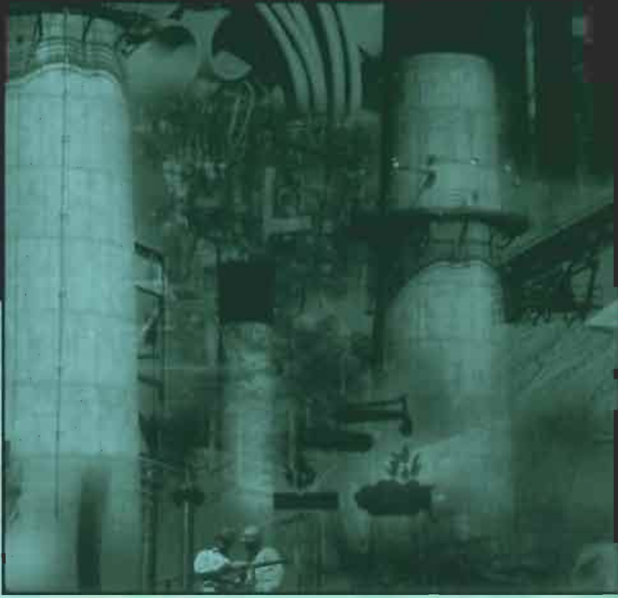
Handbook of Air Pollution Prevention and Control



Nicholas P. Cheremisinoff, Ph.D, N&P Limited

HANDBOOK OF
AIR POLLUTION PREVENTION
AND CONTROL

HANDBOOK OF AIR POLLUTION PREVENTION AND CONTROL

Nicholas P. Cheremisinoff, Ph.D.
N&P Limited

BUTTERWORTH HEINEMANN
An imprint of Elsevier Science

Amsterdam Boston London New York Oxford Paris
San Diego San Francisco Singapore Sydney Tokyo

Butterworth–Heinemann is an imprint of Elsevier Science.

Library of Congress Cataloging-in-Publication Data

Cheremisinoff, Nicholas P.
Handbook of air pollution prevention and control / Nicholas P. Cheremisinoff.
p. cm.
Includes bibliographical references and index.
ISBN 0-7506-7499-7 (alk. paper)
1. Air quality management. 2. Air—Pollution. 3. Factory and trade waste—Environmental aspects. I. Title.

TD883 .C435 2002
628.5'3—dc21

2002018563

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

The publisher offers special discounts on bulk orders of this book.
For information, please contact:

Manager of Special Sales
Elsevier Science
225 Wildwood Avenue
Woburn, MA 01801-2041
Tel: 781-904-2500
Fax: 781-904-2620

For information on all Butterworth–Heinemann publications available, contact our World Wide Web home page at: http://www.bh.com

10 9 8 7 6 5 4 3 2 1

Printed in the United States of America

CONTENTS

PREFACE

This volume covers the practices and technologies that are applied to the prevention of air pollution, and to the cleaning and control of industrial air emissions. Although there are numerous publications that address these subjects, rarely are prevention and control concepts considered together in a single volume. This book provides a bridge for today's environmental manager by focusing on an integrated approach to managing air pollution problems within industrial operations. There are eight chapters.

Chapter 1 provides orientation and an introduction to the subject of air quality. The focus of this book is on industrial air pollution problems. We begin by reviewing the regulatory driving force in the United States for air pollution abatement. To appreciate the objectives of our Federal air pollution control regulations, an understanding of the fate and transport mechanisms in the environment is important. Hence, some general discussions on the behavior of pollutants in the atmosphere are included in this chapter. There are only two general methods for ensuring high quality air. These options are the application of control technologies that clean air or remove pollutants, and methods of prevention. In general, prevention is more cost-effective than the application of end-of-pipe treatment technologies, however, there are many situations where control technologies represent the only feasible methods to managing air pollution problems. Both approaches are presented in this volume, and the reader will need to assess which is the most appropriate means on a case by case basis. At the end of Chapter 1 you will find a summary of the topics to be discussed in this volume. This will help you to focus on specific areas of reading that are most useful to you. There is also a list of recommended resources, including Web sites, as well as a review section.

In Chapter 2 we focus our attention on some of the point sources of air emissions within different types of plant operations, along with the methods of abatement and prevention. Although we do not make direct comparisons between prevention and control methodologies until Chapter 6, the reader should gain an appreciation for the simplicity of applying pollution prevention as opposed to incorporating engineering controls in many situations. While we will not cover all the important industry sector sources of air pollution in this chapter, an attempt is made to examine a broad spectrum of so-called "heavy-industries". These are industry sectors that are plagued with air pollution problems, and have had a long history in battling them.

There are literally many thousands of chemical compounds that may pose potential air pollution problems. It would be impossible to present all the pertinent data and information needed to evaluate each and every air pollution scenario. There are, however, a wealth of information and data bases that are available on the World Wide Web, along with a number of standard hard copy references to obtain information on the chemical and physical properties, and health risks of potential atmospheric contaminants. Chapter 3 provides information on the following three areas:

1. Selected chemical and physical properties, and data of common and potential atmospheric contaminants.
2. An overview of important terms and definitions useful in assessing the potentially harmful effects of air pollutants.
3. A summary of Web site sources that provide extensive data bases on the chemical and physical properties, as well as health risk effects associated with air contaminants.

Chapter 4 provides an overview of indoor air quality (IAQ) issues and management practices, with emphasis given to industrial operations. Proper indoor air quality management is an integral part of any program dealing with safe industry practices. It is an area of concern because improperly designed ventilation systems lead to significant health risk exposures through inhalation hazards, as well as energy inefficiencies, which increase the overhead costs of an operation. IAQ is an area where control and operational options may present significant pollution prevention opportunities through the capturing of energy credits, in increasing the productivity of workers through improved comfort, reducing loss time from illness and injury, reducing medical costs by minimizing or eliminating inhalation hazards, and reducing facility insurance premiums by providing a safer work environment.

Chapter 5 describes simplified methods of estimating airborne pollutant concentration distributions associated with stationary emission sources. There are sophisticated models available to predict and to assist in evaluating the impact of pollutants on the environment and to sensitive receptors such as populated areas. In this chapter we will explore the basic principles behind dispersion models and then apply a simplified model that has been developed by EPA to analyzing air dispersion problems. There are practice and study problems at the end of this chapter. A screening model for air dispersion impact assessments called SCREEN, developed by USEPA is highlighted in this chapter, and the reader is provided with details on how to download the software and apply it.

Chapter 6 makes a strong argument for pollution prevention (P2) practices, but is prudent in pointing out that there are many situations where conventional pollution control technologies will suffice. The general approach to pollution prevention and the pollution prevention assessment or auditing technique is discussed in detail. The overall concepts discussed in this chapter are:

1. The benefits of P2 to an organization.
2. The basic approach to applying and integrating P2 into an organization, with emphasis given to managing air pollution problems.
3. When P2 should and should not be applied.

Chapter 7 focuses on hardware. The intent is to provide a working description of pollution control hardware, as well as to highlight those technologies and equipment that may be applicable to pollution prevention opportunities. As stated in this chapter, we should never approach an air pollution problem (or any pollution and waste problem) without first considering other options to end-of-pipe treatment and controls. If the waste or pollution can be prevented or minimized without the use of controls that require long-term O&M and other recurring costs, then that should be the first choice, provided there is sufficient financial justification. But, the absolutely wrong reason for selecting pollution prevention (P2) over conventional wisdom is to do P2 for the sake of doing it. This chapter will provide you with a good overview of the technology options for air pollution control, as well an arsenal of important references.

Chapter 8 covers the principles of cost accounting. The focus of this chapter is *project cost estimating*. This is sometimes referred to as *total cost accounting*. The term total-cost accounting (TCA) has also come to be commonly known as *life-cycle costing* (LCC). LCC is a method aimed at analyzing the costs and benefits associated with a piece of equipment, plant, or a project over the entire time of intended use. Experience has shown that the up-front purchase price alone is a poor measure of the total cost. Instead, costs such as those associated with maintainability, reliability, disposal, and salvage value, as well as employee training and education, must be given equal weight in making financial decisions. By the same token, justifying the investment into a piece of equipment requires that all benefits and costs be clearly defined in the most concrete terms possible, and projected over the life of each technology option.

References are noted throughout the book for further information. Particular attention is given to Web site sources where detailed equipment design information and chemical property data bases exist.

At the end of the book is a glossary containing several hundred terms commonly used in pollution prevention and control practices. You can rely on the glossary for terms not identified in the text discussions, and as a general reference.

You will also find a liberal application of sidebar discussions at various points in different chapters. Here you will find some interesting and useful facts and formulas.

This handbook is intended for environmental managers and process engineers. Some subject matter is covered in survey or overview form, whereas others are treated in more depth. In both cases, important references are noted where detailed information can be obtained. The overall objective of this volume is not simply to provide a general reference, but to serve as a resource for developing approaches to managing air pollution problems. If the reader can get just one good idea from reading over the material in this volume to solve an air pollution problem, and further, capture some economic incentives that normally accompany a pollution prevention practice, then I have not only done a good job in writing this book, but you have made a wise investment in its purchase.

A heartfelt thanks goes to Butterworth Heinemann for their patience during the writing of this book, and to their fine production. A special thank you is extended to Laura Berendson and Tara Habhegger for their creative efforts throughout the production of this volume.

Nicholas P. Cheremisinoff, Ph.D.

ABOUT THE AUTHOR

Nicholas P. Cheremisinoff is a consultant to industry, lending institutions and donor agencies, and environmental litigation firms, specializing in pollution prevention and environmental due care issues. His career now spans nearly 25 years with experiences in manufacturing, applied research and development, and business development. He has assisted and led hundreds of pollution prevention programs and remediation projects, assisted in the privatization of major overseas industrial complexes, and consulted on developing foreign national policies on waste management. Among his client base are the World Bank Organization, the U.S. Trade and Development Agency, the U.S. Department of Energy, and numerous private sector companies. He has contributed extensively to the industrial press, having authored, co-authored, or edited more than 100 technical books, including Butterworth-Heinemann's *Handbook of Water and Wastewater Treatment Technologies*. Dr. Cheremisinoff received his B.S., M.S., and Ph.D. degrees in chemical engineering from Clarkson College of Technology.

HANDBOOK OF
AIR POLLUTION PREVENTION
AND CONTROL

Chapter 1

INTRODUCTION TO AIR QUALITY

INTRODUCTION

This chapter provides orientation and an introduction to the subject of air quality. As a part of this introduction, we begin exploring the options for ensuring high quality air in the environment. The focus of this book is on industrial air pollution problems, and hence, the term "environment" refers to the universal ecosystem that humans live and interact in, as well as the workplace.

We begin by reviewing the regulatory driving force in the United States for air pollution abatement. To appreciate the objectives of our Federal air pollution control regulations, an understanding of the fate and transport mechanisms in the environment is important. Hence, some general discussions on the behavior of pollutants in the atmosphere are included in this chapter.

Obviously, the overall motivation for clean air is protection of health. There are essentially only two general methods for ensuring high quality air. These options are the application of control technologies that clean air or remove pollutants, and methods of prevention. As a general rule of thumb, prevention is more cost-effective than the application of so-called end-of-pipe treatment technologies. However, there are many situations where control technologies represent the only feasible methods to managing air pollution problems. Both approaches are presented in this volume, and the reader will need to assess which is the most appropriate means on a case by case basis.

At the end of this chapter you will find a summary of the topics discussed in this volume. This will help you to focus on specific areas of reading that are most useful to you. There is also a list of recommended resources, including Web sites.

AN OVERVIEW OF THE CLEAN AIR ACT AMENDMENTS

The regulatory driving force for air pollution control in the United States is the

Clean Air Act. Many countries around the world have similar legislation and national policies aimed at protecting air quality.

The Clean Air Act Amendments of 1990 included sweeping revisions to the Clean Air Act, building on U.S. Congressional proposals advanced during the 1980s.The legislation is designed to curb three major threats to the nation's environment and to the health of millions of Americans: acid rain, urban air pollution, and toxic air emissions. Our focus is on toxic air emissions, but we will review the other revisions to gain an overall appreciation of the law.

The law also established a national permitting program. Provisions include the phaseout of ozone-depleting chemicals, roughly according to the schedule outlined in international negotiations (known as the Revised Montreal Protocol). Several progressive and creative new themes are embodied in the Amendments; themes necessary for effectively achieving the air quality goals and regulatory reform expected from these far-reaching amendments. Specifically the law:

- encourages the use of market-based principles and other innovative approaches, like performance-based standards and emission banking and trading;
- provides a framework from which alternative clean fuels will be used by setting standards in the fleet and California pilot program that can be met by the most cost-effective combination of fuels and technology;
- promotes the use of clean low sulfur coal and natural gas, as well as innovative technologies to clean high sulfur coal through the acid rain program;
- reduces enough energy waste and creates enough of a market for clean fuels derived from grain and natural gas to cut dependency on oil imports by one million barrels/day;
- promotes energy conservation through an acid rain program that gives utilities flexibility to obtain needed emission reductions through programs that encourage customers to conserve energy.

One component of urban smog - hydrocarbons - comes from automobile emissions, petroleum refineries, chemical plants, dry cleaners, gasoline stations, house painting, and printing shops. Another key component - nitrogen oxides - comes from the combustion of fuel for transportation, utilities and industries.

Although the original Clean Air Act of 1977 brought about significant improvements in air quality, the urban air pollution problems of ozone (known as smog), carbon monoxide (CO), and particulate matter (PM_{10}) persist. Currently, over 100 million Americans live in cities which are out of attainment with the public health standards for ozone. The most widespread and persistent urban pollution problem is ozone. The causes of this and the lesser problem of carbon monoxide (CO) and particulate matter (PM_{10}) pollution in our urban areas are largely due to the diversity and number of urban air pollution sources. While there are various reasons for continued high levels of ozone pollution, such as growth in the number of stationary sources of hydrocarbons and continued growth in automobile travel, perhaps the most telling reason is that the remaining sources of hydrocarbons are also the most difficult to control. These are the small sources - generally those that emit less than 100 tons of hydrocarbons per year. These sources, such as auto body shops and dry cleaners, may individually emit less than 10 tons per year, but collectively emit many hundreds of tons of pollution.

The Clean Air Act Amendments of 1990 created a new, balanced strategy to attack the problem of urban smog. While it gives states more time to meet the air quality standard (up to 20 years for ozone in Los Angeles), it also requires states to make constant formidable progress in reducing emissions. It requires the Federal government to reduce emissions from cars, trucks, and buses; from consumer products such as hair spray and window washing compounds; and from ships and barges during loading and unloading of petroleum products.

Under **Title I**, the Federal government must develop the technical guidance that states need to control stationary sources. The law addresses the urban air pollution problems of ozone (smog), carbon monoxide (CO), and particulate matter (PM_{10}). Specifically, it clarifies how areas are designated and redesignated "attainment". It also allows EPA (Environmental Protection Agency) to define the boundaries of "nonattainment" areas: geographical areas whose air quality does not meet Federal air quality standards designed to protect public health. The law also establishes provisions defining when and how the federal government can impose sanctions on areas of the country that have not met certain conditions.

For ozone, the law establishes nonattainment area classifications ranked according to the severity of the areas's air pollution problem. These classifications are *marginal*, *moderate*, *serious*, *severe* and *extreme*. The EPA assigns each nonattainment area one of these categories, thus triggering varying requirements the area must comply with in order to meet the ozone standard. Nonattainment areas must implement different control measures, depending upon their classification. Marginal areas, for example, are the closest to meeting the standard. They are required to conduct an inventory of their ozone-causing emissions and institute a permit program. Nonattainment areas with more serious air quality problems must implement various control measures. The worse the air quality, the more controls areas must implement.

The law also establishes similar programs for areas that do not meet the federal health standards for the pollutants carbon monoxide and particulate matter. Areas exceeding the standards for these pollutants are divided into "moderate" and "serious" classifications. Depending upon the degree to which they exceed the carbon monoxide standard, areas are required to implement programs introducing oxygenated fuels and/or enhanced emission inspection programs, among other measures. Depending upon their classification, areas exceeding the particulate matter standard must implement either *reasonably available control measures* (RACM) or *best available control measures* (BACM), among other requirements. For **Title II**: Provisions Relating to Mobile Sources - while motor vehicles built today emit fewer pollutants (60% to 80% less, depending on the pollutant) than those built in the 1960s, cars and trucks still account for almost half the emissions of the ozone precursors VOCs and NO_x, and up to 90% of the CO emissions in urban areas. The principal reason for this problem is the rapid growth in the number of vehicles on the roadways and the total miles driven. This growth has offset a large portion of the emission reductions gained from motor vehicle controls. In view of the unforeseen growth in automobile emissions in urban areas combined with the serious air pollution problems in many urban areas, the Congress has made significant changes to the motor vehicle provisions of the 1977 Clean Air Act.

The Clean Air Act of 1990 establishes tighter pollution standards for emissions from automobiles and trucks. These standards are aimed at reducing tailpipe emissions of hydrocarbons, carbon monoxide, and nitrogen oxides on a phased-in basis that began in model year 1994. Automobile manufacturers are also required to reduce vehicle emissions resulting from the evaporation of gasoline during refueling. Fuel quality is also controlled. Scheduled reductions in gasoline volatility and sulfur content of diesel fuel, for example, are being required. New programs requiring cleaner (so-called "reformulated" gasoline) were initiated in 1995 for the nine cities with the worst ozone problems. Other cities can "opt-in" to the reformulated gasoline program. Higher levels (2.7%) of alcohol-based oxygenated fuels are being produced and sold in 41 areas during the winter months that exceed the federal standard for carbon monoxide.

The law also establishes a clean fuel car pilot program in California, requiring the phase-in of tighter emission limits for 150,000 vehicles in model year 1996 and 300,000 by the model year 1999. These standards can be met with any combination of vehicle technology and cleaner fuels. The standards became even stricter in 2001. Other states can "opt-in" to this program, though only through incentives, not sales or production mandates. Further, twenty-six of the dirtiest areas of the country must adopt a program limiting emissions from centrally-fueled fleets of 10 or more vehicles.

Title III: Air Toxics - Toxic air pollutants are those pollutants which are hazardous to human health or the environment but are not specifically covered under another portion of the Clean Air Act. These pollutants are typically carcinogens, mutagens, and reproductive toxins. The Clean Air Act Amendments of 1977 failed to result in substantial reductions of the emissions of these very threatening substances. In fact, over the history of the air toxics program only seven pollutants have been regulated. It is well-recognized that the toxic air pollution problem is widespread. Information generated from The Superfund "Right to Know" rule (SARA Section 313) indicates that more than 2.7 billion pounds of toxic air pollutants are emitted annually in the United States. EPA studies suggest that exposure to such quantities of air toxics result in 1000 to 3000 cancer deaths each year. The Clean Air Act of 1990 offers a comprehensive plan for achieving significant reductions in emissions of hazardous air pollutants from major sources. Very early industry reports dating back to 1987 conservatively suggest that an estimated 2.7 billion pounds of toxic air pollutants were emitted into the atmosphere, contributing to approximately 300-1500 cancer fatalities annually.

The law includes a list of 189 toxic air pollutants of which emissions must be reduced. The list of source categories includes: (1) major sources emitting 10 tons/year of any one, or 25 tons/year of any combination of those pollutants; and (2) area sources (smaller sources, such as dry cleaners).

EPA also develops and issues "Maximum Achievable Control Technology" (MACT) standards for each listed source category according to a prescribed schedule. These standards are based on the best demonstrated control technology or practices within the regulated industry. The remaining source categories are controlled according to a schedule that ensures all controls will be achieved within 10 years of enactment. Companies that voluntarily reduce emissions according to certain conditions can get a six year extension from meeting the MACT requirements. This is an obvious incentive for doing pollution prevention. Eight years after MACT is installed on a source, EPA must examine the risk levels remaining at the regulated facilities and determine whether additional controls are necessary to reduce unacceptable residual risk. The law also establishes a Chemical Safety Board to investigate accidental releases of chemicals. This safety board has been aggressive in challenging industry practices, especially with regard to properly implementing preventive maintenance programs that should eliminate unintended releases. In some cases, accidental releases have resulted in criminal charges due to a perceived lack of or inappropriate preventive maintenance programs. Further, the law requires EPA to issue regulations controlling air emissions from municipal, hospital, and other commercial and industrial incinerators.

Title IV: Acid Deposition Control - As we all know, acid rain occurs when sulfur dioxide and nitrogen oxide emissions are transformed in the atmosphere and return to the earth in rain, fog, or snow. Approximately 20 million tons of SO_2 are emitted annually in the United States, mostly from the burning of fossil fuels by electric utilities. Acid rain damages lakes, harms forests and buildings, contributes to reduced visibility, and is suspected of damaging health. The Clean Air Act Amendments result in a permanent 10 million ton reduction in sulfur dioxide (SO_2) emissions from 1980 levels. To achieve this, EPA allocates allowances in two phases permitting utilities to emit one ton of sulfur dioxide. The first phase, that became effective January 1, 1995, requires 110 powerplants to reduce their emissions to a level equivalent to the product of an emissions rate of 2.5 lbs of SO_2/mm Btu × an average of their 1985-1987 fuel use. Plants that use certain control technologies to meet their Phase I reduction requirements may receive a two year extension of compliance (this extension ended in 1997). The law also allows for a special allocation of 200,000 annual allowances per year each of the 5 years of Phase I to power plants in Illinois, Indiana, and Ohio. The second phase became effective January 1, 2000, requiring approximately 2000 utilities to reduce their emissions to a level equivalent to the product of an emissions rate of 1.2 lbs of SO_2/mm Btu × the average of their 1985-1987 fuel use. In both phases, affected sources are required to install systems that continuously monitor emissions in order to track progress and assure compliance.

The law allows utilities to trade allowances within their systems and/or buy or sell allowances to and from other affected sources. Each source must have sufficient allowances to cover its annual emissions. If not, the source is subject to a $2,000/ton excess emissions fee and a requirement to offset the excess emissions in the following year. Nationwide, plants that emit SO_2 at a rate below 1.2 lbs/mm Btu were able to increase emissions by 20% between a baseline year and 2000. Bonus allowances will be distributed to accommodate growth by units in states with a statewide average below 0.8 lbs/mm Btu. Plants that repower with a qualifying clean coal technology receive a 4 year extension of the compliance date for Phase II emission limitations. The law also includes specific requirements for reducing emissions of nitrogen oxides, based on EPA regulations for certain boilers.

Title V: Permits - The law introduced an operating permits program modeled after a similar program under the Federal *National Pollution Elimination Discharge System* (NPDES) law. The purpose of the operating permits program is to ensure compliance with all applicable requirements of the Clean Air Act and to enhance EPA's ability to enforce the Act. Air pollution sources subject to the program must obtain an operating permit, states must develop and implement the program, and EPA must issue permit program regulations, review each state's proposed program (known as a SIP, or *State Implementation Plan*), and oversee the state's efforts to implement any approved program. EPA must also develop and implement a federal permit program when a state fails to adopt and implement its own program. This program, in many ways the most important procedural reform contained in the law, greatly strengthens enforcement of the Clean Air Act. It enhances air quality control in a variety of ways. First, adding such a program updates the Clean Air

Act, making it more consistent with other environmental statutes. The Clean Water Act, the Resource Conservation and Recovery Act, and the Federal Insecticide, Fungicide, and Rodenticide Act all require permits.

The 1977 Clean Air laws also requires a construction permit for certain pollution sources, and about 35 states have their own laws requiring operating permits. The program clarifies and makes more enforceable a source's pollution control requirements. Currently, a source's pollution control obligations may be scattered throughout numerous hard-to-find provisions of state and federal regulations, and in many cases, the source is not required under the applicable SIP to submit periodic compliance reports to EPA or the states. The permit program ensures that all of a source's obligations with respect to its pollutants are contained in one permit document, and that the source files periodic reports identifying the extent to which it has complied with those obligations. Both of these requirements greatly enhance the ability of Federal and state agencies to evaluate its air quality situation. In addition, the program provides a ready vehicle for states to assume administration, subject to federal oversight, of significant parts of the air toxics program and the acid rain program. And, through the permit fee provisions, discussed below, the program greatly augments a state's resources to administer pollution control programs by requiring sources of pollution to pay their fair share of the costs of a state's air pollution program.

Under the law, the EPA must issue program regulations within one year of enactment. Within three years of enactment, each state must submit to EPA a permit program meeting these regulatory requirements. After receiving the state submittal, EPA has one year to accept or reject the program. EPA must levy sanctions against a state that does not submit or enforce a permit program. Each permit issued to a facility will be for a fixed term of up to five years. The law establishes a permit fee whereby the state collects a fee from the permitted facility to cover reasonable direct and indirect costs of the permitting program. All sources subject to the permit program must submit a complete permit application within 12 months of the effective date of the program. The state permitting authority must determine whether or not to approve an application within 18 months of the date it receives the application. EPA has 45 days to review each permit and to object to permits that violate the Clean Air Act. If EPA fails to object to a permit that violates the Act or the implementation plan, any person may petition EPA to object within 60 days following EPA's 45-day review period, and EPA must grant or deny the permit within 60 days. Judicial review of EPA's decision on a citizen's petition can occur in the Federal court of appeals.

Title VI: Stratospheric Ozone and Global Climate Protection - The law builds on the market-based structure and requirements currently contained in EPA's regulations to phase out the production of substances that deplete the ozone layer.

The law requires a complete phase-out of CFCs and halons with interim reductions and some related changes to the existing Montreal Protocol. Under these provisions, EPA must list all regulated substances along with their ozone depletion potential, atmospheric lifetimes and global warming potentials within 60 days of enactment. In addition, EPA must ensure that Class I chemicals be phased out on a schedule similar to that specified in the Montreal Protocol - CFCs, halons, and carbon tetrachloride by 2000; methyl chloroform by 2002 - but with more stringent interim reductions. Class II chemicals (HCFCs) will be phased out by 2030. Regulations for Class I chemicals were required within 10 months, and Class II chemical regulations were required by December 31,1999. The law also requires EPA to publish a list of safe and unsafe substitutes for Class I and II chemicals and to ban the use of unsafe substitutes. The law requires nonessential products releasing Class I chemicals to be banned within 2 years of enactment. In 1994 a ban went into effect for aerosols and non-insulating foams using Class II chemicals, with exemptions for flammability and safety. Regulations for this purpose were required within one year of enactment, and became effective two years afterwards.

Title VII: Provisions Relating to Enforcement - The Clean Air Act of 1990 contains a broad array of authorities to make the law more readily enforceable, thus bringing it up to date with the other major environmental statutes. EPA has authorities to issue administrative penalty orders up to $200,000, and field citations up to $5000 for lesser infractions. Civil judicial penalties are enhanced. Criminal penalties for knowing violations are upgraded from misdemeanors to felonies, and criminal authorities for knowing and negligent endangerment are established. In addition, sources must certify their compliance, and EPA has authority to issue administrative subpoenas for compliance data. EPA is also authorized to issue compliance orders with compliance schedules of up to one year. The citizen suit provisions have also been revised to allow citizens to seek penalties against violators, with the penalties going to a U.S. Treasury fund for use by EPA for compliance and enforcement activities.

Other Titles - The Clean Air Act Amendments of 1990 continue the federal acid rain research program and contain several provisions relating to research, development and air monitoring. They also contain provisions to provide additional unemployment benefits through the Job Training Partnership Act to workers laid off as a consequence of compliance with the Clean Air Act. The Act also contains provisions to improve visibility near National Parks and other parts of the country. Strict enforcement of the Clean Air Act Amendments is the driving force behind pollution abatement. Non-compliance is simply not an option, since there are both financial and criminal liabilities that outweigh any benefits derived from a business.

LEGAL MOTIVATION FOR AIR POLLUTION PREVENTION AND CONTROL

THE CLEAN AIR ACT

Title I - Overall Intent of the Law and RACM and BACM
Title II - Provisions Relating to Mobile Sources
Title III - Air Toxics
Title IV - Acid Deposition Control
Title V - Permits
Title VI - Stratospheric Ozone and Global Climate
Title VII - Provisions Relating to Enforcement

FATE AND TRANSPORT IN THE ENVIRONMENT

The reasons for such strict regulation of air pollution are obvious: protecting human health and the environment. Potential air pollutants are not only toxic in many cases, but they can travel over great distances, thereby impacting areas remote from the sources of emissions. There are two environments that are of concern, once chemicals are emitted to the surroundings:

- the general atmosphere, and
- the work space.

In the first environment, we are concerned with the potential health risks that chemicals pose to the public, as well as possible impacts on the ecology. In the latter case, we are concerned with indoor air quality and its possible adverse impacts on the health and safety of the workforce. In both cases the health dangers may be either acute, or long-term chronic health risks. We will first discuss general concepts of air pollution and table our discussions on indoor air quality for a later chapter.

Atmospheric chemistry influences human health, climate, food production, and through its impact on visibility, our view of the world. Chemicals in the air affect us with each breath we take. Suspended particulate matter that form from gas-phase reactions affect the amount of solar energy reaching the earth's surface.

Not all, but certainly many chemicals, when initially emitted to the atmosphere, are relatively harmless by themselves. However, in the presence of sunlight or other pollutants, such innocuous emissions can be transformed into hazardous pollutants that present a threat to mankind and our ecology. In addition, pollutants can be transported over long distances from their sources, causing impacts hundreds or even thousands of kilometers downwind. For these reasons considerable effort is expended in conducting research on the factors that affect atmospheric pollutant transformations, the rates of these transformations, and the corresponding lifetimes of the chemicals involved. Such research includes basic kinetic studies to determine reaction rate constants; smog chamber studies to establish the reactivity, reaction products, and persistence of chemicals in various atmospheric situations; ground-level and airborne field experiments to define the rates and products of atmospheric reactions; and modeling studies to predict the impact of atmospheric reactions. This requires extensive experience in the application of aircraft, chemical tracers, and dispersion modeling to assess the extent and importance of pollutant transport. The simplified diagram in Figures 1 illustrates pollutant pathways in the environment for the case of acid rain. As shown, air pollution just doesn't impact on the air we breathe. It results in ground, groundwater, and can have impact on the food chain.

Atmospheric particulates (sea salt, carbonaceous soot, and sulfuric acid aerosols) are known to provide a condensed phase for complex heterogeneous chemistry to occur. Although the presence of atmospheric particulates are known to alter trace gas concentrations, details of the specific chemical mechanisms for condensed phase chemistry have not been identified.

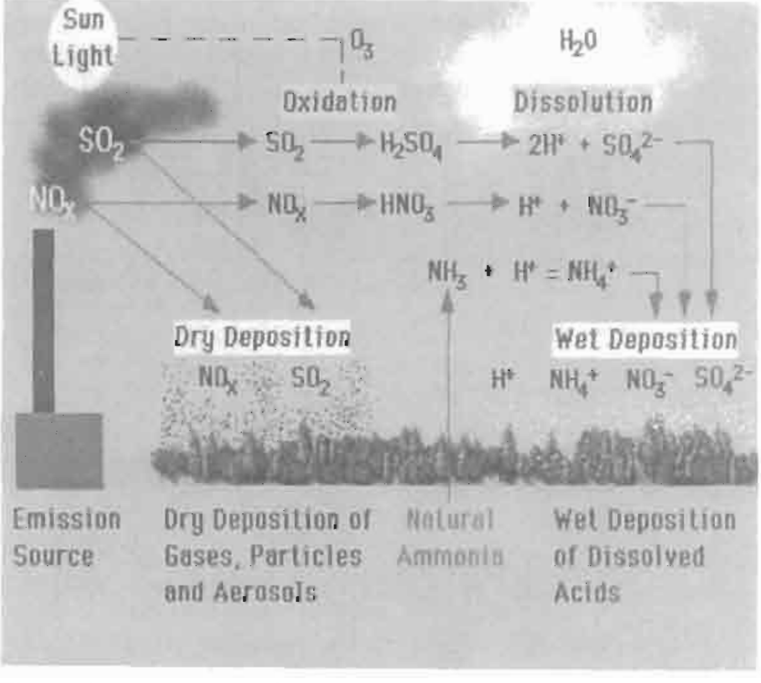


Figure 1. Mechanisms of acid rain and impact on the environment.

Clouds cover roughly two-thirds of our earth's surface and play an important role in influencing global climate by affecting the radiation budget. *Cirrus clouds* are one example of a cloud type whose optical properties are not accurately known. Cirrus clouds form in the upper troposphere and are composed almost exclusively of non-spherical ice crystal particles. The impact of cloud coverage on dispersion of pollution in the atmosphere is an area of great concern and intensive study.

Although prognostic atmospheric models have been used routinely for many years for synoptic and mesoscale applications, their computational demands have, until recently, limited their use in predicting mesoscale and microscale circulations and dispersion in complex terrain. Modeling efforts, in conjunction with observational and theoretical studies, will improve our understanding of mesoscale and microscale circulations. Mesoscale modeling studies contribute to the understanding of lower atmospheric processes and the findings of these studies are applicable to emergency preparedness and response concerns, air quality issues, and the relationship between regional and global climate change.

Local and regional pollution takes place in the lowest layer of the atmosphere, the troposphere, which extends from the earth's surface to about 16 km (about 10 mi). The troposphere is the region in which most weather occurs. If the load of pollutants added to the troposphere were equally distributed, the pollutants would be spread over vast areas and the air pollution might almost escape our notice. Also, pollution sources tend to be concentrated, especially in cities. In the weather phenomenon known as a *thermal inversion*, a layer of cooler air is trapped near the ground by a layer of warmer air above. When this occurs, normal air mixing almost ceases and pollutants are trapped in the lower layer. Local topography, or the shape of the land, can worsen this effect—an area ringed by mountains, for example, can become a pollution trap. These concepts are discussed at greater lengths in later chapters.

SMOG AND ACID PRECIPITATION

Smog is defined as intense local pollution usually trapped by a thermal inversion. Before automobiles came along, most smog came from burning coal and was so severe that in 19th-century London, street lights were turned on by noon because soot and smog darkened the midday sky. There are still parts of the industrialized world that face comparable air quality impairment. Figure 2 is a photograph of a coke-chemical plant in the city of Mariupol, Ukraine. Air quality conditions are so severe at times that poor visibility conditions caused by air pollution problems from several plants, like the one in Figure 2 hamper local air traffic.

Burning gasoline in motor vehicles is the main source of smog in most regions of the world today. Powered by sunlight, oxides of nitrogen and volatile organic compounds react in the atmosphere to produce photochemical smog.

In 1948 in the steel-mill town of Donora, Pennsylvania, intense local smog killed nineteen people. In 1952 in London over 3000 people died in one of the most notorious smog events known as London Fogs; in 1962 another 700 Londoners died.

Smog contains ozone. Ozone (O_3) in the lower atmosphere is a poison; it damages vegetation, kills trees, irritates lung tissues, and attacks rubber and various plastics. Environmental officials measure ozone to determine the severity of smog. When the ozone level is high, other pollutants, including carbon monoxide, are usually present at high levels as well. In the presence of atmospheric moisture, sulfur dioxide and oxides of nitrogen (NO_x) turn into droplets of pure acid floating in smog. These airborne acids are bad for the lungs and attack anything made of limestone, marble, or metal. In cities around the world, smog acids are eroding precious artifacts, including the Parthenon temple in Athens, Greece, and the Taj Mahal in Agra, India. Oxides of nitrogen and sulfur dioxide pollute places far from the points where they are released into the air. Carried by winds in the troposphere, they can reach distant regions where they precipitate in acid form, usually as rain or snow. Such acid precipitation can burn the leaves of plants and make lakes too

Figure 2. A coke-chemical plant in Ukraine.

acidic to support fish and other living organisms. Because of acidification, sensitive species, such as the popular brook trout, can no longer survive in many lakes and streams in the eastern United States. Smog spoils views and makes outdoor activity unpleasant. For the very young, the very old, and people who suffer from asthma or heart disease, the effects of smog are even worse: it may cause headaches or dizziness and can cause breathing difficulties. In extreme cases, smog can lead to mass illness and death, mainly from carbon monoxide poisoning. With stronger pollution controls and less reliance on coal for heat, today's chronic smog is rarely so obviously deadly. However, under adverse weather conditions, accidental releases of other toxic substances can be equally disastrous. The worst such accident occurred in 1984 in Bhopal, India, when *methyl isocyanate* released from an American-owned factory during a thermal inversion caused at least 3300 deaths.

GLOBAL SCALE POLLUTION

Air pollution can expand beyond a regional area to cause global effects. The stratosphere is the layer of the atmosphere between 16 km (10 mi) and 50 km (30 mi) above sea level. It is rich in ozone, the same molecule that acts as a pollutant when found at lower levels of the atmosphere in urban smog. Up at the stratospheric level, however, ozone forms a protective layer that serves a vital function: it absorbs the wavelength of solar radiation known as ultraviolet-B (UV-B). UV-B damages deoxyribonucleic acid (DNA), the genetic molecule found in every living cell, increasing the risk of such problems as cancer in humans. Because of its protective function, the ozone layer is essential to life on earth.

OZONE DEPLETION

Several pollutants attack the ozone layer. Chief among them is the class of chemicals known as chlorofluorocarbons (CFCs), used as refrigerants (notably in air conditioners), as agents in several manufacturing processes, and formerly as propellants in spray cans. CFC molecules are virtually indestructible until they reach the stratosphere. Here, intense ultraviolet radiation breaks the CFC molecules apart, releasing the chlorine atoms they contain. These chlorine atoms begin reacting with ozone, breaking it down into ordinary oxygen molecules that do not absorb UV-B. The chlorine acts as a catalyst—that is, it takes part in several chemical reactions—yet at the end emerges unchanged and able to react again. A single chlorine atom can destroy up to 100,000 ozone molecules in the stratosphere. Other pollutants, including nitrous oxide from fertilizers and the pesticide methyl bromide, also attack atmospheric ozone. Under this assault the protective ozone layer in the stratosphere is thinning. In the Antarctic region, it vanishes almost entirely for a few weeks every year. Although CFC use has been greatly reduced in recent years, CFC molecules already released into the lower atmosphere will be making their way to the stratosphere for decades, and further ozone loss is expected. As a result, experts anticipate an increase in skin cancer, more cataracts (clouding of the lens of the eye), and reduced yields of some food crops.

GLOBAL WARMING

Industry is possibly bringing about another global-scale change in the atmosphere: the increase in what are called *greenhouse gases*. Like glass in a greenhouse, these gases admit the sun's light, but tend to reflect back downward the heat that is radiated from the ground below, trapping heat in the earth's atmosphere. This process is known as the greenhouse effect. Carbon dioxide is the most significant of these gases—there is 25 percent more carbon dioxide in the atmosphere today than there was a century ago, the result of our burning coal and fuels derived from oil. Methane, nitrous oxide, and CFCs are greenhouse gases as well. Scientists predict that increases in these gases in the atmosphere will make the earth warmer. They expect a global rise in average temperature somewhere between 1.0° and 3.5°C (1.8° and 6.3°F) in the next century. Average temperatures have in fact been rising, and the years from 1987 to 1997 were the warmest ten years on record. Many experts are reluctant to say that global warming has actually begun, because climate naturally varies from year to year and decade to decade, and it takes many years of records to be sure of a fundamental change. There is little disagreement, though, that global warming is on its way.

Global warming will have different effects in different regions. A warmed world is expected to have more extreme weather, with more rain during wet periods, longer droughts, and more powerful storms. Although the effects of future climate change are unknown, some predict that exaggerated weather conditions may translate into better agricultural yields in areas such as the western United States, where temperature and rainfall are expected to increase, while dramatic decreases in rainfall may lead to severe drought and plunging agricultural yields in parts of Africa, for example. Warmer temperatures are expected to partially melt the polar ice caps, leading to a projected sea level rise of 50 cm (20 in) by the year 2050. A sea level rise of this magnitude would flood coastal cities, force people to abandon low-lying islands, and completely inundate coastal wetlands. If sea levels rise at projected rates, the Florida Everglades will be completely under water in less than 50 years. Diseases like malaria, which at present are primarily found in the tropics, may become more common in the regions of the globe between the tropics and the polar regions, called the temperate zones. For many of the world's plant species, and for animal species that are not easily able to shift their territories as their habitat grows warmer, climate change may bring extinction.

A FEW OF THE PRIORITY AIR POLLUTANTS

In addition to the law, the motivation for pollution prevention and control is the elimination or reduction of health risks. There are 189 toxic air pollutants that EPA has on its list to guard against and regulate. While we will not come close to describing even a fraction of the chemicals on this list, a few of the priority pollutants and their health risks are worth noting as part of this introduction to the subject of air pollution abatement technologies. At the same time, we may note some general pollution prevention options for each of these priority pollutants, as well as the control technologies that are available.

AIRBORNE PARTICULATE MATTER

Airborne particulate matter, which includes dust, dirt, soot, smoke, and liquid droplets emitted into the air, is small enough to be suspended in the atmosphere. Airborne particulate matter may be a complex mixture of organic and inorganic substances. They can be characterized by their physical attributes, which influence their transport and deposition, and their chemical composition, which influences their effect on health. The physical attributes of airborne particulates include mass concentration and size distribution. Ambient levels of mass concentration are measured in micrograms per cubic meter (mg/m^3); size attributes are usually measured in aerodynamic diameter. Particulate matter (PM) exceeding 2.5 microns (μ) in aerodynamic diameter is generally defined as coarse particles, while particles smaller than 2.5 mm ($PM_{2.5}$) are called fine particles.

The acid component of particulate matter, and most of its mutagenic activity, are generally contained in fine particles, although some coarse acid droplets are also present in fog. Samples reportedly taken in the United States showed that about 30% of particulate matter was in the fine fraction range. Particles interact with various substances in the air to form organic or inorganic chemical compounds. The most common combinations of fine particles are those with sulfates. In the United States, sulfate ions account for about 40% of fine particulate matter and may also be present in concentrations exceeding about 10 micrograms per normal cubic meter (mg/Nm^3). The smaller particles contain the secondarily formed aerosols, combustion particles, and recondensed organic and metal vapors. The carbonaceous component of fine particles - products of incomplete combustion - contains both elemental carbon (graphite and soot) and nonvolatile organic carbon (hydrocarbons emitted in combustion exhaust, and secondary organic compounds formed by photochemistry). These species may be the most abundant fine particles after sulfates. Additionally, atmospheric reactions of nitrogen oxides produce nitric acid vapor (HNO_3) that may accumulate as nitrate particles in both fine and coarse forms. The most common combination of coarse particles consists of oxides of silicon, aluminum, calcium, and iron.

There are several terms that are used to describe particulate matter. Generally, these terms are associated with the sampling method, and are briefly described as follows:

Total suspended particulates (TSP) include particles of various sizes. Some proportion of TSP consists of particles too large to enter the human respiratory tract; therefore, TSP is not a good indicator of health-related exposure. TSP is measured by a high-volume gravimetric sampler that collects suspended particles on a glass-fiber filter. The upper limit for TSP is 45 mm in diameter in the United States and up to 160 μm in Europe. TSP sampling and TSP-based standards were used in the United States until 1987. Several countries in Central and Eastern Europe, Latin America, and Asia still monitor and establish standards based on measurements of TSP. As monitoring methods and data analysis have become more sophisticated, the focus of attention has gradually shifted to fine particulates. Recent evidence shows that fine particulates, which can reach the thoracic regions of the respiratory tract, or lower, are responsible for most of the excess mortality and morbidity associated with high levels of exposure to particulates. Most sophisticated studies suggest that fine particulates are the sole factor accounting for this health damage, while exposure to coarse particulates has little or no independent effect.

The particles most likely to cause adverse health effects are the *fine particulates*, in particular, particles smaller than 10 μ and 2.5 mm in aerodynamic diameter, respectively. They are sampled using (a) a high-volume sampler with a size-selective inlet using a quartz filter or (b) a dichotomous sampler that operates at a slower flow rate, separating on a Teflon filter particles smaller than 2.5 mm and sizes between 2.5 mm and 10 mm. No generally accepted conversion method exists between TSP and PM_{10}, which may constitute between 40% and 70% of TSP. In 1987, the USEPA switched its air quality standards from TSP to PM_{10}. PM_{10} standards have also been adopted in, for example, Brazil, Japan, and the Philippines. In light of the emerging evidence on the health impacts of fine particulates, the USEPA has proposed that U.S. ambient standards for airborne particulates be defined in terms of fine particulate matter.

Black smoke (BS) is a particulate measure that typically contains at least 50% respirable particulates smaller than 4.5 mm in aerodynamic diameter, sampled by the British smokeshade (BS) method. The reflectance of light is measured by the darkness of the stain caused by particulates on a white filter paper. The result of BS sampling depends on the density of the stain and the optical properties of the particulates. Because the method is based on reflectance from elemental carbon, its use is recommended in areas where coal smoke from domestic fires is the dominant component of ambient particulates.

Most investigators conclude that BS is roughly equivalent to PM_{10}. However, there is no precise equivalence of the black smoke measurements with other methods. The BS measure is most widely used in Great Britain and other parts of Europe.

Some particulates come from natural sources such as evaporated sea spray, windborne pollen, dust, and volcanic or other geothermal eruptions. Particulates from natural sources tend to be coarse. Almost all fine particulates are generated as a result of combustion processes, including the burning of fossil fuels for steam generation, heating and household cooking, agricultural field burning, diesel-fueled engine combustion, and various industrial processes. Emissions from these anthropogenic sources tend to be in fine fractions. However, some industrial and other processes that produce large amounts of dust, such as cement manufacturing, mining, stone crushing, and flour milling, tend to generate particles larger than 1 mm and mostly larger than 2.5 mm. In cold and temperate parts of the world, domestic coal burning has been a major contributor to the particulate content of urban air. Traffic-related emissions may make a substantial contribution to the concentration of suspended particulates in areas close to traffic. Some agroindustrial processes and road traffic represent additional anthropogenic sources of mostly coarse particulate emissions. The largest stationary sources of particulate emissions include fossil-fuel-based thermal power plants, metallurgical processes, and cement manufacturing. The physical and chemical composition of particulate emissions is determined by the nature of pollution sources.

Most particles emitted by anthropogenic sources are less than 2.5 mm in diameter and include a larger variety of toxic elements than particles emitted by natural sources. Fossil fuel combustion generates metal and sulfur particulate emissions, depending on the chemical composition of the fuel used. The EPA estimates that more than 90% of fine particulates emitted from stationary combustion sources are combined with sulfur dioxide (SO_2). Sulfates, however, do not necessarily form the largest fraction of fine particulates. In locations such as Bangkok, Chongqing (China), and Sao Paulo (Brazil), organic carbon compounds account for a larger fraction of fine particulates, reflecting the role of emissions from diesel and two-stroke vehicles or of smoke from burning coal and charcoal. Although sulfates represent a significant share (30 to 40%) of fine particulates in these cases, caution is required before making general assertions about the relationship between sulfates and fine particulates, since the sources and species characteristics of fine particulates may vary significantly across locations. Combustion devices may emit particulates comprised of products of incomplete combustion and toxic metals, which are present in the fuel and in some cases may also be carcinogenic. Particulates emitted by thermal power generation may contain lead, mercury, and other heavy metals. The melting, pouring, and torch-cutting procedures of metallurgy emit metal particulates containing lead, cadmium, and nickel. Particles emitted by the cement industry are largely stone or clay-based particulate matter that may contain toxic metals such as lead.

Vegetation exposed to wet and dry deposition of particulates may be injured when particulates are combined with other pollutants. Coarse particles, such as dust, directly deposited on leaf surfaces can reduce gas exchange and photosynthesis, leading to reduced plant growth. Heavy metals that may be present in particulates, when deposited on soil, inhibit the process in soil that makes nutrients available to plants. This, combined with the effects of particulates on leaves, may contribute to reduction of plant growth and yields. In addition, particulates contribute to the soiling and erosion of buildings, materials, and paint, leading to increased cleaning and maintenance costs and to loss of utility.

The respiratory system is the major route of entry for airborne particulates. The deposition of particulates in different parts of the human respiratory system depends on particle size, shape, density, and individual breathing patterns (mouth or nose breathing). The effect on the human organism is also influenced by the chemical composition of the particles, the duration of exposure, and individual susceptibility. While all particles smaller than 10 mm in diameter can reach the human lungs, the retention rate is largest for the finer particles. Products of incomplete combustion, which form a significant portion of the fine particulates, may enter deep into the lungs. Clinical, epidemiologic, and toxicological sources are used to estimate the mortality and morbidity effects of short- and long-term exposure to various particulate concentration levels. Several studies have found statistically significant relationships between high short-term ambient particulate concentrations and excess mortality in London and elsewhere. The estimated 4,000 excess deaths in the London metropolitan area in December 1952 were associated with BS measurements equivalent to a 4,000 mg/m^3 maximum daily average ambient concentration of particulates. Studies have also found a significant association between daily average PM_{10} concentrations and mortality at concentrations below the current U.S. standard of 150 mg/ m^3 for short-term PM_{10} concentrations.

Particulate emissions have their greatest impact on terrestrial ecosystems in the vicinity of emissions sources. Ecological alterations may be the result of particulate emissions that include toxic elements. Furthermore, the presence of fine particulates may cause light scattering, known as *atmospheric haze*, reducing visibility and adversely affecting transport safety, property values, and aesthetics.

The most frequently used reference guidelines for ambient particulate concentration are those of WHO, the EU, and the USEPA. These guidelines are based on clinical, toxicological, and epidemiologic evidence and were established by determining the concentrations with the lowest observed adverse effect (implicitly accepting the notion that a lower threshold exists under which no adverse human health effects can be detected), adjusted by an arbitrary margin of safety factor to allow for uncertainties in extrapolation from animals to humans and from small groups of humans to larger populations. The WHO (World Health Organization) guidelines are based on health considerations alone; the EU (European Union) and USEPA standards also reflect the technological feasibility of meeting the standards. In the EU, a prolonged consultation and legislative decision making process took into account the environmental conditions and the economic and social development of the various regions and countries and acknowledged a phased approach to compliance. A potential tradeoff was also recognized in the guidelines for the combined effects of sulfur dioxide and particulate matter.

The main objective of air quality guidelines and standards is the protection of human health. Since fine particulates (PM_{10}) are more likely to cause adverse health effects than coarse particulates, guidelines and standards referring to fine particulate concentrations are preferred to those referring to TSP, which includes coarse particulate concentrations. Scientific studies provide ample evidence of the relationship between exposure to short-term and long-term ambient particulate concentrations and human mortality and morbidity effects. However, the dose-response mechanism is not yet fully understood. Furthermore, according to the WHO, there is no safe threshold level below which health damage does not occur.

A difficulty that should not be overlooked is that airborne particulates are rarely homogeneous. They vary greatly in size and shape, and their chemical composition is determined by factors specific to the source and location of the emissions. The combined effects and interactions of various substances mixed with particulates have not yet been established (except for sulfur dioxide), but they are believed to be significant, especially where long-term exposure occurs. Measurement techniques and their reliability may vary across regions and countries, and so may other factors, such as diet, lifestyle, and physical fitness, that influence the human health effects of exposure to particulates.

Pollution Prevention Practices and Control Technologies

Airborne particulate matter emissions can, to a great extent, be minimized by pollution prevention and emission control measures. Prevention is frequently more cost-effective than control and, therefore, should be emphasized. Special attention should be given to pollution abatement measures in areas where taxies and buses associated with particulate emissions may pose a significant environmental risk.

Measures such as improved process design, operation, maintenance, housekeeping, and other management practices can reduce emissions. By improving combustion efficiency, the amount of products of incomplete combustion (PICs), a component of particulate matter, can be significantly reduced. Proper fuel-firing practices and combustion zone configuration, along with an adequate amount of excess air, can achieve lower PICs.

Atmospheric particulate emissions can be reduced by choosing cleaner fuels. Natural gas used as fuel emits negligible amounts of particulate matter. Oil-based processes also emit significantly fewer particulates than coal-fired combustion processes. Low-ash fossil fuels contain less noncombustible, ash-forming mineral matter and thus generate lower levels of particulate emissions. Lighter distillate oil-based combustion results in lower levels of particulate emissions than heavier residual oils. However, the choice of fuel is usually influenced by economic as well as environmental considerations.

The use of more efficient technologies or process changes can reduce PIC emissions. Advanced coal combustion technologies such as coal gasification and fluidized-bed combustion are examples of cleaner processes that may lower PICs by approximately 10%. Enclosed coal crushers and grinders emit lower PM.

Reduction of ash by fuel cleaning reduces the generation of PM emissions. Physical cleaning of coal through washing and beneficiation can reduce its ash and sulfur content, provided that care is taken in handling the large quantities of solid and liquid wastes that are generated by the cleaning process. An alternative to coal cleaning is the co-firing of coal with higher and lower ash content. In addition to reduced particulate emissions, low-ash coal also contributes to better boiler performance and reduced boiler maintenance costs and downtime, thereby recovering some of the coal cleaning costs.

A variety of particulate removal technologies, with different physical and economic characteristics, are available. Some of these are as follows:

Inertial or impingement separators rely on the inertial properties of the particles to separate them from the carrier gas stream. Inertial separators are primarily used for the collection of medium-size and coarse particles. They include settling chambers and centrifugal cyclones (straight-through, or the more frequently used reverse-flow cyclones). Cyclones are low-cost, low-maintenance centrifugal collectors that are typically used to remove particulates in the size range of 10-100 μ. The fine-dust-removal efficiency of cyclones is typically below 70%, whereas electrostatic precipitators (ESPs) and baghouses can have removal efficiencies of 99.9% or more. Cyclones are therefore often used as a primary stage before other PM removal mechanisms. They typically cost about US$35 per cubic meter/minute flow rate (m^3/min), or US$1 per cubic foot/minute.

Electrostatic precipitators (ESPs) remove particles by using an electrostatic field to attract the particles onto the electrodes. Collection efficiencies for well-designed, well-operated, and well-maintained systems are typically in the order of 99.9% or more of the inlet dust loading. ESPs are especially efficient in collecting fine particulates and can also capture trace emissions of some toxic metals with an efficiency of 99%. They are less sensitive to maximum temperatures than are fabric filters, and they operate with a very low pressure drop. Their consumption of electricity is similar to that of fabric filters. ESP performance is affected by fly-ash loading, the resistance of fly ash, and the sulfur content of the fuel. Lower sulfur concentrations in the flue gas can lead to a decrease in collection efficiency. ESPs have been used for the recovery of process materials such as cement, as well as for pollution control. They typically add 1-2% to the capital cost of a new industrial plant.

Filters and dust collectors (baghouses) collect dust by passing flue gases through a fabric that acts as a filter. The most commonly used is the bag filter, or baghouse. The various types of filter media include woven fabric, needled felt, plastic, ceramic, and metal. The operating temperature of the baghouse gas influences the choice of fabric. Accumulated particles are removed by mechanical shaking, reversal of the gas flow, or a stream of high-pressure air. Fabric filters are efficient (99.9% removal) for both high and low concentrations of particles but are suitable only for dry and free-flowing particles. Their efficiency in removing toxic metals such as arsenic, cadmium, chromium, lead, and nickel is greater than 99%. They also have the potential to enhance the capture of sulfur dioxide (SO_2) in installations downstream of sorbent injection and dry-scrubbing systems. They typically add 1-2% to the capital cost of new power plants.

Wet scrubbers rely on a liquid spray to remove dust particles from a gas stream. They are primarily used to remove gaseous emissions, with particulate control a secondary function. The major types are venturi scrubbers, jet (fume) scrubbers, and spray towers or chambers. Venturi scrubbers consume large quantities of scrubbing liquid (such as water) and electric power and incur high pressure drops. Jet or fume scrubbers rely on the kinetic energy of the liquid stream. The typical removal efficiency of a jet or fume scrubber (for particles 10 μ or less) is lower than that of a venturi scrubber. Spray towers can handle larger gas flows with minimal pressure drop and are therefore often used as precoolers. Because wet scrubbers may contribute to corrosion, removal of water from the effluent gas of the scrubbers may be necessary.

Another consideration is that wet scrubbing results in a liquid effluent. Wet-scrubbing technology is used where the contaminant cannot be removed easily in a dry form, soluble gases and wettable particles are present, and the contaminant will undergo some subsequent wet process (such as recovery, wet separation or settling, or neutralization). Gas flow rates range from 20 to 3,000 (m^3/min), Gas flow rates of approximately 2,000 (m^3/min) may have a corresponding pressure drop of 25 cm water column. The selection of PM emissions control equipment is influenced by environmental, economic, and engineering factors.

- *Environmental factors* include (a) the impact of control technology on ambient air quality; (b) the contribution of the pollution control system to the volume and characteristics of wastewater and solid waste generation; and (c) maximum allowable emissions requirements.
- *Economic factors* include (a) the capital cost of the control technology; (b) the operating and maintenance costs of the technology; and (c) the expected lifetime and salvage value of the equipment.
- *Engineering factors* include (a) contaminant characteristics such as physical and chemical properties - concentration, particulate shape, size distribution, chemical reactivity, corrosivity, abrasiveness, and toxicity; (b) gas stream characteristics such as volume flow rate, dust loading, temperature, pressure, humidity, composition, viscosity, density, reactivity, combustibility, corrosivity, and toxicity; and (c) design and performance characteristics of the control system such as pressure drop, reliability, dependability, compliance with utility and maintenance requirements, and temperature limitations, as well as size, weight, and fractional efficiency curves for particulates and mass transfer or contaminant destruction capability for gases or vapors.

ESPs can handle very large volumetric flow rates at low pressure drops and can achieve very high efficiencies (99.9%). They are roughly equivalent in costs to fabric filters and are relatively inflexible to changes in process operating conditions. Wet scrubbers can also achieve high efficiencies and have the major advantage that some gaseous pollutants can be removed simultaneously with the particulates. However, they can only handle smaller gas flows (up to 3,000 m^3/min), can be very costly to operate (owing to a high pressure drop), and produce a wet sludge that can present disposal problems. For a higher flue gas flow rate and greater than 99% removal of PM, ESPs and fabric filters are the equipment of choice, with very little difference in costs.

NITROGEN OXIDES

Nitrogen oxides (NO_x) in the ambient air consist primarily of nitric oxide (NO) and nitrogen dioxide (NO_2). These two forms of gaseous nitrogen oxides are significant pollutants of the lower atmosphere. Another form, nitrous oxide (N_2O), is a greenhouse gas. At the point of discharge from man-made sources, nitric oxide, a colorless, tasteless gas, is the predominant form of nitrogen oxide. Nitric oxide is readily converted to the much more harmful nitrogen dioxide by chemical reaction with ozone present in the atmosphere. Nitrogen dioxide is a yellowish-orange to reddish-brown gas with a pungent, irritating odor, and it is a strong oxidant.

A portion of nitrogen dioxide in the atmosphere is converted to nitric acid (HNO_3) and ammonium salts. Nitrate aerosol (acid aerosol) is removed from the atmosphere through wet or dry deposition processes similar to those that remove sulfate aerosol. Only about 10% of all NO_x emissions come from anthropogenic sources. The rest is produced naturally by anaerobic biological processes in soil and water, by lightning and volcanic activity, and by photochemical destruction of nitrogen compounds in the upper atmosphere. About 50% of emissions from anthropogenic sources come from fossil-fuel-fired heat and electricity generating plants and slightly less from motor vehicles. Other sources include industrial boilers, incinerators, the manufacture of nitric acid and other nitrogenous chemicals, electric arc welding processes, the use of explosives in mining, and farm silos. Worldwide annual emissions of anthropogenic nitrogen oxides are estimated at approximately 50 million metric tons.

Annual mean concentrations of nitrogen dioxide in urban areas throughout the world are in the range of 20 to 90 mg/m^3. Maximum half-hour values and maximum 24-hour values of nitrogen dioxide can approach 850 and 400 mg/m^3, respectively. Hourly averages near very busy roads often exceed 1,000 mg/m^3. Urban outdoor levels of nitrogen dioxide vary according to time of day, season, and meteorological conditions. Typically, urban concentrations peak during the morning and afternoon rush hours. Levels are also higher in winter in cold regions of the world than in other seasons because of the increased use of heating fuels. Finally, since the conversion of nitrogen dioxide from nitric oxide depends on solar intensity, concentrations are often greater on warm sunny days. Nitrogen oxides decay rapidly as polluted air moves away from the source. Concentrations of nitrogen oxides in rural areas without major sources are typically close to background levels. However, nitrogen oxides can travel long distances in the upper atmosphere, contributing to elevated ozone levels and acidic depositions far from sources of emissions.

The United States generates about 20 million metric tons of nitrogen oxides per year, about 40% of which is emitted from mobile sources. Of the 11 million to 12 million metric tons of nitrogen oxides that originate from stationary sources, about 30% is the result of fuel combustion in large industrial furnaces and 70% is from electric utility furnaces.

Concentrations of nitrogen dioxide in homes may considerably exceed outdoor levels and may therefore be more important for human health. Large sources of indoor nitrogen dioxide include cigarette smoke, gas-fired appliances, and space heaters. Nitrogen dioxide concentrations in kitchens with unvented gas appliances can exceed 200 mg/m^3 over a period of several days. Maximum 1-hour concentrations during cooking may reach 500 to 1,900 mg/m^3, and 1,000-2,000 mg/m^3 where a gas-fired water heater is also in use. The smoke from one cigarette may contain 150,000 to 225,000 mg/m^3 of nitric oxide and somewhat less nitrogen dioxide. Epidemiologic studies have rarely detected effects on children or adults from exposure to outdoor nitrogen dioxide. Available data from animal toxicological experiments rarely indicate effects of acute exposure to nitrogen dioxide concentrations of less than 1,880 mg/m^3. Asthmatics are likely to be the group most sensitive to exposure to nitrogen oxides.

Some studies have reported reversible effects on pulmonary function of asthmatics exercising intermittently after 30 minutes of exposure to nitrogen dioxide concentrations as low as 560 mg/m^3. However, the health impact of the change in pulmonary function is unclear; the change of about 10% is within the range of physiological variation and is not necessarily adverse. At levels above 3,760 mg/m^3, normal subjects have demonstrated substantial changes in pulmonary function. Studies with animals have found that several weeks to months of exposure to nitrogen dioxide concentrations less than 1,880 mg/m^3 causes both reversible and irreversible lung effects and biochemical changes. Animals exposed to nitrogen dioxide levels as low as 940 mg/m^3 for six months may experience destruction of cilia, alveolar tissue disruption, obstruction of the respiratory bronchioles, and increased susceptibility to bacterial infection of the lungs. Rats and rabbits exposed to higher levels experience more severe tissue damage, resembling emphysema. The available data suggest that the physiological effects of nitrogen dioxide on humans and animals are due more to peak concentrations than to duration or to total dose.

In addition to the health risks, nitrogen dioxide in reaction to textile dyes can cause fading or yellowing of fabrics. Exposure to nitrogen dioxide can also weaken fabrics or reduce their affinity for certain dyes. Industry has devoted considerable resources to developing textiles and dyes resistant to nitrogen oxide exposure.

Nitrogen oxides are precursors of both acid precipitation and ozone, each of which is blamed for injury to plants. While nitric acid is responsible for only a smaller part of hydrogen ion (H^+) concentration in wet and dry acid depositions, the contribution of nitrogen oxide emissions to acid deposition could be more significant. It is nitrogen oxide that absorbs sunlight, initiating the photochemical processes that produce nitric acid. Approximately 90 to 95% of the nitrogen oxides emitted from power plants are nitric oxide; this slowly converts to nitrogen dioxide in the presence of ozone.

The extent and severity of the damage attributable to acid depositions are difficult to estimate, since impacts vary according to soil type, plant species, atmospheric conditions, insect populations, and other factors that are not well understood. Nitrates in precipitation may actually increase forest growth in areas with nitrogen-deficient soils.

However, the fertilizing effect of nitrates (and sulfates) may be counterbalanced by the leaching of potassium, magnesium, calcium, and other nutrients from forest soils. There is little evidence that agricultural crops are being injured by exposures to nitrates in precipitation. The amount of nitrates in rainwater is almost always well below the levels applied as fertilizer.

The most evident damage from acid depositions is to freshwater lake and stream ecosystems. Acid depositions can lower the pH of the water, with potentially serious consequences for fish, other animal, and plant life. Lakes in areas with soils containing only small amounts of calcium or magnesium carbonates that could help neutralize acidified rain are especially at risk. Few fish species can survive the sudden shifts in pH (and the effects of soluble substances) resulting from atmospheric depositions and runoff of contaminated waters; affected lakes may become completely devoid of fish life. Refer back to Figure 1 for the mechanisms responsible for acid deposition and rain in the environment.

Acidification also decreases the species variety and abundance of other animal and plant life. "Acid pulses" have been associated with the fish kills observed in sensitive watersheds during the spring meltdown of the snowpack. The atmospheric deposition of nitrogen oxides is a substantial source of nutrients that damage estuaries by causing algal blooms and anoxic conditions. Emissions of nitrogen oxides are also a precursor of ground-level ozone (O_3), which is potentially a more serious problem.

Plant scientists blame tropospheric ozone for 90% of the injury to vegetation in North America. Ozone can travel long distances from the source and can contribute to elevated ozone concentrations even in rural areas. Since the meteorological and climatic conditions that favor the production of ozone-abundant sunshine are also good for agriculture, ozone has the potential to cause large economic losses from reductions in crop yields. Nitrogen dioxide affects visibility by absorbing short-wavelength blue light. Since only the longer wavelengths of light are visible to the eye, nitrogen dioxide appears yellowish to reddish brown in color. Nitrogen oxides can also combine with photochemical oxidants to form smog.

Pollution Prevention Practices and Control Technologies

The first priority in designing a strategy to control nitrogen oxides is to protect human health. Human health impacts appear to be related to peak exposures to nitrogen oxides (NO_x). In addition to potentially damaging human health, nitrogen oxides are precursors to ozone (O_3) formation, which can harm human health and vegetation. Finally, nitrogen oxides contribute to acid deposition, which damages vegetation and aquatic ecosystems. The extent to which NO_x emissions harm human health depends on ground-level concentrations and the number of people exposed. Source location can affect these parameters. Gases emitted in areas with meteorological, climatological, and topographical features that favor dispersion will be less likely to concentrate near the ground. However, some meteorological conditions, such as inversion, may result in significantly higher ambient levels. Sources away from population centers will expose fewer people to harmful pollution. Plant siting is a critical feature in any air pollution management strategy. However, due to the dispersion of nitrogen oxides that may contribute to ozone formation and acid deposition far from the source, relying on plant siting alone is not a recommended strategy. The long-term objective must be to reduce total emissions. Effective control of NO_x emissions require controls on both stationary sources and mobile transport sources. Each requires different strategies.

Nitrogen oxides are produced in the combustion process by two different mechanisms: (a) the burning the nitrogen in the fuel, primarily coal or heavy oil fuel NO_x and (b) high-temperature oxidation of the molecular nitrogen in the air used for combustion (thermal NO_x). Formation of fuel NO_x depends on combustion conditions, such as oxygen concentration and mixing patterns, and on the nitrogen content of the fuel. Formation of thermal NO_x depends on combustion temperature. Above 1,538° C, NO_x formation rises exponentially with increasing temperature. The relative contributions of fuel NO_x and thermal NO_x to emissions from a particular plant depend on the combustion conditions, the type of burner, and the type of fuel. Approaches for controlling NO_x from stationary sources can address fuel NO_x, thermal NO_x, or both. One way of controlling NO_x emissions is to use low-nitrogen fuels. Another is to modify combustion conditions to generate less NO_x. Flue gas treatment techniques, such as selective catalytic reduction (SCR) processes, can remove NO_x. Coals and residual fuel oils containing organically bound nitrogen contribute to over 50% of total emissions of NO_x according to some estimates. The nitrogen content of U.S. coal ranges between 0.5% and 2% and that of residual fuel oil between 0.1% and 0.5%. In many circumstances, the most cost-effective means of reducing NO_x emissions will be to use low-nitrogen fuels such as natural gas. Natural gas used as fuel can emit 60% less NO_x than coal and virtually no particulate matter or sulfur oxides.

Combustion control may involve any of three strategies: (a) reducing peak temperatures in the combustion zone; (b) reducing the gas residence time in the high-temperature zone; and (c) reducing oxygen concentrations in the combustion zone. These changes in the combustion process can be achieved either through process modifications or by modifying operating conditions on existing furnaces. Process modifications include using specially designed low-NO_x burners, reburning, combustion staging, gas recirculation, reduced air preheat and firing rates, water or steam injection, and low excess air (LEA) firing. These modifications are capable of reducing NO_x emissions by 50 to 80%. The method of combustion control used depends on the type of boiler and the method of firing fuel.

New low-NO_x burners are effective in reducing emissions from both new power plants and existing plants that are being retrofitted. Low NO_x burners limit the formation of nitrogen oxides by controlling the mixing of fuel and air, in effect automating low-excess-air firing or staged combustion. Compared with older conventional burners, low-NO_x burners reduce emissions of NO_x by 40 to 60%. Because low-NO_x, burners are relatively inexpensive, power utilities have been quick to accept them; in fact, low-NO_x burners are now a standard part of new designs. Capital costs for low-NO_x burners with overfire air (OFA) range between US$20 and US$25 per kilowatt. Unfortunately, low-NO_x burners are not suitable for reducing NO_x emissions from cyclone fired boilers, which emit large quantities of NO_x due to their high operating temperatures. Because combustion takes place outside the main furnace, the use of low-NO_x burners is not suitable for these applications. However, reburning technology can reduce NO_x emissions.

Reburning is a technology used to reduce NO_x emissions from cyclone furnaces and other selected applications. In reburning, 75 to 80% of the furnace fuel input is burned in the furnace with minimum excess air. The remaining fuel (gas, oil, or coal) is added to the furnace above the primary combustion zone. This secondary combustion zone is operated substoichiometrically to generate hydrocarbon radicals that reduce to nitrogen the nitrogen oxides that are formed. The combustion process is then completed by adding the balance of the combustion air through overfire air ports in a final burnout zone at the top of the furnace.

Staged combustion (off-stoichiometric combustion) burns the fuel in two or more steps. Staged combustion can be accomplished by firing some of the burners fuel-rich and the rest fuel-lean, by taking some of the burners out of service and allowing them only to admit air to the furnace, or by firing all the burners fuel-rich in the primary combustion zone and admitting the remaining air over the top of the flame zone. Staged combustion techniques can reduce NO_x emissions by 20 to 50%. Conventional OFA alone can reduce emissions of NO_x by 30%, and advanced OFA has the potential of reducing them still further, although potential for corrosion and slagging exists. Capital costs for conventional and advanced OFA range between US$5 and $10 per kilowatt.

Flue gas recirculation (FGR) is the rerouting of some of the flue gases back to the furnace. By using the flue gas from the economizer outlet, both the furnace air temperature and the furnace oxygen concentration can be reduced. However, in retrofits FGR can be very expensive. Flue gas recirculation is typically applied to oil- and gas-fired boilers and reduces NO_x emissions by 20 to 50%. Modifications to the boiler in the form of ducting and an energy efficiency loss due to the power requirements of the recirculation fans can make the cost of this option higher.

Reduced air preheat and reduced firing rates lower peak temperatures in the combustion zone, thus reducing thermal NO_x. This strategy, however, carries a substantial energy penalty. Emissions of smoke and carbon monoxide need to be controlled, which reduces operational flexibility.

Water or steam injection reduces flame temperatures and thus thermal NO_x. Water injection is especially effective for gas turbines, reducing NO_x emissions by about

80% at a water injection rate of 2%. For a gas turbine, the energy penalty is about 1%, but for a utility boiler it can be as high as 10%. For diesel-fired units, 25 to 35% reductions in NO_x emissions can be achieved using water fuel mixtures.

Low-excess-air firing (LEA) is a simple, yet effective technique. Excess air is defined as the amount of air in excess of what is theoretically needed to achieve 100% combustion. Before fuel prices rose, it was not uncommon to see furnaces operating with 50 to 100% excess air. Currently, it is possible to achieve full combustion for coal-fired units with less than 15-30% excess air. Studies have shown that reducing excess air from an average of 20% to an average of 14% can reduce emissions of NO_x by an average of 19%.

Techniques involving low-excess-air firing staged-combustion, and flue gas recirculation are effective in controlling both fuel NO_x and thermal NO_x. The techniques of reduced air preheat and reduced firing rates (from normal operation) and water or steam injection are effective only in controlling thermal NO_x. These will therefore not be as effective for coal-fired units since about 80% of the NO_x emitted from these units is fuel NO_x.

Flue gas treatment (FGT) is more effective in reducing NO_x emissions than are combustion controls, although at higher cost. FGT is also useful where combustion controls are not applicable. Pollution prevention measures, such as using a high-pressure process in nitric acid plants, is more cost-effective in controlling NO_x emissions. FGT technologies have been primarily developed and are most widely used in Japan. The techniques can be classified as selective catalytic reduction, selective noncatalytic reduction, and adsorption.

The most cost-effective methods of reducing emissions of NO_x are the use of low-NO_x burners and the use of low nitrogen fuels such as natural gas. Natural gas has the added advantage of emitting almost no particulate matter or sulfur dioxide when used as fuel. Other cost-effective approaches to emissions control include combustion modifications. These can reduce NO_x emissions by up to 50% at reasonable cost. Flue gas treatment systems can achieve greater emissions reductions, but at a much higher cost.

Selective catalytic reduction (SCR) is currently the most developed and widely applied FGT technology. In the SCR process, ammonia is used as a reducing agent to convert NO_x to nitrogen in the presence of a catalyst in a converter upstream of the air heater. The catalyst is usually a mixture of titanium dioxide, vanadium pentoxide, and tungsten trioxide. SCR can remove 60-90% of NO_x from flue gases. Unfortunately, the process is very expensive (US$40-$80/kilowatt), and the associated ammonia injection results in an ammonia slip stream in the exhaust. In addition, there are safety and environmental concerns associated with anhydrous ammonia storage.

Selective noncatalytic reduction (SNCR) using ammonia- or urea-based compounds is still in the developmental stage. Early pilot studies indicate that SNCR systems can reduce NO_x emissions by 30 to 70%. Capital costs for SNCR are expected to be much lower than for SCR processes, ranging between US$10 and US$20 per kilowatt. Several dry adsorption techniques are available for simultaneous control of NO_x and sulfur oxides (SO_x). One type of system uses activated carbon with ammonia (NH_3) injection to simultaneously reduce the NO_x to nitrogen (N_2) and oxidize the SO_2 to sulfuric acid (H_2SO_4). If there is no sulfur in the fuel, the carbon acts as a catalyst for NO_x reduction only. Another adsorption system uses a copper oxide catalyst that adsorbs sulfur dioxide to form copper sulfate. Both copper oxide and copper sulfate are reasonably good catalysts for the selective reduction of NO_x with NH_3. This process, which has been installed on a 40-megawatt oil-fired boiler in Japan, can remove about 70% of NO_x and 90% of SO_2 from flue gases. For *coal-fired boilers* the most widely applied control technologies involve combustion modifications, including low-excess-air firing, staged combustion, and use of low-NO_x burners. For *oil-fired* boilers, the most widely applied techniques include flue gas recirculation, in addition to the techniques used for coal-fired units. For *gas-fired units,* which in any case emit 60% less NO_x than coal-fired units, the primary control technologies include flue gas recirculation and combustion modifications. Finally, for *diesel plants,* the common technologies are water-steam injection, and SCR technology.

GROUND-LEVEL OZONE

Ozone (O_3) is a colorless, reactive oxidant gas that is a major constituent of atmospheric smog. Ground-level ozone is formed in the air by the photochemical reaction of sunlight and nitrogen oxides (NO_x), facilitated by a variety of volatile organic compounds (VOCs), which are photochemically reactive hydrocarbons. The relative importance of the various VOCs in the oxidation process depends on their chemical structure and reactivity. Ozone may be formed by the reaction of NO_x and VOCs under the influence of sunlight hundreds of kilometers from the source of emissions. Ozone concentrations are influenced by the intensity of solar radiation, the absolute concentrations of NO_x and VOCs, and the ratio of NO_x to VOCs. Diurnal and seasonal variations occur in response to changes in sunlight. In addition, ground-level ozone accumulation occurs when sea breezes cause circulation of air over an area or when temperature-induced air inversions trap the compounds that produce smog. Peak ground-level ozone concentrations are measured in the afternoon. Mean concentrations are generally highest during the summer. Peak concentrations of ground-level ozone rarely last longer than two to three hours. Registered average natural background concentrations of ground-level ozone are around 30 to 100 $\mu g/m^3$. Short-term (one-hour) mean ambient concentrations in urban areas may exceed 300 to 800 $\mu g/m^3$. Both natural and anthropogenic sources contribute to the emission of ground-level ozone precursors, and the composition of emissions sources may show large variations across locations. VOCs occurring naturally due to emissions from trees and plants may account for as much as two thirds of ambient VOCs in some locations. Anaerobic biological processes, lightning, and volcanic activity are the main natural contributors to atmospheric NO_x occasionally accounting for as much as 90% of all NO_x emissions.

The main health concern of exposure to ambient ground-level ozone is its effect on the respiratory system, especially on lung function. Several factors influence these health impacts, including the concentrations of ground-level ozone in the atmosphere, the duration of exposure, average volume of air breathed per minute (ventilation rate), and the length of intervals between short-term exposures. Most of the evidence on the health impacts of ground-level ozone comes from animal studies and controlled clinical studies of humans focusing on short-term acute exposure. Clinical studies have documented an association between short-term exposure to ground-level ozone at concentrations of 200 to 500 $\mu g/m^3$ and mild temporary eye and respiratory irritation as indicated by symptoms such as coughing, throat dryness, eye and chest discomfort, thoracic pain, and headache. Temporary decrements in pulmonary function have been found in children at hourly average ground-level ozone concentrations of 160 to 300 $\mu g/m^3$. Similar impacts have been observed after 2.5-hour exposure of heavily exercising adults and children to concentrations of 240 $\mu g/m^3$. Lung function losses, however, have been reversible and relatively mild even at concentrations of 360 $\mu g/m^3$, with a great variety of personal responses. Full recovery of respiratory functions normally occurs within 24 to 48 hours after exposure.

Animal studies have also demonstrated an inflammatory response of the respiratory tract following exposure to ground-level ozone at 1,000 $\mu g/m^3$ for four hours. Although biochemical and morphological alterations in the red blood cells were found in several animal species after exposure to ground-level ozone concentrations of 400 $\mu g/m^3$ for four hours, no consistent changes have been demonstrated in humans, even at concentrations as high as 1,200 $\mu g/m^3$, and extrapolation of such impacts to humans has not been supported. Exposure to elevated concentrations of ground-level ozone has been shown to reduce physical performance, since the increased ventilation rate during physical exercise increases the effects of exposure to ground-level ozone. There is no evidence that smokers, children, older people, asthmatics, or individuals with chronic obstructive lung disease are more responsive to ground-level ozone exposure than others. Ground-level ozone may, however, make the respiratory airways more responsive to other inhaled toxic substances and bacteria. In addition, a synergistic effect of ground-level ozone and sulfur dioxide has been found, indicating that sulfur dioxide potentiates the effects of ground-level ozone.

Besides short-term impacts, the potential for irreversible damage to the lungs from repeated exposure over a longer period of time has been a health concern. Some studies have found an association between accelerated loss of lung function over a longer period of time (five years) and high oxidant levels in the atmosphere. The WHO has noted that the length of the recovery period between successive episodes of high ground-level ozone concentrations and the number of episodes in a season may be important factors in the nature and magnitude of health impacts, since prolonged acute exposure to ground-level ozone concentrations of 24 to 360 $\mu g/m^3$ result in progressively larger changes in respiratory function. However, a cross-sectional analysis based on large samples from multiple locations in the United States found no correlation between chronic ground-level ozone pollution and reduced lung function except for the highest 20% of ground-level ozone exposures, suggesting the possibility of a lower threshold for effects of chronic ground-level ozone exposure. No evidence has been found of an association between peak oxidant concentrations and daily mortality rates of the general population.

Elevated ground-level ozone exposures affect agricultural crops and trees, especially slow growing crops and long-lived trees. Ozone damages the leaves and needles of sensitive plants, causing visible alterations such as defoliation and change of leaf color. In North America, tropospheric ozone is believed responsible for about 90% of the damage to plants. Agricultural crops show reduced plant growth and decreased yield. According to the U.S. Office of Technology Assessment (OTA), a 120 $\mu g/m^3$ seasonal average of seven-hour mean ground-level ozone concentrations is likely to lead to reductions in crop yields in the range of 16 to 35% for cotton, 0.9 to 51% for wheat, 5.3 to 24% for soybeans, and 0.3 to 5.1% for corn. In addition to physiological damage, ground-level ozone may cause reduced resistance to fungi, bacteria, viruses, and insects, reducing growth and inhibiting yield and reproduction. These impacts on sensitive species may result in declines in agricultural crop quality and the reduction of biodiversity in natural ecosystems. The impact of the exposure of plants to ground-level ozone depends not only on the duration and concentration of exposure but also on its frequency, the interval between exposures, the time of day and the season, site-specific conditions, and the developmental stage of plants. Additionally, ground-level ozone is part of a complex relationship among several air pollutants and other factors such as climatic and meteorological conditions and nutrient balances. For example, the presence of sulfur dioxide may increase the sensitivity of certain plants to leaf injury by ground-level ozone. Also the presence of ground-level ozone may increase the growth-suppressing effects of nitrogen dioxide.

Pollution Prevention Practices and Control Technologies

Since ground-level ozone is formed by the photochemical reaction of nitrogen oxides and certain hydrocarbons, abatement strategies should focus not only on reduction of emissions of these substances but also on their ratio and balance. In areas where NO_x concentrations are high relative to VOCs, the abatement of VOC emissions can reduce the formation of ground-level ozone, while reduction in nitrogen oxides may actually increase it. In areas where the relative concentration of VOCs is high compared with nitrogen oxides, ground-level ozone formation is "NO_x-limited," and NO_x reductions generally work better than VOC abatement.

To recap, surrounding the earth at a height of about 25 kilometers is the stratosphere, which is rich in ozone, and its purpose is to prevent the sun's harmful ultraviolet (UV) rays from reaching the earth. UV rays have an adverse effect on all living organisms, including marine life, crops, animals and birds, and humans. In humans, UV is known to affect the immune system; to cause skin cancer, eye damage, and cataracts; and to increase susceptibility to infectious diseases, such as malaria. In 1974, it was hypothesized that chlorinated compounds were able to persist in the atmosphere long enough to reach the stratosphere, where solar radiation would break up the molecules and release chlorine atoms that would destroy the ozone layer. Mounting evidence and the discovery of the Antarctic ozone hole in 1985 led to the global program to control chlorofluorocarbons (CFCs) and other ozone-destroying chemicals. In addition to Antarctica, ozone loss is now present over New Zealand, Australia, southern Argentina and Chile, North America, Europe, and Russia. The ozone-depleting substances (ODSs) of concern are CFCs, halons, methyl chloroform (1,1,1,-trichloroethane; MCF), carbon tetrachloride (CTC), hydrochlorofluorocarbons (HCFCs), and methyl bromide. CFC-11 was assigned an ODP of 1.0; all other chemicals have an ODP relative to that of CFC-11. An ODP higher than 1.0 means that the chemical has a greater ability than CFC-11 to destroy the ozone layer; an ODP lower than 1.0 means that the chemical's ability to destroy the ozone layer is less than that of CFC-11. In September 1987, the Montreal Protocol on *Substances that Deplete the Ozone Layer* (the *Protocol*) was signed by 25 nations and the European Community. The Protocol was the first international environmental agreement, and its signing by so many nations represented a major accomplishment, and a major shift in the approach to handling global environmental problems. The Protocol called for a freeze on the production of halons and a requirement to reduce the production of CFCs by 50% by 1999. However, new scientific evidence surfaced after the entry into force of the Protocol, indicating that ozone depletion was more serious than originally thought. Accordingly, in 1990 (London), 1992 (Copenhagen), and 1995 (Vienna), amendments were made to the Protocol to regulate the phaseout of the original chemicals and the control and phase-out of additional chemicals. The principal provisions of the Montreal Protocol as it now stands are as follows:

- Production of CFCs, halons, methyl chloroform, and CTC ceased at the end of 1995 in industrial countries and will cease by 2010 in developing countries. Developing countries are defined in the Protocol as those that use less than 0.3 kilograms (kg) of ODS per capita per year. These are called

Article 5 countries in reference to the defining article in the Montreal Protocol.

- HCFCs, originally developed as a less harmful class of CFC alternatives, will be phased out by 2020 in industrial countries, with some provisions for servicing equipment to 2030. Developing countries are to freeze consumption by 2016 (base year 2015) and phase out use by 2040.
- Consumption and production of methyl bromide will end in 2005 in industrial countries (subject to phase-out stages and exemptions) and in 2015 in developing countries.

It was early recognized that undue hardships might be experienced by industry in developing countries as they implemented replacement technologies. Therefore, a fund was established under the Montreal Protocol to pay for incremental costs such as technical expertise and new technologies, processes, and equipment associated with the phase-out. The Multilateral Fund of the Montreal Protocol is managed by an executive committee consisting of delegates from seven developing countries and seven industrial countries.

In general, ODSs are most often used in the following applications: as propellants in aerosols (CFCs and HCFCs); in refrigeration, air conditioning, chillers, and other cooling equipment (CFCs and HCFCs); to extinguish fires (halons); in the manufacture of foams (CFCs and HCFCs); as solvents for cleaning printed circuit boards and precision parts and degreasing metal parts (CFCs, HCFCs, methyl chloroform, and CTC); in a variety of other areas, such as inks and coatings and medical applications (CFCs, HCFCs, methyl chloroform, and CTC); as a fumigant (methyl bromide). The following discussion provides a brief overview of the alternatives to ODSs that have been developed in various industry sectors. It is not intended to be an exhaustive listing of all alternatives, but it does summarize some proven alternatives. The selection of any alternative should be made with due consideration of other issues that could affect the final choice. Identification, development, and commercialization of alternatives to ODSs are going on constantly. For this reason it is important to seek information on the latest alternatives. For any alternative, consideration needs to be given to, for example, its compatibility with existing equipment, its health and safety aspects, its direct global-warming potential, whether it increases or decreases energy consumption, and the costs that may be incurred in eventual conversion to a non-ODS technology if an interim HCFC alternative is chosen. New ways of doing business may also develop in the course of selecting alternatives. For example, many electronics companies have now converted their manufacturing plants to "no-clean" technology. The benefits include elimination of circuit board cleaning after soldering, savings in chemical costs and waste disposal costs, savings in maintenance and energy consumption, improved product quality, and advances toward new technologies such as fluxless soldering. The selection of any alternative should not be made in isolation from the factors listed above.

Flexible and Rigid Foams

Zero-ODP alternatives are the substitutes of choice in many foam-manufacturing applications. However, the use of HCFCs is sometimes necessary in order to meet some product specifications. The viability of liquid hydrofluorocarbon (HFC) isomers in this industry remains to be proved, and hydrocarbon alternatives need to be better qualified, as well.

The issues in these evaluations are safety as related to toxicity and flammability, environmental impact as related to the generation of volatile organic compounds and global warming, product performance as related to insulating properties, conformity to fire codes, and the like, cost and availability, and regulatory requirements.

Some of the alternatives for specific products of the foam manufacturing sector are described briefly below. The alternatives are listed as short-term and long-term options, without an elaboration of the merits of each.

Rigid polyurethane foams used in refrigerators and freezers - Alternatives include hydrocarbons (pentane) and HCFC-141b; long-term alternatives include HFCs (134a, -245, -356, -365). Vacuum panels may be used in the future.

Rigid polyurethane for other appliances. Alternatives include HCFC-141b, HCFC-22, blends of -22 and HCFC-142b, pentane, and carbon dioxide/water blowing. In the long term, the alternatives include HFCs.

Rigid polyurethane used for boardstock and flexible-faced laminations - Alternatives include HCFC-141b and pentane; in the long term, the use of HFCs should be developed.

Sandwich panels of rigid polyurethane - HCFC-141b, HCFC-22, blends of HCFC-22 and -141b, pentane, and HFC-134a are now used as alternatives to CFCs in this application. In the long term, HFCs and carbon dioxide/water will be the replacement technologies.

Spray applications of rigid polyurethane - Alternatives currently in use for spray applications include carbon dioxide/water and HCFC-141b. Long-term alternatives will be HFCs.

Slabstock of rigid polyurethane - Alternatives include HCFC-141b; long-term alternatives include HFCs and carbon dioxide/water. Pentane may also be used.

Rigid polyurethane pipe construction - CFCs in this application are being replaced by carbon dioxide/water, HCFC-22, blends of HCFC-22 and -142b, HCFC-141b, and pentanes. Long-term alternatives will include HFCs and carbon dioxide/water. For district central heating pipes, pentane and carbon dioxide/water are the preferred technologies.

Polyurethane flexible slab - Many alternatives now exist for flexible slab construction, including extended range polyols, carbon dioxide/water, softening agents, methylene chloride, acetone, increased density, HCFC-141b, pentane, and other alternative technologies such as accelerated cooling and variable pressure. The long term will probably see the use of injected carbon dioxide and alternative technologies.

Molded flexible polyurethane - The standard now is carbon dioxide/water blowing.

Integral-skin polyurethane products - The current alternatives for these products include HCFC-22, hydrocarbons, carbon dioxide/water, HFC-134a, pentanes, and HCFC-141b. The long-term alternate is expected to be carbon dioxide/water.

Phenolic foams - Phenolic foams can now be made using HCFC-141b, hydrocarbons, injected carbon dioxide, or HFC-152a instead of CFCs. In the long term, HFCs may be the predominant alternative.

Extruded polystyrene sheet - Alternatives currently include HCFC-22, hydrocarbons, injected carbon dioxide, and HFC-152a. In the long term, these same alternatives (except for HCFC-22) will be used, along with possible use of atmospheric gases.

Extruded polystyrene boardstock - HCFC-22 and -142b and injected carbon dioxide are the current alternatives. Long-term alternatives will be HFCs and injected carbon dioxide.

Polyolefins - Polyolefins are now manufactured using alternatives such as hydrocarbons, HCFC22 and -142b, injected carbon dioxide, and HFC152a. Hydrocarbons and injected carbon dioxide will be long-term alternatives.

Refrigeration, Air Conditioning, and Heat Pumps - Immediate replacements for many applications include hydrocarbons, HFCs, and HCFCs. Some of these will also be candidates for long-term replacement of the currently used CFCs. This following briefly describes the alternatives that are available for specific refrigeration, air conditioning, and heat pump applications.

Refrigeration, Air Conditioning, and Heat Pump Application

Domestic refrigeration - Two refrigerant alternatives are predominant for the manufacture of new domestic refrigerators. HFC-134a has no ozone depletion potential and is nonflammable, but it has a high global-warming potential (GWP). HC-600a is flammable, has a zero ODP, and has a GWP approaching zero. Other alternatives for some applications include HFC-152a and binary and ternary blends of HCFCs and HFCs. Retrofitting alternatives may include HCFC/HFC blends, after CFCs are no longer available. However, the results obtained so far are still not satisfactory. Neither HC-600a nor HFC-134a is considered an alternative for retrofitting domestic refrigeration appliances, but preliminary data indicate that a combination of the two may be a retrofit, or "servicing," candidate.

Commercial refrigeration - Alternatives to CFCs for new commercial refrigeration equipment include HCFCs (including HCFC mixtures) and HFCs and HFC mixtures. Retrofit of existing equipment is possible by using both HCFCs and HFCs, in conjunction with reduced charges and more efficient compressors. Hydrocarbons are, to a limited extent, applied in hermetically sealed systems.

Cold storage and food processing - Although there has been a return to the use of ammonia for some cold storage facilities, there are safety issues, and some regulatory jurisdictions restrict its use. Other alternatives to CFCs in cold storage and large commercial food preservation facilities include HCFC-22 and HFC blends. Hydrocarbons and HCFC-22 will continue to be the favored alternatives until equipment using other alternatives is developed; ammonia will be used in selected applications.

Industrial refrigeration - New industrial refrigeration systems that are used by the chemical, petrochemical, pharmaceutical, oil and gas, and metallurgical industries, as well for industrial ice making and for sports and leisure facilities, can use ammonia and hydrocarbons as the refrigerant. Although the product base concerned is small, existing CFC equipment can be retrofitted to use HCFC-22, HFCs and HFC blends, and hydrocarbons.

Air conditioning and heat pumps (air-cooled systems) - Equipment in this category generally uses HCFC-22 as the refrigerant. Alternatives under investigation include HFCs and HCs (in particular, propane). The most promising of these are the nonflammable, nontoxic HFC compounds, although there is more interest in propane in various regions. HCFs have been criticized for their global warming potential, but their total equivalent warming impact (TEWI), a measure that combines GWP and energy efficiency, is equal to or lower than that of the other alternatives.

Air conditioning (water chillers) - HCFC-22 has been used in small chillers, and CFC-11 and -12 have been used in large chillers that employ centrifugal compressors. HFC blends are now beginning to be introduced to replace HCFC-22 in small chillers; HCFC-123 and HFC-134a are the preferred replacements for large units. Chillers that have used CFC-114 can be converted to use HCFC-124 or can be replaced by HFC-134a units.

Transport refrigeration - HCFC-22 and CFC-502 have been the refrigerants of choice for transport refrigeration units, although some applications are using ammonia as the refrigerant. The alternatives include various HFC blends.

Automotive air conditioning - The manufacturers of new automobiles have chosen HFC-134a as the fluid for air conditioning units, and retrofit kits are now available to allow older automobiles to convert to this alternative.

Heat pumps (heating-only and heat recovery) - New heating-only heat pumps use HCFC-22. HFC-134a is an alternative for retrofitting existing heat pumps, and investigation into the use of ammonia for large-capacity heat pumps is continuing. Other alternatives being explored include propane, other hydrocarbons, and hydrocarbon blends.

Solvents, Coatings, Inks, and Adhesives Applications

There now exist alternatives or sufficient quantities of controlled substances for almost all applications of ozone-depleting solvents. Exceptions have been noted for certain laboratory and analytical uses and for manufacture of space shuttle rocket motors. HCFCs have not been adopted on a large scale as alternatives to CFC solvents. In the near term, however, they may be needed as the conventional substances in some limited and unique applications. HCFC-141b is not a good replacement for methyl chloroform (1,1,1-trichloroethane) because its ODP is three times higher. Alternatives for specific uses of ozone-depleting solvents are briefly described below.

Electronics cleaning - For most uses in the electronics industry, ozone-depleting solvents can be replaced easily and, often, economically. A wide choice of alternatives exists. If technical specifications do not require postsolder cleaning, no-clean is the preferred technology. If cleaning is required, the use of water-soluble chemistry has generally proved to be reliable. There are however limitations, whereby water-soluble chemistry is not suitable for all applications.

Precision cleaning - Precision cleaning applications are defined as requiring a high level of cleanliness in order to maintain low-clearance or high-reliability components in working order. To meet rigorous specifications, the alternatives that have been developed include solvent and nonsolvent applications. Solvent options include alcohols, aliphatic hydrocarbons, HCFCs and their blends, and aqueous and semi-aqueous cleaners. Nonsolvent options include supercritical cleaning fluid (SCF), ultraviolet (UV)/ozone cleaning, pressurized gases, and plasma cleaning.

Metal cleaning - Oils and greases, particulate matter, and inorganic particles are removed from metal parts prior to subsequent processing steps such as further machining, electroplating, painting. Alternatives to ozone-depleting solvents that have been developed include solvent blends, aqueous cleaners, emulsion cleaners, mechanical cleaning, thermal vacuum deoiling, and no-clean alternatives.

Dry cleaning - Several solvents exist to replace the ozone-depleting solvents that have traditionally been used by the dry cleaning industry. Perchloroethylene has been used for more than three decades. Petroleum solvents, while flammable, can be safely used when appropriate safety precautions are taken. They include white spirit, Stoddard solvent, hydrocarbon solvents, isoparaffins, and n-paraffin. A number of HCFCs can also be used but should be considered only as transitional alternatives.

Adhesives - Methyl chloroform has been used extensively by the adhesives manufacturing industry because of its characteristics - it is nonflammable and quick drying, and it does not contribute to local air pollution. One alternative for some applications is water-based adhesives.

SULFUR OXIDES

Sulfur oxides (SO_x) are compounds of sulfur and oxygen molecules. Sulfur dioxide (SO_2) is the predominant form found in the lower atmosphere. It is a colorless gas that can be detected by taste and smell in the range of 1,000 to 3,000 $\mu g/m^3$. At concentrations of 10,000 $\mu g/m^3$, it has a pungent, unpleasant odor. Sulfur dioxide dissolves readily in water present in the atmosphere to form sulfurous acid (H_2SO_3). About 30% of the sulfur dioxide in the atmosphere is converted to sulfate aerosol (acid aerosol), which is removed through wet or dry deposition processes. Sulfur trioxide (SO_3), another oxide of sulfur, is either emitted directly into the atmosphere or produced from sulfur dioxide and is readily converted to sulfuric acid (H_2SO_4).

Most sulfur dioxide is produced by burning fuels containing sulfur or by roasting metal sulfide ores, although there are natural sources of sulfur dioxide (accounting for 35-65% of total sulfur dioxide emissions) such as volcanoes. Thermal power plants burning high-sulfur coal or heating oil are generally the main sources of anthropogenic sulfur dioxide emissions worldwide, followed by industrial boilers and nonferrous metal smelters. Emissions from domestic coal burning and from vehicles can also contribute to high local ambient concentrations of sulfur dioxide.

Periodic episodes of very high concentrations of sulfur dioxide are believed to cause most of the health and vegetation damage attributable to sulfur emissions. Depending on wind, temperature, humidity, and topography, sulfur dioxide can concentrate close to ground-level. During the London fog of 1952, levels reached 3,500 $\mu g/m^3$ (averaged over 48 hours) in the center of the city and remained high for a period of 5 days. High levels have been recorded during temperature inversions in Central and Eastern Europe, in China, and in other parts of the world.

Exposure to sulfur dioxide in the ambient air has been associated with reduced lung function, increased incidence of respiratory symptoms and diseases, irritation of the eyes, nose, and throat, and premature mortality. Children, the elderly, and those already suffering from respiratory ailments, such as asthmatics, are especially at risk. Health impacts appear to be linked especially to brief exposures to ambient concentrations above 1,000 $\mu g/m^3$ (acute exposures measured over 10 minutes). Some epidemiologic studies, however, have shown an association between relatively low annual mean levels and excess mortality. It is not clear whether long-term effects are related simply to annual mean values or to repeated exposures to peak values.

Health effects attributed to sulfur oxides are likely due to exposure to sulfur dioxide, sulfate aerosols, and sulfur dioxide adsorbed onto particulate matter. Alone, sulfur dioxide will dissolve in the watery fluids of the upper respiratory system and be absorbed into the bloodstream. Sulfur dioxide reacts with other substances in the atmosphere to form sulfate aerosols. Since most sulfate aerosols are part of $PM_{2.5}$, they may have an important role in the health impacts associated with fine particulates. However, sulfate aerosols can be transported long distances through the atmosphere before deposition actually occurs. Average sulfate aerosol concentrations are about 40% of average fine particulate levels in regions where fuels with high sulfur content are commonly used. Sulfur dioxide adsorbed on particles can be carried deep into the pulmonary system. Therefore, reducing concentrations of particulate matter may also reduce the health impacts of sulfur dioxide. Acid aerosols affect respiratory and sensory functions.

Sulfur oxide emissions cause adverse impacts to vegetation, including forests and agricultural crops. Studies have shown that plants exposed to high ambient concentrations of sulfur dioxide may lose their foliage, become less productive, or die prematurely. Some plant species are much more sensitive to exposure than others. Plants in the immediate vicinity of emissions sources are more vulnerable. Studies have shown that the most sensitive species of plants begin to demonstrate visible signs of injury at concentrations of about 1,850 $\mu g/m^3$ for 1 hour., 500 $\mu g/m^3$ for 8 hours, and 40 $\mu g/m^3$ for the growing season. Canadian studies showed that chronic effects on pine forest growth were prominent where concentrations of sulfur dioxide in air averaged 44 $\mu g/m^3$, the arithmetic mean for the total 10 year measurement period; the chronic effects were slight where annual concentrations of sulfur dioxide averaged 21 $\mu g/m^3$.

Trees and other plants exposed to wet and dry acid depositions at some distance from the source of emissions may also be injured. Impacts on forest ecosystems vary greatly according to soil type, plant species, atmospheric conditions, insect populations, and other factors that are not well understood. Agricultural crops may also be injured by exposure to depositions. Alfalfa and rye grass are especially sensitive. It appears that leaf damage must be extensive before exposure affects the yields of most crops. It is possible that over the long-term, sulfur input to soils will affect yields. However, sulfur dioxide may not be the primary cause of plant injury, and other pollutants such as ozone may have a greater impact. Acid depositions can damage freshwater lake and stream ecosystems by lowering the pH of the water. Lakes with low buffering capacity, which could help neutralize acid rain, are especially at risk. Few fish species can survive large or dramatic shifts in pH, and affected lakes could become completely devoid of fish life. Acidification also decreases the species variety and abundance of other animal and plant life. Sulfate aerosols, converted from sulfur dioxide in the atmosphere, can reduce visibility by scattering light. In combination with warm temperatures, abundant sunlight, high humidity, and reduced vertical mixing, such aerosols can contribute to haziness extending over large areas.

Sulfur dioxide emissions may affect building stone and ferrous and nonferrous metals. Sulfurous acid, formed from the reaction of sulfur dioxide with moisture, accelerates the corrosion of iron, steel, and zinc. Sulfur oxides react with copper to produce the green patina of copper sulfate on the surface of the copper. Acids in the form of gases, aerosols, or precipitation may chemically erode building materials such as marble, limestone, and dolomite. Of particular concern is the chemical erosion of historical monuments and works of art. Sulfurous and sulfuric acids formed from sulfur dioxide and sulfur trioxide when they react with moisture may also damage paper and leather.

Pollution Prevention Practices and Control Technologies

Historically, measures designed to reduce localized ground-level concentrations of sulfur oxides (SO_x) used high-level dispersion principles (i.e., dispersion of pollutants by emitting them from tall stacks). Although these measures reduced localized health impacts, it is now more widely recognized that sulfur compounds travel long distances in the upper atmosphere and can cause damage far from their sources of origin. This means then that emphasis must be to reduce total emissions. The extent to which SO_x emissions pose health risks depends primarily on ground-level ambient concentrations, the number of people exposed, and the duration of exposure. Source location can affect these parameters; thus, plant siting is a critical factor in any SO_x management strategy.

The human health impacts of concern are short-term exposure to sulfur dioxide (SO_x) concentrations above 1,000 $\mu g/m^3$, measured as a 10-minute average. Priority must be given to limiting exposures to peak concentrations. Industrial sources of sulfur oxides should have emergency management plans that can be implemented when concentrations reach predetermined levels. Emergency management plans may include actions such as using alternative low-sulfur fuels.

Since high-level dispersion methods do not address the problem of long-range transport and deposition of sulfur, and merely disperses the pollutant, reliance on this strategy is no longer recommended. Stack height should be designed in accordance with good engineering practice (see, for example, United States, 40 CFR, Part 50, 100(ii)). The principal approaches to controlling SO_x emissions include use of low-sulfur fuel; reduction or removal of sulfur in the feed; use of appropriate combustion technologies; and emissions control technologies such as sorbent injection and flue gas desulfurization (FGD). Since sulfur emissions are proportional to the sulfur content of the fuel, an effective means of reducing SO_x

emissions is to burn low-sulfur fuel such as natural gas, low-sulfur oil, or low-sulfur coal. Natural gas has the added advantage of emitting no particulate matter when burned.

The most significant option for reducing the sulfur content of fuel is called beneficiation. Up to 70% of the sulfur in high-sulfur coal is in pyritic or mineral sulfate form, not chemically bonded to the coal. Coal beneficiation can remove 50% of pyritic sulfur and 20 to 30% of total sulfur. Note that it is not effective in removing organic sulfur. Beneficiation also removes ash responsible for particulate emissions. This approach may in some cases be cost-effective in controlling emissions of sulfur oxides, but it may generate large quantities of solid waste and acid wastewaters that must be properly treated and disposed of. Sulfur in oil can be removed through chemical desulfurization processes, but this is not a widely used commercial technology outside the petroleum industry. Processes using fluidized-bed combustion (FBC) reduce air emissions of sulfur oxides. A lime or dolomite bed in the combustion chamber absorbs the sulfur oxides that are generated.

Today's major emissions control methods are sorbent injection and flue gas desulfurization. Sorbent injection involves adding an alkali compound to the coal combustion gases for reaction with the sulfur dioxide. Typical calcium sorbents include lime and variants of lime. Sodium-based compounds are also used. Sorbent injection processes remove 30 to 60% of sulfur oxide emissions.

Flue gas desulfurization may be carried out using either of two basic FGD systems: regenerable and throwaway. Both methods may include wet or dry processes. Currently, more than 90% of utility FGD systems use a wet throwaway system process. Throwaway systems use inexpensive scrubbing mediums that are less costly to replace than to regenerate.

Regenerable systems use expensive sorbents that are recovered by stripping sulfur oxides from the scrubbing medium. These produce useful by-products, including sulfur, sulfuric acid, and gypsum. Regenerable FGDs generally have higher capital costs than throwaway systems but they tend to have lower waste disposal requirements and costs. In wet FGD processes, flue gases are scrubbed in a liquid or liquid/solid slurry of lime or limestone. Wet processes are highly efficient and can achieve SO_x removal of 90% or more. With dry scrubbing, solid sorbents capture the sulfur oxides. Dry systems have 70 to 90% sulfur oxide removal efficiencies and often have lower capital and operating costs, lower energy and water requirements, and lower maintenance requirements, in addition to which there is no need to handle sludge. However, the economics of the wet and dry (including "semi-dry" spray absorber) FGD processes vary considerably from site to site. Wet processes are available for producing gypsum as a byproduct. Table 1 provides some comparisons between the different pollution control methods that dominate today.

Table 1. SO_x Pollution Control Process Comparisons.

Process	% SO_x Reduction	Capital Costs ($/kilowatt)
Sorbent injection	30-70	50-100
Dry flue gas desulfurization	70-90	80-170
Wet flue gas desulfurization	>90	80-160

INDOOR AIR QUALITY

WHAT OCCUPATIONAL DISEASES ARE

Environmental and occupational illnesses are caused by exposure to disease-causing agents in the environment, as opposed to illnesses related primarily to an individual's genetic makeup or to immunological malfunctions. In everyday use, the term *environmental disease* is confined to noninfectious diseases and to diseases caused largely by exposures beyond the immediate control of the individual; the latter restriction eliminates diseases related to personal habits such as smoking or to the use or abuse of medications or drugs such as alcohol. Occupational disease, a major category of environmental disease, refers to illness resulting from job-related exposures.

Historically, awareness of environmental diseases began with the recognition of occupational illnesses, because exposures are usually more intense in work settings than in the general environment and therefore can more readily produce overt illnesses. Examples include silicosis, a lung disease of miners, industrial workers, and potters exposed to silica dust; scrotal skin cancer in chimney sweeps exposed to soot; neurological disease in potters exposed to lead glazes; and bone disease in workers exposed to phosphorus in the manufacture of matches. Many such diseases first gained public attention during the Industrial Revolution in the 19th century.

Environmental diseases are caused by chemical agents, radiation, and physical hazards. The effects of exposure, in both natural and work settings, are greatly influenced by the exposure routes: primarily air pollution and water pollution, contaminated food, and direct contact with toxins. Synergistic effects—two or more toxic exposures acting together—are also important, as illustrated by the greatly increased risk of lung cancer in asbestos workers who smoke cigarettes. The potential interaction of multiple hazardous chemicals at toxic waste dumps poses a current public health problem that is of unknown dimensions.

Modern society has introduced or increased human exposure to thousands of chemicals in the environment. Examples are inorganic materials such as lead, mercury, arsenic, cadmium, and asbestos, and organic substances such as polychlorinated biphenyls (PCBs), vinyl chloride, and the pesticide DDT. Of particular concern is the delayed potential for these chemicals to produce cancer, as in the cases of lung cancer and mesothelioma caused by asbestos, liver cancer caused by vinyl chloride, and leukemia caused by benzene. Minamata disease, caused by food contaminated with mercury, and Yusho disease, from food contaminated with chlorinated furans, are examples of acute toxic illnesses occurring in nonoccupational settings. The full toxic potential of most environmental chemicals has not been completely tested. The extent and frequency of an illness are related to the dose of toxin, in degrees depending on the toxin. For chronic or delayed effects such as cancer or adverse reproductive effects, no "safe" dose threshold may exist below which disease is not produced. Thus, the cancer-producing potential of ubiquitous environmental contaminants such as DDT or the PCBs remains undefined.

MULTIPLE CHEMICAL SENSITIVITY DISORDER

What has become an even greater concern in recent years is the phenomenon known as *multiple chemical sensitivity disorder* triggered by exposures to many chemicals in the environment. Synthetic chemicals are all around us. They are in the products we use, in the clothes we wear, in the food we eat, in the air we breathe at work. Because chemicals are everywhere in the environment, it is not possible to escape exposure. For this reason many people have become sensitized to the chemicals around them. In fact, it is estimated that 15% of the population has become sensitized to common household and commercial products. For some people the sensitization is not too serious a problem. They may have what appears to be a minor allergy to one or more chemicals. Other people are much more seriously affected. They may feel tired all the time, and suffer from mental confusion, breathing problems, sore muscles, and a weakened immune system. Such people suffer from a condition known as Multiple Chemical Sensitivity (MCS).

MCS is a disorder triggered by exposure to chemicals in the environment. Individuals with MCS can have symptoms from chemical exposure at concentrations far below the levels tolerated by most people. Symptoms occur in more than one organ system in the body, such as the nervous system and the lungs. Exposure may be from the air, from food or water, or through skin contact. The symptoms may look like an allergy because they tend to come and go with exposure, though some people's reactions may be delayed. As MCS gets worse, reactions become more severe and increasingly chronic, often affecting more bodily functions. No single widely available medical test can explain symptoms. In the early stages of MCS, repeat exposure to the substance or substances that caused the initial health effects provokes a reaction. After a time, it takes less and less exposure to this or related chemicals to cause symptoms. As the body breaks down, an ever increasing number of chemicals, including some unrelated to the initial exposure, are found to trigger a reaction.

MCS affects the overall health and feeling of well-being of those with the disorder. It typically impairs many bodily functions including the nervous system and digestion. Each individual affected by MCS has a unique set of health problems. A chemically sensitive person may also have other preexisting health conditions. Many affected people experience a number of symptoms in relation to their chemical exposures. Typical symptoms include headaches, flu-like symptoms, asthma or other breathing problems, dizziness, increased sensitivity to odors, mental confusion, bloating or other intestinal problems, fatigue and depression, short- and long-term memory loss, chronic exhaustion. People with MCS report many other health conditions such as: persistent skin rashes and sores, inflammation, muscle weakness and joint pains, food allergies, numbness and tingling, visual disturbance, ear, nose, and throat problems, autoimmune disorders, cardiovascular irregularities, seizure disorders, genitourinary problems, irritability, persistent infections, behavioral problems, and learning disabilities in children.

MCS may result from a single massive exposure to one or more toxic substances or repeated exposure to low doses. On one hand, some people may become chemically sensitive following a toxic chemical spill at work or in their community or after being sprayed directly with pesticides. On the other, individuals may develop this condition from spending forty hours each week in a poorly ventilated building where they breathe a profusion of chemicals common to our modern way of life.

In many cases, MCS has been brought on by a wide array of chemicals found at home and work. Studies show that many people diagnosed with MCS are: industrial workers, teachers, students, office and health care workers in tight buildings, chemical accident victims, people living near toxic waste sites, people whose air or water is highly polluted, people exposed to various chemicals in consumer products, food, and pharmaceuticals, and Gulf War veterans. Not all people with MCS fit these categories. For example, some may have experienced a toxic exposure from flea or roach sprays or from (urea formaldehyde) foam insulation in their home. Other people with MCS cannot identify any situations where they had unusual exposures to chemicals. People with MCS may become partially or totally disabled for several years or for life. This physical condition affects every aspect of their life.

In nonindustrial settings, MCS substances are the cause of indoor air pollution and are the contaminants in air and water. Many of the chemicals which trigger MCS symptoms are known to be irritants or toxic to the nervous system. As an example, volatile organic compounds readily evaporate into the air at room temperature. Permitted airborne levels of such contaminants can still make ordinary people sick. When the human body is assaulted with levels of toxic chemicals that it cannot safely process, it is likely that at some point an individual will become ill. For some, the outcome could be cancer or reproductive damage. Others may become hypersensitive to these chemicals or develop other chronic disorders, while some people may not experience any noticeable health effects. Even where high levels of exposure occur, generally only a small percentage of people become chemically sensitive.

The threshold for toxic injury is not the same for everyone because sensitivity varies greatly among individuals. Most chemicals in consumer products remain untested for health effects, such as cancer, reproductive problems, and the impacts of long-term, low level exposure. How these substances affect women, children, and people with existing conditions is also little studied. Once a person's defenses have been broken down and he or she has become hypersensitive, a wide variety of common chemical exposures can trigger a reaction. Just what products and other chemicals which cause problems varies greatly among affected individuals.

Treatment of MCS is difficult for physicians to define and diagnose. There is no single set of symptoms which fit together as a syndrome, nor a single diagnostic test for MCS. Instead, physicians should take a complete patient history which includes environmental and occupational exposures, and act as detectives in diagnosing this problematic condition. After the onset of MCS, a person's health generally continues to deteriorate. It may only begin to improve once the chemical sensitivity condition is uncovered. While a number of treatments may help improve the baseline health status for some patients, at the present time, there is no single "cure" except avoidance. Avoiding the chemicals which may trigger reactions is an essential part of treating MCS. Those with MCS who are able to strictly avoid exposures often experience dramatic improvement in their health over the period of a year or more. Yet the profusion of new and untested synthetic chemicals makes this extremely difficult. Individuals affected by MCS often create a "sanctuary" relatively free from chemical emissions in their home, where they spend as much time as possible. Because of the serious impact of even an accidental unavoidable exposure, MCS sufferers often spend as much time at home as possible and often must choose not to participate in society.

Many traditional allergists and other physicians discount the existence of an MCS diagnosis. They claim that there is not yet sufficient evidence that MCS exists. Research efforts regarding the mechanisms that cause MCS have been inadequate and unfortunately are often financed and supported by the industries which benefit from chemical proliferation. Generally medical doctors have not been trained to understand or seriously investigate conditions such as MCS. In fact, the vast majority of physicians receive very little training in occupational and environmental medicine or in toxicology and nutrition. Therefore, it is not surprising that many affected individuals consult with a large number of specialists. People with MCS are often even diagnosed with serious degenerative diseases. Often baffled doctors tell their patients with MCS that their illness is entirely psychosomatic. And many whose health is impaired by MCS have never heard of the condition. The lack of support and understanding from physicians and the stress created by having no explanation for symptoms tend to produce a high level of anxiety and distress in people with MCS. At this time, conventional medicine offers very few medical treatments for MCS besides avoiding offending products. Unfortunately, medications and other conventional medical treatments offer little or no relief and may even prompt new sets of symptoms. Treatment with anti-depressants masks the underlying condition and can also cause other serious problems. Physicians who clearly recognize the MCS phenomenon include some occupational and environmental health specialists and those MDs who specialize in the new field of clinical ecology. A wide range of new or "alternative" treatments have been utilized by MCS sufferers with varying success. Though some of these treatments are still experimental in nature, they seem to help some individuals with MCS. These treatments may include a combination of the following: nutritional programs, immunotherapy vaccines, food-allergy testing, detoxification regimens through exercise and sweating, chelation for heavy metals, as well as any number of non-Western healing methods.

Diagnosis may involve unconventional laboratory tests not customary in conventional medicine, including tests for the presence of chemical contaminants, such as total body burden of accumulated pesticides. Many workers have shown improvement with these treatments, though others have not. Unfortunately, these treatments are not usually reimbursed by insurance plans, since few participating practitioners support alternative approaches. Yet some disabled workers have won reimbursement for such treatments through successful Workers' Compensation claims. MCS is now recognized as a disability. Both the U.S. Department of Housing and Urban Development (HUD) and the Social Security Administration (SSA) have recognized MCS as a disabling condition. People with MCS have won Workers' Compensation cases. A recent human rights lawsuit in Pennsylvania established the right of an affected person to safe living space in subsidized housing. Both the Maryland State Legislature and New Jersey State Department of Health have officially commissioned studies of MCS. The New Jersey study provides an excellent overview of medical and legal issues related to MCS. Just as physical barriers prevent wheelchair access, chemical use and emissions can prevent entry to those with MCS. A new federal law called the Americans with Disabilities Act (ADA) will protect the disabled from many types of discrimination. This law provides for reasonable access to people with disabilities. Reasonable accommodations enable people with MCS to enjoy access to work, public facilities, and other necessary settings. Whether an individual developed MCS at work or was already sensitized prior to employment, the right to a safe workplace should be insured. For injured workers who have a right to Workers' Compensation or Disability, it is necessary to find a physician who can diagnose MCS and who will also support the patient's legitimate claims. Finding such a physician is very important in winning such a claim and for gaining reasonable accommodation at work or in rental housing. Major physical hazards include traumatic injuries and noise. Trauma arising from unsafe environments accounts for a large proportion of preventable human illness, and noise in the workplace is responsible for the most prevalent occupational impairment: hearing loss or permanent deafness.

Environmental diseases can affect any organ system of the body. How the diseases are expressed depends on how the particular environmental agent enters the body, how it is metabolized, and by what route it is excreted. The skin, lungs, liver, kidneys, and nervous system are commonly affected by different agents in different settings. Of particular concern is the capacity of many environmental agents to cause various cancers, birth defects or spontaneous abortions (through fetal exposure), and mutations in germ cells, the last-named raising possibilities of environmentally caused genetic diseases in later generations. Environmental illnesses can be mild or severe and can range from transient to chronic, depending on the doses of toxin received. Some diseases occur abruptly after a toxic exposure, whereas the time of onset of other diseases varies after exposure. Environmentally induced cancers, for example, commonly involve latency periods of 15 to 30 years or more. Those illnesses that occur directly after a distinct toxic exposure are usually identified as being environmentally or occupationally caused. If the exposure is not clear-cut or illness is delayed, however, the cause is difficult to identify, as clinical features alone are usually nonspecific. In addition, many different causes, environmental or otherwise, may produce identical illnesses. In such instances, epidemiological studies of exposed populations can help relate exposures to the illnesses they cause.

Total frequencies of environmental illness are difficult to measure. When causes can be identified, however, scientists observe that frequencies of occurrence of a particular illness vary directly with the severity and extent of exposure. Particularly frequent in the workplace are skin lesions from many different causes and pulmonary diseases related to the inhalation of various dusts, such as coal dust (black lung), cotton dust (brown lung), asbestos fibers (asbestosis), and silica dust (silicosis). Environmental agents can also cause biological effects without overt clinical illness (for example, chromosome damage from irradiation).

CONTROL MOTIVATION: WORKER SAFETY AND HEALTH

The motivation for ensuring good indoor air quality should be obvious. The Occupational Safety and Health Act of 1970 emphasizes the need for standards to protect the health and safety of workers. To fulfill this need, the National Institute for Occupational Safety and Health (NIOSH) has developed a strategy for disseminating information that assists employers to protect their workers from workplace hazards. This strategy includes the development of Special NIOSH Hazard Reviews, which support and complement the major standards development and hazard documentation activities of the Institute. These documents deal with hazards that merit research and concern from the scientific community, even though they are not currently suitable for comprehensive review in a criteria document or a Current Intelligence Bulletin. Special NIOSH Hazard Reviews are distributed to the occupational health community at large—industries, trade associations, unions, and members of the academic and scientific communities. Some of the information provided in this chapter is derived from NIOSH Hazard Reviews, and the emphasis is on inhalation hazards.

Refer to the handbook's Glossary. The definitions provided are universally recognized. Many of these terms are not just pertinent to inhalation hazards. It would be remiss not to mention other risks beyond inhalation from chemical exposure in a work environment and to the general public.

ORGANIZATION OF HANDBOOK SUBJECTS

The following chart can serve as your road map to the subjects covered in this handbook. The chart provides a brief overview of the subjects covered in each chapter, and will help direct you to specific topical information. Use this along with the subject index to find the information you need.

Each chapter contains a section on recommended resources, which includes Web sites. Some of these sites contain additional tools such as software that you can download for calculation purposes or for equipment selection information or financial calculations. Developing a strong library of references and Web sites is important to acquiring skills and staying abreast with the technology advances in air pollution abatement.

Subject Organization Chart

Chapter	Title	General Subject	Specific Topics Covered
1	**Introduction to Air Quality**	General overview and introduction to the subject.	• General forms of pollution • Motivations for control and pollution prevention • Clean Air Act • Basic terminology and definitions • Overview of atmospheric fate and transport • Overview of indoor air quality issues • Cost sensitivities issues
2	**Industrial Air Pollution Sources and Prevention**	Examples of point sources of air pollution, general control methods, and pollution prevention and energy saving practices	• Chemical Process Industries • Petroleum industry • Iron and steel manufacturing • Lead and zinc smelting • Nickel ore processing and refining • Aluminum refining • Copper smelting
3	**Properties of Air Pollutants**	Physical and chemical properties of select air pollutants	• Web site data bases • General properties information
4	**Ventilation and Indoor Air Quality Control**	Methods, technologies, and energy-efficient practices for indoor-air quality control	• HVAC and ASHRAE guidelines • Indoor air quality • Biological contaminants • Sick building syndrome • Multiple chemical sensitivity

Chapter	Title	General Subject	Specific Topics Covered
5	**Air Pollution Dispersion**	Application of air dispersion modeling principles and EPA tools to assessing environmental impacts from stack and area releases of pollutants	• Dispersion theory • Gaussian plume model • Ground-level concentrations • Worst case scenarios • Air quality impact assessments • Stationary source emissions
6	**Prevention versus Control**	Principles of pollution prevention	• How pollution prevention works • Pollution prevention auditing • Comparing P2 to control options
7	**Prevention and Control Hardware**	Equipment and technology descriptions	• Dry and wet control hardware • NO_x control and application of pollution prevention technologies • Flue gas scrubbing and control technologies • Incineration and high temperature technologies
8	**Environmental Cost Accounting**	Project cost estimating principles	• Return on investment calculations • Project cost estimating principles
Glossary		Definitions of air pollution prevention and control terms	
Subject Index		Alphabetical subject index	

RECOMMENDED RESOURCES FOR THE READER

The following are Web sites that are worth while visiting for more detailed information on general subjects covered in this chapter:

1. www.epa.gov/oar/oaq-caa.html: This site provides a full text version of the Clean Air Act and its amendments.
2. www.fedworld.gov/cleanair/search.htm: This site allows you to search and view record on the Clean Air Act.
3. www.4cleanair.org/caa-links.html: The site provides links to various state and territorial air pollution program administrators.
4. www.eap.state.il.us/air/caap/: This site is maintained by the Illinois EPA Bureau of Air and contains their Clean Air Act Permit Program.
5. www.repp.org/articles/issuebr15/03emTrade.htm: An interesting site that provides a guide to the Clean Air Act for the renewable energy community.
6. www.epa.gov/region08/air/planningsec/planningsec.html: Provides a general overview on fate and transport mechanisms in outdoor air pollution. Provides and explanation of air quality data.
7. www.epa.gov/airmarkets/acidrain: Provides an overview of EPA's clean air market programs (emissions trading) along with general information on acid rain.
8. pubs.water.usga.gov/acidrain: On-line data and reports by the USGS on acid rain, atmospheric deposition and precipitation chemistry. You can view and download U.S. maps of atmospheric deposition.
9. www.climatehotmap.org/: This site provides a world map showing early warning signs and projected implications from global warming effects.
10. www.epa.gov/globalwarming/: EPA provides this Web site as an introduction to global warming and greenhouse gases. You can find detailed information on the types and quantities of emissions.
11. www.osha-slc.gov/SLTC/indoorairquality: This is OSHA's Web site providing general information and links to indoor air quality issues.

REVIEW AND QUESTIONS TO GET YOU THINKING

1. List several reasons why pollution prevention tends to be more cost-effective than end-of-pipe treatment. Be specific with some concrete examples.

2. An acid dipping operation for metal parts involves the use of a 75% strength sulfuric acid solution. Develop recommendations for the Maximum Achievable Control Technology for controlling the air emissions from such an operation. Hint: *Take some time to look at the EPA Web sites dealing with MACT standards and pollution prevention.*
3. Describe how the EPA permitting system works. Go to www.eap.state.il.us/air/caap/ (*this site is maintained by the Illinois EPA Bureau of Air and contains their Clean Air Act Permit Program*) and determine the requirements. List the specific information you will need for the different types of air permits.
4. List several chemicals that are ozone depleting substances. Why are we concerned with regulating these chemical compounds, and what are the regulations that address them?
5. Describe the phenomenon of acid rain and the different pathways that it impacts on in the environment.
6. What are some of the global implications from global warming? Visit www.climatehotmap.org/ (*this site provides a world map showing early warning signs and projected implications from global warming effects*) and obtain information on projected impacts on your region of the country. Discuss the implications as a group.
7. Which component of suspended particulate matter is generally thought to be mutagenic?
8. Describe how impingement separators work.
9. List several types of air cleaning devices that can be used to remove airborne particulate matter. Rank these in order of their collection efficiency and typical maximum size particle capture.
10. List the important economic factors to consider when selecting emissions control equipment.
11. Determine the health risks associated with long-term exposures to nitrous oxides.
12. What are the mechanisms in combustion that result in the formation of nitrogen oxides?
13. List several pollution prevention and control technologies aimed at reducing nitrogen oxides in combustion processes. Among these, which are considered the most cost-effective methods for reducing NO_x emissions?
14. Describe the process of flue gas desulfurization.
15. What is *multiple chemical sensitivity*?

Chapter 2

INDUSTRIAL AIR POLLUTION SOURCES AND PREVENTION

INTRODUCTION

In this chapter we focus our attention on some of the point sources of air emissions within different types of plant operations, along with the methods of abatement. Although we do not make direct comparisons between prevention and control methodologies until Chapter 6, the reader should gain an appreciation for the simplicity of applying pollution prevention as opposed to incorporating engineering controls in many situations.

While we will not cover all the important industry sector sources of air pollution in this chapter, an attempt is made to examine a broad spectrum of so-called heavy-industries. These are industry sectors that are plagued with air pollution problems, and have had a long history in battling them. The chemical, oil, and gas sectors in particular are worthy of attention because of the enormous diversity of processes and products. Note that our intent is not to focus on the global magnitude of air pollution problems by sector. For those readers that need to gain a perspective of emissions statistics by industry sector, the EPA Web site is a good starting place to obtain such information (e.g., through the TRI or *Toxic Release Inventory*). Our focus is more on a micro-scale, i.e., to examine point sources common within different industry sectors.

AIR POLLUTION IN THE CHEMICAL PROCESS INDUSTRIES

NATURAL GAS AND CRUDE DISTILLATES

Natural gas and crude distillates such as naphtha from petroleum refining are used as feedstocks to manufacture a wide range of petrochemicals that are in turn used in the manufacture of consumer goods. Basic petrochemicals are manufactured by cracking, reforming, and other processes, and include olefins (such as ethylene, propylene, butylenes, and butadiene) and aromatics (such as benzene, toluene, and xylenes). The capacity of naphtha crackers is generally of the order of 250,000 to 750,000 metric tons per year (tpy) of ethylene production. Some petrochemical plants also have alcohol and oxo-compound manufacturing units on site. The base petrochemicals or products derived from them, along with other raw materials, are converted to a wide range of products. Among them are:

- Resins and plastics such as low-density polyethylene (LDPE), high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), polypropylene, polystyrene, and polyvinyl chloride (PVC);
- Synthetic fibers such as polyester and acrylic engineering polymers such as acrylonitrile butadiene styrene (ABS);
- Rubbers, including styrene butadiene rubber (SBR) and polybutadiene rubber (PBR);
- Solvents;
- Industrial chemicals, including those used for the manufacture of detergents such as linear alkyl benzene (LAB) and of coatings, dyestuffs, agrochemicals, pharmaceuticals, and explosives.

Chemical compounds manufactured at petrochemical plants include methanol, formaldehyde, and halogenated hydrocarbons. Formaldehyde is used in the manufacture of plastic resins, including phenolic, urea, and melamine resins. Halogenated hydrocarbons are used in the manufacture of silicone, solvents, refrigerants, and degreasing agents.

Olefins (organics having at least one double bond for carbon atoms) are typically manufactured from the steam cracking of hydrocarbons such as naphtha. Major olefins manufactured include ethylene, propylene, butadiene, and acetylene. The olefins manufactured are used in the manufacture of polyethylene, including low-density polyethylene (LDPE) and high-density polyethylene (HDPE), and for polystyrene, polyvinyl chloride, ethylene glycol (used along with dimethyl terphthalate, DMT, as feedstock to the polyester manufacturing process), ethanol amines (used as solvents), polyvinyl acetate (used in plastics), polyisoprene (used for synthetic rubber manufacture), polypropylene, acetone (used as a solvent and in cosmetics), isopropanol (used as a solvent and in pharmaceuticals manufacturing), acrylonitrile (used in the production of acrylic fibers and nitrile rubber), propylene glycol (used in pharmaceuticals manufacturing), and polyurethane. Butadiene is used in the manufacture of polybutadiene rubber (PBR) and styrene butadiene rubber (SBR). Other C_4 compounds manufactured include butanol, which is used in the manufacture of solvents such as methyl ethyl ketone.

The major aromatics (organics having at least one ring structure with six carbon atoms) manufactured include benzene, toluene, xylene, and naphthalene. Other aromatics manufactured include phenol, chlorobenzene, styrene, phthalic and maleic anhydride, nitrobenzene, and aniline. Benzene is generally recovered from cracker streams at petrochemical plants and is used for the manufacture of phenol, styrene, aniline, nitrobenzene, sulfonated detergents, pesticides such as hexachlorobenzene, cyclohexane (an important intermediate in synthetic fiber manufacture), and caprolactam, used in the manufacture of nylon. Benzene is also used as a general purpose solvent.

The main uses of toluene are as a solvent in paints, rubber, and plastic cements and as a feedstock in the manufacture of organic chemicals, explosives, detergents, and polyurethane foams. Xylenes (which exist as three isomers) are used in the manufacture of DMT, alkyd resins, and plasticizers. Naphthalene is mainly used in the manufacture of dyes, pharmaceuticals, insect repellents, and phthalic anhydride (used in the manufacture of alkyd resins, plasticizers, and polyester).

The largest user of phenol in the form of thermosetting resins is the plastics industry. Phenol is also used as a solvent and in the manufacture of intermediates for pesticides, pharmaceuticals, and dyestuffs. Styrene is used in the manufacture of synthetic rubber and polystyrene resins. Phthalic anhydride is used in the manufacture of DMT, alkyd resins, and plasticizers such as phthalates. Maleic anhydride is used in the manufacture of polyesters and, to some extent, for alkyd resins. Minor uses include the manufacture of malathion and soil conditioners. Nitrobenzene is used in the manufacture of aniline, benzidine, and dyestuffs and as a solvent in polishes. Aniline is used in the manufacture of dyes, including azo dyes, and rubber chemicals such as vulcanization accelerators and antioxidants.
A number of alternative methods for manufacturing the desired products are available; however, it is beyond the scope of this book to discuss these processes and products.

Distributed Non-Point Sources of Air Emissions

In technologically advanced countries, it is fair to say that fugitive air emissions from pumps, valves, flanges, storage tanks, loading and unloading operations, and wastewater treatment operations are of greatest concern. Major point source emissions such as reactor venting and stack emissions are regulated and controlled using conventional pollution hardware. As such, fugitive emissions pose the greatest challenges and are often so large in numbers that significant quantities of air pollutants are emitted over time. Some of the compounds released to air are carcinogenic or toxic. Ethylene and propylene emissions are of concern because their release can lead to the formation of extremely toxic oxides.

Compounds considered carcinogenic that may be present in air emissions include benzene, butadiene, 1,2-dichloroethane, and vinyl chloride. A typical naphtha cracker at a petrochemical complex may release annually about 2,500 metric tons of alkenes, such as propylenes and ethylene, in producing 500,000 metric tons of ethylene. Boilers, process heaters, flares, and other process equipment (which in some cases may include catalyst regenerators) are responsible for the emission of PM (particulate matter), carbon monoxide, nitrogen oxides (200 tpy), based on 500,000 tpy of ethylene capacity, and sulfur oxides (600 tpy).

The release of volatile organic compounds (VOCs) into the air depends on the products handled at the plant. VOCs released may include acetaldehyde, acetone, benzene, toluene, trichloroethylene, trichlorotoluene, and xylene. VOC emissions are mostly fugitive and depend on the production processes, materials-handling and effluent-treatment procedures, equipment maintenance, and climatic conditions. VOC emissions from a naphtha cracker range from 0.6 to 10 kilograms per metric ton (kg/t) of ethylene produced. Of these emissions, 75% consists of alkanes, 20% of unsaturated hydrocarbons, about half of which is ethylene, and 5% of aromatics.

For a vinyl chloride plant, VOC emissions are 0.02-2.5 kg/t of product; 45% is ethylene dichloride, 20% vinyl chloride, and 15% chlorinated organics; for an SBR plant, VOC emissions are typically 3 or more kg/t of product; for an ethyl benzene plant, 0.1-2 kg/t of product; for an ABS plant, 1.4-27 kg/t of product; for a styrene plant, 0.25-18 kg/t of product; and for a polystyrene plant, 0.2-5 kg/t of product.

Petrochemical units generate waste waters from process operations such as vapor condensation, from cooling tower blowdown, and from stormwater runoff. Process waste waters are generated at a rate of about 15 cubic meters per hour (m^3/hr), based on 500,000 tpy ethylene production, and may contain biochemical oxygen demand (BOD) levels of 100 mg/l, as well as chemical oxygen demand (COD) of 1,500 to 6,000 mg/l, suspended solids of 100 to 400 mg/l, and oil and grease of 30 to 600 mg/l. Phenol levels of up to 200 mg/l and benzene levels of up to 100 mg/l may also be present.

Of great concern in this industry are accidental discharges as a result of abnormal operation, especially from polyethylene and ethylene-oxide-glycol plants in a petrochemical complex. These can be a major environmental hazard, releasing large quantities of pollutants and products into the environment. The universe of chemical accidents within the United States cannot now be accurately tallied. No comprehensive, reliable historical records exist. Further, the EPA acknowledges that many accidents occurring today at fixed facilities and during transport are not reported to the federal government. This underreporting is documented by several studies (National Environmental Law Center et al. 1994). What is known, however, is that in 1991 the National Response Center received over 16,300 calls reporting the release or potential release of a hazardous material (USEPA 1993). Also, NTSB's statistics indicate that, in 1992, chemicals were involved in 3,500 fatal highway accidents and 6,500 railroad accidents (NTSB 1992). One study analyzed information contained in the EPA's Emergency Response Notification System (ERNS) database. ERNS is acknowledged to be the largest and most comprehensive United States database of chemical accident notifications, covering both transportation and fixed facility accidents. The study found that from 1988 through 1992 an average of 19 accidents occurred each day, or about 6,900 per year, with more than 34,500 accidents involving toxic chemicals occurring over the five-year period. The study's report emphasized that the findings gravely understated the severity of the United States' chemical accident picture (*National Environmental Law Center et al. 1994*).

Although the absolute numbers vary depending on the source of statistics and period of time examined, there is no doubt about the effects of chemical accidents on human life. Every year, large numbers of people are killed and injured. Added to these imprecise numbers must be those long-term consequences of exposure that are not immediately discernable and may not be reflected in studied databases. The low-level exposure to some chemicals may result in debilitating diseases that appear only years later. During the years 1988 through 1992, 6%, or 2,070, of the 34,500 accidents that occurred resulted in immediate death, injury and/or evacuation; an average of two chemical-related injuries occurred every day during those five years (*National Environmental Law Center et al. 1994*). Between 1982 and 1986, the EPA's Acute Hazard Events (AHE) database, which contains information only for chemical accidents having acute hazard potential, recorded 11,048 events involving releases of extremely

NOTE - Petrochemical plants also generate significant amounts of solid wastes and sludges, some of which may be considered hazardous because of the presence of toxic organics and heavy metals. Spent caustic and other hazardous wastes may be generated in significant quantities; examples are distillation residues associated with units handling acetaldehyde, acetonitrile, benzyl chloride, carbon tetrachloride, cumene, phthallic anhydride, nitrobenzene, methyl ethyl pyridine, toluene diisocyanate, trichloroethane, trichloroethylene, perchloroethylene, aniline, chlorobenzenes, dimethyl hydrazine, ethylene dibromide, toluenediamine, epichlorohydrin, ethyl chloride, ethylene dichloride, and vinyl chloride.

hazardous substances; these events resulted in 309 deaths, 11,341 injuries and, based on evacuation information for the one-half of the recorded events reporting whether such activity occurred, evacuation of 464,677 people from their homes and jobs (USEPA 1989). During the years 1987 through 1991, chemical accidents resulted in 453 deaths and 1,576 injuries at fixed facilities, while transportation accidents involving chemicals claimed 55 lives and injured 1,252 persons (*USEPA 1993*).

Application of Pollution Prevention Practices

Petrochemical plants are typically large and complex, and the combination and sequence of products manufactured are often unique to the plant. Specific pollution prevention practices or source reduction measures are best determined by a dedicated technical staff. In fact, without such a dedicated resource made available to a typical plant operation, efforts to reduce chronic emissions problems can be futile. There are a number of broad areas where improvements are often possible, and site-specific emission reduction measures in these areas should be designed into the plant and targeted by plant management. General areas where efforts should be concentrated are listed in Table 1. Table 1, along with the sidebar discussion on this page, can serve as a guide.

The examples listed in Table 1 are based on actual practices, and although they are not necessarily universal, they provide examples of the types of measures that can be applied within chemical plant operations. After reviewing some of the principles in Chapters 6 and 8, it's a good idea to come back and review this and other tables like it in this chapter. A good practice target for a petrochemical complex is to reduce total organic emissions (including VOCs) from the process units to 0.6% of the throughput. Target maximum levels for air releases, per ton of product, are, for ethylene, 0.06 kg; for ethylene oxide, 0.02 kg; for vinyl chloride, 0.2 kg; and for 1,2-dichloroethane, 0.4 kg.

Table 1. Examples of Pollution Prevention Practices in the Chemical Process Industries.

SOURCE CATEGORY	POLLUTION PREVENTION PRACTICE
Reduction of Air Emissions	1. Minimize leakages of volatile organics, including benzene, vinyl chloride, and ethylene oxide, from valves, pump glands (through use of mechanical seals), flanges, and other process equipment by following good design practices and equipment maintenance procedures. 2. Use mechanical seals where appropriate.

SOURCE CATEGORY	POLLUTION PREVENTION PRACTICE
	3. Minimize losses from storage tanks, product transfer areas, and other process areas by adopting methods such as vapor recovery systems and double seals (for floating roof tanks). 4. Recover catalysts and reduce particulate missions. 5. Reduce nitrogen oxide NO_x emissions by using low-NO_x burners. Optimize fuel usage. 6. In some cases, organics that cannot be recovered are effectively destroyed by routing them to flares and other combustion devices.
Elimination or Reduction of Pollutants	7. Use nonchrome-based additives in cooling water. 8. Use long-life catalysts and regeneration to extend the cycle.
Recycling and Reuse	9. Recycle cooling water and treated wastewater to the extent feasible. 10. Recover and reuse spent solvents and other chemicals to the extent feasible.
Improved Operating Procedures	11. Segregate process waste waters from stormwater systems. 12. Optimize the frequency of tank and equipment cleaning. 13. Prevent solids and oily wastes from entering the drainage system. 14. Establish and maintain an emergency preparedness and response plan.

Vapor recovery systems to control losses of VOCs from storage tanks and loading areas should achieve close to 100% recovery. In addition, a wastewater generation rate of 15 cubic meters per 100 tons of ethylene produced is achievable with good design and operation. New petrochemical complexes should strive to achieve this. Control of air emissions normally includes the capturing and recycling or combustion of emissions from vents, product transfer points, storage tanks, and other handling equipment.

Catalytic cracking units are provided with particulate removal devices. Particulate removal technologies include fabric filters, ceramic filters, wet scrubbers, and electrostatic precipitators. Gaseous releases are minimized by condensation, absorption, adsorption (using activated carbon, silica gel, activated alumina, and zeolites), and, in some cases, biofiltration and bioscrubbing (using peat or heather, bark, composts, and bioflora to treat biodegradable organics), and thermal decomposition. Dilution of air emissions to achieve legal guidelines is unacceptable. All of the maximum levels should be achieved for at least 95% of the time that the plant or unit is operating, to be calculated as a proportion of annual operating hours. The WHO (World Health Organization) recommended air emissions levels are summarized in Table 2. Although these are not legal standards, they provide us with a general sense of emission targets to strive for to meet safe health risk exposure levels.

Table 2. Target Ambient Levels to Achieve.

PARAMETER	MAXIMUM VALUE
PM	20 mg/m^3
Nitrogen oxides	300 mg/m^3
Hydrogen chloride	10 mg/m^3
Sulfur oxides	500 mg/m^3
Benzene	5 mg/m^3 for emissions; 0.1 ppb at the plant fence
1,2-dichloroethane	5 mg/m^3 for emissions;
	1.0 ppb at the plant fence
Vinyl chloride	5 mg/m^3 for emissions;
	0.4 ppb at the plant fence
Ammonia	15 mg/m^3

Note: Maximum ambient levels for ethylene oxide are 0.3 ppb at the plant fence. Maximum total emissions of the VOCs acetaldehyde, acrylic acid, benzyl chloride, carbon tetrachloride, chlorofluorocarbons, ethyl acrylate, halons, maleic anhydride, 1,1,1-trichlorethane, trichloroethylene, and trichlorotoluene are 20 mg/Nm^3. Maximum total heavy metal emissions are 1.5 mg/Nm^3.

AIR POLLUTION FROM CHLOR-ALKALI PLANTS

There are three basic processes for the manufacture of chlorine and caustic soda from brine: the mercury cell, the diaphragm cell, and the membrane cell. Among these technologies, the membrane cell is the most modern and has both economic and environmental advantages. The other two processes generate hazardous wastes containing mercury or asbestos. Mercury cell technology is being phased out in worldwide production.

In the membrane process, the chlorine (at the anode) and the hydrogen (at the cathode) are kept apart by a selective polymer membrane that allows the sodium ions to pass into the cathodic compartment and react with the hydroxyl ions to form caustic soda. The depleted brine is dechlorinated and recycled to the input stage. As noted already, the membrane cell process is the preferred process for new plants. Diaphragm processes may be acceptable, in some circumstances, but only if nonasbestos diaphragms are used. The energy consumption in a membrane cell process is of the order of 2,200 to 2,500 kilowatt-hours per metric ton (kWh/t), as compared with 2,400 to 2,700 kWh/t of chlorine for a diaphragm cell process.

Chlorine is a highly toxic gas, and strict precautions are necessary to minimize risk to workers and possible releases during its handling. Major sources of fugitive air emissions of chlorine and hydrogen are vents, seals, and transfer operations.

For the chlor-alkali industry, an emergency preparedness and response plan is mandatory for potential uncontrolled chlorine and other releases. Carbon tetrachloride is sometimes used to scrub nitrogen trichloride (formed in the process) and to maintain its levels below 4% to avoid fire and explosion. Substitutes for carbon tetrachloride may have to be used, as the use of carbon tetrachloride may be banned in the near future due to its carcinogenicity.

Implementation of cleaner production processes and pollution prevention measures can yield both economic and environmental benefits. The primary treatment technologies afforded to this manufacturing include the following:

- Caustic scrubber systems should be installed to control chlorine emissions from condensers and at storage and transfer points for liquid chlorine.
- Sulfuric acid used for drying chlorine should be neutralized before discharge.
- Chlorine monitors should be strategically located within the plant to detect chlorine releases or leaks on a continuous basis. Monitoring data should be analyzed and reviewed at regular intervals and compared with the operating standards so that any necessary corrective actions can be taken.
- Records of monitoring results should be kept in an acceptable format. The results should be reported to the responsible authorities and relevant parties, as required.

Preference should be given to the membrane process due to its less polluting characteristics over other technologies. In addition, the scrubbing of chlorine from tail gases to produce hypochlorite is highly recommended.

AIR POLLUTION FROM AGRO-INDUSTRY CHEMICALS

Mixed Fertilizer Plants

Mixed fertilizers contain two or more of the elements nitrogen, phosphorus, and potassium (NPK), which are essential for good plant growth and high crop yields. This subsection briefly addresses the production of ammonium phosphates (monoammonium phosphate, or MAP, and diammonium phosphate, or DAP), nitrophosphates, potash, and compound fertilizers.

Ammonium phosphates are produced by mixing phosphoric acid and anhydrous ammonia in a reactor to produce a slurry. This is referred to as the *mixed acid route* for producing NPK fertilizers; potassium and other salts are added during the process. The slurry is sprayed onto a bed of recycled solids in a rotating granulator, and ammonia is sparged into the bed from underneath. Granules pass to a rotary dryer followed by a rotary cooler. Solids are screened and sent to storage for bagging or for bulk shipment.

Nitrophosphate fertilizer is made by digesting phosphate rock with nitric acid. This is the nitrophosphate route leading to NPK fertilizers; as in the mixed-acid route, potassium and other salts are added during the process. The resulting solution is cooled to precipitate calcium nitrate, which is removed by filtration methods. The filtrate is neutralized with ammonia, and the solution is evaporated to reduce the water content. The process of prilling may follow. The calcium nitrate filter cake can be further treated to produce a calcium nitrate fertilizer, pure calcium nitrate, or ammonium nitrate and calcium carbonate.

Nitrophosphate fertilizers are also produced by the mixed-acid process, through digestion of the phosphate rock by a mixture of nitric and phosphoric acids. Potash (potassium carbonate) and sylvine (potassium chloride) are solution-mined from deposits and are refined through crystallization processes to produce fertilizer. Potash may also be dry-mined and purified by flotation. Compound fertilizers can be made by blending basic fertilizers such as ammonium nitrate, MAP, DAP, and granular potash; this route may involve a granulation process.
The principal pollutants from the production of MAP and DAP are ammonia and fluorides, which are given off in the steam from the reaction. Fluorides and dust are released from materials-handling operations. Ammonia in uncontrolled air emissions has been reported to range from 0.1 to 7.8 kilograms of nitrogen per metric ton (kg/t) of product, with phosphorus ranging from 0.02 to 2.5 kg/t product (as phosphorous pentoxide, P_2O_5).

In nitrophosphate production, dust will also contain fluorides. Nitrogen oxides NO_x are given off at the digester. In the evaporation stage, fluorine compounds and ammonia are released. Unabated emissions for nitrogen oxides from selected processes are less than 1,000 milligrams per cubic meter (mg/m^3) from digestion of phosphate rock with nitric acid, 50 to 200 (mg/m^3) from neutralization with ammonia, and 30 to 200 mg/m^3 from granulation and drying. Dust is the primary air pollutant from potash manufacturing.

