AIR POLLUTION TRAINING INSTITUTE

COURSE 415: CONTROL OF GASEOUS EMISSIONS

STUDENT MANUAL

EPA

EPA

ACKNOWLEDGEMENTS

NOTICE

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LIST OF ACRONYMS

ACRONYM	DEFINITION
ACFM	Actual cubic square feet per minute
BACT	Best available control technology
CAAA	Clean Air Act Amendments
CEM	Continuous emission monitors
CFC	Chlorofluorocarbon
Cgs	Centimeter gram second
DAS	Data acquisition
DP	Differential pressure
FGD	Flue gas desulfurization
FGR	Flue gas recirculation
FID	Flame ionization detector
FRP	Fiberglass reinforced plastic
GFC	Gas filter correlation
HAP	Hazardous air pollutants
HFL	Hydrofluoric fluoride
HTU	Height of transfer unit
LEL	Lower explosive level
L/G	Liquid-to-gas
MACT	Maximum achievable control technology
MSDS	Material data safety sheets
MTZ	Mass transfer zone
MW	Molecular weight
NAAQS	National Ambient Air Quality Standards
NDIR	Nondispensive infrared
NDUV	Nondispersive ultraviolet
NESHAP	National Emission Standards for Hazardous Air Pollutants
NSPS	New Source Performance Standards
NTU	Number of transfer units
OFA	Overfire air parts
ORD	Office of Research and Development
P&I	Piping and instrumentation
PID	Photoionization detector
Psi	Pounds per square inch
SCFM	Standard cubic feet per minute
SCR	Selective catalytic reduction
SIP	State implementation plan
SLA	Solvent laden air
SNCR	Selective noncalytic reduction system
TRS	Total reduced sulfur
UEL	Lower explosive limit
VOC	Volatile organic compound
W.C	Water column

COURSE INTRODUCTION

WELCOME

Welcome to Environmental Protection Agency Training Course 415: Control of Gaseous Emissions.

Purpose

The purpose of this course is to provide general instruction about the control of gaseous emissions, as outlined by the Environmental Protection Agency (EPA).

Course Topics Covered

This course includes ten chapters which cover the following topics:

- Introduction to Control of Gaseous Emissions
- Control Techniques for Gaseous Pollutants
- Air Pollution Control Systems
- Adsorption
- Absorption
- Oxidation
- Condensation
- Control Techniques for Nitrogen Oxides
- Control Techniques for Sulfur Oxides
- Control of Greenhouse Gas Emissions

COURSE COMPLETION REQUIREMENTS

Upon conclusion of this each chapter, participants will complete a two-part assessment that includes several review questions.

1.0 INTRODUCTION TO GASEOUS EMISSIONS

1.1 INTRODUCTION

To comply with environmental laws, you must first understand why the laws exist and what they are to accomplish. This lesson introduces primary and secondary gaseous pollutants, and prepares you to recognize the sources of gaseous pollutants, as well as the regulations that pertain to them.

LEARNING OBJECTIVES

At the conclusion of this training students will be able to:

- Differentiate between primary and secondary gaseous pollutants.
- Identify the sources of gaseous pollutants.
- Recognize the regulations that pertain to gaseous pollutants.

1.2 INTRODUCTION TO GASEOUS POLLUTANTS

A BRIEF HISTORY

The control of gaseous pollutants from industrial sources in the United States began with efforts to recover useful raw materials and products entrained in gas streams. Some of the high-efficiency pollutant control techniques in use today had their origins in the 1940s and 1950s as low-to-moderate efficiency collectors used strictly for process purposes. Starting in the 1950s and 1960s, control equipment for gaseous pollutants was used primarily for environmental purposes. The environmental control programs were stimulated by concerns about (1) possible health effects, (2) apparent crop and vegetation damage, and (3) the impact on buildings and other structures.

PRIMARY AND SECONDARY GASEOUS POLLUTANTS

Primary pollutants and secondary pollutants comprise the two main category divisions of gaseous pollutants. Primary pollutants are compounds that are emitted by the source directly from the stack and/or process equipment. Examples of primary pollutants include sulfur dioxide (SO_2) emissions from combustion sources and organic compound emissions from surface coating facilities. Secondary pollutants are gaseous and vapor phase compounds that form due to reactions between primary pollutants in the atmosphere or between a primary

pollutant and naturally occurring compounds in the atmosphere. Important categories of secondary pollutants include ozone (O_3) and other photochemical oxidants formed through sunlight-initiated reactions of nitrogen oxides (NO_x), organic compounds, and carbon monoxide (CO). A summary of the main categories of gaseous pollutants follows.

Examples of Primary Gaseous Pollutants

- Sulfur dioxide (SO_2) and sulfuric acid vapor (H_2SO_4)
- Nitrogen oxide (NO) and nitrogen dioxide (NO_2)
- Carbon monoxide (CO) and partially oxidized organic compounds
- Volatile organic compounds (VOCs) and other organic compounds
- Hydrogen chloride (HCl) and hydrogen fluoride (HF)
- Hydrogen sulfide (H_2S) and other reduced sulfur compounds
- Ammonia (NH_3)

Examples of Secondary Gaseous Pollutants

- Nitrogen dioxide (NO_2)
- Ozone (O_3) and other photochemical oxidants
- Sulfuric acid (H_2SO_4)

Nitrogen oxide (NO_2) and sulfuric acid (H_2SO_4) can either be emitted directly from a stack (primary pollutants), or be formed in the atmosphere from reactions of primary pollutants (secondary pollutants).

SULFUR DIOXIDE

Sulfur dioxide (SO_2) is a colorless gas formed primarily during the combustion of a sulfur-containing fuel, such as coal, No. 6 oil, or sulfur-containing industrial waste gases. Once released into the atmosphere, SO_2 reacts slowly because of photochemically initiated reactions and reactions with cloud and fog droplets. The rates range between approximately 0.1% and 3% per hour. These atmospheric reactions yield sulfuric acid (H_2SO_4), inorganic sulfate compounds, and organic sulfate compounds. A major fraction of SO_2 is ultimately captured on vegetation and soil surfaces because of adsorption and absorption. These processes are collectively termed *deposition*. Rates of deposition are not accurately quantified and vary both regionally and seasonally. SO_2 is moderately soluble in water and is a strong irritant, due in part to its solubility and tendency to form sulfurous acid (H_2SO_3) following absorption in water. SO_2 is one of the seven criteria pollutants subject to National Ambient Air Quality Standards (NAAQS).

SULFURIC ACID VAPOR

During the combustion of sulfur-containing fuels, approximately 95% of the sulfur is converted to SO_2, while 0.5% to 2% of the fuel's sulfur is converted to sulfur trioxide (SO_3). Sulfur trioxide (SO_3) remains in the vapor state until temperatures decrease below approximately 600 °F (315 °C), this is referred to as the sulfuric acid dew point. At or below this temperature, sulfur trioxide (SO_3) reacts with water to form sulfuric acid (H_2SO_4) as indicated in Reaction 1-1.

Reaction 1-1 $SO_3 + H_2O \rightarrow H_2SO_4$

Because of the corrosiveness of sulfuric acid, it is important to keep gas streams at temperatures above the sulfuric acid dew point. Damage to air pollution control equipment, ductwork, and fans can occur if the gas temperature falls below the sulfuric acid dew point in localized areas.

NITRIC OXIDE AND NITROGEN DIOXIDE

These two compounds, collectively referred to as NO_x, are formed during the combustion of all fuels. They are also released from nitric acid plants and other industrial processes involving the generation and/or use of nitric acid (HNO_3). The term "NO_x" does not include nitrous oxide (N_2O), which is emitted in small quantities from some processes.

Three complex chemical mechanisms are responsible for NO_x formation: (1) thermal fixation of atmospheric nitrogen (N_2), (2) oxidation of organic nitrogen compounds in the fuel, and (3) reaction with partially oxidized compounds within the flame. These mechanisms are referred to as thermal, fuel, and prompt NO_x, respectively.

Nitric oxide (NO) is an odorless gas that is insoluble in water. Nitrogen dioxide (NO_2) is moderately soluble in water and has a distinct reddish-brown color. This compound contributes to the brown haze that is often associated with photochemical smog conditions in urban areas. At low temperatures, such as those often present in ambient air, nitrogen dioxide can form a dimer compound (N_2O_4). Both compounds, but particularly NO_2, are associated with adverse effects on the respiratory tract. NO_2 has been regulated since 1971 as one of the seven criteria pollutants subject to National Ambient Air Quality Standards (NAAQS).

The ambient concentrations of NO and NO_2 are usually well below the NO_2 NAAQS. This is due to the rapid photochemically initiated reactions and liquid phase reactions (clouds and fog droplets) that result in the conversion of NO_x in the atmosphere to secondary reaction products. In fact, NO_2 is the main chemical compound responsible for the absorption of the ultraviolet light that drives photochemical reactions. Until the January 2010 revisions to the NO_2 NAAQS standard, all regions of the country were compliant with the standard.

CARBON MONOXIDE AND OTHER PARTIALLY OXIDIZED ORGANIC COMPOUNDS

Carbon monoxide (CO) is a partially oxidized compound that results from incomplete combustion of fuel and other organic compounds. It forms when either the gas temperature is too low to, or the oxygen concentration is insufficient to allow complete oxidation to carbon dioxide (CO_2).

Carbon monoxide is colorless, odorless, and only very slightly soluble in water. It is a chemical asphyxiant with significant adverse health effects at high concentrations. Carbon monoxide readily participates in photochemically initiated reactions that result in smog formation. It is emitted from automobiles, trucks, boilers, and industrial furnaces; generally due to incomplete combustion as a result of insufficient oxygen (O_2).

Partially oxidized organic compounds (POCs) refer to a broad range of species formed during the combustion process, including polyaromatic compounds, unsaturated hydrocarbon

compounds, aldehydes, and organic acids. Some POCs readily condense on the surface of particulate matter (PM) while others remain in the gas phase. Combustion conditions used to minimize the formation of NO_x, such as reducing the excess O_2 concentration, actually promote the formation of CO and POCs.

VOLATILE ORGANIC COMPOUNDS OR OTHER ORGANIC COMPOUNDS

Volatile organic compounds (VOCs) are organic compounds that can volatilize and participate in photochemical reactions once released to the ambient air. Almost all of the several thousand organic compounds used as solvents and as chemical feedstock in industrial processes are classified as VOCs. The few organic compounds that are *not* considered VOCs because of their lack of photochemical reactivity are listed in Table 1-1.

Table 1-1. Organic compounds NOT classified as VOCs.

- Methane;
- Ethane;
- Methylene chloride (dichloromethane);
- 1,1,1-trichloroethane (methyl chloroform);
- 1,1,2-trichloro-1,2,2-trifluoroethane (CFC–113);
- Trichlorofluoromethane (CFC–11);
- Dichlorodifluoromethane (CFC–12);
- Chlorodifluoromethane (HCFC–22);
- Trifluoromethane (HFC–23);
- 1,2-dichloro 1,1,2,2-tetrafluoroethane (CFC–114);
- Chloropentafluoroethane (CFC–115);
- 1,1,1-trifluoro 2,2-dichloroethane (HCFC–123);
- 1,1,1,2-tetrafluoroethane (HFC–134a);
- 1,1-dichloro 1-fluoroethane (HCFC–141b);
- 1-chloro 1,1-difluoroethane (HCFC–142b);
- 2-chloro-1,1,1,2-tetrafluoroethane (HCFC–124);
- Pentafluoroethane (HFC–125);
- 1,1,2,2-tetrafluoroethane (HFC–134);
- 1,1,1-trifluoroethane (HFC–143a);
- 1,1-difluoroethane (HFC–152a);
- Parachlorobenzotrifluoride (PCBTF);
- cyclic, branched, or linear completely methylated siloxanes;
- Acetone;
- Perchloroethylene (tetrachloroethylene);
- 3,3-dichloro-1,1,1,2,2-pentafluoropropane (HCFC–225ca);
- 1,3-dichloro-1,1,2,2,3-pentafluoropropane (HCFC–225cb);
- 1,1,1,2,3,4,4,5,5,5-decafluoropentane (HFC 43–10mee);
- Difluoromethane (HFC–32);
- Ethylfluoride (HFC–161);
- 1,1,1,3,3,3-hexafluoropropane (HFC–236fa);
- 1,1,2,2,3-pentafluoropropane (HFC–245ca);

- 1,1,2,3,3-pentafluoropropane (HFC–245ea);
- 1,1,1,2,3-pentafluoropropane (HFC–245eb);
- 1,1,1,3,3-pentafluoropropane (HFC–245fa);
- 1,1,1,2,3,3-hexafluoropropane (HFC–236ea);
- 1,1,1,3,3-pentafluorobutane (HFC–365mfc);
- Chlorofluoromethane (HCFC–31);
- 1 chloro-1-fluoroethane (HCFC–151a);
- 1,2-dichloro-1,1,2-trifluoroethane (HCFC–123a);
- 1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxy-butane ($C_4F_9OCH_3$ or HFE–7100);
- 2-(difluoromethoxymethyl)-1,1,1,2,3,3,3-heptafluoropropane ((CF_3)2CFCF_2OCH_3);
- 1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane ($C_4F_9OC_2H_5$or HFE–7200);
- 2-(ethoxydifluoromethyl)-1,1,1,2,3,3,3-heptafluoropropane ((CF_3)2CFCF_2OC_2H_5);
- 1,1,1,2,2,3,3-heptafluoro-3-methoxypropane (n-C_3F7OCH_3, HFE–7000);
- 3-ethoxy-1,1,1,2,3,4,4,5,5,6,6,6-dodecafluoro-2-(trifluoromethyl) hexane (HFE–7500);
  1,1,1,2,3,3,3-heptafluoropropane (HFC 227ea);
- Methyl formate (HCOOCH3);
- 1,1,1,2,2,3,4,5,5,5-decafluoro-3-methoxy-4-trifluoromethyl-pentane (HFE–7300);
- Propylene carbonate;
- Dimethyl carbonate;
- Methyl acetate and perfluorocarbon compounds which fall into these classes:
  - (i) Cyclic, branched, or linear completely fluorinated alkanes
  - (ii) Cyclic, branched, or linear completely fluorinated ethers with no unsaturations
  - (iii) Cyclic, branched, or linear completely fluorinated tertiary amines with no unsaturations
  - (iv) Sulfur containing perfluorocarbons with no unsaturations and with sulfur bonds only to carbon and fluorine

Refer to 40 CFR 51.100(s) for future listings.

The dominant source of VOC emissions is the vaporization of organic compounds used as solvents in industrial processes; however, VOCs are also released during surface coating operations, painting, gasoline distribution, and synthetic organic chemical manufacturing. VOC emissions may be categorized as either contained or fugitive. Contained VOC emissions are those that are captured in hoods, penetrate through the air pollution control equipment, and are released from the stack. Fugitive emissions consist of those that escape from process hoods as well the numerous small leaks from pumps, valves, pipe joints or connectors and other process equipment, especially in the pressurized components of a process.

Hazardous Air Pollutants (HAPs)

Approximately 200 specific organic compounds and classes of compounds that have known adverse health effects are regulated and classified as hazardous air pollutants (HAP list, Section 112(b) of the Clean Air Act). These compounds are subject to Maximum Achievable Control Technology (MACT) standards promulgated by EPA. A partial list of the more common hazardous air pollutants is presented in Table 1-2.

Table 1-2. Organic HAP compounds.			
Compound	**CAS Number**	**Compound**	**CAS Number**
Acetaldehyde	75070	Methylene chloride	75092
Acetonitrile	75058	Methyl isocyanate	624839
Acrolein	107028	Naphthalene	91203
Acrylonitrile	107131	Nitrobenzene	98953
Aniline	62533	Phenol	108952
Benzene	71432	Phosgene	75445
13, Butadiene	106990	Phthalic anhydride	85449
Carbon disulfide	75150	Styrene	100425
Chlorobenzene	108907	Tetrachloroethylene	127184
Chloroform	67663	Toluene	108883
Ethyl benzene	100414	2,4 Toluene diisocyanate	584849
Ethylene oxide	75218	1,2,4 Trichlorobenzene	120821
Compound	**CAS Number**	**Compound**	**CAS Number**
Ethylene glycol	107211	Trichloroethylene	79016
Formaldehyde	50000	Xylenes	95476
Hexane	110543		
Methanol	67561		

HYDROGEN CHLORIDE AND HYDROGEN FLUORIDE

Hydrogen chloride (HCl) and hydrogen fluoride (HF) (known as hydrochloric acid and hydrofluoric acid), are inorganic acid gases that may be released from processes such as waste incinerators, fossil fuel-fired boilers, chemical reactors, or ore-roasting operations. They are also generated and released from air pollution control systems in which chlorine- or fluorine-containing organic compounds are oxidized. They are gases at the normal stack concentrations; however, at high concentrations, HCl can nucleate to form submicrometer acid mist particles.

Both HCl and HF are extremely soluble in water and are strong irritants. Both compounds can cause adverse health effects. HCl and HF are regulated as hazardous air pollutants.

The quantities of HCl and HF formed during waste incineration and fossil fuel combustion are directly related to the concentrations of chlorine and fluorine in the waste or fuel being fired. Essentially all of the chlorine and fluorine atoms are converted to HCl or HF as long as sufficient hydrogen is present from hydrocarbons or water vapor in the gas stream. Very few of the chlorine or fluorine atoms remain in the ash of combustion processes.

Chlorine-, fluorine-, bromine-, or other halogen-containing organic compounds are part of the larger group of "halogenated hydrocarbons," some of which can contribute to the degradation of stratospheric ozone and, in the opinion of many experts, to global warming/climate change. This includes hydrochlorocarbons (HCCs), hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs), chlorofluorocarbons (CFCs), perfluorocarbons (PFCs), etc.

HYDROGEN SULFIDE AND OTHER TOTAL REDUCED SULFUR COMPOUNDS

Hydrogen sulfide (H_2S) is emitted from a number of metallurgical, petroleum, and petrochemical processes. Fugitive emissions of H_2S occur from sour natural gas wells and certain petrochemical processes. H_2S is a highly toxic chemical asphyxiant. Despite its strong rotten-egg odor, it is often difficult to detect at high concentrations due to rapid olfactory fatigue. H_2S is highly soluble in water and can be easily oxidized to form sulfur dioxide. Total reduced sulfur compounds (TRSs) are emitted primarily from kraft pulp mills and consist primarily of the following four chemicals.

- Hydrogen sulfide, H_2S
- Methyl mercaptan, CH_3SH
- Dimethyl sulfide, $(CH_3)_2S$
- Dimethyl disulfide, $(CH_3)_2S_2$

All have extremely strong and unpleasant odors. Facilities generating TRS compounds have been subject to source-specific control regulations since the early 1970s due to the associated odor problems. All of these compounds are water-soluble. They all participate readily in atmospheric reactions that eventually yield sulfur dioxide as the main reaction product. TRS compounds are usually controlled by oxidation.

AMMONIA

Ammonia (NH_3) is a common chemical used in a large number of synthetic organic chemical manufacturing processes. Emissions of ammonia from such sources are usually quite small and are well below the natural emissions from microbial activity. Ammonia is not considered to be toxic at the levels generated by anthropogenic or natural emissions and is not regulated as a hazardous air pollutant.

Ammonia is of interest in Course 415 primarily because it is a reactant in two main types of NO_x control systems. A small fraction of the ammonia fed to these NO_x control systems can be emitted to the atmosphere, and these emissions are regulated in some states.

OZONE AND OTHER PHOTOCHEMICAL OXIDANTS

Ozone (O_3) is an oxidant that forms in the troposphere (at ground level) as a result of evolving photochemically initiated reactions between nitrogen oxides, volatile organic compounds, and carbon monoxide. Course 415 does not explicitly cover the control of ozone because it is a secondary pollutant. Control of ozone is achieved by the control of precursor compounds such as NO_x, VOCs, and CO.

The general cycle of pollutant concentrations associated with photochemical reactions is

illustrated in Figure 1-1. The reactions typically begin quickly in the mid-to-late morning following the increase in concentrations of NO_x, organic compounds, and CO from motor vehicles and other sources. Photochemically initiated reactions rapidly convert NO to NO_2. The formation of NO_2 further stimulates the photochemical smog-forming reactions because nitrogen dioxide is very efficient in absorbing ultraviolet light.
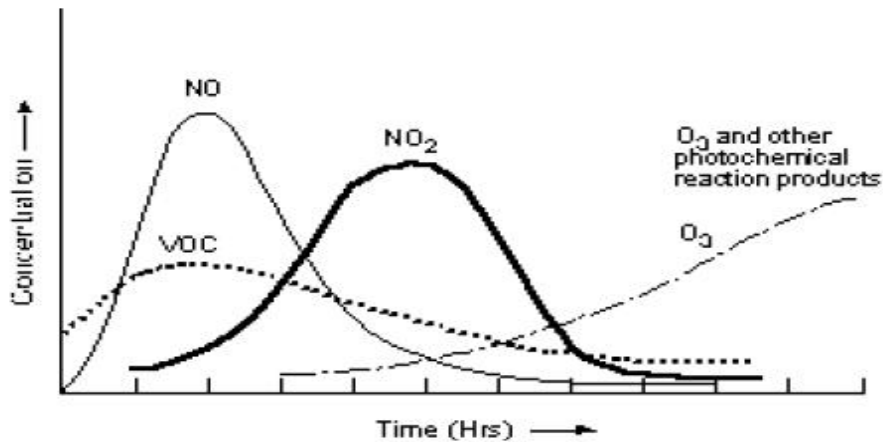
Figure 1-1. Pollutant concentration profiles due to photochemical reactions.

Explanation of Figure 1-1

As the NO_2 concentration peaks and then decreases as it is consumed to form particulate matter (PM) and vapor phase nitrates. As the NO_2 concentration drops, the levels of ozone rise rapidly. Along with the increase in ozone, the levels of various partial oxidation products also increase. Some of the photochemical reaction products are in the form of particulate matter (PM) that scatters light.

The formation of ozone is greatest during the "ozone season," usually defined as May through September. The intensity of sunlight for the photochemically initiated reactions is highest during this time period, and the high temperatures promote thermal reactions associated with the photochemical reactions.

Ozone can also form, to a limited extent, in clean rural environments. The "pollutants" involved in these reactions are low levels of organic compounds emitted from vegetation and low levels of NO_x emitted from natural biological activity. While the photochemical reactions are similar to those found in polluted urban areas, the concentrations of rural ozone are limited by the low concentrations of NO_x usually present.

In the stratosphere, ozone forms naturally from the irradiation of molecular oxygen by sunlight. The presence of ozone in the stratosphere is beneficial because it absorbs ultraviolet radiation from the sun. The stratospheric ozone concentrations are decreasing over North America because of the presence of ozone-depleting chlorinated and fluorinated organic compounds and nitrous oxide (N_2O) compounds that are not especially reactive near the Earth's surface. Once these compounds are transferred convectively to the stratosphere, they can initiate free radical chain reactions that reduce the equilibrium concentrations of ozone. The depletion of ozone in the stratosphere is not within the scope of this course.

The control of precursor gases, such as NO_x, to minimize ground level (or tropospheric) ozone concentrations, will not have an adverse effect on the beneficial ozone levels in the stratosphere. The formation mechanisms for ozone in the stratosphere are different from those in the troposphere.

LEAD

Lead is a metal found naturally in the environment as well as in manufactured products. It occurs both in its elemental form, Pb, as well as in compounds. Airborne lead compounds are designated as HAPs and may cause a range of health effects, from behavioral problems and learning disabilities, to seizures and death. Lead is persistent in the environment and accumulates in soils and sediments through deposition from air sources, direct discharge of waste streams to water bodies, mining, and erosion. Depending on the level of exposure, lead can adversely affect the nervous system, kidney function, immune system, reproductive and developmental systems and the cardiovascular system.

The major anthropogenic sources of lead emissions have historically been motor vehicles (such as cars and trucks) and industrial sources. As a result of the EPA's regulatory efforts to reduce lead in gasoline, air emissions of lead from the transportation sector, and particularly the automotive sector, have greatly declined over the past three decades. Today industrial processes, primarily metals processing, are the major source of lead emissions to the air. The highest air concentrations of lead are usually found near lead smelters. Other stationary sources are waste incinerators, utilities, and lead-acid battery manufacturers.

MERCURY

Mercury enters the environment as a result of both natural and human activities. While elemental mercury (Hg) is toxic to humans, the methylmercury ion (CH_3Hg^+) is the compound of most concern. Methylmercury is formed from other forms of mercury by microbial action in sediments and soils, and is taken up by aquatic organisms and bioaccumulates in the aquatic food chain.

Other Sources of Mercury Emissions

Anthropogenic mercury enters the atmosphere primarily due to the combustion of coal and other fossil fuels that contain trace quantities of mercury. Other significant sources of mercury emissions include certain chlor-alkali chlorine manufacturing processes, mining operations, metal refining, and products that contain elemental mercury, such as batteries, lamps, and thermometers.

Mercury Reduction Efforts

The EPA has focused most of its mercury reduction efforts on large point source emissions from chlor-alkali facilities and combustion sources ranging from power plants and industrial boilers to hazardous waste and medical incinerators. Significant reductions in mercury emissions have already been made, and total air emissions in 1999 were estimated to be only about one-half of the 1990 emissions. The greatest emission reductions during that period occurred from municipal waste and medical waste incinerators. In 2010, the EPA proposed regulations to control mercury emissions from industrial boilers. These regulations were finalized in January 2011. These regulations will reduce mercury emissions from these sources by approximately 7 tons per year. In March 2011, the EPA also proposed regulations to significantly limit air toxics emissions from

coal- and oil-fired power plants.

GREENHOUSE GASES AND EMISSION SOURCES

Greenhouse gases trap heat in the atmosphere. In the absence of greenhouse gases, the earth would be too cold to sustain human life. However, in the opinion of many experts, the increasing concentrations of greenhouse gases (principally CO_2) since the beginning of the industrial revolution have led to global warming. The most important greenhouse gases that enter the atmosphere as a result of human activity are carbon dioxide, methane, nitrous oxide, and fluorinated gases. Information about each of these greenhouse gases follow.

Carbon Dioxide

Carbon Dioxide (CO_2) is a primary product from the combustion of fossil fuels (coal, oil, and natural gas), solid waste, and trees and other wood products. Significant amounts are also liberated during the manufacture of cement and other products. CO_2 is removed from the atmosphere by plants as part of the natural biological carbon cycle and by dissolution into the oceans. In the opinion of many experts, in recent times, the rate of emissions is exceeding the rate of removal, and the average CO_2 concentration has been increasing at a rate of one to three ppm/yr.

Methane

Methane (CH_4) discharges to the atmosphere during the production and transportation of coal, oil, and natural gas. CH_4 emissions also result from livestock and other agricultural activities and from the decay of organic waste.

Nitrous Oxide

Nitrous Oxide (N_2O) is emitted from the combustion of fossil fuels. Quantities are much smaller than the emissions of NO and NO_2. Historically, the majority of N_2O emissions are a result of agricultural activities.

Fluorinated Gases

Fluorinated Gases such as hydrofluorocarbons, perfluorocarbons, and sulfur hexafluoride are greenhouse gases that are emitted from various industrial processes. A large fraction of the fluorinated gases were introduced as substitutes for stratospheric ozone-depleting chlorinated gases (CFCs and HCFCs). The absolute quantities are small, although their greenhouse warming potential is high.

GLOBAL WARMING POTENTIAL

Different greenhouse gases have widely different potential impacts, which are measured by the Global Warming Potential (GWP). Among other factors, the GWP depends on the average atmospheric lifetime of individual greenhouse gases. CO_2 was chosen as the reference point and assigned a GWP of 1.0. Estimated atmospheric lifetimes and GWPs of the major greenhouse gases are summarized in Table 1-3.

Table 1-3. Global warming potentials (GWP) and atmospheric lifetimes (years).		
Gas	**Atmospheric Lifetime**	**100-Year GWP**
Carbon dioxide, CO_2	50-200	1
Methane, CH_4	12±3	25
Nitrous oxide, N_2O	120	298
Fluorinated gases as a group	1.5–209	124–22,800

1.3 EMISSION RATES AND SOURCES OF GASEOUS POLLUTANTS

ANNUAL EMISSION RATES

The gaseous pollutants emphasized in this course include sulfur dioxide, nitrogen oxides, and organic compounds (including VOCs). Emissions data from the EPA emissions inventory for SO_2, NO_x, and VOC, for the period 1970–2008, are shown in Figure 1-2. Significant emissions reductions in each pollutant have been achieved. On a percentage basis, the reductions range from 63% for SO_2 to 54% for VOC to 40% for NO_x. These reductions were achieved in spite of population increases and economic growth during the time period.

SO_2 emission reductions have been reasonably steady throughout the period. NO_x emissions were relatively constant from 1970 to 1995, while reductions have accelerated since that time. VOC emissions decreased steadily from 1970 to 2000, but there was a significant increase between 2000 and 2005. However, the increase was reversed between 2005 and 2008.

Controls on the release of mercury to the atmosphere are just now being implemented and emissions data are relatively scarce. EPA estimates that the annual emission rate of 220 short tons per year in 1990 was reduced to 115 short tons per year by 1999.
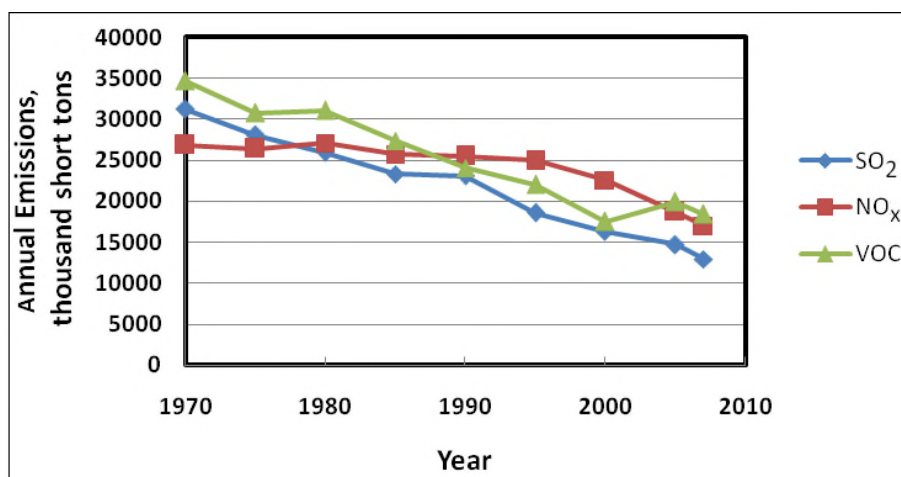
Figure 1-2. SO_2, NO_x, and VOC emissions history.

Greenhouse Emissions by Gas

Estimated annual emissions of greenhouse gases between 1990 and 2006 are shown in Figure 1-3. The units on the ordinate are teragrams of CO_2 equivalent (1 teragram = 10^{12} g). That is, emissions of CH_4 and other greenhouse gases are multiplied by their global warming potential so that the total emissions are on a CO_2-equivalent basis. We see that CO_2, with the smallest GWP of one, is easily the most significant greenhouse gas, followed by CH_4, N_2O, and the fluorinated compounds. To put the numbers into somewhat better perspective, the 1990 emissions rate of 6.14 Tg is the equivalent of 6.14 x 10^6 short tons. The overall data show an approximate 15% increase in GHG emissions during the 1990–2006 period.
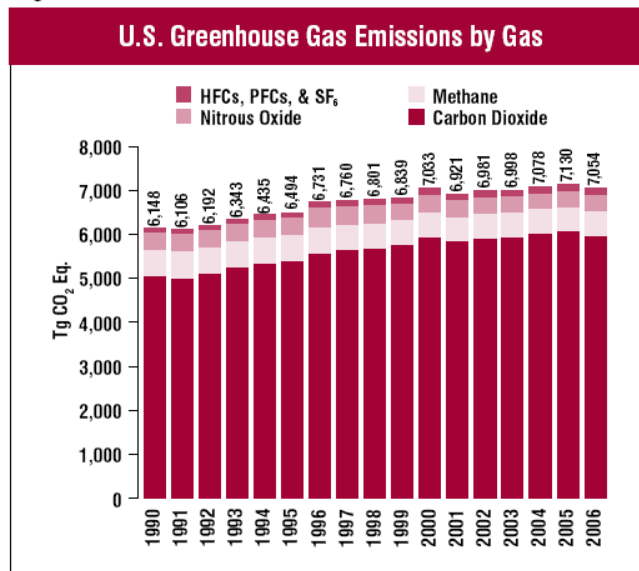
Figure 1-3. Estimated greenhouse gas emissions in terms of CO_2- equivalent.

EMISSION SOURCE CATEGORIES

The total emissions described in the previous section are subdivided into source categories, and 2008 results compared to the 1970 values for SO_2 (Table 1-4), NO_x (Table 1-5), and VOCs (Table 1-6). Table 1-4 shows that 1970 SO_2 emissions were dominated by fuel combustion in electric utilities, followed by metal processing and fuel combustion in industrial boilers.

The three fuel combustion categories – electric utilities, industrial, and other – accounted for about 75% of the total. Highway and off-highway vehicles, in contrast, accounted for only about 2% of the total. All source categories (except "other") experienced large decreases between 1970 and 2008, with the largest percentage decrease (95%) associated with metals processing. Electric utility emissions decreased by 57% during that time, but remained the largest source category. The reductions were accomplished by installing flue gas desulfurization processes and by switching to lower sulfur content fuels. Reductions occurred in spite of a large increase in demand for electricity during that time period.

Table 1-4. SO$_2$ emissions by source category, 1970 and 2008.				
Source Category	1970		2008	
	Thousands of Short Tons	Percent of Total	Thousands of Short Tons	Percent of Total
Fuel combustion, electric utilities	17,398	56	7552	66
Fuel combustion, industrial	4568	15	1670	14
Fuel combustion, other	1490	5	578	5
Chemical and allied products	591	2	255	2
Metals processing	4775	15	203	2
Petroleum and related industries	881	3	206	2
Other industrial processes	846	3	329	3
Highway vehicles	273	1	64	1
Off-highway vehicles	278	1	456	4
Other	118	0	116	1
Total	31,218	101	11,429	100

The reduction in NO$_x$ emissions shown in Figure 1-2, while significant, are less significant than the 63% reductions achieved for SO$_2$. Most of the overall reduction occurred after 1995. These trends reflect the significance of vehicle emissions to NO$_x$ levels, and the relative difficulty of controlling NO$_x$ emissions from electric utility plants as compared to SO$_2$ emissions. Table 1-5 compares NO$_x$ emissions from 1970 and 2008 by source category. Highway vehicles were the largest source of NO$_x$ in both 1970 and 2008, but off-highway vehicles supplanted electric utilities as the second most significant source in 2008. Overall, the combined combustion operations from stationary and mobile sources accounted for over 90% of the total NO$_x$ emissions in 2008. The largest percentage decrease between 1970 and 2008 came in the category of highway vehicles. Off-highway vehicles were the only category showing an absolute increase between 1970 and 2008.

Table 1-5. NOₓ emissions by source category, 1970 and 2008.				
Source Category	1970		2008	
	Thousands of Short Tons	Percent of Total	Thousands of Short Tons	Percent of Total
Fuel combustion, electric utilities	4900	18	3006	18
Fuel combustion, industrial	4325	16	1838	11
Fuel combustion, other	836	3	727	4
Highway vehicles	12,624	47	5206	32
Off-highway vehicles	2652	10	4255	26
Other	1545	6	1307	8
Total	26,882	100	16,339	99

VOC emissions, shown in Figure 1-2, decreased significantly from 1970 to 2000, but then increased by about 5% between 2000 and 2005 before dropping off again between 2005 and 2008. Overall, between 1970 and 2008, the VOC emissions decreased by 54%. Table 1-6 compares VOC emissions during 1970 and 2008 by source category. Highway vehicles, followed by solvent utilization were the largest emitting source categories in 1970. Emissions from highway vehicles were due primarily to evaporative emissions from gasoline tanks. By 2008, however, reductions in vehicle evaporative losses had decreased to the point that solvent utilization had become the largest source, and highway vehicle losses being second place. Unlike SO_2 and NO_x emissions, combustion processes contribute only a small amount of the VOC emissions.

Table 1-6. VOC emissions by source category, 1970 and 2008.				
Source Category	1970		2008	
	Thousands of Short Tons	Percent of Total	Thousands of Short Tons	Percent of Total
Fuel combustion, electric utilities	30	0	50	0
Fuel combustion, industrial	150	0	130	1
Fuel combustion, other	541	2	1269	8
Chemicals manufacture	1341	4	228	1
Petroleum industry	1194	3	561	4
Solvent utilization	7174	21	4226	27
Storage and transport	1954	6	1303	8
Waste disposal & recycling	1984	6	374	2
Highway vehicles	16,910	47	3418	21
Off-highway vehicles	1616	5	2586	16
Other	1765	5	1782	11
Total	34,659	99	15,927	99

MERCURY EMISSIONS

According to available data, the most significant sources of mercury emissions in 1990 were municipal solid waste incinerators, coal-fired electric utility boilers, and medical waste incinerators. Each of these categories contributed about 25% of the total. Relatively small additional mercury emissions were contributed by institutional boilers, chlorine production, hazardous waste incineration, gold mining, and "other." According to the data, by 1999, mercury had been largely eliminated from municipal waste and medical waste incinerators, and coal-fired utility boilers contributed about 40% of the total estimated emissions of 115 short tons. CO_2, the dominant greenhouse gas, was associated almost entirely with fuel combustion, both in stationary and mobile sources. CH_4 is emitted during the production and transport of coal, oil, and natural gas, by livestock and other agricultural practices, and by the decay of organic materials in municipal solid waste landfills. Nitrous oxide (N_2O) is emitted from agricultural and industrial activities, and small amounts are emitted during combustion of fossil fuels. The fluorinated gases, many of which were introduced as substitutes for ozone-depleting chlorinated compounds, are emitted in small quantities from a number of industrial sources.

1.4 POLLUTION CONTROL

GASEOUS POLLUTION CONTROL REGULATIONS

Pollution Control

From 1950 through 1970, gaseous pollutant control regulations were enacted by state and local agencies for pollutants such as SO_2, VOCs, and HF. These regulations were aimed at alleviating localized health and welfare effects relating to these emissions.

The Clean Air Act

Public environmental awareness that began to increase during the 1950s and 1960s culminated in the enactment of the Clean Air Act of 1970 (CAA). This act strengthened the federal program and was associated with the formation of the U.S. EPA from a variety of agencies sharing environmental responsibility before this time. The CAA substantially increased the pace of gaseous pollutant control. Since 1970, a myriad of new regulations have been established, many of these apply, in one way or another, to gaseous emissions. The following paragraphs provide only a brief overview of the most important laws and regulations that have been developed.

National Ambient Air Quality Standards

In 1971, the EPA circulated primary and secondary National Ambient Air Quality Standards (NAAQS) for sulfur dioxide, nitrogen oxides, photochemical oxidants, and carbon monoxide. These standards were based on available ambient air monitoring and health/welfare effects research data. The country was divided into a number of Air Quality Control Regions, each of which was intended to reflect common air pollution problems. Areas whose measured ambient concentrations exceeded the NAAQS levels were labeled as nonattainment areas for the specific gaseous pollutant. Nonattainment areas were required to devise a set of emission regulations and other procedures that would reduce the particular pollutant concentration in the ambient air to

levels below the NAAQS specified limit. Both primary and secondary standards have been specified for certain compounds. Primary standards are more restrictive and are designed to protect human health. Secondary standards are intended to reduce adverse material effects, such as crop damage and building soiling.

New Source Performance Standards (NSPS)

Individual states are responsible for developing control strategies for the achievement of the NAAQS as part of the State Implementation Plan (SIP) required by the Clean Air Act. Emission regulations were adopted by many state and local agencies to ensure that the NAAQS would be met.

These emission regulations take different forms in different areas. For example, in some areas, regulations limit SO_2 emissions by specifying a maximum sulfur content (e.g., ≤ 1% sulfur by weight) on the fuel being burned. In other instances, emission limitations for SO_2 and NO_x are based on an allowable mass per unit of heat input (e.g., 0.1 lb NO_x /MM Btu) or strictly on a concentration basis (e.g., 500 ppm). Likewise, emissions of VOCs are restricted based on the allowable mass per unit time (e.g., pounds per hour) or a VOC content per unit of coating.

Regulations were adopted to control process-related fugitive emissions. Because of the diversity of these sources and the difficulty of measuring these emissions, these regulations have taken many forms, including (1) required work practices, (2) leak detection and repair programs, and (3) hood capture efficiency requirements.

Regulations adopted under SIPs apply to existing sources within the state. There are substantial differences in the stringency of the regulations from state to state, depending on the pollutant control strategy believed necessary and advantageous to achieve the NAAQS.

The CAA also stipulated that New Source Performance Standards (NSPS) were to be developed on a nationwide basis to apply to all new (and substantially modified) sources. The purpose of the NSPS was to ensure continued improvements in air quality as new sources replaced existing sources. The EPA adopted these NSPSs on a source category-specific basis. Sources subject to these regulations are required to install air pollution control systems that represent the "best demonstrated technology" for that particular source category. The first set of NSPS standards (often termed Group I) included emission limitations for SO_2 and NO_x from large combustion sources. The EPA has included continuous monitoring requirements in many of the new and revised NSPS standards applicable to SO_2 and NO_x emissions.

National Emission Standards for Hazardous Air Pollutants (NEHAPs)

The CAA also authorized the promulgation of especially stringent regulations for pollutants considered to be highly toxic or hazardous. EPA was charged with identifying these pollutants and developing appropriate regulations to protect human health. The set of regulations that apply to toxic or hazardous chemicals is titled the National Emission Standards for Hazardous Air Pollutants (NESHAPs). Because of regulatory complexities occurring from 1971 to 1990, only a few of these were promulgated, and none of these involved gaseous pollutants.

Clean Air Act Amendments Expansion of NESHAPs

The Clean Air Act Amendments of 1990 required a major revision and expansion of NESHAPs. Regulations have been developed for 187 specific compounds and classes of compounds, including many that are normally in gaseous form. Sources subject to NESHAPs are required to limit emissions to levels consistent with Maximum Achievable Control Technology (MACT). The MACT requirements are based on technology currently used by the best performing sources within that category.

NEW SOURCE REVIEW

Before construction begins, new sources (or major modifications to existing sources) are required to undergo a New Source Review (NSR) and receive a pre-construction permit. In areas where NAAQS are currently satisfied, the permit is based on Prevention of Significant Deterioration (PSD) requirements. PSD requires the use of Best Available Control Technology (BACT). BACT is determined on a case-by-case evaluation that considers energy, environmental, and economic impact. In areas where the NAAQS are not satisfied, the NSR permit requires that new emissions must be offset with emission reductions from other sources and to install Lowest Achievable Emissions Rate (LAER) technology. Under LAER the applicant must achieve (1) the most stringent emission limitation in the SIP for a similar source or (2) the most stringent emission achieved in practice.

In 1997, EPA added a new NAAQS applicable to particulate matter (PM) having a diameter equal to or less than 2.5 μm (termed $PM_2.5$). EPA concluded that the $PM_{2.5}$ NAAQS were needed because health effects research indicated that particulate matter in this size category is most closely associated with adverse health effects. Control of $PM_{2.5}$ is directly relevant to APTI 413, Control of Particulate Emissions, but it is also important to gaseous emission control because atmospheric chemistry research indicates that the atmospheric reactions of SO_2, NO_x, VOCs and CO have a significant role in the formation of $PM_{2.5}$ particles. The $PM_{2.5}$ regulations will continue to drive gaseous pollutant control in the future.

Mercury is one of the 187 compounds defined as a hazardous or toxic material and is, therefore, subject to NESHAP regulations. In addition, there are mercury-specific laws and regulations. For example, the Mercury Containing and Rechargeable Battery Management Act of 1996 required phasing out the use of mercury in batteries. The Resource Conservation and Recovery Act (RCRA) set emission limits for the incineration of mercury-containing hazardous waste.

The Clean Air Mercury Rule (CAMR), issued in 2005, and subsequently overturned by federal court action in 2008, was meant to establish the first-ever limitations on mercury emissions from coal-fired power plants. The EPA proposed air toxics standards for coal- and oil-fired electric generating units in 2011, but these are not yet final. No specific limitations on mercury from coal-fired power plants currently exist as a result of the court action.

Currently, there are no U.S. limitations on greenhouse gas emissions. However, the anticipation of future regulations has spurred research in the use of non-carbon energy sources and in the capture and sequestration of carbon from fossil fuels. In October of 2009 the EPA released the Mandatory GHG Emission Reporting Rule requiring large sources and suppliers to report their GHG emissions. This information will be used by the EPA to inform future GHG rulemaking decisions. In addition, in May of 2010 the EPA released the GHG Tailoring Rule, which sets

GHG emissions thresholds to define when permits under the NSR, PSD, and Title V Operating Permit programs are required for new and existing industrial facilities. Future regulations of GHG under the CAA are anticipated to be promulgated and phased-in over the coming years.

NEW SOURCE PERFORMANCE STANDARDS (NSPS)

New source performance standards have been promulgated for about 70 industrial categories. Because of their legal standing, the standards are quite complex and require a lawyer for full interpretation. An abbreviated and simplified version of the NSPS for fossil fuel–fired electric power generation facilities is presented in Table 1-7. This is meant only to provide a rough guide for this course and should not be used in actual work. Complete New Source Performance Standards may be found in the Code of Federal Regulations, 40 CFR Part 60, Subpart Da.

The performance standard for SO_2 from any fuel type is 1.2 $lb_m/10^6$ Btu heat input, along with 90% reduction from the amount that would be emitted in the absence of controls. If, however, the emission rate is less than 0.6 $lb_m/10^6$ Btu heat input, only 70% reduction from the uncontrolled rate is required. Separate NO_x emission standards and reduction requirements have been promulgated for different fuel types. The different emission standards generally reflect differences in the nitrogen content of the fuel.

Table 1-7. New source performance standards for fossil fuel-fired electric power generating facilities.			
Category	**Fuel Type**	**Emission Limit**	**Reduction Requirement**
Particulate Matter	Solid	0.015 $lb_m/10^6$ Btu[A]	99.9%
SO_2	Liquid	1.4 lb_m/MWh	95%
SO_2	Coal Refuse	1.4 lb_m/MWh	94%
		<0.6 $lb_m/10^6$ Btu	70%
NOx	Solid	0.5 $lb_m/10^6$ Btu	65%
NOx	Liquid	0.3 $lb_m/10^6$ Btu	30%
NOx	Gas	0.2 $lb_m/10^6$ Btu	20%
NOx		1.0 lb_m/MWh	
NOx	Liquid Backup Fuel[B]	1.5 lb_m/MWh	
A: The owner/operator of a facility with a PM Continuous Emission Monitoring System (CEMS) may elect to comply with an alternate 0.14 lb_m/MWh standard. B: For the owner/operator of an IGCC facility			

NATIONAL AMBIENT AIR QUALITY STANDARDS

National Ambient Air Quality Standards (NAAQS), shown in Table 1-8, have been circulated for seven criteria pollutants. Separate standards exist for particulate matter depending on particle size. PM2.5 refers to particles with diameters less than 2.5 microns (μm), while PM10 refers to particles with diameters less than 10 microns (μm). SO_2 has its own primary and secondary standards, while the primary and secondary standards for the other pollutants are the same. Primary standards are designed to protect public health, including the health of sensitive

populations such as asthmatics, children, and the elderly. Secondary standards are designed to protect public welfare, including protection against decreased visibility and damage to animals, crops, vegetation, and buildings. These standards also have legal meaning, and their interpretation can be quite complex as indicated by the extensive list of explanatory material below the table. Notice that some of the standards have changed with time as continued research expands the knowledge base concerning the pollutant effects.

Table 1-8. National ambient air quality standards.

	Primary Standards		Secondary Standards	
Pollutant	**Level**	**Averaging Time**	**Level**	**Averaging Time**
Carbon Monoxide	9 ppm (10 mg/m^3)	8-hour [1]	None	
	35 ppm (40 mg/m^3)	1-hour [1]		
Lead	0.15 µg/m^3 [2]	Rolling 3-Month Average	Same as Primary	
	1.5 µg/m^3	Quarterly Average	Same as Primary	
Nitrogen Dioxide	53 ppb [3]	Annual (Arithmetic Average)	Same as Primary	
	100 ppb	1-hour [4]	None	
Particulate Matter (PM$_{10}$)	150 µg/m^3	24-hour [5]	Same as Primary	
Particulate Matter (PM$_{2.5}$)	15.0 µg/m^3	Annual [6] (Arithmetic Average)	Same as Primary	
	35 µg/m^3	24-hour [7]	Same as Primary	
Ozone	0.075 ppm (2008 std)	8-hour [8]	Same as Primary	
	0.08 ppm (1997 std)	8-hour [9]	Same as Primary	
	0.12 ppm	1-hour [10]	Same as Primary	
Sulfur Dioxide	0.03 ppm	Annual (Arithmetic Average)	0.5 ppm	3-hour [1]
	0.14 ppm	24-hour [1]		
	75 ppb [11]	1-hour	None	

[1] Not to be exceeded more than once per year.
[2] Final rule signed October 15, 2008.
[3] The official level of the annual NO$_2$ standard is 0.053 ppm, equal to 53 ppb, which is shown here for the purpose of clearer comparison to the 1-hour standard
[4] To attain this standard, the 3-year average of the 98th percentile of the daily maximum 1-hour average at each monitor within an area must not exceed 100 ppb (effective January 22, 2010).
[5] Not to be exceeded more than once per year on average over 3 years.
[6] To attain this standard, the 3-year average of the weighted annual mean PM2.5 concentrations from single or multiple community-oriented monitors must not exceed 15.0 µg/m3.
[7] To attain this standard, the 3-year average of the 98th percentile of 24-hour concentrations at each population-oriented monitor within an area must not exceed 35 µg/m3 (effective December 17, 2006).
[8] To attain this standard, the 3-year average of the fourth-highest daily maximum 8-hour average ozone concentrations measured at each monitor within an area over each year must not exceed 0.075 ppm. (effective May 27, 2008)
[9] (a) To attain this standard, the 3-year average of the fourth-highest daily maximum 8-hour average ozone concentrations measured at each monitor within an area over each year must not exceed 0.08 ppm.
(b) The 1997 standard—and the implementation rules for that standard—will remain in place for implementation purposes as EPA undertakes rulemaking to address the transition from the 1997 ozone standard to the 2008 ozone standard.
(c) EPA is in the process of reconsidering these standards (set in March 2008).

(10)   (a) EPA revoked the 1-hour ozone standard in all areas, although some areas have continuing obligations under that standard ("anti-backsliding").
(b) The standard is attained when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 ppm is ≤ 1.

(11)   (a) Final rule signed June 2, 2010. To attain this standard, the 3-year average of the 99th percentile of the daily maximum 1-hour average at each monitor within an area must not exceed 75 ppb.

Explanation of Figure 1-4

EPA data showing the number of people living in counties with pollutant concentrations above NAAQS levels during 2007 are shown in Figure 1-4. All counties were in compliance with the NAAQS for CO, NO_x, and SO_2. Significant fractions of the population were exposed to ozone (O_3) and $PM_{2.5}$ concentrations that exceeded the standard, while smaller numbers were exposed to Lead (Pb) and PM_{10} concentrations in excess of their respective standards. Much of the difficulty in reaching the ozone standard stems from the fact that ozone is a secondary pollutant. Direct emissions of ozone are negligible and control strategies must address ozone precursors, many of which are naturally occurring.
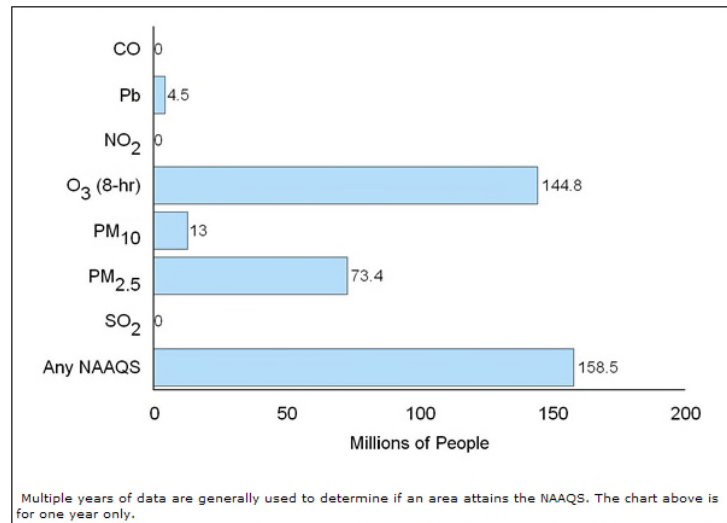
Figure 1-4. Number of people living in counties with air quality concentrations above the level of the NAAQS in 2007.

1.5 SUMMARY

CONTROL OF GASEOUS EMISSIONS

This lesson provided an overview of the following:

- Differences between primary and secondary gaseous pollutants.
- Emission rates and sources of gaseous pollutants.
- Air quality regulations pertaining to gaseous emissions.

1.6 REVIEW EXERCISES

INSTRUCTIONS

Select the best response(s) for each of the following multiple-choice questions.

MULTIPLE CHOICE QUESTIONS

1. What fraction of the sulfur present in a fossil fuel (i.e., coal, oil) is converted to sulfur dioxide in a utility or industrial boiler?

   a. 25% to 30%
   b. 50% to 75%
   c. 75% to 90%
   d. 94% to 95%

2. What factors influence the formation of NO_x in a boiler?

   a. Temperature
   b. Oxygen concentration
   c. Fuel nitrogen content
   d. All of the above

3. Which categories of air pollutants are responsible for the formation of photochemical smog? Select all that apply.

   a. Volatile organic compounds (VOC)
   b. Nitrogen oxides (NO_x)
   c. Sulfur dioxide (SO_2)
   d. Carbon monoxide (CO)

4. Ozone is a _____ air pollutant.

   a. primary
   b. secondary

5. Which category of sources is most responsible for VOC emissions?

   a. Transportation (automobiles, trucks, aircraft)
   b. Fuel handling and distribution
   c. Solvent utilization
   d. Fuel combustion

6. Which category of sources is most likely to be responsible for sulfur dioxide emissions?

   a. Utility and industrial boilers

b. Industrial processes
c. Transportation
d. None of the above

7. Which category of sources has the highest NO_x emissions?

a. Transportation (automobiles, trucks, aircraft)
b. Fuel handling and distribution
c. Solvent utilization
d. Fuel combustion (electric utilities)

8. When were National Ambient Air Quality Standards (NAQS) initiated for sulfur dioxide?

a. 1961
b. 1970
c. 1977
d. 1990

9. What type of regulation limits the emission of toxic pollutants?

a. New Source Performance Standards (NSPS)
b. National Ambient Air Quality Standards (NAAQS)
c. Maximum Achievable Control Technology Standards (MACTs)
d. Best Available Control Technology (BACT)

10. Why are VOC emissions controlled?

a. To achieve the ozone NAAQS
b. To achieve the hydrocarbon NAAQS
c. To achieve the NO_x NAAQS
d. To achieve the MACTs

1.7 REVIEW EXERCISES: SOLUTIONS

This Student Guide includes separate exercises and solutions, which allow students to check their work.

MULTIPLE CHOICE ANSWERS

1. What fraction of the sulfur present in a fossil fuel (i.e., coal, oil) is converted to sulfur dioxide in a utility or industrial boiler?

   a. 25% to 30%
   b. 50% to 75%
   c. 75% to 90%
   d. 94% to 95%

2. What factors influence the formation of NO_x in a boiler?

   a. Temperature
   b. Oxygen concentration
   c. Fuel nitrogen content
   d. All of the above

3. Which categories of air pollutants are responsible for the formation of photochemical smog? Select all that apply.

   a. Volatile organic compounds (VOC)
   b. Nitrogen oxides (NO_x)
   c. Sulfur dioxide (SO_2)
   d. Carbon monoxide (CO)

4. Ozone is a _____ air pollutant.

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   b. secondary

5. Which category of sources is most responsible for VOC emissions?

   a. Transportation (automobiles, trucks, aircraft)
   b. Fuel handling and distribution
   c. Solvent utilization
   d. Fuel combustion

6. Which category of sources is most likely to be responsible for sulfur dioxide emissions?

   a. **Utility and industrial boilers**
   b. Industrial processes
   c. Transportation
   d. None of the above

7. Which category of sources has the highest NO_x emissions?

   a. **Transportation (automobiles, trucks, aircraft)**
   b. Fuel handling and distribution
   c. Solvent utilization
   d. Fuel combustion (electric utilities)

8. When were National Ambient Air Quality Standards (NAQS) initiated for sulfur dioxide?

   a. 1961
   b. **1970**
   c. 1977
   d. 1990

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   c. **Maximum Achievable Control Technology Standards (MACTs)**
   d. Best Available Control Technology (BACT)

10. Why are VOC emissions controlled?

    a. **To achieve the ozone NAAQS**
    b. To achieve the hydrocarbon NAAQS
    c. To achieve the NO_x NAAQS
    d. To achieve the MACTs

1.8 REFERENCES

1.   National Air Quality and Emissions Trend Report, 1997; EPA 454/R-98-016; U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards: Research Triangle Park, NC, 1998.

2.0 CONTROL TECHNIQUES FOR GASEOUS CONTAMINANTS

2.1 OVERVIEW

PURPOSE

This chapter introduces the various control technologies used to remove gaseous contaminants from industrial gas streams. Determining which technology to use depends, in part, on the chemical and physical characteristics of the specific gas or vapor phase compounds present in the gas stream. This chapter summarizes data concerning the chemical compounds.

There are several gas stream characteristics to consider when selecting or designing a gaseous control system. This chapter includes a brief introduction of these characteristics, and more detail is included in subsequent chapters pertaining to each major control technique.

LEARNING OBJECTIVES

At the conclusion of this training, students will be able to:

- Identify potentially explosive gases and vapors that are collected in contaminant control systems.
- Recognize the explosive range of gases.
- Identify the six major techniques for controlling gaseous contaminants.

2.2 GAS STREAM CHARACTERISTICS

IMPORTANT GAS STREAM PROPERTIES

Before selecting a design for a gaseous contaminant control system, it is important to consider specific information about the gas stream, including its physical properties. The following is a partial list of the gas stream parameters that are often useful in this determination:

- Flow rate
- Temperature
- Pressure
- Contaminant concentration
- Contaminant ignition characteristics
- Oxygen concentration

Information concerning the gas flow rate, temperature, and pressure are needed to determine the physical size of the collector for the expected process operating conditions. Many gaseous contaminant control systems have a relatively narrow range of operating conditions. In situations where these parameters vary with time, it is important to know, whenever available, the minimum, average, and maximum parameter values. In situations where the gas stream also contains particulate matter, it is important to know the concentration, particle size distribution, and composition of the particulate.

Particulate matter (PM) entrained in the gas stream with the gaseous contaminants can have a severe impact on the efficiency and reliability of the collector. Certain types of gaseous contaminant control systems use beds of collecting media (e.g., fixed adsorption beds and catalyst beds) or pre-collector heat exchangers. PM can accumulate in these systems and disrupt proper gas flow and collection efficiency. The impact of particulate matter is especially severe if it is relatively large (>3 micrometers, μm) or sticky. If the gaseous contaminant control system is vulnerable to particulate matter–related problems, a pre-collector might be needed to remove the PM prior to this system.

EXPLOSION LIMITS

Information concerning the oxygen concentration and ignitability of the gases and vapors is needed to determine the allowable contaminant concentrations. A number of potentially explosive gases and vapors are collected in gaseous contaminant control systems, including:

- Organic compounds
- Carbon monoxide (CO)
- Ammonia (NH_3)
- Hydrogen gas (H_2, sometimes present with organic compounds)
- Hydrogen sulfide (H_2S)

One of the main factors to consider in designing a gaseous contaminant control system is the concentration range at which one or more of the contaminants can be ignited. It is important to anticipate potentially explosive conditions and conscientiously avoid them in the design of the control system.

Explosive Limit Concentrations

The explosive range is bound by two limits: the lower explosive limit (LEL) and the upper explosive limit (UEL). At contaminant concentrations below the LEL, there is insufficient contaminant (fuel) for an explosion and the mixture is described as too "lean" for combustion (ignition). At contaminant concentrations above the UEL, there is insufficient oxygen for the oxidation of the compounds present and the mixture is described as too "rich" for combustion (ignition). Theoretically, a gaseous control system could be designed for any contaminant concentrations below the LEL or above the UEL. However, almost all systems (with the exception of flares) are designed for concentrations below the LEL. Because of the uncertainties in the LEL values and the monitors used for real-time measurement, gaseous contaminant systems are usually designed for concentrations less than 25% of the LEL, providing some margin of protection from fires and explosions in the control system.