Materials handling and milling of phosphate rock should be carried out in closed buildings. Fugitive emissions can be controlled by, for example, hoods on conveying equipment, with capture of the dust in fabric filters. In the ammonium phosphate plant, the gas streams from the reactor, granulator, dryer, and cooler should be passed through cyclones and scrubbers, using phosphoric acid as the scrubbing liquid, to recover particulates, ammonia, and other materials for recycling. In the nitrophosphate plant, nitrogen oxide (NO_x) emissions should be avoided by adding urea to the digestion stage. Fluoride emissions should be prevented by scrubbing the gases with water. Ammonia should be removed by scrubbing. Phosphoric acid may be used for scrubbing where the ammonia load is high. The process water system should be balanced, if necessary, by the use of holding tanks to avoid the discharge of an effluent.

Additional pollution control devices beyond the scrubbers, cyclones, and baghouses that are an integral part of the plant design and operations are generally not required for mixed fertilizer plants.

Air emissions at point of discharge should be monitored continuously for fluorides and particulates and annually for ammonia and nitrogen oxides. Monitoring data should be analyzed and reviewed at regular intervals and compared with the operating standards so that any necessary corrective actions can be taken. Records of monitoring results should be kept in an acceptable format. The results should be reported to the responsible authorities and relevant parties, as required.

The key production and control practices that will lead to compliance with emissions requirements can be summarized as follows:

- Maximize product recovery and minimize air emissions by appropriate maintenance and operation of scrubbers and baghouses.
- Prepare and implement an emergency preparedness and response plan. Such a plan is required because of the large quantities of ammonia and other hazardous materials stored and handled on site.

Nitrogenous Fertilizer Plants

This subsection discusses the production of ammonia, urea, ammonium sulfate, ammonium nitrate (AN), calcium ammonium nitrate (CAN), and ammonium sulfate nitrate (ASN). The manufacture of nitric acid used to produce nitrogenous fertilizers typically occurs on site and is therefore included here.

Ammonia (NH_3) is produced from atmospheric nitrogen and hydrogen from a hydrocarbon source. Natural gas is the most commonly used hydrocarbon feedstock for new plants; other feedstocks that have been used include naphtha, oil, and gasified coal. Natural gas is favored over the other feedstocks from an environmental perspective.

Ammonia production from natural gas includes the following processes: desulfurization of the feedstock; primary and secondary reforming; carbon monoxide shift conversion and removal of carbon dioxide, which can be used for urea manufacture; methanation; and ammonia synthesis. Catalysts used in the process may include cobalt, molybdenum, nickel, iron oxide/chromium oxide, copper oxide/zinc oxide, and iron.

Urea fertilizers are produced by a reaction of liquid ammonia with carbon dioxide. The process steps include solution synthesis, where ammonia and carbon dioxide react to form ammonium carbamate, which is dehydrated to form urea; solution concentration by vacuum, crystallization, or evaporation to produce a melt; formation of solids by prilling (pelletizing liquid droplets) or granulating; cooling and screening of solids; coating of the solids; and bagging or bulk loading. The carbon dioxide for urea manufacture is produced as a by-product from the ammonia plant reformer.

Ammonium sulfate is produced as a caprolactam by-product from the petrochemical industry, as a coke by-product, and synthetically through reaction of ammonia with sulfuric acid. Only the third process is covered in our discussion. The reaction between ammonia and sulfuric acid produces an ammonium sulfate solution that is continuously circulated through an evaporator to thicken the solution and to produce ammonium sulfate crystals. The crystals are separated from the liquor in a centrifuge, and the liquor is returned to the evaporator. The crystals are fed either to a fluidized bed or to a rotary drum dryer and are screened before bagging or bulk loading.

Ammonium nitrate is made by neutralizing nitric acid with anhydrous ammonia. The resulting 80 to 90% solution of ammonium nitrate can be sold as is, or it may be further concentrated to a 95 to 99.5% solution (melt) and converted into prills or granules. The manufacturing steps include solution formation, solution concentration, solids formation, solids finishing, screening, coating, and bagging or bulk shipping. The processing steps depend on the desired finished product. Calcium ammonium nitrate is made by adding ammonia calcite or dolomite to the ammonium nitrate melt before prilling or granulating. Ammonium sulfate nitrate is made by granulating a solution of ammonium nitrate and ammonium sulfate. The production stages for nitric acid manufacture include vaporizing the ammonia; mixing the vapor with air and burning the mixture over a platinum/rhodium catalyst; cooling the resultant nitric oxide (NO) and oxidizing it to nitrogen dioxide (NO_2) with residual oxygen; and absorbing the nitrogen dioxide in water in an absorption column to produce nitric acid (HNO_3). Because of the large quantities of ammonia and other hazardous materials handled on site, an emergency preparedness and response plan is required.

Emissions to the atmosphere from ammonia plants include sulfur dioxide (SO_2), nitrogen oxides (NO_x), carbon monoxide (CO), carbon dioxide (CO_2), hydrogen sulfide (H_2S), volatile organic compounds (VOCs), particulate matter, methane, hydrogen cyanide, and ammonia. The two primary sources of pollutants, with typical reported values, in kilograms per ton (kg/t) for the important pollutants, are as follows:

- Flue gas from primary reformer: CO_2: 500 kg/t NH_3, NO_x: 0.6 to 1.3 kg/t NH_3 as NO_2, SO_2: less than 0.1 kg/t; CO: less than 0.03 kg/t.
- Carbon dioxide removal: CO_2: 1,200 kg/t.

Nitrogen oxide emissions depend on the process features. Nitrogen oxides are reduced, for example, when there is low excess oxygen, with steam injection; when post-combustion measures are in place; and when low-NO_x burners are in use. Other measures will also reduce the total amount of nitrogen oxides emitted. Concentrations of sulfur dioxide in the flue gas from the reformer can be expected to be significantly higher if a fuel other than natural gas is used. Energy consumption ranges from 29 to 36 gigajoules per metric ton (GJ/t) of ammonia. Process condensate discharged is about 1.5 cubic meters per metric ton (m^3/t) of ammonia. Ammonia tank farms can release upward of 10 kg of ammonia per ton of ammonia produced. Emissions of ammonia from the process have been reported in the range of less than 0.04 to 2 kg/t of ammonia produced.

In a urea plant, ammonia and particulate matter are the emissions of concern. Ammonia emissions are reported as recovery absorption vent (0.1 to 0.5 kg/t), concentration absorption vent (0.1 to 0.2 kg/t), urea prilling (0.5 to 2.2 kg/t), and granulation (0.2 to 0.7 kg/t). The prill tower is a source of urea dust (0.5 to 2.2 kg/t), as is the granulator (0.1 to 0.5 kg/t).

Particulate matter is the principal air pollutant emitted from ammonium sulfate plants. Most of the particulates are found in the gaseous exhaust of the dryers. Uncontrolled discharges of particulates may be of the order of 23 kg/t from rotary dryers and 109 kg/t from fluidized bed dryers. Ammonia storage tanks can release ammonia, and there may be fugitive losses of ammonia from process equipment.

The production of ammonium nitrate yields emissions of particulate matter (ammonium nitrate and coating materials), ammonia, and nitric acid. The emission sources of primary importance are the prilling tower and the granulator. Total quantities of nitrogen discharged are in the range of 0.01 to 18.4 kg/t of product. Values reported for calcium ammonium nitrate are in the range of 0.13 to 3 kg nitrogen per ton of product.

Nitric acid plants emit nitric oxide, nitrogen dioxide (the visible emissions), and trace amounts of nitric acid mist. Most of the nitrogen oxides are found in the tail gases of the absorption tower. Depending on the process, emissions in the tail gases can range from 215 to 4,300 milligrams per cubic meter (mg/m^3) for nitrogen oxides. Flow may be of the order of 3,200 m^3 per ton of 100% nitric acid. Nitrogen oxide values will be in the low range when high-pressure absorption is used; medium-pressure absorption yields nitrogen oxide emissions at the high end of the range. These values are prior to the addition of any abatement hardware.

The following describes production-related targets that can be achieved by measures such as those described above. The numbers relate to the production processes before the addition of pollution control measures.

Ammonia Plants - New ammonia plants should set as a target the achievement of nitrogen oxide emissions of not more than 0.5 kg/t of product (expressed as NO_2 at 3%). Ammonia releases in liquid effluents can be controlled to 0.1 kg/t of product. Condensates from ammonia production should be reused.

Nitric Acid Plant - Nitrogen oxide levels should be controlled to a maximum of 1.6 kg/t of 100% nitric acid. Extended absorption and technologies such as nonselective catalytic reduction (NSCR) and selective catalytic reduction (SCR) are used to control nitrogen oxides in tail gases.

To attain a level of 150 parts per million by volume (ppmv) of nitrogen oxides in the tail gases, the following approaches should be considered: high-pressure, single-pressure process with absorbing efficiency high enough to avoid additional abatement facilities; dual-absorption process with an absorption efficiency high enough to avoid additional treatment facilities; dual-pressure process with SCR; medium-pressure, single-pressure process with SCR.

Urea Plants - In urea plants, wet scrubbers or fabric filters are used to control fugitive emissions from prilling towers; fabric filters are used to control dust emissions from bagging operations. These equipment are an integral part of the operations, to retain product. New urea plants should achieve levels of particulate matter in air emissions of less than 0.5 kg/t of product for both urea and ammonia.

Ammonium Sulfate Plants - In ammonium sulfate plants, use of fabric filters, with injection of absorbent as necessary, is the preferred means of control. Discharges of not more than 0.1 kg/t of product should be attainable for particulate matter.

Ammonium Nitrate Plants - In ammonium nitrate plants, wet scrubbers can be considered for prill towers and the granulation plant. Particulate emissions of 0.5 kg/t of product for the prill tower and 0.25 kg/t of product for granulation should be the target. Similar loads for ammonia are appropriate. Other effluents that originate in a nitrogenous fertilizer complex include boiler blowdown, water treatment plant backwash, and cooling tower blowdown from the ammonia and nitric acid plants. They may require pH adjustment and settling. These effluents should preferably be recycled or reused. Spent catalysts are usually sent for regeneration or disposed of in a secure landfill. Air emissions should be monitored annually, except for nitrate acid plants, where nitrogen oxides should be monitored continuously. Effluents should be monitored continuously for pH and monthly for other parameters. Monitoring data should be analyzed and reviewed at regular intervals and compared with the operating standards so that any necessary corrective actions can be taken. Records of monitoring results should be kept in an acceptable format. The results should be reported to the responsible authorities and relevant parties, as required. Table 3 highlights some of the pollution prevention practices that are applied to controlling air emissions. There are many other pollution prevention practices that can be applied to wastewater and solid wastes. Can you think of some of these?

Production and control practices that will lead to compliance with emissions requirements can be summarized as follows:

- ***Choose natural gas, where possible, as feedstock for the ammonia plant.***
- ***Give preference to high-pressure processes or absorption process in combination with catalytic reduction units.***
- ***Use low-dust-forming processes for solids formation.***
- ***Reuse condensates and other waste waters.***
- ***Maximize product recovery and minimize air emissions by appropriate maintenance and operation of scrubbers and baghouses.***

Table 3. Recommended Pollution Prevention Practices in the Fertilizer Plants.

PROCESS	POLLUTION PREVENTION PRACTICE
Ammonia Plant	1. Where possible, use natural gas as the feedstock for the ammonia plant, to minimize air emissions. 2. Use hot process gas from the secondary reformer to heat the primary reformer tubes (the exchanger-reformer concept), thus reducing the need for natural gas.

PROCESS	POLLUTION PREVENTION PRACTICE
	3. Direct hydrogen cyanide (HCN) gas in a fuel oil gasification plant to a combustion unit to prevent its release. 4. Consider using purge gases from the synthesis process to fire the reformer; strip condensates to reduce ammonia and methanol. 5. Use carbon dioxide removal processes that do not release toxics to the environment. When monoethanolamine (MEA) or other processes, such as hot potassium carbonate, are used in carbon dioxide removal, proper operation and maintenance procedures should be followed to minimize releases to the environment.
Urea Plant	6. Use total recycle processes in the synthesis process; reduce microprill formation and carryover of fines in prilling towers.
Ammonium Nitrate Plant	7. *Prill tower*: reduce microprill formation and reduce carryover of fines through entrainment. 8. *Materials handling*: where feasible use covers and hoods on conveyors and transition points. Good cleanup practices must be in place to minimize contamination of stormwater runoff from the plant property. 9. *Granulators*: reduce dust emissions from the disintegration of granules.

Phosphate Fertilizer Plants

Phosphate fertilizers are produced by adding acid to ground or pulverized phosphate rock. If sulfuric acid is used, single or normal, phosphate (SSP) is produced, with a phosphorus content of 16 to 21% as phosphorous pentoxide (P_2O_5). If phosphoric acid is used to acidulate the phosphate rock, triple phosphate (TSP) is the result. TSP has a phosphorus content of 43 to 48% as P_2O_5. SSP production involves mixing the sulfuric acid and the rock in a reactor. The reaction mixture is discharged onto a slow-moving conveyor in a den. The mixture is cured for 4 to 6 weeks before bagging and shipping.

Two processes are used to produce TSP fertilizers: run-of-pile and granular. The run-of-pile process is similar to the SSP process. Granular TSP uses lower-strength phosphoric acid (40%, compared with 50% for run-of-pile). The reaction mixture, a slurry, is sprayed onto recycled fertilizer fines in a granulator. Granules grow and are then discharged to a dryer, screened, and sent to storage.

Phosphate fertilizer complexes often have sulfuric and phosphoric acid production facilities. Sulfuric acid is produced by burning molten sulfur in air to produce sulfur dioxide, which is then catalytically converted to sulfur trioxide for absorption in oleum. Sulfur dioxide can also be produced by roasting pyrite ore. Phosphoric acid is manufactured by adding sulfuric acid to phosphate rock. The reaction mixture is filtered to remove phosphogypsum, which is discharged to settling ponds or waste heaps.

Fluorides and dust are emitted to the air from the fertilizer plant. All aspects of phosphate rock processing and finished product handling generate dust, from grinders and pulverizers, pneumatic conveyors, and screens. The mixer/reactors and dens produce fumes that contain silicon tetrafluoride and hydrogen fluoride. A sulfuric acid plant has two principal air emissions: sulfur dioxide and acid mist. If pyrite ore is roasted, there will also be particulates in air emissions that may contain heavy metals such as cadmium, mercury, and lead.

The phosphoric acid plant generates dust and fumes, both of which contain hydrofluoric acid, silicon tetrafluoride, or both.

In a fertilizer plant, the main source of potential air pollution is dusts and fumes from spills, operating upsets, and dust emissions. It is essential that tight operating procedures be in place and that close attention be paid to constant cleanup of spills and to other housecleaning measures.

The discharge of sulfur dioxide from sulfuric acid plants should be minimized by using the double-contact, double-absorption process, with high efficiency mist eliminators. Spills and accidental discharges should be prevented by using well-bunded storage tanks, by installing spill catchment and containment facilities, and by practicing good housekeeping and maintenance.

In the phosphoric acid plant, emissions of fluorine compounds from the digester/reactor should be minimized by using well-designed, well-operated, and well-maintained scrubbers. The management of phosphogypsum tailings is a major problem because of the large volumes and large area required and because of the potential for release of dust and radon gases and of fluorides and cadmium in seepage. The following measures help to minimize the impacts:

- Maintain a water cover to reduce radon gas release and dust emissions.
- Where water cover cannot be maintained, keep the tailings wet or revegetate to reduce dust. (Note, however, that the revegetation process may increase the rate of radon emissions.)

Implementation of cleaner production processes and pollution prevention measures can yield both economic and environmental benefits. The following production-related targets can be achieved by measures such as those described above. The numbers relate to the production processes before the addition of pollution control measures. In sulfuric acid plants that use the double-contact, double absorption process, emissions levels of 2 to 4 kilograms of sulfur dioxide per metric ton (kg/t) of sulfuric acid can be achieved, and sulfur trioxide levels of the order of 0.15 to 0.2 kg/t of sulfuric acid are attainable. Scrubbers are used to remove fluorides and acid from air emissions. The effluent from the scrubbers is normally recycled to the process.

Pesticide Formulation

This subsection describes formulation of pesticides from active ingredients. Manufacture of pesticides merits an entirely separate discussion. The major chemical groups that are formulated include: Insecticides (organophosphates, carbamates, organochlorines, pyrethroids, biorationals, and botanicals); Fungicides (dithiocarbamates, triazoles, MBCs, morpholines, pyrimidines, phthalamides, and inorganics); Herbicides (triazines, carbamates, phenyl ureas, phenoxy acids, bipyridyls, glyphosates, sulfonyl ureas, amide xylenols, and imidazole inones); Rodenticides (coumarins).

The main purpose of pesticide formulation is to manufacture a product that has optimum biological efficiency, is convenient to use, and minimizes environmental impacts. The active ingredients are mixed with solvents, adjuvants (boosters), and fillers as necessary to achieve the desired formulation. The types of formulations include wettable powders, soluble concentrates, emulsion concentrates, oil-in-water emulsions, suspension concentrates, suspoemulsions, water-dispersible granules, dry granules, and controlled release, in which the active ingredient is released into the environment from a polymeric carrier, binder, absorbent, or encapsulant at a slow and effective rate. The formulation steps may generate air emissions, liquid effluents, and solid wastes.

The principal air pollutants are particulate matter (PM) and volatile organic compounds (VOCs). These are released from mixing and coating operations. Pollution prevention practices generally employed to reduce air emissions include:

- The use of dedicated dust collectors to recycle recovered materials.
- The use suction hoods to collect vapors and other fugitive emissions.

A pesticide formulation plant should prepare and implement an emergency preparedness and response plan that takes into account neighboring land uses and the potential consequences of an emergency or accidental release of harmful substances. Measures to avoid the release of harmful substances should be incorporated in the design, operation, maintenance, and management of the plant. Pollution control equipment employed in this sector include baghouses for removal of particulate matter and carbon adsorption for removal of VOCs.

Pesticides Manufacturing

The following discussion deals with the synthesis of the active ingredients used in pesticide formulations. The major chemical groups manufactured include:

- Carbamates and dithiocarbamates (carbofuran, carbaryl, ziram, and benthiocarb)
- Chlorophenoxy compounds (2,4-D, 2,4,5-T, and silvex)
- Organochlorines (dicofol and endosulfan)
- Organophosphorus compounds (malathion, dimethoate, phorate, and parathion methyl)
- Nitro compounds (trifluralin)
- Miscellaneous compounds such as biopesticides (for example, *Bacillus thuringiensis* and pherhormones), heterocycles (for example, atrazine), pyrethroids (for example, cypermethrin), and urea derivatives (for example, diuron).

Special attention must be given to restricted substances. Production proposals for the following pesticides should be carefully evaluated: hexachlorobenzene, toxaphene, chlordane, aldrin, DDT, mirex, dieldrin, endrin, and heptachlor. The principal manufacturing steps are (a) preparation of process intermediates; (b) introduction of functional groups; (c) coupling and esterification; (d) separation processes, such as washing and stripping; and (e) purification of the final product. Each of these steps may generate air emissions, liquid effluents, and solid wastes.

The principal air pollutants are VOCs and PM. Typical pollution prevention practices aimed at reducing air emissions include:

- The use of "closed" feed systems for batch reactors.
- The use of nitrogen blanketing where appropriate on pumps, storage tanks, and other equipment to minimize the release of toxic organics.
- Giving preference to nonhalogenated and nonaromatic solvents where feasible.
- The use of dedicated dust collectors to recycle recovered materials.
- Venting equipment through a recovery system.
- Maintain losses from vacuum pumps (such as water ring and dry) at low levels.

Specific reduction targets for the different processes are not well established. In the absence of specific pollution reduction targets, new plants should always achieve better than the industry averages and should approach the load-based effluent levels.

Typical air pollution control equipment employed by the industry include the following: stack gas scrubbing and/or carbon adsorption (for toxic organics) and baghouses (for particulate matter removal) are applicable and effective technologies for minimizing the release of significant pollutants to air. Combustion is used to destroy toxic organics. Combustion devices should be operated at temperatures above 1,100°C with a flame residence time of at least 0.5 second to achieve acceptable destruction efficiency of toxics. However, temperatures of around 900°C are acceptable provided that at least 99.99% destruction and removal efficiency of toxics is achieved.

A pesticide manufacturing plant should prepare a hazard assessment and operability study and also prepare and implement an emergency preparedness and response plan that takes into account neighboring land use and the potential consequences of an emergency. Measures to avoid the release of harmful substances should be incorporated in the design, operation, maintenance, and management of the plant. Implementation of cleaner production processes and pollution prevention measures can yield both economic and environmental benefits.

Contaminated solid wastes are generally incinerated, and the flue gases are scrubbed. The emissions levels cited in Table 4 are those recommended by the World Bank Organization that should be achieved.

Table 4. Emissions from Pesticides Manufacturing.

PARAMETER	**MAXIMUM LEVEL** ***milligrams per normal cubic meter***
PM	20;5 where very toxic compounds are present[a]
VOCs	20
Chlorine (or chloride)	5

a. See the World Health Organization's list of extremely hazardous substances (WHO 1996).

Monitoring of air emissions should be done on a continuous basis when the mass flow of toxic substances exceeds 0.5 kg per hour. Otherwise, it can be done annually.

AIR POLLUTION FROM COKE MANUFACTURING

This subsection provides an overview of the production of metallurgical coke and the associated by-products using intermittent horizontal retorts, as well as the pollution prevention practices. Coke and coke by-products, including coke oven gas, are produced by the pyrolysis (heating in the absence of air) of suitable grades of coal. The process also includes the processing of coke oven gas to remove tar, ammonia (usually recovered as ammonium sulfate), phenol, naphthalene, light oil, and sulfur before the gas is used as fuel for heating the ovens.

Coke chemical plants are interesting and complex. Although the basic unit processes are the same, there are often significant enough differences between plants that distinguish one from another. In general, the coking industry is a heavy polluting industry. While in the United States, the coking industry is at a tiny fraction of its capacity of some 30 years ago, it is still very much alive in many parts of the world. In Russia and in many parts of Eastern Europe, coke serves as a merchant supply industry to the iron and steel sector. In the coke-making process, bituminous coal is fed (usually after processing operations to control the size and quality of the feed) into a series of ovens, which are sealed and heated at high temperatures in the absence of oxygen, typically in cycles lasting 14 to 36 hours. Volatile compounds that are driven off the coal are collected and processed to recover combustible gases and other by-products. The solid carbon remaining in the oven is coke.

The coke is taken to a quench tower, where it is cooled with a water spray or by circulating an inert gas (e.g., nitrogen), a process known as dry quenching. The coke is then screened and sent to a blast furnace or to storage.

The coke oven gas is cooled, and by-products are recovered. Flushing liquor, formed from the cooling of coke oven gas, and liquor from primary coolers contain tar and are sent to a tar decanter. Note that the coke oven gas has a heating value and can be used effectively in the cogeneration of heat or electricity, which can be used by the plant, or if available in sufficient quantities, can be sold into local grids.

An electrostatic precipitator is used to remove more tar from coke oven gas. The tar is then sent to storage. Ammonia liquor is also separated from the tar decanter and sent to wastewater treatment after ammonia recovery. Coke oven gas is further cooled in a final cooler. Naphthalene is removed in a separator on the final cooler. Light oil is then removed from the coke oven gas and is fractionated to recover benzene, toluene, and xylene. Some facilities may include an onsite tar distillation unit. The Claus process is normally used to recover sulfur from coke oven gas. During the coke quenching, handling, and screening operation, coke breeze is produced. The breeze is either reused on site (e.g., in the sinter plant) or sold offsite as a by-product.

Coke ovens are major sources of fugitive air emissions. The coking process emits particulate matter (PM), volatile organic compounds (VOCs), polynuclear aromatic hydrocarbons (PAHs), methane, at approximately 100 grams per metric ton (g/t) of coke, ammonia, carbon monoxide, hydrogen sulfide (50 to 80 g/t of coke from pushing operations), hydrogen cyanide, and sulfur oxides - SO_x, (releasing 30% of sulfur in the feed).

Significant amount of VOCs may also be released in by-product recovery operations. For every ton of coke produced, approximately 0.7 to 7.4 kilograms (kg) of PM, 2.9 kg of SO_x (ranging from 0.2 to 6.5 kg), 1.4 kg of nitrogen oxides NO_x, 0.1 kg of ammonia, and 3 kg of VOCs (including 2 kg of benzene) may be released into the atmosphere if there is no vapor recovery system. Coal-handling operations may account for about 10% of the particulate load. Coal charging, coke pushing, and quenching are major sources of dust emissions.

Pollution prevention in coke making focuses on reducing coke oven emissions and developing cokeless iron- and steel-making techniques. Table 5 provides a list of pollution prevention and control measures commonly applied. The World Bank Organization recommends that benzene emissions should not be more than 5 milligrams per normal cubic meter (mg/Nm^3) in leaks from light oil processing, final cooler, tar decanter, tar storage, weak ammonia liquor storage, and the tar/water separator. VOC emissions should be less than 20 mg/Nm^3. Particulate matter emissions from the stacks should not exceed 50 mg/Nm^3. Sulfur recovery from coke oven gas should be at least 97% but preferably over 99%. Air emission control technologies include scrubbers (removal efficiency of 90%) and baghouses and electrostatic precipitators (ESPs), with removal efficiencies of 99.9%.

Baghouses are preferred over venturi scrubbers for controlling particulate matter emissions from loading and pushing operations because of the higher removal efficiencies. ESPs are effective for final tar removal from coke oven gas. Stack air emissions should be monitored continuously for particulate matter. Alternatively, opacity measurements of stack gases can suffice. Fugitive emissions should be monitored annually for VOCs.

Table 5. Examples of Pollution Prevention Practices in the Coke Industry.

PROCESS	POLLUTION PREVENTION PRACTICE
General	1. Use cokeless iron- and steel-making processes, such as the direct reduction process, to eliminate the need to manufacture coke. 2. Use beneficiation (preferably at the coal mine) and blending processes that improve the quality of coal feed to produce coke of desired quality and reduce emissions of sulfur oxides and other pollutants.

PROCESS	POLLUTION PREVENTION PRACTICE
	3. Use enclosed conveyors and sieves for coal and coke handling. Use sprinklers and plastic emulsions to suppress dust formation. Provide windbreaks where feasible. Store materials in bunkers or warehouses. Reduce drop distances.
Coke Oven Emissions	4. *Charging:* dust particles from coal charging should be evacuated by the use of jumper-pipe systems and steam injection into the ascension pipe or controlled by fabric filters 5. *Coking:* use large ovens to increase batch size and reduce the number of chargings and pushings, thereby reducing the associated emissions. Reduce fluctuations in coking conditions, including temperature. Clean and seal coke oven openings to minimize emissions. Use mechanical cleaning devices (preferably automatic) for cleaning doors, door frames, and hole lids. Seal lids, using a slurry. Use low leakage door construction, preferably with gas sealings. 6. *Pushing:* emissions from coke pushing can be reduced by maintaining a sufficient coking time, thus avoiding "green push." Use sheds and enclosed cars, or consider use of traveling hoods. The gases released should be removed and passed through fabric filters. 7. *Quenching:* where feasible, use dry instead of wet quenching. Filter all gases extracted from the dry quenching unit. If wet quenching, is used, provide interceptors (baffles) to remove coarse dust. When wastewater is used for quenching, the process transfers pollutants from the wastewater to the air, requiring subsequent removal. Reuse quench water. 8. *Conveying and sieving:* enclose potential dust sources, and filter evacuated gases.
By-Product Recovery	9. Use vapor recovery systems to prevent air emissions from light oil processing, tar processing, naphthalene processing, and phenol and ammonia recovery processes. 10. Reduce fixed ammonia content in ammonia liquor by using caustic soda and steam stripping. 11. Recover sulfur from coke oven gas. Recycle Claus tail gas into coke oven gas system.

AIR POLLUTION FROM DYE MANUFACTURING

This section provides an overview of the synthesis of dyes and pigments used in textiles and related industries. Dyes are soluble at some stage of the application process, whereas pigments, in general, retain essentially their particulate or crystalline form during application. A dye is used to impart color to materials of which it becomes an integral part. An aromatic ring structure coupled with a side chain is usually required for resonance and thus to impart color. Resonance structures cause displacement or appearance of absorption bands in the visible spectrum of light, and hence they are responsible for color. Correlation of chemical structure with color has been accomplished in the synthesis of dye using a chromogen-chromophore with auxochrome. Chromogen is the aromatic structure containing benzene, naphthalene, or anthracene rings. A chromophore group is a color giver or donor and is represented by the following radicals, which form a basis for the chemical classification of dyes when coupled with the chromogen: azo (-N=N-); carbonyl (=C=O); carbon (=C=C=); carbon-nitrogen (>C=NH or -CH=N-); nitroso (-NO or N-OH); nitro ($-NO_2$ or =NO-OH); and sulfur (>C=S, and other carbon-sulfur groups). The chromogen-chromophore structure is often not sufficient to impart solubility and cause adherence of dye to fiber. The auxochrome or bonding affinity groups are amine, hydroxyl, carboxyl, and sulfonic radicals, or their derivatives. These auxochromes are important in the use classification of dyes. A listing of dyes by use classification comprises the following:

- *Acetate rayon dyes:* developed for cellulose acetate and some synthetic fibers.
- *Acid dyes:* used for coloring animal fibers via acidified solution (containing sulfuric acid, acetic acid, sodium sulfate, and surfactants) in combination with amphoteric protein.
- *Azoic dyes:* contain the azo group (and formic acid, caustic soda, metallic compounds, and sodium nitrate); especially for application to cotton.
- *Basic dyes:* amino derivatives (and acetic acid and softening agents); used mainly for application on paper.
- *Direct dyes:* azo dyes, and sodium salts, fixing agents, and metallic (chrome and copper) compounds; used generally on cotton-wool, or cotton-silk combinations.
- *Mordant or chrome dyes:* metallic salt or lake formed directly on the fiber by the use of aluminum, chromium, or iron salts that cause precipitation in situ.
- *Lake or pigment dyes:* form insoluble compounds with aluminum, barium, or chromium on molybdenum salts; the precipitates are ground to form pigments used in paint and inks.
- *Sulfur or sulfide dyes:* contain sulfur or are precipitated from sodium sulfide bath; furnish dull shades with good fastness to light, washing, and acids but susceptible to chlorine and light.
- *Vat dyes:* impregnated into fiber under reducing conditions and reoxidized to an insoluble color.

Chemical classification is based on chromogen. For example, nitro dyes have the chromophore $-NO_2$. The *Color Index (C.I.),* published by the Society of Dyers and Colourists (United Kingdom) in cooperation with the American Association of Textile Chemists and Colorists (AATC), provides a detailed classification of commercial dyes and pigments by generic name and chemical constitution.

In general, organic compounds such as naphthalene are reacted with an acid or an alkali along with an intermediate (such as a nitrating or a sulfonating compound) and a solvent to form a dye mixture. The dye is then separated from the mixture and purified. On completion of the manufacture of actual color, finishing operations, including drying, grinding, and standardization, are performed; these are important for maintaining consistent product quality.

Dyes are synthesized in a reactor, then filtered, dried, and blended with other additives to produce the final product. The synthesis step involves reactions such as sulfonation, halogenation, amination, diazotization, and coupling, followed by separation processes that may include distillation, precipitation, and crystallization.

The principal air pollutants from dye manufacturing are VOCs, nitrogen oxides (NO_x), hydrogen chloride (HCl), and sulfur oxides (SO_x). Stack gas scrubbing and/or carbon adsorption (for toxic organics) are applicable and effective technologies for minimizing the release of significant pollutants to air. Combustion is used to destroy toxic organic compounds. Combustion devices should be operated at temperatures above 1,100°C (when required for the effective destruction of toxic organics), with a residence time of at least 0.5 sec. Dilution of air emissions or effluents to achieve guidelines is considered unacceptable. Maximum levels should be achieved for at least 95% of the time that the plant or unit is operating, to be calculated as a proportion of annual operating hours. Because of the toxicity of many of the pollutants from this industry sector, it is recommended that monitoring of air emissions be done on a continuous basis.

AIR POLLUTION FROM PHARMACEUTICALS MANUFACTURING

The pharmaceutical industry includes the manufacture, extraction, processing, purification, and packaging of chemical materials to be used as medications for humans or animals. Pharmaceutical manufacturing is divided into two major stages: the production of the active ingredient or drug (primary processing, or manufacture) and secondary processing, the conversion of the active drugs into products suitable for administration. This section briefly deals with the synthesis of the active ingredients and their usage in drug formulations to deliver the prescribed dosage. Formulation is also referred to as galenical production. The main pharmaceutical groups manufactured include:

- Proprietary ethical products or prescription only medicines (POM), which are usually patented products.
- General ethical products, which are basically standard prescription-only medicines made to a recognized formula that may be specified in standard industry reference books.
- Over-the-counter (OTC), or nonprescription, products.

The products are available as tablets, capsules, liquids (in the form of solutions, suspensions, emulsions, gels, or injectables), creams (usually oil-in-water emulsions), ointments (usually water-in-oil emulsions), and aerosols, which contain inhalable products or products suitable for external use. Propellants used in aerosols include chlorofluorocarbons (CFCs), which are being phased out. Recently, butane has been used as a propellant in externally applied products. The major manufactured groups include:

- Antibiotics such as penicillin, streptomycin, tetracyclines, chloramphenicol, and antifungals;
- Other synthetic drugs, including sulfa drugs, antituberculosis drugs, antileprotic drugs, analgesics, anesthetics, and antimalarials;
- Vitamins;
- Synthetic hormones;
- Glandular products, drugs of vegetable origin, such as quinine, strychnine and brucine, emetine, and digitalis glycosides;
- Vaccines and sera;
- Other pharmaceutical chemicals such as calcium gluconate, ferrous salts, nikethamide, glycerophosphates, chloral hydrate, saccharin, antihistamines (including meclozine, and buclozine), tranquilizers (including meprobamate and chloropromazine), antifilarials, diethylcarbamazine citrate, and oral antidiabetics, including tolbutamide and chloropropamide;
- Surgical sutures and dressings.

The principal manufacturing steps are
(a) preparation of process intermediates;
(b) introduction of functional groups;
(c) coupling and esterification;
(d) separation processes such as washing and stripping; and
(e) purification of the final product.

Additional product preparation steps include granulation; drying; tablet pressing, printing, and coating; filling; and packaging. Each of these steps may generate air emissions, liquid effluents, and solid wastes.

The manufacture of penicillin, for example, involves batch fermentation using

100 to 200 m^3 batches of maize steep liquor or a similar base, with organic precursors added to control the yield. Specific mold culture such as ***Penicillium chrysogenum*** for Type 11 is inoculated into the fermentation medium. Penicillin is separated from the fermentation broth by solvent extraction. The product is further purified using acidic extraction. This is followed by treatment with a pyrogen-free distilled water solution containing the alkaline salt of the desired element. The purified aqueous concentrate is separated from the solvent in a supercentrifuge and pressurized through a biological filter to remove the final traces of bacteria and pyrogens. The solution can be concentrated by freeze drying or vacuum spray drying. Oil-soluble procaine penicillin is made by reacting a penicillin concentrate (20 to 30%) with a 50% aqueous solution of procaine hydrochloride. Procaine penicillin crystallizes from this mixture. In some countries, the manufacture of pharmaceuticals is controlled by Good Management Practices (GMP). Some countries require an environmental assessment (EA) report addressing the fate and toxicity of drugs and their metabolized by-products. Note that the principal air pollutants are volatile organic compounds (VOCs) and particulate matter (PM).

AIR POLLUTION IN THE PETROLEUM INDUSTRY

INDUSTRY OVERVIEW

This section describes the major industrial processes within the petroleum refining industry, including the materials and equipment used, and the processes employed. The section is necessary for an understanding of the interrelationships between the industrial processes, the types of air emissions, and control and pollution prevention approaches. Descriptions of commonly used production processes, associated raw materials, by-products produced are first described.

Petroleum refining is the physical, thermal, and chemical separation of crude oil into its major distillation fractions, which are then further processed through a series of separation and conversion steps into finished petroleum products. The primary products of the industry fall into three major categories:

- fuels (motor gasoline, diesel and distillate fuel oil, liquefied petroleum gas, jet fuel, residual fuel oil, kerosene, and coke);
- finished nonfuel products (solvents, lubricating oils, greases, petroleum wax, petroleum jelly, asphalt, and coke); and
- chemical industry feedstocks (naphtha, ethane, propane, butane, ethylene, propylene, butylenes, butadiene, benzene, toluene, and xylene). These petroleum products comprise about 40% of the total energy consumed in the U.S. and are used as primary input to a vast number of products, including: fertilizers, pesticides, paints, waxes, thinners, solvents, cleaning fluids, detergents, refrigerants, anti-freeze, resins, sealants,

insulations, latex, rubber compounds, hard plastics, plastic sheeting, plastic foam, and synthetic fibers.

About 90% of the petroleum products used in the U.S. are fuels with motor gasoline accounting for about 43% of the total. Figure 1 provides a conceptual breakdown of the products. The Standard Industrial Classification (SIC) code established by the Bureau of Census to track the flow of goods and services within the economy is 29 for the Petroleum Refining and Related Industries. The petroleum refining industry is classified as SIC 2911, which includes the production of petroleum products through distillation and fractionation of crude oil, re-distillation of unfinished petroleum derivatives, cracking, or other processes.

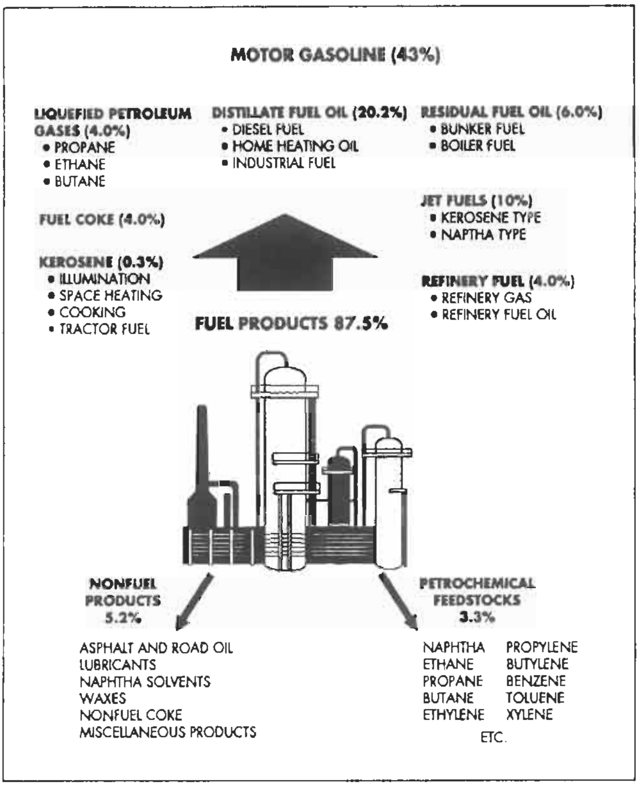


Figure 1. Refinery products and yields.

The related industries under SIC 29 are: 2951, Asphalt Paving Mixtures and Blocks; 2952, Asphalt Felts and Coatings; 2992, Lubricating Oils and Greases; and 2999, Petroleum and Coal Products, Not Elsewhere Classified. Certain products that are produced by the petroleum refining industry are also produced by other industries, including: 2865, Cyclic Organic Crudes and Intermediates, and Organic Dyes and Pigments; 2869, Industrial Organic Chemicals; 2819, Industrial Inorganic Chemicals, Not Elsewhere Classified; 2821, Plastic Materials, Synthetic Resins, Nonvulcanizable Elastomers; 2873, Nitrogenous Fertilizers; 4613, Refined Petroleum Pipelines; and 5171, Petroleum Bulk Stations and Terminals.

Most crude oil distillation capacity is owned by large, integrated companies with multiple high capacity refining facilities. Small refineries with capacities below 50,000 barrels per day, however, make up about half of all facilities, but only 14% of the total crude distillation capacity.

The United States is a net importer of crude oil and petroleum products. In 1994, imports accounted for more than 50% of the crude oil used in the U.S. and about 10% of finished petroleum products. The imported share of crude oil is expected to increase as U.S. demand for petroleum products increases and the domestic production of crude oil declines. Imported finished petroleum products serve specific market niches arising from logistical considerations, regional shortages, and long-term trade relations between suppliers and refiners. Exports of refined petroleum products, which primarily consist of petroleum coke, residual fuel oil, and distillate fuel oil, account for about 4% of the U.S. refinery output. Exports of crude oil produced in the U.S. account for about 1% of the total U.S. crude oil produced and imported.

The petroleum refining industry in the U.S. has felt considerable economic pressures in the past two decades arising from a number of factors including: increased costs of labor; compliance with new safety and environmental regulations; and the elimination of government subsidies through the Crude Oil Entitlements Program which had encouraged smaller refineries to add capacity throughout the 1970s. A rationalization period began after crude oil pricing and entitlements were decontrolled in early 1981. The market determined that there was surplus capacity and the margins dropped to encourage the closure of the least efficient capacity. Reflecting these pressures, numerous facilities have closed in recent years. Between 1982 and 1994, the number of U.S. refineries as determined by the Department of Energy dropped from 301 to 176. Most of these closures have involved small facilities refining less than 50,000 barrels of crude oil per day. Some larger facilities, however, have also closed in response to economic pressures. Industry representatives cited complying with the increasing environmental regulations, particularly the requirements of the Clean

Air Act Amendments of 1990, as the most important factor affecting petroleum refining in the 1990s. Despite the closing of refineries in recent years, total refinery output of finished products has remained relatively steady with slight increases in the past two to three years. Increases in refinery outputs are attributable to higher utilization rates of refinery capacity, and to incremental additions to the refining capacity at existing facilities as opposed to construction of new refineries.

Demand for refined petroleum products is expected to increase on the average by about 1.5% per year, which is slower than the expected growth of the economy. This slower rate of increase of demand will be due to increasing prices of petroleum products as a result of conservation, the development of substitutes for petroleum products, and rising costs of compliance with environmental and safety requirements.

Recent and future environmental and safety regulatory changes are expected to force the petroleum refining industry to make substantial investments in upgrading certain refinery processes to reduce emissions and alter product compositions. For example, industry estimates of the capital costs to comply with the 1990 Clean Air Act Amendments, which mandate specific product compositions are about $35 to $40 billion. There is concern that in some cases it may be more economical for some refineries to close down partially or entirely rather than upgrade facilities to meet these standards. In fact, the U.S. Departments of Energy and Commerce expect refinery shutdowns to continue through the early part of the new decade; however, total crude oil distillation capacity is expected to remain relatively stable as a result of increased capacity and utilization rates at existing facilities. Increases in demand for finished petroleum products will be filled by increased imports. Pressure to meet the Clean Air Act Amendments is a major driving force for pollution prevention programs in this industry sector.

PROCESS OPERATIONS AND SOURCES OF AIR EMISSIONS

Crude oil is a mixture of many different hydrocarbons and small amounts of impurities. The composition of crude oil can vary significantly depending on its source. Petroleum refineries are a complex system of multiple operations and the operations used at a given refinery depend upon the properties of the crude oil to be refined and the desired products. For these reasons, no two refineries are alike. Portions of the outputs from some processes are re-fed back into the same process, fed to new processes, fed back to a previous process, or blended with other outputs to form finished products. The major unit operations typically involved at petroleum refineries are described briefly below. In addition to those listed below, there are also many special purpose processes that cannot be described here and which may play an important role in a facility's efforts to comply with pollutant discharge and product specification requirements.

Refining crude oil into useful petroleum products can be separated into two phases and a number of supporting operations. The first phase is desalting of crude oil and the subsequent distillation into its various components or "fractions." The second phase is made up of three different types of "downstream" processes: combining, breaking, and reshaping.
Downstream processes convert some of the distillation fractions into petroleum products (residual fuel oil, gasoline, kerosene, etc.) through any combination of different cracking, coking, reforming, and alkylation processes. Supporting operations may include wastewater treatment, sulfur recovery, additive production, heat exchanger cleaning, blowdown systems, blending of products, and storage of products. Refinery pollutant outputs are discussed in more detail later.

Crude Oil Distillation and Desalting

One of the most important operations in a refinery is the initial distillation of the crude oil into its various boiling point fractions. Distillation involves the heating, vaporization, fractionation, condensation, and cooling of feedstocks. This subsection discusses the atmospheric and vacuum distillation processes which when used in sequence result in lower costs and higher efficiencies. This subsection also discusses the important first step of desalting the crude oil prior to distillation.

Desalting - Before separation into fractions, crude oil must first be treated to remove corrosive salts. The desalting process also removes some of the metals and suspended solids which cause catalyst deactivation. Desalting involves the mixing of heated crude oil with water (about 3 to 10% of the crude oil volume) so that the salts are dissolved in the water. The water must then be separated from the crude oil in a separating vessel by adding demulsifier chemicals to assist in breaking the emulsion and/or, more commonly, by applying a high potential electric field across the settling vessel to coalesce the polar salt water droplets. The desalting process creates an oily desalter sludge and a high temperature salt water waste stream which is typically added to other process waste waters for treatment in the refinery wastewater treatment facilities. The water used in crude desalting is often untreated or partially treated water from other refining process water sources.

Atmospheric Distillation - The desalted crude oil is then heated in a heat exchanger and furnace to about 750°F and fed to a vertical, distillation column at atmospheric pressure where most of the feed is vaporized and separated into its various fractions by condensing on 30 to 50 fractionation trays, each corresponding to a different condensation temperature. The lighter fractions condense and are collected towards the top of the column. Heavier fractions, which may not vaporize in the column, are further separated later by vacuum distillation. Within each atmospheric distillation tower, a number of side streams (at least four) of low-boiling point components are removed from the tower from different trays. These low-boiling point mixtures are in equilibrium with heavier components which must be removed. The side streams are each sent to a different small stripping tower containing four to 10 trays with steam injected under the bottom tray. The steam strips the light-end components from the heavier components and both the steam and light-ends are fed back to the atmospheric distillation tower above the corresponding side stream draw tray. Fractions obtained from atmospheric distillation include naphtha, gasoline, kerosene, light fuel oil, diesel oils, gas oil, lube distillate, and heavy bottoms. Most of these can be sold as finished products, or blended with products from downstream processes. Another product produced in atmospheric distillation, as well as many other refinery processes, is the light, noncondensible refinery fuel gas (mainly methane and ethane).

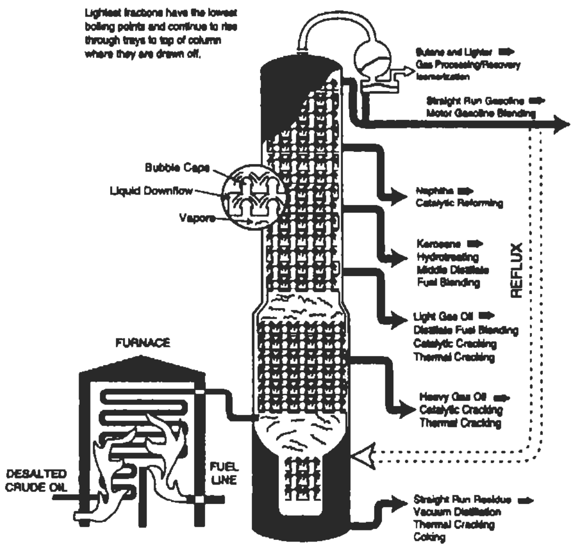


Figure 2. Crude oil distillation.

Typically this gas also contains hydrogen sulfide and ammonia gases. The mixture of these gases is known as "sour gas" or "acid gas." The sour gas is sent to the refinery sour gas treatment system which separates the fuel gas so that it can be used as fuel in the refinery heating furnaces. Air emissions during atmospheric distillation arise from the combustion of fuels in the furnaces to heat the crude oil and to process vents and fugitive emissions. Oily sour water (condensed steam containing hydrogen sulfate and ammonia) and oil are also generated in the fractionators (refer to Figure 2).

Vacuum Distillation - Heavier fractions from the atmospheric distillation unit that cannot be distilled without cracking under its pressure and temperature conditions are vacuum distilled. Vacuum distillation is simply the distillation of petroleum fractions at a very low pressure (0.2 to 0.7 psia) to increase volatilization and separation. In most systems, the vacuum inside the fractionator is maintained with steam ejectors and vacuum pumps, barometric condensers, or surface condensers.

The injection of superheated steam at the base of the vacuum fractionator column further reduces the partial pressure of the hydrocarbons in the tower, facilitating vaporization and separation. The heavier fractions from the vacuum distillation column are processed downstream into more valuable products through either cracking or coking operations.

A potential source of emissions from distillation of crude oil is the combustion of fuels in the furnace and some light gases leaving the top of the condensers on the vacuum distillation column. A certain amount of noncondensable light hydrocarbons and hydrogen sulfide pass through the condenser to a hot well, and then are discharged to the refinery sour fuel system or are vented to a process heater, flare, or another control device to destroy hydrogen sulfide. The quantity of these emissions depends on the size of the unit, the type of feedstock, and the cooling water temperature. If barometric condensers are used in vacuum distillation, significant amounts of oily wastewater can be generated. Vacuum pumps and surface condensers have largely replaced barometric condensers in many refineries to eliminate this oily wastewater stream. Oily sour water is also generated in the fractionators.

Downstream Processing

Certain fractions from the distillation of crude oil are further refined in thermal cracking (visbreaking), coking, catalytic cracking, catalytic hydrocracking, hydrotreating, alkylation, isomerization, polymerization, catalytic reforming, solvent extraction, Merox, dewaxing, propane deasphalting, and other operations. These downstream processes change the molecular structure of hydrocarbon molecules either by breaking them into smaller molecules, joining them to form larger molecules, or reshaping them into higher quality molecules. For many of the operations, a number of different techniques are used in the industry.

Thermal Cracking/Visbreaking - Thermal cracking, or visbreaking, uses heat and pressure to break large hydrocarbon molecules into smaller, lighter molecules. The process has been largely replaced by catalytic cracking and some refineries no longer employ thermal cracking. Both processes reduce the production of less valuable products such as heavy fuel oil and cutter stock and increase the feed stock to the catalytic cracker and gasoline yields. In thermal cracking, heavy gas oils and residue from the vacuum distillation process are typically the feed stocks. The feed stock is heated in a furnace or other thermal unit to up to 1,000°F and then fed to a reaction chamber which is kept at a pressure of about 140 psig. Following the reactor step, the process stream is mixed with a cooler recycle stream, which stops the cracking reactions. The product is then fed to a flasher chamber, where pressure is reduced and lighter products vaporize and are drawn off. The lighter products are fed to a fractionating tower where the various fractions are separated. The "bottoms" consist of heavy residue, part of which is recycled to cool the process stream leaving the reaction chamber; the remaining bottoms are usually blended into residual fuel (refer to Figure 3). Air emissions from thermal cracking include emissions from the combustion of fuels in the process heater, vents, and fugitive emissions.

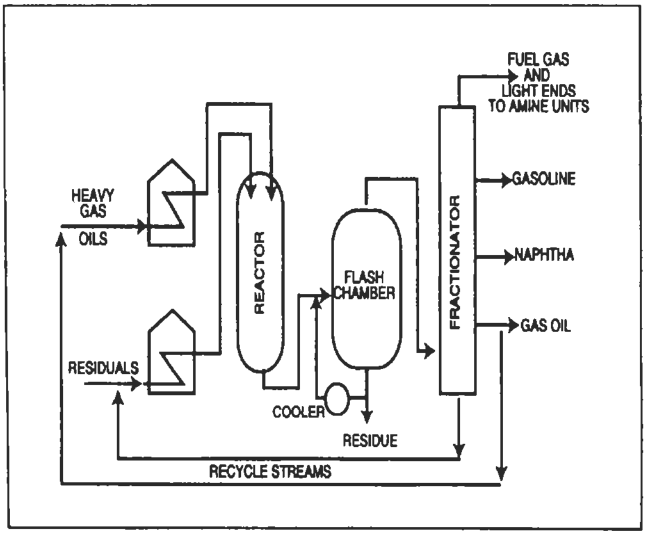


Figure 3. Thermal cracker flow diagram.

Coking - A coker flow diagram is shown in Figure 4. Coking is a cracking process used primarily to reduce refinery production of low-value residual fuel oils to transportation fuels, such as gasoline and diesel. As part of the upgrading process, coking also produces petroleum coke, which is essentially solid carbon with varying amounts of impurities, and is used as a fuel for power plants if the sulfur content is low enough.

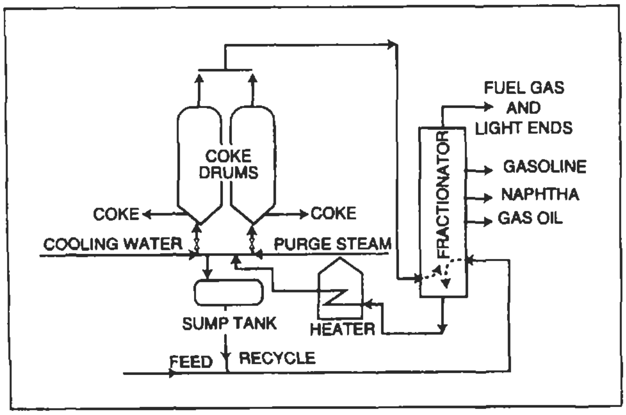


Figure 4. Coker flow diagram.

Coke also has nonfuel applications as a raw material for many carbon and graphite products including anodes for the production of aluminum, and furnace electrodes for the production of elemental phosphorus, titanium dioxide, calcium carbide, and silicon carbide. A number of different processes are used to produce coke; both *delayed coking* and *fluid coking* are the most widely used processes. Fluid coking produces a higher grade of coke. In delayed coking operations, the same basic process as thermal cracking is used except feed streams are allowed to react longer without being cooled.

The delayed coking feed stream of residual oils from various upstream processes is first introduced to a fractionating tower where residual lighter materials are drawn off and the heavy ends are condensed. The heavy ends are removed and heated in a furnace to about 900 to 1,000°F and then fed to an insulated vessel called a coke drum where the coke is formed. When the coke drum is filled with product, the feed is switched to an empty parallel drum. Hot vapors from the coke drums, containing cracked lighter hydrocarbon products, hydrogen sulfide, and ammonia, are fed back to the fractionator where they can be treated in the sour gas treatment system or drawn off as intermediate products.

Steam is then injected into the full coke drum to remove hydrocarbon vapors, water is injected to cool the coke, and the coke is removed. Typically, high pressure water jets are used to cut the coke from the drum.

Air emissions from coking operations include the process heater flue gas emissions, fugitive emissions, and emissions that may arise from the removal of the coke from the coke drum. The injected steam is condensed and the remaining vapors are typically flared. Wastewater is generated from the coke removal and cooling operations and from the steam injection. In addition, the removal of coke from the drum can release particulate emissions and any remaining hydrocarbons to the atmosphere.

Catalytic Cracking - Catalytic cracking uses heat, pressure, and a catalyst to break larger hydrocarbon molecules into smaller, lighter molecules. Catalytic cracking has largely replaced thermal cracking because it is able to produce more gasoline with a higher octane and less heavy fuel oils and light gases. Feed stocks are light and heavy oils from the crude oil distillation unit which are processed primarily into gasoline as well as some fuel oil and light gases. Most catalysts used in catalytic cracking consist of mixtures of crystalline synthetic silica-alumina, termed "zeolites," and amorphous synthetic silica alumina.

The catalytic cracking processes, as well as most other refinery catalytic processes, produce coke which collects on the catalyst surface and diminishes its catalytic properties. The catalyst, therefore, needs to be regenerated continuously or periodically essentially by burning the coke off the catalyst at high temperatures.

The method and frequency in which catalysts are regenerated are major factors in the design of catalytic cracking units. A number of different catalytic cracking designs are currently in use, including fixed-bed reactors, moving-bed reactors, fluidized-bed reactors, and once-through units. The fluidized- and moving-bed reactors are by far the most prevalent.

Fluidized-bed catalytic cracking units (FCCUs) are the most common catalytic cracking units. In the fluidized-bed process, oil and oil vapor preheated to 500 to 800°F is contacted with hot catalyst at about 1,300°F either in the reactor itself or in the feed line (called the riser) to the reactor. The catalyst is in a fine, granular form which, when mixed with the vapor, has many of the properties of a fluid. The fluidized catalyst and the reacted hydrocarbon vapor separate mechanically in the reactor and any oil remaining on the catalyst is removed by steam stripping.

The cracked oil vapors are then fed to a fractionation tower where the various desired fractions are separated and collected. The catalyst flows into a separate vessel(s) for either single- or two-stage regeneration by burning off the coke deposits with air.

In the moving-bed process, oil is heated to up to 1,300°F and is passed under pressure through the reactor where it comes into contact with a catalyst flow in the form of beads or pellets. The cracked products then flow to a fractionating tower where the various compounds are separated and collected. The catalyst is regenerated in a continuous process where deposits of coke on the catalyst are burned off.

Some units also use steam to strip remaining hydrocarbons and oxygen from the catalyst before being fed back to the oil stream. In recent years moving-bed reactors have largely been replaced by fluidized-bed reactors.

Catalytic cracking is one of the most significant sources of air pollutants at refineries. Figure 5 shows a flow scheme for a catalytic cracking unit. Air emissions from catalytic cracking operations include: the process heater flue gas emissions, fugitive emissions, and emissions generated during regeneration of the catalyst. Relatively high concentrations of carbon monoxide can be produced during regeneration of the catalyst which is typically converted to carbon dioxide either in the regenerator or further downstream in a carbon monoxide waste heat boiler.

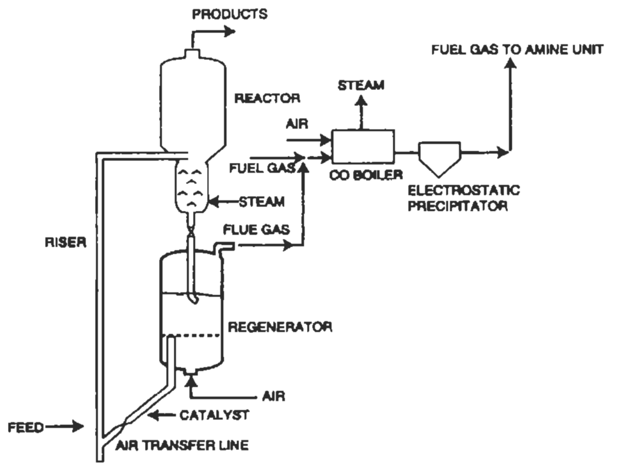


Figure 5. Catalytic cracking flow diagram.

In addition, a significant amount of fine catalyst dust is produced in FCCUs as a result of the constant movement of the catalyst grains against each other. Much of this dust, consisting primarily of alumina and relatively small amounts of nickel, is carried with the carbon monoxide strewn to the carbon monoxide burner.

The catalyst dust is then separated from the resulting carbon dioxide stream via cyclones and/or electrostatic precipitators and is sent off-site for disposal or treatment. Generated wastewater is typically sour water from the fractionator containing some oil and phenols. Wastewater containing metal impurities from the feed oil can also be generated from the steam used to purge and regenerate catalysts.

Catalytic Hydrocracking - Catalytic hydrocracking normally utilizes a fixed-bed catalytic cracking reactor with cracking occurring under substantial pressure (1,200 to 2,000 psig) in the presence of hydrogen. Feedstocks to hydrocracking units are often those fractions that are the most difficult to crack and cannot be cracked effectively in catalytic cracking units. The feedstocks include: middle distillates, cycle oils, residual fuel oils, and reduced crudes. The hydrogen suppresses the formation of heavy residual material and increases the yield of gasoline by reacting with the cracked products. However, this process also breaks the heavy, sulfur and nitrogen bearing hydrocarbons and releases these impurities to where they could potentially foul the catalyst. For this reason, the feedstock is often first hydrotreated to remove impurities before being sent to the catalytic hydrocracker.

Sometimes hydrotreating is accomplished by using the first reactor of the hydrocracking process to remove impurities. Water also has a detrimental effect on some hydrocracking catalysts and must be removed before being fed to the reactor. The water is removed by passing the feed stream through a silica gel or molecular sieve dryer. Depending on the products desired and the size of the unit, catalytic hydrocracking is conducted in either single stage or multi-stage reactor processes. Most catalysts consist of a crystalline mixture of silica-alumina with small amounts of rare earth metals. Hydrocracking feedstocks are usually first hydrotreated to remove the hydrogen sulfide and ammonia that will poison the catalyst. Sour gas and sour water streams are produced at the fractionator; however, if the hydrocracking feedstocks are first hydrotreated to remove impurities, both streams will contain relatively low levels of hydrogen sulfide and ammonia. Hydrocracking catalysts are typically regenerated off-site after two to four years of operation. Therefore, few or no emissions are generated from the regeneration processes. Air emissions arise from the process heater, vents, and fugitive emissions.

Hydrotreating/Hydroprocessing - Hydrotreating and hydroprocessing are similar processes used to remove impurities such as sulfur, nitrogen, oxygen, halides, and trace metal impurities that may deactivate process catalysts. Hydrotreating also upgrades the quality of fractions by converting olefins and diolefins to paraffins for the purpose of reducing gum formation in fuels. Hydroprocessing, which typically uses residuals from the crude distillation units, also cracks these heavier molecules to lighter more saleable products. Both hydrotreating and hydroprocessing units are usually placed upstream of those processes in which sulfur and nitrogen could have adverse effects on the catalyst, such as catalytic reforming and hydrocracking units.

The processes utilize catalysts in the presence of substantial amounts of hydrogen under high pressure and temperature to react the feedstocks and impurities with hydrogen. The reactors are nearly all fixed-bed with catalyst replacement or regeneration done after months or years of operation often at an off-site facility. In addition to the treated products, the process produces a stream of light fuel gases, hydrogen sulfide, and ammonia. The treated product and hydrogen-rich gas are cooled after they leave the reactor before being separated. The hydrogen is recycled to the reactor. The off-gas stream may be very rich in hydrogen sulfide and light fuel gas. The fuel gas and hydrogen sulfide are typically sent to the sour gas treatment unit and sulfur recovery unit. Catalysts are typically cobalt or molybdenum oxides on alumina, but can also contain nickel and tungsten.

Air emissions from hydrotreating may arise from process heater flue gas, vents, and fugitive emissions. Figure 6 provides a simplified flow diagram.

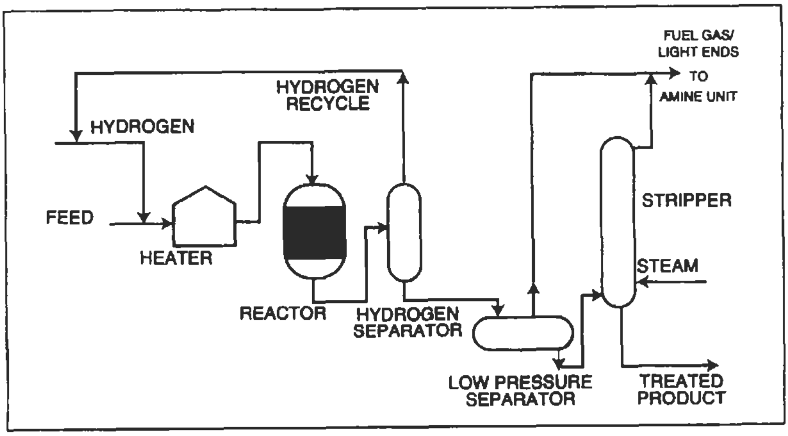


Figure 6. Flow diagram for hydrotreating.

Alkylation - Alkylation is used to produce a high octane gasoline blending stock from the isobutane formed primarily during catalytic cracking and coking operations, but also from catalytic reforming, crude distillation, and natural gas processing. Alkylation joins an olefin and an isoparaffin compound using either a sulfuric acid or hydrofluoric acid catalyst. The products are alkylates including propane and butane liquids. When the concentration of acid becomes less than 88%, some of the acid must be removed and replaced with stronger acid. In the hydrofluoric acid process, the slip stream of acid is redistilled. Dissolved polymerization products are removed from the acid as a thick dark oil. The concentrated hydrofluoric acid is recycled and the net consumption is about 0.3 pounds per barrel of alkylates produced. Hydrofluoric acid alkylation units require special engineering design, operator training and safety equipment precautions to protect operators from accidental contact with hydrofluoric acid.
In the sulfuric acid process, the sulfuric acid removed must be regenerated in a sulfuric acid plant which is generally not a part of the alkylation unit and may be located off-site. Spent sulfuric acid generation is substantial; typically in the range of 13 to 30 pounds per barrel of alkylate. Air emissions from the alkylation process may arise from process vents and fugitive emissions.

Isomerization - Isomerization is used to alter the arrangement of a molecule without adding or removing anything from the original molecule. Typically, paraffins (butane or pentane from the crude distillation unit) are converted to isoparaffins having a much higher octane. Isomerization reactions take place at temperatures in the range of 200 to 400°F in the presence of a catalyst that usually consists of platinum on a base material. Two types of catalysts are currently in use. One requires the continuous addition of small amounts of organic chlorides which are converted to hydrogen chloride in the reactor. In such a reactor, the feed must be free of oxygen sources including water to avoid deactivation and corrosion problems. The other type of catalyst uses a molecular sieve base and does not require a dry and oxygen free feed. Both types of isomerization catalysts require an atmosphere of hydrogen to minimize coke deposits; however, the consumption of hydrogen is negligible. Catalysts typically need to be replaced about every two to three years or longer. Platinum is then recovered from the used catalyst off site. Light ends are stripped from the product stream leaving the reactor and are then sent to the sour gas treatment unit. Some isomerization units utilize caustic treating of the light fuel gas stream to neutralize any entrained hydrochloric acid. This will result in a calcium chloride (or other salts) waste stream. Air emissions may arise from the process heater, vents, and fugitive emissions.

Polymerization - Polymerization is occasionally used to convert propene and butene to high octane gasoline blending components. The process is similar to alkylation in its feed and products, but is often used as a less expensive alternative to alkylation. The reactions typically take place under high pressure in the presence of a phosphoric acid catalyst. The feed must be free of sulfur, which poisons the catalyst; basic materials, which neutralize the catalyst; and oxygen, which affects the reactions. The propene and butene feed is washed first with caustic to remove mercaptans (molecules containing sulfur), then with an amine solution to remove hydrogen sulfide, then with water to remove caustics and amines, and finally dried by passing through a silica gel or molecular sieve dryer. Air emissions of sulfur dioxide may arise during the caustic washing operation.

Catalytic Reforming - Catalytic reforming uses catalytic reactions to process primarily low octane heavy straight run (from the crude distillation unit) gasolines and naphthas into high octane aromatics (including benzene). There are four major types of reactions which occur during reforming processes: (1) dehydrogenation of naphthenes to aromatics; (2) dehydrocyclization of paraffins to aromatics; (3) isomerization; and (4) hydrocracking. The dehydrogenation reactions are very endothermic, requiring that the hydrocarbon stream be heated between each catalyst bed. All but the hydrocracking reaction release hydrogen which can be used in the hydrotreating or hydrocracking processes. Fixed-bed or moving bed processes are utilized in a series of three to six reactors. Feedstocks to catalytic reforming processes are usually hydrotreated first to remove sulfur, nitrogen and metallic contaminants. In continuous reforming processes, catalysts can be regenerated one reactor at a time, once or twice per day, without disrupting the operation of the unit. In semi-regenerative units, regeneration of all reactors can be carried out simultaneously after 3 to 24 months of operation by first shutting down the process. Because the recent reformulated gasoline rules have limited the allowable amount of benzene in gasoline, catalytic reforming is being used less as an octane enhancer than in past years. Air emissions from catalytic reforming arise from the process heater gas and fugitive emissions. The catalysts used in catalytic reforming processes are usually very expensive and extra precautions are taken to ensure that catalyst is not lost. When the catalyst has lost its activity and can no longer be regenerated, the catalyst is usually sent off-site for recovery of the metals. Subsequent air emissions from catalyst regeneration are, therefore, relatively low. Relatively small volumes of wastewater containing sulfides, ammonia, and mercaptans may be generated from the stripping tower used to remove light ends from the reactor effluent.

Solvent Extraction - Solvent extraction uses solvents to dissolve and remove aromatics from lube oil feed stocks, improving viscosity, oxidation resistance, color, and gum formation. A number of different solvents are used, with the two most common being furfural and phenol. Typically, feed lube stocks are contacted with the solvent in a packed tower or rotating disc contactor. Each solvent has a different solvent-to-oil ratio and recycle ratio within the tower.

Solvents are recovered from the oil stream through distillation and steam stripping in a fractionator. The stream extracted from the solvent contains high concentrations of hydrogen sulfide, aromatics, naphthenes and other hydrocarbons, and is often fed to the hydrocracking unit.

Chemical Treating - In petroleum refining, chemical treating is used to remove or change the undesirable properties associated with sulfur, nitrogen, or oxygen compound contaminants in petroleum products. Chemical treating is accomplished by either extraction or oxidation (also known as sweetening), depending upon the product. Extraction is used to remove sulfur from the very light petroleum fractions, such as propane/propylene (PP) and butane/butylene (BB). Sweetening, though, is more effective on gasoline and middle distillate products. A typical extraction process is "Merox" extraction. Merox extraction is used to remove mercaptans (organic sulfur compounds) from PP and BB streams. PP streams may undergo amine treating before the Merox extraction to remove excess H_2S which tends to fractionate with PP and interferes with the Merox process. A caustic prewash of the PP and BB removes any remaining trace H_2S prior to Merox extraction. The PP and BB streams are passed up through the trays of an extraction tower. Caustic solution flowing down the extraction tower absorbs mercaptan from the PP and BB streams. The rich caustic is then regenerated by oxidizing the mercaptans to disulfide in the presence of aqueous Merox catalyst and the lean caustic recirculated to the extraction tower. The disulfide is insoluble in the caustic and can be separated.

Oxidation or "sweetening" is used on gasoline and distillate fractions. A common oxidation process is also a Merox process that uses a solid catalyst bed. Air and a minimum amount of alkaline caustic ("mini-alky" operation) is injected into the hydrocarbon stream. As the hydrocarbon passes through the Merox catalyst bed, sulfur mercaptans are oxidized to disulfide. In the sweetening Merox process, the caustic is not regenerated. The disulfide can remain with the gasoline product, since it does not possess the objectionable odor properties of mercaptans; hence, the product has been sweetened.

In the extraction process, a waste oily disulfide stream leaves the separator. Air emissions arise from fugitive hydrocarbons and the process vents on the separator which may contain disulfides.

Dewaxing - Dewaxing of lubricating oil base stocks is necessary to ensure that the oil will have the proper viscosity at lower ambient temperatures. Two types of dewaxing processes are used: selective hydrocracking and solvent dewaxing. In selective hydrocracking, one or two zeolite catalysts are used to selectively crack the wax paraffins. Solvent dewaxing is more prevalent. In solvent dewaxing, the oil feed is diluted with solvent to lower the viscosity, chilled until the wax is crystallized, and then filtered to remove the wax. Solvents used for the process include propane and mixtures of methyl ethyl ketone (MEK) with methyl isobutyl ketone (MIBK) or MEK with toluene. Solvent is recovered from the oil and wax through heating, two-stage flashing, followed by steam stripping. The solvent recovery stage results in solvent contaminated water which typically is sent to the wastewater treatment plant. The wax is either used as feed to the catalytic cracker or is deoiled and sold as industrial wax. Air emissions may arise from fugitive emissions of the solvents.

Propane Deasphalting - Propane deasphalting produces lubricating oil base stocks by extracting asphaltenes and resins from the residuals of the vacuum distillation unit. Propane is usually used to remove asphaltenes due to its unique solvent properties. At lower temperatures (100 to 140°F), paraffins are very soluble in propane and at higher temperatures (about 200°F) all hydrocarbons are almost insoluble in propane. The propane deasphalting process is similar to solvent extraction in that a packed or baffled extraction tower or rotating disc contactor is used to mix the oil feed stocks with the solvent.

In the tower method, four to eight volumes of propane are fed to the bottom of the tower for every volume of feed flowing down from the top of the tower. The oil, which is more soluble in the propane, dissolves and flows to the top. The asphaltene and resins flow to the bottom of the tower where they are removed in a propane mix. Propane is recovered from the two streams through two-stage flash systems followed by steam stripping in which propane is condensed and removed by cooling at high pressure in the first stage and at low pressure in the second stage. The asphalt recovered can be blended with other asphalts or heavy fuels, or can be used as feed to the coker. The propane recovery stage results in propane contaminated water which typically is sent to the wastewater treatment plant. Air emissions may arise from fugitive propane emissions and process vents.

Supporting Operations

Many important refinery operations are not directly involved in the production of hydrocarbon fuels but serve in a supporting role. Some of the major supporting processes are described below.

Wastewater Treatment

Relatively large volumes of water are used by the petroleum refining industry. Four types of wastewater are produced: surface water runoff, cooling water, process water, and sanitary wastewater. Surface water runoff is intermittent and will contain constituents from spills to the surface, leaks in equipment, and any materials that may have collected in drains. Runoff surface water also includes water coming from crude and product storage tank roof drains.

A large portion of water used in petroleum refining is used for cooling. Cooling water typically does not come into direct contact with process oil streams and therefore contains less contaminants than process wastewater. Most cooling water is recycled over and over with a bleed or blowdown stream to the wastewater treatment unit to control the concentration of contaminants and the solids content in the water. Cooling towers within the recycle loop cool the water using ambient air. Some cooling water, termed "once through," is passed through a process unit once and is then discharged directly without treatment in the wastewater treatment plant. The water used for cooling often contains chemical additives such as chromates, phosphates, and antifouling biocides to prevent scaling of pipes and biological growth. It should be noted, however, that many refineries in the United States no longer use chromates in cooling water as antifouling agents; however, this is not the case in other parts of the world. Although cooling water usually does not come into direct contact with oil process streams, it also may contain some oil contamination due to leaks in the process equipment.

Water used in processing operations also accounts for a significant portion of the total wastewater. Process wastewater arises from desalting crude oil, steam stripping operations, pump gland cooling, product fractionator reflux drum drains and boiler blowdown. Because process water often comes into direct contact with oil, it is usually highly contaminated. Petroleum refineries typically utilize primary and secondary wastewater treatment technologies. Primary wastewater treatment consists of the separation of oil, water, and solids in two stages. During the first stage, an API separator, a corrugated plate interceptor, or other separator design is used. Wastewater moves very slowly through the separator allowing free oil to float to the surface and be skimmed off, and solids to settle to the bottom and be scraped off to a sludge collecting hopper. The second stage utilizes physical or chemical methods to separate emulsified oils from the wastewater. Physical methods may include the use of a series of settling ponds with a long retention time, or the use of dissolved air flotation (DAF). In DAF, air is bubbled through the wastewater, and both oil and suspended solids are skimmed off the top. Chemicals, such as ferric hydroxide or aluminum hydroxide, can be used to coagulate impurities into a froth or sludge which can be more easily skimmed off the top. Some wastes associated with the primary treatment of wastewater at petroleum refineries may be considered hazardous and include: API separator sludge, primary treatment sludge, sludges from other gravitational separation techniques, float from DAF units, and wastes from settling ponds.

After primary treatment, the wastewater can be discharged to a publicly owned treatment works or undergo secondary treatment before being discharged directly to surface waters under a National Pollution Discharge Elimination System (NPDES) permit. In secondary treatment, dissolved oil and other organic pollutants may be consumed biologically by microorganisms. Biological treatment may require the addition of oxygen through a number of different techniques, including activated sludge units, trickling filters, and rotating biological contactors. Secondary treatment generates bio-mass waste which is typically treated anaerobically, and then dewatered.

Some refineries employ an additional stage of wastewater treatment called polishing to meet discharge limits. The polishing step can involve the use of activated carbon, anthracite coal, or sand to filter out any remaining impurities, such as biomass, silt, trace metals, and other inorganic chemicals, as well as any remaining organic chemicals.

Certain refinery wastewater streams are treated separately, prior to the wastewater treatment plant, to remove contaminants that would not easily be treated after mixing with other wastewater. One such waste stream is the sour water drained from distillation reflux drums. Sour water contains dissolved hydrogen sulfide and other organic sulfur compounds and ammonia which are stripped in a tower with gas or steam before being discharged to the wastewater treatment plant.

Wastewater treatment plants are also a significant source of refinery air emissions and solid wastes. Air releases arise from fugitive emissions from the numerous tanks, ponds, and sewer system drains. Solid wastes are generated in the form of sludges from a number of the treatment units.

Gas Treatment and Sulfur Recovery

Sulfur is removed from a number of refinery process off-gas streams (sour gas) in order to meet the SO_x emissions limits of the CAA and to recover saleable elemental sulfur. Process off-gas streams, or sour gas, from the coker, catalytic cracking unit, hydrotreating units, and hydroprocessing units can contain high concentrations of hydrogen sulfide mixed with light refinery fuel gases. Before elemental sulfur can be recovered, the fuel gases (primarily methane and ethane) need to be separated from the hydrogen sulfide. This is typically accomplished by dissolving the hydrogen sulfide in a chemical solvent. Solvents most commonly used are amines, such as diethanolamine (DEA). Dry adsorbents such as molecular sieves, activated carbon, iron sponge, and zinc oxide are also used. In the amine solvent processes, DEA solution or another amine solvent is pumped to an absorption tower where the gases are contacted and hydrogen sulfide is dissolved in the solution. The fuel gases are removed for use as fuel in process furnaces in other refinery operations. The amine-hydrogen sulfide solution is then heated and steam stripped to remove the hydrogen sulfide gas.

Current methods for removing sulfur from the hydrogen sulfide gas streams are typically a combination of two processes: the Claus Process followed by the Beaven Process, SCOT Process, or the Wellman-Land Process.

The Claus process consists of partial combustion of the hydrogen sulfide-rich gas stream (with one-third the stoichiometric quantity of air) and then reacting the resulting sulfur dioxide and unburned hydrogen sulfide in the presence of a bauxite catalyst to produce elemental sulfur. Refer to the process flow diagram in Figure 7.

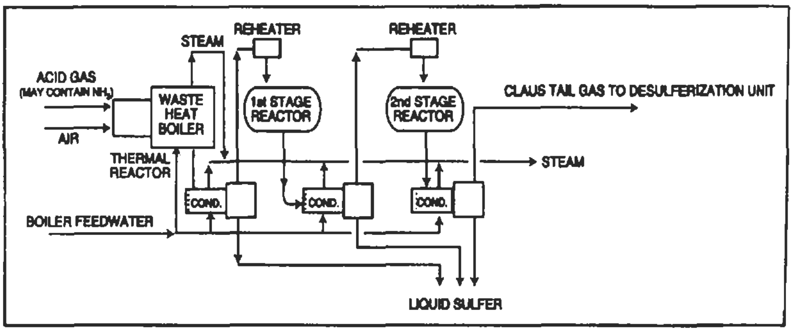


Figure 7. Claus sulfur recovery flow diagram.

Since the Claus process by itself removes only about 90% of the hydrogen sulfide in the gas stream, the Beaven, SCOT, or Wellman-Lord processes are often used to further recover sulfur. In the Beaven process, the hydrogen sulfide in the relatively low concentration gas stream from the Claus process can be almost completely removed by absorption in a quinone solution.

The dissolved hydrogen sulfide is oxidized to form a mixture of elemental sulfur and hydro-quinone. The solution is injected with air or oxygen to oxidize the hydro-quinone back to quinone. The solution is then filtered or centrifuged to remove the sulfur and the quinone is then reused.

The Beaven process is also effective in removing small amounts of sulfur dioxide, carbonyl sulfide, and carbon disulfide that are not affected by the Claus process. These compounds are first converted to hydrogen sulfide at elevated temperatures in a cobalt molybdate catalyst prior to being fed to the Beaven unit. Air emissions from sulfur recovery units will consist of hydrogen sulfide, SO_x, and NO_x in the process tail gas as well as fugitive emissions and releases from vents.

The SCOT process is also widely used for removing sulfur from the Claus tail gas. The sulfur compounds in the Claus tail gas are converted to hydrogen sulfide by heating and passing it through a cobalt-molybdenum catalyst with the addition of a reducing gas. The gas is then cooled and contacted with a solution of di-isopropanolamine (DIPA) which removes all but trace amounts of hydrogen sulfide. The sulfide-rich DIPA is sent to a stripper where hydrogen sulfide gas is removed and sent to the Claus plant. The DIPA is returned to the absorption column.

Additive Production

A number of chemicals (mostly alcohols and ethers) are added to motor fuels to either improve performance or meet federal and state environmental requirements. Since the 1970s, alcohols (methanol and ethanol) and ethers have been added to gasoline to increase octane levels and reduce carbon monoxide generation in place of the lead additives which were being phased out as required by the 1970 Clean Air Act. In 1990, the more stringent Clean Air Act Amendments established minimum and maximum amounts of chemically combined oxygen in motor fuels as well as an upper limit on vapor pressure. As a result, alcohol additives have been increasingly supplemented or replaced with a number of different ethers which are better able to meet both the new oxygen requirements and the vapor pressure limits.

The most common ethers being used as additives are methyl tertiary butyl ether (MTBE), and tertiary amyl methyl ether (TAME). Many of the larger refineries manufacture their own supplies of MTBE and TAME by reacting isobutylene and/or isoamylene with methanol. Smaller refineries usually buy their supplies from chemical manufacturers or the larger refineries.

Isobutylene is obtained from a number of refinery sources including: the light naphtha from the FCCU and coking units, the by-product from steam cracking of naphtha or light hydrocarbons during the production of ethylene and propylene, catalytic dehydrogenation of isobutane, and conversion of tertiary butyl alcohol recovered as a by-product in the manufacture of propylene oxides. Several different processes are currently in use to produce MTBE and TAME from isobutylene and methanol. Most processes use a two-stage acidic ion exchange resin catalyst. The reaction is exothermic and cooling to the proper reaction temperature is critical in obtaining the optimal conversion efficiency. The process usually produces an MTBE or TAME stream and a relatively small stream of unreacted hydrocarbons and methanol. The methanol is extracted in a water wash and the resulting methanol-water mixture is distilled to recover the methanol for recycling.

Blowdown System

Most refinery process units and equipment are manifolded into a collection unit, called the blowdown system. Blowdown systems provide for the safe handling and disposal of liquids and gases that are either automatically vented from the process units through pressure relief valves, or that are manually drawn from units. Recirculated process streams and cooling water streams are often manually purged to prevent the continued buildup of contaminants in the stream. Part or all of the contents of equipment can also be purged to the blowdown system prior to shutdown before normal or emergency shutdowns.

Blowdown systems utilize a series of flash drums and condensers to separate the blowdown into its vapor and liquid components. The liquid is typically composed of mixtures of water and hydrocarbons containing sulfides, ammonia, and other contaminants, which are sent to the wastewater treatment plant.

The gaseous component typically contains hydrocarbons, hydrogen sulfide, ammonia, mercaptans, solvents, and other constituents, and is either discharged directly to the atmosphere or is combusted in a flare. The major air emissions from blowdown systems are hydrocarbons in the case of direct discharge to the atmosphere and sulfur oxides when flared.

Blending

Blending is the final operation in petroleum refining. It consists of mixing the products in various proportions to meet specifications such as vapor pressure, specific gravity, sulfur content, viscosity, octane number, initial boiling point, and pour point. Blending can be carried out inline or in batch blending tanks. Air emissions from blending are fugitive VOCs from blending tanks, valves, pumps, and mixing operations.

Storage Tanks

Storage tanks are used throughout the refining process to store crude oil and intermediate process feeds for cooling and further processing. Finished petroleum products are also kept in storage tanks before transport off site. Storage tank bottoms are mixtures of iron rust from corrosion, sand, water, and emulsified oil and wax, which accumulate at the bottom of tanks. Liquid tank bottoms (primarily water and oil emulsions) are periodically drawn off to prevent their continued buildup.

Tank bottom liquids and sludge are also removed during periodic cleaning of tanks for inspection. Tank bottoms may contain amounts of tetraethyl or tetramethyl lead (although this is increasingly rare due to the phaseout of leaded products), other metals, and phenols. Solids generated from leaded gasoline storage tank bottoms are listed as an RCRA hazardous waste. Even if equipped with floating tops, storage tanks account for considerable VOC emissions at petroleum refineries. A study of petroleum refinery emissions found that the majority of tank losses occurred through tank seals on gasoline storage tanks.

EMISSIONS ESTIMATES

Raw material input to petroleum refineries is primarily crude oil; however, petroleum refineries use and generate an enormous number of chemicals, many of which leave the facilities as discharges of air emissions, wastewater, or solid waste. Pollutants generated typically include VOCs, carbon monoxide (CO), sulfur oxides (SO_x), nitrogen oxides (NO_x), particulates, ammonia (NH_3), hydrogen sulfide (H_2S) metals, spent acids, and numerous toxic organic compounds.

When discussing material outputs of the petroleum refining industry, it is important to note the relationship between the outputs of the industry itself and the outputs resulting from the use of refinery products. Petroleum refineries play an important role in the U.S. economy, supplying approximately 40% of the total energy used in the U.S. and virtually all of the energy consumed in the transportation sector.

The pollutant outputs from the refining facilities, however, are modest in comparison to the pollutant outputs realized from the consumption of petroleum products by the transportation sector, electric utilities, chemical manufacturers, and other industrial and commercial users.

Air emissions from refineries include fugitive emissions of the volatile constituents in crude oil and its fractions, emissions from the burning of fuels in process heaters, and emissions from the various refinery processes themselves. Fugitive emissions occur throughout refineries and arise from the thousands of potential fugitive emission sources such as valves, pumps, tanks, pressure relief valves, flanges, etc.

While individual leaks are typically small, the sum of all fugitive leaks at a refinery can be one of its largest emission sources. Fugitive emissions can be reduced through a number of techniques, including improved leak resistant equipment, reducing the number of tanks and other potential sources, and, perhaps the most effective method, an ongoing Leak Detection and Repair (LDAR) program. The numerous process heaters used in refineries to heat process streams or to generate steam (boilers) for heating or steam stripping, can be potential sources of SO_x, NO_x, CO, particulate matter, and hydrocarbon emissions. When operating properly and when burning cleaner fuels such as refinery fuel gas, fuel oil, or natural gas, these emissions are relatively low. If, however, combustion is not complete, or heaters are fired with refinery fuel pitch or residuals, emissions can be significant. The majority of gas streams exiting each refinery process contain varying amounts of refinery fuel gas, hydrogen sulfide, and ammonia. These streams are collected and sent to the gas treatment and sulfur recovery units to recover the refinery fuel gas and sulfur. Emissions from the sulfur recovery unit typically contain some H_2S, SO_x, and NO_x. Other emissions sources from refinery processes arise from periodic regeneration of catalysts. These processes generate streams that may contain relatively high levels of carbon monoxide, particulates, and VOCs. Before being discharged to the atmosphere, such off-gas streams may be treated first through a carbon monoxide boiler to burn carbon monoxide and any VOCs, and then through an electrostatic precipitator or cyclone separator to remove particulate matter. Metals from catalysts and from the crude oil that have deposited on the catalyst during the production often are recovered by third party recovery facilities.

Table 6 lists typical air emissions from petroleum refining operations. Where possible, typical quantities and concentrations of pollutants are reported. These should be considered very approximate figures since no two refinery operations are identical. However, they do provide a general idea of the quantities, flows, and levels of different types of priority pollutants handled by refinery operations.

Table 6. Air Emission Outputs from Petroleum Refining Operations.

Process	Pollutants
Crude Oil Desalting	Heater stack gas (CO, SO_x, NO_x, hydrocarbons and particulates), fugitive emissions (hydrocarbons).
Atmospheric Distillation and Vacuum Distillation	Heater stack gas (CO, SO_x, NO_x, hydrocarbons and PM), vents and fugitive emissions (hydrocarbons) Steam ejector emissions (hydrocarbons), heater stack gas (CO, SO_x, NO_x, hydrocarbons and PM), vents and fugitive emissions (hydrocarbons).

Process	Pollutants
Thermal Cracking/Visbreaking	Heater stack gas (CO, SO_x, NO_x, HCs and PM), vents and fugitive emissions (HCs).
Coking	Heater stack gas (CO, SO_x, NO_x, hydrocarbons and PM), vents and fugitive emissions (HCs) and decoking emissions (HCs and PM).
Catalytic Cracking	Heater stack gas (CO, SO_x, NO_x, HCs and PM), fugitive emissions (HCs) and catalyst regeneration (CO, NO_x, SO_x, and PM).
Catalytic Hydrocracking	Heater stack gas (CO, SO_x, NO_x, hydrocarbons and PM), fugitive emissions (hydrocarbons) and catalyst regeneration (CO, NO_x, SO_x, and catalyst dust).
Hydrotreating/Hydroprocessing	Heater stack gas (CO, SO_x, NO_x, hydrocarbons and PM), vents and fugitive emissions (HCs) and catalyst regeneration (CO, NO_x, SO_x).
Alkylation	Heater stack gas (CO, SO_x, NO_x, HCs and PM), vents and fugitive emissions (HCs).
Isomerization	Heater stack gas (CO, SO_x, NO_x, HCs and PM), HCl (potentially in light ends), vents and fugitive emissions (Hcs).
Polymerization	H_2S, from caustic washing.
Catalytic Reforming	Heater stack gas (CO, SO_x, NO_x, HCs and PM), fugitive emissions (hydrocarbons) and catalyst regeneration (CO, NO_x, SO_x).
Solvent Extraction	Fugitive solvents.
Dewaxing	Fugitive solvents, heaters.
Propane Deasphalting	Heater stack gas (CO, SO_x, NO_x, HCs and PM), fugitive propane.
Merox treating	Vents and fugitive emissions (HCs and disulfides).

Process	Pollutants
Wastewater treatment	Fugitive emissions (H_2S, NH_3, and HCs).
Gas Treatment and Sulfur Recovery	SO_x, NO_x, and H_2S from vent and tail gas emissions.
Blending	Fugitive emissions (HCs).
Heat exchanger cleaning	Periodic fugitive emissions (HCs.)
Storage Tanks	Fugitive emissions (hydrocarbons).
Blowdown and Flaring Operations	Combustion products (CO, SO_x, NO_x, and HCs) from flares, fugitive emissions.

Sources: Assessment of Atmospheric Emissions from Petroleum Refining, Radian Corp., 1980; Petroleum Refining Hazardous Waste Generation, U.S. EPA, Office of Solid Waste, 1994.

POLLUTION PREVENTION AND CONTROL

The Pollution Prevention Act of 1990 (PPA) requires facilities to report information about the management of TRI chemicals in waste and efforts made to eliminate or reduce those quantities. These data have been collected annually in the TRI reporting Form R beginning with the 1991 reporting year. The TRI data require filers to list releases to air, water, and land separately. The distribution across media can also be compared to the profile of other industry sectors. The petroleum refining industry releases 75% of its total TRI poundage to the air, 24 percent to the water (including 20 percent to underground injection and 4 percent to surface waters), and 1 percent to the land. This release profile differs from other TRI industries which average approximately 59% to air, 30% to water, and 10% to land. Examining the petroleum refining industry's TRI reported toxic chemical releases highlights the likely origins of the large air releases for the industry.

According to TRI data, the petroleum refining industry releases (discharges to the air, water, or land without treatment) and transfers (shipped off-site) a total of 482 million pounds of pollutants per year, made up of 103 different chemicals. This represents about 11% of the total pounds of TRI chemicals released and transferred by all manufacturers in a year. In comparison, the chemical industry generates on the average 2.5 billion pounds per year, accounting for 33% of all releases and transfers.

Overall, the petroleum refining industry's releases declined between 1988 and

1993. Between 1991 and 1993 the decrease in releases was 6.7% compared to the average for all industries of 18%. In the same period, however, transfers were reported to increase 65% which is higher than the average increase in transfers of 25% for all manufacturing industries.

A large portion of the increases were in the form of transfers to recycling. Spent sulfuric acid generated in the alkylation process makes up about half of all transfers of TRI listed chemicals off-site. At the facility level, the industry reported a level of pollution prevention activities of 42% of all refineries which is slightly higher than the overall average of about 35% of TRI reporting facilities. Comparisons of the reported pounds released or transferred per facility demonstrate that the petroleum refining industry is far above average in its pollutant releases and transfers per facility when compared to other TRI industries. Of the twenty manufacturing SIC codes listed in the TRI database, the mean amount of pollutant release per facility (including petroleum refining) was approximately 120,000 pounds.

The TRI releases of the average petroleum refining facility (SIC 2911) were 404,000 pounds, making the industry 3.4 times higher in per facility releases than for other industries. For transfers, the mean of petroleum refining facilities was about 13 times as much that of all TRI manufacturing facilities (202,000 pounds transferred off-site per facility compared to 2,626,000 per refinery). These high releases and transfers per facility reflect the large volumes of material processed at a relatively small number of facilities.

Of the top ten most frequently reported toxic chemicals on the TRI list, the prevalence of volatile chemicals explains the air intensive toxic chemical loading of the refining industry. Nine of the ten most commonly reported toxic chemicals are highly volatile. Seven of the ten are aromatic hydrocarbons (benzene, toluene, xylene, cyclohexane, 1,2,4-trimethylbenzene, and ethylbenzene).

Aromatic hydrocarbons are highly volatile compounds and make up a portion of both crude oil and many finished petroleum products. Ammonia, the ninth most commonly reported toxic chemical, is also released and transferred from petroleum refineries in large quantities. Ammonia may be found in high concentrations in refinery sour gas. The primary means of release to the environment is through underground injection of wastewater and emissions to air. Gasoline blending additives (i.e., methanol, ethanol, and MTBE) and chemical feedstocks (propylene, ethylene, and naphthalene) are also commonly reported to TRI. Additives and chemical feedstocks are, for the most part, released as air emissions due to their high volatility. A significant portion of the remaining chemicals of the reported TRI toxic chemicals are metals compounds, which are typically transferred off-site for recovery or as a component of hazardous wastes.

Toxicity and Environmental Fate Information for Ammonia CAS #7664-41-7

Sources. *Ammonia is formed from the nitrogen bearing components of crude oil and can be found throughout petroleum refineries in both the gaseous and aqueous forms. Gaseous ammonia often leaves distillation, cracking, and treating processes mixed with the sour gas or acid gas along with refinery fuel gases and hydrogen sulfide. Aqueous ammonia is present in the sourwater generated in the vacuum distillation unit and steam strippers or fractionators. Some release sources include fugitive emissions, sour gas stripper, sulfur unit, and wastewater discharges.*

Toxicity. *Anhydrous ammonia is irritating to the skin, eyes, nose, throat, and upper respiratory system. Ecologically, ammonia is a source of nitrogen (an essential element for aquatic plant growth), and may therefore contribute to eutrophication of standing or slow-moving surface water, particularly in nitrogen-limited waters such as the Chesapeake Bay. In addition, aqueous ammonia is moderately toxic to aquatic organisms.*

Carcinogenicity. *There is currently no evidence to suggest that this chemical is carcinogenic.*

Environmental Fate. *Ammonia combines with sulfate ions in the atmosphere and is washed out by rainfall, resulting in rapid return of ammonia to the soil and surface waters. Ammonia is a central compound in the environmental cycling of nitrogen. Ammonia in lakes, rivers, and streams is converted to nitrate.*

Although it is not the most frequently reported toxic chemical released or transferred, sulfuric acid is, by far, generated in the largest quantities. Spent sulfuric acid is primarily generated during the alkylation process. The acid is typically transferred off-site for regeneration.

As you continue to read, scan over the sidebar discussions. These provide a summary of the toxicity and fate data for the principal hazardous chemicals released by petroleum refinery operations. The sidebar discussions also provide descriptions of the most common routes by which these pollutants enter the environment as a result of common refinery practices and operations.

In addition to chemicals covered under TRI, many other chemicals are released. For example, the EPA Office of Air Quality Planning and Standards has compiled air pollutant emission factors for determining the total air emissions of priority pollutants (e.g., VOCs, SO_x, NO_x, CO, particulates, etc.) from many refinery sources. The EPA Office of Aerometric Information Retrieval System (AIRS) contains a wide range of information related to stationary sources of air pollution, including the emissions of a number of air pollutants which may be of concern within a particular industry. With the exception of volatile organic compounds (VOCs), there is little overlap with the TRI chemicals reported above.

Control technologies employed for the handling of air emissions normally include the capture and recycling or combustion of emissions from vents, product transfer points, storage tanks, and other handling equipment. Boilers, heaters, other combustion devices, cokers, and catalytic units may require particulate matter controls. Use of a carbon monoxide boiler is normally a standard practice in the fluidized catalytic cracking units. Catalytic cracking units should be provided with particular removal devices. Steam injection in flaring stacks can reduce particulate matter emissions.

Implementation of P2 (pollution prevention) measures can yield both economic and environmental benefits. However, a balance on energy usage and environmental impacts may have to be struck. New refineries should be designed to maximize energy conservation and reduce hydrocarbon losses.

A good target for simple refineries (i.e., refineries with distillation, catalytic reforming, hydrotreating, and offsite facilities) is that the total quantity of oil consumed as fuel and lost in production operations should not exceed 3.5% of the throughput. For refineries with secondary conversion units (i.e., hydrocrackers or lubricating oil units), the target should be 5 to 6% (and, in some cases, up to 10%) of the throughput. Fugitive VOC emissions from the process units can be reduced to 0.05% of the throughput, with total VOC emissions of less than 1 kg per ton of crude (or 0.1% of throughput). Methods of estimating these figures include emissions monitoring, mass balance, and inventories of emissions sources. Design assumptions should be recorded to allow for subsequent computation and reduction of losses. Vapor recovery systems to control losses of VOCs from storage tanks and loading areas should achieve 90 to 100% recovery.

Plant operators should aim at using fuel with less than 0.5% sulfur (or an emissions level corresponding to 0.5% sulfur in fuel). High-sulfur fuels should be directed to units equipped with SO_x controls. Fuel blending is another option. A sulfur recovery system that achieves at least 97% (but preferably

Toxicity and Environmental Fate Information for Toluene CAS #108-88-3

Sources. *Toluene is a component of crude oil and is therefore present in many refining operations. Toluene is also produced during catalytic reforming and is sold as one of the large volume aromatics used as feedstocks in chemical manufacturing. Its volatile nature makes fugitive emissions its largest release source. Point air sources may arise during the process of separating toluene from other aromatics and from solvent dewaxing operations where toluene is often used as the solvent.*

Toxicity. *Inhalation or ingestion of toluene can cause headaches, confusion, weakness, and memory loss. Toluene may also affect the way the kidneys and liver function. Reactions of toluene in the atmosphere contribute to ozone formation. Ozone can affect the respiratory system, especially in sensitive individuals such as asthma or allergy sufferers. Unborn animals were harmed when high levels of toluene were inhaled by their mothers, although the same effects were not seen when the mothers were fed large quantities of toluene. Note that these results may reflect similar difficulties in humans.*

Carcinogenicity. *There is currently no evidence to suggest carcinogenicity.*

Environmental Fate. *A portion of releases of toluene to land and water will evaporate. Toluene may also be degraded by microorganisms. Once volatilized, toluene in the lower atmosphere will react with other atmospheric components contributing to the formation of ground-level ozone and other air pollutants.*

over 99%) sulfur recovery should be used when the hydrogen sulfide concentration in tail gases exceeds 230 mg/Nm^3. The total release of sulfur dioxide should be below 0.5 kg per ton for a hydroskimming refinery and below 1 kg per ton for a conversion refinery.

Toxicity and Environmental Fate
Information for
Xylenes (Mixed Isomers)
CAS #1330-20-7

Sources. *Xylene isomers are a component of crude oil. They are also produced during catalytic reforming and are sold as one of the large volume aromatics used as feedstocks in chemical manufacturing. Xylene's volatile nature make fugitive emissions the largest release source. Point air sources may arise during the process of separating xylene from other aromatics.*

Toxicity. *Xylenes are rapidly absorbed into the body after inhalation, ingestion, or skin contact. Short-term exposure of humans to high levels of xylene can cause irritation of the skin, eyes, nose, and throat, difficulty in breathing, impaired lung function, impaired memory, and possible changes in the liver and kidneys. Both short- and long-term exposure to high concentrations can cause effects such as headaches, dizziness, confusion, and lack of muscle coordination. Reactions of xylene in the atmosphere contribute to the formation of ozone in the lower atmosphere. Ozone can affect the respiratory system, especially in sensitive individuals such as asthma or allergy sufferers.*

Carcinogenicity. *There is currently no evidence to suggest that this chemical is carcinogenic.*

Environmental Fate. *A portion of releases to land and water will quickly evaporate, although some degradation by microorganisms will occur. Xylene are moderately mobile in soils and may leach into groundwater, where they may persist for many years. Xylenes are VOCs. As such, xylene will react with other atmospheric components, contributing to the formation of ground-level ozone and other air pollutants.*

A wastewater generation rate of 0.4 m^3/t of crude processed is achievable with good design and operation, and new refineries should achieve this target as a minimum. As already noted, petroleum refineries are complex plants, and the combination and sequence of processes are usually very specific to the characteristics of the raw materials (crude oil) and the products. Specific pollution prevention or source reduction measures can often be determined only by the technical staff of the specific refinery operation. However, there are a number of general areas where improvements are often possible, and site-specific waste reduction measures in these areas should be designed into the plant and targeted by management of operating plants.

Areas where efforts can be concentrated in reducing air emissions include the following:

✓ ***Minimize losses from storage tanks and product transfer areas by methods such as vapor recovery systems and double seals.***

✓ ***Minimize SO_x emissions either through desulfurization of fuels, to the extent feasible, or by directing the use of high-sulfur fuels to units equipped with SO_x emissions controls.***

✓ ***Recover sulfur from tail gases in high-efficiency sulfur recovery units.***

✓ ***Recover nonsilica-based (i.e., metallic) catalysts and reduce par-ticulate emissions.***

✓ ***Use low-NO_x burners to reduce nitrogen oxide emissions.***

✓ ***Avoid and limit fugitive emissions by proper process design and maintenance.***

✓ ***Keep fuel usage to a minimum.***

Although numerous cases have been documented where petroleum refineries have simultaneously reduced pollution outputs and operating costs through pollution prevention techniques, there are often barriers to their im-plementation. The primary barrier to most pollution prevention projects is cost. Many pollution prevention options simply do not pay for themselves, or the economics often appear marginal. Corporate investments typically must earn an adequate return on invested capital for the shareholders and some pollution prevention options at some facilities may not meet the requirements set by company policies.

Toxicity and Environmental Fate
Information for
Methyl Ethyl Ketone
CAS #78-93-3

Sources. *Methyl ethyl ketone (MEK) is used in some refineries as a solvent in lube oil dewaxing. Its extremely volatile characteristic makes fugitive emissions its primary source of releases to the environment.*

Toxicity. *Breathing moderate amounts of methyl ethyl ketone (MEK) for short periods of time can cause adverse effects on the nervous system ranging from headaches, dizziness, nausea, and numbness in the fingers and toes to unconsciousness. Its vapors are irritating to the skin, eyes, nose, and throat and can damage the eyes. Repeated exposure to moderate to high amounts may cause liver and kidney effects.*

Carcinogenicity. *No agreement exists over the carcinogenicity of MEK. One source believes MEK is a possible carcinogen in humans based on limited animal evidence. Other sources believe that there is insufficient evidence to make any statements about possible carcinogenicity.*

Environmental Fate. *Most of the MEK released to the environment will end up in the atmosphere. MEK can contribute to the formation of air pollutants in the lower atmosphere. It can be degraded by microorganisms living in water and soil.*

Additionally, the equipment used in the petroleum refining industry are very capital intensive and have very long lifetimes. This reduces the incentive to make process modifications to (expensive) installed equipment that is still useful.

It should be emphasized, however, that pollution prevention techniques are, nevertheless, often more cost-effective than pollution reduction through end-of-pipe treatment technologies. A case study based on the Amoco/EPA joint study claimed that the same pollution reduction currently realized through end-of-pipe regulatory requirements at the Amoco facility could be achieved at 15% of the current costs using pollution prevention techniques.

To better understand some of the broad areas of pollution prevention practices, the following provides a summary of some pollution prevention techniques found to be effective at petroleum refineries.

Toxicity and Environmental Fate Information for Propylene CAS #115-07-1

Sources. *Propylene (propene) is one of the light ends formed during catalytic and thermal cracking and coking operations. It is usually collected and used as a feedstock to the alkylation unit. Propylene is volatile and soluble in water making releases to both air and water significant.*

Toxicity. *At low concentrations, inhalation of propylene causes mild intoxication, a tingling sensation, and an inability to concentrate. At higher concentrations, unconsciousness, vomiting, severe vertigo, reduced blood pressure, and disordered heart rhythms may occur. Skin or eye contact with propylene causes freezing burns. Reaction of propylene (see environmental fate) in the atmosphere contributes to the formation of ozone in the lower atmosphere. Ozone can affect the respiratory system, especially in sensitive individuals, such as asthma or allergy sufferers. Ecologically, similar to ethylene, propylene has a stimulating effect on plant growth at low concentrations, but inhibits plant growth at high levels.*

Carcinogenicity. *There is currently no evidence to suggest that this chemical is carcinogenic.*

Environmental Fate. *Propylene is degraded principally by hydroxyl ions in the atmosphere. Propylene released to soil and water is removed primarily through volatilization. Hydrolysis, bioconcentration, and soil adsorption are not expected to be significant fate processes of propylene in soil or aquatic ecosystems. Propylene is readily biodegraded by microorganisms in surface water.*

Place secondary seals on storage tanks - One of the largest sources of fugitive emissions from refineries is storage tanks containing gasoline and other volatile products. These losses can be significantly reduced by installing secondary seals on storage tanks. An Amoco/EPA joint study estimated that VOC losses from storage tanks could be reduced 75 to 93%. Equipping an average tank with a secondary seal system was estimated to cost about $20,000.

Establish leak detection and repair program - Fugitive emissions are one of the largest sources of refinery hydrocarbon emissions. A leak detection and repair (LDAR) program consists of using a portable VOC detecting instrument to detect leaks during regularly scheduled inspections of valves, flanges, and pump seals. Leaks are then repaired immediately or are scheduled for repair as quickly as possible. A LDAR program could reduce fugitive emissions 40 to 64%, depending on the frequency of inspections.

Install vapor recovery for barge loading - Although barge loading is not a factor for all refineries, it is an important emissions source for many facilities. One of the largest sources of VOC emissions identified during the Amoco/EPA study was fugitive emissions from loading of tanker barges. It was estimated that these emissions could be reduced 98% by installing a marine vapor loss control system. Such systems could consist of vapor recovery or VOC destruction in a flare.

Eliminate use of open ponds - Open ponds used to cool, settle out solids and store process water can be a significant source of VOC emissions. Wastewater from coke cooling and coke VOC removal is occasionally cooled in open ponds where VOCs easily escape to the atmosphere. In many cases, open ponds can be replaced with closed storage tanks.

Remove unnecessary storage tanks from service - Since storage tanks are one of the largest sources of VOC emissions, a reduction in the number of these tanks can have a significant impact. The need for certain tanks can often be eliminated through improved production planning and more continuous operations. By minimizing the number of storage tanks, tank bottom solids and decanted wastewater may also be reduced.

Replace old boilers - Older refinery boilers can be a significant source of SO_x, NO_x and particulate emissions. It is possible to replace a large number of old boilers with a single new cogeneration plant with emissions controls.

Modify the FCCU to allow the use of catalyst fines - Some FCCUs can be modified to recycle some of the catalyst fines generated.

Install rupture discs and plugs - Rupture discs on pressure relieve valves and plugs in open ended valves can reduce fugitive emissions.

Install high pressure power washer - Chlorinated solvent vapor degreasers can be replaced with high pressure power washers which do not generate spent solvent hazardous wastes or toxic fugitive emissions.

Toxicity and Environmental Fate Information for Benzene CAS # 71-43-2

Sources. *Benzene is a component of crude oil. It is also produced during catalytic reforming and is sold as one of the large volume aromatics used as feedstocks in chemical manufacturing. Benzene's volatile nature makes fugitive emissions the largest release source.*

Toxicity. *Short-term inhalation of benzene affects the central nervous system and respiratory system. Chronic exposure causes bone marrow toxicity in animals and humans, causing suppression of the immune system and development of leukemia. Ingestion of benzene is rare. Reaction of benzene in the atmosphere contributes to the formation of ozone in the lower atmosphere (troposphere).*

Environmental Fate. *A portion of benzene releases to soil and surface waters evaporate rapidly. Benzene is highly mobile in the soil and may leach to groundwater. Once in groundwater, it is likely biodegraded by microorganisms only in the presence of oxygen. Benzene is not expected to significantly adsorb to sediments, bioconcentrate in aquatic organisms, or break down in water. Atmospheric benzene is broken down through reacting with chemical ions in the air; this process is greatly accelerated in the presence of other air pollutants such as nitrogen oxides or sulfur dioxide. Benzene is fairly soluble in water and is removed from the atmosphere in rain. As a volatile chemical, benzene in the lower atmosphere will react with other atmospheric components, contributing to the formation of ground-level ozone and other air pollutants, which can contribute to respiratory illnesses in both the general and highly susceptible populations, such as asthmatics and allergy sufferers.*

Recycle and regenerate spent caustics - Caustics used to absorb and remove hydrogen sulfide and phenol contaminants from intermediate and final product streams can often be recycled. Spent caustics may be saleable to chemical recovery companies if concentrations of phenol or hydrogen sulfide are high enough. Process changes in the refinery may be needed to raise the concentration of phenols in the caustic to make recovery of the contaminants economical. Caustics containing phenols can also be recycled on-site by reducing the pH of the caustic until the phenols become insoluble thereby allowing physical separation. The caustic can then be treated along with the refinery waste waters.

Control and reuse FCCU and coke fines - Significant quantities of catalyst fines are often present around the FCCU catalyst hoppers and reactor and regeneration vessels. Coke fines are often present around the coker unit and coke storage areas. The fines can be collected and recycled before being washed to the sewers or migrating off-site via the wind. Collection techniques include dry sweeping the catalyst and coke fines and sending the solids to be recycled or disposed of as nonhazardous waste. Coke fines can also be recycled for fuel use. Another collection technique involves the use of vacuum ducts in dusty areas (and vacuum hoses for manual collection) which run to a small baghouse.

Use nonhazardous degreasers - Spent conventional degreaser solvents can be reduced or eliminated through substitution with less toxic and/or biodegradable products.

AIR POLLUTION FROM IRON AND STEEL MANUFACTURING

STEELMAKING PROCESS

There are two process routes for making steel in the UK today: the electric arc furnace and the basic oxygen converter. The latter requires a charge of molten iron, which is produced in blast furnaces. The raw materials for producing molten iron are iron ore, coking coal, and fluxes (materials that help the chemical process) - mainly limestone.

Blended coal is first heated in coke ovens to produce coke. This process is known as carbonization. The gas produced during carbonisation is extracted and used for fuel elsewhere in the steelworks. Other by-products (such as tar and benzole) are also extracted for further refining and sale. Once carbonised, the coke is pushed out of the ovens and allowed to cool.

Fine-sized ore is first mixed with coke and fluxes and heated in a sinter plant. This is a continuous moving belt on which the coke is ignited. The high temperatures generated fuse the ore particles and fluxes together to form a porous clinker called sinter. The use of sinter in the blast furnace helps make the ironmaking process more efficient. Iron ore lumps and pellets, coke, sinter, and possibly extra flux are carried to the top of the blast furnace on a conveyor or in skips and then tipped, or charged, into the furnace. Hot air (circa 900°C) is blasted into the bottom of the furnace through nozzles called tuyeres. The oxygen in the air combusts with the coke to form carbon monoxide gas, and this generates a great deal of heat. Frequently oil or coal is injected with the air, which enables less (relatively expensive) coke to be used. The carbon monoxide flows up through the blast furnace and removes oxygen from the iron ores on their way down, thereby leaving iron. The heat in the furnace melts the iron, and the resulting liquid iron (or hot metal as it is called in the industry) is tapped at regular intervals by opening a hole in the bottom of the furnace and allowing it to flow out.

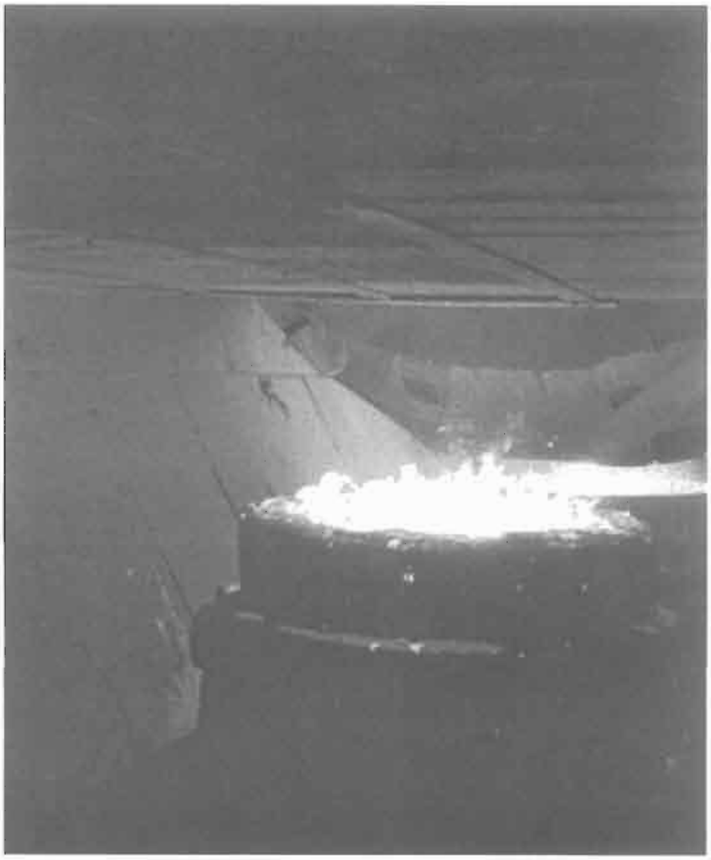


Figure 9. Shows BOF pouring molten steel into ladles.

The fluxes combine with the impurities in the coke and ore to form a molten slag, which floats on the iron and is also removed (tapped) at regular intervals. The hot metal flows into torpedo ladles. These are specially constructed railway containers which transport iron, still in liquid form, to the steel furnace. Refer to Figure 8 for an example of furnace tapping and hot molten steel being poured into a ladle. The process described above goes on continuously for ten years or more. (This is known as a campaign.) If the furnace were allowed to cool, damage could be caused to its lining of refractory bricks as a result of their contracting as they cooled. Eventually the refractory brick linings are worn away, and at that stage the process is stopped and the furnace relined with new bricks, ready to begin its next campaign.

The iron produced by the blast furnace has a carbon content of 4 to 4.5% as well as a number of other impurities. This makes it relatively brittle. Steelmaking refines iron, amongst other things by reducing its carbon content, to make it a stronger and more manipulable product.

The Basic Oxygen Converter

The BOS (Basic Oxygen Steelmaking) process is the major modern process for making bulk steels. Apart from special quality steels (such as stainless steel), all flat products, and long products over a certain size, are rolled from steel made by the BOS process.

The BOS vessel is first tilted to allow materials to be tipped into it (charged). Scrap steel is first charged into the vessel, followed by hot metal (liquid iron) from the blast furnace. A water-cooled lance is lowered into the vessel through which very pure oxygen is blown at high pressure. The oxygen, through a process known as oxidation, combines with the carbon, and with other unwanted elements, separating them from the metal, leaving steel. Lime-based fluxes (materials that help the chemical process) are charged, and they combine with the "impurities" to form slag. The main gas formed as a by-product of the oxidation process is carbon monoxide, and this is sometimes collected for use as a fuel elsewhere in the works.

A careful balance between the amounts of hot metal and scrap charged into the converter is maintained as a means of controlling the temperature and to ensure that steel of the required specification is produced. After a sample has been taken to check that the chemical content of the steel is correct, the vessel is again tilted to allow the molten steel to flow out. This is known as tapping. The steel is tapped into a ladle, in which secondary steelmaking frequently takes place. During tapping small quantities of other metals and fluxes are often added to control the state of oxidation and to meet customer requirements for particular grades of steel.

Finally the vessel is turned upside down and the slag tipped out into a container. Steelmaking slag is sometimes recycled to make road building materials.
The modern BOS vessel makes up to 350 tonnes of steel at a time, and the whole process takes about 40 minutes.

The Electric Arc Furnace

The electric arc furnace (EAF) (together with the basic oxygen vessel) is one of the two modern ways of making steel. EAFs are used to produce special quality steels (steels alloyed with other metals) and some ordinary (non-alloy) quality steels - the lighter long products such as those used for reinforcing concrete.

Unlike the basic oxygen route, the EAF does not use hot metal. It is charged with "cold" material. This is normally steel scrap (recycled goods made from steel which have reached the end of their useful life). Other forms of raw material are, however, available which have been produced from iron ore. These include direct reduced iron (DRI) and iron carbide, as well as pig iron, which is iron from a blast furnace which has been cast and allowed to go cold, instead of being charged straight into a basic oxygen vessel.

Steel scrap (or other ferrous material) is first tipped into the EAF from an overhead crane. A lid is then swung into position over the furnace. This lid contains electrodes which are lowered into the furnace. An electric current is passed through the electrodes to form an arc. The heat generated by this arc melts the scrap. The electricity needed for this process is enough to power a town with a population of 100,000.

During the melting process, other metals (ferro-alloys) are added to the steel to give it the required chemical composition. As with the basic oxygen process, oxygen is blown in to the furnace to purify the steel and lime and fluorspar are added to combine with the impurities and form slag.

After samples have been taken to check the chemical composition of the steel, the furnace is tilted to allow the slag, which is floating on the surface of the molten steel, to be poured off. The furnace is then tilted in the other direction and the molten steel poured (tapped) into a ladle, where it either undergoes secondary steelmaking or is transported to the caster.

The modern electric arc furnace typically makes 150 tonnes in each melt, which takes around 90 minutes.

Special quality steels - A vast range of special quality steels is made in electric arc furnaces by adding other metals to form steel alloys. The most commonly known of these is stainless steel, which has chromium and nickel added to form a corrosion-resistant steel. There are very many others however: the very hard steels used to make machine tools, the steels specially formulated to make them suitable for engineering, steels developed to survive for decades the hostile environment of nuclear reactors, light but strong steels used in aerospace, extra tough steels for armor plating - to name but a few.

Secondary Steelmaking

Increasingly today, steels after they have been tapped (poured) from the furnace undergo a further stage of processing called secondary steelmaking before the steel is cast. This applies to both the basic oxygen process route and to the electric arc furnace route.

The molten steel is tapped from the furnace into a ladle. A lid is placed over the ladle to conserve heat. A range of different processes is then available, such as stirring with argon, adding alloys, vacuum de-gassing or powder injection. The objective in all cases is to fine tune the chemical composition of the steel and/or to improve homogenization of temperature (making sure that the steel is the same temperature throughout) and remove impurities. Ladle arc heating is a process used to ensure that the molten steel is at exactly the correct temperature for casting.

Continuous Casting

Not that many years ago, molten steel used to be poured (teemed) into a large mold where it would be allowed to cool and solidify to form an ingot. The ingot was then put into an oven called a soaking pit, where it would be gently heated to the correct and uniform temperature. This red hot ingot would then be rolled in primary mills, in the first stage of its transformation into a usable steel product, into one of three forms of semi-finished product: a slab (a long, thick, flat piece of steel, with a rectangular cross-section), a bloom (a long piece of steel with a square cross-section), or a billet (like a bloom, but with smaller cross-section).

In modern plants, this process has largely been superseded by the continuous casting process (concaster), although the ingot route is retained for certain applications where it is the most suitable way of producing the steel required. Note that there are still many steelmaking plants in parts of Eastern Europe that rely heavily on the old ingot route.

In a continuous casting machine, molten steel is poured into a reservoir at the top of the machine. It passes at a controlled rate into a water cooled mold where the outer shell of the steel becomes solidified. The steel is drawn down into a series of rolls and water sprays, which ensure that it is both rolled into shape and fully solidified at the same time. At the end of the machine, it is straightened and cut to the required length. Fully formed slabs, blooms, and billets emerge from the end of this continuous process.

Thus the concaster combines in a single process what previously took two separate processes. This is both highly energy-efficient and produces a better quality product.

The slabs, blooms, or billets are then transported to the hot rolling mill for rolling into steel products which can be used by the manufacturing industry.

Hot Rolling

Semi-finished products called blooms, billets and slabs are transported from the steelmaking plant to the rolling mills. In many plants steelmaking and rolling are both carried out on the same site. However, there are also many stand-alone rolling mills (some are independently owned while others are typically a part of a larger group but located away from the steelmaking works).

Steel products can be classified into two basic types according to their shape: flat products and long products. Slabs are used to roll flat products, while blooms and billets are mostly used to roll long products. Billets are smaller than blooms, and therefore are used for the smaller type of long product. In some cases slabs are used to roll large long products (such as beams).

Semi-finished products are first heated in a re-heat furnace until they are red hot (around 1200°C). On all types of mill the semi-finished products go first to a roughing stand. A stand is a collection of steel rolls (or drums) on which pressure can be applied to squeeze the hot steel passing through them, and arranged so as to form the steel into the required shape. The roughing stand is the first part of the rolling mill. The large semi-finished product is often passed backwards and forwards through it several times. Each pass gradually changes the shape and dimension of the steel closer to that of the required finished product.

Plate Mills

Slabs are used to make plate. Typically, after leaving the plate mill's roughing stand, they are passed through a finishing stand. This is a reversing mill: like on the roughing stand, the steel is passed backwards and forwards through the mill. It is also turned 90° and rolled sideways at one stage during the process. Plate is a large, flat piece of steel perhaps 10mm or 20mm thick (although it can be up to 50mm thick) and up to 5 meters wide. It is used for example to make the hulls and decks of ships or to make large tanks and industrial boilers. It can also be rolled up and welded to form a large steel tube, used for oil and gas pipelines.

Strip Mills

Slabs are also used to make steel strip, normally called hot rolled coil. After leaving the roughing stand, the slab passes continuously through a series of finishing stands which progressively squeeze the steel to make it thinner. As the steel becomes thinner, it also of course becomes longer, and starts moving faster. And because the single piece of steel will be a whole range of different thicknesses along its length as each section of it passes through a different stand, different parts of the same piece of steel are traveling at different speeds. This requires very close control of the speeds at which each individual stand rolls. In modern plants the entire process is computer controlled. By the time it reaches the end of the mill, the steel is traveling at about 40 miles per hour. Finally the long strip of steel is coiled and allowed to cool. Hot rolled strip is a flat product which has been coiled to make storage and handling easier. It is a lot thinner than plate, typically a few millimeters thick, although it can be as thin as 1mm. Its width can vary from 150mm to nearly 2 meters. It frequently goes through further stages of processing such as cold rolling and is also used to make tubes (smaller tubes than those made from plate).

Long Product Mills

Blooms and billets are used to make long products. After leaving the roughing stand, the piece of steel passes through a succession of stands which do not just reduce the size of the steel, but also change its shape. In a universal mill, all faces of the piece of steel are rolled at the same time. In other mills, only two sides of the steel are rolled at any one time, the piece of steel being turned over to allow the other two sides to be rolled. Long products are so called because they come off the mill as long bars of steel. They are however produced in a vast range of different shapes and sizes. They can have cross-sections shaped like an H or I (called joists, beams, and columns), a U (channels) or a T. These types of steel section are used for construction. Bars can have cross-sections the shape of squares, rectangles, circles, hexagons, angles. These bars can also be used for construction, but many types of bars are also used for engineering purposes. Rod is coiled up after use and is used for drawing into wire or for fabricating into products used to reinforce concrete buildings, as are some types of bars. Other types of long products include railway rails and piling. Some long product mills make unique shapes of steel to a customer's individual specification. These are known as special sections.

Cooling

In all rolling processes, cooling the steel is a critical factor. The speed at which the rolled product is cooled will affect the mechanical properties of the steel. Cooling speed is controlled normally by spraying water on the steel as it passes through and/or leaves the mill, although occasionally the rolled steel is air-cooled using large fans.

Further Processing

Hot rolled products can undergo many forms of further processing before they are finally used to make an end-product (such as a steel-framed building or a consumer product). Such processing includes:

- ☐ **Cold rolling and drawing** (described below)
- ☐ **Fabricating** - Steel sections are cut, welded and otherwise prepared to form the steel frame of a building. Rods and bars are similarly cut and shaped to form the steel reinforcement for concrete buildings.
- ☐ **Coating** (described below)
- ☐ **Cutting and slitting** - Service centers cut steel into many complex shapes.
- ☐ **Profiling** - Sheet steel may be pressed into the correct shape for crash barriers or the cladding of buildings (known as profiling).

Cold Rolling & Drawing

After hot rolling, many steel products undergo a further processing in the cold state. This stage of processing does not alter the shape of the steel product, but it does reduce it in thickness and significantly improve its performance characteristics. Hot rolled coil is commonly cold rolled (also known as cold reduced). The strip is first de-coiled (uncoiled) and then passes through a series of rolling mill stands which apply pressure to the strip and progressively reduce its thickness - down to as low as 0.15 mm. The strip is then recoiled. Cold rolling processes are also used to improve the surface quality of the steel. Cold rolling also has the effect of hardening steel, so cold reduced strip is subsequently annealed: a process of very carefully controlled heating and cooling to soften it. Another form of cold processing is cold drawing. Steel rod is dragged at pressure (drawn) through a series of dies which progressively reduce the rod's circumference to produce wire. The drawing process substantially increases the steel's tensile strength - steel wires can be spun into huge ropes strong enough to support the world's largest suspension bridges. See Figure 9 for an example of cold rolling and drawing operations.

Figure 9. Example of hot wire drawing operation.

Coating

Most steels when exposed to air will gradually rust. (This does not apply to all steels: stainless steel for example was invented - in Sheffield - specifically to resist rust.) Steel has therefore always been covered - frequently painted for example - by its users in order to protect it. Nowadays the steelmaker can improve steel's corrosion resistance by coating it in the factory prior to delivery to the end-user. A wide range of different coatings is available, including:

- ☐ Zinc coating, normally called galvanizing. The zinc can be applied either electrolytically (which gives a thinner coating) or by dipping the steel in a bath of molten zinc. Much of the sheet used to produce car bodies is zinc coated. This has enabled thinner steels to be used for car bodies, thus saving weight and improving fuel consumption. (Without this coating, the thinner steels would have rusted, shortening the car's life.) Wire is also frequently galvanized to extend the product's life.

- Organic coatings (plastic and paint) can be applied to extend the steel's life, while at the same time giving it an attractive appearance. The walls of many industrial and commercial buildings are made from pre-painted steel sheets. Frequently, a combination of galvanizing and organic coatings is used.
- Tinplate is thin steel sheet with a minute coating of tin applied. This is used for producing food and drinks cans, where rust must be prevented at all costs.
- Other metals used are chromium, lead, and aluminum. Electro-chromium coated sheet is used for the tops of steel drinks cans. Aluminium coated sheet provides a combination of corrosion and heat resistance ideal for car exhaust pipes.

For further background reading on steelmaking processes, along with some informative process diagrams, visit the Web site http://www.uksteel.uk.

POLLUTION PREVENTION AND CONTROL

Steelmaking is a sophisticated and complex process, with many secondary production operations, each having unique air pollution problems to varying degrees. Figures 10, 11, and 12 provide some examples of common air pollution problems.

There are a large number of outputs that are produced as a result of the manufacturing of coke, iron, and steel, the forming of metals into basic shapes, and the cleaning and scaling of metal surfaces. For example:

- Sintering operations can emit significant dust levels of about 20 kilograms per metric ton (kg/t) of steel.
- Pelletizing operations can emit dust levels of about 15 kg/t of steel.
- Air emissions from pig iron manufacturing in a blast furnace include PM, ranging from less than 10 kg/t of steel manufactured to 40 kg/t; sulfur oxides SO_x mostly from sintering or pelletizing operations (1.5 kg/t of steel); nitrogen oxides NO_x mainly from sintering and heating (1.2 kg/t of steel); hydrocarbons; carbon monoxide; in some cases dioxins (mostly from sintering operations); and hydrogen fluoride.

- ☐ Air emissions from steel manufacturing using the BOF may include PM (ranging from less than 15 kg/t to 30 kg/t of steel).
- ☐ For closed systems, emissions come from the desulfurization step between the blast furnace and the BOF; the particulate matter emissions are about 10 kg/t of steel.

The toxic chemical release data obtained from TRI provides detailed information on the majority of facilities in the iron and steel industry in the United States. It also allows for a comparison across years and industry sectors. Reported chemicals are limited however to the 316 reported chemicals. The TRI is important to look at not only from understanding the magnitude and types of pollutants, but from the standpoint of individual plant operations benchmarking their environmental performance against industry averages.

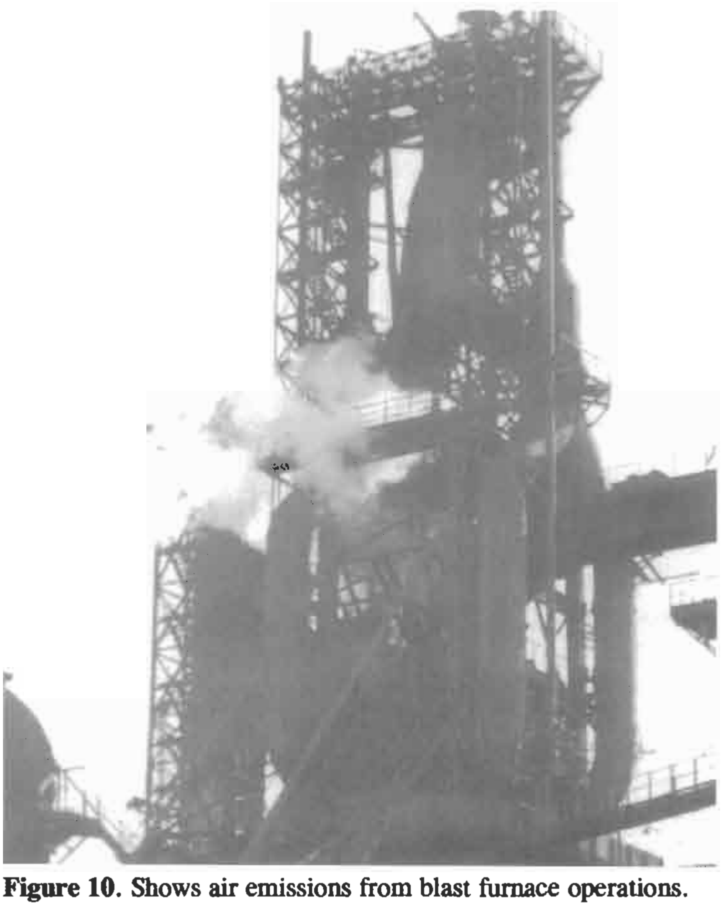


Figure 10. Shows air emissions from blast furnace operations.

Most of the hydrocarbon emissions from iron and steel facilities are not captured by TRI. The EPA Office of Air Quality Planning and Standards has compiled air pollutant emission factors for determining the total air emissions of priority pollutants (e.g., total hydrocarbons, SO_x, NO_x, CO, particulates, etc.) from many iron and steel manufacturing sources.

Figure 11. Example of air emissions from pig iron loading in sintering operations.

Figure 12. Air emissions from sludge water generated from scrubbing blast furnace off-gases.

The Aerometric Information Retrieval System (AIRS) contains a wide range of information related to stationary sources of air pollution, including the emissions of a number of air pollutants which may be of concern within a particular industry. With the exception of VOCs, there is little overlap with the TRI chemicals reported above. By way of comparison to other industry sectors, the steel industry in the U.S. emits about 1.5 million short tons/year of carbon monoxide, which is more than twice as much as the next largest releasing industry, pulp and paper. The iron and steel industry also ranks as one of the top five releasers for NO_2, PM_{10}, and SO_2. Carbon monoxide releases occur during ironmaking (in the burning of coke, CO produced reduces iron oxide ore), and during steelmaking (in either the basic oxygen furnace or the electric arc furnace). Nitrogen dioxide is generated during steelmaking. Particulate matter may be emitted from the coke-making (particularly in quenching operations), ironmaking, basic oxygen furnace (as oxides of iron that are emitted as submicron dust), or from the electric arc furnace (as metal dust containing iron particulate, zinc, and other materials associated with the scrap). Sulfur dioxide can be released in ironmaking or sintering.

With regard to coke-making, this process is seen by industry experts as one of the steel industry's areas of greatest environmental concern, with coke oven air emissions among the major problems. In response to expanding regulatory constraints in the U.S., including the Clean Air Act National Emission Standards for coke ovens, U.S. steelmakers are turning to new technologies to decrease the sources of pollution from, and their reliance on, coke. Pollution prevention in coke-making has focused on two areas: reducing coke oven emissions and developing coke-less ironmaking techniques. Although these processes have not yet been widely demonstrated on a commercial scale, they may provide important benefits, especially for the integrated segment of the industry, by potentially lowering air emissions and wastewater discharges. Several technologies are available or are under development to reduce the emissions from coke ovens. Typically, these technologies reduce the quantity of coke needed by changing the method by which coke is added to the blast furnace or by substituting a portion of the coke with other fuels. The reduction in the amount of coke produced proportionally reduces the coking emissions. Some of the most prevalent or promising coke reduction technologies are listed in the sidebar discussion that follows. Coke-less technologies substitute coal for coke in the blast furnace, hence eliminating the need for coke-making. Such technologies have enormous potential to reduce pollution generated during the steelmaking process. The drawbacks with these technologies are:

- the capital investment required for retrofits is very significant, and
- some countries whose economies are dependent upon the steel industry need to undergo significant industry rationalization and restructuring in order to justify investments into these technologies. For example, Russia and Ukraine, which have significant steel production and export capabilities heavily depend on a labor intensive and "dirty" coking industry. The elimination of the coking industry in these countries would likely result in significant social implications, such as mass unemployment in certain regions of these countries. Additionally, there are implications of domino effects on other industries, such as coal mining.

Reducing coke oven emissions with other technologies - The use of pulverized coal injection technology substitutes pulverized coal for a portion of the coke in the blast furnace. Use of pulverized coal injection can replace about 25 to 40% of coke in the blast furnace, substantially reducing emissions associated with coke-making operations. This reduction ultimately depends on the fuel injection rate applied to the blast furnaces which will, in turn, be dictated by the aging of existing coking facilities, fuel costs, oxygen availability, capital requirements for fuel injection, and available hot blast temperature. Another novel approach is the use of a nonrecovery coke battery. As opposed to the by-product recovery coke plant, the nonrecovery coke battery is designed to allow combustion of the gasses from the coking process, thus consuming the by-products that are typically recovered. The process results in lower air emissions and substantial reductions in coking process wastewater discharges. A third option is the Davy Still Auto-process. In this pre-combustion cleaning process for coke ovens, coke oven battery process water is utilized to strip ammonia and hydrogen sulfide from coke oven emissions. Still another option is the use of alternative fuels. Steel producers can inject other fuels, such as natural gas, oil, and tar/pitch, instead of coke into the blast furnace, but these fuels can only replace coke in limited amounts.

Eliminating Coke with Cokeless Technologies

The Japanese Direct Iron Ore Smelting (DIOS) process. This process produces molten iron directly with coal and sinter feed ore. A 500 ton per day pilot plant was started up in October, 1993 and the designed production rates were attained as a short term average. Data generated is being used to determine economic feasibility on a commercial scale.

HIsmelt process. A plant using the HIsmelt process for molten iron production, developed by HIsmelt Corporation of Australia, was started up in late 1993. The process, using ore fines and coal, has achieved a production rate of 8 tons per hour using ore directly in the smelter. Developers anticipate reaching the production goal of 14 tons per hour. The data generated is being used to determine economic feasibility on commercial scale. If commercial feasibility is realized, Midrex is expected to become the U.S. engineering licensee of the HIsmelt process.

Corex process. The Corex or Cipcor process has integral coal desulfurizing, is amenable to a variety of coal types, and generates electrical power in excess of that required by an iron and steel mill which can be sold to local power grids. A Corex plant is in operation in South Africa, and other plants are expected to be operational in South Korea and India.

It is important to note that EAF dust is a hazardous waste because of its high concentrations of lead and cadmium. With 550,000 tons of EAF dust generated annually in the U.S., there is great potential to reduce the volume of this hazardous waste. The motivation for reducing this waste not only lies with the cost of air pollution controls, but with the cost for disposal. U.S.

steel companies typically pay a disposal fee of $150 to $200 per ton of dust. With an average zinc concentration of 19%, much of the EAF dust is sent off-site for zinc recovery. Most of the EAF dust recovery options are only economically viable for dust with a zinc content of at least 15 to 20%. Facilities that manufacture specialty steels such as stainless steel with a lower zinc content still have opportunities to recover chromium and nickel from the EAF dust. In-process recycling of EAF dust involves pelletizing and then reusing the pellets in the furnace, however, recycling of EAF dust on-site has not proven to be technically or economically competitive for all mill operations. Improvements in technologies have made off-site recovery a cost-effective alternative to thermal treatment or secure landfill disposal. Table 7 provides some examples of pollution prevention practices aimed at reducing air emissions and capturing energy credits. Remember that this is a very energy intensive manufacturing process, so any efforts aimed at reducing energy requirements are of particular interest to plant managers.

Table 7. Examples of P2 Practices in the Iron and Steel Industry.

PROCESS	RECOMMENDED POLLUTION PREVENTION PRACTICE
Pig Iron Manufacturing	1. Improve blast furnace efficiency by using coal and other fuels (such as oil or gas) for heating instead of coke, thereby minimizing air emissions. 2. Recover the thermal energy in the gas from the blast furnace before using it as a fuel. 3. Increase fuel efficiency and reduce emissions by improving blast furnace charge distribution. 4. Recover energy from sinter coolers and exhaust gases. 5. Use dry SO_x removal systems such as carbon absorption for sinter plants or lime spraying in flue gases. 6. Recycle iron-rich materials such as iron ore fines, pollution control dust, and scale in a sinter plant. 7. Use low-NO_x burners to reduce NO_x emissions from burning fuel in ancillary operations. 8. Improve productivity by screening the charge and using better taphole practices. 9. Reduce dust emissions at furnaces by covering iron runners when tapping the blast furnace and by using nitrogen blankets during tapping. 10. Use pneumatic transport, enclosed conveyor belts, or self-closing conveyor belts, as well as wind barriers and other dust suppression measures, to reduce the formation of fugitive dust.
Steel Manufacturing	11. Use dry dust collection and removal systems to avoid the generation of wastewater. Recycle collected dust. 12. Use BOF gas as fuel. 13. Use enclosures for BOF. 14. Use a continuous process for casting steel to reduce energy consumption.

MINI STEEL MILLS

Mini steel mills normally use the electric arc furnace (EAF) to produce steel from returned steel, scrap, and direct reduced iron. EAF is a batch process with a cycle time of about two to three hours. Since the process uses scrap metal instead of molten iron, coke-making and ironmaking operations are eliminated. EAFs can economically serve small, local markets. Further processing of steel can include continuous casting, hot rolling and forming, cold rolling, wire drawing, coating, and pickling. As already noted, the continuous casting process bypasses several steps of the conventional ingot teeming process by casting steel directly into semifinished shapes. The casting, rolling, and steel finishing processes are also used in iron and steel manufacturing. Hot steel is transformed in size and shape through a series of hot rolling and forming steps to manufacture semifinished and finished steel products. The hot rolling process consists of slabheating (as well as billet and bloom), rolling, and forming operations. Several types of hot forming mills (primary, section, flat, pipe and tube, wire, rebar, and profile) manufacture a variety of steel products. For the manufacture of a very thin strip or a strip with a high-quality finish, cold rolling must follow the hot rolling operations. Lubricants emulsified in water are usually used to achieve high surface quality and to prevent overheating of the product.

Wire drawing includes heat treatment of rods, cleaning, and sometimes coating. Water, oil, or lead baths are used for cooling and to impart desired features. To prepare the steel for cold rolling or drawing, acid pickling is performed to chemically remove oxides and scale from the surface of the steel through use of inorganic acid water solutions. Mixed acids (nitric and hydrofluoric) are used for stainless steel pickling; sulfuric or hydrochloric acid is used for other steels. Other methods for removing scale include salt pickling, electrolytic pickling, and blasting; blasting is environmentally desirable, where feasible. EAFs produce metal dusts, slag, and gaseous emissions.

The primary hazardous components of EAF dust are zinc, lead, and cadmium; nickel and chromium are present when stainless steels are manufactured.

Generally, an EAF produces 10 kilograms of dust per metric ton (kg/t) of steel, with a range of 5 to 30 kg/t, depending on factors such

The composition of EAF dust can vary greatly, depending on scrap composition and furnace additives. EAF dust usually has a zinc content of more than 15%, with a range of 5 to 35%. Other metals present in EAF dust include lead (2-7%), cadmium (generally 0.1-0.2% but can be up to 2.5% where stainless steel cases of nickel-cadmium batteries are melted), chromium (up to 15%), and nickel (up to 4%).

as furnace characteristics and scrap quality. Major pollutants present in the air emissions include particulates (1,000 milligrams per normal cubic meter, mg/Nm^3), nitrogen oxides from cutting, scarfing, and pickling operations, and acid fumes (3,000 mg/Nm^3) from pickling operations. Both nitrogen oxides and acid fumes vary with steel quality.

Table 8 provides a list of pollution prevention practices for reducing air emissions in mini steel mills. Standard treatment technologies for air emissions are as follows. Dust emission control technologies include cyclones, baghouses, and ESPs. Scrubbers are used to control acid mists.

Table 8. P2 Practices for Reducing Air Emissions in Mini Steel Mills.

Locate EAFs in enclosed buildings.
Improve feed quality by using selected scrap to reduce the release of pollutants to the environment.
Use dry dust collection methods such as fabric filters.
Replace ingot teeming with continuous casting.
Use continuous casting for semifinished and finished products wherever feasible. In some cases, continuous charging may be feasible and effective for controlling dust emissions.
Use bottom tapping of EAFs to prevent dust emissions.
Use acid-free methods (mechanical methods such as blasting) for descaling, where feasible.
In the pickling process, use countercurrent flow of rinse water; use indirect methods for heating and pickling baths.
Use closed-loop systems for pickling; regenerate and recover acids from spent pickling liquor using resin bed, retorting, or other regeneration methods such as vacuum crystallization of sulfuric acid baths.
Reduce nitrogen oxide emissions by use of natural gas as fuel, use low-NO$_x$ burners, and use hydrogen peroxide and urea in stainless steel pickling baths.
Recover zinc from EAF dust containing more than 15% total zinc; recycle EAF dust to the extent feasible.

Fugitive emissions from charging and tapping of EAFs should be controlled by locating the EAF in an enclosed building or using hoods and by evacuating the dust to dust arrestment equipment to achieve an emissions level of less than 0.25 kg/t.

AIR POLLUTION FROM LEAD AND ZINC SMELTING

Lead and zinc can be produced pyrometallurgically or hydrometallurgically, depending on the type of ore used as a charge. In the pyrometallurgical process, ore concentrate containing lead, zinc, or both is fed, in some cases after sintering, into a primary smelter. Lead concentrations can be 50 to 70%, and the sulfur content of sulfidic ores is in the range of 15 to 20%. Zinc concentration is in the range of 40 to 60%, with sulfur content in sulfidic ores in the range of 26 to 34%. Ores with a mixture of lead and zinc concentrate usually have lower respective metal concentrations. During sintering, a blast of hot air or oxygen is used to oxidize the sulfur present in the feed to sulfur dioxide. Blast furnaces are used in conventional processes for reduction and refining of lead compounds to produce lead. Modern direct smelting processes include QSL, Kivcet, AUSMELT, and TBRC.

Primary Lead Processing

The conventional pyrometallurgical primary lead production process consists of four steps: sintering, smelting, drossing, and refining. A feedstock made up mainly of lead concentrate is fed into a sintering machine. Other raw materials may be added, including iron, silica, limestone flux, coke, soda, ash, pyrite, zinc, caustic, and particulates gathered from pollution control devices. The sintering feed, along with coke, is fed into a blast furnace for reducing, where the carbon also acts as a fuel and smelts the lead-containing materials. The molten lead flows to the bottom of the furnace, where four layers form: "speiss" (the lightest material, basically arsenic and antimony), “matte" (copper sulfide and other metal sulfides), blast furnace slag (primarily silicates), and lead bullion (98% by weight). All layers are then drained off. The speiss and matte are sold to copper smelters for recovery of copper and precious metals. The blast furnace slag, which contains zinc, iron, silica, and lime, is stored in piles and is partially recycled. Sulfur oxide emissions are generated in blast furnaces from small quantities of residual lead sulfide and lead sulfates in the sinter feed.

Rough lead bullion from the blast furnace usually requires preliminary treatment in kettles before undergoing refining operations. During drossing, the bullion is agitated in a drossing kettle and cooled to just above its freezing point, 370 to 425°C (700 to 800°F). A dross composed of lead oxide, along with copper, antimony, and other elements, floats to the top and solidifies above the molten lead. The dross is removed and is fed into a dross furnace for recovery of the nonlead mineral values.

The lead bullion is refined using pyrometallurgical methods to remove any remaining nonlead materials (e.g., gold, silver, bismuth, zinc, and metal oxides such as oxides of antimony, arsenic, tin, and copper). The lead is refined in a cast-iron kettle in five stages. First, antimony, tin, and arsenic are removed. Next, gold and silver are removed by adding zinc. The lead is then refined by vacuum removal of zinc. Refining continues with the addition of calcium and magnesium, which combine with bismuth to form an insoluble compound that is skimmed from the kettle. In the final step, caustic soda, nitrates, or both may be added to remove any remaining traces of metal impurities. The refined lead will have a purity of 99.90 to 99.99%. It may be mixed with other metals to form alloys, or it may be directly cast into shapes.

Secondary Lead Processing

The secondary production of lead begins with the recovery of old scrap from worn-out, damaged, or obsolete products and with new scrap. The chief source of old scrap is lead-acid batteries; other sources include cable coverings, pipe, sheet, and other lead-bearing metals. Solder, a tin-based alloy, may be recovered from the processing of circuit boards for use as lead charge.

Prior to smelting, batteries are usually broken up and sorted into their constituent products. Fractions of cleaned plastic (such as polypropylene) case are recycled into battery cases or other products. The dilute sulfuric acid is either neutralized for disposal or recycled to the local acid market. One of the three main smelting processes is then used to reduce the lead fractions and produce lead bullion.

Most domestic battery scrap is processed in blast furnaces, rotary furnaces, or reverberatory furnaces. A reverberatory furnace is more suitable for processing fine particles and may be operated in conjunction with a blast furnace.