Example data concerning the LELs and UELs for specific contaminants are provided in Table 2-

1. These data are usually expressed in terms of volume percent.

For example, the LEL for benzene (C_6H_6) is 1.2% by volume, which is equivalent to 12,000 ppm. If the gas stream concentration cannot exceed 25% of the LEL, the maximum benzene concentration should be 25% of 12,000 ppm, or 3000 ppm (0.3% by volume).

When using the 25% LEL safety limit, it usually restricts the maximum contaminant concentration in the gas stream to be treated to less than 10,000 ppm (1% by volume).

Table 2-1. LEL and UEL at room temperature and ambient oxygen concentration.		
Compound	Lower Explosive Limit, Percent by Volume*	Upper Explosive Limit, Percent by Volume*
Acetone	2.5	12.8
Acrylonitrile	3.0	17.0
Ammonia	15.0	28.0
Benzene	1.2	7.8
Carbon Disulfide	1.3	50.0
Ethyl Alcohol	3.3	19.0
Formaldehyde	7.0	73.0
Gasoline	1.4	7.6
Hydrogen	4.0	80.0
Methylene Chloride	13.0	23.0
Octane	1.0	6.5
Propane	2.1	9.5
Styrene	0.9	6.8
Toluene	1.1	7.1
Xylenes	0.9	7.0
*Note: to convert from percent by volume to ppm, multiply by 10,000 (2% by volume is equivalent to 20,000 ppm).		

Additional LEL and UEL Considerations

A gas stream having contaminants with a large explosive range requires extreme caution in control system design and operation. For example, hydrogen gas (H_2), used as a feedstock or produced as an intermediate reaction product, has an especially large explosive concentration range.

The LEL and UEL concentrations for specific compounds can be found in Material Data Safety Sheets (MSDS) or other reference books. However, these data and the values listed in Table 2-1 should *not* be taken as absolutely correct. Some of the data were measured at temperatures, pressures, and oxygen concentrations different from the specific application of current interest. Furthermore, the evaluation of references used in the LEL and UEL tables shows that some of the measurements were conducted from the 1920s through the 1950s, using analytical methods that have long since been abandoned. Unfortunately, there is no easy way to identify data based on out-of-date test methods other than by conducting an exhaustive reference review.

The caveats discussed above with respect to tabulated data also apply to the empirical equations used to estimate LEL and UEL concentrations. These equations only provide a useful approximation of LEL and UEL concentrations.

Estimating LEL and UEL: The Jones Method

Equipment design based on a maximum of 25% of the LEL provides a safety factor to account for the uncertainties in the actual values. One of the estimation techniques is the Jones method, summarized in Equations 2-1 through 2-3.

(Eq. 2-1)
$$C_mH_xO_y + zO_2 \rightarrow mCO_2 + \frac{x}{2}H_2O$$
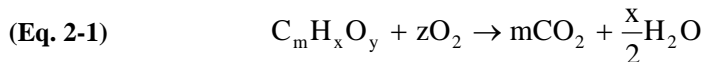
(Eq. 2-2)
$$LEL, \% = \frac{0.55(100)}{(4.76m + 1.19x + 1 - 2.38y)}$$

(Eq. 2-3)
$$UEL, \% = \frac{3.50(100)}{(4.76m + 1.19x + 1 - 2.38y)}$$

LEL of Mixtures

Industrial processes often generate gas streams having more than one potentially ignitable gas or vapor contaminant. Therefore, it is necessary to estimate the LEL and UEL for the gas mixture. Because of the number of site-specific variables involved, one of the best approaches is to have a qualified laboratory measure the LEL and UEL for the exact range of conditions anticipated. If that is not possible, it is sometimes assumed that all of the contaminants have a LEL at a level equivalent to the lowest LEL value of any contaminant present, as is illustrated in Problem 2-1.

PROBLEM 2-1

A gas stream contains acetone (C_3H_6O) at 1000 ppm, benzene (C_6H_6) at 2000 ppm, and toluene (C_7H_8) at 500 ppm.

Is this mixture at a level equivalent to 25% of the LEL for the overall gas stream?

SOLUTION

The following LEL limits are taken from Table 2-1.

Acetone, LEL = 25,000 ppm
Benzene, LEL = 12,000 ppm
Toluene, LEL = 11,000 ppm

The lowest LEL limit is 11,000 ppm (toluene).
25% of 11,000 ppm = 2750 ppm

The total contaminant concentration:
1000 ppm + 2000 ppm + 500 ppm = 3500 ppm

The total concentration exceeds the 25% LEL value.

Le Chatelier Equations

An alternative, less conservative approach for determining the concentration limits for gas mixtures in air is provided by the Le Chatelier equations (2-4, 2-5). These are simply weighted averages of the LELs and UELs of each of the combustible constituents in the gas stream.

(**Eq. 2-4**)

$$LEL_{mixture},\% = \frac{1}{\sum \dfrac{y_i}{LEL_i}}$$

(**Eq. 2-5**)

$$UEL_{mixture},\% = \frac{1}{\sum \dfrac{y_i}{UEL_i}}$$

Where: y_i = concentration of component *i* on a combustible-only basis

Problem 2-2 illustrates the use of the Le Chatelier approach and clarifies the definition of y_i.

PROBLEM 2-2

Using the same gas stream mixture discussed in Problem 2-1, estimate the LEL for the gas mixture using Equation 2-4.

SOLUTION

The following LEL limits apply for the compounds, assuming that the LELs in Table 2-1 have been verified by reference review or independent laboratory study.

> Acetone, LEL = 25,000 ppm
> Benzene, LEL = 12,000 ppm
> Toluene, LEL = 11,000 ppm

$$\text{LEL}_{\text{mixture}} = \cfrac{1}{\left[\left(\cfrac{\left(\cfrac{1000}{3500}\right)}{\left(\cfrac{25{,}000}{10{,}000}\right)}\right) + \left(\cfrac{\left(\cfrac{2000}{3500}\right)}{\left(\cfrac{12{,}000}{10{,}000}\right)}\right) + \left(\cfrac{\left(\cfrac{500}{3500}\right)}{\left(\cfrac{11{,}000}{10{,}000}\right)}\right)\right]}$$

The values of y_i, the numerator terms within the summation, represent the concentration of component '*i*' divided by the sum of the concentrations of all combustible components.

$$\text{LEL}_{\text{mixture}} = \frac{1}{0.1143 + 0.4762 + 0.1299} = 1.3881\%$$

$$25\% \text{ of the LEL} = 0.25(13{,}881) = 3470 \text{ ppm}$$

Using this approach, the gas mixture concentration is just above the 25% of LEL safety limit.

Sources of Ignition

The removal of obvious sources of ignition from the system does not provide a satisfactory solution to the potential contaminant explosion problem. If portions of the gas stream are above the LEL, even on an intermittent basis, there is a significant risk of serious fires or explosions, because the energy requirement to ignite the gas mixture is extremely small. A number of subtle conditions can create sources of ignition in the system, including:

- Static electricity due to movement of the gas stream through the equipment
- Static electricity due to particle impaction with metal components in the ductwork
- Sparks due to metal-to-metal contact
- Hot surfaces
- Electrically powered instruments mounted in the gas stream

It is usually assumed that a gas stream in the explosive range will eventually ignite because of the difficulty in avoiding all sources of ignition on a long-term basis.

Problems Monitoring LEL Contaminant Concentrations

There are a variety of fixed and portable instruments available for directly measuring LEL levels in an existing gas stream. These instruments are particularly useful for the detection of short-term, intermittent conditions that increase the concentration of contaminants to levels approaching the LEL. If the concentration of contaminants exceeds the 25% LEL level, the control system and associated process equipment can be de-energized, and the problem can be corrected safely. The LEL readings can be in error when one or more of the following conditions exist:

- Oxygen (O_2) levels are either lower or higher than the 21% level at which the instruments were calibrated.
- The presence of acid gases may have damaged the sensor.
- The gas stream pressure is either significantly higher or lower than atmospheric

pressure.
- The gas stream contains combustible particles and/or fibers.

The oxygen levels are important because the instruments use combustion air in the sample stream to measure the concentration of LEL. When oxygen concentrations are low, the instrument is not able to detect increased contaminant concentrations. The measurement of LEL is also in error at oxygen levels above 21%, because oxygen-rich environments are inherently more ignitable.

The presence of corrosive gases and vapors in the gas stream can damage the sensor in the LEL meter and bias the measurement results. Common corrosive gases and vapors include sulfuric acid (H_2SO_4), hydrogen chloride (HCl), and hydrogen fluoride (HF).

The performance of the LEL monitor at high and low absolute pressures should be checked with the instrument manufacturer. The response of the meter is subject to change due to the gas pressure in the sensing cell.

Potentially Explosive Materials Not Monitored by LEL Meters

LEL monitors are not designed to measure the concentration and ignitability of particulate matter and fibers. Common ignitable particulate matter and fibers include but are not limited to the following:

- Coal dust
- Wood sander dust
- Flour and related grain dusts
- Metal dusts such as aluminum
- Carbonaceous dusts
- Organic fibers

The ignitability of these materials is strongly dependent on the particle size distribution, because small particles provide a high surface area for oxidation reactions (i.e., combustion).

2.3 GASEOUS CONTAMINANT CONTROL TECHNIQUES

SIX MAJOR CONTROL TECHNOLOGIES

There are six major control technologies that are used commercially to capture and/or destroy gaseous contaminants, including:

- Absorption into liquids
- Biological treatment
- Adsorption onto solid surfaces
- Chemical oxidation
- Chemical reduction
- Condensation of vapors

This section introduces the uses and limitations of these gaseous control technologies.

ABSORPTION

Gaseous contaminants that are soluble in aqueous liquids can be removed by absorption, which involves the transfer of contaminant from the gas to a liquid phase. Absorption is one of the main mechanisms used for the removal of acid gas compounds (e.g., sulfur dioxide, hydrogen chloride, and hydrogen fluoride) and water-soluble organic compounds (e.g., alcohols, aldehydes, and organic acids).

When a contaminant meets the liquid, it is absorbed from the gas stream into the liquid and the rate of absorption increases as the efficiency of contact between the liquid and gas streams increases. Therefore, factors such as turbulent mixing between the two streams and large gas-liquid interfacial area promote absorption. Like adsorption processes, absorption may be operated in either a regenerative or a 'once-through' mode. When regeneration is used, the recovered contaminant may be recycled, disposed of, land filled if a solid product is formed, or it may be destroyed by an oxidation process.

Once the contaminant enters the liquid phase, it can simply dissolve, or it can react irreversibly with other chemicals added to the liquid. The behavior distinguishes the two fundamentally different types of absorption processes: simple dissolution systems and reactant-based dissolution systems. Simple dissolution systems, which are limited by the solubility of the contaminant in the liquid at the prevailing temperature of the liquid, are often used for the removal of soluble organic compounds.

Reactant-based dissolution systems are used for the removal of less soluble compounds. For example, sulfur dioxide (SO_2) may be captured by absorption when a compound such as calcium hydroxide ($Ca(OH)_2$), with which SO_2 reacts irreversibly, is added to the liquid. Such systems are limited primarily by the amount of reactant available in the liquid phase to react with the contaminant as it diffuses into the liquid.

Biological Oxidation Systems

Biological treatment systems are termed either *biological oxidation* or *biofiltration* systems. Regardless of the term, the fundamental processes involved are the collection of contaminants on the surface of a media that contains viable microorganisms. The contaminant is metabolized by the organism, and carbon dioxide (CO_2) and water vapor are produced. Accordingly, biofiltration can be classified as a special type of absorption system using microorganisms and irreversible processes to control the gaseous contaminant.

Applicability of Absorption Processes

The general applicability of simple dissolution-type absorbers is indicated by solubility relationships such as Henry's Law. This law states that the amount of contaminant that can be dissolved into a liquid is proportional to the concentration (or partial pressure) of the contaminant in the gas. Henry's Law is often valid for the low concentrations normally encountered in pollution situations, but cannot be used at high contaminant concentrations. One of the most common forms of Henry's Law is given in Equation 2-6.

(Eq. 2-6) $$y^* = Hx$$

Where   **y** = Mole fraction of contaminant in the gas phase in equilibrium with the liquid

        H = Henry's Law constant, mole fraction contaminant in gas / mole fraction contaminant in liquid

        x = Mole fraction of contaminant in the liquid phase

Equation 2-6 is the equation of a straight line that passes through the origin with a slope of H. If more than one contaminant is interacting with a liquid, Henry's Law is applied to each compound individually.

The general applicability of absorbers using irreversible chemical reactions is limited by the ability to capture and retain the contaminant in solution for a sufficient time to complete the necessary reactions. It is also important to maintain the proper concentrations of components in the liquid to ensure that these components do not exceed their solubility limits and precipitate in spray nozzles or other wetted portions of the absorption vessel.

The primary factor affecting the applicability of a biological oxidation system is the contaminants' compatibility with the microorganisms. Most organic compounds present at moderate-to-low concentrations can be controlled. However, a few organics are toxic to the microorganisms and, therefore, cannot be effectively treated. In addition, some gas stream contaminants may affect the pH levels, thereby reducing the microorganism population.

The suitability of biological oxidation can be determined in consultation with the system suppliers. A reasonably complete summary of the contaminants present in the gas stream and their concentrations will be needed in order to evaluate the feasibility of this type of control system.

FACTORS AFFECTING ABSORPTION

Concentration Dependence

Essentially all absorbers operate at their highest removal efficiency when the contaminant concentrations are high because this maximizes the driving force for mass transfer into the liquid phase. When the contaminant concentration is low (i.e., less than 100 ppm), the absorber must be designed with special attention to ensure highly effective gas-liquid contact to maximize mass transfer conditions. Biological systems are generally designed for moderate-to-low concentrations.

Gas Temperature Dependence

Absorption processes operate best when the gas and liquid temperatures are low because gas solubility increases with decreasing temperature. In most cases, the cooling provided by evaporating a portion of the absorption liquid sufficiently reduces gas temperature to levels appropriate for absorption. When the gas temperatures are very hot, a pre-cooler, such as a spray chamber or an evaporative cooling vessel, can be used upstream of the absorber. Biological systems must operate at temperatures that are reasonable for the microorganism population, normally less than 110 °F (45 °C). If the inlet gas stream temperature is higher, cooling with water sprays or a similar technique is needed to protect the microorganisms. An

additional advantage of cooling water sprays is that the increased relative humidity of the gas stream reduces the likelihood that the biofiltration bed will dry out.

Multiple Contaminant Removal

Absorption processes are often effective for the removal of multiple contaminants, although a sophisticated separation process is required if each contaminant needs to be recovered individually. However, in many absorption processes, the collected contaminants are subsequently destroyed or otherwise discarded.

Many biological systems can handle a wide range of organic compounds present at low concentration. However, the removal efficiencies for each of these contaminants might vary slightly due to the differences in their capture in the support media and their metabolism by the microorganisms.

Particulate Matter Limitations

The vulnerability of an absorption process to particulate matter depends on the type of absorption equipment used for gas-liquid contact. Many absorption processes are well suited for removal of particulate matter with aerodynamic diameters greater than approximately 3 micrometers (>3 μm). In many cases, this will not impair the removal efficiency for gaseous materials. However, the accumulation of particulate matter on packed beds or at the outlet of spray nozzles may have an adverse effect on gas-liquid contact. The presence of particulate matter in the liquid stream could also add to the wastewater treatment requirements. For these reasons, knowledge of the concentration and other characteristics of particulate matter in the contaminated gas stream is important. In some cases, it may be necessary to install a separate particulate control device upstream of the gas absorption process.

The microorganisms used in biological systems are maintained on media that form a bed. Particulate matter that impacts on the inlet of the bed can partially or completely block access to the microorganism and reduce the overall contaminant removal efficiency. For this reason, gas streams with high particulate matter concentrations often use a particulate matter pretreatment system.

ADSORPTION

Adsorption involves transferring the contaminant from the gas to the surface of a solid adsorbent. The adsorbent can be in a wide variety of physical forms, such as pellets in a thick bed, small beads in a fluidized bed, or fibers pressed onto a flat surface. Adsorption only results in phase transfer—the chemical nature of the contaminant is not altered. In nonregenerative adsorption, the adsorbent containing the contaminant is normally disposed of by land filling. In regenerative adsorption, the contaminant is subsequently desorbed so that the adsorbent may be used in multiple cycles. The desorbed contaminant, normally present in significantly higher concentrations, may be recycled or further treated using a destruction process.

Chemical and Physical Adsorption

There are two types of adsorption mechanisms: physical and chemical. The basic difference is in how strongly the contaminant molecule is held to the adsorbent surface.

In physical adsorption, intermolecular cohesion holds the contaminant molecule to the adsorbent

surface weakly. It is possible to reverse physical adsorption by applying heat or reducing the pressure surrounding the adsorbing material. It is generally not possible to reverse chemical adsorption, since a chemical reaction occurs between the adsorbent and the contaminant.

Applicability of Adsorption Processes

Physical adsorption systems are used extensively for the capture and recovery of organic solvents used in printing operations, surface coating operations, and a variety of chemical manufacturing applications.

One of the main factors determining the suitability of physical adsorption for the capture of an organic compound is how strongly the adhesive forces hold the molecule to the surface of the adsorbent. A very general and imperfect indicator of that adhesion force is the molecular weight of the compound. Most organic compounds with molecular weights between approximately 50 and 200 can be collected with high efficiency. Methane, with a molecular weight of 16, has almost negligible adhesion to most adsorbents and therefore cannot be controlled by adsorption.

Compounds with molecular weights greater than 200 can be collected with very high efficiency, but the adhesion forces are often too large to overcome in normal regeneration systems. In fact, the presence of the (nonregenerative) high-molecular-weight trace contaminants in gas streams containing other organic compounds otherwise suitable for adsorption is one of the major limits to the applicability of physical adsorption.

In addition to molecular weight, other parameters, such as boiling point and empirical adsorption correlation coefficients may be used to evaluate the applicability of physical adsorption to the problem of interest. Overall, physical adsorption is a viable technology for the control of a diverse range of organic compounds. The development of new types of adsorbents and improved properties of existing adsorbents is partly responsible for the increasing applicability of physical adsorption systems.

Chemical adsorption may provide high-efficiency control of a variety of acid gases, including hydrogen sulfide (H_2S), hydrogen chloride (HCl), and hydrogen fluoride (HF). In addition, there are now increasing applications for the control of vapor-phase mercury (Hg) using chemical adsorption systems.

FACTORS AFFECTING ADSORPTION

Concentration Dependence

The efficiency of both physical and chemical adsorption systems increases with high contaminant concentrations, due to the larger concentration driving force, which causes transfer of the contaminant from the bulk gas to the surface of the adsorbent. Adsorption may also be used at low contaminant concentrations (e.g., 1 to 100 ppm levels), although larger quantities of adsorbent are needed to ensure efficient collection. Thus, adsorption control systems are applicable to concentrations ranging from trace levels associated with some odor sources to levels approaching 25% of the lower explosive limit (e.g., organic compounds and hydrogen sulfide). Some adsorption systems also operate on gasoline recovery systems at concentrations well above the UEL levels.

Temperature Dependence

Essentially all adsorption processes work best when the gas temperature is low and the adsorption capacity is high. In physical adsorption, the gas temperature is usually maintained at levels less than approximately $120°F$ ($50°C$). As new adsorbents are developed, the operating range will probably increase above this level. If the inlet gas temperatures are higher than $120°F$ on a continuous or short-term peak basis, pre-cooling is often needed. Chemical adsorption can be conducted at higher temperatures due to the increased strength of the chemical bond formed. Many chemical adsorption processes operate in the $100°F$ ($40°C$) to $400°F$ ($200°C$) range.

Multiple Contaminant Limitations

Physical adsorption systems used for the recovery and reuse of solvents are usually limited to gas streams with one to three organic compounds. In these regenerative systems, the cost of separating more than three compounds is often prohibitive. However, in nonregenerative systems the number of organic compounds in the contaminated gas stream does not limit the system used to collect the contaminants.

In regenerative systems, the presence of trace quantities of high molecular weight compounds must be avoided since they are not sufficiently desorbed from the adsorbent surface during the regeneration process. As a result, they will eventually cover all of the adsorption surface (breakthrough), reducing efficiency and preventing the adsorption of additional compounds.

Particulate Matter Limitations

Most physical adsorption systems are sensitive to particulate matter in the contaminated gas stream. Deposition of particulate matter in the adsorbent bed restricts access of the organics to a portion of adsorbent surface. Pretreatment is often required when particulate matter concentrations are high on either an intermittent or continuous basis.

OXIDATION

Oxidization can be used to *destroy* a wide variety of organic contaminants. Oxidation processes may be divided into three main categories:

- Thermal oxidizers
- Catalytic oxidizers
- Flares

Thermal oxidizers and catalytic oxidizers are used for sources such as surface coaters, gasoline storage and distribution terminals, and organic chemical plants. Flares are used primarily to treat emergency vent gases in organic chemical plants and petroleum refineries. The majority of thermal and catalytic oxidizers operate with inlet contaminant concentrations less than 25% of the LEL. Flares can be used for sources that are well below the LEL or well above the UEL.
All chemical oxidation systems destroy organic compounds in the contaminated gas stream by converting them to carbon dioxide and water (i.e., combustion). Accordingly, they are used when economic recovery of the compounds is impractical.

Applicability of Oxidizers

Oxidization is applicable to essentially all organic compounds. The practicality of thermal oxidation depends on the contaminant's concentration and the operating temperature required for complete oxidation. In most thermal oxidizers, the heating value of the contaminants provides a major fraction of the total energy input necessary for combustion. The required operating temperature is usually 200°F (95°C) to 300°F (150°C) above the auto-ignition temperature of the organic compound of concern. If more than one organic compound is present, **thermal oxidizers** operate at a temperature 200°F to 300°F above the auto-ignition temperature of the most difficult-to-oxidize compounds. Auto-ignition temperatures of many compounds may be found in standard chemistry and physics reference books. Most thermal oxidizers operate at temperatures ranging from 1200°F (650°C) to more than 1800°F (980°C).

The suitability of catalytic oxidation is normally determined in consultation with catalyst suppliers and catalytic oxidizer manufacturers. The necessary operating temperature and the destruction capability for specific compounds will vary, depending on the type of catalyst used. The supplemental fuel requirements depend, in part, on the concentration of organic contaminants and the efficiency of the heat exchanger used ahead of the catalytic oxidizer.

Catalytic oxidizers cannot be used on systems that have high concentrations of materials that will poison the catalyst or otherwise interfere with the gas's access to the catalyst's surface (often termed masking).

Flares are used as emergency controls for a wide variety of organic compounds. To improve destruction efficiencies in the short time periods available later at peak gas stream temperatures, flares often include steam injection to improve mixing and to accelerate oxidation reactions.

FACTORS AFFECTING OXIDATION SYSTEMS

Concentration Dependence

Oxidation systems provide high-efficiency destruction of a wide variety of organic compounds, regardless of the inlet concentrations of the contaminants. The supplemental energy requirement(s) needed to maintain the necessary operating temperature decreases as the contaminant concentration increases.

Gas Temperature Dependence

The contaminated gas stream is almost always preheated prior to entering the oxidizer. For this reason, oxidation systems are effectively independent of the temperature of the contaminated gas stream.

Multiple Contaminant Capability

All oxidation systems are capable of treating contaminated gas streams containing a large number of compounds.

Particulate Matter Limitations

Thermal oxidation systems are generally capable of treating contaminated gas streams containing particulate matter. In fact, particulate matter containing organic species may also be destroyed. However, the particulate matter can deposit in the heat exchangers, which reduces the heat

exchange efficiency and eventually plugs the system. Catalytic oxidation systems are much more sensitive to particulate matter. In addition to reducing the efficiency and potentially plugging heat exchangers, particulate matter can also accumulate in catalyst beds and destroy the catalyst activity. Accumulated particulate material in heat exchangers and in catalyst beds must be removed on a routine basis to provide the necessary gas flow rates and to reduce the vulnerability of the system to bed fires caused by the ignition of these materials.

CHEMICAL REDUCTION SYSTEMS

Chemical reduction is used primarily for the destruction of NO_x compounds emitted from combustion processes. These systems include selective noncatalytic reduction (SNCR) and selective catalytic reduction (SCR). The chemistry is effectively the same in both systems. A chemically reduced form of nitrogen, ammonia or urea, is injected into the gas stream to react with the oxidized nitrogen compounds, NO and NO_2. These reactions result in the formation of molecular nitrogen (N_2), the major constituent of clean air.

Ammonia (NH_3) can be used in either the anhydrous (compressed gas) or aqueous form. Urea [$CO(NH_2)_2$] is available in liquid form. Either of these compounds is fed to the combustion system to mix with the combustion gases at the temperature range required for the reactions to occur. SCR processes normally operate at temperatures in the range of $550°F$ ($290°C$) to $750°F$ ($400°C$), while a higher temperature range of $1600°F$ ($870°C$) to $2000°F$ ($1100°C$) is required for SNCR. In the case of ammonia systems, dilution is also needed for ammonia-air mixtures to remain below the LEL.

Applicability of Reduction Systems

For **SNCR**, injection must occur at a position where the combustion gases are in the temperature range required for the reduction reactions to occur, generally between $1600°F$ and $2000°F$ ($870°C$ to $1100°C$). Sufficient space must be available at this position to install the ammonia or urea injection nozzles. This space is not always available on existing boilers and gas turbines installed long before SNCR became commercially available. Injection of ammonia or urea into a portion of the gas stream that is too cold will result in an incomplete reaction and the emission of ammonia or urea (often termed *slip*). Injection into a portion of the gas stream that is too hot will result in oxidation of the ammonia or urea to form additional NO_x. Due to the gas temperature range limitations, SNCR systems usually have NO_x destruction efficiencies in the range of 20% to 60%.

The same chemistry is used in **SCR** systems, but the presence of the catalyst allows the reactions to occur at significantly lower temperatures, generally $550°F$ ($290°C$) to $750°F$ ($400°C$). Sufficient space must be available for the moderately large reaction vessel in the area of the boiler where the combustion gases are in the desired temperature range. The unintentional conversion of sulfur dioxide (SO_2) to sulfuric acid (H_2SO_4) and the formation of very sticky ammonium bisulfate (NH_4HSO_4) and ammonium sulfate [$(NH_4)_2SO_4$] deposits in downstream boiler equipment can result in boilers using high sulfur fuels. High particulate matter levels can also create problems in gas flow through the catalyst bed or can mask the catalyst surfaces. Trace components may also tend to poison the catalyst. When properly operated, SCR systems are capable of achieving NO_x reduction efficiencies ranging from 60% to more than 90%.

FACTORS AFFECTING REDUCTION SYSTEMS

Concentration Dependence

SNCR and SCR systems achieve the high reduction efficiencies when the inlet NO_x levels range from a low of about 100 ppm to a high of 1000 ppm.

Gas Temperature Dependence

For effective reduction, both SNCR and SCR systems must operate in a relatively narrow temperature range as specified above. Furthermore, the spatial distribution of the gas temperatures at the points of reagent injection must be relatively uniform.

Multiple Contaminant Capability

SNCR and SCR systems are effective for the reduction of both NO, which comprises 90% to 95% of the NO_x, and NO_2.

Particulate Matter Limitations

SNCR systems are not sensitive to particulate matter concentrations, except in extreme circumstances when solid deposition on the injection nozzles may disrupt proper reagent spray patterns. In contrast, accumulated particulate matter on the catalyst bed in SCR systems can cause flow alterations and catalyst surface masking.

CONDENSATION SYSTEMS

Condensation systems are used exclusively for the recovery of organic compounds present at moderate-to-high concentrations in industrial process effluent gas steams. There are three main categories of condensation systems based on the general operating temperature range:

- Water-based direct and indirect condensers ($40°F$ to $80°F$ / $5°C$ to $27°C$)
- Refrigeration condensers ($-50°F$ to $-150°F$ / $-45°C$ to $-100°C$)
- Cryogenic condensers ($-100°F$ to $-320°F$ / $-75°C$ to $-195°C$)

The most common condensers are those using cooling water in direct contact or indirect contact vessels. Refrigeration and cryogenic systems are used primarily for high-efficiency recovery of high-value contaminants.

Applicability of Condensation Systems

The applicability of condensation systems is determined by the concentration and vapor pressure of the contaminant or contaminants being controlled. Condensation systems reduce the gas stream contaminant's partial pressure to a value equivalent to the vapor pressure of the compound at the condenser's operating temperature. Procedures for estimating the vapor pressure are discussed later in this course.

FACTORS AFFECTING CONDENSATION SYSTEMS

Concentration Dependence

Condensation systems are used primarily for the control of high concentrations of high-value

organic contaminants.

Gas Temperature Dependence

Condenser systems operate at low temperatures to take advantage of the decrease in vapor pressure with decreasing temperature.

Multiple Contaminant Capability

Condensers can be used for the simultaneous removal of multiple organic compounds present in the gas stream. However, the cost of separation and recovery of individual components from the condensed mixture can be high. Consequently, most condenser systems are used when the gas stream contains only a single contaminant or a mixture of compounds that does not require separation (e.g., gasoline).

Particulate Matter Limitations

Condensers operate by transferring heat from the gas stream being treated to the cooling media used in the system. Since the accumulation of particulate matter on heat transfer surfaces can reduce the effectiveness of the system, it is sometimes necessary to remove particulate matter prior to the condenser.

SUMMARY OF CONTROL TECHNIQUES

Table 2-2 summarizes the general properties and characteristics of the main control technologies used for the control of gaseous contaminants. Essentially all of the control techniques exhibit maximum control efficiency when the inlet concentration is high. All of the technologies are also sensitive to the gas stream temperature. Absorption, adsorption, biological treatment, and condensation work best at low temperatures, while oxidation and reduction systems operate in narrowly limited high-temperature ranges.

Table 2-2. Summary of the general applicability of gaseous contaminant techniques.					
Control Technique	**General Applicability**	**Typical Concentration Range**	**Typical Gas Temperature Range**	**Applicable for Control of Multiple Contaminants?**	**Applicable for Control of Gas Streams with Particulate Matter?**
Absorption	Acid Gases and Organic Compounds	< 1 ppm to > 100,000 ppm[1]	<150°F[b]	Yes[g]	Yes
Adsorption	Acid Gases and Organic Compounds	< 1 ppm to 25% of LEL[1]	<130°F[b]	Yes[g,h]	Pretreatment Often Required
Biological Treatment	Organic Compounds	< 1 ppm to ~1000 ppm	<110°F[c]	Yes	Pretreatment Often Required

Control Technique	General Applicability	Typical Concentration Range	Typical Gas Temperature Range	Applicable for Control of Multiple Contaminants?	Applicable for Control of Gas Streams with Particulate Matter?
Oxidation	Organic Compounds	< 1 ppm to 25% of LEL[a]	600°F to 2000°F[d]	Yes	Pretreatment Often Required
Reduction	NO and NO_2	< 100 ppm to 1,000 ppm[a]	550°F to 2000°F[e]	Yes[i]	Yes
Condensation	Organic Compounds	> 100 ppm[a]	-320°F to 80°F[f]	Yes[g,h]	Pretreatment Often Required

Notes:

   a. Maximum removal efficiency usually occurs at maximum contaminant inlet concentration.
   b. Gas stream precooling is needed in some applications to reduce operating temperatures.
   c. Gas stream precooling and humidification is needed in some applications to reduce operating temperatures and to increase gas stream humidity.
   d. Catalytic systems operate in the 500°F to 1000°F range. Thermal oxidizers and flares operate in the 1200°F to 2000°F range.
   e. SCR systems operate in the 550°F to 750°F range. SNCR systems operate in the 1600°F to 1900°F range.
   f. Cryogenic systems operate in the -100°F to -320°F range. Refrigeration systems operate in the -50°F to -150°F range. Water condensers operate in the 40°F to 80°F range.
   g. Multiple compound separation and recovery can be difficult in some applications.
   h. Generally used for systems having one to three organic compounds in the gas stream.
   i. Used for control of nitric oxide (NO) and nitrogen dioxide (NO_2).

While these data provide a general indication of the most common operating characteristics, specific systems can be designed to operate at high efficiency outside the ranges described in Table 2-2.

Although APTI 415 is limited to the six major control techniques summarized in this section, it is important to note that a number of additional techniques in commercial service and under development can also be used in specific cases.

2.4 SUMMARY

CONTROL TECHNIQUES FOR GASEOUS CONTAMINANTS

This chapter covered the following topics:

- Gas stream characteristics that affect the selection of a gaseous control system.
- Control technologies to remove gaseous contaminants from gas streams.
- Techniques to control gaseous contaminants.

2.5 REVIEW EXERCISES

INSTRUCTIONS

Select the best response(s) for each of the following multiple-choice questions.

MULTIPLE CHOICE QUESTIONS

1. What is the typical concentration limit for ignitable organic compounds in the inlet gas stream to an air pollution control system?

    a) 10% of the LEL
    b) 25% of the LEL
    c) 50% of the LEL
    d) 100% of the LEL

2. What factors influence the actual site-specific LEL value?

    a) Composition of the gas mixture
    b) Oxygen concentration
    c) Gas temperature
    d) All of the above

3. What type of adsorption mechanism is used in regenerative systems for organic compound removal?

    a) Physical adsorption
    b) Chemisorption
    c) Both of the above
    d) Neither of the above

4. Physical adsorption is more effective when the gas temperature is _____.

    a) high
    b) low
    c) independent of gas temperature
    d) near $200°$F

5. The capacity of an adsorbent for a gaseous contaminant (grams per 100 grams of adsorbent) increases with _____.

    a) reduced gas temperature
    b) decreased contaminant concentration
    c) decreased gas pressure
    d) the presence of multiple contaminants

6. In simple dissolution, the mass transfer of a gaseous contaminant to the liquid stream is limited by_____.

      a) solubility equilibrium
      b) availability of reactive alkali
      c) the degree of gas-liquid contact
      d) the gas and liquid stream temperatures

7. Thermal oxidizers usually operate at gas temperatures that are _____.

      a) above the auto-ignition temperature of the most difficult-to-oxidize major constituent
      b) $200°F$ to $300°F$ above the auto-ignition temperature of the most difficult to oxidize major constituent
      c) $400°F$ to $500°F$ above the auto-ignition temperature of the most difficult to oxidize major constituent
      d) between $550°F$ and $800°F$

8. A catalytic oxidizer used for organic compounds usually operates with a catalyst bed inlet temperature that is _____.

      a) above the auto-ignition temperature of the most difficult-to-oxidize major constituent
      b) $200°F$ to $300°F$ above the auto-ignition temperature of the most difficult-to-oxidize major constituent
      c) $400°F$ to $500°F$ above the auto-ignition temperature of the most difficult-to-oxidize major constituent
      d) between $400°F$ and $800°F$

2.6 REVIEW EXERCISES: SOLUTIONS

This Student Guide includes separate exercises and solutions, which allow students to check their work.

MULTIPLE CHOICE ANSWERS

1. What is the typical concentration limit for ignitable organic compounds in the inlet gas stream to an air pollution control system?

    a) 10% of the LEL
    b) 25% of the LEL
    c) 50% of the LEL
    d) 100% of the LEL

2. What factors influence the actual site-specific LEL value?

    a) Composition of the gas mixture
    b) Oxygen concentration
    c) Gas temperature
    d) All of the above

3. What type of adsorption mechanism is used in regenerative systems for organic compound removal?

    a) Physical adsorption
    b) Chemisorption
    c) Both of the above
    d) Neither of the above

4. Physical adsorption is more effective when the gas temperature is _____.

    a) high
    b) low
    c) independent of gas temperature
    d) near 200° F

5. The capacity of an adsorbent for a gaseous contaminant (grams per 100 grams of adsorbent) increases with _____.

    a) reduced gas temperature
    b) decreased contaminant concentration
    c) decreased gas pressure
    d) the presence of multiple contaminants

6. In simple dissolution, the mass transfer of a gaseous contaminant to the liquid stream is limited by_____.

      a) solubility equilibrium
      b) availability of reactive alkali
      c) the degree of gas-liquid contact
      d) the gas and liquid stream temperatures

7. Thermal oxidizers usually operate at gas temperatures that are _____.

      a) above the auto-ignition temperature of the most difficult-to-oxidize major constituent
      b) $200°$F to $300°$F above the auto-ignition temperature of the most difficult to oxidize major constituent
      c) $400°$F to $500°$F above the auto-ignition temperature of the most difficult to oxidize major constituent
      d) between $550°$F and $800°$F

8. A catalytic oxidizer used for organic compounds usually operates with a catalyst bed inlet temperature that is _____.

      a) above the auto-ignition temperature of the most difficult-to-oxidize major constituent
      b) $200°$F to $300°$F above the auto-ignition temperature of the most difficult-to-oxidize major constituent
      c) $400°$F to $500°$F above the auto-ignition temperature of the most difficult-to-oxidize major constituent
      d) between $400°$F and $800°$F

2.7 REFERENCES

1.   U.S. Department of Health and Human Services. *NIOSH Pocket Guide to Chemical Hazards*; 1997.

2.   Yaws, C. L. *Chemical Properties Handbook;* McGraw Hill: New York, 1999.

3.   Himmelblau, D. *Basic Principles and Calculations in Chemical Engineering*; Prentice Hall, Inc.: Englewood Cliffs, NJ, 1962.

4.   Lange, N.C. *Lange's Handbook of Chemistry, 9th Edition*; Handbook Publishers: Sandusky, OH, 1956.

3.0 AIR POLLUTION CONTROL SYSTEMS

3.1 OVERVIEW

INDUSTRIAL PROCESS SYSTEMS

Industrial process systems include the process equipment that generates the pollutants, the air pollution control equipment that removes them, and the fan that moves the gas stream. The process equipment and the air pollutant control devices do not work independently; the operating conditions of all the system components are closely linked together by the fans, hoods, and ductwork. In addition to discussing how hoods and fans operate in an industrial system, this chapter introduces the preparation and use of industrial process system flowcharts, an important tool for evaluating the overall system.

Understanding and evaluating the industrial process as a whole is important for several reasons, including the following:

- Changes in the process equipment can have a major impact on the efficiency of the control device.
- Changes in the air pollution control device can affect the ability of the process hoods to capture the pollutants at the point of generation.
- The operating data from one unit in the system can be valuable in evaluating the operating conditions in another unit in the system.
- Hoods and fans can influence the efficiency of the air pollution control equipment and the release of fugitive emissions from the process equipment.

LEARNING OBJECTIVES

At the conclusion of this training students will be able to:

- Evaluate air pollution control system performance.
- Recognize the components in a basic system flowchart.
- Identify the variables that contribute to hood efficiency.
- Identify the variables that contribute to fan performance.

3.2 FLOWCHARTS

Evaluating Overall System Performance

Flowcharts are a useful tool for evaluating the performance of an overall system because they provide a means for organizing and presenting operating data. More specifically, flowcharts can be used for the following purposes:

- Evaluating process operation changes that affect control device performance
- Identifying instruments that are not working properly
- Identifying health and safety problems
- Communicating effectively

An expanded block diagram flowchart has been adopted for use in this course. Major components, such as absorbers, are shown as a simple block rather than as a complex sketch resembling the actual absorber. Instrument and major equipment symbols have been adopted primarily from conventional chemical engineering practice. Most of the standard symbols are reproduced on the back of the flowchart sheet so that you do not need to remember all of the specific information included within this course.

FLOWCHART SYMBOLS

A complete flowchart consists of several symbols representing major and minor pieces of equipment and numerous material flow streams. It is important to be able to differentiate between the various types of material flow streams without sacrificing simplicity and clarity.

Material Streams

The recommended symbols selected for the material streams are presented in Figure 3-1.
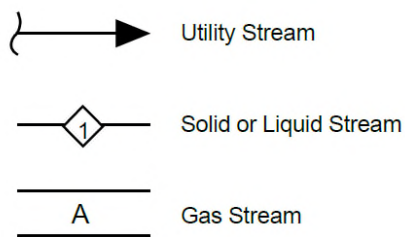
Figure 3-1. Material stream symbols.

Gas flow streams are indicated by two closely spaced parallel lines, which make them appear larger than other streams. This size difference is important so that the inspector can quickly scan the flowchart and differentiate between gas flow streams and liquid or solid flow streams. Segments of ductwork connecting one major piece of equipment to another are labeled with an alphabetic character. Important liquid and solid material flow streams are shown as solid, single lines. Diamonds with enclosed numbers are used to identify each of the streams.

To avoid cluttering the drawing, some of the liquid and solid streams for which operating data will not be necessary may be unnumbered. These *utility streams* provide necessary materials to the system and the characteristics of these streams are relatively constant. Typical utility streams for air pollution control equipment systems include make-up water, cooling water, and low-pressure steam. Natural gas, oil, and other fossil fuels can also be treated as utility streams to simplify the drawings. Instead of the numbered diamonds, these utility streams are identified either by using one of the codes listed in Table 3-1 or by a one- or two-word title. The codes or work titles are placed next to a "stretched S" symbol, which is used to indicate that the source of the utility stream is outside the scope of the drawing.

Table 3-1. Codes for utility streams.			
Cal	Compressed calibration gas	HS	High pressure steam
CA	Compressed air	IA	Instrument air
CD	Condensate	LS	Low pressure steam
CW	City (or plant) fresh water	Oil	No. 2 or No. 6 oil
Gas	Natural gas		

Major Components of Systems

A square or rectangle is used to denote major equipment such as air pollution control devices, tanks and vessels, or process equipment. Fans are denoted using a relatively large circle with a set of tangential lines to indicate the discharge point. A stack is shown as a slightly tapered rectangle. All of these symbols are shaded or filled with crosshatched diagonal lines as shown in Figure 3-2, so that it is easy to pick out the major equipment items from the gas handling ductwork and other streams leaving these units.
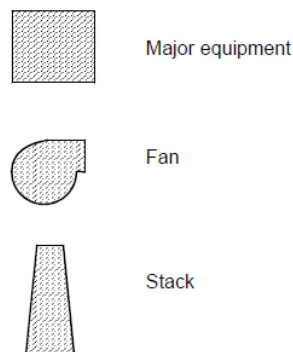
Figure 3-2. Major equipment symbols.

Whether items are treated as major equipment depends on the overall complexity of the system and on individual preference. The decision is based primarily on the types of data and observations that are possible and the level of detail that is needed to evaluate the performance of the overall system.

Emission discharge points, such as stacks and storage piles, are obviously important due to the visible emission observations and the presence of continuous emission monitors and stack sampling ports in some systems. These emission points are identified by a set of inverted

triangles immediately above the source, as shown in Figure 3-3. These are numbered whenever it is possible to confuse different sources within a single industrial complex. The numbers used in the triangles should correspond with the emission point identification numbers used in the inspector's working files. Identification numbers in the form of E_1, E_2, E_n are typically used for enclosed emission points, such as stacks, and F_1, F_2, F_n are used for fugitive emission points, such as storage piles and material handling operations.
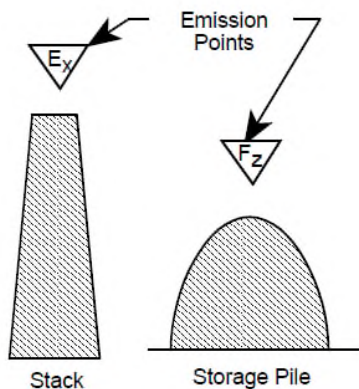
Figure 3-3. Identification of emission points.

Minor Components of Systems

A number of relatively minor components in air pollution control systems, such as those listed in Table 3-2, may be shown on the block-diagram flowcharts in order to clarify how the system operates. Symbols for the minor components listed in Table 3-2 are shown in Figure 3-4.

Table 3-2. Minor components.

Fabric Filters
- Bypass dampers
- Relief dampers
- Outlet dampers
- Reverse air fans

Wet Scrubbers
- Pumps
- Nozzles
- Manual valves
- Automatic valves

Carbon Adsorbers and Oxidizers
- Indirect heat exchangers
- Fans
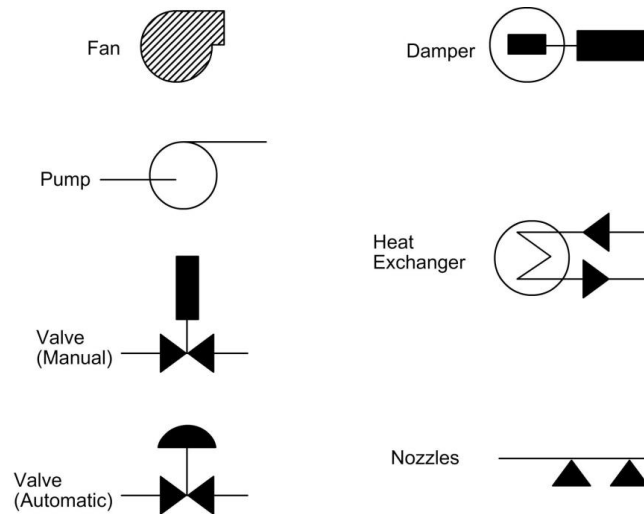
Figure 3-4. Minor component symbols.

Instruments

The presence of an instrument or a sampling port is indicated by a small circle with a short dashed line connecting it to the appropriate stream as shown in Figure 3-5. The type of instrument is indicated using the symbols listed in Table 3-3.

Direct reading
instrument

Panel mounted
instrument

Panel mounted instrument
with continuous recorder
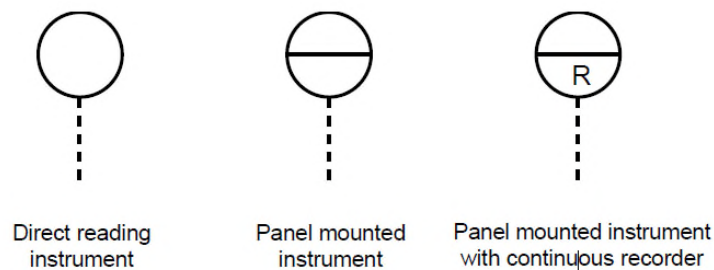
Figure 3-5. Instrument symbols.

Table 3-3. Instrument codes.			
A	Motor current	pH	Liquid or slurry pH
CEM	Continuous emission monitor	Δp	Static pressure drop
Den	Density	SP	Gas static pressure
F	Flow	SSP	Stack sampling port
L	Liquid level	T	Temperature
LEL	Lower explosive limit	V	Vacuum gauge
MP	Measurement port	VOC	Low concentration VOC monitor
Op	Opacity	W	Weight
P	Gas or liquid pressure		

Instruments such as manometers and dial-type thermometers can only be read at the gauge itself. These direct reading gauges, shown in Figure 3-5, are simply denoted by the instrument circle and the instrument code. More sophisticated instruments with panel-mounted readout gauges (normally located in the control room) are indicated using a horizontal line bisecting the instrument circle. In this case, the instrument code is placed directly above the line. When the instrument readout is a continuous strip chart recorder or data acquisition system, the letter "R" for "Recording" is placed below the line.

Materials of Construction

The materials of construction are relevant whenever a potential corrosion problem exists that could affect either system performance or safety. On a single-page flowchart, it is impractical to specify the exact materials and protective coatings used on each vulnerable component, because several hundred combinations of materials and coatings are in common use. However, the general type of material used in key portions of the system may be important. For example, it would be helpful to know that a stack discharging high concentrations of sulfuric acid vapor is composed of carbon steel, because this material is easily attacked by sulfuric acid. The stack platform and access ladders could be vulnerable to failure, as the corrosion problem gets progressively worse. An abbreviated set of symbols is presented in Table 3-4 for identifying materials of construction.

Table 3-4. Codes for construction materials.		
CS	Carbon steel	RL Rubber-lined
FRP	Fiberglass-reinforced plastic	SS Stainless steel
N	Nickel alloy	WD Wood

These symbols should be placed next to the major equipment item (e.g., stack, fan, air pollution control device) or the gas handling ductwork segment.

DIAGRAMS

Basic Flowcharting Techniques

Flowcharts are used for many purposes; therefore, many levels of sophistication in flowchart preparation exist. The most complex are design-oriented piping and instrumentation drawings (termed *P & I drawings*), which show every major component, valve, and pipe within the system. Even a drawing for a relatively simple system (or part of a system) can have several hundred separate items shown on it. Conversely, a simple block diagram used as a field sketch may have only three to five symbols on the drawing.

Flowcharts for air pollution control studies should be relatively simple. Generally, more equipment detail than shown on a simple block diagram is needed, but far less than provided by the standard P & I drawing. The flowcharts should not be so cluttered with details that it is difficult to include present system operating conditions to help identify performance problems

and health and safety risks. Since these are primarily "working" drawings, they must be small enough to be carried easily while walking around the facility and should not require a lot of time to prepare or to revise.

For these reasons, an expanded block diagram flowchart has been adopted for use in this course. Only the system components directly relevant to the study are included. Major components such as absorbers are shown as a simple block rather than a complex sketch resembling the actual absorber. Most minor components and material flow streams are omitted to avoid cluttering the drawing.

The flowchart is designed so that it fits entirely on a single 8½-by-11-inch page and can be carried on a standard clipboard or in a notebook. Furthermore, most of the standard symbols are reproduced on the back of the flowchart sheet for easy reference.

Flowchart Diagrams

An example flowchart for a relatively complicated air pollution source, a waste solvent incinerator, is shown in Figure 3-6. The process equipment in this example consists of a starved air modular incinerator with primary and secondary chambers. The air pollution control system consists of a venturi scrubber followed by a mist eliminator.
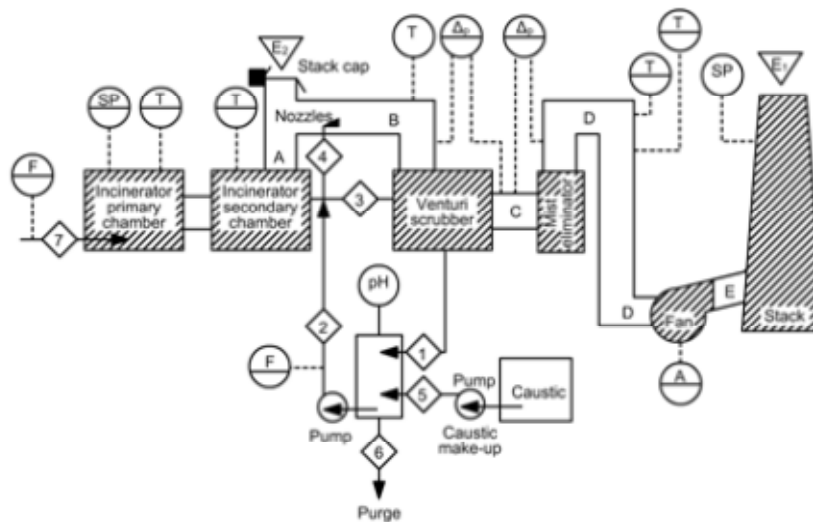
Figure 3-6. Example flowchart of a waste solvent system.

The primary and secondary chambers of the waste solvent incinerator have been shown separately because data from each chamber is important to the inspection. However, many components of the incinerator and wet scrubber systems have not been shown because their operating conditions are not central to the potential air pollution emission problems or health and safety problems.

A somewhat simpler flowchart for a hot-mix asphalt plant equipped with a spray scrubber is shown in Figure 3-7. Most of the plant is not shown since the scrubber only controls the air emissions from the mixing of hot, new aggregate with cold, aged recycled asphaltic concrete. It

is apparent in Figure 3-7 that the duct labeled as section C serves as the discharge point. The liquid recycle pond is shown using an irregular shape so that it is easy to differentiate between the pond and the major equipment items.
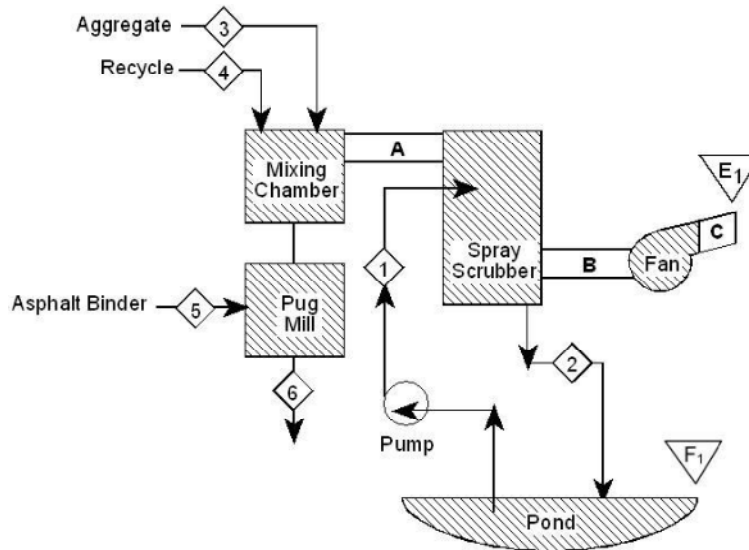
Figure 3-7. Example flowchart of an asphalt plant.

The symbols for the major pieces of equipment and other parts of the system should be located in logical positions. For example, the pond in Figure 3-7 is placed near the bottom of the sketch, and the discharge point is in a relatively high location.

The following problems illustrate how flowcharts can be helpful during the inspection of air pollution control systems. They serve as tools for organizing relevant data and determining if further investigation is needed.

Follow these steps when evaluating the overall system:

- Determine whether the operating data are consistent and logical.
- Compare current data against site-specific baseline data.
- Determine specific areas that may need emphasis during the inspection.
- Determine potential health and safety problems that may be encountered during the inspection.

PROBLEM 3-1

A regulatory agency is conducting an inspection of a soil remediation unit at a hazardous waste site. The site is an abandoned chemical plant where several nonvolatile carcinogens (chlorinated organic compounds) are present in old lagoons. The plant uses a rotary kiln for destruction of the carcinogens and two side-by-side pulse jet fabric filter units for control of particulate matter (PM) generated in the kiln. Based on the data shown in Figure 3-8 (present situation) and Table 3-5 (baseline data), determine the following:

A. Is the operating data for the system consistent and logical?
B. Do any important discrepancies exist between the current and baseline data?
C. What areas of the facility should be emphasized during the inspection?
D. What health and safety issues should be considered during the inspection?
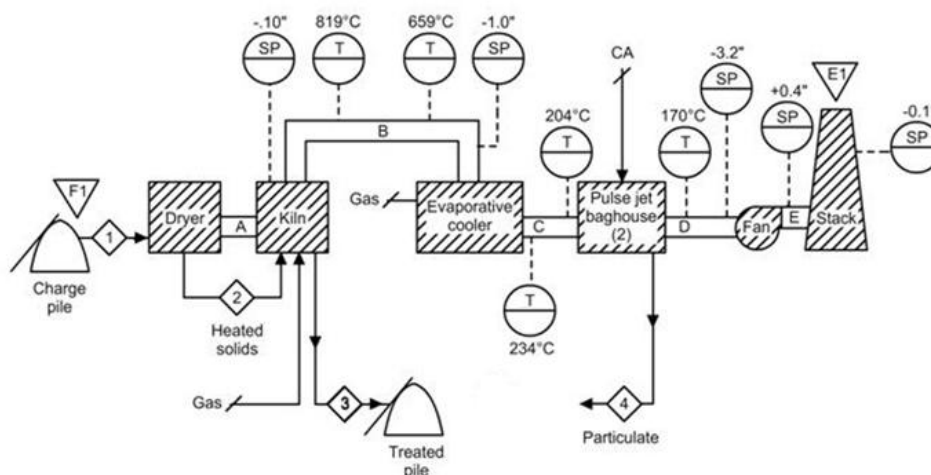
Figure 3-8. Example flowchart of a hazardous waste incinerator and pulse jet baghouse system.

Table 3-5. Baseline data for the hazardous waste incinerator.		
Location	**Temperature (C)**	**Static Pressure (in. W.C.)**
Kiln hood	810	–0.1
Evaporative cooler inlet	785	–1.0
Evaporative cooler outlet	240	No Data
Baghouse inlet	195	No Data
Baghouse outlet	190	–5.1
Duct E	No Data	–1.5
Stack	No Data	–1.0

SOLUTION: PART A

Determine if the operating data for the system are consistent and logical. There should be logical trends in the gas temperatures, gas static pressures, gas oxygen concentrations (combustion sources), and other parameters along the direction of gas flow. Figure 3-9 contains plots of static pressure and gas temperature versus "position" in the process.
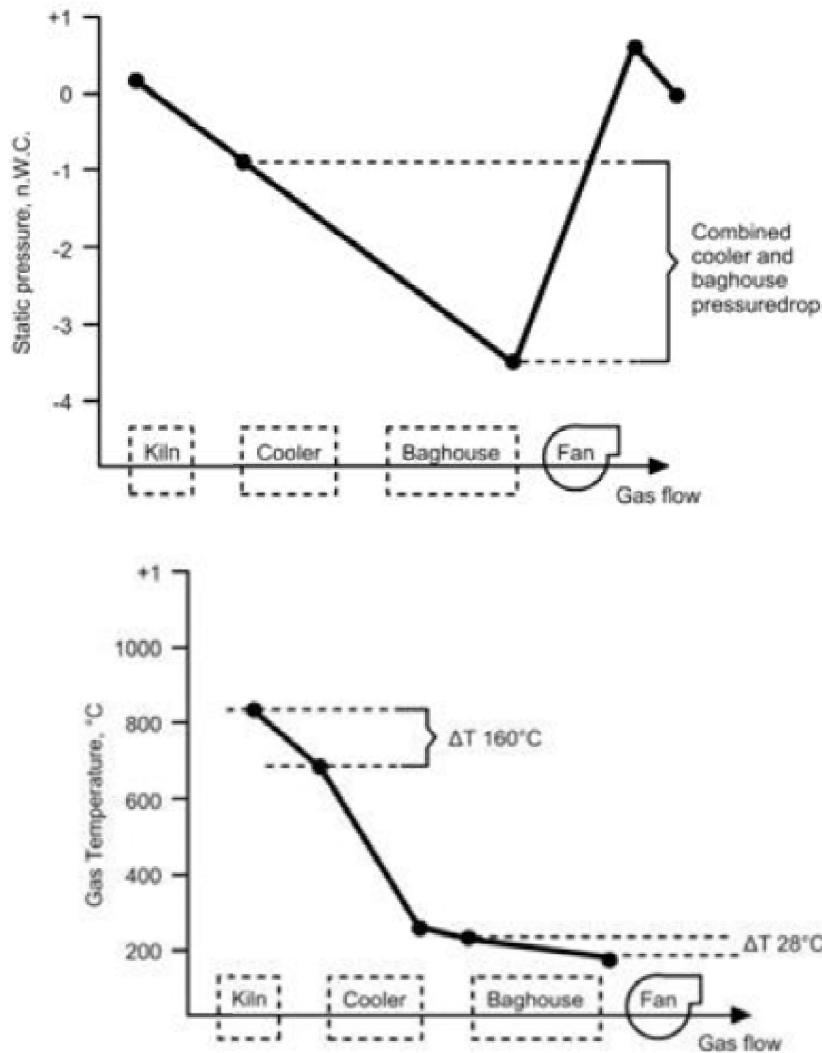
Figure 3-9. Static pressure and temperature profile for present data.

First, examine the present trends in both the gas temperature and static pressure (the present values are compared to baseline values in part B). Both the temperature and static pressure trends through the system appear to be logical. The gas temperature is a maximum at the discharge of the combustion source, and decreases in the direction of gas flow. The gas temperature at the fan outlet is not provided for this example. Note that the gas temperature at the fan outlet may be slightly higher than that at the fan inlet, due to compression that occurs as the gas moves through the fan (the Joule-Thompson effect).[2] The static pressure becomes progressively more negative as the gas approaches the fan. After the fan, the static pressure is significantly higher, as expected. Since the plant instruments provide consistent and logical profiles through the system, they are probably relatively accurate.

SOLUTION: PART B

Compare the present and the site-specific baseline data to the extent possible. The gas temperature and static pressure data for present and baseline conditions are listed in Tables 3-6 and 3-7 in the direction of gas flow.

Table 3-6. Gas temperature profile for the hazardous waste incinerator (°C).

	Present	Baseline
Kiln hood	819	810
Evaporative cooler inlet	659	785
Evaporative cooler outlet	234	240
Baghouse inlet	204	195
Baghouse outlet	176	190

Table 3-7. Gas static pressure profile for the hazardous waste incinerator (in W.C.).

	Present	Baseline
Kiln hood	–0.10	–0.10
Evaporative cooler inlet	–1.0	–1.0
Evaporative cooler outlet	No Data	No Data
Baghouse inlet	No Data	No Data
Baghouse outlet	–3.2	–5.1
Duct E	+0.4	–1.5
Stack	–0.1	–1.0

Step 1. Compare the current temperature data against the site-specific baseline data.

a. Compare the temperature data for Duct B using Table 3-6.