Blast furnaces produce hard lead from charges containing siliceous slag from previous runs (about 4.5% of the charge), scrap iron (about 4.5%), limestone (about 3%), and coke (about 5.5%). The remaining 82.5% of the charge is made up of oxides, pot furnace refining drosses, and reverberatory slag. The proportions of rerun slags, limestone, and coke vary but can run as high as 8% for slags, 10% for limestone, and 8% for coke. The processing capacity of the blast furnace ranges from 20 to 80 metric tons per day (tpd).

Newer secondary recovery plants use lead paste desulfurization to reduce sulfur dioxide emissions and generation of waste sludge during smelting. Battery paste containing lead sulfate and lead oxide is desulfurized with soda ash, yielding market-grade sodium sulfate as a by-product. The desulfurized paste is processed in a reverberatory furnace, and the lead carbonate product may then be treated in a short rotary furnace. The battery grids and posts are processed separately in a rotary smelter.

Zinc Manufacturing

In the most common hydrometallurgical process for zinc manufacturing, the ore is leached with sulfuric acid to extract the lead/zinc. These processes can operate at atmospheric pressure or as pressure leach circuits. Lead/zinc is recovered from solution by electrowinning, a process similar to electrolytic refining. The process most commonly used for low-grade deposits is heap leaching. Imperial smelting is also used for zinc ores.

POLLUTION PREVENTION AND CONTROL

The principal air pollutants emitted from the processes are particulate matter and sulfur dioxide. Fugitive emissions occur at furnace openings and from launders, casting molds, and ladles carrying molten materials, which release sulfur dioxide and volatile substances into the working environment. Additional fugitive particulate emissions occur from materials handling and transport of ores and concentrates. Some vapors are produced in hydrometallurgy and in various refining processes.

The principal constituents of the particulate matter are lead/zinc and iron oxides, but oxides of metals such as arsenic, antimony, cadmium, copper, and mercury are also present, along with metallic sulfates. Dust from raw materials handling contains metals, mainly in sulfidic form, although chlorides, fluorides, and metals in other chemical forms may be present. Off-gases contain fine dust particles and volatile impurities such as arsenic, fluorine, and mercury.

Air emissions for processes with few controls may be of the order of 30 kilograms lead or zinc per metric ton (kg/t) of lead or zinc produced. The presence of metals in vapor form is dependent on temperature. Leaching processes will generate acid vapors, while refining processes result in products of incomplete combustion (PICs). Emissions of arsine, chlorine, and hydrogen chloride vapors and acid mists are associated with electrorefining.

The most effective pollution prevention option is to choose a process that entails lower energy usage and lower emissions. Modern flash-smelting processes save energy, compared with the conventional sintering and blast furnace processes. Process gas streams containing over 5% sulfur dioxide are usually used to manufacture sulfuric acid. The smelting furnace will generate gas streams with SO_2 concentrations ranging from 0.5% to 10%, depending on the method used. It is important, therefore, to select a process that uses oxygen-enriched air or pure oxygen. The aim is to save energy and raise the SO_2 content of the process gas stream by reducing the total volume of the stream, thus permitting efficient fixation of sulfur dioxide. Processes should be operated to maximize the concentration of the sulfur dioxide. An added benefit is the reduction (or elimination) of nitrogen oxides NO_x. Regarding standard treatment technologies, ESPs and baghouses are used for product recovery and for the control of particulate emissions. Dust that is captured but not recycled will need to be disposed of in a secure landfill or in another acceptable manner (note: *this is an additional cost to control and an added incentive for pollution prevention*).

Arsenic trioxide or pentoxide is in vapor form because of the high gas temperatures and must be condensed by gas cooling so that it can be removed in fabric filters. Collection and treatment of vent gases by alkali scrubbing may be required when sulfur dioxide is not being recovered in an acid plant. These also represent high cost control options with post-disposal of waste problems. Table 9 provides some common examples of pollution prevention practices, along with energy efficiency programs. All of these fit into the category of relatively low-cost investments.

Table 9. Examples of Pollution Prevention and Energy Saving Practices.

Use doghouse enclosures where appropriate; use hoods to collect fugitive emissions.
Mix strong acidic gases with weak ones to facilitate production of sulfuric acid from sulfur oxides, thereby avoiding the release of weak acidic gases.
Maximize the recovery of sulfur by operating the furnaces to increase the SO_x content of the flue gas and by providing efficient sulfur conversion. Use a double-contact, double-absorption process.
Desulfurize paste with caustic soda or soda ash to reduce SO_2 emissions.
Use energy-efficient measures such as waste heat recovery from process gases to reduce fuel usage and associated emissions.
Recycle condensates, rainwater, and excess process water for washing, for dust control, for gas scrubbing, and for other process applications where water quality is not of particular concern.
Give preference to natural gas over heavy fuel oil for use as fuel and to coke with lower sulfur content.
Use low-NO_x burners.
Use suspension or fluidized bed roasters, where appropriate, to achieve high SO_2 concentrations when roasting zinc sulfides.

Give preference to fabric filters over wet scrubbers or wet electrostatic precipitators (ESPs) for dust control.
Good housekeeping practices are key to minimizing losses and preventing fugitive emissions. Losses and emissions are minimized by enclosed buildings, covered conveyors and transfer points, and dust collection equipment. Yards should be paved and runoff water routed to settling ponds.

AIR POLLUTION FROM NICKEL ORE PROCESSING AND REFINING

Primary nickel is produced from two very different ores, lateritic and sulfidic. Lateritic ores are normally found in tropical climates where weathering, with time, extracts and deposits the ore in layers at varying depths below the surface. Lateritic ores are excavated using large earth-moving equipment and are screened to remove boulders. Sulfidic ores, often found in conjunction with copper-bearing ores, are mined from underground. Following is a description of the processing steps used for the two types of ores.

LATERITIC ORE PROCESSING

Lateritic ores have a high percentage of free and combined moisture, which must be removed. Drying removes free moisture; chemically bound water is removed by a reduction furnace, which also reduces the nickel oxide. Lateritic ores have no significant fuel value, and an electric furnace is needed to obtain the high temperatures required to accommodate the high magnesia content of the ore. Some laterite smelters add sulfur to the furnace to produce a matte for processing. Most laterite nickel processors run the furnaces so as to reduce the iron content sufficiently to produce ferronickel products. Hydrometallurgical processes based on ammonia or sulfuric acid leach are also used. Ammonia leach is usually applied to the ore after the reduction roast step.

SULFIDIC ORE PROCESSING

Flash smelting is the most common process, but electric smelting is used for more complex raw materials when increased flexibility is needed. Both processes use dried concentrates. Electric smelting requires a roasting step before smelting to reduce sulfur content and volatiles. Older nickel-smelting processes, such as blast or reverberatory furnaces, are no longer acceptable because of low energy efficiencies and environmental concerns.

In flash smelting, dry sulfide ore containing less than 1% moisture is fed to the furnace along with preheated air, oxygen-enriched air (30 to 40% oxygen), or pure oxygen. Iron and sulfur are oxidized. The heat that results from exothermic reactions is adequate to smelt concentrate, producing a liquid matte (up to 45% nickel) and a fluid slag. Furnace matte still contains iron and sulfur, and these are oxidized in the converting step to sulfur dioxide and iron oxide by injecting air or oxygen into the molten bath. Oxides form a slag, which is skimmed off. Slags are processed in an electric furnace prior to discard to recover nickel. Process gases are cooled, and particulates are then removed by gas-cleaning devices.

NICKEL REFINING

Various processes are used to refine nickel matte. Fluid bed roasting and chlorine-hydrogen reduction produce high-grade nickel oxides (more than 95% nickel). Vapor processes such as the carbonyl process can be used to produce high-purity nickel pellets. In this process, copper and precious metals remain as a pyrophoric residue that requires separate treatment. Use of electrical cells equipped with inert cathodes is the most common technology for nickel refining. Electrowinning, in which nickel is removed from solution in cells equipped with inert anodes, is the more common refining process. Sulfuric acid solutions or, less commonly, chloride electrolytes are used.

POLLUTION PREVENTION AND CONTROL

Sulfur dioxide is a major air pollutant emitted in the roasting, smelting, and converting of sulfide ores. (Nickel sulfide concentrates contain 6 to 20% nickel and up to 30% sulfur.) SO_2 releases can be as high as 4 metric tons (t) of sulfur dioxide per metric ton of nickel produced, before controls. Reverberatory furnaces and electric furnaces produce SO_2 concentrations of 0.5 to 2.0%, while flash furnaces produce SO_2 concentrations of over 10% - a distinct advantage for the conversion of the sulfur dioxide to sulfuric acid. Particulate emission loads for various process steps include 2.0 to 5.0 kilograms per metric ton (kg/t) for the multiple hearth roaster; 0.5 to 2.0 kg/t for the fluid bed roaster; 0.2 to 1.0 kg/t for the electric furnace; 1.0 to 2.0 kg/t for the Pierce-Smith converter; and 0.4 kg/t for the dryer upstream of the flash furnace. Ammonia and hydrogen sulfide are pollutants associated with the ammonia leach process; hydrogen sulfide emissions are associated with acid leaching processes. Highly toxic nickel carbonyl is a contaminant of concern in the carbonyl refining process. Various process off-gases contain fine dust particles and volatilized impurities. Fugitive emissions occur at furnace openings, launders, casting molds, and ladles that carry molten product. The transport and handling of ores and concentrates produce windborne dust.

Pyrometallurgical processes for processing sulfidic ores are generally dry, and effluents are of minor importance, although wet ESPs are often used for gas treatment, and the resulting wastewater could have high metal concentrations. Process bleed streams may contain antimony, arsenic, or mercury. Large quantities of water are used for slag granulation, but most of this water should be recycled.

Pollution prevention is always preferred to the use of end-of-pipe pollution control facilities. Therefore, every attempt should be made to incorporate cleaner production processes and facilities to limit, at source, the quantity of pollutants generated. The choice of flash smelting over older technologies is the most significant means of reducing pollution at source. Sulfur dioxide emissions can be controlled by:

- Recovery as sulfuric acid,
- Recovery as liquid sulfur dioxide (absorption of clean dry off-gas in water or chemical absorbtion by ammonium bisulfite or dimethyl aniline),
- Recovery as elemental sulfur, using reductants, such as hydrocarbons, carbon, or hydrogen sulfide.

Toxic nickel carbonyl gas is normally not emitted from the refining process because it is broken down in decomposer towers. However, very strict precautions throughout the refining process are required to prevent the escape of the nickel carbonyl into the workplace. Continuous monitoring for the gas, with automatic isolation of any area of the plant where the gas is detected, is required. Impervious clothing is used to protect workers against contact of liquid nickel carbonyl with skin. Preventive measures for reducing emissions of particulate matter include encapsulation of furnaces and conveyors to avoid fugitive emissions. Covered storage of raw materials should be considered. Wet scrubbing should be avoided, and cooling waters should be recirculated. Stormwaters should be collected and used in the process. Process water used to transport granulated slag should be recycled. To the extent possible, all process effluents should be returned to the process. The discharge of particulate matter emitted during drying, screening, roasting, smelting, and converting is controlled by using cyclones followed by wet scrubbers, ESPs, or bag filters. Fabric filters may require reduction of gas temperatures by, for example, dilution with low temperature gases from hoods used for fugitive dust control. Preference should be given to the use of fabric filters over wet scrubbers.

AIR POLLUTION FROM ALUMINUM MANUFACTURING

The production of aluminum begins with the mining and beneficiation of bauxite. At the mine (usually of the surface type), bauxite ore is removed to a crusher. The crushed ore is then screened and stockpiled, ready for delivery to an alumina plant. In some cases, ore is upgraded by beneficiation (washing, size classification, and separation of liquids and solids) to remove unwanted materials such as clay and silica.

At the alumina plant, the bauxite ore is further crushed to the correct particle size for efficient extraction of the alumina through digestion by hot sodium hydroxide liquor. After removal of "red mud" (the insoluble part of the bauxite) and fine solids from the process liquor, aluminum trihydrate crystals are precipitated and calcined in rotary kilns or fluidized bed calciners to produce alumina (Al_2O_3). Some alumina processes include a liquor purification step.

Primary aluminum is produced by the electrolytic reduction of the alumina. The alumina is dissolved in a molten bath of fluoride compounds (the electrolyte), and an electric current is passed through the bath, causing the alumina to dissociate to form liquid aluminum and oxygen. The oxygen reacts with carbon in the electrode to produce carbon dioxide and carbon monoxide. Molten aluminum collects in the bottom of the individual cells or pots and is removed under vacuum into tapping crucibles. There are two prominent technologies for aluminum smelting: prebake and Soderberg. The following discussion focuses on the prebake technology, with its associated reduced air emissions and energy efficiencies.

Raw materials for secondary aluminum production are scrap, chips, and dross. Pretreatment of scrap by shredding, sieving, magnetic separation, drying, and so on is designed to remove undesirable substances that affect both aluminum quality and air emissions. The prevailing process for secondary aluminum production is smelting in rotary kilns under a salt cover. Salt slag can be processed and reutilized. Other processes (smelting in induction furnaces and hearth furnaces) need no or substantially less salt and are associated with lower energy demand, but they are only suitable for high-grade scrap.

Depending on the desired application, additional refining may be necessary. For demagging (removal of magnesium from the melt), hazardous substances such as chlorine and hexachloroethane are often used, which may produce dioxins and dibenzofurans. Other, less hazardous methods, such as adding chlorine salts, are available.

Because it is difficult to remove alloying elements such as copper and zinc from an aluminum melt, separate collection and separate reutilization of different grades of aluminum scrap are necessary. Note that secondary aluminum production uses substantially less energy than primary production (less than 10 to 20 gigajoules per metric ton (GJ/t) of aluminum produced, compared with 164 GJ/t for primary production).

POLLUTION PREVENTION AND CONTROL

At the bauxite production facilities, dust is emitted to the atmosphere from dryers and materials-handling equipment, through vehicular movement, and from blasting. Although the dust is not hazardous, it can be a nuisance if containment systems are not in place, especially on the dryers and handling equipment. Other air emissions could include NO_x, SO_x, and other products of combustion from the bauxite dryers. Ore washing and beneficiation yield process waste waters containing suspended solids. Runoff from precipitation may also contain suspended solids. At the alumina plant, air emissions can include bauxite dust from handling and processing, limestone dust from limestone handling, burnt lime dust from conveyors and bins, alumina dust from materials handling, red mud dust and sodium salts from red mud stacks (impoundments), caustic aerosols from cooling towers, and products of combustion such as sulfur dioxide and nitrogen oxides from boilers, calciners, various mobile equipment, and kilns. The calciners may also emit alumina dust and the kilns, and burnt lime dust.

In the aluminum smelter, air emissions include alumina dust from handling facilities; coke dust from coke handling; gaseous and particulate fluorides; sulfur and carbon dioxides and various dusts from the electrolytic reduction cells; gaseous and particulate fluorides; sulfur dioxide; tar vapor and carbon particulates from the baking furnace; coke dust, tars, and polynuclear aromatic hydrocarbons (PAHs) from the green carbon and anode-forming plant; carbon dust from the rodding room; and fluxing emissions and carbon oxides from smelting, anode production, casting, and finishing operations. The electrolytic reduction cells (pot line) are the major source of the air emissions, with the gaseous and particulate fluorides being of prime concern. The anode effect associated with electrolysis also results in emissions of carbon tetrafluoride (CF_4) and carbon hexafluoride (C_2F_6), which are greenhouse gases of concern because of their potential for global warming. Emissions numbers that have been reported for uncontrolled gases from smelters are 20 to 80 kg/t for particulates, 6 to 12 kg/t for hydrogen fluoride, and 6 to 10 kg/t for fluoride particulates. Corresponding concentrations are 200 to 800 mg/m^3; 60 to 120 mg/m^3; and 60 to 100 mg/m^3. An aluminum smelter produces 40 to 60 kg of mixed solid wastes per ton of product, with spent cathodes (spent pot and cell linings) being the major fraction. The linings consist of 50% refractory material and 50% carbon. Over the useful life of the linings, the carbon becomes impregnated with aluminum and silicon oxides (averaging 16% of the carbon lining), fluorides

(34% of the lining), and cyanide compounds (about 400 parts per million). Contaminant levels in the refractories portion of linings that have failed are generally low. Other by-products for disposal include skim, dross, fluxing slags, and road sweepings.

Atmospheric emissions from secondary aluminum melting include hydrogen chloride and fluorine compounds. Demagging may lead to emissions of chlorine, hexachloroethane, chlorinated benzenes, and dioxins and furans. Chlorinated compounds may also result from the melting of aluminum scrap that is coated with plastic. Salt slag processing emits hydrogen and methane. Solid wastes from the production of secondary aluminum include particulates, pot lining refractory material, and salt slag. Particulate emissions containing heavy metals are also associated with secondary aluminum production.

Pollution prevention is always preferred to the use of end-of-pipe pollution control facilities. Therefore every attempt should be made to incorporate cleaner production processes and facilities to limit, at source, the quantity of pollutants generated.

Using the prebake technology rather than the Soderberg technology for aluminum smelting is a significant pollution prevention measure. In the smelter, computer controls and point feeding of aluminum oxide to the centerline of the cell help reduce emissions, including emissions of organic fluorides such as CF_4, which can be held at less than 0.1 kg/t aluminum. Energy consumption is typically 14 megawatt hours per ton (MWh/t) of aluminum, with prebake technology. Soderberg technology uses 17.5 MWh/t. Gas collection efficiencies for the prebake process is better than for the Soderberg process: 98% vs. 90%. Dry scrubber systems using aluminum oxide as the adsorbent for the cell gas permits the recycling of fluorides. The use of low-sulfur tars for baking anodes helps control SO_2 emissions. Spent pot linings are removed after they fail, typically because of cracking or heaving of the lining. The age of the pot linings can vary from 3 to 10 years. By improving the life of the lining through better construction and operating techniques, discharge of pollutants can be reduced. Note that part of the pot lining carbon can be recycled when the pots are relined. Emissions of organic compounds from secondary aluminum production can be reduced by thoroughly removing coatings, paint, oils, greases, and the like from raw feed materials before they enter the melt process. At bauxite facilities, the major sources of dust emissions are the dryers, and emissions are controlled with electrostatic precipitators (ESPs) or baghouses. Removal efficiencies of 99% are achievable. Dust from conveyors and material transfer points is controlled by hoods and enclosures. Dust from truck movement can be minimized by treating road surfaces and by ensuring that vehicles do not drop material as they travel. Dusting from stockpiled material can be minimized by the use of water sprays or by enclosure in a building. At the alumina plant, pollution control for the various production and service areas is implemented as follows:

- *Bauxite and limestone handling and storage:* dust emissions are controlled by baghouses.
- *Lime kilns*: dust emissions are controlled by baghouse systems. Kiln fuels can be selected to reduce SO_x emissions; however, this is not normally a problem, since most of the sulfur dioxide that is formed is absorbed in the kiln.
- *Calciners:* alumina dust losses are controlled by ESPs; SO_2 and NO_x emissions are reduced to acceptable levels by contact with the alumina.
- *Red mud disposal*: the mud impoundment area must be lined with impervious clay prior to use to prevent leakage. Water spraying of the mud stack may be required to prevent fine dust from being blown off the stack. Longer-term treatment of the mud may include reclamation of the mud, neutralization, covering with topsoil, and planting with vegetation.

In the smelter, primary emissions from the reduction cells are controlled by collection and treatment using dry sorbent injection; fabric filters or ESPs are used for controlling particulate matter. Primary emissions comprise 97.5% of total cell emissions; the balance consists of secondary emissions that escape into the potroom and leave the building through roof ventilators. Wet scrubbing of the primary emissions can also be used, but large volumes of toxic waste liquors will need to be treated or disposed of. Secondary emissions result from the periodic replacement of anodes and other operations; the fumes escape when the cell hood panels have been temporarily removed. While wet scrubbing can be used to control the release of secondary fumes, the high-volume, low-concentration gases offer low scrubbing efficiencies, have high capital and operating costs, and produce large volumes of liquid effluents for treatment. Wet scrubbing is seldom used for secondary fume control in the prebake process.

When anodes are baked on site, the dry scrubbing system using aluminum oxide as the adsorbent is used. It has the advantage of being free of waste products, and all enriched alumina and absorbed material are recycled directly to the reduction cells. Dry scrubbing may be combined with incineration for controlling emissions of tar and volatile organic compounds (VOCs) and to recover energy. Wet scrubbing can also be used but is not recommended, since a liquid effluent, high in fluorides and hydrocarbons, will require treatment and disposal.

Dry scrubber systems applied to the pot fumes and to the anode baking furnace result in the capture of 97% of all fluorides from the process.

The aluminum smelter solid wastes, in the form of spent pot lining, are disposed of in engineered landfills that feature clay or synthetic lining of disposal pits, provision of soil layers for covering and sealing, and control and treatment of any leachate. Treatment processes are available to reduce hazards associated with spent pot lining prior to disposal of the lining in a landfill. Other solid wastes such as bath skimmings are sold for recycling, while spalled refractories and other chemically stable materials are disposed of in landfill sites.

Modern smelters using good industrial practices are able to achieve the following in terms of pollutant loads (all values are expressed on an annualized basis): hydrogen fluoride, 0.2 to 0.4 kg/t; total fluoride, 0.3 to 0.6 kg/t; particulates, 1 kg/t; sulfur dioxide, 1 kg/t; and nitrogen oxides, 0.5 kg/t. CF_4 emissions should be less than 0.1 kg/t.

For secondary aluminum production, the principal treatment technology downstream of the melting furnace is dry sorbent injection using lime, followed by fabric filters. Waste gases from salt slag processing should be filtered as well. Waste gases from aluminum scrap pretreatment that contain organic compounds of concern may be treated by post-combustion practices.

Air emissions should be monitored regularly for particulate matter and fluorides. Hydrocarbon emissions should be monitored annually on the anode plant and baking furnaces. Liquid effluents should be monitored weekly for pH, total suspended solids, fluoride, and aluminum and at least monthly for other parameters. Monitoring data should be analyzed and reviewed at regular intervals and compared with the operating standards so that any necessary corrective actions can be taken.

AIR POLLUTION FROM COPPER SMELTING

Copper can be produced either pyrometallurgically or hydrometallurgically. The hydrometallurgical route is used only for a very limited amount of the world's copper production and is normally only considered in connection with in situ leaching of copper ores. From an environmental point of view, this is a questionable production route. Several different processes can be used for copper production. The traditional process is based on roasting, smelting in reverbatory furnaces (or electric furnaces for more complex ores), producing matte (copper-iron sulfide), and converting for production of blister copper, which is further refined to cathode copper. This route for production of cathode copper requires large amounts of energy per ton of copper: 30 to 40 million British thermal units (Btu) per ton cathode copper. It also produces furnace gases with low sulfur dioxide concentrations from which the production of sulfuric acid or other products is less efficient. The sulfur dioxide concentration in the exhaust gas from a reverbatory furnace is about 0.5 to 1.5%; that from an electric furnace is about 2 to 4%. So-called flash smelting techniques have therefore been developed that utilize the energy released during oxidation of the sulfur in the ore. The flash techniques reduce the energy demand to about 20 million Btu/ton of produced cathode copper. The SO_2 concentration in the off gases from flash furnaces is also higher, over 30%, and is less expensive to convert to sulfuric acid. The INCO process results in 80% sulfur dioxide in the off gas. Flash processes have been in use since the early 1950s.

In addition to the above processes, there are a number of newer processes such as Noranda, Mitsubishi, and Contop, which replace roasting, smelting, and converting, or processes such as ISA-SMELT and KIVCET, which replace roasting and smelting. For converting, the Pierce-Smith and Hoboken converters are the most common processes.

The matte from the furnace is charged to converters, where the molten material is oxidized in the presence of air to remove the iron and sulfur impurities (as converter slag) and to form blister copper. Blister copper is further refined as either fire-refined copper or anode copper (99.5% pure copper), which is used in subsequent electrolytic refining. In fire refining, molten blister copper is placed in a fire-refining furnace, a flux may be added, and air is blown through the molten mixture to remove residual sulfur. Air blowing results in residual oxygen, which is removed by the addition of natural gas, propane, ammonia, or wood. The fire-refined copper is then cast into anodes for further refining by electrolytic processes or is cast into shapes for sale.

In the most common hydrometallurgical process, the ore is leached with ammonia or sulfuric acid to extract the copper. These processes can operate at atmospheric pressure or as pressure leach circuits. Copper is recovered from solution by electrowinning, a process similar to electrolytic refining. The process is most commonly used for leaching low-grade deposits in situ or as heaps.

Recovery of copper metal and alloys from copper-bearing scrap metal and smelting residues requires preparation of the scrap (e.g., removal of insulation) prior to feeding into the primary process. Electric arc furnaces using scrap as feed are also common.

POLLUTION PREVENTION AND CONTROL

The principal air pollutants emitted from the processes are sulfur dioxide and particulate matter. The amount of sulfur dioxide released depends on the characteristics of the ore-complex ores which may contain lead, zinc, nickel, and other metals, and on whether facilities are in place for capturing and converting the sulfur dioxide. SO_2 emissions may range from less than 4 kilograms per metric ton (kg/t) of copper to 2,000 kg/t of copper. Particulate emissions can range from 0.1 kg/t of copper to as high as 20 kg/t of copper. Fugitive emissions occur at furnace openings and from launders, casting molds, and ladles carrying molten materials. Additional fugitive particulate emissions occur from materials handling and transport of ores and concentrates. Some vapors, such as arsine, are produced in hydrometallurgy and various refining processes. Dioxins can be formed from plastic and other organic material when scrap is melted. The principal constituents of the particulate matter are copper and iron oxides. Other copper and iron compounds, as well as sulfides, sulfates, oxides, chlorides, and fluorides of arsenic, antimony, cadmium, lead, mercury, and zinc, may also be present. Mercury can also be present in metallic form. At higher temperatures, mercury and arsenic could be present in vapor form. Leaching processes will generate acid vapors, while fire-refining processes result in copper and SO_2 emissions. Emissions of arsine, hydrogen vapors, and acid mists are associated with electrorefining. Wastewater from primary copper production contains dissolved and suspended solids that may include concentrations of copper, lead, cadmium, zinc, arsenic, and mercury and residues from mold release agents (lime or aluminum oxides). Fluoride may also be present, and the effluent may have a low pH. Normally there is no liquid effluent from the smelter other than cooling water; waste waters do originate in scrubbers (if used), wet electrostatic precipitators, cooling of copper cathodes, and so on. In the electrolytic refining process, by-products such as gold and silver are collected as slimes that are subsequently recovered. Note that a significant sources of wastewater is derived air scrubbers.

Process gas streams containing sulfur dioxide are processed to produce sulfuric acid, liquid sulfur dioxide, or sulfur. The smelting furnace will generate process gas streams with SO_2 concentrations ranging from 0.5% to 80%, depending on the process used. It is important, therefore, that a process be selected that uses oxygen-enriched air (or pure oxygen) to raise the SO_2 content of the process gas stream and reduce the total volume of the stream, thus permitting efficient fixation of sulfur dioxide. Processes should be operated to maximize the concentration of the sulfur dioxide. An added benefit is the reduction of NO_x. Some pollution prevention practices for this industry include the following:

- Closed-loop electrolysis plants will contribute to prevention of pollution.
- Furnaces should be enclosed to reduce fugitive emissions, and dust from dust control equipment should be returned to the process.
- Energy efficiency measures (such as waste heat recovery from process gases) should be applied to reduce fuel usage and associated emissions.
- Recycling should be practiced for dust control and gas scrubbing, as well as for cooling water, condensates, rainwater, and excess process water used for washing.
- Good housekeeping practices are key to minimizing losses and preventing fugitive emissions. Such losses and emissions are minimized by enclosed buildings, covered or enclosed conveyors and transfer points, and dust collection equipment. Yards should be paved and runoff water routed to settling ponds. Regular sweeping of yards and indoor storage or coverage of

concentrates and other raw materials also reduces materials losses and emissions.

Pollution control technologies acceptable for this industry are as follows. Fabric filters are used to control particulate emissions. Dust that is captured but not recycled will need to be disposed of in a secure landfill or other acceptable manner. Vapors of arsenic and mercury present at high gas temperatures are condensed by gas cooling and removed. Additional scrubbing may be required. Effluent treatment by precipitation, filtration, and so on, of process bleed streams, filter backwash waters, boiler blowdown, and other streams may be required to reduce suspended and dissolved solids and heavy metals. Residues that result from treatment are sent for metals recovery or to sedimentation basins. Stormwaters should be treated for suspended solids and heavy metals reduction. Slag should be landfilled or granulated and sold. Modern plants using good industrial practices should set as targets total dust releases of 0.5 to 1.0 kg/t of copper and SO_2 discharges of 25 kg/t of copper. A double-contact, double-absorption plant should emit no more than 0.2 kg of sulfur dioxide per ton of sulfuric acid produced (based on a conversion efficiency of 99.7%).

RECOMMENDED RESOURCES FOR THE READER

1. Bounicore, Anthony J., and Wayne T. Davis, eds. 1992. *Air Pollution Engineering Manual*. New York: Van Nostrand Reinhold.
2. European Fertilizer Manufacturers' Association. 1995a. "Production of NPK Fertilizers by the Nitrophosphate Route." Booklet 7 of 8. Brussels. and 1995b. "Production of NPK Fertilizers by the Mixed Acid Route." Booklet 8 of 8. Brussels.
3. Sauchelli, Vincent. 1960. *Chemistry and Technology of Fertilizers*. New York: Reinhold Publishing.
4. Sittig, Marshall. 1979. *Fertilizer Industry; Processes, Pollution Control and Energy Conservation*. Park Ridge, N.J.: Noyes Data Corporation.
5. UNIDO (United Nations Industrial Development Organization). 1978. *Process Technologies for Nitrogen Fertilizers*. New York and 1978. *Process Technologies for Phosphate Fertilizers*. New York.
6. European Union. 1996. "Best Available Technology Notes on Various Pesticides Manufacturing Processes." Brussels.
7. Sittig, Marshall. *Pesticide Manufacturing and Toxic Materials Control Encyclopedia*. Park Ridge, N.J.: Noyes Data Corporation.
8. UNIDO (United Nations Industrial Development Organization). 1992.

International Safety Guidelines for Pesticides Formulation in Developing Countries. Vienna.

9. USEPA (U.S. Environmental Protection Agency). 1988. *Pesticide Waste Control Technology*. Park Ridge, N.J.: Noyes Data Corporation.
10. WHO (World Health Organization). 1996. *International Programme on Chemical Safety (IPCS): The WHO Recommended Classification of Pesticides by Hazard and Guidelines to Classification 1996-1997.* Geneva.
11. World Bank. 1993. "Agricultural Pest Management." Guidelines and Best Practice, GB 4.03. *World Bank Operational Manual.* April, Washington.
12. 1996. "Pollution Prevention and Abatement: Pesticides Manufacturing." Draft Technical Background Document. Environment Department, Washington, D.C.
13. ACS (American Chemical Society). 1983. *Advances in Pesticide Formulation Technology*. ACS Symposium Series 254. Washington, D.C.
14. Seaman, D. 1990. "Trends in the Formulation of Pesticides: An Overview." *Pesticide Science* 29:437-49.
15. Bounicore, Anthony J., and Wayne T. Davis, eds. 1992. *Air Pollution Engineering Manual.* New York: Van Nostrand Reinhold.
16. European Community. 1993. "Technical Note on the Best Available Technologies to Reduce Emissions into Air from Coke Plants." Paper presented to BAT Exchange of Information Committee, Brussels, 1993. "Study on the Technical and Economic Aspects of Measures to Reduce the Pollution from the Industrial Emissions of Cokeries." Paper presented to BAT Exchange of Information Committee, Brussels.
17. USEPA (United States Environmental Protection Agency). 1982. *Development Document for Effluent Limitations Guidelines and Standards for the Iron and Steel Manufacturing Point Source Subcategory*. EPA440/ 1-82/024. Washington, D.C.
18. United States. 1992. *Federal Register,* vol. 57, no. 160, August 18. Washington, D.C.: Government Printing Office.
19. World Bank. 1995. "Industrial Pollution Prevention and Abatement: Coke Manufacturing." Draft Technical Background Document. Washington, D.C.
20. WHO (World Health Organization). 1989. *Management and Control of the Environment*. WHO/PEP/89.1. Geneva.
21. Kirk, Raymond E., and Donald F. Othmer. *1980. KirkOthmer Encyclopedia of Chemical Technology*. 3d ed. New York: John Wiley and Sons.

22. Austen, George T., R. N. Shreve, and Joseph A. Brink. *1984. Shreve's Chemical Process Industries*. New York: McGraw-Hill.
23. *Cleaner Technologies Substitute Assessments: A Methodology and Resource Guide*, USEPA, EPA Document Number EPA 744-R-95-002, December 1996.

REVIEW AND QUESTIONS TO GET YOU THINKING

1. Describe typical sources and types of air emissions resulting from steelmaking. What are some pollution prevention practices used in this industry? What are some of the emission control devices used and for what purposes?
2. Describe typical sources and types of air emissions resulting from petroleum refining. What are some pollution prevention practices used in this industry? What are some of the emission control devices used and for what purposes?
3. Describe typical sources and types of air emissions resulting from fertilizer manufacturing. What are some pollution prevention practices used in this industry? What are some of the emission control devices used and for what purposes?
4. Describe typical sources and types of air emissions resulting from pharmaceutical manufacturing. What are some pollution prevention practices used in this industry? What are some of the emission control devices used and for what purposes?
5. Describe typical sources and types of air emissions resulting from dye manufacturing. What are some pollution prevention practices used in this industry? What are some of the emission control devices used and for what purposes?
6. Describe how you would determine the nature and extent of fugitive air emissions in a large plant operation like a refinery. Save these notes and refer to them when you read over Chapter 6.
7. Develop a simplified process flow sheet for the basic steelmaking process. Indicate on the schematic where and what types of air emissions take place.
8. List the major types of air pollution control devices used for particulate removal. Visit the Web and make a list of equipment suppliers for these hardware.

9. Among the principal air emissions associated with petroleum refining operations, which ones pose the greatest health risks and why?

10. Estimate some typical emission factors and make a comparison between industry sectors. One way to express an emission factor is in terms of the tons of pollution produced per year per unit capita of production. Develop a table for several common pollutants (e.g., SO_x, NO_x, HCs, others) for each industry sector you select. What conclusions can you draw from these comparisons.

11. A VCM (vinyl chloride monomer) production unit uses three vertically mounted agitated reactors for the polymerization of vinyl chloride. Crude material balances infer about 8 to 10% monomer losses. Describe how you would go about assessing whether these losses are due to leaks such as fugitive air emissions. Be specific in recommending procedures and instruments.

12. A refinery operation produces about 500,000 barrels of crude per year. There are approximately 1500 gate valves used in the operation. Develop an estimate of the potential hydrocarbon emissions resulting from valve leakage. What is this worth in terms of lost revenues to the facility? You can find some information on typical valve leakage rates from searching on www.google.com.

13. Make a list of all the costs associated with running a wet scrubbing operation to remove particulates and SO_x. What cost factors could be eliminated or reduced if a pollution prevention technology or practice that used about the same energy and manpower requirements was applied.

14. A coking operation has about 1 million cubic meters per year of excess coke oven gas that it generally sends to flares. (A) Instead of burning this offgas in flares, what else could be done with it? (B) What is the value of this gas (assume it to be essentially natural gas or methane)?

Chapter 3

PROPERTIES OF AIR POLLUTANTS

INTRODUCTION

There are literally many thousands of chemical compounds that are potential air pollutants. It would be impossible to present all the pertinent data and information needed to evaluate each and every air pollution scenario. There are, however, a wealth of information and data bases that are available on the worldwide Web, along with a number of standard hard copy references to obtain information on the chemical and physical properties, and health risks of potential atmospheric contaminants.

This chapter provides information on the following three areas:

1. Selected chemical and physical properties, and data of common and potential atmospheric contaminants,
2. An overview of important terms and definitions useful in assessing the potentially harmful effects of air pollutants, and
3. A summary of several Web site sources that provide extensive data bases on the chemical and physical properties, as well as health risk effects associated with air contaminants.

The reader will find a list of Recommended References at the end of this chapter.

SELECTED CHEMICAL AND PHYSICAL PROPERTIES OF POTENTIAL ATMOSPHERIC POLLUTANTS

Table 1 is a compilation of chemical and physical properties data for selected atmospheric contaminants. This information is useful for evaluating pollution problems. The following are abbreviations used in the table.

A, specific gravity with reference to air = 1

p., para position

abs., absolute
al., alcohol
atm., atmosphere
c., cold
ca., approximately
cc., cubic centimeters
cryst., crystal
d., decomposes or decomposed
d.h., decomposes hot
dil., dilute
expl., explodes
h., hot
i., insoluble
ign., ignites
m., meta position
n, normal
o, ortho position
prim., primary
s., soluble
s. abs., soluble in absolute alcohol
s.h., soluble hot
sl. d., slight or slightly soluble
sl. s., slight or slightly soluble
subl., sublimes
v., very
v.s., very soluble
v.s.h., very soluble hot
v. sl., very slight or very slightly
v.sl.s., very slightly soluble
∞, soluble in all proportions
α, alpha form or position
β, beta form or position
ω, omega position

Table 1. Selected Chemical and Physical Data on Potential Atmospheric Contaminants.

Compound and Chemical Formula	Specific Gravity or Density	Solubility in 100 Parts		Diffusion Coefficient in Air (cm²/sec)	Melting Point, °C	Boiling Point, °C
		Water	Alcohol			
Acetaldehyde (ethanol) $CH_3{\cdot}CHO$	0.783 (18°/4)	∞	∞		-123.5	20.2
Acetic Acid (ethanoic acid) $CH_3{\cdot}COOH$	1.049 (20°/4)	∞	∞	0.1061 (0°) 0.1065 (0°) 0.1061 (0°)	16.7	118.1

Compound and Chemical Formula	Specific Gravity or Density	Solubility in 100 Parts		Diffusion Coefficient in Air (cm^2/sec)	Melting Point, °C	Boiling Point, °C
		Water	Alcohol			
Acetic Anhydride $(CH_3CO)_2O$	1.082 (20°/4)	12c; d.h.	∞		-73	139.6
Acetone (propanone) $CH_3 \cdot CO \cdot CH_3$	0.792 (20°/4)	∞	∞		-94.6	56.5
Acetylene tetrachloride (sym-tetrachloroethane) $Cl_2CH \cdot CHCl_2$	1.6000 (20°/4)	i.	∞		-36	146.3
Acrolein (acrylic aldehyde) $CH_2{:}CH \cdot CHO$	0.841 (20°/4)	40	s.		-87.7	52.5
Acrylonitrile (vinyl cyanide) $CH_2{:}CH \cdot CN$	0.811 (0°)	s.	s.		-82	78.9
Allyl ether (diallyl ether) $(CH{:}CH \cdot CH_2)_2O$	0.826 (20°/4)	0.3	s.		—	94.3
Ammonia NH_3	0.817	89.9 (0°) 7.4 (96°)	89.9 (0°) 7.4 (96°)		-77.7	-33.4
Amyl acetate (iso) (common amyl acetate) $CH_3CO_2 \cdot (CH_2)_2 \cdot CH{:}(CH_3)_2$	0.876 (15°/4)	0.25 (15°)	∞		—	142 @ 742 mm
Arsenic trichloride (butter of arsenic) $AsCl_3$	liq. 2.163	d.	—		-18	130
Arsine (arsenous hydride) AsH_3	2.695 (A)	20 cc.	—		-113.3	-55; d. 230
Barium peroxide BaO_2	4.958	v.sl.s.	—		-0.8	—

Compound and Chemical Formula	Specific Gravity or Density	Solubility in 100 Parts		Diffusion Coefficient in Air (cm^2/sec)	Melting Point, °C	Boiling Point, °C
		Water	Alcohol			
Benzene (benzol) C_6H_6	0.879 (20°/4)	0.07 (22°)	∞	0.0751 (0°)	5.45	80.1
Benzine (mixture, gasoline)	less than water	—	—		—	—
Benzoyl chloride $C_6H_5{\cdot}CO{\cdot}Cl$	1.212 (20°/4)	d.	d.h.		-0.5	197.2
Benzyl amine (ω-amino-toluene) $C_6H_5{\cdot}CH_2{\cdot}NH_2$	0.982 (20°/4)	∞	∞		—	184.5
Bromine Br_2	3.2 (0°/4)	3.13 (30°)	s.		-7.2	58.78
Bromobenzene (phenyl bromide) C_6H_5Br	1.495 (20°/4)	i.	s.		-30.6	156.2
Bromoethane (ethyl bromide) $C_2H_5{\cdot}Br$	1.460 (20°/4)	1.06 (0°) 0.9 (30°)	∞		-118.9	38.4
Bromoethylene (vinyl bromide) $CH_2{\cdot}CH{\cdot}Br$	1.529 (11°/4)	i.	∞		-137.8	15.8
Bromomethane (methyl bromide) $CH_3{\cdot}Br$	1.732 (0°/0)	v. sl. s.	s.		-93	4.5 @ 758mm
Bromopropane (propyl bromide) $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}Br$	1.353 (20°/4)	0.25 (20°)	∞	0.085	-109.9	70.8
Bromopropene (allyl bromide) $CH_3{\cdot}CH{\cdot}CH_2{\cdot}Br$	1.398 (20°/4)	i.	∞		-119.4	70.1 @ 753mm
ω-Bromotoluene (benzyl bromide) $C_6H_5{\cdot}CH_2{\cdot}Br$	1.443 (17°)	i., sl. d.	∞		-4	198.9
Bromoxylene (bromo-o-xylene[3]) $Br{\cdot}C_6H_3{\cdot}(CH_3)_2$	1.365 (20°/4)	i.	---		—	213.5

Compound and Chemical Formula	Specific Gravity or Density	Solubility in 100 Parts		Diffusion Coefficient in Air (cm^2/sec)	Melting Point, °C	Boiling Point, °C
		Water	Alcohol			
1,3-Butadiene (erythrene) $CH_2:CH\cdot CH:CH_2$	0.621 (20°/4)	i.	∞		-108.9	-4.41
Butane (diethyl) $CH_3\cdot CH_2\cdot CH_2\cdot CH_3$	liq. 0.60 (0°)	15 cc. (17°/722)	1883 (17°/773)		-135	-0.6
n-Butanol $C_2H_5\cdot CH_2\cdot CH_2OH$	0.810 (20°/4)	9 (15°)	∞	0.0703 0.0681 (0°)	-79.9	117
2-Butanone (methylethyl ketone) $CH_3\cdot CO\cdot C_2H_5$	0.805 (20°/4)	37	∞		-85.9	79.6
Butene-1 (butylene) $C_2H_5\cdot CH:CH_2$	liq. 0.6 (9°)	i.	v.s.		-130	-5
n-Butyl acetate $CH_3CO_2\cdot (CH_2)_3\cdot CH_3$	0.882 (20°)	0.7	∞	0.058	-76.3	125.1
n-Butyl cellosolve $C_4H_9\cdot O\cdot CH_2CH_2OH$	0.905 (20°/4)	∞	∞		—	171.2
n-Butyl formate $HCO_2\cdot (CH_2)_3\cdot CH_3$	0.911 (0°)	v.sl.s.	∞		—	106.9
Butyl ether (n-dibutyl ether) $(C_2H_5\cdot CH_2\cdot CH_2)_2O$	0.769 (20°/20°)	< 0.05	∞		-98	142.4
n-Butyl nitrite $C_4H_9\cdot O\cdot NO$	0.911 (0°)	---	∞		—	78
Cacodyl oxide (cacodylic oxide) $[(CH_3)_2As]_2O$	1.486 (15°)	sl.s.	s.		-57	150
Cadmium Cd	8.65 (20°)	i.	—		320.9	767

Compound and Chemical Formula	Specific Gravity or Density	Solubility in 100 Parts		Diffusion Coefficient in Air (cm^2/sec)	Melting Point, °C	Boiling Point, °C
		Water	Alcohol			
Carbon dioxide CO_2	solid 1.56 (-79°)	179.7 cc (0°)	---	0.138	-56.5 @ 5.2 atm.	subl. -78.5
Carbon disulfide CS_2	liq. 1.262 (22°/20)	0.2 (0°)	∞	0.0892 0.0883 (0°)	-108.6	46.3
Carbon monoxide CO	liq. 0.814 (-195°/4)	0.0044 (0°)	—		-207	-192
Carbon tetrachloride CCl_4	1.595 (20°/4)	0.097 (0°)	∞		-22.6	76.8
Cellosolve (2-ethoxy-ethanol-1) $C_2H_5{\cdot}O{\cdot}(CH_2)_2OH$	0.931 (20°/4)	∞	∞		-70	135.1
Chlorine Cl_2	liq. 1.56 (-33.6°)	1.46 g (0°) 310 cc (10°)	—		-101.6	-34.6
Chlorine dioxide (chlorine peroxide) ClO_2	2.4 (11°) A	2,000 cc (4°)	expl.		-76	9.9 @730 mm expl. 100
Chlorine monoxide Cl_2O	2.9 A	20,000 cc (0°)	expl.		-20	3.8 @ 766 mm expl.
Chloroacetone $Cl{\cdot}CH_2{\cdot}CO{\cdot}CH_3$	1.162 (16°)	∞	∞		-44.5	121
Chlorobenzene (phenyl chloride) $C_6H_5{\cdot}Cl$	1.107 (20°/4)	i.	∞		-45.2	132.1
2-Chlorobutadiene (chloroprene) $CH_2{:}CCl{\cdot}CH{:}CH_2$	0.958 (20°/20)	sl.s.	∞		—	59.4

Compound and Chemical Formula	Specific Gravity or Density	Solubility in 100 Parts		Diffusion Coefficient in Air (cm^2/sec)	Melting Point, °C	Boiling Point, °C
		Water	Alcohol			
o-Chlorodiphenyl (chlorobiphenyl) $Cl\cdot C_6H_4\cdot C_6H_5$	---	i.	—		34	267
Chloroform (trichloromethane) $CHCl_3$	1.489 (20°)	0.82 (20°)	∞		-63.5	61.2
1-Chloro-1-nitro-propane $C_2H_5\cdot CH(Cl)NO_2$	1.209 (20°/20°)	< 0.8 (20°)	---		—	140
Chloropropane (n-propyl chloride) $CH_3\cdot CH_2\cdot CH_2Cl$	0.890 (20°/4)	0.27 (20°)	∞		-122.8	46.4
3-Chloropropene-1 (allyl chloride) $CH_2{:}CH\cdot CH_2Cl$	0.938 (20°/4)	< 0.1	∞		-136.4	44.6
Chloropicrin (nitrochloroform) $NO_2\cdot CCl_3$	1.651 (22.8°/4)	0.17 (18°)	37 cc 80 % al.		-64	112.3
ω-Chlorotoluene (benzyl chloride) $C_6H_5\cdot CH_2\cdot Cl$	1.100 (20°/20)	i.	∞		-39	179.4
Chloro-vinyldichloroarsine $ClCH{:}CHAsCl_2$	1.888 (20°/4)	i.	---		---	190
Chloroxylene (o-xylychloride) $Cl\cdot C_6H_3(CH_3)_2$	---	i.	∞		< -20	189.5
Chromic acid (chromium trioxide) CrO_3	2.70	164.9 (0°)	s.		197 d.	---
o-Cresol $CH_3\cdot C_6H_4\cdot OH$	1.048 (20°/4)	2.5	∞		30.8	190.8
m-Cresol $CH_3\cdot C_6H_4\cdot OH$	1.034 (20°/4)	0.5	∞		10.9	202.8
p-Cresol $CH_3\cdot C_6H_4\cdot OH$	1.035 (20°/4)	1.8	∞		35	202

Compound and Chemical Formula	Specific Gravity or Density	Solubility in 100 Parts		Diffusion Coefficient in Air (cm^2/sec)	Melting Point, °C	Boiling Point, °C
		Water	Alcohol			
Cyanogen C_2N_2	liq. 0.866 (-17.2°)	450 cc (20°)	2,300 cc (20°)		-34.4	-20.5
Cyanogen bromide $Br{\cdot}CN$	2.015 (20°/4)	s.	s.		52	61.3 @ 750 mm
Cyanogen bromide $Cl{\cdot}CN$	1.222 (0°)	2,500 cc (20°)	10,000 cc (20°)		-6.5	12.5
Dichloroethyl ether (β, β_1-dichloro ether)	1.222 (20°/20)	1.07 (20°)	s.		---	178.5
Dichlorodiethyl sulfide (mustard gas) $(Cl{\cdot}CH_2{\cdot}CH_2)_2S$	1.275 (20°/4)	0.07 (25°)	s.		13.5	217 sl.d.
Dichloromethane (methylene chloride) CH_2Cl_2	1.336 (20°/4)	2 (20°)	∞		-96.7	40.5
Diethyl amine $(C_2H_5)_2NH$	0.712 (15°/15)	v.s.	∞		-38.9	55.5
Diethylene glycol (glycol ether) $(HO{\cdot}CH_2{\cdot}CH_2)_2O$	1.118 (20°/20)	∞	∞		—	244.8
Diethyl amine $(CH_3)_2NH$	0.680 (0°/4)	v.s.	s.		-96	7.4
Dimethyl mercury (mercury dimethyl) $(CH_3)_2Hg$	2.954 (22°/4)	v.sl.s.	v.s.		—	95
Dimethyl sulfate (methyl sulfate) $(CH_3)_2SO_2$	1.352 (0°/4)	v.sl.s.	∞		-26.8	188
Ethane $(CH_3{\cdot}CH_3)$	0.546 (-88°)	4.7 cc (20°)	150 cc		-172	-88.6
Ethyl acetate $CH_3CO_2{\cdot}C_2H_5$	0.901 (20°/4)	8.5 (15°)	∞	0.0715	-82.4	77.1

Compound and Chemical Formula	Specific Gravity or Density	Solubility in 100 Parts		Diffusion Coefficient in Air (cm^2/sec)	Melting Point, °C	Boiling Point, °C
		Water	Alcohol			
Ethyl alcohol (ethanol) $CH_3{\cdot}CH_2OH$	0.789 (20°/4)	∞	---	0.102	-112	78.4
Ethyl benzene (phenyl ethane) $C_6H_5{\cdot}C_2H_5$	0.867 (20°/4)	0.01 (15°)	∞	0.0658	-94.4	136.2
n-Ethyl butyrate $C_2H_5{\cdot}CH_2{\cdot}CO_2{\cdot}C_2H_5$	0.879 (20°/4)	0.68 (25°)	∞	0.0579	-93.3	120
Ethyl ether (ether) $(C_2H_5)_2O$	0.708 (25°/4)	7.5 (20°)	∞	0.0778	-116.3	34.6
Ethyl formate ($HCOO{\cdot}C_2H_5$)	0.923 (20°/4)	11 (18°)	∞	0.0840	-79	54
Hydrogen sulfide H_2S	1.1895 A	437 cc (0°) 186 cc (40°)	9.54 cc (15°)		-82.9	-59.6
Iodine I_2	4.93 (20°)	0.0162 (0°)	s.	0.097	113.5	184.4
Mercury Hg	13.546 (20°)	i.	---		-38.87	356.9
Methane CH_4	0.554	0.35 cc (20°)	47.1 cc (20°)		-182.6	-161.4
Methanol (methyl alcohol, wood alcohol) $CH_3{\cdot}OH$	0.792 (20°/4)	∞	∞	0.1325	-97.8	64.7
Methylacetate $CH_3{\cdot}CO_2{\cdot}CH_3$	0.924 (20°/4)	33 (22°)	∞	0.084	-98.7	57.1
Methyl butyrate $C_2H_5{\cdot}CH_2{\cdot}CO_2{\cdot}CH_3$	0.898 (20°/4)	1.7	∞	0.0633	< -95	102.3
Methyl ethyl ketone (butanone) $CH_3{\cdot}CO{\cdot}C_2H_5$	0.805 (20°/4)	37	∞		-85.9	79.6

Compound and Chemical Formula	Specific Gravity or Density	Solubility in 100 Parts		Diffusion Coefficient in Air (cm^2/sec)	Melting Point, °C	Boiling Point, °C
		Water	Alcohol			
Methyl nitrite $CH_3O \cdot NO$	liq. 0.991 (15°)	—	s.		—	-12
Naphtha (coal tar) contains mostly xylenes and higher homologues					—	cc. 160
Neon Ne	0.674 A	2.6 cc (0°)	s.		-248.7	-245.9
Nitric oxide NO or $(NO)_2$	1.0367 A	7.34 cc (0°)	26.6 cc		-161	-151
Nitrogen dioxide NO_2 or $(NO_2)_2$	1.052 (20°)	d.	---		-9.3	21.3
Nitrous oxide N_2O	1.530 A	130.5 cc	s.		-102.3	-90.7
Nitroglycerine $(O_2N \cdot O)_3C_3H_5$	1.601 (15°)	0.18 (20°)	54 (20°) abs.		13.3	160
Ozone O_3	1.658 A	0.494 cc (0°)	—		-251	-112
n-Pentane $(C_2H_5)_2CH_2$	0.630 (18°/4)	i.	∞		-129.7	36.3
n-Pentanol (amyl alcohol) $CH_3 \cdot (CH_2)_3 \cdot$ CH_2OH	0.817 (20°/20)	2.7 (22°)	∞		—	137.8
Phenol (carbolic acid) $C_6H_5 \cdot OH$	1.071 (20°/4)	8.2 (15°) ∞ (65.3°)	∞		42	181.4
Phosphine PH_3	1.146 A	26 cc (17°)	s.		-132.5	-85
iso-propanol (isopropyl alcohol) $(CH_3)_2CHOH$	0.789 (20°/4)	∞	∞		-85.8	82.5
Propenol (allyl alcohol) $CH_2{:}CH \cdot CH_2OH$	0.854 (20°/4)	∞	∞		-129	96.6

Compound and Chemical Formula	**Specific Gravity or Density**	**Solubility in 100 Parts**		**Diffusion Coefficient in Air (cm^2/sec)**	**Melting Point, °C**	**Boiling Point, °C**
		Water	**Alcohol**			
isopropyl ether (iso-dipropyl ether) $[(CH_3)_2CH]_2O$	0.725	0.2	∞		-60	68.7
Radon Rn	liq. 5.5	51 cc (0°)	—		-71	-62
Styrene monomer (phenyl ethylene) $C_6H_5 \cdot CH:CH_2$	0.903 (20°/4)	v.sl.s.	∞		-31	145.5
Sulfur dioxide SO_2	2.264 A	22.8 (0°)	s.		-75.5	-10.0
Sulfuric acid H_2SO_4	1.834 (18°/4)	∞	d.		10.49	d. 340
Toluene $C_6H_5 \cdot CH_3$	0.866 (20°/4)	i.	∞		-95	110.8
Trichloroethane (1,1,1) (methyl chloroform) $CH_3 \cdot CCl_3$	1.325 (26°/4)	i.	∞		—	74.1
Trichloroethylene (TCE) $ClCH:CCl_2$	1.466 (20°/20)	0.1 (25°)	∞		-73	87.2
Triethyl amine $ClCH:CCl_2$	0.729 (20°/20)	∞	∞		-114.8	89.4
Turpentine $C_{10}H_{16}$	0.863	---	---		---	155-162
Vinyl chloride $CH_2:CH \cdot Cl$	0.908 (25°/25)	sl.s.	s.		-160	-12
o-Xylene $C_6H_4(CH_3)_2$	0.881 (20°/4)	i.	∞ abs.		-25	144

BASIC PROPERTIES AND TERMINOLOGY

CHEMISTRY OF HAZARDOUS MATERIALS

There are a number of important terms that should be committed to memory. These terms include important properties of general classes of chemicals and of a few commonly used industrial chemicals. This section will familiarize you with the main points. This section is not intended for practicing industrial chemists, nor is it intended as anything other than a refresher for those with strong backgrounds in chemistry. It is intended to provide a brief introduction to the properties and characteristics considered important when evaluating health risks from exposure to chemicals, especially as air pollutants.

Chemical Properties

All chemicals, including hazardous ones, are commonly described in terms of their physical, chemical, and biological properties. To use this information fully, it is necessary to understand the meaning and importance of the various individual properties, and also to have some grasp of the significance of the various numerical values within the context of chemicals at large. These properties can then be used along with other information to predict the likely behavior of hazardous chemicals, and to recognize and avoid potentially dangerous situations. The first step is to define and comment on several of the more critical properties that are useful in the handling of hazardous materials. Some basic terminology is listed in Table 2.

Table 2. List of Commonly Measured Physical/Chemical Properties

Color	Vapor density (VD)
Odor	Fire point
Physical state at 20°C	Auto-ignition temperature
Molecular weight (MW)	Flashpoint
Chemical formula	Explosive limits
Melting point (MP)	Heat content
Boiling point (BP)	Threshold limit value (TLV)
Vapor pressure (VP)	Specific gravity (SG)
Density	Solubility (water; other solvents)

Physical State at 20°C — the physical nature of the chemical (solid, liquid, or gas) at 20°C (i.e., room temperature). Changing the temperature may alter the physical state, depending on the magnitude and direction of the change relative to the melting and boiling points of the chemical.

Boiling Point (BP) — the temperature at which a liquid changes to gas under standard atmospheric pressure (760 mm mercury). The BP of water is 100°C, while the BPs of ethyl alcohol and n-hexane are 78.4°C and 68.7°C, respectively. Lowering the atmospheric pressure (e.g., by applying a vacuum) will lower the BP; conversely, higher pressures result in elevated boiling points.

Melting Point (MP) — the temperature at which a solid changes to a liquid. The melting point is not particularly sensitive to atmospheric pressure, but it is responsive to dissolved salts which depress the melting point. Thus, in winter, it is usual to salt sidewalks to keep water from freezing.

Vapor Pressure (VP) — the pressure exerted by the vapor in equilibrium with its liquid at a given temperature. Vapor pressure is a measure of the relative volatility of chemicals. Liquids with high vapor pressures generally represent a greater fire hazard than those with lower vapor pressures. For a given liquid the vapor pressure increases with increasing temperature. Consequently, drummed materials with high vapor pressures in particular should not be stored in direct sunlight, as overheating of the materials and resultant increases in vapor pressures could result in "pregnant" drums with failed or weakened seams. When used with solubility data, vapor pressure values can be used to predict the rate of evaporation of dissolved solvents from water. At 20°C, water, ethanol, and benzene exert vapor pressures of 17.5, 43.9, and 74 mm of mercury, respectively.

Vapor Density (VD) — the mass per unit volume of a given vapor/gas relative to that of air. Thus, acetaldehyde with a vapor density of 1.5 is heavier than air and will accumulate in low spots, while acetylene with a vapor density of 0.9 is lighter than air and will rise and disperse. Heavy vapors present a particular hazard because of the way they accumulate: if toxic they may poison workers; if nontoxic they may displace air and cause suffocation by oxygen deficiency; if flammable, once presented with an ignition source, they represent a fire or explosion hazard. Gases heavier than air include carbon dioxide, chlorine, hydrogen sulfide, and sulfur dioxide.

Density — the mass per unit volume of any substance, including liquids. The density of a liquid determines whether a spilled material that is insoluble in or immiscible with water will sink or float on water. Knowledge of this behavior is essential in checking whether to use water to suppress a fire involving the material.

Specific Gravity (SG) — the ratio of the density of a liquid as compared with that of water. Insoluble materials will sink or float in water depending on the SG. Materials heavier than water have SGs >1, and materials lighter than water have SGs <1. Thus, lead, mercury, and carbon tetrachloride with SGs of 11.3, 13.6, and 1.6, respectively, will sink, whereas gasoline with a SG of 0.66 to 0.69, will float on water. This is an important property to know when a material has spilled, particularly in a water body.

Solubility — the amount of a given substance (the solute) that dissolves in a unit volume of a liquid (the solvent). This property is of importance in the handling and recovery of spilled hazardous materials. Water-insoluble chemicals are much easier to recover from water than spills of water-soluble chemicals. Acetone, which is miscible/soluble in water in all proportions, is not readily recoverable from water. In contrast, benzene, which is lighter than water and insoluble as well, can be readily trapped with a skimmer. For organic compounds, solubility tends to decrease with increasing molecular weight and chlorine content.

Flashpoint — the lowest temperature of a liquid at which it gives off enough vapor to form an ignitable mixture with air near the surface of the liquid within the vessel used. Two tests are used—Open Cup and Closed Cup. Generally, the Open Cup method results in flashpoints 5° to 10° higher than the Closed Cup method. Flashpoint $< 140°F$ (Closed Cup) is the criterion used by EPA to decide whether a chemical is hazardous by ignitability. DOT defines materials with flashpoints of $< 100°F$ as flammable materials, and between 100° and 200°F as combustible.

Fire Point — the temperature at which a liquid gives off enough vapor to continue to burn when ignited.

Auto-Ignition Temperature — the temperature at which ignition occurs without an ignition source and the material continues to burn without further heat input.

Flammable or Explosive Limits — the upper and lower vapor concentrations at which a mixture will burn or explode. The lower explosive limit of p-xylene is 1.1 percent by volume in air, whereas the upper explosive limit is 7.0 percent in air. A mixture of p-xylene vapor and air having a concentration of < 1.1 percent in air is too lean in p-xylene vapor to burn. Conversely, a mixture containing more than 7.0 percent is too rich in p-xylene to burn. By subtraction (7.0 - 1.1), p-xylene is said to have a flammable range of 5.9. Materials having low explosive limits and wide flammable ranges are extremely dangerous.

Heat Content — the heat released by complete combustion of a unit weight of material. Methane has a heat content of about 21,500 Btu/lb while benzene contains about 17,250 Btu/lb.

Threshold Limit Value (TLV) — the exposure level under which most people can work for eight hours a day, day after day, with no harmful effects. A table of these values and accompanying precautions for most common industrial materials is published annually by the American Conference of Governmental Industrial

Hygienists (ACGIH). TLV values for specific chemicals can be found in this handbook.

pK$_a$ — the negative logarithm of the equilibrium constant for acids or bases. This parameter is an indicator of the strength of an acid or base. Strong acids, such as H_2SO_4, and HCl, have low pK$_a$s (i.e., ~1.0) while strong bases such as KOH and NaOH, have pK$_a$s close to 14.0. Weak acids and weak bases fall in the intermediate range.

Key Concepts

Concentrations — Chemists and engineers seldom work with pure solutions of materials. In fact, more often than not we work with very minute amounts of materials dispersed in environmental media. A knowledge of units of concentration is required. Units of concentration in common usage for aqueous solutions include parts per million (ppm) and with increasing analytical capability and environmental awareness, parts per billion (ppb), and even parts per trillion (ppt), milligrams per liter (equivalent to ppm for dilute aqueous solutions), moles per liter or molar solutions (a weight of substance equivalent to the gram-molecular or gram atomic weight in a liter of solution), equivalents per liter (commonly used for acids and bases; a one equivalent per liter solution is stated to be a one normal solution), and finally percent by weight or volume. For vapors and gases, mists, and particulates in air, common units of concentration are ppm, micrograms per m^3, and percent by volume.

Solubility Product — The solubility product constant commonly referred to as the solubility product provides a convenient method of predicting the solubility of a material in water at equilibrium. Copper hydroxide, for example, dissolves according to the following equilibrium:

$$Cu(OH)_2\ (s) \leftrightarrows Cu^{2+} + 2OH^- \tag{1}$$

The resultant solubility product is represented in the following manner:

$$[Cu^{2+}][OH^-]^2 = K_{sp} \tag{2}$$

Note that the brackets, [ ], refer to the concentration of the species. K_{sp} is the solubility product constant; hence $[Cu^{2+}]$ and $[OH^-]^2$ are equal to the molar concentrations of copper and hydroxyl ions, respectively. The K_{sp} is commonly used in determining suitable precipitation reactions for removal of ionic species from solution. In the same example, the pH for removal of copper to any specified concentration can be determined by substituting the molar concentration into the following equation:

$$[OH^-][H^+] = \sqrt{\frac{K_{sp}}{[Cu^{2+}]}} \qquad (3)$$

and then applying the derived values in turn to this other equation:

$$[OH^-][H^+] = 10^{-14} \text{ and } pH = -\log [H^+] \qquad (4)$$

Use of the K_{sp} for precipitation information is often complicated by a number of interfering factors including complexation of metallic ions, high ionic strength solutions, and high solids contents. This principle is applicable solely to ionic compounds, i.e., primarily inorganic compounds.

Adsorption — An important physico-chemical phenomenon used in treatment of hazardous wastes or in predicting the behavior of hazardous materials in natural systems is adsorption. Adsorption is the concentration or accumulation of substances at a surface or interface between media. Hazardous materials are often removed from water or air by adsorption onto activated carbon. Adsorption of organic hazardous materials onto soils or sediments is an important factor affecting their mobility in the environment. Adsorption may be predicted by use of a number of equations most commonly relating the concentration of a chemical at the surface or interface to the concentration in air or in solution, at equilibrium. These equations may be solved graphically using laboratory data to plot "isotherms." The most common application of adsorption is for the removal of organic compounds from water by activated carbon.

Volatilization — Volatilization is a physico-chemical phenomenon of particular interest to environmental managers as well as safety managers. It is the tendency of a material to transfer from a liquid phase (either pure or dissolved as in aqueous systems) to a gaseous phase (commonly air). The volatilization, or evaporation as it is more commonly called, is controlled by a number of factors, the most important of which are the vapor pressure of the material, temperature (vapor pressure increases with temperature), and air/material interfacial surface area, and the action of active mass transfer agents such as wind.

The processes of dissolution/precipitation (for inorganics), dissolution/phase separation (for organics), adsorption, and volatilization control the distribution of a spilled material in the environment. Conversely, knowledgeable manipulation of these same processes can be used to advantage in either cleaning up or mitigating the effects of spilled material. Thus, for example, groundwater contaminated with volatile organics of limited aqueous solubility can be decontaminated by air stripping of these compounds which can then be concentrated by adsorption on activated carbon for subsequent disposal. From a safety standpoint, if a volatile hazardous chemical is spilled, the concern over inhalation exposure may warrant the need for respirators.

Hazard Categories and Chemistry Principles

The testing of chemicals/wastes to establish the nature of their hazard capacity/threat in accordance with regulatory requirements falls into four categories: (1) reactivity, (2) ignitability/flammability, (3) corrosivity, and (4) EP toxicity. Commercial chemical products, specific wastes, and wastes from specific processes may be listed as hazardous wastes because they are known to present toxic hazards in the manner of the tests above and/or are known to present serious toxic hazards to mammals/humans. In the discussion to follow, various chemical groups will be examined primarily in the context of reactivity, ignitability, and corrosivity.

Chemistry of Corrosives

The EPA defines corrosivity in terms of pH (i.e., wastes with pH <2 or >2.5) or in terms of ability to corrode steel (SAE 20) at a rate of >6.35 mm (0.250 in.) per year at a temperature of 55°C (13°F). This discussion will address corrosivity as it applies to acids and caustics. Acids are compounds that yield H^+ions (actually H_3O^+ ions) when dissolved in water. Common industrial acids include acetic, nitric, hydrochloric, and sulfuric acids. The terms *concentrated* and *dilute* refer to the concentrations in solution. Mixing a concentrated acid with enough water will produce a dilute acid. For example, a bottle of concentrated HCl direct from the manufacturer is approximately 12 N in HCl, while a solution of HCl used in a titration may be only 0.5 N. The latter is a dilute acid solution.

Strong and *weak* acids are classified by how completely they ionize in solution. For example, HCl is classified as a strong acid because it is completely ionized to H^+ and Cl^- ions. Acetic acid is classified as a weak acid because it does not totally ionize in solution. As mentioned earlier, weak acids such as acetic acid have higher pK_as. The pK_a for acetic acid is 4.75. The negative antilog of this value (1.76×10^{-5}) can be used to calculate the concentrations at equilibrium of the acetate and hydrogen ions. Strong acids include perchloric, hydrochloric, sulfuric, nitric, and hydriodic acids. Examples of weak acids include boric, hydrocyanic, carbonic, and acetic acids. Thus, the terminology "strong versus weak acid" may bear little relationship to the nature or extent of potential hazard, while the terms "concentrated versus dilute" most often do.

The acidic nature of a given solution is characterized by its pH, where pH is the negative logarithm of the molar H^+ concentration (-log $[H^+]$). A solution with pH <7 is acid, a solution with pH 7 is neutral, and a solution with pH >7 is basic. For example, the pH of lemon juice is 2, while the pH of lye is about 14.

Acids

Acids may be inorganic, such as H_2SO_4, and are then known as mineral acids, or they may be organic, like acetic acid. Mineral acids may be weak or strong, but organic acids tend to be uniformly weak. Table 3 gives a list of commonly occurring acids along with their relative strengths. It should be noted that salts of several metals (e.g., Al^{3+}, Fe^{3+}, and Zn^{4+}) dissolve in water to produce acid solutions. Acids include a variety of compounds, many of which have other significant properties that contribute to their "reactivity." Typical reactions of acids are: neutralization of bases (strong and weak) and oxidation of substances. Characteristics of common acids are presented in Table 4. Examples of neutralization of bases are the following reactions:

$H^+ + OH^- \rightarrow H_2O$
$HCl + NaOH \rightarrow H_2O + NaCl$
$CaCO_3 + 2HCl \rightarrow CaCl_2 + H2O + CO_2$

Examples of oxidation reactions are as follows:

$Zn^\circ + 2HCl \rightarrow Zn^{2+} + 2Cl^- + H^2\uparrow$
$2NaI + 2H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O + Na_2SO_4$

Bases

A base is any material that produces hydroxide ions when it is dissolved in water. The words alkaline, basic, and caustic are often used synonymously. Common bases include sodium hydroxide (lye), potassium hydroxide (potash lye), and calcium hydroxide (slaked lime). The concepts of strong versus weak bases, and concentrated versus dilute bases are exactly analogous to those for acids. Strong bases such as sodium hydroxide dissociate completely while weak bases such as the amines dissociate only partially. As with acids, bases can be either inorganic or organic. Typical reactions of bases include neutralization of acids, reaction with metals, and reaction with salts:

Table 3. Relative Strengths of Acids in Water

Perchloric acid	$HClO_4$	↑
Sulfuric acid	H_2SO_4	↑
Hydrochloric acid	HCl	↑
Nitric acid	HNO_3	↑

Phosphoric acid	H_3PO_4	Increasing
Hydrofluoric acid	HF	Acid
Acetic acid	CH_3COOH	Strength
Carbonic acid	H_2CO_3	↑
Hydrocyanic acid	HCN	↑
Boric acid	H_3BO_3	↑

Table 4. Properties of Some Common Acids and Bases

Acids—Sulfuric, Nitric, Hydrochloric, Acetic

a. *These acids are highly soluble in water.*
b. *Concentrated solutions are highly corrosive and will attack materials and tissue.*
c. *If spilled on skin, flush with lots of water.*
d. *Sulfuric and nitric acids are strong oxidizers and should not be stored or mixed with any organic material.*
e. *Sulfuric, nitric, and hydrochloric acids will attack metals upon contact and generate hydrogen gas which is explosive.*
f. *Acetic acid (glacial) is extremely flammable. Its vapors form explosive mixtures in the air. It is dangerous when stored with any oxidizing material, such as nitric and sulfuric acids, peroxides, sodium hypochlorite, etc.*
g. *Breathing the concentrated vapors of any of these acids can be extremely harmful. Wear appropriate equipment.*
h. *When mixing with water, always add acids to water, never water to acids.*

Bases (Caustics)—Sodium Hydroxide, Ammonium Hydroxide, Calcium Hydroxide (Slaked Lime), Calcium Oxide (Quick Lime)

a. *These bases are highly soluble in water.*
b. *Concentrated solutions are highly corrosive. They are worse than most acids because they penetrate the skin (Saponification reactions).*
c. *If spilled on skin, flush immediately with lots of water.*
d. *When mixed with water, they generate a significant amount of heat - especially sodium hydroxide and calcium oxide.*
e. *Unless unavoidable, do not store or mix concentrated acids and bases, as this gives off much heat- diiute, then mix.*
f. *Do not store or mix ammonium hydroxide with other strong bases. It can release ammonia gas which is extremely toxic.*
g. *Do not store or mix ammonium hydroxide with chlorine compounds (i.e., sodium hypochlorite). It can release chlorine gas which is extremely toxic.*

An example of a reaction with a metal is

$2Al + 6NaOH \rightarrow 2Na_3AlO_3 + 3H_2 \uparrow$
(reaction goes slowly)

An example of a reaction involving salt is:

$Pb(NO_3)_2 + 2NaOH \rightarrow Pb(OH)_2 + 2NaNO_3$

Characteristics to remember about some common bases are presented in Table 3.

General Properties and Nomenclature of Organics

Most compounds in which carbon is the key element are classified as organic. Common examples of organic compounds include degreasing solvents, lubricants, and heating and motor fuels. This subsection highlights some of the more common characteristics of organics as they relate to hazards. Various relevant classes of organics are presented in terms of chemical behavior and physical properties. In order to facilitate the discussion to follow, a few basic definitions will be presented first.

Definitions

Covalent — refers to a chemical bond in which there is an equal/even sharing of bonding electron pairs between atoms. This is typical of the bonding between carbon atoms and between carbon and hydrogen atoms in organic compounds.

Hydrocarbons — chemical compounds consisting primarily of carbon and hydrogen.

Aliphatic — organic compound with the carbon backbone arranged in branched or straight chains (e.g., propane).

Aromatic — organic molecular structure having the benzene ring (C_6H_6) as the basic unit (e.g., toluene, xylene).

Saturated — the condition of an organic compound in which each constituent carbon is covalently linked to four different atoms. This is generally a stable configuration (e.g., $CH_3CH_2CH_3$ - propane).

Isomers — different structural arrangements with the same chemical formula (e.g., n-butane and t-butane).

Unsaturated — an organic compound containing double or triple bonds between carbons (e.g., ethylene [$CH_2=CH_2$]). Multiple bonds tend to be sites of reactivity.

Functional Group — an atom or group of atoms, other than hydrogen, bonded to the chain or ring of carbon atoms (e.g., the -OH group of alcohols, the -COOH group of carboxylic acids, the -O- group of ethers). Functional groups determine the behavior of molecules. Consequently, the unique hazards of an organic compound are often determined by its functional group(s).

General Properties

Most organic compounds are flammable. They tend to melt and boil at lower temperatures than most inorganic substances. Because many organic compounds volatilize easily at room temperature and possess relatively low specific heats and ignition temperatures, they tend to burn easily. Moreover, organic vapors often have high heats of combustion which, upon ignition, facilitate the ignition of surrounding chemicals, thus compounding the severity of the hazard.

Most organic compounds are less stable than inorganics. However, the presence of one or more halogen atoms (F,Cl,Br,I) in the molecular structure of an organic compound increases its stability and inertness to combustion. Thus, partially halogenated hydrocarbons burn with less ease than their nonhalogenated analogs. Fully halogenated derivatives, such as carbon tetrachloride (CCl_4) and certain polychlorinated biphenyls (PCBs), are almost noncombustible.

Most organic compounds are water-insoluble. Notable exceptions are the lower molecular weight alcohols, aldehydes, and ketones, all known to be "polar" molecules. This characteristic is of importance to firefighting because the specific gravity of the compound will then be a major determinant of the suitability of water for the suppression of fires involving the chemical.

Except for alkanes and organic acids, organic compounds tend to react easily with oxidizing agents such as hydrogen peroxide or potassium dichromate. Moreover, a mixture of an oxidizing agent and organic matter is usually susceptible to spontaneous ignition. Notably, except for flammability and oxidation, organic compounds tend to react slowly with other chemicals.

Nomenclature

This subsection will familiarize the reader with some of the more common and simple organic groups.

Alkenes and alkynes are similar in structure to the alkanes except the alkenes contain a carbon-to-carbon double bond ($C=C$) and the alkynes contain a carbon-to-carbon triple bond ($C\equiv C$). The name prefixes are exactly the same as for the alkanes with the same number of carbons, but the endings are -one for compounds with double bonds and their derivatives and -yne for compounds with triple bonds and their derivatives. Ethene (ethylene) and propene (propylene) are alkenes. Ethyne (acetylene) is an alkyne.

Aromatics are molecules based on single or triple benzene rings. Some of the more common aromatics include benzene, toluene, xylene, and phenol. As previously mentioned, benzene is a 6-carbon ring with the formula C_6H_6. The ring has alternating double and single bonds, and is quite stable. The substitution of a methyl group ($-CH_3$) for one of the hydrogens gives methyl benzene or toluene. The substitution of another methyl group gives dimethyl benzene or xylene. Substitution of a hydroxyl ($-OH$) for a hydrogen on the benzene ring gives hydroxy benzene or phenol. Aromatics can also be named more specifically based on a system of assigning names or numbers to various positions on the benzene ring. By using the numbering system for the carbons on single or multiple benzene rings in combination with the names of the relevant substituents, any aromatic compound can be assigned a unique name.

Properties of Individual Functional Groups

Alkanes — Presented as (C_nH_{2n+2}), these are saturated hydrocarbons. The lower molecular weight alkanes (ethane through butane) are gases at standard temperature and pressure. The remainder are water-insoluble liquids that are lighter than water and thus form films or oil slicks on the surface of water. Hence, water is not used to suppress fires involving materials, such as gasoline, that include substantial proportions of liquid alkanes. Alkanes are relatively unreactive with most acids, bases, and mild oxidizing agents. However, with addition of sufficient heat, alkanes will react and burn in air or oxygen when ignited. In fact, low molecular weight alkanes (LPG, butane, gasoline) are commonly used as fuels. Consequently, the biggest hazard from alkanes is flammability.

Organic Carboxylic Acids — (RCOOH) are usually weak acids but can be very corrosive to skin. However, The substitution of Cl atoms on the carbon next to the carboxylic carbon produces a stronger acid. Thus, trichloroacetic acid is almost a strong acid whereas acetic acid is a weak one.

Organic Sulfonic Acids — (RSO_2H) are generally stronger acids than organic carboxylic acids.

Organic Bases — (such as amines, RNH_2) are weak bases but can be corrosive to skin or other tissue.

Alcohols — (ROH) are not very reactive. The lower molecular weight alcohols (methanol, ethanol, propanol) are completely miscible with water, but the heavier alcohols tend to be less soluble. Most common alcohols are flammable. Aromatic alcohols like phenol are not as flammable (flashpoint = 79°C) and are fairly water soluble (~9 g/L).

Alkenes — Also known as olefins, and denoted as C_nH_{2n} the compounds are unsaturated hydrocarbons with a single carbon-to-carbon double bond per molecule. The alkenes are very similar to the alkanes in boiling point, specific gravity, and other physical characteristics. Like alkanes, alkenes are at most only weakly polar. Alkenes are insoluble in water but quite soluble in nonpolar solvents like benzene. Because alkenes are mostly insoluble liquids that are lighter than water and flammable as well, water is not used to suppress fires involving these materials. Because of the double bond, alkenes are more reactive than alkanes.

Esters — These are not very reactive. Only the lowest molecular weight esters have appreciable solubility in water (e.g., ethyl acetate, 8%). Methyl and ethyl esters are more volatile than the corresponding unesterified acids. Most common esters are flammable. Esters are often easily recognizable due to their sweet to pungent odors.

Ethers — (R-O-R) are low on the scale of chemical reactivity. Aliphatic ethers are generally volatile, flammable liquids with low boiling points and low flashpoints. Well known hazardous ethers include diethyl ether, dimethyl ether, tetrahydrofuran. Beyond their flammability, ethers present an additional hazard: they react with atmospheric oxygen in the presence of light to form organic peroxides.

Organic Peroxides — (R-O-O-R) are very hazardous. Most of the compounds are so sensitive to friction, heat, and shock that they cannot be handled without dilution. As a result, organic peroxides present a serious fire and explosion hazard. Commonly encountered organic peroxides include benzoyl peroxide, peracetic acid, and methyl ethyl ketone peroxide.

Aldehydes and Ketones — These share many chemical properties because they possess the carbonyl (C=O) group as a common feature of their structure. Aldehydes and ketones have lower boiling points and higher vapor pressures than their alcohol counterparts. Aldehydes and ketones through C_4 are soluble in water and have pronounced odors. Ketones are relatively inert while aldehydes are easily oxidized to their counterpart organic acids.

Chemistry of Flammables

Flammability, the tendency of a material to burn, can only be subjectively defined. Many materials that we normally do not consider flammable will burn, given high enough temperatures. Neither can flammability be gauged by the heat content of materials. Fuel oil has a higher heat content than many materials considered more flammable because of their lower flashpoint. In fact, flashpoint has become the

SOME IMPORTANT FIRE TERMS:
- ***LEL - Lower Explosion Limit***
- ***UEL - Upper Explosion Limit***
- ***Flammability Limits***
- ***Auto-ignition Temperature***
- ***Fire Point Temperature***
- ***Fire Triangle***
- ***Flash Point Temperature***

standard for gauging flammability. The most common systems for designating flammability are the Department of Transportation (DOT) definitions, the National Fire Protection Association's (NFPA) system, and the Environmental Protection Agency's (EPA) Resource Conservation and Recovery Act's (RCRA) definition of ignitable wastes, all of which use flashpoint in their schemes. The NFPA diamond, which comprises the backbone of the NFPA Hazard Signal System, uses a four-quadrant diamond to display the hazards of a material. The top quadrant (red quadrant) contains flammability information in the form of numbers ranging from zero to four. Materials designated as zero will not burn. Materials designated as four rapidly or completely vaporize at atmospheric pressure and ambient temperature, and will burn readily (flashpoint <73°F and boiling point < 100°F). The NFPA defines a flammable liquid as one having a flashpoint of 200°F or lower, and divides these liquids into five categories:

1. Class IA: liquids with flashpoints below 73°F and boiling points below 100°F. An example of a Class IA flammable liquid is n-pentane (NFPA Diamond: 4).
2. Class IB: liquids with flashpoints below 73°F and boiling points at or above 100°F. Examples of Class IB flammable liquids are benzene, gasoline, and acetone (NFPA Diamond: 3).
3. Class IC: liquids with flashpoints at or above 73°F and below 100°F. Examples of Class IC flammable liquids are turpentine and n-butyl acetate (NFPA Diamond: 3).
4. Class II: liquids with flashpoints at or above 100°F but below 140°F. Examples of Class II flammable liquids are kerosene and camphor oil (NFPA Diamond: 2).
5. Class III: liquids with flashpoints at or above 140°F but below 200°F. Examples of Class III liquids are creosote oils, phenol, and naphthalene. Liquids in this category are generally termed combustible rather than flammable (NFPA Diamond: 2). The DOT system designates those materials with a flashpoint of 100°F or less as flammable, those between 100°F and 200°F as combustible, and those with a flashpoint of greater than 200°F as nonflammable. EPA designates those wastes with a flashpoint of less than 140°F as ignitable hazardous wastes. To facilitate the comparison of these systems they are presented graphically in Figure 1.

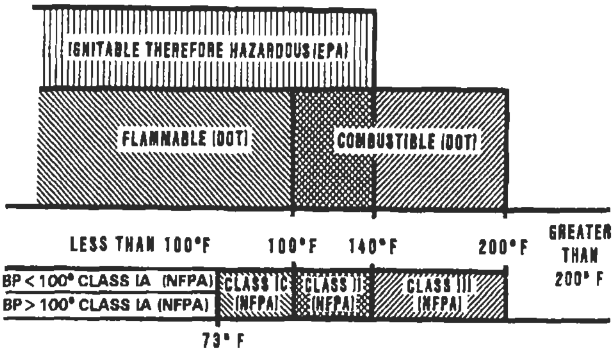


Figure 1. Illustrative classification of flashpoint designators.

These designations serve as useful guides in storage, transport, and spill response. However, they do have limitations. Since these designations are somewhat arbitrary, it is useful to understand the basic concepts of flammability.

The elements required for combustion are few--a substrate, oxygen, and a source of ignition. The substrate, or flammable material, occurs in many classes of compounds but most often is organic. Generally, compounds within a given class exhibit increasing heat contents with increasing molecular weights (MW).

Other properties specific to the substrate that are important in determining flammable hazards are the auto-ignition temperature, boiling point, vapor pressure, and vapor density. Auto-ignition temperature (the temperature at which a material will spontaneously ignite) is more important in preventing fire from spreading (e.g., knowing what fire protection is needed to keep temperatures below the ignition point) but can also be important in spill or material handling situations. For example, gasoline has been known to spontaneously ignite when spilled onto an overheated engine or manifold. The boiling point and vapor pressure of a material are important not only because vapors are more easily ignited than liquids, but also because vapors are more readily transportable than liquids (they may disperse, or when heavier than air, flow to a source of ignition and flash back). Vapors with densities greater than one do not tend to disperse but rather to settle into sumps, basements, depressions in the ground, or other low areas, thus representing active explosion hazards.

Oxygen, the second requirement for combustion, is generally not limiting. Oxygen in the air is sufficient to support combustion of most materials within certain limits. These limitations are compound specific and are called the explosive limits in air. The upper and lower explosive limits (UEL and LEL) of several common materials are given in Table 5. The source of ignition may be physical (such as a spark, electrical arc, small flame, cigarette, welding operation, or a hot piece of equipment), or it may be chemical in nature, such as an exothermic reaction. In any case, when working with or storing flammables, controlling the source of ignition is often the easiest and safest way to avoid fires or explosions.

Once a fire has started, control of the fire can be accomplished in several ways: through water systems (by reducing the temperature), carbon dioxide or foam systems (by limiting oxygen), or through removal of the substrate (by shutting off valves or other controls). Chapter 4 provides detailed discussion on the theories of fire and specific information on hydrocarbons, as well as chemical specific fire characteristics.

Table 5. Explosive Limits of Hazardous Materials

Compound	**LEL %**	**UEL %**	**Flashpoint °F**	**Vapor Density**
Acetone	2.15	13	-4	2.0
Acetylene	2.50	100	Gas	0.9
Ammonia, anhydrous	16	25	Gas	0.6
Benzene	1.30	7.1	12	7.8
Carbon monoxide	12.4	74	Gas	1.0
Gasoline	1.4	7.6	-45	3-4
Hexane	1.1	7.5	-7	3.0
Toluene	1.2	7.1	40	3.1
Vinyl chloride	3.6	33	Gas	2.2
p-xylene	1.0	6.0	90	3.7

Chemistry of Water Reactive Materials

The characteristics of a chemical or substance that would categorize it as a reactive material include (1) it reacts violently with water, (2) it forms potentially explosive mixtures with water, or (3) when mixed with water or other chemicals, it generates toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment. Because water is the most common fire suppressant, the characteristic of reactivity is especially relevant since the application of water to eliminate or prevent the spread of fires may be counter-productive rather than helpful. Several categories of chemicals will be discussed from this standpoint; however, several of these same chemicals also present additional hazards.

Substances That Produce H_2

Metals — Several metals react with water and air with the extent of reactivity being dependent upon the physical state of the metal. The highly reactive metals such as lithium, sodium, and potassium are pyrophoric (i.e., they ignite spontaneously in air without an ignition source). In contrast, the less reactive metals such as magnesium, zirconium, titanium, aluminum, and zinc are highly pyrophoric only as dusts.

Lithium, sodium, and potassium (alkali metals) react rapidly with water to release hydrogen (H_2) gas:

$$2Na + 2H_2O \rightarrow 2Na^+ + 2OH^- + H_2\uparrow$$

Sufficient heat is generated to ignite the hydrogen gas so that it can react explosively with the oxygen in air. Metals like magnesium, aluminum, titanium, and zirconium in pure form also react with water to release H_2, but heat must be supplied to initiate the reaction. The generalized representation is:

$$metal + water + heat \rightarrow metal\ oxide\ or\ hydroxide + H_2\uparrow$$

Hydrides — True hydrides (i.e., those in which the hydrogen is in its anionic or most reduced form) are salt-like compounds in which the hydrogen is combined with alkali metals, either alone as simple hydrides or in association with other elements as complex hydrides. Hydrides react with water to release hydrogen.

Simple hydrides:

$$LiH + H_2O \rightarrow H_2\uparrow + LiOH$$

Complex hydrides:

$$LiAlH_4 + 4H_2O \rightarrow Al(OH)_3 + LiOH + 4H_2\uparrow$$

Peroxides — Compounds containing the O^{2-} ion are hazardous primarily as oxidizing agents but also as water reactives. An example is the liberation of oxygen from the mixture of sodium peroxide and water:

$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2 \uparrow$

Substances That Produce Alkaline Aqueous Solutions

This group is exemplified by nitrides, carbides, and phosphides. Nitrides will react with water to generate ammonia (NH_3), which can be released depending on how alkaline the solution becomes. It is unlikely that sufficient NH_3 will be produced under normal circumstances to create a hazard.

$N_3 + 3H_2O \rightarrow NH_3\uparrow + 3OH^-$
$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3 \uparrow$

Carbides, which are binary compounds containing anionic carbon, occur as covalent and as salt-like compounds. The salt-like carbides are water-reactive and, upon hydrolysis, yield flammable hydrocarbons. Typical hydrolysis reactions include:

$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2 \uparrow$ (acetylene)
$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4 \uparrow$ (methane)

Other similar carbides are Be_2C and Mg_2C_3. Notably, each reaction is sufficiently exothermic to ignite the specific RBS formed upon hydrolysis.

Phosphides are binary compounds containing anionic phosphorus (P^{3-}). Heavy metal, alkali, and alkaline earth metal phosphides exist but few of them are commercially important. Phosphides hydrolyze to the flammable and toxic gas phosphine (PH_3). The hydrolysis reaction of aluminum phosphide is given below:

$AlP + 3H_2O \rightarrow PH_3 \uparrow + Al(OH)_3$

Substances That Produce Acidic Aqueous Solutions

Inorganic Chlorides/Halides — These metallic salts are formed from the reaction of a weak base with the strong acid HCl. Salts such as these dissolve in water to produce a markedly acidic solution. This is exemplified by aluminum chloride, which is corrosive due to the acidity resulting from the hydrolysis that produces aluminum and chlorine ions. Anhydrous $AlCl_3$ hydrolyzes violently when contacted by water.

Several nonmetallic chlorides also react with water with varying degrees of violence to produce hydrochloric acid. Although these compounds are themselves nonflammable, the heat generated by hydrolysis is sufficient to ignite adjacent flammable materials. These nonmetallic chlorides include antimony pentachloride ($SbCl_5$), boron trichloride (BCl_3), phosphorus oxychloride ($POCl_3$), phosphorus pentachloride (PCl_5), phosphorus trichloride (PCl_3), silicon tetrachloride ($SiCl_4$), thionyl chloride ($SOCl_2$), sulfuryl chloride (SO_2Cl_4) and titanium tetrachloride ($TiCl_4$). Because of their acid-producing tendencies, many of these chlorides are considered to be corrosive.

Organic Chlorides/Halides — Several organic compounds also are hydrolyzed (or react with water) to produce corrosive materials. Notable inclusions among these compounds are acetic anhydride ($[CH_3CO_2]_2O$), and acetyl chloride (CH_3COCl), both of which produce acetic acid upon reaction with water. Both acetic anhydride and acetyl chloride are corrosive; in addition, mixtures of the vapors of acetic anhydride and acetic acid are flammable in air, and acetyl chloride itself is flammable.

Oxidation/Reduction Phenomena

The explosive potential of oxidation/reduction reactions has resulted time and time again in chemical disasters. Perhaps the largest of these was the explosion of the S.S. Grandcamp at Texas City, Texas, in 1947, where thermal decomposition (redox reactions of ammonium nitrate and subsequent oxidation reactions of the decomposition products) led to the deaths of over 600 people and over $33 million (1947 dollars) damage. The addition or loss of electrons involves an accompanying transfer of energy, often a violently exothermic transfer. The substance that gives up electrons (and is therefore oxidized) is the reducing agent. The substance that gains electrons (and is therefore reduced) is the oxidizing agent.

Oxidizing agents are generally recognizable by their structures or names. They tend to have oxygen in their structures and often release oxygen as a result of thermal decomposition. Oxidizing agents often have "per-" prefixes (perchlorate, peroxides, permanganate) and often end in "-ate" (chromate, nitrate, chlorate).

Strong oxidizers have more potential incompatibilities than perhaps any other chemical group (with the exception of water reactive substances). It is safe to assume that they should not be stored or mixed with any other material except under carefully controlled conditions. Common oxidizing agents listed in decreasing order of oxidizing strength include:

Fluorine
Ozone
Hydrogen peroxide
Hypochlorous acid
Chlorine
Sulfuric acid (concentrated)
Oxygen
Metallic iodates

Metal chlorates
Lead dioxide
Metallic permanganates
Metallic dichromates
Nitric acid (concentrated)
Bromine
Ferric salts
Iodine
Sulfur
Stannic salts

Reducing agents present similar problems. They react with a broad spectrum of chemical classes, and the reactions can be exothermic and violent. Reducing agents are, by definition, highly oxidizable and may react with air or moisture in the air. Common reducing agents include:

Hydrogen
Metals (Li, Na, K, Ca, Sr, Ba)
Hydrazine
Metal acetylides
Complex hydrides
Metal hydrides
Metal hypoborates
Metal hypophosphites
Sulfides
Sulfites
Iodides
Nitrides
Nitrites
Phosphites
Metallic azides

Toxics

This subsection provides only a general overview of toxic substances. Detailed information on specific chemicals are provided in Chapter 5.

Toxic Metals

The most common toxic metals in industrial use are cadmium, chromium, lead, silver, and mercury; less commonly used are arsenic, selenium (both metalloids), and barium. Cadmium, a metal commonly used in alloys and myriads of other industrial uses, is fairly mobile in the environment and is responsible for many maladies including renal failure and a degenerative bone disease called "ITA ITA" disease. Chromium, most often found in plating wastes, is also environmentally mobile and is most toxic in the Cr^{+6} valence state. Lead has been historically used as a component of an antiknock compound in gasoline and, along with chromium (as lead chromate), in paint and pigments.

Lead, because of its history as an air emission, has been fairly mobile and is particularly soluble in acid environments. Silver is used widely in the electronics industry. Intake of silver compounds can result in permanent discoloration of the skin and may result in damage to kidneys, lungs, mucous membranes, and other organs.

Mercury enjoys its seeming environmental ubiquity due to its use as a fungicide and as an electrode in the chlorine production process. Elemental mercury is relatively immobile, but is readily transformed to more mobile organometallic compounds through bacterial action. Mercury is the responsible agent for the infamous Minimata syndrome which is characterized by degeneration of the central nervous system. Arsenic and selenium are both commonly used to decolorize glass or to impart a desirable color. Arsenic occurs in a number of important forms, many of which have been used as contact herbicides. Important forms of arsenic include arsenic trioxide and pentoxide, and arsenic acids, arsenites and arsenates, and various organic arsenic compounds. Selenium often occurs as selenous acid. Both arsenic and selenium are fairly mobile and toxic. In general, toxic metals can be readily removed from aqueous solution through precipitation reactions, either as the sulfide or (more commonly) as the hydroxide.

Cyanides

Cyanides are dangerously toxic materials that can cause instantaneous death. They occur in a number of industrial situations but are commonly associated with plating operations, and sludges and baths from such sources. Cyanide is extremely soluble and many cyanide compounds, when mixed with acid, release deadly hydrogen cyanide gas. Cyanide is sometimes formed during the combustion of various nitrile, cyanohydrin, and methacrylate compounds. Cyanides (CN^-) are commonly treated by chlorine oxidation to the less toxic cyanate (CNO^-) form, then acid hydrolyzed to CO_2 and N_2. Obviously, care should be taken that the cyanide oxidation is complete prior to acid hydrolysis of the cyanate.

Hydrogen Sulfide

Hydrogen sulfide is a commonly occurring decomposition product of organic matter. It is relatively water soluble at higher pHs where it is predominantly dissociated as H^+ and $S^=$ ions. As the pH is decreased below 7, undissociated gas H_2S begins to predominate and is released. Since its vapor density is > 1.0, H_2S gas tends to settle in low places and creates a toxicity hazard. H_2S is readily oxidizable by a number of means to less toxic $SO_3^=$ or $SO_4^=$ forms.

Pesticides and Bioaccumulators

Pesticides include the broad categories of insecticides, fungicides, rodenticides, and herbicides. Insecticides in common use fall into three categories. The chloroinsecticides have chlorine in their structure. They are less soluble than the other insecticide forms and much less biodegradable (i.e., more persistent). While they are less acutely toxic, several have been identified as potential carcinogens. Carbamatea are a relatively new form of pesticide. They are less persistent and less toxic than chloroinsecticides, but some are also suspected carcinogens. Organophosphate insecticides are generally more acutely toxic than the other categories but they are not persistent.

Many formerly common herbicides now have been banned or restricted in their use, e.g., 2,4-D and 2,4,5-T. However, the number and diversity of herbicides far exceeds that of insecticides. There are both organic and inorganic herbicides. Examples of inorganic herbicides are $CuSO_4$ and $NaClO_4$.

There are at least 22 chemical families of organic herbicides. Even a cursory treatment of the chemistry of these materials would be extensive. Herbicides of limited toxicity (Treflan, Atrazine) as well as extremely toxic ones (Paraquat, Dinoseb) are in use in many parts of the world. They range from water soluble to insoluble. The detailed chemistry of each should be determined prior to handling.

Chemical Compatibility

Chemical incompatibility can manifest itself in many ways; however, discussions will be limited to those combinations resulting in fires, explosions, extreme heat, evolution of gas (both toxic and nontoxic), and polymerization.

Because of the number of chemicals and subsequent multiple number of potential reactions, it is impractical and (perhaps impossible) to list all potential reactions. Several systems exist for determining the reactions between classes of chemicals, however, none of them is definitive. Because all of the potential reactions for individual chemicals are not cataloged and because there are no (or very few), pure solutions of waste materials, laboratory compatibility testing is recommended for most materials. An appropriate protocol for compatibility testing would involve the following steps:

- Obtain all available information about the material. If it is a surplus or off-specification product, obtain an analysis or a Material Safety Data Sheet. If it is a waste, check for previous analyses, and if none exists, obtain one. (Even if a previous analysis exists, consider running a few screening-type field analyses for confirmation of important properties such as pH, redox potential, or other oxidizer test such as cyanide, sulfide, and flashpoint.)
- Once the identity of the material is known, the literature can be consulted to determine potential reactions. At this point, incompatibility may be obvious. If not, then laboratory testing for compatibility is required.

Compatibility testing is almost by nature an experiment with the unknown. As such, safety must be the watchword. Procedures for compatibility testing should take into account the most severe adverse reaction possible, not just that expected. Such testing should always be performed under a vent hood while wearing, as a minimum, face shield, rubber apron, and gloves. Generally, compatibility testing entails mixing a small volume of one substance with another and observing for heat, gas generation, or polymerization. Polymerization need not be violent to cause problems. Anyone who has ever had to chisel out or replace a tank of solidified material can attest to this. Often it is advisable to heat the mixture to expected storage or process temperature and then observe for further heat, gas, or polymerization.

Observation of a reaction does not necessarily preclude mixing. Moderate heat or gas generation may not present a problem. However, a number of safety precautions should be taken before mixing the material if any heat or gas generation occurs. If heat is generated, the amount should be determined and a heat balance calculated so that effects of heating on the storage tank and tank base can be calculated. Expansion of the material with heating should also be considered so as to avoid overfilling the receiving tank.

Generation of gas requires a gas analysis before mixing. If the gas is toxic or if discharge of the resultant gas violates an air quality constraint, the materials should not be mixed. If the gas is nontoxic, care should still be taken to assure that the gas generation rate does not exceed the design venting capacity of the tank. Remember that most tanks are designed to withstand a water gauge internal pressure of only about eight inches. (A typical person can provide about 24 inches water gauge by blowing). Secondly, even if the gas is nontoxic, it may still displace air and (for inside tanks especially) create an asphyxiation hazard.

Toxicology Principles

Toxicology is the science that studies the harmful effects chemicals can have on the body. All chemicals affect man to some degree, depending on the time of exposure, concentration, and human susceptibility. One chemical may only cause a slight rash or dizziness while another may result in cancer or death. It is the degree of exposure and toxicity that are of practical concern. The means by which chemicals enter the body are inhalation (breathing), ingestion (swallowing), and absorption (skin or living tissue contact). Once in the system these chemicals may produce such symptoms as tissue irritation, rash, dizziness, anxiety, narcosis, headaches, pain, fever, tremors, shortness of breath, birth defects, paralysis, cancer, and death, to mention a few. The amount of chemical that enters the body is called the "dose." The relationship that defines the body response to the dose given is called the "dose-response curve." The lowest dose causing a detectable response is the "threshold limit." The "limit" is dependent on factors such as particle size of contaminant, solubility, breathing rate, residence time in the system, and human susceptibility.

To accomplish meaningful studies, measurements of various parameters are essential. Dose is one of them, and in inhalation studies dose is proportional to the air concentration of the contaminant multiplied by the length of time it is breathed. The units of concentration are ppm (a volume/volume description of concentration--parts of air contaminant per one million parts of the air mixture) for gases and vapors, and mg/m^3 (a weight/volume description—milligrams of air contaminant per cubic meter of air mixture). Other concentration units exist, such as fibers per cubic centimeter (f/cc) for asbestos, and "rems" for radiation. Dose for oral or skin applications is measured by weight or volume in assigned units such as grams or cubic centimeters.

Toxicity data are presented in the literature by such terms as "LD_{50}" and "LC_{50}," that lethal dose per kilogram of body weight or lethal concentration that can kill 50 percent of an animal population. Such data are found, for example, in the Registry of Toxic Effects of Chemical Substances (RTECS). With data such as these obtained from animals closely resembling the human in biochemistry, relative toxicities can be established to characterize chemicals. These data in conjunction with air contaminant threshold limit values (TLV) or permissible exposure limits (PEL), set by law for short periods of exposure or eight-hour, time-weighted average exposure, have produced safe working exposure limits for the worker. Many of these values are contained in the OSHA Standards and the American Conference of Governmental Industrial Hygienist's (ACGIH) in their publications on *Threshold Limit Values and Biological Exposure Indices*.

Human response to chemicals may be described by two types of biological effects--acute and chronic. An acute effect generally results after a single significant exposure, with severe symptoms developing rapidly and coming quickly to a crisis. An example of an acute effect is a few minutes' exposure to carbon monoxide of various concentrations that cause headache, dizziness, or death. The chronic effect results from a repeated dose or exposure to a substance over a relatively prolonged period of time. Examples of chronic effects are possible reduction in life span, increased susceptibility to other diseases, and cancer as a result of smoking. Some materials, such as lead, can bioaccumulate (be stored in the body) and cause continuing effects, or reach a threshold value where an effect on the body occurs after a prolonged period of time, or "latency" period. An example of such a chemical is asbestos, which may produce asbestosis twenty years after the initial exposure. An effect which exists but has not been widely studied because of its immensity and related problems is "synergism." Synergism occurs when the effect of two chemicals is greater than or less than either chemical alone. Inhalation of isopropyl alcohol and carbon tetrachloride can be well below safe concentration limits separately, but together, produce severe effects including renal failure. Toxicology and epidemiology, the sciences that study diseases in a general population, are closely related. Most of the present occupational concentration limits for hazardous material have resulted from illnesses and deaths of workers, and from use of both disciplines. Some materials cause genetic changes that can cause cancer (carcinogen), mutation (mutagens), and birth defects (teratogens). These effects are often hard to document due to latency periods and synergisms. The USOSH Hazard Communication Standard, 29 CFR 1910.1200, has categorized certain target organ effects, including examples of signs and symptoms and chemicals which have been found to cause such effects. These examples are presented to illustrate the range and diversity of effects and hazards found in the workplace, and the broad scope employers must consider in this area, but they are not intended to be all-inclusive. These are summarized for the reader in Table 6.

Table 6. Target Organ Effects Categorized Under the Hazard Communication Act

A. **Hepatotoxins:** Chemicals which produce liver damage;
Signs and Symptoms: Jaundice; liver enlargement;
Chemicals: Carbon tetrachloride; nitrosamines.

B. **Nephrotoxins:** Chemicals which produce kidney damage;
Signs and Symptoms: Edema; proteinuria;
Chemicals: Halogenated hydrocarbons; uranium.

C. **Neurotoxins:** Chemicals which produce their primary toxic effects on the nervous system;
Signs and Symptoms Narcosis: Behavioral changes; decrease in motor functions;
Chemicals: Mercury; carbon disulfide.

D. **Agents which act on the blood or hematopoietic system:** Decreases hemoglobin function; deprive body tissues of oxygen;
Signs and Symptoms: Cyanosis; loss of consciousness;
Chemicals: Carbon monoxide; cyanides.

E. **Agents which damage the lung:** Chemicals which irritate or damage the pulmonary tissue;
Signs and Symptoms: Cough; tightness in chest; shortness of breath;
Chemicals: Silica; asbestos.

F. **Reproductive toxins:** Chemicals which affect the reproductive capabilities including chromosomal damage (mutations) and effects on fetuses (teratogenesis);
Signs and Symptoms: Birth defects; sterility;
Chemicals: Lead; KEPONE.

G. **Cutaneous hazards:** Chemicals which affect the dermal layer of the body;
Signs and Symptoms: Defatting of the skin; rashes; irritation;
Chemicals: Ketones; chlorinated compounds.

H. **Eye hazards:** Chemicals which effect the eye or visual capacity;
Signs and Symptoms: Conjunctivitis; corneal damage;
Chemicals: Organic solvents; acids

ACCESSING THE WORLD-WIDE WEB FOR DATA BASES

The reader can find an almost endless supply of chemical and physical properties for hundreds of thousands of chemicals and tradename products on the Web. The easiest access to general information resources that contain health risk and some air transport properties are those sites which contain Material Safety Data Sheets (MSDSs). The following are a list of but a few sites worth exploring for chemical-specific information:

- Visit http://cortex.uchc.edu/~safety/ehs/msds-1.html. This site is accessible by UCHC network registered users only. Once registered, you can access 70,000 MSDSs from Sigma, Aldrich, and Fluka on-line. The MSDSs are available in several languages (English, French, German, Spanish and Italian languages). Updates are done on a quarterly basis.
- Visit http://ntp-support.niehs.nih.gov/Main_Pages/Chem-HS.html. This is the site for the National Institute of Environmental Health Science. You will find MSDS-type chemical health and safety information from the National Toxicology Program. Chemical searches can be performed by chemical name, synonym, or CAS (Chemical Abstract Service) number.
- Visit gopher://atlas.chem.Utah.edu/11/MSDS. This site is run by the University of Utah. To search, you choose the alphabetical folder that contains the chemical of interest. You will be presented with a list of chemicals to select from.
- Visit gopher://quasar.tach.net:3020/71/msds. This is the Vermont state SIRI Web. You will find a searchable (manufacturer or product name) gopher index of MSDSs.
- Visit http://www1.fishersci.com/catalogs/. This site is the Fisher Scientific on-line catalogue. Once connected, double click on the Catalogue. Double click on the Fisher Chemical catalogue. Then select the alphabetical group containing your chemical's name or type in the product in the Search box. When you find the chemical of interest, scroll down and click on the MSDS icon found within the other product information for the chemical.
- Visit gopher://ecosys.drdr.virginia.edu:70/00/library/gen/toxics. This site contains EPA Fact Sheets. For each chemical list on the site you will find general hazard information.
- Visit http://www-portfolio.stanford.edu/100369. This is Stanford University general chemical safety information from their Portfolio Information System. Also included are storage groups for compatible segregation of chemicals. Chemicals are searchable by scrolling to the end of the section titled Chemical Safety and entering the chemical name. Then select that chemical or other chemical with that chemical root as part of its name.
- Visit http://www.boc.com/gases/msds_us/. This site provides downloadable MSDS documents in the Adobe pdf file format.

- Visit http://msds.pdc.cornell.edu/msdssrch.asp. This site, operated by Cornell University, has a searchable database of MSDS files.
- Make sure to pay a visit to the Agency for Toxic Substances and Disease Registry (ATSDR). You can perform quick searches by clicking onto the first letter of a chemical listed. The web-site address is the following: http://atsdr1.atsdr.cdc.gov:8080/toxfaq.html. This site also provides some links to other sites with chemical specific information and health risk data.
- A commercially available product containing about 260,000 MSDSs on a CD-Rom can be purchased for around $ 400. For more information, visit www.fastsearch-msds.com.
- Another site to visit is the Risk Management Internet Services. This site enables you to conduct online searches on numerous chemical databases to obtain such information as: MSDSs, toxicology profiles, chemical health hazards, Threshold Limit Values (TLVs), government lists of hazardous substances, pesticide information, storage compatibility, chemical safety guides and related materials. Examples of databases that are accessible are: CCRS, DART, EMIC, EMCI, ETICBACK, GENE-TOX, IRIS, HESIS, HSDB, ISSDS, OPPT, RTECS, SAGE, SOLV-DB, SSDS, TOXNET, TRI. Visit this site at http://www.rmis.com/db/dbchemicals.htm.

RECOMMENDED RESOURCES FOR THE READER

Journals & Monographs

1. Aetiological Agents in Occupational Asthma, Chan-Yeung M., Malo J. (Eur Respir J. 1994;7:346-371).
2. Occupational Sentinel Health Events: An Up-Dated List for Physician Recognition and Public Health Surveillance, Mullan RJ, Murthy LI. (Am J Ind Med. 1991;19:775-799).
3. ATSDR Case Studies in Environmental Medicine, Lum, M, Ortyl D, Project Officers, published by the Agency for Toxic Substances and Disease Registry.

Books

1. Cheremisinoff, N. P., Handbook of Hazardous Chemical Properties, Butterworth-Heinemann, United Kingdom, 2000.
2. Cheremisinoff, N. P., Handbook of Industrial Toxicology and Hazardous Materials, Marcel Dekker, Inc., New York, 1999.
3. Contact and Occupational Dermatology, 2nd ed., Marks JG, DeLeo VA. (Mosby, 1997).
4. Control of Communicable Diseases Manual, 16th ed., Benenson AS, ed. (APHA, 1995).

5. Environmental & Occupational Medicine, 3rd ed., Rom WN, ed. (Lippincott-Raven, 1998).
6. Hawley's Condensed Chemical Dictionary, 12th ed., Lewis, RJ. (Van Nostrand Reinhold Company, 1993).
7. Hazardous Materials Toxicology. Sullivan J, Krieger G, eds. (Williams & Wilkins, 1992).
8. Occupational & Environmental Medicine, 2nd ed., LaDou J, ed. (Appleton & Lange, 1997).
9. Occupational and Environmental Respiratory Diseases, Harber P, Schenker MB, Balmes JR, eds. (Mosby, 1996).
10. Occupational Health: Recognizing and Preventing Work-Related Disease, 3rd ed., Levy BS, Wegman DH, eds. (Little, Brown and Company, 1995).
11. Preventing Occupational Disease and Injury, Weeks JL, Levy BS, Wagner GR, eds. (APHA, 1991).
12. Textbook of Clinical Occupational and Environmental Medicine, Rosenstock L, Cullen MR, eds. (W.B. Saunders, 1994).
13. Recognition and Management of Pesticide Poisonings, 5th ed. Reigart JR, Roberts JR, eds.(EPA, 1999).
14. The Merck Index, An Encyclopedia of Chemicals, Drugs, and Biologicals, 11th ed., Budavari S, O'Neil MJ, Smith A, Heckelman PE, eds. (Merck & Co., Inc., 1989).
15. The Merck Manual, 16th ed. Berkow, R., ed. (Merck & Co., Inc., 1992).
16. Recognition of Health Hazards in Industry, 2nd ed., Burgess WA. (John Wiley & Sons, 1995).

Computer Databases

1. ATSDR's Toxicological Profiles on compact disc. (Lewis Publishers, 1997 CRC Press, Inc.).
2. Encyclopaedia of Occupational Health and Safety, 4th ed., CD-ROM. Stellman JM, ed. (ILO, 1998).
3. Hazardous Substances Data Bank (HSDB) on compact disc from the Canadian Center for Occupational Health and Safety (can buy at CCOHS web site). "The HSDB(R) (Hazardous Substances Data Bank(R)) database contains data profiles on 4,500 potentially toxic chemical substances. It is created and updated by specialists at the U.S. National Library of Medicine. Compiled from an extensive range of authoritative sources, HSDB is widely recognized as a reliable and practical source of health and safety information. Much of the data is peer reviewed.

4. NIOSHTIC on compact disc from the Canadian Center for Occupational Health and Safety (can buy at CCOHS web site). "NIOSHTIC(R) is a bibliographic database which provides comprehensive international coverage of documents on occupational health and safety, as well as related fields. It contains detailed summaries of over 200,000 articles, reports and publications, spanning over 100 years. NIOSHTIC(R) sources include over 160 scientific and technical journals, NIOSH reports (published and unpublished), NIOSH research bibliographies, abstracts from CIS Abstracts, and personal files from respected professionals on selected topics.
5. Quick Guide: The Electronic NIOSH Pocket Guide to Chemical Hazards, Version 4.0.
6. TLVs and other Occupational Exposure Values—1995 on compact disc from the American Conference of Governmental Industrial Hygienists.
7. BC Cancer Agency: Carcinogens CDC National Center for Infectious Diseases
8. ChemIDplus at the National Library of Medicine is a database of 56,645 chemical structures. Code of Federal Regulations.

REVIEW AND QUESTIONS TO GET YOU THINKING

1. Consider an above ground storage vessel of capacity 30,000 gallons that is three quarters full with gasoline. The tank is equipped with a simple vent. The vessel is exposed to a mean ambient air temperature of 90° F for most of the day. In the late afternoon a severe thunderstorm occurs, with rain for several hours and the mean ambient temperature falling to 75° F. (A) Would you expect the tank to vent during or before the thunderstorm, and why? (B) What concentration range would you expect in the headspace of the vessel throughout the day and during the rainfall?
2. Trichloroethylene, hydrogen sulfide, and toluene vapors are emitted from an open top degreasing operation used for cleaning metal parts. Under relatively quiescent air flow patters in the immediate vicinity, where would you expect these vapors to collect (i.e., will these vapors rise and dissipate rapidly, or will any of them tend to concentrate near the grade)? What physical property is most important to making this assessment?
3. The laboratory you work in has benzene, methyl ethyl ketone, trichloroethane (TCA), and acetone as general purpose solvents. Rank these in order of their risk for fire. State the reasons why one is more dangerous from another in terms of fire safety.

4. Obtain the TLVs for the following chemicals: carbon tetrachloride, chlorobenzene, iodine, ethyl formate, phenol, methanol, and MEK (methyl ethyl ketone). Rank these in order of greatest health risk. *Here's a chance for you to become acquainted with some of the Web sites referred to earlier.*
5. Describe the processes of adsorption and absorption. Give examples of how these would be applied in air pollution control applications.
6. What are the hazard categories used to define regulated hazardous wastes?
7. Explain what a neutralization reaction is. Write a stoichiometric expression for a common neutralization reaction (give an example other than the one used in the text).
8. Give some examples of chemicals that have isomers.
9. What is an unsaturated organic compound? Give some examples.
10. Draw the fire triangle and explain the simple theory of combustion.
11. Why is a flammable gas more dangerous than a flammable liquid? Give examples of both types.
12. What is a pyrophoric material? Give an example.
13. Ethyl aluminum dichloride (EADC) is used in the manufacture of certain catalysts for making LDPE. Occasionally, the batch operation involving the catalyst production results in an off-spec lot. This off-spec lot is washed from the reactor (impregantor) with water and hexane, and must be sent to a waste disposal facility. The facility treats this waste in a hydrolysis reaction (i.e., with water and mild agitation). If the reaction is exothermic, what are the potential air pollution and fire problems associated with the waste treatment?
14. For question 13, what types of testing would you recommend to ensure uniformity of waste batches that enter the treatment facility to minimize violent exothermic reactions from occurring between waste treatments?

Chapter 4

VENTILATION AND INDOOR AIR QUALITY CONTROL

INTRODUCTION

This chapter provides an overview of indoor air quality issues and management practices, with emphasis given to industrial operations. Proper indoor air quality management is an integral part of any program dealing with safe industry practices and in the control of air pollution problems. It is an area of concern because improperly designed ventilation systems lead to significant health risk exposures through inhalation hazards, as well as energy inefficiencies which increase the overhead costs of an operation. Therefore, it is an area where control and operational options may present significant pollution prevention opportunities through the capturing of energy credits, in increasing the productivity of workers through improved comfort, reducing loss time from illness and injury, reducing medical costs by minimizing or eliminating inhalation hazards, and reducing facility insurance premiums by providing a safer work environment.

AN OVERVIEW OF INDOOR AIR QUALITY

The quality of the indoor environment in any building complex depends on a large number of variables, a few of which are: the interactions between the site, climate, building system (original design and later modifications in the structure and mechanical systems), construction techniques, contaminant sources (building materials and furnishings, moisture, processes and activities within the building and outdoor sources), and the activities of the building occupants and operations they perform. To generalize, the following factors are involved in the development of indoor air quality problems:

Source: there is a source of contamination or discomfort indoors, outdoors, or within the mechanical systems of the building.

HVAC: the HVAC system is not able to control existing air contaminants and ensure thermal comfort (temperature and humidity conditions that are comfortable for most occupants).

Pathways: one or more pollutant pathways connect the pollutant source to the occupants and a driving force exists to move pollutants along the pathway(s). *Occupants:* building occupants are present.

It is important to understand the role that each of these factors may play in order to prevent, investigate, and resolve and manage indoor air quality problems.

Indoor air contaminants can originate within the building or be drawn in from outdoors. If contaminant sources are not controlled, problems can arise, even if the HVAC system is properly designed and well-maintained. Sources can be from outside the building; from operating equipment, from human activities, and other or miscellaneous sources. Sources outside a building include contaminated outdoor air, emissions from nearby sources, soil gas, or moisture or standing water.

Contaminated outdoor air can include pollen, dust, fungal spores, industrial pollutants, general vehicle exhaust. Emissions from nearby sources include exhaust from vehicles on nearby roads or in parking lots or garages, loading docks, odors from dumpsters, re-entrained (drawn back into the building) exhaust from the building itself or from neighboring buildings, unsanitary debris near the outdoor air intake, emissions from industrial sources such as stacks from neighboring building operations, or even backwash from the stacks of buildings we are trying to control the indoor air quality in. Soil gas generally refers to radon, leakage from underground fuel tanks, contaminants from previous uses of the site (e.g., landfills), pesticides. Moisture or standing water promotes excess microbial growth; rooftops after rainfall, crawlspace can also be a major source of indoor air quality problems.

Equipment sources can be of two types; namely, HVAC system and non-HVAC system equipment. In an HVAC system, the sources of contamination may be dust or dirt in ductwork or other components, microbiological growth in drip pans, humidifiers, ductwork, coils, improper use of biocides, sealants, and/or cleaning compounds, improper venting of combustion products, refrigerant leakage. From non-HVAC equipment, the emissions can be from office equipment (volatile organic compounds, ozone), supplies (solvents, toners, ammonia), emissions from shops, labs, cleaning processes, elevator motors, and other mechanical systems.

The human or personal activities that can contribute to poor indoor air quality are actions such as smoking, cooking, body odor, cosmetic odors. Personal activities sources can also be related to housekeeping activities, such as cleaning materials and procedures emissions from stored supplies or trash, use of deodorizers and fragrances, airborne dust or dirt (e.g., circulated by sweeping and vacuuming). Another source may be maintenance activities - microorganisms in mist from improperly maintained cooling towers, airborne dust or dirt, volatile organic compounds from use of paint, caulk, adhesives, and other products, pesticides from pest control activities, emissions from stored supplies.

Building components and furnishings may also be a contributing factor or source. These can be locations that produce or collect dust or fibers; including textured surfaces such as carpeting, curtains, and other textiles, open shelving, old or deteriorated furnishings, materials containing damaged asbestos.

Unsanitary conditions and water damage can harbor microbiological growth on or in soiled or water-damaged furnishings, microbiological growth in areas of surface condensation, standing water from clogged or poorly designed drains, dry traps that allow the passage of sewer gas. In addition, chemicals released from building components or furnishings such as volatile organic compounds or, inorganic compounds can create problems.

Other or miscellaneous sources can be accidental releases, such as spills of water or other liquids, microbiological growth due to flooding or to leaks from roofs, piping, fire damage (soot, PCBs from electrical equipment, odors). Special use areas and mixed use buildings, although intended to isolate problems, can be a source of contamination in the common-use areas of a building. These can be smoking lounges, laboratories, print shops, art rooms, exercise rooms, beauty salons, and food preparation areas.

Other potential sources are redecorating/remodeling/repair activities, emissions from new furnishings, dust and fibers from demolition resulting in odors and volatile organic and inorganic compounds from paint, caulk, adhesives, and microbiologicals released from demolition, or remodeling activities.

Indoor air often contains a variety of contaminants at concentrations that are far below any standards or guidelines for occupational exposure. Given our present knowledge, it is difficult to relate complaints of specific health effects to exposures to specific pollutant concentrations, especially since the significant exposures may be to low levels of pollutant mixtures.

THE BASICS OF HVAC SYSTEMS

When we talk about an HVAC system, recognize that the discussion includes all heating, cooling, and ventilation equipment that services a building: that is, it includes furnaces or boilers, chillers, cooling towers, air handling units, exhaust fans, ductwork, filters, steam (or heating water) piping. The general comments that follow apply both to central HVAC systems and to individual components used as stand-alone units.

A number of variables interact to determine whether people are comfortable with the temperature of the indoor air. The activity level, age, and physiology of each person affect the thermal comfort requirements of that individual.

A proper HVAC system provides thermal comfort, distributes adequate amounts of outdoor air to meet ventilation needs of all building occupants, isolates and removes odors and contaminants through pressure control, filtration, and exhaust fans. One of the import roles of any HVAC system is to provide thermal comfort. The American Society of Heating, Refrigerating, and Air Conditioning Engineers (ASHRAE) Standard 55-1981 describes the temperature and humidity ranges that are comfortable for most people engaged in largely sedentary activities.

The ASHRAE standard assumes "normal" indoor clothing. Added layers of clothing reduce the rate of heat loss. Uniformity of temperature is important to comfort. When the heating and cooling needs of rooms within a single zone change at different rates, rooms that are served by a single thermostat may be at different temperatures. Temperature stratification is a common problem caused by convection, which is the tendency of light, warm air to rise and heavier, cooler air to sink, thus causing a circulation of air patterns. If the air is not properly mixed by the ventilation system, the temperature near the ceiling can be several degrees warmer than at floor level. Even if air is properly mixed, insulated floors over unheated spaces can create discomfort in some climate zones. Large fluctuations of indoor temperature can also occur when controls have a wide "dead band" (a temperature range within which neither heating nor cooling takes place).

Large vertical surfaces can also produce a significant flow of naturally convecting air, resulting in drafty conditions. Adding insulation to walls helps to moderate the temperature of interior wall surfaces. Closing curtains reduces heating from direct sunlight and isolates building occupants from exposure to window surfaces (which, lacking insulation, are likely to be much hotter or colder than the walls).

Radiant heat transfer may cause people located near very hot or very cold surfaces to be uncomfortable even though the thermostat setting and the measured air temperature are within the comfort range. Buildings with large window areas sometimes have acute problems of discomfort due to radiant heat gains and losses, with the locations of complaints shifting during the day as the sun angle changes.

Humidity is an important factor in achieving thermal comfort. Raising relative humidity reduces the ability to lose heat through perspiration and evaporation, so that the effect is similar to raising the temperature. Humidity extremes can also create other IAQ (Indoor Air Quality) problems. Excessively high or low relative humidity can produce discomfort, while high relative humidity can promote the growth of mold and mildew.

Most air handling units distribute a blend of outdoor air and recirculated indoor air. HVAC designs may also include units that introduce 100% outdoor air or that simply transfer air within the building. Uncontrolled quantities of outdoor air enter buildings by infiltration through windows, doors, and gaps in the exterior construction of the building.

Thermal comfort and ventilation needs are met by supplying "conditioned" air (a blend of outdoor and recirculated air that has been filtered, heated or cooled, and sometimes humidified or dehumidified).

Large buildings often have exterior ("core") spaces in which constant cooling is required to compensate for heat generated by occupants, equipment, and lighting, while perimeter rooms may require heating or cooling depending on outdoor conditions. Two of the most common HVAC designs used in modern public and commercial buildings are *constant volume* and *variable air volume* systems.

Constant volume systems are designed to provide a constant airflow and to vary the air temperature to meet heating and cooling needs. The percentage of outdoor air may be held constant, but is often controlled either manually or automatically to vary with outdoor temperature and humidity. Controls may include a mini setting that should allow the system to meet ventilation guidelines for outdoor air quantities under design conditions.

In contrast, variable air volume (VAV) systems condition supply air to a constant temperature and ensure thermal comfort by varying the airflow to occupied spaces. Most early VAV systems did not allow control of the outdoor air quantity, so that a decreasing amount of outdoor air was provided as the flow of supply air was reduced. More recent designs ensure a minimum supply of outdoor air with static pressure devices in the outdoor air stream. Additional energy-conserving features such as economizer control or heat recovery are also found in some buildings. Quality design, installation, and testing and balancing are essential to the proper operation of all types of HVAC systems, especially VAV systems, as are regular inspections and maintenance.

CONTROLLING ODORS AND AIR POLLUTANTS

One technique for controlling odors and contaminants is to dilute them with outdoor air. Dilution can work only if there is a consistent and appropriate flow of supply air that mixes effectively with room air. The term "ventilation efficiency" is used to describe the ability of the ventilation system to distribute supply air and remove internally generated pollutants.

Another technique for isolating odors and contaminants is to design and operate the HVAC system so that pressure relationships between rooms are controlled. This type of control technique is accomplished by adjusting the air quantities that are supplied to and removed from each room. If more air is supplied to a room than is exhausted, the excess air leaks out of the space and the room is said to be under *positive pressure*. If less air is supplied than is exhausted, air is pulled into the space and the room is said to be under *negative pressure*. This technique can result in incremental energy savings over time, depending on the size and complexity of the building operation. Control of pressure relationships is critically important in mixed use buildings or buildings with special use areas. Lobbies and buildings in general are often designed to operate under positive pressure to minimize the infiltration of unconditioned air, with its potential to cause drafts and introduce dust, dirt, and thermal discomfort. Without proper operation and maintenance, these pressure differences are not likely to remain as originally designed.

A third technique is to use local exhaust systems (sometimes known as *dedicated exhaust ventilation systems*) to isolate and remove contaminants by maintaining negative pressure in the area around the contaminant source. Local exhaust can be linked to the operation of a particular piece of equipment used to treat an entire room. Air should be exhausted to the outdoors, not recirculated, from locations which produce significant odors and high concentrations of contaminants. Spaces where local exhaust is used must be provided with make-up air and the local exhaust must function in coordination with the rest of the ventilation system. Under some circumstances, it may be acceptable to transfer conditioned air from relatively clean parts of a building to comparatively dirty areas and use it as make-up air for a local exhaust system. The advantage of such a transfer is that it can achieve significant energy savings.

The stack effect exists whenever there is an indoor-outdoor temperature difference and becomes stronger as the temperature difference increases. As heated air escapes from upper levels of the building, indoor air moves from lower to upper floors, and replacement outdoor air is drawn into openings at the lower levels of buildings. Stack effect airflow can transport contaminants between floors by way of stairwells, elevator shafts, utility chases, or other openings. Wind effects are transient, creating local areas of high pressure (on the windward side) and low pressure (on the leeward side) of buildings.

Air cleaning and filtration devices designed to control contaminants are found as components of HVAC systems (for example, filter boxes in ductwork) and can also be installed as independent units. The effectiveness of air cleaning depends upon proper equipment selection, installation operation, and maintenance.

UNDERSTANDING CONTAMINANT PATHWAYS

Airflow patterns in buildings result from the combined action of mechanical ventilation systems, human activity, and natural forces. Pressure differentials created by these forces move airborne contaminants from areas of relatively higher pressure to areas of relatively lower pressure through any available openings.

The HVAC system is generally the predominant pathway and driving force for air movement in buildings. However, all of a building's components (walls, ceilings, floors, penetrations, HVAC equipment, and occupants) interact to affect the distribution of contaminants. For example, as air moves from supply registers or diffusers to return air grilles, it is diverted or obstructed by partitions, walls, and furnishings, and redirected by openings that provide pathways for air movement. On a localized basis, the movement of people has a major impact on the movement of pollutants. Some of the pathways change as doors and windows open and close. It is useful to think of the entire building - the rooms and the connections (e.g., chases, corridors, stairways, elevator shafts) between them as part of the air distribution system. Additionally, natural forces exert an important influence on air movement between zones and between the building's interior and exterior.

Both the stack effect and wind can overpower a building's mechanical system and disrupt air circulation and ventilation, especially if the building envelope is leaky. Stack effect is defined as the pressure driven flow produced by convection (the tendency of warm air to rise).

Depending on the leakage openings in the building exterior wind can affect the pressure relationships within and between rooms. The basic principle of air movement from areas of relatively higher pressure to areas of relatively lower pressure can produce many patterns of contaminant distribution, including: local circulation in the room containing the pollutant source, air movement into adjacent spaces that are under lower pressure, recirculation of air within the zone containing the pollutant source or in adjacent zones where return systems overlap, movement from lower to upper levels of the building, air movement into the building through either infiltration of outdoor air or reentry of exhaust air. Air moves from areas of higher pressure to areas of lower pressure through any available openings. A small crack or hole can admit significant amounts of air if the pressure differentials are high enough (which may be very difficult to assess).

Even when the building as a whole is maintained under positive pressure, there is always some location (for example, the outdoor air intake) that is under negative pressure relative to the outdoors. Entry of contaminants may be intermittent, occurring only when the wind blows from the direction of the pollutant source. The interaction between pollutant pathways and intermittent or variable driving forces can lead to a single source causing IAQ complaints in areas of the building that are distant from each other and from the source.

IAQ ISSUES AND IMPACTS ON OCCUPANTS

The term "building occupants" refers to people who spend extended time periods (e.g., a full workday) in the building. Visitors are also occupants; they may have different tolerances and expectations from those who spend their entire workdays in the building, and are likely to be more sensitive to odors. Groups that may be particularly susceptible to effects of indoor air contaminants include allergic or asthmatic individuals, people with respiratory disease, people whose immune systems are suppressed due to chemotherapy, radiation therapy, disease, or other causes, contact lens wearers. Some other groups are particularly vulnerable to exposures of certain pollutants. For example, people with heart disease may be more affected by exposure at lower levels of carbon monoxide than healthy individuals. Children exposed to environmental tobacco smoke have been shown to be at higher risk of respiratory illnesses and those exposed to nitrogen dioxide have been shown to be at higher risk from respiratory infections. Because of varying sensitivity among people, one individual may react to a particular IAQ problem while surrounding occupants have no ill effects. Symptoms that are limited to a single person can also occur when only one work station receives the majority of the pollutant dose. In other cases, complaints may be widespread. A single indoor air pollutant or problem can trigger different reactions in different people. Some may not be affected at all. Information about the types of symptoms can sometimes lead directly to solutions. However, symptom information is more likely to be useful for identifying the timing and conditions under which problems occur.

The effects of IAQ problems are often nonspecific symptoms rather than clearly defined illnesses. Symptoms commonly attributed to IAQ problems include: headache, fatigue, shortness of breath, sinus congestion, coughing, sneezing, eye, nose, and throat irritation, skin irritation, dizziness, nausea. All of these symptoms, however, may also be caused by other factors, and are not necessarily due to air quality deficiencies. Health and comfort are used to describe a spectrum of physical sensations. For example, when the air in a room is slightly too warm for a person's activity level, that person may experience mild discomfort. If the temperature continues to rise, discomfort increases and symptoms such as fatigue, stuffiness, and headaches can appear. Some complaints are often related to the discomfort end of the spectrum. One of the most common IAQ complaints is related to the presence of a strange odor. Odors are often associated with a perception of poor air quality, whether or not they cause symptoms. Environmental stressors such as improper lighting, noise, vibration, overcrowding, ergonomic stressors, and job-related psychosocial problems (such as job stress) can produce symptoms that are similar to those associated with poor air quality.

CONDITIONS RESULTING FROM POOR INDOOR AIR QUALITY

The term *sick building syndrome* (SBS) is used to describe cases in which building occupants experience acute health and comfort effects that are linked to the time they spend in the building, but in which no specific illness or cause can be identified. The complaints may be localized in a particular room or zone or may be widespread throughout the building. Many different symptoms have been associated with SBS, including respiratory complaints, irritation, and fatigue. Analysis of air samples often fails to detect high concentrations of specific contaminants. The problem may be caused by any or all of the following: the combined effects of multiple pollutants at low concentrations, other environmental stressors (e.g., overheating, poor lighting, noise), ergonomic stressors, job-related psychosocial stressors (e.g., overcrowding, labor-management problems).

Building-related illness (BRI) is a term referring to illness brought on by exposure to the building air, where symptoms of diagnosable illness are identified (e.g., certain allergies or infections) and can be directly attributed to environmental agents in the air. Legionnaire's disease and hypersensitivity pneumonitis are examples of BRI that can have serious, even life threatening consequences.

A small percentage of the population may be sensitive to a number of chemicals in indoor air, each of which may occur at very low concentrations. The existence of this condition, which is known as *multiple chemical sensitivity* (MCS), is a matter of considerable controversy. MCS is not currently recognized by the major medical organizations. Medical opinion is divided, and further research is needed. The applicability of access for the disabled and worker's compensation regulations to people who believe they are chemically sensitive is becoming a concern for facility managers.

SOME HELPFUL HINTS

Sometimes a number of building occupants experience serious health problems (e.g., cancer, miscarriages, Lou Gehrig's disease) over a relatively short time period. These clusters of health problems are occasionally blamed on indoor air quality, and can produce anxiety among building occupants. Establishing a communication system that can help prevent indoor air quality problems and resolve problems if they do arise is a critical issue in the proper management of IAQ problems. Effective communication can encourage building occupants to improve their work environment through positive contributions. Many indoor air quality problems can be prevented if staff and building occupants understand how their activities affect IAQ. If a company already has a health and safety committee functioning to promote good working conditions, it is easy to add indoor air quality to their list of concerns. It is important to define the responsibilities of building management, staff, and occupants in relation to indoor air quality. These responsibilities can be formalized by incorporating them into documents such as employee manuals or lease agreements. Educate occupants about the permitted uses and maximum occupancy of different areas within the building and make sure that appropriate ventilation is provided for the activities that are permitted.

Inform occupants about the importance of keeping the building management informed about significant changes in the number of people regularly using particular areas of the building. The ventilation systems in buildings are designed and operated to supply air to projected ranges of occupants. If the occupancy rate becomes a problem, it may be helpful to refer to a standard reference such as ASHRAE Standard 62-1989 to show occupants that keeping occupancy within the ventilation capacity serves the goal of providing a quality work environment and is not an arbitrary decision by building management. Management should review plans that may involve increases in the number of occupants, relocation of walls or partitions, installation of new equipment, or changes in the use of space. Building owners, facility managers, and occupants share responsibility for monitoring new equipment installation and changes in the use of space. The review process allows potential indoor air quality problems to be identified so that the HVAC system can be modified as needed. Only authorized maintenance personnel should adjust air supply or exhaust vents; however, if occupants are expected to follow such a "hands-off' policy, facility management must respond promptly to IAQ complaints. Many organizations have established procedures for responding to occupant complaints that can be modified to include indoor air quality concerns. To avoid frustrating delays, building occupants need to know how to express their complaints about IAQ. Most importantly, they need to know how to locate responsible staff and where to obtain complaint forms. This information can be posted on bulletin boards, circulated in memos or newsletters, or publicized by some other means. Complaints should be handled promptly, with every incident given serious attention. It is advisable to establish a recordkeeping system that cross-references documentation on complaints with records of equipment operation and maintenance. The recordkeeping system can help to resolve complaints by collecting information in a form that highlights patterns of problems (for example, complaints that occur at a regular time of day or in the same area of the building). In many cases, building managers may be alerted to potential indoor air quality problems by complaints from occupants. The complaints can be vague, to the effect that one or more people feel "sick" or "uncomfortable" or that someone has noticed an unusual odor. They may be specific, blaming a particular material as the cause of discomfort or health problems. People are usually reacting to a real problem, so their complaints should be taken seriously. However, they may attribute their symptoms to the wrong cause, so their theories about the problem should be heard respectfully but weighed cautiously. Indoor air quality problems can sometimes be identified and resolved quickly. On other occasions, complaints originate from the interaction of several variables, and detailed investigation may be necessary in order to resolve the problem.

Listening and responding to building occupants is critical to achieving a successful resolution of indoor air quality complaints. IAQ complaints may be grounded in poor indoor air quality, thermal conditions, noise, glare, or even job stress. However, it is in the building manager's best interest to respond to all complaints about the indoor environment promptly and seriously and to establish credibility through open communication with building occupants. The biggest mistake that building managers can make in the face of an IAQ complaint is to underestimate the problems that can result if building occupants believe that no action is being taken or that important information is being withheld. Without open communication, any IAQ problem can become complicated by anxiety, frustration, and distrust, delaying its resolution. Paying attention to communication, as well as problem-solving, helps to ensure proper support and cooperation of building occupants as the complaint is investigated and resolved. The messages to convey are that management believes it is important to provide a healthy and safe building, that good indoor air quality is an essential component of a healthful indoor environment, and that complaints about indoor air quality are taken seriously. Make certain that occupants know how to contact the responsible personnel who can receive and respond to IAQ complaints. Tenants may also have an internal system for channeling complaints, for example through a health and safety representative, supervisor, or company doctor. Indoor air quality complaints that can be resolved quickly and that involve small numbers of people (e.g., annoying but harmless odors from an easily-identified source) can be handled matter-of-factly like other minor problems without risking confusion and bad feeling among other building occupants. Communication becomes a more critical issue when there are delays in identifying and resolving the problem and when serious health concerns are involved. If the problem seems to be widespread or potentially serious, it is advisable to work with your health and safety committee. If you do not have a health and safety committee, consider forming one, or establishing a joint management-tenant IAQ task force. Productive relations will be enhanced if occupants are given basic information during the process of investigation and mitigation.

Potential critics can become allies if they are invited to be part of the problem-solving process and become better educated about IAQ and building operations. Building managers may be understandably reluctant to share test results or consultants' reports with their tenants or employees, but secrecy in such matters can backfire if information leaks out at a later time. Building management staff can be encouraged to talk directly with occupants both at the time a complaint occurs and later during a diagnostic investigation. Their observations about patterns of symptoms or building conditions may provide helpful information.

Confidentiality of records can be important to occupants, especially if they are concerned that IAQ complaints will lead to negative reactions from their employers. There may be legal penalties for violating confidentiality of medical records. By reassuring occupants that privacy will be respected, investigators are more likely to obtain honest and complete information. It is advisable to explain the nature of investigative activities, so that rumors and suspicions can be countered with factual information.

Notices or memoranda can be delivered directly to selected occupants or posted in general use areas. Newsletter articles or other established communication channels can also be used to keep building occupants up-to-date. Problems can arise from saying either too little or too much. Premature release of information when data-gathering is still incomplete can produce confusion, frustration, and mistrust at a later date. Similar problems can result from incorrect representation of risk - assuming the worst case (or the best). However, if progress reports are not given, people may think nothing (or something terrible) is happening.

It is good practice to clear each piece of information with the facility manager, building owner, or legal counsel. Vague discomfort, intermittent symptoms, and complex interactions of job stress with environmental factors, which make IAQ problems difficult to investigate, can also obscure the effects of mitigation efforts. Even after the proper mitigation strategy is in place, it may take days or weeks for contaminants to dissipate and symptoms to disappear. If building occupants are informed that their symptoms may persist for some time after mitigation, the inability to bring instant relief is less likely to be seen as a failure.

APPLICATION OF AUDITS TO DEVELOPING AN IAQ PROFILE

An IAQ profile enables us to develop a description of the features of the building structure, function, and occupancy that impact indoor air quality. Upon completion of the IAQ profile, one should have an understanding of the current status of air quality in the building and baseline information on the factors that have a potential for causing problems in the future. The IAQ profile can help building management to identify potential problem areas and prioritize budgets for maintenance and future modifications. Combined with information on lighting, security, and other important systems, it can become an owner's manual that is building-specific and will serve as a reference in a variety of situations. The key questions to answer while developing the IAQ profile are: How was this building originally intended to function? Consider the building components and furnishings, mechanical equipment (HVAC and non HVAC), and the occupant population and associated activities. Is the building functioning as designed? Find out whether it was commissioned. Compare the information from the commissioning to its current condition. What changes in building layout and use have occurred since the original design and construction? Find out if the HVAC system has been reset and retested to reflect current usage. What changes may be needed to prevent IAQ problems from developing in the future? Consider potential changes in future uses of the building.

The process of developing an IAQ profile should require only a modest effort, from a few days to a few weeks of staff time, depending on the complexity of the building and the amount of detailed information collected. The work can be done in pieces over a longer period, if necessary, to fit into a building manager's busy schedule. Over time, it is desirable to make some actual measurements of airflow, temperature, relative humidity, carbon dioxide (CO), and/or pressure differentials (e.g., in each of the air handling zones or other subareas of the building). These measurements provide far better information on current conditions than can be obtained from the plans and specifications, even if as-built records are available. Also, few buildings have been adequately commissioned, so the system may never have delivered the airflows shown on the design drawings. In the event of litigation around future IAQ complaints, the value of the IAQ profile as a resource document will be enhanced by real-world measurements. Refer to the ASHRAE standard on commissioning. The EPA document on designing for good indoor air quality also contains information on the process of commissioning buildings.

Many of the resources necessary for the IAQ profile should already be on hand. Additional information can be collected by the staff person or persons who have the following skills: basic understanding of HVAC system operating principles, ability to read architectural and mechanical plans and understand manufacturer's catalog data on equipment ability to identify items of office equipment, ability to work cooperatively with building occupants and gather information about space usage ability to collect information about HVAC system operation, equipment condition, and maintenance schedules, authority to collect information from subcontractors about work schedules and materials used (particularly cleaning and pest control activities), ability to understand the practical meaning of the information contained in the Material Safety Data Sheets (MSDSs). If direct measurements are to be included in the IAQ profile, the staff should have the tools and training to make the following measurements: air volumes at supply diffusers and exhaust grilles, CO concentration, temperature, relative humidity at different pressure differentials, assessment of thermal and ventilation load requirements. The type of information needed for an IAQ profile is similar to that which is collected when solving indoor air quality problems, but includes the entire building rather than focusing on areas that may have caused an identified problem. The IAQ profile should be an organized body of records that can be referred to in planning for renovations, negotiating leases and contracts, or responding to future complaints.

The process of gathering information for the IAQ profile can be divided into three major stages: (1) Collect and review existing records. (2) Conduct a walkthrough inspection of the building. (3) Collect detailed information on the HVAC system, pollutant pathways, pollutant sources, and building occupancy. These three steps constitute an indoor air quality audit. The first two stages should be carried out as quickly as possible, but the third stage can be handled as time allows so that it does not interfere with other staff responsibilities.

RECORDKEEPING PRACTICES

Initial efforts should be devoted to collecting any available documents that describe the construction and operation of the building: architectural and mechanical plans, specifications, submittals, sheet metal drawings, commissioning reports, adjusting and balancing reports, inspection records, and operating manuals. Many buildings may lack some or all of these documents. If there are no commissioning reports or balancing reports, actual ventilation quantities may be different from those indicated on mechanical design drawings. If there are no operating or maintenance manuals for HVAC equipment, it is difficult for staff to carry out an adequate preventive maintenance program.

An examination of the original architectural and mechanical design should be made to gain an understanding of the building's layout and intended functions. Identify and note locations in which changes in equipment or room usage create a potential for indoor air quality problems and give them special attention during the walkthrough inspection. Items of interest and the questions they suggest could include the following:

- Commissioning reports: Was the building properly commissioned when it was first constructed, including testing and balancing of the HVAC system?
- Operating manuals: Do staff members understand how the HVAC equipment is intended to operate?
- Remodeled areas: Has the HVAC system layout been changed to accommodate new walls, rearranged partitions, or similar architectural modifications?
- Addition, removal, or replacement of HVAC equipment: Where the original equipment has been replaced, do the newer units have the same capacity as the originals? Has new equipment been properly installed and tested? Where equipment has been removed, is it no longer needed?
- Changes in room use: Is there a need for additional ventilation (supply and/or exhaust) due to increased occupant population or new activities within any area of the building? Have new items of equipment (non-HVAQ been provided with local exhaust where needed? Look for unusual types or quantities of equipment such as copy machines or computer terminals.

Check HVAC maintenance records against equipment lists. Collect existing maintenance and calibration records and check them against the construction documents (e.g., equipment lists and mechanical plans). Equipment that has been installed in inaccessible or out-of-the-way locations is frequently overlooked during routine maintenance.

This is particularly true of items such as filter boxes and small capacity exhaust fans. If there is an organized record of past occupant complaints about the building environment, review those complaints to identify building areas that deserve particular attention.

WALKTHROUGH INSPECTIONS

The intent of the walkthrough inspection is to acquire a good overview of occupant activities and building functions and to look for IAQ problem indicators. No specific forms are suggested for this stage of IAQ profile development. However, the investigator should have a sketch plan of the building, such as a small floor plan showing fire exits, so that his or her notes can be referenced to specific locations.

Detailed measurements of temperature, humidity, airflow, or other parameters are more appropriate to a later stage of profile development. However, chemical smoke can be used to observe airflow patterns and pressure relationships between special use areas or other identified pollutant sources and surrounding rooms. Odors in inappropriate locations may indicate that ventilation system components require adjustment or repair.

The value of IAQ ventilation measurement tools to your operation will grow as you become more familiar with handling indoor air quality concerns. For example, if you do not own a direct-reading carbon dioxide monitor, it is not necessary to acquire one for the IAQ profile. Those who already have access to this type of instrument can take readings during the walkthrough as a way to obtain baseline information about normal operating conditions or identify problem locations. If you begin to suspect that underventilation is a consistent problem, you may decide that it would be helpful to obtain more ventilation monitoring equipment.

A walkthrough inspection provides an opportunity to introduce facility staff and other building occupants to the topic of indoor air quality and to understand current staff (and contractor) responsibilities in relation to housekeeping and maintenance activities. Advance notice of the inspection will make it seem less intrusive and may encourage staff and other occupants to remember important information. Discussion of routine activities in the building will help to clarify elements that should be included in the IAQ management plan. Ask staff members about their job responsibilities, training, and experience. It will be helpful to meet with responsible staff and contractors to discuss facility operation and maintenance issues (e.g., HVAC, plumbing, electric, interior maintenance). HVAC maintenance schedule (e.g., filter changes, drain pan maintenance), use and storage of chemicals, schedule of shipping and receiving, handling of vehicles at loading dock scheduling, and other procedures for isolating odors, dust, and emissions from painting, roof repair, and other contaminant-producing activities should be examined. Others areas to examine include budgeting (e.g., including staff influence on budget decisions), housekeeping, cleaning schedules, trash storage and schedule of refuse removal, use and storage of chemicals, pest control, schedule and location of pesticide applications, use and storage of chemicals, pest control activities other than use of pesticides.