The 160°C temperature drop (from 819°C to 659°C) in the short duct (B) between the kiln and the evaporative cooler is significantly greater than the 25°C decrease under the baseline conditions. A small temperature decrease due to radiant and convective heat losses is expected. However, the significantly greater temperature drop suggests that air infiltration is occurring or that the second temperature-measuring device is malfunctioning. Air infiltration could reduce the amount of combustion gas being pulled through the kiln, which would result in fugitive emissions from the kiln. Thus, a check for fugitive emissions should be included in the scope of the inspection.

b. Evaluate the destruction efficiency of the rotary kiln using the kiln outlet temperature data in Figure 3-9 and Table 3-6.

The primary function of this portable plant is to incinerate carcinogens contained in the contaminated soil. The single parameter most useful for evaluating the destruction efficiency is the kiln outlet temperature monitored by the temperature gauge on the left side of duct B. The present value of 819°C compares well with the baseline data obtained during the trial burn tests in which the unit demonstrated good performance. Accordingly, it appears that the unit is presently in compliance.

c. Evaluate the temperature data for the evaporative cooler. See Figure 3-9 and Table 3-6.

The evaporative cooler protects the temperature-sensitive Nomex® bags used in the downstream pulse jet baghouses. The present temperature drop of 425°C across the evaporative cooler coupled with the present outlet gas temperature of 234°C demonstrates that this unit is operating as intended. It is not necessary to climb to the top of the unit to check the spray nozzles.

    d.   Evaluate the temperature data for the baghouse. See Figure 3-9 and Table 3-6.

The present temperature drop across the baghouse of 28°C is significantly larger than the 5°C drop at baseline conditions. This could be an indication of air infiltration, which should be investigated in the field evaluation.

Step 2. Compare the current pressure drop data against the site-specific baseline data.

    1.   Evaluate the static pressure data across the kiln using Figure 3-9 and Table 3-7.

The present and baseline pressure readings agree.

    2.   Evaluate the static pressure data from the evaporative cooler inlet to the baghouse outlet. See Figure 3-9 and Table 3-7.

The baseline static pressure drop of 4.1 in. W.C. is significantly higher than the present pressure drop of 2.2 in. W.C. Pressure drop across evaporative coolers tends to remain constant. However, the pressure drop across baghouses will vary with time depending on the particulate loading on the bags. The decrease in pressure drop may result from air inleakage at the bag connection points or could be due to worn or torn bags. This possibility should be investigated during the inspection.

    3.   Evaluate the static pressure data from the baghouse exit to the stack. See Figure 3-9 and Table 3-7.

The static pressure increase created by the fan (3.6 in. W.C.) is similar for the baseline and present conditions. The static pressure drop from the fan exit to the stack also agrees.

SOLUTION: PART C

Determine the areas that should be emphasized during equipment performance evaluation.

They are as follows:

1. Check for air infiltration in Duct B.
2. Check for fugitive emissions from rotary kiln.
3. Investigate the reason for the temperature drop across the pulse jet baghouses.
4. Check for air inleakage across the pulse jet baghouses.

SOLUTION: PART D

Determine what health and safety issues should be considered during the performance evaluation.

The pulse jet baghouses should be investigated during the field inspection. However, this work must be conducted carefully in order to minimize safety hazards. The uninsulated metal housing at 176°C is a definite burn hazard. Incineration of the chlorinated compounds forms HCl, which in turn is likely to lead to corrosion of the housing. The probable air infiltration identified previously could be caused by corrosion. The roof of the baghouse should be avoided both because of high temperature and the possibility that it has been weakened by corrosion.

The possibility of fugitive emissions from the kiln, as indicated by the large temperature decrease along ductwork B, should be investigated. This is particularly important since the soil is contaminated with several suspected carcinogens. This should be noted on the flowchart to serve as a reminder to stay out of areas where inhalation problems or skin absorption hazards could exist.

Summary of Health and Safety Issues:

1. Avoid roof of pulse jet baghouses.
2. Remain aware that chemicals in the process are possible carcinogens. Avoid areas where inhalation or absorption may become dangerous.

PROBLEM 3-2

A company is evaluating the performance of a venturi scrubber serving a hazardous waste incinerator. They are using an Enhanced Monitoring Protocol that is based on the static pressure drop gauge across the venturi. Answer the following questions based on the data shown in Figure 3-10.

A. Is there any reason to believe that the venturi scrubber pressure drop gauge is malfunctioning?
B. Is there any reason to be concerned about fugitive emissions from the emergency bypass stack? (The emergency bypass stack has the stack cap covering the outlet.)

The present data and the corresponding baseline data are provided in Tables 3-8 and 3-9.
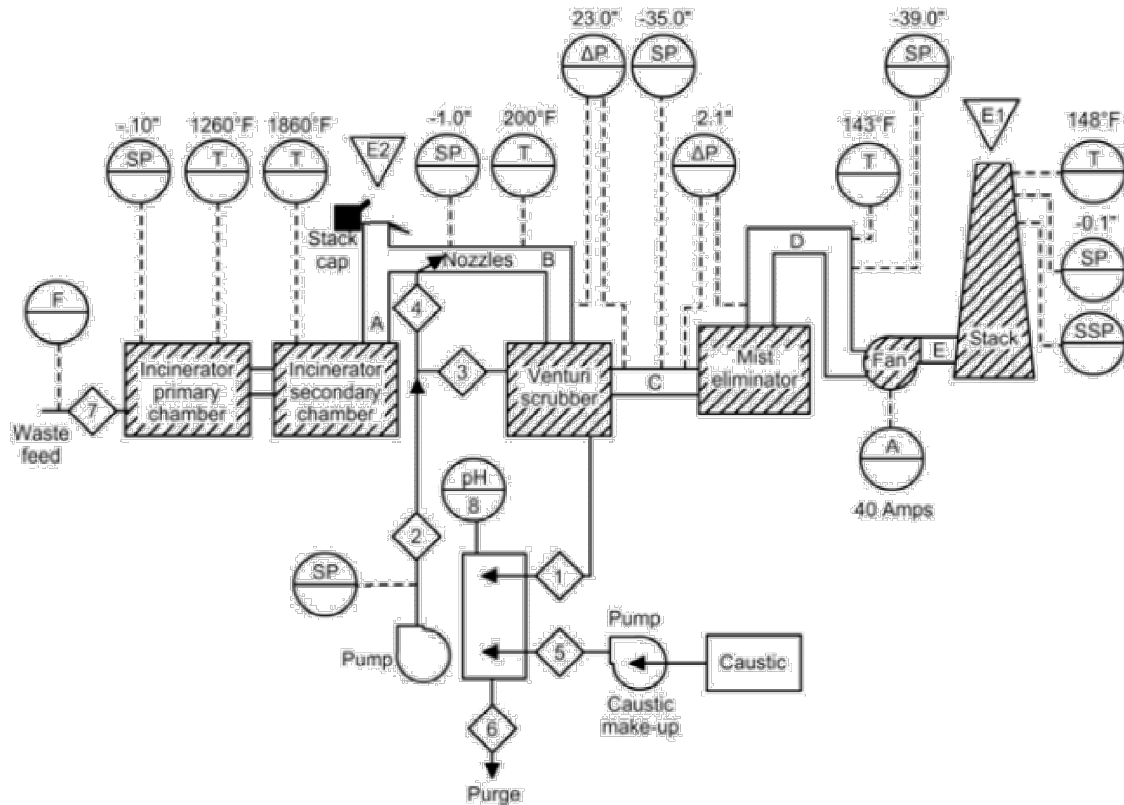
Figure 3-10. Example flowchart of a hazardous waste incinerator and venturi scrubber system.

Table 3-8. Static pressures and static pressure drops (in. W.C.).		
Static Pressures	**Present**	**Baseline**
Incinerator primary chamber	–0.10	–0.12
Duct B	–1.0	–1.10
Mist eliminator	–35.0	–38.0
Fan inlet (Duct D)	–39.0	–40.0
Stack	–0.1	–0.1
Static Pressure Drop	**Present**	**Baseline**
Venturi scrubber	23.0	36.0
Mist eliminator	2.1	1.6

Table 3-9. Gas temperatures (°F).		
	Present	**Baseline**
Incinerator secondary chamber	1860	1835
Duct B	200	197
Fan inlet	143	142
Stack	148	147

SOLUTION: PART A

First, evaluate the quality of data before attempting to evaluate the system. There should be logical trends for the static pressure, gas temperature, and other relevant parameters. The static pressure and pressure drop data for present and baseline conditions have been combined into a single graph (Figure 3-11), which can be used to evaluate the static pressures along the entire gas flow path. It is apparent that present static pressure drop data for the venturi scrubber does not make sense. However, the inlet static pressure to the mist eliminator is near the baseline value. This suggests that the static pressure drop gauge is malfunctioning. In addition, the static pressure drop across the mist eliminator is larger than expected. This suggests that the mist eliminator may be partially plugged and that a more vigorous or more frequent cleaning is needed.

SOLUTION: PART B

There is no reason to suspect fugitive emissions from the emergency bypass stack. The static pressures upstream and downstream of the bypass stack are negative. Accordingly, ambient air could leak into a poorly sealed stack, but untreated combustion gas could not escape to the atmosphere.
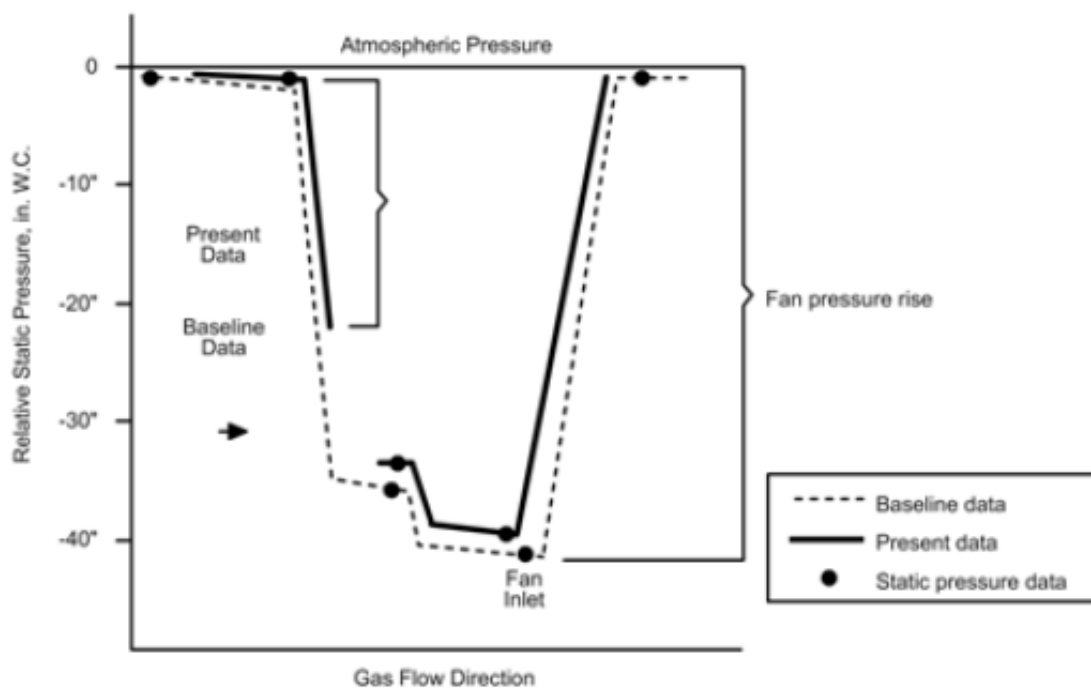

Figure 3-11. Static pressure profiles.

FLOWCHARTS SUMMARY

A flowchart of the process system can be used to:

- Identify changes in performance of the control device or other process units due to

> process changes or equipment malfunction
> - Identify instruments that are not consistent with other similar instruments in the system
> - Communicate effectively with other personnel
> - Avoid potential health and safety hazards

Flowcharts used for agency inspections should be prepared prior to or in the early stages of the inspection. If flowcharts for the system being inspected have been prepared previously, they should be reviewed prior to the on-site work and updated as necessary.

3.3 HOODS

TRANSPORTING POLLUTANTS

The pollutants generated or released in process equipment must be captured so that they can be transported to the air pollution control device. Many processes are totally enclosed so that the pollutant is automatically transferred to the control device. For example, coal-fired boilers generate pollutants within an enclosed furnace area that is maintained at a slightly negative pressure of –0.05 to –0.25 in. W.C. In this case, the furnace walls serve as a totally enclosed hood. Other processes, however, are open to the surroundings, and the pollutant is prevented from escaping by the use of a hood.

Hoods are an integral part of the process equipment. The hood can consist of a simple, stationary plenum mounted above or to the side of the source, a large moveable plenum, or the process equipment itself.

Figure 3-12. Stationary hood in an industrial process.

Pollutants from an open process that are not captured by a hood disperse directly into the plant air and eventually pass through roof vents and doors into the atmosphere. Evaluation of the ability of the hoods to capture pollutants at the point of generation is important in many inspections and engineering studies. Pollutants that are not captured by the hood are considered fugitive emissions. According to the EPA definition, these include "emissions that (1) escape capture by process equipment exhaust hoods; (2) are emitted during material transfer; (3) are emitted to the atmosphere from the source area; and (4) are emitted directly from process equipment."

(Eq. 3.1)   Fugitive emissions $=$ Total emissions $-$ Emissions captured by hood

(Eq. 3.2) $\text{Stack emissions} = \text{Emissions captured by hood} \times \left(\dfrac{100\% - \eta}{100\%} \right)$

Where: η = collection efficiency of the pollution control device $(\%)$

The importance of hood performance is illustrated by Problems 3-3 and 3-4, which are based on the simplified industrial process shown in Figure 3-13. This system consists of a process unit that generates pollutants, two hoods associated with the process equipment, the ductwork, an air pollution control device, a fan, and a stack.
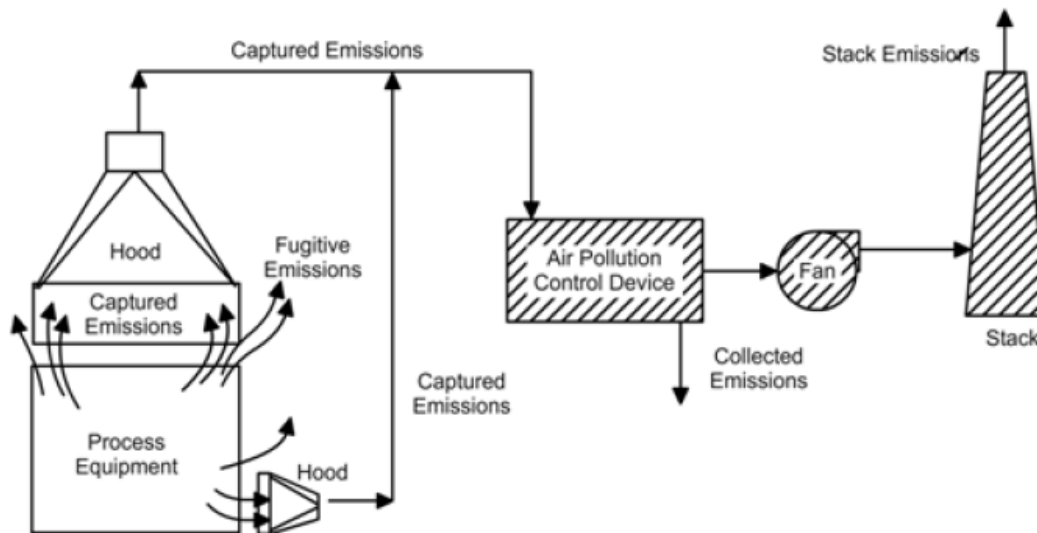
Figure 3-13. Role of hoods in an industrial process.

PROBLEM 3-3

Calculate the fugitive emissions and the stack emissions if the process equipment generates 100 lb$_m$/hr of volatile organic compounds (VOCs), the hood capture efficiency is 95%, and the collection efficiency of the air pollution control device is 95%.

SOLUTION

1. Calculate fugitive emissions.

   Fugitive emissions = Total emissions – Emissions captured by hood

   $100 \text{ lb}_m/\text{hr} - 95 \text{ lb}_m/\text{hr} = 5 \text{ lb}_m/\text{hr}$

2. Calculate stack emissions.

   Stack emissions = Emissions captured by hood $\times \left(\dfrac{100\% - \eta}{100\%} \right)$

   Where: η = collection efficiency of the pollution control device $(\%)$

$$\text{Stack emissions} = \left(95\ \text{lb}_m/\text{hr}\right)\left(\frac{100\% - 95\%}{100\%}\right) = 4.75\ \text{lb}_m/\text{hr}$$

3. Calculate total emissions.

    Total emissions = Hood emissions + Stack emissions

    $$5\ \text{lb}_m/\text{hr} + 4.75\ \text{lb}_m/\text{hr} = 9.75\ \text{lb}_m/\text{hr}$$

The capture of fugitive emissions is a key step in an air pollution control system. It is crucial that emissions escaping the hood be minimized so that the maximum amount of the pollutants generated are transported to the air pollution control device. Problem 3-3 shows that even with hood capture efficiencies approaching 100%, fugitive emissions can be higher than emissions leaving the stack.

PROBLEM 3-4

Calculate the stack emissions and fugitive emissions if the process equipment generates 100 lb$_m$/hr of VOCs, the hood capture efficiency is 90%, and the collection efficiency of the air pollution control device is 95%.

SOLUTION

$$\text{Fugitive emissions} = 100\ \text{lb}_m/\text{hr} - 90\ \text{lb}_m/\text{hr} = 10\ \text{lb}_m\text{hr}$$
$$\text{Stack emissions} = \frac{\left(100\% - 95\%\right)}{100\%}\left(90\text{lb}_m/\text{hr}\right) = 4.5\ \text{lb}_m/\text{hr}$$
$$\text{Total emissions} = 10\ \text{lb}_m/\text{hr} + 4.5\ \text{lb}_m/\text{hr} = 14.5\ \text{lb}_m/\text{hr}$$

Explanation:

These two problems illustrate the importance of hoods. Slight changes in the ability of the hood to capture the pollutants can have a large impact on the total amount of the pollutants that are actually released into the atmosphere.

Unfortunately, it is not always possible to see the fugitive emissions. Gaseous and vapor emissions such as carbon monoxide (CO), sulfur dioxide (SO$_2$), hydrogen chloride (HCl), and nitric oxide (NO) are not visible. Even particulate emissions may be hard to see if there are numerous small fugitive sites, if one major site cannot be seen from normal areas accessible to personnel, or if the PM is not in the size range that causes light scattering.

HOOD OPERATING PRINCIPLES

Hoods are generally designed to operate under negative (sub-atmospheric) pressure. The air is drawn into the hood due to static pressures that are lower inside the hood than those in the process equipment and the surrounding air. Since air from all directions moves toward the low-pressure hood, the hood must be as close as possible to the process equipment in order to capture the pollutant-laden air and not just the surrounding air. Figure 3-14 illustrates, for an

unbaffled hood, how quickly the gas velocity decreases as distance from the hood increases. At approximately one-hood-diameter away from the hood entrance, the gas velocities are often less than 10% of the velocity at the hood entrance.
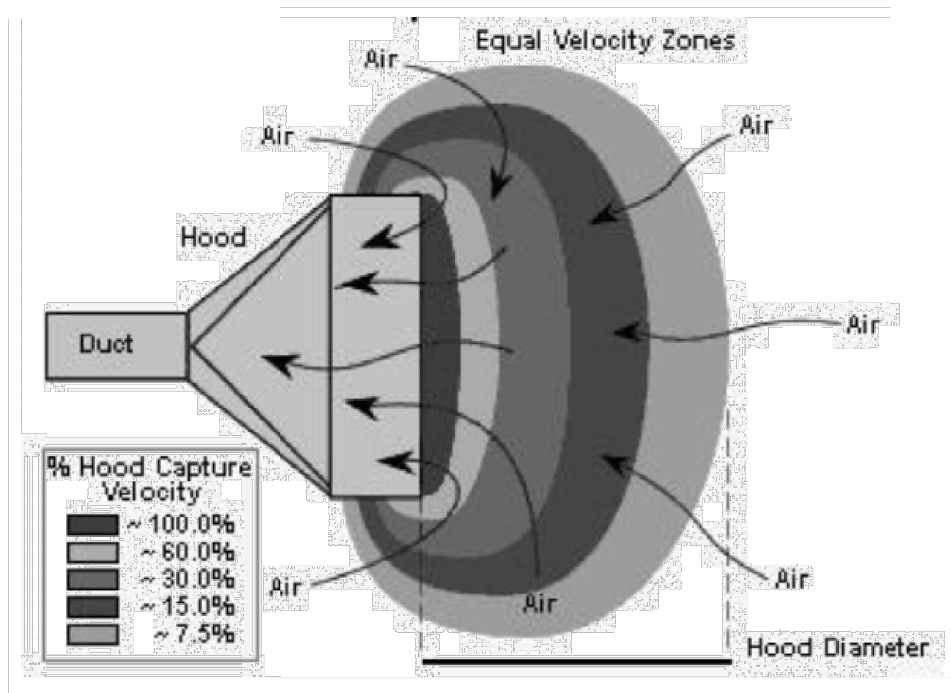
Figure 3-14. Hood capture velocities.

Figure 3-14 indicates that the hood has relatively little influence on gas flow except in the area very close to the hood entrance. Therefore, in order to ensure good capture of the pollutant-laden gas streams, the hood must be as close to the emission source as possible. The capture velocity of a hood is defined as the air velocity at any point in front of the hood or at the hood opening necessary to overcome opposing air currents and to capture the contaminated air at that point by pulling it into the hood.

The following equation relating volumetric flow rate, air velocity, and distance from the hood face for a freely suspended hood without a flange demonstrates the importance of the proximity of the hood to the source.

(Eq. 3-3)
$$Q = v_h \left(10x^2 + A_h\right)$$

Where:
Q = volumetric airflow rate (ACFM)
X = distance from hood face to point of contaminant (ft)
V_h = hood capture velocity at distance of X (ft/min)
A_h = area of hood opening (ft^2)

Note that this equation should be used for *estimation purposes only*. The equation is also limited to situations in which the distance (X) is less than or equal to 1.5 hood diameters.[1]

PROBLEM 3-5

The recommended capture velocity for a certain pollutant is 300 fpm entering a 16-inch diameter hood. What is the volumetric flow rate needed to achieve the recommended capture velocity for the following distances between the hood face and the emission source (X)?

A. X = 12 in. (75% of hood diameter)
B. X = 24 in. (150% of hood diameter)

SOLUTION: PART A

$$Q = v_h \left(10x^2 + A_h \right)$$

1. Calculate the area of the hood opening.

$$Area = \frac{\pi D^2}{4}$$

$$\frac{3.14(16\,in.)^2}{4} = 201\,in.^2$$

2. Calculate the volumetric flow rate, Q, required to achieve the recommended capture velocity of 300 fpm at a distance of 12 inches from the hood.

$$Q = \frac{300\,ft}{min} \left[10\left(1\,ft\right)^2 + \left(201\,in.^2\right)*\left(\frac{1\,ft^2}{144\,in.^2} \right) \right]$$

$$= 3{,}420\,ACFM$$

SOLUTION: PART B

$$Q = v_h \left(10x^2 + A_h \right)$$

Calculate the volumetric flow rate, Q, required to achieve the recommended capture velocity of 300 fpm at a distance of 24 inches from the hood.

$$Q = \frac{300\,ft}{min} \left[10\left(2\,ft\right)^2 + \left(201\,in.^2\right)*\left(\frac{1\,ft^2}{144\,in.^2} \right) \right]$$

$$= 12{,}420\,ACFM$$

The required volumetric flow rate increases approximately *four times* when the distance between the hood and the contaminant source is *doubled*.

The recommended capture velocity equations for a variety of hoods with different locations and arrangements can be obtained from the ACGIH *Industrial Ventilation Manual*, 23rd edition.

Hood Designs for Improved Performance

There are many ways to design hoods to improve capture effectiveness. For example, when the pollutant-laden gas stream is hot, the hood is often positioned above the point of pollutant release to take advantage of the buoyancy of the low-density, hot gas stream. Variations from the standard hood design shown in Figure 3-14 may also be used to improve hood performance.

Side baffles or *flanges* can be used to restrict the flow of clean air into the hood. The beneficial effect of side baffles on the gas velocities near the hood entrance is seen when comparing Figure 3.14 to Figure 3-15 below.
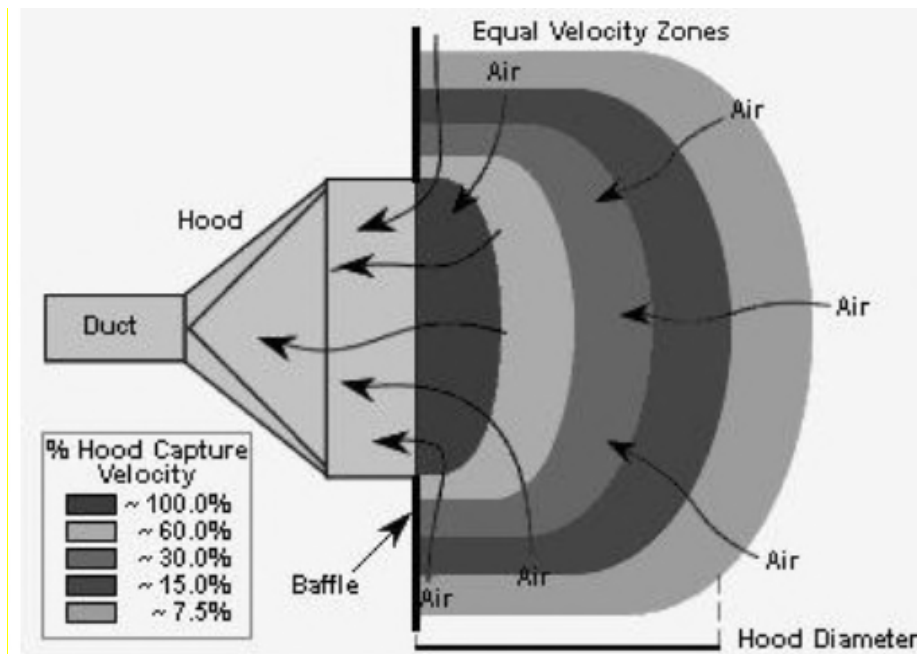
Figure 3-15. Beneficial effect of side baffles on hood capture velocities.

Hood capture is greatly improved when the enclosure comprised of the hood and the side baffles can completely encompass the source of pollutant generation. The side baffles can be in the form of metal sheets, strips of fabric or plastic, or any other material that blocks the movement of clean air into the low-pressure area of the hood.

Side baffles should be made of materials that are compatible with the gas stream and pollutants, to prevent corrosion or other unwanted side reactions from taking place between the gas stream and the baffles themselves.

In addition to reducing the unintentional capture of clean air, these side baffles minimize crossdrafts, which can limit the intended movement of the pollutant-laden gas into the hood. The recommended width of a flange for most situations is equal to the square root of the hood area.

Another hood design that is used to improve capture effectiveness is called the push-pull hood. As shown in Figure 3-16, a high-velocity clean air stream is "pushed" across the area of pollutant generation into a "pull" hood on the opposite side.
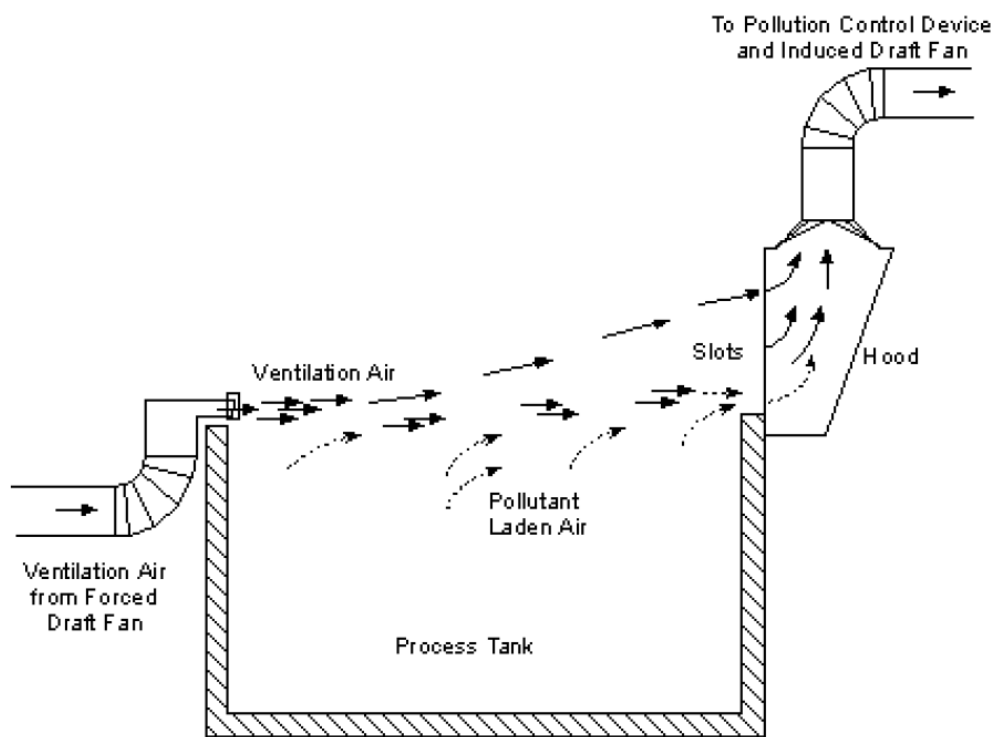
Figure 3-16. Push-pull hood.

The high-velocity gas stream does not inherently disperse rapidly. Therefore, it flows toward the "pull" hood and the pollutants are captured. These types of hoods are sometimes used on open tanks and other sources where access from the top is necessary in order to operate the equipment. However, they should not be used when the ventilation air would significantly increase the quantities of pollutants vaporized. Push-pull hoods can provide very high capture efficiencies where they are applicable.

The hood arrangement may also be altered when personnel must have access to the open vessel where the pollutants are generated. As shown in Figure 3-17, the hood located directly above the source would result in the contaminated air flowing directly over the personnel working on the unit. The side-mounted hood, in contrast, would pull clean air over the worker before mixing with the contaminated air.
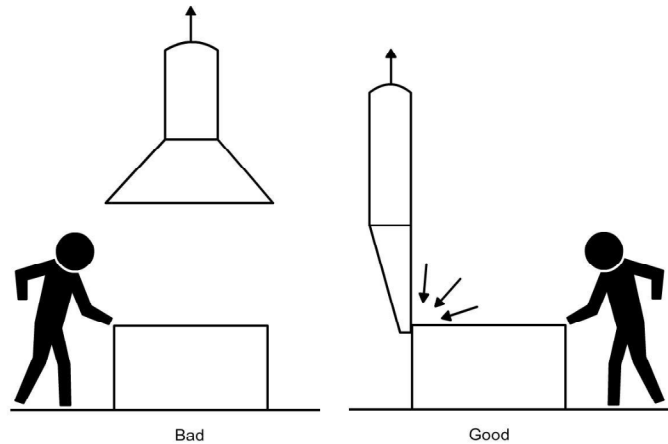
Figure 3-17. Hood design for protection of plant personnel.

MONITORING HOOD CAPTURE EFFECTIVENESS

Hood performance should be monitored on a regular basis to confirm that the capture effectiveness has not decreased since it was installed or last tested. Visible emission observations for fugitive emissions should be conducted in the case of particulate sources. In general, you should confirm that the hood has not been moved away from the point of pollutant generation and that side baffles and other equipment necessary to maintain good operation have not been damaged or removed.

The hood static pressure should be monitored to ensure that the appropriate gas flow rate is being maintained. The *hood static pressure,* which is simply the static pressure in the duct immediately downstream from the hood, is entirely dependent on the hood geometry and the gas flow rate. As long as the hood has not been damaged or altered, the hood static pressure provides an indirect but relatively accurate measurement of the gas flow rate. The hood static pressure is made up of two components: (1) the velocity pressure in the duct from the hood and (2) the hood entry loss.

(Eq. 3-4) $$SP_h = -(VP_d) - h_e$$

Where: SP_h = hood static pressure (in. W.C.)
VP_d = duct velocity pressure (in. W.C.)
h_e = overall hood entry loss (in. W.C.)

The loss of pressure caused by airflow moving into the hood is referred to as entry loss, and is given by the following equation.

(Eq. 3-5) $$h_e = (F_h)(VP_d)$$

Where: F_h = hood entry loss coefficient (dimensionless)
VP_d = duct velocity pressure (in. W.C.)

(Eq. 3-6) $$SP_h = -(VP_d) - (F_h)(VP_d)$$

The velocity pressure term in Equations 3-5 and 3-6 is associated with the energy necessary to accelerate the air from zero velocity to the velocity in the duct. The hood entry loss coefficient, F_h, is shown below (Figure 3-18) for three common geometries, and tabulated values may be found in standard texts for other geometries.

When air enters a duct under suction, the flow separates from the wall and forms a jet. The area of minimum cross-sectional area is referred to as the *vena contracta*. After passing through the vena contracta, the flow expands to fill the duct. As the flow expands, some of the velocity pressure converts to static pressure. The magnitude of the vena contracta, which determines the hood entry loss coefficient, is dependent on the hood geometry. As shown in Figure 3-18, the hood entry loss coefficient ranges from a value of 0.04, when the hood has a bell-mouth entry, to 0.93 for a plain-end duct entry.
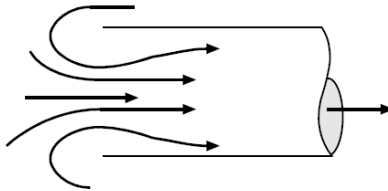
Figure 3-18a-c. Plain duct end with a hood entry loss coefficient of 0.93.
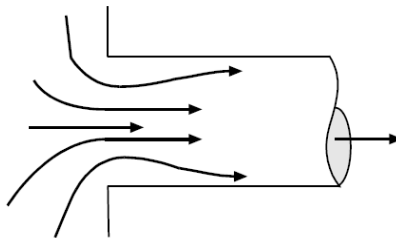
Figure 3-18b. Flanged opening with a hood entry loss coefficient of 0.49.
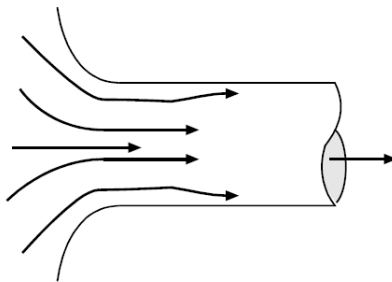
Figure 3-18c. Bell-mouth inlet with a hood entry loss coefficient of 0.04.

The velocity pressure is related to the square of the velocity of the gas stream in the duct and the gas density, as shown in Equation 3-7. Note that this is a dimensional equation, with the coefficient 4005, responsible for converting the velocity in ft/min to the velocity pressure units

of inches of Water Column (in. W.C.). Any consistent units of density may be used, as the density ratio is dimensionless.

(Eq. 3-7)
$$VP_d = \left(\frac{v}{4005}\right)^2 \frac{\rho_{Actual}}{\rho_{Standard}}$$

Where:

VP_d = velocity of duct (in. W.C.)

v = gas velocity (ft/min)

ρ_{Actual} = density at actual conditions (lb_m/ft^3)

$\rho_{Standard}$ = density at standard conditions (lb_m/ft^3)

The hood static pressure increases as the gas flow rate increases, as shown in Figure 3-19. In this figure, a flanged hood with an entry loss coefficient (F_h) of 0.49 and gas density equal to standard gas density have been assumed in evaluating the gas flow rate versus hood static pressure curve.

The hood static pressure can be measured by relatively simple gauges, such as water-filled manometers and Magnehelic® gauges. The normal range of hood static pressures is –0.2 to –2.0 in. W.C.
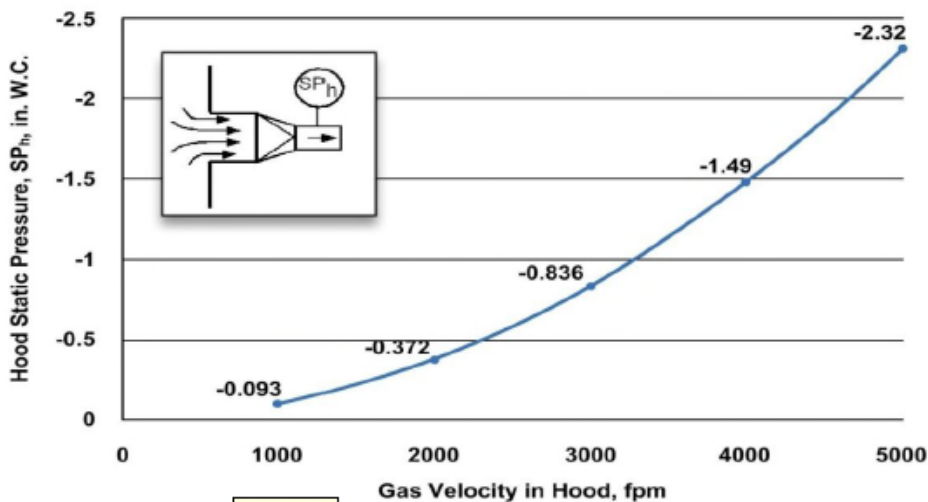
Figure 3-19

Figure 3-19. Relationship between hood static pressure and gas velocity.
(A flanged hood with $F_h = 0.49$ and $Q_{actual} = Q_{standard}$ has been assumed.)

A decrease in hood static pressure (i.e., a less negative value), corrected for gas density changes, usually indicates that the gas flow rate entering the hood has decreased from previous levels. This may reduce the effectiveness of the hood by reducing the capture velocity at the hood entrance.

PROBLEM 3-6

A hood serving a paint dipping operation has a hood static pressure of –1.10 in. W.C. The baseline hood static pressure was –1.70 in. W.C. The temperature is 68°F. Estimate the gas flow rate:

     (A) At present operating conditions
     (B) At baseline levels

Use the data provided below:
- Hood $F_h = 0.93$
- Baseline air temperature $= 68°F$
- Duct diameter$= 2$ ft (inside diameter)

SOLUTION: PART A

Calculate the gas velocity and flow rate at present conditions.

Step 1. Calculate the velocity pressure (VP) using the following equation:

$$SP_h = -(VP_d) - h_e$$

   1.   Calculate the value for the hood entry loss, he, as follows:

$$h_e = (F_h)(VP_d)$$
$$= (0.93)(VP_d)$$
$$SP_h = -VP_d - 0.93(VP_d) = -1.93(VP_d)$$

Given: $SP_h = -1.10$ in. W.C.

$$-1.1 \text{ in. W.C.} = -1.93(VP_d)$$

$$VP_d = \frac{-1.1 \text{ in. W.C.}}{-1.93} = 0.57 \text{ in. W.C.}$$

Step 2. Calculate the gas velocity using a variation of Equation 3-7.

     At 68°F, $\rho_{act} = \rho_{std} = 0.075 \text{ lb}_m/\text{ft}^3$.

$$v = 4{,}005\sqrt{VP_d}$$
$$v = 4{,}005\sqrt{0.57}$$
$$v = 3{,}024 \text{ ft/min}$$

Step 3. Calculate the gas flow rate as follows:

     Flow rate = Velocity × Area of duct

$$\text{Area of duct} = \frac{\pi D^2}{4}$$

$$\frac{3.14(2\,\text{ft})^2}{4} = 3.14\,\text{ft.}^2$$

$$\text{Flow rate} = 3{,}024\,\text{ft/min} * (3.14\,\text{ft}^2) = 9{,}495 \text{ ACFM}$$

SOLUTION: PART B

Calculate the gas flow rate at baseline conditions.

Step 1. Calculate the velocity pressure using the following.

$$SP_h = -(VP_d) - h_e$$

$$= -(VP_d) - (0.93)(VP_d)$$

$$= -(VP_d) - 0.93\,VP_d = -1.93(VP_d)$$

Given: $SP_h = -1.7$ in. W.C.

$$-1.7\,\text{in.W.C.} = -1.93(VP_d)$$

$$VP_d = 0.88\,\text{in. W.C.}$$

Step 2. Calculate the gas velocity using Equation 3-7.

$$v = 4{,}005\sqrt{VP_d}$$

$$v = 4{,}005\sqrt{0.88}$$

$$v = 3{,}757 \text{ ft/min}$$

Step 3. Calculate the gas flow rate. The duct area was calculated in Part A.

$$\text{Flow rate} = \text{Velocity} \times \text{Area}$$

$$3{,}757 \text{ ft/min} \times (3.14 \text{ ft}^2)$$

$$= 11{,}797 \text{ ACFM}$$

Explanation:

The reduction in hood static pressure from –1.7 in. W.C. to –1.1 in. W.C. corresponds to a 20%

decrease in the gas volumetric flow rate from 11,797 ACFM to 9,495 ACFM.
The flow-capture velocity equation, Equation 3-3, may be modified with different hood designs. For example, with a wide flanged hood, Equation 3-3 should be multiplied by 0.75, which indicates that the volumetric flow rate may be decreased by 25% when a flanged hood is used.

Transport Velocity

When a particulate-laden gas stream is captured by the hood system and enters the ductwork, a minimum transport velocity must be maintained to keep the particulate from settling out of the gas flow stream and depositing in the ductwork. This will lead to decreased hood capture efficiencies and increased fugitive emissions. Systems having particulate-laden gas streams should have clean-out ports installed to remove particulate that has settled out.

The duct diameter is a key element when addressing minimum transport velocity. Particles will settle out if a section of ductwork has a larger than necessary diameter. However, if a section of ductwork is too small, the pressure drop will increase across this section, thus requiring the fan to handle more static pressure. Another concern when dealing with transport velocities is the abrasion of the ductwork, especially of the bends or elbows. Abrasion is dependent upon several factors, including the duct velocity, the amount and type of particulate in the gas stream, and the construction of the ductwork.

Example transport velocities are found in Table 3-10. More details can be found in standard texts concerning hoods and ventilation systems.

Table 3-10. Commonly recommended transport velocities.	
Type of Pollutant	**Transport Velocity**
Gases	~1,000–2,000 ft/min
Light particulate loading	~3,000–3,500 ft/min
Normal particulate loading	~3,500–4,500 ft/min

PROBLEM 3-7

A duct system transporting a very light dust requires a minimum transport velocity of 2,800 ft/min. The volumetric flow rate for the system is 978 ACFM. What is the necessary duct diameter in inches for this section of ductwork to maintain the minimum transport velocity?

Given: Minimum transport velocity = 2,800 ft/min
                   Volumetric flow rate = 978 ACFM

SOLUTION

Step 1. Calculate the duct area.

$$\text{Duct area} = \frac{\text{Gas volumetric flow rate}}{\text{Minimum transport velocity}}$$

$$= \frac{978\text{ft}^3\,\min}{2{,}800\text{ft/min}}$$

$$= 0.349\text{ft}^2$$

Step 2. Calculate the duct diameter.

$$\text{Duct Area} = \frac{\pi D^2}{4}$$

$$D^2 = \frac{4\left(0.349\text{ft}^2\right)}{3.14}$$

$$= 8\text{ inches}$$

HOODS SUMMARY

Hoods are the first component of the air pollution control system and are of critical importance. Fugitive emissions from a hood reduce the overall collection efficiency of the system. While many factors affect hood capture efficiency, the most important is the distance between the pollutant source and the hood entrance.

The geometry of the hood entrance influences the hood entry loss coefficient and the hood static pressure due to the formation of the vena contracta. Comparing the hood static pressure against baseline conditions provides a good indicator if the system has developed any problems. When the gas stream contains PM, it is necessary to maintain a minimum transport velocity to prevent particulate build-up in the ductwork.

3.4 FANS

Introduction

Fans are used to control the gas flow rate from the point of pollutant generation from the process equipment, through the air pollution control devices, and out through the stack to the atmosphere. Fans provide the energy required for the gas stream to overcome the flow resistance associated with the hood, ductwork, and air pollution control devices. Fan performance is an important component of inspections and other evaluations of system performance.

TYPES OF FANS AND FAN COMPONENTS

There are two main types of fans: axial and centrifugal. Air pollution control systems normally use centrifugal fans.

Axial Fans

An axial fan, shown in Figure 3-20, utilizes a set of propeller blades mounted on a rotating shaft, similar to a standard house ventilation fan. It is commonly used for moving large quantities of air against very low static pressures.
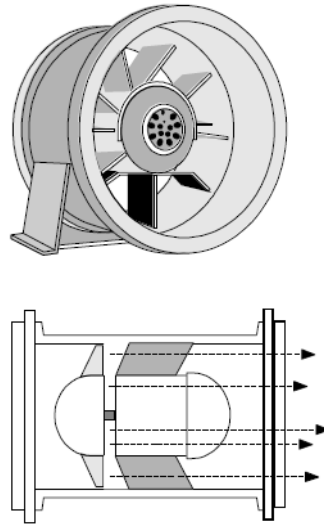
Figure 3-20. Axial fan.

Centrifugal Fans

A centrifugal fan, shown in Figure 3-21, contains a number of fan blades mounted around a hub, which turns on a shaft that passes through the fan housing. The gas enters from the side of the fan wheel, turns 90° and is accelerated as it passes over the fan blades. The term *centrifugal* refers to the trajectory of the gas stream as it passes out of the fan housing.
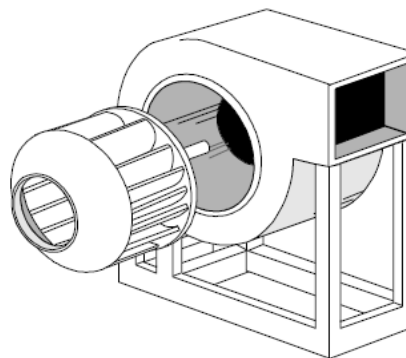
Figure 3-21. Centrifugal fan.

Centrifugal fans are capable of generating higher pressures than axial fans. Accordingly, they are well suited for industrial processes and air pollution control systems. The remainder of this section concerns centrifugal fans.

Components of Centrifugal Fans

The major components of a centrifugal fan include the fan wheel, fan housing, drive mechanism, and inlet and/or outlet dampers. A wide variety of fan designs serve different applications.

The *fan drive* determines the speed of the fan wheel and the extent to which this speed can be varied. Fan drives can be grouped into three basic categories:

1. Direct drive
2. Belt drive
3. Variable drive

In a *direct drive* arrangement, the fan wheel is linked directly to the shaft of the motor. Therefore, the fan wheel speed is identical to the motor rotational speed and cannot be varied (as with variable drive fans).

Belt-driven fans are connected to the drive motor by a belt mounted on sheaves connected to the motor and fan wheel shafts as shown in Figure 3-22.
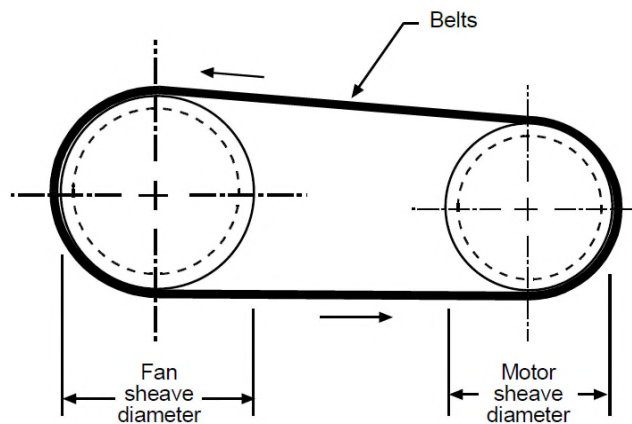
Figure 3-22. Centrifugal fan and motor sheaves.

The fan wheel speed is related to the motor speed and the ratio of the fan wheel sheave diameter to the motor sheave diameter, as indicated in Equation 3-8.

(Eq. 3-8)
$$RPM_{(Fan)} = RPM_{(Motor)} * \frac{D_{(Motor)}}{D_{(Fan)}}$$

Where:
$$RPM_{(Fan)} = \text{fan speed} (\text{revolutions per minute})$$
$$RPM_{(Motor)} = \text{motor speed} (\text{revolutions per minute})$$

$D_{(Fan)}$ = diameter of fan sheave(inches)

$D_{(Motor)}$ = diameter of fan sheave(inches)

Fan Speed

The fan speed can be adjusted by changing the diameter of either the fan or motor sheave. However, there are very definite safety limits to the extent to which the fan speed can be increased. If the fan rotational speed is excessive, the fan can disintegrate. For given sheave sizes, the fan wheel speed is fixed unless the belts slip. Belt slippage normally reduces fan wheel speed several hundred rpm and creates a noticeable squeal.

Variable-speed fans use hydraulic or magnetic couplings that allow the operator to control the fan wheel speed independent of the motor speed. Fan speed controls are often automated to maintain the desired fan performance over a variety of process operating conditions.

Inlet and/or outlet dampers are used with centrifugal fans. Dampers on the outlet side impose a flow resistance that is used to control gas flow. Dampers on the inlet side control gas flow and affect how the gas enters the fan wheel at different operating conditions. Inlet dampers conserve fan energy due to their ability to affect the airflow pattern into the fan. The fan wheel consists of a hub and a number of fan blades that can be forward-curved, backward-curved, or radial.

Forward-curved fans (Figure 3-23A) use blades that curve toward the direction of rotation of the fan wheel. These fans are used against low to moderate static pressures, but they are not recommended for particulate-laden gas streams.

Backward-curved fan blades (Figure 3-23B) provide high-energy efficiency and intrinsic non-overloading characteristics. These fans are also prone to solids build-up and should only be used when the air contains no condensable or particulate matter.

Radial blades (Figure 3-23C) extend straight out from the hub. The radial blade fan is the "workhorse" for most exhaust systems and is less sensitive to solids build-up on the blades.
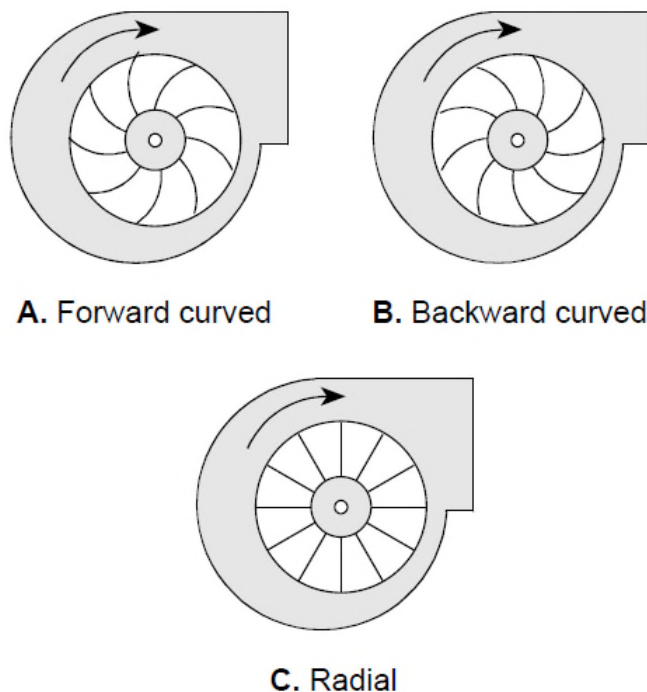
Figure 3-23. Types of centrifugal fan wheels.

CENTRIFUGAL FAN OPERATING PRINCIPLES

A basic understanding of fan operating principles is necessary to evaluate their performance in industrial air pollution control processes. The fan operating speed is one of the most important operating variables. Most fans, such as the example radial blade centrifugal fan shown in Figure 3-24, can operate over a modest range of speeds.
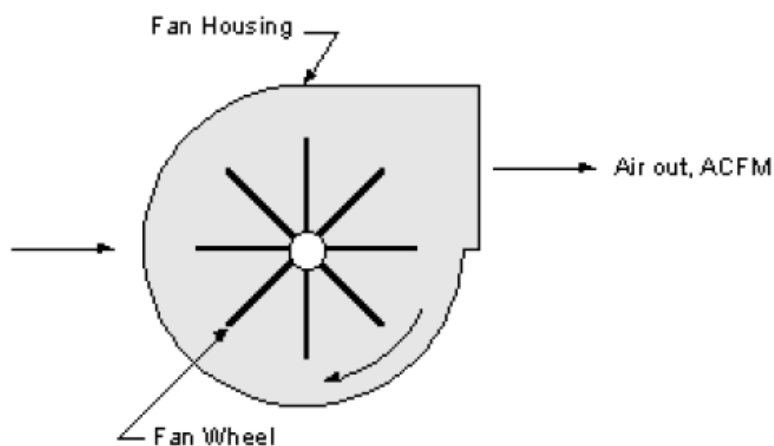
Figure 3-24. Centrifugal fan with radial blade.

The First Fan Law (Equation 3-9) states that the gas volumetric flow rate is directly proportional to the fan rotational speed.

(Eq. 3-9)
$$Q_2 = Q_1 \left(\frac{RPM_2}{RPM_1} \right)$$

Where:

Q_1 = baseline air flow rate $(ACFM)$

Q_2 = present air flow rate $(ACFM)$

RPM_1 = baseline fan wheel rotation speed (revolutions per minutes)

RPM_2 = present fan wheel rotation speed (revolutions per minutes)

Explanation

A 50% increase in rotational speed will produce a 50% increase in volumetric gas flow rate, which is generally expressed in ACFM. This is helpful because this value is independent of gas density. In this respect, a fan is much like a shovel. It moves a specific volume of gas per minute regardless of the gas temperature (density).

The static pressure of the gas stream moving through the fan increases due to the mechanical energy expended by the rotating fan wheel. As indicated in Figure 3-25, the static pressure at the fan outlet is always higher than the static pressure at the inlet. The static pressure rise across the fan is denoted by Fan ΔSP.

Fan ΔSP = 0.05 - (-10) - (0.50) = 9.55 in. W.C.
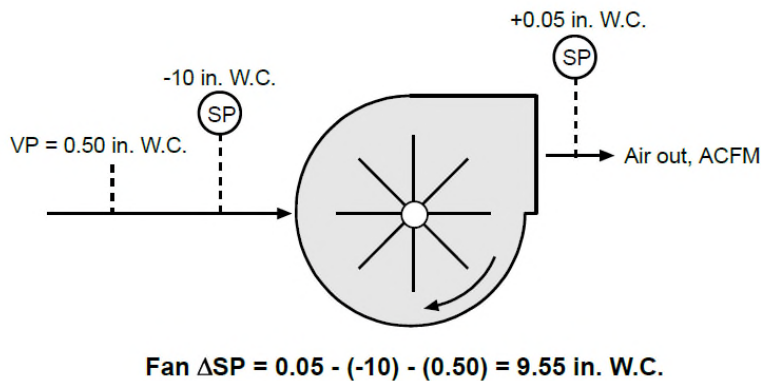
Figure 3-25. Fan static pressure rise.

The Second Fan Law (Equation 3-10) states that the Fan ΔSP is proportional to the square of the fan speed. Thus, a 50% increase in fan speed will result in an increase in Fan ΔSP by a factor of 2.25. The fan static pressure rise is usually expressed in units of inches of water column (in. W.C.).

(Eq. 3-10)
$$Fan\Delta SP_2 = Fan\Delta SP_1 \left(\frac{RPM_1}{RPM} \right)$$

Where:

$$\text{Fan}\Delta SP_1 = \text{baseline fan static pressure rise (in. W.C.)}$$
$$\text{Fan}\Delta SP_2 = \text{present fan static pressure rise (in. W.C.)}$$
$$RPM_1 = \text{baseline fan wheel rotation speed (revolutions per minute)}$$
$$RPM_2 = \text{present fan wheel rotation speed (revolutions per minute)}$$

The fan specifications for an air pollution control system are based on the gas flow rate and fan static pressure rise needed to properly capture, transport, and control the emissions. As indicated in the block flowcharts introduced earlier in this chapter, each process to be controlled may include one or more capture hoods, ductwork, air pollution control systems, the fan, and a stack. The gas flow rate must be sufficient to provide adequate pollutant capture at the hoods and to ensure proper transport of the pollutant-laden air through the entire system.

The fan static pressure rise must be sufficient to accelerate the air entering the hoods and to overcome the flow resistances of the hoods, ductwork, air pollution control systems, and stack at the prescribed volumetric flow rates. The changes in the gas stream static pressure from the point of entry into the hood to the point of entry into the fan are illustrated in Figure 3-26 for an example process.
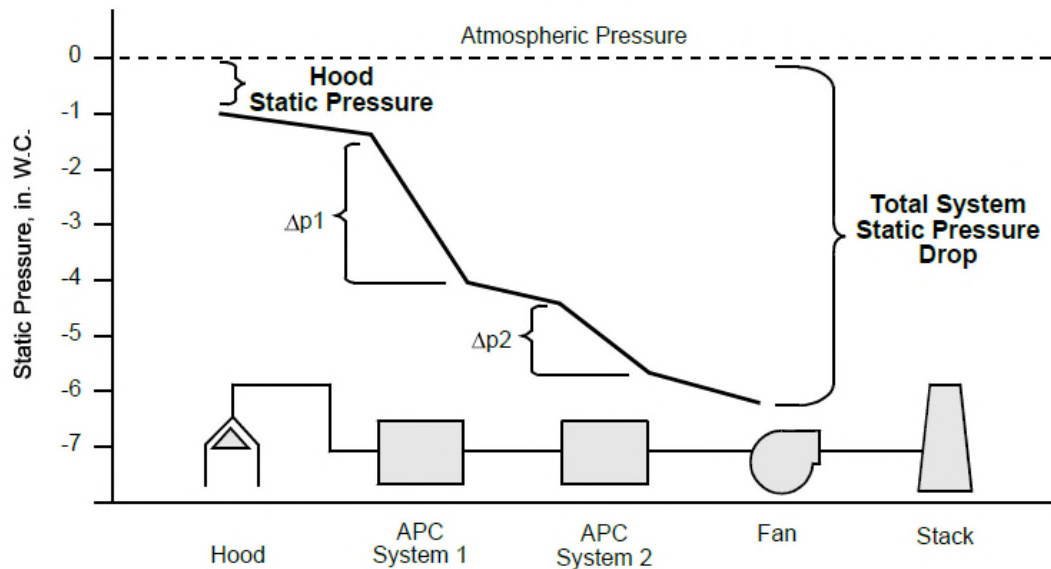
Figure 3-26. Total system static pressure drop.

The design of a system, such as the one shown in Figure 3-26, starts by specifying the air velocities in the hoods, ductwork, air pollution control system, and stack. These velocities are selected based on established engineering design principles to ensure high efficiency hood capture, proper operation of the air pollution control systems, and proper dispersion of the effluent gas stream from the stack. The total static pressure drop across each component of the overall system is related to the square of the gas flow rate, as illustrated in Figure 3-27.
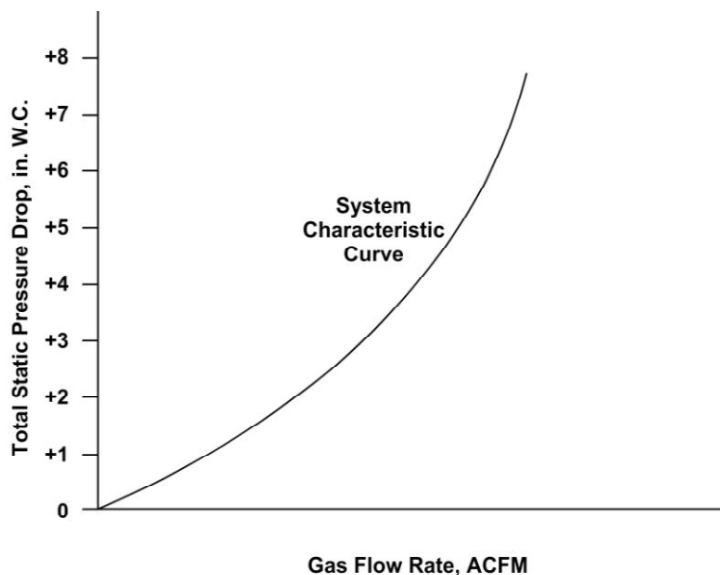
Figure 3-27. System characteristic curve.

This general relationship between total system static pressure drop and gas flow rate is termed the *system characteristic curve*. As an example, let us assume that a gas flow rate of 12,000 ACFM is needed and that the total static pressure drop across the system is 10 in. W.C. Therefore, the fan selected must be able to provide the flow rate and static pressure rise.

The fan supplies sufficient energy to increase the gas static pressure from the minimum level exiting the last air pollution control system to a static pressure slightly above ambient absolute pressure. This is illustrated in Figure 3-28, which is simply the static pressure profile chart shown in Figure 3-26 with the addition of the static pressure increase associated with the fan.
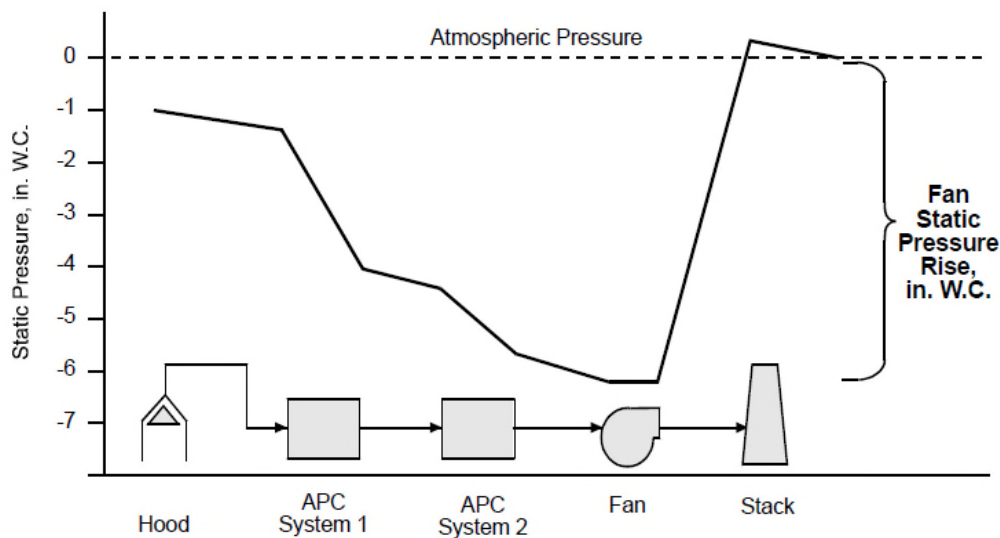
Figure 3-28. Fan static pressure rise profile.

An appropriate fan may be selected based on fan manufacturer's performance data, usually provided as multi-ratings tables published for each specific fan model and size. From the multi-rating table it is possible to select a fan model, the specific size of that model, and the fan speed necessary to achieve the gas flow rate and static pressure rise conditions required for the overall air pollution control system. Most fans are selected to operate at a speed near the middle of its safe operating range. An excerpt from a multi-rating table for a centrifugal fan is shown below in Figure 3-29.

194 LS

Inlet diameter: 11" O.D. | Wheel diameter: 19⅛"
Outlet area: .660 sq. ft. inside | Wheel circumference: 5.01 ft

CFM	OV	2"SP RPM	2"SP BHP	4"SP RPM	4"SP BHP	6"SP RPM	6"SP BHP	8"SP RPM	8"SP BHP	10"SP RPM	10"SP BHP	12"SP RPM	12"SP BHP	14"SP RPM	14"SP BHP	16"SP RPM	16"SP BHP	18"SP RPM	18"SP BHP
660	1000	995	0.48	1392	1.01	1698	1.60	1960	2.27	2191	2.98	2399	3.74	2592	4.55	2769	5.38	2938	6.27
792	1200	1008	0.55	1398	1.11	1703	1.75	1962	2.45	2192	3.20	2398	3.99	2588	4.83	2767	5.71	2936	6.65
924	1400	1023	0.62	1405	1.23	1708	1.90	1965	2.64	2194	3.43	2401	4.27	2589	5.14	2766	6.05	2932	7.01
1056	1600	1042	0.71	1418	1.35	1716	2.07	1971	2.84	2197	3.67	2401	4.53	2593	5.46	2769	6.42	2935	7.41
1188	1800	1061	0.80	1431	1.49	1726	2.24	1980	3.06	2203	3.92	2407	4.83	2593	5.78	2771	6.79	2936	
1320	2000	1084	0.90	1447	1.64	1739	2.44	1987	3.29	2209	4.19	2414	5.15	2600	6.13	2773	7.16	2940	
1452	2200	1109	1.01	1465	1.80	1753	2.65	1999	3.54	2221	4.49	2422	5.47	2607	6.50	2778	7.55	2943	
1584	2400	1136	1.13	1485	1.98	1769	2.87	2012	3.80	2229	4.78	2431	5.82	2612	6.87	2786	7.98	2949	
1716	2600	1162	1.26	1505	2.16	1784	3.10	2025	4.08	2242	5.11	2441	6.18	2623	7.28	2791	8.40	2956	
1980	3000	1223	1.56	1554	2.58	1824	3.62	2059	4.70	2272	5.82	2464	6.95	2644	8.14	2815	9.38	2973	
2244	3400	1290	1.91	1606	3.04	1867	4.19	2098	5.38	2305	6.59	2495	7.83	2671	9.09	2838	10.4	2995	
2508	3800	1361	2.33	1661	3.56	1917	4.84	2141	6.12	2345	7.44	2531	8.78	2703	10.1	2866	11.5	30	
2772	4200	1439	2.83	1723	4.16	1968	5.54	2189	6.95	2387	8.37	2569	9.80	2740	11.3	2900	12.8		
3036	4600	1519	3.40	1788	4.84	2025	6.32	2239	7.85	2432	9.36	2611	10.9	2780	12.5	2937	14.1		
3300	5000	1603	4.07	1855	5.58	2086	7.20	2294	8.83	2483	10.5	2660	12.1	2825	13.8	2978	15.5		
3564	5400	1691	4.84	1929	6.45	2148	8.14	2350	9.88	2536	11.6	2708	13.4	2859	15.2	3024	17.0		
3828	5800	1781	5.73	2005	7.41	2214	9.18	2409	11.01	2591	12.9	2759	14.8	2917	16.7	3069	18		

Figure 3-29. Portion of a typical multi-rating table.
(Reprinted courtesy of the New York Blower Company).

The match between the fan performance data and the system characteristic curve is illustrated in Figure 3-30 for the specific fan rotational speed chosen. As long as the overall system and the fan remain in good condition, the system will operate at the *operating point*, shown in Figure 3-30.
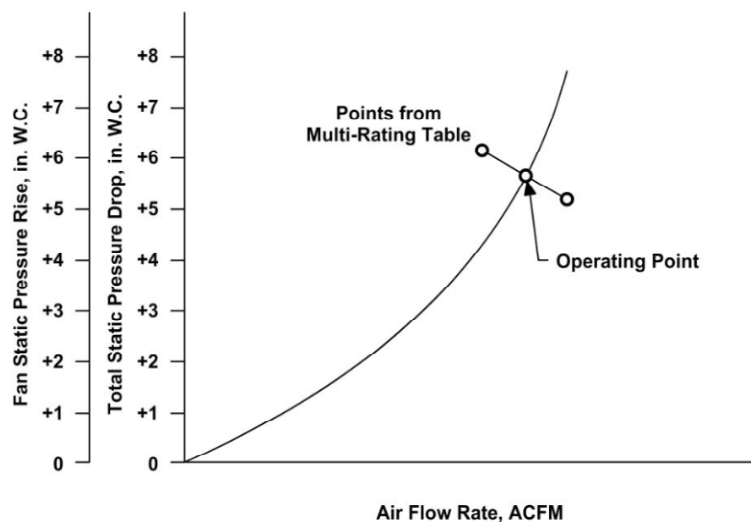
Figure 3-30. Operating point.

When the total system static pressure drop and the fan static pressure rise are shown on the same graph, as in the case with Figure 3-30, it is convenient to simply delete the total system static pressure drop axis.

Figure 3-31 illustrates the system characteristic curve and a complete fan curve determined using the multi-rating table for a particular fan model, size, and rotational speed. The intersection of the two curves at Point A is the operating point for the process.
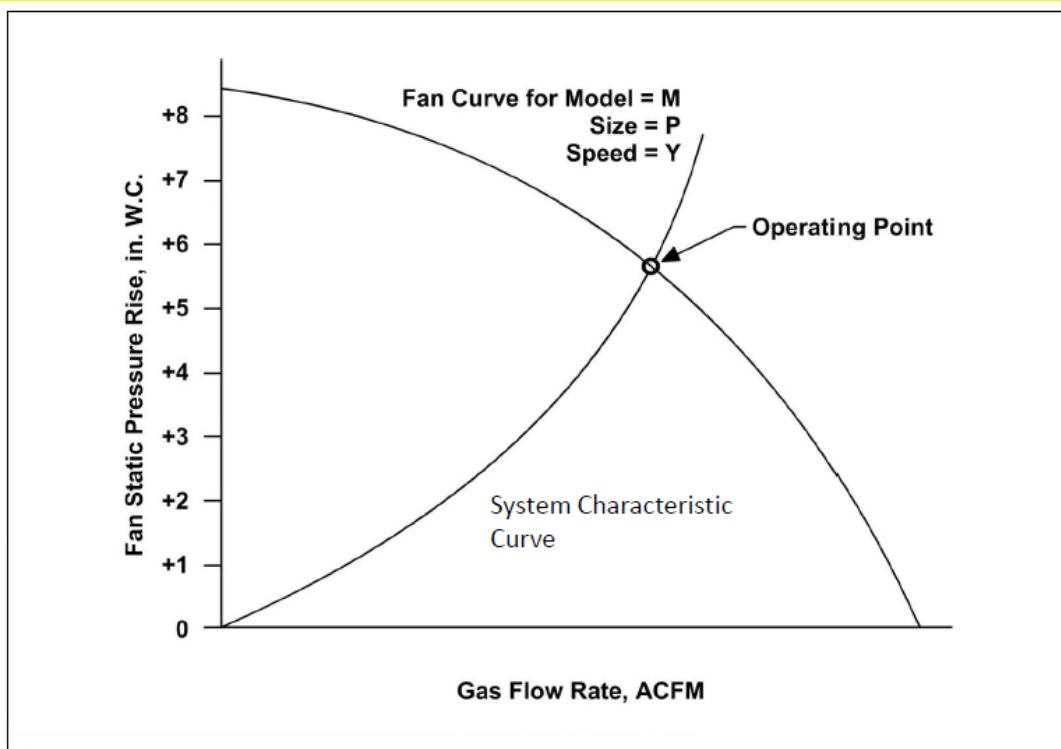
Figure 3-31. Fan characteristic curve.

Air pollution control systems, however, do not necessarily remain exactly at the conditions anticipated by the system designer and the fan manufacturer. For example, system changes such as an increase or decrease in gas flow rate will cause the system characteristic curve to change, which, in turn, will cause the system static pressure to change. The results of specified changes are illustrated in Figures 3-32 through 3-34, based on the system and fan characteristic curves.

If the gas flow resistance increases due, for example, to the build-up of PM in the air pollution control device or partially closing a damper, the system characteristic curve will shift upward and a new operating point, labeled B in Figure 3-32, will be established. At this new operating point, the fan static pressure rise will be slightly higher, while the airflow rate will be slightly lower.

If the airflow resistance decreases due to a damper being opened, for example, the system characteristic curve will shift downwards, and a new operating point, labeled C, will be established at a slightly reduced fan static pressure and increased air flow rate.

Decreased system resistance, resulting in increased gas flow rate and reduced static pressure increase, can create problems. While this change would favor improved hood capture, it could reduce the collection efficiency of the air pollution control device. Increased gas velocities through certain types of air pollution control systems, such as fabric filters, electrostatic precipitators, carbon bed adsorbers, and catalytic oxidizers, can reduce capture or destruction efficiency.
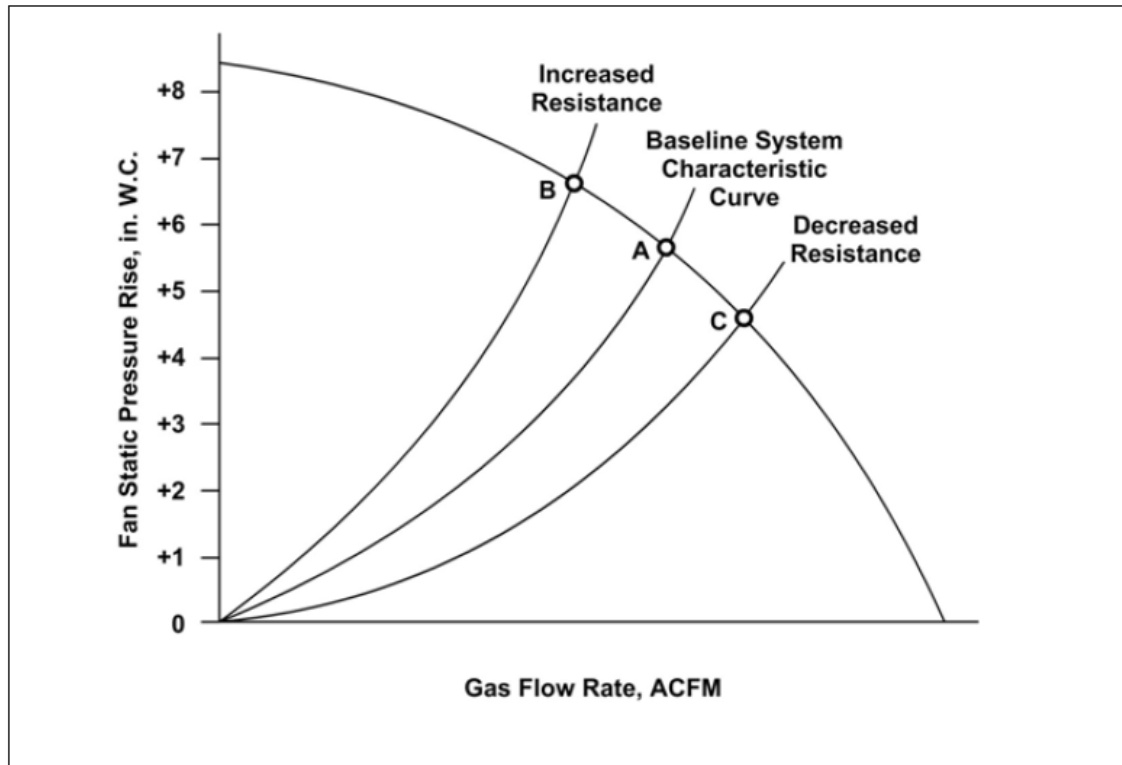
Figure 3-32. Changes in the system resistance curve.

Some changes in the system characteristic curve are to be expected due to factors such as (1) air pollution control system cleaning cycles, (2) gradually increasing air infiltration between maintenance cycles, and (3) the opening and closing of dampers on individual process sources ducted into the overall ventilation system. The system must be designed to provide adequate pollutant capture even at the lowest normally occurring airflow rates.

When changes in the system characteristic curve are outside of the anticipated range, fan-operating conditions may be modified. Increases (or decreases) in the fan speed will result in increased (or decreased) gas flow rates and static pressure rises without exceeding the safe operating speed limits. Results of this type of change are illustrated in Figure 3-33.
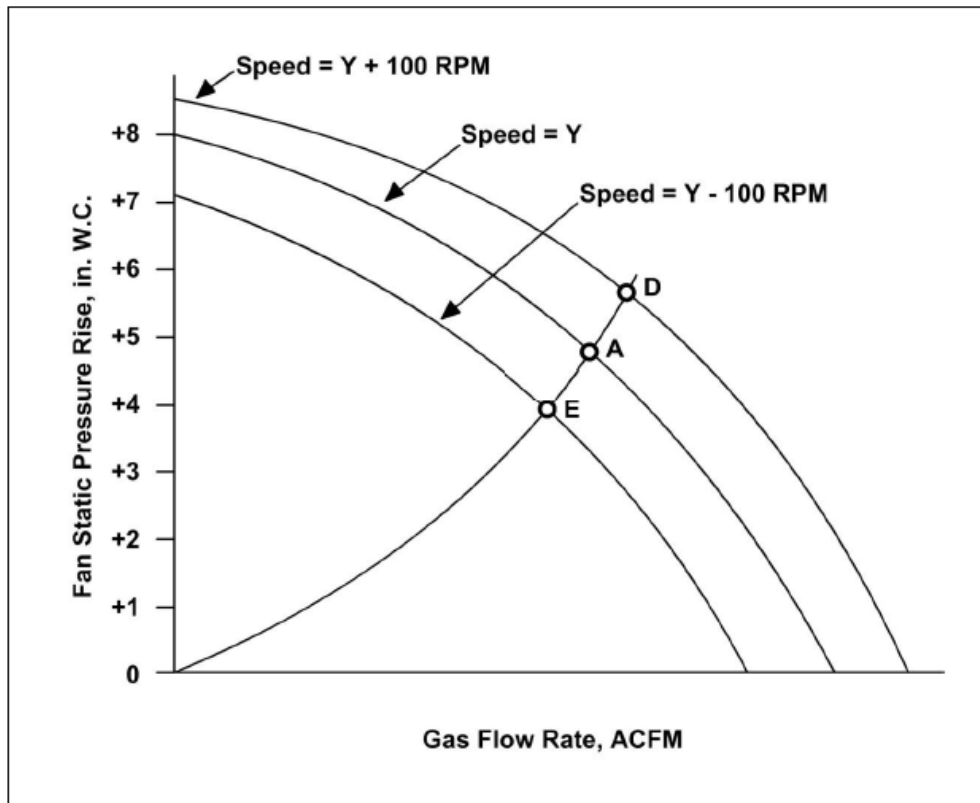
Figure 3-33. Changes in the fan speed.

Increased fan speed results in a new operating point, labeled D, having an air flow rate and fan static pressure rise that are both larger than the normal conditions represented by operating point A. Not all fans can be easily adjusted to change the fan speed. Direct drive fans where the fan wheel shaft is directly driven by the fan motor operate only at the motor rotation speed and cannot be adjusted. Belt-driven fans can be adjusted, but only by changing one or both of the sheaves on the fan and motor. Some large fans with hydraulic or magnetic drives have easily adjusted fan speeds.

Inadvertent reductions in fan speed are possible for belt-driven fans due to belt slippage. As shown in Figure 3-33, this would result in a decrease in both gas flow rate and system static pressure.

The system operating point can also change as a result of opening or closing the fan inlet damper, as illustrated in Figure 3-34. It is apparent that the operating point changes to a lower gas flow rate and fan static pressure rise as the inlet damper is closed. The opposite effect results from opening the inlet damper.
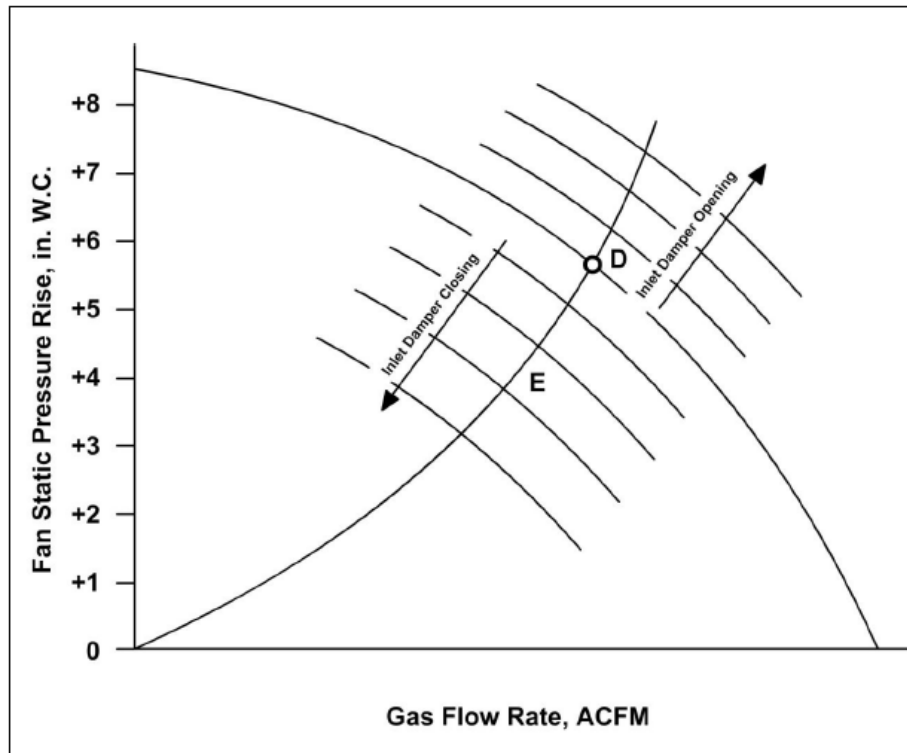
Figure 3-34. Changes in the inlet damper position.

The fan inlet damper is often used to ensure safe operation of a fan when the gas stream is at an elevated temperature. During start-up when the gas is cold, the fan inlet damper is kept partially closed to minimize the quantity of dense cold air moved through the system. As the air heats and becomes less dense, the fan inlet damper is opened to increase the gas flow rate and the fan static pressure rise. This approach minimizes the electrical power demand on the fan motor. Starting with the fan inlet dampers wide open causes the motor to draw excessive current that could result in burnout of the motor windings. It is very important to avoid exceeding the maximum fan motor current specification.

PROBLEM 3-8

A portion of a ventilation system is shown in Figure 3-35. The static pressure drop across the system measured at the fan inlet is -16.5 in. W.C. at a gas flow rate of 8,000 ACFM. Estimate the static pressure drop if the flow rate increased to 12,000 ACFM.
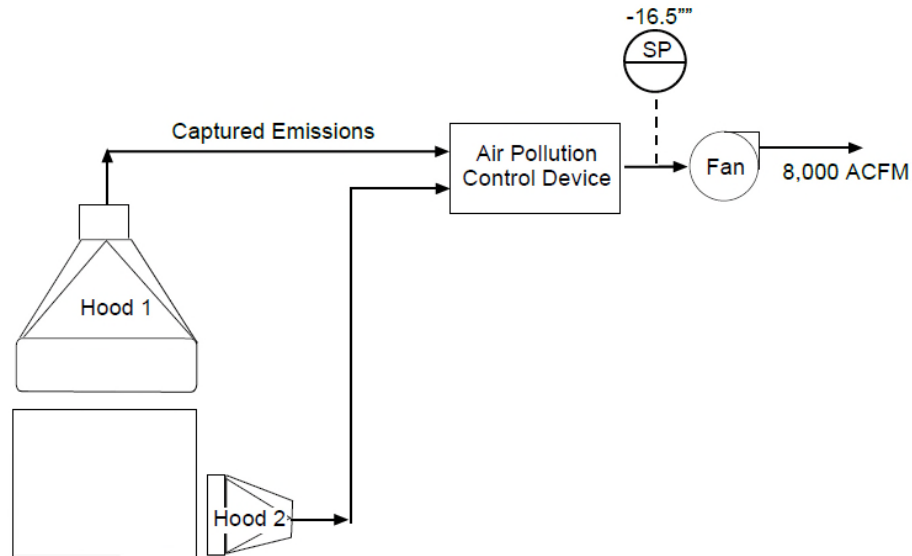
Figure 3-35. Portion of a ventilation system.

SOLUTION

By combining the First and Second Fan Laws (Equations 3-9 and 3-10), we find that:

$$\frac{SP_{@High\ flow}}{SP_{@Low\ flow}} = \frac{(12,000\ ACFM)^2}{(8,000\ ACFM)^2} = 2.25$$

$$\begin{aligned} SP_{@High\ flow} &= SP_{@Low\ flow}\ (2.25) \\ &= -16.5\ in.\ W.C. * (2.25) \\ &= -37.13\ in.\ W.C. \end{aligned}$$

Note: This solution is based on the assumption that there are no significant changes in gas density due to the increase in gas flow rate.

Problem 3-8 illustrates that an increase in the gas flow rate of 50% more than doubles the static pressure drop across the system.

It is helpful to be able to determine when the system characteristic curve has shifted. While the most direct method is to measure the gas flow rate, this is time-consuming. The fan motor current provides an indirect but useful indication of gas flow changes from the baseline conditions. An increase in gas flow rate causes an increase in fan motor current, while a decreased flow rate results in decreased motor current. Unfortunately, the relationship between gas flow rate and motor current is not linear. The nonlinear characteristic of the relationship is indicated by the *brake horsepower curve*, shown in Figure 3-36. The fan motor current is directly proportional to the brake horsepower as indicated by Equation 3-11, which applies to three-phase motors.

(Eq. 3-11) $$\text{BHP} = \frac{\text{I} \times \text{E} \times 1.73 \times \text{Eff} \times \text{P.F.}}{745}$$

Where:

BHP	= brake horsepower (total power consumed by the fan)
I	= fan motor current (amperes)
E	=voltage (volts)
E	= efficiency expressed as decimal
P.F.	= Power Factor

While the exact shape of the horsepower curve varies for different types of fans, the general relationship applies to all centrifugal fans in their normal operating range.
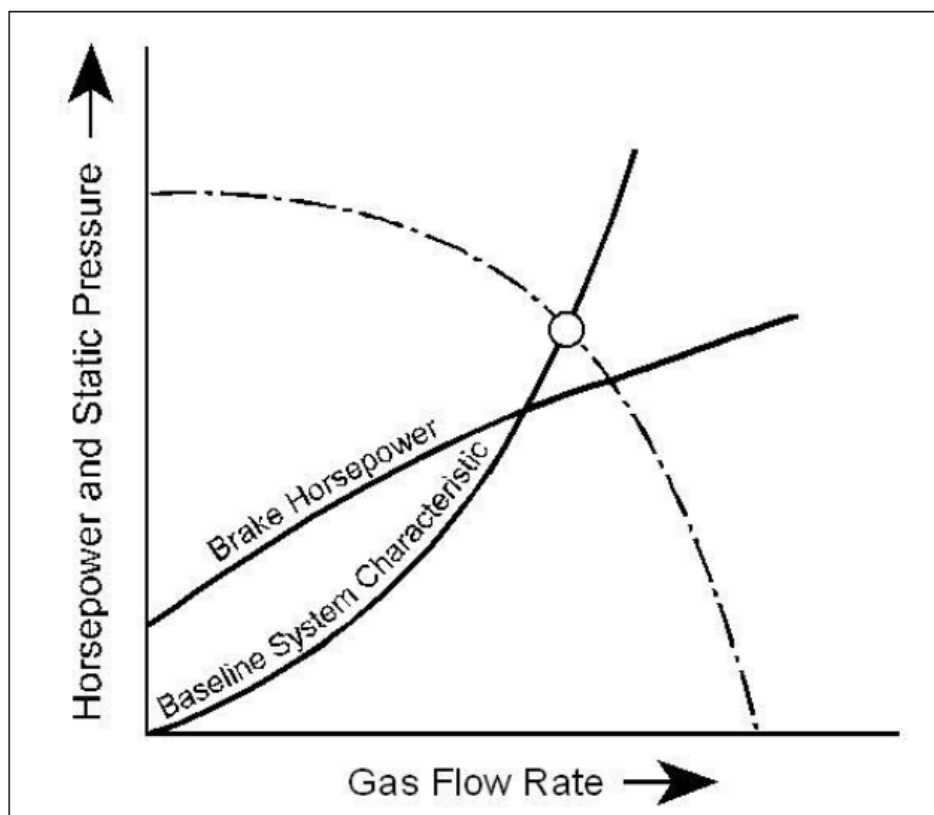
Figure 3-36. Example of a brake horsepower curve.

The Third Fan Law states that the brake horsepower is proportional to the cube of the fan rotational speed, as shown in Equation 3-12.

(Eq. 3-11) $$\text{BHP}_2 = \text{BHP}_1 \left(\frac{\text{RPM}_2}{\text{RPM}_1} \right)^3$$

Where:

$\text{BHP}_1 = \text{baseline brake horsepower (BHP)}$

$\text{BHP}_2 = \text{present brake horsepower (BHP)}$

$$\text{RPM}_1 = \text{baseline fan wheel rotation speed (revolutions per minute)}$$
$$\text{RPM}_2 = \text{present fan wheel rotation speed (revolutions per minute)}$$

The fan motor current is measured by the fan ammeter, which is monitored either in the main control room or in a remote fan control room.

EFFECT OF GAS TEMPERATURE AND DENSITY ON CENTRIFUGAL FANS

A fan operates like a high-speed shovel. Every rotation of the fan wheel at a given set of operating conditions moves a constant volume of gas. While the volume is constant, the weight of the air being moved depends on the air density. At high temperature, the gas has a low density, but when the gas is at low temperature, the density is higher. The density of a gas at pressures near ambient is given by a form of the ideal gas law:

(Eq. 3-13) $$\rho = \frac{PM}{RT}$$

Where
$$\rho = \text{gas density,} \text{lb}_m/\text{ft}^3$$
$$P = \text{pressure, atm}$$
$$M = \text{molecular weight of gas,} \text{lb}_m/\text{lb mol} \ (M = 29 \text{ for air})$$
$$T = \text{absolute temperature, } °R$$
$$R = \text{gas constant} = 0.7302 \text{ ft}^3 \text{ atm/lb mol } °R$$

The density ρ_2, at temperature T_2 and pressure P_2, compared to the density ρ_1, at temperature T_1 and pressure P_1, can be found by using a ratio of the ideal gas law. This eliminates the effect of molecular weight and the gas constant.

(Eq. 3-14) $$\frac{\rho_2}{\rho_1} = \left(\frac{P_2}{P_1}\right)\left(\frac{T_1}{T_2}\right)$$

Recall that the density of air at EPA standard conditions of 1 atm and 68°F is 0.075 lb$_m$/ft^3. Thus the density of air at any temperature, T_2, and pressure, P_2, can be easily calculated.

$$\rho_2 = (0.075 \text{ lb}_m/\text{ft}^3)(P_2/1 \text{ atm})(528 \ °R/T_2) = 39.6 \ (P_2/T_2)$$

In the above equation, the units of ρ_2 are lb$_m$/ft^3, the units of P_2 are atm, and the units of T_2 are °R.

The gas density has a direct effect on the fan motor current. When the gas is at low temperature (with corresponding high density), such as during process start-up, the current will be high. If steps are not taken to minimize gas flow during cold operating periods, the fan motor could burn out due to excessive current flow. To prevent the possibility of burning out the fan motor during these periods, the fan inlet or outlet dampers are usually partially closed during start-up to restrict the gas flow. The dampers may then be gradually opened as the gas is heated to the normal operating temperature. When using the fan motor current as an indicator of gas flow rate, it is important to correct the motor current at the actual conditions back to standard conditions. This correction can be performed using Equation 3-15.

(Eq. 3-15) $$I_{STD} = I_{Actual}\left(\frac{\rho_{STP}}{\rho_{Actual}}\right)$$

Where: I_{STP} = fan motor current at standard conditions (amperes)

                I_{Actual} = fan motor current at actual conditions (amperes)

                ρ_{STP} = gas density at standard conditions $\left(lb_m/ft^3\right)$

                ρ_{Actual} = gas density at actual conditions $\left(lb_m/ft^3\right)$

PROBLEM 3-9

A fan motor is operating at 80 amps and the airflow rate through the system is 10,000 ACFM at 300°F and -10 in. W.C. (fan inlet). What is the motor current at standard conditions?

SOLUTION

Step 1. Calculate the gas density at actual conditions.

As a basis, use 1 lb$_{mol}$ of gas. Assume 1 lb$_{mol}$ of gas has a mass of 29 pounds (this implies that the gas is air).

     a)   Convert pressure from inches of water (gauge) to atm (absolute).

$$\left[\frac{\left(407 \text{ in. W.C.} - 10 \text{ in. W.C.}\right)}{407 \text{ in. W.C.}}\right] = 0.975 \text{ atm } \left(\text{or } 14.34 \text{ psia}\right)$$

     b)   Calculate the gas volume (per lb$_{mol}$) at actual conditions using the ideal gas law equation.

$$V \ (per \ lb_{mol}) = \frac{RT}{P}$$

$$V = \frac{\left(0.7302 \frac{ft^3 * atm}{lb_{mol} * °R}\right)\left(300°F + 460°F\right)}{0.975 \text{ atm}}$$

$$= 569 \text{ ft}^3 \left(per \ lb_{mol}\right)$$

     c)   Calculate the gas density, ρ.

$$\rho = \frac{\text{Mass}}{\text{Volume}}$$

Mass = 29 lb_m / lb_{mol}

Volume = 569 ft^3 / lb_{mol} (*at actual conditions*)

$$\rho = \frac{29 \text{ lb}_m/\text{lb}_{mol}}{569 \text{ ft}^3/\text{lb}_{mol}} = 0.051 \frac{\text{lb}_m}{\text{ft}^3}$$

Step 2. Calculate the gas density at standard conditions.

a) Calculate the gas volume at standard conditions using the ideal gas law.

$$V\left(\text{per lb}_{mol}\right) = \frac{RT}{P}$$

$$V = \frac{\left(0.7302 \dfrac{\text{ft}^3 * \text{atm}}{\text{lb}_{mol} * {}^\circ R}\right)\left(68^\circ + 460^\circ F\right)}{1 \text{ atm}}$$

$$= 385.5 \text{ft}^3 \left(\text{per lb}_{mol}\right)$$

b) Calculate the gas density, ρ.

$$\rho = \frac{29 \text{ lb}_m/\text{lb}_{mol}}{385.5 \text{ ft}^3/\text{lb}_{mol}} = 0.075 \frac{\text{lb}_m}{\text{ft}^3}$$

Step 3. Correct the motor current for the change in gas density.

$$I_{STP} = I_{Actual}\left(\frac{\rho_{STP}}{\rho_{STP}}\right)$$

$$= 80 \text{ amps}\left(\frac{0.075 \text{ lb}_m/\text{ft}^3}{0.051 \text{ lb}_m/\text{ft}^3}\right)$$

$$= 80 \text{ amps}(1.47)$$

$$= 118 \text{ amps}$$

The temperature and pressure corrections for gas density must also be used when selecting a fan. The fan multi-ratings tables are expressed in standard temperatures and pressures. These corrections are needed to ensure that the fan will deliver the necessary gas flow rates and absolute pressure increases under the actual operating conditions anticipated in the process.

The gas temperature is a weak function of pressure. When the gas reaches the fan, the gas flow changes from negative to positive pressure. This increase in pressure can cause the temperature to increase slightly.

FANS – FINAL POINTS

Centrifugal fans are the most commonly used type of fan in industrial processes due to their ability to generate high-pressure rises in the gas stream. The major components of a typical centrifugal fan include the fan wheel, fan housing, drive mechanism, and inlet and/or outlet dampers.

The intersection of the fan characteristic curve and the system characteristic curve establishes the operating point for the fan. The factors that affect the fan characteristic curve are the type of fan wheel and blade, the fan rotational speed, and the shape of the fan housing. The system characteristic curve takes into account the energy losses as the gas flows through the hood, ductwork, and air pollution control device. These curves are helpful indicators in determining if a change in the system has occurred. The fan motor current, which varies nonlinearly with the gas flow rate, can also be used to identify changes in system operating conditions.

The fan laws describe how a fan will be affected by a change in operating conditions. The fan laws apply to fans having the same geometric shape and a system having fixed physical characteristics.

At a fixed rotation speed, a fan will move a constant volume of gas. However, the work required to move this constant gas volume is dependent on the density of the gas. Two factors that affect gas density are temperature and pressure. The gas density has a direct effect on the fan motor current.

3.5 SUMMARY

AIR POLLUTION CONTROL SYSTEMS SUMMARY

This lesson covered the following topics:

- Benefits and components of a basic system flowchart.
- Hood designs and operating principles.
- Identify the variables that contribute to hood efficiency.
- Types of fans and fan components.
- Variables that contribute to fan performance.

Conclusions
- Fan performance is important because it influences pollutant capture efficiency at the point of pollutant generation.
- The fan characteristic curve is determined by the fan wheel design, fan wheel housing configuration, fan speed, damper positions, and inlet and outlet duct configurations.
- The system operating point is the intersection of the fan characteristic curve and the system resistance curve.
- Changes in gas flow rate can be caused by changes in the system resistance curve, fan speed, or damper positions.
- Changes in the gas flow rate are qualitatively indicated by changes in the fan motor current. As current increases, gas flow rate increases.
- Fan motor currents are also a function of gas density. Current should be corrected to standard conditions when comparing operating conditions at two significantly different gas temperatures.

3.6 REVIEW EXERCISES

INSTRUCTIONS

Select the best response(s) for these multiple-choice questions. Use the drawing shown below (Figure 3-37) to answer Review Exercises 1-3.

Figure 3-37. Example flowchart.

1. Which static pressure reading appears to be illogical according to the flowchart?

    a) Duct A
    b) Duct B
    c) Duct D
    d) They all appear logical

2. Calculate the static pressure at the inlet to the centrifugal fan. (Exclude frictional losses of ducts and entry losses.)

    a) 0.7 in. W.C.
    b) –1.7 in. W.C.
    c) –9.2 in. W.C.
    d) None of the above

3. The temperature in Duct A was checked by plant personnel and determined to be correct. Which of the other temperature readings appears to be illogical according to the flowchart?

    a) Duct B
    b) Duct C
    c) Duct D
    d) They all appear logical .

4. The gas flow rate in Duct A is 5,000 SCFM, the temperature is 350°F, and the pressure is –32 in. W.C. The gas flow rate in Duct B is 4,000 ACFM, the temperature is 400°F, and the pressure is –35 in. W.C. Calculate the total gas flow rate in a combined Duct C (SCFM) handling the flows from Ducts A and B. Use a barometric pressure of 29.15 in Hg.

5. Calculate the hood static pressure if the hood coefficient of entry is 0.49 and the gas flow rate through a 1.5-foot diameter duct from the hood is 6,200 ft^3/min. Use standard temperatures and pressures.

   a) –2.1 in W.C.
   b) –1.15 in. W.C.
   c) –0.38 in W.C.
   d) 0.85 in W.C.

6. Find the farthest distance away that a flanged hood, 6 in. × 12 in., can be placed away from the contaminant source and maintain the capture velocity of 300 fpm and a volumetric flow rate of 2,000 ACFM. The equation for a flanged hood is:

   $$Q = (0.75) * v_h \lfloor 10X^2 + A_h \rfloor$$

   a) 15 inches
   b) 24 inches
   c) 3 inches
   d) 11 inches

7. Estimate the rotational speed of a belt-driven centrifugal fan based on the following data:

   Motor rotational speed, $RPM_{Motor} = 1778 RPM$
   Motor sheave diameter, $D_{Motor} = 8$ in.
   Fan sheave diameter, $D_{Fan} = 14$ in.

   a) 1239 RPM_{fan}
   b) 2000 RPM_{fan}
   c) 400 RPM_{fan}
   d) 1016 RPM_{fan}

8. A system consists of the following components (in order): hood, fabric filter, centrifugal fan, and stack. The fabric filter static pressure drop has increased from 4.5 inches of water to 6.5 inches of water. If the fan dampers do not move to compensate for this change, what will happen to the hood static pressure?

   a) It will be less negative (closer to zero)
   b) It will be more negative
   c) It will become positive
   d) It will remain unchanged

9. A centrifugal fan moves 1,000 cubic feet of air per minute at a temperature of 450°F and a fan inlet pressure of –15 inches of water. Calculate the actual air flow rate if the gas temperature decreases to 68°F and the inlet pressure and fan rotational speed remains the same.

   a) The air flow rate will increase to 1,580 ACFM
   b) The air flow rate will decrease to 580 ACFM
   c) The air flow rate will remain at 1,000 ACFM
   d) It is impossible to calculate the air flow rate at the new conditions

10. A centrifugal fan is operating with a motor current of 120 amps. The gas density entering the fan at the operating conditions is 0.045 pounds per cubic foot. Estimate the motor current at standard conditions when the gas density is approximately 0.075 pounds per cubic foot.

   a) 500 amps
   b) 200 amps
   c) 159 amps
   d) 90 amps

11. The static pressure drop through a section of ductwork is –1.2 inches of water when the gas flow rate is 5,000 ACFM. Estimate the static pressure drop across this section of ductwork if the gas flow rate increases to 8,000 ACFM. Assume that there is no gas density change associated with the increased gas flow rate.

   a) 3.07 in. W.C.
   b) 1.1 in. W.C.
   c) 2 in. W.C.
   d) 4 in. W.C.

12. The hood capture efficiency is 92% and the wet scrubber control system has a collection efficiency of 95%. If the process served by this system generates 140 pounds of pollutant per hour, calculate the fugitive emissions and the stack emissions.

    a) 20.50 lb$_m$/hr fugitive emissions and 9.80 lb$_m$/hr stack emissions
    b) 1.50 lb$_m$/hr fugitive emissions and 0.80 lb$_m$/hr stack emissions
    c) 11.20 lb$_m$/hr fugitive emissions and 6.4 lb$_m$/hr stack emissions
    d) 14.0 lb$_m$/hr fugitive emissions and 3.54 lb$_m$/hr stack emissions

13. Assume a fan is presently operating with the following conditions: 20,000 ACFM, –2.5 in. W.C. static pressure, 400 RPM, and 12 brake horsepower. Use the fan laws to determine the new RPM, brake horsepower, and static pressure when the volumetric flow rate increases to 22,500 ACFM.

    a) 490 RPM, 19.1 BHP, –5.7 in. W.C.
    b) 350 RPM, 9.5 BHP, –3.9 in. W.C.
    c) 400 RPM, 10.2 BHP, –2.8 in. W.C.
    d) 450 RPM, 17.1 BHP, –3.2 in. W.C.

14. What would happen to the desired operating point of a fan if a hole developed in the ductwork? Which characteristic curve will shift, what will happen to the operating point, volumetric flow rate, and hood static pressure?

    a) The system characteristic curve will shift down, the volumetric flow rate will increase, and the hood static pressure will increase.
    b) The system characteristic curve will shift down, the volumetric flow rate will decrease, and the hood static pressure will decrease.
    c) The system characteristic curve will shift down, the volumetric flow rate will increase, and the hood static pressure will decrease.
    d) The system characteristic curve will shift up, the volumetric flow rate will increase, and the hood static pressure will decrease.

3.7 REVIEW EXERCISES: SOLUTIONS

This Student Guide includes separate exercises and solutions, which allow students to check their work.
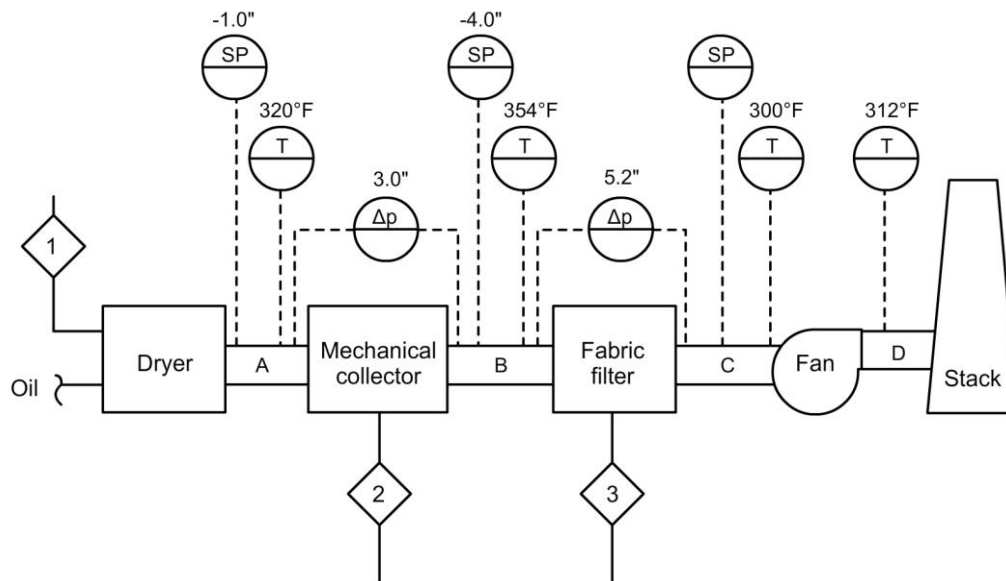
MULTIPLE CHOICE ANSWERS
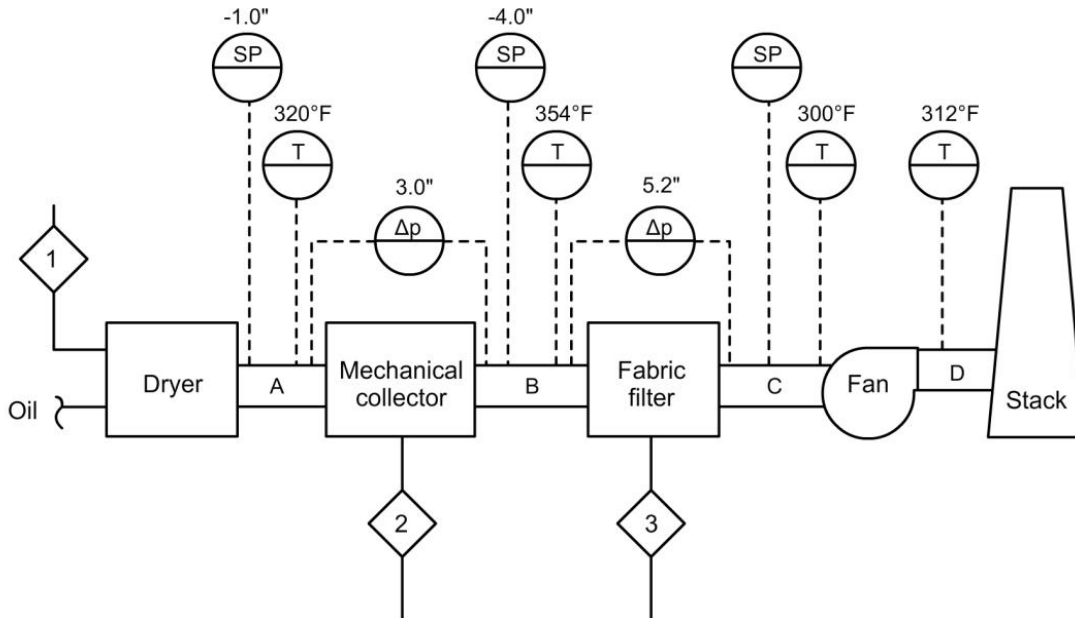
Figure 3-38. Example flowchart.

1. Which static pressure reading appears to be illogical according to the flowchart?

a) Duct A
b) Duct B
c) Duct D
d) They all appear logical

Explanation:
The gas stream decreases in pressure as it approaches the fan inlet.

2. Calculate the static pressure at the inlet to the centrifugal fan. (Exclude frictional losses of ducts and entry losses.)

a) 0.7 in. W.C.
b) –1.7 in. W.C.
c) –9.2 in. W.C.
d) None of the above

SOLUTION

$$\mathrm{SP_{Duct\,C}} = \mathrm{SP_{Duct\,B}} - \Delta\mathrm{SP_{Fabric\,filter}}$$

$$= -4.0 \text{ in. W.C.} - 5.2 \text{ in. W.C.}$$

$$= -9.2 \text{ in. W.C.}$$

3. The temperature in Duct A was checked by plant personnel and determined to be correct. Which of the other temperature readings appears to be illogical according to the flowchart?

    a) Duct B
    b) Duct C
    c) Duct D
    d) They all appear logical

    Explanation:

    The temperatures should decrease as the gas moves through the system since no significant source of energy is added to the gas. There is no reason for the gas stream in Duct B to be hotter than the gas stream in Duct A. Otherwise the temperature trend appears logical.

4. The gas flow rate in Duct A is 5,000 SCFM, the temperature is 350°F, and the pressure is –32 in. W.C. The gas flow rate in Duct B is 4,000 ACFM, the temperature is 400°F, and the pressure is –35 in. W.C. Calculate the total gas flow rate in a combined Duct C (SCFM) handling the flows from Ducts A and B. Use a barometric pressure of 29.15 in Hg.

SOLUTION

Calculate the absolute pressure in Duct B.

$$SP = \left(\frac{407 \text{ in. W.C.}}{29.92 \text{ in. Hg}} \right) * 29.15 \text{ in. Hg} + \left(-35 \text{ in. W.C.} \right)$$

$$= 361.5 \text{ in. W.C.}$$

Convert the flow in Duct B to SCFM using the ideal gas law.

$$V_{STP} = V_B * \left(\frac{T_{STP} * P_B}{T_B * P_{STP}} \right)$$

$$SCFM = \left(4{,}000 \text{ ACFM} \right) \left(\frac{528° R}{400° F + 460° F} \right) \left(\frac{361.5 \text{ in. W.C.}}{407 \text{ in. W.C.}} \right)$$

$$= 2{,}181 \text{ SCFM}$$

Flow in Duct C = Flow in Duct A + Flow in Duct B

$$= 5{,}000 \text{ SCFM} + 2{,}181 \text{ SCFM}$$
$$= 7{,}181 \text{ SCFM}$$

5. Calculate the hood static pressure if the hood coefficient of entry is 0.49 and the gas flow rate through a 1.5-foot diameter duct from the hood is 6,200 ft^3/min. Use standard temperatures and pressures.

   a) –2.1 in W.C.
   b) –1.15 in. W.C.
   c) –0.38 in. W.C.
   d) 0.85 in. W.C.

SOLUTION

To calculate the hood static pressure (SP$_h$), use the following equation:

$$SP_h = -VP_d - h_e$$

Step 1. Calculate the velocity pressure (VP) using the following equation.

At standard conditions, = 0.075 lb$_m$/ft^3. Actual ρ

$$VP_d = \left(\frac{v}{4005} \right)^2 \times \frac{\rho_{Actual}}{0.075}$$

$$\text{Velocity} = v = \frac{6{,}200 \text{ ft}^3/\text{min}}{\pi D^2/4}$$

$$= \frac{6{,}200 \text{ ft}^3/\text{min}}{(3.14)(1.5 \text{ft})^2/4}$$

$$= 3{,}510 \text{ ft/min}$$

$$VP_d = \left[\frac{3510}{4005}\right]^2$$

$$VP_d = 0.77$$

Step 2. Calculate the hood entry loss (he) as follows:

$$h_e = F_h(VP_d)$$

Given: $\quad F_h = 0.49$

$$h_e = 0.49(0.77 \text{ in. W.C.})$$

$$= 0.38 \text{ in. W.C.}$$

Step 3. Calculate the hood static pressure (SPh).

$$SP_h = -0.77 \text{ in. W.C.} - 0.38 \text{ in. W.C.}$$

$$= -1.15 \text{ in. W.C.}$$

6. Find the farthest distance away that a flanged hood, 6 in. × 12 in., can be placed away from the contaminant source and maintain the capture velocity of 300 fpm and a volumetric flow rate of 2,000 ACFM. The equation for a flanged hood is:

$$Q = (0.75) * v_h \lfloor 10X^2 + A_h \rfloor$$

a) 15 inches
b) 24 inches
c) 3 inches
d) 11 inches

SOLUTION

Solve for X using the following equation.

$$\frac{2{,}000 \text{ ACF}}{\text{min}} = (0.75)\left(\frac{300\,\text{ft}}{\text{min}}\right)\left[10X^2 + \left(\frac{72\,\text{in.}^2}{1} \times \frac{1\,\text{ft}^2}{144\,\text{in.}^2}\right)\right]$$

$$\frac{2{,}000 \text{ ACF}}{\text{min}} = \left(\frac{225\,\text{ft}}{\text{min}}\right)\left[10X^2 + 0.5\,\text{ft}^2\right]$$

$$8.89\,\text{ft}^2 = 10X^2 + 0.5\,\text{ft}^2$$

$$8.39\,\text{ft}^2 = 10X^2$$

$$\sqrt{0.839\,\text{ft}^2} = X$$

$$X = 0.916\,\text{ft} * \left(\frac{12\,\text{in}}{1\,\text{ft}}\right) = 11\,\text{in.}$$

7. Estimate the rotational speed of a belt-driven centrifugal fan based on the following data:

Motor rotational speed, $\text{RPM}_{\text{Motor}} = 1778\,\text{RPM}$
Motor sheave diameter, $D_{\text{Motor}} = 8$ in.
Fan sheave diameter, $D_{\text{Fan}} = 14$ in.

a) 1239 RPM$_{\text{fan}}$
b) 2000 RPM$_{\text{fan}}$
c) 400 RPM$_{\text{fan}}$
d) 1016 RPM$_{\text{fan}}$

SOLUTION

Calculate the fan speed (RPM$_{\text{fan}}$) using the following equation.

$$\text{RPM}_{\text{Fan}} = \text{RPM}_{\text{Motor}} \times \frac{D_{\text{Motor}}}{D_{\text{Fan}}}$$

$$= \frac{1778}{1}\left|\frac{8\,\text{in.}}{14\,\text{in.}}\right. = 1016 \text{ RPM}$$

8. A system consists of the following components (in order): hood, fabric filter, centrifugal fan, and stack. The fabric filter static pressure drop has increased from 4.5 inches of water to 6.5 inches of water. If the fan dampers do not move to compensate for this change, what will happen to the hood static pressure?

    a) **It will be less negative (closer to zero)**
    b) It will be more negative
    c) It will become positive
    d) It will remain unchanged

Explanation:

The hood static pressure will decrease due to reduced gas flow rate caused by the increased blockage of airflow from the fabric filters.

9. A centrifugal fan moves 1,000 cubic feet of air per minute at a temperature of 450°F and a fan inlet pressure of –15 inches of water. Calculate the actual air flow rate if the gas temperature decreases to 68°F and the inlet pressure and fan rotational speed remains the same.

    a) The air flow rate will increase to 1,580 ACFM
    b) The air flow rate will decrease to 580 ACFM
    c) **The air flow rate will remain at 1,000 ACFM**
    d) It is impossible to calculate the air flow rate at the new conditions

Note: Fans move a constant volume of air.

10. A centrifugal fan is operating with a motor current of 120 amps. The gas density entering the fan at the operating conditions is 0.045 pounds per cubic foot. Estimate the motor current at standard conditions when the gas density is approximately 0.075 pounds per cubic foot.

    a) 500 amps
    b) **200 amps**
    c) 159 amps
    d) 90 amps

SOLUTION

$$I_{STP} = I_{Actual} \left(\rho_{STP} / \rho_{Actual} \right)$$

$$= 120 \, amps \frac{0.075 \, lb_m / ft^3}{0.045 \, lb_m / ft^3} = 200 \, amps$$

11. The static pressure drop through a section of ductwork is –1.2 inches of water when the gas flow rate is 5,000 ACFM. Estimate the static pressure drop across this section of ductwork if the gas flow rate increases to 8,000 ACFM. Assume that there is no gas density change associated with the increased gas flow rate.

    a) **3.07 in. W.C.**
    b) 1.1 in. W.C.
    c) 2 in. W.C.
    d) 4 in. W.C.

SOLUTION

$$\frac{SP_{@Highflow}}{SP_{@Lowflow}} = \frac{(8,000\,ACFM)^2}{(5,000\,ACFM)^2} = 2.56$$

Given: $SP_{@Lowflow} = -1.2$ in. W.C.

               $SP_{@Highflow} = -1.2$ in. W.C. $(2.56) = -3.07$ in. W.C.

12. The hood capture efficiency is 92% and the wet scrubber control system has a collection efficiency of 95%. If the process served by this system generates 140 pounds of pollutant per hour, calculate the fugitive emissions and the stack emissions.

a) 20.50 lb_m/hr fugitive emissions and 9.80 lb_m/hr stack emissions
b) 1.50 lb_m/hr fugitive emissions and 0.80 lb_m/hr stack emissions
c) **11.20 lb_m/hr fugitive emissions and 6.4 lb_m/hr stack emissions**
d) 14.0 lb_m/hr fugitive emissions and 3.54 lb_m/hr stack emissions

SOLUTION

$$\text{Fugitive emissions} = (140\ lb_m/hr)\left[\frac{100\% - 92\%}{100\%}\right] = 11.2\ lb_m/hr$$

$$\text{Capture emissions} = 140\ lb_m/hr - 11.20\ lb_m/hr = 128.8\ lb_m/hr$$

$$\text{Stack emissions} = (128.8\ lb_m/hr)\left[\frac{100\% - 95\%}{100\%}\right] = 6.44\ lb_m/hr$$

13. Assume a fan is presently operating with the following conditions: 20,000 ACFM, –2.5 in. W.C. static pressure, 400 RPM, and 12 brake horsepower. Use the fan laws to determine the new RPM, brake horsepower, and static pressure when the volumetric flow rate increases to 22,500 ACFM.

    a) 490 RPM, 19.1 BHP, –5.7 in. W.C.
    b) 350 RPM, 9.5 BHP, –3.9 in. W.C.
    c) 400 RPM, 10.2 BHP, –2.8 in. W.C.
    d) **450 RPM, 17.1 BHP, –3.2 in. W.C.**

SOLUTION

New fan speed:

$$\frac{Q_2}{Q_1} = \frac{RPM_2}{RPM_1}$$

$$\frac{22,500\,ACFM}{20,000\,ACFM} = \frac{RPM_2}{400\,RPM}$$

$$RPM_2 = 450\,RPM$$

Brake horsepower:

$$\frac{BHP_2}{BHP_1} = \left(\frac{RPM_2}{RPM_1}\right)^3$$

$$\frac{BHP_2}{12\,BHP} = \frac{450^3}{400^3} = \frac{91,125,000}{64,000,000}$$

$$BHP_2 = 17.1\,BHP$$

Static pressure

$$\frac{SP_2}{SP_1} = \left(\frac{RPM_2}{RPM_1}\right)^2$$

$$\frac{SP_2}{-2.5\,in.W.C.} = \left(\frac{450}{400}\right)^2 = \frac{202,500}{160,000}$$

$$SP_2 = -3.2\ in.\ W.C.$$

14. What would happen to the desired operating point of a fan if a hole developed in the ductwork? Which characteristic curve will shift, what will happen to the operating point, volumetric flow rate, and hood static pressure?

    a. The system characteristic curve will shift down, the volumetric flow rate will increase, and the hood static pressure will increase.
    b. The system characteristic curve will shift down, the volumetric flow rate will decrease, and the hood static pressure will decrease.
    c. **The system characteristic curve will shift down, the volumetric flow rate will increase, and the hood static pressure will decrease.**
    d. The system characteristic curve will shift up, the volumetric flow rate will increase, and the hood static pressure will decrease.

SOLUTION

The system characteristic curve will shift down due to a decrease in the system resistance, causing the static pressure to decrease and the gas flow rate to increase. The hood static pressure will decrease because the hole in the ductwork will allow air to enter the system prior to the hood. The gas flow rate will increase due to the air inleakage.

3.8 REFERENCES

1.   American Conference of Governmental Industrial Hygienists (ACGIH). *Industrial Ventilation—A Manual of Recommended Practice*, 23rd ed.; ACGIH: Lansing, MI, 1998.

2.   Cengel, Y. A.; Boles, M. A. *Thermodynamics: An Engineering Approach*; McGraw-Hill: New York, 1989.

3.   *Code of Federal Regulations*, 40 Part 60, Method 22; July 1, 1997.

CHAPTER 4

4.0 ADSORPTION

4.1 OVERVIEW

INTRODUCTION

Adsorption processes have been used since the 1950s for high-efficiency removal of a wide variety of organic vapors and several types of inorganic gases. Adsorption is the term used to describe the accumulation of gases, liquids, or solutes on the surface of a solid or liquid. The use of adsorption processes has been expanding recently due to innovations in the designs of the systems and to the development of new adsorbents.

Nonregenerative

Adsorption systems designed for odor control and other low contaminant concentration applications (<10 ppm) are relatively simple. In these cases, the adsorbent bed is discarded as it approaches saturation with the contaminant. These systems are termed *nonregenerative* because the absorbent material is not reused.

Adsorption processes are also used extensively on large-scale applications having solvent vapor concentrations in the range of 10 to 10,000 ppm. Because of the large quantities of adsorbent needed, it is not economical to discard the adsorbent. Prior to becoming saturated with the solvents, the adsorbent is isolated from the gas stream and treated to drive the solvent compounds out of the solid adsorbent and into a small-volume, high-concentration gas stream. The desorbed gas stream is then treated to recover and reuse the solvents. The adsorbent is cooled (if necessary) and returned to adsorption service.

Regenerative

Adsorber systems that operate continuously must have (1) multiple fixed-beds of adsorbent, (2) fluidized bed contactors with separate adsorption and desorption vessels, or (3) rotary bed adsorbents that cycle continuously between adsorption and desorption operations. Because the adsorbent is treated and placed back in service, these adsorption processes are termed *regenerative*.

Adsorption systems are used as preconcentrators for thermal or catalytic oxidizer systems. The high-concentration, lower-volume organic vapor stream generated during adsorber bed desorption is well-suited for oxidation because fuel requirements in the oxidizer are minimized. This preconcentrator application expands the use of adsorption for low-concentration sources (10 to 1,000 ppm organic vapor) and for multi-component organic vapor streams.

Adsorption processes usually operate at efficiencies of 90% to 98% over long periods. They can be vulnerable to a variety of operating problems, such as the gradual loss of adsorption capacity, plugging of the adsorbent beds, and corrosion. These problems can usually be identified by shifts in the operating conditions and by increases in the stack contaminant concentrations.