The walkthrough inspection can be used to identify areas with a high potential for

IAQ problems. The following are general indicators of IAQ problems: odors, dirty or unsanitary conditions (e.g., excessive dust), visible fungal growth or moldy odors (often associated with problem of too much moisture), sanitary conditions in equipment such as drain pans and cooling towers, poorly-maintained filters, signs of mold or moisture damage at walls (e.g., below windows, at columns, at exterior corners), ceilings, and floors, such as staining and discoloration.

The walkthrough should focus on uneven temperatures, persistent odors, drafts, sensations of stuffiness. You may find that occupants are attempting to compensate for an HVAC system that doesn't meet their needs. Look for propped-open corridor doors, blocked or taped-up diffusers, popped-up ceiling tiles, people using individual fans/heaters or wearing heavier (or lighter) clothing than normal.

Overcrowding issues should be noted. Future occupant density is estimated when the ventilation system for a building is designed. When the actual number of occupants approaches or exceeds this occupant design capacity, managers may find that IAQ complaints increase. At that point, the outdoor air ventilation rate will have to be increased. However, the ventilation and cooling systems may not have sufficient capacity to handle the increased loads from the current use of the space.

Check for underventilation caused by obstructed vents, faulty dampers or other HVAC system malfunctions, or from problems within the occupied space. Furniture, papers, or other materials can interfere with air movement around thermostats or block airflow from wall or floor-mounted registers. If office cubicles are used, a small space (i.e., two to four inches) between the bottom of the partitions and the floor may improve air circulation.

Lift a ceiling tile and examine the plenum for potential problems. Walls or full-height partitions that extend to the floor above can obstruct or divert air movement in ceiling plenums unless transfer grilles have been provided. If fire dampers have been installed to allow air circulation through walls or partitions, confirm that the dampers are open. Construction debris and damaged or loose material in the plenum area may become covered with dust and can release particles and fibers.

Be aware of areas that contain unusual types or quantities of equipment such as copy machines or computer terminals. Also look for instances of over-illumination. High concentrations of electrical fixtures and equipment can overwhelm the ventilation and cooling systems.

Confirm that the HVAC system maintains appropriate pressure relationships to isolate and contain odors and contaminants in mixed use buildings and around special use areas. Examples of special use areas include attached parking garages, loading docks, print shops, smoking lounges, janitorial closets, storage areas, and kitchens.

The collection of detailed information for the IAQ profile can be handled as time is available. Areas that have been identified as presenting potential IAQ problems should be given the highest priority.

Check the outdoor air intakes to see whether they are located near contaminant sources (e.g., plumbing vents, exhaust outlets, dumpsters, loading docks, or other locations where vehicles idle). See if the space containing the HVAC system is clean and dry. Examples of problems include: cleaning or other maintenance supplies stored in mechanical room; dust and dirt buildup on floors and equipment; moisture in mechanical room because of inadequate insulation, lack of conditioned air, or failure to provide for air movement. Unsanitary conditions in the mechanical room are particularly a problem if unducted return air is dumped into and circulated through the mechanical room.

Use maintenance records to inspect HVAC equipment and make sure that it is in good operating condition. Identify items of equipment that need to be repaired, adjusted, or replaced. Record control settings and operating schedules for HVAC equipment for comparison to occupancy schedules and current uses of space.

Using a sketch plan of the building that was begun during the walkthrough inspection, indicate architectural connections (e.g., chases) and mechanical connections (e.g., ductwork, temperature control zones). Observe and record airflow between spaces intended to run positive or negative and the areas that surround them (including airflow between perimeter rooms and outdoors). Note that hidden pathways such as chases may travel both vertically and horizontally and transport pollutants over long distances.

Record potential pollutant sources in the building. Note the locations of major sources. Major sources such as large items of equipment can be recorded on the floor plan. Record the names and locations of chemicals or hazardous substances used or stored within the building, such as those that may be contained in cleaning materials, biocides, paints, caulks, and adhesives. Ask your suppliers to provide you with Material Safety Data Sheets. You may be unaware of the potential hazards of some materials that are commonly used in public and commercial buildings. For example: In 1990, EPA eliminated the sale of mercury-containing interior latex paint. (Enamel paints do not contain mercury.) People are urged not to use exterior latex paint indoors, as it may contain mercury. If you have paint in storage that may have been manufactured before August 20, 1990, you may contact the manufacturer, the National Pesticide Telecommunication Network (1-800-858-7378), or your State Health Department for guidance. In 1990, EPA banned the use of chromium chemicals in cooling towers, because the chemicals have been shown to be carcinogenic. Heating system steam should not be used in the HVAC humidification system, as it may contain potentially harmful chemicals such as corrosion inhibitors.

Part of the walkthrough should focus on collecting information on building occupancy. This should include information on the way each area of the building is used, its source of outdoor air, and whether or not it is equipped with local exhaust. If underventilation is suspected, estimate ventilation rates in cubic feet per minute per person or per square foot floor area, for comparison to guidelines such as design documents, applicable building codes, or the recommendations of ASHRAE 621989. Underventilation problems can occur even in areas where ventilation rates apparently meet ASHRAE guidelines; proper distribution and mixing of supply air with room air are also essential for good ventilation.

If the information collected as you develop the IAQ profile indicates that you have one or more IAQ problems, prioritize these problems by considering the apparent seriousness of their consequences. For example, combustion gas odors demand a more rapid response than thermostats that are out of calibration.

DEVELOPING MANAGEMENT PLANS

Any IAQ management system will be successful only if it is organized to fit the specific needs of the building. Managing a building for good indoor air quality involves reviewing and amending current practice (and establishing new procedures, if necessary) to:

Operate and maintain HVAC equipment: keep all equipment and controls in proper working order and to keep interior of equipment and ductwork clean and dry.

Oversee activities of staff, tenants, contractors, and other building occupants that impact indoor air quality: smoking, housekeeping, building maintenance, shipping and receiving, pest control, food preparation, and other special uses.

Maintain communications with occupants so that management will be informed of *complaints about the indoor environment in a timely way*: identify building management and staff with IAQ responsibilities use health and safety committees.

Educate staff, occupants, and contractors about their responsibilities in relation to indoor air quality: staff training , lease arrangements , contracts.

Identify aspects of planned projects that could affect indoor air quality and manage projects so that good air quality is maintained: this includes redecorating, renovation, or remodeling, relocation of personnel or functions within the building, new construction.

Development of the management plan involves reviewing and revising staff responsibilities so that IAQ considerations become incorporated into routine procedures. Organizations may assign responsibility for operations, recordkeeping, purchasing, communications, planning, and policymaking in many different ways. However, the key elements of good IAQ management remain the same: *It is important to understand the fundamental influences that affect indoor air quality.* This can be achieved by becoming familiar with literature on IAQ and keeping abreast of new information. Select an IAQ manager with the following attributes: clearly defined responsibilities, adequate authority and resources.

Use the IAQ profile and other available information to: evaluate the design, operation, and usage of the building, identify potential IAQ problem locations, identify staff and contractors whose activities affect indoor air quality. Review and revise staff responsibilities to ensure that responsibilities that may affect indoor air quality are clearly assigned.

In addition, establish lines of communication for sharing information pertaining to: equipment in need of repair or replacement, plans to remodel, renovate, or redecorate, new uses of building space or increases in occupant population, installation of new equipment.

Review standard procedures and make necessary revisions to promote good indoor air quality, such as: terms of contracts (e.g., pest control, leases), scheduling of activities that produce dust, emissions, odors, scheduling of equipment operation, inspection, and maintenance, specifications for supplies (e.g., cleaning products, construction materials, furnishings), policy regarding tobacco smoking within the building.

Review the existing recordkeeping system and make necessary revisions to: establish a system for logging IAQ related complaints, obtain Material Safety Data Sheets for hazardous materials used and stored in the building. Educate building staff, occupants, and contractors about their influence on indoor air quality by: establishing a health and safety committee, instituting training programs as needed. IAQ problems may occur even in buildings whose owners and managers conscientiously apply the best available information to avoid such problems. Those who can demonstrate their ongoing efforts to provide a safe indoor environment are in a strong legal and ethical position if problems do arise.

IAQ management will be facilitated if one individual is given overall responsibility for IAQ. Whether or not this person is given the title of "IAQ Manager," he or she should have a good understanding of the building's structure and function and should be able to communicate with tenants, facility personnel, and building owners or their representatives about IAQ issues. The IAQ manager's ongoing responsibilities might include: developing the IAQ profile, overseeing the adoption of new procedures, establishing a system for communicating with occupants about IAQ issues, coordinating staff efforts that affect indoor air quality, and making sure that staff have the information (e.g., operating manuals, training) and authority to carry out their responsibilities, reviewing all major projects in the building for their IAQ implications, reviewing contracts and negotiating with contractors (e.g., cleaning services, pest control contractors) whose routine activities in the building could create IAQ problems, periodically inspecting the building for indicators of IAQ problems, managing IAQ-related records, responding to complaints or observations regarding potential IAQ problems, conducting an initial walkthrough investigation of any IAQ complaints. If the IAQ manager was not actively involved in developing the IAQ profile, one of the first tasks will be to review the profile carefully. The manager can start by also identifying building locations with a potential for IAQ problems, staff and contractors whose activities impact indoor air quality, and other building occupants whose activities impact indoor air quality. In addition to information from the IAQ profile, it may be helpful to review lease forms and other

> ***As new practices are introduced to prevent indoor air quality problems, an organized system of recordkeeping will help those practices to become part of routine operations and to "flag" decisions that could affect IAQ. The best results can be achieved by taking time to think about the established channels of communication within your organization, so that new forms can be integrated into decision making with minimum disruption of normal procedures.***

contractual agreements for an understanding of the respective legal responsibilities of the building management, tenants, and contractors. Incorporation of IAQ concerns into legal documents helps to ensure the use of proper materials and procedures by contractors and can help to limit the load placed on ventilation equipment by occupant activities. The assignment of responsibilities varies widely between organizations, depending upon the routine activities to be carried out and the capabilities of the available personnel. It would not be appropriate for this document to suggest how IAQ-related responsibilities should be allocated in your organization.

Using information from the IAQ profile, the IAQ manager should work with staff and contractors to ensure that building operations and planning processes incorporate a concern for indoor air quality. New procedures, recordkeeping requirements, or staff training programs may be needed. The flow of information between the IAQ manager and staff, occupants, and contractors is particularly important. Good indoor air quality requires prompt attention to changing conditions that could cause IAQ problems, such as installation of new equipment or furnishings, increases in occupant population, or new uses of rooms. Indoor air quality can be affected both by the quality of maintenance and by the materials and procedures used in operating and maintaining the building components including the HVAC system. Facility staff who are familiar with building systems in general and with the features of their building in particular are an important resource in preventing and resolving indoor air quality problems. Facility personnel can best respond to indoor air quality concerns if they understand how their activities affect indoor air quality. It may be necessary to change existing practices or introduce new procedures in relation to the following:

Equipment operating schedules: Confirm that the timing of occupied and unoccupied cycles is compatible with actual occupied periods, and that the building is flushed by the ventilation system before occupants arrive. ASHRAE 62-1989 provides guidance on lead and lag times for HVAC equipment. In hot, humid climates, ventilation may be needed during long unoccupied periods to prevent mold growth.

Control of odors and contaminants: Maintain appropriate pressure relationships between building usage areas. Avoid recirculating air from areas that are strong sources of contaminants (e.g., smoking lounges, chemical storage areas, beauty salons). Provide adequate local exhaust for activities that produce odors, dust, or contaminants, or confine those activities to locations that are maintained under negative pressure (relative to adjacent areas). For example, loading docks are a frequent source of combustion odors. Maintain the rooms surrounding loading docks under positive pressure to prevent vehicle exhaust from being drawn into the building. Make sure that paints, solvents and other chemicals are stored and handled properly, with adequate (direct exhaust) ventilation provided. If local filter traps and adsorbents are used, they require regular maintenance. Have vendors provide Material Safety Data Sheets (MSDSs).

Ventilation quantities: Compare outdoor air quantities to the building design goal and local and State building codes and make adjustments as necessary. It is also informative to see how your ventilation rate compares to ASHRAE 62-1989, because that guideline was developed with the goal of preventing IAQ problems.

HVAC equipment maintenance schedules: Inspect all equipment regularly (per recommended maintenance schedule) to ensure that it is in good condition and is operating as designed (i.e., as close to the design setpoints for controls as possible). Most equipment manufacturers provide recommended maintenance schedules for their products. Components that are exposed to water (e.g., drainage pans, coils, cooling towers, and humidifiers) require scrupulous maintenance in order to prevent microbiological growth and the entry of undesired microbiologicals or chemicals into the indoor airstream.

HVAC inspections: Be thorough in conducting these inspections. Items such as small exhaust fans may operate independently from the rest of the HVAC system and are often ignored during inspections. As equipment is added, removed, or replaced, document any changes in function, capacity, or operating schedule for future reference. It may also be helpful to store equipment manuals and records of equipment operation and maintenance in the same location as records of occupant complaints for easy comparison if IAQ problems arise.

Building maintenance schedules: Try to schedule maintenance activities that interfere with HVAC operation or produce odors and emissions (e.g., painting, roofing operations) so that they occur when the building is unoccupied. Inform occupants when such activities are scheduled and, if possible, use local ventilation to ensure that dust and odors are confined to the work area.

Purchasing: Review the general information provided by MSDS and request information from suppliers about the chemical emissions of materials being considered for purchase.

PREVENTIVE MAINTENANCE PRACTICES

An HVAC system requires adequate preventive maintenance (PM) and prompt attention to repairs in order to operate correctly and provide suitable comfort conditions and good indoor air quality. The HVAC system operator(s) must have an adequate understanding of the overall system design, its intended function, and its limitations. The preventive maintenance program must be properly budgeted and implemented. A well-implemented PM plan will improve the functioning of the mechanical systems and usually save money when evaluated on a life-cycle basis. However, in some buildings, because of budgetary constraints, maintenance is put off until breakdowns occur or complaints arise, following the "if it isn't broken, don't fix it" philosophy. This type of program represents a false economy and often increases the eventual cost of repairs. Poor filter maintenance is a common example of this phenomenon. Filters that are not changed regularly can become a bed for fungal growth, sometimes allowing particles or microorganisms to be distributed within the building. When filters become clogged, the fans use more energy to operate and move less air. If the filters are an inexpensive, low-efficiency type that becomes clogged and then "blows out," the coils then accumulate dirt, causing another increase in energy consumption. Poor air filter efficiency and poor maintenance may cause dirt to build up in ducts and become contaminated with molds, possibly requiring an expensive duct cleaning operation.

The elements of a PM plan include: periodic inspection, cleaning, and service as warranted, adjustment and calibration of control system components, maintenance equipment and replacement parts that are of good quality and properly selected for the intended function. Critical HVAC system components that require PM in order to maintain comfort and deliver adequate ventilation air include: a outdoor air intake opening, damper controls, air filters, drip pans, cooling and heating coils, fan belts, humidification equipment and controls, distribution systems, exhaust fans.

Maintenance "indicators" are available to help facility staff determine when routine maintenance is required. For example, air filters are often neglected (sometimes due to reasons such as difficult access) and fail to receive maintenance at proper intervals. Installation of an inexpensive manometer, an instrument used to monitor the pressure loss across a filter bank, can give an immediate indication of filter condition without having to open the unit to visually observe the actual filter. Computerized systems are available that can prompt staff to carry out maintenance activities at the proper intervals. Some of these programs can be connected to building equipment so that a signal is transmitted to staff if a piece of equipment malfunctions. Individual areas can be monitored for temperature, air movement, humidity, and carbon dioxide, and new sensors are constantly entering the market.

These sensors can be programmed to record data and to control multiple elements of the HVAC system.

Indoor air quality complaints can arise from inadequate housekeeping that fails to remove dust and other dirt. On the other hand, cleaning materials themselves produce odors and emit a variety of chemicals. As they work throughout a building, cleaning staff or contractors may be the first to recognize and respond to potential IAQ problems.

SHIPPING AND RECEIVING

Shipping and receiving areas can create indoor air quality problems regardless of the types of materials being handled. Vehicle exhaust fumes can be minimized by prohibiting idling at the loading dock. This is particularly important if the loading dock is located upwind of outdoor air intake vents. You can also reduce drafts and pollutant entry by pressurizing interior spaces (e.g., corridors) and by keeping doors closed when they are not in use.

PEST CONTROL

Pest control activities that depend upon the use of pesticides involve the storage, handling, and application of materials that can have serious health effects. Common construction, maintenance practices, and occupant activities provide pests with air, moisture, food, warmth, and shelter. Caulking or plastering cracks, crevices, or holes to prevent harborage behind walls can often be more effective than pesticide application at reducing pest populations to a practical minimum. Integrated Pest Management (IPM) is a low-cost approach to pest control based upon knowledge of the biology and behavior of pests. Adoption of an IPM program can significantly reduce the need for pesticides by eliminating conditions that provide attractive habitats for pests. If an outside contractor is used for pest control, it is advisable to review the terms of the contract and include IPM principles where possible. The following items deserve particular attention. Schedule pesticide applications for unoccupied periods, if possible, so that the affected area can be flushed with ventilation air before occupants return. Pesticides should only be applied in targeted locations, with minimum treatment of exposed surfaces. They should be used in strict conformance with manufacturers' instructions and EPA labels. General periodic spraying may not be necessary. If occupants are to be present, they should be notified prior to the pesticide application. Particularly susceptible individuals could develop serious illness even though they are only minimally exposed. Select pesticides that are species specific and attempt to minimize toxicity for humans and non-target species. Ask contractors or vendors to provide EPA labels and MSDSs. Make sure that pesticides are stored and handled properly consistent with their EPA labels. If only limited areas of the building are being treated, adjust the HVAC system so that it does not distribute contaminated air throughout the rest of the building. Consider using temporary exhaust systems to remove contaminants during the work. It may be necessary to modify HVAC system operation during and after pest control activities (e.g., running air handling units on 100% outdoor air for some period of time or running the system for several complete air exchanges before occupants re-enter the treated space).

HOW TO DIAGNOSE IAQ PROBLEMS

Another name for the indoor air quality audit is a diagnostic building investigation. Remember, the goal is to identify and solve the indoor air quality complaint in a way that prevents it from recurring and that does not create other problems. An IAQ investigator should use only the investigative techniques that are needed. Many indoor air quality complaints can be resolved without using all of the diagnostic tools described in this chapter. For example, it may be easy to identify the source of odors that are annoying nearby office workers and solve the problem by controlling pressure relationships (e.g., installing exhaust fans). The use of in-house personnel builds skills that will be helpful in minimizing and resolving future problems. On the other hand, some jobs may be best handled by contractors who have specialized knowledge and experience. In the same way, diagnosing some indoor air quality problems may require equipment and skills that are complex and more sophisticated.

Any IAQ investigation begins with one or more reasons for concern, such as occupant complaints. Some complaints can be resolved very simply (e.g., by asking a few common sense questions of occupants and facility staff during the walkthrough). At the other extreme, some problems could require detailed testing by an experienced IAQ professional. The major steps are information gathering, hypothesis formation, and hypothesis testing. The goal of the investigation is to understand the IAQ problem well enough so that it can be resolved. Many IAQ problems have more than one cause and may respond to (or require) several corrective actions.

An initial walkthrough of the problem area provides information about all four of the basic factors influencing indoor air quality (occupants, HVAC system, pollutant pathways, and contaminant sources). The initial walkthrough may provide enough information to resolve the problem. At the least, it will direct further investigation. For example, if the complaint concerns an odor from an easily identified source, one may want to study pollutant pathways as a next step, rather than interviewing occupants about their patterns of discomfort. As one develops an understanding of how the building functions, where pollutant sources are located, and how pollutants move within the building, several hypotheses or potential explanations of the IAQ complaint may be formed. Building occupants and operating staff are often a good source of ideas about the causes of the problem. For example, they can describe changes in the building that may have occurred shortly before the IAQ problem was noticed (e.g., relocated partitions, new furniture or equipment). Hypothesis development is a process of identifying and narrowing down possibilities by comparing them with observations. Whenever a hypothesis suggests itself, it is reasonable to pause and consider it. Is the hypothesis consistent with the facts collected so far? One may be able to test the hypothesis by modifying the HVAC system or attempting to control the potential source or pollutant pathway to see whether the symptoms or other conditions in the building can be relieved. If the hypothesis successfully predicts the results of planned manipulations, then corrective action can be considered. Sometimes it is difficult or impossible to manipulate the factors you think are causing the IAQ problem; in that case, you may be able to test the hypothesis by trying to predict how building conditions will change over time (e.g., in response to extreme outdoor temperatures).

If the hypothesis or "model" does not seem to be a good predictor of what is happening in the building, you probably need to collect more information about the occupants, HVAC system, pollutant pathways, or contaminant sources. Under some circumstances, detailed or sophisticated measurements of pollutant concentrations or ventilation quantities may be required. Outside assistance may be needed if repeated efforts fail to produce a successful hypothesis or if the information required calls for instruments and procedures that are not available in-house. Analysis of the information collected during the IAQ investigation could produce any of the following results:

The apparent cause(s) of the complaint(s) is (are) identified: Remedial action and follow-up evaluation will confirm whether the hypothesis is correct.

Other IAQ problems are identified that are not related to the original complaints: These problems (e.g., HVAC malfunctions, strong pollutant sources) should be corrected when appropriate.

A better understanding of potential IAQ problems is needed in order to develop a plan for corrective action: It may be necessary to collect more detailed information and/or to expand the scope of the investigation to include building areas that were previously overlooked. Outside assistance may be needed.

The cause of the original complaint cannot be identified: A thorough investigation has found no deficiencies in HVAC design or operation or in the control of pollutant sources, and there have been no further complaints. In the absence of new complaints, the original complaint may have been due to a single, unrepeated event or to causes not directly related to IAQ.

An investigation may require one or many visits to the complaint area. The amount of preparatory work needed before the initial walkthrough varies with the nature and scope of the complaint and the expertise of the investigator, among other factors. For example, an in-house investigator who is already familiar with the layout and mechanical system in the building may begin responding to a complaint about discomfort by going directly to the complaint area to check the thermostat setting and see whether air is flowing from the supply outlets. If the investigator is not familiar with the building or is responding to complaints that suggest a serious health problem, more preparation may be needed before the initial walkthrough. The activities listed below can be directed at a localized "problem area" or extended to include the entire building:

Collect easily-available information about the history of the building and the complaints.

Identify known HVAC zones and complaint areas: Begin to identify potential sources and pollutants (e.g., special use areas near the complaint location). Having a copy of mechanical and floor plans can be helpful at this stage, especially if they are reasonably up-to-date.

Notify the building occupants of the upcoming investigation: Tell them what it means and what to expect.

Identify key individuals needed for access and information: A person familiar with the HVAC systems in the building should be available to assist the investigator at any time during the onsite phase. Individuals who have complained or who are in charge of potential sources (e.g., housekeeping, non- HVAC equipment) should be aware that their information is important and should be contacted for appointments or telephone interviews if they will not be available during the onsite visit.

The initial walkthrough provides an opportunity to question complainants about the nature and timing of their symptoms and to briefly examine the immediate area of the complaint. The investigator attempts to identify pollutant sources and types and observes the condition and layout of the HVAC system serving the complaint area. Staff can be asked to describe the operating schedule of equipment. Obvious problems (e.g., blocked diffusers, malfunctioning air handlers) can be corrected to see if the complaints disappear. The walkthrough can solve many routine IAQ problems and will suggest directions for a more complex investigation, should one be necessary. Some investigators avoid taking any measurements during the initial walkthrough so that they are not distracted from "getting the big picture." Others find that using smoke sticks, digital thermometers, and direct reading CO_2 meters or detector tubes to take occasional measurements helps them develop a feel for the building. Any instruments that will be used should be inspected to make sure they are in working order and calibrated. IAQ investigations generally include the use of, at a minimum: heatless chemical smoke devices and instruments for measuring temperature and humidity. Carbon dioxide measuring devices (detector tubes with a hand pump or a direct reading meter) are helpful for most investigations. Other instruments may be needed as the investigation progresses.

Collecting information on complaints is an essential part of the investigation. Occupant data falls into two categories: complaints of discomfort or other symptoms (e.g., teary eyes, chills) and perceptions of building conditions (e.g., odors, draftiness). Investigators can gather valuable information about potential indoor air problems by listening to occupants, and use that information for: defining the complaint area within the building; suggesting directions for further investigation, either by identifying other events that seem to happen at the same time as the incidents of symptoms or discomfort, or by identifying possible causes for the types of symptoms or discomfort that are occurring; indicating potential measures to reduce or eliminate the problem. If there is a record of occupant complaints, a review of that record can help to define the location of the IAQ problem and identify people who should be interviewed as part of the investigation. Information about the history of complaints could also stimulate theories about potential causes of the problem. The most obvious way to collect information from building occupants is to talk to them in person. If it is not possible to interview everyone who has complained about building conditions, the investigator should attempt to interview a group of individuals that reflects the concerns of the affected areas. The investigation may also include occupant interviews with building occupants who do not have complaints. Then conditions in the complaint area can be compared to conditions in similar building locations where there are no complaints. Many events occur simultaneously in and around a complex building, and it can be very difficult to judge which of those events might be related to the IAQ complaints. In trying to resolve stubborn problems, professional investigators sometimes ask occupants and facility staff to keep day-by-day records. Occupants are asked to record the date and time of symptoms, where they are when the symptoms appear, and any other information that might be useful. Such information could include observations about the severity and duration of symptoms and comments on weather conditions, events, and activities that are happening at the same time. Facility staff are asked to record the date and time of events such as maintenance work, equipment cycles, or deliveries. If symptoms seem to occur at particular times of day, staff can focus their attentions on recording events that occur before and during those periods. Such records are likely to produce more accurate and detailed information than can be obtained by relying on memory.

The pattern of complaints within the building helps to define the complaint area. The timing of symptoms and the types of symptoms reported may provide clues about the cause of the problem. The investigator should look for symptom patterns, and define the complaint area. Use the spatial pattern (locations) of complaints to define the complaint area. Building locations where symptoms or discomfort occur define the rooms or zones that should be given particular attention during the initial investigation. However, the complaint area may need to be revised as the investigation progresses. Pollutant pathways can cause occupant complaints in parts of the building that are far removed from the source of the problems. The investigator should also look for patterns in the timing of complaints. The timing of symptoms and complaints can indicate potential causes for the complaints and provide directions for further investigation. Review the data for cyclic patterns of symptoms (e.g., worst during periods of minimum ventilation or when specific sources are most active) that may be related to HVAC system operation or to other activities in and around the building. Look for patterns in the types of symptoms or discomfort. IAQ investigations often fail to prove that any particular pollutant or group of pollutants is the cause of the problem. Such causal relationships are extremely difficult to establish. There is little information available about the health effects of many chemicals. Typical indoor levels are much lower than the levels at which toxicology has found specific effects. Therefore, it may be more useful to look for patterns of symptoms than for specific pollutant and health effect relationships. Investigators who are not medically trained cannot make a diagnosis and should not attempt to interpret medical records. Also, confidentiality of medical information is protected by law in some jurisdictions and is a prudent practice everywhere. In general terms, indoor air quality is judged to be worse as temperatures rise above 76°F, regardless of the actual air quality. There is controversy concerning recommended levels of relative humidity. In general, the range of humidity levels recommended by different organizations seems to be 30% to 60% RH. Relative humidities below this level may produce discomfort from dryness. On the other hand, maintaining relative humidities at the lowest possible level helps to restrict the growth of mold and mildew.

The concerns (comfort for the most part) associated with dry air must be balanced against the risks (enhanced microbiological growth) associated with humidification. If temperatures are maintained at the lower end of the comfort range (68 to 70°F) during heating periods, relative humidity in most climates will not fall much below 30% (also within the comfort range) in occupied buildings.

IAQ complaints often arise because the quantity or distribution of outdoor air is inadequate to serve the ventilation needs of building occupants. Problems may also be traced to air distribution systems that are introducing outdoor contaminants or transporting pollutants within the building. The investigation should begin with the components of the HVAC system(s) that serve the complaint area and surrounding rooms, but may need to expand if connections to other areas are discovered. Your goal is to understand the design and operation of the HVAC system well enough to answer the following questions:

- Are the components that serve the immediate complaint area functioning properly?
- Is the HVAC system adequate for the current use of the building?
- Are there ventilation (or thermal comfort) deficiencies?
- Should the definition of the complaint area be expanded based upon the HVAC layout and operating characteristics?

An evaluation of the HVAC system may include limited measurements of temperature, humidity, air flow, as well as smoke tube observations. Complex investigations may require more extensive or sophisticated measurements of the same variables (e.g., repeated CO_2 measurements taken at the same location under different operating conditions, continuous temperature and relative humidity measurements recorded with a data logger).

A detailed engineering study may be needed if the investigation discovers problems such as the following:

- airflows are low
- HVAC controls are not working or are working according to inappropriate strategies
- building operators do not understand (or are unfamiliar with) the HVAC system

A review of existing documentation (e.g., plans, specifications, testing and balancing reports) should provide information about the original design and later modifications, particularly: the type of HVAC system (e.g., constant volume, VAV); locations and capacities of HVAC equipment serving the complaint area; the planned use of each building area; supply, return, and exhaust air quantities; location of the outdoor air intake and of the supply, return, and exhaust registers, diffusers, and grilles that serve the complaint area.

The most useful way to record this information is to make a floor plan of the complaint area and surrounding rooms. You may be able to copy an existing floor plan from architectural or mechanical drawings, fire evacuation plans, or some other source. If there is no documentation on the mechanical system design, much more onsite inspection will be required to understand the HVAC system. The HVAC system may have been installed or modified without being commissioned, so that it may never have performed according to design. In such cases, good observations of airflow and pressure differentials are essential. In addition, load analyses may be required.

It is important to note that IAQ complaints are often intermittent. Discussions with staff may reveal patterns that relate the timing of complaints to the cycles of equipment operation or to other events in the building such as painting, installation of new carpeting, or pest control. These patterns are not necessarily obvious. Keeping a day-to-day record may help to clarify subtle relationships between occupant symptoms, equipment operation, and activities in and around the building. If the building is new or if there is a preventive maintenance program with recent test and balance reports, it is possible that the HVAC system is functioning according to its original design. Otherwise it is probable that one or more features of building usage or system operation have changed in ways that could affect indoor air quality. Elements of the on-site investigation can include the following:

Check temperature and/or humidity to see whether the complaint area is in the comfort range: Take more than one measurement to account for variability over time and from place to place. Check thermostat operation. Check whether the supply air temperature corresponds to the design criteria. Use a hygrothermograph (if available) to log temperature and humidity changes in the complaint area.

Check for indicators of inadequate ventilation: Check supply diffusers to see if air is moving (using chemical smoke). If it is not, confirm that the fan system is operating, and then look for closed dampers, clogged filters, or signs of leaks. Compare design air quantities to building codes for the current occupancy or ventilation guidelines (e.g., ASHRAE 62-1989). If the HVAC system, performing as designed, would not provide enough ventilation air for current needs, then there is good reason to believe that actual ventilation rates are inadequate. Measure carbon dioxide in the complaint area to see whether it indicates ventilation problems. Measure air quantities supplied to and exhausted from the complaint area, including calculation of outdoor air quantities. Be aware of damper settings and equipment cycles when you are measuring (e.g., are you evaluating minimum outdoor air, "normal" conditions, or maximum airflow?). Note that evaluation of variable air volume (VAV) systems requires considerable expertise. Compare the measured air quantities to your mechanical system design specifications and applicable building codes. Also compare ventilation rates to ASHRAE 62-1989.

Check that equipment serving the complaint area (e.g., grilles, diffusers, fans) is operating properly: Confirm the accuracy of reported operating schedules and controls sequences; for example, power outages may have disrupted time clocks, fans reported as "always running" may have been accidentally switched off, and controls can be in need of calibration. Check to see that equipment is properly installed. For example, look for shipping screws that were never removed or fans that were reversed during installation, so that they move air in the wrong direction.

Compare the current system to the original design: Check to see that all equipment called for in the original design was actually installed. See whether original equipment may have been replaced by a different model (i.e., a model with less capacity or different operating characteristics).

See whether the layout of air supplies, returns, and exhausts promotes efficient air distribution to all occupants and isolates or dilutes contaminants: If supplies and returns are close together, heatless chemical smoke can be used to check for short-circuiting (supply air that does not mix properly with air in the breathing zone, but moves directly to the return grille). CO_2 can also be used to evaluate air mixing. Use heatless chemical smoke to observe airflow patterns within the complaint area and between the complaint area and surrounding spaces, including outdoors. Compare airflow directions under various operating conditions. If the system layout includes ceiling plenums, look above the ceiling for interruptions such as walls or full-height partitions.

Consider whether the HVAC system itself may be a source of contaminants: Check for deterioration or unsanitary conditions (e.g., corrosion, water damage or standing water, mold growth or excessive dust in ductwork, debris or damaged building materials in ceiling plenums). If the mechanical room serves as a mixing plenum (i.e., return and outdoor air are drawn through the room into the air handler), check very carefully for potential contaminants such as stored solvents and deteriorated insulation.

In reviewing the HVAC data, consider whether the system is adequate to serve the use of the building and whether the timing, location, and impact of apparent deficiencies appear related to the IAQ complaint. Deficiencies in HVAC design, operation, or maintenance may exist without producing the complaint under investigation; some defects may not cause any apparent IAQ problems. Strategies for corrective actions should be based on comparisons between the original design and the current system; comparing the original uses of space to current uses, and a consideration of the condition of the HVAC system.

Normal safety precautions observed during routine operation of the building must be followed closely during IAQ inspections. When the IAQ investigator is not familiar with the mechanical equipment in that particular facility, an operator or engineer should be present at all times in equipment areas. Potential safety hazards include:

- electrocution;
- injury from contacting fans, belts, dampers or slamming doors;
- burns from steam or hot water lines;
- falls in ventilation shafts or from ladders or roofs.

Investigators evaluating building IAQ generally do not encounter situations in which specific personal protection measures (e.g., protective garments and respirators) are required. However, safety shoes and eyeglasses are generally recommended for working around mechanical equipment. When severe contamination is present (e.g., microbiological, chemical, or asbestos), IAQ investigators may need additional protection in the vicinity of certain building areas or equipment. Such decisions are site-specific and should be made in consultation with an experienced industrial hygienist. General considerations include the following:

Microbiological: Care must be taken when serious building-related illness (e.g., Legionnaire's disease) is under investigation or when extensive microbiological growth has occurred. Investigators with allergy problems should be especially cautious. The array of potential contaminants makes it difficult to know what sort of personal protection will be effective. At a minimum, investigators should minimize their exposure to air in the interior of ducts or other HVAC equipment unless respiratory protection is used. If there is reason to suspect biological contamination (e.g., visible mold growth), expert advice should be obtained about the kind of respiratory protection to use and how to use it. Possible protective measures against severe microbiological contamination include disposable coveralls and properly fitted respirators.

Chemical: Where severe chemical contamination is suspected, specific precautions must be followed if OSHA action levels are approached. Such instances rarely occur in IAQ investigations. One possible exception might be a pesticide spill in a confined space. In this case, an appropriate respirator and disposable coveralls may be needed.

Asbestos: An IAQ investigation often includes inspection above accessible ceilings, inside shafts, and around mechanical equipment. Where material suspected of containing asbestos is not only present, but also has deposited loose debris, the investigator should take appropriate precautions. This might include disposable coveralls and a properly fitted respirator.

POLLUTANT PATHWAYS AND DRIVING FORCES

Unless the IAQ problem is caused by an obvious contaminant located in the complainant's immediate workspace, you will need to understand the patterns of airflow into and within the complaint area. Correction of IAQ problems often involves controlling pollutant movement through sealing of pollutant pathways or manipulation of the pressure relationships. If the complaints being investigated are limited to a few areas of the building, pollutant pathways can be evaluated so that the complaint area is properly defined before conducting the source inventory. If complaints are spread throughout the building, evaluation of pathways could be a very time-consuming process, and it may be more practical to look for major contaminant sources before trying to discover how the contaminants move within the building.

Architectural and mechanical pathways allow pollutants to enter the complaint area from surrounding spaces, including the outdoors. An examination of architectural and mechanical plans can help in developing a list of connections to surrounding areas. These include: doors, operable windows, stairways, elevator shafts with utility chases, ductwork and plenums, areas served by common HVAC controls (e.g., shared thermostats). Onsite inspection is needed to confirm the existence of these connections and to identify other openings (e.g., accidental openings such as cracks and holes). Fire codes usually require that chases and hidden openings be firestopped. Check for the existence and condition of firestops in chases, especially those that connect both vertically and horizontally.

The airflow quantities shown in mechanical plans or in testing and balancing reports can be used to determine the direction of air movement intended by the designer. Onsite examination is necessary to determine the actual direction of airflow at each available pathway. Chemical smoke tubes can be used to determine airflow directions between the complaint area and surrounding spaces (including the outdoors), and to reveal air circulation patterns within the complaint area. A micromanometer (or equivalent) can measure the magnitude of pressure differences between these areas. It may be necessary to make observations under different conditions, as airflow direction can change depending upon weather conditions, windspeed and direction, equipment operation within the building, traffic through doors, and other factors (e.g., as VAV systems throttle back).

Switching air handlers or exhaust fans on and off, opening and closing doors, and simulating the range of operating conditions in other ways can help to show the different ways that airborne contaminants move within the building. Dust tracking patterns around door frames can reveal the dominant direction of air and pollutant movement.

Some investigators study air movement by releasing a small amount of peppermint oil at the opening to a suspected pathway and asking an assistant to sniff for the "toothpaste" smell. If this technique is used, it is important that the assistant have an acute sense of smell. If the building is in use during the investigation, occupants may also notice the odor and could find it distracting. Some investigators prefer to use methods that release an odor during unoccupied periods. Investigators should note two common causes of false negative results (falsely concluding that no pathway exists):

- The nose quickly becomes tolerant of strong odors, so that the assistant may need to take a long rest (breathing fresh air) between tests.
- If there is substantial airflow through the pathway, the peppermint oil odor could be diluted so that it is imperceptible. Tracer gases such as sulfur hexafluoride (SF_6) can provide qualitative and quantitative information on pollutant pathways and ventilation rates. Use of tracer gases to obtain quantitative results requires considerable technical expertise. If it appears that a sophisticated study of pathways (or ventilation rates) is required, you need to use trained investigators.

Pollutant pathway information helps the investigator to understand airflow patterns in and around the complaint area. The pollutant pathway data may indicate a need to enlarge the complaint area, or may direct attention toward contaminant sources that deserve close study.

Evaluate airflow patterns into and within the complaint area. Because of the complexity and variability of airflow patterns, investigators cannot be expected to understand how air moves within the building under all potential operating conditions. However, data on pathways and driving forces can help to locate potential pollutant sources and to understand how contaminants are transported to building occupants. The discovery of unexpected pollutant pathways can show a need to study areas of the building that may be distant from the original complaint area.

Throughout the investigation, the building investigator will try to identify pollutant sources that may be causing the occupant complaints. Any public or commercial building is likely to contain a number of sources that produce odors, contaminants, or both.

The investigator's task is to identify the source(s) that may be responsible for the complaint(s). The area included in the pollutant source inventory should be defined by the investigator's understanding of the building's architectural and mechanical layout, as well as the pollutant pathways. Common sense will help to differentiate unusual sources (e.g., spills, strong odors from new furnishings or equipment, stains, vapors) from those that are normally found within or near the building. It is important to note that few sources of indoor air contaminants are both continuous and constant in volume over time. Pollutant concentrations often vary in strength over time, and may not be evident at the time of the site visit. Some sources are subtle and might only be noticed by a trained investigator. As the investigation progresses, the inventory of pollutant sources may need to be revised by expanding the definition of the complaint area or examining specific locations more closely (e.g., under various operating conditions).

Depending upon the nature of the complaint, the investigator may find some of the following activities to be useful: inventory outdoor sources; inventory equipment sources; review building components and furnishings; inventory other potential sources.

If a strong pollutant source is identified in the immediate vicinity of the complaint, a simple test (e.g., sealing, covering, or removing the source) can sometimes reveal whether or not it is the cause of the IAQ problem. If a number of potential sources have been found in and around the complaint area, other data (e.g., the pattern of symptoms, the HVAC system design and operation, and pollutant pathways) may be needed in order to determine which source(s), if any, may be related to the complaint. Strategies for using source information include: identify patterns linking emissions to complaints; evaluate unrelated sources; look for patterns linking emissions from potential sources to the IAQ complaints.

A detailed study of pollutants and sources may involve an engineering evaluation of equipment that is releasing IAQ contaminants, diagnostic sampling to assess sources in operation, or other measurements. These may require skills or instruments that are not available in-house. Although air sampling might seem to be the logical response to an air quality problem, such an approach may not be required to solve the problem and can even be misleading. Air sampling should not be undertaken until some or all of the other investigative activities mentioned previously have been used to collect considerable information. Before beginning to take air samples, investigators should develop a sampling strategy that is based on a comprehensive understanding of how the building operates, the nature of the complaints, and a plan for interpreting the results. It may be desirable to take certain routine air quality measurements during an investigation to obtain a "snapshot" of current conditions. These tests should be limited to those that are indicative of very common IAQ concerns such as temperature, relative humidity, air movement, or carbon dioxide (CO_2). Unusual readings may or may not indicate a problem, and should always be interpreted in perspective, based upon site-specific conditions.

Measurement of specific chemical or biological contaminants can be very expensive. Before expending time and money to obtain measurements of indoor air pollutants, you must decide: how the results will be used (e.g., comparison to standards or guidelines, comparison to levels in complaint-free areas); what substances(s) should be measured; where to take, samples; when to take samples; what sampling and analysis method to use so that the results provide useful information.

It is often worthwhile for building staff to develop skills in making temperature, humidity, airflow, and CO_2 measurements and assessing patterns of air movement (e.g., using chemical smoke).

Although air sampling will generate numbers, it will not necessarily help resolve the IAQ problem. Many IAQ complaints are resolved without sampling or with inconclusive sampling results. The design of an air sampling strategy should fit the intended use of the measurements. Potential uses of indoor air measurements include:

- Comparing different areas of the building or comparing indoor to outdoor conditions in order to: confirm that a control approach has the desired effect of reducing pollutant concentrations or improving ventilation. Establish baseline conditions so that they can be compared to concentrations at other times or locations, such as concentrations in outdoor air, concentrations in areas where no symptoms are reported, expected "background" range for typical buildings without perceived IAQ problems.
- Test a hypothesis about the source of the problem, such as: checking emissions from a piece of equipment. Testing for "indicator" compounds associated with particular types of building conditions: Peak carbon dioxide (CO_2) concentrations over 1000 ppm (parts per million) are an indicator of underventilation. Carbon monoxide (CO) over several ppm indicates inappropriate presence of combustion by-products (which may also account for high CO_2 readings). Compare any measured concentrations to guidelines or standards.

The following occupational exposure standards and guidelines should be referred to: OSHA PELs (Occupational Safety and Health Administration's Permissible Exposure Limits), NIOSH RELs (National Institute for Occupational Safety and Health's Recommended Exposure Limits), ACGIH TLVs (American Conference of Governmental Industrial Hygienists' Threshold Limit Values). Public health guidelines for specific pollutants can be found in the following: EPA National Ambient Air Quality Standards, the World Health Organization Air Quality Guidelines, and the Canadian Exposure Guidelines for Residential Air Quality.

There are no widely accepted procedures to define whether IAQ test results are acceptable. Caution must be used in comparing contaminant concentrations to existing occupational standards and guidelines. Although a contaminant concentration above those guidelines is a problem indicator, occupants may still experience health and comfort problems at concentrations well within those guidelines. It is extremely rare for occupational standards to be exceeded, or even approached in public and commercial buildings, including those experiencing indoor air quality problems. Where specific exposure problems are suspected, more detailed diagnostic testing may be needed to locate or understand major sources, confirm the exposure, and to develop appropriate remedial actions. For example, the control of microbial or pesticide contamination may involve surface or bulk sampling. Surface sampling involves wiping a measured surface area and analyzing the swab to see what organisms are present, while bulk sampling involves analyzing a sample of suspect material. Specialized skills, experience, and equipment may be needed to obtain, analyze, and interpret such measurements.

The conditions experienced by building occupants are best simulated by sampling air from the "breathing zone" away from the influence of any particular individual. However, if an individual sits at a desk all day (except for brief periods), samplers placed on the desk when the individual is elsewhere can provide a good estimate of that person's exposure.

Measurement of "indicator" compounds such as CO_2 or CO can be a cost-effective strategy. Such measurements can help the investigator understand the nature of the problem and define the complaint area. Air sampling for specific pollutants works best as an investigative tool when it is combined with other types of information gathering. It is prudent to begin a program of chemical sampling only if symptoms or observations strongly suggest that a specific pollutant or a specific source may be the cause of the complaint and if sampling results are important in determining an appropriate corrective action. The identified problem area is an obvious site for air sampling.

Measurements taken outdoors and in a control location (e.g., a complaint-free area of the building) are helpful in interpreting results from the complaint area.

There are several ways to locate sampling sites for an IAQ investigation. One approach first divides the building into homogeneous areas based on key factors identified in the building inspection and interviews. Examples of how a building might be divided include: control zones (e.g., individual rooms); types of HVAC zones (e.g., interior vs. perimeter); complaint versus noncomplaint areas that define a relationship to major sources (e.g., spaces directly, indirectly, or not impacted by smoking areas or exhaust fumes from a piece of equipment); complaint types. Test sites can then be selected to represent complaints, controls, and potential sources with a reasonable number of samples.

Samples may be designed to obtain "worst case" conditions, such as measurements during periods of maximum equipment emissions, minimum ventilation, or disturbance of contaminated surfaces. Worst-case sample results can be very helpful in characterizing maximum concentrations to which occupants are exposed and identifying sources for corrective measures. It is also helpful to obtain samples during average or typical conditions as a basis of comparison. It may, however, be difficult to know what conditions are typical. Exposure to some pollutants may vary dramatically as building conditions change. Devices that allow continuous measurements of key variables can be helpful.

Symptoms or odors that only occur occasionally will not generally be seen during the IAQ investigation. Air samples should not be taken if an incident is not occurring, unless the purpose of the sample is to establish a baseline for future comparisons. One approach to intermittent IAQ problems is for the IAQ investigator to ask appropriate building staff or other occupants to document changes over time using day-to-day records such as an Occupant Diary and Log of Activities and System Operation. When an odor episode does occur, the building engineer could inspect the air handler and intake area while another staff member documents the status of several potential sources. Another strategy is to manipulate building conditions to create worst-case conditions during the building investigation. Chemical smoke and tracer gases can be used to assess where emissions may travel under various building conditions. Such strategies should be carried out in ways that minimize occupant exposure. Care should be taken in selecting the appropriate measurement techniques and to provide proper analysis so that the results provide useful information.

CONTROL

Many types of mitigation (correction) strategies have been implemented to solve indoor air quality problems. Mitigation of indoor air quality problems may require the involvement of building management and staff representing such areas of responsibility as: facility operation and maintenance, housekeeping, shipping and receiving, purchasing, policymaking, staff training. Successful mitigation of IAQ problems also requires the cooperation of other building occupants, including the employees of building tenants. Occupants must be educated about the cause(s) of the IAQ problems and about actions that must be taken or avoided to prevent a recurrence of the problems. Efforts to control indoor air contaminants change the relationships between these factors. There are many ways that people can intervene in these relationships to prevent or control indoor air contaminant problems. Control strategies can be categorized as: source control, ventilation, air cleaning, and exposure control. Successful mitigation often involves a combination of these strategies.

SOURCE CONTROL

All efforts to prevent or correct IAQ problems should include an effort to identify and control pollutant sources. Source control is generally the most cost effective approach to mitigating IAQ problems in which point sources of contaminants can be identified. In the case of a strong source, source control may be the only solution that will work. The following are categories and examples of source control:

Remove or reduce the source: Prohibit smoking indoors or limit smoking to areas from which air is exhausted, not recirculated (NIOSH regards smoking areas as an interim solution). Relocate contaminant-producing equipment to an unoccupied, better ventilated, or exhaust-only ventilated space. Select products which produce fewer or less potent contaminants while maintaining adequate safety and efficiency. Modify other occupant activities.

Seal or cover the source: Improve storage of materials that produce contaminants. Seal surfaces of building materials that emit VOCs such as formaldehyde.

Modify the environment: After cleaning and disinfecting an area that is contaminated by fungal or bacterial growth, control humidity to make conditions inhospitable for regrowth.

Source removal or reduction can sometimes be accomplished by a one-time effort such as thorough cleaning of a spill. In other cases, it requires an ongoing process, such as establishing and enforcing a non-smoking policy. Sealing or covering the source can be a solution in some cases; application of a barrier over formaldehyde-emitting building materials is an example.

Sealing may also involve educating staff or building occupants about the contaminant-producing features of materials and supplies and inspecting storage areas to ensure that containers are properly covered. In some cases, modification of the environment is necessary for effective mitigation. If the indoor air problem arises from microbiological contaminants, for example, disinfection of the affected area may not eliminate the problem.

Regrowth of microbiologicals could occur unless humidity control or other steps, such as adding insulation to prevent surface condensation, are taken to make the environment inhospitable to microbiologicals.

VENTILATION

Ventilation modification is often used to correct or prevent indoor air quality problems. This approach can be effective either where buildings are underventilated or where a specific contaminant source cannot be identified. Ventilation can be used to control indoor air contaminants by:

Diluting contaminants with outdoor air may increase the total quantity of supply air (including outdoor air): Increase the proportion of outdoor air to total air, and also the improve air distribution.

Isolating or removing contaminants by controlling air pressure relationships and install effective local exhaust at the location of the source: Avoid recirculation of air that contains contaminants. Locate occupants near supply diffusers and sources near exhaust registers. Use air-tightening techniques to maintain pressure differentials and eliminate pollutant pathways. Make sure that doors are closed where necessary to separate zones. Diluting contaminants by increasing the flow of outdoor air can be accomplished by increasing the total supply airflow in the complaint area (e.g., opening supply diffusers, adjusting dampers) or at the air handling unit, (e.g., cleaning the filter on the supply fan). An alternative is to increase the proportion of outdoor air (e.g., adjusting the outdoor air intake damper, installing minimum stops on variable air volume (VAV) boxes so that they satisfy the outdoor air requirements of ASHRAE 62-1989). Increasing ventilation rates to meet ASHRAE Standard 62-1989 (e.g., from 5 to 15 or 20 cfm/person) does not necessarily significantly increase the total annual energy consumption. The increase appears to be less than 5% in typical commercial buildings. The cost of ventilation is generally overshadowed by other operating costs, such as lighting. Further, improved maintenance can produce energy savings to balance the costs that might otherwise result from increased ventilation. The cost of modifying an existing HVAC system to condition additional outdoor air can vary widely depending upon the specific situation. In some buildings, HVAC equipment may not have sufficient capacity to allow successful mitigation using this approach. Original equipment is often oversized so that it can be adjusted to handle the increased load, but in some cases additional capacity is required. Most ventilation deficiencies appear to be linked to inadequate quantities of outdoor air. However, inadequate distribution of ventilation air can also produce IAQ problems. Diffusers should be properly selected, located, installed, and maintained so that supply air is evenly distributed and blends thoroughly with room air in the breathing zone. Short- circuiting occurs when clean supply air is drawn into the return air plenum before it has mixed with the dirtier room air and therefore fails to dilute contaminants. Mixing problems can be aggravated by temperature stratification. Stratification can occur, for example, in a space with high ceilings in which ceiling-mounted supply diffusers distribute heated air.

The side effects of increased ventilation include:

- mitigation by increasing the circulation of outdoor air requires good outdoor air quality
- increased supply air at the problem location might mean less supply air in other areas
- increased total air in the system and increased outdoor air will both tend to increase energy consumption and may require increased equipment capacity
- any approach which affects airflow in the building can change pressure differences between rooms (or zones) and between indoors and outdoors, and might lead to increased infiltration of unconditioned outdoor air
- increasing air in a VAV system may overcool an area to the extent that terminal reheat units are needed

Ventilation equipment can be used to isolate or remove contaminants by controlling pressure relationships. If the contaminant source has been identified, this strategy can be more effective than dilution. Techniques for controlling air pressure relationships range from adjustment of dampers to installation of local exhaust.

Using local exhaust confines the spread of contaminants by capturing them near the source and exhausting them to the outdoors. It also dilutes the contaminant by drawing cleaner air from surrounding areas into the exhaust airstream. If there are return grilles in a room equipped with local exhaust, the local exhaust should exert enough suction to prevent recirculation of contaminants. Properly designed and installed local exhaust results in far lower contaminant levels in the building than could be accomplished by a general increase in dilution ventilation, with the added benefit of costing less.

Replacement air must be able to flow freely into the area from which the exhaust air is being drawn. It may be necessary to add door or wall louvers in order to provide a path for the make-up air. (Make sure that this action does not violate fire codes.)

Identification of the pollutant source and installation of the local exhaust is critically important. For example, an improperly designed local exhaust can draw other contaminants through the occupied space and make the problem worse. The physical layout of grilles and diffusers relative to room occupants and pollutant sources can be important. If supply diffusers are all at one end of a room and returns are all at the other end, the people located near the supplies may be provided with relatively clean air while those located near the returns breathe air that has already picked up contaminants from all the sources in the room that are not served by local exhaust.

Elimination of pollutant pathways by air sealing (e.g., caulking cracks, closing holes) is an approach that can increase the effectiveness of other control techniques. It can be a difficult technique to implement because of hidden pathways (e.g., above drop ceilings, under raised flooring, against brick or block walls). However, it can have other benefits such as energy savings and more effective pest control (by eliminating paths used by vermin).

AIR CLEANING

Another IAQ control strategy is to clean the air. Air cleaning is usually most effective when used in conjunction with either source control or ventilation; however, it may be the only approach when the source of pollution is outside of the building. Most air cleaning in large buildings is aimed primarily at preventing contaminant buildup in HVAC equipment and enhancing equipment efficiency. Air cleaning equipment intended to provide better indoor air quality for occupants must be properly selected and designed for the particular pollutants of interest (for example, gaseous contaminants can be removed only by gas sorption). Once installed, the equipment requires regular maintenance in order to ensure good performance; otherwise it may become a major pollutant source in itself. This maintenance requirement should be borne in mind if an air cleaning system involving a large number of units is under consideration for a large building. If room units are used, the installation should be designed for proper air recirculation. There are four technologies that remove contaminants from the air: particulate filtration, electrostatic precipitation, negative ion generation, and gas sorption. The first three approaches are designed to remove particulate matter, while the fourth is designed to remove gases.

Particulate filtration removes suspended liquid or solid materials whose size, shape, and mass allow them to remain airborne at the air velocity conditions present. Filters are available in a range of efficiencies, with higher efficiency indicating removal of a greater proportion of particles and of smaller particles. Moving to medium efficiency pleated filters is advisable to improve IAQ and increase protection for equipment. However, the higher the efficiency of the filter, the more it will increase the pressure drop within the air distribution system and reduce total airflow (unless other adjustments are made to compensate). It is important to select an appropriate filter for the specific application and to make sure that the HVAC system will continue to perform as designed. Filters are rated by different standards which measure different aspects of performance.

Electrostatic precipitation is another type of particulate control. It uses the attraction of charged particles to oppositely charged surfaces to collect airborne particulate matter. In this process, the particles are charged by ionizing the air with an electric field. The charged particles are then collected by a strong electric field generated between oppositely-charged electrodes. This provides relatively high efficiency filtration of small respirable particles at low air pressure losses. Electrostatic precipitators may be installed in air distribution equipment or in specific usage areas. As with other filters, they must be serviced regularly. Note, however, that electrostatic precipitators produce some ozone. Because ozone is harmful at elevated levels, EPA has set standards for ozone concentrations in outdoor air, and NIOSH and OSHA have established guidelines and standards, respectively, for ozone in indoor air. The amount of ozone emitted from electrostatic precipitators varies from model to model.

Negative ion generators use static charges to remove particles from the indoor air. When the particles become charged, they are attracted to surfaces such as walls, floors, table tops, draperies, and occupants. Some designs include collectors to attract the charged particles back to the unit. Negative ion generators are not available for installation in ductwork, but are sold as portable or ceiling-mounted units. As with electrostatic precipitators, negative ion generators may produce ozone, either intentionally or as a by-product of use.

Gas sorption is used to control compounds that behave as gases rather than as particles (e.g., gaseous contaminants such as formaldehyde, sulfur dioxide, ozone, and oxides of nitrogen). Gas sorption involves one or more of the following processes with the sorption material (e.g., activated carbon, chemically treated active clays): a chemical reaction between the pollutant and the sorbent; a binding of the pollutant and the sorbent; or diffusion of the contaminant from areas of higher concentration to areas of lower concentration. Gas sorption units are installed as part of the air distribution system. Each type of sorption material performs differently with different gases. Gas sorption is not effective for removing carbon monoxide. There are no standards for rating the performance of gaseous air cleaners, making the design and evaluation of such systems problematic. Operating expenses of these units can be quite high, and the units may not be effective if there is a strong source nearby.

Exposure control is an administrative approach to mitigation that uses behavioral methods, such as:

Scheduling contaminant-producing activities to avoid complaints: Schedule contaminant-producing activities to occur during unoccupied periods. Notify susceptible individuals about upcoming events (e.g., roofing, pesticide application) so that they can avoid contact with the contaminants. Scheduling contaminant-producing activities for unoccupied periods whenever possible is simple common sense. It may be the best way to limit complaints about activities (such as roofing or demolition) which unavoidably produce odors or dust.

Relocating or rotating susceptible individuals: Move susceptible individuals away from the area where they experience symptoms. Controlling exposure by relocating susceptible individuals may be the only practical approach in a limited number of cases, but it is probably the least desirable option and should be used only when all other strategies are ineffective in resolving complaints.

Mitigation efforts should be evaluated at the planning stage by considering the following criteria: permanence, operating principle, degree to which the strategy fits the job, ability to institutionalize the solution, durability, installation and operating costs, conformity with codes. Mitigation efforts that create permanent solutions to indoor air problems are clearly superior to those that provide temporary solutions (unless the problems are also temporary). Opening windows or running air handlers on full outdoor air may be suitable mitigation strategies for a temporary problem such as outgasing of volatile compounds from new furnishings, but would not be good ways to deal with emissions from operating equipment. A permanent solution to microbiological contamination involves not only cleaning and disinfection, but also modification of the environment to prevent regrowth.

The most economical and successful solutions to IAQ problems tend to be those in which the operating principle of the correction strategy makes sense and is suited to the problem. If a specific point source of contaminants has been identified, treatment at the source (e.g., by removal, scaling, or local exhaust) is almost always a more appropriate correction strategy than dilution of the contaminant by increased general ventilation. If the IAQ problem is caused by the introduction of outdoor air that contains contaminants, increased general ventilation will only make the situation worse (unless the outdoor air is cleaned). It is important to make sure that one understands the IAQ problem well enough to select a correction strategy whose size and scope fit the job. If odors from a special use area such as a kitchen are causing complaints in a nearby office, increasing the ventilation rate in the office may not be a successful approach. The mitigation strategy should address the entire area affected.

If mechanical equipment is needed to correct the IAQ problem, it must be powerful enough to accomplish the task. For example, a local exhaust system should be strong enough and close enough to the source so that none of the contaminant is drawn into nearby returns and recirculated. A mitigation strategy will be most successful when it is institutionalized as part of normal building operations. Solutions that do not require exotic equipment are more likely to be successful in the long run than approaches that involve unfamiliar concepts or delicately maintained systems. If maintenance or housekeeping procedures or supplies must change as part of the mitigation, it may be necessary to plan for additional staff training, new inspection checklists, or modified purchasing practices. Operating schedules for HVAC equipment may also require modification.

IAQ mitigation strategies that are durable and low-maintenance are more attractive to owners and building staff than approaches that require frequent adjustment or specialized maintenance skills. New items of equipment should be quiet, energy-efficient, and durable, so that the operators are encouraged to keep them running.

The approach with the lowest initial cost may not be the least expensive over the long run. Other economic considerations include: energy costs for equipment operation; increased staff time for maintenance; differential cost of alternative materials and supplies; and higher hourly rates if odor-producing activities (e.g., cleaning) must be scheduled for unoccupied periods. Although these costs will almost certainly be less than the cost of letting the problem continue, they are more readily identifiable, so an appropriate presentation to management may be required. Any modification to building components or mechanical systems should be designed and installed in keeping with applicable fire, electrical, and other building codes.

Two kinds of criteria can be used to judge the success of an effort to correct an indoor air problem: reduced complaints, and measurement of properties of the indoor air. Reduction or elimination of complaints appears to be a clear indication of success, but that is not necessarily the case. Occupants who see that their concerns are being heard may temporarily stop reporting discomfort or health symptoms, even if the actual cause of their complaints has not been addressed. Lingering complaints may also continue after successful mitigation if people have become upset over the handling of the problem. Ongoing (but reduced) complaints could also indicate that there were multiple IAQ problems and that one or more problems are still unresolved. However, it can be very difficult to use measurements of contaminant levels as a means of determining whether air quality has improved. Concentrations of indoor air pollutants typically vary greatly over time; further, the specific contaminant measured may not be causing the problem. If air samples are taken, readings taken before and after mitigation should be interpreted cautiously. It is important to keep the "before" and "after" conditions as identical as possible, except for the operation of the control strategy. For example, the same HVAC operation, building occupancy and climatic conditions should apply during both measurement periods. "Worst-case" conditions identified during the investigation should be used.

Measurements of airflows, ventilation rates, and air distribution patterns are the more reliable methods of assessing the results of control efforts. Airflow measurements taken during the building investigation can identify areas with poor ventilation; later they can be used to evaluate attempts to improve the ventilation rate, distribution, or direction of flow. Studying air distribution patterns will show whether a mitigation strategy has successfully prevented a contaminant from being transported by airflow.

Solving an indoor air quality problem is a cyclical process of data collection and hypothesis testing. Deeper and more detailed investigation is needed to suggest new hypotheses after any unsuccessful or partially-successful control attempt. Even the best planned investigations and mitigation actions may not produce a resolution to the problem. You may have made a careful investigation, found one or more apparent causes for the problem, and implemented a control system. Nonetheless, your correction strategy may not have caused a noticeable reduction in the concentration of the contaminant or improvement in ventilation rates or efficiency. Worse, the complaints may persist even though you have been successful at improving ventilation and controlling all of the contaminants you could identify.

When you have pursued source control options and have increased ventilation rates and efficiency to the limits of your expertise, you must decide how important it is to pursue the problem further. If you have made several unsuccessful efforts to control a problem, then it may be advisable to seek outside assistance. The problem is probably fairly complex, and it may occur only intermittently or cross the borders that divide traditional fields of knowledge. It is even possible that poor indoor air quality is not the actual cause of the complaints. Bringing in a new perspective at this point can be very effective.

Many IAQ problems are simple to resolve when facility staff have been educated about the investigation process. In other cases, however, a time comes when outside assistance is needed. Professional help might be necessary or desirable in the following situations, as examples:

- Mistakes or delays could have serious consequences (e.g., health hazards, liability exposure, regulatory sanctions).
- Building management feels that an independent investigation would be better received or more effectively documented than an in-house investigation.
- Investigation and mitigation efforts by facility staff have not relieved the IAQ problem.
- Preliminary findings by staff suggest the need for measurements that require specialized equipment and training beyond in-house capabilities.

Aside from private consultants, local, state, or federal government agencies may be able to provide expert assistance or direction in solving IAQ problems. It is particularly important to contact a local or state health department if one suspects that there is a serious building-related illness potentially linked to biological contamination in a building.

If available government agencies do not have personnel with the appropriate skills to assist in solving your IAQ problem, they may be able to direct you to firms in your area with experience in indoor air quality work. Note that even certified professionals from disciplines closely related to IAQ issues (such as industrial hygienists, ventilation engineers, and toxicologists) may not have the specific expertise needed to investigate and resolve indoor air problems. Individuals or groups that offer services should be questioned closely about their related experience and their proposed approach to the problem. As with any hiring process, the better you know your own needs, the easier it will be to select a firm or individual to service those needs. Firms and individuals working in IAQ may come from a variety of disciplines.

Typically, the skills of HVAC engineers and industrial hygienists are useful for this type of investigation, although input from other disciplines such as chemistry, chemical engineering, architecture, microbiology, or medicine may also be important. If problems other than indoor air quality are involved, experts in lighting, acoustic design, interior design, psychology, or other fields may be helpful in resolving occupant complaints about the indoor environment.

Building owners and managers who suspect that they may have a problem with a specific pollutant (such as radon, asbestos, or lead) may be able to obtain assistance from local and state health departments. Government agencies and affected industries have developed training programs for contractors who diagnose or mitigate problems with these particular contaminants.

Consultants being considered should have familiarity with state and local regulations and codes. For example, in making changes to the HVAC system, it is important to conform to local building codes. Heating, cooling, and humidity control needs are different in different geographic regions, and can affect the selection of an appropriate mitigation approach. Getting assurances that all firms under consideration have this knowledge becomes particularly important if it becomes necessary to seek expertise from outside the local area.

Firms should be asked to provide references from clients who have received comparable services. In exploring references, it is useful to ask about long-term follow-up. After the contract was completed, did the contractor remain in contact with the client to ensure that problems did not recur?

If projected costs jump suddenly during the investigation process, the consultants should be able to justify that added cost. The budget will be influenced by a number of factors, including: the complexity of the problem, the size and complexity of the building and its HVAC system(s), the quality and extent of recordkeeping by building staff and management, the type of report or other product required, the number of meetings required (formal presentations can be quite expensive), air sampling (e.g., use of instruments, laboratory analysis) if required.

QUANTIFICATION AND MEASUREMENT

The following is a brief introduction to making measurements that might be needed in the course of developing an IAQ profile or investigating an IAQ complaint. Emphasis has been placed on the parameters most commonly of interest in non-research studies, highlighting the more practical methods and noting some inappropriate tests to avoid. Most of the instruments discussed in this section are relatively inexpensive and readily available from many local safety supply companies. Air contaminants of concern in IAQ can be measured by one or more of the methods described below.

VACUUM PUMP

A vacuum pump with a known airflow rate draws air through collection devices, such as a filter (catches airborne particles), a *sorbent tube* (which attracts certain chemical vapors to a powder such as carbon), or an *impinger* (bubbles the contaminants through a solution in a test tube). Tests originated for industrial environments typically need to be adjusted to a lower detection limit for IAQ work. Labs can be asked to report when trace levels of an identifiable contaminant are present below the limit of quantification and detection. In adapting an industrial hygiene sorbent tube sampling method for IAQ, the investigator must consider at least two important questions.

- First: are the emissions to be measured from a product's end use the same as those of concern during manufacturing?
- Second: is it necessary to increase the air volume sampled? Such an increase may be needed to detect the presence of contaminants at the low concentrations usually found in non-industrial settings. *For example, an investigator might have to increase sampling time from 30 minutes to 5 hours in order to detect a substance at the low concentrations found during IAQ investigations.* In cases where standard sampling methods are changed, qualified industrial hygienists and chemists should be consulted to ensure that accuracy and precision remain acceptable.

DIRECT-READING METER AND DETECTOR TUBE KIT

Direct-reading meters estimate air concentrations through one of several detection principles. These may report specific chemicals (e.g., CO_2 by infrared light), chemical groups (e.g., certain volatile organics by photoionization potential), or broad pollutant categories (e.g., all respirable particles by scattered light). Detection limits and averaging time developed for industrial use may or may not be appropriate for IAQ.

Detector tube kits generally include a hand pump that draws a known volume of air through a chemically treated tube intended to react with certain contaminants. The length of color stain resulting in the tube correlates to chemical concentration.

PERSONAL MONITORING DEVICES

Personal monitoring devices (sometimes referred to as "dosimeters") are carried or worn by individuals and are used to measure that individual's exposure to particular chemical(s). Devices that include a pump are called "active" monitors; devices that do not include a pump are called "passive" monitors. Such devices are currently used for research purposes. It is possible that sometime in the future they may also be helpful in IAQ investigations in public and commercial buildings.

PERSONAL SAMPLING

The following are OSHA recommended guidelines for air sampling programs normally implemented under the guidance of an industrial hygienist. Unnecessary air sampling can tie up laboratory resources and produce delays in reporting results of necessary sampling. One must evaluate the potential for employee overexposure through observation and screening samples before any partial or full-shift air sampling is conducted. Do not overexpose the employee to gather a sample. Screening with portable monitors, gravimetric sampling, or detector tubes can be used to evaluate the following:

a. Processes, such as electronic soldering,

b. Exposures to substances with exceptionally high PELs (Permissible Exposure Limits) in relatively dust-free atmospheres, e.g., ferric oxide and aluminum oxide,

c. Intermittent processes with substances without STELs (Short Term Exposure Limits),

d. Engineering controls, work practices, or

e. To assess the need for personal protection.

The objective of a proper sampling program is to take a sufficient number of samples to obtain a representative estimate of exposure. Contaminant concentrations vary seasonally, with weather, with production levels, and in a single location or job class. The number of samples taken depends on the error of measurement and differences in results. It is important also that if the employer has conducted air sampling and monitoring in the past, a thorough review of the records should be made.

Bulk Samples are often required to assist the laboratory in the proper analysis of field samples. The following are some general sampling procedures:

1. Screen the sampling area using detector tubes, if appropriate. Determine the appropriate sampling technique. Prepare and calibrate the equipment and prepare the filter media.
2. Select the employee to be sampled and discuss the purpose of the sampling. Inform the employee when and where the equipment will be removed. Stress the importance of not removing or tampering with the sampling equipment. Turn off or remove sampling pumps before an employee leaves a potentially contaminated area (such as when he/she goes to lunch or on a break).
3. Instruct the employee to notify the supervisor if the sampler requires temporary removal.
4. Place the sampling equipment on the employee so that it does not interfere with work performance.
5. Attach the collection device (filter cassette, charcoal tube, etc.) to the shirt collar or as close as practical to the nose and mouth of the employee). Employee exposure is that exposure which would occur if the employee were not using a respirator. The inlet should always be in a downward vertical position to avoid gross contamination. Position the excess tubing so as not to interfere with the work of the employee.
6. Turn on the pump and record the starting time.
7. Observe the pump operation for a short time after starting to make sure it is operating correctly.
8. Record the information required.

9. Check pump status every two hours. More frequent checks may be necessary with heavy filter loading. Ensure that the sampler is still assembled properly and that the hose has not become pinched or detached from the cassette or the pump. For filters, observe for symmetrical deposition, fingerprints, or large particles, etc. Record the flow rate, if possible.
10. Periodically monitor the employee throughout the work day to ensure that sample integrity is maintained and cyclical activities and work practices are identified.
11. Take photographs, as appropriate, and detailed notes concerning visible airborne contaminants, work practices, potential interferences, movements, and other conditions to assist in determining appropriate engineering controls.
12. Prepare a blank(s) during the sample period for each type of sample collected. For any given analysis, one blank will suffice for up to 20 samples collected. These blanks may include opened but unused charcoal tubes, and so forth.
13. Before removing the pump at the end of the sample period, check the flow rate to ensure that the rotameter bail is still at the calibrated mark (if there is a pump rotameter). If the ball is no longer at the mark, record the pump rotameter reading.
14. Turn off the pump and record the ending time.
15. Remove the collection device from the pump and seal it as soon as possible. The seal should be attached across sample inlet and outlet so that tampering is not possible.
16. Prepare the samples for transport to laboratory for analysis.
17. Recalibrate pumps after each day of sampling (before charging).

The reader should refer to the OSHA Technical Manual, issued February 5, 1990, for specific air sampling procedures.

1. Detector Tubes

a. Each pump should be leak-tested before use. Calibrate the detector tube pump for proper volume at least quarterly or after 100 tubes.

2. Total Dust and Metal Fume

a. Collect total dust on a pre-weighed, low-ash polyvinyl chloride fitter at a flow rate of about 2 liters per minute (lpm), depending on the rate required to prevent overloading.

b. Collect metal fumes on a 0.8 micron mixed cellulose ester filter at a flow rate of approximately 1.5 lpm, not to exceed 2.0 lpm. Do not collect metal fumes on a low-ash polyvinyl chloride filter.

c. Avoid any overloading of the filter, as evidenced by any loose particulate.

d. Calibrate personal sampling pumps before and after each day of sampling, using a bubble meter method (electronic or mechanical) or the precision rotameter method (that has been calibrated against a bubble meter).

e. Weigh filters before and after taking the sample.

3. Respirable Dust

a. Collect respirable silica dust using a clean cyclone equipped with a pre-weighed low-ash polyvinyl chloride filter.

b. Collect silica only as a respirable dust. A bulk sample should be submitted to the laboratory.

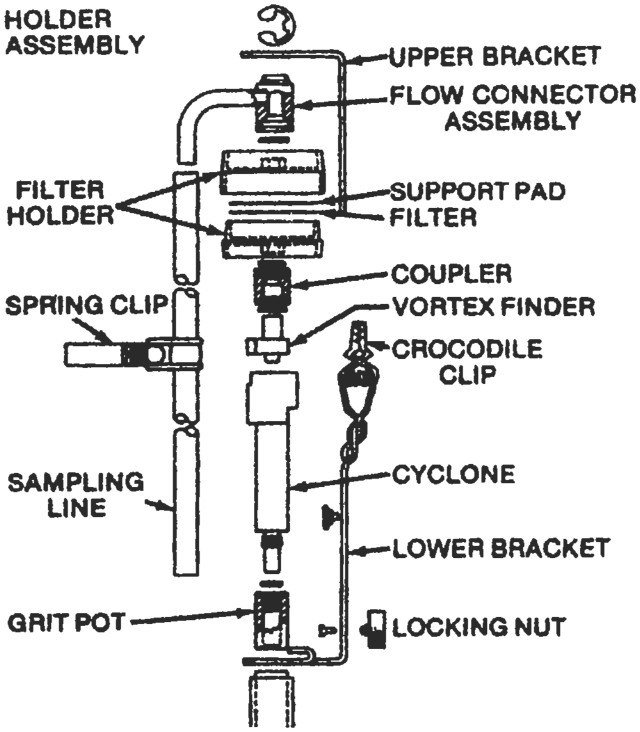


Figure 1. Cyclone (chamber).

c. All filters used should be pre-weighed and post-weighed.

d. Calibration Procedures:(1) Do the calibration at the pressure and temperature where the sampling is to be conducted. (2) Replace the filter with a 1-liter jar containing the cassette holder assembly and cyclone or the open face filter cassette. (3) Connect the tubing from the electronic bubble meter to the inlet of the jar. (4) Connect the tubing from the outlet of the cyclone holder assembly or from the filter cassette to the outlet of the jar and then to the sampling pump. (5) Calibrate the pump. The calibration readings must be within 5% of each other.

e. Cyclone cleaning: (1) Clean the cyclone thoroughly after each use to prevent excess wear or damage and to prevent contamination of a sample. Inspect the cyclone after cleaning for signs of wear or damage, such as scoring. Replace the unit if it appears damaged. (2) Gently clean the interior, avoid scoring the interior surfaces. Never insert anything into the cyclone during cleaning. Refer to Figure 1. (3) Leak test the cyclone at least once a month with regular usage.

4. Organic Vapors and Gases

a. Organic vapors and gases may be collected on activated charcoal, silica gel, or other adsorption tubes using low flow pumps.

b. Immediately before sampling, break off the ends of the charcoal tube so as to provide an opening approximately one-half the internal diameter of the tube. Wear eye protection when breaking ends. Use tube holders, if available, to minimize the hazards of broken glass. Do not use the charging inlet or the exhaust outlet of the pump to break the ends of the charcoal tubes.

c. Use the smaller section of the charcoal tube as a back-up and position it near the sampling pump. The charcoal tube shall be held or attached in an approximately vertical position with the inlet either up or down during sampling.

d. Draw the air to be sampled directly into the inlet of the charcoal tube and do not allow it to pass through any hose or tubing before entering the pump tubing.

e. Draw the air to be sampled directly into the inlet of the charcoal tube and do not allow it to pass through any hose or tubing before entering the pump tubing.

f. Cap the charcoal tube with the supplied plastic caps immediately after sampling and seal as soon as possible.

g. For other adsorption tubes, follow the same procedures as those for the charcoal tube, with the following exceptions:

(1) Set up the calibration apparatus as shown in Figure 2 replacing the cassette with the solid sorbent tube to be used in the sampling (e.g., charcoal, silica

gel, etc.). If a sampling protocol requires the use of two charcoal tubes, then the calibration train must include two charcoal tubes. The air flow must be in the direction of the arrow on the tube.

(2) Calibrate the pump.

5. Midget Impingers/Bubblers

a. Method:

1) Take care in preparing bubblers and impingers to see that frits or tips are not damaged and that joints can be securely tightened.

2) Rinse the impinger/bubbler with the appropriate reagent. Then, add the specified amount of this reagent to the impinger flask. If flasks containing the reagent are transported, caps must be placed on the impinger stem and side arm. To prevent overflowing, do not add over 10 milliliters of liquid to the midget impingers.

3) Collect contaminants in an impinger at a maximum flow rate of 1.0 lpm.

4) The impinger may either be hand-held by the industrial hygienist or attached to the employee's clothing using an impinger holster; in either case, it is very important that the impinger does not tilt, causing the reagent to flow down the side arm to the hose and into the pump.

5) In some instances, it will be necessary to add additional reagent during the sampling period to prevent the amount of reagent from dropping below one-half of the original amount.

6) After sampling, remove the glass stopper and stem from the impinger flask.

7) Rinse the absorbing solution adhering to the outside and inside of the stem directly into the impinger flask with a small amount (1 or 2 ml.) of the sampling reagent. Stopper the flask tightly with the plastic cap provided or pour the contents of the flask into a 20 cc. glass bottle. Rinse the flask with a small amount of the reagent and pour the rinse solution into the bottle. Tape the cap shut to prevent it from coming loose due to vibration. If electrial tape is used, do not "stretch" the tape since it will contract and loosen the cap.

b. Calibration Procedure:

1) Set up the calibration apparatus, replacing the cassette with the impinger/bubbler lined with the amount of liquid reagent specified in the sampling method.

2) Connect the tubing from the electronic bubble meter to the inset of the impinger/bubbler.

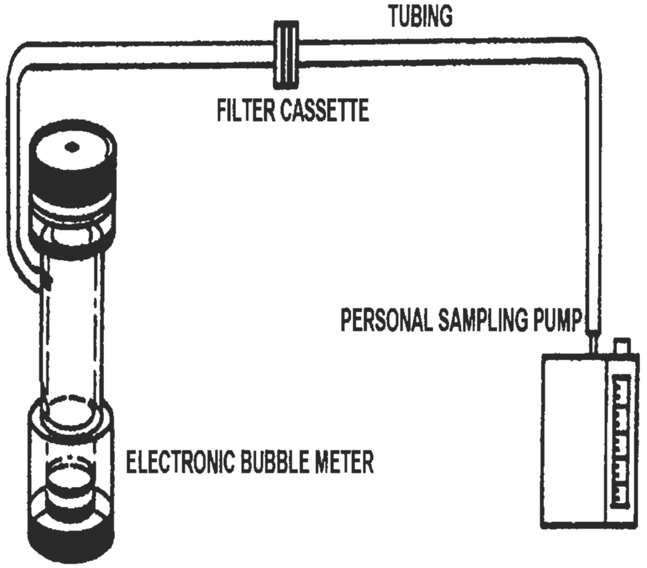


Figure 2. For calibration, the cassette is attached to an electronic bubble meter as shown in the illustration.

3) Connect the outlet of the impinger/bubbler to the tubing to the pump.
4) Calibrate the pump at a maximum flow rate of 1.0 lpm.

6. Vapor Badges

a. Passive diffusion sorbent badges are useful for screening and monitoring certain chemical exposures, especially vapors and gases.
b. Badges are available to detect mercury, nitrogen oxides, ethylene oxide, formaldehyde, etc.
c. Interfering substances should be noted.

For asbestos sampling:

a. Collect asbestos on a special, 0.8 micrometer pore size, 25 mm diameter mixed cellulose ester filter, using a back-up pad.
b. Use fully conductive cassette with conductive extension cowl.
c. Sample open face in worker's breathing zone.
d. Assure that the bottom point (between the extension and the conical black piece) of the cassette is sealed tightly with a shrink band of electrical tape. Point the open end of the cassette down to minimize contamination.

e. Use a flow rate in the range of 0.5 to 2.5 liters per minute. One liter per minute is suggested for general sampling. Office environments allow flow rates of up to 2.5 lpm. Calibrate pump before and after sampling.

f. Sample for as long a time as possible without overloading (obscuring) the filter.

g. Submit at the most 10 blanks, with a minimum in all cases of 2 blanks. Where possible, collect and submit to the laboratory a bulk sample of the material suspected to be in the air.

h. Mail bulks and air samples separately to avoid cross-contamination. Pack the samples securely to avoid any rattle or shock damage (do not use expanded polystyrene "packing"). Use bubble sheeting as packing. Put identifying paperwork in every package. Do not send samples in plastic bags or in envelopes.

i. Instruct the employee to avoid knocking the cassette and to avoid using a compressed air source that might dislodge the sample.

EQUIPMENT PREPARATION AND CALIBRATION

1. Replace alkaline batteries frequently (once a month). Also carry fresh replacement batteries with the equipment.
2. Check the rechargeable Ni-Cad batteries under load (e.g., turn pump on and check voltage at charging jack) before use.
3. Calibrate personal sampling pumps before and after each day of sampling, using either the electronic bubble meter method or the precision rotameter method (that has been calibrated against a bubble meter).
4. Electronic Flow Calibrators:

   a. These units are high accuracy electronic bubble flowmeters that provide instantaneous air flow readings and a cumulative averaging of multiple samples. These calibrators measure the flow rate of gases and present the results as volume per unit of time.

   b. These calibrators should be used to calibrate all air sampling pumps.
5. When a sampling train requires an unusual combination of sampling media (e.g., glass fiber filter proceeding impinger), the same media/devices should be in line during calibration.

The electronic bubble meter method consists of the following:

(1) Allow the pump to run 5 minutes prior to voltage check.

(2) Assemble the polystyrene cassette filter holder, using the appropriate filter for the sampling method. Compress cassette by using a mechanical press or other means of applying pressure. Use shrink tape around cassette

> to cover joints and prevent leakage. If a cassette adapter is used, care should be taken to ensure that it does not come in contact with the back-up pad. When calibrating with a bubble meter, the use of cassette adapters can cause moderate to severe pressure drop at high flow rates in the sampling train, which will affect the calibration result, If adapters are used for sampling, then they should be used when calibrating. Nylon adapters can restrict air flow due to plugging over time. Stainless steel adapters are preferred.
>
> (3) Connect the collection device, tubing, pump, and calibration apparatus.
>
> (4) A visual inspection should be made of all Tygon tubing connections.
>
> (5) Wet the inside of the electronic flow cell with the supplied soap solution by pushing on the button several times.
>
> (6) Turn on the pump and adjust the pump rotameter, if available, to the appropriate flow rate setting.
>
> (7) Press the button on the electronic bubble meter. Visually capture a single bubble and electronically time the bubble. The accompanying printer will automatically record the calibration reading in liters per minute.
>
> (8) Repeat step 7 until two readings are within 5%.
>
> (9) While the pump is still running, adjust the pump, if necessary.
>
> (10) Repeat the procedures described above for all pumps to be used for sampling. The same cassette and filter may be used for all calibrations involving the same sampling method.

The precision rotameter is a secondary calibration device. If it is to be used in place of a primary device such as a bubble meter, care must be taken to ensure that any introduced error will be minimal and noted. The precision rotameter may be used for calibrating the personal sampling pump in lieu of a bubble meter provided it is: (a) Calibrated with an electronic bubble meter or a bubble meter. (b) Disassembled, cleaned as necessary, and recalibrated. It should be used with care to avoid dirt and dust contamination which may affect the flow. (c) Not used at substantially different temperature and/or pressure from those conditions present when the rotameter was calibrated against the primary source. (d) Used such that pressure drop across it is minimal. If altitude or temperature at the sampling site are substantially different from the calibration site, it is necessary to calibrate the precision rotameter at the sampling site where the same conditions are present.

Filter Weighing Procedure: The step-by-step procedure for weighing filters depends on the make and model of the balance. Consult the manufacturer's instruction book for directions. In addition, follow these guidelines:

1. There shall be no smoking or eating in the weighing area. All filters will be handled with tongs or tweezers. Do not handle the filters with bare hands.
2. Dessicate all filters at least 24 hours before weighing and sampling. Change deSsicant before it completely changes color (e.g., before blue dessicant turns all pink). Evacuate dessicator with a sampling or vacuum pump.
3. Zero the balance prior to use.
4. Calibrate the balance prior to use and after every 10 samples.
5. Immediately prior to placement on the balance, pass all filters over an ionization unit after 12 months of use to the distributor for disposal.
6. Weigh all filters at least twice.
   a. If there is more than 0.005 milligram difference in the two weighings, repeat the zero and calibration and reweigh the filter.
   b. If there is less than 0.005 milligram difference in the two weighings, average the weights for the final weight.
7. Record all the appropriate weighing information in the weighing log.
8. In reassembling the cassette assembly, remember to add the unweighed backup pad.
9. When weighing the filter after sampling, include any loose material from an overloaded filter and cassette. At all times take care not to exert downward pressure on the weighing pans. Such action may damage the weighing mechanism.

Detector Tubes/Pumps: Detector tube pumps are portable equipment which, when used with a variety of commercially available detector tubes, are capable of measuring the concentrations of a wide variety of compounds in industrial atmospheres. Operation consists of using the pump to draw a known volume of air through a detector tube designed to measure the concentration of the substance of interest. The concentration is determined by a colorimetric change of an indicator which is present in the tube contents.

Detector tubes/pumps are screening instruments which may be used to measure hundreds of organic and inorganic gases and vapors or for leak detection. Some aerosols can also be determined. Detector tubes of a given brand are to be used only with a pump of the same brand.

The tubes are calibrated specifically for the same brand of pump and may give erroneous results if used with a pump of another brand. A limitation of many detector tubes is the lack of specificity. Many indicators are not highly selective and can cross-react with other compounds. Manufacturers' manuals describe the effects of interfering contaminants. Another important consideration is sampling time. Detector tubes give only an instantaneous interpretation of environmental hazards. This may be beneficial in potentially dangerous situations or when celling exposure determinations are sufficient. When long-term assessment of occupational environments is necessary, short-term detector tube measurements may not reflect time-weighted average levels of the hazardous substances present. Detector tubes normally have a shelf-life at 25°C of 1 to 2 years. Refrigeration during storage lengthens the shelf-life. Outdated detector tubes (i.e., beyond the printed expiration date) should never be used.

Detectable concentration ranges are tube-dependent and can be anywhere from one-hundredth to several thousand ppm. The limits of detection depend on the particular detector tube. Accuracy ranges vary with each detector tube. The pump may be handheld during operation (weighing from 8 to 11 ounces), or it may be an automatic type (weighing about 4 pounds) which collects a sample using a preset number of pump strokes.

A full pump stroke for either type of short-term pump has a volume of about 100 cc. In most cases where only one pump stroke is required, sampling time is about one minute. Determinations for which more pump strokes are required take proportionately longer.

Each day prior to use, perform a pump leakage test by inserting an unopened detector tube into the pump and attempt to draw in 100 ml of air. After a few minutes, check for pump leakage by examining pump compression for bellows-type pumps or return to resting position for piston-type pumps. Automatic pumps should be tested according to the manufacturer's instructions. In the event of leakage which cannot be repaired in the field, send the pump to the manufacturer. Record the leakage test data.

Calibrate the detector tube pump for proper volume measurement at least quarterly. Simply connect the pump directly to the bubble meter with a detector tube in-line. Use a detector tube and pump from the same manufacturer. Wet the inside of the 100 cc bubble meter with soap solution. For volume calibration, experiment to get the soap bubble even with the zero ml mark of the buret. For piston-type pumps, pull the pump handle all the way out (full pump stroke) and note where the soap bubble stops; for bellows-type pumps, compress the bellows fully; for automatic pumps, program the pump to take a full pump stroke.

For either type pump, the bubble should stop between the 95 cc and 105 cc marks. Allow 4 minutes for the pump to draw the full amount of air. Also check the volume for 50 cc (1/2 pump stroke) and 25 cc (1/4 pump stroke) if pertinent. A +5 percent error is permissible. If error is greater than +8 percent, send the pump for repair and recalibration. Record the calibration information required on a calibration log. It may be necessary to clean or replace the rubber bung or tube holder if a large number of tubes have been taken with the pump.

Draeger, Model 31 (bellows): When checking the pump for leaks with an unopened tube, the bellows should not be completely expanded after 10 minutes. Draeger, Quantimeter 1000, Model 1 (automatic): A battery pack is an integral part of this pump. The pack must be charged prior to initial use. One charge is good for 1000 pump strokes. During heavy use, it should be recharged daily. If a "U" (undervoltage) message is continuously displayed in the readout window of this pump, the battery pack should be immediately recharged. Matheson-Kitagawa, Model 8014-400A (piston): When checking the pump for leaks with an unopened tube, the pump handle should be pulled back to the 100-ml mark and locked. After 2 minutes, the handle should be released carefully. After taking 100 to 200 samples, the pump should be cleaned and relubricated. This involves removing the piston from the cylinder, removing the inlet and pressure-relief valve from the front end of the pump, cleaning, and relubricating. Mine Safety Appliances, Samplair Pump, Model A, Part No. 463998 (piston): The pump contains a flow-rate control orifice protected by a plastic filter which periodically needs to be cleaned or replaced. To check the flow rate, the pump is connected to a buret and the piston is withdrawn to the 100 ml position with no tube in the tube holder. After 24 to 26 seconds, 80 ml of air should be admitted to the pump. Every 6 months the piston should be relubricated with the oil provided. Sensidyne-Gastec, Model 800, Part No. 7010657-1 (piston): This pump can be checked for leaks as mentioned for the Kitagawa pump; however, the handle should be released after 1 minute. Periodic relubrication of the pump head, the piston gasket, and the piston check valve is needed and is use-dependent.

Detector tubes should be refrigerated when not in use to prolong shelf life. They should not be used when cold. They should be kept at room temperature or in a shirt pocket for one hour prior to use. Lubrication of the piston pump may be required if volume error is greater than 5%.

Electronic Flow Calibrators: These units are high accuracy electronic bubble flowmeters that provide instantaneous air flow readings and a cumulative averaging of multiple samples. These calibrators measure the flow rate of gases and report volume per unit of time. The timer is capable of detecting a soap film at 80 microsecond intervals. This speed allows under steady flow conditions an accuracy of +/- 0.5% of any display reading. Repeatability is +/- 0.5% of any display. The range with different cells is from 1 cc/min to 30 lpm. Battery power will last 8 hours with continuous use. Charge for 16 hours. Can be operated from an A/C charger.

Manual Buret Bubble Meter Technique: When a sampling train requires an unusual combination of sampling media (e.g., glass fiber filter proceeding impinger), the same media/devices should be in line during calibration. Calibrate personal sampling pumps before and after each day of sampling. Allow the pump to run 5 minutes prior to voltage check and calibration. Assemble the polystyrene cassette filter holder using the appropriate filter for the sampling method.

If a cassette adapter is used, care should be taken to ensure that it does not come in contact with the back-up pad. When calibrating with a bubble meter, the use of cassette adapters can cause moderate to severe pressure drop in the sampling train, which will affect the calibration result. If adapters are used for sampling, then they should be used when calibrating. Connect the collection device, tubing, pump, and calibration apparatus. A visual inspection should be made of all Tygon tubing connections. Wet the inside of a 1-liter buret with a soap solution. Turn on the pump and adjust the pump rotameter to the appropriate flow rate setting. Momentarily submerge the opening of the buret in order to capture a film of soap.

Draw two or three bubbles up the buret in order to ensure that the bubbles will complete their run. Visually capture a single bubble and time the bubble from 0 to 1000 ml for high flow pumps or 0 to 100 ml for low flow pumps. The timing accuracy must be within +1 second of the time corresponding to the desired flow rate. If the time is not within the range of accuracy, adjust the flow rate and repeat the last two steps until the correct flow rate is achieved. While the pump is still running, mark the center of the float in the pump rotameter as a reference. Repeat the procedures described above for all pumps to be used for sampling. The same cassette and filter may be used for all calibrations involving the same sampling method.

SAMPLING FOR SPECIAL ANALYSES

Air Samples: Respirable dust samples are analyzed for quartz and cristobalite by x-ray diffraction (XRD). XRD is the preferred analytical method due to its sensitivity, minimum requirements for sample preparation, and ability to identify polymorphs (different crystalline forms) of free silica.

a. The analysis of free silica by XRD requires that the particle size distribution of the samples be matched as closely as possible to the standards. This is best accomplished by collecting a respirable sample. (1) Respirable dust samples are collected on a low ash PVC filter using a 10 mm nylon cyclone at a flow rate of 1.7 lpm. (2) A sample not collected in this manner is considered a total dust (or nonrespirable) sample. Total dust samples do not allow for an accurate analysis by XRD.

b. Quartz (or cristobalite) is identified by its major (primary) X-ray diffraction peak. Because other substances also have peaks at the same position, it is necessary to confirm quartz (or cristobalite) principally by the presence of secondary and/or tertiary peaks.

c. If they are considered to be present in the work environment, the following major chemicals which can interfere with an analysis should be noted: Aluminum phosphate, Feldspars (microcline, orthoclase, piagiodase), Graphite, Iron carbide, Lead sulfate, Micas (biotite, muscovite), Potash, Silver chloride, Talc, Zircon (Zirconium silicate).

d. A sample weight and total air volume shall accompany all filter samples. Sample weights of 0.1 to 5.0 milligrams are acceptable. Sample weights of 0.5 to 3.0 milligrams are preferred. (1) Do not submit a sample(s) unless its weight or the combined weights of all filters representing an individual exposure exceed 0.1 mg. (2) If heavy sample loading is noted during the sampling period, it is recommended that the filter cassette be changed to avoid collecting a sample with a weight greater than 5.0 milligrams. If a sample weight exceeds 5.0 mg, another sample of a smaller air volume, whenever possible, should be collected to obtain a sample weight of less than 5.0 mg. Laboratory results for air samples are usually reported under one of four categories: (1) Percent Quartz (or Cristobalite). Applicable for a respirable sample in which the amount of quartz (or cristobalite) in the sample was confirmed. (2)"Less than or equal to" value in units of %. Less or equal to values are used when the adjusted 8-hour exposure is found to be less than the PEL, based on the sample's primary diffraction peak. The value reported represents the maximum amount of quartz (or cristobalite) which could be present. However, the presence of quartz (or cristobalite) was not confirmed using secondary and/or tertiary peaks in the sample since the sample could not be in violation of the PEL. (3) Approximate Values in Units of Percent: The particle size distribution in a total dust sample is unknown and error in the XRD analysis may be greater than for respirable samples. Therefore, for total dust samples, an approximate result is given. (4) Nondetected: A sample reported as nondetected indicates that the quantity of quartz (or cristobalite) present in the sample is not greater than the detection limit of the instrument. The detection limit is usually 10 micrograms for quartz and 50 micrograms for cristobalite. If less than a full-shift sample was collected, one should evaluate a nondetected result to determine whether adequate sampling was performed. If the presence of quartz (or cristobalite) is suspected in this case, the Industrial Hygienist may want to sample for a longer period of time to increase the sample weights.

Bulk Samples: Bulk samples must be submitted for all silica analyses. They have two purposes: (1) For laboratory use only, to confirm the presence of quartz or cristobalite in respirable samples, or to assess the presence of other substances that may interfer in the analysis of respirable samples. (2) To determine the approximate percentage of quartz (or cristobalite) in the bulk sample. A bulk sample submitted "for laboratory use only" must be representative of the airborne free silica content of the work environment sampled: otherwise it will be of no value. The order of preference for an evaluation is:

- A high volume respirable area sample.
- A high volume area sample.
- A representative settled dust (rafter) sample.
- A bulk sample of the raw material used in the manufacturing process.

A bulk sample is the last choice and the least desirable. It should be submitted "for laboratory use only" if there is a possibility of contamination by other matter. The type of bulk sample submitted to the laboratory should be cross-referenced to the appropriate air samples. A reported bulk sample analysis for quartz (or cristobalite) will be semi-quantitative in nature because: (1) The XRD analysis procedure requires a thin layer deposition for an accurate analysis. (2) The error for bulk samples analyzed by XRD is unknown because the particle size of nonrespirable bulk samples varies from sample to sample.

Samples Analyzed by Inductively Coupled Plasma (ICP): **Metals** — Where two or more of the following analytes are requested on the same filter, an ICP analysis may be conducted. However, the Industrial Hygienist should specify the metals of interest in the event samples cannot be analyzed by the ICP method. A computer print-out of the following 13 analytes may be typically reported: Antimony, Beryllium, Cadmium, Chromium, Cobalt, Copper, Iron, Lead, Manganese, Molybdenum, Nickel, Vanadium, Zinc. **Arsenic** — Lead, cadmium, copper, and iron can be analyzed on the same filter with arsenic.

AIR SAMPLING AND PERSONAL SAFETY MONITORING

On and off the job, everyone is exposed to a great variety of chemical and physical agents, most of which do no harm under ordinary circumstances, but all of which have the potential for being injurious at some level and under some conditions of exposure. How a material is used is the major determinant of the hazard potential.

Any substance contacting or entering the body can be injurious at some degree of exposure and will be tolerated without effect at some lower exposure. The practice of industrial hygiene or environmental health is based on the concept that for each substance there is a safe or tolerable lower level of exposure below which significant injury, illness or discomfort will not occur. The industrial hygienist protects the health of the worker by determining this safe limit of exposure for a substance and then controlling the environmental conditions so that exposure does not exceed that limit.

The toxicity, or hazard properties, of a chemical refer generally to the capacity of the substance to injure an individual. Frequently the word poison is used to mean a substance with some capability of producing adverse reaction on the health or well-being of an individual. Whether or not any ill effects occur depends on: (1) the properties of the chemical, (2) the dose (the amount of the chemical acting on the body or system), (3) the route by which the substance enters the body, and (4) the susceptibility or resistance of the exposed individual. There are four routes of entry or means by which a substance may enter or act on the body: (1) inhalation, (2) ingestion, (3) injection, and (4) contact or absorption through the skin. Of these, inhalation is the most important insofar as serious and acute industrial poisoning is concerned, but contact of the skin with corrosive or irritating chemicals is the most frequently encountered.

Ingestion of toxic materials occurs only through accidental or careless procedures in the industrial environment and, while it cannot be ignored, it is seldom a significant factor in exposure.

However, there are multiple routes of entry to the body for some materials. When a toxic chemical acts on the body or system, the nature and extent of the injurious response depends upon the dose received, that is, the amount of the chemical actually entering the body or system. This relationship of dose and response is shown in Figure 3. The dose-response curve varies with the type of material and the response.

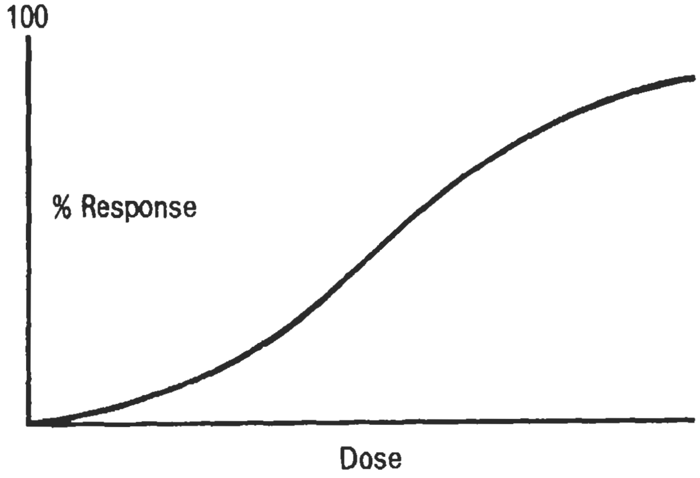


Figure 3. The dose-response curve.

Typically, there would be no response up to a certain dose, then a gradually increasing response to an increasing dose. At the upper part of the curve, the increase in response to an increase in dose would diminish, and would gradually approach 100% response in all exposed animals or individuals. However, no such curve is precise, because there is great variation in the susceptibility or resistance of individuals to a fixed dose of any material and, in addition, the biological response covers a rather wide range of effects for any given dose.

In experimental work, some accidental exposures, or in the administration of medicine, the dose may be a certain quantity of the chemical administered at one time, such as in a pill, an injection, or an accidentally swallowed poison. In industry, time is a factor in most exposures, and the dose is the result of both the concentration of the toxic agent and the duration of the exposure.

In exposures by inhalation of airborne materials, the dose is the concentration multiplied by the time (CT), and is roughly a constant for any given material and specified effect. The CT value can be used to provide a rough approximation of other combinations of concentration and time which would have about the same effect. Although this concept must be used very cautiously and cannot be applied at extreme conditions of either concentration or time, it is most important in setting limits for airborne contaminants and physical agents in respect to environmental exposures. The worker is exposed for various periods of time, day after day, to the materials in his environment, and the safe limits are set so that the combinations of concentrations and durations are below the levels which will produce injury.

Over the years, various individuals proposed different limits, and some states, as well as, and the American Conference of Governmental Industrial Hygienists (ACGIH) began to develop limits or standards. In 1945, W. A. Cook compiled a list of concentration limits for 150 substances. The ACGIH adopted this list and developed an active program which continues to this day.

In the early development of such limits, they were generally known as Maximum Allowable Concentrations or MACs, sometimes called Maximum Acceptable Concentrations, or Maximum Permissible Concentrations.

The early concept was that these were values which must not be exceeded; in other words, they were truly maximum values. As the understanding of limits and the development of the philosophy for such limits grew, it was realized that short-term exposures to somewhat higher concentrations could be permitted without undue harm if the total exposure during the day was sufficiently below the maximum limit. This led to the development of the concept of Threshold Limit Values (TLV's) by the ACGIH.

The TLVs, as recommended and published by the ACGIH, refer to concentrations of airborne contaminants or levels of physical agents, and represent the conditions to which it is believed nearly all workers may be repeatedly exposed day after day without adverse effects. TLVs are based on the results of animal experiments, limited human experiments, some industrial experience and, when possible, a combination of all three.

The basis on which the TLVs are set may differ from substance to substance. For some, such as levels for silica dust, a guiding factor is protection against impairment of health. For others, it is the comfort level of the individual, such as freedom from irritation, nuisance, or other forms of stress; for example, the TLV for sulfur dioxide is based on irritation and not on toxicity per se. The TLV list is reviewed annually resulting in some revisions in values and some additions to the list.

It is most important that TLV data be correctly used. Misuse can occur when uninformed individuals view these levels as magic numbers, below which workers are safe and above which they become ill. It should be remembered that there is wide variation in individual susceptibility to air contaminants and physical agents. Some workers may experience some discomfort from exposures at or below the TLV, and a much smaller number may be affected more seriously by aggravation of a pre-existing condition or by development of an occupational illness. Therefore, the TLVs as published were intended to be used only as guides in the control of health hazards and not as levels which separate safe from dangerous exposures. In addition, a TLV is not intended as a relative index of hazard or toxicity, nor to be mathematically manipulated by applying physical constants to derive a relative hazard.

Basically a TLV refers to a time-weighted averaged exposure for a 7 or 8-hour work day and a 40-hour work week. In other words, it is a level directed toward chronic (long-term) exposure and not toward acute (short-term) exposure. Generally, toxicity data for acute exposures is obtainable largely from animal experimentation, early medical data, and limited information from accidental exposures. In the use of TLVs, it is important to recognize that the levels are generally developed for normal individuals doing normal work. Under conditions of high heat, unusual humidity, heavy exertion, abnormal pressure, or other work factors which may place added stress on the body, the effects from exposure to an air contaminant at its TLV may be altered. Generally, most of these stresses act adversely to increase the toxic response to a substance, and proper downward adjustment of the level should be made.

The TLVs for airborne contaminants are based on the premise that although all chemical substances are toxic at some concentration for some period of time, a concentration exists for all substances from which no toxicity may be expected no matter how often the exposure is repeated. A similar premise holds for substances producing irritation, discomfort and nuisance. In using these limits, items such as excursion factors, ceiling values, "skin" notations, mixtures of substances, and inert material should be considered. These factors are discussed below.

Excursion Factors: Most TLVs refer to time-weighted average exposures for an 8-hour work day and a 40-hour work week. However, in calculating time-weighted average exposure, excursions above the limit are permitted provided they are compensated for by equivalent excursions below the limit during the same work day. The question here is: "How much of a fluctuation above the limit is permissible in developing the average?" These fluctuations above the limits are related to the magnitude of the TLV for the particular substance (refer to Table 1).

Table 1. Permissible Excursions for Time-Weighted Average Limits

TLV (ppm or mg/m^3)	**Excursion factor**	**TLV (ppm or mg/m^3)**	**Excursion factor**
0-1	3	10-100	1.5
1-10	2	100-1000	1.25

Note: These excursions are for a duration of only 15 min or less.

Following are two examples of the use of excursion factors:

Example 1: Carbon monoxide has a TLV of 50 ppm. Therefore, the maximum concentration permitted for a short time would be 75 ppm (50 ppm x 1.5 = 75 ppm).

Example 2: Lead has a TLV of 0.2 mg/m^3. Therefore, the maximum concentration permitted for a short time would be 0.6 mg/m^3 (0.2 mg/m^3 x 3 = 0.6 mg/m^3).

The limiting excursion factors should be considered "rule-of-thumb" guidelines for listed substances, but are not appropriate for all materials (such as those designated "C").

Ceiling "C" Values: "C" designations following the names of some substances refer to a ceiling value which should not be exceeded for that substance for any period of time. In other words, the time-weighted average exposure should fluctuate below the C value. Generally, C values are assigned to substances whose action is chiefly irritation, narcosis, or productive of serious long-term effects from a single or a few peak exposures. These are usually fast-acting substances whose TLV is more appropriately based on a ceiling value than on a time-weighted average which allows excursions above listed values.

"Skin" Notation: The designation "skin" refers to the potential contribution to the overall exposure by the cutaneous route, including mucous membranes and eyes, either by airborne, or more particularly by direct, contact with the substance. Examples of such substances are phenol (cresol and cumene), hydrogen cyanide, and mercury. The "skin" notation is intended to make known the need to prevent cutaneous absorption so that the TLV is not violated.

Mixtures: Special consideration should be given to the application of TLVs in assessing health hazards which may be associated with mixtures of two or more substances.

Generally, when two or more hazardous materials are present, their combined effect rather than either individual effect should be considered. In other words, the effects of the different hazards in a mixture should be considered additive.

An exception may be made when there is good reason to believe that the chief effects of the different harmful substances are not in fact additive, but independent, such as a combined exposure to silica dust and lead dust. In the determination of whether or not the additive effects are excessive, the following formula should be used:

$$C = C_1/T_1 + C_2/T_2 + \cdots C_n/T_n$$

where C indicates the observed concentration and T the corresponding TLV. If the sum of the fractions exceeds unity, then the mixture should be considered as being excessive.

"Inert" or Nuisance Particulates: Some materials may be classified as "inert" or nuisance particulates. Table 2 gives some examples. Generally, these materials have a long history of little adverse effect on the lungs and do not produce significant organic disease or toxic effect when exposures are kept under reasonable control. However, excessive concentrations of "inert" or nuisance particulates in the work air may seriously reduce visibility (iron oxide), may cause unpleasant deposits in the eyes, ears and upper respiratory passages (e.g., Portland cement and limestone dust), or may cause injury to the skin or mucous membranes during rigorous cleaning or mechanical action. To control these effects, a TLV for particulates with less than 1% free silica has been set at 10 mg/m^3 or 30 ppm cf (whichever is less) of total dust. The mg/m^3 refers to a gravimetric standard and the mppcf to a particle count standard. The limits do not apply to brief exposures to higher concentrations during a normal work day, nor do they apply to substances which may cause physiologic impairment at lower concentrations, for which no TLV has been indicated. Time-weighted average exposures for an 8-hour work shift are calculated by the following formula (where E = time-weighted average exposure, C = concentration during any period of time where the concentration remains constant, and T = duration, hrs.):

$$E = \frac{(C_1\,T_1) + (C_2\,T_2) + \ldots (C_n\,T_n)}{Daily\ hours\ of\ work}$$

As an example, several air samples collected during an 8-hour work shift for benzene (8-hour time-weighted average = 10 ppm) were 3 hours at 4 ppm, 1 hour at 15 ppm, 2 hours at 6 ppm and 2 hours at 9 ppm. The employee's time-weighted average exposure would be:

$$\frac{(3\,hrs \times 4\,ppm) + (1\times 15) + (2\times 6) + (2\times 9)}{8\,hours} = 7\,ppm$$

Table 2. Typical "Inert" or Nuisance Particulates

Alundum (Al_2O_3)	Glass, fiber/dust	Kaolin	Pentaerythritol
Calcium carbonate	Glycerin Mist	Limestone	Plaster of Paris
Cellulose	Graphite	Magnesite	Sawdust
Portland Cement	Gypsum	Marble	Rouge
Corundum (Al_2O_3)	Vegetable oil mists (except castor cashew nut, or similar irritant oils)	Sucrose, Tin Oxide, Titanium Dioxide	Silicon Carbide

This exposure is not excessive since 7 ppm is below the 8-hour time-weighted average of 10 ppm. Mixtures of air contaminants are additive and calculated in the manner described previously; that is, the fractions (concentration divided by limit for each material) are added together and if the sum does not exceed unity, the exposure is not excessive.

The primary purpose of monitoring the air in the work environment is to determine the level of employee exposure to airborne contaminants and to protect his health. Generally, where employees may be overexposed to potential health hazards, such sampling or measurements is performed on a routine basis. In addition to the above, sampling for air contaminants may be performed for one or more of the following reasons: (1) to determine the magnitude of employee exposure at the start-up of a new process or a change in a process or material used; (2) to determine the justification of employee grievances concerning an alleged health hazard; (3) to determine the performance or effectiveness of engineering control measures; (4) for research purposes, such as to determine the chemical and/or physical characteristics of contaminants, or (5) to investigate a potential health problem on a corporate wide basis. However, the majority of the sampling with which plant personnel will be concerned will be performed because of local or federal regulations. Those health standards under the Occupational Safety and Health Act (OSHA) require monitoring, on a periodic basis, of all employees who are exposed to harmful materials.

While the concept of air sampling and the use of air monitoring devices may appear to be simple, the details of a good monitoring program may be misunderstood unless the person engaged in sampling is adequately trained and technical supervision is provided by a professional industrial hygienist. Consequently, misapplication of techniques, errors in instrument performance, and errors in interpretation of sampling data are common when monitoring is conducted by those individuals whose training is limited solely to undertaking the monitoring required by federal and state regulations without the essential professional guidance.

The major problems arise from accepting an instrument reading as reliable without determining its calibration and the reproducibility of its response; and in not obtaining representative tests. Plant personnel must have some experience with and knowledge of the resolution of these problems.

This knowledge is also important in order to determine if air tests conducted by OSHA compliance officers are valid. For example, if threshold limit value in the health standard is an 8-hour time-weighted average, the air sample should be obtained by sampling over the entire shift in the employee's breathing zone. It cannot be measured by a few short term samples, even if spaced over the full shift unless the worker is in a relatively fixed location with no variation in his work procedure or in the process. Such an event is generally the exception rather than the rule.

Unless established monitoring practices are conducted by plant personnel or the OSHA compliance officer, the results are of limited value in determining compliance with a standard, and what is more important, protecting the worker's health. The conduct of air monitoring by untrained, or poorly trained, persons relegates the program to a "numbers game" which serves no useful purpose.

A characteristic of the air contamination in most occupational environments is that there is most always a continual change in concentration with respect to time and location. This is particularly the case with respect to airborne particulates (dust, fumes and mists). Air currents within a room, process variations, changes in the work practice performed by an operator, and variation in the emission rate of contaminants are a few of the more significant factors resulting in this continual change in concentration throughout a work shift. This change in concentration will be less pronounced with gases and vapors than with particulates. However, generally speaking, marked concentration gradients can exist in most work areas which may be transient or relatively constant depending upon the contaminant sources and their number. Therefore, it is apparent that it would be most unrealistic to assume that the concentration of air contamination exists uniformly throughout a room or area.

The problem of determining the exposure of a worker to air contaminants is further complicated by the mobility of most workers who move about, in and out of, many areas of a workroom. This mobility is characteristic of many assigned jobs. Therefore, the concentration of contaminants in each work area, and the time spent in each must be considered in determining the full shift time-weighted average concentration to which each worker is exposed. Exposure is concentration averaged over a time period, which in the general case is a full 8-hour shift. However, threshold limit values in the list published in the OSHA safety and health standards are peak concentrations or "ceiling values." Such standards indicate the maximum concentration which is allowed for any time period. Although a single specific sampling strategy cannot be applicable for all air monitoring, general principles or considerations, which should be incorporated in such a strategy, can be developed.

There are a variety of air sampling instruments, as indicated previously, the normal variability of the concentration of air contaminants and the mobility of workers, the average full-shift exposure of a worker is a to different concentrations during a workday. This can be ascertained by determining each concentration and exposure period, which is an extremely time-consuming and costly procedure; however, a more effective procedure involves the use of a personal sampling device worn by the worker during his full working shift, or any portion thereof which may be under inquiry. It is important to recognize that no perfect instrument exists nor can any be worn by a worker or placed in a location without periodic observation if for no other purpose than to note variation in process operating conditions or work practices. Both people and instruments malfunction and environmental conditions can readily depart from normality. It is such observations which must be noted if sampling data is to be properly evaluated.

Standard sampling instruments and procedures have been developed by OSHA with the assistance of the National Institute of Occupational Safety and Health (NIOSH).

These are developed to have OSHA industrial hygienists and compliance officers operate under a necessary standardized practice to determine compliance with standards. A principal consideration in their selection has been simplicity in operation and direct-reading response. Both of these requirements are important for any inspectorate as these individuals must engage in considerable travel and desire to ascertain compliance status as soon as possible. However, these OSHA sampling instruments and practices are not necessarily the optimum for individual plant use to provide the most accurate data, but a number of them can be so categorized as they have been selected from those long accepted by the industrial hygiene profession. Air samples to be obtained generally consist of breathing zone and fixed position samples. While both have application in hazard evaluation, the former is to be recommended for general use in determining compliance with standards. The exposure of a worker can be measured most accurately by determining the concentration of the contaminant in the air which he breathes. This does not imply that the sampling instrument must be located a few inches from his nose, as such a location would be impractical and unnecessary. The instrument should be held or located as close to an employee's nose and mouth without interfering with his freedom of movement in the normal conduct of his work. While some individuals have indicated sharp concentration gradients around a contaminant source, sample locations for exposure measurement located 1-2 feet from the nose is adequately representative.

Of more significance is the need for more than one full-shift sample if representative exposure data is to be obtained. Unfortunately OSHA standards for air contaminants are based upon a single 8-hour time-weighted average except where "ceiling value" standards are involved. Such a basis of determining compliance with standards for materials such as pneumoconiosis-producing dusts do not recognize that these materials only produce long-term effects and hazard evaluation should be based on more than a single 8-hour sample. Such a single sample can be at considerable variance with the true exposure averaged over two or more days, nor is one rarely occurring excessive exposure hazardous to the employee. Nevertheless, the regulations require that samples must be based upon the sampling period prescribed in the standards. Frequently it is desirable to obtain fixed position samples. For example, a worker may spend only a fraction of an hour in a job involving exposure to a contaminant and the remaining time in uncontaminated air. Such a breathing zone sample would collect such a small quantity of the contaminant that an accurate chemical analysis cannot be made. It would be preferable to locate a sampling instrument in a fixed position within the breathing zone of a worker when in the area and to sample for the entire shift. However, the concentration derived from such a sample must be time-weighted only for the actual time spent at the job to obtain the exposure of the worker involved. There are other instances when fixed position samples are desired, such as in control cabs, pulpits, etc., where the effectiveness of engineering controls or the contribution of this location to the total exposure is desired. Another application for fixed position samples is to determine whether employees located at distances from an operation should be sampled. This can be readily determined by locating several fixed position samplers at different distances from a source of contamination. Still another type of fixed position sampling, although not directly a measure of employee exposure is the use of continuous fixed position sampling stations, such as commonly used in blast furnace divisions for carbon monoxide. These types of samplers may be the sequential multiple point sampler type or the single point sampler. They are generally arranged so that the sampling point is located in close proximity to points where accidental release of high concentration of gases having an acute effect may develop. Their principal use is to warn employees by means of an audible alarm to immediately leave the area. Such instruments also can provide a continuous recorded measurement of some gases or vapors which may or may not be exposure related.

Number of Samples: A reliable estimate of an employee's exposure requires replicate samples irrespective of their duration. This is basic whether or not one is concerned with 8-hour time-weighted concentrations, operational exposures or areal contamination. Differences involving a factor of five or more are not rare. Therefore, a minimum of three samples should be obtained, until experience dictates an upward or downward revision, based upon the variability so determined. One cannot emphasize too greatly that the objective of a sampling program is worker protection and not the collection of numbers. An occasional exposure to a concentration which exceeds the threshold limit values would result in a violation if the compliance officer is sampling on the day that such an exposure exists, even though the average of several daily samples obtained during the same week is within the standard. This demonstrates the difference between good evaluation techniques and the mere application of numbers.

In the development of a sampling schedule, one should remember that if an operation continues more than one shift, it may be prudent to collect samples during each shift, as exposure to airborne contaminants may be different for each shift. Furthermore, sampling should be performed during all seasons of the year (winter, spring, summer and fall). This is especially true for locations in areas where large temperature variations occur during the different seasons of the year. Generally, there is more natural ventilation in the warmer months with the buildings open, which tends to dilute air contaminants, than in the colder weather when natural ventilation may be limited due to closing of doors and windows. In summary, the minimum number and type of samples is dictated by OSHA standards. However, it would be highly desirable to obtain more than this minimum number of samples.

Duration of Samples: For a practical viewpoint the duration of samples will be dictated by the requirements in the OSHA standards. These are continuous 8-hour samples or short-term samples when the standard has a "ceiling value" or peak concentration limit. Scientifically speaking, the minimum volume of air to be sampled, or the duration of sampling, is based on the following considerations: (1) the threshold limit value (TLV) or regulatory standard; (2) the sensitivity of the analytical procedure; or (3) the estimated air concentration. Thus, the volume of sample needed may vary from a few liters, where the estimated concentration is high to several cubic meters where low concentrations are expected. Then, knowing the sensitivity of the analytical procedure, the TLV and the sampling rate of the particular instrument in use, one can determine the minimum time necessary for an adequate sample. However, the collected sample should represent some identifiable period of time — usually a complete cycle of an operation or so many minutes out of each hour. This will enable the worker's exposure on a time-weighted average basis to be calculated.

Preparation for Sampling: The successful application of any sampling program requires that one be knowledgeable of the processes involved, the potential hazards and be able to recognize hazardous work conditions. Therefore, the first step in evaluating the occupational environment is to become familiar with the operations in the plant. This is best obtained by a preliminary, or "walk-through," survey during which information is obtained on the job categories and the operations in each, the raw materials used, the process by-products, and the type of control measures afforded for the protection of the workers. This information should be recorded on an appropriate form following which the data is reviewed and the potential hazards. Discussions should be held with supervisory personnel and industrial engineering personnel to obtain such details. It is imperative that plant personnel responsible for environmental health tests be considerably more knowledgeable of work practices and their environmental impact than one can expect from a regulatory official. Only by such experience can plant personnel determine if samples obtained are representative and accurate.

Sampling for Gases and Vapors: Many gases and vapors can be sampled by devices which indicate the concentration of the substance during sampling or shortly thereafter, without the necessity for chemical analysis. These direct reading devices are convenient and useful when properly calibrated. Other substances cannot be sampled by this method, because no appropriate instrument is available, and indirect methods which require laboratory analysis of the sample must therefore be used. Such analyses are often delayed by days or weeks, depending upon laboratory schedules.

Direct reading samplers include simple devices such as colorimetric indicating tubes in which a color change indicates the presence of the contaminant in air passed through the tube, or instruments which are more or less specific for a particular substance. In the latter category are carbon monoxide indicators, combustible gas indicators (explosimeters) and mercury vapor meters, as well as a number of other instruments.

All instruments for sampling gases or vapors must be calibrated before use and their limitations and possible sources of error must be fully understood. Every instrument has a lower limit of sensitivity which can be too high, making the instrument useless for health hazard evaluation. For example, some explosimeters are so insensitive that they show only the presence of nearly explosive mixtures of some solvent vapors, and give no response of levels which may be harmful to health. To be useful for environmental health purposes, an instrument should give a substantial reading at or near the TLV concentration and preferably should accurately indicate the presence of air contaminants as low as 10% of this concentration. Most direct reading instruments and many colorimetric indicating tubes are not sufficiently sensitive for this kind of sampling. The manufacturer's specifications should be reviewed before a sampling device is selected. But it should be remembered that specifications may be optimistic, and that it may not be possible to detect with certainty the concentration which is listed as the lower limit of detection.

Since no device is completely specific for the substances of interest, care must be taken that interferences do not invalidate the sampling results. Many common gases and vapors react with the same chemicals, or have similar physical properties, so that the instrument may give falsely high or low readings for the substance being sampled. The manufacturer's data for colorimetric indicating tubes lists those substances which may interfere with the desired determination.

If there is reason to think that interfering substances may be present, it is advisable to sample them to determine whether their concentrations are sufficiently high to actually constitute an interference. It is very important to establish that an instrument responds properly to the substance it is designed to sample. This is generally done by calibration procedures with standard concentrations of the substance of interest.

It is also desirable to spot test the instrument's response between calibrations. For this purpose, several suppliers of compressed gas prepare cylinders containing almost any desired concentration of the gas or vapor of interest. If it is not practical to keep such cylinders on hand, other procedures may be used. For example, a carbon monoxide meter can usually be checked by exposing it to a small amount of diluted automobile exhaust; a mercury meter can be checked by holding it above an open bottle of mercury; a combustible gas indicator (explosimeter) can be checked by exposing it to a solvent mixture such as gasoline, lighter fluid, or paint thinner. Although such rough checks are not quantitative, they indicate whether the meter is responding to the substance for which it is to be used. Indicating tubes cannot be tested in this way, since they are usually designed for one-time use. If there is any doubt about the response of indicating tubes, it is advisable to sacrifice one tube from the box, to be sure that the tubes in the particular batch are, in fact, responsive to the substance being sampled. In any case, it is desirable to check one tube from each batch with a calibrating gas of known concentration.

A sampling device may use one of three basic methods for collecting gaseous air contaminants. The first involves passing air through a direct reading instrument which indicates, without further analysis, the actual concentration of the substance at the time the sample is taken. The second method involves passing a known volume of air through an absorbing solution (a liquid which takes up and retains the gas or vapor), or an adsorbing medium (a solid substance which mechanically holds a solvent or vapor on its surface), to remove the desired contaminant or contaminants from the air. The absorbing solution may be a weak alkali solution (0.01% normal sodium hydroxide) in a fritted glass bubbler and the adsorbing medium may be chemically treated silica gel or activated charcoal sealed in a glass tube. In the third method, an air sample of definite volume at known temperature and pressure is collected in a container (an evacuated flask, a bottle, or a plastic bag) which is resealed immediately to prevent sample loss. It should be noted that samples collected by the second and third methods must be sent to a laboratory for analysis. All three sampling methods should:

1. Provide an acceptable efficiency of collection for the air contaminant involved;
2. Maintain this efficiency at a specified air flow;
3. Have a high degree of reproducibility;
4. Require minimal manipulation in the field;
5. Avoid, if possible, the use of corrosive or otherwise hazardous sampling media.

The first (direct reading) method is fairly simple and results are available immediately. However, the instruments have limited sensitivity and must be recalibrated periodically. The second (absorption in a liquid or adsorption on a medium) and third (gas container) methods are generally considered more sensitive and more accurate method for trace analysis by gas chromatographs, infrared spectrophotometers, and similar instruments. However, because of their sophistication, both of these methods require careful handling to insure representative tests. Direct reading instruments enable the operator to obtain immediate indications of gas or vapor concentration by reading a meter dial or by noting the length of stain on an indicator tube. This does not mean, however, that the mere reading of a meter implies a valid test. On the contrary, the operator must be thoroughly familiar with the use and limitations of the instruments and devices.

Direct Reading Instruments: Combustible gas explosimeters are one of the most useful instruments of the direct reading type, also known as a combustible gas indicator. As the names suggest, instruments of this type were designed to detect the presence of explosive or combustible gases in the air. Safety checking is still their principal application, and many of them are suitable only for this purpose. To understand the principle on which these instruments operate, the terms lower and upper explosive limits must be defined. When certain proportions of combustible vapor are mixed with air, ignition will produce an explosion. The range of concentrations over which this will occur is called the explosive range. It includes all concentrations in which a flash will occur or a flame will travel if the mixture is ignited. The lowest percentage at which this occurs is the lower explosive limit (LEL), and the highest percentage is the upper explosive limit (UEL). Mixtures below the LEL are too lean to ignite, and mixtures above the UEL are too rich.

Explosive limits are expressed in percent by volume of vapor in air. LELs and UELs have been determined in fire and safety, and health laboratories for all substances likely to be found in industry. Typical values for some solvents and gases are given in Table 3.

Table 3. Explosion Limits for Common Materials.

	Flashpoint °F		**Explosive Limits in air % by Volume**			**Density**
Name	**Closed Cup**	**Open Cup**	**Lower**	**Upper**	**Autoignition Temp. °F**	**Air = 1.0**
Acetaldehyde	-36	—	4.0	55.0	365	1.52
Acetone	0	15	2.1	13.0	1000	2.00
Ammonia (Anhydrous)	Gas	Gas	15	28	1204	0.596
Amyl Acetate-n	76	80	1.1	7.5	714	4.49
Amyl Alcohol-n	91	120	1.2	—	572	3.04
Benzene	12	—	1.4	7.1	1044	2.77
Benzine	<0	—	1.4	5.9	550	2.50
Butyl Acetate-n	72	90	1.4	7.6	790	4.00

	Flashpoint °F		Explosive Limits in air % by Volume			Density
Name	Closed Cup	Open Cup	Lower	Upper	Autoignition Temp. °F	Air = 1.0
Butyl Alcohol-n	84	110	1.4	11.2	693	2.55
Camphor	150	200			871	5.24
Carbon Disulfide	-22	—	1.0	50	257	2.64
Carbon Tetrachloride	None	None				
Cellosolve	104	120	2.6	15.7	460	3.10
Chloroform	None	None	—	—		4.13
Coal Tar Oil	80-160	—	—			
Coal Tar Pitch	405	490	—	—		
O-Cresol	178	—	1.3 at 300° F	—	1038	3.72
Cyclohexanol	154	—	—		572	3.45
Denatured Alcohol	60	—	—		750	1.60
Ethyl Acetate	24	30	2.2	11	800	3.04
Ethylene Glycol	232	240	3.2	—	775	2.14
Ethyl n-propyl ether		—	1.9	24	—	—
Formaldehyde, 37% in water	130	200	—	—	795	1.03
Fuel oil No. 1	114-185	—	0.6	5.6	445-560	—
Fuel oil No. 1-D	100 min	—	1.3	6	350-625	
Fuel oil No. 2	126-230	—	—	—	500-705	—
Fuel oil No. 2-D	100 min	—	1.3	6	490-545	—
Fuel oil No. 4	154-240	—	1	5	505	
Fuel oil No. 5	130-310	—	1	5	—	—
Fuel oil No. 6	150-430	—	1	5	765	—
Gasoline Automotive premium	-50+	—	1.3-1.4	6.0-7.6	770	3.0-4.0
Gasoline Automotive regular	-50 ±	—	1.3-1.4	6.0-7.6	700	3.0-4.0
Gasoline Aviation commercial	-50 ±	—	1	6.0-7.6	800-880	3.0-4.0
Gasoline Aviation military	-50 ±	—	1	6.0-7,6	800-880	3.0-4.0
Hexane-n	-7	—	1.2	7.5	453	2.91
Hexane-iso	< -20	—	1	7	—	3.00
Hydrogen sulfide	Gas	Gas	4.3	45.5	500	1.18
Jet fuel JP-1	110-125	—	0.6	5.6	442-560	—
Jet fuel JP-4	26-36	—	0.8	6.2	468	—
Lacquer	0.86	—	—	—	—	—
Maieic Anhydride	218	240	—	—	890	3.38
Methyl Acetate	15	20	3.1	16	935	2.56
Mineral spirits	100 min	110	0.77@212°F	—	475	3.9

	Flashpoint °F		Explosive Limits in air % by Volume			Density
Name	Closed Cup	Open Cup	Lower	Upper	Autoignition Temp. °F	Air = 1.0
Naphtha	100-110	—	0.8	5	440-500	—
Naphtha VM&P	20-45	—	0.9	6.0	450-500	3.75
Naphthalene	174	190	0.9	5.9	979	4.42
Petroleum crude	20-90	—				—
Petroleum ether	<0	—	1.4	5.9	550	2.50
Phenol	175	185	—	—	1319	3.24
Phthalic Anhydride	305	330	1.7	10.5	1083	5.10
Pine oil	172	175	—	—	—	—
Propane	<-100	Gas	2.2	9.6	871	1.56
Propyl Acetate-n	58	70	1.7	8.0	842	3.52
Stoddard solvent	100-110	—	0.8	5	440-500	—
Styrene	90	—	1.1	6.1	914	3.60
Sulfur	405	440	—	—	450	—
Toluene	40	45	1.3	7.0	997	3.14
Trichloroethylene	Weakly Flammable		10 in O_2	65 in O_2	—	4.53
Turpentine	95	—	0.8	—	488	4.84
p-Xylene	77	—	1.1	7.0	984	3.66

Several manufacturers make explosimeters or combustible gas indicators. Although they differ somewhat in design and operating features, their operation is based on the fact that a measurable amount of heat is released when a combustible gas or vapor is burned. Most meters contain a battery-operated electrical circuit known as a Wheatstone bridge, which is balanced by means of controls on the outside of the instrument.

On the simplest type of instrument (an explosimeter) only one scale is provided, usually with readings from 0 to 100% LEL. However, the detectable changes produced by combustion are too small to be measured accurately in the presence of the low concentrations of contaminants usually encountered in evaluating potential health hazards. For example, the LEL of even the most explosive gas is of the order of 1%, or 10,000 ppm, which is well in excess of the toxic limit for any gas. Therefore, explosimeters or combustible gas indicators which have only a 0-to-100% LEL explosive scale are not suitable for environmental health testing in the ppm range. More sensitive instruments, including the type used in sampling for environmental health purposes, have a dual scale, in which the second, more sensitive scale, expands the 0-to-10% LEL part of the instrument's response to full-scale reading. Refer to Figure 4.

While this permits more sensitive and accurate reading of concentrations in the 0-to-10% range, this type of instrument is not sufficiently sensitive to give precise indications of concentrations at the TLV of many toxic gases and vapors. In addition, they lack specificity, do not read directly in TLV units (ppm), and are subject to interferences. All combustible gas and vapor indicators are calibrated by the manufacturer using one specific gas or vapor such as methane, and a calibration curve is provided, in percent LEL, for the calibration gas only.

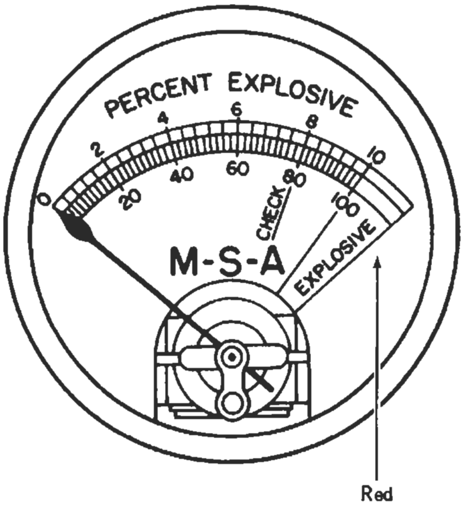


Figure 4. Scale on an explosion meter.

Obviously, accurate concentrations of other gases or vapors cannot be indicated unless the instrument has been appropriately calibrated for each of these gases. Furthermore, the manufacturer's calibration may not be sufficiently accurate and a correction may be required. For example, a meter reading of 2.0 on the 0 to 10% LEL scale of one instrument would indicate, for a solvent having an LEL of 1.4%, a concentration of 280 ppm (0.02 x 14,000 ppm). Benzene, methyl isobutyl ketone (MIBK). For example, a meter reading of 2.0 on the 0-to-10% LEL scale of one instrument would indicate, for a solvent having an LEL of 1.4%, a concentration of 280 ppm (0.02 x 14,000 ppm). Benzene, methyl isobutyl ketone (MIBK) and toluene all have LEL's of 1.4%, but actual concentrations at a meter reading of 2.0 would be 294 ppm for benzene, 350 ppm for MIBK and 231 ppm for toluene. Therefore, unless the scale reading is corrected according to a calibration chart, to indicate actual ppm values, the reading can be seriously in error.

The manufacturer's instructions for operating a combustible gas indicator should be carefully reviewed before the device is used. In general, all explosimeters require a brief initial warm-up period so that the batteries can heat the filaments. Then battery strength should be checked, and the zero scale adjusted. When zero is established and the indicating needle is stable, the instrument is ready for use.

The zero adjustment must be made by taking the instrument to a source of air which does not contain combustible gases or vapors, or by passing air into it through an activated carbon filter which will remove combustible vapors and gases except methane. Since methane is not removed by activated charcoal filters, extra caution is required if the presence of methane is suspected. In addition, the filter should be changed periodically because it tends to become saturated during prolonged use and will no longer remove many of the combustible gases and vapors. If the zero adjustments are made in fresh air, care must be taken that no combustible gas or vapor is present in an amount which would influence the instrument's response.

Most combustible gas indicators are equipped with a length of sampling tubing with a metal probe at the end. The probe is held at the sampling point (usually near the breathing zone of the worker) and, a few seconds later, the response can be read on the meter. Generally, the air is drawn through the probe and meter by means of a hand-operated rubber squeeze bulb. In some instances, however, a small electrically-operated pump in the instrument case is used for this purpose. In most work areas, the concentration of combustible gas or vapor fluctuates constantly, and it is necessary to observe the instrument carefully and to make a judgment concerning average and peak readings.

Sometimes the probe of a combustible gas indicator or explosimeter is placed in a manhole or other space not normally occupied by people, to determine if there is a potentially explosive or dangerous concentration of gas present. When the instrument is used in this way, it may show a zero response for several different reasons. Assuming that the batteries are working and the instrument is functional, the absence of meter response can mean either that there is little or no combustible gas in the space being tested, or that the concentration is so high that it is above the UEL and combustion cannot occur because of lack of oxygen. A very high concentration can be identified by carefully watching the needle as the probe is moved into and withdrawn from the space being tested. At some point during entry and withdrawal, the probe must pass through the LEL concentration and enter the flammable range. At this point, the needle will jump briefly, then settle back to zero. This "chink" or jump is a clear indication that a high concentration is present. Dual scale combustible gas indicators are rugged, relatively lightweight, and portable so they are widely used for checking work operations like solvent cleaning or painting, or locations such as coal chemical areas where organic solvents are emitted. Their limitations must be realized, however, and where there is a possibility that benzene or an unknown and possibly toxic solvent may be present, they cannot be relied upon. In such cases, sampling must be performed by other means. The user of any instrument should be thoroughly familiar with precautions to be taken in its operation; users of combustible gas indicators must also be aware of interfering gases and vapors which can create major aberrations in instrument response. One such precaution is that the 0 to 100% scale should be used first, to determine whether an explosive atmosphere exists and to prevent overloading to 0 to 10% LEL scale. Interfering gases and vapors can seriously affect instrument response, and an experienced tester recognizes the indications of their presence. The manufacturer's instructions should be thoroughly understood. For example, high concentrations of chlorinated hydrocarbons (i.e., trichloroethylene) or of an acid gas (sulfur dioxide) may cause depressed meter readings when high concentrations of combustibles are also present. Trace amounts of these interferences may not affect the readings directly, but can corrode the sensitive detector elements. High molecular alcohols in the atmosphere may burn out the filaments, making the instrument inoperative. If such limitations are understood, the tester can obtain sufficiently valid results.

For calibration of the 0 to 100% LEL scale, test kits containing known concentrations of combustible gases (usually either 2.5% methane or 2.5% natural gas) are available from the instrument manufacturers. In using these kits, it should be borne in mind that the calibration is only for that specific gas and indicates only that the meter is operational on the 0 to 100% LEL scale. To calibrate to 0 to 10% scale, it is necessary to use purchased or specifically prepared known concentrations of gases in the TLV ranges.

Carbon Monoxide Testers: Carbon monoxide is one of the most commonly encountered toxic gases and may result from many industrial processes as well as from automobile or truck exhaust. Since pure CO is colorless, odorless, and tasteless, the senses cannot be relied on to give warning of its presence. Carbon monoxide may be sampled in several ways, including the use of the colorimetric indicating tubes, but for making repeated measurements over a period of time, a direct reading meter is frequently used. Such a meter is similar to a combustible gas indicator in that its operation involves combustion of the CO and measurement of the heat released by this combustion. However, both the design of the instrument and its method of measuring heat are considerably different from those in combustible gas indicators.

Carbon monoxide is combustible, but does not burn readily at low concentrations such as the present TLV of 50 ppm. However, it will burn at low concentrations in the presence of a catalyst such as hopcalite, a granular mixture originally developed for use in gas masks. A conventional meter contains one cell of inactive chemical (reference cell) and one cell of hopcalite (detector cell), each containing a number of electric wires or thermocouples which generate a small electric current when heated. The detector cell is surrounded by two thermistors (heat sensitive resistors) which are part of a Wheatstone bridge circuit. When air containing carbon monoxide is drawn through the detector cell, it is oxidized by the hopcalite. The heat created by this oxidation causes a change in the electrical resistance of the system which is registered by an upward deflection of the meter. The reference cell compensates for all temperature changes caused by the surrounding air or by variations within the instrument, so that the net reading is a measure of the concentration of CO in the air. Since the performance of the hopcalite is hampered by water vapor, the air must be dried before entering the catalyst chamber. The drying agent built into the instrument should be checked periodically, and replaced when necessary.

Oxygen Indicators: Air normally contains about 21% oxygen, and in most working places the concentration of contaminants is so low that this oxygen level remains essentially unchanged at all times. Even if there is a relatively high concentration (such as 1,000 ppm) of a vapor in the work atmosphere, there are still 999,000 ppm of air present, and for all practical purposes, this is no different from pure air insofar as its oxygen content is concerned.

In many locations, however, such as mines, manholes, tunnels, or other confined spaces, it is possible for the oxygen content to be sufficiently low that it is hazardous to life. In such situations, it is necessary to determine the oxygen content and, in addition, to sample to determine whether combustible gases are present in dangerous concentrations.

When oxygen reaches the inside of the cell, it generates a minute electric current which is converted to a voltage and is registered on a meter as a per cent of oxygen. The instrument is basically stable, automatically compensates for temperature changes between freezing and about 100°F, and is not affected by carbon dioxide or relative humidity. It is readily calibrated by sampling ordinary air and, according to the manufacturer, this single point calibration is adequate. Complete instructions for its use, operation and maintenance are supplied by the manufacturer.

Indicator (Colorimetric) Tubes: The use of solid chemical detectors (indicating tubes) is common practice. They are simple devices to operate which tends to cause many users to ignore their limitations which must be recognized if they are to be useful in evaluating potential hazards due to air contaminants. This apparent simplicity increases the number of people who attempt to use them, which in turn results in wide variations in both individual competence and the accuracy of the data obtained.

It is essential for all users of air sampling devices to recognize that, while collecting an air sample is a simple procedure, it is only one part of the total procedure for proper evaluation of the environment. Only minimal skills are required to operate the instrument. Far greater knowledge and skill are required to recognize its limitations, to maintain and calibrate it properly, to obtain representative tests, and to know the strategy for obtaining valid data on workers' exposures. These are problems which require experienced and well-trained personnel who either are, or are under the direction of, professional industrial hygienists.

Making reliable tests with indicating tubes requires thorough knowledge of their limitations and care in their use. Experience has shown that the following measures help to minimize some errors:

1. Test each batch of tubes with a known gas concentration.
2. Read the length of stain in a well-lighted area.
3. Read the longest length of stain if stain development is not sharp or even.
4. Observe the manufacturer's expiration date closely, and discard outdated tubes.
5. Keep detector tubes in a shirt pocket or other warm place until time to start the test.
6. Refer to the manufacturer's data for a list of interfering materials.
7. Calibrate for the proper flow rate.

Indirect Sampling Devices for Gases and Vapors: As stated earlier in this chapter, not every contaminant can be sampled by a direct reading device. In such cases (or even in some situations involving contaminants which can be measured with direct reading devices) an indirect reading sampler must be used when the sample must be sent to a laboratory for analysis of the components. For this purpose, a number of glass or plastic bubblers are available, containing water or some other liquid to capture gases or dusts when air is drawn through them. Occasionally, filter papers are used, but since ordinary filter paper cannot trap gas or vapor, the paper must be treated with chemicals which will react with the substance of interest and retain it on the paper. For many purposes, gases and vapors can also be collected in bottles, in plastic bags, or in tubes which contain activated charcoal or some other adsorbent. Each of these methods is discussed below, since the person responsible for monitoring in each plant will be required to use them at some time.

Bubblers: Bubblers are ordinarily made of glass, although some are made of clear plastic. A stated amount of absorbing liquid is placed in a sample bottle which also contains the bubbler. When air is drawn through the bubbler, the contaminant is retained in the absorbing solution. The most efficient unit for sampling gases and vapors is a fritted bubbler, which is a piece of glass with thousands of small holes which disperse the air as it bubbles through the solution.

The choice of absorbing solution, the strength (normality or pH) of the solution, the sampling rate (generally 1 to 3 liters per minute), and the size of the bottle (20 cc, 50 cc, or 125 cc), are some of the variables which must be considered in using bubblers.

It should also be emphasized that the air flow calibration of bubblers should be done before field use. The calibration should be done with the same type and amount of absorbing solution as will be used in the actual testing, since absorbing solutions vary in viscosity and can directly affect the pressure drop in the sampling system. The pressure drop is also directly affected when the pores of the fritted bubbler become clogged thus lowering the efficiency of the bubbler and materially influencing the collection rate. To avoid such clogging, a filter must be used ahead of the bubbler.

Charcoal Tubes: Reference has been made earlier to adsorption, which is the property of some solid materials, such as activated charcoal, to physically retain solvent vapors on their surfaces. In environmental health testing, the adsorbed vapors are removed, generally with a solvent, in a laboratory. The solvent is then analyzed by physical methods (gas chromatography, etc.) to determine the individual compounds whose vapors, such as benzene, were present in the sampled air. Industrial atmospheric samples can be collected in small glass tubes (4 mm ID) packed with two sections of activated charcoal, separated and retained with fiberglass plugs. To obtain an air sample, the sealed ends of the tube are broken off, and air is drawn through the charcoal at the rate of 1 liter per minute by means of a personal sampler. After sampling, the tubes are resealed and sent to a laboratory for analysis.

Four precautions must be observed when this type of collection device is used:

1. The shorter (backup, or second) section of the charcoal tube should be inserted into the sampling line so that the air is drawn through the longer section first. When analyzed, the backup section should be void of solvent vapors - in other words, there should have been no carry-over from the first section.
2. The sampling rate must be maintained at 1 liter per minute. Sampling at a higher rate may elutriate the solvent vapors from the first section, in which case they may be adsorbed in, or even elutriated from, the second section.
3. Because of the limited adsorption capacity of the tube, the sampling period should not exceed 15 to 30 minutes. The time will depend to some degree on the expertise of the observer, since high concentrations of solvent vapors could saturate the first charcoal section in a few minutes.
4. The tubes should be carefully resealed, with the caps provided for that purpose, immediately after use.

Plastic Bags: Sometimes it is possible to sample simply by filling a bag, bottle, or other container with air from the working area and sending the container to a laboratory. Plastic bags have several advantages over bottles for this purpose. First, of course, they require little storage space and can be kept on hand at all times. In addition, they are available in relatively large sizes so that a much larger volume of air can be sampled than might be practical with a bottle. Finally, they are lightweight even when filled.

Among the materials used for these bags are Myler, Saran, and a laminated material called Scotch Pak. These bags are, in general, strong and impermeable, do not react with many of the common vapors which must be sampled, and do not themselves add contaminants to the air after it is collected. Commercially available bags come in various sizes ranging upward from 1 liter, and have built-in tubes for sampling purposes. There are several ways to fill a sampling bag. The most common is to attach to the bag inlet a rubber bulb containing two valves, one to draw air in, the other to blow air out. If the bulb is squeezed rapidly, the bag can be filled in a very short time. If a rubber bulb is not suitable for the vapors of interest, some other means must be used to fill the bag.

Instrument Limitations: Every instrument has certain limitations which must be recognized. A number of these have already been discussed, and it is very important that they be kept in mind at all times. Otherwise, serious errors can result, rendering the tests meaningless or misleading. Following is a brief summary of limitations common to many instruments, but it must be emphasized that any given instrument may not be susceptible to any particular error:

1. All instruments are limited in specificity of response to the contaminant they are supposed to measure. Interferences may cause false readings and, as pointed out earlier, care must be taken to identify (and, if possible, compensate for) these interferences.
2. Any instrument is suitable for only a given range of contaminant concentration. This means that at certain very low levels, the instrument will not respond while, at very high levels, the reading may be grossly inaccurate or even meaningless. As discussed earlier, combustible gas indicators can even register zero in the presence of very high concentrations of vapors or gases.
3. Every instrument is likely to have a slight error, and the magnitude of this error, if it exists, must be known. It is meaningless, for example, to record an instrument reading as 51.3 ppm when in fact there is a known instrument error of ± 5%. It is also meaningless to report the average of several readings by a number which cannot be read on the instrument itself.
4. Every instrument which requires that air be passed through it, must be operated at a specific flow rate, or within a certain range of flow. Failure to sample at the correct flow rate can produce inaccurate or meaningless results.
5. A number of limitations are imposed by the construction of the instrument and its operating parts, including such factors as fully charged or new dry cell batteries, replacement of drying agents or other chemicals and, of course, how well the moving or consumable parts such as filaments have been maintained. Most instrument failures from these causes can be prevented by routine care and maintenance, and by periodic calibrations.

RECOMMENDED RESOURCES FOR THE READER

1. www.epa.gov/iaq/ - EPA's indoor air quality web site. Provides general information and publication links.
2. www.osha-slc.gov/SLTC/indoorairquality - OSHA web site devoted to indoor air quality issues.