LEARNING OBJECTIVES

At the conclusion of this training students will be able to:

- Identify various types of adsorption systems.
- Identify principles of operation that apply to adsorption.
- Identify the factors that affect the performance of an adsorption system.
- Determine the areas that need to be monitored in an adsorption system.

4.2 TYPES AND COMPONENTS OF ADSORPTION SYSTEMS

Adsorbents

During adsorption, the gas stream passes through a bed or layer of highly porous material called the *adsorbent*. The compound or compounds to be removed, termed the *adsorbate(s)*, diffuse to the surface of the adsorbent and are retained because of weak attractive forces, while the carrier gas passes through the bed without being adsorbed. Adsorption occurs on the internal surfaces of the materials as shown in Figure 4-1. The term adsorbate is defined here for reference but it is used extensively throughout this chapter.

The most common types of adsorbents for pollution control applications are activated carbons, zeolites (molecular sieves), and synthetic polymers. Other types of adsorbents, such as silica gel and activated alumina, are used primarily for dehydrating gas streams.
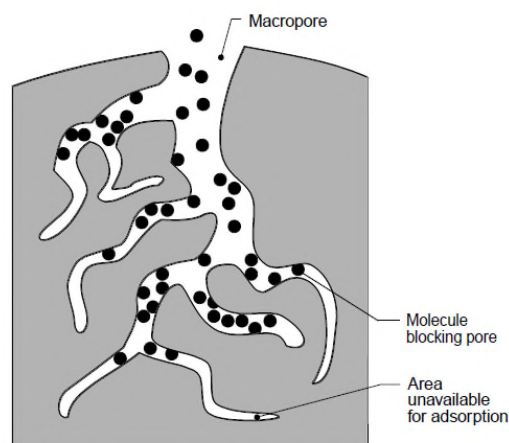
Figure 4-1. Vapor adsorbed into pores of adsorbent.

Activated Carbon

Activated carbon can be produced from a variety of raw materials such as wood, coal, coconut, nutshells, and petroleum-based products.

The activation process takes place in two steps:

1. First, the feedstock is *pyrolyzed*. This involves heating the material in the absence of air to a temperature high enough (e.g., 1,100°F or 593°C) to drive off all volatile material. Carbon and small quantities of ash are left.

2. To increase the surface area, the carbon is then "activated" by using steam, air, or carbon dioxide at higher temperatures. These gases attack the carbon and increase the pore structure. The temperatures involved, the amount of oxygen present, and the type of feedstock all greatly affect the adsorption qualities of the carbon.

Manufacturers vary these parameters to produce activated carbons suitable for specific purposes. There are a large number of commercial brands available that have significantly different properties to serve various applications. Accordingly, the term *activated carbon* applies to an entire category of diverse materials, not to a specific material.

Because of its nonpolar surface, activated carbon is used to control emissions of a wide variety of organic solvents and toxic gases. Carbons used in gas phase adsorption systems are manufactured in a granular form or in a carbon fiber form. The granular carbon pellets are usually between 4×6 and 4×20 mesh. Bulk density of the granular-pellet-packed beds can range from 5 to 30 lb_m/ft^3 (0.08 to 0.48 g/cm^3), depending on the internal porosity of the carbon. Total surface area of the macropores and micropores in activated carbon can range from 600 to 1,600 m^2/g (2.9-7.8 x 10^6 ft^2/lb_m).

Zeolites (Molecular Sieves)

Unlike activated carbon adsorbents that are amorphous in nature, molecular sieves have a crystalline structure. The pores are uniform in diameter.[1,2] Molecular sieves can be used to capture or separate gases on the basis of molecular size and shape. Simplified sketches of several zeolites are shown in Figure 4-2.

Type A   Sodalite   Faujasite
                                  (Type X, Y)
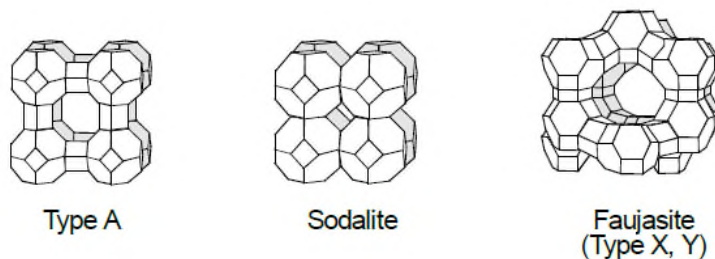
Figure 4-2. Sketches of zeolites.[3]
(Reprinted by permission of Chemical Engineering Progress, American Institute of Chemical Engineers.)

The main uses of molecular sieves have been to remove moisture from exhaust streams, to separate hydrocarbons in refining processes, and to remove nitrogen oxide compounds from air pollution sources. Because of the development of new synthetic zeolites, their applications are expanding into the volatile organic compound (VOC) control field. The surface areas of molecular sieves range from 590 to 700 m^2/g (2.9-3.4 x 10^6 ft^2/lb_m).

Synthetic Polymers

Polymeric adsorbents are formed by crosslinking long chain polymers that have a variety of functional groups. The polymeric materials have a rigid microporous structure with surface areas of more than 1,000 m^2/g (4.9 x 10^6 ft^2/lb_m).[4] The ash content is less than 0.01%.[4,5] The chemical structure of one commercial brand of synthetic polymer is shown in Figure 4-3.

These materials have very high adsorption capacities for selected organic compounds, and they can be regenerated more rapidly than activated carbon adsorbents. Regeneration can occur using hot air, hot nitrogen, steam, indirect contact heating, and microwaves. The main applications of this type of adsorbent are the control of organic compounds such as ketones, aldehydes, and reactive compounds that can undergo various chemical reactions on the surfaces of activated carbon.
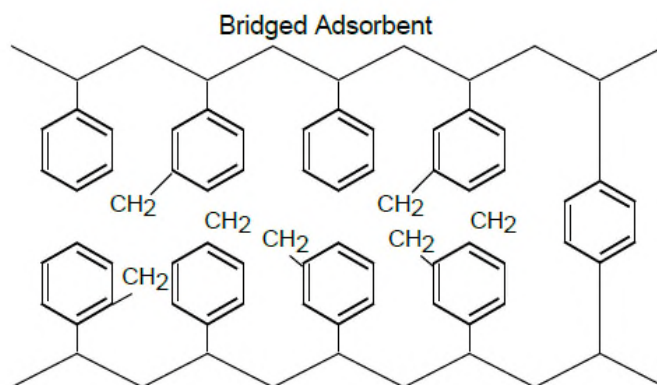
Figure 4-3. Example of a synthetic polymer.
(Reprinted courtesy of Dow Chemical, Inc.; Midland, Michigan.)

Polymeric adsorbents are also used for gas streams containing high water vapor concentrations (>50% relative humidity) because they are less prone to adsorb water vapor than conventional activated carbon adsorbents. The main limitation to the use of polymeric adsorbents is cost. These materials are more expensive than activated carbon and zeolite adsorbents.[4]

Silica Gel

Silica gels are made from sodium silicate. Sodium silicate is mixed with sulfuric acid, resulting in a jelly-like precipitant from which the name "gel" comes. This precipitant is then dried and roasted. Different grades can be produced depending on the processes used in manufacturing the gel. Silica gels have surface areas of approximately 750 m^2/g (3.7 x 10^6 ft^2/lb_m). They are

used primarily to remove moisture from exhaust streams. Silica gels are ineffective at temperatures above 500°F (260°C).

Activated Alumina (Aluminum Oxides)

Activated alumina is an amorphous form of aluminum oxide manufactured by heating aluminum trihydrate in an inert atmosphere to produce a porous, high-surface-area adsorbent. The primary use of activated alumina is for drying gases and they are not commonly used in air pollution applications. The surface areas of activated alumina adsorbents can range from 200 to 300 m^2/g (1.0-1.5 x 10^6 ft^2/lb_m).

PHYSICAL PROPERTIES OF ADSORBANTS

The physical properties of the adsorbent affect the adsorption capacity, adsorption rate, and pressure drop across the adsorbent bed. Table 4-1 summarizes these properties for the adsorbents discussed earlier.

Table 4-1. Physical properties of major types of adsorbents.					
Adsorbent	**Internal Porosity (%)**	**Surface Area (m^2/g)**	**Pore Volume (cm^3/g)**	**Bulk Dry Density (g/cm^3)**	**Mean Pore Diameter (Å)**
Activated Carbon	55-75	600-1600	0.80-1.20	0.30-0.50	20-35
Activated Alumina	30-40	200-300	0.29-0.37	0.80-1.00	18-34
Zeolites (Molecular Sieves)	40-55	600-700	0.27-0.38	0.70-0.80	3-12
Silica Gel	30-40	650-750	--	0.80	21
Synthetic Polymers[1]	--	1080-1100	0.94-1.16	0.34-0.40	--

[1]Data provided applied to Dow XUS-43493.02 and XUS-43502.01 adsorbents.[4]

Because adsorption occurs at the gas-solid interface, the surface area available to the vapor molecules determines the effectiveness of the adsorbent. Generally, the larger the surface area, the higher the adsorbent's capacity is. However, the surface area must be available in certain pore sizes if it is to be effective as a vapor adsorber.

Dubinin[6] classified the pores in activated carbon as *micropores*, *macropores*, or *transitional pores*. Micropores have diameters of 10-100 Angstroms (Å; Angstrom = 1.0×10^{-10} meters) or less. Pores larger than 1,000 Å are considered macropores, and pores with diameters in the range of 100 to 1,000 Å are defined as transitional.

Many gaseous air pollutant molecules are in the 40 to 60 Angstrom size range. Thus, if a large

portion of an adsorbent's surface area is associated with pores smaller than 60 Å, many contaminant molecules will be unable to reach these sites.

The large pores serve mainly as passageways to the smaller pores where the adsorption forces are stronger. These forces are strongest in pores that are smaller than approximately twice the size of the contaminant molecule where the molecules experience overlapping attraction of the closely-spaced walls.

Capillary condensation occurs when mulitiple layers of adsorbed contaminant molecules build up from both sides of the pore wall, totally packing the pore and condensing in it. This activity usually occurs only in the micropores. The amounts of contaminant removed increase because additional molecules condense on the surface of the liquid that has formed.

ADSORPTION SYSTEMS

Nonregenerative Adsorption Systems

Nonregenerative adsorption systems are manufactured in a wide variety of physical configurations. They usually consist of thin adsorbent beds, ranging in thickness from 0.5 to 4 inches (1 to 10 cm). These thin beds have low pressure drops, normally below 0.25 in. W.C. (0.06 kPa) depending on the bed thickness, gas velocity, and particle size of the adsorbent. Bed areas are sized to control the gas velocity through them from 20 to 60 ft/min (6 to 18 m/min). Service time for these adsorption units can range from six months for "heavy" odor concentrations to two years for trace concentrations or intermittent operations.[7] Nonregenerative adsorption systems are used mainly as air purification devices for small airflow streams such as offices and laboratory exhausts.

These thin bed adsorbers are flat, cylindrical, or pleated. The granules of activated carbon are retained by porous support material, usually perforated sheet metal. An adsorber system usually consists of a number of retainers or panels placed in one frame. Figure 4-4 shows a nine-panel, thin-bed adsorber. The panels are similar to home air filters except that they contain activated carbon as the filter instead of fiberglass.
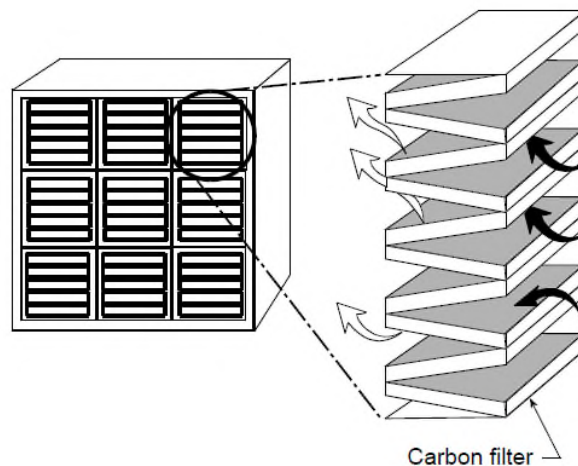
Figure 4-4. Thin-bed adsorber — nine-cell system.

Explanation of Figure

The pleated cell adsorber (Figure 4-5) consists of one continuous retainer of activated carbon, rather than individual panels. Cylindrical canisters (Figure 4-5) are usually small units designed to handle low flow rates of approximately 25 ACFM (0.7 m³/min). Cylindrical canisters are made of the same materials as the panel and pleated adsorbers, but their shape is round rather than square. Panel and pleated beds are dimensionally about the same size, normally 2 ft by 2 ft (0.6 m by 0.6 m). Flat panel beds are sized to handle higher exhaust flow rates of approximately 2,000 ACFM (57 m³/min), while pleated beds are limited to flow rates of 1,000 ACFM (28 m³/min).

Pleated thin bed   Canister
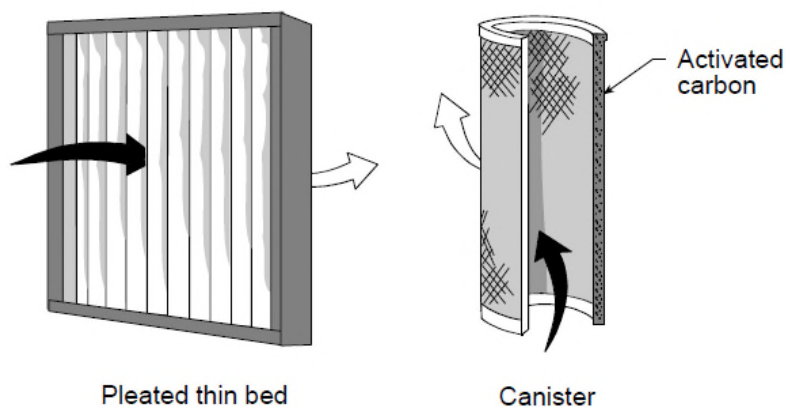
Figure 4-5. Nonregenerative adsorbers.

Thick-bed nonregenerative systems are also available. One system, shown in Figure 4-6, is essentially a 55-gallon drum. The bottom is filled with a material such as gravel to support a bed of activated carbon weighing approximately 150 lb$_m$ (70 kg). These units are used to treat small flow rates of 100 ACFM (2.8 m³/min) from laboratory hoods, chemical storage tank vents, or chemical reactors.
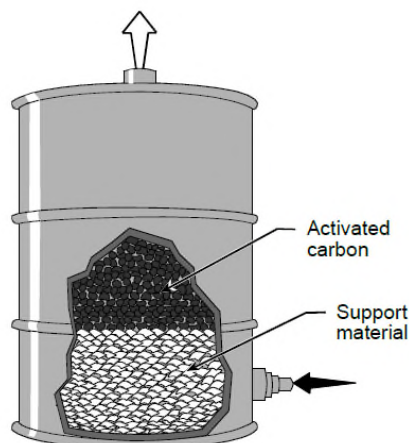
Figure 4-6. Thick-bed nonregenerative adsorber.

A flowchart of a simple system containing a small-scale nonregenerative adsorber is shown in Figure 4-7. Solvent-laden air (SLA) is generated in a laboratory hood or small-scale industrial process that is almost entirely enclosed in a hood. A centrifugal fan discharges the SLA at positive pressure first to a particulate filter and then into the activated carbon panels or barrels. The cleaned gas stream is then exhausted directly to the atmosphere.
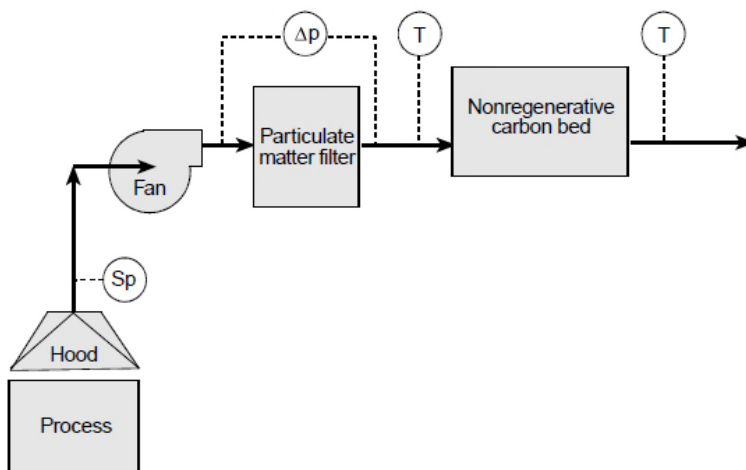
Figure 4-7. Flowchart of a simple nonregenerative adsorber.

The instrumentation on these systems is usually limited. In some cases, gas stream temperature monitors (usually dial-type thermometers) are mounted in the inlet and outlet ducts of the activated carbon panel units or barrels. An increase in the inlet temperature from the design or baseline levels may cause the service life of the activated carbon to be reduced. An increase in the outlet temperature compared to the inlet temperature may indicate that liquid droplets of solvent are being captured in the bed and increasing the bed temperature. High outlet temperatures must be monitored to prevent fires.

Particulate filters may be used to prevent the accumulation of dusts, fibers, and other debris from plugging the passages through the activated carbon bed. The static pressure drop across these filters provides an indication of filter overloading, which reduces gas flow through the system.

Due to the physical scale of the nonregenerative systems, it is uneconomical to include outlet organic vapor concentration monitors since these instruments can cost several times the total cost of the control system. Accordingly, with these small systems, there is no direct indication that the unit is approaching saturation.

Regenerative Adsorption Systems

Large regenerative adsorption systems can be categorized as *fixed*, *moving*, or *fluidized* beds. The name refers to the manner in which the gas stream and adsorbent are brought into contact. The choice of a particular system depends on the pollutants to be controlled and the recovery requirements.

Fixed-Bed Designs

Fixed carbon adsorption beds are commonly used to control a variety of organic vapors and are often regenerated by low-pressure steam. They are best used when the liquid organic is immiscible with water when steam is used during the regeneration step. Relatively pure organic liquids may be recovered by condensing the regeneration exhaust and separating the water and the organic based on different densities.

Fixed-bed adsorption systems usually involve multiple beds. One or more beds treat the process exhaust, while the other beds are either being regenerated or cooled. A flowchart of a typical two-bed adsorption system is shown in Figure 4-8.
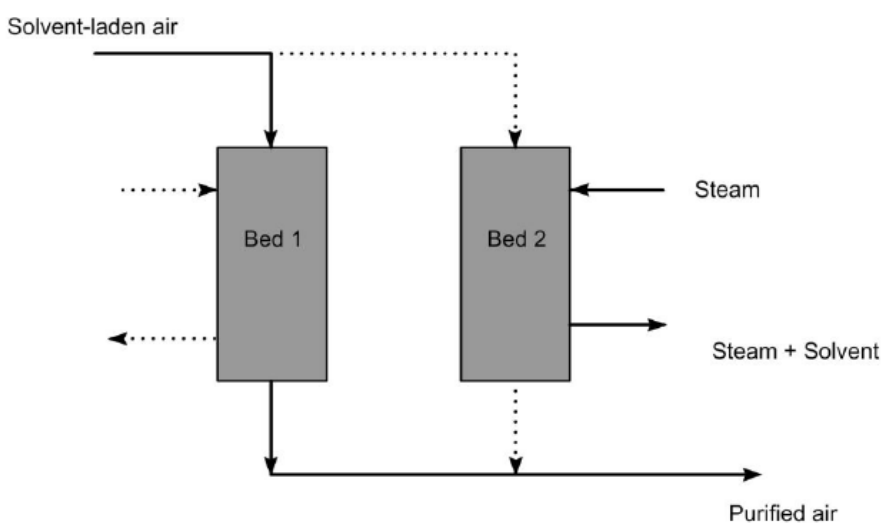
Figure 4-8. Two-bed adsorption system.

As shown, solvent-laden air enters Bed 1, which is in the adsorption mode. Gas flow is usually in the downward direction to avoid possible entrainment of carbon particles that might occur in the upflow mode. Solvent is adsorbed while purified air is discharged to the atmosphere. At the same time, Bed 2 is in the regeneration mode. Steam is fed to Bed 2 and steam plus solvent exit the bed and are fed to the solvent recovery system. Opening and closing appropriate dampers switch the functions of the two beds periodically. The switching may be based upon either a time cycle or when the adsorption bed approaches saturation and the solvent concentration in the purified air increases to some predetermined level. Three or more beds may be required if the duration of the adsorption and regeneration/cooling cycles cannot be matched.

A more complete three-bed system is shown in Figure 4-9. The SLA stream is first pretreated to remove any solid particles that could plug the carbon bed and prevent proper contact between the gas stream and the adsorbent bed. The solvent-laden air stream is often passed through an indirect heat exchanger (cold water tubes) to lower the gas temperature to the range of 60°F to 100°F (15°C to 38°C) where adsorption efficiency and adsorbent service life are both optimum. The pretreated gas stream then enters one of the parallel vessels that house the adsorbent beds. In Figure 4-9, we can imagine that the top bed is in the adsorption mode while the second bed is

being regenerated and the third is cooling prior to its next adsorption phase. The steam plus regenerated solvent passes first to a condenser and, if the steam and solvent are immiscible, to a decanter where separation occurs due to density differences in the two phases. If the solvent and steam are miscible, distillation may be required for separation.
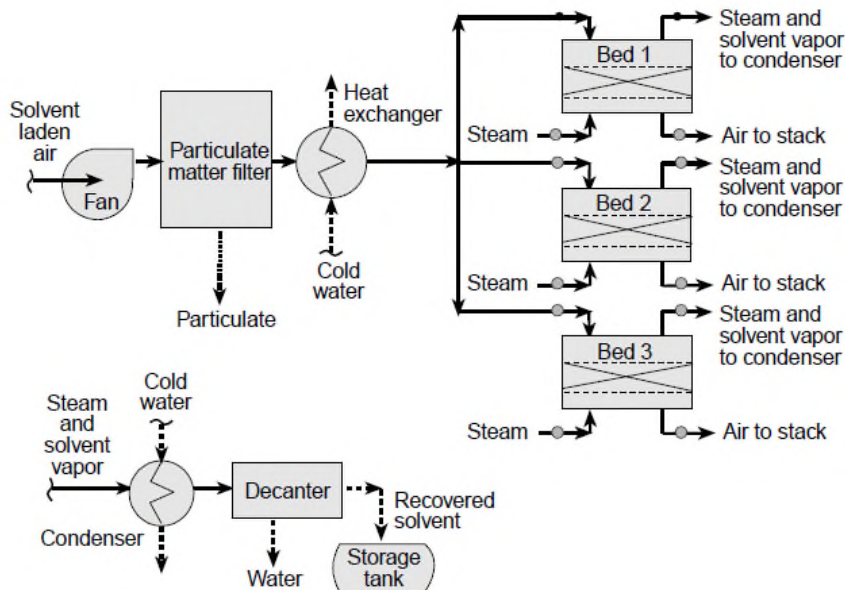
Figure 4-9. Multi-bed, fixed-bed-type adsorption system.

Regenerative fixed carbon beds are usually from 1 to 4 ft (0.3 to 1.2 m) thick. The maximum adsorbent depth of 4 ft (1.2 m) is based on pressure drop considerations.[8] Superficial gas velocities through the adsorber range from 20 to 100 ft/min (6 to 30 m/min). Pressure drops normally range from 3 to 15 in. W.C. (0.75 to 3.75 kPa), depending on the gas velocity, bed depth, and carbon pellet size.[3] A cutaway sketch of a fixed-bed adsorber vessel is shown in Figure 4-10.
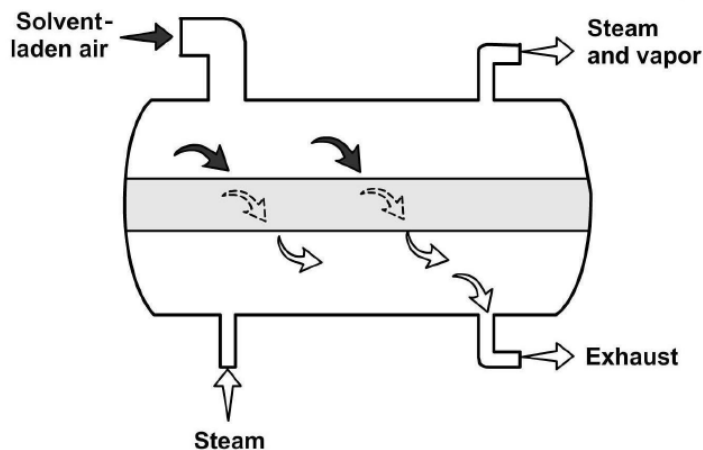
Figure 4-10. Cutaway sketch of horizontal adsorber vessel.

Adsorbers of this type are manufactured as a package system capable of handling flow rates up to 400,000 ACFM (11,500 m³/min). Larger units must be engineered and fabricated for the specific application.

Some fixed-bed adsorbers have been designed recently with "multi-pass" capability in order to increase the solvent vapor removal efficiency. The last adsorber vessel that has been regenerated is placed as a second stage[9] by using a series of dampers and connecting ductwork. The air stream passing out of the first adsorber is then directed through this second vessel in order to remove the solvent vapors that penetrated the first unit. This approach is also called *series/parallel*.

Carbon Fiber System

Two-chamber, fixed-bed adsorbers have also been developed using carbon fiber adsorbent elements. The activated carbon is prepared as fiber-coated surfaces, a number of which are mounted in a single chamber. The carbon fiber is a thin layer of material with micropores leading directly from the adsorbent surface.[10] With the two-chamber design; one of the chambers is in adsorption mode, while the other is desorbed using hot steam. Because of the thin depth of the material, desorption times are shorter than the conventional deep-bed, carbon pellet designs. A diagram of a two-bed, carbon fiber adsorber appears in Figure 4-11.
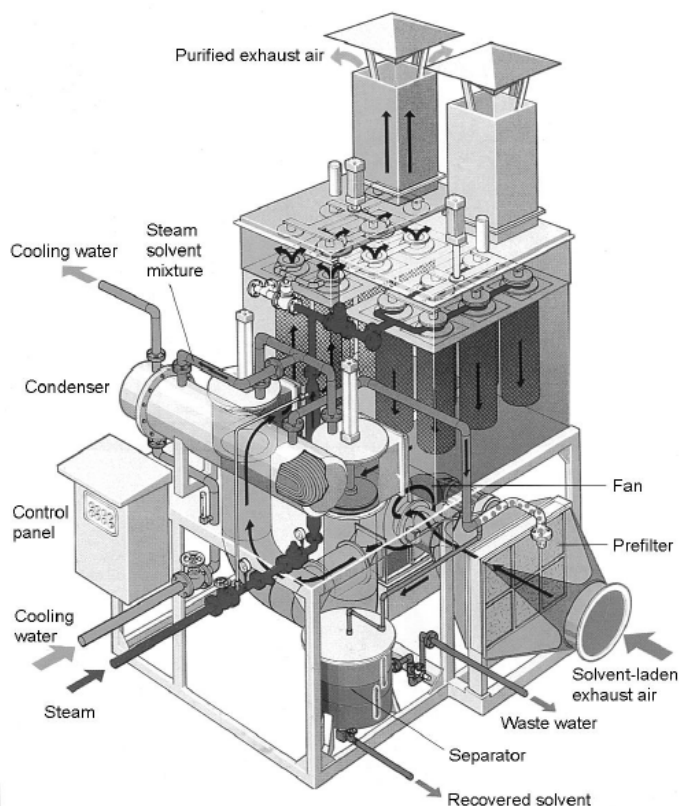
Figure 4-11. Carbon fiber system.
(Reprinted courtesy of Durr Industries, Inc.; Plymouth, Michigan.)

Regenerative Adsorption Systems – Moving-Bed Designs

Moving-bed systems can use a carbon bed more effectively than a fixed-bed system because the solvent-laden air stream passes only through the unsaturated portion of the carbon bed, reducing the distance the air stream travels through the bed; therefore, the static pressure drop is low.

One type of moving-bed adsorber is the rotary wheel zeolite adsorber, as shown in Figure 4-12. The zeolite adsorbent is mounted in a vertically oriented wheel that rotates at a rate of approximately five revolutions per hour. Three quarters of the wheel are in adsorption service while one quarter is being desorbed using hot air. The desorbed gas stream has a VOC content that is concentrated by approximately a factor of 10 to 15 over the inlet level and a flow rate that is less than 10% of the inlet gas stream. Overall VOC adsorption efficiencies are in the range of 90% to 98%.
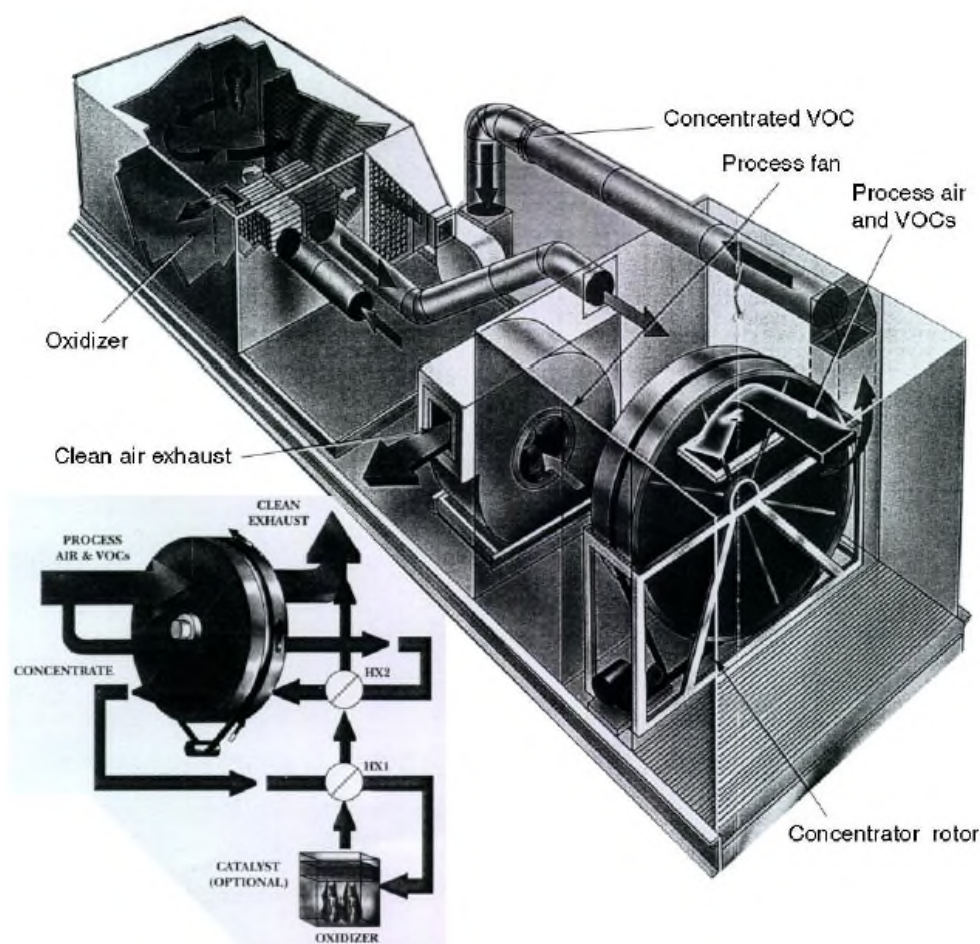
Figure 4-12. Rotary wheel zeolite adsorber.

Another type of moving-bed adsorber is the rotary carbon-fiber adsorber. This adsorber uses activated carbon-fiber paper prepared in a corrugated honeycomb arrangement (Figure 4-13a).

The adsorbent is mounted in a rotor that turns continuously at a speed of 1 to 9 revolutions per hour.[12] Desorption is accomplished using hot air that passes through the honeycomb as it rotates into position.
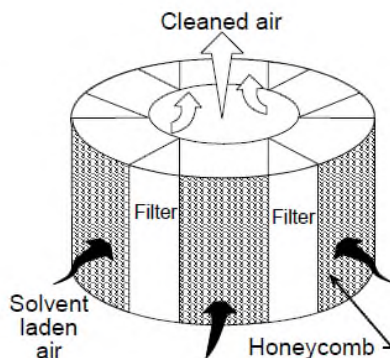
Figure 4-13.a. Rotor for carbon-fiber system.
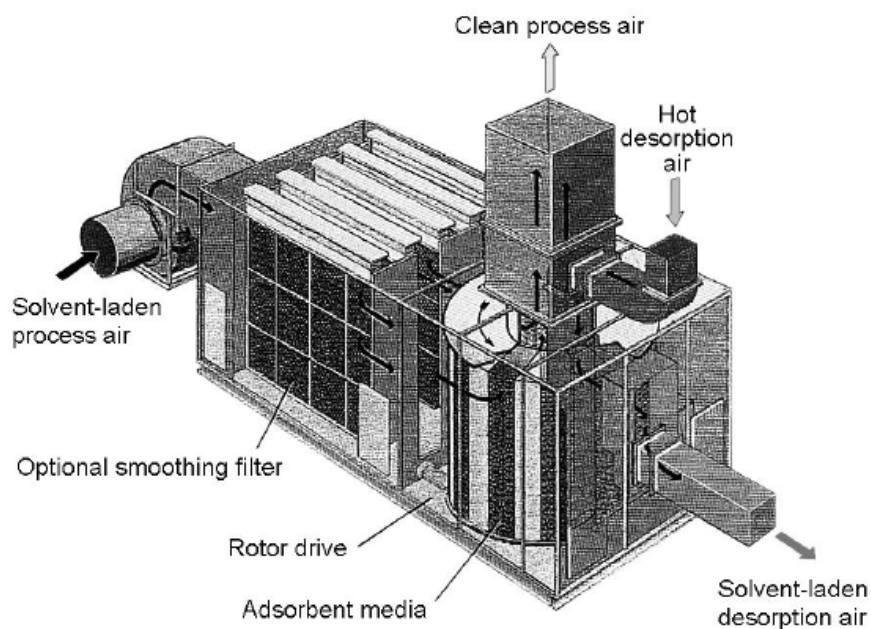
Figure 4-13b. Rotor system.
(Reprinted courtesy of Durr Industries, Inc.; Plymouth, Michigan.)

Adsorption and desorption are performed simultaneously on different sectors of the rotor. The desorbed solvent vapors are at concentrations of 5 to 15 times the inlet levels. Accordingly, the system is attractive for the pretreatment of dilute solvent-laden air streams prior to incineration. The carbon-fiber rotor system is shown in Figure 4-13b.

Regenerative Adsorption Systems – Fluidized Bed Adsorbers

A fluidized bed system, shown in Figure 4-14, uses the motion of the solvent-laden gas stream to entrain adsorbent material and thereby facilitate good gas-solid contact. The VOC-laden gas stream enters at the bottom of the adsorber vessel and passes upward through the fluidized adsorbent with the purified gas exiting at the top. The adsorbent plus VOC is pneumatically conveyed to the desorption vessel for regeneration. Regeneration gas plus VOC exit from the top and are ready for further treatment. The regenerated adsorbent is pneumatically conveyed back to the adsorption vessel. Because the adsorption and desorption processes are physically separate, organic contaminants can be concentrated by a factor of 10 to 50.
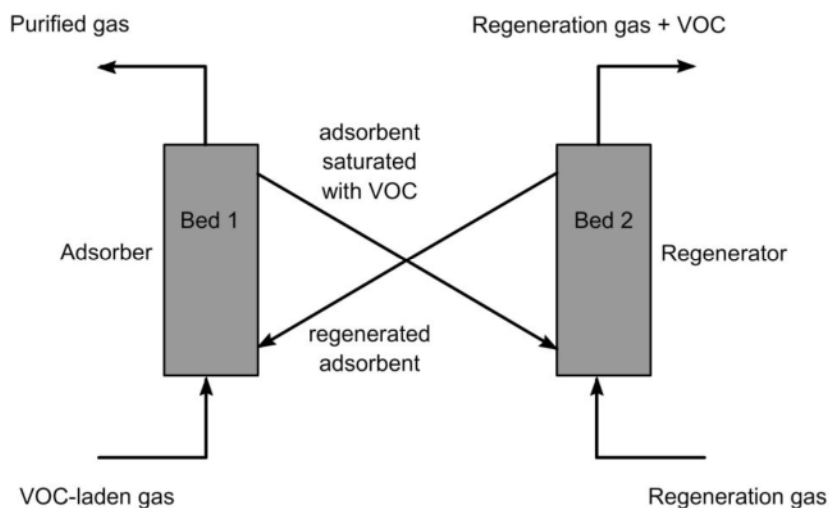
Figure 4-14. Fluidized bed adsorber/regenerator.

A system that consists of multiple fluidized beds appears in Figure 4-15. VOC-laden gas enters at the bottom of the adsorber and passes upward through a series of beds. The adsorbent flows downward from bed to bed until it reaches the bottom. The saturated adsorbent is then transported pneumatically to the desorption vessel for regeneration. In this system, regeneration occurs through indirect contact with steam. The regenerated adsorbent is transported back to the adsorption vessel.

Both the moving bed and fluidized bed systems provide continuous operation and efficient utilization of the adsorbent. These systems are used with either polymeric adsorbents or activated carbon adsorbents. It is necessary to use an adsorbent that can withstand the physical attrition inherent in the system. A "beaded" activated carbon that minimizes attrition loss has been developed. The beaded shape is inherently stronger and has better fluidity properties than granular carbon. This type of carbon has been used in a few installations and is reported to reduce the attrition loses to 2% to 5% per year.
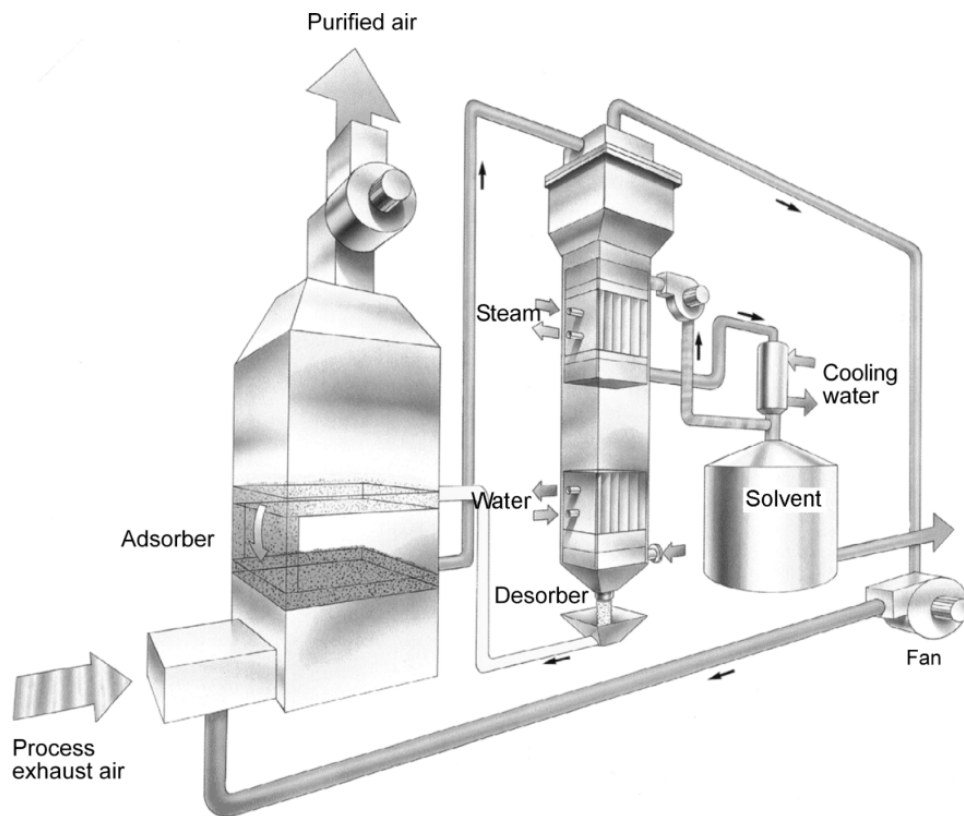
Figure 4-15. Fluidized bed adsorber.
(Reprinted courtesy of Weatherly, Inc., Atlanta, Georgia.)

4.3 OPERATING PRINCIPLES

Adsorption Steps

Adsorption occurs in a series of three steps. In the first step, the contaminant is transferred from the bulk gas stream to the external surface of the adsorbent material. In the second step, the contaminant molecule diffuses from the relatively small area of the external surface (a few square meters per gram) into the macropores, transitional pores, and micropores within each adsorbent. Most adsorption occurs in the micropores because the majority of available surface area is there (hundreds of square meters per gram). In the third step, the contaminant molecule adsorbs to the surface in the pore. Figure 4-16 illustrates this overall mass transfer, diffusion, and adsorption process.
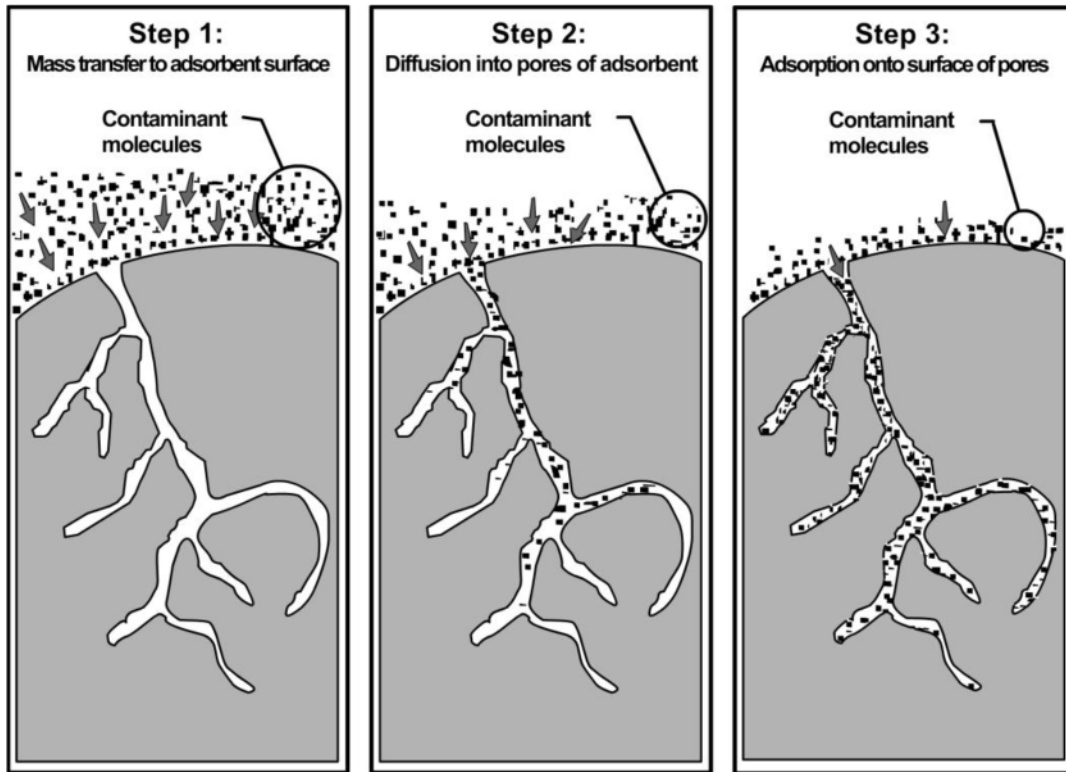
Figure 4-16. Adsorption steps.

Steps 1 and 2 occur because of the concentration difference between the bulk gas stream passing through the adsorbent and the gas near the surface of the adsorbent. Step 3 is the actual physical bonding between the molecule and the adsorbent surface. This step normally occurs more rapidly than steps 1 and 2.

ADSORPTION FORCES

The adsorption process is classified as either *physical* or *chemical*. The basic difference is the strength in which the gas molecule is bonded to the adsorbent. In physical adsorption, the gas molecule is held to the solid surface by weak forces of intermolecular cohesion. The chemical nature of the adsorbed gas remains unchanged; therefore, physical adsorption is a readily reversible process. In chemical adsorption a strong chemical bond is formed between the gas molecule and adsorbent. Chemical adsorption, or chemisorption, is not easily reversed.

Physical Adsorption

The forces active in physical adsorption (or physisorption) are electrostatic in nature and occur under suitable conditions in most gas-solid systems. These forces are present in all states of matter: gas, liquid, and solid. They are the same forces of attraction that cause gases to condense and deviate from ideal behavior under extreme conditions. Physical adsorption is also referred to as van der Waals' adsorption. Because of van der Waals' forces, physical adsorption can form multiple layers of adsorbate molecules, one on top of another.

The electrostatic effect that produces van der Waals' forces depends on the polarity of both the gas and solid molecules. Molecules in any state are either polar or nonpolar depending on their chemical structure. Polar substances exhibit a separation of positive and negative charges within the compound, which is referred to as a *permanent dipole*. Water is a prime example of a polar substance. Nonpolar substances have both their positive and negative charges in one center so they have no permanent dipole. Most organic compounds are nonpolar because of their symmetry.

Physical adsorption can result from three different effects: orientation, dispersion, or induction (Figure 4-17). For polar molecules, attraction occurs because of the *orientation effect*. The negative charge of one molecule is attracted to the positive charge of the other. An example of this type of adsorption is the removal of water vapor (polar) from an exhaust stream using silica gel (polar).
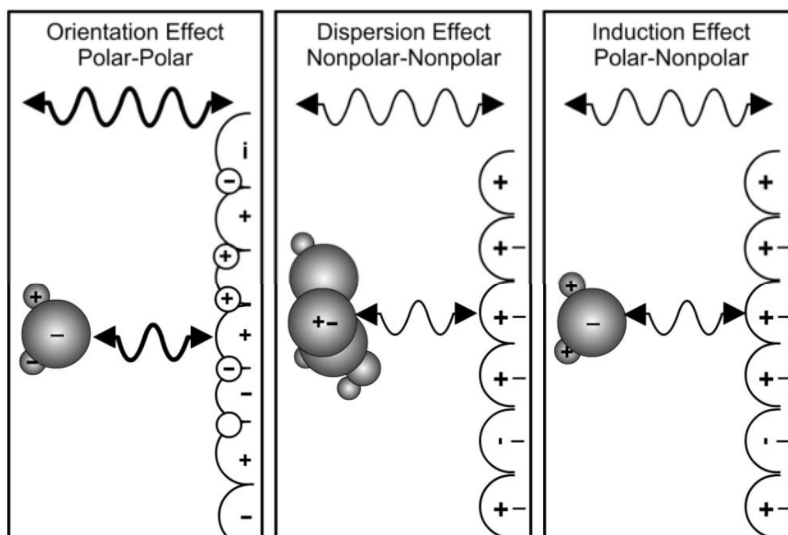
Figure 4-17. Physical forces causing adsorption.

The adsorption of a nonpolar gas molecule onto a nonpolar surface is accounted for by the *dispersion effect*. This effect is based on the fact that although nonpolar substances do not possess a permanent dipole, they do have a fluctuating or oscillating dipole. Fluctuating dipoles are a result of momentary changes in electron distribution around the atomic nuclei. In a nonpolar substance, when two fluctuating dipoles come close to one another, their total energy decreases, and they fluctuate in phase with each other. This is the origin of the name *dispersion effect*. The adsorption of organic vapors onto activated carbon is an example of nonpolar molecular attraction.

The attraction between a molecule with a permanent dipole (polar molecule) and a nonpolar molecule is caused by the *induction effect*. A molecule with a permanent dipole can induce polarity into a nonpolar molecule when they come in close contact. The energy of this effect is determined by the polarizability of the nonpolar molecules. The induction effect is, however,

small when compared to the orientation or dispersion effects. Therefore, adsorption systems use polar adsorbents to remove polar contaminants. This ensures that the inter-molecular forces of attraction between the gas and solid will be greater than those between similar molecules in the gas phase.

Chemisorption

Chemical adsorption (chemisorption) results from a chemical interaction between the gas and the solid. The gas is held to the surface of the adsorbate by the formation of a chemical bond. Adsorbents used in chemisorption can be either pure substances or chemicals deposited on an inert carrier material. One example of the former is the use of pure iron oxide chips to adsorb hydrogen sulfide gas. An example of the latter is the use of activated carbon that has been impregnated with potassium iodide to remove mercury vapors.

All adsorption processes are exothermic whether adsorption occurs from chemical or physical forces. The fast-moving gas molecules lose kinetic energy when adsorbed on the solid, which results in the liberation of heat.

In chemisorption, the heat of adsorption is comparable to the heat evolved from an exothermic chemical reaction, usually over 10 kcal/mol. The heat given off by physical adsorption is much lower, approximately 0.1 kcal/mol, which is comparable to the heat of condensation. Molecules that are chemisorbed are very difficult (and in some cases, impossible) to remove from the adsorbent surface, as opposed to physically adsorbed molecules which can usually be easily removed by either increasing the operating temperature or reducing the pressure of the adsorbent bed. Chemisorption stops when all the active sites on the surface of the adsorbent have reacted, forming only a monolayer of adsorbate molecules on the surface. In contrast, multilayers of adsorbed molecules can often be formed in physisorption. While the physical adsorption rate decreases with increasing temperature, the chemisorption rate increases with increasing temperature. Chemisorption is a highly selective process in which the gas molecule must be capable of forming a chemical bond with the adsorbent surface for chemisorption to occur. Physisorption, however, is a more general process than the much more specific chemisorption. For these reasons, physical adsorption is more desirable for air pollution control. A summary of the characteristics of physical versus chemical adsorption is presented in Table 4-2.

Table 4-2. Summary of the characteristics of chemisorption and physical adsorption.	
Chemisorption	**Physical Adsorption**
Releases high heat, 10 kcal/mol	Releases low heat, 0.1 kcal/mol
Forms a chemical compound	Gas retained by dipolar interaction
Desorption difficult	Desorption easy
Adsorbate recovery impossible	Adsorbate recovery easy

ADSORPTION-CAPACITY RELATIONSHIPS

Adsorption Equilibrium Conditions

Most available data on adsorption systems are determined at equilibrium conditions. The equilibrium capacity is the maximum amount of vapor that can be adsorbed at a given set of operating conditions. Adsorption equilibrium is the set of conditions at which the number of molecules arriving on the surface of the adsorbent equals the number of molecules leaving. The adsorbent bed becomes "saturated with vapors" and cannot remove any more vapors from the exhaust stream. Although a number of variables affect adsorption capacity, gas temperature and pressure are the two most important.

Adsorption equilibrium data may be presented in three forms: isotherm at constant temperature, isobar at constant pressure, and isostere at constant amount of vapor adsorbed.

Isotherm

The most common and useful method of presenting adsorption equilibrium data is the adsorption isotherm, a plot of the adsorbent capacity versus the partial pressure of the adsorbate at a constant temperature. Figure 4-18 is an example of an adsorption isotherm for carbon tetrachloride (CCl_4) on one specific activated carbon. Adsorption capacity may be presented in many different units, with pounds of adsorbate per 100 pounds of adsorbent being typical. Data of this type are used to estimate the size of adsorption systems as demonstrated in Problem 4-1.

Attempts have been made to develop generalized equations to predict adsorption equilibrium from physical data. This is difficult because adsorption isotherms take many shapes depending on the forces involved. Isotherms can be concave upward, concave downward, or "S" shaped. To date, most of the theories agree with data only for specific adsorbate-adsorbent systems and are valid over limited concentration ranges.
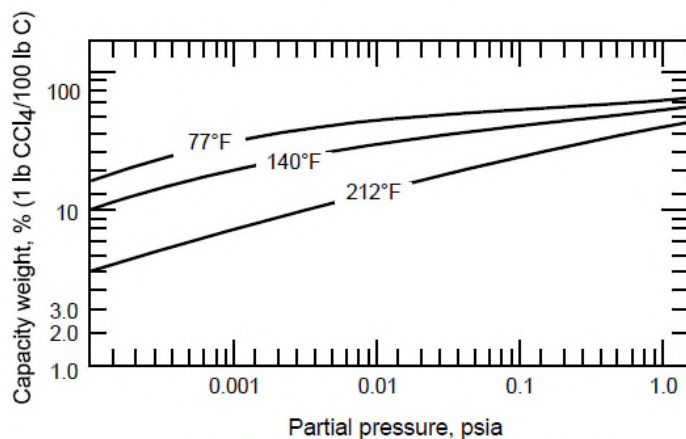
Figure 4-18. Adsorption isotherm for carbon tetrachloride (CCl_4) on one specific commercial activated carbon adsorbent product.

PROBLEM 4-1

A dry cleaning process exhausts a 15,000 SCFM air stream containing 680 ppm carbon tetrachloride (CCl_4). Given Figure 4-18, and assuming that the exhaust stream is at approximately 140°F and 14.7 psia, determine the saturation capacity of the activated carbon.

SOLUTION

Step 1. In the gas phase, the mole fraction (y) is equal to the ppm divided by 10^6.

y = 680 ppm = 0.00068

The partial pressure is the product of the total pressure and the mole fraction.

P* = yP = (0.00068)(14.7 psia) = 0.010 psia

Step 2. From Figure 4-18, at a partial pressure of 0.01 psia and a temperature of 140°F, the carbon capacity is read as approximately 45 lb CCl_4/ 100 lb C, or 45%. This is also equal to 45 g CCl_4/100 g C.

It must be noted that, in practical applications, adsorbers use more carbon than is required at saturation to ensure that uncaptured vapors are not exhausted to the atmosphere. Problem 4-2, presented later in this chapter, illustrates this point.

Isostere

The isostere is a plot of the natural log of the pressure versus the reciprocal of absolute temperature (ln[P] vs. 1/T) at a constant amount of vapor adsorbed. Adsorption isostere lines are straight for most adsorbate-adsorbent systems. Figure 4-19 shows isosteres for the adsorption of H_2S gas onto molecular sieves. The isostere chart is important because the slope of the isostere corresponds to the differential heat of adsorption. The total or integral heat of adsorption is determined by integration over the total quantity of material adsorbed.
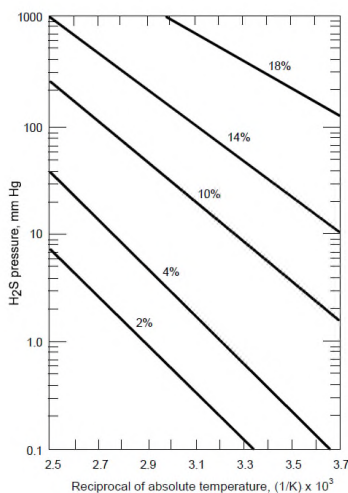
Figure 4-19. Adsorption isosteres of H_2S on 13X molecular sieve (loading in % H_2S by weight).

Isobar

The isobar is a plot of the amount of vapor adsorbed versus temperature at a constant partial pressure of the adsorbate. Figure 4-20 shows an isobar for the adsorption of benzene vapors on an activated carbon.
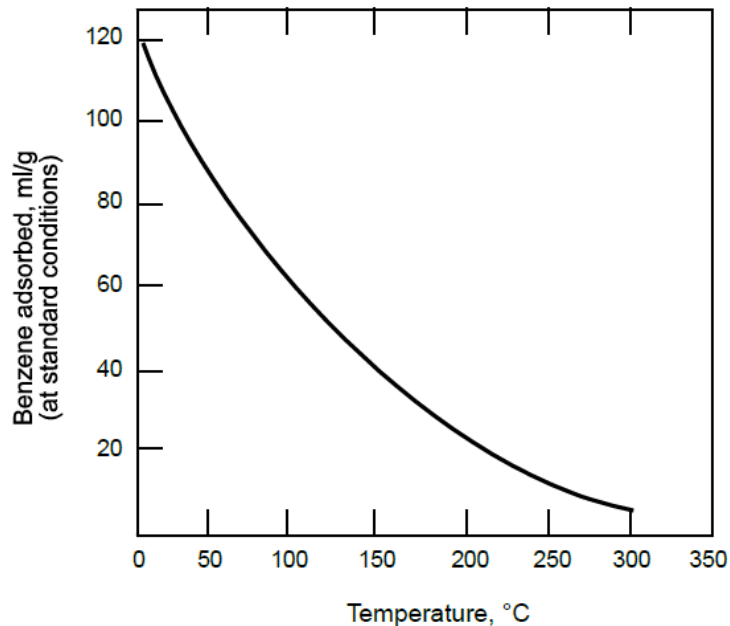
Figure 4-20. Adsorption isobar for benzene on an activated carbon ($P_{benzene} = 10.0$ mm Hg).

Note that the capacity units in this isobar are ml benzene/g C. Also note that the amount adsorbed decreases with increasing temperature. This is always the case for physical adsorption.

Because the isotherm, isostere, and isobar for a given adsorbate-adsorbent system are developed at equilibrium conditions, they are mutually dependent. By determining one, such as the isotherm, the other two relationships can be determined. In the design of an air pollution control system, the adsorption isotherm is by far the most commonly used equilibrium relationship.

4.4 ADSORPTION SYSTEM PERFORMANCE

APPLICABILITY

Nonregenerative Systems

Nonregenerative systems are applicable to a wide variety of small, low-concentration organic vapor sources. As a very approximate guideline, organic compounds having molecular weights greater than 50 and/or boiling points greater than 68°F (20°C) can be adsorbed. Because these units are not regenerated, it is often possible to use them up to 50% of the saturation level indicated by the applicable adsorption isotherm. This is generally a higher adsorbent utilization than is practical in regenerative systems. Accordingly, nonregenerative units can have a relatively long service life despite the limited quantity of adsorbent present.

Regenerative Systems

Conventional regenerative carbon bed adsorbers are used primarily for the removal and/or recovery of organic compounds having molecular weights between approximately 50 and 200.[10] These compounds usually have boiling points between 68°F and 350°F (20°C to approximately 175°C).[10] Very high molecular weight, high boiling point compounds have such a strong affinity for the adsorbent that it is impractical to desorb these materials.

Table 4-3 presents examples of organic compounds suitable for regenerative carbon adsorption. This is not a complete list because carbon adsorption is used for a wide variety of organic compounds. Other compounds, such as those listed in Table 4-4, are not suitable for regenerative adsorption because of their reactivity or high molecular weights and boiling temperatures.

Table 4-3. Examples of organic compounds suitable for carbon adsorption.					
Organic Compound	**Boiling Point °F (°C)**	**Molecular Weight**	**Water Soluble**	**Flammable Liquid**	**Lower Explosive Limit, % Vol**
Aliphatic					
Heptane	209 (98.4)	100.2	No	Yes	1.20
Hexane	156 (68.7)	86.2	No	Yes	1.20
Pentane	97 (36.1)	72.2	No	Yes	1.20
Naptha	288 (142)	-	No	Yes	0.92
Mineral Spirits	381 (194)	-	No	Yes	<1.00
Stoddard Solvent	379 (193)	-	No	Yes	1.10

Table 4-4. Examples of organic compounds suitable for carbon adsorption (cont'd).					
Organic Compound	**Boiling Point °F (°C)**	**Molecular Weight**	**Water Soluble**	**Flammable Liquid**	**Lower Explosive Limit, % Vol**
Aromatic					
Benzene	176 (80.0)	78.1	No	Yes	1.40
Toluene	231 (110.6)	92.1	No	Yes	1.40
Xylene	292 (144.4)	106.2	No	Yes	1.00
Ester					
Butyl Acetate	259 (126.1)	116.2	No	Yes	7.60
Ethyl Acetate	171 (77.2)	88.1	Yes	Yes	2.50
Halogenated					
Carbon Tetrachloride	170 (76.7)	153.8	No	No	N.F.
Ethylene Dichloride	210 (98.9)	85.0	No	Yes	6.20
Methylene Chloride	104 (40.0)	84.9	Yes	No	N.F.
Perchloroethylene	250 (121.1)	165.8	No	No	N.F.
Trichloroethylene	189 (87.2)	131.4	No	No	N.F.
Trichloroethane	165 (73.9)	133.4	No	No	N.F.
Ketones					
Acetone	133 (56.1)	58.1	Yes	Yes	2.60
Diacetone Alcohol	293 (145.0)	116.2	Yes	Yes	-
Methyl Ethyl KetoneMethyl	174 (78.9)	72.1	Yes	Yes	1.80
Isobutyl Ketone	237 (113.9)	100.2	Yes	Yes	1.20
Alcohols					
Butyl Alcohol	241 (116.1)	74.1	Yes	Yes	1.40
Ethanol	165 (73.9)	46.1	Yes	Yes	4.30
Propyl Alcohol	205 (96.1)	60.1	Yes	Yes	2.10

<table>
<tr><td colspan="2">**Table 4-5. Organic compounds not usually suitable for carbon adsorption.**</td></tr>
</table>

Reactive Compounds	High Boilers
Organic acids	Plasticizers
Aldehydes	Resins
Monomers (some)	Long Chain HCs (+C14)
Ketones (some)	Glycols, Phenols, Amines

ADSORPTION CAPACITY

Three important terms are used in actual systems to describe the capacity of the adsorbent bed, measured, for example, in pounds of vapor per pound of adsorbent.

- *Breakthrough capacity* is defined as the capacity of the bed at the time where unadsorbed vapor begins to be emitted.
- *Saturation capacity* (or equilibrium capacity) is the maximum amount of vapor that can be adsorbed per unit weight of carbon. This is the capacity read from the adsorption isotherms.
- *Working capacity* is a fraction of the saturation capacity, often in the range from 0.1 to 0.5 of the saturation capacity, that is used for design purposes. Smaller working capacities increase the amount of carbon required. The designer selects the appropriate fraction for individual systems by balancing the cost of carbon and adsorber operation versus preventing breakthrough.

It is generally uneconomical to desorb all vapor during the regeneration cycle. The small amount of residual vapor left in the bed is referred to as the *heel,* which accounts for a large portion of the difference between the saturation capacity and the working capacity. In some cases, the working capacity can be estimated by assuming that it is equal to the saturation capacity minus the heel.[16] Problem 4-2 illustrates one method of estimating the working capacity. In all of the examples in this course, a design factor of 0.25 of the saturation capacity is used. This is the same as assuming that the working amount of carbon is four times the amount required at saturation.

PROBLEM 4-2

A dry cleaning process exhausts a 15,000 SCFM air stream containing 680 ppm carbon tetrachloride (CCl_4). Based on Figure 4-18 and gas stream conditions of 140°F and 14.7 psia, estimate the amount of carbon required if the adsorber operates on a four-hour cycle. Note that saturation capacity of the activated carbon is 45% by weight. The molecular weight of CCl_4 is 154. Use a working capacity of 25% of the saturation capacity.

SOLUTION

Step 1. Compute the flow rate of CCl₄.

$$Q_{CCl_4} = 15,000 \text{ SCFM} \times 0.00068 = 10.2 \text{ SCFM CCl}_4$$

Convert to pounds per hour:

$$\frac{10.2 \text{ ft}^3}{\text{min}} \times \frac{\text{lb mol}}{385.4 \text{ ft}^3} \times \frac{154 \text{ lb}_m}{\text{lb mol}} \times \frac{60 \text{ min}}{\text{hour}} = 245 \text{ lb}_m \text{ CCl}_4 / \text{hour}$$

For a four-hour cycle:

$$4 \times 245 = 980 \text{ lb}_m \text{ CCl}_4$$

Explanation:

The value 385.4 ft³/lb mol is derived from the Ideal Gas Law at standard temperature and pressure (STP) as shown here:

Standard Temperature & Pressure (STP)

Temperature:	68 °F	To convert from °F to °R:	
	528 °R	$T_R = T_F + 460$	
Pressure:	1 atm		
	29.92 in. Hg		
	407 in. W.C.		
	14.7 psia		

Volume of 1 lb mol of gas @ STP:

V/n: 385.4 ft³/lb mol

Derived from the Ideal Gas Law [PV = nRT]:

$$\frac{V}{n} = \frac{RT}{P} = \frac{\left(\dfrac{0.7302 \text{ ft}^3 \text{ atm}}{\text{lb mol }^\circ R}\right)\left(68^\circ F + 460^\circ R\right)}{1 \text{ atm}} = 385.4 \frac{\text{ft}^3}{\text{lb mol}} @ \text{STP}$$

Step 2. The amount of activated carbon (at saturation) required is:

$$980 \text{ lb}_m \text{ CCl}_4 \times \left(\frac{100 \text{ lb}_m \text{ carbon}}{45 \text{ lb}_m \text{ CCl}_4}\right) = 2,178 \text{ lb}_m \text{ activated carbon}$$

The actual amount of activated carbon required can be estimated by multiplying the amount

needed at saturation by four (based on the working capacity of 25% of the saturation capacity).

$4 \times 2{,}178 = 8{,}712$ lb$_m$ carbon per four-hour cycle, per adsorber.

This gives only a rough estimate of the amount of carbon needed. Actual working capacity may be 25% to 75% of the saturation capacity.

FACTORS AFFECTING ADSORPTION SYSTEM PERFORMANCE

A number of factors or system variables that influence the performance of a physical adsorption system are discussed in the following sections.

Temperature

The capacity of an adsorbent decreases as the temperature of the system increases, as illustrated in Figure 4-21. As the temperature increases, the vapor pressure of the adsorbate increases, raising the energy level of the adsorbed molecules. Adsorbed molecules now have sufficient energy to overcome the van der Waals' attraction and migrate back to the gas phase. Molecules already in the gas phase tend to stay there due to their high vapor pressure. As a general rule, adsorber temperatures are kept below 130°F (54°C) to ensure adequate bed capacities. Temperatures above this limit can be avoided by cooling the exhaust stream to be treated.
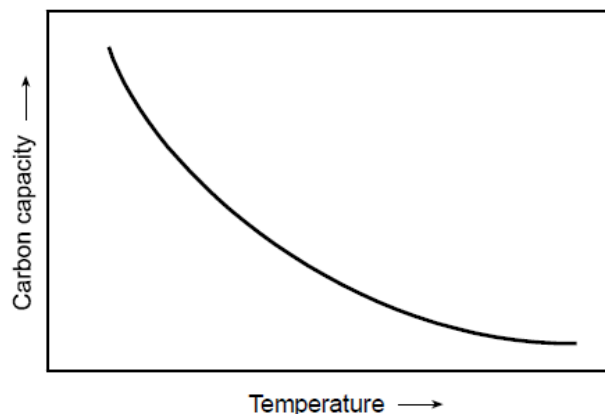
Figure 4-21. Carbon capacity versus gas stream temperature.

Adsorption is an exothermic process with the heat released for physical adsorption approximately equal to the heat of condensation. At low concentrations (below 1,000 ppm), the heat release is minimal and is quickly dissipated by the gas flowing through the bed. At higher concentrations (e.g., 5,000 ppm), the bed temperature can increase, thus causing the adsorption capacity to decrease. In addition, granular carbon is a good insulator that inhibits heat dissipation from the interior of the bed. In some cases, especially ketone recovery, the temperature rise can cause auto-ignition of the carbon bed.

Pressure

Adsorption capacity increases with an increase in the partial pressure of the vapor, which is proportional to the total pressure of the system. Any increase in pressure will increase the adsorption capacity. The increase in capacity occurs because of a decrease in the mean free path of vapor at higher pressures. Simply, the molecules are packed more tightly together. More molecules have a chance to "hit" the available adsorption sites, increasing the number of molecules adsorbed.

Gas Velocity

The gas velocity through the adsorber bed determines the contact or residence time between the gas stream and adsorbent. The residence time directly affects capture efficiency. The lower the gas velocity (the longer the contact time) through the adsorbent bed, the greater is the probability of a contaminant molecule reaching an available site. In order to achieve 90% or more capture efficiency, most carbon adsorption systems are designed for a maximum gas velocity of 100 ft/min (30 m/min) through the adsorber. A lower limit of at least 20 ft/min (6 m/min) is maintained to avoid flow problems such as channeling.

Gas velocity through the adsorber is determined by dividing the gas volumetric flow rate by the cross-sectional area of the adsorber. By specifying the gas velocity through the adsorber, the cross-sectional area is also specified.

PROBLEM **4-3**

A regenerative carbon bed system has three beds in parallel, each having a gas flow rate of 9,000 SCFM, a gas temperature of 100°F, and a gas pressure of +4 in. W.C. The barometric pressure is 30.3 in. Hg. What is the minimum cross-sectional area of each bed if the gas velocity must be maintained below 100 feet per minute?

SOLUTION

Step 1. Calculate the absolute static pressure.

$$SP_{absolute} = \left(4\,\text{in. W.C.}\right) + 30.3\,\text{in. Hg}\left(\frac{407\,\text{in. W.C.}}{29.92\,\text{in.Hg}}\right) = 416\,\text{in. W.C.}$$

Step 2. Calculate the gas flow rate in ACFM.

Use the Ideal Gas Law to calculate gas flow rate:

$$Q_{actual} = Q_{STP} \left[\left(\frac{T_{actual}}{T_{STP}} \right) \left(\frac{P_{STP}}{P_{actual}} \right) \right]$$

$$ACFM = 9,000 \, SCFM \left(\frac{100 + 460\,°R}{68 + 460\,°R} \right) \left(\frac{407 \, in.\,W.C.}{416 \, in.\,W.C.} \right) = 9,339 \, ACFM$$

Step 3. Calculate the minimum cross-sectional area of the bed to maintain a maximum of 100 ft/min.

$$Velocity = \left(\frac{Gas\,flow\,rate\,in\,ACFM}{Area} \right)$$

$$100\,ft/min = \left(\frac{9,340\,ACFM}{Area} \right)$$

Area = 93.4 ft²

Increasing the gas flow rate through the adsorber increases the pressure drop. Within the above stated maximum and minimum flow rates, the allowable pressure drop usually dictates the required tower cross-sectional area and flow rate. The pressure drop across the bed also depends on the depth of adsorbent.

Humidity

As stated previously, activated carbon will preferentially adsorb nonpolar hydrocarbons over polar water vapor. The water vapor molecules in the exhaust stream exhibit stronger attractions for each other rather than the adsorbent. However, at high relative humidity the number of water molecules in an exhaust stream may increases to the extent that they begin to compete with the hydrocarbon molecules for active adsorption sites, thus reducing the capacity and efficiency of the adsorption system.
Exhaust streams with relative humidities greater than 50% may require installation of additional equipment. Condensers to remove a portion of the water are one solution. Dilution air containing less moisture than the process stream has also been used. The contaminant stream may also be heated to reduce the humidity as long as the increase in temperature does not greatly affect adsorption efficiency. Additional adsorbent can be added to help offset the reduced efficiency.

Bed Depth

Providing a sufficient depth of adsorbent is very important in achieving efficient VOC removal due to the fact that adsorption rate is not infinitely fast. There are practical minimum and maximum limits to the bed depth.

The minimum depth is based primarily on the length of the mass transfer zone (MTZ) that, at fixed conditions such as temperature, partial pressure, and gas velocity, is related to the rate of adsorption. The MTZ is the volume of the bed where mass transfer occurs at any one time. The MTZ starts on the gas inlet side of the bed and moves through the bed as illustrated in Figure 4-22. The actual length of the MTZ remains fairly constant throughout the adsorption step. As long as the leading edge of the MTZ is above the bed outlet, the effluent concentration c_2 remains very low, because that portion of the bed in front of the MTZ has not yet been exposed to VOC.
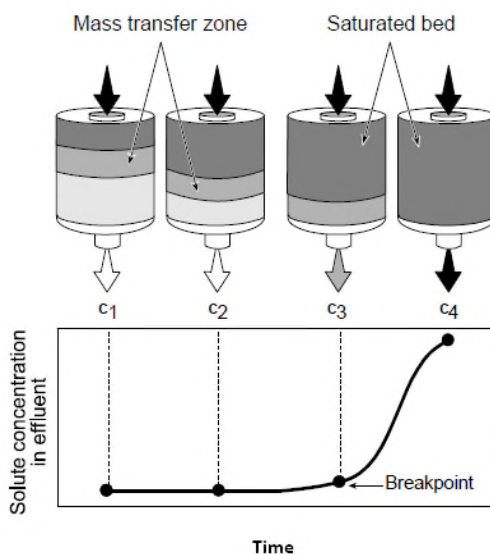
Figure 4-22. Mass transfer zone.

Breakthrough

When the leading edge of the MTZ reaches the outlet of the bed, the concentration of contaminant in the effluent suddenly begins to rise. This is referred to as the breakthrough point. If the contaminated gas stream is not switched to a newly regenerated bed, the concentration of contaminant in the outlet will quickly rise until it equals the initial concentration, c_4. If the adsorber bed depth is shorter than the required MTZ, breakthrough will occur almost immediately, rendering the system ineffective. Estimating the MTZ is important in determining the minimum bed depth.

Factors for determining MTZ length

Estimating the length of the MTZ is difficult because it depends on six separate factors: (1) adsorbent particle size, (2) gas velocity, (3) adsorbate concentration, (4) fluid properties of the gas stream, (5) temperature of the system, and (6) pressure of the system. The MTZ can be estimated from experimental data using Equation 4-1.[17] To obtain the necessary data, vendors will usually test a small portion of the exhaust stream on a pilot adsorber column, operating at several different bed depths.

(Eq. 4-1)
$$MTZ = \frac{1}{1 - X_S} D \left(1 - \frac{C_B}{C_S} \right)$$

Where: MTZ   = length of MTZ (meters)
X_S = degree of saturation in the MTZ (%), usually assumed to be 50%
D   = bed depth (meters)
C_B = breakthrough capacity (%)
C_S = saturation capacity (%)

In the absence of experimental data, empirical factors are often used to estimate the MTZ. Actual bed depths are usually several times longer than the length of the MTZ. The additional bed depth allows for adequate cycle times. Equation 4-1 can be rearranged to solve for breakthrough capacity for a fixed-bed depth.

(Eq. 4-2)
$$C_B = \frac{(X_S)(C_S)(MTZ) + C_S(D - MTZ)}{D}$$

Bed Depth

Often the actual adsorbent depth is fixed by the maximum allowable static pressure drop across the bed. Pressure drop data for typical carbons are presented in Figure 4-23.[16] The pressure drop per meter of bed depth is plotted versus the gas velocity with the carbon mesh size as a parameter. From the figure, an adsorber with a flow rate of 80 ft/min (24 m/min) using 4x10 mesh carbon will have a pressure drop of approximately 6 in. W.C. per foot (4.9 kPa per meter) of bed depth. Therefore, if the total pressure drop across the bed is limited to 18 in. W.C. (4.5 kPa), the total bed depth should not exceed 3 ft (0.9 m).

Contaminants

Particulate matter, organic compounds that have high boiling points, and entrained liquid droplets can also reduce adsorber efficiency if present in the gas stream.

Dust or lint greater than 3 micrometers ($\Box$m) in size can cover the surface of the adsorbent and reduce the surface area available to the gas molecules for adsorption. Covering active adsorption sites by an inert material is referred to as "blinding" or "deactivation." To avoid this situation, almost all industrial adsorption systems are equipped with some type of upstream particulate matter removal device.

High boiling point and high molecular weight compounds have such an affinity for the carbon that it is extremely difficult to remove them by standard desorption practices. These compounds also tend to react chemically on the carbon surface, forming solids or polymerization products that are extremely difficult to desorb. Loss of carbon activity in this manner is termed chemical deactivation.

Entrained liquid droplets can also cause operational problems. Liquid droplets that are non-adsorbing can act the same way as particulate matter by covering the surface and blinding the

bed. Liquid adsorbate droplets result in high heats of adsorption, thereby increasing the temperature and decreasing the adsorption capacity. In extreme cases, the liquid organic droplets carried over from the process can cause bed fires from the released heat. An entrainment separator may be required when liquid droplets are present.
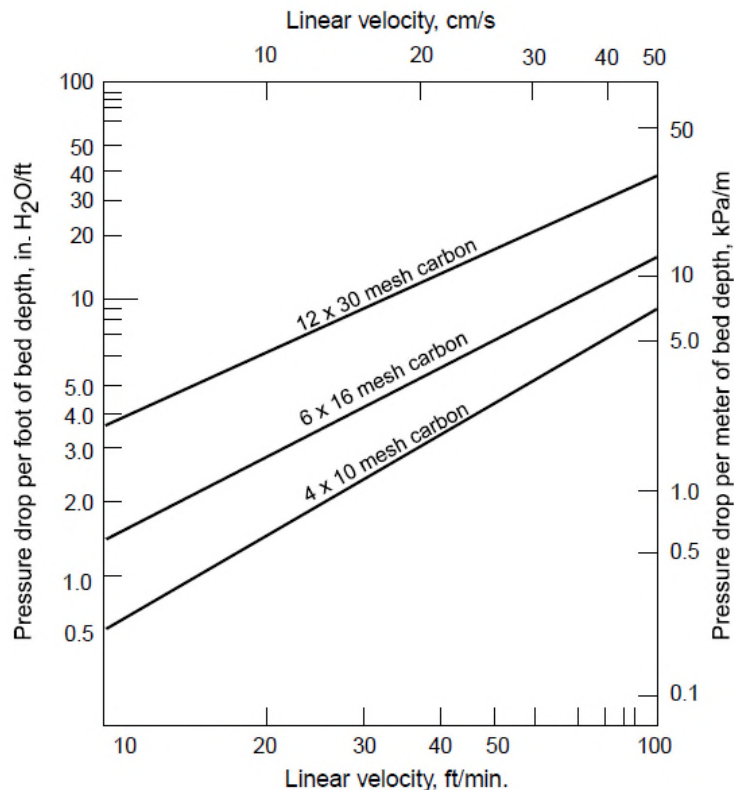
Figure 4-23. Pressure drop versus gas velocity through a deep bed granular carbon.

ABSORBENT REGENERATION METHODS

Periodic replacement or regeneration of the adsorbent bed is mandatory in order to maintain continuous operation. When the adsorbate concentration is high, and/or the cycle time is short (less than 12 hours), replacement of the adsorbent is not feasible, and in situ regeneration is required. Regeneration is accomplished by reversing the adsorption process, usually increasing the temperature or decreasing the pressure. Four methods are used commercially for regeneration.

Thermal Swing

The bed is heated so that the adsorption capacity is reduced. The adsorbate leaves the surface of the carbon and is removed from the vessel by a stream of purge gas. Cooling must be provided before the subsequent adsorption cycle begins. Steam regeneration is a common example of thermal swing regeneration.

Pressure Swing

The pressure is lowered at a constant temperature to reduce the adsorbent capacity.

Inert Purge Gas Stripping

Purging with an inert gas reduces the partial pressure of the contaminant in the gas phase, reversing the concentration driving force. Molecules desorb from the surface into the gas stream.

Displacement Cycle

The adsorbates are displaced by a compound that is preferentially adsorbed. This method is usually a last resort for situations in which the adsorbate is both valuable and heat sensitive and in which pressure swing regeneration is ineffective.

Thermal Swing—Steam Stripping

Steam stripping is the most common desorption technique because it is simple and relatively inexpensive.

There are several additional advantages to using steam for desorption.
- A low steam temperature of 230°F (110°C) is sufficient to desorb most adsorbates of interest without damaging the carbon.
- Steam readily condenses in the adsorber bed, releasing its (the steam's) heat of condensation and aiding in desorption.
- Immiscible organic compounds can be easily separated from the steam by condensation and decantation.
- Miscible compounds will require condensation followed by distillation.
- Residual moisture in the bed can be removed easily by a stream of cool, dry air (either pure or process-effluent).
- Steam is a more concentrated source of heat than hot air and is effective in raising the temperature of the adsorber bed quickly. Steam also avoids the potential fire hazard associated with air.

The amount of steam required for regeneration depends on the adsorbate and the adsorbate loading of the bed. The longer a carbon bed is steamed, the more adsorbate will be desorbed. It is usually not cost-effective to try to desorb all of the adsorbate. Acceptable working capacities can be achieved by using less steam and leaving a small portion of adsorbate in the bed (the heel). During the initial heating period, only a small amount of organic is desorbed because a fixed amount of steam is first required to raise the temperature of the bed to the desorption temperature. As the bed temperature increases, the rate of desorption increases until a plateau is reached. The plateau represents the optimum steam requirement, usually in the range of 0.25 to 0.35 pound of steam/pound of carbon.[17] The steam is usually supplied at pressures ranging from 3 to 15 psig, and steam usage can range anywhere from 0.3 to 10 pounds of steam per pound of solvent removed.

Some disadvantages are associated with steam regeneration:

- The aqueous effluent from the condenser can pose a water pollution problem unless the condensate is sent to a wastewater treatment facility.
- Some organic compounds may hydrolyze or form corrosive solutions in the presence of water. Corrosive substances can greatly reduce the life of the adsorption equipment unless expensive corrosive resistant materials are used.
- A hot, wet carbon bed will not effectively remove organic vapors. The bed will need to be cooled and dried to ensure adequate removal efficiencies at the beginning of a subsequent cycle.

Pressure Swing - Vacuum Desorption

Pressure swing or vacuum desorption has one primary advantage over thermal (steam) desorption. Desorption is accomplished by a change in pressure rather than temperature, so the time required to heat and cool the carbon bed is avoided. Thus pressure swing allows the bed to be in the adsorption mode for a greater fraction of the total cycle time. Smaller units may also be used because there is no increase in air volume due to heating of the bed. Both of these conditions allow for higher throughputs or smaller adsorber designs than can be accommodated by thermal swing desorption systems. Importantly, the desorbed vapors can be condensed directly, thus avoiding the need for additional downstream processing equipment, such as decanters or distillation columns.

The principle disadvantages of a pure pressure swing cycle are its high operating and construction costs. A vacuum system is required, unless the adsorber is initially operated at elevated pressures so that the pressure swing can be accomplished by reducing the vessel to atmospheric pressures. In vacuum systems, the adsorber vessel and valving must be constructed of materials capable of withstanding vacuums of 28 in. Hg (380 in. W.C.). Vacuum systems operating cyclically may require more operating attention than other regeneration systems. To be effective, pressure regeneration systems must operate so that a small decrease in pressure will result in a drastic shift in the direction of mass transfer.

PROBLEM 4-4

A solvent degreaser is designed to recover toluene from an 8,000 ACFM air stream at 77°F (25°C) and atmospheric pressure. The company is planning to use a two-bed carbon adsorption system with a cycle time of 4 hours. The average concentration of toluene is 2,400 ppm. Given the adsorption isotherm for toluene (Figure 4-24), and the additional operational data given below, estimate the following:

- The amount of carbon required for a 4-hour operating cycle (operating time between desorption steps).
- The square feet of cross-sectional area required based on a 100 ft/min maximum velocity.
- The depth of the carbon bed.

Given:

Molecular weight of toluene = 92.1
Activated carbon density = (30 lb_m/ft^3)
Working capacity is 25% of saturation capacity

SOLUTION

Step 1. First calculate the toluene flow rate.

$$\left(8,000 \text{ ACFM }\right)\frac{68 + 460\,^\circ\text{R}}{77 + 460\,^\circ\text{R}} = 7,866 \text{ SCFM}$$

$$\left(7,866\,\text{SCFM }\right)\left(\frac{\text{lb mol total}}{385.4\,\text{scf}}\right)\left(\frac{0.0024\,\text{lb mol toluene}}{\text{lb mol total}}\right) = 0.049\,\text{lb mol toluene / min}$$

The mass flow rate of toluene is:

$$\left(0.049\,\text{lb mol / min }\right)\left(92.1\text{lb}_\text{m}\text{ / mol}\right) = 4.51\,\text{lb}_\text{m}\text{ / min}$$

Step 2. To determine the saturation capacity of the carbon, calculate the partial pressure of toluene at the adsorption conditions.

$$\text{P}^* = \text{yP} = \left(\frac{2,400\,\text{ppm}}{1,000,000}\right)\left(14.7\,\text{psia }\right) = 0.0353\,\text{psia}$$

From Figure 4-24, the saturation capacity of the carbon is 43% or 43 pounds toluene per 100 pounds of carbon at 0.0353 psia.
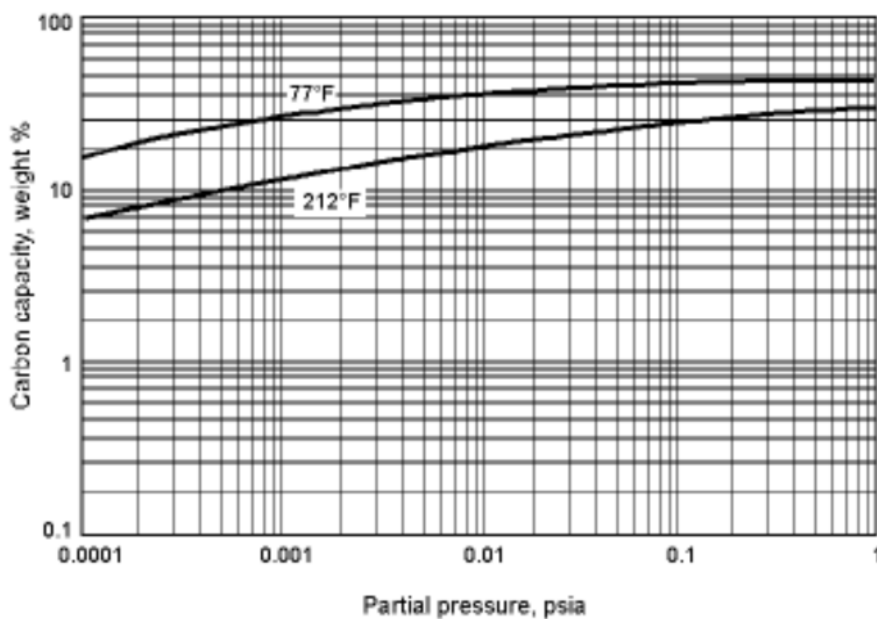
Figure 4-24. Toluene isotherm.

Step 3. Determine the amount of carbon at saturation for a 4-hour cycle:

$$\left(4.51\frac{lb_m\ toluene}{min}\right)\left(\frac{60\ min}{hr}\right)\left(\frac{100\ lb_m\ carbon}{43\ lb_m\ toluene}\right)\left(4\frac{hr}{cycle}\right)=2,517\ lb_m$$

The working charge of carbon can be estimated by multiplying the charge at saturation by four. Therefore, the working charge is:

$$(4)(2,517\ lb_m\ of\ carbon\ )=10,068\ lb_m\ of\ carbon$$

The cross-sectional area of the bed is the volumetric flow rate divided by the allowable velocity of 100 ft/min through the adsorber.

The required cross-sectional area is:

$$A=\frac{Q}{Maximum\ Velocity}=\frac{8,000\ ACF/min}{100\ ft/min}=80\ ft^2$$

Step 4. Estimate the bed depth.

Each bed of the proposed two-bed system would have to handle the 8,000 ACFM gas flow rate because one bed would be in desorption mode a portion of the operating time.

At a carbon density of 30 lb_m/ft^3, the bed depth would be:

Vol. carbon = 10,068 lb_m carbon/ 30 $lb_m/\ ft^3$) = 336 ft^3

Bed depth = 336 ft^3 / 80 ft^2 = 4.2 ft

This bed depth may result in excessively high pressure drop, so it may be preferable to use a larger vessel and a lower gas velocity. The required cross-sectional area is recalculated below using an average velocity of 60 ft/min rather than the 100 ft/min value used earlier in this problem.

$$A=\frac{Q}{Maximum\ Velocity}=\frac{8,000\ ACF/min}{60\ ft/min}=133\ ft^2$$

The bed depth for this modified approach would be:

336 ft^3/133 ft^2 = 2.5 ft

4.5 PERFORMANCE MONITORING

Premature Breakthrough

The factors that contribute to premature organic breakthrough in a large fixed-bed, regenerative system or a large nonregenerative system are relatively similar. The problems include but are not limited to the following:

- Corrosion and subsequent collapse of the pellet beds
- Infrequent desorption (not applicable to nonregenerative systems)
- Loss of adsorptive capacity due to high boiling point compounds
- Plugging of activated carbon pellet beds due to particulate matter
- Physical deterioration of the activated carbon pellets or carbon fiber materials
- Increased operating temperature
- Increased organic vapor concentration

A conventional, regenerative, deep, fixed-bed system will be used to illustrate the techniques available to evaluate performance and to identify the problems listed above. Although the techniques are relatively similar for all types of fixed-bed systems, some small-scale fixed-bed units will not have all of the on-site instruments that are economically reasonable for the large installations.

The example fixed-bed system flowchart is shown in Figure 4-25. This shows three adsorber beds in parallel. The SLA stream from the process equipment is discharged by the centrifugal fan through a particulate matter filter and an indirect heat exchanger into the top of the on-line adsorber vessel. Low-pressure steam is used to desorb the organic vapors from the off-line adsorber vessel. The typical types of instruments present on a large-scale system are shown in this flowchart.
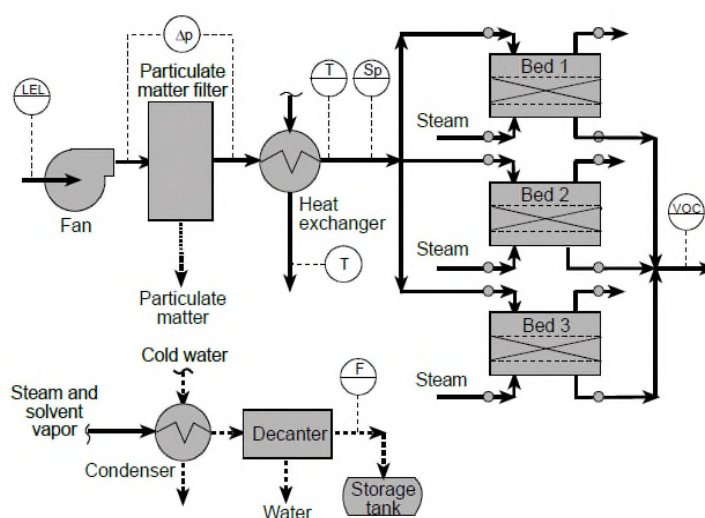
Figure 4-25. Flowchart of a three-bed (deep bed) absorber.

A control room or control panel for the adsorber system is usually located in an area close to the adsorber vessels. One or more storage tanks are usually also close to the system.

OUTLET VOC CONCENTRATION MONITOR

The most direct measure of the performance of the adsorber is provided by the outlet VOC concentration monitor. This instrument draws a sample gas stream from the outlet of each bed on a frequent basis. Common types of instruments include photoionization and flame ionization detectors (FID). The outlet concentrations are determined and recorded on a data acquisition system (DAS) or strip chart recorder at the control panel for the adsorber system. Premature breakthrough or other improper operation will be indicated by high outlet concentrations.

It should be noted that these instruments provide an accurate indication of the outlet concentration only when they are calibrated for the specific organic compound, or compounds, present in the gas stream. The instruments are usually calibrated using a readily-available organic compound such as methane, propane, n-hexane, or 1,3-butadiene that can be prepared in a stable form at relatively high concentrations (100 to 10,000 ppm). Stable gas samples are much more difficult to prepare for compounds such as toluene, halogenated organics, and ketones. When calibration gases such as methane, propane, or 1,3-butadiene are used for calibration, the instrument reading is only a qualitative indicator of performance. However, instrument readings above baseline levels for the unit are a clear indication of adsorber performance problems.

The accuracy of the VOC data should be checked regularly. The instruments should be calibrated on a daily basis using gas cylinders. Calibration gas is usually injected near the sample port on each adsorber bed (Figure 4-26) so that the integrity of the sample line to the instrument can be confirmed. A variety of problems in these sample lines can lead to lower-than-actual organic vapor concentration readings; these include:

- VOC outlet monitor sample line problems
- Air infiltration due to leaking connections or corroded tubing
- Adsorption and absorption along the tubing walls due to low surface temperatures and water condensation
- Reduced sample gas flow rates due to partial plugging of the tubing (primarily affects flame ionization detectors)
- Inoperative valves controlling sample gas flow from each adsorber vessel

The calibration frequencies and procedures for the instruments should be checked. A single point calibration and a zero check should be made on a daily basis. Outlet concentration data obtained since the last calibration period may be corrected for calibration drift and zero drift by computerized data acquisition systems.
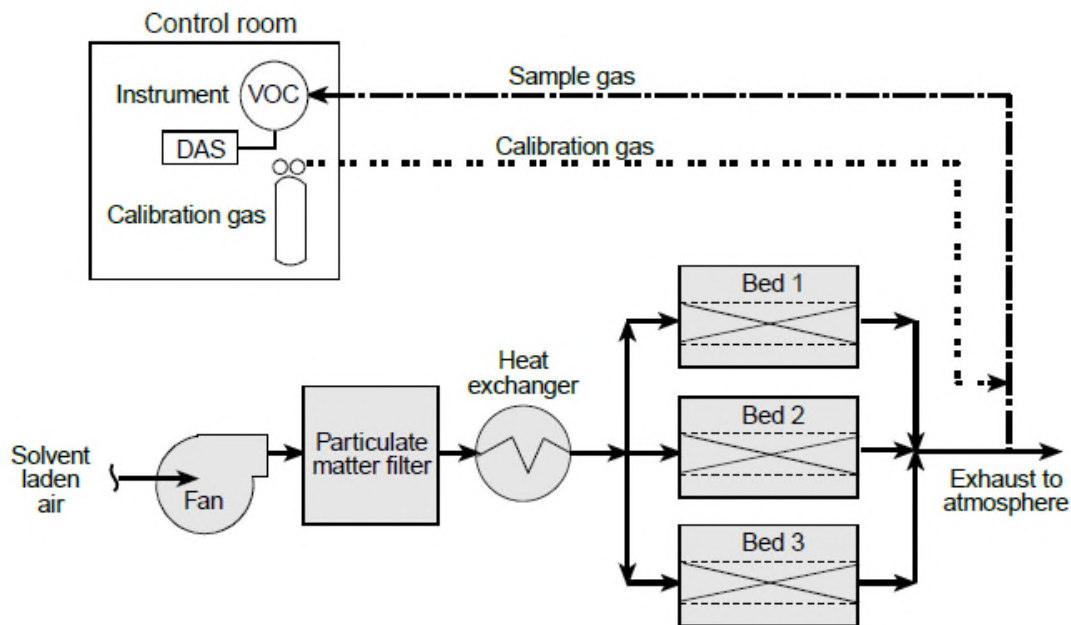
Figure 4-26. Calibration gas injection locations to check for sample line tubing problems.

PORTABLE ORGANIC VAPOR CONCENTRATION DETECTORS

There are a variety of portable detectors (often termed portable VOC analyzers) that can be used for small-scale fixed-bed adsorbers where it is uneconomical to have permanently mounted instruments. The most common types include (1) flame ionization detectors, (2) catalytic combustion analyzers, and (3) photoionization detectors. All of these are battery-powered instruments that can be used to obtain a small gas sample and provide a qualitative indication of the total outlet VOC concentration. These instruments are subject to the same calibration gas limitations that affect the permanently mounted units on large-scale adsorber systems.

Flame Ionization Detectors

The flame ionization detector (FID) extracts 10 to 50 cc/min of the sample gas that is mixed with either pure hydrogen or a hydrogen/helium blend. The mixture is injected and combusted along with "clean" air in the FID. The organic compounds oxidized in the hydrogen flame form positive gas ions that are driven to a collector electrode in the burner chamber. The electrical current flowing through this electrode is amplified and provides an indication of the total mass of organic vapor in the sample gas stream. Any compounds that can be oxidized in the burner chamber can be detected, including essentially all organic compounds with the exception of low molecular weight, highly oxygenated or halogenated compounds, such as formaldehyde (CH_2O) and carbon tetrachloride (CCl_4).

Catalytic Combustion Analyzers

The catalytic combustion analyzer is similar to the FID analyzer in that the organic compounds in the sample gas stream are entirely oxidized during the analysis. A small sample gas stream

passes through a sintered metal detector that has a catalyst-coated wire. Oxidation of the organic compounds in this detector changes the electrical resistance of the coated wire. This change in resistance is converted to a current signal that is proportional to the total organic vapor concentration. This type of instrument responds to approximately the same types of compounds as the flame ionization detector; however, it is not quite as sensitive.

Photoionization Detectors

A photoionization detector (PID) pulls a sample gas stream through a small chamber where the organic compounds are irradiated with ultraviolet light. A small fraction of the organics is photoionized to form positive ions that are accumulated on an electrode creating a current proportional to the organic vapor concentration. The current is amplified to indicate the total organic vapor concentration. Unlike the flame ionization analyzer, the photoionization detector is essentially nondestructive. The sample gas stream passing through the instrument can be recovered in a sample gasbag and returned to a laboratory for more detailed analysis.

Photoionization detectors can detect organic compounds with ionization potentials close to or below the ionization energy level of the lamp (e.g., 9.0, 10.0, 10.2, and 11.3 electron volts). Most organic compounds can be detected, including the highly oxygenated or halogenated compounds that cannot be measured by the flame ionization detector.

Photoionization detectors are not useful for low molecular weight paraffinic compounds such as methane, propane, and butane, because these compounds have high ionization potentials. This is not a problem with respect to carbon adsorber system evaluations, however, because these same compounds have a very low affinity for activated carbon and are not controlled by these systems.

All three types of instruments can be used to measure the outlet VOC concentration from an adsorber. Because of the limited pump capacity of all three instrument types, the sample should be obtained from a positive pressure portion of the outlet duct. A single point measurement can usually be made, and the monitoring times are relatively short.

Organic vapor concentration measurements using portable VOC analyzers should be made near the end of the adsorption cycle. At this time, the outlet VOC concentration is at a maximum. The measurements must not be conducted when the adsorber is in the cooldown-purge cycle just prior to returning to adsorption service. During this period, the gas stream humidity is high and water droplets may be present. Moisture can damage the sensors of all three types of instruments.

ADDITIONAL MONITORING CONSIDERATIONS

LEL Inlet Monitor

Adsorbers designed to operate with feed gas containing more than 10% to 25% of the LEL usually have an LEL monitor in the inlet duct to the adsorber system. The primary purpose of this instrument is to shut down the fan and other system components in the event that the inlet concentration increases above the safety limit.

This instrument can be used to provide a qualitative indication of changes in the inlet VOC concentration. Increased inlet concentrations could lead to organic vapor breakthrough unless

the adsorption cycle time is decreased.

Gas Inlet Temperature

The gas inlet temperature is one of the most important variables affecting performance. Due to the weak physical forces involved in adsorption, increased gas temperatures result in substantially reduced adsorption capacity which leads to increased pre-breakthrough concentrations and premature breakthrough. The inlet gas temperatures should be compared during the last several months to identify significant increases above baseline values. Furthermore, gas inlet temperatures above 100°F (38°C) may lead to inadequate adsorber performance.

Adsorber Vessel Bed Static Pressure Drop

The static pressure drop across a fixed-bed adsorber is usually between 0.5 and 3.0 in. W.C. (0.1 and 0.75 kPa) per foot of bed. The static pressure drop across moving-bed adsorbers is usually considerably lower than the levels for the fixed-bed designs.

Changes from baseline pressure drop levels are usually associated with conditions that adversely affect performance. An increase in the static pressure drop (no change in the gas flow rate) can be caused by the accumulation of dust and particulate matter on the inlet side of the bed. Gas flow maldistribution will lead to decreased adsorption efficiency. A decrease in the static pressure drop may indicate partial or complete collapse of the fixed-bed due to corrosion of the support grid.

Gas Flow Rate

Gas flow rates above the design range of the absorber vessel create a longer-than-anticipated MTZ. Breakthrough will occur if the MTZ reaches the outlet of the carbon bed before the adsorber is brought off-line for desorption. Usually, the maximum gas velocities through the bed are limited to less than 100 feet per minute. Increased gas flow rates are indicated by increased centrifugal fan motor currents, increased adsorber vessel pressure drop, and/or increased hood static pressures.

Decreased gas flow rates may also indicate performance problems. Increased fugitive emissions from the process equipment served by the adsorber could be due to reduced gas flow rates. This problem may be indicated by reduced fan motor current, decreased hood static pressure, decreased static pressure drop across the adsorber vessels, and/or decreased static pressure drop across the particulate matter filter.

Hood Static Pressure

The hood static pressure provides a useful indicator of the gas flow conditions at the pick-up point on the process equipment where the organic vapors are being released. The typical values of the hood static pressure range from approximately -0.3 in. W.C. (-0.075 kPa) to more than -2.0 in. W.C. (-0.5 kPa). If the hood static pressure becomes less negative (moves toward 0.0 in. W.C.), the gas flow rate has probably decreased, and fugitive emissions have probably increased.

4.6 SUMMARY

ADSORPTION SUMMARY

This lesson covered the following topics:

- Several types of adsorption systems used for various organic compounds.
- Principles of operation that apply to adsorption, and common adsorbants.
- Factors that affect the performance of an adsorption system.
- Areas of an adsorption system that require monitoring.

4.7 REVIEW EXERCISES

INSTRUCTIONS

Select the best response(s) for these multiple-choice questions.

1. What types of adsorbents are most often used in VOC adsorption systems? Select all that apply.

    a) Activated carbon
    b) Carbon fiber
    c) Zeolites
    d) Polymeric materials

2. What is the primary purpose for using a pre-concentrator adsorption system?

    a) Achieve high VOC concentrations to facilitate higher saturation capacities
    b) Improve collection efficiency in the adsorber vessel
    c) Reduce the gas stream volume and increase the VOC concentration in an incinerator inlet gas stream
    d) Increase the gas stream concentration prior to treatment in a condenser

3. What materials and/or techniques are used to desorb VOCs from regenerative type adsorption systems? Select all that apply.

    a) Low pressure steam
    b) Hot air
    c) Vacuum
    d) Hot water flush

4. What is the adsorber bed inlet concentration limit for VOC-containing gas streams

    a) 25% of the LEL
    b) 75% of the LEL
    c) 95% of the LEL
    d) 99% of the LEL

5. What problems can potentially be created by the presence of particles larger than approximately 3 micrometers? Select all that apply.

    a) Plugging of the inlet side of the bed
    b) Increased channeling of the solvent-laden air through the bed
    c) Increased static pressure drop
    d) Reduction in adsorbent saturation capacity

6. What is the normal maximum gas temperature used in VOC adsorption systems?

   a) 75°F
   b) 100°F
   c) 130°F
   d) 160°F

7. What type of solvent separator is needed for an activated carbon adsorber system that uses low-pressure steam for desorption and is collecting water-insoluble organic compounds?

   a) Condenser and decanter
   b) Distillation column
   c) Stripping column
   d) None of the above

8. What is the typical VOC removal efficiency of a properly designed and operated adsorption system?

   a) 50% to 75%
   b) 75% to 90%
   c) 90% to 98%
   d) 98% to 99.5%

9. Is an activated carbon adsorber system applicable to the removal of methane and ethane from a gas stream?

   a) Yes
   b) No
   c) It depends on the solvent-laden gas temperature
   d) It depends on the solvent-laden gas pressure

Operating Principles of Adsorption Systems

10. How does the saturation capacity of an activated carbon bed change when the VOC concentration increases?

    a) It increases
    b) It decreases
    c) It remains unchanged
    d) It depends on the specific VOC

11. How does the saturation capacity of an activated carbon bed change when the temperature of the solvent-laden air increases?

    a) It increases
    b) It decreases
    c) It remains unchanged
    d) It depends on the specific VOC

12. How does the saturation capacity of an activated carbon bed change when the humidity of the solvent-laden air increases?

    a) It increases
    b) It decreases
    c) It remains unchanged
    d) It depends on the specific VOC

13. Can the adsorption isotherm shown in Figure 4-20 be used for sizing an adsorber using a different commercial activated carbon product?

    a) Yes
    b) No
    c) It depends on the temperature of the solvent-laden air entering system and the sample gas used to develop the isotherm
    d) It depends on the temperature and relative humidity of the solvent-laden air entering the system and the sample gas used to develop the isotherm

14. Why are high molecular weight compounds (> molecular weight of 200) difficult to handle in a regenerative adsorber system?

    a) They are not adsorbed efficiently
    b) They have too high an affinity and cannot be efficiently desorbed
    c) They cannot be separated in decanters, condensers, and distillation columns
    d) They are likely to decompose at the elevated adsorption temperature

Adsorption System Performance

15. Using Figure 4-24, what is the saturation capacity of activated carbon for toluene at a temperature of 77°F and a toluene concentration of 600 ppm?

16. Based on the saturation capacity determined in Question 15, how much activated carbon would be needed in a three-bed regenerative system to treat a gas stream having a toluene concentration of 600 ppm and a gas flow rate of 30,000 SCFM? Assume that each bed is desorbed every third hour and that two beds are in service during all operating times. Assume that the working capacity is 15% of the saturation capacity.

17. Is the superficial velocity within the normal range for activated carbon fixed-bed systems if the three beds evaluated in Question 16 have cross-sectional areas of 180 ft^2 each? Use a gas temperature of 77°F, an inlet static pressure of + 6 in. W.C., and a barometric pressure of 29.65 in. Hg, if necessary in solving the problem.

18. What is the approximate static pressure drop across the carbon bed described in Questions 16 and 17? The bed contains 4×10 mesh carbon having a density of 30 lb$_m$/ft^3.

19 The static pressure drop of a fixed-bed carbon adsorber system has increased from 4 in. W.C. to 5.5 in. W.C. The static pressure drop across the particulate matter filter has decreased from 1.5 in. W.C. to 1.3 in. W.C. The fan motor current has also decreased. Have the fugitive emissions from the process equipment probably increased or decreased due to these changes?

   a) Increased
   b) Decreased

20 Which techniques are used to determine the adsorption isotherms that are used to size adsorbent beds?

   a) Pilot plant tests
   b) Laboratory tests with the specific type or brand of adsorbent
   c) Theoretical adsorption models
   d) Other

Performance Monitoring

21 What technique can be used to determine if breakthrough is occurring on a VOC adsorption system handling toluene?

   a) Monitoring of the outlet VOC concentration
   b) Measuring the bed static pressure drop
   c) Measuring the bed inlet gas temperature
   d) All of the above

22 What is the primary purpose of measuring the hood static pressure?

   a) Evaluate changes in the gas flow rate that could adversely affect the adsorption bed
   b) Determine if there is a need to adjust the desorption frequency
   c) Identify possible increases in fugitive emissions from process equipment
   d) Identify need to change the rate of water flow to an indirect heat exchanger upstream of the adsorber beds

23 What is the primary purpose of installing the adsorber bed inlet LEL gauge?

   a) Detect potentially explosive conditions so that the system can be rapidly de-energized
   b) Detect increased VOC concentrations that could require increased desorption frequency

c) Detect increased VOC concentrations that could confirm improved fugitive emission capture at the process source

d) Provide data for compiling a material balance of VOC materials around the adsorption system

24 What is the purpose of installing a solvent-laden air temperature gauge at the inlet of the adsorption beds?

a) Detect potentially explosive conditions so that the system can be rapidly de-energized
b) Detect increased gas temperatures that could require increased desorption frequency
c) Detect decreased gas temperatures that could indicate impaired fugitive emission capture at the process source
d) Detect increased gas temperatures that could cause the VOCs to decompose

4.8 REVIEW EXERCISES: SOLUTIONS

This Student Guide includes separate exercises and solutions, which allow students to check their work.

MULTIPLE CHOICE ANSWERS

1. What types of adsorbents are most often used in VOC adsorption systems? Select all that apply.

   a) **Activated carbon**
   b) **Carbon fiber**
   c) Zeolites
   d) Polymeric materials

2. What is the primary purpose for using a pre-concentrator adsorption system?

   a) Achieve high VOC concentrations to facilitate higher saturation capacities
   b) Improve collection efficiency in the adsorber vessel
   c) **Reduce the gas stream volume and increase the VOC concentration in an incinerator inlet gas stream**
   d) Increase the gas stream concentration prior to treatment in a condenser

3. What materials and/or techniques are used to desorb VOCs from regenerative type adsorption systems? Select all that apply.

   a) **Low pressure steam**
   b) **Hot air**
   c) **Vacuum**
   d) Hot water flush

4. What is the adsorber bed inlet concentration limit for VOC-containing gas streams

   a) **25% of the LEL**
   b) 75% of the LEL
   c) 95% of the LEL
   d) 99% of the LEL

   In some facilities, 10% of the LEL is the maximum allowed.

5. What problems can potentially be created by the presence of particles larger than approximately 3 micrometers? Select all that apply.
   a) **Plugging of the inlet side of the bed**
   b) **Increased channeling of the solvent-laden air through the bed**
   c) **Increased static pressure drop**
   d) Reduction in adsorbent saturation capacity

6. What is the normal maximum gas temperature used in VOC adsorption systems?

   a) 75°F
   b) 100°F
   c) **130°F**
   d) 160°F

7. What type of solvent separator is needed for an activated carbon adsorber system that uses low-pressure steam for desorption and is collecting water-insoluble organic compounds?

   a) **Condenser and decanter**
   b) Distillation column
   c) Stripping column
   d) None of the above

8. What is the typical VOC removal efficiency of a properly designed and operated adsorption system?

   a) 50% to 75%
   b) 75% to 90%
   c) **90% to 98%**
   d) 98% to 99.5%

9. Is an activated carbon adsorber system applicable to the removal of methane and ethane from a gas stream?

   a) Yes
   b) **No**
   c) It depends on the solvent-laden gas temperature
   d) It depends on the solvent-laden gas pressure

Operating Principles of Adsorption Systems

10. How does the saturation capacity of an activated carbon bed change when the VOC concentration increases?

    a) **It increases**
    b) It decreases
    c) It remains unchanged
    d) It depends on the specific VOC

11. How does the saturation capacity of an activated carbon bed change when the temperature of the solvent-laden air increases?

    a) It increases
    b) **It decreases**
    c) It remains unchanged
    d) It depends on the specific VOC

Increased temperature increases the vapor pressure and internal energy of the pollutants, making them less likely to adsorb to the surface (increased energy allows more pollutant molecules to overcome the adsorption energy and remain in the gas phase), thus the saturation capacity decreases.

12. How does the saturation capacity of an activated carbon bed change when the humidity of the solvent-laden air increases?

    e) It increases
    f) It decreases
    g) It remains unchanged
    h) It depends on the specific VOC

13. Can the adsorption isotherm shown in Figure 4-20 be used for sizing an adsorber using a different commercial activated carbon product?

    a) Yes
    b) No
    c) It depends on the temperature of the solvent-laden air entering system and the sample gas used to develop the isotherm
    d) It depends on the temperature and relative humidity of the solvent-laden air entering the system and the sample gas used to develop the isotherm

14. Why are high molecular weight compounds (> molecular weight of 200) difficult to handle in a regenerative adsorber system?

    a) They are not adsorbed efficiently
    b) They have too high an affinity and cannot be efficiently desorbed
    c) They cannot be separated in decanters, condensers, and distillation columns
    d) They are likely to decompose at the elevated adsorption temperature

Adsorption System Performance

15. Using Figure 4-24, what is the saturation capacity of activated carbon for toluene at a temperature of 77°F and a toluene concentration of 600 ppm?

SOLUTION

Step 1. In the gas phase, the mole fraction (y) is equal to the ppm divided by 10^6.

    y = 600 ppm = 0.0006

    P* = yP = (0.0006)(14.7 psia) = 0.0088 psia

Step 2. From Figure 4-24, at a partial pressure of 0.0088 psia and a temperature of 77°F the carbon saturation capacity is read as about 40%.

16. Based on the saturation capacity determined in Question 15, how much activated carbon would be needed in a three-bed regenerative system to treat a gas stream having a toluene concentration of 600 ppm and a gas flow rate of 30,000 SCFM? Assume that each bed is desorbed every third hour and that two beds are in service during all operating times. Assume that the working capacity is 15% of the saturation capacity.

SOLUTION

Step 1. First calculate the toluene flow rate per bed.

$$\left(15,000\,\text{SCFM}\right)\left(\frac{\text{lb mol total}}{385.4\,\text{scf}}\right)\left(\frac{0.0006\,\text{lb mol toluene}}{\text{lb mol total}}\right) = 0.0234 \;\text{lb mol toluene / min}$$

The mass flow rate of toluene is:

$$\left(0.0234\,\text{lb mol / min}\right)\left(92.1\,\text{lb}_m\,/\,\text{mol}\right) = 2.16\,\text{lb}_m\,/\,\text{min}$$

From Question 15, the saturation capacity of the activated carbon is 40% or 40 pounds toluene per 100 pounds of carbon at 0.0088 psia.

Step 2. The amount of carbon at saturation for a 2-hour cycle is:

$$\left(\frac{2.16\,\text{lb}_m}{\text{min}}\right)\left(\frac{100\,\text{lb}_m\,\text{carbon}}{40\,\text{lb}_m\,\text{toluene}}\right)\left(\frac{60\,\text{min}}{\text{hr}}\right)\left(\frac{2\,\text{hours}}{\text{cycle}}\right) = 648\,\text{lb}_m\,\text{carbon per bed}$$

The working charge of carbon can be estimated by dividing the charge at saturation by 0.15. Therefore, the working charge is calculated as:

$$\frac{648\,\text{lb}_m}{0.15} = 4,320\,\text{lb}_m\,\text{of carbon}$$

17. Is the superficial velocity within the normal range for activated carbon fixed-bed systems if the three beds evaluated in Question 16 have cross-sectional areas of 180 ft^2 each? Use a gas temperature of 77°F, an inlet static pressure of + 6 in. W.C., and a barometric pressure of 29.65 in. Hg, if necessary in solving the problem.

SOLUTION

Step 1. Calculate the absolute static pressure.

$$SP_{absolute} = (6\,in.\,W.C.) + 29.65\,in.\,Hg\left(\frac{407\,in.\,W.C.}{29.92\,in.\,Hg.}\right) = 409\,in.\,W.C.$$

Step 2. Calculate the gas flow rate in ACFM.

$$= (15,000\,SCFM)\left(\frac{77 + 460\,^\circ R}{68 + 460\,^\circ R}\right)\left(\frac{407\,in.\,W.C.}{409\,in.\,W.C.}\right) = 15,181\,ACFM$$

Step 3. Determine the superficial velocity through bed.

Velocity = Flow Rate/Area = $(15,181\,ft^3/min)/180\,ft^2 = 84.3\,ft/min$

Yes, the velocity is in the normal range (<100 ft/min).

18. What is the approximate static pressure drop across the carbon bed described in Questions 16 and 17? The bed contains 4×10 mesh carbon having a density of 30 lb_m/ft^3.

SOLUTION

Step 1. Calculate the depth of the activated carbon bed.

At a carbon density of 30 lb_m/ft^3, the bed depth would be:

Vol. carbon = 4,320 lb_m carbon/(30 lb_m/ft^3) = 144 ft^3

Bed depth = 144 ft^3/180 ft^2 = 0.8 ft

Step 2. Calculate the static pressure drop.

From Question 17, linear velocity = 84 ft/min. From Figure 4-23, the pressure drop per foot of bed depth is approximately 7 in. W.C./ft.

Static pressure drop = 0.8 ft (7.0 in. W.C./foot of bed) = 5.6 in. W.C.

19. The static pressure drop of a fixed-bed carbon adsorber system has increased from 4 in. W.C. to 5.5 in. W.C. The static pressure drop across the particulate matter filter has decreased from 1.5 in. W.C. to 1.3 in. W.C. The fan motor current has also decreased. Have the fugitive emissions from the process equipment probably increased or decreased due to these changes?

c) **Increased**
d) Decreased

Explanation:

Due to the decreased fan motor current, there is likely less air and contaminants being drawn into the hood, and therefore fugitive emissions would increase.

20. Which techniques are used to determine the adsorption isotherms that are used to size adsorbent beds?

    a) Pilot plant tests
    b) Laboratory tests with the specific type or brand of adsorbent
    c) Theoretical adsorption models
    d) Other

Performance Monitoring

21. What technique can be used to determine if breakthrough is occurring on a VOC adsorption system handling toluene?

    a) Monitoring of the outlet VOC concentration
    b) Measuring the bed static pressure drop
    c) Measuring the bed inlet gas temperature
    d) All of the above

22. What is the primary purpose of measuring the hood static pressure?

    a) Evaluate changes in the gas flow rate that could adversely affect the adsorption bed
    b) Determine if there is a need to adjust the desorption frequency
    c) Identify possible increases in fugitive emissions from process equipment
    d) Identify need to change the rate of water flow to an indirect heat exchanger upstream of the adsorber beds

23. What is the primary purpose of installing the adsorber bed inlet LEL gauge?

    a) Detect potentially explosive conditions so that the system can be rapidly de-energized
    b) Detect increased VOC concentrations that could require increased desorption frequency
    c) Detect increased VOC concentrations that could confirm improved fugitive emission capture at the process source
    d) Provide data for compiling a material balance of VOC materials around the adsorption system

24. What is the purpose of installing a solvent-laden air temperature gauge at the inlet of the adsorption beds?

    a) Detect potentially explosive conditions so that the system can be rapidly de-energized
    b) Detect increased gas temperatures that could require increased desorption frequency
    c) Detect decreased gas temperatures that could indicate impaired fugitive emission capture at the process source
    d) Detect increased gas temperatures that could cause the VOCs to decompose

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5.0 ABSORPTION

5.1 OVERVIEW

INTRODUCTION

Absorbers in air pollution control applications use aqueous scrubbing liquids to remove gases and vapors. Absorber design has benefited substantially from the extensive development of these types of systems for non-pollution-control process applications and is, therefore, a relatively mature technical field.

The use of absorbers has increased since 1990 because of increased concerns about gaseous contaminants, which are classified as air toxic or volatile organic compounds (VOCs). In addition to stand-alone systems, absorbers are frequently used downstream of thermal and catalytic incinerators to remove acid gases generated from the combustion of sulfur-containing and/or halogenated compounds present in the incinerator feed.

Absorption refers to the transfer of a gaseous component from the gas phase to a liquid phase. The opposite operation, known as stripping, involves the transfer of the contaminant from the liquid to the gas phase and is important in water pollution control applications. Absorption occurs into liquid droplets dispersed in the gas stream, sheets of liquid covering packing material, or jets of liquid within the vessel. The liquid surface area available for mass transfer and the time available for diffusion of the gaseous molecules into the liquid are important factors affecting performance. Absorption can be divided into two broad classifications: straight dissolution of *absorbate* (contaminant gas) into *absorbent* (liquid), and dissolution accompanied by irreversible chemical reaction. The majority of this chapter covers only straight dissolution. Dissolution accompanied by chemical reaction, which is important in air pollution control applications such as flue gas desulfurization, is covered briefly at the end of Section 5.4 Capability and Sizing.

The gaseous contaminant being absorbed (absorbate) must be at least slightly soluble in the scrubbing liquid (absorbent). Mass transfer to the liquid continues until the liquid approaches saturation. At saturation, equilibrium is established between the two phases. The mass transfer rate of the contaminant into the liquid is equal to the mass transfer rate of the dissolved species back into the gas phase. Accordingly, the solubility of the contaminant in the liquid creates a limit to the amount of pollutant removal that can occur with a given quantity of liquid. This solubility limit can be overcome by providing reactants in the liquid phase that react with the dissolved gas contaminant, forming a dissolved compound that cannot exit the liquid. This is the case in flue gas desulfurization (covered in Chapter 9: Sulfur Oxides Control), where a compound that reacts irreversibly with SO_2, such as lime [$Ca(OH)_2$], is added to the liquid.

LEARNING OBJECTIVES

At the conclusion of this training, students will be able to:

- Identify various types of absorbers.
- Identify the principles of operation that influence the efficiency of absorbers.
- Determine the capability and sizing parameters of an absorber system.
- Identify the instrumentation requirements for an absorber system.

5.2 TYPES AND COMPONENTS OF ABSORBERS

TYPES OF ABSORBERS

Spray-Tower Absorbers

Spray towers are the simplest devices used for gas absorption. They consist of an open vessel and one or more sets of liquid spray nozzles to distribute the scrubbing liquid (absorbent). Typically, the flow is countercurrent, with the contaminant gas stream entering near the bottom of the tower and flowing upward, while the liquid enters near the top and flows downward. The most dilute gas is exposed to the most dilute liquid at the top of the column while the most concentrated gas and liquid are in contact near the bottom. Figure 5-1 illustrates a typical countercurrent-flow spray-tower absorber. Spray towers range in size (throughput) from 5 to 100,000 ACFM (0.14 to 2800 m^3/min).
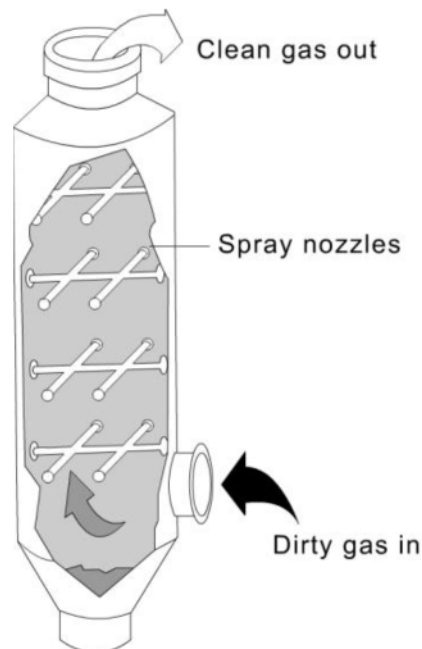
Figure 5-1. Countercurrent spray-tower scrubber.

Spray chambers can also operate in crosscurrent- or cocurrent-flow arrangements when there is limited space in an industrial facility. In crosscurrent absorbers, the gas flow is perpendicular to the liquid flow. In cocurrent absorbers, the gas and liquid flow in the same direction. Because the gas stream does not "push" against the liquid stream as in countercurrent-flow, higher gas stream velocities can be used. With higher gas stream velocities, the size of the unit can be reduced. However, crosscurrent or cocurrent spray towers are not usually as efficient as countercurrent units.