3. www.cpsc.gov/cpscpub/pubs/iaq.html - U.S. Consumer Product Safety Commission site. Contains publications on various IAQ issues and technical reports.
4. www.who.int/peh/air/Airqualitygd.htm - World Health Organization web site for indoor air quality management.

REVIEW AND QUESTIONS TO GET YOU THINKING

1. What are some of the benefits beyond reduced health risks from high quality indoor air?
2. Examine your building operation. Make an inventory list of all the sources of contaminants that impact on indoor air quality. Determine which among these are likely to have first order effects on air quality.
3. Continuing with Question 2, which sources could potentially be the focus of a pollution prevention opportunity?
4. Define conditioned air. Does the air supply in your building or workplace meet the criteria for conditioned air?
5. List several elements important to developing a meaningful indoor air quality management plan.
6. Examine health records in your plant. Organize these by work areas and assess whether there are statistically higher incidents that support respiratory ailments, including cold and flu statistics. If the data supports a particular work area as having a problem, can you identify the reasons? If so, what are they and how would you go about better defining the problem and a solution?
7. Air samples are collected over an 8 hour work shift for MEK. Measurements showed 3 ppm after 2 hours, 24 ppm after 4.5 hours, 12 ppm after 6 hours, and 2 ppm after 8 hours. Calculate the TWA concentration and compare this value against the OSHA safe level of exposure.
8. Rank the following materials in terms of their relative fire risks: amyl alcohol, acetone, benzene, ethyl acetate, fuel oil, hexane, coal tar, mineral spirits, styrene monomer.
9. Develop a checklist f items that should be addressed in an IAQ audit.
10. What specific OSHA standards are applicable to indoor air quality?
11. Identify up to 10 chemicals handled at your facility and obtain information on their flammability limits.
12. Go to the Web and identify several sites that provide information on the MSDSs for chemicals.

13. Go to the Web and identify several sites that address indoor air quality issues.
14. Define what Ceiling, Short term limit, and time weighted average values are.
15. What are some pollution prevention opportunities you could focus on in an indoor air quality audit.
16. Define multiple chemical sensitivity.
17. Describe several instruments suitable for indoor air quality testing.
18. What instruments would you use to measure air flow direction and intensity in an indoor air quality audit.
19. What are some of the criteria to use when selecting a consultant for indoor air quality assessments.
20. Describe what wipe samples are and how they can be applied to an IAQ assessment.

Chapter 5

AIR POLLUTION DISPERSION

INTRODUCTION

This chapter describes simplified methods of estimating airborne pollutant concentration distributions associated with stationary emission sources. Methods of estimating concentrations of airborne effluents have been studied for a long time and have undergone considerable revision because of experimental results. There are sophisticated models available to predict and to assist in evaluating the impact of pollutants on the environment and to sensitive receptors such as populated areas. In this chapter we will explore the basic principles behind dispersion models and then apply a simplified model that has been developed by EPA to analyzing air dispersion problems. The software can be downloaded from Butterworth-Heinemann's Web site and is called SCREEN3. This model provides a simulation of point and area source dispersion calculations which can help develop air quality impact assessments, assess worst-case scenarios for catastrophic releases from elevated point sources such as stacks and flares and area sources such as fires, and help guide in the selection of control equipment and schemes by assessing different dispersion scenarios that are discussed below.

It is important to note that the modeling techniques discussed in this chapter are limited to nonreactive effluents. For a nonreactive effluent, meteorology specifies what happens to a puff or plume of pollutant from the time it is emitted to the time it is detected at some other location. This is a very limiting case since many pollutants undergo significant biotransformations when emitted into the atmosphere, where they interact with other pollutants, undergo reactions when exposed to UV light, experience half-life transformations, and/or are impacted by temperature and humidity conditions. Models based on nonreactive effluents must be used with caution and the calculations viewed as gross estimates only. Kinetics describing biotransformations can be built into the model however, this needs to be done on a pollutant-specific basis.

The principal shortcoming with SCREEN3 is the lack of graphical displays. Interactive graphics that enable plume tracking are invaluable in assessing potential environmental impacts and public health risks from episodic releases. There are a number of commercial and EPA software products that enable this more sophisticated type of analysis to be performed. Some are cited in this chapter; however, no specific endorsements of individual software products are made. The reader also has the option of working with consulting firms that specialize in developing and applying such models. One of these is Principia Mathematica, located in Lakewood, Colorado. Their Web site can be visited at www.prinmath.com. The author has worked closely with this group on a number of environmental litigation problems involving both groundwater and air contamination issues, and recommends their services.

In a traditional sense, dispersion models themselves are generally not thought of as pollution prevention tools. Most often they have been applied to environmental impact assessments (EIA) or an air quality assessment (AQA), evaluating worst-case catastrophic air release scenarios for emergency planning purposes, and in assessing environmental impacts from releases for health-risk evaluations and/or litigation purposes. Nonetheless, they are a tool that can be applied in assessing the benefits of an air pollution prevention type project opportunity, by applying the tool in the same manner as for an EIA.

DISPERSION THEORY BASICS

The earliest and still widely used dispersion model to compute pollutant concentration profiles is the Gaussian plume model for single or multiple source pollution problems. Box-type model techniques, which can take into account nonlinear interactions among different species arising from chemical reactions, have been used in longer-range dispersion computations.

In Gaussian plume computations the change in wind velocity with height is a function both of the terrain and of the time of day. We model the air flow as turbulent flow, with turbulence represented by eddy motion. The effect of eddy motion is important in diluting concentrations of pollutants. If a parcel of air is displaced from one level to another, it can carry momentum and thermal energy with it. It also carries whatever has been placed in it from pollution sources. Eddies exist in different sizes in the atmosphere, and these turbulent eddies are most effective in dispersing the plume.

TOPOGRAPHICAL EFFECTS

Surface topography can affect the local wind patterns; one example is the onshore and offshore breeze, and another example is the heat island over large urban areas. Another manmade effect is the generation of mechanical turbulence caused by the nonuniform height of buildings in a city. We will discuss this effect in more depth later on.

TEMPERATURE IN THE ATMOSPHERE

Temperature change with altitude has great influence on the motion of air pollutants. For example, inversion conditions result in only limited vertical mixing. The amount of turbulence available to diffuse pollutants is also a function of the temperature profile. The decrease of temperature with altitude is known as the *lapse rate*. The normal or standard lapse rate in the United States is -3.5° F/1,000 ft. An adiabatic lapse rate has a value of -5.4° F/1,000 ft. Temperature as a function of altitude is expressed by the following equation:

$$Z_2 - Z_1 = -nR(T_2 - T_1)/[(n - 1)g] \tag{1}$$

where:
Z = vertical distance from a reference point
R = the Universal gas constant = $53.341b_f/lb_m$--°R for air
g = gravitational constant
T = absolute temperature
n = a thermodynamic constant = C_p/C_v = 1 for isothermal process = 1.4 for adiabatic process

ATMOSPHERIC STABILITY

Consider a sphere of air which is carried upward over a distance from Z_1 to Z_2 in the atmosphere. This parcel travels through a region of decreasing pressure, and consequently expands. The expansion requires work, and the air sphere temperature drops. Since the process is usually reasonably rapid, it is a good approximation to assume that this process occurs adiabatically. If the atmospheric lapse rate were exactly the adiabatic lapse rate, then the parcel of air would reach its new position, Z_2, at the same temperature as the surroundings, and there would be no buoyant force. We consider this process as having a *neutral stability*, a displaced mass of air neither tending to return to its original position nor tending to continue its displacement.

If the sphere of air mass moves upward in an adiabatic process but in an atmosphere with a *subadiabatic lapse rate*, the sphere follows a temperature change given by the adiabatic slope; but when it arrives at point Z_2, it is at a lower temperature than its surroundings, but at the same pressure. As a result, it is heavier than the surroundings and tends to fall back to its original position. This condition is called *stable*. In a stable atmosphere pollutants will only slowly disperse, and turbulence is suppressed.

In another case, when the air motion results in a temperature rise, the density of the air sphere is less than the surroundings, and the sphere of air continues to rise. Such an atmosphere is ***unstable***. An unstable condition is favorable for pollutant dispersion. While turbulent diffusion in the mixing layer depends in a fundamental sense on temperature structure, an empirical system due to Pasquill (see your list of ***Recommended Resources***) is often used in urban dispersion models to denote stability. Here, common meteorological observations - insolation (incident solar radiation) during the day or degree of cloudiness at night- are used in lieu of temperature profile measurements for reasons of practicality and availability of data. Stability classes defined in this system are given in Table 1. The table can also be used to find dispersion coefficients which, in turn, are used to estimate concentrations of pollutants.

Table 1. Relations Between Turbulent Conditions and the Weather.[a,b]

Surface wind speed (at 10 m), m/s	**Daytime Insolation Conditions**			**Nighttime conditions**	
	Strong	**Moderate**	**Slight**	**Thin overcast or ≥ 4/8 cloudiness [c]**	**Thin overcast or ≤ 3/8 cloudiness**
< 2	A	A-B	B		
2 - 3	A-B	B	C	E	F
3 - 5	B	B-C	C	D	E
5 - 6	C	C-D	D	D	D
> 6	C	D	D	D	D

[a] A, extremely unstable conditions; B, moderately unstable; C, slightly unstable; D, neutral conditions [b]; E, slightly stable conditions; F, moderately stable conditions; [b] Applicable to heavy overcast, day or night; [c] The degree of cloudiness is defined as that fraction of the sky above the local apparent horizon which is covered by clouds.

WHAT IS MEANT BY ATMOSPHERIC DISPERSION

Methods of estimating gaseous effluent concentrations have undergone many revisions. For a number of years, estimates of concentrations were calculated from the equations of Sutton, with the atmospheric dispersion parameters C_y, C_z, and n, or from the equations of Bosanquet with the dispersion parameters p and Q. More common approaches are based on experimental observation that the vertical distribution of spreading particles from an elevated point is related to the standard deviation of the wind elevation angle, σ_E, at the point of release.

The *Gaussian Plume Model* is the most well-known and simplest scheme to estimate atmospheric dispersion. This is a mathematical model which has been formulated on the assumption that horizontal advection is balanced by vertical and transverse turbulent diffusion and terms arising from creation of depletion of species i by various internal sources or sinks. In the wind-oriented coordinate system, the conservation of species mass equation takes the following form:

$$\partial C_i/\partial t + U\,\partial C_i/\partial x = \partial_i/\partial y(K_y\,\partial C_i/\partial y) + \partial/\partial z(K_z\,\partial C_i/\partial z) + C_i \qquad (2)$$

where:
C_i = average concentration, g/m^3 or μg/m^3
U = average wind speed, m/s
t = time
x = x axis extending horizontally in the direction of mean wind
y = y axis in the horizontal plane perpendicular to the x axis
z = z axis extending vertically
C_I = rate of loss or gain by chemical reactions, precipitation (washout), or adsorption by suspended particles
$K_y = U\,\sigma_y^2/2x$
$K_z = U\,\sigma_z^2/2x$

The wind-oriented coordinate system is shown in Figure 1.

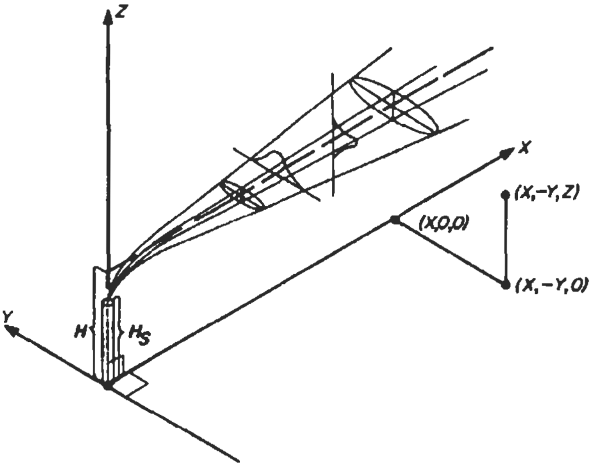


Figure 11. Coordinate systems for Gaussian plume model.

Considering an analytical solution for the simplest case of dispersion from an isolated source, we note that sources may be located at any point along the z axis, such as sources from industrial chimneys or power plant stacks at some height H_S above the ground. These usually continue to rise an incremental height ΔH, either by virtue of buoyancy forces acting on the heated effluent, or because their momentum carries them aloft, or both.
For the special case of a uniform wind, where K_z and K_y are constants, an isolated source located at (0,0,H) continuously emits a mass per unit time of species i at a constant rate Q_i, and the removal rate from internal sinks is governed by linear processes, $C_i = -C_i/t_c$ with t_c being a characteristic decay time.

The following expression provides a solution:

$$C_i(x,y,z,H) = (Qi/2\pi\sigma_y\sigma_z U)\exp[-x/Ut_c]\exp[-\tfrac{1}{2}(y/\sigma_y)^2]\{\exp[-\tfrac{1}{2}((z-H)/\sigma_z)^2] + \exp[-\tfrac{1}{2}((z+H)/\sigma_z)^2]\} \qquad (3)$$

where: Q_i = source strength, g/s
t_c = decay time, s ($t_c = \infty$ for nonactive species)
H = effective stack height
σ_y = diffusion coefficient in the y-direction, m
σ_z = diffusion coefficient in the z-direction, m

The solution to the above expression assumes no diffusion along the horizontal axis (i.e., no diffusion in the downwind (x) direction). This assumption makes the model applicable to a plume, but not to a puff of pollution.

Since U is a function of z, some mean value must be used. The appropriate value is the mean through the plume. However, the time-averaged wind speed at the stack height is commonly used. Often, even this value may not be known, in which case an estimate must be made. This estimate could be based on an assumed power law velocity profile such as:

$$U = U_1(H/Z_1)^n \qquad (4)$$

DIFFUSION COEFFICIENTS

To apply Equation (3), it is necessary to determine the diffusion coefficients σ_y and σ_z. The diffusion coefficients can be related to the deviation in the wind direction, given by σ_a in the azimuth angle (azimuth refers to the lateral or cross-wind direction), and σ_e in the deviation angle (deviation refers to vertical - z direction). The variation of these angles as a function of wind speed and stability condition is reported in older literature to be related through empirical observation of meteorological parameters, and in particular wind vectors. Table 1 notes the atmospheric conditions, and Figures 2 and 3 give results for the diffusion coefficients. These values assume:

- a sampling time of about 10 min,
- the height values of interest to be in the lowest several hundred meters of the atmosphere, and
- a surface corresponding to conditions of open country. For urban areas there are heat island effects and the mechanical turbulence generated by surface roughness. The diffusion coefficients are greater; therefore, Figures 2 and 3 will produce a conservative result.

Maximum ground level concentration and its location can be calculated from the following expression:

$$C_i(x,0,0,H) = (Q/\pi\sigma_y\sigma_z U)\exp(-H^2/2\sigma z^2) \qquad (5)$$

MULTISOURCE GAUSSIAN PLUME MODEL

Using the Gaussian plume model and the other relations presented, it is possible to compute ground level concentrations C_i at any receptor point (x_0, y_0) in the region resulting from each of the isolated sources in the emission inventory. Since Equation (2) is linear for zero or linear decay terms, superposition of solutions applies. The concentration distribution is available by computing the values of C_i at various receptors and summing over all sources.

A graphical representation can be made by plotting x_{max} as a function of $(C_iU/Q_i)max$ using Equation (5). Later in this chapter we will examine a formalized model that was developed by the US EPA that uses the basic principles discussed thus far. The model that we will become familiar with is a software package that you can download from the Butterworth-Heinemann Web-site. We can evaluate maximum ground-level concentrations from various point source scenarios, using these as a guide to assessing the impact on air quality from episodic releases. Some shortcomings with the model are:

- the lack of interactive graphics that enables visual tracking of a plume progression;
- the lack of kinetic model components within the dispersion calculations that would account for biotransformations of the pollutant species and interactions between species;

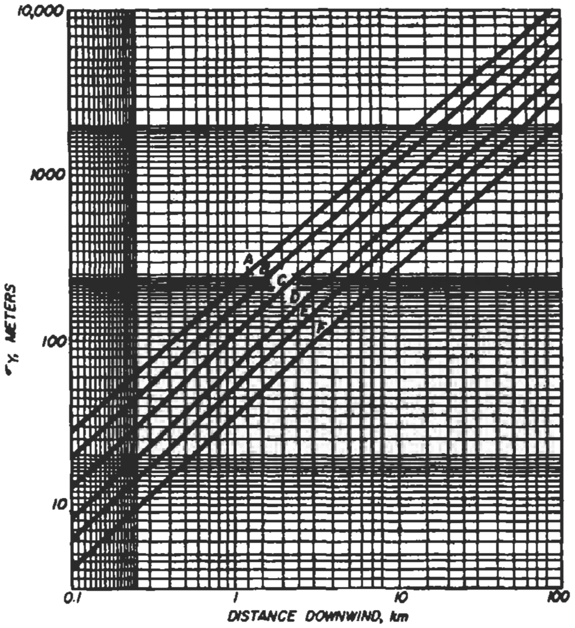


Figure 2. Horizontal dispersion coefficient as a function of downwind distance from the source.

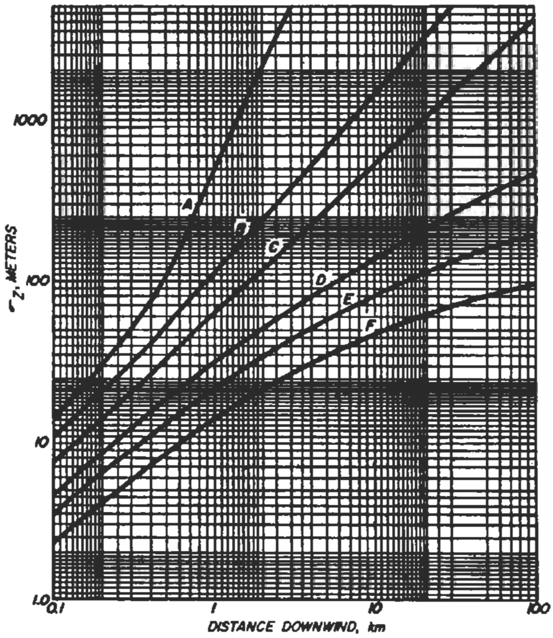


Figure 3. Vertical dispersion coefficient as a function of downwind distance from the source.

- inflexible terrain parameters that do not necessarily simulate actual conditions.

Despite these shortcomings, SCREEN3 is still a useful tool in evaluating air dispersion problems.

ELEVATED POINT SOURCE DISCHARGES

This section defines the principal factors which must be accounted for when designing a stack for air pollution control purposes. These factors govern the dispersion and transport of the pollutants and define the performance criteria against which the stack will be compared. These factors include (1) air quality standards, (2) meteorological conditions, and (3) topographical peculiarities. The problem of designing a stack to exploit its air pollution control potential largely reduces to a problem of determining a stack height which will assure non-polluting performance. This means designing a stack to meet some performance standard (usually legally binding) given the meteorological conditions, topographic influences, and process exit conditions. Usually, the exit gas conditions are unstable and the topographic influences are unknown or speculative. This leaves the meteorology and the air quality standards as the governing design criteria.

First order parameters affecting dispersion stem from meteorological conditions. These, as much as any other consideration, determine how a stack is to be designed for air pollution control purposes. Since the operant transport mechanisms are determined by the micro-meteorological conditions, any attempt to predict ground-level pollutant concentrations is dependent on a reasonable estimate of the convective and dispersive potential of the local air. The following are meteorological conditions which need to be determined:

- Mean wind speed and direction: The air flow is assumed to be horizontal, but the flow may be tilted (to yield a vertical component) due to local topographic effects. The mean wind speed determines the convection of the stack emissions.
- Intensity of turbulence: These factors, represented by the standard deviations of the horizontal wind direction, σ_θ, the standard deviation of the vertical wind component, σ_ϕ, and the gustiness as measured by the standard deviation of the wind speed, all have significant bearing on the dispersion of emissions from a stack.
- Vertical temperature gradient: The lapse rate (rate of decrease in temperature with increases in height) must be taken into account because it affects the final height to which a buoyant plume rises.

These meteorological parameters, with the possible exception of the mean wind speed and direction, are not generally available for inclusion in calculations. Even wind speed measurements, which are usually taken at 20 ft above grade, must be corrected to the release point elevation. The correction applied to the wind speed depends on the turbulence of the air. The wind speed is the key determinant of the convection of pollutant in a plume.

The vertical temperature gradient (the lapse rate) is usually not monitored by routine meteorological observation, and it, too, must be approximated from estimates of solar insolation, solar angle, and differential heating due to uneven cloud cover. For purposes of diffusion analyses, the lapse rate is usually approximated by a constant.

The parameters about which the least is known are the diffusion parameters σ_ϕ and σ_θ, which govern diffusion transport of pollutants within a plume. These parameters are not monitored by meteorological stations and must always be approximated through indirect methods. Figure 4 illustrates the role each of these parameters has on the transport of airborne pollutants.

It is known that the vertical distribution of diffusing particles from an elevated point source is a function of the standard deviation of the vertical wind direction σ_ϕ at the release point. The standard deviations of the vertical and horizontal wind directions are related to the standard deviations of particle concentrations in the vertical and horizontal directions within the plume itself. This is equivalent to saying that fluctuations in stack top conditions control the distribution of pollutant in the plume. Furthermore, it is known that the plume pollutant distributions follow a familiar Gaussian diffusion equation.

The Gaussian diffusion equation is known as the Pasquill and Gifford model, and is used to develop methods for estimating the required diffusion coefficients. The basic equation, already presented in a slightly different form, is restated below:

$$\chi(x,y,z,h_e) = (Q/2\pi\sigma_y\sigma_z U)\exp(A_1)[\exp(A_2) + \exp(A_3)] \qquad (6)$$

where:
$A_1 = -½(y/\sigma_y)^2$
$A_2 = -½((z - h_e)/\sigma_z)^2$
$A_3 = -½((z + h_e)/\sigma_z)^2$

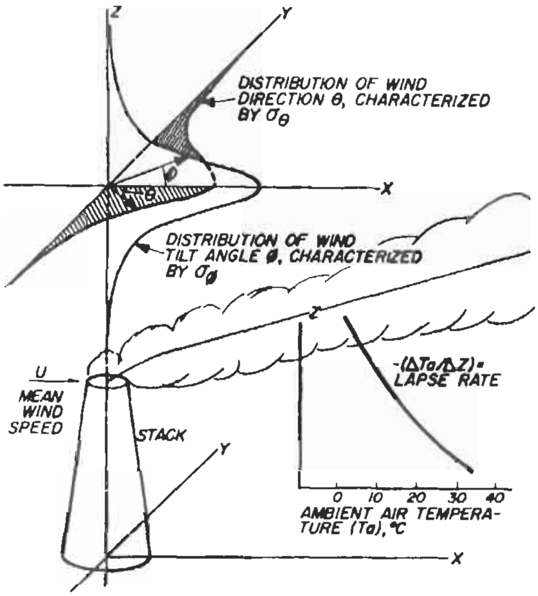


Figure 4. Role of meteorological parameters on transport of air pollutants.

The Pasquill and Gifford approach presented here removes the need to relate σ_ϕ to σ_z and σ_θ to σ_y, and concentrates on determining σ_z and σ_y directly from weather data. In order to do this, Pasquill introduced the concept of the *atmospheric stability class*. Pasquill defined six stability classes ranging from highly stable, low-turbulence Class F, to unstable, highly turbulent Class A, and he identified the surface wind speed, intensity of solar radiation, and nighttime sky cover as being the prime factors controlling atmospheric stability. These stability classes were then correlated with observations of the behavior of plumes in terms of their dispersion with the identified prime meteorological factors. Look back at Table 1 and also the sidebar discussion for reminders on these definitions.

Relation Between Stability Classes and Meteorological Observations

Stability Class	
A	Extremely unstable conditions
B	Moderately unstable conditions
C	Slightly unstable conditions
D	Neutral conditions
E	Slightly stable conditions
F	Moderately stable

Local Topographical Factors

The following discussion clarifies the effect that topographic factors can have on the transport of pollutants and, consequently, on the design and especially the siting of the stack.

Effects of Nearby Ridges - An example of the effect that nearby mountain ridges may have on pollutant transport is shown in Figure 5. High concentrations of pollutants emitted from the source stack would probably be expected to occur on the windward slope of the ridge shown, but, in fact, observations at smelting plants and thermal generating stations located in valleys indicate that the leeward side of the ridge often experiences the more severe pollution due to wind-induced eddy formation. Probably there is little that can be done in the design of a stack to avoid this problem, although raising the elevation could be of value. In such cases, air pollution control can probably be implemented only by process reduction during unfavorable wind conditions or by permanent stack gas cleaning devices. In the lee of a cliff there may be eddies of the type shown in Figure 6. If a stack is sited in the downdraft of one of these eddies, the plume may be brought directly to the ground. One of the central problems in stack design for pollution control: local, short-term effects may be the most important stack design consideration, but will usually be the aspect of the problem about which the least information is available.

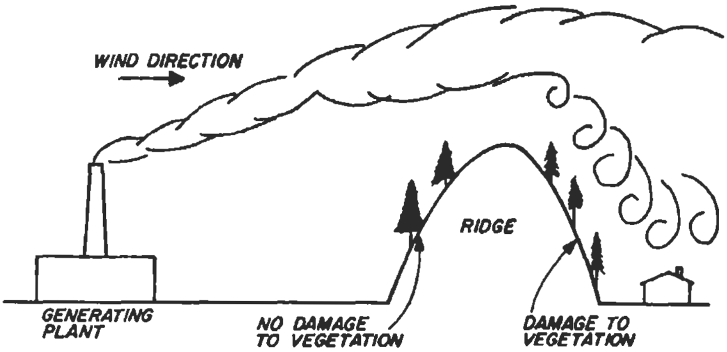


Figure 5. Shows effect of nearby mountain ridges on pollutant transport.

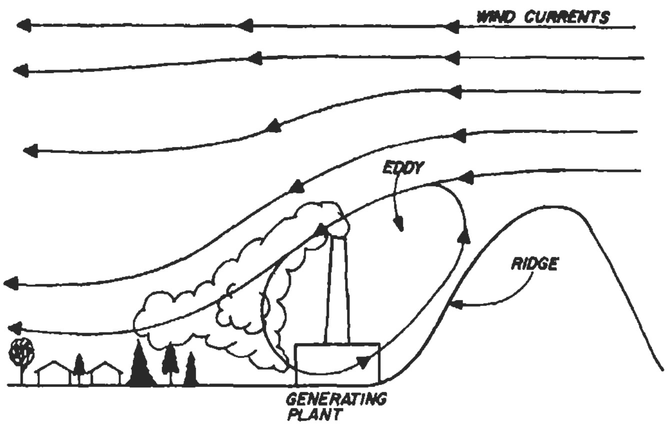


Figure 6. Shows turbulent eddy formation in the lee of a cliff.

Diurnal Air Circulation Effects in Valleys - Figure 7 shows some of the complications associated with siting a stack in a valley. When the winds are light, the air in a valley becomes stagnant and stratified, especially at night and particularly in winter. Pollutants emitted at night may be drawn down to the valley floor by cold air sinking down the hillside. During the day most of the air in the valley remains stably stratified while warm air flows up the hillsides, receiving heat from them as it ascends. As shown in Figure 7, a circulation pattern is set up where the plume is forced to fan out.

Effects of Large Local Water Bodies - The siting of a stack along the shoreline of a large lake or along an ocean front may be accompanied by unique air pollution transport phenomena. Figure 8 shows how thermal convection wind currents arising from differences in the temperatures of land and water masses can influence transport properties. Such convection phenomena may be highly dependent on meteorological and seasonal conditions and may defy the available methods to estimate them quantitatively. The pattern shown in Figure 8 is appropriate for an occasion when the land mass is warmer than the water, a frequently encountered summer air circulation phenomenon which reverses in the evening as the land cools off faster than the lake or ocean. It is doubtful that stack design would have any significant influence on controlling this type of atmospheric transport problem, and it is more unlikely that such an influence could be quantified. Hence, if sea breeze-induced air pollution effects were found to be objectionable, the only control options remaining to the source operator would be: (1) process reduction during periods of high air pollution potential, or (2) installation of a stack gas cleaning device.

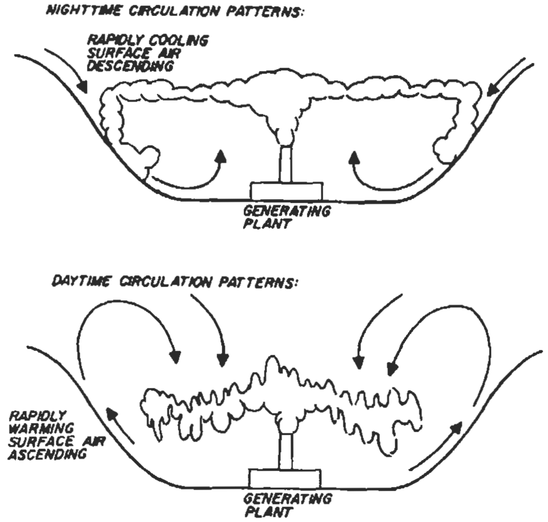


Figure 7. Diurnal air circulation effects associated with valleys.

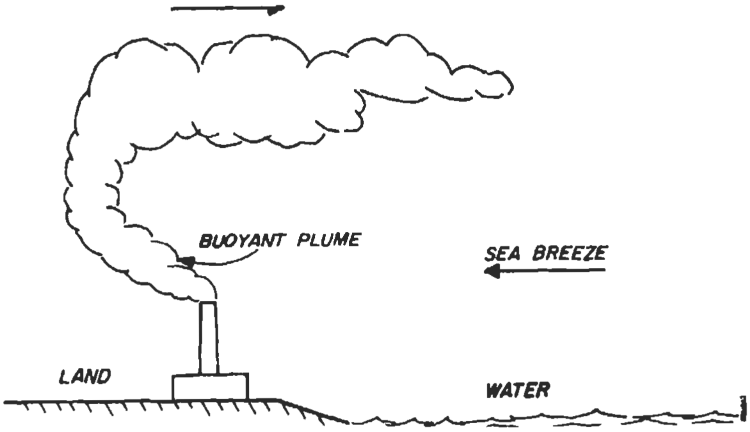


Figure 8. Shows effect of large water bodies on pollutant transport.

Given the factors which influence the design of the stack, it is logical to proceed with the question of relating these factors to stack performance. It has already been proposed that a Gaussian distribution of pollutant concentration be used to predict the concentration of pollutant at any point within the plume. This procedure requires knowledge of meteorological conditions as they affect the standard deviations of plume concentration in the vertical and horizontal directions. Use of the stability class approach leads to a determination of σ_z and σ_y.

One major item remains before we can apply the dispersion methodology to elevated emission sources, namely plume height elevation or rise. Once the plume rise has been determined, diffusion analyses based on the classical Gaussian diffusion model may be used to determine the ground-level concentration of the pollutant. Comparison with the applicable standards may then be made to demonstrate compliance with a legal discharge standard.

Plume Rise Determination

A particularly difficult aspect of the problem of diffusion of atmospheric pollution is the determination of the height to which a buoyant plume with an initial exit velocity will rise. Plume rise, which is defined as the distance between the top of the stack and the axis of the centroid of the pollutant distribution, has been found to depend on:

- The exit velocity of the stack, V_s
- The diameter of the stack, d
- The mean wind (horizontal) speed, U_s
- The atmospheric stability class
- The lapse rate $(\partial T_a/\partial z)$
- The temperature difference between the exit gases and ambient air

Clearly, there exists a large degree of interrelation between certain of the "independent" variables given above. Unfortunately, the exact form of the interrelationship depends on highly speculative local circumstances, such as terrain roughness and variable orographic effects. For this reason the problem of plume rise determination has remained particularly difficult to solve in a general, broadly applicable sense. All plume rise formulas contain at least one dimensionless constant that must be evaluated experimentally, and the value of these so-called constants varies from stack to stack. Unfortunately, the experimental data from which the constants are derived are of highly variable quality. The shortcomings of these data stem from several sources including the following:

- Observations were made too close to the source before the plume became horizontal.

- Critical meteorological variables were not always measured, especially vertical wind and temperature gradients.
- Early measurements were frequently confined to relatively short stacks and to areas with a high concentration of interfering industrial and residential structures.

Thus, based on the above, it is not surprising that even under the best conditions an uncertainty factor of approximately 2 is likely in estimates of the plume rise. Despite this somewhat pessimistic introduction, estimations of plume rise are worthwhile and an integral part of the dispersion analysis. Table 2 presents some of the well-known plume rise formulas used in different model approaches. The two major controlling variables which appear in many, if not all, of the plume rise formulas surveyed are:

- A momentum term: $C_1d(V_sU)^{C2}$
- A heat flux term: $C_3(Q_h/U)^{C4}$

Multiple regression techniques have been applied by investigators to determine the coefficients in a plume rise equation containing both of the above terms:

$$\Delta h = [C_1d(V_s/U)^{C2} + C_3(Q_h/U)^{C4}] \tag{7}$$

where C_1, C_2, C_3, and C_4 are coefficients of regression.
Plume rise observations based on single-stack operation were regressed into the above expression and empirically fitted to the following expression, which incorporates atmospheric stability classes into the coefficients:

$$\Delta h = A[-0.029V_sd/U + 5.35Q_h^{1/2}/U] \tag{8}$$

where A = 2.65, 1.08, and 0.68 for unstable, neutral, and stable conditions, respectively.

Table 2. Examples of Plume Rise Formulas Reported in the Literature.

Investigator	Formula	Comment
Holland	**$\Delta h = (1.5V_sd + 0.04Q_h)/U$** where Δh = plume rise (m), V_s = stack exit velocity (m/s), d = stack diameter (m), Q_h = heat emission rate (kcal/s), U = stack top wind speed (m/s)	Highly empirical. Requires stack testing confirmation on case-by-case basis

Investigator	Formula	Comment
Concawe	$\Delta h = 5.53Q_h^{1/2}/U^{3/4}$	Regression formula best suited for large buoyant plumes
Stumke	$\Delta h = (d/U)[1.5V_s + 65d^{1/2}\Theta^{0.25}]$ where $\Theta = (T_a - T_s)/T_s$ Ta = ambient air temperature, °K Ts = stack gas temperature, °K	Same as Holland formula
Lucas-Moore-Spurr	$\Delta h = 135Q_h^{1/4}/U$	Regression formula with ill-defined statistics
Rauch	$\Delta h = 47.2Q_h^{1/4}/U$	Same as Lucas formula
Stone-Clark	$\Delta h = (104.2 + 0.17h_p)Q_h^{1/4}/U$ where h_p = physical stack height (m)	Modification of Lucas-Moore expression, takes into account effect of physical stack
Moses and Carson	$\Delta h = (A/U)(-0.029V_s + 5.53Q_h^{1/2})$ A = coefficient dependent on atmospheric stability: A = 2.65; Unstable A = 1.08; Neutral A = 0.68; Stable	Regression formula
Briggs	For unstable and neutral conditions: $\Delta h = 0.25Q_h^{1/3}h_p^{2/3}U$ For stable conditions: $\Delta h = 0.296[Q_h/U(\partial\theta/\partial z)]^{1/3}$ where $\partial\theta/\partial z$ = variation of potential temperature with height ≈ 0.03 °K/m	Nonempirical formulation

We direct attention to procedures for estimating the air quality impact of stationary sources based on an approach developed by the US EPA.

ESTIMATING THE AIR QUALITY IMPACT OF STATIONARY SOURCES

In this section we will learn how to use one of EPA's simpler air dispersion models for evaluating the air quality impact of stationary sources. The model is known as SCREEN3, and it was developed to provide an easy-to-use method of obtaining pollutant concentration estimates based on a screening procedures document that we will discuss.

SCREEN will run on an IBM-PC compatible personal computer with at least 256K of RAM. The program will run with or without a math coprocessor chip. Execution time will be greatly enhanced with a math coprocessor chip present (about a factor of 5 in computer time) and will also benefit from the use of a hard disk drive.

The reader can purchase the software package and user guide from NTIS, or you can simply follow the discussions below and download the software directly from the Butterworth Heinemann Web site. There are no charges for the software from the publisher's site.

SCREEN3 (or simply, SCREEN) runs interactively on the PC, meaning that the program asks the user a series of questions in order to obtain the necessary input data, and to determine which options to exercise. SCREEN can perform single-source, short-term calculations, including estimating maximum ground-level concentrations and the distance to the maximum ground-level concentration, incorporating the effects of building downwash on the maximum concentrations for both the near wake and far wake regions, estimating concentrations due to inversion break-up and shoreline fumigation, and determining plume rise for flare releases. Each of these cases is described later on.

The model can incorporate the effects of simple elevated terrain on maximum concentrations, and can also estimate 24-hour average concentrations due to plume impaction in complex terrain using the VALLEY model 24-hour screening procedure. Simple area sources can be modeled with SCREEN using a numerical integration approach. The model can also be used to simulate the effects of simple volume sources using a virtual point source procedure. The model can also calculate the maximum concentration at any number of user-specified distances in flat or elevated simple terrain, including distances out to 100 km for long-range transport.

SCREEN can not explicitly determine maximum impacts from multiple sources, except for the procedure to handle multiple nearby stacks by merging emissions into a single "representative" stack. The reader is directed to the MPTER (Pierce and Turner, 1980) or ISC (EPA, 1995b) models on EPA's Support Center for Regulatory Air Models (SCRAM) Bulletin Board System (BBS) to model short-term impacts for multiple sources. With the exception of the 24-hour estimate for complex terrain impacts, the results from SCREEN are estimated maximum 1-hour concentrations. To handle longer period averages, the screening procedures document contains recommended adjustment factors to estimate concentrations out to 24 hours from the maximum 1-hour value. For seasonal or annual averages, the screening procedures document contains a procedure using hand calculations, but the use of ISCLT (EPA, 1995b) or another long-term model on the SCRAM BBS is recommended. The SCREEN model can provide estimated concentrations for distances less than 100 meters (down to one meter as in other regulatory models), whereas the nomographs used in the hand calculations are limited to distances greater than or equal to 100 meters. The SCREEN model is also not limited to plume heights of 300 meters, whereas the nomographs are. In both cases, caution should be used in interpreting results that are outside the range of the nomographs.

In addition, SCREEN examines a full range of meteorological conditions, including all stability classes and wind speeds to find maximum impacts, whereas to keep the hand calculations tractable only a subset of meteorological conditions (stability classes A, C, and E or F) likely to contribute to the maximum concentration is examined. The use of a full set of meteorological conditions is required in SCREEN because maximum concentrations are also given as a function of distance, and because An E or F stability may not be controlling for sources with building downwash (not included in the hand calculations). SCREEN explicitly calculates the effects of multiple reflections of the plume off the elevated inversion and off the ground when calculating concentrations under limited mixing conditions.

A TUTORIAL FOR THE SOFTWARE

The executable file that you can download is called SCREEN3.EXE. You can download the software from Butterworth Heinemann's companion Web site at www.bh.com/companions/0750674497. Since this is an interactive program, SCREEN is normally executed by simply typing SCREEN from any drive and directory that you have downloaded the program into containing the SCREEN3.EXE file. Then simply respond to the prompts provided by the program.

As noted, the SCREEN model is written as an interactive program for the PC. Therefore, SCREEN is normally executed by simply typing SCREEN from any drive and directory that contains the SCREEN3.EXE file, and responding to the prompts provided by the program. However, a mechanism has been provided to accommodate the fact that for some applications of SCREEN the user might want to perform several runs for the same source changing only one or a few input parameters. This mechanism takes advantage of the fact that the Disk Operating System (DOS) on PCs allows for the redirection of input that is normally provided via the keyboard to be read from a file instead. As an example, to run the sample problem provided on the disk one would type the following at the DOS prompt:

```
SCREEN3 <EXAMPLE.DAT
```

The SCREEN model will then read the responses to its prompts from the EXAMPLE.DAT file rather than from the keyboard. The output from this run will be stored in a file called SCREEN, which can then be compared with the EXAMPLE.OUT file provided on the program. The file containing the redirected input data may be given any valid DOS pathname. To facilitate the creation of the input file for the SCREEN model, SCREEN has been programmed to write out all inputs provided to a file called SCREEN.DAT during execution. Therefore, at the completion of a run, if the user types the following, the last run will be exactly duplicated:

```
SCREEN3 <SCREEN.DAT
```

Alternatively, the SCREEN.DAT file may be edited as an ASCII file using a text or line editor, and selected input parameters changed before rerunning the model. Since the original SCREEN.DAT file will be overwritten each time the model is run, it is advisable to save the modified inputs under a different file name.

Some cautions are needed regarding the use of redirected input with SCREEN. Because of the way some input errors are handled by SCREEN, the SCREEN.DAT file may contain some of the errors from the original input.

While SCREEN.DAT should still reproduce the correct results, it will be easier to work with the file if the original input does not contain any errors.

More importantly, since the inputs requested by SCREEN depend on the options selected, it is not advisable to edit the SCREEN.DAT file and try to change the options selected. An experienced user may be able to do this, but it may be easier simply to rerun SCREEN with the new options.

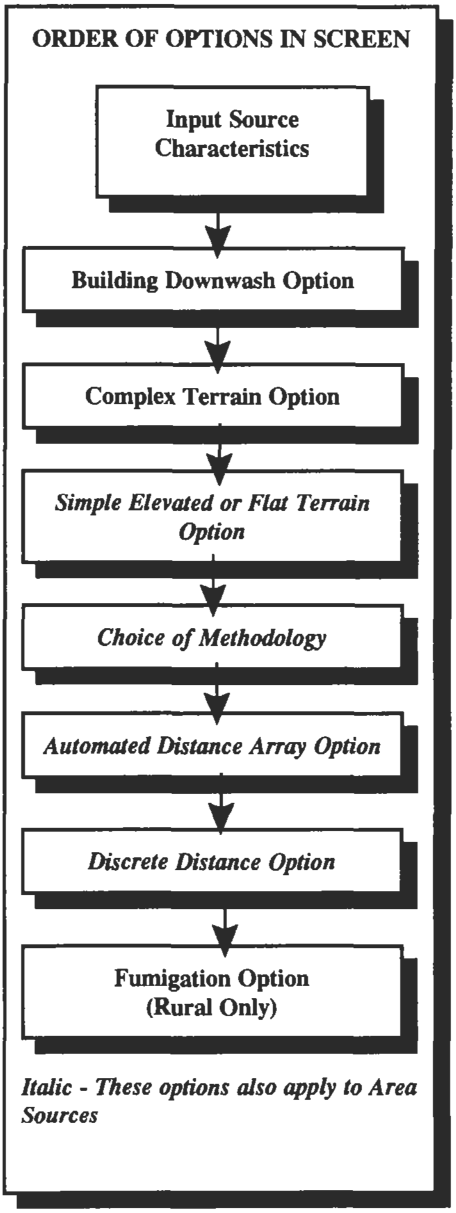
As noted later on in this chapter, there are other software options that can be downloaded for more sophisticated and detailed analyses.

Point Source Example

When running SCREEN for a point source, or for flare releases and area sources discussed below, you are first asked to provide a one line title (up to 79 characters) that will appear on the output file. You will then be asked to identify the source type, and should enter 'P' or 'p' for a point source (the model will identify either upper or lowercase letters and will repeat the prompt until a valid response is given). For a point source, you will be asked to provide the following inputs:

- Point Source Inputs Emission rate (g/s)
- Stack height (m)
- Stack inside diameter (m)
- Stack gas exit velocity (m/s) or flow rate (ft^3/min or m^3/s)
- Stack gas temperature (°K)
- Ambient temperature (°K) (use default of 293° K if not known)
- Receptor height above ground (may be used to define flagpole receptors) (m)
- Urban/rural option (U = urban, R = rural)

The SCREEN model uses free format to read the numerical input data, with the exception of the exit velocity/flow rate option. The default choice for this input is stack gas exit velocity, which SCREEN will read as free format. However, if the user precedes the input with the characters VF= in columns 1-3, then SCREEN will interpret the input as flow rate in actual cubic feet per minute (ACFM). Alternatively, if the user inputs the characters VM= in columns 1-3, then SCREEN will interpret the



Italic - These options also apply to Area Sources

input as flow rate in m^3/s. The user can input either upper or lowercase characters for VF and VM. The flow rate values are then converted to exit velocity in m/s for use in the plume rise equations, based on the diameter of the stack.

SCREEN allows for the selection of urban or rural dispersion coefficients. The urban dispersion option is selected by entering a 'U' (lower or upper case) in column 1, while the rural dispersion option is selected by entering an 'R' (upper or lower case) in column 1. Determination of the applicability of urban or rural dispersion is based upon land use or population density. In general, if 50 percent or more of an area 3 km around the source satisfies the urban criteria (Auer, 1978), the site is deemed in an urban setting. Of the two methods, the land use procedure is considered more definitive.
The sidebar discussion presents the order of regulatory options within the SCREEN model for point sources.

In order to obtain results from SCREEN corresponding to the procedures for the simple elevated or flat terrain option, the user should select the full meteorology option, the automated distance array option, and, if applicable for the source, the simple elevated terrain option. The simple elevated terrain option would be used if the terrain rises above the stack base elevation but is less than the height of the physical stack. These, as well as the other options listed in the sidebar, are explained in more detail below.

In the model, a *flagpole receptor* is defined as any receptor, which is located above local ground level, e.g., to represent the roof or balcony of a building.

Building Downwash Option

There are two downwash options available with this model, a regulatory and a non-regulatory option. Both are summarized below.

Regulatory Building Downwash Option - Following the basic input of source characteristics, a SCREEN prompt asks if building downwash is to be considered, and if so, prompts for building height, minimum horizontal dimension, and maximum horizontal dimension, in meters, are presented. The downwash screening procedure assumes that the building can be approximated by a simple rectangular box. Wake effects are included in any calculations made using the automated distance array or discrete distance options (described below). Cavity calculations are made for two building orientations - first with the minimum horizontal building dimension along-wind, and second with the maximum horizontal dimension along-wind. The cavity calculations are summarized at the end of the distance-dependent calculations.

Non-Regulatory Building Downwash Option - A Schulman-Scire Building Downwash/Cavity option can be selected along with two other non-regulatory options by entering the appropriate flag, SS, on the line containing the source type input. The program will later ask for the building height, minimum horizontal dimension, and maximum horizontal dimension in meters as is done for the regulatory cavity option. However, for this option only, the program will ask for the position of the source on the building with respect to the two building orientations. The response will need to be in the form of a ratio of the stack distance from a building centerline drawn perpendicular to the wind over the horizontal dimension of the side of the building which is parallel to the wind. The program will show a figure on how to calculate the correct ratio for an articular orientation.

Complex Terrain Option

The complex terrain option of SCREEN allows the user to estimate impacts for cases where terrain elevations exceed stack height. If the user elects this option, then SCREEN will calculate and print out a final stable plume height and distance to final rise for the VALLEY model 24-hour screening technique. This technique assumes stability class F (E for urban) and a stack height wind speed of 2.5 m/s. For complex terrain, maximum impacts are expected to occur for plume impaction on the elevated terrain under stable conditions. The user is therefore instructed to enter minimum distances and terrain heights for which impaction is likely, given the plume height calculated, and taking into account complex terrain closer than the distance to final rise. If the plume is at or below the terrain height for the distance entered, then SCREEN will make a 24-hour concentration estimate using the VALLEY screening technique. If the terrain is above stack height but below the plume centerline height for the distance entered, then SCREEN will make a VALLEY 24-hour estimate (assuming E or F and 2.5 m/s), and also estimate the maximum concentration across a full range of meteorological conditions using simple terrain procedures with terrain "chopped off" at physical stack height. The higher of the two estimates is selected as controlling for that distance and terrain height (both estimates are printed out for comparison).

The simple terrain estimate is adjusted to represent a 24-hour average by multiplying by a factor of 0.4, while the VALLEY 24-hour estimate incorporates the 0.25 factor used in the VALLEY model. Calculations continue for each terrain height/distance combination entered until a terrain height of zero is entered. The user will then have the option to continue with simple terrain calculations or to exit the program. It should be noted that SCREEN will not consider building downwash effects in either the VALLEY or the simple terrain component of the complex terrain screening procedure, even if the building downwash option is selected. SCREEN also uses a receptor height above ground of 0.0 m (i.e., no flagpole receptors) in the complex terrain option even if a non-zero value is entered. The original receptor height is saved for later calculations.

Simple Elevated or Flat Terrain Option

You are given the option in SCREEN of modeling either simple elevated terrain, where terrain heights exceed stack base but are below stack height, or simple flat terrain, where terrain heights are assumed not to exceed stack base elevation. If the user elects not to use the option for simple terrain screening with terrain above stack base, then flat terrain is assumed and the terrain height is assigned a value of zero. If the simple elevated terrain option is used, SCREEN will prompt the user to enter a terrain height above stack base. If terrain heights above physical stack height are entered by the user for this option, they are chopped off at the physical stack height. The simple elevated terrain screening procedure assumes that the plume elevation above sea level is not affected by the elevated terrain. Concentration estimates are made by reducing the calculated plume height by the user-supplied terrain height above stack base. Neither the plume height nor terrain height is allowed to go below zero. The user can model simple elevated terrain using either or both of the distance options described below, i.e., the automated distance array or the discrete distance option. When the simple elevated terrain calculations for each distance option are completed, the user will have the option of continuing simple terrain calculations for that option with a new terrain height. For conservatism and to discourage the user from modeling terrain heights that decrease with distance, the new terrain height for the automated distances cannot be lower than the previous height for that run. The user is still given considerable flexibility to model the effects of elevated terrain below stack height across a wide range of situations.

For relatively uniform elevated terrain, or as a "first cut" conservative estimate of terrain effects, the user should input the maximum terrain elevation (above stack base) within 50 km of the source, and exercise the automated distance array option out to 50 km. For isolated terrain features a separate calculation

For flat terrain the user will not be given the option to continue with a new terrain height.

can be made using the discrete distance option for the distance to the terrain feature, with the terrain height input as the maximum height of the feature above stack base. Where terrain heights vary with distance from the source, then the SCREEN model can be run on each of several concentric rings using the minimum and maximum distance inputs of the automated distance option to define each ring, and using the maximum terrain elevation above stack base within each ring for terrain height input. As noted above, the terrain heights are not allowed to decrease with distance in SCREEN. If terrain decreasing with distance (in all directions) can be justified for a particular source, then the distance rings would have to be modeled using separate SCREEN runs, and the results combined. The overall maximum concentration would then be the controlling value. The optimum ring sizes will depend on how the terrain heights vary with distance, but as a "first cut" it is suggested that ring sizes of roughly 5 km be used (i.e., 0 to 5 km, 5 to 10 km, etc.). The application of SCREEN to evaluating the effects of elevated terrain should be done in consultation with the permitting agency.

Choice of Meteorology

For simple elevated or flat terrain screening, the user will be given the option of selecting from three choices of meteorology:

- full meteorology (all stability classes and wind speeds);
- specifying a single stability class; or
- specifying a single stability class and wind speed.

Generally, the full meteorology option should be selected. The other two options were originally included for testing purposes only, but may be useful when particular meteorological conditions are of concern.

Automated Distance Array Option

The automated distance array option of SCREEN gives the user the option of using a preselected array of 50 distances ranging from 100 m out to 50 km. Increments of 100 m are used out to 3,000 m, with 500 m increments from 3,000 m to 10 km, 5 km increments from 10 km to 30 km, and 10 km increments out to 50 km.

When using the automated distance array, SCREEN prompts the user for a minimum and maximum distance to use, which should be input in free format, i.e., separated by a comma or a space. SCREEN then calculates the maximum concentration across a range of meteorological conditions for the minimum distance given (≥ 1 meter), and then for each distance in the array larger than the minimum and less than or equal to the maximum.

Thus, the user can input the minimum site boundary distance as the minimum distance for calculation and obtain a concentration estimate at the site boundary and beyond, while ignoring distances less than the site boundary. If the automated distance array is used, then the SCREEN model will use an iteration routine to determine the maximum value and associated distance to the nearest meter. If the minimum and maximum distances entered do not encompass the true maximum concentration, then the maximum value calculated by SCREEN may not be the true maximum. Therefore, it is recommended that the maximum distance be set sufficiently large initially to ensure that the maximum concentration is found. This distance will depend on the source, and some trial and error may be necessary; however, the user can input a distance of 50,000 m to examine the entire array. The iteration routine stops after 50 iterations and prints out a message if the maximum is not found. Also, since there may be several local maxima in the concentration distribution associated with different wind speeds, it is possible that SCREEN will not identify the overall maximum in its iteration. This is not likely to be a frequent occurrence, but will be more likely for stability classes C and D due to the larger number of wind speeds examined.

Discrete Distance Option

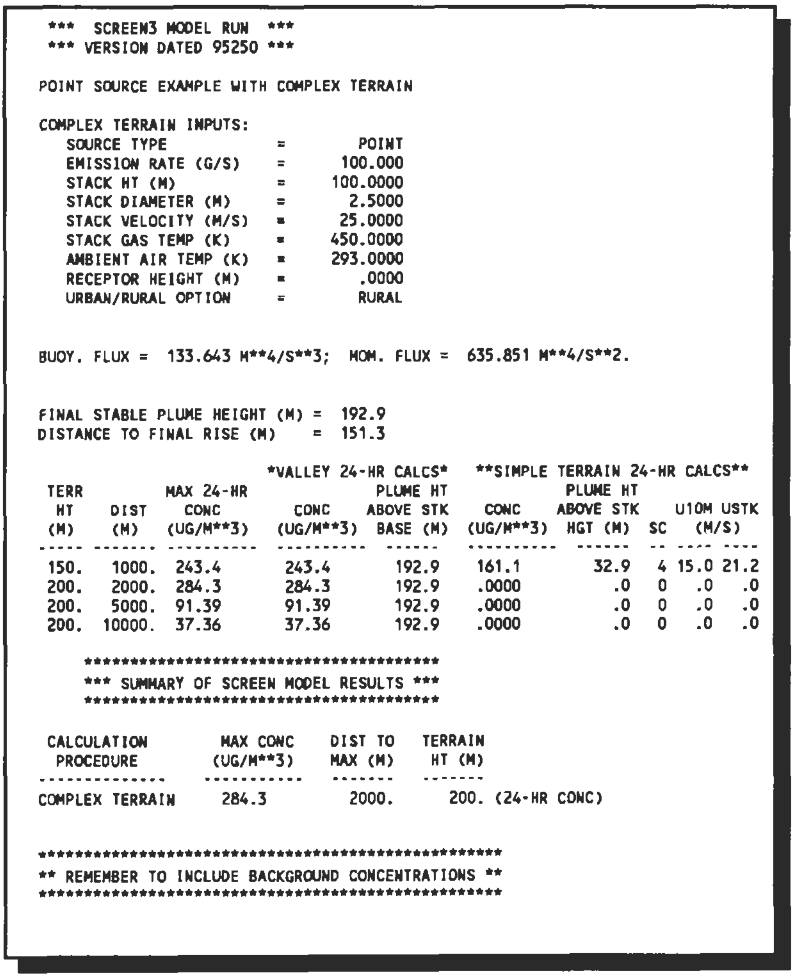
The discrete distance option of SCREEN allows the user to input specific distances. Any number of distances (≥ 1 meter) can be input by the user and the maximum concentration for each distance will be calculated. The user will always be given this option whether or not the automated distance array option is used. The option is terminated by entering a distance of zero. SCREEN will accept distances out to 100 km for long-range transport estimates with the discrete distance option. However, for distances greater than 50 km, SCREEN sets the minimum 10 meter wind speed at 2 m/s to avoid unrealistic transport times.

Fumigation Option

Once the distance-dependent calculations are completed, SCREEN will give the user the option of estimating maximum concentrations and distance to the maximum associated with inversion break-up fumigation, and shoreline fumigation. The option for fumigation calculations is applicable only for rural inland sites with stack heights greater than or equal to 10 meters (within 3,000 m onshore from a large body of water). The fumigation algorithm also ignores any potential effects of elevated terrain.

Once all computations are completed, SCREEN summarizes the maximum concentrations for each of the calculation procedures examined. Before execution terminates, whether it is after complex terrain calculations are completed or at the end of the simple terrain calculations, you are given the option of printing a hardcopy of the results.

Regardless of whether or not a hardcopy is printed, the results of the session, including all input data and concentration estimates, are stored in a file called SCREEN.OUT. This file is opened by the model each time it is run. If a file named SCREEN.OUT already exists, then its contents will be overwritten or lost.



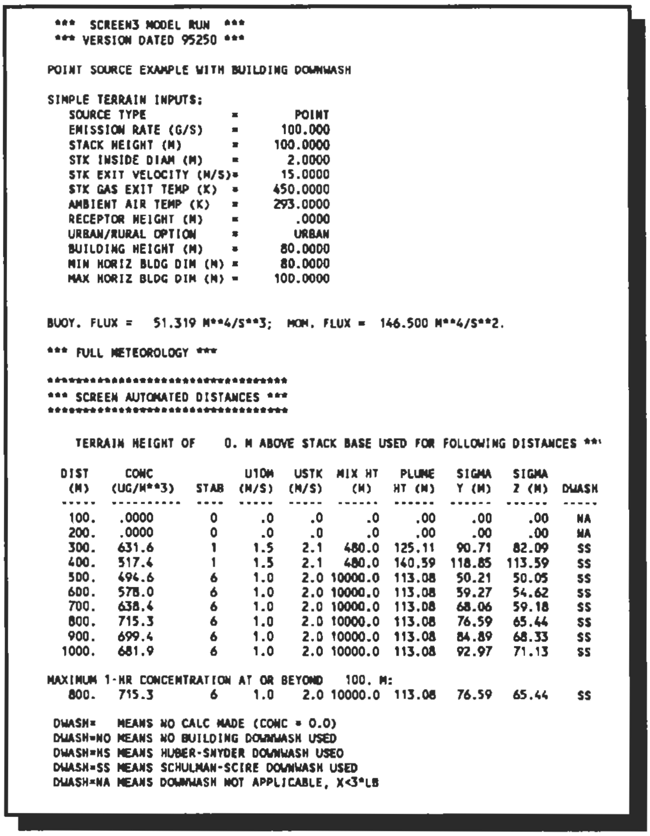
```
 ***  SCREEN3 MODEL RUN  ***
 *** VERSION DATED 95250 ***

POINT SOURCE EXAMPLE WITH COMPLEX TERRAIN

COMPLEX TERRAIN INPUTS:
   SOURCE TYPE             =        POINT
   EMISSION RATE (G/S)     =       100.000
   STACK HT (M)            =      100.0000
   STACK DIAMETER (M)      =        2.5000
   STACK VELOCITY (M/S)    =       25.0000
   STACK GAS TEMP (K)      =      450.0000
   AMBIENT AIR TEMP (K)    =      293.0000
   RECEPTOR HEIGHT (M)     =         .0000
   URBAN/RURAL OPTION      =        RURAL


BUOY. FLUX =  133.643 M**4/S**3;  MOM. FLUX =  635.851 M**4/S**2.


FINAL STABLE PLUME HEIGHT (M) =  192.9
DISTANCE TO FINAL RISE (M)    =  151.3

                         *VALLEY 24-HR CALCS*  **SIMPLE TERRAIN 24-HR CALCS**
 TERR         MAX 24-HR             PLUME HT              PLUME HT
  HT    DIST    CONC         CONC   ABOVE STK   CONC     ABOVE STK     U10M USTK
 (M)    (M)   (UG/M**3)   (UG/M**3)  BASE (M)  (UG/M**3)  HGT (M)  SC   (M/S)
----- ------- ----------  ----------   ------  ----------   ------ -- ---- ----
 150.   1000.  243.4        243.4       192.9   161.1         32.9  4 15.0 21.2
 200.   2000.  284.3        284.3       192.9   .0000           .0  0   .0   .0
 200.   5000.  91.39        91.39       192.9   .0000           .0  0   .0   .0
 200.  10000.  37.36        37.36       192.9   .0000           .0  0   .0   .0

     ***************************************
     *** SUMMARY OF SCREEN MODEL RESULTS ***
     ***************************************

 CALCULATION         MAX CONC     DIST TO   TERRAIN
  PROCEDURE         (UG/M**3)     MAX (M)    HT (M)
--------------     -----------   -------    -------
COMPLEX TERRAIN      284.3          2000.      200. (24-HR CONC)

***************************************************
** REMEMBER TO INCLUDE BACKGROUND CONCENTRATIONS **
***************************************************
```

Figure 9. SCREEN point source example for complex terrain.

Thus, if you wish to save the results of a particular run, you must change the name of the output file using the DOS RENAME command (e.g., type REN SCREEN.OUT RUN1.OUT), or simply print the file using the option at the end of the program.

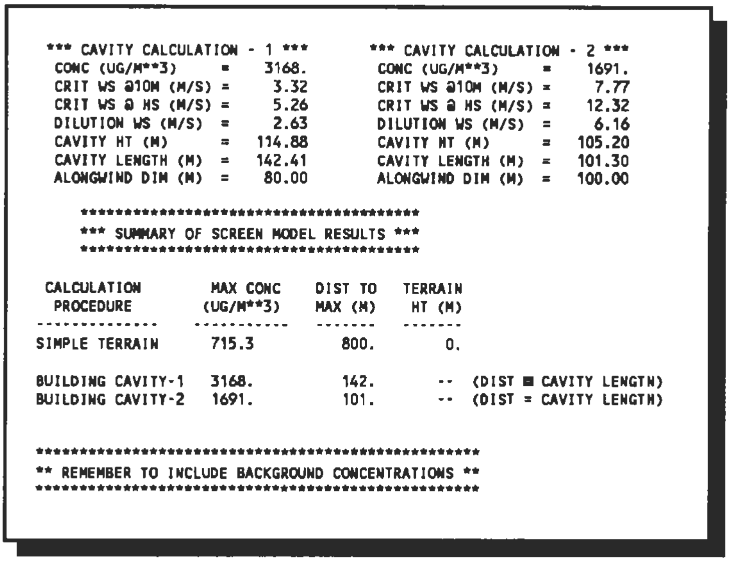
Figure 9 shows an example using the complex terrain screen only. Figures 10 and 11 show an example for an urban point source which uses the building downwash option.

In the DWASH column of the output, 'NO' indicates that no downwash is included, 'HS' means that Huber-Snyder downwash is included, 'SS' means that Schulman-Scire downwash is included, and 'NA' means that downwash is not applicable since the downwind distance is less than $3L_b$. A blank in the DWASH column means that no calculation was made for that distance because the concentration was so small.



```
 ***  SCREEN3 MODEL RUN  ***
 *** VERSION DATED 95250 ***

POINT SOURCE EXAMPLE WITH BUILDING DOWNWASH

SIMPLE TERRAIN INPUTS:
   SOURCE TYPE              =        POINT
   EMISSION RATE (G/S)      =      100.000
   STACK HEIGHT (M)         =     100.0000
   STK INSIDE DIAM (M)      =       2.0000
   STK EXIT VELOCITY (M/S)=        15.0000
   STK GAS EXIT TEMP (K)    =     450.0000
   AMBIENT AIR TEMP (K)     =     293.0000
   RECEPTOR HEIGHT (M)      =        .0000
   URBAN/RURAL OPTION       =        URBAN
   BUILDING HEIGHT (M)      =      80.0000
   MIN HORIZ BLDG DIM (M) =        80.0000
   MAX HORIZ BLDG DIM (M) =       100.0000


BUOY. FLUX =   51.319 M**4/S**3;  MOM. FLUX =  146.500 M**4/S**2.

*** FULL METEOROLOGY ***

************************************
*** SCREEN AUTOMATED DISTANCES ***
************************************

   TERRAIN HEIGHT OF    0. M ABOVE STACK BASE USED FOR FOLLOWING DISTANCES **'

 DIST     CONC              U10M   USTK  MIX HT   PLUME  SIGMA   SIGMA
  (M)   (UG/M**3)   STAB   (M/S)  (M/S)    (M)   HT (M)  Y (M)   Z (M)  DWASH
 -----  ----------  ----   -----  -----  ------  ------  ------  ------  -----
  100.   .0000        0       .0     .0      .0     .00     .00     .00    NA
  200.   .0000        0       .0     .0      .0     .00     .00     .00    NA
  300.   631.6        1      1.5    2.1   480.0  125.11   90.71   82.09    SS
  400.   517.4        1      1.5    2.1   480.0  140.59  118.85  113.59    SS
  500.   494.6        6      1.0    2.0 10000.0  113.08   50.21   50.05    SS
  600.   578.0        6      1.0    2.0 10000.0  113.08   59.27   54.62    SS
  700.   638.4        6      1.0    2.0 10000.0  113.08   68.06   59.18    SS
  800.   715.3        6      1.0    2.0 10000.0  113.08   76.59   65.44    SS
  900.   699.4        6      1.0    2.0 10000.0  113.08   84.89   68.33    SS
 1000.   681.9        6      1.0    2.0 10000.0  113.08   92.97   71.13    SS

MAXIMUM 1-HR CONCENTRATION AT OR BEYOND   100. M:
  800.   715.3        6      1.0    2.0 10000.0  113.08   76.59   65.44    SS

 DWASH=   MEANS NO CALC MADE (CONC = 0.0)
 DWASH=NO MEANS NO BUILDING DOWNWASH USED
 DWASH=HS MEANS HUBER-SNYDER DOWNWASH USEO
 DWASH=SS MEANS SCHULMAN-SCIRE DOWNWASH USED
 DWASH=NA MEANS DOWNWASH NOT APPLICABLE, X<3*LB
```

Figure 10. SCREEN point source example with building downwash (page 1 of 2 results).



```
*** CAVITY CALCULATION - 1 ***          *** CAVITY CALCULATION - 2 ***
 CONC (UG/M**3)     =    3168.           CONC (UG/M**3)     =    1691.
 CRIT WS @10M (M/S) =     3.32           CRIT WS @10M (M/S) =     7.77
 CRIT WS @ HS (M/S) =     5.26           CRIT WS @ HS (M/S) =    12.32
 DILUTION WS (M/S)  =     2.63           DILUTION WS (M/S)  =     6.16
 CAVITY HT (M)      =   114.88           CAVITY HT (M)      =   105.20
 CAVITY LENGTH (M)  =   142.41           CAVITY LENGTH (M)  =   101.30
 ALONGWIND DIM (M)  =    80.00           ALONGWIND DIM (M)  =   100.00

    ****************************************
    *** SUMMARY OF SCREEN MODEL RESULTS ***
    ****************************************

 CALCULATION         MAX CONC     DIST TO    TERRAIN
  PROCEDURE         (UG/M**3)     MAX (M)     HT (M)
--------------     -----------    -------    -------
SIMPLE TERRAIN       715.3          800.         0.

BUILDING CAVITY-1    3168.          142.        --   (DIST = CAVITY LENGTH)
BUILDING CAVITY-2    1691.          101.        --   (DIST = CAVITY LENGTH)


*******************************************************
** REMEMBER TO INCLUDE BACKGROUND CONCENTRATIONS **
*******************************************************
```

Figure 11. SCREEN point source example with building downwash (page 2 of 2 results).

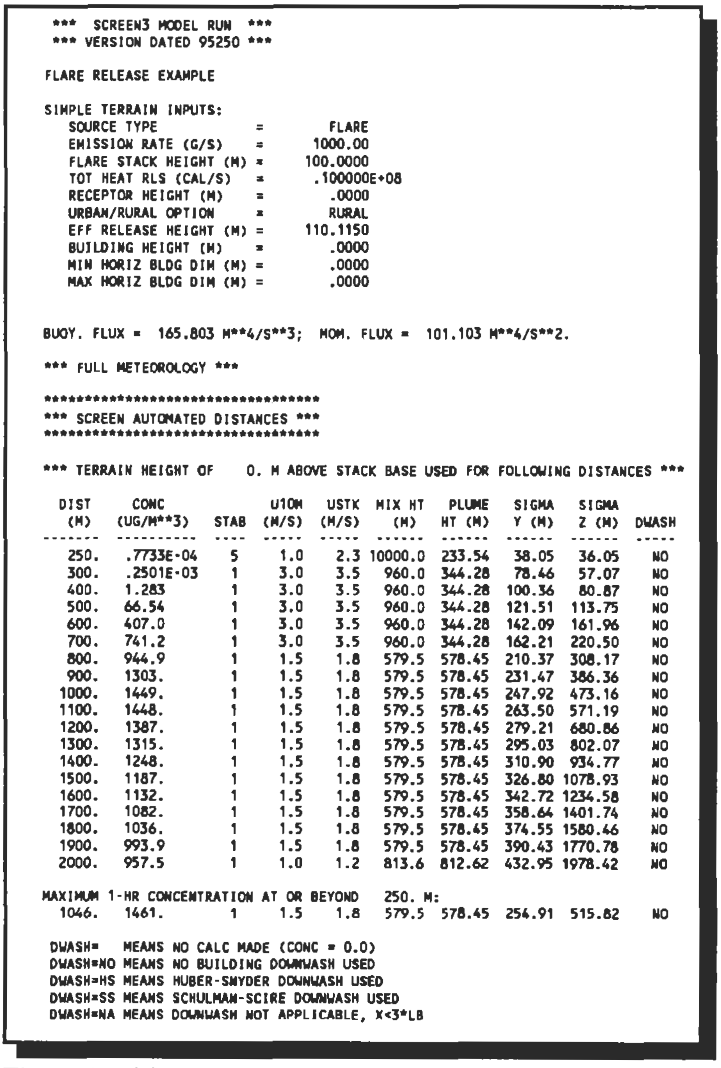
Flare Release Example

By answering 'F' or 'f' to the question on source type the user selects the flare release option. This option is similar to the point source described above except for the inputs needed to calculate plume rise. The inputs for flare releases are described below.

Flare Release Inputs:
- Emission rate (g/s)
- Flare stack height (m)
- Total heat release rate (cal/s)
- Receptor height above ground (m)
- Urban/rural option (U = urban, R = rural)

The SCREEN model calculates plume rise for flares based on an effective buoyancy flux parameter. An ambient temperature of 293° K is assumed in this calculation and therefore none is input by the user. It is assumed that 55 percent of the total heat is lost due to radiation.

For the flare release example, plume rise is calculated from the top of the flame, assuming that the flame is bent 45 degrees from the vertical. SCREEN calculates and prints out the effective release height for the flare. SCREEN provides the same options for flares as described earlier for point sources, including building downwash, complex and/or simple terrain, fumigation, and the automated and/or discrete distances. The order of these options and the user prompts are the same as described for the point source example. While building downwash is included as an option for flare releases, it should be noted that SCREEN assumes an effective stack gas exit velocity (V_s) of 20 m/s and an effective stack gas exit temperature (T_e) of 1,273° K, and calculates an effective stack diameter based on the heat release rate.



```
 ***  SCREEN3 MODEL RUN  ***
 *** VERSION DATED 95250 ***

FLARE RELEASE EXAMPLE

SIMPLE TERRAIN INPUTS:
   SOURCE TYPE            =        FLARE
   EMISSION RATE (G/S)    =      1000.00
   FLARE STACK HEIGHT (M) =     100.0000
   TOT HEAT RLS (CAL/S)   =      .100000E+08
   RECEPTOR HEIGHT (M)    =        .0000
   URBAN/RURAL OPTION     =        RURAL
   EFF RELEASE HEIGHT (M) =     110.1150
   BUILDING HEIGHT (M)    =        .0000
   MIN HORIZ BLDG DIM (M) =        .0000
   MAX HORIZ BLDG DIM (M) =        .0000


BUOY. FLUX =  165.803 M**4/S**3;  MOM. FLUX =  101.103 M**4/S**2.

*** FULL METEOROLOGY ***

**********************************
*** SCREEN AUTOMATED DISTANCES ***
**********************************

*** TERRAIN HEIGHT OF    0. M ABOVE STACK BASE USED FOR FOLLOWING DISTANCES ***

  DIST     CONC              U10M   USTK  MIX HT   PLUME   SIGMA   SIGMA
   (M)   (UG/M**3)    STAB  (M/S)  (M/S)    (M)    HT (M)   Y (M)   Z (M)  DWASH
 -------  ----------  ----  -----  -----  ------   ------  ------  ------  -----
   250.   .7733E-04     5    1.0     2.3 10000.0  233.54   38.05   36.05    NO
   300.   .2501E-03     1    3.0     3.5   960.0  344.28   78.46   57.07    NO
   400.   1.283         1    3.0     3.5   960.0  344.28  100.36   80.87    NO
   500.   66.54         1    3.0     3.5   960.0  344.28  121.51  113.75    NO
   600.   407.0         1    3.0     3.5   960.0  344.28  142.09  161.96    NO
   700.   741.2         1    3.0     3.5   960.0  344.28  162.21  220.50    NO
   800.   944.9         1    1.5     1.8   579.5  578.45  210.37  308.17    NO
   900.   1303.         1    1.5     1.8   579.5  578.45  231.47  386.36    NO
  1000.   1449.         1    1.5     1.8   579.5  578.45  247.92  473.16    NO
  1100.   1448.         1    1.5     1.8   579.5  578.45  263.50  571.19    NO
  1200.   1387.         1    1.5     1.8   579.5  578.45  279.21  680.86    NO
  1300.   1315.         1    1.5     1.8   579.5  578.45  295.03  802.07    NO
  1400.   1248.         1    1.5     1.8   579.5  578.45  310.90  934.77    NO
  1500.   1187.         1    1.5     1.8   579.5  578.45  326.80 1078.93    NO
  1600.   1132.         1    1.5     1.8   579.5  578.45  342.72 1234.58    NO
  1700.   1082.         1    1.5     1.8   579.5  578.45  358.64 1401.74    NO
  1800.   1036.         1    1.5     1.8   579.5  578.45  374.55 1580.46    NO
  1900.   993.9         1    1.5     1.8   579.5  578.45  390.43 1770.78    NO
  2000.   957.5         1    1.0     1.2   813.6  812.62  432.95 1978.42    NO

MAXIMUM 1-HR CONCENTRATION AT OR BEYOND   250. M:
  1046.   1461.         1    1.5     1.8   579.5  578.45  254.91  515.82    NO

 DWASH=   MEANS NO CALC MADE (CONC = 0.0)
 DWASH=NO MEANS NO BUILDING DOWNWASH USED
 DWASH=HS MEANS HUBER-SNYDER DOWNWASH USED
 DWASH=SS MEANS SCHULMAN-SCIRE DOWNWASH USED
 DWASH=NA MEANS DOWNWASH NOT APPLICABLE, X<3*LB
```

Figure 12. SCREEN flare release example (page 1 of 2 results).

These effective stack parameters are somewhat arbitrary, but the resulting buoyancy flux estimate is expected to give reasonable final plume rise estimates for flares. However, since building downwash estimates depend on transitional momentum plume rise and transitional buoyant plume rise calculations, the selection of effective stack parameters could influence the estimates. Therefore, building downwash estimates should be used with extra caution for flare releases.

If more realistic stack parameters can be determined, then the estimate could alternatively be made with the point source option of SCREEN. In doing so, care should be taken to account for the vertical height of the flame in specifying the release height. Figure 12 shows an example for a flare release.

Area Source Example

The third source type option in SCREEN is for area sources, which is selected by entering 'A' or 'a' for source type. The area source algorithm in SCREEN is based on a numerical integration approach, and allows for the area source to be approximated by a rectangular area. The inputs requested for area sources are as follows:

- Area Source Inputs Emission rate [g/(s-m^2)]
- Source release height (m)
- Length of larger side of the rectangular area (m)
- Length of smaller side of the rectangular area (m)
- Receptor height above ground (m)
- Urban/rural option (U = urban, R = rural)
- Wind direction search option (if no, specify desired angle)

Since the concentration at a particular distance downwind from a rectangular area is dependent on the orientation of the area relative to the wind direction, the SCREEN model provides the user with two options for treating wind direction. The first option, which should be used for most applications of SCREEN and is the regulatory default, is for the model to search through a range of wind directions to find the maximum concentration.

The range of directions used in the search is determined from a set of look-up tables based on the aspect ratio of the area source, the stability category, and the downwind distance. The SCREEN model also provides the user an option to specify a wind direction orientation relative to the long axis of the rectangular area. The second option may be used to estimate the concentration at a particular receptor location relative to the area. The output table for area sources includes the wind direction associated with the maximum concentration at each distance.

The user has the same options for handling distances and the same choices of meteorology as described above for point sources, but no complex terrain, elevated simple terrain, building downwash, or fumigation calculations are made for area sources. Distances are measured from the center of the rectangular area. Since the numerical integration algorithm can estimate concentrations within the area source, the user can enter any value for the minimum distance.

Volume Source Example

The fourth source type option in SCREEN is for volume sources, which is selected by entering 'V' or 'v' for source type. The volume source algorithm is based on a virtual point source approach, and may be used for non-buoyant sources whose emissions occupy some initial volume. The inputs requested for volume sources are as follows:

- Volume Source Inputs Emission rate (g/s)
- Source release height (m)
- Initial lateral dimension of volume (m)
- Initial vertical dimension of volume (m)
- Receptor height above ground (m)
- Urban/rural option (U = urban, R = rural)

The user must determine the initial dimensions of the volume source plume before exercising the SCREEN model volume source. Table 3 provides guidance on determining these inputs.

Table 3. Procedures for Estimating Initial Lateral Dimensions (σ_{y0}) and Initial Vertical Dimensions (σ_{z0}) for Volume Sources.

Source Description	**Initial Dimension**
Initial Lateral Dimensions (σ_{y0})	
Single Volume Source	σ_{y0} = length of side divided by 4.3
Initial Vertical Dimensions (σ_{z0})	
Surface-Based Source ($h_e \sim 0$)	σ_{z0} = vertical dimension of source divided by 2.15
Elevated Source ($h_e > 0$) on or Adjacent to a Building	σ_{z0} = building height divided by 2.15
Elevated Source ($h_e > 0$) not on or Adjacent to a Building	σ_{z0} = vertical dimension of source divided by 4.3

Since the volume source algorithm cannot estimate concentrations within the volume source, the model will give a concentration of zero for distances (measured from the center of the volume) of less than 2.15 σ_{y0}.

Non-regulatory Options

On the same source type input line, the program allows the input of three additional inputs, N, nn.n, and SS, where 'nn.n' represents a numerical anemometer height such as 7.5 meters. These inputs, when entered, cause the program to use the nonregulatory Brode 2 Mixing Height (1991) option (N), a user-specified anemometer height (nn.n), and/or non-regulatory building downwash/cavity option (Schulman and Scire, 1993) (SS, in SCREEN printout). While additional input is required for the Schulman-Scire Building Downwash/Cavity option, as discussed earlier, no additional input data are required for the other two options.

DISPERSION THEORY ELEMENTS OF THE SCREEN MODEL

Many of the techniques used in the SCREEN model are based on assumptions and methods common to other EPA dispersion models. SCREEN uses a Gaussian plume model that incorporates source-related factors and meteorological factors to estimate pollutant concentration from continuous sources. It is assumed that the pollutant does not undergo any chemical reactions, and that no other removal processes, such as wet or dry deposition, act on the plume during its transport from the source. The basic Gaussian model equations and the interactions of the source-related and meteorological factors were discussed earlier. The basic equation for determining ground-level concentrations under the plume centerline is:

$$\begin{aligned}\chi &= Q/(2\pi u_s\sigma_y\sigma_z)\ \{\exp[-\tfrac{1}{2}((Z_r - h_e)/\sigma_z)^2] + \exp[-\tfrac{1}{2}((Z_r + h_e)/\sigma_z)^2]\\ &+ \sum_{N=1}^{k}[\exp[-\tfrac{1}{2}((z_r - h_e - 2NZ_i)/\sigma_z)^2] + \exp[-\tfrac{1}{2}((Z_r + h_e - 2NZ_i)/\sigma_z)^2]\\ &+ \exp[-\tfrac{1}{2}((Z_r - h_e + 2NZ_i)/\sigma_z)^2] + \exp[-\tfrac{1}{2}((Z_r + h_e + 2NZ_i)/\sigma_z)^2]]\} \qquad (9)\end{aligned}$$

where:
χ = concentration (g/m^3)
Q = emission rate (g/s)
π = 3.141593
u_s = stack height wind speed (m/s)
σ_y = lateral dispersion parameter (m)
σ_Z = vertical dispersion parameter (m)
Z_r = receptor height above ground (m)

h_e = plume centerline height (m)
Z_i = mixing height (m)
k = summation limit for multiple reflections of plume off of the ground and elevated inversion, usually ≤ 4

Note that for stable conditions and/or mixing heights greater than or equal to 10,000 m, unlimited mixing is assumed and the summation term is assumed to be zero, as noted by expressions presented earlier in this chapter. Equation (9) is used to model the plume impacts from point sources, flare releases, and volume releases in SCREEN. The SCREEN volume source option uses a virtual point source approach. The model uses a numerical integration algorithm for modeling impacts from area sources.

Table 4. SCREEN's Wind Speed and Stability Class Combinations.

10-m Wind Speed (m/s)	**Stability Class**					
	A	**B**	**C**	**D**	**E**	**F**
1	■	■	■	■	■	■
1.5	■	■	■	■	■	■
2	■	■	■	■	■	■
2.5	■	■	■	■	■	■
3	■	■	■	■	■	■
3.5		■	■	■	■	■
4		■	■	■	■	■
4.5		■	■	■	■	
5		■	■	■	■	
8			■	■		
10			■	■		
15				■		
20				■		

The area source is assumed to be a rectangular shape, and the model can be used to estimate concentrations within the area. SCREEN examines a range of stability classes and wind speeds to identify the "worst case" meteorological conditions, i.e., the combination of wind speed and stability that results in the maximum ground-level concentrations. The wind speed and stability class combinations used by SCREEN are given in Table 4.

The 10-meter wind speeds given in Table 4 are adjusted to stack height by SCREEN using wind profile power law exponents. For release heights of less than 10 meters, the wind speeds listed in Table 4 are used without adjustment. For distances greater than 50 km (available with the discrete distance option), SCREEN sets 2 m/s as the lower limit for the 10-meter wind speed to avoid unrealistic transport times. Table 4 includes some cases that may not be considered standard stability class/wind speed combinations, namely E with winds less than 2 m/s, and F with winds greater than 3 m/s. The combinations of E and winds of 1 to 1.5 m/s are often excluded because the algorithm developed by Turner (1964) to determine stability class from routine National Weather Service (NWS) observations excludes cases of E stability for wind speeds less than 4 knots (2 m/s). These combinations are included in SCREEN because they are valid combinations that could appear in a data set using on-site meteorological data with another stability class method. A wind speed of 6 knots (the highest speed for F stability in Turner's scheme) measured at a typical NWS anemometer height of 20 feet (6.1 meters) corresponds to a 10 meter wind speed of 4 m/s under F stability. Therefore the combination of F and 4 m/s has been included.

The user has three choices of meteorological data to examine. The first choice, which should be used in most applications, is to use "Full Meteorology" which examines all six stability classes (five for urban sources) and their associated wind speeds. Using full meteorology with the automated distance array, SCREEN prints out the maximum concentration for each distance, and the overall maximum and associated distance. Full meteorology is used instead of the A, C, and E or F subset used by the hand calculations because SCREEN provides maximum concentrations as a function of distance, and stability classes A, C, and E or F may not be controlling for all distances. The use of A, C, and E or F may also not give the maximum concentration when building downwash is considered. The second choice is to input a single stability class (1 = A, 2 = B, ..., 6 = F). SCREEN will examine a range of wind speeds for that stability class only. Using this option the user is able to determine the maximum concentrations. The third choice is to specify a single stability class and wind speed. The last two choices were originally put into SCREEN to facilitate testing only, but they may be useful if particular meteorological conditions are of concern. However, they are not recommended for routine uses of SCREEN.

The mixing height used in SCREEN for neutral and unstable conditions (classes A-D) is based on an estimate of the mechanically driven mixing height. The mechanical mixing height, z_m(m), is calculated (Randerson, 1984) as:

$$Z_m = 0.3\ u^*/f \tag{10}$$

where:
u^* = friction velocity (m/s)
f = Coriolis parameter ($9.374 \times 10^{-5}\ s^{-1}$ at 40° latitude)

Using a log-linear profile of the wind speed, and assuming a surface roughness length of about 0.3 m, u^* is estimated from the 10-meter wind speed, u_{10}, as:

$$u^* = 0.1\ u_{10} \tag{11}$$

Substituting for u^* into the above expression, we obtain:

$$Z_m = 320\ u_{10} \tag{12}$$

The mechanical mixing height is taken to be the minimum daytime mixing height. To be conservative for limited mixing calculations, if the value of Z_m from the above expression is less than the plume height, h_e, then the mixing height used in calculating the concentration is set equal to $h_e + 1$. For stable conditions, the mixing height is set equal to 10,000 m to represent unlimited mixing.

Plume Rise for Point Sources

The use of the methods of Briggs to estimate plume rise are relied on in the SCREEN model. Stack tip downwash is estimated following Briggs (1973, p.4) for all sources except those employing the Schulman-Scire downwash algorithm. Buoyancy flux for non-flare point sources is calculated from:

$$F_b = gvsds^2(T_s - T_a) / (4T_s) \tag{13}$$

Buoyancy flux for flare releases is estimated from:

$$F_b = 1.66 \times 10^{-5} \times H \tag{14}$$

where H is the total heat release rate of the flare (cal/s). This formula was derived from Briggs (1969), assuming T_a = 293° K, p = 1205 g/m, c_p= 0.24 cal/g-°K, and that the sensible heat release rate, Q_H = 0.45H. The sensible heat rate is based on the assumption that 55 percent of the total heat released is lost due to radiation (Leahey and Davies, 1984). The buoyancy flux for flares is calculated in SCREEN by assuming effective stack parameters of $V_s = 20$ m/s, $T_s = 1{,}273°$ K, and solving for an effective stack diameter, $d_s = 9.88 \times 10^{-4} (Q_H)^{0.5}$.

The momentum flux, which is used in estimating plume rise for building downwash effects, is calculated from:

$$F_m = v_s^2 d_s^2 T_a/(4T_s) \tag{15}$$

The ISC user's guide (EPA, 1995b) describes the equations used to estimate buoyant plume rise and momentum plume rise for both unstable/neutral and stable conditions. Also described are transitional plume rise and how to estimate the distance to final rise.

Final plume rise is used in SCREEN for all cases with the exception of the complex terrain screening procedure and for building downwash effects. The buoyant line source plume rise formulas that are used for the Schulman-Scire downwash scheme are described in EPA (1995b). These formulas apply to sources where $h_s \leq H_b + 0.5L_b$.

For sources subject to downwash but not meeting this criterion, the downwash algorithms of Huber and Snyder (EPA, 1995b) are used, which employ the Briggs plume rise formulas referenced above.

Dispersion Parameters

The formulas used for calculating vertical (σ_z) and lateral (σ_y) dispersion parameters for rural and urban sites were described earlier and are discussed in greater detail in EPA (1995b).

Buoyancy Induced Dispersion

Throughout the SCREEN model, with the exception of the Schulman-Scire downwash algorithm, the dispersion parameters, σ_y and σ_z, are adjusted to account for the effects of buoyancy induced dispersion as follows:

$$\sigma_{ye} = (\sigma_y^2 + (\Delta h/3.5)^2)^{0.5} \tag{16}$$

$$\sigma_{ze} = (\sigma_z^2 + (\Delta h/3.5)^2)^{0.5} \tag{17}$$

where Δh is the distance-dependent plume rise. (Note that for inversion break-up and shoreline fumigation, distances are always beyond the distance to final rise, and therefore Δh = final plume rise).

Building Downwash

Cavity Recirculation Region - The cavity calculations are based largely on results published by Hosker (1984). If non-zero building dimensions are input to SCREEN for either point or flare releases, then cavity calculations will be made as follows. The cavity height, h_c(m), is estimated based on the following equation from Hosker (1984):

$$h_c = h_b(1.0 + 1.6 \exp(-1.3L/h_b)) \tag{18}$$

where:
h_b = building height (m)
L = alongwind dimension of the building (m)

Using the plume height based on momentum rise at two building heights downwind, including stack tip downwash, a critical (i.e., minimum) stack height wind speed is calculated that will just put the plume into the cavity (defined by plume centerline height = cavity height). The critical wind speed is then adjusted from stack height to 10 m using a power law with an exponent of 0.2 to represent neutral conditions (no attempt is made to differentiate between urban or rural sites or different stability classes). If the critical wind speed (adjusted to 10 m) is less than or equal to 20 m/s, then a cavity concentration is calculated; otherwise the cavity concentration is assumed to be zero. Concentrations within the cavity, χ_c, are estimated by the following approximation (Hosker, 1984):

$$\chi_c = Q/(1.5\, A_p u) \tag{19}$$

where:
Q = emission rate (g/s)
Ap = $H_b W$ = cross-sectional area of the building normal to the wind (m^2)
W = crosswind dimension of the building (m)
u = wind speed (m/s)

For u, a value of one-half the stack height critical wind speed is used, but not greater than 10 m/s and not less than 1 m/s. Thus, the calculation of χ_c is linked to the determination of a critical wind speed. The concentration, χ_c, is assumed to be uniform within the cavity.

The cavity length, x_r, measured from the lee side of the building, is estimated by the following (Hosker, 1984):

for short buildings ($L/h_b \leq 2$), $x_r = AW/(1.0 + B(W/h_b))$ (20A)

for long buildings ($L/h_b \geq 2$), $x_r = 1.75W/(1.0 + 0.25(W/h_b))$ (20B)

where:
h_b = building height (m)
L = alongwind building dimension (m)
W = crosswind building dimension (m)
$A = -2.0 + 3.7(L/hb)^{-1/3}$, and
$B = -0.15 + 0.305(L/h_b)^{-1/3}$

The above expressions for cavity height, concentration and cavity length are all sensitive to building orientation through the terms L, W, and A_p. Therefore, the entire cavity procedure is performed for two orientations, first with the minimum horizontal dimension alongwind and second with the maximum horizontal dimension alongwind. For screening purposes, this is thought to give reasonable bounds on the cavity estimates. The first case will maximize the cavity height, and therefore minimize the critical wind speed. However, the A_P term will also be larger and will tend to reduce concentrations. The highest concentration that potentially effects ambient air should be used as the controlling value for the cavity procedure.

Wake Region - Wake effects are divided into two regions, one referred to as the "near wake" extending from $3L_b$ to $10L_b$ (L_b is the lesser of the building height, h_b, and maximum projected width), and the other as the "far wake" for distances greater than $10L_b$. For the SCREEN model, the maximum projected width is calculated from the input minimum and maximum horizontal dimensions as $(L^2 + W^2)^{0.5}$. Unlike the cavity calculation, the comparison of plume height (due to momentum rise at two building heights) to wake height to determine if wake effects apply does not include stack tip downwash.

Fumigation

Inversion Break-up Fumigation - The inversion break-up screening calculations are based on procedures described in the Workbook of Atmospheric Dispersion Estimates (Turner, 1970). The distance to maximum fumigation is based on an estimate of the time required for the mixing layer to develop from the top of the stack to the top of the plume, using:

$$\begin{aligned} x_{max} &= ut_m \\ &= (u\rho_a c_p/R)(\Delta\Theta/\Delta Z)(h_i - h_{s)}[(hi + h_s)/2] \end{aligned} \qquad (21)$$

where:
x_{max} = downwind distance to maximum concentration (m)
t_m = time required for mixing layer to develop from top of stack to top of plume(s)
u = wind speed (2.5 m/s assumed)
ρ_a = ambient air density (1205 g/m^3 at 20°C)
c_p = specific heat of the air at constant pressure (0.24 cal/g-°K)
R = net rate of sensible heating of an air column by solar radiation (about 67 cal/m^2/s)
$\Delta\Theta/\Delta Z$ = vertical potential temperature gradient (assume 0.035° K/m for F stability)
h_i = height of the top of the plume (m) = $h_e + 2\sigma_{ze}$ (h_e is the plume centerline height)
h_s = physical stack height (m)
σ_{ze} = vertical dispersion parameter incorporating buoyancy induced dispersion (m)
The values of u and $\Delta\Theta/\Delta Z$ are based on assumed conditions of stability class F and stack height wind speed of 2.5 m/s for the stable layer above the inversion. The value of h_i incorporates the effect of buoyancy induced dispersion on σ_z; however, elevated terrain effects are ignored. The equation above is solved by iteration, starting from an initial guess of x_{max} = 5,000 m. The maximum ground-level concentration due to inversion break-up fumigation, χ_f, is calculated from:

$$\chi_f = Q/[(2\pi)^{0.5}u(\sigma_{ye} + h_e/8)(h_e + 2\,\sigma_{ze})] \qquad (22)$$

where Q is the emission rate (g/s), and other terms are defined above. The dispersion parameters, σ_{ye} and σ_{ze}, incorporate the effects of buoyancy induced dispersion. If the distance to the maximum fumigation is less than 2000 m, then SCREEN sets $\chi_f = 0$ since for such short distances the fumigation concentration is not likely to exceed the unstable/limited mixing concentration estimated by the simple terrain screening procedure.

Shoreline Fumigation - For rural sources within 3000 m of a large body of water, maximum shoreline fumigation concentrations can be estimated by SCREEN. A stable onshore flow is assumed with stability class F ($\Delta\Theta/\Delta Z$ = 0.035° K/m) and stack height wind speed of 2.5 m/s. Similar to the inversion break-up fumigation case, the maximum ground-level shoreline fumigation concentration is assumed to occur where the top of the stable plume intersects the top of the well-mixed thermal internal boundary layer (TIBL). An evaluation of coastal fumigation models (EPA, 1987b) has shown that the TIBL height as a function of distance inland is well-represented in rural areas with relatively flat terrain by an equation of the form:

$$h_T = A'[x]^{0.5} \tag{23}$$

where:
h_T = height of the TIBL (m)
A' = TIBL factor containing physics needed for TIBL parameterization (including heat flux) (m)
x = inland distance from shoreline (m)

The TIBL factor, A', ranges from about 2 to 6. For screening purposes, A' is conservatively set equal to 6, since this will minimize the distance to plume/TIBL intersection, and therefore tend to maximize the concentration estimate.

As with the inversion break-up case, the distance to maximum ground-level concentration is determined by iteration. The equation used for the shoreline fumigation case is:

$$x_{max} = [(h_e + 2\sigma_{ze})/6]2 - x_s \tag{24}$$

where:
x_{max} = downwind distance to maximum concentration (m)
x_s = shortest distance from source to shoreline (m)
h_e = plume centerline height (m)
σ_{ze} = vertical dispersion parameter incorporating buoyancy induced dispersion (m)

Plume height is based on the assumed F stability and 2.5 m/s wind speed, and the dispersion parameter (σ_{ze}) incorporates the effects of buoyancy induced dispersion. If x_{max} is less than 200 m, then no shoreline fumigation calculation is made, since the plume may still be influenced by transitional rise and its interaction with the TIBL is more difficult to model.

The maximum ground-level concentration due to shoreline fumigation, χ_f, is calculated from:

$$\chi_f = Q/[(2\pi)^{0.5}u(\sigma_{ye} + h_e/8)(h_e + 2\,\sigma_{ze})] \tag{25}$$

with σ_{ye} and σ_{ze} incorporating the effects of buoyancy induced dispersion.

Even though the calculation of x_{max} above accounts for the distance from the source to the shoreline in x_s, extra caution should be used in interpreting results as the value of x_s increases. The use of A'= 6 may not be conservative in these cases since there will be an increased chance that the plume will be calculated as being below the TIBL height, and therefore no fumigation concentration estimated. Whereas a smaller value of A′ could put the plume above the TIBL with a potentially high fumigation concentration. Also, this screening procedure considers only TIBLs that begin formation at the shoreline, and neglects TIBLs that begin to form offshore.

Complex Terrain 24-Hour Screen

As noted earlier, the SCREEN model also contains the option to calculate maximum 24-hour concentrations for terrain elevations above stack height. A final plume height and distance to final rise are calculated based on the VALLEY model screening technique (Burt, 1977) assuming conditions of F stability (E for urban) and a stack height wind speed of 2.5 m/s. Stack tip downwash is incorporated in the plume rise calculation. The user then inputs a terrain height and a distance (m) for the nearest terrain feature likely to experience plume impaction, taking into account complex terrain closer than the distance to final rise. If the plume height is at or below the terrain height for the distance entered, then SCREEN will make a 24-hour average concentration estimate using the VALLEY screening technique devised by EPA.

If the terrain is above stack height but below plume centerline height, then SCREEN will make a VALLEY 24-hour estimate (assuming F or E and 2.5 m/s), and also estimate the maximum concentration across a full range of meteorological conditions using simple terrain procedures with terrain "chopped off" at physical stack height, and select the higher estimate. Calculations continue until a terrain height of zero is entered. For the VALLEY model concentration SCREEN will calculate a sector-averaged ground-level concentration with the plume centerline height (h_e) as the larger of 10.0 m or the difference between plume height and terrain height. The equation used is:

$$\chi = (2.032Q/ux\sigma_{ze}) \exp [-0.5(he/\sigma_{ze})^2] \qquad (26)$$

Note that for screening purposes, concentrations are not attenuated for terrain heights above plume height. The dispersion parameter, σ_{ze}, incorporates the effects of buoyancy induced dispersion (BID). For the simple terrain calculation SCREEN examines concentrations for the full range of meteorological conditions and selects the highest ground-level concentration. Plume heights are reduced by the chopped off terrain height for the simple terrain calculation. To adjust the concentrations to 24-hour averages, the

VALLEY screening value is multiplied by 0.25, as done in the VALLEY model, and the simple terrain value is multiplied by 0.4 factor.

Non-regulatory Options

Mixing Height Option - The Brode 2 Mixing Height (Brode, 1991) option calculates a mixing height that is calculated based on the calculated plume height, the anemometer height wind speed, and a stability-dependent factor which is compared to a stability-dependent minimum mixing height. The algorithm is expressed as:

$$\mathrm{ZI} = \mathrm{MAX}\,(\mathrm{ZI}_{\mathrm{min}},\ \mathrm{HE}(1.0 + \mathrm{ZI}_{\mathrm{fact}}\mathrm{U}_{10})) \tag{27}$$

where $\mathrm{ZI}_{\mathrm{min}}$ is 300 m for A, 100 m for B, and 30 m for both C and D stabilities, and $\mathrm{ZI}_{\mathrm{fact}}$ is 0.01 for A, 0.02 for B, 0.03 for C, and 0.04 for D stability. Brode found that the results of using this algorithm appear to provide a fairly consistent level of conservatism.

Variable Anemometer Height Option - The anemometer height is used in adjusting the wind speed to stack height wind speed for cavity calculations based on the following power law function:

$$\mathrm{UO} = \mathrm{UOTEN}(\mathrm{AMAX1}(10,\mathrm{HS})/\mathrm{ZREF})^{0.20} \tag{28A}$$

$$\mathrm{U1} = \mathrm{UITEN}(\mathrm{AMAX1}\ (10,\mathrm{HS})\ /\mathrm{ZREF})^{0.20} \tag{28B}$$

where:
U0TEN = initial wind speed value set to 20 m/s
UITEN = initial wind speed value set to 1 m/s
HS- stack height
ZREF - anemometer height

U0TEN is adjusted downward in speed and UITEN is adjusted upward in speed in an iterative process until the minimum wind speed, UC, that will entrain the plume into a building's cavity is found. The critical wind speed is then adjusted to the anemometer height, using the reverse of the power law above, as follows:

$$\mathrm{UC10M} = \mathrm{UC}(\mathrm{ZREF}/\mathrm{AMAX1}(10,\mathrm{HS})^{\,0.20} \tag{29}$$

where UC10M represents the critical wind speed at anemometer height, ZREF. The variables HANE and ZREF are used interchangeably.

Schulman-Scire Building Downwash/Cavity Option - A nonregulatory building downwash/cavity algorithm (Schulman and Scire, 1993) is used as a non-regulatory option. This option is based on the diffusing plume approach with fractional capture of the plume by the near-wake recirculation cavity. Extensive parameterization is used to define a building length scale, roof recirculation cavity, maximum height of the roof cavity, and the length of the downwind recirculation cavity (as measured from the lee face of the building). A building length scale for flow and diffusion is defined as:

$$R = BS\{\exp(2/3)\}BL\exp(1/3) \qquad (30)$$

where BS is the smaller of the building height and projected width for the minimum side orientation, BL is the larger of the building height and projected width for the maximum side orientation. The length of the roof recirculation cavity is estimated as:

$$LC = 0.9R \qquad (31)$$

The roof cavity will reattach to the roof if $LC < L$, where L is the downwind length of the roof. The maximum height of the roof cavity is defined as:

$$HC = 0.22R, \text{ at } x = 0.5R \qquad (32)$$

where x is the downwind distance. The program uses two algorithms to determine the height and width of the downwind recirculation cavity or near-wake. If the roof cavity reattaches to the roof, the height and width are:
$HR = H$ where H is the building height
$WR = W$ where W is the projected width normal to the wind. If the roof cavity does not reattach, the height and width are:

$$HR = H + HC \qquad (33A)$$
$$WR = 0.6H + 1.1W \qquad (33B)$$

and measured from the lee face of the building.
The length of the recirculation region is calculated using the formula:

$$LR = 1.8W/[(L/H)^{0.3}(1.0 + 0.24W/H)] \qquad (34)$$

with the restriction that L/H is set equal to 0.3 if $L/H < 0.3$, and L/H is set equal to 3.0 if $L/H > 3.0$.

The ground-level concentration in the recirculation region is calculated assuming the mass fraction of the plume, below HR at the downwind end of the region, is captured into the region. The calculation assumes a Gaussian distribution of the vertical mass of the plume at that point using the following formula:

$$\sigma_z = 0.21R^{0.25}x^{0.75} \tag{35}$$

The cavity concentration, C, is then calculated as a fraction of the plume content using the following empirical formula:

$$C = fcB_0Q/(B_0w_0A_0 + u_Hs^2) \tag{36}$$

where f_c is the mass fraction of the plume captured in the recirculation region, B_0 is an empirical constant approximately equal to 16, w_0 is the stack exit speed, A_0 is the stack exit face area, u_H is the upwind wind speed at roof level, and s^2 is the "stretched string" distance between the stack base and the receptor.

The position of the stack on the roof is taken into consideration. A ratio is calculated based on the distance of the stack from a centerline of the building perpendicular to the wind flow for each of two orientations divided by the along wind flow length of the building. Below is an example where the along wind flow length is HW and the distance of the stack from the centerline is "x"; producing a ratio of 0.4. Note that the ratio is always a positive number. Ratios greater than 0.5 indicate that the stack is not on the roof. Refer to Figure 13.

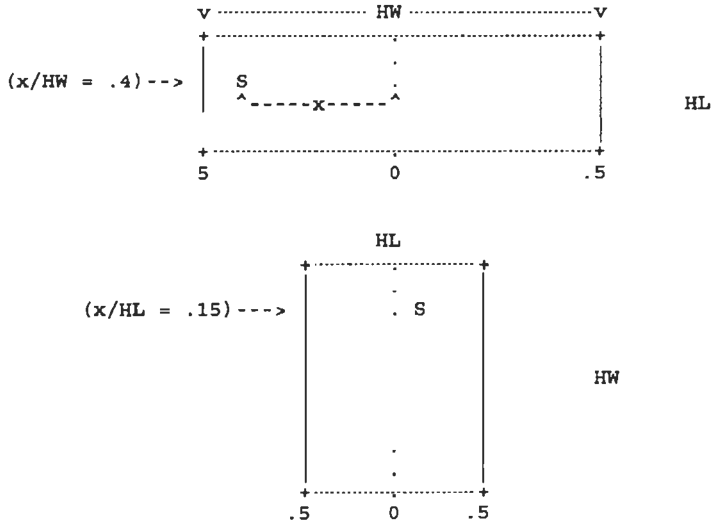


Figure 13. System diagram for building downwash/cavity option.

OTHER MODELS AND RESOURCES

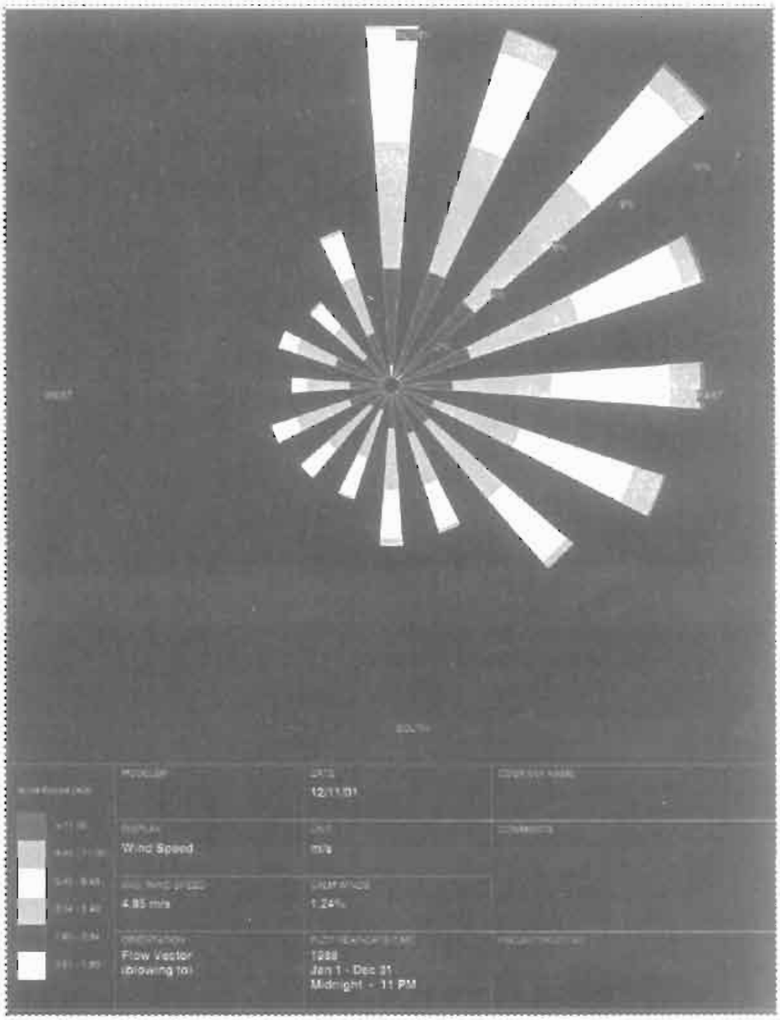
In this section several free air dispersion software products that can be downloaded from the Web are cited. First, SCREEN can be downloaded from the Butterworth-Heinemann site www.bh.com/companions/0750674997. You can obtain a brief description of the software along with the download, but must mainly rely on the chapter discussions to learn how to use and apply the program.

A second important Web site to visit is that of **Lakes Environmental Software** (450 Phillip Street,Suite 2, Waterloo, Ontario N2L 5J2, Canada; Phone: +1 519 746 6157; +1 519 746 5995; Fax: +1 519 746 0793). The home page site address is http://www.lakes-environmental.com. Lakes Environmental specializes in environmental software and training. This company develops and supplies human health and ecological risk assessment software, emergency planning software, and air dispersion modeling software to consultants, industries, governmental agencies, and academia. The company markets a wide variety of sophisticated software products for air dispersion analyses, and is considered a leader in this consulting field. In addition to their own software, however, the site provides easy access to free EPA software which can be downloaded. The downloadable software products that you can access and learn to use are described below. All of the software is equipped with Windows-based interfaces.

One free software package worth downloading is **WRPLOT View**, which is a fully operational wind rose Windows program for your meteorological data. **WRPLOT View** is the logical replacement for the popular U.S. EPA DOS utility WRPLOT (this second program is also available at the site and is noted below). WRPLOT View's main features are:

- Reads surface data files in SCRAM, CD144, and SAMSON formats.
- Reads ISC "pre-processed" meteorological data files.
- Reads California Air Resources Board data files.
- Wind rose plots for wind speed and stability classes.
- Rain Intensity plots for met data files containing precipitation data.
- Frequency distribution tables for wind speed and stability classes.
- Specifies adjacent or non-adjacent dates and hours to be read for plotting.
- Color wind rose and rain intensity plots.
- Prints wind rose plots or copy them for use in other applications.

This self-extracting EXE can be installed in Windows 95/98/Me, NT, or 2000. You will easily find this product on the main site page. Figure 14 shows a sample graphical printout from the program. Once executed, the program will link you to a meteorological Web site where you can download historical and current weather information for a region or city into a file for construction of the wind rose plots. You may also perform statistical analysis to ascertain trends on wind speed, direction, and seasonal variations. This type of information is obviously needed when you perform an air dispersion study (e.g., in assessing average conditions and worst case scenario dispersion calculations).



12/11/01

Wind Speed

m/s

4.85 m/s

1.24%

Flow Vector
(blowing to)

1988
Jan 1 - Dec 31
Midnight - 11 PM

Figure 214. Sample printout of windrose from WRPlot View.

DOWNLOADABLE U.S. EPA MODELS

To download any or all of the programs cited below, go to http://www.lakes-environmental.com/lakeepa.html.

Screening Procedures

In addition to SCREEN3, you can also download TSCREEN, VISCREEN, and CTSCREEN. **TSCREEN** is a screening model for determining maximum short-term impact from toxic releases. Click the filename to download the file.

- TSCREEN1.ZIP 567,607 bytes 12/02/92 (TSCREEN, File 1)
- TSCREEN2.ZIP 193,114 bytes 12/02/92 (TSCREEN, File 2)
- TSCREEN3.ZIP 342,711 bytes 10/02/95 (TSCREEN, File 3)
- TSCREEN4.ZIP 182,152 bytes 10/02/95 (TSCREEN, File 4)
- TSCRCODE.ZIP 418,871 bytes 10/02/95 (TSCREEN Source Code)
- TSCREEND.ZIP 40,448 bytes 07/24/94 (TSCREEN User's Guide - WP 5.1)
- TSCRD1.ZIP 345,611 bytes 06/15/93 (TSCREEN Workbook, File 1)
- TSCRD2.ZIP 598,241 bytes 06/15/93 (TSCREEN Workbook, File 2)
- TSCRD3.ZIP 693,239 bytes 06/15/93 (TSCREEN Workbook, File 3)
- TSCRD4.ZIP 438,688 bytes 06/16/93 (TSCREEN Workbook, File 4)

VISCREEN is an initial screening model for visual impact caused by emissions to the atmosphere. Click the filename to download the file.

- VISCREEN.ZIP 121,369 bytes 08/11/92 (PC version EXE Included)
- VISCRDU.ZIP 35,813 bytes 07/16/93 (User's Guide Update-WP 5.1)

CTSCREEN is a complex terrain screening model of CTDMPLUS. Click the filename (highlighted in blue) to download the file:

- CTSCRN1.ZIP 332,248 bytes 03/30/94 (Readme, PC EXE, Test Case)
- CTSCRN1E.ZIP 254,194 bytes 03/30/94 (Extended memory executable)
- CTSCRN2.ZIP 125,887 bytes 05/25/94 (Source Code)
- CTSCSUP.ZIP 12,823 bytes 03/17/93 (Supplement to User's Guide)

- CTPLSMOD.ZIP 117,813 bytes 03/18/93 (Report on modifications to CTSCREEN/CTD)
- CTSCREEN.ZIP 109,925 bytes 04/30/91 (User's Guide-WP 5.1)
- CT-NOTES.TXT 9,904 bytes 08/09/93 (Notes on Terrain Input to CTDM+/CTSCREEN)

Regulatory Models

The following EPA regulatory models can be downloaded:

***ISCST3 - Industrial Source Complex - Short Term**:* This model is used in more detailed studies of maximum air quality impacts (Phase 3 - Refined Modeling Analysis). The purpose is to compute short term concentration or deposition values, from multiple sources, on specified locations (i.e., receptors). To download the file, click the filename. This is the latest version of the regulatory model ISCST3 (00101) which was released by U.S. EPA on April 27, 2000. The file ISCST.ZIP is 1.60 MB (Executable, Source, Test Cases). You can also download the ISCST3 model evaluation references.

ISCLT3 - Industrial Source Complex - Long Term: The ISC3 Long Term dispersion model is used to model emissions with long-term averaging periods. Click the filename to download the file. You will see the following codes to download:

- ISCLT3-L.ZIP 220,542 bytes 09/18/95 (ISCLT3 *.EXE(Lahey))
- ISCLTSRC.ZIP 134,493 bytes 09/18/95 (ISCLT3 Source Code (Lahey and Microsoft))
- AREALTL.ZIP 7,787 bytes 09/18/95 (Area Source Test Case (Lahey))
- DEPLTL.ZIP 6,647 bytes 09/18/95 (Deposition Test Case (Lahey))
- TEST-LTL.ZIP 19,979 bytes 09/18/95 (Original ISCLT Test Case (Lahey))

You can also download the ISC3 User's Guide (ISCST3 & ISCLT3). To download, click onto the following:

- ISC3V1.PDF 1.16Mb (User's Guide - Volume 1 - with Addendum)
- ISC3V2.PDF 570 Kb (User's Guide - Volume 2 - with Addendum)

- ISC3UG.ZIP 552 Kb 04/27/00 (User's Guides - All Volumes - WP format)

ISC-PRIME - Industrial Source Complex - Plume RIse Model Enhancements: ISC-PRIME dispersion model is being evaluated as the next generation building downwash model. This version of the ISC model has a new set of algorithms and has been named ISC-PRIME. The files below are made available for review and evaluation only, but you can get some insight into how they work and the types of applications:

- ISCPRIME.TXT 6.07 KB 08/24/98 (ISC-PRIME ReadMe (Read First))
- USEGUIDE.PDF 229 KB 08/24/98 (ISC-PRIME User's Guide)
- ISCPRMSR.ZIP 213 KB 1/28/99 (ISC-PRIME and BPIPPRM source codes)
- PRMTESTS.ZIP 624 KB 1/28/99 (ISC-PRIME and BPIPRM Executables, Met Data and Test Cases)
- PRIMPLDN.PDF 589 KB 10/25/99 (Draft: Development and Evaluation of the PRIME Plume Rise and Building Downwash Model)

AERMOD: AERMOD is the next generation air dispersion modeling system and consists of 3 components - AERMOD (air dispersion model), AERMET (meteorological data preprocessor) and AERMAP (terrain preprocessor). A brief overview of the model can be found in the mod-desc.txt file which can be downloaded from the site.

Update: AERMOD (with PRIME downwash) and AERMET version 01247 Beta:

- AERMODB.ZIP 533 KB 10/11/01 (AERMOD Executable)
- AERMODUGB.ZIP 236 KB 10/11/01 (AERMOD User's Guide)
- AERMODSRB.ZIP 361 KB 10/11/01 (AERMOD Source Code)
- AERMODEXB.ZIP 19 KB 10/11/01 (AERMOD Test Case)
- AERMETREADB.TXT 2.40 KB 10/15/01 (AERMET readme - read first)
- AERMETSRB.ZIP 305 KB 10/15/01 (AERMET Source Code)
- AERMETTCB.ZIP 3.25 MB 10/15/01 (AERMET Test Case)

- STAGE1N2B.ZIP 252 KB 10/15/01 (AERMET Stage 1&2 Executable)
- STAGE3B.ZIP 206 KB 10/15/01 (AERMET Stage 3 Executable)
- CHANGES.TXT 9.19 KB 10/15/01 (List of changes to develop current version)
- AERMETUGB.ZIP 317 KB 10/15/01 (AERMET User's Guide - with Addendum changes)

Previous AERMOD/AERMET Version and Related Files (AERMAP): Click the following filenames to download:

- MOD-DESC.TXT 2.39 Kb 1/11/99 (Brief description of AERMOD)
- DEGRADE.ZIP 45.9 Kb 12/14/98 (Min. met data recommendations and analysis - WP format)
- FIGDEG.ZIP 478 Kb 12/14/98 (Figures for DEGRADE file - BMP format)
- AERMODUG.PDF 624 Kb 11/10/98 (AERMOD User's Guide)
- AERMETUG.PDF 454 Kb 11/30/98 (AERMET User's Guide)
- AERMAPUG.PDF 127 Kb 11/10/98 (AERMAP User's Guide)
- AERMOD.ZIP 305 Kb 04/24/00 (AERMOD Executable)
- AERMODEX.ZIP 23 Kb 04/24/00 (AERMOD Test Case)
- AERMODSR.ZIP 203 Kb 04/24/00 (AERMOD Source Code)
- AERMET.ZIP 457 Kb 02/14/00 (AERMET Executable)
- AERMETEX.ZIP 45 Kb 12/06/99 (AERMET Test Case)
- AERMETSR.ZIP 204 Kb 12/06/99 (AERMET Source Code)
- AERMAP.ZIP 190 Kb 12/06/99 (AERMAP Executable)
- MAPTEST.ZIP 1.53 Mb 12/06/99 (AERMAP Test Case)
- AERMAPSR.ZIP 57 Kb 12/06/99 (AERMAP Source Code)

CALINE3 (California Line Source Dispersion Model): These are air quality models used to predict pollutant concentration near roadway intersections. CAL3QHC is an enhanced version of CALINE3, with the additional traffic algorithm to estimate vehicular queue lengths at intersections with traffic stop lights. It is recommended that you get both models. The theoretical information regarding the CALINE3 implementation in CAL3QHC is only presented in CALINE3 User's Guide. To download, click the following filenames:

- CALINE3.ZIP 52,564 bytes 06/13/91 (PC version EXE included)
- CALINE3D.ZIP 23,009 bytes 08/31/93 (CALINE3 WP Format)

CALINE4 (California Line Source Dispersion Model): CALINE4 is a modeling program to assess air quality impacts near transportation facilities. It is based on the Gaussian diffusion equation and employs a mixing zone concept to characterize pollutant dispersion over the roadway. CALINE4 comes with a Windows user interface. Click the following filenames to download the file.

- ZCALINE4.EXE 2,127KB 04/13/99 (Windows Interface and EXE included)
- CL4GUIDE.PDF 390 KB 09/10/98 (User's Guide for CALINE4 Interface)
- CALINE41989.PDF 7.7 MB 06/89 (Manual for the CALINE4 Model)

FDM: FDM (Fugitive Dust Model) is an air quality model designed for computing concentration and deposition impacts from fugitive dust sources. Click the following filenames to download the file:

- FDM1.ZIP 383,939 bytes 10/08/93 (FDM.EXE, Source Code, and Readme.txt)
- FDM2.ZIP 389,660 bytes 10/07/93 (FDM test case and postprocessor)
- FDMD.ZIP 116,736 bytes 10/07/93 (FDM User's Guide in WP5.1)

UAM-IV (Urban Airshed Model): UAM-IV is an urban scale, three dimensional, grid type numerical simulation model. The model incorporates a condensed photochemical kinetics mechanism for urban atmospheres. UAM-IV is designed for computing ozone (O_3) concentrations under short-term, episodic conditions lasting one or two days resulting from emissions of oxides of nitrogen (NO_x), volatile organic compounds (VOC), and carbon monoxide (CO). The model treats VOC emissions as their carbon-bond surrogates. Click the following filename to download the file:

- UAMREAD.TXT 3 KB (Read This First)
- UAM.ZIP 5.33 MB (UAM-IV Modeling System)
- UAMUG.ZIP 226 KB (User's Guide for UAM-IV)

Emergency Release Models

SLAB: SLAB is an atmospheric dispersion model for denser-than-air releases. Three types of releases can be treated by the model:

- ➞ a ground-level evaporating pool, an elevated horizontal jet,
- ➞ a stack or elevated jet, and
- ➞ an instantaneous volume source.

To download, click the filename SLAB.ZIP 111,139 bytes 04/06/94 (SLAB Model for dense gas dispersion). Don't forget to download the user's manual (**SLAB User's Manual (Full Version)** - SLAB.PDF 6.09 MB 11/18/99 (SLAB User's Manual - Adobe Acrobat), and **SLAB User's Manual (Abridged Version)** - SLABMAN.PDF 385,339 bytes 08/26/97 (SLAB User's Manual - Adobe Acrobat); SLABMPS.ZIP 395,495 bytes 07/08/97 (SLAB User's Manual - Postscript)). Note, to read and print PDF files, you will need the Adobe Acrobat Reader. If your browser does not support PDF files yet, you may download the Adobe Acrobat Reader, free of charge, at http://www.adobe.com. Also, if you downloaded the SLABMPS.ZIP, then unzip this file and in a DOS window give the following command: **COPY SLABMPS.PRN LPT1:** (This file can be printed on postscript printers only). If you are using Windows 95/98 or NT, drag the file and drop over your printer icon.

DEGADIS: DEGADIS is a mathematical dispersion model that can be used as a refined modeling approach to estimate short-term ambient concentrations and the expected area of exposure to concentrations above specified threshold values for toxic chemical releases. To download, Click the following filenames:

- DEGSRC.ZIP 265,013 bytes 09/15/92 (DEGADIS Fortran Source Code)
- DEGEXE.ZIP 691,191 bytes 11/24/92 (DEGADIS executable)
- README.DOC 33,654 bytes 08/24/92 (Installation and information)
- DEGUGV1.PDF 2.50 MB 11/18/99 (Technical Document)
- DEGUGV2.PDF 3.77 MB 11/18/99 (DEGADIS User's Guide)

Miscellaneous Programs

It is recommended that you download some of these files also.

BPIP: BPIP (Building Profile Input Program) calculates building downwash, building heights, and projected building widths, for input into ISC3 model (ISCST3 and ISCLT3).
PCRAMMET: PCRAMMET is a very useful utility program to convert meteorological data from National Weather Service (NWS) to be used by EPA's short term air quality dispersion models such as ISCST3.
BINTOASC: This is a utility program that converts unformatted (binary) meteorological data files generated by the RAMMET, PCRAMMET, or MPRM preprocessor programs to the default ASCII format for applications that do not involve dry deposition.
STAR: The STAR program summarizes National Weather Services (NWS) meteorological data, by generating joint frequencies of 6 wind speeds, 16 wind directions, and 6 stability categories for the station and time period desired.

Emissions Modeling

FIRE: The **Factor Information REtrieval (FIRE)** Data System is a database containing EPA's recommended emission estimation factors for criteria and hazardous air pollutants. **FIRE 6.23** (released October, 2000) is a 32-bit Windows program. Users can browse through records in the database or select specific emission factors by source category, source classification code (SCC), pollutant name, CAS number, or control device. The fire623.exe file is a self-extracting installation program which will install and configure the FIRE Software and data on your computer. Click the filename to download the file (FIRE623.EXE 4.1MB (Complete Installation)).

PM CALCULATOR: PM Calculator will calculate controlled emissions for filterable PM2.5 and filterable PM10 for point sources. Click the filename to download the file:

- PMCALC.ZIP 12.2 MB (Complete Installation)
- PMCALCMAN.PDF 184 KB (PM Calculator User's Guide)

TANKS: This program estimates volatile organic compound (VOC) and hazardous air pollutant (HAP) emissions from fixed- and floating-roof storage tanks. *TANKS* is based on the emission estimation procedures from

Chapter 7 of EPA's *Compilation Of Air Pollutant Emission Factors* (AP-42). Click the filename to download the file.

- TANKS409.EXE 641 KB (Complete Installation)
- INSTALL.TXT 11 KB (Installation Instructions)
- TANK4MAN.PDF 13.6 MB (TANKS User's Guide)

There are a number of Web sites where meteorological information can be obtained, and a simple search on www.google.com will help you to identify sources. Two sites that are recommended are:

- the National Center for Atmospheric Research (NCAR) at http://ncardata.ucar.edu/datasets/ds464.0/MASTER, and
- Infor@wunderground.com.

CASE STUDY APPLYING SCREEN

The following case study illustrates the use of SCREEN. In this example we analyze a fire incident that occurred at a wood preserving facility. The incident involved a fire and explosion of six cylindrical vessels containing creosote and pentachlorophenol. Refer to Figure 15.

In general, the environmental consequences resulting from emissions generated by the combustion of treated wood and the chemicals used to treat them are not well understood. Combustion of the materials involved in the incident unquestionably produced hazardous products of incomplete combustion emissions (e.g., dioxins and furans).

The characterization of PIC (products of incomplete combustion) from the combustion of wood treated with pentachlorophenol (penta) is more widely documented in the open literature than creosote alone. However, both products are similar in chemical composition and likely result in comparable forms and concentrations of PIC. Literature reported studies on the combustion of these chemicals and wood treated by them, and the PIC generated are based upon optimal conditions. Optimal conditions are defined as those in which the fuel burns at the designed heat release rate with nominally 160% excess air and a low level ($<$ 100 ppm) of carbon monoxide (CO) emissions in combustion (flue) gases.

Figure 15. Destroyed penta vessels from fire.

This clearly was not the condition of the fire incident, since a potion of the fire occurred within a confined space, followed by tank bursting, and complex hydrodynamics brought on by the application of water during fire fighting practices.

The principal PIC for penta and penta-treated wood would include volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), dioxins and furans, as well as SO_2, CO_2, NO, and HCl. Penta would be expected to have undergone a very high destruction efficiency (DRE) during the fire ($> 99.99\%$). Among the VOC emissions, the following chemicals likely contributed to air pollution problems: benzene, bromobenzene, chloromethane, 1,3-butadiene, iodomethane, acetone, chloroform, and 1,2-dichloroethane.

Among the SVOCs emissions, the following chemicals likely contributed to air pollution problems: phenol, acetophenone, naphthalene, 2-nitophenol, and phenanthrene. It is important to note that the application of water for fire fighting purposes results in a lowering of the localized combustion zone temperature, resulting in the formation of both high levels of PIC formation as well as other PIC not included in this list. Total polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran (PCDD/PCDF) would most certainly have been among the PIC in the fire incident. Literature reported values for concentrations in flue gases range from 0.274 to 1.190 ng/dscm. A portion of these emissions would be associated with flyash and heavy soot, which would be expected to settle out of the atmosphere close to the fire emission source. The PCDF concentrations in the literature are significantly greater than PCDD concentrations, indicating *de novo* synthesis formation reactions rather than condensation reactions. The literature also substantiates long half-lives and great transport distances in the atmosphere.

Multiple pathways are a major concern since depostion of PIC would have occurred. Specific soil conditions determine attenuation rates of penta PIC leachate. Once penta reaches the water table, other transport and fate processes become important. Penta exists in two forms: ionized and non-ionized. The ionized form is soluble in water, while the non-ionized form is not. The ratio of the two forms in water is dependent on the pH of the aquifer. In alkaline environments penta PIC tend to be more soluble and more susceptible to advective transport and biological decay. Half-lives of penta leachate in groundwater have been estimated ranging from 27 days to 58 years.

Creosote is a complex mixture of toxic chemicals, which can have both immediate and chronic effects on exposed organisms. PIC of creosote are of particular concern due to long half-lives of some chemicals, and because of multiple pathways to the environment from ash and soot.

Of great concern for air pollution problems resulting from the incident are dioxin-like compounds. In general, dioxin-like compounds can be generated when chlorine donor compounds are present. Depending on the source of the coal tar, chlorine content may range between 1 and 5000 ppm.

The specific molecular mechanisms by which PCDDs and PCDFs are initially formed and become part of the PIC remain largely unknown and are theoretical. The theoretical basis for conjecture is derived primarily from direct observations in municipal solid waste incinerators. The emissions of

PCDDs and PCDFs can be explained by three principal theories, which should not be regarded as being mutually exclusive. The first is that PCDD/PCDFs are present as contaminants in creosote or tar oil. The second is that PCDDs/PCDFs are ultimately formed from the thermal breakdown and molecular rearrangement of precursor compounds, which are chlorinated aromatic hydrocarbons having a structural resemblance to the PCDD/PCDF molecules. The third theory, similar to the second is that PCDDs/PCDFs are synthesized *de novo;* this means they are formed from organic and inorganic substrates comprised of singular or mixtures of molecules bearing little resemblance to the molecular structure of PCDDs or PCDFs.

The fuels consumed in the fire were treated wood, penta, and creosote (coal tars). Both are considered combustible liquids, with flash points above 160° F (CC). Vapor conditions within the headspaces of tanks can, however, reach explosive conditions, and the introduction of an ignition source resulted in spontaneous combustion. Under ideal conditions, creosote burns similar to crude oil, and in standard lab burn tests, has an average burn rate of 4 mm/min. There is no data on the burn rate of penta; however, its vapors would have likely burned at much slower rates and a series of complex chemical transformations would have occurred.

The early stages of the fire were characterized by a series of eruptions from successive tank ruptures. This would precipitate well controlled released of PIC into the atmosphere, comparable to point source emissions from stacks. However, once fire conditions spread, catastrophic tank failures resulting from bursting and explosion occurred, resulting in a small area fire with large quantities of black, toxic, and sooty smoke emitted to the atmosphere. The application of water in fire fighting would have greatly aggravated the problem. This action contributed greatly to the formation of toxic condensation products containing PCDD/PCDF. In addition to PIC in condensible forms, a considerable amount of flyash would have been generated. The compositions of flyash vary significantly, but these would have contained PCDD/PCDF, lead, possibly chromium, copper, and other heavy metals (these constituents may have been present in both the creosote and as additives in the wood treating process).

In this evaluation SCREEN was applied to calculating Ground Level Concentrations (GLCs). In this analysis, we assume an average emission rate over the length of the fire incident. Literature information supports that a fire of this magnitude and under uncontrolled conditions, would consume anywhere from 70 to 90 % of the products. The entire fire scenario is believed to have ranged from 8 to 12 hours. We conservatively use as a basis 75 % of the fuel as being consumed by the fire, and treat the entire fuel blend as a homogeneous mixture. Of the 75 % fuel consumed, we apply the following assumptions:

- Creosote and penta are assumed to be present in a 50/50 mix;
- Penta undergoes 99.99% DRE, resulting in negligible penta air pollution, although an average emission concentration of 190 ng/dscm could be used as a background concentration from wood burning;
- Creosote PIC are comprised of PCDD/PCDF, flyash and soot, NO, SO_2, CO_2, HCl, and various PAHs;
- Flyash is assumed to settle out of the atmosphere close to the source;
- Although ultra conservative, the wood consumed in the fire is not considered in the analysis, other than contributing to short-range ash deposition;
- Of the fuel blend portion (creosote and penta) consumed by combustion, 60% is assumed converted directly to energy to support the fire;
- Of the fuel blend portion resulting in PIC, 15% is attributed to large particulate flyash;
- Among the remaining air pollutants, 99.5% is considered to be NO_x, SO_x, CO, and HCl;
- It is assumed that 0.5% of the PIC are comprised of gaseous forms of PCDD/PCDF.

The fire area is assumed to be rectangular, and estimated from the dimensions of the vessels and assuming they were within close proximity of each other. Area source inputs to the model are:

- Emission rate (g/s-m^2)
- Source release height (estimated 6 m)
- Length of larger side of the rectangular area (estimated as 30.5 m)
- Lenght of smaller side of the rectangular area (13.4 m)
- Receptor height above ground (0 m)

SCREEN was run for an urban setting and simple terrain. Table 5 provides a tabulation of the input terms and other information gathered for the analysis. Two fire case scenarios are considered: an 8-hour and a 12-hour continuous fire.

Table 5. Source Terms Used in the Dispersion Calculations.

	Available Fuel, Lbs	**Lbs Fuel for Energy**	**Lbs Flyash**	**Total Lbs Gaseous + PM**	**Lbs NO_x, SO_x, CO, Other**	**Lbs PCDD/ PCDF**
Penta	910,535	546,321	54.6	309,582	308,034	1,548
Tar	492,057	295,234	29,523	167,299	166,463	836
Total	1,402,592	841,555	84,156	476,881	474,497	2,384

The area source emission used in the calculations are:

- For an 8-hour fire: 0.092 g/s-m^2
- For a 12-hour fire: 0.061 g/s-m^2

Table 6 summarizes the stability classes and wind speeds used in the calculations.

Table 6. Meteorological Data and Stability Classes Used in Calculations.

Time, Hours	**Wind Speed, m/s**	**Atmospheric Stability Class**
12:00	2.0	
13:00	1.5	A
14:00	2.0	A
15:00	1.0	A
16:00	2.0	A-B
17:00	3.0	A-B
18:00	2.5	A-B
19:00	2.5	E
20:00	3.0	F

Time, Hours	Wind Speed, m/s	Atmospheric Stability Class
21:00	2.5	F
22:00	2.0	F
23:00	1.0	D-F
24:00	0	D-F

GLCs (ground level concentrations) for the two fire scenarios are tabulated in Table 7. The calculations show that up to 5,000 meters from the fire scene significant levels of PCDD/PCDF persisted. Also, the analysis shows that on the day of the incident, nighttime conditions significantly worsened the air dispersion, leading to very high concentrations of PCDD/PCDF for brief periods but over greater distances.

Table 7. Tabulation of SCREEN Calculations.

Time, Hrs	Distance from Source, m	PCDD/PCDF Concentration, $\mu g/m^3$	
		8-Hr Burn	12-Hr Burn
12:00-15:00	100	9,334	6,189
	400	553	367
	800	130	86
	1000	70	47
	2000	38	25
	3000	28	19
	5000	20	13
16:00-18:00	100	5974	3961
	400	354	235
	800	83	55
	1000	52	34
	2000	16	11
	3000	14	9
	5000	8	8

Time, Hrs	Distance from Source, m	PCDD/PCDF Concentration, $\mu g/m^3$	
		8-Hr Burn	12-Hr Burn
19:00-21:00	100	38,000	24,930
	400	4153	2753
	800	1326	879
	1000	934	619
	2000	336	223
	3000	194	129
	5000	101	67
22:00-24:00	100		50,110
	400		4,969
	800		1,540
	1000		1074
	2000		379
	3000		223
	5000		125

REFERENCES AND RECOMMENDED RESOURCES FOR THE READER

1. Auer, Jr., A.H., 1978. Correlation of Land Use and Cover with Meteorological Anomalies. Journal of Applied Meteorology, 17 (5): 636-643.
2. Briggs, G.A., 1969. Plume Rise. USAEC Critical Review Series, TID-25075, National Technical Information Service, Springfield, Virginia 22151.
3. Briggs, G.A., 1973. Diffusion Estimation for Small Emissions NOAA ATDL, Contribution File No. 79 (Draft), Oak Ridge.
4. Briggs, G.A., 1975. Plume Rise Predictions, In: Lectures on Air Pollution and Environmental Impact Analysis, Haugen, D.A. (ed.), American Meteorological Society, Boston, MA, pp. 59-111.

5. Brode, R.W., 1991. A Comparison of SCREEN Model Dispersion Estimates with Estimates From a Refined Dispersion Model. Seventh Joint Conference on Applications of Air Pollution Meteorology with A&WMA, 93-96.
6. Burt, E.W., 1977. Valley Model User's Guide. EPA-450/2-77-018 U.S. Environmental Protection Agency, Research Triangle Park, NC.
7. Environmental Protection Agency, 1977. Guidelines for Air Quality Maintenance Planning and Analysis, Volume 10 (Revised): Procedures for Evaluating Air Quality Impact of New Stationary Sources. EPA-450/4-77-001 (OAQPS Number 1.2029R), Research Triangle Park, NC.
8. Environmental Protection Agency, 1983, Regional Workshops on Air Quality Modeling: A Summary Report and Addendum. EPA-450/4-82-015. U.S. Environmental Protection Agency, Research Triangle Park, NC.
9. Environmental Protection Agency, 1987a. Guideline On Air Quality Models (Revised) and Supplement A. EPA-450/2-78-027R. U.S. Environmental Protection Agency, Research Triangle Park, NC. Environmental Protection Agency, 1987b. Analysis and Evaluation of Statistical Coastal Fumigation Models. EPA-450/4-87-002. U.S. Environmental Protection Agency, Research Triangle Park, NC.
10. Environmental Protection Agency, 1988. Screening Procedures for Estimating the Air Quality Impact of Stationary Sources - Draft for Public Comment. EPA-450/4-88-010. U.S. Environmental Protection Agency, Research Triangle Park, NC.
11. Environmental Protection Agency, 1995a: Screening Procedures for Estimating the Air Quality Impact of Stationary Sources, Revised. EPA-450/R-92-019. U.S. Environmental Protection Agency, Research Triangle Park, NC.
12. Environmental Protection Agency, 1995b, Industrial Source Complex (ISC3) Dispersion Model User's Guide. EPA-454/B-95003b. U.S. Environmental Protection Agency, Research Triangle Park, NC.
13. Hosker, R.P., 1984. Flow and Diffusion Near Obstacles. In: Atmospheric Science and Power Production. Randerson, D. (ed.), DOE/TIC-27601, U.S. Department of Energy, Washington, D.C.
14. Leahey, D.M. and M.J.E. Davies, 1984. Observations of Plume Rise from Sour Gas Flares. Atmospheric Environment, 18, 917-922. Misra, P.K. and S. Onlock, 1982. Modelling Continuous Fumigation of Nanticoke Generating Station Plume. Atmospheric Environment, 16, 479-482.

15. Pierce, T.E., D.B. Turner, J.A. Catalano, and F.V. Hale, 1982. PTPLU - A Single Source Gaussian Dispersion Algorithm User's Guide. EPA-600/8-82-014. U.S. Environmental Protection Agency, Research Triangle Park, NC.
16. Pierce, T.E., 1986. Addendum to PTPLU - A Single Source Gaussian Dispersion Algorithm. EPA/600/8-86-042. U.S. Environmental Protection Agency, Research Triangle Park, NC.(Available only from NTIS. NTIS Accession Number PB87-145 363.)
17. Pierce, T.E. and D.B. Turner, 1980. User's Guide for MPTER - A Multiple Point Gaussian Dispersion Algorithm With Optional Terrain Adjustment. EPA-600/8-80-016. U.S. Environmental Protection Agency, Research Triangle Park, NC.
18. Randerson, D., 1984. Atmospheric Boundary Layer. In: Atmospheric Science and Power Production. Randerson, D. (ed.), DOE/TIC-27601, U.S. Department of Energy, Washington, D.C.
19. Schulman,L.L. and Scire, J.S., 1993. Building Downwash Screening Modeling for the Downwind Recirculation Cavity. Air and Waste, August, 1122-1127.
20. Turner, D. B., 1964. A Diffusion Model for an Urban Area. Journal of Applied Meteorology, 3, 83-91.
21. Turner, D. B., 1970, Workbook of Atmospheric Dispersion Estimates, Revised, 6th Printing, Jan, 1973, Office of Air Programs Pub. No. AP-26.

REVIEW AND QUESTIONS TO GET YOU THINKING

1. Have a discussion on the major parameters that influence pollution dispersion. List these parameters in terms of first order effects in dispersing pollutants.
2. Download a copy of SCREEN (SCREEN can be downloaded from the publisher's site www.bh.com/companions/0750674997.) Try a few test cases (follow the examples in this chapter) to become familiar with the software.
3. Visit http://ncardata.ucar.edu/datasets/ds464.0/MASTER and/or Infor@wunderground.com. Become familiar with the types of meteorological data and formats that you can download in.

4. Select a region or perhaps, the city you live in and develop a wind rose for several months. Meteorological data can be obtained from the sites noted in Question 3. Use **WRPLOT View** to construct the plots and generate tables. The program can be downloaded from http://www.lakes-environmental.com.

5. Describe how you would go about applying dispersion calculations to developing a an emergency response plan for a catastrophic release of an air pollutant. As an example, consider a VCM (vinyl chloride monomer reactor). How would you apply a model like SCREEN to evaluate emergency response and evacuation plans in the event that the reactor ruptured or exploded? List all the information and sources you would require to perform the analysis and to develop a worst-case scenario plan of action.

6. Download **FIRE**: **Factor Information REtrieval**, and apply this to the case study described on pages 323 through 330.

7. To increase the capacity of a natural gas processing plant, a facility decides to invest into four booster station compressors. This will increase the existing wellhead pressure, thereby enabling the gas processing plant to provide uninterrupted supply for the next ten years. (For those readers who are not familiar with such plant operations, Figures 16 and 17 show some photographs.) The project is to be financed through a lending institution that favors green technologies (i.e., pollution prevention type technologies). The environmental guidelines issued by the lending institution concerning the performance of gas turbines fueled by gaseous fossil fuel permit the emission of a maximum concentration of 86 nanograms of oxides of nitrogen (as NO_2) per Joule of heat input. This requirement would make it necessary to install DLE (Dry Low Emissions) type compressor engines at the proposed booster station. The selection of DLE over non-DLE (higher NO_x emitting compressor engines), along with a requirement to install anti-ice systems that would be needed to operate these machines under severe weather conditions, would result in a capital cost increase to the investment in excess of 10 million dollars. Based on the design information provided below, along with information on the local site conditions you will select as a part of the exercise, perform an analysis to ascertain whether the investment into the pollution prevention technology is justified. In other words, is there a significant enough environmental impact from NO_x emissions from the proposed project to justify the higher investment into the pollution prevention technology?

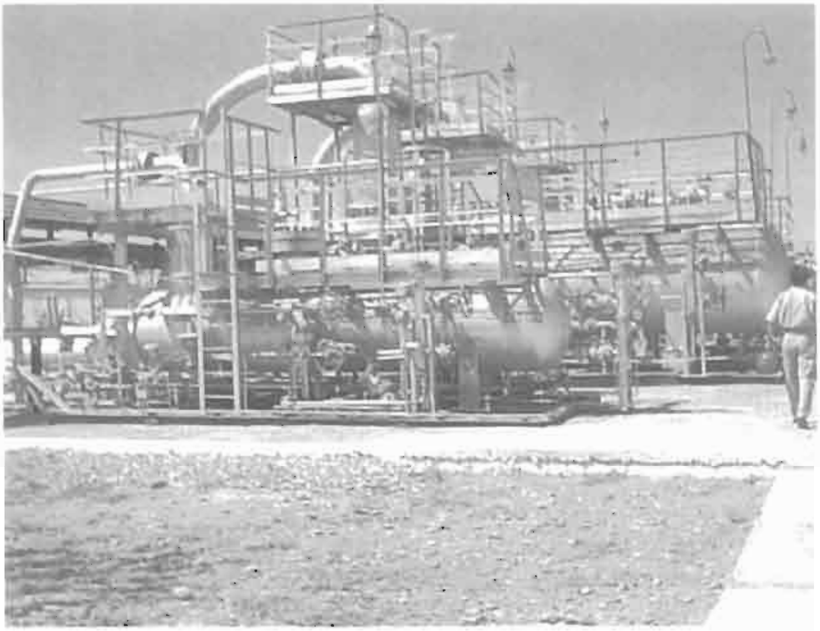


Figure 16. Gas processing plant.

Figure 17. Gas processing plant operations.

Data Inputs and Boundary Conditions for Question 7

(a) Perform the analysis for two different receptor scenarios. The first scenario is a densely populated urban region. The second should be a remote, rural setting. Select two cities or regions of the country that meet these criteria and for which historical meteorological data can be downloaded from the Web. (b) Assume that there are no other major industrial point source emitters in the regions except for the existing gas processing plant. The yearly average emissions levels for the base plant are 60.9 tons NO and 236 tons NO_2. (c) The compressors are planned to be operated in three different modes: summer mode (3 months operation or 2000 hours), normal mode (6 months operation or 4000 hours), and winter mode (3 months or 2000 hours). (d) There is a significant difference between the emissions from the non-DLE and DLE-type machines. When compared on a side-by-side basis for similar operating conditions, NO_x emissions for the non-DLE machines are 3 to 7 times higher, depending on inlet ambient air conditions. Table 8 provides a comparison of the emissions from each type of machine. (e) Only three of the machines will operate continuously in any of the three operational modes, with one machine as swing (i.e., as a spare).

Table 8. Comparison of DLE and Non-DLE Machine Emissions.

Ambient Temp. (°C)	**-28**	**-10**	**0**	**10**	**15**	**28**
DLE Machine						
Heat Rate (KJ/KW-Hr)	9580	9630	9661	9702	9736	9884
Cor. NO_x @ 15% O_2 (mg/mm$_3$)	82	51	51	51	51	51
NO_x Emission (kg/hr)	15.2	10	9.7	9.3	9.2	8.7
Non-DLE Machine						
Heat Rate (KJ/KW-Hr)	9500	9573	9597	9652	9688	9853
Cor. NO_x @ 15% O_2 (mg/mm$_3$)297	344	344	334	324	281	281
NO_x Emission (kg/hr)56.4	67.1	64.6	60.3	57.4	47	47

Chapter 6

PREVENTION VERSUS CONTROL

INTRODUCTION

Make no mistake about it - air pollution abatement, especially based upon end-of-pipe treatment technologies is expensive. Not too long ago the prevailing attitude among industry stakeholders was that air pollution control was simply a part of the cost of doing business, and that add-on costs associated with compliance simply had to be passed on to the consumer's purchase price for products. With the intensity of international competition in the chemical and allied industries, this philosophy simply does not cut it anymore.

Furthermore, although the U.S. EPA argues that the cost of compliance for all environmental regulations is small in comparison to overall industry expenditures, there are many hidden costs that oftentimes are not considered, and go beyond the capital investment for a piece of equipment. These so-called other costs are not necessarily incremental, depending upon the size of a company and the magnitude of its environmental management issues. They include, but are not limited to:

- engineering costs,
- tender and bidding costs on large capital projects,
- operational costs, the largest of which are usually energy related,
- maintenance costs,
- the cost for training personnel and maintaining a dedicated staff for operational purposes,
- the cost for space - since a piece of equipment will occupy floorspace that could be used for other purposes in manufacturing, the allocated space has a value,
- costs for recordkeeping, fees for permits to construct, permits to operate, and renewal of operating permits. This in itself requires dedicated staff to maintain emission contrivances for many point sources within an operating plant,
- there are also costs associated with monitoring, which may include laboratory support, either on-site or off-site,

- there are the costs associated with developing an environmental impact statement,
- and, we should not forget that if money is allocated for a piece of equipment for pollution control purposes, we loose the use of that money or the interest it would accrue if we simply left it in an interest bearing account, or invested it in other equipment or a project that enhances our manufacturing productivity or product quality (the *time-value-of money*, discussed in Chapter 8).

The more that can be done on the prevention side of the formula in managing any pollution problem, *not just air pollution*, the lower are our operating and hidden costs, and hence, the higher our profit margin. These cost saving categories can represent an enormous motivation for doing pollution prevention.

There are, however, limits to pollution prevention, and indeed, there are simply situations where it is more costly to invest in so-called *green technologies*, as opposed to relying on traditional pollution control systems.

In this chapter, we examine the following:

- the benefits of P2 to an organization,
- the basic approach to applying and integrating P2 into an organization, with emphasis given to managing air pollution problems, and
- when P2 should and should not be applied.

The last factor might seem strange to many readers, because in today's industry vernacular, P2 is politically correct (for a lot of reasons). Staunch supporters will argue that P2 is the only meaningful approach to managing pollution issues, and there seem to be an almost endless collection of success stories touting the financial and environmental benefits behind these practices. But it is human nature to remember and highlight the successes in life, and to dwell less on the failures. The fact of the matter is, P2 works a great deal of the time, but not always. P2 does make the most sense when we are concerned with long-term liability issues, and in this regard we need to step back and assess whether or not a waste generated poses an issue in the future. From that standpoint, P2 technologies that are more costly than conventional control techniques can be justified more readily.