The liquid is distributed through a series of spray nozzles. Full-cone nozzles are generally used. The full-cone nozzle generates a spray pattern that completely fills the target area, as shown in Figure 5-2. The spray angle is a function of the liquid pressure in the supply header.
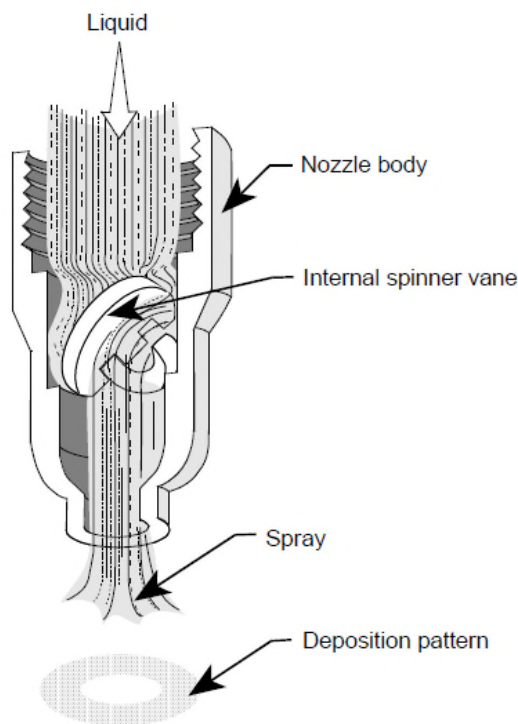
Figure 5-2. Full-cone spray nozzle.

The quantity of liquid, normally characterized by the liquid-to-gas ratio (L/G), is a key parameter in gas absorption. The (L/G) is frequently expressed in units of gallons per minute of liquid divided by the gas flow rate in units of 1,000 ACFM. Typical (L/G) ratios for spray-tower absorbers can vary from 5 to more than 50 gallons per 1,000 ACF. The (L/G) is determined by the solubility of the contaminant in the liquid and by the mass transfer characteristics in the spray tower. Contaminant capture efficiency increases with increasing (L/G) and one important aspect of the design problem amounts to determining the optimum (L/G) required to satisfy emission specifications at the minimum cost.

Because of limited contact between the liquid droplets and the gas stream, spray-tower absorbers are used primarily in applications where the gases are extremely soluble in the absorbent, where high pollutant removal efficiency is not required, or where the chemical reactions in the absorbing liquid could result in salts that could cause plugging in other types of

absorber vessels. They have been used to control SiF_4 and HF generated in fertilizer plants during the production of superphosphate. Spray towers are also used in a number of flue gas desulfurization systems.

The main advantage of spray-tower absorbers is that they are completely open. They have no internal components except for the spray nozzles and connecting piping. Therefore, they have a very low gas-stream static pressure drop, which ranges from 1 to 3 in. W.C. (0.25 to 0.75 kPa) for the absorber vessel.

Mist eliminators, which are used to prevent liquid droplets from exiting the absorber with the gas stream, are used in all types of gas absorber equipment. Mist eliminators used in spray towers can add a 0.3 to 4 in. W.C. (0.075 to 1.0 kPa) to the total gas-phase static pressure drop.

Packed-Bed Absorbers

Packed-bed absorbers are the most common absorbers used for gas removal. The absorbing liquid is dispersed over the packing material, which provides a large surface area for gas-liquid contact. Packed beds are classified according to the relative direction of gas-to-liquid flow.

Types of Packed Bed Absorbers. The most common packed-bed absorber is the countercurrent-flow tower shown in Figure 5-3. The gas stream enters the bottom of the tower and flows upward through the packing material and exits from the top after passing through a mist eliminator.

Liquid is introduced at the top of the packed-bed by sprays or weirs and flows downward over the packing. In this manner, the most dilute gas contacts the least saturated absorbing liquid and the concentration difference between the liquid and gas phases, which is necessary for mass transfer, is reasonably constant through the column length. The maximum (L/G) in countercurrent-flow is limited by flooding, which occurs when the upward force exerted by the gas is sufficient to prevent the liquid from flowing downward. The minimum (L/G) is fixed by the need to ensure that all of the packing is covered by a thin liquid film.
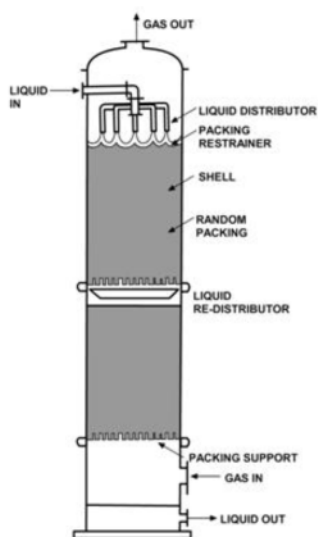
Figure 5-3. Countercurrent packed-tower.

In a cross-flow absorber, the gas stream flows horizontally through the packed bed, which is irrigated by the scrubbing liquid flowing down through the packing material. A typical cross-flow absorber is shown in Figure 5-4. Inlet sprays aimed at the face of the bed may also be included. The leading face of the packed bed is often slanted in the direction of the incoming gas stream, as shown in Figure 5-4. The force exerted by the gas stream deflects the liquid from straight downward flow. Slanting the bed allows for this deflection and ensures complete wetting of the packing.
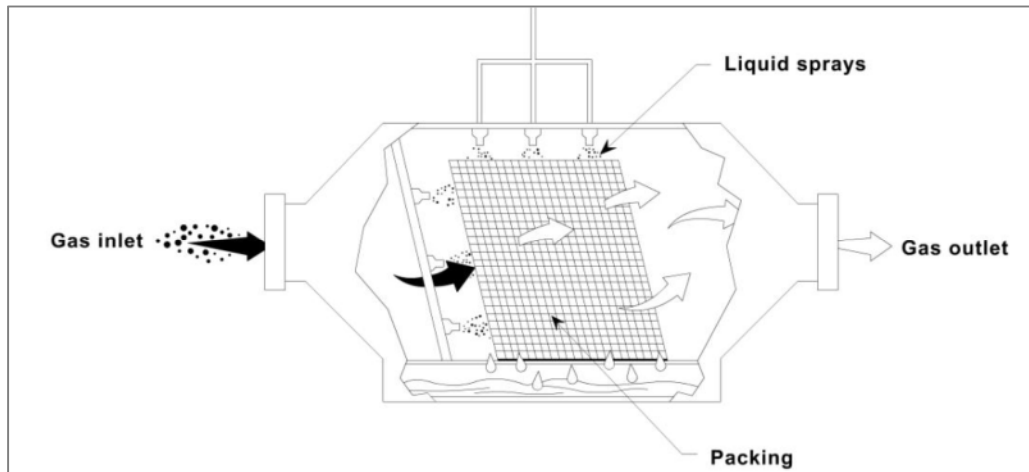
Figure 5-4. Flowchart of cross-flow scrubber.

The design procedure for cross-flow absorbers is more complex because concentration gradients exist in two directions: from top to bottom and from front to rear. Gas-phase static pressure drop in packed bed absorbers ranges from 0.25 to 1 in. W.C. per ft of packing (0.06 to 0.25 kPa) when the unit operates at typical gas flow rates. Large variations in liquid or gas flow rates cause loading and flooding of this type of absorber.

Packed-bed absorbers are most suited to applications where high gas-removal efficiency is required, and the feed gas stream is relatively free from particulate matter. In the production of both sulfuric and hydrochloric acids, packed bed absorbers are used to control tail and exhaust emissions (i.e., SO_2 and HCl, respectively). The scrubbing liquor for these processes can be a weak acid solution with the spent liquor from the packed-tower sent back to the process. Packed-towers are also used to control HCl and H_2SO_4 fume emissions from pickling operations in the primary metals industry. They are used to control odors in rendering plants, petroleum refineries, and sewage treatment plants. For odor control applications, the packed bed scrubbing liquor usually contains an oxidizing reagent, such as sodium hypochlorite (NaOCl). In these applications, an acid backwash must be added if a precipitate is formed or if plugging can be a problem. The gas flow rate through packed-towers can vary from 5 to 30,000 ACFM (0.14 to 850 m^3/min).

Packing Material. The primary purpose of the packing material is to provide a large surface area for mass transfer. Figure 5-5 illustrates some of the most commonly used packings. These packings are usually made of plastic (polyethylene, polypropylene, or polyvinylchloride), but can be ceramic or metal. A specific packing is described by its trade name and overall size. For

example, a column can be packed with 2-inch (5-centimeter) Raschig^{TM} rings or 1-inch (2.5-centimeter) Tellerettes^{TM}. The overall dimensions of packing materials normally range from 1 to 4 inches (2.5 to 10 centimeters).

Raschig™ ring   Pall ring   Berl saddle

Intalox saddle   Tellerette™

Figure 5-5. Types of packing.

The specific packing selected depends on the corrosiveness of the contaminants and scrubbing liquid, the size of the absorber, the static pressure drop, and the cost. Specific considerations involved in the selection of packing materials are summarized below.

Cost	Plastic packings are generally cheaper than metal, with ceramic being the most expensive.
Low pressure drop	Pressure drop is a function of the volume of void space in a tower when filled with packing. Generally, the larger the packing size, the smaller the pressure drop.
Corrosion resistance	Ceramic or porcelain packing is commonly used in a very corrosive atmosphere.
Structural strength	Packing must be strong enough to withstand normal loads during installation, service, physical handling, and thermal fluctuations. Ceramic packing is subject to cracking under sudden temperature changes.
Weight	Heavier packing may require additional support materials or heavier tower construction. Plastics are much lighter than either ceramic or metal packings.

Design flexibility   The efficiency of a scrubber changes as the liquid and gas flow rates are varied. Packing material must be able to handle the process changes without substantially affecting the removal efficiency.

Packing material may be arranged in an absorber in either of two ways. The packing may be dumped into the column randomly (as indicated in Figure 5-3) or stacked as structured material. Randomly packed-towers provide a higher surface area per unit volume (ft^2/ft^3), but also cause a higher-pressure drop than stacked packing. In addition to the lower pressure drop, the stacked packing provides better liquid distribution over the entire surface of the packing. However, the labor cost of installing stacked packing can be a major drawback, particularly for large systems.

Liquid Distribution. One of the requirements for efficient absorption is good gas-liquid contact throughout the entire packed bed. At the top of the column, liquid should be distributed over the entire upper surface of the packed bed. This is commonly achieved by the trough and weir or the perforated pipe arrangements shown in Figure 5-6, which provide flexibility with variations in liquid flow rate. Arrays of spray nozzles are also used.

(a) Trough and weir type   (b) Perforated pipe
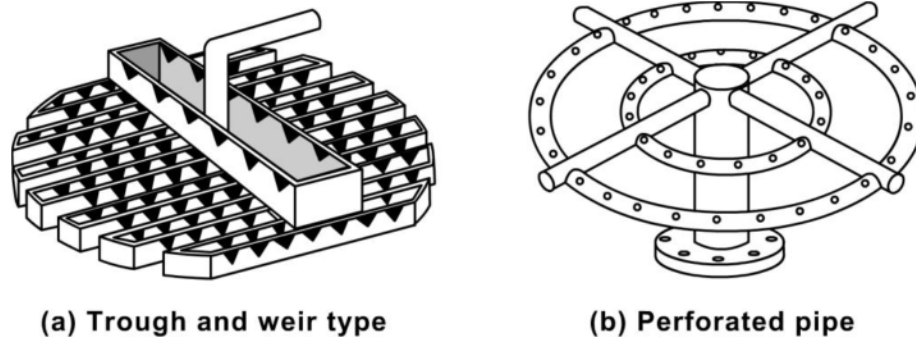
Figure 5-6. Types of liquid distributors for packed-bed absorbers.

Once the liquid is distributed over the packing, it flows down by the force of gravity through the packing, following the path of least resistance. The liquid tends to flow toward the tower wall where the void spaces are greater than in the center. Once the liquid hits the wall, it flows straight down the tower (known as *channeling*). With taller columns, it is necessary to redirect the liquid from the tower wall back to the center of the column using liquid redistributors. Redistributors are usually placed at intervals of no more than 10 feet (3 meters), or five tower diameters, whichever is smaller.[1]

Uniform distribution of the inlet gas stream is also important for achieving good gas-liquid contact. This is accomplished by properly designing the inlet gas ducts and the support trays that hold the packing material.

Tray-Tower Absorbers

A tray-tower absorber is a vertical column with one or more trays mounted horizontally inside

for gas-liquid contact. The gas stream enters at the bottom and flows upward, passing through openings in the trays. Liquid enters at the top of the tower, and travels across each tray and then through a downcomer to the tray below until it reaches the bottom of the tower. Mass transfer occurs in the liquid spray created by the gas velocity through the openings in the tray. Figure 5-7 illustrates a typical bubble cap–tray tower unit. Note that Figure 5-7 shows the capability for the addition and removal of liquid at an intermediate position in the column. Such an arrangement would be unusual in pollution control applications.
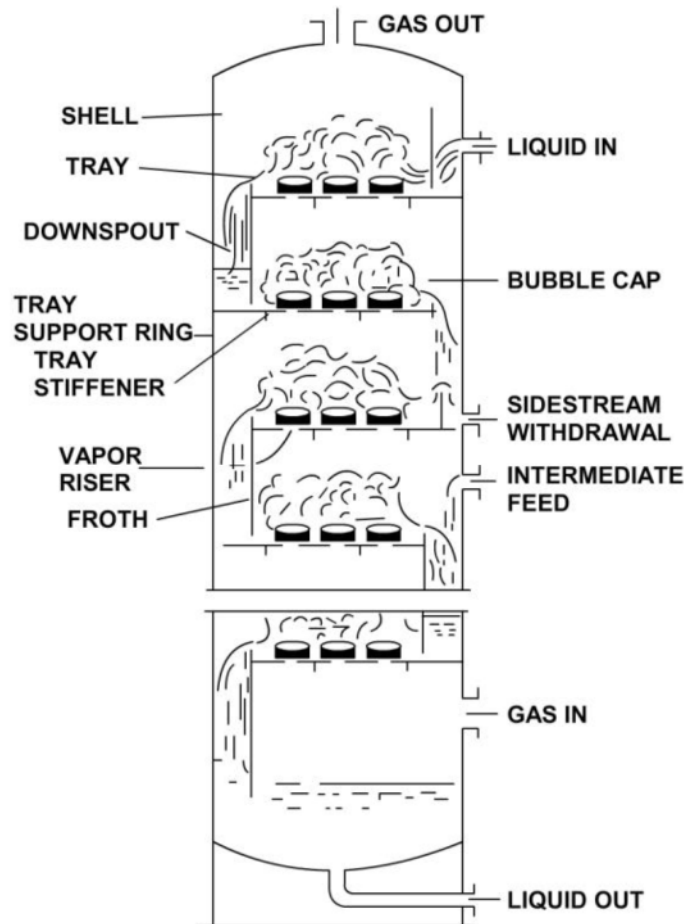
Figure 5-7. Bubble-cap tray.

The function of the trays is to provide a liquid depth through which the gas bubbles and creates liquid droplets, creating large gas-liquid interface areas for mass transfer. The depth of liquid on each tray is controlled by a weir at the position where liquid enters the downcomer. The pressure of the gas below each tray must be sufficient to prevent liquid droplets from falling through the openings in the trays, a condition known as *weeping*. A variety of different tray designs are used for air pollution control.

Bubble-Cap Trays. A bubble-cap tray is illustrated in Figure 5-7. The gas stream enters the liquid layer through holes or slots in the bubble caps mounted on each tray. This type of unit can

handle wide ranges of gas and liquid rates without adversely affecting efficiency because the bubble caps are liquid-tight.

Sieve Trays. Sieve trays contain a number of orifices ranging from 0.25 to 1 in. (0.6 to 2.5 cm) in diameter. Because of these relatively large openings, the sieve trays are less prone to solids accumulation and plugging than other types of trays that have smaller orifices.

Figure 5-7 provides a more detailed picture of gas-liquid contact in bubble-cap trays. The liquid flow direction in the bubble cap tray is as described above (i.e., across the tray). However, the geometry of the sieve tray shown in Figure 5-8 is the disk-and-donut arrangement. A central downcomer is used to provide radial liquid flow from the center outward, and then from the outer edge to the center in successive trays. Sieve trays may also be operated with liquid flow across each tray in alternating directions, much like the bubble-cap liquid flow.
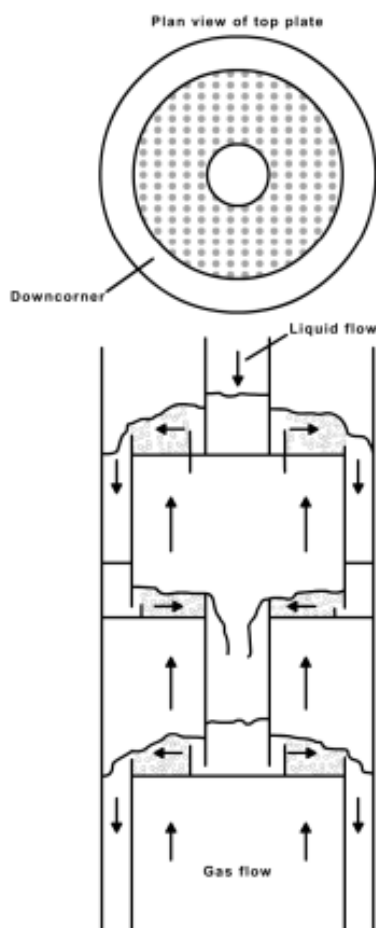
Figure 5-8. Gas-liquid contact in a disk-and-donut sieve tray.

Impingement Trays. The gas stream passes through small orifices in the impingement tray that are usually 3/16 in. (0.48 cm) in diameter. Small impingement targets above each orifice are used to promote gas-liquid contact immediately above the tray. Mass transfer is enhanced since a portion of the liquid is actually atomized due to the high gas velocities created by the small

orifices and impingement targets. The liquid layer across the impingement tray is maintained at 0.75 to 1.5 in. (1.9 to 3.8 cm) by means of an overflow weir on the discharge side of the tray. Impingement trays are somewhat more prone to plugging by solids present in the feed gas because of the smaller orifices.

Float Valve™ Trays. The gas stream flows up through small holes in the tray and lifts metal valves or caps that cover the openings. The valves are restrained by legs that limit vertical movement. The liftable caps act as variable orifices and adjust the size of the opening depending on gas flow rate through the absorber.

High removal efficiencies are possible in all properly designed tray towers because of the good gas-liquid contact that can be achieved on a tray. The use of several trays in series also ensures that uneven distribution of the gas and liquid on a single tray does not severely limit the efficiency of the overall absorber.

Venturi and Ejector Absorbers

Venturi absorbers are used primarily when there is a need to simultaneously remove particulate matter and absorb gaseous contaminants. Ejector absorbers are used primarily in small-scale systems where it is uneconomical to provide a fan for gas movement. The gas stream flows through the absorber simply by the aspiration (suction) effect of the high-velocity ejector liquid stream. The ejectors function in a manner similar to aspirators on laboratory sinks. Ejector absorbers are also used in series arrangements for the concentration of acids in manufacturing processes.

Venturis. A typical venturi configuration, shown in Figure 5-9, consists of a converging section for the acceleration of the approaching gas stream containing the contaminant, a means to introduce the liquid absorbent stream, a gas-liquid contacting throat, and a diverging section for decelerating the gas stream and atomized liquid droplets.

Some venturis have a baffle-type adjustable throat mechanism that permits the velocity of the gas stream passing through the throat to be adjusted. This enables the unit to maintain conditions favorable for particle impaction, despite changes in the gas flow at different process operating rates. There are many different commercial designs of adjustable throat mechanisms.

Venturi absorbers normally operate with high gas-phase static pressure drops ranging from 10 to 100 in. W.C. (2.5 to 25 kPa). The necessary pressure drop is based primarily on the particle size distribution of the incoming gas stream and the applicable particulate matter removal requirements and is not directly related to the capability of the venturi to absorb gaseous contaminants.
In the throat, gas velocities can vary between 100 and 600 ft/sec (30 to 180 m/sec). These high velocities effectively create large interfacial surface area by atomizing the liquid. There is very limited time for gas absorption. In fact, at normal venturi throat velocities, the gas stream and the liquid droplets are in close contact for periods of less than 0.002 seconds. There is a strong tendency for droplets to be entrained because of their small size. For this reason, both the gas and liquid exit through a cyclonic mist eliminator, where centrifugal force causes the small droplets to separate by migrating to the wall of the vessel. The cyclonic mist eliminator is then followed by a standard mist eliminator at the top of the vessel.
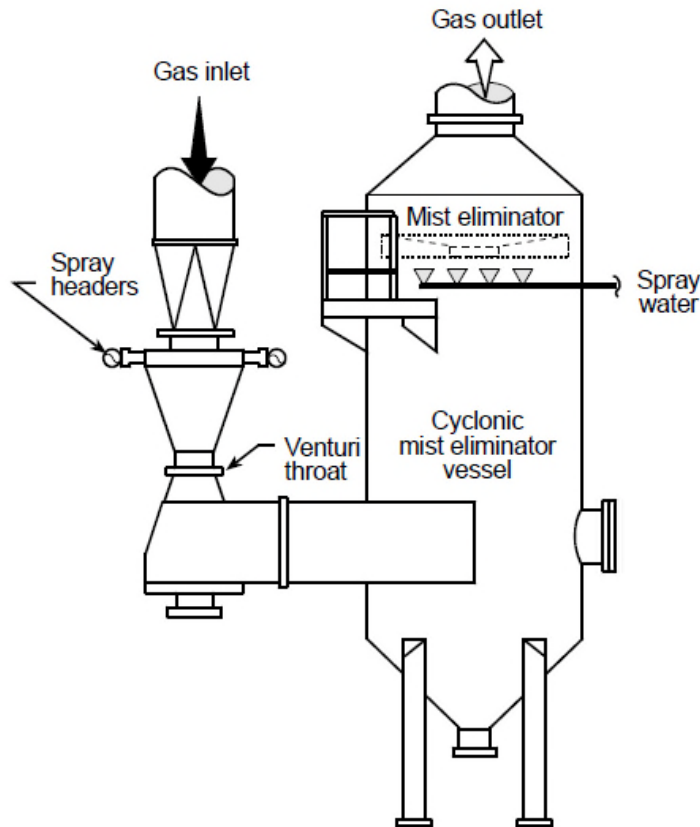
Figure 5-9. Venturi absorber.

To overcome the short residence time, some venturi systems used primarily for gaseous absorption operate at high (L/G) ratios ranging from 20 to 100 gallons per 1,000 ACF (2.7 to 13 liters per m³ of gas). For comparison purposes, it should be noted that venturi (L/G) ratios for particulate matter removal are usually optimal in the range of 4 to 20 gallons per 1,000 ACF (0.5 to 2.7 liters per m³).

Ejector Absorbers. Ejector absorbers are often used in series, as shown in Figure 5-10, where three ejector absorbers are followed by a packed-bed absorber. Solvent-laden gas is introduced near the top of the first ejector absorber and passes through the remaining ejector absorbers in series, and finally enters the packed-tower absorber for final polishing. The treated gas from the top of the packed-bed absorber is emitted to the atmosphere. Make-up absorbing liquid is introduced into the packed bed and then passes from ejector to ejector in a direction opposite to that of the gas flow. This overall countercurrent-flow arrangement results in the most concentrated liquid contacting the most concentrated gas in the first ejector and fresh liquid contacting the least concentrated gas in the packed bed. "Product" liquid is removed from the system from the first ejector absorber stage.

Liquid is added to each ejector through a high-pressure spray nozzle operating at more than 80 psig aimed at the throat section of the ejector. This creates an aspiration effect that pulls the gas stream through each vessel and eliminates the need for a fan or blower to move the gas stream. The high-pressure sprays also form very small liquid droplets that provide a large gas-liquid interfacial area for absorption of gases. Mass transfer is aided by the highly turbulent conditions

around the droplets, but is limited by the relatively short contact time between the droplets and the gas stream.

Ejector absorbers operate at high liquid-to-gas ratios (around 100 gallons/1,000 ACF). The gas-phase static pressure rises (pressure increases in absorber) usually range between 4 and 8 in. W.C. (1 to 2 kPa). However, the overall power consumption is high because of the liquid pumping requirements.
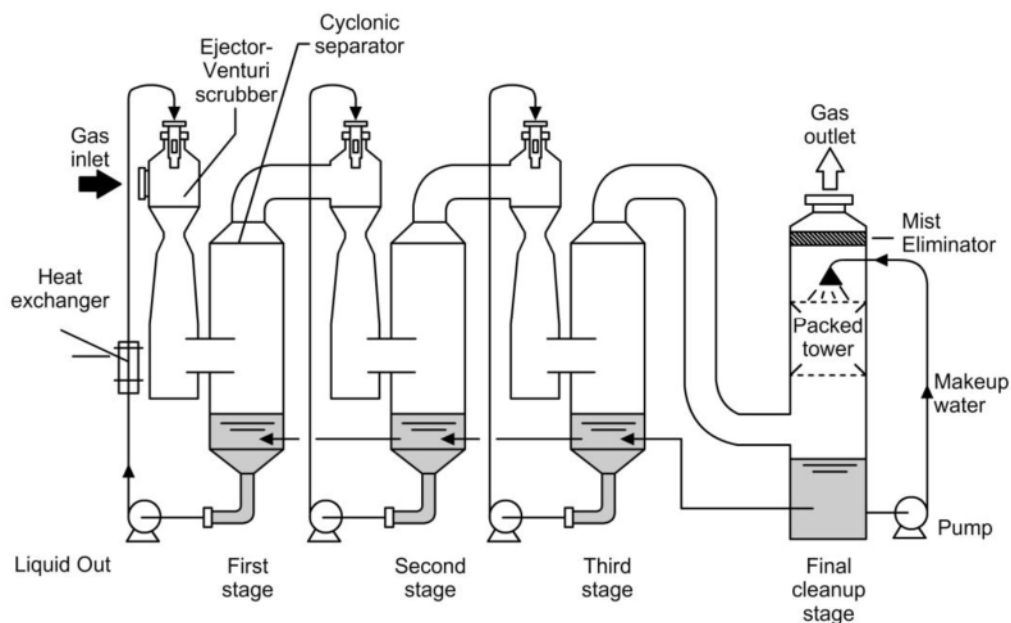
Figure 5-10. Ejector absorber.

Ejector absorbers are used in acid production facilities and also for some types of emergency scrubbers. Emergency scrubbers are often required in enclosed areas in the event of an accidental release of compressed gases such as ammonia or chlorine.

Biofiltration Beds

Biofiltration systems use aerobic microorganisms in a packed bed to consume organic compounds. The microorganisms are present in a thin layer over porous support packing composed of soil, compost, peat, or vegetation wastes. A simplified flowchart of a biofiltration system is shown in Figure 5-11.

The inlet gas stream must be humidified to approximately 95% relative humidity in order to avoid drying the bed and killing the microorganisms.[2] Water may be sprayed on the top of the bed in order to maintain total moisture levels equivalent to 40% to 60% of the total weight.[2] A portion of this water drains from the bed and is recirculated to minimize make-up water requirements and reduce wastewater discharge quantities.

The bed temperature must be maintained between approximately 68°F and 105°F (20°C and 40°C).[3,4] High-temperature excursions can kill the organisms while low-temperature operations

can suppress the biological activity. For cold weather operations, it is necessary to supply supplemental heat or to design the unit for the low levels of biological activity that exist at these temperatures.
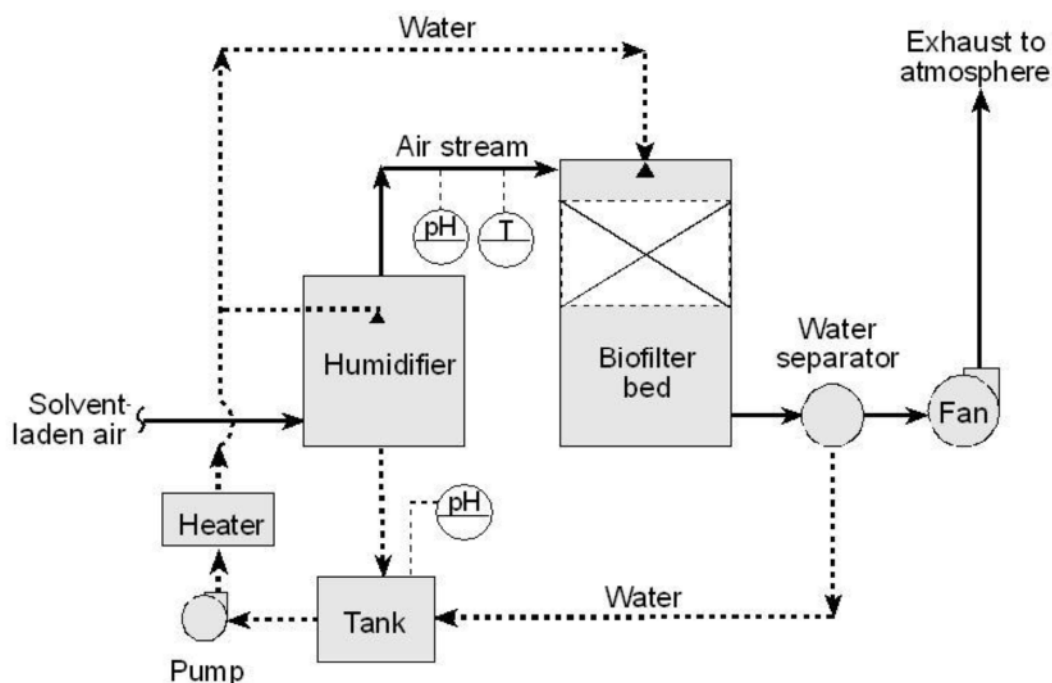
Figure 5-11. Biological oxidation system.[5]

The organic vapor contaminants passing through the bed must be water-soluble in order to enter the water layers surrounding the packing material. Once in the water layers, the compounds must be biodegradable. The highly variable rates at which organic compounds are consumed must be taken into account when sizing the unit.

Sulfur- and nitrogen-containing organic compounds can generate acidic compounds during biodegradation. Alkali additives may be necessary to maintain the pH level in the range of six- to eight- where the organisms are viable.[2]

The packed beds are usually approximately 3 feet (1 m) in height and have gas-flow static pressure drops between 4 and 12 in. W.C. (1 and 3 kPa).[2,3,4] The pressure drop may increase over time because of the gradual compaction of the bed and the buildup of mineral matter within the bed. The beds must be replaced on a two- to five-year cycle.

Biological oxidation systems are used primarily for low concentration (< 500 ppm) organic vapor streams. They can tolerate short-term spikes of relatively high concentrations and periods when the process is not operational.

COMMON ABSORPTION SYSTEM COMPONENTS

Most absorption systems generate liquid droplets that tend to be entrained in the gas stream leaving the treatment area. The mist eliminator is used to remove these entrained droplets prior to entering the induced draft fan (if present) and prior to discharge of the effluent from the stack. The droplets and the suspended and dissolved solids within the droplets emitted from the stack can create nuisance damage in the immediate vicinity.

The droplet sizes generated in absorbers range from approximately 200 to 1,000 micrometers (μm). While larger droplets quickly settle out of the gas stream, the small droplets are easily entrained and must be removed by means of impaction or centrifugal collection. Common types of mist eliminators used on absorbers include cyclonic vessels (Figure 5-9), chevrons (Figure 5-12), radial vanes (Figure 5-13), and mesh-pads (Figure 5-14).

The cyclonic vessels have a tangential inlet and operate much like a conventional large-diameter cyclone used for particulate removal. Droplets are accelerated toward the vessel wall by centrifugal forces imparted by the spinning gas. Depending on the gas velocity, the gas stream spins one-half to two revolutions prior to discharge. They have reasonable efficiencies when operated close to the design inlet gas velocities; however, droplet removal decreases rapidly at very low or very high gas velocities. Because of the spinning action of the gas stream, it is often necessary to install anti-vortex baffles in the stack in order to eliminate cyclonic flow conditions at emission testing locations.
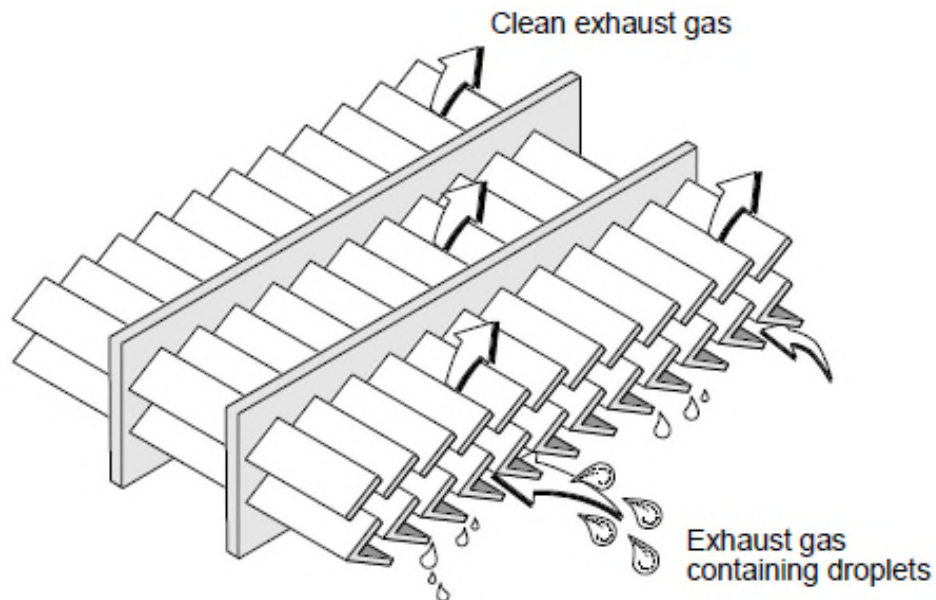
Figure 5-12. Chevron mist eliminator.

Chevrons are simply zigzag baffles that force the gas to turn sharply several times while passing through the mist eliminator. Water droplets collect on the chevron blades and coalesce into larger droplets that fall downward into the absorber. Chevron mist eliminators are generally limited to gas velocities of less than approximately 20 ft/sec (6 m/sec). At higher velocities, liquid on the blades can be driven toward the outlet side of the chevron, where it can be reentrained in the gas stream. High velocities are usually caused by the unintentional build-up of solids on part of the chevron. This increases the velocity in the portion of the mist eliminator still open for flow. In order to minimize solids accumulation, clean water spray headers are placed on the inlet and/or outlet sides. These are activated intermittently on a once-per-shift or once-per-day basis, depending on the severity of the solids buildup problem.

Radial-vane mist eliminators, shown in Figure 5-13, are conceptually similar to chevrons. The droplet-laden gas stream is forced through a set of turning vanes at the top of the absorption vessel.

Impaction of droplets occurs on the vanes as the gas stream turns to pass through the mist eliminator. A set of sprays is used to clean the vanes on an intermittent basis.
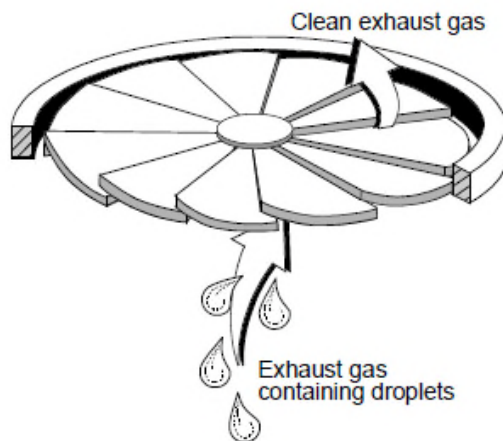
Figure 5-13. Radial-vane mist eliminator.
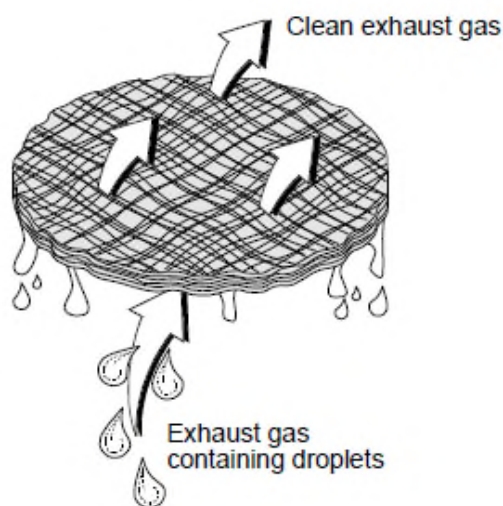
Figure 5-14. Mesh-pad mist eliminator.

Mesh-pads are formed from woven or randomly interlaced metal or plastic fibers that serve as impaction targets. The pads can be up to six inches thick. As with the chevrons, there is a maximum gas velocity above which reentrainment is possible. This maximum gas velocity, which depends on the density of the mesh (usually 5 to 9 lb_m/ft^3), on the materials of construction, and on the gas density, is usually in the range of 12 ft/sec (3.7 m/sec).

Mesh-pads are often layered, with the inlet layers capable of removing large quantities of large diameter droplets without overloading. The middle- and outlet-side layers are more compact and have high removal efficiencies for smaller liquid droplets. These units have maximum velocities of 8 to 15 ft/sec (2.4 to 4.6 m/sec), depending on the pad construction characteristics. Mesh-pad mist eliminators usually have clean water spray systems to remove solids. Blinding of these mist

eliminators (i.e., where solids/particulates have covered the mesh-pad to the point where the gas stream is unable to pass through) can lead to excessive pressure drops and liquid reentrainment.

Normal static pressure drops across mist eliminators range from 0.5 to more than 4 in. W.C. (0.12 to 1.0 kPa). Static pressure drop gauges are useful for monitoring the pressure drop and providing an early warning of solids accumulation.

Pumps and Piping Systems

Centrifugal pumps are commonly used for absorber systems. In these pumps, the liquid enters axially and is accelerated by the rotating impeller. As the liquid leaves the impeller radially, the liquid velocity decreases and the pressure increases.

The piping system generally consists of a number of components, including the suction pipe, strainer, suction-side check valve, and discharge control valve. The strainer is used for removal of small bits of metal and other contaminants that can be caught in the liquid stream. The suction-side check valve is used to reduce the risk of air infiltration into the suction-side piping during an outage of the system. The discharge valve is used to adjust liquid flow from the pump.

Instrumentation

Instruments are used throughout the absorber system to protect components and to monitor performance. A partial list of the parameters and common monitoring locations for most systems include the following:

Gas Temperature
- Absorber inlet
- Absorber outlet

Liquid Flow Rate
- Recirculation liquid stream
- Purge liquid stream

Liquid Pressure
- Recirculation pump discharge
- Absorber liquid distribution headers

Liquid pH
- Recirculation liquid tank
- Recirculation liquid stream

Static Pressure Drop
- Absorber vessel
- Mist eliminator

The absorber inlet temperature gauge is used to detect high gas temperatures that would impair absorption efficiency and could damage the absorber system. Many absorbers are constructed of fiberglass-reinforced plastics (FRP) or have corrosion-resistant liners that have maximum temperature limits ranging from 200°F to 400°F (90°C to 200°C). In the event of high inlet gas

temperature, emergency flush systems may be included to protect the system during an emergency shutdown.

The outlet gas temperature gauge is useful for evaluating absorber performance and to protect the downstream fan. Loss of scrubbing liquid flow because of pump failure, pipe freezing, pipe breakage, or pipe blockage could result in higher-than-desirable gas temperatures.

Liquid flow monitors, which are used to ensure that the flow rates remain within the intended operating range, are often required by both U.S. EPA and state regulations. They are especially important on systems that do not add alkali or other additives to react with the pollutants absorbed in the system. In these cases, the liquid flow must be maintained at a rate above the solubility limits for the pollutants being removed from the gas stream. The type of liquid flow monitor used depends on the size of the facility and the characteristics of the liquid being monitored. Relatively clean liquid streams can be monitored by orifice meters, swinging vane meters, and rotameters. Magnetic flow meters and ultrasonic meters can be used on streams with moderate solids levels.

Liquid pressure gauges are used on supply headers to the absorber to monitor for problems such as nozzle pluggage, nozzle orifice erosion, and header pluggage. Pluggage problems are indicated by higher than normal pressures. Most liquid pressure gauges are direct-indicating-type instruments. pH instruments are used to control the alkaline feed rate to absorber systems (for acid gas removal applications). It is usually advantageous to maintain the pH at levels between 5 and 9. At low pH, the materials are vulnerable to corrosion. At high levels, calcium and magnesium compounds can precipitate out of solution and create scale in piping, nozzles, scrubber walls, and mist eliminators.

The static pressure gauge across the absorber vessel is used primarily to evaluate routine performance. In large units, the static pressure is measured by a differential pressure transmitter, and an electrical signal is sent to a monitoring system in the control room. Direct-indicating gauges, such as manometers and Magnehelic® gauges, are used in many smaller systems.

Static pressure–drop gauges are used on mist eliminators to monitor for excessive solids build-up that could lead to droplet reentrainment and fan operating problems, and to indicate the need to activate the cleaning sprays.

5.3 OPERATING PRINCIPLES

PURPOSE

The purpose of this section is to introduce important variables that influence the gaseous pollutant-removal efficiency of absorbers. These operating principles apply to essentially all types of absorbers discussed previously.

MECHANISMS OF ABSORPTION

Two-Film Theory

The basic model for describing the absorption process is the *two film* or *double resistance* theory, which was first proposed by Whitman in 1923. The two film model, illustrated in Figure 5-15, starts by assuming that the gas and liquid phases are in turbulent contact with each other, separated by an interface. Further, the model proposes that a mass transfer zone exists to include a small film of the gas and liquid phases on either side of the interface. These films are assumed to be laminar.
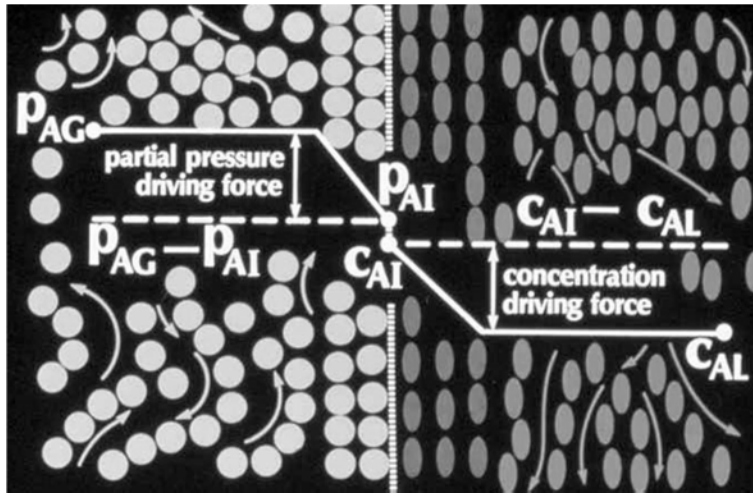
Figure 5-15. Two-film theory of absorption.

According to the two film theory, for a molecule of substance A to be absorbed it must proceed through a series of five steps. The molecule must diffuse:

1. From the bulk phase to the gas film
2. Through the gas film
3. Across the interface
4. Through the liquid film
5. Into the bulk liquid phase

The theory assumes that there is complete mixing in both the gas and liquid bulk phases and that the interface is at equilibrium. This implies that all resistance to diffusion occurs when the molecule is diffusing through the gas and liquid films, hence the name *double resistance* theory.

A gas concentration is expressed by its partial pressure. Accordingly, the concentration in the gas phase changes for p_{AG} in the bulk gas to p_{AI} at the interface. Similarly, the molar concentration in the liquid changes from c_{AI} at the interface to c_{AL} in the bulk phase. The rate of mass transfer is then equal to the amount of molecule A transferred, times the resistance molecule A encounters in diffusing through the films:

(Eq. 5-1) $\qquad\qquad\qquad N_A = k_g(p_{AG} - p_{AI})$

(Eq. 5-2) $\qquad\qquad\qquad N_A = k_l(c_{AI} - c_{AL})$

where:

N_A = rate of transfer of component A, lbmole/hr·ft^2
k_g = mass transfer coefficient for gas film, lbmole/hr·ft^2·atm
k_l = mass transfer coefficient for liquid film, lbmole/hr·ft^2·(lbmole/ft^3)

The mass transfer coefficients, k_g and k_l, represent the resistance molecule A encounters in diffusing through each film.

In practice, Equations 5-1 and 5-2 are difficult to use, since it is impossible to measure the interface concentrations p_{AI} and c_{AL}. These interface concentrations can be avoided by defining the mass transfer system at equilibrium conditions and combining the individual film resistances into an overall resistance. If the equilibrium line is straight, the rate of absorption is given by:

(Eq. 5-3) $N_A = K_{OG}(p_{AG} - p_A^*)$

(Eq. 5-4) $N_A = K_{OL}(c_A^* - c_{AL})$

where:

p_A^* = equilibrium partial pressure of component A, atm
c_A^* = equilibrium concentration of component A, lbmole/ft^3
K_{OG} = overall mass transfer coefficient for gas phase, lbmole/hr·ft^2·atm
K_{OL} = overall mass transfer coefficient for liquid phase, lbmole/hr·ft^2·(lbmole/ft^3)

The rate of mass transfer is dependent on the concentration departure from equilibrium in either the gas ($p_{AG} - p_A^*$) or liquid (c_A^* - c_{AL}) phase. The larger these concentration differences are, the greater the rate of mass transfer. If equilibrium is ever reached ($p_{AG} = p_A^*$ or $c_{AL} = c_A^*$) absorption stops and no net transfer occurs. Accordingly, it is important to design and operate absorbers so that saturation conditions are not reached. There are two ways to achieve this goal:

- Provide sufficient liquid so that the dissolved contaminants do not reach their solubility limit.
- Chemically react the dissolved contaminants so that they cannot return to the gas phase.

At equilibrium, the overall mass transfer coefficients are related to the individual mass transfer coefficients by:

(Eq. 5-5) $$\frac{1}{K_{OG}} = \frac{1}{k_g} + \frac{H}{k_l}$$

(Eq. 5-6) $$\frac{1}{K_{OL}} = \frac{1}{k_l} + \frac{1}{H \cdot k_g}$$

Here, H is Henry's Law constant, the slope of the equilibrium curve. Equations 5-5 and 5-6 are useful in determining which phase controls the rate of absorption. From Equation 5-5, if H is very small (which means the gas is very soluble in the liquid) then $K_{OG} \sim k_g$, and absorption is

said to be gas film controlled. The major resistance to mass transfer is in the gas phase. Conversely, if a gas has limited solubility then H is large, and Equation 5-6 reduces to $K_{OL} \sim k_l$. The mass transfer rate is liquid film controlled and depends on the contaminant diffusion rate in the liquid phase. Most systems in the air pollution control field are gas phase controlled, since the liquid is chose so that the contaminant will have a high degree of solubility.

Mass transfer coefficients are often expressed by the symbols $K_{OG}a$, $k_g a$, etc., where "a" represents the surface area available for absorption per unit volume of the absorber. This allows experimental data to be applied to absorbers with different configurations from the experimental apparatus. A typical $K_{OG}a$ plot is shown in Figure 5-15a.
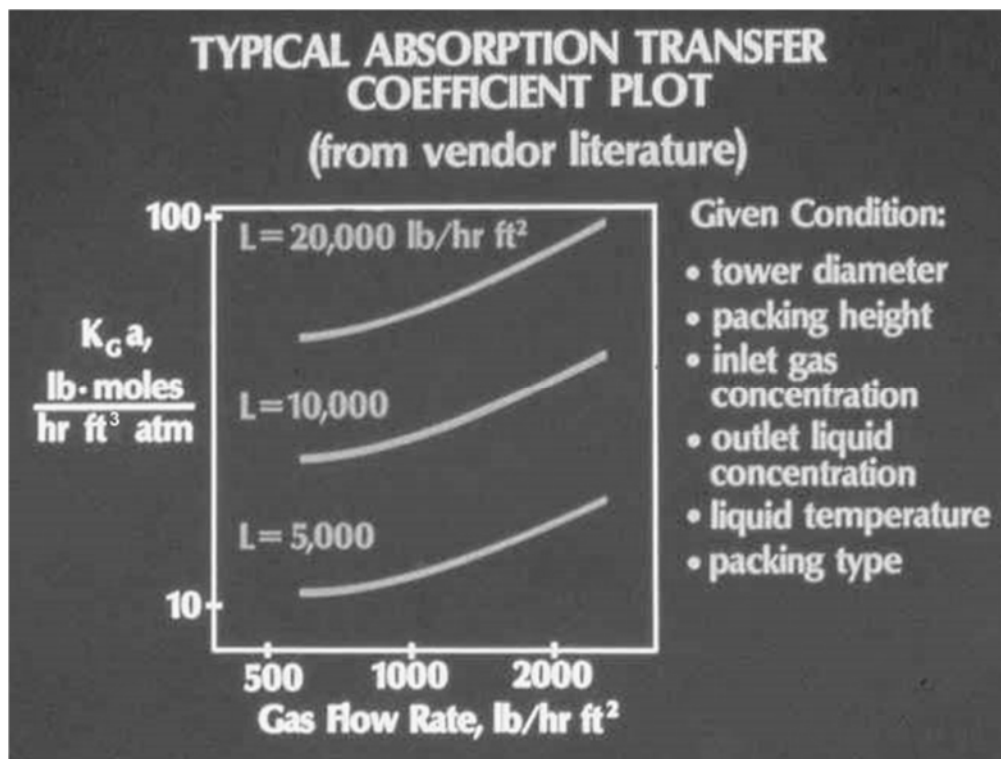
Figure 5-15a. Typical absorption transfer coefficient plot.

Solubility

The solubility of a gas in a liquid is a function of the temperature and partial pressure of the contaminant in the gas phase. Gas phase total pressure can also influence solubility, but this is not a major variable in absorbers used for air pollution control since they operate near atmospheric pressure.

Solubility data for an ammonia-water (NH_3-H_2O) system are presented in Table 5-1 as a function of temperature. Ammonia concentration in the gas phase is expressed as partial pressure in units of mm Hg, while liquid phase ammonia concentration is expressed in weight of NH_3 per 100 weights of H_2O. The data are taken from Perry's *Chemical Engineers Handbook*.[8]

Table 5-1. Equilibrium Partial pressure of ammonia over aqueous solutions, mm Hg.							
Wt. NH₃ per 100 wts. H₂O	0°C	10°C	20°C	30°C	40°C	50°C	60°C
20.0	64	103.5	166	260	395	596	834
15.0	42.7	70.1	114	179	273	405	583
10.0	25.1	41.8	69.6	110	167	247	361
7.5	17.7	29.9	50	79.7	120	179	261
5.0	11.2	19.1	31.7	51	76.5	115	165
4.0		16.1	24.9	40.1	60.8	91.1	129.2
3.0		11.3	18.2	29.6	45	67.1	94.3
2.5			15.0	24.4			77.0
2.0			12.0	19.3			61.0
1.6				15.3			48.7
1.2				11.5			36.3
1.0							30.2
0.5							

The most common method of analyzing solubility data is to use an equilibrium diagram. This is a plot of the mole fraction of solute (contaminant) in the liquid phase, denoted as x, versus the mole fraction of solute in the gas phase, denoted as y. Equilibrium data for the NH₃-H₂O system given in Table 5-1 are plotted in Figure 5-16 at 0°C, 20°C and 40°C.

Figure 5-16 illustrates the temperature dependence of the absorption process. At a constant mole fraction of solute in the gas (y), the mole fraction of NH₃ in the liquid (x) increases as the liquid temperature decreases.
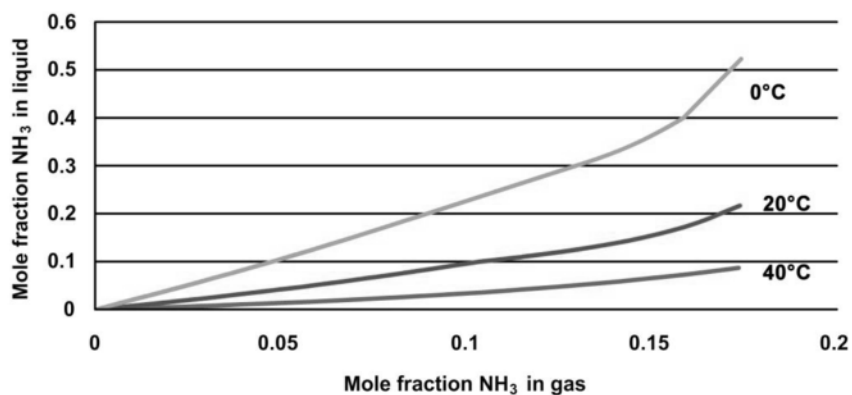
Figure 5-16. Ammonia-water (NH₃-H₂O) system.

Henry's Law

Under certain conditions (as described in the paragraphs following Eq. 5-8), the relationship

between the gas phase concentration and the liquid phase concentration of the contaminant at equilibrium can be expressed by Henry's Law.

(Eq. 5-7) $$P_A = H_P x_A$$

Where: P_A = partial pressure of contaminant in gas phase at equilibrium
H_p = Henry's Law constant when the gas concentration is expressed in partial pressure
x_A = mole fraction of contaminant dissolved in the liquid phase at equilibrium

Henry's Law can be written in an alternate form that is consistent with the data in Figure 5-16 by dividing both sides of Equation 5-7 by the total pressure, P, of the system. The left side of the equation becomes the partial pressure divided by the total pressure, which (according to Dalton's Law) is equal to the mole fraction in the gas phase, y_A. The new value of Henry's constant H_y is simply the old value H_p divided by the total pressure P. It is important to express the contaminant concentrations in mole fraction as indicated in Equation 5-8.

(Eq. 5-8) $$y_A = H_y x_A$$

Where: y_A = mole fraction of the contaminant in the gas phase at equilibrium
H_y = Henry's Law constant when the gas concentration is expressed in mole fraction
x_A = mole fraction of contaminant dissolved in the liquid phase at equilibrium.

(Note: H is now dependent on the total pressure.)

Equation 5-8 is the equation of a straight line where the slope (m) is equal to H_y. Thus, Henry's Law can be used to predict solubility when the equilibrium line is straight. This is the often the case when the contaminant concentration is very small, as in many air pollution control applications. For example, Figure 5-16 shows that the equilibrium line is approximately straight to gas phase mole fractions of NH_3 up to about 0.15.

Another restriction on using Henry's Law is that it does not hold true for gases that react or dissociate upon dissolution. If this happens, the gas no longer exists as a simple molecule. For example, scrubbing hydrofluoric acid (HF) or hydrochloric acid (HCl) gases with water causes both compounds to dissociate in solution. In these cases, the equilibrium lines are curved rather than straight. Data on systems that exhibit curved equilibrium lines must be obtained from experiments.

PROBLEM 5-1

Use the NH_3-H_2O data in Table 5-1 to show that Henry's Law is valid at low concentrations of NH_3 and calculate H_p and H_y at 20°C in this low concentration range.

SOLUTION

Step 1. From Equation 5-7, $H_{PA} = P_A / x_A$. The mass concentration data from

Table 5-1 must be converted to x_A, the mole fraction of NH_3 in the liquid.

$$x_A = \text{(mol A)}/\text{(mol A + mol H}_2\text{O)}$$
$$= (m_A/M_A)/[(m_A/M_A) + (m_{H2O}/M_{H2O})]$$

Use the first data entry from Table 5-1 as an example:

$$m_A = 20, \; m_{H2O} = 100, \; M_A = 17, \text{ and } M_{H2O} = 18$$
$$x_A = (20/17)/[(20/17) + (100/18)] = 0.175$$

Step 2. Converting the remaining mass concentration data in the same manner leads to the following table of x_A, P_A, and H_p.

Conversion data.		
x_A	P_A	H_p
0.1748	166	950
0.1371	114	832
0.0957	69.6	727
0.0736	50	680
0.0503	31.7	630
0.0406	24.9	613
0.0308	18.2	591
0.0258	15.0	582
0.0207	12.0	579

It is clear from examining the values of H_p that Henry's Law is not valid over the entire concentration range. However, this is not surprising since Henry's Law is known to be valid only at low concentrations. The last three entries, for x_A less than or equal to 0.0308, are effectively constant at an average value of $H_p = 584$. This value can be accepted to be approximately correct at low concentrations.

Step 3. In deriving Equation 5-8:

$$H_y = H_p/P$$
$$H_y = 584/760$$
$$H_y = 0.768$$

The final values with units are:

$$H_p = 584 \text{ mm Hg/mole fraction NH}_3 \text{ in liquid}$$
$$H_y = 0.768 \text{ mole fraction NH}_3 \text{ in gas/mole fraction NH}_3 \text{ in liquid}$$

5.4 CAPABILITY AND SIZING

PURPOSE

This section concerns the evaluation of new absorber systems. The primary issues are (1) the ability of the scrubbing system to achieve efficient gaseous pollutant removal and (2) the adequacy of the mist eliminator to remove entrained droplets.

GASEOUS POLLUTANT REMOVAL CAPABILITY

There are two general approaches to evaluating the capability of an absorber system: (1) empirical evaluations based on previously installed units on similar sources and (2) pilot scale tests.

Site-Specific Data

Most absorber manufacturers have extensive databases describing the performance of their commercial absorbers and the common types of packing materials. These data provide a starting point in determining if a given type of absorber will be able to meet the performance requirements specified by the purchaser. Site-specific information is considered along with this historical performance data to determine if an absorber would be appropriate. The most important site-specific data to be considered are listed below.

- Gas flow rates (average and maximum)
- Types of gaseous pollutants present
- Concentrations of the gaseous pollutants
- Removal efficiency requirements
- Make-up water availability
- Purge liquid flow limitations
- Inlet gas temperatures (average and maximum)
- Particulate matter loadings
- Operating schedule

These data can also be used to determine the absorber liquid-to-gas ratio, the alkali requirement (if needed), the make-up liquid and purge liquid flow rates, and the basic sizing parameters, such as the absorber diameter and absorber height.

Empirical Model Approach

Most absorber manufacturers have incorporated the empirical data from prior installations into mass transfer rate models. These models calculate (1) the liquid-to-gas ratios required at the minimum and average gas temperatures, (2) the number of beds or trays needed for the required removal efficiency, and (3) the diameter of the absorber based on the liquid-to-gas ratio and the maximum gas flow rate.

The advantage of the empirical/mass transfer rate model approach is that most absorber manufacturers have an extensive database concerning the mass transfer and overall performance capability of absorbers for similar applications. The primary disadvantage of this approach is that occasionally the data provided to the manufacturers may be inaccurate or incomplete. For example, the intermittent process operating conditions of some sources can

generate high particulate matter loadings that could plug a packed bed or an impingement tray scrubber. In other cases, the estimated gas flow rate for a new process is less than the actual gas flow rate from the operating system. Some types of absorbers cannot maintain high removal efficiencies at gas flow rates significantly above or below the design levels. Accordingly, the success of the empirical approach depends, in part, on the completeness and accuracy of the source descriptive data provided to the absorber designer.

Pilot-Scale Tests

Pilot-scale performance tests can be conducted when there is uncertainty concerning the applicability of an absorber or the necessary size of an absorber. These tests are preferably conducted on the specific source to be controlled so that the characteristics of the gas stream are inherently taken into account. If this is an entirely new application that has not yet been built, a similar existing unit can be tested.

The tests are normally conducted using a small skid-mounted absorber system capable of handling 100 to 1,000 ACFM (2.8 to 28 m^3/min). The gas is pulled from the effluent duct from the process source. The performance of the pilot-scale scrubber system is usually determined using conventional U.S. EPA reference method air emission tests.

The primary advantage of pilot-scale tests is that the performance of an absorber very similar to the proposed unit can be evaluated on the actual gas stream. Site-specific problems, such as the presence of sticky particulate matter, short-term spikes in the gaseous pollutant concentration (e.g., reactor charging), and severe temperature variations, can be taken into account. Furthermore, a test can be conducted to identify the optimal operating conditions. These tests include the liquid-to-gas ratio, the recirculation liquid pH, and the recirculation liquid purge rate. The main disadvantage is that pilot-scale tests are both time-consuming and expensive. Also, pilot-scale tests usually indicate slightly higher pollutant-removal efficiencies than can be achieved by the full-scale system, because a variety of non-ideal gas flow conditions are more significant on the larger systems.

ABSORBER SIZING

Liquid-to-Gas Ratios

The liquid-to-gas ratio (L/G) is defined as the quantity of liquid fed to the absorber divided by the outlet gas flow rate, often expressed in units of gallons per 1,000 ACF. This definition is illustrated in Figure 5-17.