A P2 opportunity needs to be looked at every time when dealing with a pollution problem, but only a detailed analysis and comparison to status quo and financial benefits and drawbacks will enable an optimum solution to a problem. In this regard, one of the objectives of this chapter is to wade through the P2-propaganda, and provide some simple guidelines on how to properly apply the principles to air pollution problems.

POLLUTION PREVENTION: WHEN AND HOW

DEFINING POLLUTION PREVENTION AND THE BENEFITS

To understand the possible benefits, we must first develop a working definition of pollution prevention. Although the term seems obvious, there are often wrong interpretations given to P2 practices.

Webster's Dictionary defines *prevention* as "the act of keeping something from happening." Practices are activities aimed at keeping an operation from polluting. An example of a P2 practice is converting a coal-fired electricity generating utility plant to one that burns natural gas. In this case a technology change and a feedstock substitution are made to reduce the pollution. With a coal-fired electric utility plant, air pollution emissions include unburned hydrocarbons (UHC), particulate matter (PM), nitrogen oxides (NO_x), sulfur oxides (SO_x), carbon dioxide (CO_2), and mercury. In contrast, the combustion of natural gas only creates NO_x and lower amounts of CO_2 (there are other pollutants, depending on the specific gas turbine technologies used).

By converting the plant to natural gas, we displace the use of coal and eliminate the hazardous air emissions associated with its combustion — but we need to invest into a new technology. The new process is generically referred to as "cleaner production," simply because it is inherently cleaner or less polluting, and the technology is referred to as "green technology."

There are cost savings carried along with this investment. The savings categories include lower direct and O&M (operating and maintenance) costs, because the P2 measure eliminates the need for such air pollution control devices like electrostatic precipitators, cyclone separators, baghouses, and NO_x and SO_x scrubbers; savings from not having to treat and dispose of wastewaters and solids wastes from gas scrubbing and coal combustion operations; and lower energy costs, because, when considered over its full cycle of use, natural gas is more economical and has a higher burn efficiency than coal.

As indicated by this example, the cost savings can go beyond the list of compliance-related financial losses associated with the act of pollution itself. There can be raw materials savings, energy efficiency savings, materials substitution savings, and there can be savings associated with improved product quality and higher levels of productivity and throughput. In some industry cases, pollution streams can have valuable by-products that can be recovered, recycled, or reconstituted and sold into secondary markets, thereby generating new revenue streams.

The trade journals and general media are filled with many examples of where P2 practices have captured both environmental and economic credits. Some good examples sorted by industry category are noted in the ***Recommended References*** at the end of this chapter. And, rather than mounting a lengthy argument to convince the few readers that don't believe in the overall value of P2 practices, the sidebar discussions scattered throughout this chapter provide ample examples of the rewards associated with successful programs.

A POLLUTION PREVENTION EXAMPLE

Overview: *The U.S. Air Force has classified material that must be destroyed. Disintegrators provide an alternative to incineration for the destruction of classified materials. Disintegrators are able to handle the destruction of paper, thick documents, video cassettes, microfilm or reels, CD-ROMs, microfiche, and diskettes. Disintegrators are available with a capacity of 50 to over 7500 lbs. per hour. Disintegrators work in the following way: Waste material is fed into the machine through a safety feed hopper. The cutting mechanism consists of 2 to 5 knives mounted on a steel rotor that pass 2 stationary bed knives (0.005 inch gap) at 500-600 RPM for up to 6,000 cuts per minute. Waste is cut until small enough to fall through a perforated steel screen beneath the cutting rotor. The screens are interchangeable so that the degree of destruction can be varied from 3/32 to 3 inches. Thick, tough materials such as diskettes and CD-ROMs can be destroyed with less power and less chance of jams due to the high mass of the rotor and thickness of the knives. A vacuum or fan unit creates a constant cooling air flow, dissipates heat, and draws the waste out of the cutting chamber eliminating the melting of plastic materials. The same air flow automatically bags the waste or discharges it to a collection bin or waste compactor.*

Benefits: *Using a disintegrator for the destruction of classified materials instead of an incinerator decreases the amount of air emissions from a facility. The decrease in air emissions eliminates the need for an air permit under Title V (**40 CFR 70 and 71**). Additionally, the facility may no longer need to meet incinerator performance standards (i.e., particulate matter and stack monitoring) such as those required under **40 CFR 60, subpart E**. Since an incinerator uses natural gas but a disintegrator does not, switching to a disintegrator will decrease natural gas consumption therefore helping a facility meet the requirements under **Executive Order 12902**, Energy Efficiency and Water Conservation at Federal Facilities.*

- ✓ *Stack emissions from incinerators are eliminated.*
- ✓ *The need for air permits for the incinerators are eliminated.*
- ✓ *Operating costs are reduced.*
- ✓ *Toxic and complex environmental contaminants are not created during the destruction of the materials.*
- ✓ *On-site operation may reduce transportation and labor costs.*

Economic Analysis Summary

- ✓ *Annual Savings for Disintegrator System: $46,445*
- ✓ *Capital Cost for Equipment/Process: $46,000*
- ✓ *Payback Period for Investment in Equipment/Process: 1 year*

P2 MAY NOT ALWAYS APPLY

A good P2 program is built around a set of well-planned activities that involves re-engineering the way an operation works, so that pollution does not occur, or is at least kept to a minimum. By doing this, we have the potential to save money as well as capture environmental credits. The re-engineering can take the form of process changes, technology changes, operational changes, and, in very simple cases, nothing more than good housekeeping practices. But in other situations, as in the example noted above, the cost of an investment into a major technological change can be very substantial.

In the electric utility example, the incentives for investing in natural gas-fired plants seem to be both environmental and economic. From the environmental standpoint, both smog precursors and climate change species production (or "greenhouse gases") can be directly attributed to coal use, and hence, investments into clean technologies are a matter of global sustainability, thereby making good common sense. Or is it? It certainly makes environmental sense, but does it make economic sense?

From an economic standpoint, electricity production from a new natural gas plant versus a newly built coal-fired plant heavily favors natural gas, because natural gas-fired plants are cheaper to build. However, older coal-fired plants built 20 to 30 years ago are often more profitable than newly built gas plants, because — among other reasons — coal is cheaper than natural gas, and the older plants have long since paid for their capital investments through depreciation.

Another reason why we can question whether such a technology investment really makes sense is the fact that emissions-control requirements tend to be less stringent when it comes to older coal-fired plants. In the United States the great majority of NO_x emissions from the power sector come from existing coal-fired plants, many of which were built between 1950 and 1980.

Due to a mechanism known as "grandfathering," most existing plants are subject only to NO_x standards imposed by Title IV of the 1990 Clean Air Act Amendments, which only requires the installation of low-NO_x boiler technology or the equivalent. The standards were set at 0.45 to 0.50 pounds per million British thermal units, or MM Btu (equivalent to 1.5 to 1.7 lb/MW-hr) for wall-fired and tangentially fired coal boilers during Phase I of the Title IV program (1996–1999), and from 0.40 to 0.86 lb/MM-Btu for a wider group of boilers beginning in 2000. However, because utility companies are legally allowed to average the emissions of all their units, and because some units are exempt in Phase II (i.e., cyclone units less than 155 MW), some units continue to operate without controls while emitting NO_x at levels as high as 2.0 lb/MM-Btu (roughly 630 parts per million, or ppm). The Title IV standards for NO_x produced minor innovation, because they were set at levels that could be achieved through low-cost boiler modifications.

The intent of the U.S. Congress on this issue was quite clear, as the law allows units that could not meet the numerical limit through use of low-NO_x burner technology to meet an alternative emission limit set at the lowest level they could reach using this technology. Because the standard simply requires the use of an existing and known technology, the only innovations were to reduce the cost of low-NOx burner technology for some boiler types. In contrast, the NO_x standards for existing oil- and gas-fired plants are significantly more stringent than those for existing coal plants, as most were built after 1971 and were subject to new-source standards that establish a minimum NO_x emission limit of 0.20-0.30 lb/MM-Btu (40 CFR 60.44, 60.44a).

New-source standards for new gas-fired facilities are even more stringent, where in some states the standards are as low as 0.02 lb/MM Btu, or an order of magnitude lower than the levels mentioned above.

There are several problems with these standards for older coal-fired plants that limit a sensible NO_x-reduction policy. First, they are relatively lenient. Because they require only that low-NO_x burners be used at coal-fired plants, relatively inexpensive NO_x-reduction technologies are not being used, because the plants already meet the minimum standards. Second, standards are established on a technology-by-technology basis, and have resulted in more lenient requirements for dirtier technologies. This has created little or no incentive to switch to cleaner processes in the past decade. Thirdly, these standards are input-based, which means they provide no incentive for efficiency within any technology category.

This example leads us to a very important observation. While pollution prevention may seem like the obvious thing to do, it is not always cost effective, and investments into re-engineering processes must be carefully scrutinized. In fact, in this example, we see environmental legislation that actually discourages investments into green technologies, which in itself is contrary to national policy under the Pollution Prevention Act.

An even more striking example of a situation where P2 is not necessarily appropriate is Question 7 in Chapter 5. If you did not have the time to tackle this problem, go back now and read it over. There are some important lessons to learn from this exercise, beyond the use of air pollution software models. One lesson is that sometimes lending institutions impose technology restrictions when they may not be necessary. In this problem a green technology would add on 10 million dollars to an investment. If the intended operation is planned for a populated region (i.e., an urban setting) then the environmental benefits associated with the green technology are likely to be important, because public safety would far outweigh any financial savings. But, if the intended operation were planned in a remote or rural setting, environmental credits can reach a point of diminishing returns. In fact, Question 7 originates from a project done in a remote part of Uzbekistan in virtually the middle of a desert. Under these conditions, an extra 10 million dollars added on to the project makes little sense, neither from an economic or environmental viewpoint.

All too often activities are implemented without carefully assessing the economic attractiveness (or unattractiveness) of a P2 project. Very often, companies implement P2 programs because it seems like the right thing to do, yet in practice these implementations can cost an enterprise more than the status quo, or cause the enterprise to ignore other opportunities with a greater potential for greater cost-savings.

We could argue that protecting the environment must take priority over financial savings. After all, investments into clean technologies, such as a gas-fired plant, have global environmental implications, so why shouldn't a utility owner/operator take a little less profit?

The problem with this reasoning is two-fold. First, even if the owner/operator of an older coal-fired plant decides to make the conversion, the investments required are so high that the conversion must be done in stages. As a result, the owner/operator will inevitably dispatch electricity more frequently from the dirtier coal-fired portion of the operation, simply to recover the capital investment costs of the conversion. This means that the environmental benefits that could be achieved by clean production will not take place anyway. This general observation is in fact common to other industry categories (e.g., there is little incentive in Eastern European countries to make the enormous investments into cleaner technologies for making steel). A second problem is that NO_x--emission standards from natural gas plants are being ratcheted down to as low as 2 ppm in many states.

This ultra-low emission target is in fact at the extreme limits of today's combined-cycle natural gas technology, and to achieve these limits there are not only tradeoffs in efficiency (making gas turbines less financially attractive than coal-burning technology), but a worsening of emissions because machines produce other pollutants beyond NO_x. The lesson here is that force-fitting P2 into an enterprise or industry sector is simply not the right thing to do.

We should note that in a general sense, the objective of pollution abatement is compliance. Whether we apply conventional controls or P2, the intent is to develop corrective actions that largely focus on the *lowest achievable emission rate* (LAER) technologies, and only sometimes on *best available control technologies* (BACT), which ultimately brings the operations into compliance. To understand the importance of this, the reader must have a clear understanding of LAER and BACT.

P2 EXAMPLE OF SURFACE COATING TECHNOLOGY AIR EMISSIONS

The Clean Air Act (CAA) requires the U.S. Environmental Protection Agency (U.S. EPA) to establish standards that limit hazardous air pollutants (HAPs) and volatile organic compound (VOC) emissions from various sources. There are 188 CAA-regulated HAPs, which include many of the solvents commonly used in surface coating. Many of these solvents are VOCs. EPA is currently engaged in the development of regulations for a number of categories of industrial surface coating operations and composite operations. Collectively known as the Coatings and Composites Coordinated Rule (CCCR), the regulations under development are national emission standards for hazardous air pollutants (NESHAPs) under Section 112 of the CAA and for some of the categories, national VOC rules or control technique guidelines (CTG) under Section 183(e) of the Act. The Agency has already promulgated regulations covering the surface coating activities of aerospace facilities and shipbuilding operations. EPA is expected to issue final NESHAPs or Section 183(e) rules for the remaining categories included in the CCCR by May 2002. Examples of remaining categories include automobiles and light-duty trucks, plastic parts, and miscellaneous metal parts. These new standards will apply to facilities engaged in the surface coating of synthetic polymer components; facilities engaged in the coating of a wide range of metal products that vary in size, shape, application method, and use; and vehicle assembly operations that apply primers, guide coat/primer surfacers, top coats, and other related coatings. New surface coating technologies have lower VOCs and HAPs content than the conventional coating systems because of the reduced solvent concentration in the formulation, and due to improved coating chemistries. Six of the technologies are: Powder Coating, High-Solids Coatings, Waterborne Coatings, UNICOAT, Radiation Curable Coatings, Supercritical Carbon Dioxide (CO_2) Spraying.

Benefit: *Use of alternative surface coating technologies can help facilities comply with EPA's NESHAP for Shipbuilding and Ship Repair - Shipbuilding and Ship Repair* ***(40 CFR 63, Subpart II)*** *and for Aerospace Manufacturing and Rework Facilities* ***(40 CFR 63, Subpart GG)****. Additionally, these alternative technologies may help facilities comply with the upcoming surface coating regulations. Reduces the amounts of VOCs and HAPs emitted into the environment and improves the ability of installations to comply with EPA's current and future emission standards for surface coating.*

The term LAER from a practical standpoint refers to corrective actions (i.e., technologies) that are capable of achieving the lowest emission rates. So, if a process is emitting nitrogen oxides (NO_x) and LAER is applied as the basis for reducing NO_x emissions, then we are forced to select only those technologies that will achieve the lowest emissions (based on a legal standard), without regard to the cost of the technology.

In contrast, the term BACT (sometimes known as BAT, for best available technology) generally refers to those technologies that cost-effectively achieve the goals (reduced emissions) of the corrective action. LAER and BACT most often focus on end-of-pipe technologies. P2 technologies can be BACT, but there are far more industry examples of end-of-pipe treatment approaches.

In contrast, P2 practices are by and large corrective actions based upon cost-sensitivity considerations. A P2 project really only makes sense when it is financially attractive or, at a minimum, break-even from a cost standpoint. Also, P2 programs are not necessarily driven by regulations (though they often anticipate them) and, like environmental management systems (EMSs), they are totally voluntary. This means then that P2 practices do not necessarily apply in all situations. There are situations, as we saw with the electric utility example, where regulations establish the abatement technology. Under this condition, P2 only applies if the emission can be eliminated altogether (e.g., a technology change or material substitution).

This brings us to what the real objectives behind P2 are about. Pollution prevention is a carefully planned investment aimed at reducing an enterprise's operating costs through the elimination of harmful pollution. A successful P2 activity is a win-win type of investment — that is, the company not only eliminates pollution at the source, but does so on the condition that, at the very least, the activity pays for itself and, more favorably, provides attractive financial returns. The re-engineering considered for the pollution reduction and/or elimination must meet a set of well-defined financial goals within the enterprise; otherwise it is not a worthwhile P2 practice.

PRINCIPLES OF POLLUTION PREVENTION

Harold Babbit, a leading authority on treatment engineering, stressed that "the search for profit should be the first step in the solution of the problem of the disposal of industrial wastes." This statement was made in the publication *Sewerage and Sewage Treatment*, 7th edition (New York, John Wiley Publishers) in 1952. Associating profit with or finding means of economically disposing of industrial wastes is not a new concept. There are numerous trade journal articles dating as far back as the 1930s which tout the very same principles today's organizations apply in pollution prevention programs. What is different today, however, is a much greater incentive to eliminate pollution problems altogether. This greater incentive stems from strict enforcement of environmental laws that did not exist a generation ago.

For pollution prevention to have a significant impact on any company, it must be applied on a regular and dedicated basis. Occasional programs only have local impacts, and rarely does any one environmentally focused project have profound impacts on the bottom line economic performance of a company. Furthermore, pollution prevention should not just focus on one medium, although it may make sense to do so initially if that one medium represents the largest environmental issue for a company.

The book *Green Profits: A Manager's Handbook for ISO 14001 and Pollution Prevention* (N. P. Cheremisinoff and A. Bendavid-Val, Butterworth-Heinemann, Mass., 2001) provides a step-by-step approach to developing pollution prevention programs in an organization. In this section we summarize the basic approach for the reader, but refer you to the above publication for further details and examples.

AN OVERVIEW OF THE POLLUTION PREVENTION AUDIT

All pollution prevention programs start the same - with an audit. The objective of an audit is to gather information aimed at developing a baseline description of the operations. Once we understand how much the costs of compliance to air and other pollution media are, then we can apply engineering tools and management practices to reduce these costs.

We can also use the results of the audit to compare how well our organization manages its air or other media pollution problems against a standard. The standard by which comparisons are made to our baseline can be based on other companies within our industry sector, on industry-specific standards, on legal standards, or on internal goals set by the enterprise. This is known as *benchmarking*. By performing benchmarking, a company can formulate a basis for recommending corrective actions aimed at improving the performance of the subject.

There are four essential elements of any audit:
- ➞ **Examination**
- ➞ **Developing a baseline**
- ➞ **Benchmarking**
- ➞ **Developing recommendations for corrective actions**

A P2 audit differs from most other types of audits because it makes use of a dual benchmarking approach; namely, it uses both technical (environmental performance) and financial performance as its basis for making corrective actions. The status quo most often serves as the benchmark, though other standards certainly can be devised. A P2 audit can also affect non-environmental issues. The types of corrective actions can affect other types of wastes, energy, occupational safety, product quality, and worker productivity.

The objectives of the audit are first to develop a baseline of the environmental performance of the facility, and then to assess one or more corrective actions (P2 activities) with attractive economics which improve environmental performance.

There are three consecutive phases:

- Phase I: Pre-assessment for audit preparation
- Phase II: The in-plant assessment
- Phase III: Synthesis, benchmarking, and corrective actions

THE PRE-ASSESSMENT (PHASE I)

Step 1: Audit Focus and Preparation

Step 1.1: Getting Ready. A thorough preparation for a P2 audit is a prerequisite for an efficient and cost-effective evaluation. Gaining support for the assessment from top-level management, and for the implementation of results, is particularly important. Otherwise, there will be no real action on recommendations. Early in the process, management needs to accept that, at a bare minimum, the audit is a worthwhile exercise and that resources - human and financial - should be diverted from other activities to the task of auditing.

Step 1.2: Assemble the Audit Team. The members of the P2 auditing team should be identified and assembled. The number of people required on a team will depend on the size and complexity of the processes to be investigated. Select team members on the basis of their expertise. Don't just limit the team members to environmental specialists. Environmental and environmental health and safety (EHS) engineers and specialists will understand what the current costs are for end-of-pipe treatment technologies and for disposal, and well-trained and experienced individuals will also have a good understanding of the subject facility's compliance issues. But these team members will generally not have a keen understanding of the process details and, more importantly, of the specific hardware associated with each unit operation. Further, we must recognize that because environmental engineers traditionally are trained in pollution control technologies, they are not always a source of P2 ideas. As such, the team needs to combine the brainstorming chemistry of different disciplines - for example, between a process engineer, an operator, possibly a chemist, laboratory or product quality personnel, and the EHS personnel.

Step 1.3: Identify and Allocate Additional Resources. The audit may require external resources, such as laboratory facilities and possibly equipment for air sampling, flow measurements, energy measurements, and product-quality testing, *Step 1.4: Select the Subject Facility*. It is important to decide on the focus of your audit during the preparation stage. You may wish to audit a complete process or you may want to concentrate on a selection of unit operations within a unit process.

The focus will depend on the overall objectives of the audit. A good way to approach this is by conducting a brainstorming session with operators and environmental specialists.

Such sessions often help to bring to the surface those parts of the plant where suspect waste issues or pollution problems are most critical. Such areas of operations are most likely to benefit from an audit and P2 program.

Step 1.5: Define the Audit Objectives. If the objectives are not entirely environmental, then you may wish to look at waste minimization as a whole or you may wish to concentrate on particular wastes - for example, raw material losses, wastes that cause processing problems, wastes considered to be hazardous or for which regulations exist, and/or wastes for which disposal costs are high. A good starting point for designing a P2 audit is to determine the major problems and wastes associated with your particular process. This can be accomplished by a thorough review of existing documentation, as described in the next sub-step.

LOW NITROGEN OXIDES (NOx) BURNERS FOR REDUCTION OF NO_x EMISSIONS IN INDUSTRIAL BOILERS

Overview: *Low NOx burners (LNB) reduce the formation of NOx by staging the combustion process by producing fuel rich and fuel lean zones within the flame. The fuel rich zone is the primary combustion zone and prevents the formation of thermal NOx (formation of NOx caused by high flame temperatures) resulting from low oxygen concentration. The cooler, fuel lean zone prevents thermal and fuel NOx (formation of NOx resulting from the oxidation of fuel bound nitrogen). LNBs can reduce NOx emissions by as much as 60 percent. By replacing existing burners with burners designed to reduce the formation of NOx, reductions in NOx emissions of between 20 and 60 percent can be achieved.*

Benefit: *The use of LNB decreases the amount of NOx formation at the facility and therefore may help facilities meet state RACT or BACT (40 CFR 52) requirements. Additionally, this technology may help facilities meet standards of performance for industrial-commercial-institutional steam generating units in 40 CFR 60, Subpart Db. A decrease in a facility's NOx emissions may decrease the possibility that a facility will meet the Nox emission threshold for an air permit under 40 CFR 70 and 71.*

Economic Analysis: *In an effort to provide for the use of lower cost fuel, two 8.37 MM Btu/hr package boilers at the Naval Consolidated Brig Marine Corps Air Station (MCAS) were retrofitted as dual fuel LNBs (lower cost natural gas and oil), incorporating flue gas recirculation (FGR) and other changes. The cost of retrofitting a single boiler with a LNB was estimated at $24,000 (1992 dollars). The new system replaced an external FGR module with one that is integral to the boiler front. No operating or maintenance problems have been identified. FGR maintenance costs were reduced significantly and boiler shutdowns were almost eliminated. The Capital Cost for Equipment/Process was $24,000. The payback period, estimated at less than five years, related primarily to the use of lower cost natural gas. in addition, maintenance costs were reduced and shutdown times were largely eliminated.*

Step 1.6: Review Documentation. Collate and review all existing documentation and information regarding the process. Regional or plant surveys may have been undertaken, environmental audits may have been conducted, safety audit findings may be available; these could yield useful information indicating the areas for concern, and will show gaps where no data are available.

Step 1.7: Gain Employee Buy-in and Participation. The importance of top management support *and* employee participation cannot be overstated.

Step 2: Listing the Unit Operations

Manufacturing processes are made up of a number of *unit processes*, which are in turn made up of *unit operations*. Unit processes are distinct stages of a manufacturing operation. They each focus on one stage in a series of stages, successively bringing a product to its final form. Take a look back at some of the process flow sheets provided in Chapter 2 for some examples. A unit operation is an area where materials and energy are input, a function occurs, and materials are output, possibly in a different form, state, or composition. Unit operations, or "unit ops," are the individual process steps within each major unit process. Quite often, the same unit ops are used in different unit processes within the same plant, but they have different functions, and hence do not use the same equipment. Developing an accurate list of all the unit operations within a unit process is the starting point in identifying P2 and waste-minimization opportunities. Without such a list, the team will not be able to identify and, later on, quantify possible P2 and waste reductions. Furthermore, without the list of individual unit ops, the team cannot assess re-engineering options. Ultimately, each unit op can be related to a piece of process equipment. It is the process equipment that is ultimately modified, either physically or operationally, or that can be replaced with an alternative piece of equipment or newer technology. It is best not to think of any one unit operation in terms of process equipment at this stage of the audit. Process-equipment options for each unit operation are considered much further into the P2 audit and, indeed, may not be necessary to consider at all if the P2 or waste minimization opportunity identified falls into the best practices category.

To develop a useful list, we recommend the following sub-steps.

Step 2.1: Refine the Initial Checklist. Table 1 is a checklist of unit operations. Apply this as an initial guide and checklist that can be used to identify each unit operation within the unit process that the audit will focus on. You may have to make additions to the list, because it is meant to be a general overview. Next to each unit operation that applies to the unit process of interest, provide a brief description of its function or purpose. This will prove useful in developing a process flow scheme in Step 3. Much of this sub-step can be accomplished by sitting down with other team members and reviewing the plant or unit-process objectives. If the focus of the audit is strictly air emissions, then make a note under the Objective/Purpose columns as to whether air pollution issues exist.

Table 1. An Initial Checklist of Unit Operations.

Name of Unit Process: *Include the name, title, or general statement of the unit process in this block. Then check and briefly describe the purpose of those unit ops that apply.*					
	Unit Op	**Objective/ Purpose**		**Unit Op**	**Objective/ Purpose**
☐	Absorption		☐	Filtration (gas-PM-vapor)	
☐	Adsorption (liquid-liquid)		☐	Filtration (liquid-PM)	
☐	Adsorption (liquid-liquid)		☐	Flotation - separation	
☐	Blending and homogenization		☐	Fluid transfer	
☐	Centrifugation		☐	Fluidization (gas-solid)	
☐	Chemical reaction		☐	Fluidization (gas-liquid)	
☐	Classification (PM)		☐	Gas compression	
☐	Communition		☐	Gas Scrubbing	
☐	Crystallization		☐	Homogenization	
☐	Desalination		☐	Incineration	
☐	Distillation		☐	Ion exchange	
☐	Drying		☐	Mixing	
☐	Extraction (liquid-liquid)		☐	Sedimentation (PM-gas)	
☐	Extrusion		☐	Sedimentation (solid-liquid)	

Step 2.2: An Initial Walkthrough. The entire purpose of Step 2 is to develop an initial survey of the unit process. The step will set many of the ground rules for the audit. Using the modified checklist derived from Table 1, one or more of the team should walk around not only the unit process of interest, but neighboring unit processes that depend upon or affect the subject facility. If the plant is small enough, then take the time to walk around the entire plant, to gain a thorough understanding of all the processing operations and their interrelationships. The walkthrough will help the auditors refine their list of unit operations, and enable them to decide how best to describe a process in terms of these unit ops. During this initial overview, it is useful to record visual observations and discussions, and to make rough sketches of process layout, drainage systems, vents, plumbing, and other material-transfer areas. These help ensure that important factors are not overlooked. The team should consult the production staff about normal operating conditions. The production or plant staff, are likely to know about waste-discharge points, unplanned waste-generating operations (such as spills and washouts), and give the team a good indication of actual operating procedures. Investigations may reveal that night-shift procedures are different from day-shift procedures; also, plant personnel may disclose that actual material-handling practices are different from those set out in written procedures. A long-time employee could provide insight into recurring process problems. In the absence of any historical monitoring, this information can be very useful. Such employee participation must be free from the threat of disciplinary action. During this initial site survey, note imminent problems that need to be addressed before the assessment is complete. Set the notes generated from the initial walkthrough aside for use in Step 2.3.

Step 2.3: Organize the Collected Data. As previously noted, the audit team needs to understand the function and process variables associated with each unit operation. Similarly, the team needs to collate all the available information on the unit operations and the process in general that were collected in Steps 2.1 and 2.2. For complex unit processes and plant-wide audits, it's best to organize these materials into separate files. Always try to tabulate data, so team members can more easily review and cross-reference information. A convenient way of organizing the files is on a unit-operation basis. Identification of materials handling operations (manual, automatic, bulk, drums, etc.) covering raw materials, transfer practices, and products is also an important aspect that could usefully be included in the above organization and tabulation of information, as a prelude to developing material balances in Phase II.

Step 3: Constructing Process Flow Sheets

The next step is to connect the individual unit operations in a block diagram, creating a *process flow sheet.* Figure 1 is an example of a simplified process flow diagram for a pattern-etch process for a printed wiring-board operation. There are plenty of other examples for you to refer to in Chapter 2. The process flow sheet provides us with a description of the flow of all materials not only into and out of the entire unit process, but through each and every unit operation. Intermittent operations - such as cleaning, make-up, or tank dumping - may be distinguished by using broken lines to link the boxes. Air emissions (both primary and fugitive) can easily be identified on such schematics.

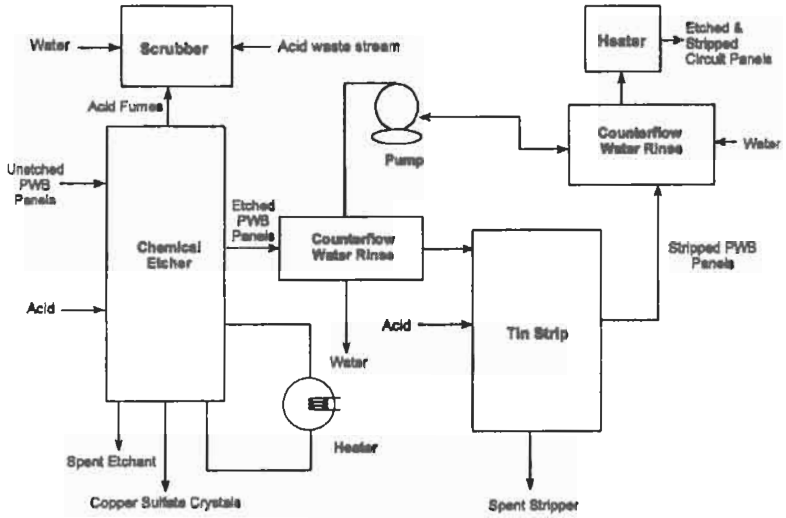


Figure 1. Example of a process flow sheet of a pattern-etch process for a wiring-board operation.

For complex processes, prepare a general flow diagram illustrating the main process areas, and then separately prepare detailed flow diagrams for each main processing area. Decide on the level of detail that you require to achieve your objectives. It is important to realize that the less detailed or more far-reaching the assessment becomes, the more information is likely to be lost or masked by oversimplification. Establishing the correct level of detail and focusing on specific areas are very important at an early stage.

Step 4: Preliminary Assessment and Next Steps

Often, the walkthrough and analysis of the process flow sheets lead to an early identification of P2 and waste-reduction opportunities. By studying the process flow sheets and information gathered from the walkthrough, and by conducting brainstorming sessions with team members, the team will be able to identify sources of pollution and waste, and their causes. Pay particular attention to any obvious waste that can be reduced or prevented easily, and correct it before proceeding to the development of a material balance (Phase II). Simple changes at this early stage and the resulting benefits will help enlist the participation and stimulate the enthusiasm of employees for the total P2 assessment and reduction program.

Summarize the findings and recommendations in a brief pre-assessment report, and present and review this with management. This will reaffirm management's commitment to the next phase. Include in the pre-assessment report a list of actions or steps that the team intends to follow in the next phase. If some of these steps involve field measurements, then highlight these and their possible effects on production schedules and personnel assignments. Use the steps in Phase II as a guide to developing the recommended actions.

THE IN-PLANT ASSESSMENT (PART 1 OF PHASE II)

An important engineering tool needed to implement Phase II is *stoichiometry*. Stoichiometry refers to the methods of *material balances,* which are defined as precise accounts of the inputs and outputs of an operation.

The first law of thermodynamics is the basis for material- and energy-balance calculations. Because there is no significant transformation of mass to energy in most manufacturing operations, for a material balance the first law can be reduced to the simplified form:

$$\text{Mass in} = \text{mass out} + \text{accumulation}$$

A similar statement, or equation, can be used to express the energy balance:

$$\text{Energy in (above datum)} + \text{energy generated} = \text{energy out (above datum)}$$

Energy balances differ from mass balances in that the total mass is known but the total energy of a component is difficult to express. Consequently, the heat energy of a material is usually expressed relative to its standard state at a given temperature. For example, the heat content, or enthalpy, of steam is expressed relative to liquid water at 273°K (0°C) at a pressure equal to its own vapor pressure.

Step 5: Determining the Inputs

Step 5.1: Determine the Total Inputs. Inputs to a process or a unit operation may include raw materials, chemicals, water, compressed air, and energy. The inputs to the unit process and to each unit operation need to be quantified; as a first step toward quantifying raw material usage, examine purchasing records. This will rapidly give you an idea of the sort of quantities of raw materials involved.

In many situations, the unit operations where raw-material losses are greatest are raw-material storage and transfer. Look at these operations in conjunction with the purchasing records to determine the actual net input to the process.

Make notes regarding raw-material storage and handling practices. Consider evaporation losses, spillages, leaks from underground storage tanks, vapor losses through storage-tank pressure-relief vents, and contamination of raw materials. These can often be rectified very simply. Record raw-material purchases and storage and handling losses in a table, to derive the net input to the process.

Step 5.2: Determine the Inputs to Unit Operations. Once you've determined the net input of raw materials to the process, quantify the raw material input to each unit operation. If accurate information about raw-material consumption rates for individual unit operations is not available, then take measurements to determine average quantities (or perform careful mass balances). Measurements should be taken for an appropriate length of time. For example, if a batch takes one week to run, then take measurements over a period of at least three weeks; these figures then can be extrapolated for monthly, quarterly, or annual figures. Some quantification is possible by observation and some simple accounting procedures. The idea is to develop a database of inputs that reflect *steady-state* operations - that is, the input amounts that reflect average or normal consumption patterns.

For liquid raw materials, such as water or solvents, check storage tank capacities and ask operators when a tank was last filled. Monitor the tank levels and the number of tankers arriving on site. Remember, open tanks are a source of fugitive air emissions. While investigating the inputs, talking to staff, and observing the unit operations in action, the auditing team should think about how to improve the efficiency of the unit operations.

The audit relies on information gathered in the field, by interviewing operators and various shop personnel. These interviews help the team identify possible ways to save raw materials, reduce pollution, and conserve energy. These discussions should not be extemporaneous; they should be thoughtout in advance, and initially formulated during the walkthrough. It's a good idea to have a list of questions and a checklist of issues for such meetings and encounters with operators. Refer to ***Green Profits*** for sample questions to ask on an audit.

Step 5.3: Consider the Energy Inputs. The energy input to a unit operation should be considered at this stage; however, energy use deserves a full assessment in its own right. For our discussions, however, we will focus on energy only as it relates to evaluating a P2 opportunity.

In other words, our primary focus is on waste- and pollution-reduction opportunities; if these could reduce energy consumption as well, all the better. If energy usage is a particularly prominent factor, then the team should recommend a separate energy audit.

Step 5.4: Record Information on Process Flow Sheets. The input data collected for the material balance can be recorded on the process flow diagram, and in tabular form on a spreadsheet.

Step 6: Accounting for Water Usage

The use of water, other than for a process reaction, is a factor that should be covered in all pollution prevention audits. The use of water to wash, rinse, and cool is often overlooked, although it represents an area where waste reductions can frequently be achieved simply and cheaply. Water inputs to a process can represent both significant pollution and raw materials savings if opportunities for recycling are identified. Using less water can be a cost-saving exercise. In many older plant operations, water conservation programs are often overlooked. Even something as straightforward as a valve-maintenance program can result in significant reductions in water consumption.

Consider the following points while investigating water use. These could wind up being recommendations, with incremental financial savings for the plant:

- Tighter control of water use can reduce the volume of wastewater requiring treatment, and result in cost savings - it can sometimes reduce volumes and increase concentrations to the point of providing economic material recovery in place of costly wastewater treatment.
- Attention to good housekeeping practices often reduces water usage and, in turn, the amount of wastewater passing to drains.
- The cost of storing wastewater for subsequent reuse may be far less than the treatment and disposal costs.
- Counter-current rinsing and rinse-water reuse are useful tips for reducing usage. Counter-current contact systems are more efficient in promoting heat and mass exchanges, which are important to gas absorption, extraction, and many types of chemical reactions.

Step 7: Measuring Current Levels of Waste Reuse and Recycling

Some wastes lend themselves to direct reuse in production and may be transferred from one unit to another; others require some modifications before they are suitable for reuse in a process. These reused waste streams should be quantified. The reuse or recycling of wastes can reduce the amount of freshwater and raw materials required for a process. While looking at the inputs to unit operations, think about the opportunities for reusing and recycling outputs from other operations. Note that if reused wastes are not properly documented, double-counting may occur in the material balance, particularly at the process or complete plant level; that is, a waste will be quantified as an output from one process and as an input to another.

FLUE GAS RECIRCULATION FOR REDUCTION OF NITROGEN OXIDES (NO_x) EMISSIONS IN INDUSTRIAL BOILERS

Overview: *Flue gas recirculation (FGR) significantly reduces nitrogen oxides (NOx) emissions (up to 60 percent) in industrial boilers by recirculating a portion of the boiler flue gas (up to 20 percent) into the main combustion chamber. This process reduces the peak combustion temperature and lowers the percentage of oxygen in the combustion air/flue gas mixture; thus retarding the formation of* NO_x *caused by high flame temperatures (thermal* NO_x*). To modify an existing boiler, ducting must be run from the stack to the boiler air supply fan. Space limitations can make routing new ductwork difficult and costly. More powerful fans, oxygen monitors, and air flow controllers are usually required.*

Benefit: *The use of FGR decreases the amount of NOx formation at the facility and therefore may help facilities meet state RACT or BACT **(40 CFR 52)** requirements. Additionally, this technology may help facilities meet standards of performance for industrial-commercial-institutional steam generating units in **40 CFR 60**, Subpart Db. A decrease in a facility's* NO_x *emissions may decrease the possibility that a facility will meet the* NO_x *emission threshold for an air permit under **40 CFR 70 and 71**.*

- ✓ *Typically costs less to implement than low NOx burners, if installing as separate unit.*
- ✓ *In most situations, would be sufficient to satisfy state* NO_x *RACT (Reasonably Available Control Technology) regulations or other* NO_x *emissions requirements.*
- ✓ *Provides potential for emission reduction credits. Provides potential for increased boiler flexibility.*
- ✓ *If part of an integral system, may reduce energy and space requirements.*

Step 8: Quantifying Process Outputs

By now, the team has half the data needed for the material-balance system. To calculate the second half of the material balance, the outputs from unit operations and the process as a whole need to be quantified. Outputs include primary product, byproducts, wastewater, gaseous wastes (emissions to atmosphere), liquid and solid wastes that need to be stored and/or sent off-site for disposal, and reusable or recyclable wastes. Your team may find that a spreadsheet will help organize the input information. It is important to identify units of measurement, and to keep them consistent.

The assessment of the amount of primary product or useful product is a key factor in process or unit-operation efficiency. If the product is sent off-site for sale, then the amount produced is likely to be documented in company re-cords. However, if the product is intermediate, meant for input to another process or unit operation, then the output may not be so easy to quantify.

➪ *Production rates may have to be measured over a period of time.*
➪ *Similarly, the quantification of any by-products may require measurement.*

Step 9: Accounting for Wastewater Flows

In many plant operations, significant quantities of both clean and contaminated water are discharged to a sewer or a watercourse.

In many cases, this wastewater has environmental implications and incurs treatment costs. In addition, wastewater may wash out valuable unused raw materials from the process areas. It is very important to know how much wastewater is going down the drain, and what that wastewater contains. The wastewater-flows from each unit operation, as well as from the process as a whole, need to be quantified, sampled, and analyzed.

Step 9.1: Identify the Effluent Discharge Points. Determine the points at which wastewater leaves the site. Wastewater may go to an effluent treatment plant, directly to a public sewer, or directly to a watercourse. One factor that is often overlooked in audits is the use of several discharge points. It is important to identify the location, type, and size of *all* discharge flows. Identify where flows from different unit operations or process areas contribute to the overall flow. In this way, it is possible to piece together the drainage network for the site. This can lead to startling discoveries of what goes where!

Once the team understands the drainage system, the enterprise can design an appropriate sampling and flow measurement program to monitor the wastewater flows and strengths from each unit operation.

Step 9.2: Plan and Implement a Monitoring Program. Plan your monitoring program thoroughly and try to take samples over a range of operating conditions, such as full production, startup, shutdown, and washing out. In the case of combined stormwater and wastewater drainage systems, ensure that sampling and flow measurements are carried out in dry weather. For small or batch wastewater flows, it may be physically possible to collect all the flow for measurement using a pail and wristwatch. Larger or continuous wastewater flows can be assessed using flow measurement techniques. Refer to the list of suggested readings at the end of this book for references on field monitoring and measurement methods.

Step 9.3: Reconcile Wastewater Flows. The sum of the wastewater generated from each unit operation should be approximately the same as the input to the process. If its not, then there are possible sources of error in your accounting. The inability to reconcile water flows is a good tip-off to P2 opportunities. To make sure it doesn't miss such an opportunity, the team should focus attention on accurate reconciliation of the inputs and outputs.

Step 9.4: Determine the Concentrations of Contaminants. Analyze wastewater to determine the concentration of contaminants. Take samples for laboratory analysis. Composite samples should be taken for continuously running wastewater. For example, a small volume - say, 100 ml - may be collected every hour through a production period of 10 hours, to gain a 1-liter composite sample. The composite sample represents the average wastewater conditions over that time.

Step 9.5: Tabulate Flows and Concentrations. Wastewater flows and concentrations should be tabulated.

Step 10: Accounting for Air Emissions

Step 10.1: Quantify the Air Emissions. It's necessary to arrive at an accurate material-balance quantification of gaseous emissions associated with the process. Consider the actual and potential gaseous emissions associated with each unit operation, from raw-material storage through product storage. Gaseous emissions are not always obvious and can be difficult to measure. Also, continuous monitoring can be expensive and not always justified. Where quantification is impossible, estimations can be made using stoichiometric information. The following example illustrates the use of indirect estimation.

Consider coal burning in a boiler house. The assessor may not be able to measure the mass of sulfur dioxide (SO_2) leaving the boiler stack, because of access problems and the lack of suitable sampling ports on the stack. The only information available is that the coal is of soft quality, containing 3% sulfur by weight and, on average, 1,000 kg of coal is burned each day.

First calculate the amount of sulfur burned:

$$1{,}000 \text{ kg coal} \times 0.03 \text{ kg sulfur/kg coal} = 30 \text{ kg sulfur/day}$$

The combustion reaction is approximately:

$$S + O_2 = SO_2$$

The number of moles of sulfur burned equals the number of moles of sulfur dioxide produced. The atomic weight of sulfur is 32 and molecular weight of sulfur dioxide is 64. Therefore:

$$\text{kg-moles S} = 30\ \text{kg}/32\ \text{kg per kg-mole} = \text{kg-moles of } SO_2 \text{ formed}$$

$$\text{kg } SO_2 \text{ formed} = (64\ \text{kg } SO_2/\text{kg-mole}) \times \text{kg-moles } SO_2 = 64 \times 30/32 = 60\ \text{kg}$$

Thus, it may be estimated that an emission of 60 kg of SO_2 will take place each day from the boiler stack.

These types of stoichiometric calculations are commonplace and can provide reliable estimates for the material balance. As with any calculation method, one should list the assumptions to qualify the accuracy of the estimate. Limited field measurements can always be done later to verify the estimated emissions.

Note that application of a systematic approach enables us to resolve a material-balance system into a number of independent equations equal to the number of unknowns that it needs to solve for. The following steps should be followed with any material-balance system, regardless of complexity:

Step 1: State the Objective. More exactly, state the unknowns that you need to solve for. The team should actually have a good idea of these by the time Phase I is complete.

Step 2: Tabulate the Available Data.

Step 3: Refer to the Process Flow Sheets. All material balances are logical. The process flow sheets are the basis for rationalizing the mathematical statement form of material balances.

Step 4: Define the System Boundaries. This depends on the nature of the unit process and individual unit operations. For example, some processes involve only mass flowthrough. An example is filtration. This unit operation involves only the physical separation of materials (e.g., particulates from air). Hence, we view the filtration equipment as a simple box on the process flow sheet, with one flow input (contaminated air) and two flow outputs (clean air and captured dust). This is an example of a system where no chemical reaction is involved. In contrast, if a chemical reaction is involved, then we must take into consideration the kinetics of the reaction, the stoichiometry of the reaction, and the by-products produced. An example is the combustion of coal in a boiler. On a process flow sheet, coal, water, and energy are the inputs to the box (the furnace), and the outputs are steam, ash, NO_x, SO_x, and CO_2.

Step 5: Establish the Basis for the System Parameters. Is the process steady-state, or do the parameters represent transient or intermittent conditions? These considerations qualify the nature of the operation, and ultimately qualify the conditions under which corrective actions are taken in any P2 activities the team recommends.

Step 6: Write the Component Material Balances. The Phase II auditing steps define the pollutants and wastes that are among the team's focus. Its objective has always been to identify specific wastes or pollutants that the enterprise can reduce; these are the components the team needs to assess in the material balances. It is important to note that once the material balance for each unit operation has been completed for raw-material inputs and waste outputs, it is necessary to repeat the procedure for each contaminant of concern.

Step 7: Write an Overall Material Balance. Remember that the P2 audit focuses on a unit process, but that there are individual unit operations that make up this process. The team will need to develop a series of material balances for each unit operation, and an overall material balance about the entire unit process, to bring closure to a solution of parameters of interest. The individual or component material balances developed may be summed to give a balance for the whole process, production area, or factory.

Step 8: Solve the Equations. Many material balances can be stated in terms of simple algebraic expressions. For complex processes, matrix-theory techniques and extensive computer calculations will be needed, especially if there are a large number of equations and parameters, and/or chemical reactions and phase changes involved.

Step 9: Develop a Final Material Balance. You must develop a final material balance to check the accuracy of the calculations. You may find that it is necessary to go back onto the production floor and gather additional information and measurements to improve the accuracy and reliability of the calculations. Note: *It is important to keep track of any assumptions made in developing the material balance. Oftentimes there are losses, emissions and, or throughputs that we cannot gain an accurate handle on. Assuming some of these to be small at one point in the analysis could lead to wrong conclusions. Therefore, assumptions or estimates will often require retesting in order to bring closure to a balance.* The material balance is really an evolving tool that the auditors may have to refine at several stages of the audit.

In situations where no chemical reaction is involved, the balances are based on the masses of the individual components appearing in more than one incoming or outgoing stream. Components that appear in only one incoming stream and one outgoing stream can be lumped together as though they are one component, to simplify the calculations and increase precision. It is important at the start to select a convenient unit of mass (usually the kilogram or pound), and then express all components in that same unit.

To describe a continuous process on a standard basis, always choose a unit of time or a consistent flow rate per-unit-of-time basis. For batch processes, select a unit-weight basis on the basis of a single batch.

Processes involving chemical reactions must be approached differently. It is best to express the compositions of flow streams entering the process or unit operation in terms of molar concentrations. Balances are developed in terms of the largest components that remain unchanged by the reactions.

In cases where the reactants involved are not present in the proper stoichiometric ratios, the limiting reactant will have to be determined and the excess amounts of the other reactants calculated. It is safe to assume that unconsumed reactants and inert components exit with the products in their original forms. Consider the following example.

Natural gas containing 98% methane and 2% nitrogen by volume is burned in a furnace with 15% excess air. The fuel consumption is 20 cubic meters per second, measured at 290°K and 101.3 kPa (or 14.7 psia). The problem is to determine how much air is required under these conditions. In addition, we want to determine the baseline environmental performance of the furnace by calculating the quantity and composition of the flue gas.

Solution. As with all material-balance systems, our first step is to start with a process flow sheet. Figure 2 provides a simplified flow scheme, along with a definition of the system boundary to be considered in the analysis. From this drawing we can establish the basis for the calculations.

To simplify calculations, but also by convention, the amount of excess reactant in a reaction is defined on the basis of the reaction going to completion for the limiting reactant. In the case of methane (CH_4) burned with excess air, the volume of air needed to combust the methane is calculated as though there is complete combustion of the methane, converting it entirely to carbon dioxide and water.

We assume one second as the basis for the calculations, and define A and F as the volumetric flow rates for air and flue gas, respectively. We will also adopt the consistent use of volumetric flow-rate units of cubic meters per second.

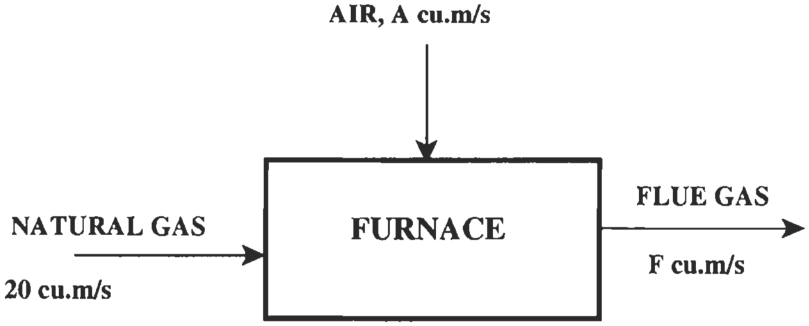


Figure 2. Process flow sheet for furnace illustration.

For our second step, we first summarize the information already known:

	Flow (m^3/s)	Component	Composition (%)	Mol. Weight
Natural gas	20	CH_4	98	16
		N_2	2	28
Air	A	O_2	21	32
		N_2	79	28

In our third step, we convert the compositions to a kg-moles-per-second basis. For this example (as well as many common industry cases), the ideal gas law can be used: n = PV/RT, where:

n = number of moles
R = ideal gas law constant, which is 8.314 kJ/(kg-mol)(K)
T = absolute temperature
P = pressure

For CH_4

$$n = (101.3 \text{ kPa})[(20 \text{ m}^3/\text{s})(0.98)]/[8.314 \text{ kJ/(kg-mol)(K)}](298^\circ \text{ K})$$
$$n = 0.80 \text{ kg-mol/s}$$

For N_2, because the volumetric concentration is 98% CH_4 and 2% N_2, then:

$$n = (0.02/0.98)(0.80) = 0.016 \text{ kg-mol/s}$$

In our fourth step, we determine the amount of oxygen needed and the air-flow rate. To determine this, we must note the following stoichiometric reaction taking place in the furnace:

$$CH_4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O$$

From this, we know that 0.80 mol/s of CH_4 requires 2 H 0.80 = 1.60 mol/s O_2 for stoichiometric combustion.

Because 15% excess air is used, the number of moles of O_2 in the air is:

$$(1.15)(1.60) = 1.84 \text{ kg-mol/s}$$

The amount of N_2 in with the air is:

$$[(0.79 \text{ mol } N_2/\text{mol air})/(0.21 \text{ mol } O_2/\text{mol air})](1.84 \text{ kg-mol/s } O_2)$$
$$= 6.92 \text{ kg-mol/s}$$

The total moles in the incoming air are:

$$1.84 + 6.92 = 8.76 \text{ kg-mol/s}$$

Now rearrange the ideal gas law to convert to volumetric flow rate:

$$V = nRT/P, \text{ or } (8.76)(8.314)(289)/101.3 = 207.8 \text{ m}^3\text{/s}$$

Our next step is to write the material balances and calculate the composition and quantity of flue gas. Unless there is a conversion between mass and energy, calculations such as these can be handled on a mass basis. We shall make this assumption, and also note that there is no accumulation.

The flue gas includes N_2 from the air and from the natural gas, plus the 15% excess O_2, plus the reaction products (0.80 mol/s CO_2 and 2 H 0.80 = 1.60 mol/s H_2O).

The following tabulation summarizes the data available for the analysis.

Component	kg-mol x	kg per mole	= kg
Inputs			
Natural gas:			
CH_4	0.80	16	12.8
N_2	0.016	28	0.448
Air:			
N_2	6.92	28	193.8
O_2	1.84	32	58.9
Total:			265.9
Outputs			
Flue gas:			
N_2	(6.92 + .016)	28	194.2
O_2	(1.84 - 1.60)	32	7.68
CO_2	0.80	44	35.2
H_2O	1.60	18	28.8
Total:			265.9

The accumulation is zero. The overall material balance is 265.9 = 265.9 + 0. Thus the total quantity of flue gas is 265.9 kg/s.

Step 10.2: Tabulate Flows and Concentrations. Record the quantified emission data in tabular form and indicate which figures are estimates and which are actual measurements. The team should consider qualitative characteristics when it quantifies gaseous wastes.

The following are some typical questions to address when developing the material balance around the gaseous emissions components.

- Are odors associated with a unit operation?
- Are there certain times when gaseous emissions are more prominent - are they linked to temperature?
- Is any pollution-control equipment in place?
- Are gaseous emissions from confined spaces (including fugitive emissions) vented to the outside?
- If gas scrubbing is practiced, what is done with the spent scrubber solution? Could it be converted to a useful product?
- Do employees complain of irritating vapors?
- Do employees wear protective clothing, such as masks?
- Do health and safety records indicate a high incidence of respiratory problems among workers?
- Are there visible fumes at any times during the operation?

Step 11: Accounting for Off-Site Wastes

Your process may produce wastes that cannot be treated on-site, and so must be transported off-site for treatment and disposal. Wastes of this type are usually non-aqueous liquids, sludge, or solids. Often, wastes for off-site disposal are costly to transport and to treat, and represent a third-party liability. Therefore, minimization of these wastes yields a direct cost benefit, both present and future. Measure the quantity and note the composition of any wastes associated with your process that need to be sent for off-site disposal. Record your results in a table or an appropriate spreadsheet.

Step 12: Final Preparation for the Material-Balance System

The team is now at the point where it can prepare a material balance at a scale appropriate to the level of detail required in the assessment. For example, you may require a material balance for each unit operation, or one for a whole process may be sufficient. Decide on various levels of detail that may be needed.

Developing and analyzing material and energy balances usually winds up as an iterative process, one that continues until the appropriate or most revealing level of detail is achieved. Bear in mind that the idea behind performing a material balance is to gain a better understanding of the inputs and outputs (especially waste) of a unit operation, so areas where information is inaccurate or lacking can be identified. Imbalances require further investigation.

Do not expect a perfect balance - your initial balance should be considered a rough assessment, to be refined and improved. Your first action in this step should be to assemble the input and output information for each unit operation, and then decide whether all the inputs and outputs need to be included in the material balance. For example, this is not essential where the cooling water input to a unit operation equals the cooling water output.

Make sure to standardize units of measurement (liters, tons, or kilograms) on a per-day, per-year, or per-batch basis. Finally, summarize the measured values in standard units by referring to your process flow sheets (it may have been necessary to modify your process flow sheets following the in-plant assessment).

Step 13: Construct a Material Balance Information Sheet

In this step, the team organizes and makes a final review of the quantitative information on all material flows, and summarizes the data onto a spreadsheet. For each unit operation, the team should use data compiled from Steps 2 through 12 to construct the material-balance system. Organize the information clearly.

Step 14: Evaluating Material Balances

Step 14.1: Classify the Material Balances. Though each unit process is different, leading to a unique material-balance system, there are general classes of material balances, regardless of the nature of the process. By recognizing these early on in the evaluation, the team will save time in setting up the family of equations needed to calculate key parameters, such as various mass and volumetric flow rates, and concentrations of individual chemical components. Also, we can determine in this stage whether or not any portion of the material-balance system involves chemical reactions. It may be necessary to develop a kinetic model, either from experimental data or literature information, and incorporate this into the balances. Situations involving recycle streams, purge streams, and batch versus semi-batch operations can pose different constraints and boundary conditions when solving material balances.

Step 14.2: Determine the Gaps and Inaccuracies. The individual and sum totals making up the material balance should be reviewed to determine information gaps and inaccuracies. If you discover that there is a significant material imbalance, you should investigate it further. For example, if outputs are less than inputs, look for potential losses or waste discharges (such as evaporation, or fugitive emissions not accounted for, such as significant valve, pump, and reactor seals leakage). Outputs may appear to be greater than inputs if large measurement or estimating errors are made or some inputs have been overlooked. At this stage you should take time to re-examine the unit operations to attempt to identify where unnoticed losses may be occurring. It may be necessary to repeat some data-collection activities. Remember that you need to be thorough and consistent to obtain a satisfactory material balance. The material balance not only reflects the adequacy of your data collection, but, by its very nature, ensures that you have a sound understanding of the processes involved.

Step 15: Refine the Material Balances

Now you can reconsider the material balance equations by adding those additional factors identified in the previous step. If necessary, estimates of unaccountable losses will have to be calculated. Note that, in the case of a relatively simple manufacturing plant, preparation of a preliminary material-balance system and its refinement (Steps 14 and 15) can usefully be combined. For more-complex P2 assessments, however, two separate steps are likely to be more appropriate. An important rule to remember is that the *inputs should ideally equal the outputs* - but in practice this will rarely be the case. Some judgment will be required to determine what level of accuracy is acceptable, and we should have an idea as to what the unlikely sources of errors are (e.g., evaporative losses from outside holding ponds may be a materials loss we cannot accurately account for). In the case of high concentrations of hazardous wastes, accurate measurements are needed to develop cost-effective waste-reduction options. It is possible that the material balance for a number of unit operations will need to be repeated. Again, continue to review, refine, and, where necessary, expand your database. The compilation of accurate and comprehensive data is essential for a successful P2 audit and subsequent waste-reduction action plan. Remember - *you can't reduce what you don't know is there*!

By the end of Step 15, you should have assembled information covering process inputs and process outputs. These data should be organized and presented clearly in the form of material balances for each unit operation. Reflecting back on the 10 steps that constitute Phase II, the team's objective has been to arrive at a quantitative baseline that characterizes the performance of the operation. By bringing closure to the material balances, we have developed an extensive database, based on field measurements and sampling, and on calculations. The database should contain information on essentially all the mass inputs and outputs to the unit process, as well as each unit operation. Hence, Phase II has not only defined for us the amounts and concentrations of liquid, gaseous, and solid forms of pollution, but also the products, the by-products, and all other wastes. The information compiled also provides us inference on wasted energy, and might very well divert our attention toward a separate energy efficiency study. We recommend, however, that this become part of the action plans for pollution-prevention and possible waste-minimization options we uncover in Phase III.

We now are ready to move on to the next phase, which involves developing P2 recommendations.

SYNTHESIS, BENCHMARKING, AND CORRECTIVE ACTIONS (PHASE III)

Phases I and II have covered planning and undertaking a P2 audit, resulting in the preparation of a material balance for each unit operation. Phase III represents the interpretation of the material balance, to identify process areas or components of concern.

The material balance focuses the attention of the auditors on technical options for improving environmental performance and reducing wastes. The arrangement of the input and output data in the form of a material balance facilitates understanding of how materials flow through a production process. To interpret a material balance, it is necessary to have an understanding of normal operating performance C after all, how can you assess whether a unit operation is working efficiently if you do not know what is normal? Therefore, it is essential that you have a good working knowledge of the process. The results obtained from field measurements and material balance calculations will guide you to areas of concern and help to prioritize problems in the enterprise.

You should use the material balance information to identify the major sources of waste and pollution, to look for deviations from the norm in waste production, to identify areas of unexplained losses, and to pinpoint operations that contribute to flows that exceed national-, local-, or site-discharge regulations. Also, a good thing to remember is that, from a practical standpoint, *process efficiency* is synonymous with *waste minimization*.

Different pollution- and waste-reduction measures require varying degrees of effort, time, and financial resources. They can be categorized into two broad categories: *Group 1* includes obvious waste-reduction measures, including improvements in management techniques and housekeeping procedures that can be implemented cheaply and quickly. These are the best practices and minor (low-investment) re-engineering corrective actions, which can be referred to as low-cost/no-cost. They represent a category of corrective actions (P2 opportunities) where financial justifications are obvious, or trivial. For example, for a bottle-washing operation using once-through water, it is obvious that recycling would offer cost savings, especially if the re-piping required is trivial. Low-cost/no-cost P2 recommendations should be immediately reported to top management and implemented. Publicizing and monitoring the savings from such early success stories can help develop momentum for the P2 program.

Group 2 includes long-term reduction measures involving process modifications or process substitutions to eliminate problem wastes. This second group of corrective actions fall into two investment categories - moderate and high. Such projects involve re-engineering and equipment investments to the extent that a sufficiently detailed project-cost analysis will be needed to justify implementation. This involves financial benchmarking, which we discuss in Chapter 8.

The following steps will bring the team to the point of identifying options for both groups of P2 corrective actions.

Step 16: Low-Cost/No-Cost Recommendations

It may have been possible to implement very obvious waste-reduction measures already, before embarking on obtaining a material balance (even as early as at the end of Phase I). You should now consider the material balance information in conjunction with visual observations made during the data-collection period, to pinpoint areas or operations where simple adjustments in procedure could greatly improve the efficiency of the process by reducing unnecessary losses.

Use the information gathered for each unit operation to develop better operating practices for all units. Significant waste reductions can often be achieved by generally taking more care in performing operations and handling materials. Look back at some of the P2 opportunities identified in Chapter 2 for examples. Tightening up housekeeping procedures can reduce waste considerably. Simple, quick adjustments made to your process can achieve a rapid improvement in process efficiency. However, where such obvious reduction measures do not solve the entire waste-disposal problem, you will need to consider more detailed waste reduction options. These are addressed in Steps 17 through 19.

Step 17: Targeting and Characterizing Problem Wastes

Use the material balance for each unit operation to pinpoint the problem areas associated with a process. The material-balance exercise may have brought to light the origin of wastes with high treatment costs, or may indicate which wastes are causing process problems in which operations. The material balance should be used to set priorities for long-term waste reduction.

At this stage, it may be worthwhile to consider the underlying causes of why wastes are generated and what factors lead to these causes; for example, poor or outdated technology, lack of maintenance, and non-compliance with company procedures may be contributing, or even underlying, factors. Additional sampling and characterization of wastes might be necessary, involving more in-depth analysis to ascertain the exact concentrations of contaminants. A worthwhile exercise is to list the wastes in order of priority for reduction actions. This will alert both the team and top management to the most costly waste issues and also help to better define what resources may be needed to address them.

Step 18: Segregation

Segregation of wastes can offer enhanced opportunities for recycling and reuse with resultant savings in raw-material costs. Concentrated simple wastes are more likely to be of value than dilute or complex wastes. Avoid the practice of mixing wastes, because this can aggravate pollution problems. If a highly concentrated waste is mixed with a large quantity of weak, relatively uncontaminated effluent, the result is a larger volume of waste that requires treatment. Isolating the concentrated waste from the weaker waste can reduce treatment costs. The concentrated waste could be recycled/reused or may require physical, chemical, and biological treatment to comply with discharge consent levels, whereas the weaker effluent could be reused or may only require settlement before discharge. Therefore, waste segregation can provide more scope for recycling and reuse, while reducing treatment costs. Step 18 then is to review your waste-collection and storage facilities to determine if waste segregation is possible. If so, then adjust your list of priority wastes accordingly.

Step 19: Developing Long-Term P2 and Waste-Reduction Options

Waste problems that cannot be solved by simple procedural adjustments or improvements in housekeeping practices will require more substantial long-term changes. It is necessary to develop possible prevention options for the waste problems. Process or production changes that may increase production efficiency and reduce waste generation include:

- ➪ Changes in production process - continuous versus batch
- ➪ Equipment and installation changes
- ➪ Changes in process control - automation
- ➪ Changes in process conditions, such as retention times, temperatures, agitation, pressure, and catalysts
- ➪ Use of dispersants in place of organic solvents, where appropriate
- ➪ Reduction in the quantity or type of raw materials used in production
- ➪ Raw-material substitution, through the use of wastes as raw materials, or the use of different raw materials that produce less waste or less hazardous waste
- ➪ Process substitution with cleaner technology

At the end of Step 19 you and your team should have identified all the waste reduction options which could be implemented. Although we have not stated the following as a formal step, it is obvious that these options should be listed into the two general categories (Low-cost/No-cost and Longer-term/Higher Investments). There may be corrective actions among the first category that we may feel the need to justify the cost-savings further by considering the remaining steps to Phase III.

The second category does require further actions before becoming formal recommendations.

Step 20: Environmental and Economic Evaluation of P2 Options

When deciding which options to pursue as part of a waste-reduction action plan, consider each option in terms of environmental and economic benefits.

It is often taken for granted that reduction of a waste will have environmental benefits. Though this is generally true, there are exceptions to the rule. For example, reducing one waste may give rise to pH imbalances or may produce another waste which is more difficult to treat, resulting in a net environmental disadvantage. Hence, there may be environmental trade-offs between the status quo and the alternatives identified.

In many cases, the benefits may be obvious, such as the result of removing a toxic element from an aqueous effluent by segregating the polluted waste, or by changing the process so the waste is prevented from occurring. In other cases, the environmental benefits may be less tangible. Creating a cleaner, healthier workplace *will* increase production efficiency, but this may be difficult to quantify. These represent different cost-savings categories, which we discuss in Chapter 8. In addition, the team needs to begin focusing on the design aspects of the recommended options. At this stage of the audit process, detailed engineering practices begin to come into play. The possible recommendations will probably include equipment modifications, and changes involving newer and alternative pieces of equipment. At this point, the unit operations are no longer black boxes on a process flow sheet; instead, the team begins transforming these into preliminary shop drawings of actual equipment and layouts, piping changes, vendor quotes, and equipment supplier specs.

The team should also undertake a comparative economic analysis of the P2 options and the existing situation. Where it cannot quantify benefits or changes (e.g., reduction in future liability, worker health and safety costs, etc.), it should make some form of qualitative assessment.

Economic evaluations of waste-reduction options should involve a comparison of operating costs to illustrate where cost savings would accrue. For example, a waste-reduction measure that reduces the amount of raw material lost down the drain during the process will reduce raw-material costs. Raw-material substitution or process changes may reduce the amount of solid waste that must be transported off-site, reducing the transport costs for waste disposal.

In many cases, it is appropriate to compare the waste treatment costs under existing conditions with those associated with the waste-reduction option. The size of a treatment plant and the treatment processes required may be altered significantly by the implementation of waste-reduction options. This should be considered in an economic evaluation.

Calculate the annual operating costs for the existing process that needs waste treatment, and estimate how these costs would be altered by the introduction of waste-reduction options. Tabulate and compare the process and waste-treatment operating costs for both the existing and proposed waste-management options. If there are any monetary benefits (such as recycled or reused materials or wastes), then these should be subtracted from the total process or waste-treatment costs as appropriate. The expanded cost-analysis scheme discussed in Chapter 8 is appropriate to include at this point in the process.

Now that you have determined the likely savings in terms of annual process and waste-treatment operating costs associated with each option, consider the necessary investment required to implement each option. Investment can be assessed by looking at the payback period for each option that is, the time taken for a project to recover its financial outlay. A more detailed investment analysis may involve an assessment of the internal rate of return (IRR) and net present value (NPV) of the investment based on discounted cash flows. An analysis of investment risk allows you to rank the options identified.

Consider the environmental benefits and the savings in process and waste-treatment operating costs, along with the payback period for an investment, to decide which options are viable candidates. Once this is done, the audit team can develop draft recommendations to include in the final report and presentation to top management.

Step 21: Developing and Implementing the Action Plan

The immediate reduction measures identified in Step 16, along with the long-term waste reduction measures evaluated in Steps 19 and 20, should form the basis of the P2 action plan. Prepare the ground for the waste-reduction action plan - precede its implementation by explaining its goals. It is necessary to convince those who must work with the new procedures that the change in philosophy from end-of-pipe treatment to pollution prevention makes sense and improves efficiency. Use posters around the site to emphasize the importance of waste reduction in minimizing production and waste-treatment and disposal costs, and (where appropriate) for improving the health and safety of company personnel.

Set out the intended action plan, within an appropriate schedule. Remember, it may take time for the staff to feel comfortable with a new way of thinking. It's a good idea to implement waste-reduction measures slowly but consistently, to allow everyone time to adapt to these changes.

Establish a monitoring program to run alongside the P2 action plan, so actual improvements in process efficiency, as well as in environmental performance, can be measured. It is likely that you will have highlighted significant information gaps or inconsistencies during the P2 audit. You should concentrate on these gaps and explore ways of developing the additional data. Ask yourself repeatedly - is outside help required?

A good way of providing P2 incentives is to set up an internal waste-charging system, so those processes that create pollution or waste in great volume, or that are difficult and expensive to handle, have to contribute to the treatment costs on a proportional basis. Another method of motivating staff is to offer financial rewards for individual waste-saving efforts, drawing on the savings gained from implementing waste-reduction measures. P2 audits should be a regular event - attempt to develop a specific P2-assessment approach for your own situation, keeping abreast of technological advances that could lead to waste reduction and the development of cleaner products and processes. Train process employees to undertake material-balance exercises. Training people who work on a process to undertake a P2 assessment of that or other processes will help to raise awareness in the workforce. Without the support of the operators, P2 actions will be ineffectual - these are the people who can really make a difference to process performance.

The following references will help you develop techniques for applying pollution prevention audits. Use the examples in Chapter 2 as a basis to tailor audit questions and to focus on areas of opportunities. Finally, Chapter 8 will help you in developing the tools needed to assess the financial attractiveness of the pollution prevention opportunities you identify.

REFERENCES AND RECOMMENDED RESOURCES FOR THE READER

1. Cheremisinoff, N. P. and A. Bendavid-val, *Green Profits: A Manager's Guide to ISO 14000 and Pollution Prevention*, Butterworth-Heinemann Publishers, MA, 2001.
2. Ahmed, Kulsum. *Renewable Energy Technologies: A Review of the Status and Costs of Selected Technologies,* World Bank Technical Paper No. 240. Washington: World Bank Group, 1994.

3. Bernstein, Janis D. *Alternative Approaches to Pollution Control and Waste Management: Regulatory and Economic Instruments*. Washington: The World Bank, 1993.
4. Cheremisinoff, Nicholas P. *Handbook of Pollution Prevention Practices*. New York: Marcel Dekker Inc., 2001.
5. *Pollution Prevention and Abatement Handbook 1998 — Toward Cleaner Production*. Washington: The World Bank Group, 1999.
6. *Profile of the Petroleum Refining Industry,* EPA 310-R-95-013. Washington: U.S. Environmental Protection Agency, 1995.
7. *A Planner's Guide for Selecting Clean Coal Technologies for Power Plants,* Technical Paper No. 387. Washington: The World Bank, 1997.
8. *Guide to Accessing Pollution Prevention Information Electronically*. Boston: U.S. Environmental Protection Agency — Northeast Waste Management Official's Association, 1997.
9. *Profile of the Motor Vehicle Assembly Industry* EPA 310-R-95-009. Washington: U.S. Environmental Protection Agency, 1995.
10. *Prototype Study of Industry Motivation for Pollution Prevention,* EPA 100-R-96-001. Washington: U.S. Environmental Protection Agency, 1996.
11. Chopey, Nicholas P., and Tyler G. Hicks, editors. *Handbook of Chemical Engineering Calculations*. New York: McGraw-Hill Book Co., 1984.
12. Cheremisinoff, Nicholas P. *Handbook of Chemical Processing Equipment*. Boston: Butterworth-Heinemann, 2000.
13. Cheremisinoff, Nicholas P. *Chemical Engineer's Condensed Encyclopedia of Process Equipment*. Houston: Gulf Publishing Co., 2000.
14. Peters, Max S., and Klaus D. Timmerhaus. *Plant Design and Economics for Chemical Engineers*. New York: McGraw-Hill Book Co., 1968.
15. Cheremisinoff, Nicholas P. *Liquid Filtration — 2nd Edition*. Boston: Butterworth-Heinemann, 1998.
16. Cheremisinoff, Nicholas P., and Paul N. Cheremisinoff. *Compressors and Fans*. Englewood Cliffs, N.J.: Prentice-Hall Inc., 1992.
17. Cheremisinoff, Nicholas P., and Paul N. Cheremisinoff. *Carbon Adsorption for Pollution Control*. Englewood Cliffs, N.J.: Prentice-Hall Inc., 1993.
18. Block, Marilyn R., and I. Robert Marash. *Integrating ISO 14001 into a Quality Management System.* Milwaukee: ASQ Quality Press, 2000. - Explains how to expand an existing quality-management system to encompass the requirements of ISO 14001. Provides a comparison and guide to integrating ISO 9001 and ISO 14001.
19. Block, Marilyn R. *Identifying Environmental Aspects and Impacts*. Milwaukee: ASQ Quality Press, 2000.
20. Cascio, Joseph, ed. *ISO 14000 Handbook*. Milwaukee: ASQ Quality Press, 1998. - Includes checklists, case studies, and a great deal of practical information and guidance for implementing ISO 14001. Goes beyond to

discuss other standards in the ISO 14000 series. Includes contributions from professionals working on various ISO 14000 standards.

21. Edwards, A.J. *ISO 14001 Environmental Certification Step by Step.* Oxford, U.K.: Butterworth-Heinemann, 2001. - Written primarily for small and medium-sized enterprises, this book sets out an overall program for establishing an EMS, and provides step-by-step directions for implementation in conformance with ISO 14001.
22. Goetsch, David I., and Stanley B. Davis. *ISO 14000: Environmental Management.* Upper Saddle River, N.J.: Prentice Hall, 2000. - Publisher information says that this book is written as a practical teaching resource and how-to guide. Each chapter contains a list of key concepts, review questions, critical thinking problems, and discussion cases with related questions.
23. Hillary, Ruth, ed. *ISO 14001: Case Studies and Practical Experiences.* Sheffield, U.K.: The Network for Environmental Management, Greenleaf Publishing, 2000. - Contains case studies that provide experiences of companies and what certifiers look for when they visit firms. Highlights ISO 14001's strengths and weaknesses. Analyzes environmental and economic performance improvements under ISO 14001.
24. Kanholm, Jack *ISO 14001 in Our Company: Self-Study Course for Personnel.* Pasadena, Calif.: AQA Press, 1998. - A booklet that offers a general orientation to the ISO 14001 standard for self-study or group training. Could be useful for basic EMS training for employees.
25. Kanholm, Jack. *ISO 14001 Manual and Procedures: EMS Manual, 21 Procedures and Forms*, Pasadena, Calif.:AQA Press, 1999. - A CD-ROM containing a full set of formatted document templates and procedures, including a model EMS manual, that conform to the ISO 14001 standard.
26. Kanholm, Jack. *ISO 14001 Requirements: 61 Requirements Checklists and Compliance Guide.* Pasadena, Calif.: AQA Press, 1998. - Interprets and explains the ISO 14001 standard as 61 distinct requirements and discusses, with respect to each of these requirements, how to implement, required documentation, and what auditors will look for as evidence of compliance.
27. Kinsella, John, Annette Dennis McCully, and David Burngasser. *Handbook for Implementing an ISO 14001 Environmental Management System: A Practical Approach.* Bothell, Wash.: EMCON, 1999. - A guide for implementing an EMS that meets the requirements of the ISO 14001 standard. Based on work with five companies, ranging in size from 30 employees to 42,000, enabling readers to learn about the challenges they encountered and how they solved them.
28. Perry, Pam, ed. *The Bottom Line: How to Build a Business Case for ISO 14001.* Boca Raton, Fla.: CRC Press-St. Lucie Press, 1999. - Based on the experiences and data of companies that have implemented ISO 14001.

Describes how implementing the standard can benefit a company and how to build a case to convince top management to adopt ISO 14001.

29. Roberts, Hewitt, and Gary Robinson. *ISO 14001 EMS Implementation Handbook*. Oxford, U.K.: Butterworth-Heinemann, 1998. - A guide for implementing and maintaining an ISO 14001 EMS. Includes recommendations, checklists, templates, certification tips, case-study materials, and more.
30. Saponara, Anthony, and Randy A. Roig, Ph.D. *ISO 14001 Environmental Management Systems: A Complete Implementation Guide*. Vancouver: ERM-West, Inc. and STP Specialty Technical Publishers Inc., 1998. - A very extensive, two-volume ISO 14001 implementation manual containing dozens of checklists, prototype charts, templates, document examples, and other tools. Uses "Green Acres Hotel and Resort" as a case illustration for presenting implementation principles, techniques, and tools.
31. Shell , David J. *A Green Plan for Industry: 16 Steps to Environmental Excellence*. Rockville, Md.: Government Institutes, Inc., 1998. - Offers a 16-step process for developing a comprehensive environmental management plan. Written for environmental managers, this book also contains techniques and tools for implementing ISO 14001.

REVIEW AND QUESTIONS TO GET YOU THINKING

1. Does your company have a deliberate organized program that focuses on P2 opportunities? If not, then why not? If yes, what motivated top management to put it in place?
2. Does your company have regular meetings or task forces that focus on P2 opportunities? Have these meetings or task forces ever been tried before, and what kind of success did they have?
3. What are the three essential elements of a successful P2 program? Describe the objectives of each.
4. What are the three sub-elements of the P2 audit?
5. Does your company take corrective actions aimed at reducing pollution, or does it monitor and react to environmental problems? Which do you think is a better approach to managing environmental issues and why?
6. What does it cost your enterprise to comply with air pollution control regulations? What other environmental regulations is your company subject to?
7. Has your enterprise been faced with a history of environmental litigation, fines, penalties, or corrective actions? How many of these have occurred over the last five years, and what were the reasons?

8. Is your company a member of any of the EPA's voluntary programs on P2 or energy efficiency? If not, does management know about these programs and the possible benefits?
9. Try the following problem to sharpen your skills in working with material balances. Hydrogen is produced from methane by a combination steam-reforming/partial-oxidation process. Sufficient air is used in partial oxidation to give a 3.5:1 hydrogen-to-nitrogen molar ratio in the feed section to an ammonia unit. The hydrogen-nitrogen mixture is heated to reaction temperature and then fed into a fixed-bed reactor, where 19 percent conversion of reactants to ammonia is obtained per pass. After exiting the reactor, the mixture is cooled and the ammonia is removed via condensation. The unreacted hydrogen-nitrogen mixture is recycled and mixed with fresh feed. Using a basis of 150 kg-mol/hr of fresh feed, develop a material balance, and calculate the ammonia-production and recycle rates.
10. Try the following problem to sharpen your skills in working with material and energy balances. Crude oil is heated to 525° K and then charged at a rate of 0.06 m^3/hr to the flash zone of a pilot-scale distillation tower. The flash zone is maintained at an absolute temperature of 115 kPa. Calculate the percent vaporized and the amounts of the overhead and bottoms streams. Assume that the vapor and liquid are in equilibrium.
11. Develop a list of the individual unit processes at your enterprise. Among these, which are the processes that are most likely to benefit from a P2 audit? Why?
12. For one of the unit processes identified in the above exercise, develop a list of all the unit operations involved, and prepare a simplified process flow sheet. List all the material flows on the sheet, and highlight the pollution and waste streams.
13. From the process flow sheet developed in the above exercise, identify: a) those unit operations involving simple mass flows only; b) those unit operations in which phase changes are occurring; c) those operations in which there are chemical reactions taking place; d) those operations that are batch; e) those operations that are continuous.
14. From the previous set of questions, make a list of the different types of material balances that you could develop.
15. From your discussions about the previous series of questions, are there any best practices that you think might be recommended as possible low-cost/no-cost P2 actions? If so, develop a list of actions needed to verify their benefits, and how you intend to implement them.
16. Make a list of the important control variables, the dependent process variables, and the monitoring parameters important to the unit process that you have discussed in the previous series of questions.

Chapter 7

PREVENTION AND CONTROL HARDWARE

INTRODUCTION

This chapter focuses on hardware. The intent is to provide a working description of pollution control hardware, and to highlight technologies and equipment that may be applicable to pollution prevention opportunities.

We should never approach an air pollution problem (or any pollution and waste problem) without first considering other options to end-of-pipe treatment and controls. If the waste or pollution can be prevented or minimized without the use of controls that require long-term O&M costs, then that should be the first choice, provided there is sufficient financial justification. But the absolutely wrong reason for selecting pollution prevention (P2) over conventional wisdom is to do P2 for the sake of doing it. Many companies often tout that they rely on P2 practices, but upon closer examination we find that many projects implemented are more costly than putting in a simple piece of hardware. For this reason, it always pays to perform a *total cost accounting* (TCA) of a proposed project, regardless of how small the project is. Since small savings, especially when it comes to raw materials such as water usage or energy can incrementally add up to sizable savings over time, a TCA analysis should span over the intended life of the operation, and furthermore, it should focus heavily on the ROI. By closely examining the financial attractiveness of a P2 versus end-of-pipe hardware solution, we can develop ample justification for an investment, and develop recommendations for the optimum solution to the problem. TCA principles are discussed in Chapter 8.

METHODS OF PARTICULATE COLLECTION

Settling chambers, low-pressure-drop cyclones, and dynamic precipitators are among the most common and important devices applied in end-of-pipe control applications for dust and particulate matter.

GRAVITY SETTLING CHAMBERS

This section is concerned with the practical removal of air pollutants through the mechanism of downward gravitational forces. Gravity settling chambers are the oldest and simplest means of removing suspended particles from a gas. In principle, pollutants are removed by reducing the velocity of the gas stream sufficiently to allow particles to settle out under the influence of gravity. The simplest chamber is merely a horizontal duct in which large particles settle out on the floor. High-efficiency settling chambers are often fitted with baffles or deflectors to change the gas flow direction.

This type of technology is a part of the group of air pollution controls collectively referred to as "precleaners," because they are oftentimes used to reduce the inlet loading of particulate matter (PM) to downstream collection devices by removing larger, abrasive particles. Settling chambers are also referred to as gravity settling chambers, gravity collectors, expansion chambers, and outfall chambers. Multiple-tray settling chambers are also referred to as Howard settling chambers.

Particle Classification

Before selecting or sizing a specific control device, a careful evaluation of all aspects of the process and contaminants must be made. Improper terminology can lead to poor design and/or operation of any type of device. A list of contaminant definitions in accordance with the USA Standards Institute includes the following.

Liquid in Gas: These include the following terminology:

- Mists and Sprays - There are numerous industrial chemical operations which involve liquid-in-gas dispersions. These operations generate mists and sprays that consist of particles in diameter ranges of 0.1 to 5,000 μm. Engineers most commonly encounter spray droplets which are particles often formed unintentionally in chemical plant operations. For example, vapors or fumes may condense onto piping, ducts, or stack walls. Under such conditions liquid films form.

Solid in Gas:

- Dusts - Dusts are fine solid particles often formed in such operations as pulverizing, crushing, grinding, drilling, detonation, and polishing. Other industrial sources are conveying operations and screening. Particle diameters generally are in the range of 1.0 to 1,000 μm. Dusts generally do not diffuse in air, but settle out by gravity.
- Flyash - Flyashes are finely divided matter generally entrained in flue gases that arise from combustion. Particles range from 1 μm in size on down. This is not within the operational range of gravity settling chambers. Wet

scrubbers are generally employed in flyash control. In some applications high-efficiency electrostatic precipitators, baghouses, or cyclones are utilized.

- Fumes - Fumes are finely divided solid particles that are generated by the condensation of vapors. Fumes are generally the by products of sublimation, distillation, and molten metal processes. Particle diameters are generally in the range of 0.1 to 1 μm.
- Smoke - Smoke constitutes fine, solid, gasborne matters that are products of incomplete combustion of organics (wood, coal, tobacco). Smoke particles are extremely small, ranging in size from less than 0.01 μm to 1 μm.
- Smog - Smog refers to a mixture of natural fog and industrial smoke.
- Aerosols - Aerosols are an assemblage of small particles, either solid or liquid, suspended in gas. Particle sizes range from 0.01 to 100 μm. There are several classes of aerosols. Dispersion aerosols are a common class that are formed from processes such as grinding, solid and liquid atomization, and conveying powders in suspended state by vibration. Dispersion aerosols are usually composed of individual or slightly aggregated particles irregularly formed. Condensation aerosols are formed when supersaturated vapors condense or when gases react chemically to form a nonvolatile product. This latter class is usually less than 1 μm in size. Dispersion aerosols are considerably more coarse and contain a wide variety of particle sizes. Condensed aerosols usually consist of solid particles that are loose aggregates of a large number of primary particles of crystalline or spherical shape.
- Grit - The term grit is used to classify coarse particles that are unable to pass through 200-mesh screen. These particles are normally greater than 43 μm in diameter and are within the operating efficiency of gravity settling chambers.

Design Features

Figure 1 is a simplified representation of a horizontal simple gravity settling chamber. It is a long duct fitted with hoppers on the floor to collect particulates. Physical dimensions are characterized by the ductwork above the collection hoppers: length = L, width = W, and height = H.

The primary section of the chamber is characterized by its cross-sectional area (W × H) and by its length (L). The cross-sectional area is designed to be larger than the inlet and exit ducts in order to reduce substantially the gas stream's inlet linear velocity. The length of the chamber determines the amount of time the particles remain at the reduced rate. This starving of the gas's forward motion allows the particles sufficient time to settle out into the hoppers.

For dilute systems, Stoke's law is applicable to particle settling. References cited at the end of this chapter provide design and sizing information.

In specifying settling chamber dimensions, gas flow velocities must be maintained below the reentrainment velocity (pick-up velocity) of deposited particulate. As a general guideline, linear gas velocities are kept below 10 ft/sec (600 ft/min = 304.8 cm/sec). This is satisfactory for most materials; however, some low-density particulates are reentrained at lower velocities.

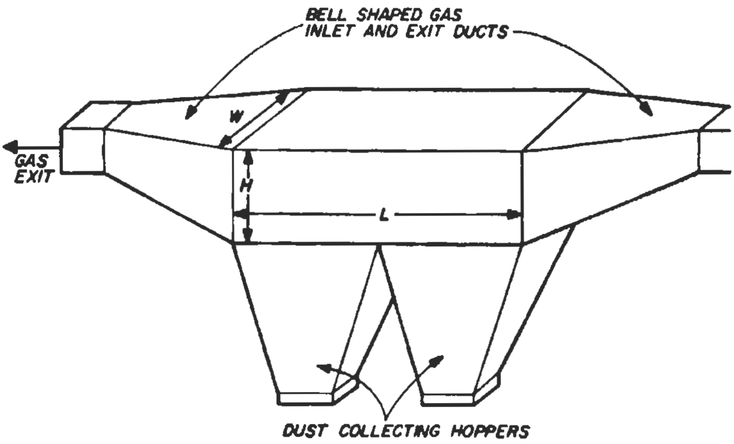


Figure 1. Simple gravity settling chamber.

Settling efficiency is normally related through a theoretical efficiency curve for a chamber of the dimensions sized. An example is illustrated in Figure 2. There may be additional factors other than space availability that may enter into sizing considerations. For example, economics may dictate the use of only a gravity settling chamber for pollution control purpose. In such a case the removal of a wider range of particle sizes may be required. Rapid removal of larger particles could be accomplished by increasing the width of the chamber, and removal of the smaller-sized particles could be accomplished by increasing the length. Several efficiency curves can be generated for various chamber dimensions, and an optimum design based on legal aspects and economics can be made.

As noted, settling chambers are used to control PM, and primarily PM greater than 10 micrometers (μm) in aerodynamic diameter. Most designs only effectively collect PM greater than approximately 50 μm (Wark, 1981; Perry, 1984; EPA, 1998).

The collection efficiency of settling chambers varies as a function of particle size and settling chamber design. Settling chambers are most effective for large and/or dense particles. Gravitational force may be employed to remove particles where the settling velocity is greater than about 13 centimeters per second (cm/s) (25 feet per minute (ft/min)). In general, this applies to particles larger than 50 μm if the particle density is low, down to 10 μm if the material density is reasonably high. Particles smaller than this would require excessive horizontal flow distances, which would lead to excessive chamber volumes. The collection efficiency for PM less than or equal to 10 μm in aerodynamic diameter (PM_{10}) is typically less than 10 percent. Multiple-tray chambers have lower volume requirements for the collection of particles as small as 15 μm (Wark, 1981; Mycock, 1995; EPA, 1998). Note that this device is used for stationary point source control applications.

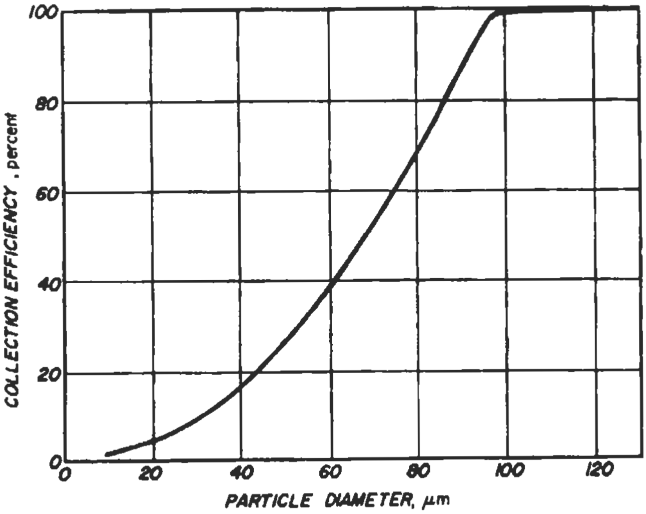


Figure 2. Example of theoretical collection efficiency curve.

Industrial Applications

Despite low collection efficiencies, settling chambers have been used extensively in the past. The metals refining industries have used settling chambers to collect large particles, such as arsenic trioxide from the smelting of copper ore.

Power and heating plants have used settling chambers to collect large unburned carbon particles for reinjection into the boiler. They are particularly useful for industries that also need to cool the gas stream prior to treatment in a fabric filter (Mycock, 1995).

Settling chambers have been used to prevent excessive abrasion and dust loading in primary collection devices by removing large particles from the gas stream, such as either very high dust loadings or extremely coarse particles which might damage a downstream collector in series with the settling chamber. The upstream use of settling chambers has declined with improvements in acceptable loading of other, more efficient, control devices and increasing space restrictions at facilities. In cases where sparks or heated material is present in the waste gas, settling chambers are still used to serve as "spark traps" to prevent a downstream baghouse or filter from catching fire (Wark, 1981; EPA, 1998; Josephs, 1999; Davis, 1999). These devices are generally constructed for a specific application from duct materials, though almost any material can be used. Settling chambers have been replaced, for most applications, by cyclones primarily due to the lower space requirements and the higher collection efficiency of cyclones. Multiple-tray settling chambers have never been widely used because of the difficulty in removing the settled dust from the horizontal trays (Mycock, 1995; Josephs, 1999).

Emission Stream Characteristics

Air Flow: The simple design and construction of settling chambers allows for almost any size and waste gas flow rate, but size is usually restricted to a 4.25 meter (14 foot) square shipping size. Units restricted by this shipping constraint will generally have flow rates which range up to 50 standard cubic meters per second (scm^3/sec) (106,000 standard cubic feet per minute (scfm)). Typical settling chamber waste gas flow capacity is 0.25 to 0.5 sm^3/sec per cubic meter of chamber volume (15 to 30 scfm per cubic foot of chamber volume) (Wark, 1981; Andriola, 1999).

Temperature: Inlet gas temperatures are only limited by the materials of construction of the settling chamber, and have been operated at temperatures as high as 540°C (1000°F) (Wark, 1981; Perry, 1984).

Pollutant Loading: Waste gas pollutant loadings can range from 20 to 4,500 grams per standard cubic meter (g/sm^3) (9 to 1,970 grains per standard cubic foot (gr/scf)). Multiple-tray settling chambers can only handle inlet dust concentrations of less than approximately 2.3 g/sm^3 (1.0 gr/scf) (Mycock, 1995; Parsons, 1999; Steinbach, 1999; Josephs, 1999).

Other Considerations: Leakage of cold air into a settling chamber can cause local gas quenching and condensation. Condensation can cause corrosion, dust buildup, and plugging of the hopper or dust removal system. The use of thermal insulation can reduce heat loss and prevent condensation by maintaining the internal device temperature of the above the dew point (EPA, 1982). No pretreatment is necessary for settling chambers.

Cost Information

The following are cost ranges (expressed in third quarter 1995 dollars) for a single conventional expansion-type settling chamber under typical operating conditions, developed using a modified EPA cost-estimating spreadsheet (EPA, 1996), and referenced to the volumetric flow rate of the waste stream treated. For purposes of calculating the example cost effectiveness, flow rates are assumed to be between 0.25 and 50 sm^3/sec (530 and 106,000 scfm), the inlet PM loading concentration is assumed to range from approximately 20 to 4,500 g/sm^3 (9 to 1,970 gr/scf) and the control efficiency is assumed to be 50 percent. The costs do not include costs for disposal or transport of collected material. Capital costs can be higher than in the ranges shown for applications which require expensive materials. As a rule, smaller units controlling a low concentration waste stream will be more expensive (per unit volumetric flow rate) than a large unit cleaning a high pollutant load flow.

- Capital Cost: $330 to $10,900 per sm^3/sec ($0.16 to $5.10 per scfm)
- O & M Cost: $13 to $470 per sm^3/sec ($0.01 to $0.22 per scfm), annually
- Annualized Cost. $40 to $1,350 per sm^3/sec ($0.02 to $0.64 per scfm), annually
- Cost Effectiveness: $0.01 to $3.90 per metric ton ($0.01 to $3.50 per short ton), annualized cost per ton per year of pollutant controlled

Theory of Operation

Settling chambers, which rely on gravitational settling as a collection mechanism, are the simplest and oldest mechanical collectors. Settling chambers are generally built in the form of long, horizontal, rectangular chambers with an inlet at one end and an exit at the side or top of the opposite end. Flow within the chamber must be uniform and without any macroscopic mixing. Uniform flow is often ensured by flow straighteners at the inlet to the chamber. Hoppers are used to collect the settled-out material, though drag scrapers and screw conveyers have also been employed. The dust removal system must be sealed to prevent air from leaking into the chamber which increases turbulence, causes dust reentrainment, and prevents dust from being properly discharged from the device (EPA, 1982; Wark, 1981; Corbitt, 1990; Perry, 1984; Mycock, 1995; Avallone, 1996; EPA, 1998).

There are two primary types of settling chambers: the expansion chamber and the multipletray chamber. In the expansion chamber, the velocity of the gas stream is significantly reduced as the gas expands in a large chamber. The reduction in velocity allows larger particles to settle out of the gas stream (EPA, 1982; Wark, 1981; Perry, 1984; Mycock, 1995; EPA, 1998). A multiple-tray settling chamber is an expansion chamber with a number of thin trays closely spaced within the chamber, which causes the gas to flow horizontally between them. While the gas velocity is increased slightly in a multiple-tray chamber, when compared to a simile extension chamber, the collection efficiency generally improves because the particles have a much shorter distance to fall before they are collected. Multiple-tray settling chambers have lower volume requirements than expansion-type settling chambers for the collection of small particles (~ 15 μm) (EPA, 1998).

The efficiency of settling chambers increases with residence time of the waste gas in the chamber. Because of this, settling chambers are often operated at the lowest possible gas velocities. In reality, the gas velocity must be low enough to prevent dust from becoming reentrained, but not so low that the chamber becomes unreasonably large. The size of the unit is generally driven by the desired gas velocity within the unit, which should be less than 3 meters per second (m/s) (10 feet per second (ft/sec)), and preferably less than 0.3 m/s (1 ft/sec) (Wark, 1981; Corbitt, 1990; Mycock, 1995; EPA, 1998).

Advantages of settling chambers include (Wark, 1981; Corbitt, 1990; Perry, 1984; Mycock, 1995; and EPA, 1998):

- Low capital cost;
- Very low energy cost;
- No moving parts, therefore, few maintenance requirements and low operating costs;
- Excellent reliability;
- Low pressure drop through device;
- Device not subject to abrasion due to low gas velocity;
- Provide incidental cooling of gas stream;
- Temperature and pressure limitations are only dependent on the materials of construction; and
- Dry collection and disposal.

Disadvantages of settling chambers include (Wark, 1981; Mycock, 1995; and EPA, 1998):

- Relatively low PM collection efficiencies, particularly for PM less than 50 μm in size;
- Unable to handle sticky or tacky materials;
- Large physical size; and
- Trays in multiple-tray settling chamber may warp during high-temperature operations.

The most common failure mode of settling chambers is plugging of the chamber with collected dust. In expansion settling chambers the plugging can result from hopper bridging or hopper discharge seal failure. Multiple-tray settling chambers may experience plugging of the individual gas passages. Such failures can be prevented or minimized by use of hopper level indicators or by continuous monitoring of the dust discharge. Scheduled internal inspection can determine areas of air leakage and condensation, both of which may cause hopper bridging. Nominal instrumentation for a settling chamber generally includes only an indicator of differential static pressure. An increase in static pressure drop can indicate plugging (EPA, 1982).

Additional Information

References 1 through 14 provide detailed information on gravity settling chambers. In addition, you can find some design case calculations for sizing chambers at http://www.chemeng.queensu.ca/chee481/Downloads.htm.

CYCLONE SEPARATORS

This type of technology is a part of the group of air pollution controls collectively referred to as "precleaners," because they are oftentimes used to reduce the inlet loading of particulate matter (PM) to downstream collection devices by removing larger, abrasive particles. Cyclones are also referred to as cyclone collectors, cyclone separators, centrifugal separators, and inertial separators. In applications where many small cyclones are operating in parallel, the entire system is called a multiple tube cyclone, multicyclone, or multiclone. Key features of the equipment are illustrated in Figures 3, 4, and 5.

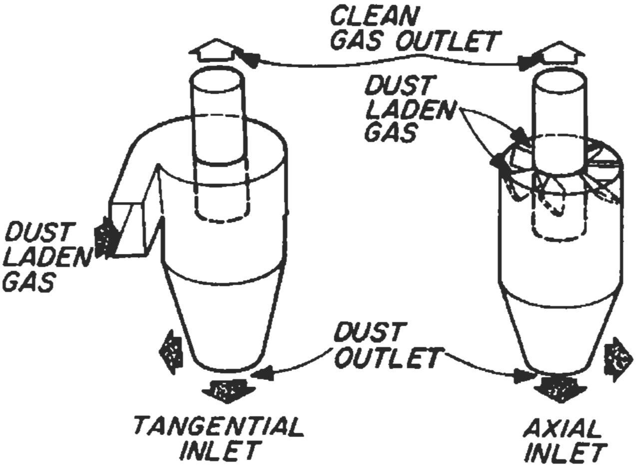


Figure 3. Basic cyclone configuration and inlet schemes.

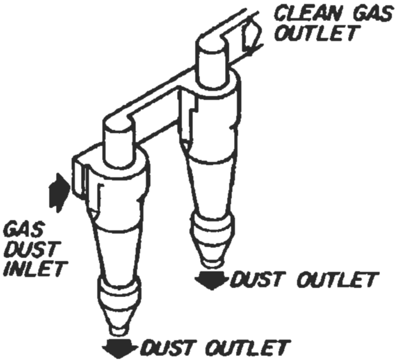


Figure 4. Cyclones arranged in series.

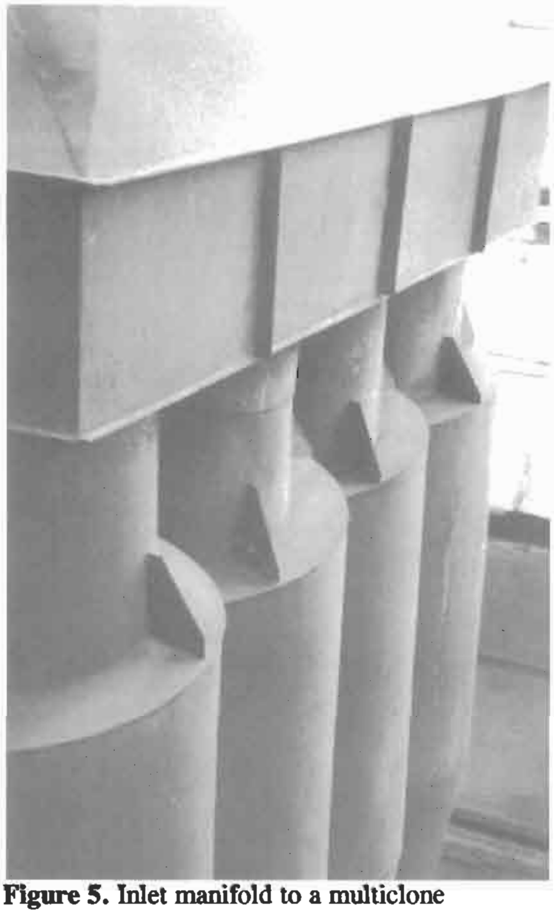


Figure 5. Inlet manifold to a multiclone arrangement.

Particle removal from a gas stream is achieved by centrifugal and inertial forces, induced by forcing particulate-laden gas to change direction. Figure 6 illustrates the steps that achieve removal. Cyclones are used to control PM, and primarily PM greater than 10 micrometers (μm) in aerodynamic diameter. However, there are high efficiency cyclones designed to be effective for PM less than or equal to 10 μm and less than or equal to 2.5 μm in aerodynamic diameter (PM_{10} and $PM_{2.5}$). Although cyclones may be used to collect particles larger than 200 μm, gravity settling chambers or simple momentum separators are usually satisfactory and less subject to abrasion (Wark, 1981; Perry, 1984).

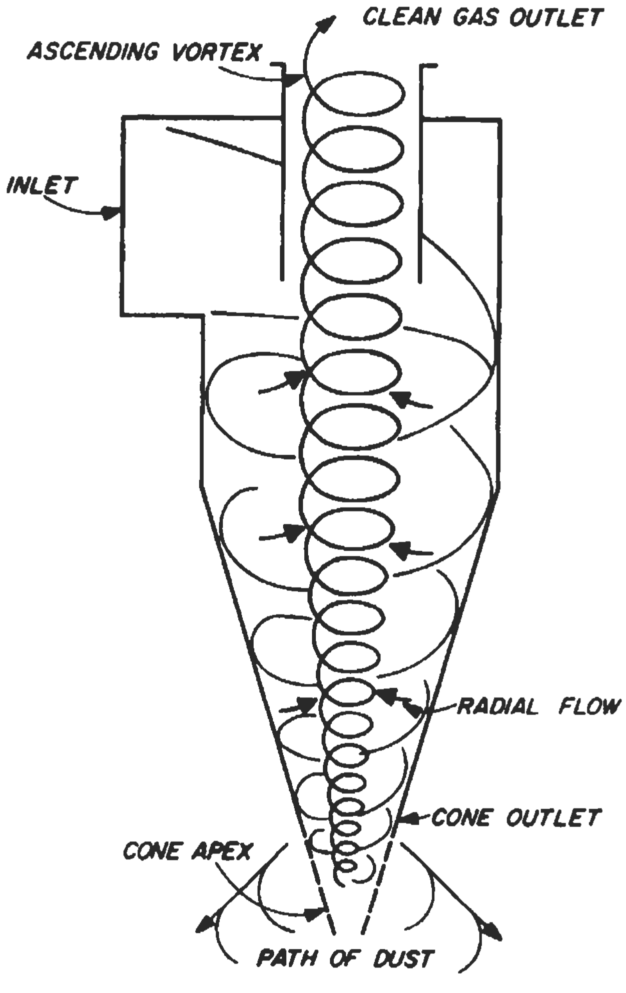


Figure 6. Steps involved in particle separation.

Achievable Emission Limits and Reductions

The collection efficiency of cyclones varies as a function of particle size and cyclone design. Cyclone efficiency generally increases with (1) particle size and/or density, (2) inlet duct velocity, (3) cyclone body length, (4) number of gas revolutions in the cyclone, (5) ratio of cyclone body diameter to gas exit diameter, (6) dust loading, and (7) smoothness of the cyclone inner wall. Cyclone efficiency will decrease with increases in (1) gas viscosity, (2) body diameter, (3) gas exit diameter, (4) gas inlet duct area, and (5) gas density. A common factor contributing to decreased control efficiencies in cyclones is leakage of air into the dust outlet (EPA, 1998).

Control efficiency ranges for single cyclones are often based on three classifications of cyclone, i.e., conventional, high-efficiency, and high-throughput. The control efficiency range for conventional single cyclones is estimated to be 70 to 90 percent for PM, 30 to 90 percent for PM_{10}, and 0 to 40 percent for $PM_{2.5}$.

High efficiency single cyclones are designed to achieve higher control of smaller particles than conventional cyclones. According to Cooper (1994), high efficiency single cyclones can remove 5 μm particles at up to 90 percent efficiency, with higher efficiencies achievable for larger particles. The control efficiency ranges for high efficiency single cyclones are 80 to 99 percent for PM, 60 to 95 percent for PM_{10}, and 20 to 70 percent for $PM_{2.5}$. Higher efficiency cyclones come with higher pressure drops, which require higher energy costs to move the waste gas through the cyclone. Cyclone design is generally driven by a specified pressure-drop limitation, rather than by meeting a specified control efficiency (Andriola, 1999; Perry, 1994).

According to Vatavuk (1990), high throughput cyclones are only guaranteed to remove particles greater than 20 μm, although collection of smaller particles does occur to some extent. The control efficiency ranges for high-throughput cyclones are 80 to 99 percent for PM, 10 to 40 percent for PM_{10}, and 0 to 10 percent for $PM_{2.5}$. Multicyclones are reported to achieve from 80 to 95 percent collection efficiency for 5 μm particles (EPA, 1998).

Note that this equipment is applicable only for stationary point source emission control.

Typical Industrial Applications

Cyclones are designed for marry applications. Cyclones themselves are generally not adequate to meet stringent air pollution regulations, but they serve an important purpose as precleaners for more expensive final control devices such as fabric filters or electrostatic precipitators (ESPs). In addition to use for pollution control work, cyclones are used in many process applications, for example, they are used for recovering and recycling food products and process materials such as catalysts (Cooper, 1994).

Cyclones are used extensively after spray drying operations in the food and chemical industries, and after crushing, grinding, and calcining operations in the mineral and chemical industries to collect salable or useful material. In the ferrous and nonferrous metallurgical industries, cyclones are often used as a first stage in the control of PM emissions from sinter plants, roasters, kilns, and furnaces. PM from the fluid-cracking process are removed by cyclones to facilitate catalyst recycling.

Fossil-fuel and wood-waste fired industrial and commercial fuel combustion units commonly use multiple cyclones (generally upstream of a wet scrubber, ESP, or fabric filter) which collect fine PM (< 2.5 μm) with greater efficiency than a single cyclone. In some cases, collected fly ash is reinjected into the combustion unit to improve PM control efficiency (AWMA, 1992; Avallone, 1996; STAPPA/ALAPCO, 1996; EPA, 1998).

Emission Stream Characteristics

Air Flow: Typical gas flow rates for a single cyclone unit are 0.5 to 12 standard cubic meters per second (sm^3/sec) (1,060 to 25,400 standard cubic feet per minute (scfm)). Flows at the high end of this range and higher (up to approximately 50 sm^3/sec or 106,000 scfm) use multiple cyclones in parallel (Cooper, 1994). There are single cyclone units employed for specialized applications which have flow rates of up to approximately 30 sm^3/sec (63,500 scfm) and as low as 0.0005 sm^3/sec (1.1 scfm) (Wark, 1981; Andriola, 1999).

Temperature: Inlet gas temperatures are only limited by the materials of construction of the cyclone, and have been operated at temperatures as high as 540°C (1000°F) (Wark, 1981; Perry, 1994).

Pollutant Loading: Waste gas pollutant loadings typically range from 2.3 to 230 grams per standard cubic meter (g/sm^3) (1.0 to 100 grains per standard cubic foot (gr/scf)) (Wark, 1981). For specialized applications, loadings can be as high as 16,000 g/sm^3 (7,000 gr/scf), and as low as 1 g/sm^3 (0.44 gr/scf) (Avallone, 1996; Andriola, 1999).

Other Considerations: Cyclones perform more efficiently with higher pollutant loadings, provided that the device does not become choked. Higher pollutant loadings are generally associated with higher flow designs (Andriola, 1999).

Cost Information

The following are cost ranges (expressed in third quarter 1995 dollars) for a single conventional cyclone under typical operating conditions, developed using an EPA cost-estimating spreadsheet (EPA, 1996), and referenced to the volumetric flow rate of the waste stream treated. For purposes of calculating the example cost effectiveness, flow rates are assumed to be between 0.5 and 12 sm^3/sec (1,060 and 25,400 scfm), the PM inlet loading is assumed to be approximately 2.3 and 230 g/sm^3 (1.0 to 100 gr/scf) and the control efficiency is assumed to be 90 percent. The costs do not include costs for disposal or transport of collected material. Capital costs can be higher than in the ranges shown for applications which require expensive materials.

As a rule, smaller units controlling a waste stream with a low PM concentration will be more expensive (per unit volumetric flow rate and per quantity of pollutant controlled) than a large unit controlling a waste stream with a high PM concentration.

- Capital Cost: $4,200 to $5,100 per sm^3/sec ($2.00 to $2.40 per scfm)
- O & M Cost: $2,400 to $27,800 per sm^3/sec ($1.10 to $13.10 per scfm), annually
- Annualized Cost: $2,800 to $28,300 per sm^3/sec ($1.30 to $13.40 per scfm), annually
- Cost Effectiveness: $0.45 to $460 per metric ton ($0.41 to $420 per short ton), annualized cost per ton per year of pollutant controlled.

Flow rates higher than approximately 10 sm^3/sec (21,200 scfm), and up to approximately 50 sm^3/sec (106,000 scfm), usually employ multiple cyclones operating in parallel. Assuming the same range of pollutant loading and an efficiency of 90 percent, the following cost ranges (expressed in third quarter 1995 dollars) were developed for multiple cyclones, using an EPA cost-estimating spreadsheet (EPA, 1996), and referenced to the volumetric flow rate of the waste stream treated.

- Capital Cost: $4,100 to $5,000 per sm^3/sec ($2.00 to *$2.40* per scfm)
- O & M Cost: $1,600 to $2,600 per sm^3/sec ($0.75 to $1.20 per scfm), annually
- Annualized Cost: $2,000 to $3,100 per sm^3/sec ($0.90 to $1.50 per scfm), annually
- Cost Effectiveness: $0.32 to $50 per metric ton ($0.29 to $46 per short ton), annualized cost per ton per year of pollutant controlled

Theory of Operation

Cyclones use inertia to remove particles from the gas stream. The cyclone imparts centrifugal force on the gas stream, usually within a conical shaped chamber. Cyclones operate by creating a double vortex inside the cyclone body (refer back to Figure 6). The incoming gas is forced into circular motion down the cyclone near the inner surface of the cyclone tube. At the bottom of the cyclone, the gas turns and spirals up through the center of the tube and out of the top of the cyclone (AWMA, 1992). Particles in the gas stream are forced toward the cyclone walls by the centrifugal force of the spinning gas but are opposed by the fluid drag force of the gas traveling through and out of the cyclone. For large particles, inertial momentum overcomes the fluid drag force so that the particles reach the cyclone walls and are collected. For small particles, the fluid drag force overwhelms the inertial momentum and causes these particles to leave the cyclone with the exiting gas. Gravity also causes the larger particles that reach the cyclone walls to travel down into a bottom hopper. While they rely on the same separation mechanism as momentum separators, cyclones are more effective because they have a more complex gas flow pattern (AWMA, 1992). Cyclones are generally classified into four types, depending on how the gas stream is introduced into the device and how the collected dust is discharged. The four types include tangential inlet, axial discharge; axial inlet, axial discharge; tangential inlet, peripheral discharge; and axial inlet, peripheral discharge. The first two types are the most common (AWMA, 1992). Pressure drop is an important parameter because it relates directly to operating costs and control efficiency. Higher control efficiencies for a given cyclone can be obtained by higher inlet velocities, but this also increases the pressure drop. In general, 18.3 meters per second (60 feet per second) is considered the best operating velocity. Common ranges of pressure drops for cyclones are 0.5 to 1 kilopascals (kPa) (2 to 4 in. H_2O) for low-efficiency units (high throughput), 1 to 1.5 kPa (4 to 6 in. H_2O) for medium-efficiency units (conventional), and 2 to 2.5 kPa (8 to 10 in. H_2O) for high-efficiency units (AWMA, 1992).

When high-efficiency (which requires small cyclone diameter) and large throughput are both desired, a number of cyclones can be operated in parallel. In a multiple tube cyclone, the housing contains a large number of tubes that have a common gas inlet and outlet in the chamber. The gas enters the tubes through axial inlet vanes which impart a circular motion (AWMA, 1992).

Another high-efficiency unit, the wet cyclonic separator, uses centrifugal force to enhance control efficiency.

- Advantages of cyclones include (AWMA, 1992; Cooper, 1994; and EPA, 1998): Low capital cost;
- No moving parts, therefore, few maintenance requirements and low operating costs;
- Relatively low pressure drop (2 to 6 inches water column), compared to amount of PM removed;

- Temperature and pressure limitations are only dependent on the materials of construction;
- Dry collection and disposal; and
- Relatively small space requirements.

Disadvantages of cyclones include (AWMA, 1992; Cooper, 1994; and EPA, 1998):

- Relatively low PM collection efficiencies, particularly for PM less than 10 μm in size;
- Unable to handle sticky or tacky materials; and
- High efficiency units may experience high pressure drops.

Using multiple cyclones, either in parallel or in series, to treat a large volume of gas results in higher efficiencies, but at the cost of a significant increase in pressure drop. Higher pressure drops translate to higher energy usage and operating costs. Several designs should be considered to achieve the optimum combination of collection efficiency and pressure drop (Cooper, 1994).

Additional Information

References 15 through 23 provide additional information on cyclone separators and the design and scale-up principles.

FABRIC FILTER PULSE-JET CLEANED TYPE

This equipment is used for the capture of Particulate Matter (PM), including particulate matter less than or equal to 10 micrometers (μm) in aerodynamic diameter (PM_{10}, particulate matter less than or equal to 2.5 μm in aerodynamic diameter ($PM_{2.5}$), and hazardous air pollutants (HAPs) that are in particulate form, such as most metals (mercury is the notable exception, as a significant portion of emissions are in the form of elemental vapor).

Typical new equipment design efficiencies are between 99 and 99.9%. Older existing equipment have a range of actual operating efficiencies of 95 to 99.9%. Several factors determine fabric filter collection efficiency. These include gas filtration velocity, particle characteristics, fabric characteristics, and cleaning mechanism. In general, collection efficiency increases with increasing filtration velocity and particle size.

For a given combination of filter design and dust, the effluent particle concentration from a fabric filter is nearly constant, whereas the overall efficiency is more likely to vary with particulate loading. For this reason, fabric filters can be considered to be constant outlet devices rather than constant efficiency devices. Constant effluent concentration is achieved because at any given time, part of the fabric filter is being resumes, the filtering capability has been reduced because of the lost filter cake and loose particles are pushed through the filter by the flow of gas. As particles are captured, the efficiency increases until the next cleaning cycle. Average collection efficiencies for fabric filters are usually determined from tests that cover a number of cleaning cycles at a constant inlet loading. Note that this equipment is applicable to stationary point source control.

Typical Industrial Applications

Fabric filters have had a long history in performing effectively in a wide variety of applications. Common applications using pulse-jet cleaning systems include:

- Utility Boilers (Coal)
- Industrial Boilers (Coal, Wood)
- Commercial/Institutional Boilers (Coal, Wood)
- Ferrous Metal Processing (e.g., Iron and Steel Production and Steel Foundries)
- Mineral Products (e.g., Cement Manufacturing, Coal Cleaning, and Stone Quarrying and Processing)
- Asphalt Manufacturing
- Grain Milling

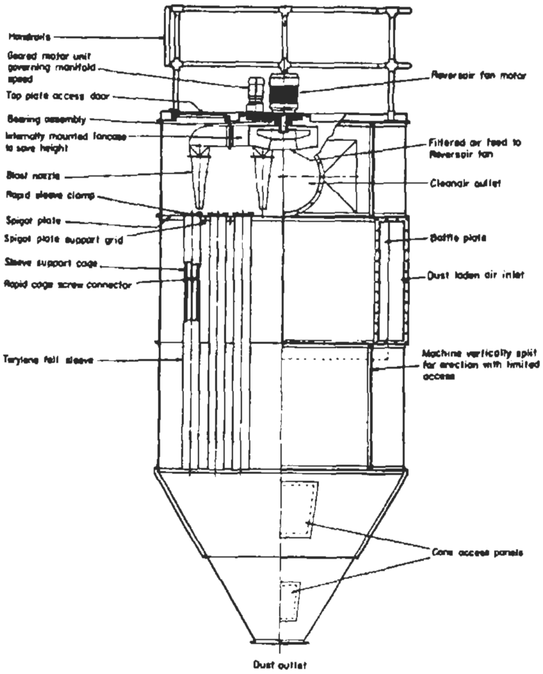
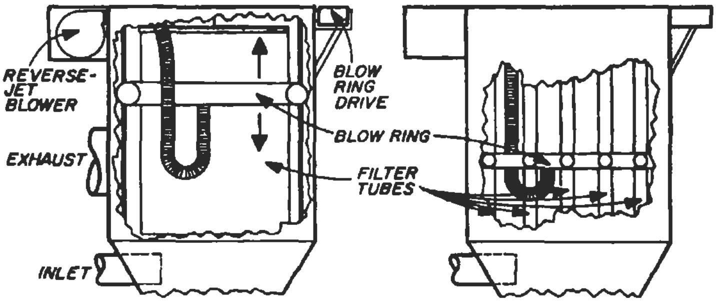


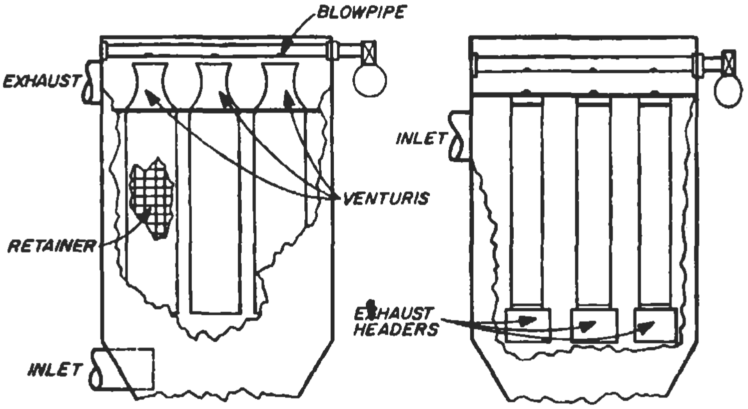
Figure 7. European design baghouse based on rotating fan principle.

It is important to note that these applications are typical, but not at all definitive. Fabric filters can be used in almost any process where dust is generated and can be collected and ducted to a centralized location. In general, fabric filters come in many different sizes and configurations. In older plants one can find makeshift operations. See Figures 7 and 8 for examples of common configurations and characteristics.



(a) SINGLE-TUBE HERSEY TYPE

(b) MULTIPLE-TUBE HERSEY TYPE



(c) PULSE-JET COLLECTOR

(d) DOWNFLOW-TYPE PULSE-JET

Figure 8. Examples of pulse-jet type collectors.

Emission Stream Characteristics

Air Flow: Baghouses are separated into two groups, standard and custom, which are either separated into low, medium, and high capacity. Standard baghouses are factory-built, off the shelf units. They may handle from less than 0.10 to more than 50 standard cubic meters per second (sm^3/sec) (("hundreds" to more than 100,000 standard cubic feet per minute (scfm)). Custom baghouses are designed for specific applications and are built to the specifications prescribed by the customer. These units are generally much larger than standard units, i.e., from 50 to over 500 sm^3/sec (100,000 to over 1,000,000 scfm).

Temperature: Typically, gas temperatures up to about 260°C (500°F), with surges to about 290°C (550°F) can be accommodated routinely, with the appropriate fabric material. Spray coolers or dilution air can be used to lower the temperature of the pollutant stream. This prevents the temperature limits of the fabric from being exceeded. Lowering the temperature, however, increases the humidity of the pollutant stream. Therefore, the minimum temperature of the pollutant stream must remain above the dew point of any condensable in the stream. The baghouse and associated ductwork should be insulated and possibly heated if condensation may occur.

Pollutant Loading: Typical inlet concentrations to baghouses are 1 to 23 grams per cubic meter (g/m^3) (0.5 to 10 grains per cubic foot (gr/ft^3)), but in extreme cases, inlet conditions may vary between 0.1 to more than 230 g/m^3 (0.05 to more than 100 gr/ft^3).

Other Considerations: Moisture and corrosives content are the major gas stream characteristics requiring design consideration. Standard fabric filters can be used in pressure or vacuum service, but only within the range of about ± 640 millimeters of water column (25 inches of water column). Well-designed and operated baghouses have been shown to be capable of reducing overall particulate emissions to less than 0.05 g/m^3 (0.010 gr/ft^3), and in a number of cases, to as low as 0.002 to 0.011 g/m^3 (0.001 to 0.0115 gr/ft^3).

Emission Stream Pretreatment Requirements

Because of the wide variety of filter types available to the designer, it is not usually required to pretreat a waste stream's inlet temperature. However, in some high temperature applications, the cost of high temperature-resistant bags must be weighed against the cost of cooling the inlet temperature with spray coolers or dilution air. When much of the pollutant loading consists of relatively large particles, mechanical collectors such as cyclones may be used to reduce the load on the fabric filter, especially at high inlet concentrations.

Cost Information

Cost estimates are presented below for pulse jet cleaned fabric filters. The costs are expressed in fourth quarter 1998 dollars. The cost estimates assume a conventional design under typical operating conditions and do not include auxiliary equipment such as fans and ductwork. The costs for pulse jet cleaned systems are generated using EPA's cost-estimating spreadsheet for fabric filters. Costs are primarily driven by the waste stream volumetric flow rate and pollutant loading. In general, a small unit controlling a low pollutant loading will not be as cost effective as a large unit controlling a high pollutant loading. The costs presented are for flow rates of 470 m^3/sec (1,000,000 scfm) and 1.0 m^3/sec (2,000 scfm), respectively, and a pollutant loading of 9 g/m^3 (4.0 gr/ft^3).

Pollutants that require an unusually high level of control or that require the fabric filter bags or the unit itself to be constructed of special materials, such as Gore-Tex or stainless steel, will increase the costs of the system. The additional costs for controlling more complex waste streams are not reflected in the estimates given below. For these types of systems, the capital cost could increase by as much as 75% and the operational and maintenance (O&M cost could increase by as much as 20%.

- Capital Cost: $13,100 to $54,900 per sm³/s ($6 to $26 per scfm)
- O&M Cost: $11,200 to $51,700 per sm³/s ($5 to $24 per scfm), annually
- Annualized Cost: $13,100 to $83,400 per sm³/s ($6 to $39 per scfm), annually
- Cost Effectiveness: $46 to $293 per metric ton ($42 to $266 per short ton)

Theory of Operation

In a fabric filter, flue gas is passed through a tightly woven or felted fabric, causing PM in the flue gas to be collected on the fabric by sieving and other mechanisms. Fabric filters may be in the form of sheets, cartridges, or bags, with a number of the individual fabric filter units housed together in a group. Bags are the most common type of fabric filter. The dust cake that forms on the filter from the collected PM can significantly increase collection efficiency. Fabric filters are frequently referred to as baghouses because the fabric is usually configured in cylindrical bags. Bags may be 6 to 9 m (20 to 30 ft) long and 12.7 to 30.5 centimeters (5 to 12 inches) in diameter. Groups of bags are placed in isolable compartments to allow cleaning of the bags or replacement of some of the bags without shutting down the entire fabric filter.

Operating conditions are important determinants of the choice of fabric. Some fabrics (e.g., polyolefins, nylons, acrylics, polyesters) are useful only at relatively low temperatures of 95 to 150°C (200 to 300°F). For high-temperature flue gas streams, more thermally stable fabrics such as fiberglass, Teflon, or Nomex must be used.

Practical application of fabric filters requires the use of a large fabric area in order to avoid an unacceptable pressure drop across the fabric. Baghouse size for a particular unit is determined by the choice of air-to-cloth ratio, or the ratio of volumetric airflow to cloth area. The selection of air-to-cloth ratio depends on the particulate loading and characteristics, and the cleaning method used. A high particulate loading will require the use of a larger baghouse in order to avoid forming too heavy a dust cake, which would result in an excessive pressure drop. As an example, a baghouse for a 250 MW utility boiler may have 5,000 separate bags with a total fabric area approaching 46,500 m^2 (500,000 square feet).

Determinants of baghouse performance include the fabric chosen, the cleaning frequency and methods, and the particulate characteristics. Fabrics can be chosen which will intercept a greater fraction of particulate and some fabrics are coated with a membrane with very fine openings for enhanced removal of submicron particulate. Such fabrics tend to be more expensive.

Pulse-jet cleaning of fabric filters is relatively new compared to other types of fabric filters. This cleaning mechanism has consistently grown in popularity because it can treat high dust loadings, operate at constant pressure drop, and occupy less space than other types of fabric filters. Pulse jet cleaned fabric filters can only operate as external cake collection devices. The bags are closed at the bottom, open at the top, and supported by internal retainers, called cages. Particulate-laden gas flows into the bag, with diffusers often used to prevent oversized particles from damaging the bags. The gas flows from the outside to the inside of the bags, and then out the gas exhaust. The particles are collected on the outside of the bags and drop into a hopper below the fabric filter.

During pulse jet cleaning, a short burst, 0.03 to 0.1 seconds in duration, of high pressure [415 to 830 kiloPascals (kPa) (60 to 120 pounds per square inch gauge (psig)] of air is injected into the bags. The pulse is blown through a venturi nozzle at the top of the bags and establishes a shock wave that continues onto the bottom of the bag. The wave flexes the fabric, pushing it away from the cage, and then snaps it back dislodging the dust cake. The cleaning cycle is regulated by a remote timer connected to a solenoid valve. The burst of air is controlled by the solenoid valve and is released into blow pipes that have nozzles located above the bags. The bags are usually cleaned row by row.

There are several unique attributes of pulse jet cleaning. Because the cleaning pulse is very brief, the flow of dusty gas does not have to be stopped during cleaning. The other bags continue to filter, taking on extra duty because of the bags being cleaned. In general, there is no change in fabric filter pressure drop or performance as a result of pulse jet cleaning. This enables the pulse jet fabric filters to operate on a continuous basis with solenoid valves as the only significant moving parts. Pulse jet cleaning is also more intense and occurs with greater frequency than the other fabric filter cleaning methods. This intense cleaning dislodges nearly all of the dust cake each time the bag is pulsed. As a result, pulse jet filters do not rely on a dust cake to provide filtration. Felted (non-woven) fabrics are used in pulse jet fabric filters because they do not require a dust cake to achieve high collection efficiencies. It has been found that woven fabrics used with pulse jet fabric filters leak a great deal of dust after they are cleaned.

Since bags cleaned by the pulse jet method do not need to be isolated for cleaning, pulse jet cleaned fabric filters do not need extra compartments to maintain adequate filtration during cleaning. Also, because of the intense and frequent nature of the cleaning, they can treat higher gas flow rates with higher dust loadings. Consequently, fabric filters cleaned by the pulse jet method can be smaller than other types of fabric filters in the treatment of the same amount of gas and dust, making higher gas-to-cloth ratios achievable.

Fabric filters in general provide high collection efficiencies on both coarse and fine (submicron) particulate matter. They are relatively insensitive to fluctuations in gas stream conditions. Efficiency and pressure drop are relatively unaffected by large changes in inlet dust loadings for continuously cleaned filters. Filter outlet air is very clean and may be recirculated within the plant in many cases (for energy conservation). Material is collected dry for subsequent processing or disposal. Corrosion and rusting of components are usually not problems. Operation is relatively simple. Unlike electrostatic precipitators, fabric filter systems do not require the use of high voltage; therefore, maintenance is simplified and flammable dust may be collected with proper care. The use of selected fibrous or granular filter aids (precoating) permits the high-efficiency collection of submicron smokes and gaseous contaminants. Filter collectors are available in a large number of configurations, resulting in a range of dimensions and inlet and outlet flange locations to suit installation requirements.

They do have some disadvantages. Temperatures much in excess of 290°C (550°F) require special refractory mineral or metallic fabrics, which can be expensive. Certain dusts may require fabric treatments to reduce dust seepage, or in other cases, assist in the removal of the collected dust. Concentrations of some dusts in the collector, approximately 50 g/m^3 (22 gr/ft^3), may represent a fire or explosion hazard if a spark or flame is accidentally admitted (i.e., risk of a dust explosion). Fabrics can burn if readily oxidizable dust is being collected. Fabric filters have relatively high maintenance requirements (e.g., periodic bag replacement). Fabric life maybe shortened at elevated temperatures and in the presence of acid or alkaline particulate or gas constituents. They cannot be operated in moist environments. Hygroscopic materials, condensation of moisture, or tarry adhesive components may cause crusty caking or plugging of the fabric or require special additives. Respiratory protection for maintenance personnel may be required when replacing fabric. Medium pressure drop is required, typically in the range of 100 to 250 mm of water column (4 to 10 inches of water column). A specific disadvantage of pulse jet units that use very high gas velocities is that the dust from the cleaned bags can be drawn immediately to the other bags. If this occurs, little of the dust falls into the hopper and the dust layer on the bags becomes too thick. To prevent this, pulse jet fabric filters can be designed with separate compartments that can be isolated for cleaning.

Fabric filters are useful for collecting particles with resistivities either too low or too high for collection with electrostatic precipitators. Fabric filters therefore may be good candidates for collecting fly ash from low-sulfur coals or fly ash containing high unburned carbon levels, which respectively have high and low resistivities, and thus are relatively difficult to collect with electrostatic precipitators.

Additional Information

References 24 through 28 provide additional information on filters and the design and scale-up principles. Note that the next section describes a variation of this technology.

EXTENDED MEDIA CARTRIDGE FILTERS

Applicable pollutants for this equipment are Particulate Matter (PM), including particulate matter less than or equal to 10 micrometers in aerodynamic diameter (PM_{10}), particulate matter less than or equal to 2.5 μm in aerodynamic diameter ($PM_{2.5}$), and hazardous air pollutants (HAPs) that are in particulate form, such as most metals (mercury is the notable exception, as a significant portion of emissions are in the form of elemental vapor).

Achievable Emission Limits/Reductions

Older existing cartridge collector types have a range of actual operating efficiencies of 99 to 99.9% for PM_{10} and $PM_{2.5}$. Typical new equipment design efficiencies are between 99.99 and 99.999+%. In addition, commercially available designs are able to control submicron PM (0.8 μm in diameter or greater) with a removal efficiency of 99.999+%.

Several factors determine cartridge filter collection efficiency including gas filtration velocity, particle characteristics, filter media characteristics, and cleaning mechanism. In general, collection efficiency increases with increasing filtration velocity and particle size.

For a given combination of filter design and dust, the effluent particle concentration from a cartridge collector is nearly constant, whereas the overall efficiency is more likely to vary with particulate loading. For this reason, cartridge collectors can be considered to be constant outlet devices rather than constant efficiency devices. Constant effluent concentration is achieved because at any given time, part of the filter media is being cleaned. As a result of the cleaning mechanisms used in cartridge collectors, the collection efficiency is constantly changing. Each cleaning cycle removes at least some of the filter cake and loosens particles that remain on the filter. When filtration resumes, the filtering capability has been reduced because the lost filter cake and loose particles are pushed through the filter by the flow of gas. As particles are captured, the efficiency increases until the next cleaning cycle. Average collection efficiencies for cartridge collectors are usually determined from tests that cover a number of cleaning cycles at a constant inlet loading. As with baghouses, this equipment is applicable for point source control.

Typical Industrial Applications

Cartridge collectors perform very effectively in many different applications. Common applications of cartridge filter systems with pulse jet cleaning are comparable to baghouses described earlier. In addition to these applications, cartridge collectors can be used in any process where dust is generated and can be collected and ducted to a central location.

Emission Stream Characteristics

Air Flow: Cartridge collectors are currently limited to low air flow capacity applications. Standard cartridge collectors are factory-built, off the shelf units. They may handle airflow rates from less than 0.10 to more than 5 standard cubic meters per second (sm^3/sec) (("hundreds" to more than 10,000 standard cubic feet per minute (scfm)).

Temperature: Temperatures are limited by the type of filter media and sealant used in the cartridges. Standard cartridges utilizing paper filter media can accommodate gas temperatures up to about 95°C (200°F). Cartridge filters utilizing synthetic, nonwoven media such as needle-punched felts fabricated of polyester or Nomex can withstand temperatures of up to 200°C (400°F) with the appropriate sealant material. Spray coolers or dilution air can be used to lower the temperature of the pollutant stream. This prevents the temperature limits of the filter media from being exceeded. Lowering the temperature can result in higher humidity of the pollutant stream. Therefore, the minimum temperature of the pollutant stream must remain above the dew point of'any condensable in the stream. The cartridge collector and associated ductwork should be insulated and possibly heated if condensation may occur.

Pollutant Loading: Typical inlet concentrations to cartridge collectors are 1 to 23 grams per cubic meter (g/m^3) (0.5 to 10 grains per cubic foot (gr/ft^3)). Cartridge filters, which utilize synthetic, nonwoven media such as needle punched felts fabricated of polyester or Nomex, are able to handle inlet concentrations up to 57 g/m^3 (25 gr/ft^3).

Other Considerations: Moisture and corrosive content in the gas streams are the major design considerations. Standard cartridge filters can be used in pressure or vacuum service, but only within the range of about ± 640 millimeters of water column (25 inches of water column). Baghouses have been shown to be capable of reducing overall particulate emissions to less than 0.05 g/m^3 (0.010 grft^3). Penetration of PM in cartridge collectors is generally many times less than in traditional baghouse designs.

Emission Stream Pretreatment Requirements

Because of the wide variety of filter types available to the designer, the inlet temperature of the waste stream usually does not require pretreatment. However, in some high temperature applications, the cost of high temperature-resistant cartridge filters must be weighed against the cost of cooling the inlet temperature with spray coolers or dilution air. When much of the pollutant loading consists of relatively large particles, mechanical collectors such as cyclones may be used to reduce the load on the filter media, especially at high inlet concentrations.

Cost Information

Cost estimates, expressed in fourth quarter 1998 dollars, are presented below for cartridge collectors with pulse jet cleaning. The cost estimates assume a conventional design under typical operating conditions. Auxiliary equipment, such as fans and ductwork, is not included. The costs are generated using EPA's cost estimating spreadsheets for fabric filters (EPA, 1998b).

Costs are primarily driven by the waste stream volumetric flow rate and pollutant loading. In general, a small unit controlling a low pollutant loading will not be as cost effective as a large unit controlling a high pollutant loading. Cartridge collectors are currently limited to low flow rate applications. The capital cost for a cartridge collector is significantly lower than for a baghouse. However, the operational and maintenance (O&M) cost tends to be higher. The costs presented are for flow rates of 5 m^3/s (10,000 scfm) and 1.0 m^3/s (2,000 scfm), respectively, and a pollutant loading of 9 g/m^3 (4.0 gr/ft^3).

Pollutants that require an unusually high level of control or that require the filter media or the unit itself to be constructed of special materials, such as Nomex or stainless steel, will increase the costs of the system. The additional costs for controlling more complex waste streams are not reflected in the estimates given below. For these types of systems, the capital cost could increase by as much as 75% and the O&M cost could increase by as much as 10%.

- Capital Cost: \$15,000 to \$27.000 per sm^3/s (\$7 to \$13 per scfm)
- O & M Cost: \$20,000 to \$52,000 per sm^3/s (\$9 to \$25 per scfm), annually
- Annualized Cost: \$26, 000 to \$80,000 per sm^3/s (\$13 to \$38 per scfm), annually
- Cost Effectiveness: \$94 to \$280 per metric ton (\$85 to \$256 per short ton)

Theory of Operation

Cartridge filters contain either a paper or nonwoven fibrous filter media. Paper media is generally fabricated of natural or synthetic materials such as cellulose and fiberglass. Nonwoven media is generally fabricated from synthetic materials such as Nomex, polyester, or polypropylene. The media is supported by inner and outer wire frameworks. The waste gas stream is passed through the fibrous filter media causing PM in the gas stream to be collected on the media by sieving and other mechanisms. The dust cake that forms on the filter media from the collected PM can significantly increase collection efficiency.

In general, the filter media is pleated to provide a larger surface area to volume flow rate. For this reason, cartridge filters are also referred to as extended media filters. Close pleating, however, can cause PM to bridge the pleat bottom, effectively reducing the surface area. Corrugated aluminum separators are often employed to prevent the pleated media from collapsing. The pleat depth can vary anywhere from 2.5 cm (1 inch) up to 40 cm (16 inches). Pleat spacing generally ranges between 12 to 16 pleats per inch, with certain conditions requiring fewer pleats, 4 to 8 pleats per inch. There are a wide variety of cartridge designs and dimensions. Typical designs include flat panels, V shaped packs or cylindrical packs. Commercially available cylindrical packs are approximately 15 to 35 centimeters (cm) (6 to 14 inches) in diameter and 40 to 122 cm (16 to 48 inches) in length.

The cartridge is closed at one end with a metal cap. The media is sealed to the cap using polyurethane plastic, epoxy, or other commercially available sealant. For certain applications, two cartridges may be placed in series. The cartridges are placed in a frame constructed of wood or metal. A neoprene or silicone gasket seals the frame to the clean air plenum of the collector. The cartridges may be mounted horizontally or vertically, if retrofitting a baghouse.

Replacement of the cartridges is generally performed outside of the collector. This reduces the risk of exposure to PM by the maintenance workers. This feature is especially important for HAPs applications. The Occupational Safety and Health Administration (OSHA) requires special filter replacement procedures, commonly referred to as bag in/bag out procedures, for many HAP applications (see Heumann, 1997).

Operating conditions are important determinants of the choice of filter media and sealant used in the cartridges. Some filter media, such as cellulose paper filters, are useful only at relatively low temperatures of 95 to 150°C (200 to 300°F). For high-temperature flue gas streams, more thermally stable filter media, such as nonwoven polyester, polypropylene, or Nomex, must be used. A variety of commercially available sealants such as polyurethane plastic and epoxy will allow fabric operating temperatures up to150°C (300°F). Selected sealants such as heat cured Plasitcol will withstand operating temperatures up to 200°C (400°F).

Practical application of cartridge collectors requires the use of a large media area in order to avoid an unacceptable pressure drop across the filter media. The number of cartridges utilized in a particular collector is determined by the choice of air-to-cloth ratio, or the ratio of volumetric air flow to filter media area. The selection of air-to-cloth ratio depends on the particulate loading, particulate characteristics, and the cleaning method used. A high particulate loading will require the use of a larger number of cartridges in order to avoid forming a heavy dust cake, which results in an excessive pressure drop. The paper and nonwoven filter media used in cartridge filters have a larger pressure drop across the filter than the woven fabric used in bags. For this reason, cartridge collectors are utilized at lower air flow rates and particulate loadings than traditional baghouse designs. Determinants of cartridge collector performance include the filter media chosen, the cleaning frequency and methods, and the particulate characteristics. Filter media can be chosen which will intercept a greater fraction of particulate, and some filter media are coated with a membrane with very fine openings for enhanced removal of submicron particulate. Such filter media tend to be more expensive.

Pulse jet cleaning of cartridge filters is relatively new, having only been used for the past 30 years. This cleaning mechanism has consistently grown in popularity because it can treat high dust loadings, operate at constant pressure drop, and occupy less space than traditional bug-type fabric filters. Pulse jet cleaned cartridge filters can only operate as external cake collection devices. The cartridges are closed at the bottom, and open at the top. Particulate laden gas flows into the collector, with diffusers often used to prevent oversized particles from damaging the filter media. The gas flows from the outside to the inside of the cartridges, and then out the gas exhaust. The particles are collected on the outside of the filter media and drop into a hopper below the cartridge after cleaning.

During pulse jet cleaning, a short burst, 0.03 to 0.1 seconds in duration, of high pressure, 415 to 830 kiloPascals (kPa) (60 to 120 pounds per square inch gauge (psig)), air is injected into the cartridges. The pulse is blown through a venturi nozzle at the top of the cartridges and establishes a shock wave that continues onto the bottom of the cartridges. The wave flexes the filter media, dislodging the dust cake. The cleaning cycle is regulated by a remote timer connected to a solenoid valve. The burst of air is controlled by the solenoid valve and is released into blow pipes that have nozzles located above the cartridges.

There are several unique attributes of pulse-jet cleaning. Because the cleaning pulse is very brief, the flow of dusty gas does not have to be stopped during cleaning. The other cartridges continue to filter, taking on extra duty because of the cartridges being cleaned. In general, there is no change in filter pressure drop or performance as a result of pulse jet cleaning. This enables the cartridge collectors with pulse jet cleaning to operate on a continuous basis with solenoid valves as the only significant moving parts. Pulse jet cleaning is also more intense and occurs with greater frequency than the other filter cleaning methods. This intense cleaning dislodges nearly all of the dust cake each time the cartridge is pulsed. As a result, pulse jet filters do not rely on a dust cake to provide filtration. Paper and nonwoven filter media are used in pulse jet cleaned cartridge collectors because they do not require a dust cake to achieve high collection efficiencies.

Since cartridges cleaned by the pulse jet method do not need to be isolated for cleaning, the collector does not need extra compartments to maintain adequate filtration during cleaning. In addition, the pleating of the filter media provides increased filter area per housing volume. Consequently, cartridge collectors cleaned by the pulse jet method can be smaller than traditional fabric filter baghouses in the treatment of the same amount of gas and dust. A cartridge collector is approximately 4 times smaller than baghouse designs for similar gas streams.

Cartridge filters in general provide high collection efficiencies on both coarse and fine (submicron) particulates. They are relatively insensitive to fluctuations in gas stream conditions. Efficiency and pressure drop are relatively unaffected by large changes in inlet dust loadings for continuously cleaned filters. Filter outlet air is very clean and may be recirculated within the plant in many cases (for energy conservation - *a pollution prevention credit*). PM is collected dry for subsequent processing or disposal. Corrosion and rusting of components are usually not problems. Operation is relatively simple. Unlike electrostatic precipitators, cartridge filter systems do not require the use of high voltage; therefore, maintenance is simplified and flammable dust may be collected with proper care. The use of selected fibrous or granular filter aids (precoating) permits the high-efficiency collection of submicron smokes and gaseous contaminants. Cartridge collectors are available in a large number of configurations, resulting in a range of dimensions and inlet and outlet flange locations to suit installation requirements.

Some of the disadvantages are as follows. Temperatures much in excess of 95°C (200°F) require special filter media, which can be expensive. Certain dusts may require filter media treatments to reduce dust seepage, or in other cases, assist in the removal of the collected dust. Concentrations of some dusts in the collector, approximately 50 g/m^3 (22 gr/ft^3), may represent a fire or explosion hazard (i.e., dust explosion) if a spark or flame is accidentally admitted. Cartridge filters can burn if readily oxidizable dust is being collected. Cartridge filters have relatively high maintenance requirements (e.g., periodic cartridge replacement). Another disadvantage is the filter life may be shortened at elevated temperatures and in the presence of acid or alkaline particulate or gas constituents. Also, they cannot be operated in moist environments; hygroscopic materials, condensation of moisture, or tarry adhesive components may cause crusty caking or plugging of the filter media or require special additives. Medium pressure drop is required, typically in the range of 100 to 250 mm of water column (4 to 10 in. of water column).

A specific disadvantage of pulse jet units that use very high gas velocities is that the dust from the cleaned cartridges can be drawn immediately to the other cartridges. If this occurs, little of the dust falls into the hopper and the dust layer on the cartridges becomes too thick. To prevent this, cartridge collectors with pulse jet cleaning can be designed with separate compartments that can be isolated for cleaning. Cartridge collectors are useful for collecting particles with resistivities either too low or too high for collection with electrostatic precipitators. They are ideal for HAP applications. Cartridge replacement procedures can be performed outside the collector housing. For similar airflow rates, cartridge collectors are compact in size compared to traditional baghouses. The application of cartridge collectors is limited to low airflow rates.

Additional Information

References 29 through 38 provide additional information on filters and the design and scale-up principles. Note that vendors are some of the best sources of information on equipment. Look at some of the Web sites noted in this and other sections describing equipment.

DRY ELECTROSTATIC PRECIPITATOR (ESP)- WIRE-PIPE TYPE

Applicable pollutants for this equipment are Particulate Matter (PM), including particulate matter less than or equal to 10 micrometers (μm) in aerodynamic diameter (PM_{10}), particulate matter less than or equal to 2.5 μm in aerodynamic diameter ($PM_{2.5}$), and hazardous air pollutants (HAPs) that are in particulate form, such as most metals (mercury is the notable exception, as a significant portion of emissions are in the form of elemental vapor).

Achievable Emission Limits Reductions

Typical new equipment design efficiencies are between 99 and 99.9%. Older existing equipment have a range of actual operating efficiencies of 90 to 99.9%. While several factors determine ESP collection efficiency, ESP size is most important. Size determines treatment time; the longer a particle spends in the ESP, the greater its chance of being collected. Maximizing electric field strength will maximize ESP collection efficiency. Collection efficiency is also affected by dust resistivity, gas temperature, chemical composition (of the dust and the gas), and particle size distribution. As with other equipment described, this hardware is applicable to point source emission control.

Typical Industrial Applications

Many older ESPs are of the wire-pipe design, consisting of a single tube placed on top of a smokestack. Dry pipe-type ESPs are occasionally used by the textile industry, pulp and paper facilities, the metallurgical industry, including coke ovens, hazardous waste incinerators, and sulfuric acid manufacturing plants, among others, though other ESP types are employed as well.

Wet wire-pipe ESPs are used much more frequently than dry wire-pipe ESPs, which are used only in cases in which wet cleaning is undesirable, such as high temperature streams or wastewater restrictions. Table 1 provides a list of typical applications.

Table 1. Typical ESP Applications

Industrial Classification	Process
Utilities and industrial power plant fuel-fired boilers	coal - pulverized coal - cyclone cole - stoker oil wood - bark bagasse fluid coke
Pulp and paper	Kraft recovery boiler Soda recovery boiler Lime kiln

Industrial Classification	Process
Rock products - kiln	Cement - dry Cement -wet Gypsum Alumina Lime Bauxite Magnesium oxide
Steel	Basic oxygen furnace Open hearth Electric furnace Ore roasters Cupola Pyrites roaster Taconite roaster Hot scarfing
Mining and metallurgical	Zinc roaster Zinc smelter Copper roaster Copper reverberatory furnace Copper converter Aluminum-Hall process Aluminum-Soderberg process Ilmenite dryer Titanium dioxide process Molybdenum roaster Ore beneficiation
Miscellaneous	Refinery catalyst regenerator Municipal incinerators Apartment incinerators Spray drying Precious metal refining

Applications listed in Table 1 are typical, but not inclusive. This is a workhorse piece of equipment used in a wide variety of versatile applications. Its high capital cost requires careful consideration of design and selection as the means of control.

Although it is generally thought of as typical end-of-pipe treatment technology, the manner in which it can be applied enables it to be used in pollution prevention applications. Figure 9 shows an installation in a steel mill operation.

Figure 9 . New ESP installation servicing blast furnaces at a steel mill.

Emission Stream Characteristics

Air Flow: Typical gas flow rates for dry wire-pipe ESPs are 0.5 to 50 standard cubic meters per second (sm^3/sec) (1,000 to 100,000 standard cubic feet per minute (scfm)).

Temperature: Dry wire-pipe ESPs can operate at very high temperatures, up to 700°C (1300°F). Operating gas temperature and chemical composition of the dust are key factors influencing dust resistivity and must be carefully considered in the design of an ESP.

Pollutant Loading: Typical inlet concentrations to a wire-pipe ESP are 1 to 10 g/m^3

(0.5 to 5 gr/scfm). It is common to pretreat a waste stream, usually with a wet spray or scrubber, to bring the stream temperature and pollutant loading into a manageable range. Highly toxic flows with concentrations well below 1 g/m^3 (0.5 gr/scfm) are also sometimes controlled with ESPs.

Other Considerations: In general, dry ESPs operate most efficiently with dust resistivities between 5 x 10^3 and 2 x 10^{10} ohm-cm. In general, the most difficult particles to collect are those with aerodynamic diameters between 0.1 and 1.0 μm. Particles between 0.2 and 0.4 μm usually show the most penetration. This is most likely a result of the transition region between field and diffusion charging.

Emission Stream Pretreatment Requirements

When much of the pollutant loading consists of relatively large particles, mechanical collectors, such as cyclones or spray coolers may be used to reduce the load on the ESP, especially at high inlet concentrations. Gas conditioning equipment to improve ESP performance by changing dust resistivity is occasionally used as part of the original design, but more frequently it is used to upgrade existing ESPs.

The equipment injects an agent into the gas stream ahead of the ESP. Usually, the agent mixes with the particles and alters their resistivity to promote higher migration velocity, and thus higher collection efficiency. Conditioning agents that are used include SO_3, H_2SO_4, sodium compounds, ammonia, and water; the conditioning agent most used is SO_3.

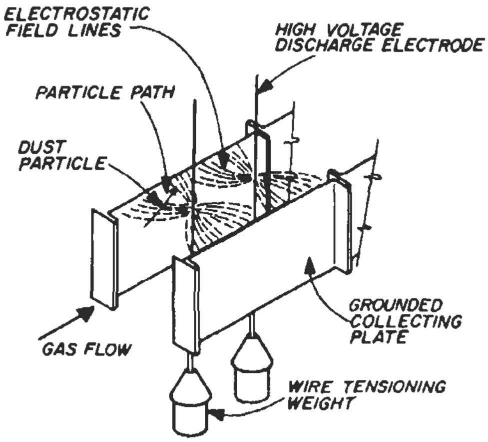
Cost Information

The following are cost ranges (expressed in third quarter 1995 dollars) for dry wire-pipe ESPs of conventional design under typical operating conditions, developed using EPA cost-estimating spreadsheets (EPA, 1996). Costs can be substantially higher than in the ranges shown for pollutants which require an unusually high level of control, or which require the ESP to be constructed of special materials such as stainless steel or titanium. In general, smaller units controlling a low concentration waste stream will not be as cost effective as a large unit cleaning a high pollutant load flow.

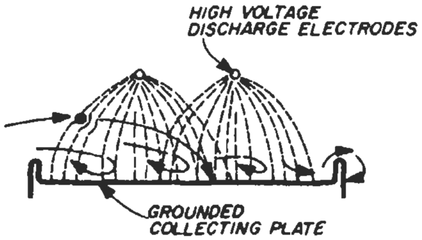
- Capital Cost: \$65,000 to \$400,000 per sm^3/sec (\$30 to \$190 per scfm)
- O&M Cost: \$10,000 to \$20,000 per sm^3/sec (\$5 to \$10 per scfm), annually
- Annualized Cost: \$20,000 to \$75,000 per sm^3/sec (\$10 to \$35 per scfm), annually
- Cost Effectiveness: \$55 to \$950 per metric ton (\$50 to \$850 per short ton)

Theory of Operation

In reading over this section, refer to Figures 10 through 12. Figure 10 shows a simplified view of how particles are collected in an ESP. An ESP is a particulate control device that uses electrical forces to move particles entrained within an exhaust stream onto collection surfaces. The entrained particles are given an electrical charge when they pass through a corona, a region where gaseous ions flow. The power system which supplies the power for the electric field and the charging of the particles consists of two major components: (1) the transformer-rectifier set (Figure 11), and (2) the auto-voltage feed-back control system. There may be one or more complete and independent power systems in a particular installation, depending upon such factors as unit size, the characteristics of the effluent, and efficiency requirements.



EFFECT OF ELECTROSTATIC CHARGING ON DUST PARTICLES



COLLECTING PARTICULATE ON COLLECTING SURFACE

Figure 10. Simplified view of how an ESP works.

Electrodes in the center of the flow lane are maintained at high voltage and generate the electrical field that forces the particles to the collector walls. In dry ESPs, the collectors are knocked, or "rapped," by various mechanical means to dislodge the particulate, which slides downward into a hopper where they are collected.

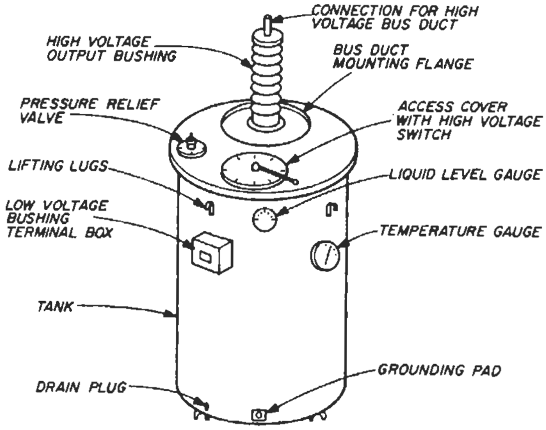


Figure 11. Illustrates the transformer-rectifier of the power supply unit.

Recently, dry wire-pipe ESPs are being cleaned acoustically with sonic horns (Flynn, 1999). The horns, typically cast metal horn bells, are usually powered by compressed air, and acoustic vibration is introduced by a vibrating metal plate that periodically interrupts the airflow (AWMA, 1992). As with a rapping system, the collected particulate slides downward into the hopper. The hopper is evacuated periodically, as it becomes full. Dust is removed through a valve into a dust-handling system, such as a pneumatic conveyor, and is then disposed of in an appropriate manner.

In a wire-pipe ESP, also called a tubular ESP, the exhaust gas flows vertically through conductive tubes, generally with many tubes operating in parallel. The tubes may be formed as a circular, square, or hexagonal honeycomb. Square and hexagonal pipes can be packed closer together than cylindrical pipes, reducing wasted space. Pipes are generally 7 to 30 cm (3 to 12 inches (in.)) in diameter and 1 to 4 meters (3 to 12 feet) in length. The high voltage electrodes are long wires or rigid "masts" suspended from a frame in the upper part of the ESP that run through the axis of each tube. Rigid electrodes are generally supported by both an upper and lower frame. In modern designs, sharp points are added to the electrodes, either at the entrance to a tube or along the entire length in the form of stars, to provide additional ionization sites (EPA, 1998; Flynn, 1999).

The power supplies for the ESP convert the industrial AC voltage (220 to 480 volts) to pulsating DC voltage in the range of 20,000 to 100,000 volts as needed. The voltage applied to the electrodes causes the gas between the electrodes to break down electrically, an action known as a "corona." The electrodes are usually given a negative polarity because a negative corona supports a higher voltage than does a positive corona before sparking occurs. The ions generated in the corona follow electric field lines from the electrode to the collection surfaces. Therefore, each electrode-pipe combination establishes a charging zone through which the particles must pass. As larger particles (>10 μm diameter) absorb many times more ions than small particles (>1 μm diameter), the electrical forces are much stronger on the large particles.

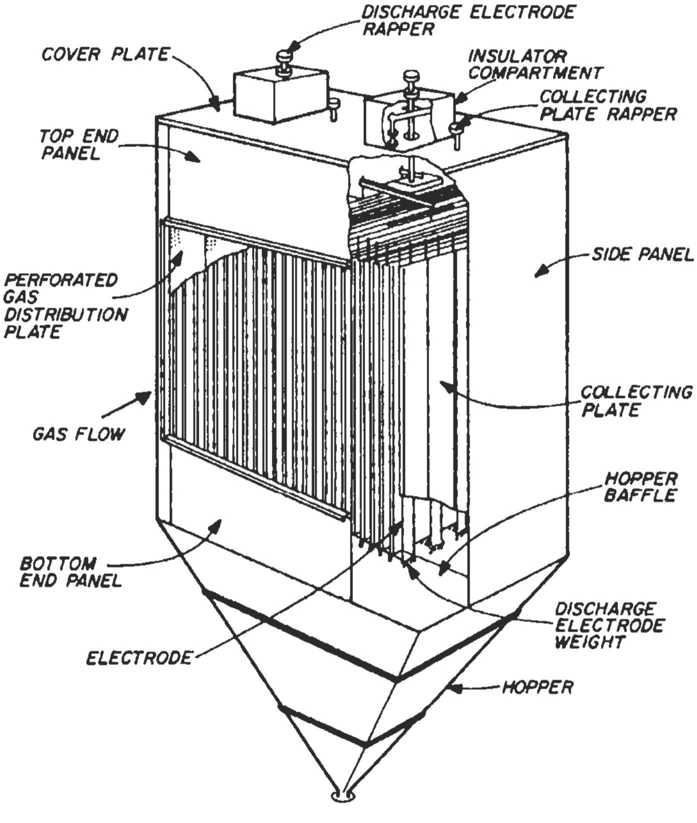


Figure 12. Internal design features of a conventional ESP.

Due to necessary clearances needed for nonelectrified internal components at the top of wire-plate ESPs, part of the gas is able to flow around the charging zones. This is called "sneakage" and places an upper limit on the collection efficiency.

Wire-pipe ESPs provide no sneakage paths around the collecting region, but field nonuniformities may allow some particles to avoid charging for a considerable fraction of the tube length. Dry wire-pipe ESPs are, however, subject to reentrainment of the collected material after cleaning the collectors with a rapping or acoustic mechanism, though the closed nature of the pipes increases chances for recollection. The internal configuration of a conventional ESP is illustrated in Figure 12.

Another major factor in the performance is the resistivity of the collected material. Because the particles form a continuous layer on the ESP pipes, all the ion current must pass through the layer to reach the ground. This current creates an electric field in the layer, and it can become large enough to cause local electrical breakdown. When this occurs, new ions of the wrong polarity are injected into the wire-pipe gap where they reduce the charge on the particles and may cause sparking. This breakdown condition is called "back corona." Back corona is prevalent when the resistivity of the layer is high, usually above 2×10^{11} ohm-cm. Above this level, the collection ability of the unit is reduced considerably because the severe back corona causes difficulties in charging the particles. Low resistivities will also cause problems. At resistivities below 10^8 ohm-cm, the particles are held on the collecting surface so loosely that general reentrainment, as well as that associated with collector cleaning, become much more severe. Hence, care must be taken in measuring or estimating resistivity because it is strongly affected by such variables as temperature, moisture, gas composition, particle composition, and surface characteristics.

Dry wire-pipe ESPs and other ESPs in general, because they act only on the particulate to be removed, and only minimally hinder flue gas flow, have very low pressure drops (typically less than 13 millimeters (mm) (0.5 in.) water column). As a result, energy requirements and operating costs tend to be low. They are capable of very high efficiencies, even for very small particles. They can be designed for a wide range of gas temperatures, and can handle high temperatures, up to 700°C (1300°F). Dry collection and disposal allows for easier handling. Operating costs are relatively low. ESPs are capable of operating under high pressure (to 1,030 kPa (150 psi)) or vacuum conditions. Relatively large gas flow rates can be effectively handled, though are uncommon in wire-pipe ESPs.

ESPs generally have high capital costs. Wire discharge electrodes (approximately 2.5 mm (0.01 in.) in diameter) are high-maintenance items. Corrosion can occur near the top of the wires because of air leakage and acid condensation. Also, long weighted wires tend to oscillate - the middle of the wire can approach the pipe, causing increased sparking and wear. Newer ESP designs are tending toward rigid electrodes, or "masts" which largely eliminate the drawbacks of using wire electrodes (Cooper and Alley, 1994; Flynn, 1999).

ESPs in general are not suited for use in processes which are highly variable because they are very sensitive to fluctuations in gas stream conditions (flow rates, temperatures, particulate and gas composition, and particulate loadings). ESPs are also difficult to install in sites which have limited space since ESPs must be relatively large to obtain the low gas velocities necessary for efficient PM collection. Certain particulates are difficult to collect due to extremely high or low resistivity characteristics. There can be an explosion hazard when treating combustible gases and/or collecting combustible particulates. Relatively sophisticated maintenance personnel are required, as well as special precautions to safeguard personnel from the high voltage. Dry ESPs are not recommended for removing sticky or moist particles. Ozone is produced by the negatively charged electrode during gas ionization (AWMA, 1992).

Dusts with very high resistivities (greater than 10^{10} ohm-cm) are also not well-suited for collection in dry ESPs. These particles are not easily charged, and thus are not easily collected. High-resistivity particles also form ash layers with very high voltage gradients on the collecting electrodes. Electrical breakdowns in these ash layers lead to injection of positively charged ions into the space between the discharge and collecting electrodes (back corona), thus reducing the charge on particles in this space and lowering collection efficiency. Fly ash from the combustion of low-sulfur coal typically has a high resistivity, and thus is difficult to collect.

Additional Information

References 39 through 46 provide additional information on ESPs, design and scale-up principles, as well as operational guidance.

WET ELECTROSTATIC PRECIPITATOR (ESP): WIRE-PIPE TYPE AND OTHERS

Applicable pollutants for this equipment are Particulate Matter (PM), including particulate matter less than or equal to 10 micrometers (μm) in aerodynamic diameter (PM_{10}), particulate matter less than or equal to 2.5 μm in aerodynamic diameter ($PM_{2.5}$), and hazardous air pollutants (HAPs) that are in particulate form, such as most metals (mercury is the notable exception, as a significant portion of emissions are in the form of elemental vapor). Wet ESPs are often used to control acid mists and can provide incidental control of volatile organic compounds.

Achievable Emission Limits Reductions

Typical new equipment design efficiencies are between 99 and 99.9%. Older existing equipment have a range of actual operating efficiencies of 90 to 99.9%.

While several factors determine ESP collection efficiency, ESP size is most important. Size determines treatment time, the longer a particle spends in the ESP, the greater its chance of being collected. Maximizing electric field strength will maximize ESP collection efficiency. Collection efficiency is also affected to some extent by dust resistivity, gas temperature, chemical composition (of the dust and the gas), and particle size distribution.

Typical Industrial Applications

Wet ESPs are used in situations for which dry ESPs are not suited, such as when the material to be collected is wet, sticky, flammable, explosive, or has a high resistivity. Also, as higher collection efficiencies have become more desirable, wet ESP applications have been increasing. Many older ESPs are of the wire-pipe design, consisting of a single tube placed on top of a smokestack. Wet pipe-type ESPs are commonly used by the textile industry, pulp and paper facilities, the metallurgical industry, including coke ovens, hazardous waste incinerators, and sulfuric acid manufacturing plants, among others, though other ESP types are employed as well (EPA, 1998; Flynn, 1999).

There are four types of precipitators which have used water in their operation:

- Intermittent-flush, parallel-plate precipitators
- Pipe-type precipitators
- Two-stage precipitators with intermittent flushing
- Continuous-spray, parallel-plate, wet electrostatic precipitators

The intermittent-flush, parallel-plate precipitator is built in either cylindrical or square housings and uses intermittent spraying to remove collected particles from the electrodes. The sprays are usually located just before or just after the precipitation fields. These sprays must not be applied at low pressure if the field strength is not to be interrupted. The intermittent-flush units are used on blast furnace applications.

The pipe-type units are usually built in a cylindrical housing having a header sheet near the inside top. In this header sheet are nested pipes which act as collecting electrodes. The discharge electrodes are supported above the header sheet and hang axially in the collecting pipes. Water is introduced onto this sheet and flows over leveled weir rings, flushing the collection walls with a thin film of water.

Charged particles are collected in the water film, neutralized, and drained off at the bottom of the unit. This type of unit is commonly used on scarfing operations, detarring, and sulfuric acid mist collection.The two-stage precipitator is used where low ozone generation is required. It is frequently applied in the cleaning of recirculated ventilation. The particles are charged in the first field and collected in a second noncorona stage. Intermittent-flush mechanical flushing is used to clean these units. They are not well suited for external industrial applications because they are capable of accepting only very light loadings. Water is used only sometimes with this type of equipment, and therefore it has been classified as a type of wet precipitator.

The continuous-spray, parallel-plate design of precipitator is constructed with a rectangular housing. The sprays used in this system to clean the electrostatic collecting plates are located above the electrostatic field. The fine water droplets formed by the sprays are electrostatically deposited on the collecting surfaces. This system does not disrupt the electrostatic field power but does provide a better wetting action than does the intermittent-spray or weir-type unit. The wetting is continuous and uniform. The continuous flushing eliminates wet/dry buildup problems experienced with other types of design. The weir-type systems do not distribute water evenly or continuously. Intermittent spray requires interruption of the gas cleaning cycle in most cases and can be used effectively only when deposit buildup is slow. The continuous wet precipitation has many broad and diverse applications. It is much more versatile and adaptable than its predecessors. An example of the construction is shown in Figure 13.

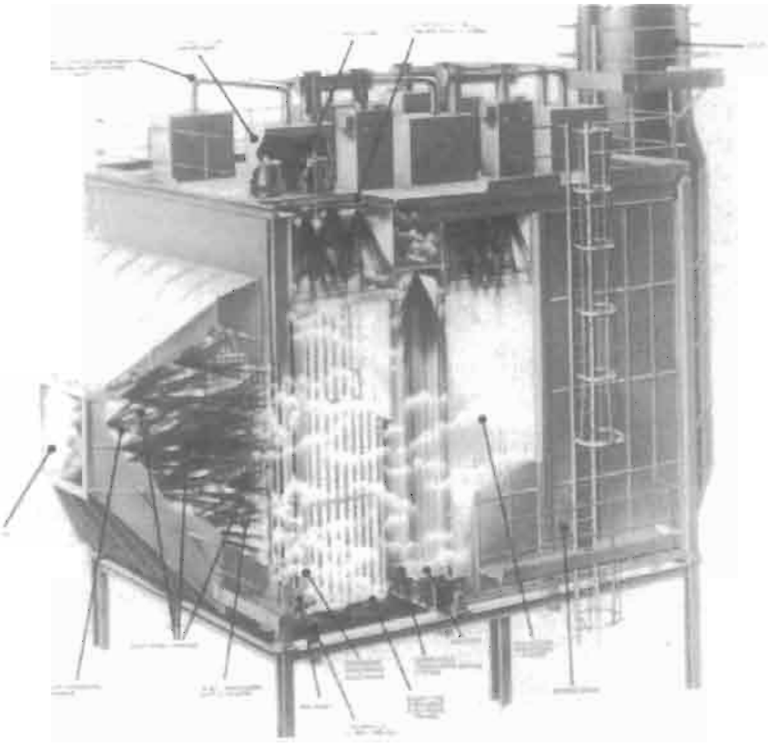


Figure 13. Continuous-spray, parallel-plate type of wet precipitator.

The continuous-spray design is ideal for any application in which there is a relatively light loading of submicron particles and/or condensed organics which form a submicron flame. Ordinarily, the only other piece of equipment applicable to this type of loading would be a high-energy scrubber. Since dust resistivity has no effect on the precipitator, it can be applied successfully on many very difficult dry applications. Continuous-spray wet electrostatic precipitators have been applied on many applications, including:

- Soderberg aluminum reduction cells for simultaneous removal of aluminum oxides, solid and gaseous fluoride, tar mist (condensible hydrocarbons), and SO_2,
- On carbon anode baking furnaces (ring furnaces) for removal of carbon particles, tar mists, and SO_2,
- On fiberglass resin application sections and forming lines to remove short particles of glass fiber, phenolic resins, and tars,
- On molybdenum sulfate roasting, downstream of a scrubber, to remove ammonium sulfite and sulfate aerosols which form in the ammonia scrubbing stage, and SO_2,
- On phosphate rock driers for removal of submicron particulate and SO_2,
- On coke batteries for the removal of fine carbon particles, condensible hydrocarbons, and SO_2

This precipitator is also applicable on all the following products:

- Acid mists and aerosols
- High-resistivity particulates
- Condensed particles or gaseous
- Oil- and tar-contaminated particles
- Oil mists and tar fogs

This particular design has a flexibility and range of applications which far exceed most other designs.

Emission Stream Characteristics

Air Flow: Typical gas flow rates for wet wire-pipe ESPs are 0.5 to 50 standard cubic meters per second (sm^3/sec) (1,000 to 100,000 standard cubic feet per minute (scfm)) (Flynn, 1999).

Temperature: Wet wire-pipe ESPs are limited to operating at temperatures lower than approximately 80 to 90°C (170 to 190°F) (EPA, 1998; Flynn, 1999).

Pollutant Loading: Typical inlet concentrations to a wire-pipe ESP are 1 to 10 grams per cubic meter (g/m^3) (0.5 to 5 gr/ft^3). It is common to pretreat a waste stream, usually with a wet spray or scrubber, to bring the stream temperature and pollutant loading into a manageable range. Highly toxic flows with concentrations well below 1 g/m^3 (0.5 gr/ft^3) are also sometimes controlled with ESPs (Flynn, 1999).

Other Considerations: Dust resistivity is not a factor for wet ESPs, because of the high humidity atmosphere which lowers the resistivity of most materials. Particle size is much less of a factor for wet ESPs, compared to dry ESPs. Much smaller particles can be efficiently collected by wet ESPs due to the lack of resistivity concerns and the reduced reentrainment (Flynn, 1999).

Emission Stream Pretreatment Requirements

When the pollutant loading is exceptionally high or consists of relatively large particles ($> 2\ \mu$m), venturi scrubbers or spray chambers may be used to reduce the load on the ESP. Much larger particles ($> 10\ \mu$m) are controlled with mechanical collectors such as cyclones. Gas conditioning equipment to reduce both inlet concentration and gas temperature is occasionally used as part of the original design of wet ESPs (AWMA, 1992; Flynn, 1999).

Cost Information

The following are cost ranges (expressed in third quarter 1995 dollars) for wire-pipe ESPs of conventional design under typical operating conditions, developed using EPA cost estimating spreadsheets for dry wire-pipe ESPs with adjustments made to reflect wet wire-pipe ESPs (EPA, 1996). Costs can be substantially higher than in the ranges shown for pollutants which require an unusually high level of control, or which require the ESP to be constructed of special materials such as titanium. Capital and operating costs are generally higher due to noncorrosive materials requirements, increased water usage, and treatment and disposal of wet effluent. In most cases, smaller units controlling a low concentration waste stream will not be as cost effective as a large unit cleaning a high pollutant load flow (EPA, 1998).

- *Capital Cost*: $125,000 to $640,000 per sm^3/sec ($60 to $300 per scfm)
- *O&M Cost*: $15,000 to $25,000 per sm^3/sec ($7 to $12 per scfm), annually
- *Annualized Cost*: $32,000 to $125,000 per sm^3/s ($15 to $60 per scfm), annually
- *Cost Effectiveness*: $90 to $950 per metric ton ($80 to $850 per ton)

Theory of Operation

An ESP is a particulate control device that uses electrical forces to move particles entrained within an exhaust stream onto collection surfaces. The basic theory has already been described under dry ESPs, but a brief summary here is included, with notable differences between the equipment. The entrained particles are given an electrical charge when they pass through a corona, a region where gaseous ions flow. Electrodes in the center of the flow lane are maintained at high voltage and generate the electrical field that forces the particles to the collector walls. In wet ESPs, the collectors are either intermittently or continuously washed by a spray of liquid, usually water. The collection hoppers used by dry ESPs are replaced with a drainage system. The wet effluent is collected, and often treated on-site (EPA, 1998).

In a wire-pipe ESP, also called a tubular ESP, the exhaust gas flows vertically through conductive tubes, generally with many tubes operating in parallel. The tubes may be formed as a circular, square, or hexagonal honeycomb. Square and hexagonal pipes can be packed closer together than cylindrical pipes, reducing wasted space. Pipes are generally 7 to 30 cm (3 to 12 inches (in.)) in diameter and 1 to 4 m (3 to 12 feet) in length. The high voltage electrodes are long wires or rigid "masts" suspended from a frame in the upper part of the ESP that run through the axis of each tube. Rigid electrodes are generally supported by both an upper and lower frame. In modern designs, sharp points are added to the electrodes, either at the entrance to a tube or along the entire length in the form of stars, to provide additional ionization sites.

The power supplies for the ESP convert the industrial AC voltage (220 to 480 volts) to pulsating DC voltage in the range of 20,000 to 100,000 volts as needed. The voltage applied to the electrodes causes the gas between the electrodes to break down electrically, an action known as a "corona." The electrodes are usually given a negative polarity because a negative corona supports a higher voltage than does a positive corona before sparking occurs. The ions generated in the corona follow electric field lines from the electrode to the collecting pipe. Therefore, each electrode-pipe combination establishes a charging zone through which the particles must pass. As larger particles (> 10 μm diameter) absorb many times more ions than small particles (> 1 μm diameter), the electrical forces are much stronger on the large particles.

Due to necessary clearances needed for nonelectrified internal components at the top of wire-pipe ESPs, part of the gas is able to flow around the charging zones. This is called "sneakage" and places an upper limit on the collection efficiency. Wire-pipe ESPs provide no sneakage paths around the collecting region, but field nonuniformities may allow some particles to avoid charging for a considerable fraction of the tube length. Wet ESPs require a source of wash water to be injected or sprayed near the top of the collector pipes either continuously or at timed intervals. This wash system replaces the rapping mechanism usually used by dry ESPs. The water flows with the collected particles into a sump from which the fluid is pumped or drained. A portion of the fluid may be recycled to reduce the total amount of water required. The remainder is pumped into a settling pond or passed through a dewatering stage, with subsequent disposal of the sludge.

Unlike dry ESPs, resistivity of the collected material is generally not a major factor in performance. Because of the high humidity in a wet ESP, the resistivity of particles is lowered, eliminating the "back corona" condition. The frequent washing of the pipes also limits particle buildup on the collectors.

The power consumed to operate a wet electrostatic precipitator is much less than that required by most other methods of control. There are four areas in which power is consumed: (1) electrostatic power, (2) fan power, (3) insulator heating power, and (4) pump power. The total electrostatic power input required for operation is 0.8 to 1.0 kW/1,000 ft^3 of collection area. A comparable piece of equipment is a venturi scrubber with 50-in.wg pressure drop. The power required for this installation would be 6 to 7 kW/1,000 cfm. This would mean that approximately seven times the power would be needed to achieve the same amount of cleaning with a venturi scrubber as opposed to using a precipitator.

Since power is a substantial component of the fixed operating cost of a unit, the operating cost would run approximately seven times more on a scrubber installation. The installation costs of a hot-rolled steel precipitator to handle 100,000 cfm would be between \$3.50 and \$4.50/cfm as opposed to \$1.40 to \$1.80/cfm for a venturi scrubbing system. Although the initial capital expenditure is high for the precipitator, if the total operating and capital costs are amortized over an acceptable period of time, 8 to 10 years, the precipitator will prove to be the more economically feasible choice because of its low operating and maintenance costs.

The advantages of this equipment are as follows. Wet wire-pipe ESPs and other ESPs in general, because they act only on the particulate to be removed, and only minimally hinder flue gas flow, have very low pressure drops (typically less than 13 millimeters (mm) (0.5 in.) water column). As a result, energy requirements and operating costs tend to be low. They are capable of very high efficiencies, even for very small particles. Operating costs are relatively low. ESPs are capable of operating under high pressure (to 1,030 kPa (150 psi)) or vacuum conditions, and relatively large gas flow rates can be effectively handled (AWMA, 1992).

Another advantage is that wet ESPs can collect sticky particles and mists, as well as highly resistive or explosive dusts. The continuous or intermittent washing with a liquid eliminates the reentrainment of particles due to rapping which dry ESPs are subject to. The humid atmosphere that results from the washing in a wet ESP enables them to collect high resistivity particles, absorb gases or cause pollutants to condense, and cools and conditions the gas stream. Liquid particles or aerosols present in the gas stream are collected along with particles and provide another means of rinsing the collection electrodes.

Wet wire-pipe ESPs have the additional advantages of reducing "sneakage" by passing the entire gas stream through the collection field, and the ability to be tightly sealed to prevent leaks of material, especially valuable or hazardous materials.

Disadvantages are as follows. ESPs generally have high capital costs. Wire discharge electrodes (approximately 2.5 mm (0.01 in.) in diameter) are high-maintenance items. Corrosion can occur near the top of the wires because of air leakage and acid condensation. Also, long weighted wires tend to oscillate - the middle of the wire can approach the pipe, causing increased sparking and wear. Newer ESP designs are tending toward rigid electrodes, or "masts" which largely eliminate the drawbacks of using wire electrodes (see Cooper and Alley, 1994; Flynn, 1999).

ESPs in general are not suited for use in processes which are highly variable because they are very sensitive to fluctuations in gas stream conditions (flow rates, temperatures, particulate and gas composition, and particulate loadings). ESPs are also difficult to install in sites which have limited space since ESPs must be relatively large to obtain the low gas velocities necessary for efficient PM collection. Relatively sophisticated maintenance personnel are required, as well as special precautions to safeguard personnel from the high voltage. Ozone is produced by the negatively charged electrode during gas ionization.

Wet ESPs add to the complexity of a wash system, because of the fact that the resulting slurry must be handled more carefully than a dry product, and in many cases requires treatment, especially if the dust can be sold or recycled. Wet ESPs are limited to operating at stream temperatures under approximately 80 to 90°C (170 to 190°F), and generally must be constructed of noncorrosive materials (EPA, 1998; Flynn, 1999).

For wet ESPs, consideration must be given to handling wastewaters. For simple systems with innocuous dusts, water with particles collected by the ESP may be discharged from the ESP system to a solids-removing clarifier (either dedicated to the ESP or part of the plant wastewater treatment system) and then to final disposal. More complicated systems may require skimming and sludge removal, clarification in dedicated equipment, pH adjustment, and/or treatment to remove dissolved solids. Spray water from an ESP preconditioner may be treated separately from the water used to wash the ESP collecting pipes so that the cleaner of the two treated water streams may be returned to the ESP. Recirculation of treated water to the ESP may approach 100 percent (AWMA, 1992).

Additional Information

References 47 through 58 provide additional information on wet ESPs, design, and scale-up principles, as well as operational guidance.

VENTURI SCRUBBERS

This type of technology is a part of the group of air pollution controls collectively referred to as "wet scrubbers." Venturi scrubbers are also known as venturi jet scrubbers, gas-atomizing spray scrubbers, and ejector-venturi scrubbers. The technology is based on the removal of air pollutants by inertial and diffusional interception.

Venturi scrubbers are primarily used to control particulate matter (PM), including PM less than or equal to 10 micrometers (μm) in aerodynamic diameter (PM_{10}), and PM less than or equal to 2.5 μm in aerodynamic diameter ($PM_{2.5}$). Though capable of some incidental control of volatile organic compounds (VOC), generally venturi scrubbers are limited to control PM and high solubility gases (EPA, 1992; EPA, 1996).

Achievable Emission Limits Reductions

Venturi scrubbers PM collection efficiencies range from 70 to greater than 99 percent, depending upon the application. Collection efficiencies are generally higher for PM with aerodynamic diameters of approximately 0.5 to 5 gm. Some venturi scrubbers are designed with an adjustable throat to control the velocity of the gas stream and the pressure drop. Increasing the venturi scrubber efficiency requires increasing the pressure drop which, in turn, increases the energy consumption.

Typical Industrial Applications

Venturi scrubbers have been applied to control PM emissions from utility, industrial, commercial, and institutional boilers fired with coal, oil, wood, and liquid waste. They have also been applied to control emission sources in the chemical, mineral products, wood, pulp and paper, rock products, and asphalt manufacturing industries; lead, aluminum, iron and steel, and gray iron production industries; and to municipal solid waste incinerators. Typically, venturi scrubbers are applied where it is necessary to obtain high collection efficiencies for fine PM. Thus, they are applicable to controlling emission sources with high concentrations of submicron PM.

Emission Stream Characteristics

Air Flow: Typical gas flow rates for a single-throat venturi scrubber unit are 0.2 to

28 standard cubic meters per second (sm^3/sec) (500 to 60,000 standard cubic feet per minute (scfm)). Flows higher than this range use either multiple venturi scrubbers in parallel or a multiple throated venturi.

Temperature: Inlet gas temperatures are usually in the range of 4 to 370° C (40 to 700° F) (see Avallone, 1996).

Pollutant Loading: Waste gas pollutant loadings can range from 1 to 115 grams per standard cubic meter (g/sm^3) (0.1 to 50 grains per standard cubic foot (gr/scf)) (Turner, 1999; Dixit, 1999).

Other Considerations: In situations where waste gas contains both particulates and gases to be controlled, venturi scrubbers are sometimes used as a pretreatment device, removing PM to prevent clogging of a downstream device, such as a packed bed scrubber, which is designed to collect primarily gaseous pollutants.

Emission Stream Pretreatment Requirements

Generally, no pretreatment is required for venturi scrubbers, though in some cases the waste gas is quenched to reduce the temperature for scrubbers made of materials affected by high temperatures (see Dixit, 1999).

Cost Information

The following are cost ranges (expressed in third quarter 1995 dollars) for venturi wet scrubbers of conventional design under typical operating conditions, developed using EPA cost estimating spreadsheets (EPA, 1996) and referenced to the volumetric flow rate of the waste stream treated. For purposes of calculating the example cost effectiveness, the pollutant is assumed to be PM at an inlet loading of approximately 7 g/sm^3 (3 gr/scf). The costs do not include costs for post-treatment or disposal of used solvent or waste. Actual costs can be substantially higher than in the ranges shown for applications which require expensive materials, solvents, or treatment methods. As a rule, smaller units controlling a low concentration waste stream will be much more expensive (per unit volumetric flow rate) than a large unit cleaning a high pollutant load flow.

- Capital Cost: \$6,700 to \$59,000 per sm^3/sec (\$3.20 to \$28 per scfm)
- O & M Cost: \$8,700 to \$250,000 per sm^3/sec (\$4.10 to \$119 per scfm), annually
- Annualized Cost: \$9,700 to \$260,000 per sm^3/sec (\$4.60 to \$123 per scfm), annually
- Cost Effectiveness: \$84 to \$2,300 per metric ton (\$76 to \$2,100 per short ton), annualized cost per ton per year of pollutant controlled

Theory of Operation

A venturi scrubber accelerates the waste gas stream to atomize the scrubbing liquid and to improve gas-liquid contact. In a venturi scrubber, a "throat" section is built into the duct that forces the gas stream to accelerate as the duct narrows and then expands (refer to Figure 14). As the gas enters the venturi throat, both gas velocity and turbulence increase.

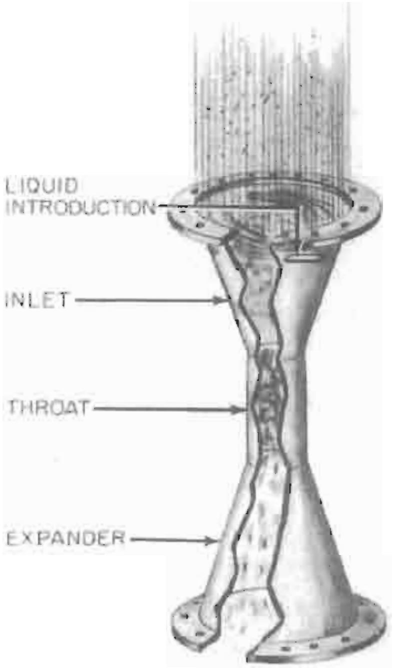


Figure 14. Typical venturi scrubber configuration.

Depending upon the scrubber design, the scrubbing liquid is sprayed into the gas stream before the gas encounters the venturi throat, or in the throat, or upwards against the gas flow in the throat. The scrubbing liquid is then atomized into small droplets by the turbulence in the throat and droplet-particle interaction is increased. Some designs use supplemental hydraulically or pneumatically atomized sprays to augment droplet creation. The disadvantage of these designs is that clean liquid feed is required to avoid clogging (EPA, 1998; AWMA, 1992; Corbitt, 1990).

After the throat section, the mixture decelerates, and further impacts occur causing the droplets to agglomerate. Once the particles have been captured by the liquid, the wetted PM and excess liquid droplets are separated from the gas stream by an entrainment section which usually consists of a cyclonic separator and/or a mist eliminator (EPA, 1998; Corbitt, 1990).

Current designs for venturi scrubbers generally use the vertical downflow of gas through the venturi throat and incorporate three features: (1) a "wet-approach" or "flooded-wall" entry section to avoid a dust buildup at a wet-dry junction; (2) an adjustable throat for the venturi throat to provide for adjustment of the gas velocity and the pressure drop; and (3) a "flooded" elbow located below the venturi and ahead of the entrainment separator, to reduce wear by abrasive particles. The venturi throat is sometimes fitted with a refractory lining to resist abrasion by dust particles. Some examples of other configurations are shown in Figures 15 and 16. Figure 15 illustrates a rectangular venturi scrubber configuration. Figure 16 shows a variable cylindrical venturi scrubber design. Still another example is a nonwetted approach, variable rectangular venturi scrubber shown in Figure 17. A wetted approach, variable rectangular venturi scrubber is shown in Figure 18. A variable venturi scrubber for flyash and sulfur dioxide removal is shown in Figure 19. Specific configurations are oftentimes established based upon available floor and headspace. As already noted, this is a versatile control technology with the dual function of removing PM and highly soluble gaseous pollutants. Some VOCs fall into the soluble gas category.

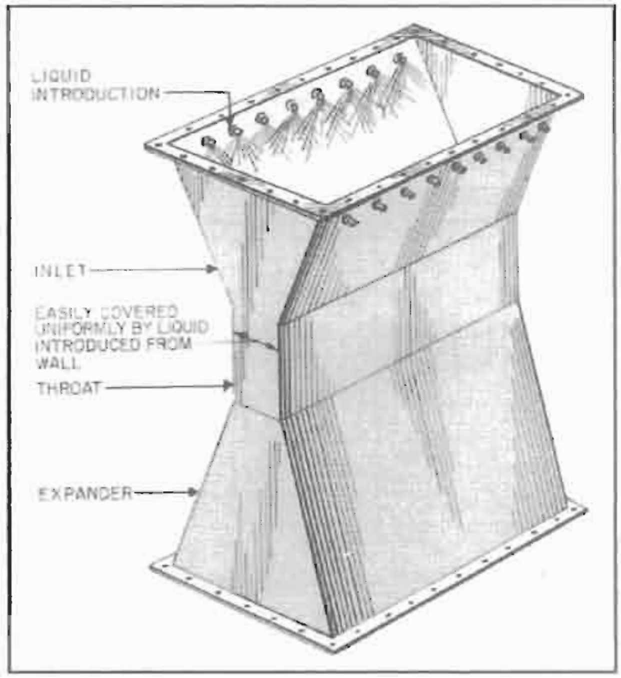


Figure 15. Rectangular venturi scrubber.

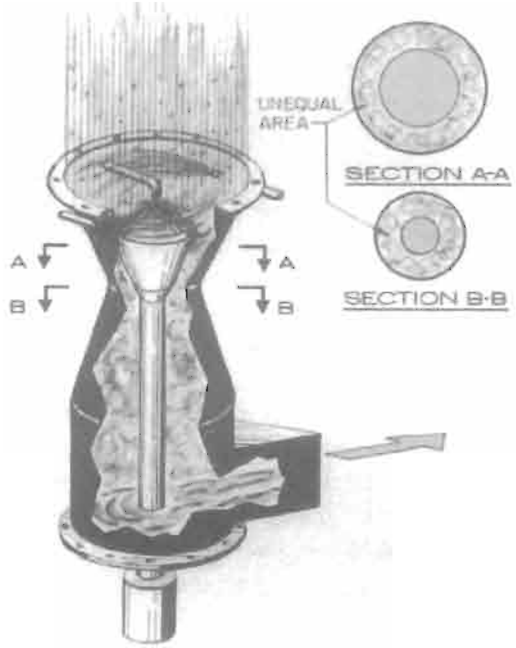


Figure 16. Variable cylindrical venturi scrubber.

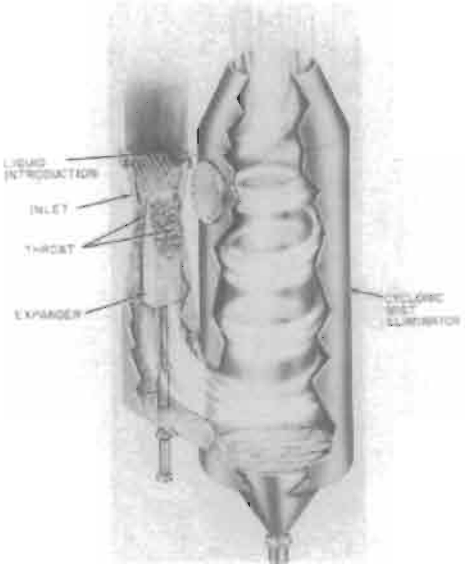


Figure 17. Nonwetted approach, variable rectangular venturi scrubber.

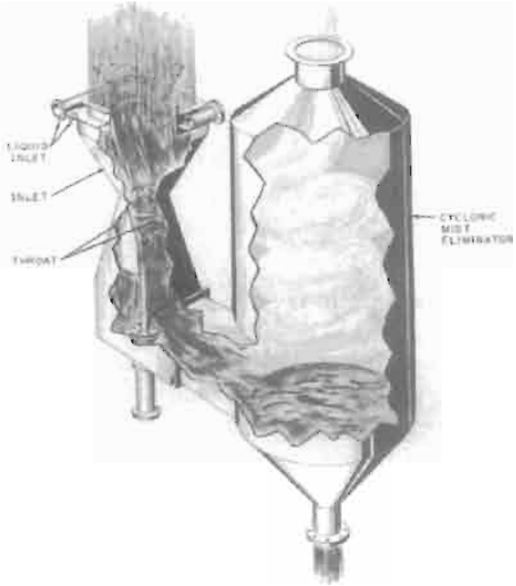


Figure 18. Wetted approach, variable rectangular venturi scrubber.

Figure 19. Variable venturi scrubber for flyash and sulfur dioxide removal.

Some of the advantages of venturi scrubbers include:

- Capable of handling flammable and explosive dusts with little risk;
- Can handle mists;
- Relatively low maintenance;
- Simple in design and easy to install;
- Collection efficiency can be varied;
- Provides cooling for hot gases; and
- Corrosive gases and dusts can be neutralized.

Disadvantages of impingement plate scrubbers include:

- Effluent liquid can create water pollution problems;
- Waste product collected wet;
- High potential for corrosion problems;
- Protection against freezing required;
- Off gas may require reheating to avoid visible plume;
- Collected PM may be contaminated, and may not be recyclable; and
- Disposal of waste sludge may be very expensive.

For PM applications, wet scrubbers generate waste in the form of a slurry or wet sludge. This creates the need for both wastewater treatment and solid waste disposal. Initially, the slurry is treated to separate the solid waste from the water. The treated water can then be reused or discharged. Once the water is removed, the remaining waste will be in the form of a solid or sludge.

If the solid waste is inert and nontoxic, it can generally be landfilled. Hazardous wastes will have more stringent procedures for disposal. In some cases, the solid waste may have value and can be sold or recycled.

Additional Information

References 59 through 67 provide additional information on venturi scrubbers, design and scale-up principles, as well as operational guidance.

ORIFICE SCRUBBER

This type of technology is a part of the group of air pollution controls collectively referred to as "wet scrubbers." Orifice scrubbers are also known as self-induced spray scrubbers, gas-induced spray scrubbers, and entrainment scrubbers. The operating principle is based on the removal of air pollutants by inertial and diffusional interception.

Orifice scrubbers are primarily used to control particulate matter (PM), including particulate matter less than or equal to 10 micrometers (μm) in aerodynamic diameter, particulate matter less than or equal to 2.5 μm in aerodynamic diameter, down to particles with an aerodynamic diameter of approximately 2 μm.

Achievable Emission Limits Reductions

Orifice scrubber collection efficiencies range from 80 to 99 percent, depending upon the application and scrubber design. This type of scrubber relies on inertial and diffusional interception for PM collection. Some orifice scrubbers are designed with adjustable orifices to control the velocity of the gas stream.

Typical Industrial Applications

Orifice scrubbers are used in industrial applications including food processing and packaging (cereal, flour, rice, salt, sugar, etc.); pharmaceutical processing and packaging; and the manufacture of chemicals, rubber and plastics, ceramics, and fertilizer. Processes controlled include dryers, cookers, crushing and grinding operations, spraying (pill coating, ceramic glazing), ventilation (bin vents, dumping operations), and material handling (transfer stations, mixing, dumping, packaging). Orifice scrubbers can be built as high-energy units, but most devices are designed for low-energy service.

Emission Stream Characteristics

Air Flow: Typical gas flow rates for an orifice scrubber unit are 0.47 to 24 standard cubic meters per second (sm^3/sec) (1,000 to 50,000 standard cubic feet per minute (scfm)).

Temperature: In general, orifice scrubbers can treat waste gases up to approximately 150°C (300°F).

Pollutant Loading: Orifice scrubbers can accept waste flows with PM loadings up to 23 grams per standard cubic meter (g/sm^3) or 10 grains per standard cubic foot (gr/scf), or higher, depending upon the nature of the PM being controlled.

Emission Stream Pretreatment Requirements

Orifice scrubbers generally do not require precleaning, unless the waste gas contains large pieces of debris. Precooling may be necessary for high temperature waste gas flows which increase the evaporation of the scrubbing liquid.

Cost Information

The following are cost ranges (expressed in third quarter 1995 dollars) for orifice wet scrubbers of conventional design under typical operating conditions, adapted from EPA cost estimating spreadsheets (EPA, 1996) and referenced to the volumetric flow rate of the waste stream treated. For purposes of calculating the example cost effectiveness, the pollutant is PM at a loading of approximately 7 g/sm^3 (3 gr/scf). The costs do not include costs for post-treatment or disposal of used solvent or waste. Costs can be higher than in the ranges shown for applications which require expensive materials, solvents, or treatment methods. As a rule, smaller units controlling a low concentration waste stream will be more expensive (per unit volumetric flow rate) than a large unit cleaning a high pollutant load flow.

- Capital Cost: $10,000 to $36,000 per sm^3/sec ($5.00 to $17 per scfm)
- O&M Cost: $8,000 to $149,000 per sm^3/sec ($3.80 to $70 per scfm), annually
- Annualized Cost: $9,500 to $154,000 per sm^3/sec ($4.50 to $73 per scfm), annually
- Cost Effectiveness: $88 to $1,400 per metric ton ($80 to $1,300 per short ton), annualized cost per ton per year of pollutant controlled

Theory of Operation

Orifice scrubbers form a category of gas-atomized spray scrubbers in which a tube or a duct of some other shape forms the gas-liquid contacting zone. The particle-laden gas stream is forced to pass over the surface of a pool of scrubbing liquid at high velocity, entraining it as droplets as it enters an orifice. The gas stream flowing through the orifice atomizes the entrained liquid droplets in essentially the same manner as a venturi scrubber. As the gas velocity and turbulence increases with the passing of the gas through the narrow orifice, the interaction between the PM and atomized liquid droplets also increases. Particulate matter and droplets are then removed from the gas stream by impingement on a series of baffles that the gas stream encounters after exiting the orifice. The collected liquid and PM drain from the baffles back into the liquid pool below the orifice.

The scrubbing liquid is fed into the pool at the bottom of the scrubber and later recirculated from the entrainment separator baffles by gravity instead of being circulated by a pump as in venturi scrubbers. Many devices using contactor ducts of various shapes are offered commercially. The principal advantage of this scrubber is the elimination of a pump for recirculation of the scrubbing liquid.

Advantages of orifice scrubbers include:

- Can handle flammable and explosive dusts with little risk;
- Can handle mists;
- Relatively low water recirculation rate;

- Collection efficiency can be varied;
- Provides cooling for hot gases; and
- Corrosive gases and dusts can be neutralized.

Disadvantages of orifice scrubbers include:

- Effluent liquid can create water pollution problems;
- Waste product collected wet;
- High potential for corrosion problems;
- Protection against freezing required;
- Off-gas may require reheating to avoid visible plume;
- Collected PM may be contaminated, and may not be recyclable; and
- Disposal of waste sludge may be very expensive.

For PM applications, wet scrubbers generate waste in the form of a slurry or wet sludge. This creates the need for both wastewater treatment and solid waste disposal. Initially, the slurry is treated to separate the solid waste from the water. The treated water can then be reused or discharged. Once the water is removed, the remaining waste will be in the form of a solid or sludge. If the solid waste is inert and nontoxic, it can generally be landfilled. Hazardous wastes will have more stringent procedures for disposal. In some cases, the solid waste may have value and can be sold or recycled.

Orifice scrubbers usually have low liquid demands, since they use the same scrubbing liquid for extended periods of time. Because orifice scrubbers are relatively simple in design and usually have few moving parts, the major maintenance concern is the removal of the sludge which collects at the bottom of the scrubber. Orifice scrubbers rarely drain continually from the bottom because a static pool of scrubbing liquid is needed at all times. Therefore, the sludge is usually removed with a sludge ejector that operates like a conveyer belt. As the sludge settles to the bottom of the scrubber, it lands on the ejector and is conveyed up and out of the scrubber.

Orifice scrubbers are relatively simple in design and usually have few moving parts, aside from a fan and possibly an automatic sludge ejector.

Additional Information

References 68 through 72 provide additional information on orifice scrubbers, design and scale-up principles, as well as operational guidance.

CONDENSATION SCRUBBERS

This type of technology is a part of the group of air pollution controls collectively referred to as "wet scrubbers." The removal of air pollutants is achieved by the use of condensation to increase pollutant particle size, followed by inertial interception. Condensation scrubbers are typically intended to control fine particulate matter (PM) with an aerodynamic diameter of between approximately 0.25 and 1.0 micrometers (μm).

Achievable Emission Limits Reductions

Collection efficiencies of greater than 99 percent have been reported for particulate emissions, based on study results. Note list of references cited at the end of this subsection for detailed studies.

Typical Industrial Applications

Condensation scrubbers are intended for use in controlling fine PM-containing waste-gas streams, and are designed specifically to capture fine PM which has escaped a primary PM control device. The technology is suitable for both new and retrofit installations.

Condensation scrubbing systems are a relatively new technology and are not yet generally commercially available. It may be argued that this is a pollution prevention type of technology since it replaces other approaches to controlling very fine PM, although the primary role is end-of-pipe treatment.

Emission Stream Characteristics

Air Flow: Typical air flows are on the order of 10 standard cubic meters per second (sm^3/sec) or 21,000 standard cubic feet per minute (scfm).

Temperature: The waste gas entering a condensation scrubber is generally cooled to saturation conditions, approximately 20 to 26°C (68 to 78°F).

Pollutant Loading: Pollutant loading is dependent upon the control effectiveness for fine PM of the primary PM control system. Fine PM may, in some cases, comprise up to 90 percent of the total mass of PM emissions from a combustion source, and many primary control technologies have relatively low collection efficiencies for fine PM.

Other Considerations: The fine fraction of PM emissions from a combustion source often contains cadmium and other metals. Use of a condensation scrubber to capture fine PM may provide an effective method of reducing the emission of metals.

Emission Stream Pretreatment Requirements

For PM control from combustion sources, the flue gas enters a coagulation area (e.g., ductwork, a chamber, or a cyclone) to reduce the number of ultrafine particles, and then a gas conditioner to cool the gas to a suitable temperature and saturation state. This is generally accomplished by means of a waste heat recovery heat exchanger to reduce the temperature of the flue gas or by spraying water directly into the hot flue gas stream.

It is usually not practical or cost effective to cool flue gases to temperatures below ambient values. Condensation scrubbers are generally intended to be used downstream of another scrubber (e.g., a venturi scrubber) which has already removed PM > 1.0 μm aerodynamic diameter.

Cost Information

The following provides cost information (expressed in fourth quarter 1993 dollars) for retrofitting an existing scrubber system with a condensation scrubber under typical operating conditions, adapted from EPA cost-estimating spreadsheets (EPA, 1996) and referenced to the volumetric flow rate of the waste stream treated. For purposes of calculating the example cost effectiveness, the pollutant is PM at a loading of approximately 7 grams per standard cubic meter (g/sm^3) or 3 grains per standard cubic foot (gr/scf). The costs do not include costs for post-treatment or disposal of used solvent or waste.

- Capital Cost: $13,000 per sm^3/sec ($6.00 per scfm)
- O&M Cost: $5,300 per sm^3/sec ($2.50 per scfm), annually
- Annualized Cost: $7,000 per sm^3/sec ($3.40 per scfm), annually
- Cost Effectiveness: $65 per metric ton ($59 per short ton), annualized cost per ton per year of pollutant controlled

Theory of Operation

Condensation scrubbing is a relatively recent development in wet scrubber technology. Most conventional scrubbers rely on the mechanisms of impaction and diffusion to achieve contact between the PM and liquid droplets. In a condensation scrubber, the PM act as condensation nuclei for the formation of droplets. Generally, condensation scrubbing depends on first establishing saturation conditions in the gas stream. Once saturation is achieved, steam is injected into the gas stream. The steam creates a condition of supersaturation and leads to condensation of water on the fine PM in the gas stream. The large condensed droplets are then removed by one of several conventional devices, such as a high efficiency mist eliminator.

Advantages of condensation scrubbers include:
- Can handle flammable and explosive dusts with little risk;
- Can handle fine PM;
- Collection efficiency can be varied; and
- Corrosive gases and dusts can be neutralized.

Disadvantages of condensation scrubbers include:
- Effluent liquid can create water pollution problems;
- Waste product collected wet;
- High potential for corrosion problems;
- Protection against freezing required;
- Off-gas may require reheating to avoid visible plume;
- Collected particulate may be contaminated, and may not be recyclable; and
- Disposal of waste sludge may be very expensive.

For PM applications, wet scrubbers generate waste in the form of a slurry. This creates the need for both wastewater treatment and solid waste disposal. Initially, the slurry is treated to separate the solid waste from the water. The treated water can then be reused or discharged.

Additional Information

References 73 through 76 provide additional information on condensation scrubbers, design and scale-up principles, as well as operational guidance.

METHODS FOR CLEANING GASEOUS POLLUTANTS

An overview of several technologies is presented in this section. Each of these technologies are point source controls for handling gaseous pollutants. They are all well-established methods of gas cleaning, some based on many decades of industry practice.

PACKED TOWER AND ABSORPTION

This type of technology is a part of the group of air pollution controls collectively referred to as "wet scrubbers." When used to control inorganic gases, they may also be referred to as "acid gas scrubbers." The technology is based on the removal of air pollutants by inertial or diffusional impaction, reaction with a sorbent or reagent slurry, or absorption into liquid solvent. This is an older technology, with much of the classical development work having been done in the 1920s and 30s. It is a very important technology, having been applied so widely, with both standard and newer applications still evolving.

Scrubbers used in air pollution control are available in a wide range of types and sizes. They are used mainly to eliminate one or more objectionable gaseous or particulate components from a gas stream. Their principle of design is based on mass transfer (diffusion), inertial impaction, or electrostatic attraction. In mass transfer, gaseous components are dissolved in liquid. When gas and liquid are brought into intimate contact, the concentration gradient is established between two phases, and diffusion takes place. Objectionable components, higher in concentration in the gaseous phase, are transferred to the liquid phase, having a lower concentration. During this diffusion process, solute is transferred in liquid with or without chemical reaction.

When fluid passes over a solid surface, its velocity at the surface of the solid is zero. The velocity of the fluid thus changes from that in the bulk stream to the solid surface across which it is flowing. The velocity rises sharply in a zone between the interface and a very small distance perpendicular to the solid interface. This small zone is called the laminar region. The fluid in the bulk stream can be in the turbulent region. The zone between the laminar and turbulent regions is known as the transition or buffer region. Intimate contact between gas and liquid is established in the laminar region over solids known as packing. The laminar region consists of stagnant gas and liquid films. As diffusing fluid passes from the main stream, it has to pass through the main stream, buffer zone, and laminar regions. Diffusion through the laminar film is on a molecular scale and is known as molecular diffusion. Molecules in gases move in random directions, and as they do so, they collide against each other. The resultant distance is, therefore, very small; hence, molecular diffusion is a slow process. If, on the other hand, the temperature of the gas is higher, molecules travel at a higher velocity and can cover larger distances, thereby increasing the rate of diffusion. At lower pressure, there is a greater distance between molecules; this can also increase the rate of diffusion.
The main concentration gradient is established in the laminar region, so the mechanism of gas absorption by diffusion is a molecular diffusion.

The technology is primarily applicable to the removal of inorganic fumes, vapors, and gases (e.g., chromic acid, hydrogen sulfide, ammonia, chlorides, fluorides, and SO_2); volatile organic compounds (VOC); and particulate matter (PM), including PM less than or equal to 10 micrometers (μm) in aerodynamic diameter (PM_{10}), PM less than or equal to 2.5 μm in aerodynamic diameter ($PM_{2.5}$), and hazardous air pollutants (HAP) in particulate form (PM_{HAP}).

Absorption is widely used as a raw material and/or product recovery technique in separation and purification of gaseous streams containing high concentrations of VOC, especially water-soluble compounds such as methanol, ethanol, isopropanol, butanol, acetone, and formaldehyde. Hydrophobic VOC can be absorbed using an amphiphilic block copolymer dissolved in water. However, as an emission control technique, it is much more commonly employed for controlling inorganic gases than for VOC. When using absorption as the primary control technique for organic vapors, the spent solvent must be easily regenerated or disposed of in an environmentally acceptable manner. When used for PM control, high concentrations can clog the bed, limiting these devices to controlling streams with relatively low dust loadings.

Achievable Emission Limits Reductions

Inorganic Gases: Control device vendors estimate that removal efficiencies range from 95 to 99%.

VOC: Removal efficiencies for gas absorbers vary for each pollutant-solvent system and with the type of absorber used. Most absorbers have removal efficiencies in excess of 90 percent, and packed-tower absorbers may achieve efficiencies greater than 99 percent for some pollutant-solvent systems. The typical collection efficiency range is from 70 to greater than 99%.

PM: Packed-bed wet scrubbers are limited to applications in which dust loading is low, and collection efficiencies range from 50 to 95%, depending upon the application. Condensation scrubbers potentially offer a means of extending the removal efficiency of PM.

Typical Industrial Applications

The suitability of gas absorption as a pollution control method is generally dependent on the following factors: 1) availability of suitable solvent; 2) required removal efficiency; 3) pollutant concentration in the inlet vapor; 4) capacity required for handling waste gas; and, 5) recovery value of the pollutant(s) or the disposal cost of the unrecoverable solvent. Packed-bed scrubbers are typically used in the chemical, aluminum, coke and ferro-alloy, food and agriculture, and chromium electroplating industries.

These scrubbers have had limited use as part of flue gas desulfurization (FGD) systems, but the scrubbing solution flow rate must be carefully controlled to avoid flooding. When absorption is used for VOC control, packed towers are usually more cost effective than impingement plate towers (discussed later).

However, in certain cases, the impingement plate design is preferred over packed-tower columns when either internal cooling is desired, or where low liquid flow rates would inadequately wet the packing.

Emission Stream Characteristics

Air Flow: Typical gas flow rates for packed-bed wet scrubbers are 0.25 to 35 standard cubic meters per second (sm^3/sec) (500 to 75,000 standard cubic feet per minute (scfm)).

Temperature: Inlet temperatures are usually in the range of 4 to 370°C (40 to 700°F) for waste gases in which the PM is to be controlled, and for gas absorption applications, 4 to 38° C (40 to 100° F). In general, the higher the gas temperature, the lower the absorption rate, and vice-versa. Excessively high gas temperatures also can lead to significant solvent or scrubbing liquid loss through evaporation.

Pollutant Loading: Typical gaseous pollutant concentrations range from 250 to 10,000 ppmv. Packed-bed wet scrubbers are generally limited to applications in which PM concentrations are less than 0.45 grams per standard cubic meter (g/sm^3) (0.20 grains per standard cubic foot (gr/scf)) to avoid clogging.

Other Considerations: For organic vapor HAP control applications, low outlet concentrations will typically be required, leading to impractically tall absorption towers, long contact times, and high liquid-gas ratios that may not be cost-effective. Wet scrubbers will generally be effective for HAP control when they are used in combination with other control devices such as incinerators or carbon adsorbers.

Emission Stream Pretreatment Requirements

For absorption applications, precoolers (e.g., spray chambers, quenchers) may be needed to saturate the gas stream or to reduce the inlet air temperature to acceptable levels to avoid solvent evaporation or reduced absorption rates.

Cost Information

The following are cost ranges (expressed in third quarter 1995 dollars) for packed-bed wet scrubbers of conventional design under typical operating conditions, developed using EPA cost estimating spreadsheets (EPA, 1996a) and referenced to the volumetric flow rate of the waste stream treated. For purposes of calculating the example cost effectiveness, the pollutant used is hydrochloric acid and the solvent is aqueous caustic soda. The costs do not include costs for post-treatment or disposal of used solvent or waste. Costs can be substantially higher than in the ranges shown for applications which require expensive materials, solvents, or treatment methods. As a rule, smaller units controlling a low concentration waste stream will be much more expensive (per unit volumetric flow rate) than a large unit cleaning a high pollutant load flow.

- Capital Cost: \$22,500 to \$120,000 per sm^3/sec (\$11 to \$56 per scfm)
- O&M Cost: \$33,500 to \$153,000 per sm^3/sec (\$16 to \$72 per scfm), annually

- Annualized Cost: \$36,000 to \$166,000 per sm^3/sec (\$17 to \$78 per scfm), annually
- Cost Effectiveness: \$0.24 to \$1.09 per metric ton (\$0.21 to \$0.99 per short ton), annualized cost per ton per year of pollutant controlled.

Theory of Operation and Design Configurations

Figure 20. Metal pall ring.

Packed-bed scrubbers consist of a chamber containing layers of variously shaped packing material, such as Raschig rings, spiral rings, or Berl saddles, that provide a large surface area for liquid-particle contact. The packing is held in place by wire mesh retainers and supported by a plate near the bottom of the scrubber. Scrubbing liquid is evenly introduced above the packing and flows down through the bed. The liquid coats the packing and establishes a thin film. The pollutant to be absorbed must be soluble in the fluid. In vertical designs (packed towers), the gas stream flows up the chamber (countercurrent to the liquid). Some packed beds are designed horizontally for gas flow across the packing (crosscurrent). Examples of common packing configurations are shown in Figures 20 through 23. Figures 24 through 27 show examples of different scrubber configurations and operating modes.

Physical absorption depends on properties of the gas stream and liquid solvent, such as density and viscosity, as well as specific characteristics of the pollutant(s) in the gas and the liquid stream (e.g., diffusivity, equilibrium solubility). These properties are temperature dependent, and lower temperatures generally favor absorption of gases by the solvent. Absorption is also enhanced by greater contacting surface, higher liquid-gas ratios, and higher concentrations in the gas stream. Chemical absorption may be limited by the rate of reaction, although the rate-limiting step is typically the physical absorption rate, not the chemical reaction rate.

Figure 21. Plastic pall ring.

Inorganic Gases Control - Water is the most common solvent used to remove inorganic contaminants. Pollutant removal may be enhanced by manipulating the chemistry of the absorbing solution so that it reacts with the pollutant. Caustic solution (sodium hydroxide, NaOH) is the most common scrubbing liquid used for acid-gas control (e.g., HCl, SO_2, or both), though sodium carbonate (Na_2CO_3) and calcium hydroxide (slaked lime, $Ca[OH]_2$) are also used. When the acid gases are absorbed into the scrubbing solution, they react with alkaline compounds to produce neutral salts. The rate of absorption of the acid gases is dependent upon the solubility of the acid gases in the scrubbing liquid.

Figure 22. Hy-pak ring.

VOC Control - Absorption is a commonly applied operation in chemical processing. It is used as a raw material and/or a product recovery technique in separation and purification of gaseous streams containing high concentrations of organics (e.g., in natural gas purification and coke by-product recovery operations). In absorption, the organics in the gas stream are dissolved in a liquid solvent. The contact between the absorbing liquid and the vent gas is accomplished in countercurrent spray towers, scrubbers, or packed or plate columns. The use of absorption as the primary control technique for organic vapors is subject to several limiting factors. One factor is the availability of a suitable solvent. The VOC must be soluble in the absorbing liquid and even then, for any given absorbent liquid, only VOC that are soluble can be removed. Some common solvents that may be useful for volatile organics include water, mineral oils, or other nonvolatile petroleum oils. Another factor that affects the suitability of absorption for organic emissions control is the availability of vapor-liquid equilibrium data for the specific organic/solvent system in question. Such data are necessary for the design of absorber systems; however, they are not readily available for uncommon organic compounds. The solvent chosen to remove the

Figure 23. Intalox saddle.

pollutant(s) should have a high solubility for the vapor or gas, low vapor pressure, low viscosity, and should be relatively inexpensive. Water is used to absorb VOC having relatively high water solubilities. Amphiphilic block copolymers added to water can make hydrophobic VOC dissolve in water. Other solvents such as hydrocarbon oils are used for VOC that have low water solubilities, though only in industries where large volumes of these oils are available (e.g., petroleum refineries and petrochemical plants).

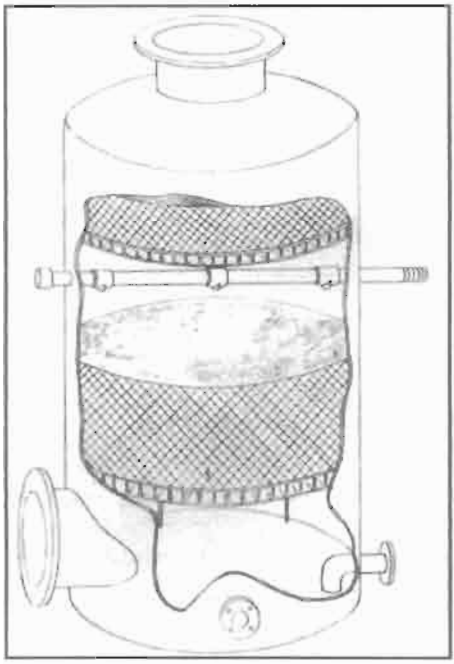


Figure 24. Countercurrent-flow packed scrubber.

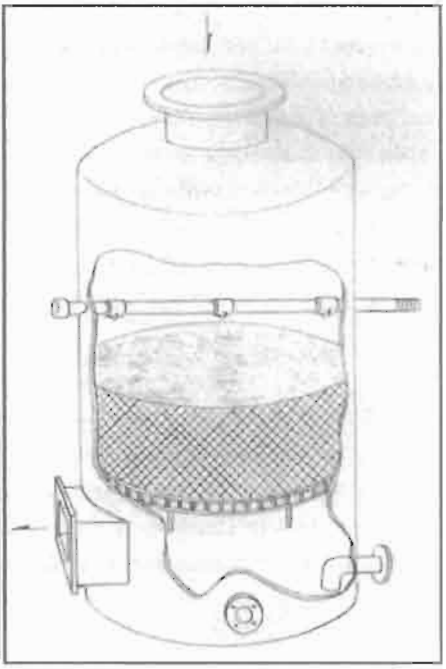


Figure 25. Co-current-flow scrubber.

Another consideration in the application of absorption as a control technique is the treatment or disposal of the material removed from the absorber. In most cases, the scrubbing liquid containing the VOC is regenerated in an operation known as stripping, in which the VOC is desorbed from the absorbent liquid, typically at elevated temperatures and/or under vacuum. The VOC is then recovered as a liquid by a condenser.

PM Control - In packed-bed scrubbers, the gas stream is forced to follow a circuitous path through the packing material, on which much of the PM impacts. The liquid on the packing material collects the PM and flows down the chamber towards the drain at the bottom of the tower. A mist eliminator (also called a "de-mister") is typically positioned above/after the packing and scrubbing liquid supply. Any scrubbing liquid and wetted PM entrained in the exiting gas stream will be removed by the mist eliminator and returned to drain through the packed bed. In a packed-bed scrubber, high PM concentrations can clog the bed, hence the limitation of these devices to streams with relatively low dust loadings. Plugging is a serious problem for packed-bed scrubbers because the packing is more difficult to access and clean than other scrubber designs. Mobile-bed scrubbers are available that are packed with low-density plastic spheres that are free to move within the packed bed. These scrubbers are less susceptible to plugging because of the increased movement of the packing material. In general, packed-bed scrubbers are more suitable for gas scrubbing than PM scrubbing because of the high maintenance requirements for control of PM.

Advantages of packed-bed towers include:

- Relatively low pressure drop;
- Fiberglass-reinforced plastic (FRP) construction permits operation in highly corrosive atmospheres;
- Capable of achieving relatively high mass-transfer efficiencies;
- The height and/or type of packing can be changed to improve mass transfer without purchasing new equipment;
- Relatively low capital cost;
- Relatively small space requirements; and
- Ability to collect PM as well as gases.

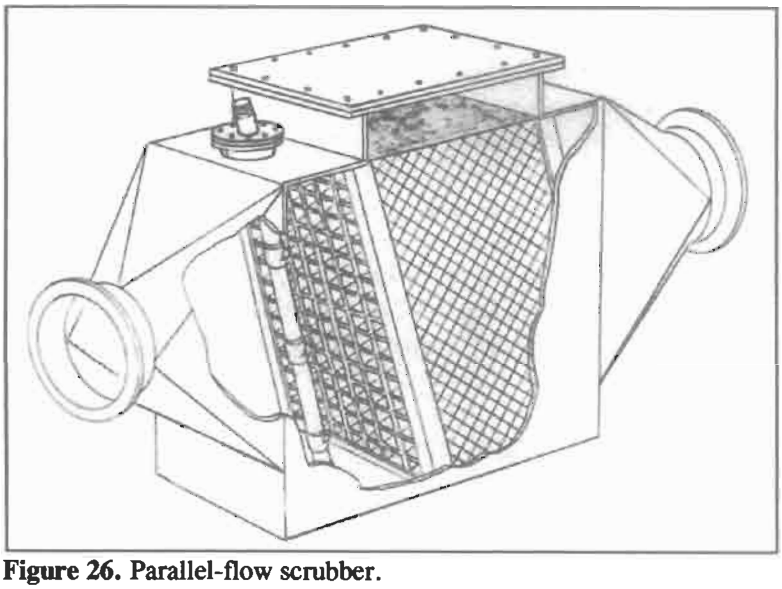


Figure 26. Parallel-flow scrubber.

Disadvantages of packed-bed towers include:

- May create water (or liquid) disposal problem;
- Waste product collected wet;
- PM may cause plugging of the bed or plates;
- When FRP construction is used, it is sensitive to temperature; and
- Relatively high maintenance costs.

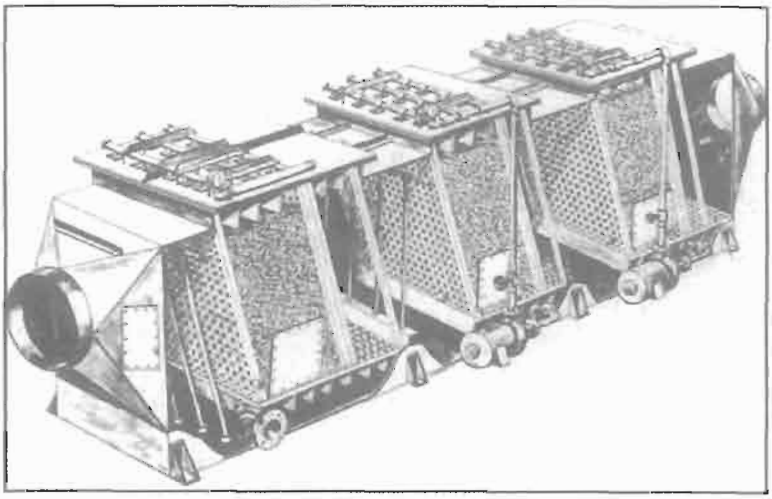


Figure 27. Cross-flow scrubber with three packed beds.

For gas absorption, the water or other solvent must be treated to remove the captured pollutant from the solution. The effluent from the column may be recycled into the system and used again. This is usually the case if the solvent is costly (e.g., hydrocarbon oils, caustic solutions, amphiphilic block copolymer). Initially, the recycle stream may go to a treatment system to remove the pollutants or the reaction product. Make-up solvent may then be added before the liquid stream reenters the column.

For PM applications, wet scrubbers generate waste in the form of a slurry. This creates the need for both wastewater treatment and solid waste disposal. Initially, the slurry is treated to separate the solid waste from the water. The treated water can then be reused or discharged. Once the water is removed, the remaining waste will be in the form of a solid or sludge. If the solid waste is inert and nontoxic, it can generally be landfilled. Hazardous wastes will have more stringent procedures for disposal. In some cases, the solid waste may have value and can be sold or recycled.

Configuring a control device that optimizes control of more than one pollutant does not achieve the highest control possible for any of the pollutants controlled alone. For this reason, waste gas flows which contain multiple pollutants (e.g., PM and SO_2, or PM and inorganic gases) are generally controlled with multiple control devices, occasionally more than one type of wet scrubber.

Additional Information

References 77 through 90 provide additional information on packed tower wet scrubbers, design and scale-up principles, as well as operational guidance.

IMPINGEMENT-PLATE/TRAY TOWER SCRUBBERS

This type of technology is a part of the group of air pollution controls collectively referred to as "wet scrubbers." When used to control inorganic gases, they may also be referred to as "acid gas scrubbers." When used to specifically control sulfur dioxide (SO_2), the term flue-gas desulfurization (FGD) may also be used. The technology is based on the removal of air pollutants by inertial or diffusional impaction, reaction with a sorbent or reagent slurry, or absorption into liquid solvent. Applicable pollutants are primarily particulate matter (PM), including particulate matter less than or equal to 10 micrometers (μm) in aerodynamic diameter (PM_{10}), particulate matter less than or equal to 2.5 μm in aerodynamic diameter ($PM_{2.5}$), and hazardous air pollutants (HAP) in particulate form (PM_{HAP}); and inorganic fumes, vapors, and gases (e.g., chromic acid, hydrogen sulfide, ammonia, chlorides, fluorides, and SO_2). These types of scrubbers may also occasionally be used to control volatile organic compounds (VOC). Hydrophilic VOC may be controlled with an aqueous fluid, and hydrophobic VOC may be controlled with an amphiphilic block copolymer in the water. However, since very little data exist for this application, VOC data are not presented. When using absorption as the primary control technique, the spent solvent must be easily regenerated or disposed of in an environmentally acceptable manner.

Achievable Emission Limits Reductions

PM: Impingement-plate tower collection efficiencies range from 50 to 99 percent, depending upon the application. This type of scrubber relies almost exclusively on inertial impaction for PM collection. Therefore, collection efficiency decreases as particle size decreases. Short residence times will also lower scrubber efficiency for small particles. Collection efficiencies for small particles ($<$ 1 μm in aerodynamic diameter) are low for these scrubbers; hence, they are not recommended for fine PM control.

Inorganic Gases: Control device vendors estimate that removal efficiencies range from 95 to 99%. For SO_2 control, removal efficiencies vary from 80 to greater than 99%, depending upon the type of reagent used and the plate tower design. Most current applications have an SO_2 removal efficiency greater than 90 percent.

Typical Industrial Applications

The suitability of gas absorption as a pollution control method is generally dependent on the following factors. 1) availability of suitable solvent; 2) required removal efficiency; 3) pollutant concentration in the inlet vapor; 4) capacity required for handling waste gas; and, 5) recovery value of the pollutant(s) or the disposal cost of the unrecoverable solvent. Impingement plate scrubbers are typically used in the food and agriculture industry, and at gray iron foundries.

FGD is used to control SO_2 emissions from coal and oil combustion from electric utilities and industrial sources. Impingement scrubbers are one wet scrubber configuration used to bring exhaust gases into contact with a sorbent designed to remove the SO_2. On occasion, wet scrubbers have been applied to SO_2 emissions from processes in the primary nonferrous metals industries (e.g., copper, lead, and aluminum), but sulfuric acid or elemental sulfur plants are more popular control devices for controlling the high SO_2 concentrations associated with these processes.

When absorption is used for VOC control, packed towers are usually more cost effective than impingement-plate towers. However, in certain cases, the impingement-plate design is preferred over packed-tower columns when either internal cooling is desired, or where low liquid flow rates would inadequately wet the packing.

Emission Stream Characteristics

Air Flow: Typical gas flow rates for a single impingement-plate scrubber unit are 0.47 to 35 standard cubic meters per second (sm^3/sec) (1,000 to 75,000 standard cubic feet per minute (scfm)).

Temperature: Inlet gas temperature is limited to 4 to 370°C (40 to 700°F) for PM control. For gaseous pollutant control, the gas temperature typically ranges between 4 to 38° C (40 to 100°F). In general, the higher the gas temperature, the lower the absorption rate, and vice-versa. Higher temperatures can lead to loss of scrubbing liquid or solvent through evaporation.

Pollutant Loading: Impingement-plate scrubbers are easy to clean and maintain and are not subject to fouling as packed-bed wet scrubbers are hence they are more suited to PM control and there are no practical limits to inlet PM concentrations.
Other Considerations: For organic vapor HAP control, low outlet concentrations will typically be required, leading to impractically tall absorption towers, long

contact times, and high liquid-gas ratios that may not be cost-effective. Wet scrubbers will generally be effective for HAP control when they are used in combination with other control devices such as incinerators or carbon adsorbers.

Emission Stream Pretreatment Requirements

For gas absorption applications, precoolers (e.g., spray chambers) may be needed to reduce the inlet air temperature to acceptable levels to avoid solvent evaporation or reduced absorption rates.

Cost Information

The following are cost ranges (expressed in third quarter 1995 dollars) for impingement plate wet scrubbers of conventional design under typical operating conditions, developed using EPA cost-estimating spreadsheets (EPA, 1996) and referenced to the volumetric flow rate of the waste stream treated. For purposes of calculating the example cost effectiveness, the pollutant is assumed to be PM at an inlet loading of approximately 7 grams per standard cubic meter (g/sm^3), or 3 grains per standard cubic foot (gr/scf). The cost estimates do not include costs for posttreatment or disposal of used solvent or waste. Actual costs can be substantially higher than in the ranges shown for applications which require expensive materials, solvents, or treatment methods. As a rule, smaller units controlling a low concentration waste stream will be much more expensive (per unit volumetric flow rate) than a large unit cleaning a high pollutant load flow.

- Capital Cost: \$4,500 to \$25,000 per sm^3/sec (\$2.10 to \$11 per scfm)
- O&M Cost: \$5,200 to \$148,000 per sm^3/sec (\$2.50 to \$70 per scfm), annually
- Annualized Cost: \$5,900 to \$151,000 per sm^3/sec (\$2.80 to \$71 per scfm), annually
- Cost Effectiveness: \$51 to \$1,300 per metric ton (\$46 to \$1,200 per short ton), annualized cost per ton per year of pollutant controlled

Theory of Operation

PM Control - An impingement-plate scrubber is a vertical chamber with plates mounted horizontally inside a hollow shell. Impingement-plate scrubbers operate as countercurrent PM collection devices. The scrubbing liquid flows down the tower while the gas stream flows upward. Contact between the liquid and the particle-laden gas occurs on the plates. The plates are equipped with openings that allow the gas to pass through. Some plates are perforated or slotted, while more complex plates have valve-like openings.

The simplest impingement-plate scrubber is the sieve plate, which has round perforations. In this type of scrubber, the scrubbing liquid flows over the plates and the gas flows up through the holes. The gas velocity prevents the liquid from flowing down through the perforations. Three phase (gas-liquid-particle) contact is achieved within the froth generated by the gas passing through the liquid layer. Complex plates, such as bubble cap or baffle plates, introduce an additional means of collecting PM. The bubble caps and baffles placed above the plate perforations force the gas to turn before escaping the layer of liquid. While the gas turns to avoid the obstacles, most PM cannot and is collected by impaction on the caps or baffles. Bubble caps and the like also prevent liquid from flowing down the perforations if the gas flow is reduced.

In all types of impingement-plate scrubbers, the scrubbing liquid flows across each plate and down the inside of the tower onto the plate below. After the bottom plate, the liquid and collected PM flow out of the bottom of the tower. Impingement-plate scrubbers are usually designed to provide operator access to each tray, making them relatively easy to clean and maintain. Consequently, impingement-plate scrubbers are more suitable for PM collection than packed-bed scrubbers. Particles greater than 1 gm in aerodynamic diameter can be collected effectively by impingement-plate scrubbers, but many particles < 1 μm in aerodynamic diameter will penetrate these devices.

Inorganic Gases Control - Water is the most common solvent used to remove inorganic contaminants, though as caustic for is used for acid-gas absorption. Amphiphilic block copolymers can be used to absorb hydrophobic VOC. When used as part of an FGD system, an impingement-plate scrubber promotes contact between the flue gas and the sorbent slurry in a vertical column with transversely mounted perforated trays. The SO_2 laden gas enters at the bottom of the column and travels upward through the perforations in the trays; the reagent slurry is fed at the top and flows over the plates toward the bottom. In most cases the sorbent is an alkaline slurry, commonly limestone, slaked lime, or a mixture of slaked lime and alkaline flyash, though many other sorbent processes exist. Absorption of SO_2 is accomplished by countercurrent contact between the gas reagent slurry. The sulfur oxides react with the sorbent, forming a wet mixture of calcium sulfite and sulfate.

Advantages of impingement plate scrubbers include:
- Can handle flammable and explosive dusts with little risk;
- Provides gas absorption and dust collection in a single unit;
- Can handle mists;
- Collection efficiency can be varied;
- Provides cooling for hot gases;
- Corrosive gases and dusts can be neutralized; and
- Improves gas-slurry contact for SO_2 removal.

Disadvantages of impingement plate scrubbers include:

- Effluent liquid can create water pollution problems;
- Waste product collected wet;
- High potential for corrosion problems;
- Protection against freezing required;
- Off-gas may require reheating to avoid visible (steam) plume;
- Collected PM may be contaminated, and may not be recyclable; and
- Disposal of waste sludge may be very expensive.

For PM applications, wet scrubbers generate waste in the form of a slurry. This creates the feed for both wastewater treatment and solid waste disposal. Initially, the slurry is treated to separate the solid waste from the water. The treated water can then be reused or discharged. Once the water is removed, the remaining waste will be in the form of a solid or sludge. If the solid waste is inert and nontoxic, it can generally be landfilled. Hazardous wastes will have more stringent procedures for disposal. In some cases, the solid waste may have value and can be sold or recycled.

For gas absorption, the water or other solvent must be treated to remove the captured pollutant from the solution. The effluent from the column may be recycled into the system and used again. This is usually the case if the solvent is costly (e.g., hydrocarbon oils, caustic solutions). Initially, the recycle stream may go to a waste treatment system to remove the pollutants or the reaction product. Make-up solvent may then be added before the liquid stream reenters the column. For FGD applications, the slurry combines with the SO_2-laden waste gas to form a waste slurry in the bottom of the scrubber. The sludge is removed from the scrubber and, depending upon the reagent or sorbent used to react with the SO_2, the waste reacted sludge is disposed of, recycled or regenerated, or, in some cases, a salable product. For slurries which produce calcium sulfate and sulfite, oxidizing the waste sludge results in gypsum.

Gypsum is a preferred product because it can be marketed and also because of its superior dewatering characteristics. Most scrubbers are operated without the oxidizing step and the waste sludge must be dewatered and disposed of properly. Some slurries can be regenerated and used again, but few such systems are in use due to high energy costs associated with the regeneration of the reagent.

Configuring a control device that optimizes control of more than one pollutant often does not achieve the highest control possible for any of the pollutants controlled alone. For this reason, waste gas flows which contain multiple pollutants (e.g., PM and SO_2, or PM and inorganic gases) are generally controlled with multiple control devices, occasionally more than one type of wet scrubber.

Additional Information

References 91 through 103 provide additional information on impingement-plate scrubbers, design and scale-up principles, as well as operational guidance.

FIBER-BED SCRUBBERS

This type of technology is a part of the group of air pollution controls collectively referred to as "wet scrubbers." Fiber-bed scrubbers are also known as wetted-filter scrubbers and mist eliminators. The technology is based on the removal of air pollutants by inertial and diffusional interception.

Fiber-bed scrubbers are used to collect fine and/or soluble particulate matter (PM) or as mist eliminators to collect liquid aerosols, including inorganic (e.g., sulfuric acid mist) and volatile organic compounds (VOC). Insoluble and/or coarse PM will clog the fiber bed with time, and VOC which are difficult to condense will not be collected efficiently.

Achievable Emission Limits Reductions

Fiber-bed scrubber collection efficiencies for PM and VOC mists generally range from 70 to greater than 99 percent, depending upon the size of the aerosols to be collected and the design of the scrubber and the fiber beds.

Typical Industrial Applications

Fiber-bed scrubbers are used to control aerosol emissions from chemical, plastics, asphalt, sulfuric acid, and surface coating industries. They are also used to control lubricant mist emission from rotating machinery and mists from storage tanks. Fiber-bed scrubbers are also applied downstream of other control devices to eliminate a visible plume. Despite their potential for high collection efficiency, fiber-bed scrubbers have had only limited commercial acceptance for dust collection because of their tendency to become plugged.

Emission Stream Characteristics

Air Flow: Fiber-bed scrubbers can treat flows from 0.5 to 47 standard cubic meters per second (sm^3/sec) (1,000 to 100,000 standard cubic feet per minute (scfm)).
Temperature: The temperature of the inlet waste gas flow is generally restricted by the choice of materials. Plastic fiber beds are generally restricted to operate below 60°C (140° F).
Pollutant Loading: Inlet flow loadings can range from 0.2 to 11 grams per standard cubic meter (g/sm^3) (0.1 to 5 grains per standard cubic foot (gr/scf)).

Emission Stream Pretreatment Requirements

Waste gas streams are often cooled before entering fiber-bed scrubbers to condense as much of the liquid in the flow as possible and to increase the size of the existing aerosol particles through condensation. A prefilter is generally used to remove larger particles from the gas stream prior to its entering the scrubber.

Cost Information

The following are cost ranges (expressed in third quarter 1995 dollars) for orifice wet scrubbers of conventional design under typical operating conditions, adapted from EPA cost estimating spreadsheets (EPA, 1996) and referenced to the volumetric flow rate of the waste stream treated. For purposes of calculating the example cost effectiveness, the pollutant is PM at a loading of approximately 7 g/sm^3 (3 gr/scf) and waste gas flow ranging from 0.5 to 47 sm^3/sec (1,000 to 100,000 scfm). The costs do not include costs for post-treatment or disposal of used solvent or waste.

- Capital Cost: \$2,100 to \$6,400 per sm^3/sec (\$1.00 to \$3.00 per scfm)
- O&M Cost: \$3,500 to \$76,000 per sm^3/sec (\$1.60 to \$36 per scfm), annually
- Annualized Cost: \$4,300 to \$77,000 per sm^3/sec (\$2.00 to \$37 per scfm), annually
- Cost Effectiveness: \$40 to \$710 per metric ton (\$36 to \$644 per short ton), annualized cost per ton per year of pollutant controlled

Theory of Operation

In fiber-bed scrubbers, moisture-laden waste gas passes through beds or mats of packing fibers, such as spun glass, fiberglass, or steel. If only mists are to be collected, small fibers may be used, but if solid particles are present, the use of fiber-bed scrubbers is limited by the tendency of the beds to plug. For PM collection, the fiber mats must be composed of coarse fibers and have a high void fraction, to minimize the tendency to plug. The fiber mats are often sprayed with the scrubbing liquid so particles can be collected by deposition on droplets and fibers. For PM removal, the scrubber design may include several fiber mats and an impingement device. The final fiber mat is typically dry for the removal of any droplets which are still entrained in the gas stream.

Advantages of fiber-bed scrubbers include:

- Can handle flammable and explosive dusts with little risk;
- Can handle mists;
- Relatively low pressure drop;
- Provides cooling for hot gases; and
- Corrosive gases and dusts can be neutralized.

Disadvantages of fiber-bed scrubbers include:

- Effluent liquid can create water pollution problems;
- Waste product collected wet;
- High potential for corrosion problems;
- Protection against freezing required;
- Collected PM may be contaminated, and may not be recyclable; and
- Disposal of waste sludge may be very expensive.

For liquid aerosols, the used scrubbing liquid must be treated to remove the captured pollutant from the solution. The effluent from the column may be recycled into the system and used again. This is usually the case if the solvent is costly (e.g., hydrocarbon oils, caustic solutions). Initially, the recycle stream may go to a waste treatment system to remove the pollutants or the reaction product. Make-up scrubbing liquid may then be added before the liquid stream reenters the column. For PM applications, wet scrubbers generate waste in the form of a slurry. This creates the need for both wastewater treatment and solid waste disposal. Initially, the slurry is treated to separate the solid waste from the water. The treated water can then be reused or discharged. Once the water is removed, the remaining waste will be in the form of a solid or sludge. If the solid waste is inert and nontoxic, it can generally be landfilled. Hazardous wastes will have more stringent procedures for disposal. In some cases, the solid waste may have value and can be sold or recycled.

Additional Information

References 104 through 109 provide additional information on fiber-bed scrubbers, design, and scale-up principles, as well as operational guidance.

USE OF ACTIVATED CARBON AND OTHER ADSORBER SYSTEMS

Adsorption is defined as the collection and concentration of a substance (e.g., an organic solvent) onto a solid surface (e.g., carbon adsorbent) from a gas (or liquid). The solvent is bound to the carbon due to the attractive forces (affinity) between the carbon and the organic solvent.

Activated carbon adsorption is a popular method of recovering solvents from air emissions as well as wastewater. At one time, adsorption systems were largely viewed as an end-of-pipe pollution control technology as opposed to today's view of a solvent recovery system. This view has altered because of technology advances that have enhanced the ability of adsorbers to recover (desorb) the solvent from the activated carbon. Further advancements in the process of regenerating the used activated carbon have made the need for replacing the adsorbent less frequently than in past practices, thus making this an economical technology.

Adsorption traditionally has found wide application in the field of odor control. Odors are generally created by the presence of small quantities of contaminants in large volumes of air. The equilibrium relationships associated with adsorption, unlike those involved in absorption, lend themselves to removal of low-concentration contaminants. However, because of the complex mass transfer mechanisms involved in adsorptions, and the great variability in adsorbent physical properties which strongly affect performance, adsorption is much less amenable to generalized design from basic physical data than is absorption. Good design requires specific data for the gas-solid system involved.

Theory of Operation

In industrial operations, adsorption is accomplished primarily on the surfaces of internal passages within small porous particles. Three basic mass transfer processes occur in series: (1) mass transfer from the bulk gas to the particle surface, (2) diffusion through the passages within the particle, and (3) adsorption on the internal particle surfaces. Each of the processes depends on the system operating conditions and the physical and chemical characteristics of the gas stream and the solid adsorbent. Often, one of the transfer processes will be significantly slower than the other two, and will control the overall transfer rate. The other process will operate nearly at equilibrium.

Heat transfer may also play an important role in an adsorption system. The adsorption process is exothermic. Physical adsorption equilibria behave in a manner similar to vapor-liquid equilibria; transfer out of the vapor phase is favored by decreasing temperature. Therefore, rapid dissipation of heat away from the adsorbing surface improves adsorption performance. Chemisorption rates, on the other hand, generally increase with increased temperature.

External mass transfer is the only process of the three involved in adsorption that can be predicted with reasonable accuracy from physical data. Mass transfer from the bulk gas to the particle surface can be considered by the film resistance approach. The rate of mass transfer is proportional to the external surface area of the adsorbent particles and the adsorbate concentration difference between the bulk gas and the particle external surface. The proportionality constant is the mass transfer coefficient, the reciprocal of the resistance to mass transfer of a hypothetical thin film at the particle surface. Correlations of mass transfer coefficients as functions of particle size, gas flows, and properties and operating conditions have been summarized extensively in the literature. The references cited at the end of this section will assist you.

Transfer of material from the particle surface to internal adsorption sites is accomplished by diffusion through the internal passages of the particle. Diffusion takes place by one or more of several mechanisms. Where passages are sufficiently large that intermolecular collisions are more likely than collisions with the passage walls, bulk diffusion predominates. In smaller passages, and at lower pressures, where collisions with the passage walls are more probable, Knudson diffusion controls. Knudson diffusion rates are often an order of magnitude lower than bulk rates for a given pore length. A third diffusion mechanism, surface diffusion, may predominate in small-passage, high-surface situations. Surface diffusion is the migration of molecules along the passage surface after adsorption. Because of the irregularity and variability of intraparticle passages, and the difficulty of measuring surface concentrations, intraparticle mass transfer is extremely difficult to predict accurately from physical data. Its effects can be determined to a degree by comparison of experimental adsorption rates for different size adsorbent particles, allowing for differences in external mass transfer rates.

The actual adsorption of vapor molecules takes place mainly on the surface of internal passages within the adsorbent particles, since that is where most of the available surface exists. The adsorption process may be either physical or chemical in nature. Physical adsorption is a readily reversible process which occurs as a result of the physical attraction between the gas molecules and the molecules of the solid surface. If the gas-solid intermolecular attraction is greater than the intermolecular attractions in the gas phase, the gas will condense on the solid surface, even though its pressure is lower than its vapor pressure at the prevailing temperature. For example, the equilibrium adsorption pressure of acetone on activated carbon may, under some conditions, be as little as 150 to 1,100 of the equilibrium vapor pressure at the same temperature. Therefore, small concentrations of contaminants can often be removed from gas streams by adsorption, but not by absorption. The heat released on adsorption is usually somewhat greater than the latent heat of vaporization and of the order of the heat of sublimation of the gas. Chemical adsorption, or chemisorption, involves formation of chemical bonds between the gas and surface molecules. The strength of the chemical bond may vary considerably, and identifiable chemical compounds in the usual sense may not actually form. However, the adhesive force is much greater than found in physical adsorption. The heat liberated during chemisorption is usually large, of the order of the heat of chemical reaction.

Equilibrium Considerations - Most of the adsorption data available from the literature are equilibrium data. Equilibrium data are useful in determining the maximum adsorbent loading which can be obtained for a specific adsorbate-adsorbent system under given operating conditions. However, equilibrium data by themselves are insufficient for design of an adsorption system. Overall mass transfer rate data are also necessary.

The equilibrium adsorption characteristics of gas or vapor on a solid resemble in many ways the equilibrium solubility of a gas in a liquid. Adsorption equilibrium data are usually portrayed by isotherms; lines of constant temperature on a plot of adsorbate equilibrium partial pressure versus adsorbent loading in mass of adsorbate per mass of adsorbent. Isotherms take many shapes, including concave upward and downward, and S-curves. Equilibrium data for a given adsorbate-adsorbent system cannot generally be extrapolated to other systems with any degree of accuracy.

Several useful methods are available for extrapolating equilibrium data for a given system to various temperatures and pressures. One convenient method is by use of a reference substance plot. Here, the adsorption equilibrium partial pressure of the adsorbate is plotted against a pure substance vapor pressure, preferably that of the adsorbate. If logarithmic coordinates are used on both axes, lines of constant adsorbent loading, isosteres, are linear for most substances. Therefore, only two datum points are required to establish each isostere. Isosteres will also generally be linear on a plot of the logarithm of the ratio of pure substance vapor pressure to adsorption equilibrium vapor pressure against reciprocal absolute temperature. A further condensation of data may be accomplished by plotting absolute temperature times the logarithm of the ratio of pure substance vapor pressure to adsorption equilibrium vapor pressure at that temperature against adsorbent loading. For most singly adsorbate systems, a single curve will result for all temperatures, at least over a moderate temperature range.

Mass Transfer Rate Considerations - As discussed previously, the mass transfer mechanism involved in industrial adsorption processes is complex. Generally, basic physical data on the materials involved are insufficient for design. Experimental mass transfer rate data for the specific adsorbate-adsorbent system are usually required for good design.

Hardware

Three basic schemes are used in adsorption systems for obtaining effective gas-solid contact: (1) the fluidized bed, (2) continuous moving bed, and (3) unsteady-state fixed-bed techniques. By far the most common is the fixed bed unsteady-state adsorber. In this system, the contaminated gas is passed through a stationary bed of adsorbent. The bed is operated in this manner until the contaminant level in the effluent begins to rise. The adsorbent must then be replaced or regenerated. Generally gas flow is diverted to a second, parallel bed to allow continued operations during adsorbent change or regeneration. Adsorbent beds range in size and form from small disposable cartridges to dumped beds contained in large vessels. Unsteady-state fixed-bed adsorbers have the advantage of being relatively simple and economical, particularly at low adsorbate rates. Since the bed is stationary, the adsorbent is handled only during replacement, which should be infrequent in a well-designed system. Continuous solids-handling systems and their inherent high cost and mechanical problems are avoided.

The primary disadvantage of fixed-bed adsorbers arises when contaminant rates are high. Because of the unsteady-state nature of the operation, a large portion of the in-process adsorbent inventory is saturated and, therefore, inactive. Where adsorbate rates are high, unduly large beds are required. In addition, gas flow rates through fixed beds are limited by pressure drop. Extremely high gas rates may require uneconomically large beds.

In fluidized-bed adsorbers, the combination of high gas rate and small adsorbent particle size results in suspension of the adsorbent, giving it many of the characteristics of a fluid. Fluidized bed adsorbers, therefore, lend themselves to truly continuous, countercurrent, multistage operation. Adsorbent inventory is minimized.

Fluidized-bed adsorbers have several disadvantages. The continuous handling and transport of solids is expensive from an equipment standpoint; fluidized-bed systems must be large to be economical. Solids handling also presents a potential for mechanical problems. Careful control is required to keep the adsorbent fluidized, while minimizing adsorbent loss with the gas-phase attrition of the adsorbent can be high, requiring substantial makeup.

Continuous moving-bed adsorbers, like fluidized-bed systems, lend themselves to true countercurrent, multistage operation. The adsorbent, however, is not fluidized, but is mechanically converged or falls by gravity through the rising stream of gas. Attrition is generally higher than in fluidized-bed systems, but control may be less critical. Other advantages and disadvantages of fluidized-bed adsorbers apply to moving-bed adsorbers.

Adsorbent Regeneration

When adsorbate rates are sufficiently high to make periodic adsorbent replacement uneconomical, regeneration of the adsorbent can usually be justified. In continuous, steady-state systems, regeneration is required for economical operation.

Adsorbent regeneration is normally accomplished by reversing the adsorption process, either by decreasing the system pressure or, more commonly, by increasing the system temperature. In some cases, particularly in chemisorption systems, the adsorbent activity can be restored by reaction with a suitable reagent. One of the inherent problems in regeneration of adsorbent beds is disposal of the desorbed material. In activated carbon systems, the most common in odor control applications, regeneration is accomplished by heating the bed with a gas or vapor which carries the desorbed contaminant out of the bed. The most commonly used carrier is superheated steam. Normally, the adsorbate is condensed along with the steam. If large quantities of adsorbate are involved, or if the adsorbate is highly water soluble, a secondary liquid waste disposal problem may result. The energy costs for a superheated steam-condensing regeneration system can be appreciable for a large adsorption system. A pollution prevention practice is to use hot combustion gases as the regeneration carrier. The energy required to heat the gas is supplied by combustion of the desorbed material; supplemental fuel is supplied, if necessary. Both the energy cost and secondary disposal problems are solved with this system. However, the cost of the additional equipment required makes this system uneconomical for small adsorption installations.

Adsorbent Selection

There are several choices for the adsorbent. Activated carbon still remains the most widely used, especially for VOC.

Activated Carbon - Activated carbon is by far the most commonly used adsorbent in odor control applications and many VOC recovery applications. Because of its relatively uniform distribution of surface electrical charge, activated carbon is not selective toward polar molecules. It can, therefore, be used to remove many organic vapors from gas streams with high water vapor contents. Water molecules, being highly polar, show strong attractions for each other, which compete with their attractions for the nonpolar carbon surface. Consequently, the large, less polar organic molecules are selectively adsorbed. Activated carbon is most effective for adsorbing organic materials which boil at normal ambient temperature or higher. In general, effectiveness increases with increasing molecular weight. Activated carbons have surface areas on the order of 300 to 700 ft^2/ft^3. Average pore diameter ranges from 20 to 40 Å, typical for most commercially used adsorbents. However, the distribution of pore sizes is substantially broader than found in other adsorbents.

Siliceous Adsorbents - The most commonly used adsorbents of the siliceous class are silica gels and synthetic zeolites, or molecular sieves. These materials are available over a wide range of adsorbent capacities. At best, their capacities are of the same order of magnitude as that of the most highly activated carbons. They exhibit a greater selectivity for polar molecules than does activated carbon. Silica gel is commonly used to remove water from gas streams. Surface areas average 200 to 700 ft^2/ft^3. Average pore diameters of various grades range from 20 to 140 Å.

Molecular Sieves - Molecular sieves are synthetic zeolites which can be manufactured with extremely close control of pore size. Therefore, they can be tailored to suit specific applications. In addition to gas drying applications, molecular sieves are used for the separation of gases and vapors on the basis of molecular size and shape. Surface areas range from 350 to 1,000 ft^2/ft^3.

Metal Oxide - Since metals are less electrophilic than silicon, metal oxide adsorbents show even stronger selectivity for polar molecules than do siliceous materials. The most commonly used metal oxide adsorbent is activated alumina, used primarily for gas drying. Occasionally, metal oxides find applications in specific chemisorption systems. For example, several processes are under development utilizing lime or limestone for removal of sulfur oxides from flue gases. Activated aluminas have surface areas in the range of 200 to 1,000 ft^2/ft^3. Average pore diameters range from about 30 to 80 Å.

Impregnated Adsorbents - For some applications, an adsorbent may be impregnated with a material which enhances its contaminant-removal ability. The improved effectiveness may be related to any of several mechanisms. The impregnating material may react with the vapor contaminant to form a compound or complex which remains on the adsorbent surface. Some impregnants react with the contaminant, or catalyze reactions of the contaminant with other gas constituents to form less noxious vapor-phase substances. In some instances, the impregnant acts as a catalyst intermittently, for example, under regeneration conditions. In this case, the contaminant is adsorbed by physical adsorption and destroyed by a catalytic reaction during regeneration.

Purchasing Guidelines for Adsorbers

Table 2 provides a list of issues you should address when considering the acquisition of an adsorber. Also, consult the references cited at the end of this section for more detailed information and guidance on adsorber equipment selection criteria. Table 3 provides a list of vendors that supply activated carbon adsorbers.

Table 2. Purchasing Guidelines for Adsorbers

Has the solvent in question been successfully recovered through activated carbon adsorption? • If there is no data available on your particular solvent, it is possible to estimate the adsorption effectiveness by comparing your solvent to solvents that are similar in chemical structure. • The best approach to evaluate the effectiveness of activated carbon adsorption is to run bench-scale tests on your waste stream.
Has the adsorber you are interested in been used for solvent recovery rather than simply for end-of-pipe pollution control? • Some adsorption equipment is effective in removing the solvent from the waste stream, but is unable to desorb (recover) the solvent from the activated carbon.
Can the unit be easily adapted to recover different solvents or is it solvent-specific?

Does the system have two or more adsorption beds that are parallel to each other so that one bed is on-line while the others are being desorbed or regenerated?

Will you need to filter the waste stream to remove contaminants that would clog the activated carbon adsorbent?

How do the solvent concentration limits of the adsorption system compare with the solvent concentration of your waste stream?

- Adsorbers have minimum and maximum solvent concentration limits; adsorbers will not function effectively outside those solvent concentration limits.

If you are considering recovering solvent from air, is the relative humidity of the air low enough to allow adsorption?

- If the relative humidity is too high you will need to add a dryer to the system to remove the excess moisture. Silica gel is a commonly used drying agent.

Would you consider a multiple stage (cascade) system of adsorbers to achieve a higher recovery rate?

- A cascade system should improve the recovery rate by trapping solvent in the second stage that escaped the first stage.
- Cascade adsorption allows you to use a cheaper adsorbent in the first stage to recover the bulk of the solvent. The second stage can then be equipped with a high efficiency adsorbent to recover remaining solvent. This approach will extend the life of the more expensive adsorbent and consequently lower the operating costs.
- Cascade adsorption will increase the initial capital cost; you should evaluate whether the increase in solvent recovery justifies the added expense.

Will you recover the solvent from the carbon adsorbent onsite or contract with a service to recover the solvent for you?

- If you plan on using a substantial amount of adsorbent, it may be more cost effective for you to purchase the solvent regeneration equipment and do it on-site.

If you want to recover the solvent and regenerate the adsorbent on-site, what method will you use?

- Thermal Regeneration
- Purging with an Inert Gas
- Brayton Cycle(a)

Are there any local, state, or federal health and safety or environmental regulations that apply to the use of this equipment?

(a) Brayton Cycle is a heat pump system licensed by Nucon International (Columbus, OH) under the name Braysorb. At the present time, it has only been installed in large industrial settings. It is offered as a service (via a mobile unit) to small quantity generators in some areas of the country and may be scaled down for on-site use in the future.

Table 3. Partial List of U.S. Carbon Adsorber Suppliers.

Company Name	Contact Coordinates
AMCEC Corp.	2625 Butterfield Rd., #225 N, Oak Brook, IL 60521 Phone: (708) 954-1515
American Air Filter	P.O. Box 35690, Louisville, KY 40232-5690 Phone: (502) 637-011
American Environmental Intl.	5 Revere Drive, Suite 200, Northbrook, IL 60062-998 Phone: (708) 272-8646
Atochem Inc./CECA Div.	266 Harrison Rd., Glen Rock, NJ 07452 Phone: (800) 248-2322
Baron-Blakeslee Inc.	2001 N. Janice Avenue, Melrose Park, IL 60160 Phone: (708) 450-3900
COH Corp.	2000 Eastern Parkway, Brooklyn, NY 11233 Phone: (718) 347-8055
Calgon Carbon Corp.	P.O. Box 717, Pittsburgh, PA 15230-0717 Phone: (800) 422-7266
Cameron-Yakima	P.O. Box 1554, Yakima, WA 98909 Phone: (509) 452-6605
Carbtrol Corp.	39 Riverside Avenue, Westport, CT 06880 Phone: (800) 242-1150
DR Technology Inc.	Hidden Pines Drive, Clarksburg, NJ 08510 Phone: (201) 780-4664
Dedert Corp.	20000 Governors Drive, Olympia Fields, IL 60461-1074 Phone: (708) 747-7000
Ducon Environmental Technology Inc.	147 East Second Street, Mineola, NY 11501 Phone: (516) 741-6100
Envirotrol Inc.	432 Green St./ P.O. Box 61, Sewickley, PA 15143 Phone: (412) 741-2030
HTC Corp.	325 Lennon Lane, Suite 200, Walnut Creek, CA 94598 Phone: (415) 934-8221
Hoyt Corp.	251 Forge Rd., Westport, MA 02790-0217 Phone: (800) 343-9411

Company Name	Contact Coordinates
Hydrogroup Inc.	97 Chimney Rock Rd., Bridgewater, NJ 08807 Phone: (201) 563-1400
Independent Equipment Corp.	Rt. 202 N/P.O. Box 460, Three Bridges, NJ 08887 Phone: (201) 782-5989
Met-Pro Corp.	160 Casell Rd., Harleysville, PA 19438 Phone: (215) 723-6751
Nuclear Consulting Services (NUCON)	P.O. Box 29151, Columbus, OH 43229 Phone: (614) 846-5710
Peroxidation Systems Inc.	4400 E. Broadway, Suite 602, Tucson, AZ 85711-3558 Phone: (602) 327-0277
Remedial Systems Inc.	29 Wall St., Foxboro, MA 02035 Phone: (508) 543-1512
Sutcliffe-Croftshaw	1301 York Rd., Lutherville, MD 21093 Phone: (301) 337-2800
Tigg Corp.	P.O. Box 11661, Pittsburgh, PA 15228 Phone: (412) 563-4300
Unisorb Corp.	1310 Genoa St., S. Houston, TX 77587 Phone: (713) 943-3753
VARA International	1201 19th Place, Vero Beach, FL 32960 Phone: (407) 567-1320
Westgates Carbon Inc.	2130 Leo Avenue, Los Angeles, CA 90040-1634 Phone: (213) 722-7500
Wintek Corp.	RR 3 Box 337/Lime Rock Lane, Califon, NJ 07830 Phone: (201) 832-9477
Zimpro/Passavant Inc.	301 Military Rd., Rothschild, WI 54474 Phone: (800) 826-1475

Additional Information

References 110 through 123 provide additional information on adsorbers, design, and scale-up principles, as well as operational guidance.

THERMAL DESTRUCTIVE TECHNOLOGIES

For more than a decade now, the baking industry, the chemical process industry, pharmaceutical industry, fabric coating, rubber extrusion, electronic components, soil remediation, metal coating, wood working, formaldehyde, and sterilizers have become the specific industries being targeted by the environmental authorities. The reason for this is clear: these industry sectors are large generators of VOC emissions. Table 4 provides a list of industry operations and the typical VOC, solvents, and other offgases associated with them.

Table 4. Examples of Gaseous Pollutants by Industry.

Industry Operation	Gaseous Pollutants Emitted
Acetate Finish Coating	Silicate Solution
Alcohol Synthesis	C_1, C_2, C_3, C_6 Hydrocarbons
Automobile Coating	Ketones, Xylene, Toluene, Phenols
Bakery Ovens	Ethanol
Can Coating	Ketones, Alcohols, Aromatic Hydrocarbons, Ethers
Chemical Processing	All of the above
Coffee Roasting	Heavy Oils from coffee beans
Coil Coating	Phosphates, Solvesso, Cyclohexanol, Alcohols, Carbitols, Hydrocarbons
Electronic Components	Butyl Acetate, Xylene, MEK, Cellosolve
Fiberglass Coating	Teflon Emulsion, Fiberglass, Synthetics, Styrene
Flexographic Printing	Flexographic Ink Derivatives, Alcohols, Glycol
Formaldehyde	Formaldehyde, Methanol, CO
Lithographic Print/Paint	Butyl Cellosolve, Ciacetone Alcohol, Solvesso, Cellosolve Acetate, Xylene, MIBK
Metal Coating	Alcohols, Cellosolve Acetate, Phthalates, Solvesso
Paper Coating	High-Boiling Organics, Latexes
Pharmaceuticals	Isopropanol, Toluene, Hydrocarbons
Phthalic Anhydride Mfg.	Organic Acids
Resin Plant	Formaldehyde, Phenols, Phthalic Anhydride

Industry Operation	Gaseous Pollutants Emitted
Rubber Processing	
Soil Remediation	Benzene, Toluene, Ethylene, Xylene
Sterilizers	Ethylene Oxide
Vinyl Surgical Glove	Polyvinyl Chloride, Cioctyl Phthalate
Wire Enameling	Cellosolve Acetate

The air pollution control solutions that are available to control these emissions are normally dictated by the volume of air that is to be processed. The volume of air flow, measured in cubic feet per minute, is designated as ACFM for Actual Cubic Feet per Minute of SCFM where "S" stands for standard cubic feet per minute, at 70°F, sea level, and one atmosphere.

Thermal destructive techniques have been widely used for many years to control some of these emissions. Thermal oxidizer sizes range from 100 SCFM up to 100,000 SCFM. Each industry has operations that dictate the exhaust flow that must be processed.

Commercially available thermal oxidizer systems are pre-engineered, that is, the equipment is designed on the principle that in order for the equipment to be competitive in the marketplace, then a series of products of fundamentally standard designs are tailored to the application by changing some of the parameters as dictated by the requirements. This is not always the case with other pollution control systems, as oftentimes custom built-systems are specified. Since thermal oxidation equipment has a burner, the designs require controls for safety and operation.

Controls are termed user friendly with control logic being relay or computer based. As noted in earlier chapters, particular hydrocarbons affect health in several ways. Some affect the respiratory system, while others are air toxins. Recall from Chapter 1 that the EPA issued new rules and regulations in 1990 regarding VOCs and air toxins. Subsequent controls or regulations have been issued which have identified that air toxins are particularly dangerous to industrial workers. One of the major air toxins is benzene, and benzene is one of the principal components of gasoline. The remediation of benzene from underground storage tanks and leaky underground petroleum bases is a significant source of air toxins. Carbon tetrachlorethylene, hydrogen cyanide, and ketones are all air toxins being controlled or regulated, since they are carcinogenic and may create an immediate problem or delayed.

Emission Stream Characteristics

In determining the most appropriate technology to controlling a process stream, it is necessary to characterize the air stream. The first step in the characterization is to establish what organics and other contaminants need to be destroyed or controlled. Recognize also that the sizing of the equipment required is dependent on the air flow and the organic loading.

There are four general oxidation technologies:

- Catalytic Recuperative,
- Thermal Recuperative,
- Regenerative Thermal, Regenerative Catalytic, and
- Rotor Concentrator.

Low flow, low concentration streams are best handled by a catalytic recuperative oxidizer. When the concentration of the stream is between 15% to 20% LEL (Lower Explosion Limit) then both a catalytic recuperative or thermal recuperative is the best technologies. For process streams between 20% to 25% LEL then thermal recuperative is the preferred solution.

It is important to establish the volume of the process stream that is to be treated. There are companies that have not needed to buy pollution control equipment in the past. Their approach to eliminating pollution has been the more exhaust, the better. This is particularly true in the low margin industries. The more complex and high volume industries, e.g., the chemical industry, have normally been concerned about the air exhausted from their plant and have paid attention to the exhaust volume by process control. The industries that have not paid attention to exhaust volume are not sufficiently aware that when buying pollution control equipment the cost of that equipment is going to depend on two elements:

- The air volume that must be processed, and
- The pounds per hour of organics that must be processed.

Process flow reduction should be targeted and must be in such a way that it will not impact upon the operation of the process or plant. The normal first response by a plant engineer is that air flow reduction cannot be done. However, subsequent investigation has resulted in that most of the time flow reduction can be done. This should be a significant area to focus on when conducting a pollution prevention audit.

Organic Loading: Determining the concentration of the organic matter in plant offgases can be difficult. However, in an operation where solvents or other organics are purchased, the number of pounds or tons of the organics that have been bought in the past year is known. Note that this information must also be supplied to the environmental authorities. Hence, examining purchasing records can provide some good insights into how much is ultimately loss as emissions. Given the tons of organics purchased in the previous years, and the number of operating hours per year, the ratio of those two numbers yields the pounds per hour, a conservative initial estimate of the average organic loading. This methodology assumes that everything that is purchased will be emitted up the stacks. In addition to the loading, it is necessary to determine if there are compounds in the exhaust stream which can be deleterious to catalysts used, thereby precluding the use of this technology. As an example, when automotive catalytic mufflers and converters were introduced many years ago, the automobile industry required the petrochemical industry to eliminate lead from gasoline since lead degraded and reduced the effectiveness of the catalyst and the destruction of the gasoline. One set of industrial compounds that can harm catalysts are halogens, a family of compounds which include chlorine, bromine, iodine, and fluorine. Bromine, while not prevalent in industry, is present in chemical plants. Freons are fluorine compounds. Silicone is another compound which is deleterious to catalyst. It is used as a *slip agent*, or a lubricant in many industrial processes. Phosphorous, heavy metals (zinc, lead), sulfur compounds, and any particulate can result in shortening the life of the catalyst. It is necessary to estimate the volume or the amount of each of those contaminants, to assess the viability of catalytic technologies for the application.

Operating Costs

RTO/RCO and Rotor/Concentrator systems are typically higher in capital costs, but the operating cost savings on high volume, low concentration streams make these technologies attractive. Subsequently the capital and operating cost of the equipment and the cost of the installation of that equipment is related to the sizing. Since oxidation equipment requires fuel and electricity, the operating costs will also depend on the hours or operation per day, per week, and per year. In addition, the costs depend on the quantity of organics that need to be processed, in pounds per hour (lb/hr), or in parts per millions by volume (ppmv). A critical consideration is whether the organic loading is steady state or if it has peaks or spikes. Since all oxidation equipment has to operate at an elevated temperature, it is necessary to know the type of auxiliary energy of fuel available. All oxidizers can operate on electric heating, natural gas, or LPG, whereas thermal oxidizer can operate with sulfur based fuels such as number two or number six fuel oil. Electric heat is only suitable for small air flows; otherwise it is too costly. No thermal oxidizer should be considered without some arrangement for heat recovery. The reason being that a continuing cost of air pollution control is the operating cost. Available heat recovery efficiencies vary depending on the type of thermal oxidation technology selected. The specific heat recovery efficiency selected for an application depends on the organic concentration. Table 5 shows an economic comparison for a particular air stream.

Table 5. Operating Cost Comparisons for Different Systems.

Process Stream % LEL	**Catalytic Recuperative Oxidizer**	**Thermal Recuperative Oxidizer**	**Regenerative Catalytic Oxidizer**	**Regenerative Thermal Oxidizer**	**Rotor Concentrator with Thermal Oxidizer**
1	$11.00/hr	$28.37/hr	$2.50/hr	$5.65/hr	$0.30/hr
10	$ 3.70/hr	$16.72/hr	$1.65/hr	$1.60/hr*	N/A

Operational Modes: The Catalytic Recuperative Oxidizer assumes a 65% efficienct heat exchanger.; The Thermal Recuperative Oxidizer assumes a 65% efficienct heat exchanger; The Regenerative Catalytic Oxidizer assumes a 95% efficienct heat exchanger; The Regenerative Thermal Oxidizer assumes a 95% efficient heat exchanger.; The rotor concentrator wheel assumes a 6:1 concentration ratio.

The comparison is for a process stream of 10,000 SCFM with an inlet temperature of 70°F. Toluene is the contaminant in this example. Toluene has a calorific content of 16,720 BTU/LB and a LEL of 1.10% by volume. For each of the technologies, an economic analysis was performed at a toluene loading of 1% LEL and at 10% LEL. The results of this analysis are reported as operational costs in $/hr. The operational cost is the sum of the fuel usage as well as the electricity needed to run the system fans. All the technologies are assumed to be running on natural gas at a cost of $4.50/MMBTU. The electricity price has been taken at $0.06/KWH. See the operating cost advantages of one technology over another at two loading conditions. A catalytic recuperative oxidizer, with a 65% effective heat exchanger, is more economical to operate at the 1% to 10% LEL range than a thermal recuperative oxidizer with a 65% effective heat exchanger. The thermal recuperative oxidizer will only begin to show a significant reduction in operational costs around the 15% to 25% LEL range. Both of the regenerative oxidizers utilize a 95% effective heat exchanger. These technologies are best suited for high air flow, low loading process streams.

Both of the regenerative oxidizers begin to show high temperature bypass at the 10% LEL loading. This means that the loading point at which the oxidizers would require zero supplemental fuel has been exceeded. Excess heat is now being produced in the oxidizer. This heat must be able to escape from the oxidizer by way of a high temperature bypass. Also, the rotor concentrator wheel is another technology suited for high airflow, low loading process streams. The rotor concentrator will concentrate the process stream from anywhere between a 6:1 to a 13:1 concentration ratio. Thus, the airflow will be reduced 6 times, while the contaminant loading will be increased 6 times. The rotor concentrator technology is not suited for process streams at a 10% LEL loading.

Destruction Efficiency

In the U.S. and many parts of Western Europe, 95% destruction of VOC is required, and when toxic chemicals are present the destruction efficiency is raised to 99%. Characterization of the VOC laden stream assists in selecting the appropriate technology to achieve the required destruction efficiency.

Theory of Operation

There are seven fundamental oxidizer technologies that achieve the oxidation of organics in alternate ways. These technologies are:

- Catalytic Recuperative
- Thermal Recuperative
- Catalytic Regenerative
- Thermal Regenerative
- Rotor Concentrators
- Flare/Burner
- Ceramic Filter

Before describing these, some general background information is presented.

Thermal oxidation, by definition, converts a hydrocarbon, in the presence of oxygen and heat, to carbon dioxide and water vapor. A general equation showing this relationship is:

$$C_nH_{2m} + (n + m/2)O_2 \rightarrow nCO_2 + mH_2O + \text{Heat}$$

The particular n and m subscripts of the equation are used to define the number of carbon atoms and hydrogen atoms. The number of oxygen atoms convert to n molecules of carbon dioxide and m molecules of water vapor and heat which is given off in the exothermic reactor.

One measure of the organic loading or the organic concentration of the process stream is the "lower explosive limit," designated as the LEL (also known as the "lower flammable limit," designated as the LFL). The LEL of a stream is the lowest organic concentration in a stream that would, in the presence of an ignition source, yield a combustible mixture. At this concentration, the stream is said to be at 100% LEL. As examples, if a steam has toluene or alcohol and it is at 100% LEL, this means that the concentration within that stream is explosive if a spark or ignition source is present (recall the so-called *fire-triangle* explanation of combustion). Look back in Chapter 3 for some common organics and their fire properties.

Let's take the example of benzene, which at 12,000 ppm, is 100% LEL. The National Fire Protection Association (NFPA) states that equipment can operate, without LEL monitors or controls, if the LEL is less than 25% LEL. For benzene then, 25% LEL is equal to 3,000 ppm. This upper boundary becomes a dictating factor in the selection and design of the oxidation equipment. If the concentration is higher than 25% LEL, the NFPA requirements state that an LEL monitor is required. Using an LEL monitor, NFPA guidelines allow operation up to 50% LEL (a 2:1 safety factor). Thus, 100% LEL is explosive; if the stream is at 25%, a factor safety of four exists.

In addition to the explosive aspects of the LEL, another issue is the heat energy given off during oxidation. An estimate of the exotherm is that there will be a 25° F rise per 1% LEL in the stream. Hence, if the process air enters the oxidizer at a given temperature, and if the stream has a concentration of 2% LEL, then a 50° F rise in process stream temperature is expected after oxidation. If the process stream were running at a 10% LEL, then a 250°F temperature rise would be predicted. A maximum LEL of 25% yields a 625°F temperature rise of the process stream.

The concentration that is required to yield 100% LEL varies with the characteristics of the identified organics. For example, ethanol has a 20,000 ppm by volume concentration whereas benzene has a 12,000 ppmv.

Not only do different organics have different LELs but every time a pound of a different organic is oxidized, a different amount of heat will be given off. An example that demonstrates this energy release is the catalytic muffler in an automobile. When mufflers were initially installed, the high level of unburned gasoline which went through the muffler caused excessive heating and subsequently caused fires if the auto had been parked on leaves. The reason for the excessive heat was that for each pound of gasoline being oxidized 20,000 BTU's were being released.

Chlorinated organics are hydrocarbons that have one or many chlorine atoms. Oxidation of chlorinated hydrocarbons yields CO_2, water vapor and hydrogen chloride (HCl) gas. Some typical chlorinated organics are TCE and PCE. These organics have calorific values as low as 5,000 BTU/lb.

We should not forget to mention the importance of the catalyst. The characteristics of oxidation catalyst are many and varied. Fundamentally, if an airstream containing organics is heated and passed across catalyst, the organics will be converted to carbon dioxide and water vapor. However, the percent conversion happens at different temperatures for different organics and for different catalysts. As an example, to destroy 25% of the toluene in an air stream, a temperature of about 300°F is required. However, the EPA does not require 25% destruction, but 95 to 99% destruction. In order to destroy 95% of the toluene, 500 to 550°F is required. Some organics require higher temperatures to be destroyed than others, catalytically. Alcohols, isopropyl alcohol and ethanol, can be destroyed relatively simply whereas the acetates, particularly the ethyl acetates and propyl acetates, may require temperatures in the 750° F range in order to achieve adequate destruction. Depending on the process stream, either a single organic may be present as found in the chemical industry, or in printing operations, a multiplicity of organics exists. Having a multiplicity of organics imposes the requirement of focusing on the ability to destroy the most difficult organic constituent.

Some organics cannot be effectively destroyed by catalyst. For example: heptane and hexane can be destroyed at temperatures of 600-700°F, whereas propane, ethane, and methane require temperatures beyond a reasonable temperature range. Since methane is not a smog producing organic, a guarantee to destroy 95% of the organics means that the methane is not considered and is removed from that stream in evaluating the process. However, if propane is the auxiliary fuel, that is, if the burners are being driven by LPG or by propane directly, it means that there will be contribution to the VOC at the end of the stack.

The catalyst is normally contained on a ceramic substrate. These ceramics are extruded in a malleable state and then fired in ovens. The process consists of starting with a ceramic and depositing an aluminum oxide coating. The aluminum oxide makes the ceramic, which is fairly smooth, have a number of bumps. On those bumps a noble metal catalyst, such as platinum, palladium, or rubidium, is deposited. The active site, wherever the noble metal is deposited, is where the conversion will actually take place. An alternate to the ceramic substrate is a metallic substrate. In this process, the aluminum oxide is deposited on the metallic substrate to give the wavy contour. The precious metal is then deposited onto the aluminum oxide. Both forms of catalyst are called monoliths.

An alternate form of catalyst is pellets. The pellets are available in various diameters or extruded forms. The pellets can have an aluminum oxide coating with a noble metal deposited as the catalyst. The beads are placed in a tray or bed and have a depth of anywhere from 6 to 10 inches. The larger the bead (1/4 inch versus 1/8 inch) the less the pressure drop through the catalyst bed. However, the larger the bead, the less surface area is present in the same volume which translates to less destruction efficiency. Higher pressure drop translates into higher horsepower required for the oxidation system. The noble metal monoliths have a relatively low pressure drop and are typically more expensive than the pellets for the same application.

Base Metal Catalyst - An alternate to a noble metal catalyst is a base metal catalyst. A base metal catalyst can be deposited on a monolithic substrate or is available as a pellet. These pellets are normally extruded and hence are 100% catalyst rather than deposition on a substrate. A benefit of base metal extruded catalyst is that if any poisons are present in the process stream, a deposition of the poisons on the surface of the catalyst occurs. Depending on the type of contaminant, it can frequently be washed away with water. When it is washed, abraded, or atritted, the outer surface is removed and subsequently a new catalyst surface is exposed. Hence, the catalyst can be regenerated. Noble metal catalyst can also be regenerated but the process is more expensive. A noble metal catalyst, depending on the operation, will typically last 30,000 hours. As a rule of thumb, a single shift operation of 40 hours a week, 50 weeks a year results in a total of 2,000 hours per year. Hence, the catalyst might have a 15 year life expectancy. From a cost factor, a typical rule of thumb is that a catalyst might be 10%-15% of the overall capital cost of the equipment.

Catalytic Recuperative Oxidizer - A catalytic recuperative oxidizer consists of several main elements:

- System Fan
- Heat Exchanger

- Reactor
- Catalyst
- Exhaust Stack

With this technology, the process stream is ducted to the oxidizer and enters a system fan. The system fan is driven by a motor and the process stream is forced under positive pressure through a heat exchanger. The heat exchanger is usually a cross flow heat exchanger of the shell and tube type. Plate type heat exchangers can also be used in the application. Normally, the process stream enters through the tube side of the heat exchanger due to the ability of cleaning the tubes. As the air enters in and goes through the heat exchanger, it is heated and will then exit into the section called the reactor. As it enters the reactor, the process stream will be further heated by a burner, controlled by a thermocouple measuring the temperature of the air and a temperature controller regulating the burner firing to bring the process stream up to the catalyzing temperature of 300-700° F. The catalyzing temperature depends on the organic, the requirement for the destruction of the organic and the type and volume of catalyst. At the catalyzing temperature, the process stream will pass through a series of beds, having catalyst in them. As the air containing organics comes across the catalyst, the organic is converted to CO_2 and water vapor and an exothermic reaction occurs. This exotherm will raise the temperature of the stream exiting the catalyst bed. Hence, the catalyst outlet temperature will be higher than the temperature going into the catalyst bed. The process stream is then directed through the shell side of the heat exchanger where it preheats the incoming air and is then exhausted to the atmosphere.

Thermal Recuperative Oxidizer - The best way to understand the theory of operation for thermal recuperative oxidation is by the three "Ts" of combustion:

- **Time**
    - **Turbulence**
        - **Temperature**

Time refers to the retention time or residence which is the length of time that an organic is at the appropriate oxidation temperature. Roughly, if a 95% destruction efficiency is required, a residence time of a half a second is adequate. That is, the organic compound is brought up to a temperature of about 1400° F, and maintained at that temperature for a retention time of half a second. Both retention time and turbulence must be achieved, where turbulence is a term which implies a required degree of mixing. If the turbulence occurs and if the 1400° F for a half a second is achieved, with adequate oxygen, then 95% of the organics will be destroyed. In some cases, oxygen must be added to a process stream. For each organic, a specific temperature and a specific retention time is required to achieve the desired level of destruction. Refer to the sidebar discussion for some examples.

One of the concerns that exists in thermally processing chlorinated organics is that the by-products of combustion that are formed may be more harmful than the initial product that is to be destroyed. A by-product of combustion is a compound formed, either catalytically or thermally, when most of the organic compound is converted to CO_2 and H_2O. For example, when 97% of the toluene in an air stream is destroyed, what happens to the other 3%? Does it remain as toluene or are new products formed? Frequently, "by products of combustion" are formed and it is not possible to predict what those by products are. They could be a mixture of the original compounds or they could be more harmful. The concern that we have in processing chlorinated organics thermally at these high temperatures is that dioxins may be generated. Dioxins are in effect much more harmful than the organic that will cause VOCs or smog in the air.

Typical Temperatures and Residence Times for Destruction of Common Organics

0.5 SEC RETENTION TIME

Organic	95% DE	99% DE
Toluene	1351	1372
Benzene	1489	1640
Styrene	1445	1480
PCE	1843	1921
TCE	1592	1675

1.0 SEC RETENTION TIME

Organic	95% DE	99% DE
Toluene	1317	1338
Benzene	1415	1640
Styrene	1391	1424
PCE	1726	1797
TCE	1972	1545

Thermal oxidizers must be built to provide the residence time and temperatures to achieve the desired destruction efficiency (DE). As such, thermal oxidizers are comparatively larger than catalytic oxidizers since their residence time is two to four times greater. Historical designs of thermal oxidizers were comprised of carbon steel for the outer shell and castable refractory or brick as the thermal liner (a refractory is like a cement, which is put on the inside of the rector shell to act as a thermal insulation barrier). Modern units are designed and built using ceramic fiber insulation on the inside, which is a lightweight material, and has a relatively long life. Old refractory would tend to fail over a period of years by attrition of expansion and contraction.

A forced draft thermal recuperative oxidizer consists of a fan which forces the process airstream through a heat exchanger. As the process flow exits the heat exchanger the burner fires and the process stream is brought up to temperature. The reactor chamber, which is lined with a high temperature ceramic fiber, is designed for the required retention time. A shell and tube heat exchanger is normally used for thermal oxidizers because of expansion concerns. The material selection for the shell and tube heat exchanger needs to be a high grade stainless, adequate for expected steady state and peak temperatures.

In addition to forced draft systems, induced draft systems are also used. The induced draft system is slightly more expensive but is recommended when particulate, or organic oils are present. Particulates impact upon a forced draft fan and will have a negative effect on the system performance. If the process stream is clean a forced draft system is appropriate.

The burners used are modulating burners, that is, if the organic is preheated to an adequate temperature, the burners will modulate down to zero so that there is no energy required for the continued oxidation.

One of the advantages of the thermal recuperative oxidizer is that it is possible to process organics that may be a poison or be detrimental to catalyst. In addition, if the organic concentration is very high, for example the organic level is of the 20 to 25% LEL, then thermal recuperative oxidation is appropriate.

For relatively large volume and low concentration streams the disadvantage with the thermal recuperative design is that the metallic heat exchanger only recovers about 70% of the heat and operating costs increase dramatically. The level of heat exchanger efficiency is limited by material cost to increase heat exchanger efficiency and the fact that autoignition, where organics ignite due to temperature alone, becomes a problem with the life of metallic heat exchangers.

Regenerative Thermal Oxidizer (RTO) - The Regenerative Thermal Oxidizer is a thermal oxidizer consisting two or more ceramic heat transfer beds, which act as heat exchangers and a Purification Chamber or Retention Chamber where the organics are oxidized and converted to CO_2 and H_2O vapor. The operation of a RTO (Dual-Bed) requires the initial preheating of the ceramic heat transfer beds to a temperature of 1500°F during the startup mode. This is accomplished by operation of fuel fired burner located in the purification chamber. To equalize the preheating of the ceramic heat transfer beds, the air is directed into and out of the ceramic heat transfer beds by operation of pneumatic diverter valves located under each ceramic heat transfer bed. During initial startup outside air is supplied to the oxidizer through the make-up air damper tee located on the inlet side of the process air fan. A Programmable Logic Controller (PLC) monitors and controls the direction of the air flow.

After the ceramic heat transfer beds have reached an operating temperature of 1500°F the unit is ready for the process airstream. As the process airstream enters the ceramic heat transfer beds, the heated ceramic media preheats the process airstream to its oxidation temperature. Oxidation of the airstream occurs when the auto-ignition of the hydrocarbon is reached. At this point the heat released by the oxidation of the process hydrocarbons is partially absorbed by the inlet ceramic heat transfer bed. The heated air passes through the retention chamber and the heat is absorbed by the outlet ceramic heat transfer bed.

During the normal Mode of Operation of the system the process air enters the RTO System Fan and passes through the Inlet Diverter Valve where the process air is forced into the bottom of the left ceramic heat transfer bed. As the process air rises through the ceramic heat transfer bed, the temperature of the process stream will rise. The tops of the beds are controlled to a temperature of 1,500°F. The bottoms of the beds will vary depending upon the temperature of the air that is coming in. If it is assumed that the process air is at ambient conditions or 70° F, then as the air enters the bottom of the bed, the bottom of the bed will approach the inlet air temperature of 70°F. The entering air is heated and the media is cooled. As the air exits the ceramic media it will approach 1500°F. The process air then enters the second bed at 1,500°F and now the ceramic media recovers the heat from the air, and increases in temperature. At a fixed time interval (usually 4 to 5 minutes), or based on thermocouple control, the diverter valves switch and the process air is directed to enter the bed on the right and exits the bed on the left. Prior to valve switching the air heated the right bed and now this bed is being cooled. The cooling starts at the bottom and continues upward because the media is hot and the energy is transferred. The process air then goes through the purification chamber and exits through the second bed. When the valves are switched, whatever organics had not been destroyed prior to the flow being reversed are then exhausted out of the stack. In addition, the rapidity of switching or closure of the valves is critical to minimize the bypass of unoxidized organics. If the emissions versus time were plotted, the graph would reflect a very low exhaust concentration level, but whenever the diverter valve switches an organic pulse occurs in the exhaust stream. Since the valves shift every four minutes these pulses reduce the overall destruction efficiency of the organics. Several methods of processing the pulse exist in order to achieve higher destruction efficiencies.

The retention chamber and heat transfer chamber are fabricated of reinforced carbon steel exterior and ceramic fiber lining. The thickness of the ceramic fiber lining is based on the required destruction temperature of the organics and the desired outside shell temperature. The ceramic heat exchange media can be of various types including ceramic saddles, tye pacs, or structured packing. The ceramic structured packing is a recent development in the industry reflecting lower pressure drops for equivalent heat transfer. A reinforced carbon steel structure is provided to support the loads of the oxidizer chambers and the structured packing support grid, and the wind and/or earthquake loads. The packing support grid is fabricated of stainless steel and is designed to support the structured packing. If organic particulates in the process exhaust builds up on the "cold" surfaces at the bottom of the oxidizer, the process must be shut down and a volatilization of these organics or a "bakeout" is required. When bake-out is activated, the flow diverter valves will stay in one position until the exhaust air temperature from the outlet bed reaches 850°F. At this temperature, most organic oils will volatilize, as in a self cleaning oven. When the first outlet bed reaches 850°F, the flow diverter valves will switch and will stay in position until the outlet temperature of the second bed reaches 850°F.

Regenerative Catalytic Oxidizer (RCO) - A catalytic oxidizer design uses the term Gas Hourly Space Velocity (GHSV) which relates the amount of air to be processed and the volume of catalyst required. The GHSV is the inverse of the residence time. We note also that lower temperature translates into lower fuel costs assuming the same heat exchanger efficiency. It takes energy to take the airstream from whatever temperature it enters, up to its operating temperature. Even though a heat exchanger will help reduce net fuel costs, the lower the operating temperature, the lower the fuel costs. The sidebar discussion provides some comparisons of oxidation temperatures for different organics.

OPERATING TEMPERATURE COMPARISONS

Catalytic Vs. Thermal Oxidation Temperatures for 99% Destruction

Organic	Catalytic	Thermal
Benzene	440	1460
Carbon TET	610	1430
MEK	600	1780
Cyanide	480	1800

Rotor Concentrator/Thermal Oxidizer - For high volume airstreams with relatively low organic concentration, the energy required to bring the process stream to thermal oxidation temperature can be significant. A technology developed uses a Rotor Concentrator in a 2 step process and has proven to be effective in high volume, low concentration air streams.

The first part of that system consists of a slowly rotating concentrator wheel, utilizing zeolites or carbon deposited on a substrate, which adsorbs the organics as they are exhausted from the original process and passed through the wheel. A sector of the concentrator wheel is partitioned off from the main section of the rotor and clean heated air is passed through this section to desorb the organics. The air volume of clean heated air varies for applications, but is roughly 10% of the original airstream volume.

As the clean heated air passes through the rotor section, the organics are desorbed, resulting in a process stream that is 10% in volume of the original process stream and 10 times the original concentration. The desorption airstream will drive off all the organics in that particular sector of the wheel and as the shell continues to turn the entire wheel is desorbed. As the concentrated organic, low volume airstream exits and in the second part of the system it is processed through a thermal recuperative oxidizer. Consequently, what is achieved is that a large air stream with low concentration, which requires considerable energy to heat up, has been reduced to a low airstream with a high concentration, which is significantly less costly to process.

A secondary fan draws the air and forces it through the secondary heat exchanger, where the reduced air volume temperature is raised to the required desorption temperature. The preheated air is then used to desorb the air in one portion of the wheel. As the air exits the desorption section the organic concentration is approximately 10 times the concentration of the original process stream. This low volume, higher concentration stream then enters the induced draft section of a catalytic or thermal recuperative oxidizer, where the organics are destroyed.

The total hydrocarbon reduction efficiency for the Rotor/Concentrator is the adsorption efficiency of the Rotor/Concentrator times the destruction efficiency of the oxidizer.

Flare and Burners - Certainly the oldest and still widely used technology through some parts of the world is flaring. Flares are used in the petroleum, petrochemical, and other industries that require the disposal of waste gases of high concentration of both a continuous or intermittent basis. As other thermal oxidation technologies, the three T's of combustion of time, temperature, and turbulence are necessary to achieve adequate emission control.

Flares ideally burn waste gas completely and smokelessly. Two types of flares are normally employed. The first is called the open flare, whereas the second is called the enclosed flare. The major components of a flare consist of the burner, stack, water seal, controls, pilot burner, and ignition system. Flares required to process variable air volumes and concentrations are equipped with automatic pilot ignition systems, temperature sensors, and air and combustion controls.

Open flares have a flare tip with no restriction to flow, the flare tip being the same diameter of the stack. Open flares are effectively a burner in a tube. Combustion and mixing of air and gas take place above the flare with the flame being fully combusted outside of the stack.

Enclosed flares are composed of multiple gas burner heads placed at ground level in a stacklike enclosure that is usually refractory or ceramic lined. Many flares are equipped with automatic damper controls that regulate the supply of combustion air depending on temperature which is monitored upstream of the mixing, but inside the stack. This class of flare is becoming the standard in the industry due to its ability to more effectively control emissions. Requirements on emissions includes carbon monoxide limits and minimal residence time and temperature. Exhaust gas temperatures may vary from 1,000 to 2,000°F.

Ceramic Filter - The ceramic filter collects, volatilizes, and destroys particulates, and condensible organics emitted from industrial process streams, such as paint spray, lost foam casting, condensible organics, tenter frames, and cured rubber operations. It may be used independently as a hot or cold filter media or coupled with an oxidization module for total odor and VOC control. The ceramic filter is designed based on exhaust airflow volume, type of contaminant, and desired collection efficiency. During operation, the process stream, containing hot or cold particulate laden air, condensible organics, or VOCs, is drawn into the ceramic filter. The process stream passes over a ceramic matrix selected on particle size and collection efficiency considerations. The ceramic matrix is periodically heated by a natural gas burner, whereby any organics collected on the ceramic matrix are volatilized. Any non-organics collected on the ceramic matrix are converted to inorganic ash and retained in the unit dropout chamber. If required, the volatilized organics can then be processed through a catalyst bed. As in the catalytic oxidizer these volatiles would be converted to CO_2 and H_2O.

Additional Information

References 124 through 130 provide additional information on thermal destructive technologies, design and scale-up principles, as well as operational guidance.

REFERENCES AND RECOMMENDED RESOURCES FOR THE READER

1. Andriola, 1999. T. Andriola, Fisher-Klosterman, Inc., (502) 572-4000, personal communication with Eric Albright, October 14, 1999.
2. AWMA, 1992. Air & Waste Management Association, Air Pollution Engineering Manual, Van Nostrand Reinhold, New York, NY, 1992.
3. Avallone, 1996. "Marks' Standard Handbook for Mechanical Engineers," edited by Eugene Avallone and Theodore Baumeister, McGraw-Hill, New York, NY, 1996.
4. Corbitt, 1990. "Standard Handbook of Environmental Engineering," edited by Robert Corbitt, McGraw-Hill, New York, NY, 1990.
5. Davis, 1999. W. Davis, Professor and Coordinator, Environmental Engineering Program, Department of Civil and Environmental Engineering, University of Tennessee, (423) 974-7728, personal communication with E. Albright, October 28, 1999.
6. EPA, 1982. U.S. EPA, Office of Air Quality Planning and Standards, "Control Techniques for Particulate Emissions from Stationary Sources, Volume 1," EPA-450/3-81-005a, Research Triangle Park, NC, September, 1982.
7. EPA, 1996. U.S. EPA, Office of Air Quality Planning and Standards, "OAQPS.
8. Control Cost Manual," Fifth Edition, EPA 453/B-96-001, Research Triangle Park, NC, February, 1996.
9. EPA, 1998. U.S. EPA, Office of Air Quality Planning and Standards, "Stationary Source Control Techniques Document for Fine Particulate Matter," EPA-452/R-97-001, Research Triangle Park, NC, October, 1998.
10. Josephs, 1999. D. Josephs, Equipment Product Manager, AAF International, (502) 637-0313, personal communication with Eric Albright, October 28, 1999.
11. Mycock, 1995. J. Mycock, J. McKenna, and L. Theodore, "Handbook of Air Pollution Control Engineering and Technology," CRC Press, Boca Raton, FL, 1995.
12. Parsons, 1999. B. Parsons, Sterling Systems, Inc., (804) 316-5310, personal communication with E. Albright, October 26, 1999.
13. Perry, 1984, "Perry's Chemical Engineer's Handbook," edited by Robert Perry and Don Green, 6th edition, McGraw-Hill, New York, NY, 1984.

14. Wark, 1981, Kenneth Wark and Cecil Warner, "Air Pollution: Its Origin and Control," Harper-Collins, New York, NY, 1981.
15. Avallone, 1996. "Marks' Standard Handbook for Mechanical Engineers," edited by Eugene Avallone and Theodore Baumeister, McGraw-Hill, New York, NY, 1996.
16. AWMA, 1992. Air & Waste Management Association, Air Pollution Engineering Manual, Van Nostrand Reinhold, New York, NY, 1992.
17. Cooper, 1994. David Cooper and F. Alley, Air Pollution Control: A Design Approach, 2nd Edition, Wave and Press, Prospect Heights, IL, 1994,
18. EPA, 1996. U.S. EPA, Office of Air Quality Planning and Standards, "OAQPS Control Cost Manual," Fifth Edition, EPA 453/B-96-001, Research Triangle Park, NC, February, 1996.
19. EPA, 1998. U.S. EPA, Office of Air Quality Planning and Standards, "Stationary Source Control Techniques Document for Fine Particulate Matter," EPA-452/R-97-001, Research Triangle Park, NC, October, 1998.
20. Perry, 1984. "Perry's Chemical Engineers' Handbook," edited by Robert Perry and Don Green, 6th Edition, McGraw-Hill, New York, NY, 1984.
21. STAPPA/ALAPCO, 1996. State and Territorial Air Pollution Program Administrators and the Association of Local Air Pollution Control Officials (STAPPA/ALAPCO), "Controlling Particulate Matter Under the Clean Air Act: A Menu of Options," STAPPA/ALAPCO, Washington, DC, July, 1996.
22. Vatavuk, 1990. W.M. Vatavuk, "Estimating Costs of Air Pollution Control," Lewis Publishers, Chelsea, MI, 1990.
23. Wark, 1981. Kenneth Wark and Cecil Warner, "Air Pollution: Its Origin and Control," Harper Collins, New York, NY, 1981.
24. EPA, 1997. U.S. EPA, Office of Air Quality Planning and Standards, "Compilation of Air Pollutant Emission Factors. Volume I, Fifth Edition, Research Triangle Park, NC., October.
25. EPA, 19.98a. US. EPA, Office of Air Quality Planning and Standards, "Stationary Source Control Techniques Document for Fine Particulate Matter, "EPA-452IR-97-001, Research Triangle Park, NC., October.
26. EPA. 1998b. U.S. EPA, Office of Air Quality Planning and Standards, "OAQPS Control Cost Manual, 5th Edition, Chapter 5, EPA 453/B-96-001, Research Triangle Park, NC, December.
27. ICAO 1999. Institute of Clean Air Companies internet web page www.icac.com, Control Technology Information; Fabric Filters, page last updated January 11, 1999. STAPPAIALAPCO, 1996. State and Territorial Air Pollution Program Administrators and Association of Local Air Pollution

Control Officials, "Controlling Particulate Matter Under the Clean Air Act: A Menu of Options," July.

28. AAF International, Inc., internet web page www.aafint/com/equipmentl, Core Products Information, last updated December, AWMA, 1992.
29. Air & Waste Management Association, Air Pollution Engineering Manual. Van Nostrand Reinhold, New York.
30. EPA, 1997. U.S. EPA, Office of Air Quality Planning and Standards, "Compilation ofAir Pollutant Emission Factors, Volume I, Fifth Edition, Research Triangle Park, NC, October.
31. EPA, 1998a. U.S. EPA, Office of Air Quality Planning and Standards, "OAQPS Control Cost Manual," 5th Edition, Chapter 5, EPA 453/B-96-001, Research Triangle Park, NC. December.
32. EPA, 1998b. U.S. EPA, Office of Air Quality Planning and Standards, "Stationary Source Control Techniques Document for Fine Particulate Matter" EPA-452/R-97-001, Research Triangle Park, NC, October.
33. Heumann, 1997. W. L. Heumann, Industrial Air Pollution Control Systems, McGraw Hill Publishers, Inc., Washington, D. C.
34. ICAO 1999. Institute of Clean Air Companies internet web page www.icac.com, Control Technology Information: Fabric Filters, page last updated January 11, 1999.
35. IFF, 1999. Industrial Filter Fabric, Inc., Internet Web page www.filters.com, Product Bulletin 003; Cartridge Filters, December, 1999.
36. STAPPAIALAPCO, 1996. State and Territorial Air Pollution Program Administrators and Association of Local Air Pollution Control Officials, "Controlling Particulate Matter Under the Clean Air Act: A Menu of Options," July.
37. Torit, 1999. Torit Products a Subsidiary of Donaldson Company, Inc. internet webpage www.torit.com/Products, Industrial Dust Collection Systems, last updated December.
38. AWMA, 1992. Air & Waste Management Association, Air Pollution Engineering Manual, Van Nostrand Reinhold, New York.
39. Cooper & Alley, 1994. C. D. Cooper and F. C. Alley, Air Pollution Control: A Design Approach, Second Edition, Waveland Press, Inc. IL.
40. EPA, 1996. U.S. EPA, Office of Air Quality Planning and Standards, "OAQPS Control Cost Manual," Fifth Edition, EPA 453/B-96-001, Research Triangle Park, NC. February.

41. EPA, 1997. U.S. EPA, Office of Air Quality Planning and Standards, "Compilation of Air Pollutant Emission Factors, Volume I, Fifth Edition, Research Triangle Park, NC, October.
42. EPA, 1998. U.S. EPA, Office of Air Quality Planning and Standards, "Stationary Source Control Techniques Document for Fine Particulate Matter," EPA-452/R-97-001, Research Triangle Park, NC, October.
43. Flynn, 1999. Brian Flynn, Beltran Associates, Inc., (718) 338-3311, personal communication with Eric Albright, February 5, 1999.
44. ICAC, 1999. Institute of Clean Air Companies internet web page www.icac.com, Control Technology Information: Electrostatic Precipitator, page last updated January 11, 1999.
45. STAPPA/ALAPCO, 1996. State and Territorial Air Pollution Program Administrators and Association of Local Air Pollution Control Officials. "Controlling Particulate Matter Under the Clean Air Act: A Menu of Options," July.
46. AWMA, 1992. Air & Waste Management Association, Air Pollution Engineering Manual, Van Nostrand Reinhold, New York.
47. Cooper & Alley, 1994. C. D. Cooper and F. C. Alley, Air Pollution Control: A Design Approach, Second Edition, Waveland Press, Inc. IL.
48. EPA, 1996. U.S. EPA, Office of Air Quality Planning and Standards, "OAQPS Control Cost Manual," Fifth Edition, EPA 453/B-96-001, Research Triangle Park, NC. February.
49. EPA, 1997. U.S. EPA, Office of Air Quality Planning and Standards, "Compilation of Air Pollutant Emission Factors, Volume I, 5th Edition, Research Triangle Park, NC, October.
50. EPA, 1998. U.S. EPA, Office of Air Quality Planning and Standards, "Stationary Source Control Techniques Document for Fine Particulate Matter," EPA-452/R-97-001, Research Triangle Park, NC, October.
51. STAPPA/ALAPCO, 1996. State and Territorial Air Pollution Program Administrators and Association of Local Air Pollution Control Officials, "Controlling Particulate Matter Under the Clean Air Act: A Menu of Options," July.
52. J. A. Danielson,"Air Pollution Engineering Manual," U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, 1967, pp. 138-139.
53. S. Oglesby and G. B: Nichols, "A Manual of Electrostatic Precipitator Technology, Part I -Fundamentals," Contract CRA 2269-73 for NAPCA, Cincinnati, Ohio, 1970, pp. 5-7.

54. H. J. White, "Industrial Electrostatic Precipitation," AddisonWesley Publishing Co., Reading, Mass., 1963.

55. A. D. Moore, "Electrostatics and Its Applications," John Wiley & Sons, New York, 1973.

56. E. Bakke, On the Application of Wet Electrostatic Precipitators for Control of Emissions from Soderberg Aluminum Reduction Cells, A.I.M.E. Meeting, Dallas, Texas, February 1974.

57. Precipitation Pamphlet, Western Precipitation Company C-103R-1, Los Angeles, Calif., 1952, p. 3, E. Bakke: The Application of Wet Electrostatic Precipitators for Control of Fine Particulate Matter, Paper presented at Symposium on Control of Fine Particulate Emissions from Industrial Sources for the Joint U.S.-U.S.S.R. Working Group, Stationary Source Air Pollution Control Technology, San Francisco, Calif., January 15-18, 1974, pp. 6-7.

58. Avallone, 1996. "Marks' Standard Handbook for Mechanical Engineers," edited by Eugene Avallone and Theodore Baumeister, 10th Edition, McGraw-Hill, New York, NY, 1996.

59. AWMA, 1992. Air & Waste Management Association, Air Pollution Engineering Manual, Van Nostrand Reinhold, New York.

60. Cooper, 1994. David Cooper and F. Alley, Air Pollution Control: A Design Approach, 2nd Edition, Waveland Press, Prospect Heights, IL, 1994.

61. Corbitt, 1990. Standard Handbook of Environmental Engineering, edited by Robert A. Corbitt, McGraw-Hill, New York, NY, 1990.

62. Dixit, 1999. Mandar Dixit, Misonix, Inc., (516) 694-9555, personal communication with Eric Albright, May 25, 1999, EPA, 1992. U.S. EPA, Office of Air Quality Planning and Standards, "Control Technologies for Volatile Organic Compound Emissions from Stationary Sources," EPA 453/R-92-018, Research Triangle Park, NC, December, 1992.

63. EPA, 1995. U.S. EPA, "Compilation of Air Pollutant Emission Factors," AP-42, Volume 1, Research Triangle Park, NC, January, 1995.

64. EPA, 1996. U.S. EPA, Office of Air Quality Planning and Standards, "OAQPS Control Cost Manual," Fifth Edition, EPA 453/B-96-001, Research Triangle Park, NC, February.

65. EPA, 1998. U.S. EPA, Office of Air Quality Planning and Standards, "Stationary Source Control Techniques Document for Fine Particulate Matter," EPA-452/R-97-001, Research Triangle Park, NC, October.

66. Perry, 1984. "Perry's Chemical Engineers' Handbook," edited by Robert Perry and Don Green, 6th Edition, McGraw-Hill, New York, NY, 1984.

67. AAF, 1999. AAF International, web site http://www.aafintl.com, accessed May 19, 1999.

68. Cooper, 1994. David Cooper and F. Alley, Air Pollution Control: A Design Approach, 2nd Edition, Waveland Press, Prospect Heights, IL, 1994.

69. Corbitt, 1990. Standard Handbook of Environmental Engineering, edited by Robert A. Corbitt, McGraw-Hill, New York, NY, 1990.

70. EPA, 1996. U.S. EPA, Office of Air Quality Planning and Standards, "OAQPS Control Cost Manual," Fifth Edition, EPA 453/B-96-001, Research Triangle Park, NC, February.

71. EPA, 1998. U.S. EPA, Office of Air Quality Planning and Standards, "Stationary Source Control Techniques Document for Fine Particulate Matter," EPA-452/R-97-001, Research Triangle Park, NC, October.

72. Cooper, 1994. David Cooper and F. Alley, Air Pollution Control: A Design Approach, 2nd Edition, Waveland Press, Prospect Heights, IL. 1994.

73. EPA, 1996. U.S. EPA, Office of Air Quality Planning and Standards, "OAQPS Control Cost Manual,; 5th Edition, EPA 453/B-96-001, Research Triangle Park, NC, February.

74. EPA 1998, U.S. EPA, Office of Air Quality Planning and Standards, "Stationary Source Control Techniques Document for Fine Particulate Matter," EPA-452/R-97-001, Research Triangle Park, NC, October.

75. Sun, 1994. Jinjun Sun, Benjamin Liu, Peter McMurry, and Stephen Greenwood, "A Method to Increase Control Efficiencies for Wet Scrubbers for Submicron Particles and Particulate Metals," J. Air & Waste Management Association, 44:2, February 1994.

76. Avallone, 1996. "Marks' Standard Handbook for Mechanical Engineers," edited by Eugene Avallone and Theodore Baumeister, 10th Edition, McGraw-Hill, New York, NY, 1996.

77. AWMA, 1992. Air & Waste Management Association, Air Pollution Engineering Manual, Van Nostrand Reinhold, New York.

78. Croll Reynolds, 1999. Croll Reynolds Company, Inc., web site http://www.croll.com, accessed May 19, 1999.

79. EC/R, 1996. EC/R, Inc., "Evaluation of Fine Particulate Matter Control Technology: Final Draft," prepared for U.S. EPA, Integrated Policy and Strategies Group, Durham, NC, September, 1996.

80. EPA, 1981. U.S. EPA, Office of Air Quality Planning and Standards, "Control Technologies for Sulfur Oxide Emission from Stationary Sources," Second Edition, Research Triangle Park, NC, April, 1981.

81. EPA, 1982. U.S. EPA, Office of Research and Development, "Control

Techniques for Particulate Emissions from Stationary Sources, Volume 1," EPA-450/3-81-005a, Research Triangle Park, NC, September, 1982.

82. EPA, 1991. U.S. EPA, Office of Research and Development, "Control Technologies for Hazardous Air Pollutants," EPA/625/6-91/014, Washington, D.C., June, 1991.
83. EPA, 1992. U.S. EPA, Office of Air Quality Planning and Standards, "Control Technologies for Volatile Organic Compound Emissions from Stationary Sources," EPA 453/R-92-018, Research Triangle Park, NC, December, 1992.
84. EPA, 1993. U.S. EPA, Office of Air Quality Planning and Standards, "Chromium Emissions from Chromium Electroplating and Chromic Acid Anodizing Operations: Background Information for Proposed Standards," EPA-453[R-93-030a, Research Triangle Park, NC, July 1993.
85. EPA, 1995. U.S. EPA, Office of Air Quality Planning and Standards, "Survey of Control Technologies for Low Concentration Organic Vapor Gas Streams," EPA-456/R-95-003, Research Triangle Park, NC, May, 1995.
86. EPA, 1996a. U.S. EPA, Office of Air Quality Planning and Standards, "OAQPS Control Cost Manual," Fifth Edition, EPA 453/13-96-001, Research Triangle Park, NC, February, 1996.
87. EPA, 1996b. U.S. EPA, Office of Air Quality Planning and Standards, "Chemical Recovery Combustion Sources at Kraft and Soda Pulp Mills," EPA-453/R-96-012, Research Triangle Park, NC, October, 1996.
88. EPA, 1998. U.S. EPA, Office of Air Quality Planning and Standards, "Stationary Source Control Techniques Document for Fine Particulate Matter," EPA-452-R-97-001, Research Triangle Park, NC, October, 1998.
89. Cheremisinoff, Paul N. and Richard A. Young, Air Pollution Control and Design Handbook, Vol. 2, Marcel Dekker Publishers, New York, 1977.
90. Avallone, 1996. "Marks' Standard Handbook for Mechanical Engineers," edited by Eugene Avallone and Theodore Baumeister, 10th Edition, McGraw-Hill, New York, NY, 1996.
91. AWMA, 1992. Air & Waste Management Association, Air Pollution Engineering Manual, Van Nostrand Reinhold, New York.
92. Cooper, 1994. David Cooper and F. Alley, Air Pollution Control: A Design Approach, 2nd Edition, Waveland Press, Prospect Heights, IL, 1994.
93. EC/R, 1996. EC/R, Inc., "Evaluation of Fine Particulate Matter Control Technology: Final Draft," prepared for U.S. EPA, Integrated Policy and Strategies Group, Durham, NC, September, 1996.
94. EPA, 1981. U.S. EPA, Office of Air Quality Planning and Standards,

"Control Technologies for Sulfur Oxide Emission from Stationary Sources," 2nd Edition, Research Triangle Park, NC, April, 1981.

95. EPA, 1991. U.S. EPA, Office of Research and Development, "Control Technologies for Hazardous Air Pollutants," EPA/625/6-91/014, Washington, D.C., June.

96. EPA, 1992. U.S. EPA, Office of Air Quality Planning and Standards, "Control Technologies for Volatile Organic Compound Emissions from Stationary Sources," EPA 453/R-92-018, Research Triangle Park, NC, December, 1992.

97. EPA, 1993. U.S. EPA, Office of Air Quality Planning and Standards, "Chromium Emissions from Chromium Electroplating and Chromic Acid Anodizing Operations: Background Information for Proposed Standards," EPA-453/R-93-030a, Research Triangle Park, NC, July 1993.

98. EPA, 1996. U.S. EPA, Office of Air Quality Planning and Standards, "OAQPS Control Cost Manual," Fifth Edition, EPA 453/13-96-001, Research Triangle Park, NC February.

99. EPA, 1998. U.S. EPA, Office of Air Quality Planning and Standards, "Stationary Source Control Techniques Document for Fine Particulate Matter," EPA-452/R-97-001, Research Triangle Park, NC, October.

100. Merrick, 1989. David Merrick and Jan Vernon, "Review of Flue Gas Desulphurization Systems," Chemistry and Industry, February 6, 1989.

101. Sondreal, 1993. Everett A. Sondreal, "Clean Utilization of Low-Rank Coals for Low-Cost Power Generation," from "Clean and Efficient Use of Coal: The New Era for Low-Rank Coal," Organization for Economic Co-Operation and Development/International Energy Agency, Paris, France, 1993.

102. Soud, et al., 1993. Hermine N. Soud, Ivlitsuru Takeshita, and Irene M. Smith, "FGC Systems and Installations for Coal-Fired Plants" from "Desulfurization 3," Institution of Chemical Engineers, Warwickshire, UK, 1993.

103. Cooper, 1994. David Cooper and F. Alley, Air Pollution Control: A Design Approach, 2nd Edition, Waveland Press, Prospect Heights, IL, 1994.

104. Enviro-Chem, 1999. Monsanto Enviro-Chew Systems, web site http://enviro-chem.com, accessed May 24, 1999.

105. EPA, 1996. U.S. EPA, Office of Air Quality Planning and Standards, "OAQPS Control Cost Manual," Fifth Edition, EPA 453/B-96-001, Research Triangle Park, NC, February.

106. EPA, 1998. U.S. EPA, Office of Air Quality Planning and Standards, "Stationary Source Control Techniques Document for Fine Particulate

Matter," EPA-452/R-97-001, Research Triangle Park, NC, October.

107. Hassan, 1999. Nadeem Hassan, Monsanto Enviro-Chem Systems, (314) 275-5782, personal communication with Eric Albright, May 26, 1999.

108. Perry, 1984. "Perry's Chemical Engineers' Handbook," edited by Robert Perry and Don Green, 6th Edition, McGraw-Hill, New York, NY, 1984.

109. H. N. Barry: Fixed-Bed Adsorption, Chemical Engineering, p. 105 (Feb. 8, 1960).

110. J. M. Campbell, F. E. Ashford, R. B. Needham, and L. S. Reid: More Insight into Adsorption Design, Hydrocarbon Processing and Petroleum Refiner, 42(12):89-96 (Dec. 1963).

111. J. R. Fair: Sorption Processes for Gas Separation, Chemical Engineering, pp. 90-110 (July 14, 1969).

112. A. Hougen and K. M. Marshall: Adsorption from a Fluid Stream Flowing Through a Stationary Granular Bed, Chemical Engineering Progress, 43:197 (1967).

113. C. L. Humphries: Now Predict Recovery from Adsorbents, Hydrocarbon Processing, 45(12):88 (Dec. 1966).

114. Octave Levenspiel: "Chemical Reaction Engineering," John Wiley & Sons, New York, 1962.

115. W. K. Lewis, E. R. Gilliland, B. Cherton, and W. P. Cadogan: Adsorption Equilibria: Hydrocarbon Gas Mixtures, Industrial and Engineering Chemistry, 42:1319 (1950).

116. W. K. Lewis, E. R. Gilliland, B. Cherton, and W. P. Cadogan: Adsorption Equilibria: Pure Gas Isotherms, Industrial and Engineering Chemistry, 42:1326 (1950).

117. M. M. Mattia: Process for Solvent Pollution Control, Chemical Engineering Progress, 66(12):74-79 (Dec. 1970).

118. A. S. Michaels: Simplified Method of Interpreting Kinetic Data in Fixed-Bed Ion Exchange, Industrial and Engineering Chemistry, 44(8):1922 (1952).

119. Donald F. Othmer and Samuel Josefowitz: Correlating Adsorption Data, Industrial and Engineering Chemistry, 40:723 (1948).

120. Robert H. Perry, Cecil H. Chilton, and Sidney D. Kirkpatrick: "Chemical Engineer's Handbook," 4th ed., McGraw-Hill Book Co., New York, 1963.

121. G. C. Ray and E. O. Box, Jr.: Adsorption of Gases on Activated Charcoal, Industrial and Engineering Chemistry, 4-2:1314 (1950).

122. H. M. Rawson, Fluid Bed Adsorption of Carbon Disulfide, British Chemical Engineering, 8(3):180 (March 1963).

123. J. M. Smith,"Chemical Engineering Kinetics," 2nd ed., McGrawHill Book Co., New York, 1970.

124. AWMA, 1992. Air & Waste Management Association, Air Pollution Manual, Van Nostrand Reinhold, New York.

125. EPA, 1991. U.S. EPS, Office of Research and Development, "Control Technologies for Hazardous Air Pollutants," EPA/625/6-91/014, Washington, D.C., June.

126. EPA, 1992, U.S. EPA, Office of Air Quality Planning and Standards, "Control Techniques for Volatile Organic Emissions from Stationary Sources," EPA-453/R-92-018, Research Triangle Park, NC, December.

127. EPA, 1995, U.S. EPA, Office of Air Quality Planning and Standards, "Survey of Control Technologies for Low Concentration Organic Vapor Gas Streams," EPA-456/R-95-003, Research Triangle Park, NC, December.

128. EPA, 1998, U.S. EPA, Office of Air Quality Planning and Standards, "Stationary Source Control Techniques Document for Fine Particulate Matter," EPA-452/R-97-001, Research Triangle Park, NC, October.

129. Cheremisinoff, P. N. and R. A. Young, Volumes 1 and 2: Air Pollution Control and Design Handbook, Marcel Dekker Publishers, New York, 1977.

130. Cheremisinoff, N. P., Pressure Safety Design Practices for Refinery and Chemical Operations, Noyes Publications, Westwood, New Jersey, 1998.

Chapter 8

ENVIRONMENTAL COST ACCOUNTING PRINCIPLES

INTRODUCTION

Make no mistake about it - air pollution control, especially based on end-of-pipe treatment technologies, is expensive! Not too long ago the attitude among industry stakeholders was that air pollution control was simply a part of the cost of doing business, and that add-on costs associated with compliance simply had to be passed on to the consumer's purchase price for products. Both intense competition as well as ever tightening regulations, have made this approach obsolete. Indeed, there are examples where more progressive companies elected to trim their profits in the short-term, having made investments into less polluting technologies and improved controls in order to meet environmental challenges in the long-term, but less than a decade ago, these were the exception rather than the norm. Today's concept of Responsible Care, as proudly touted by the chemical industry, has had a long and arduous road to get where it is today. And even now with heightened environmental awareness and sensitivities among the public, intense regulatory enforcement, and teams of specialists focusing on compliance issues within companies, we see that environmental litigations built around toxic torts have become a thriving industry unto itself. In so many ways, environmental compliance is a "catch 22" situation. It is impossible to operate a business by not complying, and it can be too costly to meet compliance if the wrong decisions and investments into controls are made.

The EPA argues that the cost of compliance to environmental regulations is small in comparison to baseline industry expenditures. However, there are many hidden costs that oftentimes are not considered when contemplating a control technology investment, and which can escalate and adversely impact on bottom-line economic performance. These so-called other costs include, but are not limited to:

- engineering costs,
- tender and bidding costs on large capital projects,

- operational costs, the largest of which are usually energy related,
- maintenance costs,
- the cost for training personnel and maintaining a dedicated staff for operational purposes,
- the cost for space - since a piece of equipment will occupy floorspace that could be used for other purposes in manufacturing (the allocated space has a value),
- costs for compliance, including fees for permits to construct, permits to operate, and renewal of operating permits. This in itself requires dedicated staff to maintain contrivances for many point sources within an operating plant,
- there are also costs associated with monitoring, which may include laboratory support, either on-site or off-site,
- there are the costs associated with developing an environmental impact statement,
- and, we should not forget that if money is allocated for a piece of equipment for pollution control purposes, we lose the use of that money or the interest it would accrue if we simply left it in an interest bearing account, or invested it in other equipment that enhances our manufacturing productivity or product quality.

Beyond these indirect costs, there are future costs associated with new or more stringent variations of existing environmental legislation. We also need to recognize that all operations, especially those within complex industry sectors like petrochemicals, carry liabilities and exposures to potential catastrophic releases. Systems do fail for a variety of reasons, leading to unplanned and sometimes innocent mistakes, that may result in third-party exposures for environmental damages or health risk exposures. These costs are related to legal fees, loss in consumer confidence, and subsequent losses in market shares for the products a company sells, as well as the clean-up associated with the spill or release.

All of these cost considerations make for the argument that the more that can be done on the prevention side of managing environmental issues, the lower are our operating costs and hidden costs. These cost saving categories are the real motivation behind doing pollution prevention. However, there are limits to pollution prevention, and indeed, there are simply situations where it is more costly to invest in so-called *green technologies*, as opposed to relying on traditional pollution control systems.

This brings us to some very basic principles of cost accounting. These concepts were covered in the first volume of this series (***Handbook of Water and Wastewater Treatment Technologies***), but we will repeat a portion of them here because of their particular relevance to planning air pollution control projects. The focus of this chapter is *project cost estimating*. This is sometimes referred to as total cost accounting. The term *total-cost accounting* (TCA) has also come to be commonly known as *life-cycle costing* (LCC). LCC is a method aimed at analyzing the costs and benefits associated with a piece of equipment, plant, or a project over the entire time of intended use. Experience has shown that the up-front purchase price alone is a poor measure of the total cost. Instead, costs such as those associated with maintainability, reliability, disposal and salvage value, as well as employee training and education, must be given equal weight in making financial decisions. By the same token, justifying the investment into a piece of equipment requires that all benefits and costs be clearly defined in the most concrete terms possible, and projected over the life of each technology option.

In reading over this chapter, glance back at Chapter 6. Many of the principles covered here complement the pollution prevention audit, and will assist you in developing approaches to assessing prevention versus control options.

TOTAL COST ACCOUNTING TERMINOLOGY

In this section, we review the basic terminology and concepts needed to making a financial analysis of an investment.

PRESENT WORTH

The importance of *present worth*, also known as *present value*, lies in the fact that time is money. The preference between a dollar now and a dollar one year from now is driven by the fact that a dollar in-hand can earn interest.

$$P = F/(1 + i)^n \quad (1)$$

In this formula, **P** is present worth or present value, **F** is future value, ***i*** is the interest or discount rate, and **n** is the number of periods. Economically, there is an additional factor at work in present value, and that factor is *pure time preference*, or *impatience*. However, this issue is generally ignored in business accounting, because the firm has no such emotions, and opportunities can be measured in terms of financial return.

AN EXAMPLE

If we have or hold \$1,000, in one year at 6 percent interest compounded annually, the \$1,000 would have a computed present value of:

$P = \$1{,}000/(1 + 0.06)^1$
$= \$\,943.40$

Because this money can "work" at 6% interest, there is no difference between \$943.40 now and \$1,000 in one year because they both have the same value now.
If the money was received in three years, the present value would be:

$P = \$1{,}000/(1 + 0.06)^3$
$= \$839.62$

In considering either multiple payments or cash into and out of a company, the present values are additive. For example, at 6 percent interest, the present value of receiving both \$1,000 in one year and \$1,000 in three years would be \$943.40 + \$839.62 = \$1,783.06. Similarly, if one were to receive \$1,000 in one year, and pay \$1,000 in 3 years the present value would be \$943.40 - \$839.62 = \$103.78. It is common practice to compare investment options based on the present-value equation shown above. We may also apply one or all of the following four factors when comparing investment options: *Payback Period*; *Internal Rate of Return*; *Benefit-to-cost Ratio*; and *Present Value of Net Benefit*. But as we will see later, it is rate of return that is usually the most enlightening when considering an investment.

PAYBACK PERIOD

The payback period of an investment is a measure of how long it takes to break even on the cost of that investment. In other words, how many weeks, months, or years does it take to earn the investment capital that was laid out for a P2 project or a piece of control hardware? Sometimes, engineers are perplexed by this concept when only end-of-pipe treatment technologies are concerned. The fact is, if there is a compliance issue, then one must install a piece of hardware to bring the operation into compliance. But even an end-of-pipe treatment approach carries a savings along with it that pays for the investment over time. The most obvious savings is the negation of fines or shut-downs imposed by regulatory inspectors. Put simply, when we consider a payback period, those projects with the fastest returns are highly attractive. The technique for determining payback period again lies within present value; however, instead of solving the present-value equation for the present value, the cost and benefit cash flows are kept separate over time.

P2 OPPORTUNITIES WITH THE FASTEST RETURNS ARE ATTRACTIVE

- **Cost and benefit cash flows should be kept separate over time**
- **Anticipated benefit and cost should be tabulated for each year of the project's life**
- **Convert these values to present values**
- **The cumulative total of the benefits (at present value) and the cumulative total of the costs (at present value) should be compared year by year**
- **At the point in time when the cumulative present value of benefits begins to exceed the cumulative present value of costs, then the P2 opportunity has reached the payback period**
- **Rank P2 and control opportunities identified according to the shortest payback period first**

First, the project's anticipated benefit and cost are tabulated for each year of the project's lifetime. Then, these values are converted to present values by using the present-value equation, with the company's discount rate plugged in as the discount factor. Finally, the cumulative total of the benefits (at present value) and the cumulative total of the costs (at present value) are compared on a year-by-year basis. At the point in time when the cumulative present value of the benefits starts to exceed the cumulative present value of the costs, the project has reached the payback period.

Ranking equipment and technology options for an intended application then becomes a matter of selecting those project options with the shortest payback period. So, for example, if we compare a baghouse versus an electrostatic filter for a dust control application, an overall payback period for each option can be determined based on the capital investment for each piece of equipment, operating, maintenance, power costs, and other factors.

Although this approach is straightforward, there are dangers in selecting technology or equipment options based upon a minimum payback-time criterion. For example, because the equipment's use generally extends far into the future, discounting makes its payoff period very long. Because the payback period analysis stops when the benefits and costs are equal, the projects with the quickest positive cash flow will dominate. Hence, for a project, with a high discount rate, the long-term costs and benefits may be so far into the future that they do not even enter into the analysis.

In essence, the importance of life-cycle costing is lost in using the minimum payback-time standard, because it only considers costs and benefits to the point where they balance, instead of considering them over the entire life of the project or piece of control or P2 equipment. The analysis is further complicated by the fact that any pollution control device may in fact be viewed as a negative cost factor, because after all, its role is ancillary to manufacturing. Therefore, one must look at the entire process economics in order to properly assess the costs of technology options. This should include an assessment of the costs to manufacturing for non-compliance, although this may not necessarily be an option in most cases.

INTERNAL RATE OF RETURN

This term is most familiar to people as the *return on investment*, or ROI. The ROI is defined as the interest rate that would result in a return on the invested capital equivalent to the project's return. For illustration, if we had an air abatement project where heat recovery was involved, and there was an overall ROI of 30 percent, that's financially equivalent to investing resources in the right stock and having its price go up 30 percent. This is called a "Primitive ROI."

For those readers that like to dabble in the market, consider the following. On 1/1/01, we purchase 10 shares of XYZ corporation at $10 per share; i.e., a $100 investment. Then on 12/31/01, we purchase another 10 shares of the stock, again at $ 10 per share. On 12/21/01 we sell the 20 shares at $11 per share. The total profit in this example is $200. So, from a "primitive" perspective, the ROI is $20/$200, or 10%. The problem with this very simple viewpoint is that it does not take into consideration the time-value-of-money (TVM).

The TVM takes into consideration the total time that the principal was tied up into the investment. For the shares that we purchased on 1/1/01, the $100 was tied up for one full year. This portion of the investment made 10% in one year. But the shares that were purchased on 12/1/01 tied up $100 for only one month, which is a significantly higher return than the 10% per year. In fact, if an investment gained 10% every month like the latter share purchase, it would gain 207.5% in one year! TVM formulas give the most accurate ROI calculation possible. They are the same formulas used by large investors and lending institutions to evaluate capital expenditures and investment alternatives. Unfortunately, in a real-world example, you would normally be unable to calculate the true TVM-ROI because the calculations require the application of advanced numerical analysis.

Fortunately, there are some simple rules of thumb to apply when considering a ROI analysis. In fact, without even opening a spreadsheet, you can apply some criteria to assessing basic project finance information to assess whether the investment is likely worth the effort. To determine the likelihood of a positive ROI, look at the following factors:

- Breadth - *How much waste or pollution will be reduced by the application or project? The greater the reduction, the greater the ROI is likely to be*;
- Repeatability - *How often and for how long will the opportunity or project be applied? The more often the application or control is used, the longer the life of the investment, and hence the greater the ROI*;
- Cost - *The more costly the investment, the longer you will likely wait for a return on the investment*;
- Knowledge capture - *The greater the potential to re-use information gathered from the project to make further improvements to productivity, or roll-out applications to other parts of the company, the greater the potential ROI.*

Note that costs and benefits can be either one-time or recurring. Be sure to include them appropriately in your analysis. Follow these basic rules when gathering information and including costs in the ROI analysis:

- Count everything that is directly associated with the project
- Don't count infrastructure items that are not used or associated with the project
- Do count infrastructure items that are driven by the project

Benefits derived from a P2 or control project are sometimes difficult to fully assess because they often include indirect productivity-based gains. For example, increased worker productivity can be a potential outfall of improving the air quality within a plant environment, but often there are no direct benefits or reductions in budgets that reflect these gains. You can account for this by considering the additional employees you would need to hire to do the same work, or take into account the increase in production from the same number of employees. In such situations, try to account fairly for the potential gains in productivity. To do this, correct for different transfer of time, meaning – the total time saved rarely equals the total additional work performed. To measure properly, follow these rules:

- measure based on fully-loaded costs
- correct for inefficient transfer of the time using a value of unity (1.0) for line workers to 0.5 for general employees
- find a corroborating measurement that supports the change (for example, if your environmental monitoring lab saves 10% of their time as a result of the investment, do you expect them to fire 10% of the technicians or to increase their productivity by 10%)

When calculating the primitive ROI, it's best to establish a criterion. For example, one acceptable ROI calculation is to take an average benefit over 3 to 5 years and divide that by the initial cost to the investment. Another calculation basis, used by the U.S. DOE (Department of Energy) for P2 assessments is as follows:

$$\mathrm{ROI} = 100 \times (C_B - C_A)/C_I \tag{2}$$

In this formula, the ROI calculated is based on comparing the projected annual cost after implementation (C_A) to a baseline annual cost before implementation (C_B). The ROI is computed as the ratio of anticipated cost savings (C_B - C_A) to the projected implementation costs (C_B), expressed as a percentage.

BENEFIT-TO-COST RATIO

The benefit-to-cost (B/C) ratio is a benchmark that is determined by taking the total present value of all of the financial benefits of an air pollution control project and dividing it by the total present value of all the costs of the project. If the ratio is greater than unity, then the benefits outweigh the costs, and we may conclude that the project is economically worthwhile.

The present values of the benefits and costs are kept separate, and expressed in one of two ways. First, there is the pure B/C ratio, which implies that if the ratio is greater than unity, the benefits outweigh the costs and the project is viable. Second, there is the net B/C ratio, which is the net benefit (benefits minus costs) divided by the costs. In this latter case, the decision criterion is that the benefits must outweigh the costs, which means that the net ratio must be greater than zero (if the benefits exactly equaled the costs, the net B/C ratio would be zero). In both cases, the highest B/C ratios are considered as the best projects.

The B/C ratio can be misleading. For example, if the present value of a cyclone's benefits were \$10,000 and costs were \$6,000, the B/C ratio would be \$10,000/\$6,000 or 1.67. But what if, upon further reassessment of the project, we find that some of the costs are not true costs, but instead simply offsets to benefits? In this case, the ratio could be changed considerably.

For argument sake, let's say that \$4,500 of the \$6,000 total cost is for lower energy and water costs over say a wet scrubber, and that \$7,000 of the \$10,000 in benefits is due to utility savings; one could then use them to offset each other. Mathematically, then, both the numerator and denominator of the ratio could be reduced by \$4,500 with the following effect:

$$(\$10,000 - \$4,500)/(\$6,000 - \$4,500) = 3.7$$

Without changing the project, the recalculated B/C ratio would make the project seem to be considerably more attractive.

PRESENT VALUE OF NET BENEFITS

The present value of net benefits (PVNB) shows the worth of a project in terms of a present-value sum. The PVNB is determined by calculating the present value of all benefits; doing the same for all costs; and then subtracting the two totals. The result is an amount of money that would represent the tangible value of undertaking the project. This comparison evaluates all benefits and costs at their current or present values. If the net benefit (the benefits minus costs) is greater than zero, the project is worth undertaking; if the net is less than zero, the project should be abandoned on a financial basis. This technique is firmly grounded in microeconomic theory and is ideal for total-cost analysis (TCA).

Even though it requires a preselected discount rate, which can greatly discount long-term benefits, it assures that all benefits and costs over the entire life of the project are included in the analysis. Once you know the present value of all options with positive net values, the actual ranking of equipment and technology options using this method is straightforward; those with the highest PVNBs are funded first. There are no hard and fast rules as to which factors one may apply in performing life-cycle costing or total-cost analysis; however, conceptually, the PVNB method is preferred. There are, however, many small-scale equipment projects where the benefits are so well defined and obvious that a comparative financial factor as simple as a ROI or the payback period will suffice.

ESTABLISHING BASELINE COSTS

To properly determine the cost of any engineering project, we first need to establish a baseline for comparative purposes. If nothing else, a baseline defines for management the option of maintaining the status quo. If we are faced with meeting a legal discharge limit, then obviously we need to do something other than status quo to remain in business. But here is where we can develop some interesting and very detailed justifications for one air pollution control technology or piece of equipment over another. Changes in material consumption, utility demands, staff time, etc., for options being considered can be measured as either more or less expensive than a certain baseline. The baseline may be arbitrary for comparison. For example, we could choose as a baseline a traditional industry average. By starting with those technologies that comprise a conventional air pollution control option, we have a baseline for the cost analysis. But to determine true cost benefits to your specific application, you really need to compare technologies and costs. This is an optimization exercise, and one which is well worthwhile in establishing the right level of investment for any air pollution control project.

The methodology of McHugh (McHugh, R.T., *The Economics of Waste Minimization*, McGraw-Hill Book Publishers, 1990) relies on four tiers of potential costs:

- *Tier 0:* Usual or normal costs, such as direct labor, raw materials, energy, equipment, etc.
- *Tier 1:* Hidden costs, such as monitoring expenses, reporting and record keeping, permitting requirements, environmental impact statements, legal, etc.
- *Tier 2:* Future liability costs, such as remedial actions, personal injury under the OSHA regulations, property damage, etc.
- *Tier 3:* Less tangible costs, such as consumer response and confidence, employee relations, corporate image, etc.

Do you see the potential advantage of P2 over an end-of-pipe treatment option?
Many conventional control technologies simply convert an air pollution problem into another form (for example: an air scrubber can create a water treatment and sludge disposal issue; a baghouse creates a solid waste disposal issue). End-of-pipe technologies generally have environmental tradeoffs, which result in additional costs. These additional costs can be avoided if we can displace the air pollution problem altogether by prevention, or by using a technology that completely destroys or neutralizes the air pollutant.

Tier 0 and Tier 1 costs are direct and indirect costs. They include the engineering, materials, labor, construction, contingency, etc., as well as waste-collection and transportation services (in many cases we simply transform an air pollution problem into a solid waste or wastewater problem that requires final treatment and disposal), raw-material consumption (increase or decrease), and production costs. Tier 2 and

Tier 3 represent intangible costs. They are much more difficult to define, and include potential corrective actions under the Clean Air Act and possibly other environmental legislation if the air pollution is converted to another waste form (hence, RCRA or the Clean Water Act could be applicable); possibly more stringent discharge limitations in the future; and benefits of improved safety and work environments. Although these intangible costs often cannot be accurately predicted, they can be very important and should not be ignored when assessing an equipment or technology option. A present-value analysis that contains such uncertain factors generally requires a little ingenuity in assessing the full merits of an engineering project.

When analyzing the financial impact of projects, it is often useful to further categorize costs as either *procurement costs* or *operations costs*. This distinction better enables the projection of costs over time, because procurement costs are short-term, and refer to all costs required to bring a new piece of equipment or a new procedure on-line. Conversely, operations costs are long-term, and represent all costs of operating the equipment or performing the procedure in the post-procurement phase.

Tier 2 and 3 costs are difficult to quantify or predict. While Tier 2 costs include potential liabilities, such as changing air discharge limits and permitting requirements, Tier 3 costs are even harder to predict -- for example, a typical Tier 3 cost could be associated with public acceptance or rejection of a particular technology. This is often the case when incineration technologies are used. In many cases, there is a probability that can be connected with a particular event. This enters into the calculation of *expected value*. The expected value of an event is the probability of an event occurring, multiplied by the cost or benefit of the event. Once all expected values are determined, they are totaled and brought back to present value as done with any other benefit or expense. Hence, the expected value measures the central tendency, or the average value that an outcome would have. For example, there are a number of games at county fairs that involve betting on numbers or colors, much like roulette. If the required bet is $1, and the prize is worth $5, and there are 10 selections, the expected value of the game can be computed as:

(Benefit of Success) $\times$ (Probability of Success) - (Cost of Failure) $\times$ (Probability of Failure), or (\$5) $\times$ (0.1) - (\$1) $\times$ (0.9) = -\$0.40

On the average, the player will lose -- meaning the game operator will win -- 40 cents on every dollar wagered. For tier 2 and 3 expenses, the analysis is the same. For example, there is a great deal of data available from Occupational Safety and Health Administration (OSHA) studies regarding employee injury in the workplace. If one technology poses a higher risk to occupational exposure than another, then the probability of injury and a cost can be found, and the benefit of the project can be computed. The concept of expected value is not complicated, though the calculations can be cumbersome. For example, even though each individual's chance of injury may be small, the number of employees, their individual opportunity costs, the various probabilities for each task, etc., could mean a large number of calculations. However, if one considers the effect of the sum of these small costs, or the large potential costs of having to replace a technology or consider significant upgrades within 5 years, then the expected value computations can be quite important in the financial analysis.

REVENUES, EXPENSES, AND CASH FLOW

Because it is the goal of any business to make a profit, the costs-and-benefits cash flows for each option can be related to the basic profit equation:

REVENUES - EXPENSES = PROFITS

The most important aspect of this is that profits can be increased by either an increase in revenues or a decrease in expenses. With end-of-pipe treatment technologies, the investments required increase expenditures and decrease profit. However, if we can capitalize on an air pollution problem by recovering a valuable product, or identifying a secondary market for the waste, then a revenue stream is created which can offset the overhead and investment requirements for the equipment. There are different categories of revenues and expenses, and it is important to distinguish between them. Obviously, revenue is money coming into the company; from the sale of goods or services, from rental fees, from interest income, etc. The profit equation shows that an increase in revenue leads to a direct increase in profit, and vice versa if all other revenues and expenses are held constant. Let's assume that other expenses/revenues are held constant in the discussions below. Revenue impacts must be closely examined. For example, if we take the two cases for an electric utility considered back in Chapter 6, one being a coal-fired plant and the other based on natural gas, air pollution control costs theoretically should be considerably lower for the case of the plant whose technology is based on a clean fuel. However, that is not necessarily the situation. In this situation, older coal burning electricity generating facilities have less stringent NO_x emission standards to meet than do newer plants based upon Combined Cycle Natural Gas (CCNG) turbine technologies in many states. The cost for converison to CCNG technologies is high, and operational costs for equipment are significantly greater in meeting the more stringent NO_x emissions standards. In addition, those plants that are in the process of conversion from the older technology to the newer face the temptation of dispatching more electricity from the coal-fired portion of the operation since their operating and depreciation costs are lower. Hence, the financial analysis for an air pollution control project or process investment offering lower pollution discharges can be complex, and is linked to local environmental statutes.

Let's turn our attention to expenses. Expenses are monies that leave the company to cover the costs of operations, maintenance, insurance, etc. There are several major cost categories:

- Insurance expenses
- Depreciation expenses
- Interest expenses
- Labor expenses
- Training expenses
- Auditing and demo expenses
- Floor-space expenses

Each of these should be carefully considered in your analysis.

Insurance Expenses - Depending upon the project, insurance expenses could either increase or decrease. Insurance premiums can be increased depending on the technology option chosen for a plant design.

Depreciation Expenses - By purchasing capital equipment with a limited life the entire cost is not charged against the current year. Instead, depreciation expense calculations spread the equipment's procurement costs (including delivery charges, installation, start-up expenses, etc.) over a period of time by taking a percentage of the cost each year over the life of the equipment. For example, if the expected life of a catalytic combustor is 10 years, each year the company would charge an accounting expense of 10 percent of the procurement cost of the equipment. This is known as the *method of straight-line depreciation*. Although there are other methods available, all investment projects under consideration at any given time should use a single depreciation method to accurately compare alternative projects' expense and revenue effects. Because straight-line depreciation is easy to compute, it is the preferred method. Note that even though a company must use a different depreciation system for tax purposes (e.g., the *Accelerated Cost Recovery System*, or ACRS), it is acceptable to use other methods for bookkeeping and analysis. In any event, any capital equipment must be expensed through depreciation.

Interest Expense - Investment in equipment implies that one of two things must occur: Either a company must pay for the project out of its own cash, or it must finance the cost by borrowing money from a bank, by issuing bonds, or by some other means. When a firm pays for a project out of its own cash reserves, the action is sometimes called an *opportunity cost*. If you must borrow the cash, there is an interest charge associated with using someone else's money. It is important to recognize that interest is a true expense and must be treated, like insurance expense, as an offset to the project's benefits. The magnitude of the expense will vary with bank lending rates, the interest rate offered on the corporate notes issued, etc. In any case, there will be an expense. The reason companies account for equipment purchases as a cost is this: **If cash is used for the purpose of pollution control, it is unavailable to use for other opportunities or investments.** Revenues that could have been generated by the cash (for example, interest from a certificate of deposit at a bank) are treated as an expense and thus reduce the value of the project. But again, we may not have a choice if the project is driven by legal requirements. Although the reasoning seems sound, opportunity costs are not really expenses. Though it is true that the cash will be unavailable for other investments, opportunity cost should be thought of as a comparison criterion and not an expense. The opportunity foregone by using the cash is considered when the project competes for funds and is expressed by one of the financial analysis factors discussed earlier (net value of present worth, payback period, etc.). It is this competition for company funds that encompasses opportunity cost, so opportunity cost should not be accounted directly against the project's benefits.

Many companies apply a minimum rate of return, or *hurdle rate*, to express the opportunity-cost competition between investments. For example, if a firm can draw 10 percent interest on cash in the bank, then 10 percent would be a valid choice for the hurdle rate as it represents the company's cash opportunity cost. Then, in analyzing investment options under a return-on-investment criterion, not only would the highest returns be selected, but any project that pays the firm a return of less than the 10 percent hurdle rate would not be considered.

Labor Expenses - In the majority of situations, projects will cause a company's labor requirements to change. This change could be a positive effect that increases available productive time, or there could be a decrease in employees' production time depending upon the practice. When computing labor expenses, the Tier 1 costs could be significant. Labor expense calculations can be simplistic or comprehensive. The most direct and basic approach is to multiply the wage rate by the hours of labor. More comprehensive calculations include the associated costs of payroll taxes, administration, and benefits. Many companies routinely track these costs and establish an internal "burdened" labor rate to use in financial analysis.

Training Expenses - A project may also involve the purchase of equipment that requires additional operator training. In computing the total training costs, the enterprise must consider as an expense both the direct costs and the staff time spent in training. Remember that some technologies require more extensive worker training than others. In addition, any other costs for refresher training, or for training for new employees, that is above the level currently needed must be included in the analysis. Computing direct costs is simply a matter of adding the costs of tuition, travel, per diem, etc. for the employees. Similarly, to compute the labor costs, simply multiply the employees' wage rates by the number of hours spent away from the job in training.

Auditing and Demo Expenses - Labor and other expenses associated with defining the engineering project are often overlooked. Although these tend to be small for low-investment projects, some contemplated operations may require pilot testing, or sending personnel off-site to work with vendors in their shops. Pilot or plant trials can incur significant up-front costs from production down times, personnel, monitoring equipment, and laboratory measurements, as well as engineering design time and consultant-time charges. Some enterprises may prefer to absorb these costs as part of their R&D budget -- for organizations these expenses simply are a part of the baseline cost of operations.

Floor Space Expenses - As with any costs, the floor-space costs must be based on the value of alternative uses. Unfortunately, computing floor-space opportunity cost is not always straightforward, as it is in the case of training costs. In instances where little square footage is required, there may be no other use for the floor space, which implies a zero cost. Alternatively, as the square footage required increases, calculating floor-space costs becomes more straightforward. For example, if a battery of fabric filters is to be installed within an existing building, it's easy to compute a cost. The average-square-foot cost for an addition to an existing building or its renovation would be based on the average market worth of a square foot of floor space. Unless there is a specific alternative proposal for the floor space, this market analysis should work as a proxy.

Finally, let's consider cash flow. Although cash flow does not have a direct effect on a company's revenues or expenses, the concept must be considered. If the project involves procurement costs, they often must be paid upon delivery of the equipment - yet cash recovery could take many months or even years. Three things about any project can affect a firm's available cash. First, cash is used at the time of purchase. Second, it takes time to realize financial returns from the project, through either enhanced revenues or decreased expenses. Depreciation expense is calculated at a much slower rate than the cash was spent. As a result of the investment, a company could find itself cash-poor. Even though cash flow does not directly affect revenues and expenses, it may be necessary to consider.

INCOME TAXES

Although most companies use only revenue and expense figures when comparing investment projects, income-tax effects can enter into each calculation if either revenues or expenses change from the baseline values. More expenses mean lower profits and fewer taxes, and vice versa. If a company needs to know the effect of income taxes on profit, the computations are simple and can be done during or after the analysis. As with expenses and revenues, you do not need to compute the total tax liability for each option. Instead, you only need to look at the options' effect on revenues and/or expenses, and the difference in tax liability resulting from deviations from the baseline. The profit equation reflects gross or pretax profits. Income tax is based on the gross profit figure from this equation and cannot be computed until you know what effect the options will have on revenues and/or expenses.

CASE STUDY

The following case study is a good example of analyzing the benefits of a P2 project, and applying the financial credits. This example is based on an air emissions credit program. In 1999, the Department of Defense (DoD) initiated the Emission Reduction Incentive Pilot Program. Military installations now have the opportunity to use the proceeds from sales of air emission credits at their installation instead of depositing them to the U.S. Treasury. Establishment of the pilot program provides military installations with a monetary incentive to incorporate more pollution prevention measures into their environmental management strategies. The Pilot Program has been in effect since September 1999. The program includes an annual cap of $500,000. The purpose of the Pilot Program is to encourage military facilities to reduce their air emissions below legal limits. The facility must be located in a state or local air quality district that provides an economic incentive program. The facility can use the net proceeds from the sale of emissions for use in the management of environmental programs subject to certain conditions. Sales are transacted similarly to the private sector, including the use of an air broker, listing in environmental trade letters and local newspapers, and through the local air pollution control district. In emissions trading programs, the commodity being traded is tons, or fractions of tons, of actual emission reductions of criteria pollutants which consist of nitrogen oxides or NO_x, sulfur oxides or SO_x, volatile organic compounds or VOC, carbon monoxide (CO), and particulate matter (referred to as PM_{10}). The emissions can be generated by either stationary or mobile sources. In most trading programs, sources trade emissions at a "rate," for example, one ton per year for some number of years, or indefinitely. Oxides of nitrogen (NO_x) and volatile organic compounds (VOC) are the pollutants most frequently traded. For all emission trading programs, emissions must be:

- Surplus, meaning that the reductions are not required by other regulations;
- Real, meaning that the reductions have already occurred and that production will not lead to an increase elsewhere in the facility;
- Quantifiable, meaning that the reductions can be measured;
- Enforceable, meaning that violations can be enforced by the agencies allowing the trade; and
- Permanent, meaning that the reductions will continue in perpetuity.

There are basically two types of emission trading programs. New Source Trading and Banking programs allow facilities to bank emissions credits to be used to offset emission increases caused by new or modified sources and/or for inter-pollutant trading (i.e., NO_2 emissions can be used for a new VOC source). Allocation trading programs define a facility's emissions allocation and create a "bubble" inside which allocations can be traded. The three established allocation trading programs (also known as cap-and-trade) currently in place include the Sulfur Dioxide (SO_2) Trading, the Ozone Depleting Chemicals (ODC) manufacturing capability trading, and the Regional Clean Air Incentives Market (RECLAIM) program in the South Coast Air Quality Air District (SCAQMD). These three programs differ in the pollutants addressed, the allocation structures, trading deadlines, expiration rules, and geographic adjustments. All are designed to provide flexibility within an area or region to implement pollution prevention measures which will ultimately improve overall air quality. Under most programs, emission reduction credits or ERC's are generated based on emission reductions achieved above and beyond the requirements of the regulations. Since these emission reductions are real, quantifiable, and impact the emissions for the life of the associated piece of equipment, the ERC certificates typically do not have an expiration date. The ERC's are a commodity that can be sold in part or as a whole. Once sold, the seller has no claim over the emissions credits.

CASE STUDY SUCCESS STORIES

March ARB is located in Riverside County in Southern California and is the first DoD installation to participate in the Emission Reduction Incentive Pilot Program. March ARB is covered by the RECLAIM Trading Program and also the Emission Reduction Credit Program in Riverside County. March ARB has a surplus of NO_x, VOC, SO_2, CO, and PM_{10} ERCs created from a reduction in base operations. In addition, the base converted from using JP-4 to JP-8 in 1994. Because JP-8 has significantly fewer VOCs than JP-4, the base was able to convert this savings in emissions into ERCs. Table 1 summarizes the ERCs and RTCs (RECLAIM Trading Credits, which are specific to the RECLAIM Trading program) sold to date. In addition, March ARB has on the market 1999 and 2000 RTCs and SO_2, PM_{10}, VOC and CO ERCs.

Table 1. Credits Achieved by the Program.

Location	Date	Quantity and Type of Pollutant Sold	Value
March Air Reserve Base	1/99	12 Lbs/day NO_x ERCs	$58,971
March Air Reserve Base	2/99	45000 Lbs CY1998 NO_x RTCs	$6,247
March Air Reserve Base	6/99	10 Lbs/day PM_{10} ERCs	$19,100

The base plans to accrue an undetermined amount of Mobile Source Emissions Reduction Credits (MSERCs) from the use of clean fuel vehicles. These MSERCs can then be converted to RTCs for that year and be sold like other RTCs. The second success story for the pilot program is the trade/sale involving 18.31 tons of NO_x RECLAIM Trading Credits (RTCs) available from MCAS El Toro. These credits became available due to the operational closure of the facility in July, 1999. After review by the Deputy Assistant Secretary of the Navy for Environment and Safety, the facility was authorized to offer the RTCs in exchange for ERCs in another Southern California air basin to accommodate emerging Marine Corps or Navy needs or to sell the RTCs if an exchange was not possible. The RTCs were subsequently exchanged for ERCs in the San Diego Air Basin. The value of the exchanged RTCs was estimated at $640,885 as of August 2000. Additional Web sites containing information on air credit programs and the DoD pilot program include: https://www.denix.osd.mil/ and http://yosemite.epa.gov/aa/programs.nsf. Use of the emission credit program may help to reduce facility-wide emissions below applicable major source thresholds and thus remove Title V permitting requirements under the Clean Air Act. In addition, inter-pollutant trading can allow a facility to offset emission increases for a new source or other source where compliance costs are more prohibitive. The pilot program allows the facility to keep the revenues generated by emission reductions that can be used to invest in development and implementation of new technologies and for certain operational costs related to pollution prevention and environmental protection. Specific pollution prevention and environmental compliance benefits include:

- Provides incentive to exceed environmental and regulatory air emissions reduction goals and reduce emission below legal requirements.
- Provides reductions that decrease facility emissions below Title V permitting thresholds.
- Reduces or eliminates local VOC requirements in ozone non-attainment and maintenance areas.
- Emission reduction credits can also be used to offset emissions increases under New Source Review, Prevention of Significant Deterioration, and Base Realignment and Closure.
- Encourages the use of cleaner fuels or less polluting raw materials.

This case study helps to illustrate an innovative approach to managing air pollution problems. Savings derived from an emissions trading program represent an excellent way of making funds available for reinvestment into a facility operation, and further, encourages wider application of pollution prevention practices. When considering P2 technologies versus straightforward control hardware, try to identify approaches that will enable possible savings to be converted into working capital that improves efficiency, quality, productivity, and more sweeping reductions in emissions.

GLOSSARY

Absorption: the process by which incident light is removed from the atmosphere and retained by a particle.

Absorption Coefficient: a number that is proportional to the "amount" of light removed from a sight path by absorption per unit distance.

Absorption Cross Section: the amount of light absorbed by a particle divided by its physical cross section.

Acid: There are several definitions for acid. The Arrhenius definition is a substance that ionizes in water to product H^+ ions. The Bronsted definition is a substance that is a proton (H^+) donor. This does not require the substances to be in aqueous (water) solution. The Lewis definition is a substance that can accept a pair of electrons. This does not require a proton or aqueous solution. There are several other definitions as well. An acidic solution is defined as one that has a pH less than 7.0. The following are examples of strong acids, meaning that they completely dissociate into ions and form H^+ in aqueous (water) solution. For example $HCl \rightarrow H^+ + Cl^-$. All of these will cause severe burns upon skin contact: Perchloric acid ($HClO_4$), Hydroiodic acid (HI), Hydrobromic acid (HBr), Hydrochloric acid (HCl), Sulfuric acid (H_2SO_4), and Nitric acid (HNO_3). Weak acids do not dissociate completely into ions. Examples of these include acetic acid (a 5% solution of acetic acid in water is called vinegar), formic acid, ammonium cation, and water itself. The strength of acids can be measured using the pH scale. The lower the pH, the greater the acidity of a solution. Just because an acid is weak does not mean that it can't be harmful. For example, HF, hydrofluoric acid, is a weak acid. When you spill it on your hand it doesn't burn, but over the course of hours it migrates to the bones in your fingers and then begins to dissolve them from the inside out (a painful process; amputation can be required). Some common properties of acids are: (1) They have a sour taste. For example, citric acid in lemons and vinegar are both sour; (2) They can react with metals such as magnesium, zinc, or iron to corrode them and produce explosive hydrogen gas. Do not store acids in metal containers; (3) Solutions of acids can conduct electricity. It is important to know the pH of substances because they may be corrosive or react with incompatible materials. For example, acids and bases should not be stored or used near each other as their accidental combination could generate a huge amount of heat and energy, possibly resulting in an explosion. pH is also important to know in case you spill the material on your skin or eyes. Whenever a substance enters the eye, flush with water for 15 minutes and get prompt medical attention.

Acid Aerosol: acidic liquid or solid particles that are small enough to become airborne. High concentrations of acid aerosols can be irritating to the lungs and have been associated with some respiratory diseases, such as asthma.

Acidification: the decrease of acid neutralizing capacity in water or base saturation in soil caused by natural or anthropogenic processes.

Acid Deposition (wet): air pollution produced when acid chemicals are incorporated into rain, snow, fog, or mist.

ACGIH - American Conference of Governmental Industrial Hygienists, Inc.: The American Conference of Governmental Industrial Hygienists, Inc., ACGIH, is an organization open to all practitioners in industrial hygiene, occupational health, environmental health, or safety. Their Web site is http://www.acgih.org/. ACGIH publishes over 400 titles in occupational and environmental health and safety. They are most famous for their Threshold Limit Values publication which lists the TLV's for over 700 chemical substances and physical agents, as well as 50 Biological Exposure Indices for selected chemicals.

Acute toxicity: Acute toxicity describes the adverse effects resulting from a single exposure to a substance. Acute toxicity helps workers understand the health consequences from a single exposure to a chemical. Acute toxicity differs from chronic toxicity, which describes the adverse health effects from repeated (lower level) exposures to a substance over a longer period (months to years). Human tests for acute toxicity are not performed because of ethical and legal prohibitions. The U.S. EPA describes the following methods for determination of acute toxicity: *Animal testing*: Animal tests are still used where other laboratory protocols are not available. These tests are combined with other assays (lethality, necroscopy, etc.) to minimize the number of animals sacrificed. Evaluation of acute toxicity data should include the relationship, if any, between the exposure of animals to the test substance and the incidence and severity of all abnormalities, including behavioral and clinical abnormalities, the reversibility of observed abnormalities, gross lesions, body weight changes, effects on mortality, and any other toxic effects. *Use of data from structurally related substances or mixtures*: In order to minimize the need for animal testing for acute effects, the EPA encourages the review of existing acute toxicity information on chemical substances that are structurally related to the agent under investigation. In certain cases it may be possible to obtain enough information to make preliminary hazard evaluations that may reduce the need for further animal testing for acute effects. *Chemical properties*: For example, if a substance is a strong acid then there is really no need to do skin and eye tests as a corrosive material such as this will obviously cause great harm. *In vitro testing* (test tube experiments): Animal rights activists advocate such methods whenever possible. *Limit testing*: A single group of animals is given a large dose of the agent. If no lethality is demonstrated, no further testing is pursued and the substance is classified in a hazard category according to the dose used.

Add-on Control Device: an air pollution control device such as carbon absorber or incinerator that reduces the pollution in an exhaust gas. The control device usually does not affect the process being controlled and thus is "add-on" technology, as opposed to a scheme to control pollution though altering the basic process itself.

Adsorption: removal of a pollutant from air or water by collecting the pollutant on the surface of a solid material; e.g., an advanced method of treating waste in which activated carbon removes organic matter from wastewater.

Aerometric Information Retrieval System (AIRS): a computer-based repository of U.S. air pollution information administered by the EPA Office of Air Quality Planning and Standards.

Aerosol: a mixture of microscopic solid or liquid particles in a gaseous medium. Smoke, haze, and fog are aerosol examples.

Air Parcel: volume of air that tends to be transported as a single entity.

Air Pollutant: an unwanted chemical or other material found in the air. *See also air pollution.*

Air Pollution: degradation of air quality resulting from unwanted chemicals or other materials occurring in the air. *See also air pollutant.*

Air Pollution Control Device: Mechanism or equipment that cleans emissions generated by a source (e.g., an incinerator, industrial smokestack or an automobile exhaust system) by removing pollutants that would otherwise be released to the atmosphere.

Air Pollution Control Permitting Process: process by which facilities are permitted to emit specified types and quantities of air pollutants

Air Quality: (in context of the national parks:) the properties and degree of purity of air to which people and natural and heritage resources are exposed.

Air Quality Related Value (AQRV): a resource, as identified by the FLM for one or more Federal areas, that may be adversely affected by a change in air quality. The resource may include visibility or a specific scenic, cultural, physical, biological, ecological, or recreational resource identified by the FLM for a particular area. "These values include visibility and those scenic, cultural, biological, and recreation resources of an area that are affected by air quality" *(43 Fed. Reg. 15016)*.

Airshed: a geographic area that, because of topography, meteorology, and/or climate, is frequently affected by the same air mass.

AIRWeb: Air Resources Web, an air quality information web site for U.S. parks and wildlife refuges developed by the Air Resources Division of the National Park Service and the Air Quality Branch of the Fish and Wildlife Service.

Allergen: a substance capable of causing an allergic reaction because of an individual's sensitivity to that substance.

Allergic Rhinitis: inflammation of the mucous membranes in the nose that is caused by an allergic reaction.

Alopecia: Alopecia is the loss of hair. Acute or chronic exposure to some chemicals may result in the temporary or permanent loss of hair.

Ambient Air: air that is accessible to the public.

Ames Test: The Ames Test is a way of determining whether a compound causes genetic mutations (changes). Animal liver cell extracts are combined with a special form of *Salmonella* bacteria. The mixture is then exposed to the test substance and examined for signs that the bacteria have mutated (a process called mutagenesis). The Ames test does not directly indicate the carcinogenic (cancer-causing) potential of the substance; however, there is a good correlation between mutagen strength and carcinogen strength in rodent studies. Avoid the use of mutagens, if at all possible. If you must work with them, be sure to utilize the proper personal protective equipment (PPE) recommended on the MSDS sheet.

Anesthesia: Anesthesia is a loss of sensation or feeling. Anesthesia (or "anesthetics") is often used deliberately by doctors and dentists to block pain and other sensations during surgical procedures. Treatment for pre- or postoperative pain is called analgesia.

Anhydride: An anhydride is a compound that gives an acid or a base when combined with water. Many substances are not themselves acids or bases, but will become such when exposed to water. This does not necessarily require the addition of water (such as from a fire hose). Many anhydrides will react readily with ambient humidity and even the water present in your skin or lungs. The reaction of anhydrides with water is often very violent and exothermic (giving off a great deal of heat energy). The reaction to form sulfuric acid is one step in the reaction of sulfur oxide emissions to form "acid rain." The reaction to form acetic acid is used in certain silicone caulks, leading to the familiar smell of vinegar (vinegar is a 5% solution of acetic acid in water), while the caulk cures.

Anhydrous: An anhydrous material does not contain any water molecules. Many substances occur naturally as hydrates, compounds that have a specific number of water molecules attached to them. This water can often be removed by heating and/or vacuum to give the anhydrous material. Anhydrous materials can absorb water from their surroundings and find use as dessicants. Examples include those packets of silica gel you find in some consumer goods, as well as dehumidifying sachets used in clothes closets. When an anhydrous material reacts with water, this could release a large amount of heat, possibly leading to a heat or pressure buildup that could result in an explosion.

Animal Dander: Tiny scales of animal skin.

Anorexia: Anorexia is loss of appetite. You may be familiar with the eating disorder, anorexia nervosa, in which the victim restricts dietary intake to starvation levels. Anorexia may be a symptom of acute or chronic exposure to certain chemicals. If you have suffered an unexplained loss of appetite in conjunction with other unusual symptoms, you may want to explore the MSDSs for chemicals that you use in your workplace.

Anosmia: Anosmia is the loss of the sense of smell. Anosmia can be fatal. Certain toxic chemicals have strong detectable odors at low levels. But at higher levels, these saturate your smell receptors ("olfactory fatigue") and you can no longer smell the material. For example, hydrogen sulfide, H_2S, has the distinctive odor of rotten eggs at or below 10 parts per million (ppm) in air. If you were exposed to an H_2S leak and the concentration went above 10 ppm, you might be lulled into thinking that the leak had stopped, because you could not smell it anymore. H_2S can be fatal at concentrations of several hundred ppm.

Anoxia: Anoxia is the absence of oxygen in inspired gases or in arterial blood and/or in the tissues. This is closely related to hypoxia, which is a severe oxygen deficiency in the tissues. One can think of anoxia as the most extreme case of hypoxia.

ANSI-American National Standards Institute: American National Standards Institute, ANSI, is a private, nonprofit membership organization representing over 1,000 public and private organizations, businesses and government agencies. They seek to develop technical, political and policy consensus among various groups. Their web site is http://www.ansi.org/. ANSI does not develop American National Standards (ANSs), but they accredit qualified groups to do so in their area(s) of technical expertise. There are over 14,000 ANSI-approved standards in use today. ANSI-approved standards are voluntary, however, it is possible that some of the content of these standards could be made into law by a governmental body. ANSI is the official U.S. representative to the International Standards Organization (ISO). ANSI standard Z400.1-1998 "Hazardous Industrial Chemicals-Material Safety Data Sheets-Preparation" is the voluntary standard commonly used to construct MSDSs. You can purchase the standard on-line for $100.00 by following links on the ANSI Web site. This standard was developed by the Chemical Manufacturers Association (CMA). The ANSI standard MSDS contains 16 sections: (1) Substance identity and company contact information, (2) chemical composition and data on components, (3) hazards identification, (4) First aid measures, (5) Fire-fighting measures, (6) Accidental release measures, (7) handling and storage, (8) exposure controls and personal protection, (9) physical and chemical properties, (10) stability and reactivity, (11) toxicological information, (12) ecological information, (13) disposal considerations, (14) transport information, (15) regulations, (16) other information. MSDSs in ANSI format have a few distinct advantages over those prepared using the standard OSHA Form 174 format. ANSI-format sheets have all of the information required on the OSHA 174 format sheets, as well as additional useful information. The information on an ANSI format sheet is arranged in a consistent format whereas OSHA has no format requirements, only content requirements. ANSI format is likely to be consistent from country to country, possibly permitting one to use the same MSDS in different markets without modification. Most businesses that issue new MSDSs today use the ANSI standard format.

Anthropogenic: produced by human activities.

AOT40: sum of all hourly average concentrations after subtracting 40 ppb from each hourly value.

Apportionment: to distribute or divide and assign proportionately.

Aqueous: Aqueous refers to a solution in water. A more exact definition is a solution, in which the solute (the substance dissolved) initially is a liquid or a solid and the solvent is water. Aqueous solutions are not usually flammable, but may be able to carry toxic materials into your body through skin contact or ingestion. Be careful with terminology. A solution of ammonia gas (NH_3) in water is often called ammonium hydroxide, NH_4OH, ammonia water, or simply ammonia. Do not confuse this aqueous solution sometimes called ammonia with ammonia gas (anhydrous ammonia). Aqueous solutions fall into three general categories, based on how well they conduct electricity. Strong electrolytes, when dissolved in water, dissociate completely into ions and conduct electricity. For example, sodium chloride, NaCl, dissociates into Na^+ and Cl^- ions in water. Other examples of strong electrolytes are nitric acid (HNO_3) and sodium hydroxide (NaOH). Weak electrolytes, when dissolved in water, do not dissociate to any large extent and, therefore, do not conduct electricity very well. Examples include ammonia (NH_3) and acetic acid (CH_3COOH). Nonelectrolytes do not dissociate to ions in water and do not conduct electricity. Examples include sugar (sucrose; $C_{12}H_{22}O_{11}$), ethanol (CH_3CH_2OH), and methanol (CH_3OH).

Asphysia: Asphysia is a lack of oxygen, which interferes with the oxygenation of the blood. This condition is the result of asphyxiation, which can result from a number of factors, such as (1) suffocation/strangulation or (2) inhalation of an asphyxiant, such as 100% nitrogen gas.

Asphyxiant: An asphyxiant is a substance that can cause unconsciousness or death by suffocation (asphyxiation). Asphyxiation is an extreme hazard when working in enclosed spaces. Be sure you are trained in confined space entry before working in sewers, storage tanks, etc. where gases, such as methane, may displace oxygen from the atmosphere. Asphyxiants themselves are not toxic materials. They work by displacing so much oxygen from the ambient atmosphere that the hemoglobin in the blood cannot pick up enough oxygen from the lungs to fully oxygenate the tissues. As a result, the victim slowly suffocates. The normal composition of air is:

Name	Formula	% by volume
Nitrogen	N_2	78.03
Oxygen	O_2	20.99
Argon	Ar	0.94
Carbon dioxide	CO_2	0.033
Neon	Ne	0.0015

According to the Canadian Center for Occupational Health and Safety (CCOHS) the health effects of asphyxiation are:

% O_2 by volume	Symptoms or effects
16 to 12	Breathing and pulse rate increased, muscular coordination slightly disturbed
14 to 10	Emotional upset, abnormal fatigue, disturbed respiration
10 to 6	Nausea and vomiting, collapse or loss of consciousness
Below 6	Convulsive movements, possible respiratory collapse and death

Examples of asphyxiating gases are nitrogen (NH_3), helium (He), neon (Ne), argon (Ar), methane (CH_4), propane ($CH_3CH_2CH_3$), and carbon dioxide (CO_2). All of the above except carbon dioxide are odorless and tasteless. You can be overcome by these gases without realizing they are present. Again, follow OSHA-approved protocols for confined space entry into sewers, storage tanks, etc. Related terms are asphyxia, asphyxiation.

Asphyxiation: Asphyxiation is the process by which asphysia (lack of oxygen which interferes with the oxygenation of the blood) occurs. Asphyxiation can result from a number of factors such as (1) suffocation/strangulation or (2) inhalation of an asphyxiant such as 100% nitrogen gas.

Asthma: Occupational asthma, one form of asthma, is a lung disease in which the airways overreact to dusts, vapors, gases, or fumes that exist in the workplace. Symptoms include wheezing, a tight feeling in the chest, coughing and shortness of breath. While occupationally related asthma is usually reversible, chronic exposure to an irritant can result in permanent lung damage. The worker may become generally asthmatic, reacting to molds, allergens, cigarette smoke, dust mites, pet dander, etc.

Asymptomatic: Asymptomatic means neither causing nor exhibiting symptoms of disease. Just because one does not display symptoms of a disease or chemical exposure does not necessarily mean that one does not have the disease or was not harmed. Certain symptoms might occur only 50% of the time...or not at all depending on the individual involved. In general, being asymptomatic is a good thing, but it is not a guarantee of health.

Atrophy: Atrophy is a wasting or decrease in size of a bodily organ, tissue, or part owing to disease, injury, or lack of use. You may have heard this term used in reference to accident or paralysis victims: "his muscles atrophied because of non-use." Exposure to certain chemicals can cause internal organs to degrade, weaken and decrease in size, particularly with chronic (long-term) exposure.

Attainment Area: a geographic area in which levels of a criterion air pollutant meet the health-based National Ambient Air Quality Standard for that specific pollutant.

Attenuation: the diminution of quantity. In the case of visibility, attenuation or extinction refers to the loss of image-forming light as it passes from an object to the observer.

Autoignition: The autoignition temperature of a substance is the temperature at or above which a material will spontaneously ignite (catch fire) without an external spark or flame. Storing a substance anywhere near its autoignition temperature is a severe safety hazard. Be careful storing substances in hot areas, such as 1) sheds or cabinets exposed to direct sunlight, 2) adjacent to furnaces, hot water heaters, or boilers or 3) places where flames or heat are often used. Knowing a substance's autoignition temperatures is also very useful in the event of a fire. The equipment for determining an autoignition temperature is very similar to that used for flash point determinations.

Back Trajectory: a trace backwards in time showing where an air mass has been.

Best Available Control Technology (BACT): the control level (or control measures) required for sources subject to the Prevention of Significant Deterioration program (see 40CFR 52.21(b)).

Best Available Control Measures (BACM): *see BACT.*

Bimodal Distribution: a plot of frequency of occurrence of a variable versus the variable. A bimodal distribution exists if there are two maxima of the frequency of occurrence separated by a minimum. *See Mode.*

Bradycardia: Bradycardia is a slow heart rate (60 beats per minute or slower) that does not meet the body's metabolic demands. Symptoms of bradycardia include dizziness, extreme fatigue, shortness of breath, or fainting spells. This can be compared to tachycardia, which is an extremely rapid heart rate, usually signified by a pulse of over 100 beats per minute. Adults usually have a resting heart rate of 70-80 beats per minute, although well-trained athletes can have resting rates in the 50's or 60's. Newborn babies have a normal heart rate of 120-160 beats per minute. A slowed heart rate can lead to a variety of other problems. First aid treatment may include administration of oxygen.

Bronchitis: Bronchitis is inflammation of the bronchi (air passages of the lungs consisting of muscle tissue lined with mucous membranes). Chronic bronchitis is defined by the presence of a mucus-producing cough most days of the month, three months of a year for two successive years without other underlying disease to explain the cough. Chronic bronchitis is usually associated with smoking. Certain occupations that involve irritating dust or fumes are at higher risk. The American Lung Association lists coal miners, grain handlers, metal molders, and other workers exposed to dust as being at a higher risk for chronic bronchitis.

Budget: *see light extinction budget.*

Building-related Illness: a discrete, identifiable disease or illness that can be traced to a specific pollutant or source within a building. (Contrast with "Sick building syndrome").

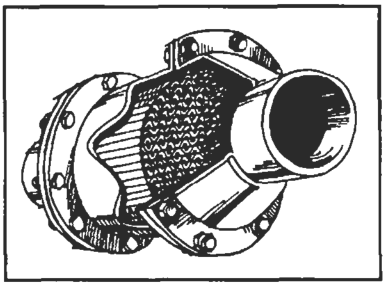
Buy-Back Center: facility where individuals or groups bring recyclable items in return for payment.

Carbon Monoxide: a criteria air pollutant that is a colorless, odorless, poisonous gas produced by incomplete combustion; particularly, incomplete burning of carbon-based fuels, e.g., gasoline, oil, and wood.

Carcinogen: A carcinogen is a substance that causes cancer (or is believed to cause cancer). A material that is carcinogenic is one that is believed to cause cancer. The process of forming cancer cells from normal cells or carcinomas is called carcinogenesis. OSHA's Hazardous Communications standard 1910.1200 accepts the following sources for establishing that a chemical is a known or potential carcinogen: National Toxicology Program (NTP), "Annual Report on Carcinogens" (latest edition); International Agency for Research on Cancer (IARC) "Monographs" (latest editions), part of the World Health Organization (WHO); 29 CFR part 1910, subpart Z, Toxic and Hazardous Substances, Occupational Safety and Health Administration. The "Registry of Toxic Effects of Chemical Substances" published by NIOSH indicates whether a chemical has been found by NTP or IARC to be a potential carcinogen.

Carcinoma: A carcinoma is a malignant (cancerous) growth that arises from the epithelium (the covering of internal and external surfaces of the body, including the lining of vessels and other small cavities). This includes the skin and lining of the organs such as breast, prostate, lung, stomach, or bowel. Carcinomas tend to spread (a process called metastasis) through the blood vessels, lymph channels or spinal fluid to other organs, such as the bone, liver, lung, or the brain. According to the American Cancer Society, at least 80% of all cancers are carcinomas.

CAS Number - Chemical Abstracts Service Registry Number: A CAS (Chemical Abstracts Service) Registry Number is a unique identifier that tells you, for example, that acetone and dimethyl ketone are actually the same substance. The Chemical Abstracts Service is a division of the American Chemical Society. OSHA only requires certain items on an MSDS and a CAS number is not one of them. However, authors of MSDS's are allowed to add additional information, such as the CAS number, if they desire. The numbers you see on trucks on the highway are not CAS Numbers, but U.S. Department of Transportation (DOT) codes, which are not necessarily specific to each chemical. Their aim is to assist emergency responders.



Catalytic Converter: an air pollution abatement device that removes pollutants from motor vehicle exhaust either by oxidizing them into carbon dioxide and water or reducing them to nitrogen. A typical catalytic oxidizer for auto emission control is illustrated in the sidebar figure.

CERCLA: Comprehensive Environmental Response Compensation and Liability Act.

Chemical Sensitization: Evidence suggests that some people may develop health problems characterized by effects such as dizziness, eye and throat irritation, chest tightness, and nasal congestion that appear whenever they are exposed to certain chemicals. People may react to even trace amounts of chemicals to which they have become "sensitized."

Chronic Health Effect: A chronic health effect is an adverse health effect resulting from long-term exposure to a substance. The effects could be a skin rash, bronchitis, cancer, or any other medical condition. An example would be liver cancer from inhaling low levels of benzene at your workplace over several years. The term is also applied to a persistent (months, years, or permanent) adverse health effect resulting from a short-term (acute) exposure. Chronic effects from long-term exposure to chemicals are fairly common. Recognize the PEL (permissible exposure level) for each substance in your workplace and minimize your exposure whenever possible.

Class I Area: as defined in the Clean Air Act, the following areas that were in existence as of August 7, 1977: national parks over 6,000 acres, national wilderness areas and national memorial parks over 5,000 acres, and international parks.

Class II Area: areas of the country protected under the Clean Air Act, but identified for somewhat less stringent protection from air pollution damage than a class I area, except in specified cases.

Clean Air Act: Originally passed in 1963, our current national air pollution control program is based on the 1970 version of the law. Substantial revisions were made by the 1990 Clean Air Act Amendments. *See also Clean Air Act pages.*

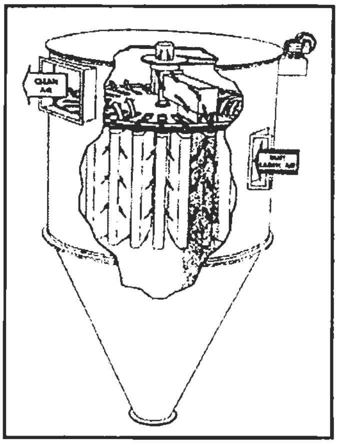
Clean Fuels: low-pollution fuels that can replace ordinary gasoline, including gasohol and natural and LP gas.

Cleanup: actions taken to deal with a release or threat of release of a hazardous substance that could affect humans and/or the environment. The term "cleanup" is sometimes used interchangeably with the terms remedial action, removal action, response action, or corrective action.

Closed-Loop Recycling: reclaiming or reusing wastewater for non-potable purposes in an enclosed process.

Coagulation: the process by which small particles collide with and adhere to one another to form larger particles.

Combined Cyclonic and Fabric Filtration: There are a number of arrangements where separate cyclones and fabric filters are combined into a single design to enhance gas cleaning. The side figure provides an example. Air carrying the pollutant particles enters the filter; heavier particles are removed through cyclonic dust separation in the lower cylindrical section of the filter; air carrying the lighter particles moves up through the fabric filter tubes and is deposited onto the outside of the filter tubes; clean air leaves the filter through the clean air outlet. To maintain the porosity of the filter sleeves, high velocity air is counter-flowed through the fabric filter tubes in a reverse of the filtering operation, cleaning each filter tube with a frequency of once per minute.



Combustible: A combustible material can be a solid or liquid. The U.S. Occupational Health and Safety Administration (OSHA) defines a combustible liquid as "any liquid having a flash point at or above 100°F (37.8°C), but below 200°F (93.3°C), except any mixture having components with flashpoints of 200°F (93.3°C), or higher, the total volume of which make up 99% or more of the total volume of the mixture." Compare this definition to flammable, which indicates a liquid that is even easier to ignite (flash point below 100°F). OSHA divides combustible (and flammable) liquids into several classes. If you'd like to see these, take a look at 29 CFR 1910.106. Combustible solids are those capable of igniting and burning. Wood and paper are examples of such materials. Proper storage and use of combustible materials are absolutely critical in maintaining a safe workplace. Avoid placing or using combustible materials near sources of heat or flame.

Compressed Natural Gas (CNG): an alternative fuel for motor vehicles; considered one of the cleanest because of low hydrocarbon emissions and its vapors are relatively non-ozone producing. However, vehicles fueled with CNG do emit a significant quantity of nitrogen oxides.

Condensation: the process by which molecules in the atmosphere collide and adhere to small particles.

Condensation Nuclei: the small nuclei or particles which gaseous constituents in the atmosphere (e.g., water vapor) collide and adhere.

Conjunctivitis: Conjunctivitis (also known as pink eye because the white part of the eye becomes pink) is inflammation (swelling) of the mucous membrane lining the eye (the conjunctiva). This is often accompanied by itching and watery eyes and sometimes blurred vision, eye pain, and sensitivity to light. This inflammation can be caused by physical injury, allergies, or chemical exposure, but is most commonly caused by bacterial or viral infection. These infections can be highly contagious and spread rapidly among schoolchildren or families. Bacterial conjunctivitis can be treated with antibiotic eye drops, prescribed by a physician, whereas viral conjunctivitis usually clears up on its own, if strict hygiene is followed. Exposure to chemicals that irritate the eyes (such as lachrymators) can cause conjunctivitis or make existing conjunctivitis worse. Seek medical treatment if the condition does not clear up on its own. If you are not certain whether a chemical was splashed in your eye or you are suffering from conjunctivitis, you should consult a physician immediately.

Continuous Sampling Device: an air analyzer that measures air quality components continuously. *See also monitoring, integrated sampling device.*

Control Technique Guidelines (CTG): EPA documents designed to assist state and local pollution authorities to achieve and maintain air quality standards for certain sources (e.g., organic emissions from solvent metal cleaning known as degreasing) through reasonably available control technologies (RACT).

Criteria: (in the context of criteria pollutants) information on health and/or environmental effects of pollution.

Criteria Air Pollutant: a group of very common air pollutants regulated by EPA on the basis of criteria, and for which a National Ambient Air Quality Standard is established (SO_2, NO_2, PM_{10}, Pb, CO, O_3).

Critical Load: the concentration of air pollution or total deposition of pollutants above which specific deleterious effects may occur.

Cumulative Effect: the impact on an AQRV resulting from total pollutant loading from all sources including the contributing effects of new and modified sources of air pollution.

Cutaneous: Cutaneous relates to or affects the skin. The term subcutaneous refers to being below the skin (as in a penetrating injury or injection). Use your MSDS to determine the required personal protective equipment (PPE) that you must use. Protecting the skin (with gloves, aprons, coveralls, face masks, etc.) is important. After all, the skin is the largest organ in the human body.

Cyanosis: Cyanosis is an abnormal bluish color of the skin or mucous membranes. The bluish (cyan) or blue-gray color arises from deoxygenated hemoglobin, the oxygen carrier in your bloodstream that carries oxygen from your lungs to your tissues. Hemoglobin and your blood are red when well-oxygenated, but blood appears to be dark red-blue if there is more than 50 g/L of hemoglobin without oxygen. Cyanosis can be seen in cases of anoxia and hypoxia (lack of oxygen) and is a symptom of asphyxiation. Cyanosis is also observed when a chemical agent blocks the ability of hemoglobin to bind oxygen. For example, carbon monoxide, CO, a product of imperfect combustion, binds to hemoglobin approximately 200 times better than oxygen. Victims of carbon monoxide poisoning often have blue lips and fingernails. Treatment for cyanosis includes administration of pure oxygen. In the case of carbon monoxide poisoning, hyperbaric oxygen treatment, placing the victim in a chamber pressurized to 2 or 3 atmospheres of pure oxygen, may be used. Cyanosis is harder to observe in dark-skinned people. The best places to look in this case are in the buccal mucosa (inside of the cheek) and hard palate (roof of the mouth). Cyanosis is an early sign of hypoxia. If you are working in a confined space, where the oxygen content may be less than normal or are working with a chemical substance that interferes with oxygen transport in the body, be sure to recognize the bluish cast of cyanosis.

Cyclone Separators: Cyclone separators are described in Chapter 7. Typically used to remove particulate from a gas stream, the gas enters tangentially at the top of a cylinder and is forced downward into a spiral motion. The particles exit the bottom while the gas turns upward into the vortex and leaves through the top of the unit. Pressure drops through cyclones are usually from 13 to 17 mm water gauge. Although seldom adequate by themselves, cyclone separators are often an effective first step in pollution control.

Damage: any reduction in the intended use or value of a biological or physical resource. For example, economic production, ecological structure or function, aesthetic value, or biological or genetic diversity that may be altered by a pollutant.

Deciview: a unit of visibility proportional to the logarithm of the atmospheric extinction. Under many circumstances a change in one deciview will be perceived to be the same on clear and hazy days.

Dermal Toxicity: Dermal toxicity is the ability of a substance to poison people or animals by contact with the skin. Toxic materials absorb through the skin to various degrees depending on their chemical composition and whether they are dissolved in a solvent. Always wear proper personal protection equipment (PPE), such as gloves and aprons, when working with a toxic (or nontoxic) substance that can be absorbed through the skin.

Desulfurization: removal of sulfur from fossil fuels to reduce pollution.

Diffraction: modification of the behavior of a light wave resulting from limitations of its lateral extent by an obstacle. For example, the bending of light into the "shadow area" behind a particle.

Diffusion: a process by which substances, heat, or other properties of a medium are transferred from regions of higher concentrations to regions of lower concentration.

Dose-response: the relationship between the dose of a pollutant and its effect on a a biological system

Dry Deposition: delivery of air pollutants in the gaseous or particle phase to surfaces.

Dyspnea: Dyspnea is shortness of breath or difficulty in breathing. The victim is usually quite aware of the unusual breathing pattern. Shortness of breath can be an indicator of many physical ailments including simple exertion, a panic attack, a blow to the chest, asthma, cardiac disease, as well as exposure to toxic chemicals. If a person is suffering from shortness of breath, evaluate them for additional symptoms and possible exposures. Keep the victim in a sitting position. Remove the victim to fresh air, if possible, and seek medical attention.

Ecological Effects: studies to determine the nature or extent of air pollution and acid deposition to ecosystems.

Edema: Edema is an abnormal accumulation of body fluid in tissues. An edema can be as trivial as a blister on your thumb, as life-threatening as a constriction of your airway. As in real estate, the three factors that determine the dangers associated with an edema are location, location, location. Exposure to toxic chemicals can cause a variety of edemas. Pulmonary edema (fluid in the lungs) is particularly dangerous, if not treated. Be sure to avoid inhalation of chemicals whenever possible and to use proper protective measures, as suggested on the MSDS (fume hoods, respirators, etc.).

Electrostatic Precipitators: ESPs are described in Chapter 7. Boasting an efficiency in excess of 99%, electrostatic precipitators are very effective at removing tiny particles from gas streams. Gas flows through a rectangular duct containing rows of metallic strips. The strips are negatively charged by way of a small voltage that is applied (about 200 W for every 1000 ft^3/min of gas). The efficiency is a result of the precipitators applying the collecting force to the particles only and not the gas. Periodically, the precipitators have to be taken offline and cleaned.

Elevated Flares: See *Flares* for a general definition. The elevated flare, by the use of steam injection and effective tip design, operates as a smokeless combustion device. Flaring generally is of low luminosity up to about 20 % of maximum flaring load. Steam injection tends to introduce a source of noise to the operation, and a compromise between smoke elimination and noise is usually necessary. When adequately elevated (by means of a stack) this type of flare displays the best dispersion characteristics for malodorous and toxic combustion products. Visual and noise pollution often creates nuisance problems. Capital and operating costs tend to be high, and an appreciable plant area can be rendered unavailable for plant operations and equipment because of excessive radiant heat.

Emergency Planning and Community Right-To-Know Act (EPCRA): The U.S. Emergency Planning and Community Right-To-Know Act (EPCRA) also known as the Community Right-To-Know Act or SARA, Title III provides for the collection and public release of information about the presence and release of hazardous or toxic chemicals in the nation's communities. The law requires industries to participate in emergency planning and to notify their communities of the existence of, and routine and accidental releases of, hazardous chemicals. The goal is to help citizens, officials, and community leaders to be better informed about toxic and hazardous materials in their communities. To implement EPCRA, Congress required each state to appoint a State Emergency Response Commission (SERC). The SERCs were required to divide their states into Emergency Planning Districts and to name a Local Emergency Planning Committee (LEPC) for each district. Broad representation by fire fighters, health officials, government and media representatives, community groups, industrial facilities, and emergency managers ensures that all necessary elements of the planning process are represented. If you have a major chemical user or manufacturer in your community, plans to deal with emergency releases have already been developed. Consult your local EPA office for more information. A list of over 600 chemicals subject to EPCRA are listed in the Toxics Release Inventory (TRI), which is maintained by the U.S. Environmental Protection Agency (EPA). EPCRA or TRI information is not equivalent to an MSDS, but does provide useful information for people concerned about the presence (or potential presence) of chemicals in their community or environment. The information found in these materials can supplement MSDS information, but is not a substitute for it.

Emissions: release of pollutants into the air from a source.

Emission Offset: a federally enforceable reduction in emissions from an existing source that mitigates the impacts on AQRVs of a proposed new or modified source, and ensures compliance with NAAQS and PSD increment.

Enforcement: legal methods used by EPA, state, and local governments to make polluters obey the Clean Air Act. In the absence of enforcement, citizens can sue EPA or the states to obtain action, and can also sue violating sources apart from any action EPA or state or local governments have taken.

Environmental Protection Agency (EPA): the federal agency responsible for regulating air quality. See also EPA Web site.

Environmental Tobacco Smoke (ETS): mixture of smoke from the burning end of a cigarette, pipe, or cigar and smoke exhaled by the smoker (also secondhand smoke or passive smoking).

Extinction: the attenuation of light due to scattering and absorption as it passes through a medium.

Extinction Coefficient: a measure of the ability of particles or gases to absorb and scatter photons from a beam of light; a number that is proportional to the number of photons removed from the sight path per unit length. See absorption.

Extinction Cross Section: the amount of light scattered and absorbed by a particle divided by its physical cross section.

Exxon Thermal DeNOx: Similar to SCR, the Exxon Thermal DeNOx process utilizes the NO_x/ammonia reaction. However, this process does not use a catalyst to aid the reaction. Rather, tightly controlled temperatures are used to steer the reactions. Optimum reaction temperatures are found between 1600°F (871°C) and

1800°F (981°C). Below the optimum temperature range, ammonia does not fully react and can be released in the flue gas. Above the optimum temperature, the following competing reaction can begin to take place:

$NH_3 + 5/4\ O_2 \dashrightarrow NO + 3/2\ H_2O$

Ammonia is injected in a 2:1 molar ratio in this process.

Feasibility Analysis Phase: The point in a pollution prevention program at which waste reduction options are evaluated technically, economically and environmentally. The results are used to select options to be recommended for implementation.

Federal Motor Vehicle Control Program: all federal actions designed to control pollution from motor vehicles by such efforts by establishing and enforcing tailpipe and evaporative emission standards for new vehicles, testing methods development, and guidance to states operating inspection and maintenance programs. May include nearby locations in the same states that share common air pollution problems.

Federal Land Manager (FLM): the Secretary of the Department with authority over such lands. [40 CFR 51.166(b)(24)] The FLM for the Department of the Interior has been delegated the Assistant Secretary for Fish and Wildlife and Parks; the FLM for the Department of Agriculture has been delegated to the Forest Service, and has been redelegated to the Regional Forester or individual Forest Supervisor.

Fine Particle: particulate matter less than 2.5 microns in diameter.

Flares: a combustion device used in the disposal of waste gas streams and/or in emergency handling of high pressure releases from a refinery or chemical plant operation. Three types of flare systems used in the past are the elevated flare, the ground flare, and the burning pit flare. Burning pit flares are no longer considered viable in the U.S. because of air pollution and safety considerations, but are employed in some parts of the world. *Refer to elevated flares and ground flares.*

Fluidized Bed Scrubber: This is an impingement-type gas-liquid scrubber, where the gas flow rate is sufficiently high to keep a packed bed of spheres in constant motion. As with the fixed bed design described in Chapter 7, liquid flow is countercurrent to the gas flow. Initial wash water distribution is accomplished by multiple spray heads wetting the entire cross section of the bed. A vane axial mist eliminator spins the escaping droplets against the cylindrical wetted wall before the demisted gas is discharges through the cleaned gas discharge. Sludge is discharged out of the bottom.

Flux: gaseous uptake into plant tissue.

Fugitive Emission: pollutant emitted from diffuse or ill-defined conditions, e.g., other than a stack or chimney.

Fungi: any of a group of parasitic lower plants that lack chlorophyll, including molds and mildews.

Gastroenteritis: Gastroenteritis is an acute inflammation of the lining of the stomach and intestines. Symptoms include anorexia, nausea, diarrhea, abdominal pain and weakness. Gastroenteritis has many causes, such as bacteria (food poisoning), viruses, parasites, consumption of irritating food or drink, as well as stress. Treatment for the condition depends on the underlying cause.

Green Line: the total pollutant loading (contributions from existing and proposed sources) below which there is a very high degree of certainty that no AQRV will be adversely affected.

Ground Flares: See *Flares* for a general definition. There are various designs, but the most widely used is the so-called multi-jet flare. Smokeless operation can be achieved, with essentially no noise or luminosity problems, provided that the design gas rate to the flare is not exceeded. However, since the flame is near the ground level, dispersion of stack releases is poor. This can result in severe air pollution or hazard if the combustion products are toxic, or in the event of a flame-out occurring. The multi jet flare is best suited for "clean burning" gases, and in those situations where noise and visual pollution problems are critical.

Gulf of Maine Oxidant Study (GOMOS): a study to investigate the sources and transport of pollutants contributing to ozone formation.

Hazardous Air Pollutants (HAP): airborne chemicals that cause serious health and environmental effects.

Haze (Hazy): an atmospheric aerosol of sufficient concentration to be visible. The particles are so small that they cannot be seen individually, but are still effective attenuating light and reducing visual range.

Hepatic: Hepatic means "pertaining to the liver." For example, hepatitis is inflammation of the liver. Liver disorders are sometimes marked by jaundice, a yellowish coloration to the whites of the eyes and skin. Certain chemicals are hepatotoxins (toxic to the liver), usually as a result of chronic exposure. One example is carbon tetrachloride (CCl_4).

Highly Toxic: A highly toxic material is defined by the U.S. Occupational Health and Safety Administration (OSHA) in CFR 29 1910.1200 Appendix A as a chemical that falls in any of these three categories: A chemical that has a median lethal dose (LD_{50}) of 50 milligrams or less per kilogram of body weight when administered orally to albino rats weighing between 200 and 300 grams each. A chemical that has a median lethal dose (LD_{50}) of 200 milligrams or less per kilogram of body weight, when administered by continuous contact for 24 hours (or less if death occurs within 24 hours) with the bare skin of albino rabbits, weighing between two and three kilograms each. A chemical that has a median lethal concentration (LC_{50}) in air of 200 parts per million by volume or less of gas or vapor, or 2 milligrams per liter or less of mist, fume, or dust, when administered by continuous inhalation for one hour (or less if death occurs within one hour) to albino rats weighing between 200 and 300 grams each. This is the greatest level of toxicity defined in the OSHA Hazard Communication Standard (OSHA does not have an "Extremely toxic" ranking). Accidental release or exposure to a highly toxic chemical can cause serious injury or death. Use proper protective equipment (gloves, safety goggles, fume hoods, etc.) when working with highly toxic materials. Know the physical properties of the material, as well as symptoms of exposure and first aid procedures.

Homogeneous Nucleation: a process by which gases interact and combine with droplets made up of their own kind. For instance, the collision and subsequent adherence of water vapor to a water droplet is a homogeneous nucleation. See nucleation.

Humidifier Fever: A respiratory illness caused by exposure to toxins from microorganisms found in wet or moist areas in humidifiers and air conditioners. Also called air conditioner or ventilation fever.

Hydrocarbons: compounds containing only hydrogen and carbon. Examples: methane, benzene, and decane.

Hygroscopic: A hygroscopic material (literally "water seeking") is one that readily absorbs water (usually from the atmosphere). In most cases, the water can be removed from the material by heating (sometimes under vacuum or under a flow of dry gas such as nitrogen). Hygroscopic materials are fairly common. Some may absorb a finite amount of water (such as magnesium sulfate, $MgSO_4$), while others may attract so much water that they form a puddle and dissolve (deliquesce). For example, solid sodium hydroxide (NaOH) pellets will form a small corrosive puddle in less than an hour in moist air. Therefore, always be sure to clean up any spills of hygroscopic materials right away. Also be aware that hygroscopic materials typically release a large amount of heat, when mixed with water. Always store hygroscopic materials in well-sealed containers (or under vacuum or an inert atmosphere). Know their physical properties, so that, if you open a container, you can tell if the material has been contaminated with water (i.e., that jar of calcium chloride, $CaCl_2$, should be a solid, not a liquid).

Hypergolic: A hypergolic mixture ignites upon contact of the components without any external source of ignition (heat or flame). The only field, in which this is a desirable event, is in rocket fuel research. Accidental mixing of incompatible materials can lead to a fire or explosion. Here is one example provided by the staff at ILPI of what can happen, when incompatibles are mixed. Always read the labels on your bottles (don't assume a chemical's identity by the shape, size, or color of the bottle), and know what materials are incompatible with the chemicals that you are using.

Hypersensitivity Pneumonitis: a group of respiratory diseases that cause inflammation of the lung (specifically granulomatous cells). Most forms of hypersensitivity pneumonitis are caused by the inhalation of organic dusts, including molds.

Hypoxia: Hypoxia is a deficiency of oxygen in inspired (inhaled) gases or in arterial blood and/or in the tissues. This is closely related to anoxia, which is a complete lack of oxygen in the tissues. One can think of anoxia as the most severe case of hypoxia. Various forms of hypoxia are recognized: anemic hypoxia, which results from a decreased concentration of hemoglobin; hypoxic hypoxia, which results from defective oxygenation of the blood in the lungs; ischemic hypoxia - results from slow peripheral circulation (also called stagnant hypoxia). Not uncommon following congestive cardiac failure; altitude sickness- nosebleed, nausea or pulmonary edema experienced at high altitudes. The most common symptom of hypoxia is cyanosis, a bluish cast to the skin, lips and/or fingernails. If your body isn't getting oxygen, you die. Make sure you recognize cyanosis when you see it. If working in an enclosed space or with an asphyxiant, move to a well-ventilated area if you become light-headed, weak, or disoriented. Related terms are anoxia, asphyxiant, cyanosis.

IARC: International Agency for Research on Cancer: The International Agency for Research on Cancer (IARC) is a part of the World Health Organization. IARC's mission is to coordinate and conduct research on the causes of human cancer, the mechanisms of carcinogenesis, and to develop scientific strategies for cancer control. Their Web home page is http://www.iarc.fr/. IARC compiles several databases on carcinogenic risk to humans, epidemiology, and cancer control. The IARC Monographs series is one of four resources that OSHA uses to list a material as a known or probable human carcinogen. You can view a list of over 800 agents covered in the monographs. IARC classifies agents (chemicals, mixtures, occupational exposures etc.) into four basic categories: **Group 1**: The agent (mixture) is carcinogenic to humans. The exposure circumstance entails exposures that are carcinogenic to humans. **Group 2**: The agent (mixture) is probably carcinogenic to humans and **Group 2A**: The exposure circumstance entails exposures that are probably carcinogenic to humans. **Group 2B**: The exposure circumstance entails exposures that are possibly carcinogenic to humans. **Group 3**: The agent (mixture, or exposure circumstance) is unclassifiable as to carcinogenicity in humans. **Group 4**: The agent (mixture, exposure circumstance) is probably not carcinogenic to humans.

Impairment: the degree to which a scenic view or distance of clear visibility is degraded by man-made pollutants.

Implementation Phase: the step in a pollution prevention assessment where procedures, training, and equipment changes are put into action to reduce waste.

IMPROVE: Interagency Monitoring of Protected Visual Environments, a collaborative monitoring program to establish present visibility levels and trends, and to identify sources of man-made impairment.

Industrial Source Reduction: Practices that reduce the amount of any hazardous substance, pollutant, or contaminant entering any waste stream or otherwise released into the environment. Also reduces the threat to public health and the environment associated with such releases. Term includes equipment or technology modifications, substitution of raw materials, and improvements in house keeping, maintenance, training or inventory control.

Injury: any physical or biological response to pollutants, such as a change in metabolism, reduced photosynthesis, leaf necrosis, premature leaf drop, or chlorosis.

Integrated Sampling Device: an air sampling device that allows estimation of air quality components over a period of time (e.g., two weeks) through laboratory analysis of the sampler's medium.

Inversion: See temperature inversion.

Iridocyclitis: Iridocyclitis is an inflammation of the iris (the colored part of the eye) and of the ciliary body (muscles and tissue involved in focusing the eye). This condition is also called "anterior uvetitis." The condition can be marked by red eye, pain, photophobia (light sensitivity, literally "fear of light"), watering of the eyes and a decrease in vision. If only one eye is affected, shining light in the good eye can produce pain in the affected eye. This is closely related to conjunctivitis, swelling of the mucous membranes around the eye. Treatments include steroid, atropine, antibiotic, or antiviral eyedrops. Exposure to chemicals that irritate the eyes (such as lachrymators) can cause iridocyclitis or aggravate an existing case. Seek medical treatment if the condition does not clear up on its own. If you are not certain whether a chemical was splashed in your eye or you are suffering from iridocyclitis, you should consult a physician immediately.

Isopleth: a line drawn on a map through all points having the same numeric value.

Isotropic: a situation where a quantity (or its spatial derivatives) is independent of position or direction.

Isotropic Scattering: the process of scattering light equally in all directions.

Ketosis: Ketosis is the presence of excess ketones in the body. Ketones are chemicals with a carbonyl unit (a carbon doubly bonded to an oxygen), that has two alkyl or aromatic (hydrocarbon) substituents bonded to the carbon atom. Ketones are a by product of fat metabolism (the breaking down of fat into energy). Normally, your body is efficient at removing these, but when certain enzymes are absent or damaged, the amount of ketones in the body can build up to dangerous levels. Certain individuals are predisposed towards ketosis. For example, those with diabetes have low insulin levels and cannot process glucose (sugar) for energy. Therefore, their bodies break down fat, leading to a rise in ketone levels. Ketones can be excreted through the urine and those that are volatile (such as acetone) can be expelled through the lungs. Diabetics can be mistaken for being drunk by the odor on their breath, and acetone being expelled through the lungs can give a false positive result on early model breathalyzers. However, don't expect to escape a ticket as driving while impaired (due to low blood sugar) is still a traffic offense whether you are drunk or not. Ketosis can lead to coma and death, if untreated.

Lachrymator: A lachrymator is an irritant that causes tearing (watering of the eyes). Examples include onions, tear gas, and pepper spray (capsaicin). Some typical lachrymating chemicals are thionyl chloride ($SOCl_2$) and acrolein ($CH_2=CH-CHO$). Certain chemicals may say lachrymator on the label so treat these with respect. Use these only in a fume hood. Goggles or safety glasses are not adequate protection for lachrymators, because the fumes can still reach your eyes directly or through inhalation.

LAER (Lowest Achievable Emissions Rate): the control level required of a source subject to nonattainment review. (See 40 CFR 51.165(a))

LC_{50}, 50% Lethal Concentration: An LC_{50} value is the concentration of a material in air that will kill 50% of the test subjects (animals, hopefully), when administered as a single exposure (typically 1 or 4 hours). This value gives you an idea of the relative toxicity of the material. This value applies to vapors, dusts, mists, and gases. Solids and liquids use the closely related LD_{50} value (50% lethal dose). The formula for determination of an LC_{50} is rather complex and can be found in 49 CFR 173.133(b)(1)(i). Both LC_{50} and LD_{50} values state the animal used in the test. This is important, because animal toxicity studies do not necessarily extrapolate (extend) to humans. For example, dioxin (of Love Canal, Times Beach, Sveso, and Agent Orange fame) is highly toxic to guinea pigs and ducklings at extremely low levels, but has never been conclusively linked to a single human death even at very high levels of acute (short term) exposure. However, it is best to err on the safe side when evaluating animal toxicity studies and assume that most chemicals that are toxic to animals are toxic to humans. Typical units for LC_{50} values are parts per million (ppm) of material in air, micrograms (10^{-6} = 0.000001 g) per liter of air and milligrams (10^{-3} = 0.001 g) per cubic meter of air. Never be exposed to an LC_{50} dose of a hazardous chemical - by definition, there is a 50% chance this will kill you and if you survive you're not going to be in good shape. Pay close attention to the permissible exposure level (PEL) instead. This is a more realistic determination of the maximum safe exposure to a material and is usually based on the known effects of the chemical on humans, rather than laboratory animals.

LD_{50}, 50% Lethal Dose: An LD_{50} value is the amount of a solid or liquid material that it takes to kill 50% of test animals in one dose. LC_{50} (50% lethal concentration) is a related term used for gases, dusts, vapors, mists, etc. The dose may be administered orally (by mouth), or injected into various parts of the body. The value is usually reported along with the administration method. Both LC_{50} and LD_{50} values state the animal used in the test. This is important, because animal toxicity studies do not necessarily extrapolate (extend) to humans. For example, dioxin (of Love Canal, Times Beach, Sveso, and Agent Orange fame) is highly toxic to guinea pigs and ducklings at extremely low levels, but has never been conclusively linked to a single human death even at very high levels of acute (short term) exposure. However, it is best to err on the safe side when evaluating animal toxicity studies and assume that most chemicals, that are toxic to animals, are toxic to humans.

Typical units for LD_{50} values are milligrams or grams of material per kilogram of body weight (mg/kg or g/kg, recall that 1 kg = 2.2 pounds). Never be exposed to an LD_{50} dose of a hazardous chemical- by definition, there is a 50% chance this will kill you and if you survive you are not going to be in good shape. Pay close attention to the permissible exposure level (PEL) instead. This is a more realistic determination of the maximum safe exposure to a material and is usually based on the known effects of the chemical on humans, rather than laboratory animals.

Light-absorbing Carbon: carbon particles in the atmosphere that absorb light. Black carbon.

Light Extinction Budget: the percent of total atmospheric extinction attributed to each aerosol and gaseous component of the atmosphere.

Long Path Measurement: an atmospheric measurement process that is made over distances in excess of a few hundred meters.

Major Source: a stationary facility that emits a regulated pollutant in an amount exceeding the threshold level (100 or 250 tons per year, depending on the type of facility). *See also source.*

Metastasis: Metastasis is the spread of a disease (usually cancer) from an original site of infection to other parts of the body. This usually happens when cancer cells break off from the original tumor and travel through the blood vessels to a new site. This kind of cancer is called malignant, meaning that it is life-threatening and usually fatal.

Micrometer: a unit of length equal to one millionth of a meter; the unit of measure for particle size.

Micron: a unit of length equal to one millionth of a meter; the unit of measure for wavelength.

MIE Theory: a complex mathematical model that allows the computation of the amount of energy (light) scattered by spherical particles.

Mobile Sources: moving objects that release regulated air pollutants, e.g., cars, trucks, buses, planes, trains, motorcycles, and gas-powered lawn mowers. *See also source; stationary source.*

Mode: the maximum point in a plot of the frequency of occurrence of a variable versus the variable.

Monitoring: measurement of air pollution. *See also continuous sampling device, integrated sampling device.*

Mutagen: A mutagen is a substance or agent that causes an increase in the rate of change in genes (subsections of the DNA of the body's cells). These mutations (changes) can be passed along as the cell reproduces, sometimes leading to defective cells or cancer. Examples of mutagens include biological and chemical agents as well exposure to ultraviolet light or ionizing radiation. There are many types of mutations, some of which are harmful and others which have little or no effect on the body's function. See the Life Science Dictionary at the University of Texas, for examples. Mutagens can be identified using the Ames test and other biochemical testing methods. Do not confuse a mutagen with a carcinogen (a substance that causes cancer). Mutagens may cause cancer, but not always. Do not confuse a mutagen with a teratogen (a substance that causes change or harm to a fetus or embryo). Whenever you work with a mutagen be sure to wear proper protective equipment (PPE) and minimize your exposure.

Narcosis: Narcosis is a state of deep stupor or unconsciousness, produced by a chemical substance, such as a drug or anesthesia. Inhalation of certain chemicals can lead to narcosis. For example, diethyl ether and chloroform, two common organic solvents, were among the first examples of anesthesia known. Many other chemicals that you would not suspect can also cause narcosis. For example, even though nitrogen gas comprises 80% of the air we breathe and is considered chemically inert (unreactive) it can cause narcosis under certain conditions. Always work with adequate inhalation and avoid inhaling chemical fumes, mists, dusts etc. whenever possible. Use fume hoods and respirators as necessary.

National Ambient Air Quality Standards (NAAQS): permissible levels of criteria air pollutants established to protect public health and welfare.

Natural Conditions: conditions substantially unaltered by humans or human activities. as applied in the context of visibility, natural conditions include naturally occurring phenomena that reduce visibility as measured in terms of light extinction, visual range, contrast, or coloration.

Natural Visibility Conditions: visibility conditions attributable to Rayleigh scattering and aerosol associated with natural processes.

Necrosis: Necrosis is the death of cells or tissue due to disease, injury, exposure to chemical agents, radiation etc. Necrotic tissue can be found anywhere in the body, but is generally a localized phenomenon. When extremely large areas of tissue are involved, the condition is generally called gangrene. Corrosive materials may cause painful chemicals burns and necrosis of the skin or eyes. Always wear proper personal protection equipment (PPE) such as gloves and goggles when dealing with such materials.

Neoplasm: A neoplasm is an abnormal growth of tissue that has no useful function. A synonym is "tumor." Neoplasms may be benign (no ability to spread to other parts of the body) or malignant (cancerous). Chronic (long-term) exposure to certain chemicals can result in the formation of neoplasms. While not all of these tumors are cancerous, benign tumors have the potential to interfere with vital body functions or become malignant. Limit your exposure to chemicals that are known to cause neoplasms (tumors). This includes reducing the usage of such chemicals in your workplace as well as using proper personal protective equipment (PPE) such as gloves, respirators and fume hoods. Related terms are carinogen, carcinoma, malignant, mutagen, and teratogen.

Nephelometer: an instrument that measures the amount of light scattered.

New Source Performance Standards (NSPS):- Uniform national EPA air emission and water effluent standards which limit the amount of pollution allowed from new sources or from modified existing sources.

NIOSH - National Institute for Occupational Safety and Health: The National Institute for Occupational Safety and Health, NIOSH, is part of the U.S. federal government's Centers for Disease Control and Prevention (CDC). NIOSH's web site is http://www.cdc.gov/niosh/homepage.html. NIOSH is the only federal Institute responsible for conducting research and making recommendations for the prevention of work-related illnesses and injuries. NIOSH was created by the Occupational Health and Safety (OHS) Act of 1970. OSHA is responsible for creating and enforcing workplace safety and health regulations while NIOSH is in the Department of Health and Human Services and is a research agency. Examples of NIOSH activities include: investigating potentially hazardous working conditions as requested by employers or employees; evaluating hazards in the workplace, ranging from chemicals to machinery; creating and disseminating methods for preventing disease, injury, and disability; conducting research and providing scientifically valid recommendations for protecting workers; providing education and training to individuals preparing for or actively working in the field of occupational safety and health; creating new ways to prevent workplace hazards. Many NIOSH-approved standards appear on MSDSs. Other examples of NIOSH's involvement with MSDSs: NIOSH cooperates with other world agencies in providing International Chemical Safety Cards which, while not strictly MSDSs, provide workers with succinct information about the hazards of chemicals; NIOSH plays a role in establishing PEL, TLV, and STELs for a variety of chemicals; the NIOSH Pocket Guide to Chemical Hazards (NPG); NIOSH publishes Occupational Health Guidelines for Chemical Hazards listed by chemical; the Registry for Toxic Effects of Chemical Substances (RTECS), a toxicology database containing over 140,000 chemical substances.

Nitrates: those gases and aerosols that have origins in the gas-to-aerosol conversion of nitrogen oxides, e.g., NO_2; of primary interest are nitric acid and ammonium nitrate. Ammonium nitrate is very hygroscopic so its contribution to visibility impairment is magnified in the presence of water vapor.

Nitrogen Dioxide: a gas (NO_2) consisting of one nitrogen and two oxygen atoms. It absorbs blue light and therefore has a reddish-brown color associated with it.

Nitrogen Oxides: a criteria air pollutant, compounds NO, NO_2, NO_3, N_2O_5, alkyl nitrates, etc.

Nonattainment Area: An area designated by the EPA Administrator pursuant to Section 107(d) of the Clean Air Act as having air quality which does not meet one or more National Ambient Air Quality Standards (NAAQS). For a list of nonattainment areas, see 40 CFR Part 81, Subpart C.

North Atlantic Regional Experiment (NARE): a study to assess the contribution of continental air pollution to the North Atlantic Ocean.
NO_x: the sum of $NO + NO_2$.
NO_y: the sum of all oxidized nitrogen species, i.e. NO, NO_2, NO_3, HNO_3, N_20_5, alkyl nitrates, PAN, etc. Does not include NH_3 or N_2O. *See also nitrogen oxides, NOx.*

NTP- National Toxicology Program: The National Toxicology Program (NTP) is a unit of the U.S. Department of Health and Human Services. NTP coordinates toxicology research and testing activities within the Department and provides information about potentially toxic chemicals to regulatory and research agencies and the public. NTP is the world leader in designing, conducting, and interpreting animal assays for toxicity and carcinogenicity. Their Web home page is http://ntp-server.niehs.nih.gov/. The NTP consists of relevant toxicology activities of the U.S. National Institutes of Health's National Institute of Environmental Health Sciences (NIH/NIEHS), the U.S. Centers for Disease Control and Prevention's National Institute for Occupational Safety and Health (CDC/ NIOSH), and the U.S. Food and Drug Administration's National Center for Toxicological Research (FDA/NCTR). The NTP's Annual Reports on Carcinogens (see the latest edition) are one of the four sources used by OSHA to declare substances as carcinogens. NTP is one of your most trusted sources when it comes to information about toxic chemicals or potential carcinogens.

Nucleation: a process by which a gas interacts and combines with droplets. See homogeneous nucleation.

Nystagmus: Nystagmus is a rapid, involuntary, motion of the eyeball (side to side, up and down, rotating and/or oscillating). Nystagmus can be caused by tumors or drugs (such as barbiturates). It can also be a congenital condition (present at birth). Exposure to certain chemicals can cause nystagmus. This condition is very easy for other persons to observe. Be certain you read the MSDSs for all chemicals that you are working with and note whether exposure to any of these can cause this condition.

Organic Compounds: Chemicals that contain carbon. Volatile organic compounds vaporize at room temperature and pressure. They are found in many indoor sources, including many common household products and building materials.

OSHA- Occupational Health and Safety Administration: The U.S. Occupational Health and Safety Administration, OSHA, is a federal government agency in the U.S. Department of Labor. OSHA's Web site is http://www.osha.gov/. The primary goals of OSHA are to save lives, prevent injuries, and protect the health of America's workers. OSHA employs over 2,000 inspectors to ensure job site safety. OSHA was created by the Occupational Health and Safety (OHS) Act of 1970. While many see OSHA as an intrusive government agency intent on enforcing arcane rules, the fact is that OSHA saves lives. And if that is not enough for you, their Voluntary Protection Plan (VPP) saves money by reducing the cost of injuries, accidents, downtime, and litigation. OSHA's Hazard Communication Standard 1910.1200 requires employers to establish hazard communication programs to transmit information on the hazards of chemicals to their employees by means of labels on containers, material safety data sheets, and training programs. Implementation of these hazard communication programs will ensure all employees have the "right-to-know" the hazards and identities of the chemicals they work with, and will reduce the incidence of chemically-related occupational illnesses and injuries. The OSHA HazCom standard specifies the required elements that must be on an MSDS among other important data. It is a very readable document, and it is suggested that anyone involved with MSDS management print out a hard copy for future reference. OSHA has a suggested format for MSDSs, Form 174 (OMB #1218-0072). You can download this form in HTML or PDF format from the U.S. Department of Labor's Occupational Safety and Health Administration World Wide Web site, if you wish. While this format is nonmandatory, it is a frequently utilized format. An MSDS can contain more information than that required by OSHA, but not less. Form 174 has the following sections: Chemical Identity - The identity of the substance as it appears on the label. Section I. Manufacturer's Name and Contact Information: Manufacturer's name, address, telephone number and emergency telephone number. Date the MSDS was prepared and an optional signature of the preparer. Section II. Hazardous Ingredients/Identity Information - Lists the hazardous components by chemical identity and other common names. Includes OSHA PEL (Permissible Exposure Limit), ACGIH TLV (Threshold Level Value) and other recommended exposure limits. Percentage listings of the hazardous components is optional. Section III. Physical/Chemical Characteristics - Boiling point, vapor pressure, vapor density, specific gravity, melting point, evaporation rate, solubility in water, physical appearance, and odor. Section IV. Fire and Explosion Hazard Data - Flash point (and method used to determine it), flammability limits, extinguishing media, special firefighting procedures, unusual fire and explosion hazards. Section V. Reactivity Data - Stability, conditions to avoid, incompatibility (materials to avoid), hazardous decomposition or by products, hazardous polymerization (and conditions to avoid). VI. Health Hazard Data - Routes of entry (inhalation, skin, ingestion), health hazards (acute = immediate and chronic = build up over time), carcinogenicity (NTP, IARC monographs, OSHA regulated), signs and symptoms of exposure, medical conditions generally aggravated by exposure, emergency, and first aid procedures.VII. Precautions for Safe Handling and Use - Steps to be taken in case material is released or spilled, waste disposal method, precautions to be taken in handling or storage, and other precautions. VIII. Control Measures - Respiratory protection (specify type), ventilation (local, mechanical exhaust, special or other), protective gloves, eye protection, other protective clothing or equipment, work/hygienic practices. A competing format, the ANSI format is emerging as the standard format for MSDS. This format contains all of the information found on

Form 174, but includes additional information/categories and has a consistent organization.

Ozone (O_3): a gas similar to oxygen that is a criteria air pollutant and a major constituent of smog. *See also reactive organic compounds; volatile organic compounds.*

Oxidant Stipple: small brown or black interveinal necrotic lesions on the adaxial surface of leaf tissue that can be attributed to exposure to ozone.

Particle Sampler: an instrument to measure particulate matter in ambient air.

Particulate Matter: dust, soot, other tiny bits of solid materials that are released into and move around in the air. See also fine particle, PM_{10}.

Perceived Visual Air Quality (PVAQ): an index that relates directly to how human observers perceive changes in visual air quality.

Permissible Exposure Limit (PEL): A Permissible Exposure Limit (PEL) is the maximum amount or concentration of a chemical that a worker may be exposed to under OSHA regulations. PEL can be defined in two different ways as discussed in the OSHA regulation on air contaminants 1910.1000: Ceiling values at no time should this exposure limit be exceeded. *8-hour Time Weighted Averages (TWA)*: This is an average value of exposure over the course of an 8 hour work shift. TWA levels are usually lower than ceiling values. Thus, a worker may be exposed to a level higher than the TWA for part of the day (but still lower than the ceiling value) as long as he is exposed to levels below the TWA for the rest of the day. See 1910.1000 for the formulas used in the calculations. PELs are defined by OSHA in 3 Tables: Table Z-1 Limits for Air Contaminants, Table Z-2 Acceptable maximum peak above the acceptable ceiling level for an 8 hour shift, Table Z-3 Mineral dusts. In general, PELs refer to substances that may be inhaled, although some can be absorbed through the skin or eyes. When working with materials that have a PEL or TWA listed use proper precautions to minimize the generation of a vapor or dust in the first place. Always use appropriate personal protective equipment (PPE) such as gloves, dust masks, and respirators to limit your exposure to chemicals. Remember, exposure limits are not some magic threshold that define the border between safe and dangerous. A PEL that was acceptable in 1950 may be recognized as dangerously high today. Therefore, always do everything reasonable to limit the airborne release of chemicals or dusts in the first place. Chemical Sampling Information at OSHA lists the PELs and/or TWAs for many substances, health effects, and equipment/manufacturers that can monitor concentration for PEL/TWA compliance.

Phase Shift: a change in the periodicity of a waveform such as light.

Photometry: instrumental methods, including analytical methods, employing measurement of light intensity. See telephotometer.

Photon: a bundle of electromagnetic energy that exhibits bothe wave-like and particle-like characteristics.

Phytotoxic: poisonous to plants.

Picocurie (pCi): a unit for measuring radioactivity, often expressed as picocuries per liter (pCi/L) of air.

Plume Blight: visual impairment of air quality that manifests itself as a coherent plume.

PM_{10}: a criteria air pollutant that is particulate matter in ambient air exceeding 10 microns in diameter.

Point Source: a source of pollution that is well defined, such as the smokestack of a coal-fired power plant or smelter.

Poison: A poison is a substance that adversely affects one's health by causing injury, illness, or death. A gas poisonous by inhalation is defined by 49 CFR 173.115 as "material which is a gas at 20 °C (68 °F) or less and a pressure of 101.3 kPa (14.7 psi) (a material which has a boiling point of 20 °C (68 °F) or less at 101.3 kPa (14.7 psi)) and which: (1) Is known to be so toxic to humans as to pose a hazard to health during transportation, or (2) In the absence of adequate data on human toxicity, is presumed to be toxic to humans because when tested on laboratory animals it has an LC_{50} value of not more than 5000 ml/m^3 ... LC_{50} values for mixtures may be determined using the formula in Sec. 173.133(b)(1)(i) of this subpart." A poisonous substance (other than a gas) is defined by 49 CFR 173.132 as a material "which is known to be so toxic to humans as to afford a hazard to health during transportation, or which, in the absence of adequate data on human toxicity: Is presumed to be toxic to humans because it falls within any one of the following categories when tested on laboratory animals (whenever possible, animal test data that has been reported in the chemical literature should be used): *Oral Toxicity*: A liquid with an LD_{50} for acute oral toxicity of not more than 500 mg/kg or a solid with an LD_{50} for acute oral toxicity of not more than 200 mg/kg. *Dermal Toxicity*: A material with an LD_{50} for acute dermal toxicity of not more than 1000 mg/kg. *Inhalation Toxicity*: A dust or mist with an LC_{50} for acute toxicity on inhalation of not more than 10 mg/L; or a material with a saturated vapor concentration in air at 20 °C (68 °F) of more than one-fifth of the LC_{50} for acute toxicity on inhalation of vapors and with an LC_{50} for acute toxicity on inhalation of vapors of not more than 5000 ml/m^3 or is an irritating material, with properties similar to tear gas, which causes extreme irritation, especially in confined spaces." Treat poisonous materials with respect! Read the MSDS sheet to find out what ways a poison can kill you, is it by inhalation, ingestion, and/or skin contact? What precautions should you take with the material? What kinds of personal protective equipment are recommended?

Pollution Prevention: the use of materials, processes, or practices that reduces or eliminates the creation of pollutants or wastes at the source. It includes practices that reduce the use of hazardous materials, energy, water, or other resources and practices that protect natural resources through conservation or efficient use.

Pollution Prevention Assessments: Systematic, periodic internal reviews or specific processes and operations designed to identify and provide information about the production and reduction of toxic and hazardous materials and waste.

Pollution Prevention Assessment Team: a group assembled within a facility to conduct waste reduction assessments. They are selected on the basis of their expertise and knowledge of the process operations.

Pollution Prevention Champion: one or more people designated to facilitate the pollution prevention program by resolving conflicts.

Pollution Prevention Task Force: overall group responsible for instituting a pollution prevention program, for performing a preliminary assessment, and for guiding the program though the development stages.

Post-construction Monitoring: monitoring required as a permit condition that the permitting authority considers necessary to determine the effect emissions from a stationary source may have, or are having, on the air quality or on the AQRV's of an area. Such monitoring includes both "ambient" monitoring and "AQRV" monitoring and may involve short-term and long-term measurements made at locations representative of the greatest expected impacts.

Pressed Wood Products: A group of materials used in building and furniture construction that are made from wood veneers, particles, or fibers bonded together with an adhesive under heat and pressure.

Prevention of Significant Deterioration (PSD): a program established by the Clean Air Act that limits the amount of additional air pollution that is allowed in Class I and Class II areas.

PSD Increments: the maximum increase in ambient pollution concentrations allowed over baseline concentrations. See 40 CFR 51.166 (c) for increments for specific pollutants.

Precusor Emissions: emissions from point or regional sources that transform into pollutants with varied chemical properties.

Primary Standard: a pollution standard based on human health effects. Primary standards are set for criteria air pollutants. *See also secondary standard.*

RACT (Reasonably Available Control Technology): the lowest emissions limit that a particular source can meet by the application of control technology that is reasonably available considering technological and economic feasibility.

Radon (Rn) and Radon Decay Products: Radon is a radioactive gas formed in the decay of uranium. The radon decay products (also called radon daughters or progeny) can be breathed into the lung where they continue to release radiation as they further decay.

Rayleigh Scattering: the scattering of light by particles much smaller than the wavelength of the light, e.g., molecular scattering in the natural atmosphere.

RCRA: Resource Conservation and Recovery Act.

Reactive Organic Compounds: (in the context of photochemically produced air pollution) organic compounds that produce ozone in the presence of nitrogen oxides and sunlight. *See also Volatile Organic Compounds.*

Reconstructed Extinction: extinction estimate that results from summing up the product of the mass of each measured particle species and the appropriate absorption or extinction coefficient.

Recycling: using, reusing, or reclaiming materials/waste, including processes that regenerate a material or recover a usable product from it.

Recycling and Reuse Business Assistance Centers: located in state solid-waste or economic-development agencies, these centers provide recycling businesses with customized and targeted assistance.

Recycling Economic Development Advocates: individuals hired by state or tribal economic development offices to focus financial, marketing and permitting resources on creating recycling businesses.

Recycling Technical Assistance Partnership National Network: A national information-sharing resource designed to help businesses and manufacturers increase their use of recovered materials.

Red Line: the total pollutant loading (contributions from existing and proposed sources) at which there is a very high degree of certainty that at least one AQRV will be adversely affected.

Reformulated Gasoline: specially refined gasoline with low levels of smog-forming volatile organic compounds and low levels of hazardous air pollutants.

Refraction: the change of direction of a ray of light in passing obliquely from one medium into another in which the speed of propagation differs.

Regional Haze: a cloud of aerosols extending up to hundreds of miles across a region and promoting noticeably hazy conditions.

Regional Haze Visibility Impairment: any humanly perceptible change in visibility (light extinction, visual range, contrast, coloration) from that which would have existed under natural conditions, caused predominantly by a combination of many sources from, and occurring over, a wide geographic area.

Registry of Toxic Effects of Chemical Substances (RTECS): The Registry of Toxic Effects of Chemical Substances (RTECS) is a toxicology database of over 140,000 chemicals compiled, maintained, and updated by the U.S. National Institute of Occupational Safety and Health (NIOSH). Its goal is to include "all known toxic substances and the concentrations at which toxicity is known to occur." RTECS was mandated by the same act that created the U.S. Occupational Health and Safety Administration (OSHA). It was originally called the Toxic Substances List. RTECS data is obtained from the open scientific literature and maintained by NIOSH. Unlike many other government databases, RTECS is only available from vendors (if you dislike this, which you should, consult your congressional representatives). NIOSH has additional info and a vendor list if you would like access to the database. The price is roughly $300 U.S. for a one-year CD-ROM subscription and $250 for renewals. RTECS data can be used to help you construct an MSDS. Six types of toxicity data are included in the file: primary irritation, mutagenic effects, reproductive effects, tumorigenic effects, acute toxicity, and other multiple dose toxicity, including LD_{50} and LC_{50} values.

Reuse: the use of previously used material in similar or different processes.

R-MAP: Resource Management Assessment Program.

Relative Humidity: the ratio of the partial pressure of water to the saturation vapor pressure, also called saturation ratio; often expressed as a percentage.

Re-opener: a permit condition that requires the permitting authority, at a specified time after permit issuance, to review and revise, if necessary, the permit based on new information such as the findings from post-construction monitoring, updated emissions inventories, updated modeling, research, or information on air pollution effects to terrestrial, aquatic, and visibility resources.

SARA: Superfund Amendments and Reauthorization Act: The U.S. Superfund Amendments and Reauthorization Act, SARA is an amendment and reauthorization of CERCLA, the Comprehensive Environmental Response, Compensation & Liability Act (CERCLA) of 1980, better known as the SuperFund Act. Both CERCLA and SARA have the goals of identifying, remediating and preventing the release of hazardous substances to the environment. SARA not only extended the life of CERCLA, but made several important changes to provide new tools for enforcement, remedies, funding, and both state and individual input. SARA also resulted in a revision of the U.S. EPA's (Environmental Protection Agency) Hazard Ranking System to assess the degree of hazard to humans and the environment. The Emergency Planning and Community Right-To-Know Act (EPCRA), also known as the Community Right-To-Know Law, is also known as Title III of SARA. This provides specific plans for preparing for, preventing, and responding to the release of over 600 chemicals listed in the Toxics Release Inventory. Any release of one or more of the roughly 800 CERCLA or 360 EPCRA hazardous substances that equals or exceeds a reportable quantity (RQ) must be reported to the National Response Center (NRC). RQs are adjusted to one of five levels: 1, 10, 100, 1,000, or 5,000 pounds. EPA bases adjustments to the RQs on the intrinsic characteristics of each hazardous substance, such as the aquatic toxicity, acute and chronic toxicity, ignitability, reactivity, and potential carcinogenicity. An RQ value is established for each of these characteristics of a hazardous substance, with the most stringent RQ value (i.e., the lowest quantity) becoming the final RQ or reporting trigger for that hazardous substance.

Scattering: an interaction of light with an object (e.g., a fine particle) that causes the light to be redirected in its path.

Scattering Angle: the angle between the direction of propagation of the scattered and incident light (or transmitted light).

Scattering Coefficient: measure of the ability of particles to scatter light; measured in number proportional to the "amount" of light scattered per unit distance.

Scattering Cross Section: the amount of light scattered by a particle divided by its physical cross section.

Screening Level or Screening Level Value (SLV): the concentration or dose of air pollution below which estimated impacts from proposed new or modified sources are considered insignificant. The SLV is dependent on existing air quality and on the condition of the AQRV of concern.

Scrubbers: Scrubbers are described in Chapter 7. Separating solids or liquids from a gas is one use of scrubbers. However, separating a soluble gas from other gases is the application where scrubbers see the most action. Typically, a gas enters the bottom of a scrubber and moves upward while a liquid is sprayed from the top. The soluble gas is carried away by the liquid exiting out the bottom of the unit. The most common application is flue gas desulfurization using ammonia as the solvent or spray liquid. Pressure drops through scrubbers are usually low if they're sized properly, and scrubbers are generally about 50% efficient so multiple units are sometimes required or packing may be used to increase efficiency. The contaminated liquid exiting the scrubber represents it's own disposal problem. *See also semi-dry scrubbers.*

Secondary Aerosols: aerosol formed by the interaction of two or more gas molecules and/or primary aerosols.

Secondary Standard: an air pollution limit based on environmental effects, e.g. damage to property, plants, visibility, etc. Secondary standards are set for criteria air pollutants. *See also primary standard.*

Selective Catalytic Reduction (SCR): SCE is a process to reduce NO_x to nitrogen and water with ammonia in the presence of a catalyst between 540-840°F (282-449°C). Ammonia is usually injected at a 1:1 molar ratio with the NOx contaminants. Ammonia is used due to its tendency to react only with the contaminants and not with the oxygen in the gas stream. Ammonia is injected by means of compressed gas or steam carriers. Efficiencies near 90% have been reported with SCR. *See Exxon Thermal DeNO*$_x$.

Semidry Scrubbers: The advantage of semidry scrubbers is in that they remove contaminants by way of a solid waste that is easier to dispose of (less expensive). Initially, the scrubbing medium is wet (such as a lime or soda ash slurry). Then a spray dryer is used to atomize the slurry into the gas which evaporates the water in the droplets. As this takes place, the acid in the gas neutralizes the alkali material and forms a fine white solid. Most of the white solids are removed at the bottom of the scrubber while some are carried into the gas stream and have to be removed by a filter or electrostatic precipitator (discussed later). Although semidry systems cost 5-15% more than wet systems, when combined with a fabric filter, they can achieve 90-95% efficiencies. Dry scrubbers are sometimes used in a very similar fashion, but without the help of gas-liquid-solid mass transfer, these systems use much higher amounts of the solid alkali materials.

Sensitive Receptor: the aqrv, or part thereof, that is the most responsive to or the most easily affected by the type of air pollution in question. For example, at Great

Smoky Mountains National Park, spruce-fir forest is a sensitive receptor indicator.

Sensitive Receptor Indicator: a measurable physical, chemical, biological, or social (e.g., odor) characteristic of a sensitive receptor. For example, for the sensitive receptor, Crater Lake, water clarity is a sensitive receptor indicator.

Sensitizer: A sensitizer is defined by OSHA as "a chemical that causes a substantial proportion of exposed people or animals to develop an allergic reaction in normal tissue after repeated exposure to the chemical." The condition of being sensitized to a chemical is also called chemical hypersensitivity. Certain chemicals have no immediate health effect. But if you are exposed to them several times, they can make you allergic or sensitive to other chemicals. A classic example is formaldehyde (HCHO). Typical reactions to sensitizers can include skin disorders such as eczema. When working with sensitizers, always use proper protective equipment such as gloves, respirators, etc. Once you are sensitized to a particular chemical, even minute amounts will cause symptoms. Sensitization is usually a life-long effect.

Short-Term Exposure Limit (STEL): A Short-Term Exposure Limit (STEL) is defined by ACGIH as the concentration to which workers can be exposed continuously for a short period of time without suffering from irritation, chronic or irreversible tissue damage, narcosis of sufficient degree to increase the likelihood of accidental injury, impair self-rescue or materially reduce work efficiency. STELs are generally used only when toxic effects have been reported from high acute (short-term) exposures in either humans or animals. A STEL is not a separate independent exposure limit, but supplements time-weighted average limits where there are recognized acute effects from a substance whose toxic effects generally chronic (long-term) in nature. For example, one cannot be exposed to a STEL concentration if the TLV-TWA (time weighted average for an 8 hour shift; see Permissible Exposure Limit (PEL)) would be exceeded. Workers can be exposed to a maximum of four STEL periods per 8 hour shift, with at least 60 minutes between exposure periods. In general, PELs and TLV-STELs refer to substances that may be inhaled, although some can be absorbed through the skin or eyes (STELs will often have "-skin" after them, when skin exposure is possible). When working with materials that have listed exposure limits, use proper precautions to minimize the generation of a vapor or dust in the first place. Always use appropriate personal protective equipment (PPE) such as gloves, dust masks, and respirators to limit your exposure to chemicals. Remember, exposure limits are not some magic threshold that define the border between safe and dangerous. A PEL or STEL that was acceptable in 1950 may be recognized as dangerously high today. Therefore, always do everything reasonable to limit the airborne release of chemicals or dusts in the first place.

Sick Building Syndrome: Term that refers to a set of symptoms that affect some number of building occupants during the time they spend in the building and diminish or go away during periods when they leave the building. Cannot be traced to specific pollutants or sources within the building. (Contrast with "Building related illness").

Smog: a mixture of air pollutants, principally ground-level ozone, produced by chemical reactions involving smog-forming chemicals. *See also haze.*

Southern Oxidant Study (SOS): a study to assess the sources and transport of air pollutants contributing to ozone formation.

Source: any place or object from which air pollutants are released. Sources that are fixed in space are stationary sources; sources that move are mobile sources. *See also major source.*

Source Reduction: As defined in the Federal Pollution Prevention Act, source reduction is "any practice which 1) reduces the amount of any hazardous substance, pollutant or contaminant entering any waste stream or otherwise released into the environment (including fugitive emissions) prior to recycling, treatment, and disposal; and 2) reduces the hazards to public health and the environment associated with the release of such substances, pollutants, or contaminants. The term includes equipment or technology modifications, process or procedure modifications, reformulation or redesign of products, substitution of raw materials and improvements in housekeeping, maintenance, training or inventory control." Source reduction does not entail any form of waste management (e.g., recycling and treatment). The Act excludes from the definition of source reduction "any practice which alters the physical, chemical, or biological characteristics or volume of a hazardous substance, pollutant, or contaminant though a process or activity which itself is not integral to and necessary for the production of a product or the providing of a service."

Source Sampling: The act of making emissions measurements from stationary emission sources. The goal is to develop information or a data base on a concentration basis, such as parts per million (ppm) or micrograms (μg) per cubic meter, or to determine a mass emission rate such as pounds per hour or pounds per million British thermal units. Samples are drawn into a sample collector through a probe and nozzle arrangement, where the pollutant sample is gathered for later laboratory analysis and computation. A pumping device is used to extract the sample, and for flow control during metering, equipment is used to determine the quantity of sample obtained. Additional measurements of temperature, pressure, moisture content, velocity, etc., are made to ensure a representative sample.

Spectral: an adjective implying a separation of wavelengths of light or other waves into a spectrum or separated series of wavelengths.

State Implementation Plan (SIP): a collection of regulations used by the state to carry out its responsibilities under the Clean Air Act.

Stable Air Mass: an air mass which has little vertical mixing. *See temperature inversion.*

Stagnant: referring to meteorological conditions that are not conducive to atmospheric mixing.

Stagnation Periods: lengths of time during which little atmospheric mixing occurs over a geographical area, making the presence of layered hazes more likely. *See temperature inversion.*

Stationary Source: a fixed source of regulated air pollutants (e.g., industrial facility). *See also source; mobile sources.*

Sulfates: those aerosols that have origins in the gas-to-aerosol conversion of sulfur dioxide; of primary interest are sulfuric acid and ammonium sulfate. Sulfuric acid and ammonium sulfate are very hygroscopic so their contribution to visibility impairment is magnified in the presence of water vapor.

Sulfur Dioxide (SO_2): a gas (SO_2) consisting of one sulfur and two oxygen atoms. Of interest because sulfur dioxide converts to an aerosol.

SUM00: the sum of all hourly average concentrations above 0.00 ppb.

SUM60: the sum of all hourly average concentrations at or above 60 ppb.

Sun Angle: refers to the angle of the sun above the horizon of the earth.

Target Load: the acceptable concentration or dose of an air pollutant that provides a reasonable margin of safety below the critical load. The target load should be achievable under existing conditions.

Target Organ Effects: Target organ effects indicate which bodily organs are most likely to be affected by exposure to a substance. Some terms used when describing target organ effects are defined as follows:

Class and Definition	Signs/Symptoms	Examples
Hepatotoxins - produce hepatic (liver) damage	Jaundice, liver enlargement	Carbon tetrachloride, nitrosamines
Nephrotoxins- produce kidney damage	Edema, proteinuria	Halogenated hydrocarbons, uranium
Neurotoxins- produce their primary toxic effects on the nervous system	Narcosis, behavioral changes, decrease in motor functions	Mercury, carbon disulfide
Hematopoietic agents- act on the blood or hematopoietic system, decrease hemoglobin function, deprive the body tissues of oxygen	Cyanosis, loss of consciousness	Carbon monoxide, cyanides
Agents which damage the lung- these irritate or damage pulmonary (lung) tissue	Cough, tightness in chest, shortness of breath	Silica, asbestos
Reproductive toxins- affect the reproductive capabilities including chromosomal damage (mutations) and effects on fetuses (terato-genesis)	Birth defects, sterility	Lead, DBCP

Class and Definition	Signs/Symptoms	Examples
Cutaneous hazards- affect the dermal layer (skin) of the body	Defatting of the skin, rashes, irritation	Ketones, chlorinated compounds
Eye hazards- affect the eye or visual capacity	Conjunctivitis, corneal damage	Organic solvents, acids

When working with chemicals that have target organ effects it is critical to prevent exposure. This is especially true if you have a pre-existing condition, disease, or injury to that particular organ. Read the MSDS to find out the most effective personal protection equipment (PPE) for dealing with the chemical and be certain to minimize release of the chemical in the first place.

Telephotometer: an instrument that measures the brightness of a specific point in either the sky or vista.

Temperature Inversion: in meteorology, a departure from the normal decrease of temperature with increasing altitude such that the temperature is higher at a given height in the inversion layer than would be expected from the temperature below the layer. This warmer layer leads to increased stability and limited vertical mixing of air.

Teratogen: A teratogen is an agent that can cause malformations of an embryo or fetus. This can be a chemical substance, a virus or ionizing radiation. Pregnant women should avoid all contact with teratogens, particularly during the first three months of pregnancy, as this can result in damage to the developing child. For example, alcohol is a teratogen and drinking during pregnancy can lead to a child born with fetal alcohol syndrome. Many drugs can also have an adverse effect on developing fetuses, the most infamous example being thalidomide. Always minimize the use and release of teratogens (or believed teratogens) in the workplace. Women who are of child-bearing age should pay particular attention to teratogenic materials because they could be pregnant without knowing it and expose their fetus. Teratogens typically cause their most severe damage during the first three months of pregnancy when many pregnancies are not yet known. Many teratogens cause effects at very low exposure levels.

Total Suspended Particulates (TSP): total particulate matter in a sample of ambient air.

Toxic Air Pollutants: see hazardous air pollutants.

Toxics Release Inventory (TRI): The Toxics Release Inventory (TRI) contains information concerning waste management activities and the release of over 600 toxic chemicals by facilities that manufacture, process, or otherwise use such materials. Using this information, citizens, businesses, and governments can work together to protect the quality of their land, air, and water. Section 313 of the Emergency Planning and Community Right-To-Know Act (EPCRA) and section 6607 of the Pollution Prevention Act (PPA), mandate that a publicly accessible toxic chemical database be developed and maintained by the U.S. Environmental Protection Agency (EPA). The TRI database includes information on: What chemicals were released into the local environment during the preceding year; How much of each chemical went into the air, water, and land in a particular year; How much of the chemicals were transported away from the reporting facility for disposal, treatment, recycling, or energy recovery; How chemical wastes were treated at the reporting facility; The efficiency of waste treatment; Pollution prevention and chemical recycling activities. TRI applies to companies that utilize 25,000 pounds of the approximately 600 designated chemicals or 28 chemical categories specified in the regulations, or uses more than 10,000 pounds of any designated chemical or category. TRI information is not equivalent to an MSDS, but does provide useful information for people concerned about the presence (or potential presence) of chemicals in their community or environment.

Toxics Use Reduction: This term refers to the activities grouped under "source reduction" where the intent is to reduce, avoid, or eliminate the use of toxics in processes and/or products so as to reduce overall risks to the health of workers, consumers, and the environment without shifting risks between workers, consumers, or parts of the environment.

Toxic: Toxic is defined by OSHA 29 CFR 1910.1200 App A as a chemical which falls in any of these three categories: (1) A chemical that has a median lethal dose (LD_{50}) of more than 50 milligrams per kilogram, but not more than 500 milligrams per kilogram of body weight when administered orally to albino rats weighing between 200 and 300 grams each; (2) A chemical that has a median lethal dose (LD_{50}) of more than 200 milligrams per kilogram, but not more than 1,000 milligrams per kilogram of body weight, when administered by continuous contact for 24 hours (or less, if death occurs within 24 hours) with the bare skin of albino rabbits weighing between two and three kilograms each; (3) A chemical that has a median lethal concentration (LC_{50}) in air of more than 200 parts per million, but not more than 2,000 parts per million by volume of gas or vapor, or more than two milligrams per liter, but not more than 20 milligrams per liter of mist, fume, or dust, when administered by continuous inhalation for one hour (or less, if death occurs within one hour) to albino rats weighing between 200 and 300 grams each. Highly toxic is defined by OSHA as: (1) A chemical that has a median lethal dose (LD_{50}) of 50 milligrams or less per kilogram of body weight, when administered orally to albino rats, weighing between 200 and 300 grams each; (2) A chemical that has a median lethal dose (LD_{50}) of 200 milligrams or less per kilogram of body weight, when administered by continuous contact for 24 hours (or less, if death occurs within 24 hours) with the bare skin of albino rabbits, weighing between two and three kilograms each; (3) A chemical that has a median lethal concentration (LC_{50}) in air of 200 parts per million by volume or less of gas or vapor, or 2 milligrams per liter or less of mist, fume, or dust, when administered by continuous inhalation for one hour (or less, if death occurs within one hour) to albino rats, weighing between 200 and 300 grams each. Toxicology is the study of the nature, effects, detection, and mitigation of poisons and the treatment or prevention of poisoning. Treat all toxic materials with great respect. Avoid their use whenever possible, but, if you do you use them, take responsible measures to limit their use and minimize hazards. Always wear appropriate personal protective equipment (PPE), such as gloves, fume hoods, respirators, etc.

Transmissometer: an instrument that measures the amount of light extinction over a fixed, specified path length.

Unstable Air Mass: an air mass that is vertically well mixed. See also stable air mass, temperature inversion.

UV Radiation: Ultraviolet Radiation emitted from the sun, which can affect health and ecosystems at elevated levels.

Ventilation Rate: The rate at which indoor air enters and leaves a building. Expressed in one of two ways: the number of changes of outdoor air per unit of time (air changes per hour, or "ACH") or the rate at which a volume of outdoor air enters per unit of time (cubic feet per minute, or "cfm").

Visibility Impairment: any humanly perceptible change in visibility (visual range, contrast, coloration) from that which would have existed under natural conditions. [40CFR 51.301(x)]

Visual Air Quality: air quality evaluated in terms of pollutant particles and gases that affect how well one can see through the atmosphere.

Visual Range: the distance at which a large black object would just disappear from view.

Volatile Organic Compounds (VOC): organic compounds that vaporize readily and contribute to the development of ozone. Many VOCs are also hazardous air pollutants. *See also reactive organic compounds.*

Waste Management: handling, treatment, storage and disposal of waste products.

Waste Exchange: a central office in which generators who want to recycle valuable components of their waste can register the waste for off-site transfer to others.

Waste Minimization: source reduction, certain types of recycling and reclamation. Waste minimization does not include recycling activities whose uses constitute disposal and burning for energy recovery.

Waste Reduction: The term has been used by the Congressional Office of Technology Assessment and INFORM to mean source reduction. On the other hand, many different groups have used the term to refer to waste minimization. Therefore, care must be employed in determining which of these different concepts is implied when the term "waste reduction" is encountered.

INDEX

Environmental Engineering

Handbook of Air Pollution Prevention and Control

Nicholas P. Cheremisinoff, Ph.D, N&P Limited

Handbook of Air Pollution Prevention and Control provides a concise overview of the latest technologies for managing industrial air pollution problems in the petrochemical, oil and gas, and allied industries. This volume uniquely combines prevention and control concepts, while providing comprehensive discussions and information on energy-efficient technologies and approaches to implementing environmental cost accounting measures. Included in the text is detailed material on equipment selection, sizing, and troubleshooting operations along with practical design methodology, as well as the practices and technologies that are applied to the prevention of air pollution and to the cleaning and control of industrial air emissions.

More than 500 pages packed with information, ideas, and solutions to today's industrial air pollution problems, this book provides a bridge for today's environmental manager by focusing on an integrated approach to managing air pollution problems within industrial operations.

- Contains tried and tested methods of successful air pollution prevention practices in the chemicals manufacturing industry, the oil and gas industry, the iron and steel industry, the pharmaceutical industry, and others.
- Contains detailed regulatory information and descriptions of air pollution control equipment and hardware.
- Contains numerous up-to-date references, including many websites where you can access databases on chemical properties and fate and transport information.
- Shows you where and how you can download free air pollution software to tackle air dispersion problems, plus numerous examples to walk you through the use of these tools.
- Shows you how to calculate financial returns from pollution prevention projects using lifecycle costing tools, and is linked to a free, downloadable EPA air dispersion model that can be used to predict and assist in evaluating the impact of pollutants on the environment and populated areas.
- Contains a glossary with hundreds of pollution prevention and control terms.

Nicholas P. Cheremisinoff, Ph.D. (Ch.E.) is an internationally recognized consulting engineer who has conducted hundreds of pollution prevention audits and demonstrations, training programs on modern process design practices and plant safety, environmental management and product quality programs, and site assessments and remediation plans for both public and private sector clients throughout the world. He frequently serves as expert witness on personal injury and third-party property damage litigations arising from environmental catastrophes. Dr. Cheremisinoff has contributed extensively to the literature of environmental and chemical engineering as author, co-author, or editor of 150 technical reference books, including Butterworth-Heinemann's *Handbook of Chemical Processing Equipment*, and *Green Profits*. He holds advanced degrees in chemical engineering from Clarkson College of Technology.

ISBN: 0-7506-7499-7
90000
9 780750 674997

BUTTERWORTH
HEINEMANN

An imprint of Elsevier Science
www.bh.com