The liquid-to-gas ratio is important for two reasons: (1) there must be sufficient liquid to avoid mass transfer equilibrium, and (2) there must be good gas-liquid contact within the absorber. The combinations of factors that influence gas-liquid contact are sometimes referred to as *hydraulic* factors.

$$\frac{L}{G} = \frac{Liquid_{IN}}{Gas_{OUT}}$$
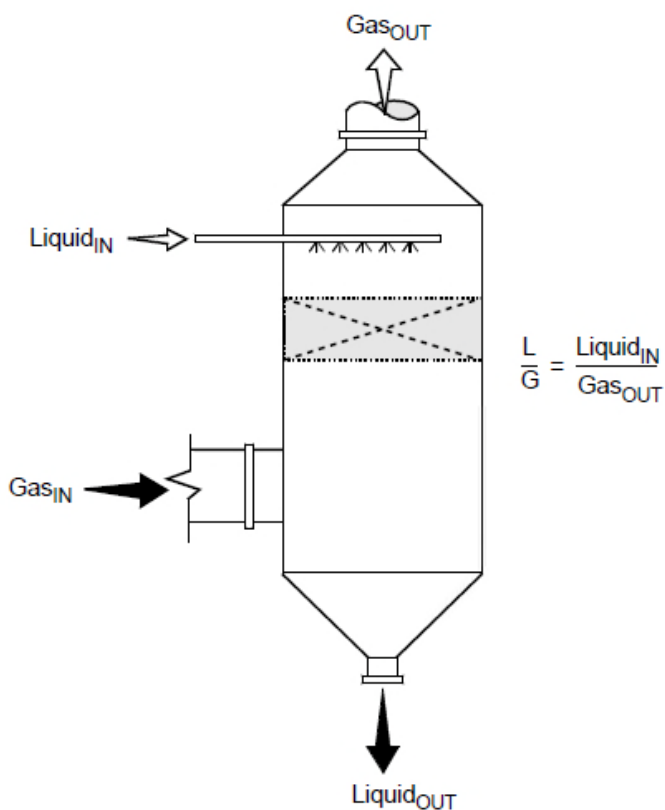
Figure 5-17. Definition of the liquid-to-gas ratio.

An estimate of the minimum required (L/G) can be obtained based on the solubility data of the contaminant and mass balance information. This procedure can be used for systems in which the contaminant is at relatively low concentrations, does not have a high heat of absorption, and does not react in solution.

Material Balance Calculations of Minimum Liquid-to-Gas Ratio

Figure 5-18 illustrates a typical countercurrent-flow absorber. For convenience, the bottom and top of the column are indicated by the subscripts 1 and 2, respectively.
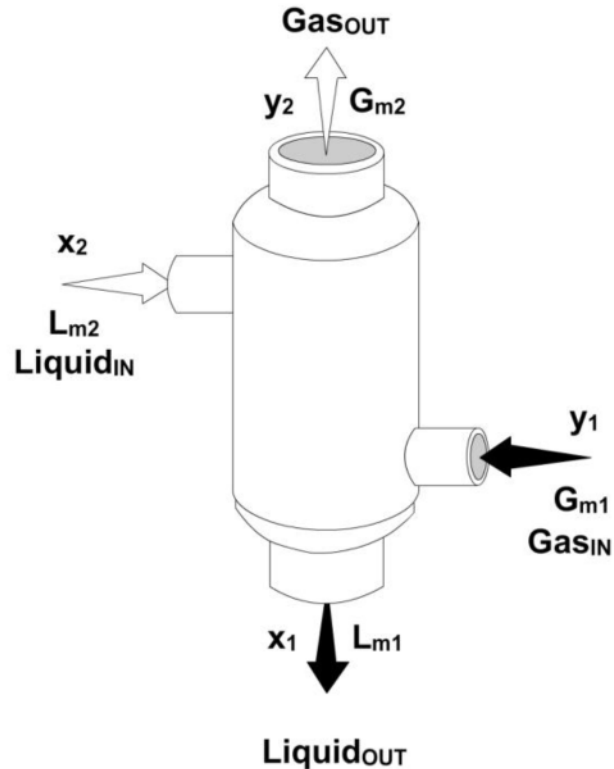
Figure 5-18. Material balance for countercurrent-flow absorber.

The following material balance equation equates the moles of contaminant entering in streams G_{m1} and L_{m2} to the moles leaving in streams G_{m2} and L_{m1}.

(Eq. 5-9) $$G_{m1}y_1 + L_{m2}x_2 = G_{m2}y_2 + L_{ml}x_1$$

Where: G_m = total gas molar flow rate (mol/hr)
    y = mole fraction of contaminant in gas stream
    L_m = total liquid molar flow rate (mol/hr)
    x = mole fraction of the contaminant in pure liquid

It turns out to be convenient to write the material balance equations on the basis of mole ratios instead of mole fractions. New concentration parameters, Y and X, are defined as follows.

(Eq. 5-10) $$Y = \frac{\text{mole fraction contaminant in gas}}{\text{mole fraction contaminant} - \text{free gas}} = \frac{y}{1-y}$$

(Eq. 5-11) $$X = \frac{\text{mole fraction contaminant in liquid}}{\text{mole fraction contaminant} - \text{free gas}} = \frac{x}{1-x}$$

In air pollution control problems, the contaminant concentrations are usually small, i.e., y and x are generally small compared to 1. Under these conditions, $Y \approx y$, and $X \approx x$. This simplification is used in the following analysis. If the mole fraction of contaminant in the inlet gas is larger than a few percent by volume, this assumption is invalid and will cause errors in

the material balance calculations.

An overall (total mole) balance across the absorber in Figure 5-18 yields the following equation:

(Eq. 5-12) $$G_{m1} + L_{m2} = G_{m2} + L_{m1}$$

Equation 5-9 is rewritten in terms of X and Y using the simplifications introduced in equations 5-10 and 5-11 to give:

(Eq. 5-13) $$G_{m1} Y_1 + L_{m2} X_2 = G_{m2} Y_2 + L_{m1} X_1$$

Equation 5-13 can be further simplified by recognizing that as the gas and liquid streams flow through the adsorber, their flow rate does not change appreciably. Therefore, it is not necessary to include the subscripts 1 and 2 on the total gas and liquid flow rates.

(Eq. 5-14) $$G_{m1} = G_{m2} = G_m \quad \text{and} \quad L_{m1} = L_{m2} = L_m$$

The contaminant material balance now becomes:

(Eq. 5-15) $$G_m (Y_1 - Y_2) = L_m (X_1 - X_2)$$

Rearranging Equation 5-15 yields Equation 5-16

(Eq. 5-16) $$Y_1 - Y_2 = \frac{L_m}{G_m} (X_1 - X_2)$$

These simplifications can be justified by the following example. Consider a 10,000 SCFM exhaust gas stream containing 1,000 ppm of contaminant. This is equivalent to a contaminant mole fraction of only 0.001 or 10 SCFM of contaminant. If the absorber removed all of the contaminant, the total gas flow rate would only change from 10,000 SCFM at the inlet to 9,990 SCFM at the outlet. The transfer of a quantity this small is negligible in an overall material balance.

Equation 5-16 is the equation of a straight line, known as an operating line, on a Y-X diagram. The operating line is nothing more than a graphical representation of the contaminant material balance. This line defines operating conditions within the absorber: the material going in and the material coming out represent the terminal points of the operating line. A typical equilibrium diagram and operating line are plotted on a Y-X diagram in Figure 5-19. The equilibrium line in this example is shown as curved, although in cases where Henry's Law is applicable, both the equilibrium and operating lines would be straight. The slope of the operating line is the ratio of the molar flow rates of liquid and gas. The driving force for mass transfer is graphically represented by the "distance" between the operating and equilibrium lines.
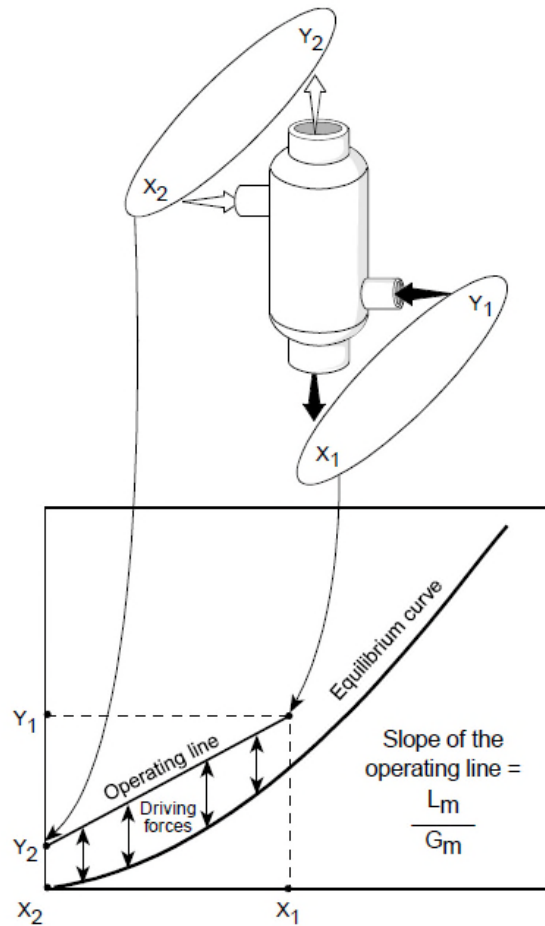
Figure 5-19. Y-X diagram showing the equilibrium and operating lines.

In the typical design problem, the quantity of gas to be treated (G_m) and the inlet contaminant concentration in the gas (Y_1) are set by process conditions. Air pollution emission limitations specify the outlet contaminant concentration (Y_2). The composition of the liquid into the absorber (X_2) is also generally known. If the inlet liquid contains no contaminant, the value of X_2 is zero. This is the situation shown in Figure 5-19. However, because of liquid recycle, the inlet liquid may contain some contaminant in which case X_2 will be somewhat greater than zero, but small. Thus, the coordinate positions Y_1, Y_2, and X_2, along with G_m are known. The unknowns are X_1 and L_m.

Figure 5-20A is a typical equilibrium diagram with the known operating points Y_1, Y_2 and X_2 designated for a countercurrent-flow absorber. For the minimum liquid rate required to achieve the specified separation, the inlet gas concentration of contaminant (Y_1) is in equilibrium with the outlet liquid contaminant concentration, designated as X_{max}. Since the gas and liquid are in equilibrium at these conditions, the coordinates of point X_{max}, Y_1 must lie on both the equilibrium and operating lines as represented by Figure 5-20B.
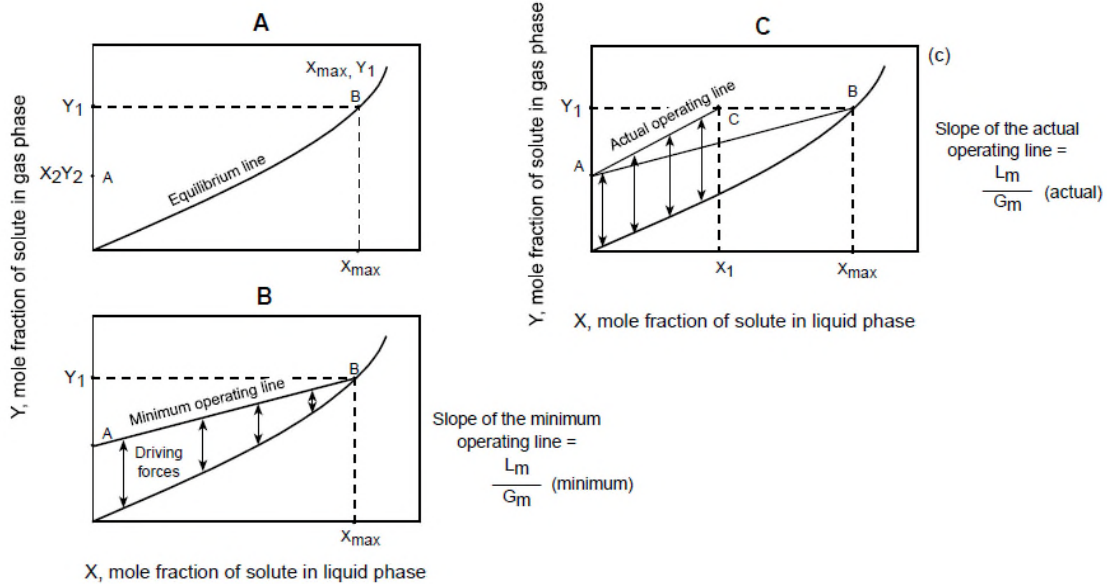
Figure 5-20. Liquid-to-gas ratio.

In Figure 5-20B, the slope of the line drawn between points A and B represents the operating conditions at minimum liquid flow rate. The driving force for mass transfer, which is represented by the distance between the equilibrium and operating lines, decreases to zero at point B. By knowing the slope (L_m/G_m) of the minimum operating line, the minimum liquid rate can easily be determined by substituting the known gas flow rate. This procedure is illustrated in Problem 5-2.

Determining the minimum liquid flow rate (L_m/G_m) is important because absorbers are usually operated at some multiple, perhaps 25% to 100% greater than the minimum. A typical absorber might operate at a liquid rate 50% greater than the minimum (i.e., 1.5 times the minimum liquid-to-gas ratio). Line AC in Figure 5-20C is drawn at a slope of 1.5 times the minimum (L_m/G_m), and is referred to as the actual operating line.

Operating at the minimum (L_m/G_m) would require an infinitely large column, as the driving force for mass transfer is zero when the operating and equilibrium lines intersect. As the actual value of (L_m/G_m) increases above the minimum, the size of the absorber decreases. The smaller column results in a decrease in capital cost but an increase in operating cost because of the larger liquid flow rate. In the real situation there is an optimum (L_m/G_m) corresponding to minimum total cost. The optimum (L_m/G_m) is often near the value of 1.5*(L_m/G_m) as described above. The following problem illustrates the calculation of (L_m/G_m).

PROBLEM 5-2

Calculate the operating liquid rate in gal/min for the removal of 90% of the NH_3 from a 85.0 m^3/min (3,000 ACFM) feed gas containing 3% NH_3 and 97% air, assuming that the operating liquid rate is 1.5 times the minimum. The inlet liquid is water and the temperature and pressure are 293 K and 1 atm, respectively. Use the results from Problem 5-1.

SOLUTION

Step 1. Sketch and label a drawing of the system. Figure 5-21 shows the pertinent parameters for this problem.
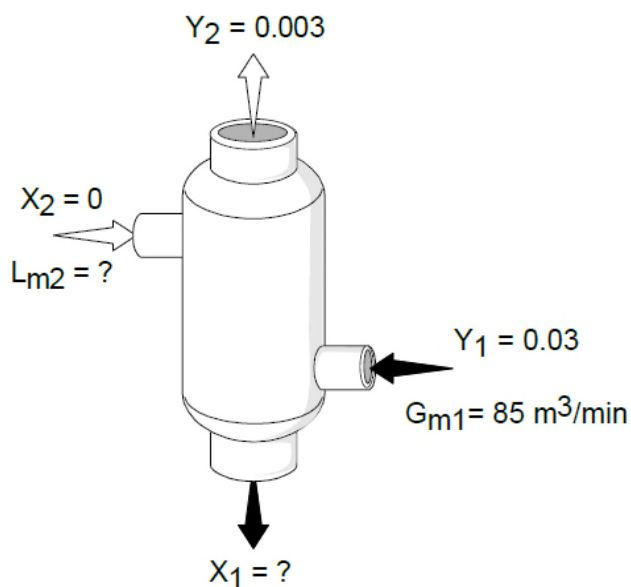
Figure 5-21. Absorber operating conditions in Problem 5-2.

Step 2. At the minimum, liquid rate Y₁ and X₁ will be in equilibrium. The liquid will be saturated with NH₃.

$$H_y = 0.768 \frac{\text{mole fraction } NH_3 \text{ in air}}{\text{mole fraction } NH_3 \text{ in water}} \quad \text{(from Problem 5-1)}$$

$$Y_1 = H_y X_1$$
$$0.03 = 0.768 \, X_1$$
$$X_1 = 0.0391 \text{ mole fraction}$$

Step 3. (Lₘ/Gₘ)ₘᵢₙ can be obtained directly by rearranging Equation 5-16.

$$Y_1 - Y_2 = \frac{L_m}{G_m}\left(X_1 - X_2\right)$$

$$\left(\frac{L_m}{G_m}\right)_{min} = \frac{Y_1 - Y_2}{X_1 - X_2}$$

$$\left(\frac{L_m}{G_m}\right)_{min} = \frac{0.03 - 0.003}{0.0391 - 0}$$

$$\left(L_m / G_m\right)_{min} = 0.6905 \text{ gmol water/gmol air}$$

Step 4. Convert m³ of air to gram moles; then compute the minimum required liquid flow rate. At 293 K and 1 atm, the molar volume of an ideal gas (air) can be calculated as follows:

$$PV = nRT$$

$$\frac{V}{n} = \frac{RT}{p} = \frac{\left(0.08206\frac{l*atm}{gmol*K}\right)(293K)}{(1atm)\left(1000\frac{l}{m^3}\right)} = 0.024\frac{m^3}{gmol}$$

$$G_m = 85.0\frac{m^3}{min}\left(\frac{gmol}{0.024\ m^3}\right) = 3{,}542\frac{gmol\ air}{min}$$

$$\left(L_m\right)_{min} = \left(0.6905\frac{gmol\ H_2O}{gmol\ air}\right)*G_m$$

$$\left(L_m\right)_{min} = (0.6905)*(3542) = 2{,}446\frac{gmol\ H_2O}{min}$$

$$L_{min} = \left(2{,}446\frac{gmol\ H_2O}{min}\right)*\left(18\frac{g\ H_2O}{gmol\ H_2O}\right) = 44{,}028\frac{g\ H_2O}{min}$$

$$L_{min} = \left(44{,}028\frac{g\ H_2O}{min}\right)*\left(\frac{1lb}{453.6\ g}\right)*\left(\frac{1\ gal}{8.34\ lb\ H_2O}\right)$$

$$L_{min} = 11.6\frac{gal\ H_2O}{min}$$

Step 5. Figure 5-22 illustrates the graphical solution to this problem. Multiply the slope of the minimum operating line by 1.5 to get the slope of the actual operating line (line AC).

$$L = 1.5*L_{min} = 1.5*\left(2{,}446\frac{gmolH_2O}{min}\right) = 3{,}669\frac{gmolH_2O}{min}, \text{ or}$$

$$= 1.5*\left(44{,}028\frac{g\ H_2O}{min}\right) = 66{,}042\frac{g\ H_2O}{min}, \text{ or}$$

$$=1.5*\left(11.6\frac{\text{gal}\,H_2O}{\text{min}}\right)=17.5\frac{\text{gal}\,H_2O}{\text{min}}$$
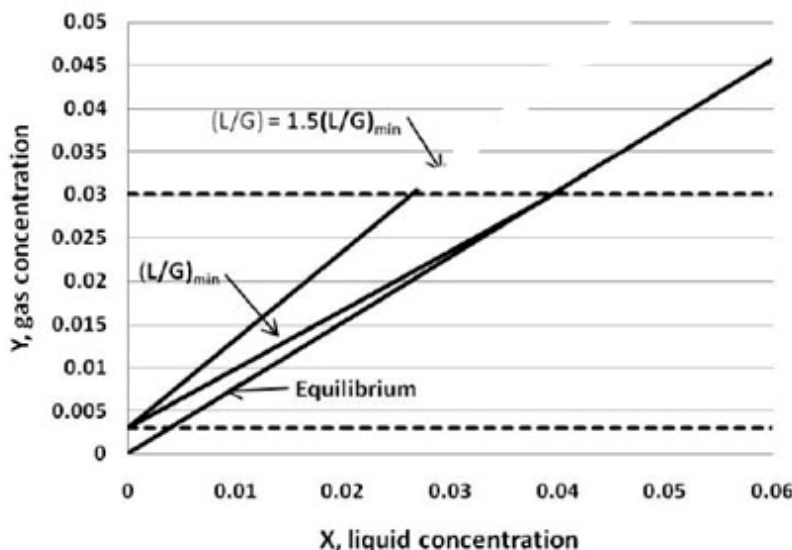
Figure 5-22. Graphical representation of NH_3 absorber problem (Problem 5-2).

The evaluation technique used in Problem 5-2 applies mainly to absorbers in which the contaminant is relatively dilute and does not react in solution. For absorbers that use alkali or other types of reagents that react with the dissolved materials, the liquid-to-gas ratio is determined based primarily on the hydraulic factors that affect gas-liquid distribution.

The relationship between the equilibrium line and the actual operating line used in the absorbers is termed the absorption factor (defined in Equation 5-17). This is simply the ratio of the slopes of the operating line and the equilibrium line.

(Eq. 5-17) $$AF = \frac{L_2}{mG_1}$$

Where: AF = absorption factor
          L_2 = molar flow rate of liquid
          m = slope of the equilibrium line on a mole fraction basis = H_y
          G_1 = molar flow rate of gas

PACKED-TOWER ABSORBER DIAMETER AND HEIGHT

The diameter and height of the bed(s) can be estimated for packed-tower absorbers. The starting point in these calculations is the adjusted liquid-to-gas ratio discussed in the previous subsection.

Packed-Tower Absorber Diameter

The main parameter that affects the diameter of a packed column is the gas velocity at which liquid droplets become entrained in the exiting gas stream. Consider a packed column operating at set gas and liquid flow rates. If the gas velocity through the column is gradually increased by using smaller and smaller diameter columns, a point is reached where the liquid flowing down over the packing begins to be held in the void spaces between the packing. This gas velocity is termed the loading point. The pressure drop across the column also increases as the velocity increases and the degree of mixing between the phases decreases. A further increase in gas velocity beyond the loading point causes the liquid to completely fill the void spaces in the packing. The liquid forms a layer over the top of the packing, and no more liquid can flow down through the tower. This condition is referred to as *flooding*, and the gas velocity at which it occurs is the *flooding velocity*. Using an extremely large diameter tower would eliminate this problem; however, as the diameter increases, the cost of the tower increases, and a point will be reached where the liquid flow rate is insufficient to wet all of the packing.

Normal practice is to fix the diameter of the packed column so that the gas velocity is at a certain percent of the flooding velocity, typically 50% to 75%. It is assumed that by operating in this range, the gas velocity will also be below the loading point.

A common and relatively simple procedure for estimating the flooding velocity (thus setting a minimum column diameter) is to use a generalized flooding and pressure drop correlation such as the Leva-Sherwood correlation shown in Figure 5-23. The correlation is based on the physical properties of the gas and liquid streams and on the tower packing characteristics. The use of the Sherwood correlation is described below.
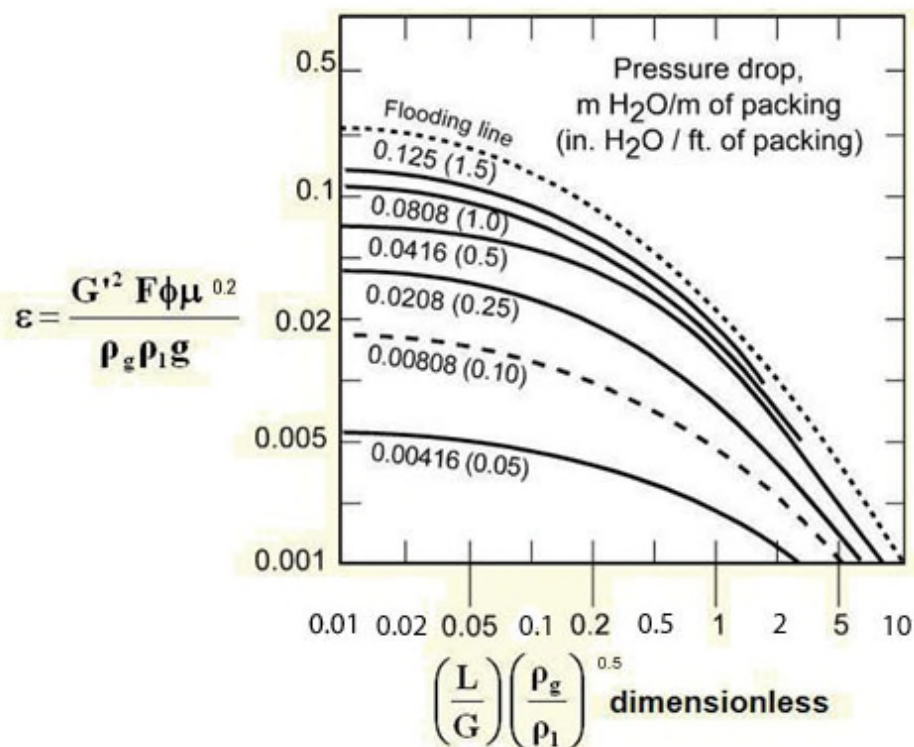
Figure 5-23. Generalized Leva-Sherwood flooding and pressure drop correlation.

Step 1. Calculate the value of the abscissa (horizontal axis) of Figure 5-23 using Equation 5-18.

(Eq. 5-18)
$$\text{Abscissa} = \left(\frac{L}{G}\right)\left(\frac{\rho_g}{\rho_1}\right)^{0.5}$$

Where
- L = mass velocity of liquid stream, lb/ft^2 sec
- G = mass velocity of gas stream, lb/ft^2 sec
- ρ_g = gas density, lb/ft^3
- ρ_1 = liquid density, lb/ft^3

Calculation of the individual values of L and G requires that the cross-sectional area of the column (and thus the column diameter) be known. However, the ratio (L/G) is simply the ratio of the mass flow rates and is independent of column diameter.

Step 2. From this point on the abscissa, move vertically up to the flooding line and read the ordinate, ε, at the flooding point.

Step 3. Calculate the gas mass velocity at flooding using Equation 5-19.

(Eq. 5-19)
$$G* = \left(\frac{\varepsilon \rho_g \rho_1 g}{F_p \varphi \mu^{0.2}}\right)^{0.5}$$

Where:
- $G*$ = gas mass velocity at flooding (lb_m/ft^2 sec)
- ε = ordinate of Leva-Sherwood correlation (Figure 5-23)
- ρ_g = density of gas (lb_m/ft^3)
- ρ_1 = density of liquid (lb_m/ft^3)
- g = gravitational acceleration constant (32.2 ft/sec^2)
- F_p = packing factor (ft^2/ft^3)
- ϕ = specific gravity of absorbent (dimensionless)
- μ_1 = viscosity of liquid (cP)

It is important to recognize that the ordinate of Figure 5-23 is not dimensionless, and the stated units must be used. Values of the packing factor, F_p, along with other properties of typical packing materials may be found in Table 5-2.

Step 4. Calculate the actual gas mass flow rate per unit area as a fraction of the gas flow rate at flooding (Equation 5-20).

(Eq. 5-20)
$$G_{op} = G^* f$$

Where: G_{op} = actual gas mass flow rate per unit area (lb_m/ft^2 sec)

  f   =   fractional approach to flooding, typically ≈ 0.75

Step 5. Calculate the packed bed diameter based on the actual gas mass velocity.

(Eq. 5-21) $\text{Tower Area, ft}^2 = \dfrac{\text{Total gas mass flow rate, lb}_m/\text{sec}}{\text{Gas mass velocity, lb}_m/\text{ft}^2}$

(Eq. 5-22) $\text{Tower Diameter} = \left[\dfrac{4 * \text{TowerArea}}{\pi} \right]^{0.5}$

(Eq. 5-23) $\text{Tower Diameter} = 1.13 \, (\text{Tower Area})^{0.5}$

Table 5-2. Packing data*.					
Packing	**Size (in.)**	**Weight (lb_m/ft^3)**	**Surface Area (ft^2/ft^3)**	**Void Fraction (%)**	**Packing Factor, F_p (ft^2/ft^3)**
Raschig™ Rings (Ceramic, Porcelain)	1.0	44	58	70	155
	1.5	42	36	72	95
	2.0	38	28	75	65
	3.0	34	19	77	37
Raschig™ Rings (Steel)	1.0x1/32	40	63	92	115
	2.0x1/16	38	31	92	57
Berl™ Saddles (Ceramic Porcelain)	1.0	48	79	68	110
	2.0	38	32	75	45
Intalox™ Saddles (Ceramic)	1.0	44	78	77	98
	2.0	42	36	79	40
Intalox™ Saddles (Plastic)	1.0	6.0	63	91	30
	2.0	3.8	33	93	20
	3.0	3.3	27	94	15
Pall™ Rings (Plastic)	1.0	5.5	63	90	52
	2.0	4.5	31	92	25
Pall™ Rings (Metal)	1.5 x 0.03	24	39	95	28
Tellerettes™	1.0	7.5	55	87	40
	2.0	3.9	38	93	20
	3.0	5.0	30	92	15

*Data for guide purposes only. Packing factor for the specific application should be obtained from the manufacturer or from other sources.

Problem 5-3 illustrates the calculation procedures for estimating the packed bed column

diameter.

PROBLEM 5-3

For the scrubber in Problem 5-2, determine the packed-bed tower diameter and the pressure drop per foot of packing depth, if the operating liquid flow rate is 1.5 times the minimum. The gas velocity should be no greater than 75% of the flooding velocity, and the packing material is two-inch ceramic Intalox^{TM} saddles.

SOLUTION

Step 1. Calculate the value of the abscissa in Figure 5-23.
From Problem 5-2:

G_m = 3542 gmol/min

L = 3669 gmol/min

Convert gas molar flow to a mass flow, assuming the gas to be air having a molecular weight of 29 g/gmol (air).

G = (3542 gmol/min)(29 g/gmol)
  = (102,718 g/min)(1 lb$_m$/453.6 g) = 226 lb$_m$/min

L = (3669 gmol/min)(18 g/gmol)
  = (66,042 g/min)(1 lb$_m$/453.6 g) = 146 lb$_m$/min

The densities of air and water at 293 K are:

$$\rho_1 = 62.4 \ \text{lb}_m/\text{ft}^3$$

$$\rho_g = 0.074 \ \text{lb}_m/\text{ft}^3$$

Calculate the abscissa using Equation 5-18.

$$\text{Abscissa} = \left(\frac{L}{G}\right)\left(\frac{\rho_g}{\rho_1}\right)^{0.5} = \left(\frac{146}{226}\right)\left(\frac{0.074}{62.4}\right)^{0.5} = 0.0222$$

Step 2. Determine the ordinate in Figure 5-23 at an abscissa of 0.0222; the ordinate is 0.2.

Step 3. Calculate the gas flow rate per unit area at flooding using Equation 5-19.

$$G^* = \left(\frac{\varepsilon \rho_g \rho_1 g}{F_p \varphi \mu_1^{0.2}}\right)^{0.5}$$

For water at 293K, φ = 1.0, and the viscosity is equal to 1 cP.

From Table 5-3, for two-inch ceramic Intalox™ saddles:

$F_p = 40 \text{ ft}^2/\text{ft}^3$

$g = 32.2 \text{ ft/sec}^2$

$$G^* = \left[\frac{(0.2)\left(0.074 \frac{\text{lb}_m}{\text{ft}^3}\right)\left(62.4 \frac{\text{lb}_m}{\text{ft}^3}\right)\left(32.2 \frac{\text{ft}}{\text{sec}^2}\right)}{\left(40 \frac{\text{ft}^2}{\text{ft}^3}\right)(1.0)(1\text{cP})^{0.2}} \right]^{0.5} = 0.862 \frac{\text{lb}_m}{\text{ft}^2 \text{sec}}$$

Step 4. Calculate the actual gas flow rate per unit area using Equation 5-20.

$G_{op} = 0.75 * (0.862 \text{ lb}_m/\text{ft}^2 \text{ sec}) = 0.647 \text{ lb}_m/\text{ft}^2 \text{ sec}$

Step 5. Calculate the tower diameter using Equations 5-21 through 5-23.

Tower Area = gas flow rate/G_{op}

$$\text{Tower Area} = \frac{\left(226 \frac{\text{lb}_m}{\text{min}}\right)\left(\frac{1 \text{min}}{60 \text{sec}}\right)}{\left(0.647 \frac{\text{lb}_m}{\text{ft}^2 \text{sec}}\right)} = 5.82 \text{ ft}^2$$

$$\text{Tower Diameter} = 1.13 A^{0.5} = 1.13 \left(5.82 \text{ ft}^2\right)^{0.5} = 2.73 \text{ ft}$$

Step 6. Calculate the pressure drop.

Use Figure 5-23 once again. The new value of the ordinate based on actual flow rate is:

$$\left(\frac{\varepsilon_{new}}{\varepsilon_{old}}\right) = \left(\frac{G_{actual}}{G_{flooding}}\right)^2 = \left(\frac{G_{op}}{G^*}\right)^2$$

$$\varepsilon_{new} = \varepsilon_{old}\left(\frac{G_{op}}{G^*}\right)^2 = (0.2)\left(\frac{0.647 \frac{\text{lb}_m}{\text{ft}^2 \text{sec}}}{0.862 \frac{\text{lb}_m}{\text{ft}^2 \text{sec}}}\right)^2 = 0.113$$

From Figure 5-23, use the original abscissa value of 0.0222 and the new ε value to estimate the pressure drop:

ΔP is approximately 1.0 in. W.C./ft of packing depth

Packed-Tower Absorber Height

The height of a packed-tower absorber refers to the height of packing material needed to accomplish the required contaminant removal. The more difficult the separation, the larger the packing height required. For example, a much larger packed height would be required to remove SO_2 than to remove Cl_2 from an exhaust stream using water as the absorbent because Cl_2 is more soluble in water than SO_2. Determining the proper height of packing is important because it affects both the rate and efficiency of absorption.

A number of theoretical equations based on diffusion principles are used to predict the required packing height. The general equation for a gas phase controlled resistance (common in air pollution systems) is given in Equation 5-24.

(Eq. 5-24)
$$Z = \frac{G^*}{K_g aP} \int_{Y_2}^{Y_1} \frac{dY}{(1-Y)(Y-Y^*)}$$

Where: Z   =   height of packing (ft)
             G^* =   molar flow rate of gas per unit cross sectional area (lbmol/hr·ft^2)
             Kg =   overall gas film coefficient (lbmole/hr·ft^2·atm)
             a   =   interfacial contact area per unit packing volume (ft^2/ft^3)
             P   =   pressure of the system (atm)
             Y   =   mole ratio of contaminant to contaminant-free gas
             Y^* =   mole ratio of contaminant to contaminant-free gas at equilibrium

In Equation 5-24, the term $G/K_g a$ has the dimension of length and is referred to as the height of a transfer unit. The term inside the integral is dimensionless and represents the number of transfer units needed to make up the total packing height. Using the concept of transfer units, Equation 5-24 can be simplified to Equation 5-25.

(Eq. 5-25)
$$Z = (HTU)(NTU)$$

Where: HTU =   height of a transfer unit (ft)
             NTU =   number of transfer units (dimensionless)

The concept of a transfer unit comes from the operation of tray-tower absorbers, where discrete stages (trays) of separation occur. These stages can be visualized as a transfer unit with the number and height of each giving the total tower height. Although packed columns operate as one continuous separation process, in design terminology the column is treated as if it were broken into discrete sections. The number and the height of a transfer unit may be based on either the gas or liquid phase so that Equation 5-25 can be modified to yield Equation 5-26.

(Eq. 5-26)
$$Z = N_{OG}H_{OG} = N_{OL}H_{OL}$$

Where: N_{OG} =   number of transfer units based on overall gas film coefficient
             H_{OG} =   height of a transfer unit based on overall gas film coefficient (ft)

N_{OL} = number of transfer units based on overall liquid film coefficient
H_{OL} = height of a transfer unit based on overall liquid film coefficient (ft)

Values for the height of a transfer unit are usually obtained from experimental data. To ensure the greatest accuracy, vendors of absorption equipment normally perform pilot plant studies to determine the height of a transfer unit. For common absorption systems, such as NH_3 in water, manufacturers have developed correlations that can be used to estimate the height of a transfer unit. These correlations do not provide the accuracy of pilot plant data, but they are less expensive, less time consuming, and are easier to use.

Figure 5-24 gives a typical correlation for the ammonia-water system for two common packing materials. In this figure, the liquid mass velocity ($lb_m/hr*ft^2$) is plotted versus the H_{OG} at a gas mass velocity of 500 $lb_m/hr*ft^2$ with the two lines representing different packing materials. In applying these data, it is important that the process conditions be similar to the conditions at which the HTU was measured.
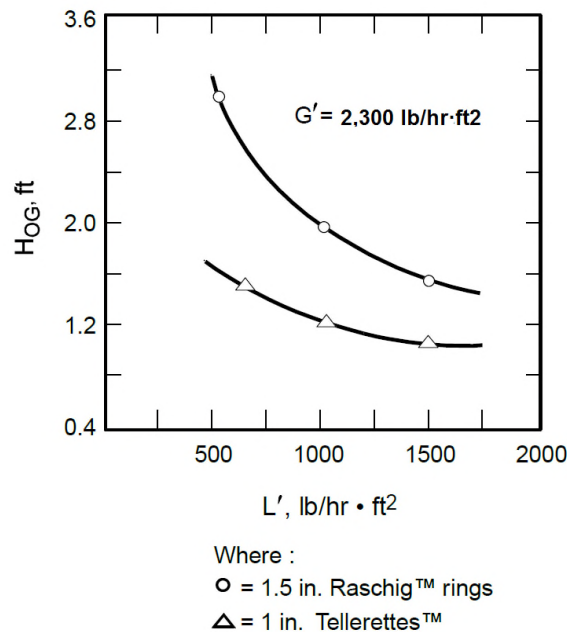
Figure 5-24. Height of a transfer unit, ammonia and water system.

When no experimental data are available, or if only a preliminary estimate of absorber efficiency is needed, generalized correlations are available to estimate the height of a transfer unit. The correlations for predicting the H_{OG} or the H_{OL} are empirical and are functions of the type of packing, liquid and gas flow rates, concentration and solubility of the contaminant, liquid properties, and system temperature. These correlations can be found in engineering texts. For most applications, the height of a transfer unit ranges between 1 and 4 feet (0.305 and 1.22 m).

The number of transfer units, NTU, can be obtained experimentally or calculated by a variety of methods. When the pollutant concentration is low, and the equilibrium line is straight, Equation 5-27 can be used to determine the number of transfer units (N_{OG}) based on the gas phase resistance. Equation 5-27 can be derived from the integral portion of Equation 5-24 when the above restrictions are satisfied.

(Eq. 5-27)
$$N_{OG} = \frac{\ln\left[\left(\frac{Y_1 - mX_2}{Y_2 - mX_2}\right)\left(1 - \frac{mG_m}{L_m}\right) + \frac{mG_m}{L_m}\right]}{1 - \frac{mG_m}{L_m}}$$

Where: Y_1 = mole ratio of contaminant to contaminant-free gas entering the absorber
                 m = slope of the equilibrium line (= Henry's Law constant)
                 X_2 = mole ratio of contaminant to contaminant-free liquid entering the absorber
                 Y_2 = mole ratio of contaminant to contaminant-free gas leaving the absorber
                 G_m = molar flow rate of gas (lbmol/hr)
                 L_m = molar flow of liquid (lbmol/hr)

Equation 5-27 can be further simplified for special situations where a chemical reaction occurs or if the pollutant is extremely soluble. In these cases, the pollutant exhibits almost no partial pressure, and, therefore, the slope of the equilibrium line approaches zero ($m = 0$). For these cases, Equation 5-21 reduces to Equation 5-28.

(Eq. 5-28)
$$N_{OG} = \ln\left(\frac{Y_1}{Y_2}\right)$$

The number of transfer units depends only on the inlet and outlet concentration of the pollutant. For example, if the conditions in Equation 5-28 are met, 2.3 transfer units are required to achieve 90% removal of any pollutant.

PROBLEM 5-4

Continue Problems 5-1 through 5-3 by estimating the required packed height and the total pressure drop across the packed bed. In order to calculate H_{OG}, use the correlation for 1.5-inch Raschig™ rings in Figure 5-24 as a substitute for the 2-inch Intalox™ saddles specified in the earlier examples.

SOLUTION

Use data from previous problems.

     $M = 0.768$ mole fraction NH_3 in air/mole fraction NH_3 in water
     $G = 226$ lb$_m$/min
     $L = 146$ lb$_m$/min
     $X_2 = 0$
     $Y_1 = 0.03$
     $Y_2 = 0.003$

Step 1. Convert mass to molar flow rates.

     $G_m = (226 \text{ lb}_m/\text{min})(\text{lbmol}/29 \text{ lb}_m) = 7.79$ lbmol/min

     $L_m = (146 \text{ lb}_m/\text{min})(\text{lbmol}/18 \text{ lb}_m) = 8.11$ lbmol/min

Step 2. Compute the N_{OG} from Equation 5-27.

$$N_{OG} = \frac{\ln\left[\frac{(Y_1 - m*X_2)}{(Y_2 - m*X_2)}\left(1 - \frac{m*G_m}{L_m}\right) + \left(\frac{m*G_m}{L_m}\right)\right]}{1 - \frac{m*G_m}{L_m}}$$

$$N_{OG} = \frac{\ln\left[\frac{(0.03)}{(0.003)}\left(1 - \frac{(0.768)(7.79)}{8.11}\right) + \left(\frac{(0.768)(7.79)}{8.11}\right)\right]}{1 - \frac{(0.768)(7.79)}{8.11}}$$

$N_{OG} = 4.62$

Step 3. Obtain H_{OG} from Figure 5-24.

$$L = \frac{\left(146\frac{lb_m}{min}\right)\left(\frac{60\,min}{hr}\right)}{5.82\,ft^2} = 1{,}505\frac{lb_m}{hr*ft^2}$$

$$G = \frac{\left(226\frac{lb_m}{min}\right)\left(\frac{60\,min}{hr}\right)}{5.82\,ft^2} = 2{,}330\frac{lb_m}{hr*ft^2}$$

$H_{OG} = 1.5$ ft

Step 4. Using Equation 5-26, the total packing height is:

$Z = (H_{OG})(N_{OG}) = (1.5\ ft)(4.62) = 6.9\ ft$

Total Pressure Drop:

$$\Delta P_{tot} = \left(1.0\frac{in\,W.C.}{ft}\right)*(6.9\,ft) = 6.9\,in.\,W.C.$$

TRAY-TOWER ABSORBER DIAMETER AND HEIGHT

In a tray-tower absorber, the liquid enters at the top of the tower, passes over the top tray, and then down over each lower tray until it reaches the bottom as shown in Figure 5-25. Absorption occurs as the gas, which enters at the bottom, passes up through the tray and contacts the liquid. In a tray tower, absorption occurs in a stepwise manner or in a stage process. Liquid and gas concentrations at the top of the tower are designated X_a and Y_a, respectively. Bottom concentrations are designated X_b and Y_b. Trays are numbered consecutively from 1 at the top to n at the bottom of the tower. Gas and liquid concentrations within the tower are subscripted according to the tray from which each originates.
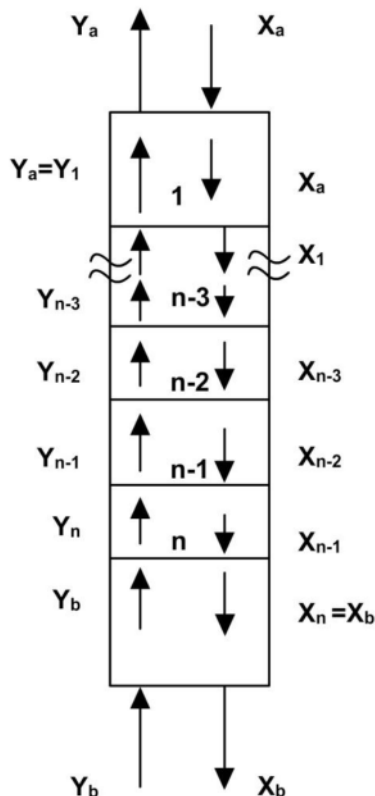
Figure 5-25. Schematic diagram of a tray-tower absorber.

There are various accepted procedures available for sizing a tray tower. Detailed summaries can be found in standard chemical engineering references.[8,9,10] The following discussion presents a simplified method for sizing or reviewing the design of a tray tower.

Tray Tower Diameter

The minimum diameter of a single-pass tray tower is determined based on the gas velocity through the tower. If the gas velocity is too great, liquid droplets are entrained to the tray above. This condition, known as priming, reduces absorber efficiency. Priming in a tray tower is somewhat analogous to flooding in a packed-tower in that it determines the minimum acceptable diameter. The actual tower diameter should be larger. Equation 5-23 expresses the smallest allowable diameter for a tray-tower absorber.

(Eq. 5-29)
$$d = \psi\left(Q\sqrt{\rho_g}\right)^{0.5}$$

Where:
- ψ = empirical constant (ft$^{0.25}$ • min$^{0.5}$ / lb$^{0.25}$)
- Q = volumetric gas flow rate (ft^3/min)
- ρ_g = gas density (lb$_m$/ft^3)

The term ψ is a function of the tray spacing and the densities of the gas and liquid streams. Values for ψ in Table 5-3 are for a tray spacing of 61 cm (24 in.) and a liquid specific gravity of 1.05.[11] If the specific gravity of a liquid varies significantly from 1.05, the values for ψ in Table 5-4 cannot be used.

Table 5-3. Tray spacing parameters.		
Tray	**Metric***	**English****
Bubble Cap	0.0162	0.1386
Sieve	0.0140	0.1198
Valve	0.0125	0.1069

* Metric expressed in m$^{0.25}$*hr$^{0.5}$/kg$^{0.25}$ for use with Q expressed in m^3/hr, and ρ_g expressed in kg/m^3

** English expressed in ft$^{0.25}$ • min$^{0.5}$/lb$^{0.25}$ for use with Q in ACFM, and ρ_g expressed in lb/ft^3

Trays are spaced sufficiently far apart to allow the gas and liquid phases to separate before reaching the plate above and also to provide space for easy maintenance and cleaning. They are normally spaced 45 cm to 70 cm (18 to 28 in.) apart. The use of Table 5-4 for tray spacing different than 61 cm (24 in.) requires that the diameter calculated from Equation 5-29 be multiplied by a correction factor that is obtained from Figure 5-26.
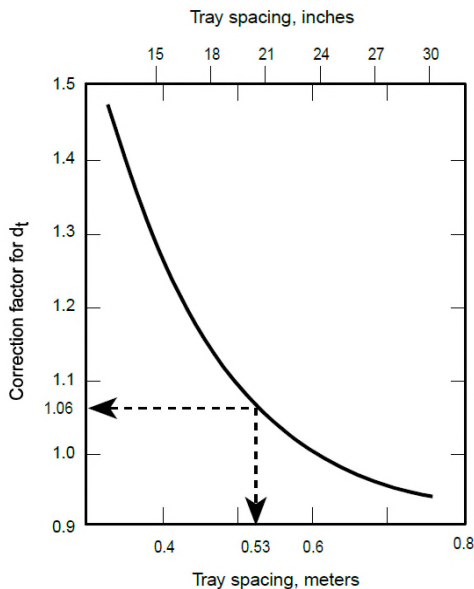
Figure 5-2626. Tray spacing correction factor.

Problem 5-5 illustrates how the minimum diameter of a tray-tower absorber is estimated.

PROBLEM 5-5

For the conditions described in Problem 5-2, determine the minimum acceptable diameter if the scrubber is a bubble-cap tray-tower absorber. The trays are spaced 0.53 m (21 in.) apart.

SOLUTION

From Problem 5-2:

Gas flow rate = Q = 85.0 m^3/min

$$\text{Density} = \rho_g = \left(\frac{\text{gmol}}{0.024 \text{ m}^3}\right)\left(\frac{29 \text{ g}}{\text{gmol}}\right)\left(\frac{\text{kg}}{1000 \text{ g}}\right) = 1.21 \text{ kg/m}^3$$

From Table 5-3 for a bubble-cup tray:

$$\psi = 0.0162 \text{ m}^{0.25} \bullet \text{hr}^{0.50}/\text{kg}^{0.25}$$

Before Equation 5-29 can be used, Q must be converted to m^3/hr

Q = (85.0 m^3/min)(60 min/hr) = 5100 m^3/hr

Step 1. Substitute these values into Equation 5-29 to obtain the minimum diameter.

$$d = \psi\left(Q\sqrt{\rho_g}\right)^{0.5}$$
$$d = (0.0162)[5100*(1.21)^{0.5}]^{0.5} = 1.21 \text{ m}$$

Step 2. Correct the diameter for a tray spacing of 0.53 m.

From Figure 5-26, read a correction factor of 1.06.
Therefore, the minimum diameter is:
d = 1.21 (1.06) = 1.28 m (4.20 ft)

Explanation: The minimum acceptable diameter based on the operating conditions. In practice, a larger diameter should be specified.

Number of Trays

There are several methods used to determine the number of ideal plates or trays required for a given removal efficiency. An ideal plate is defined as one in which the gas and liquid streams leaving the plate are in equilibrium with each other.

One method used is a graphical technique such as illustrated in Figure 5-28. The number of ideal

plates is obtained by drawing "steps" on an operating diagram. The operating and equilibrium lines are determined as previously described. The liquid and gas concentrations at the bottom of the tower, X_b and Y_b, are known as is the gas concentration at the top of the tower, X_a. A horizontal line is drawn from A, which represents conditions at the bottom of the tower, to B on the equilibrium curve. Point B establishes the concentrations of the two streams leaving the bottom plate, X_n and Y_n, which, according to the definition of an ideal plate, are in equilibrium with each other. Next, a vertical line is drawn from B to C located on the operating line. Points on the operating line represent concentrations of streams that pass, in this case X_n and Y_{n-1}. This graphical stair-step procedure is repeated until concentrations at the top of the tower are reached. Each complete step represents one ideal tray.

In the Figure 5-27 example, conditions at the top of the tower lie between points E and F. Visual interpolation indicates that the point X_a, Y_a is about 0.3 of the distance between E and F. Thus, we estimate that 2.3 ideal trays are required for the specified separation. In effect, each horizontal line is a graphical statement that streams leaving an ideal tray are in equilibrium while each vertical line is a representation of a contaminant material balance at that position in the tower. In reality, equilibrium on each tray may be approached, but never truly achieved. To account for this, the number of actual trays will be greater than the ideal trays based on an efficiency correction that is described in below.
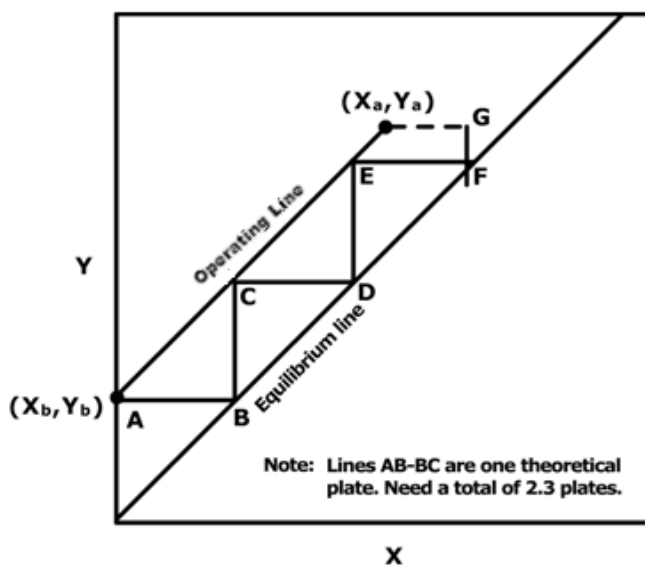
Figure 5-27. Graphical determination of the number of theoretical plates.

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When both the equilibrium and operating lines are straight, which is often the case in air pollution problems, the number of ideal trays can be calculated analytically using Equation 5-30. Note that Equation 5-30 is similar but not identical to Equation 5-27 for computing the N_{OG} of a packed-tower.

(Eq. 5-30)
$$N_{OG} = \frac{\ln\left[\frac{(Y_1 - mX_2)}{(Y_2 - mX_2)}\left(1 - \frac{mG_m}{L_m}\right) + \left(\frac{mG_m}{L_m}\right)\right]}{\ln\left(\frac{L_m}{mG_m}\right)}$$

Equation 5-30 is used to predict the number of theoretical trays required to achieve a given removal efficiency. The operating conditions for a theoretical tray assume that the gas and liquid streams leaving the plate are in equilibrium with each other. This ideal condition is never achieved in practice. A larger number of actual trays are required to compensate for this decreased tray efficiency.

Three types of efficiencies have been proposed to correct for the fact that true equilibrium is not actually achieved: (1) the overall efficiency, which is applied equally to all trays within the column; (2) the Murphree efficiency, which may vary from tray to tray; and (3) the local efficiency, which pertains to a specific location on a tray. While methods for estimating the Murphree and local efficiencies are available, the methods are complex and are of questionable reliability.

For the present purposes, the overall efficiency, which is the ratio of the number of theoretical trays to the actual number of trays, is satisfactory. Values of the overall efficiency are often based on operating experience with systems that are similar to the system of current interest. For a rough estimate, overall tray efficiencies for absorbers operating with low-viscosity liquid normally fall in the 20% to 40% range for gas streams having high inert gas concentrations (typical air pollution control applications).

PROBLEM 5-6

Calculate the number of theoretical trays required for the NH_3 absorber considered in the previous example problems. Estimate the total height of the absorber if the trays are spaced at 0.53 m intervals, and assume an overall tray efficiency of 40%.

SOLUTION

From Problem 5-5 and the previous examples, the following data is obtained.

$Y_1 = 0.03$
$Y_2 = 0.003$
$X_2 = 0$
$L_m = 3669 \dfrac{\text{gmol } H_2O}{\text{min}}$
$G_m = 3542 \dfrac{\text{gmol air}}{\text{min}}$
$m = H_y = 0.768$

Step 1. The number of theoretical plates from Equation 5-30 is:

$$N_{OG} = \frac{\ln\left[\frac{(Y_1 - mX_2)}{(Y_2 - mX_2)}\left(1 - \frac{mG_m}{L_m}\right) + \left(\frac{mG_m}{L_m}\right)\right]}{\ln\left(\frac{L_m}{mG_m}\right)}$$

$$N_{OG} = \frac{\ln\left[\frac{(0.03 - 0)}{(0.003 - 0)}\left(1 - \frac{(0.768)(3542)}{(3669)}\right) + \left(\frac{(0.768)(3542)}{(3669)}\right)\right]}{\ln\left(\frac{(3669)}{(0.768)(3542)}\right)}$$

N_{OG} = 4.02 theoretical plates

Step 2. Assuming the overall plate efficiency is 40%, the actual number of trays is:

$$\text{Overall Plate Efficiency} = \frac{\#\text{Theoretical Plates}}{\#\text{Actual Plates}}$$

$$\#\text{Actual Plates} = \frac{\#\text{Theoretical Plates}}{\text{Overall Plate Efficiency}}$$

$$\#\text{ActualPlates} = \frac{4.02}{0.40} = 10.0\text{plates}(\text{trays})$$

Step 3. The height of the tower is given by:

$$Z = N_p * \text{tray spacing} + \text{top height}$$

The top height is the distance over the top plate that allows the gas-vapor mixture to separate. This distance (sometimes termed the *freeboard*) is usually the same as the tray spacing.

Z = 10.0 trays * (0.53 m/tray) + 0.53 m
Z = 5.83 meters (19.1 ft)

This height of the tray-tower absorber calculated in Problem 5-6 is higher than the 6.9 ft estimated for the packed-tower in Problem 5-4. This is logical because the tray tower is often less efficient for gas absorption than a similarly sized packed-bed scrubber. Because of the many assumptions and simplifications made in these example problems, no generalization should be made concerning the relative capabilities of the two common types of absorbers.

MIST ELIMINATOR EVALUATION

There are limits to the gas velocity through the mist eliminator since, at high gas velocities, liquid can be forced toward the trailing edge of the mist eliminator elements and reentrained in the gas stream. General guidelines concerning the maximum velocities are presented in Table 5-4.

Table 5-4. Gas velocities through mist eliminators.		
Mist Eliminator Type	Orientation	Maximum Gas Velocity (ft/sec)
Chevron*	Horizontal	15-20
Chevron*	Vertical	12-15
Mesh-Pad	Horizontal	15-23
Mesh-Pad	Vertical	10-15
Woven Pad[13]	Vertical	7-15
Tube Bank	Horizontal	18-23
Tube Bank	Vertical	12-16

*Also known as zigzag

The actual maximum velocity that applies to the specific type of mist eliminator should be determined from the manufacturers' specification sheet. This data can then be used to confirm that the mist eliminator is located in an area where the gas velocity is below the maximum level. The average gas velocity through the mist eliminator can be calculated simply by dividing the actual gas flow rate by the open area of the mist eliminator, as shown in Equation 5-31.

(Eq. 5-31) $$\text{Velocity} = \frac{\text{Gas flow fate, ft}^3/\text{min}}{\text{Mist eliminator open area, ft}^2} \left(\frac{\text{min}}{60 \, \text{sec}} \right)$$

Alkali Requirements

Absorption systems may require an alkali addition system if the gas stream is acidic. The most common acid gases are sulfur dioxide (SO_2), hydrogen chloride (HCl), and hydrogen fluoride (HF). Carbon dioxide (CO_2), which is formed in all combustion processes involving fossil fuels, wood fuels, and waste fuels, is also acidic. Calcium hydroxide [$Ca(OH)_2$] is the most common alkali material used to neutralize the acid gas. The alkali requirement is usually calculated based on the quantity of acid gas and the stoichiometry of the neutralization reaction.

Reaction 5-1 $\quad SO_2 + Ca(OH)_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 + H_2O$

Reaction 5-2 $\quad 2HCl + Ca(OH)_2 \rightarrow Ca^{2+} + 2Cl^- + 2H_2O$

Reaction 5-3 $\quad 2HF + Ca(OH)_2 \rightarrow Ca^{2+} + 2F^- + 2H_2O$
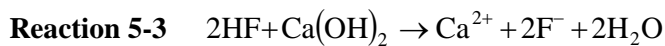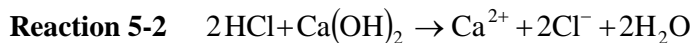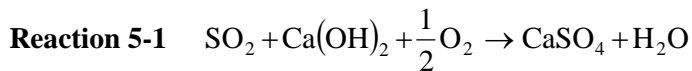
PROBLEM 5-7

Calculate the amount of calcium hydroxide (lime) needed to neutralize the HCl absorbed from a gas stream having 50 ppm HCl and a flow rate of 10,000 SCFM. Assume an HCl absorption efficiency of 95%.

SOLUTION

The quantity of HCl to be neutralized in the scrubbing liquid is calculated as follows:

First, calculate the molar density of the gas stream using the Ideal Gas Law.

$$PV = nRT \rightarrow \frac{V}{n} = \frac{RT}{P}$$

$$\frac{V}{n} = \frac{\left(0.7302 \frac{ft^3 * atm}{lb\,mol * R}\right)\left(68°F + 459.7°R\right)}{\left(1 atm\right)}$$

$$\frac{V}{n} = 385.3 \frac{ft^3}{lb\,mol}$$

Then calculate the amount of HCl in the gas stream to be absorbed.

$$HCl = 10,000 SCFM * \left(\frac{lb\,mol}{385.3 ft^3}\right)\left(\frac{0.00005\,lb\,mol\,HCl}{lb\,mol\,total}\right) = 0.0013 \frac{lb\,mol\,HCl}{min} \text{ in the gas stream}$$

$$HCl = \left(0.0013 \frac{lb\,mol\,HCl}{min}\right)(0.95) = 0.00123 \frac{lb\,mol\,HCl}{min} \text{ absorbed in the scrubbing liquid}$$

Next calculate the amount of lime needed to neutralize the HCl in the scrubbing liquid, using the stoichiometry from Reaction 5-2.

1 lbmol of lime [Ca(OH)₂] will neutralize 2 lbmol of HCl

$$Ca(OH)_2 \text{ required} = \left(\frac{1\,lb\,mol\,Ca(OH)_2}{2\,lb\,mol\,HCl}\right)\left(0.00123 \frac{lb\,mol\,HCl}{min}\right) = 0.000615 \frac{lb\,mol\,Ca(OH)_2}{min}$$

The molecular weight of lime [Ca(OH)₂] is 74.09 lb/lbmol, therefore:

$$\left(0.000615 \frac{lb\,mol\,Ca(OH)_2}{min}\right)\left(\frac{74.09\,lb_m}{lb\,mol}\right)\left(\frac{60\,min}{hr}\right) = 2.73 \frac{lb_m\,Ca(OH)_2}{hr}$$

The alkali feed system should be designed to provide sufficient alkali during times of peak acid gas concentrations. In some processes, the acid gas concentration can vary by more than a factor of 2. If these peaks last for long periods of time, the alkali system must have sufficient capacity to prevent the pH from dropping to values less than approximately 5, where the rate of corrosion begins to accelerate, especially in the presence of chlorides and fluorides.

5.5 INSTRUMENTATION

Common Problems Affecting Absorbers

Properly designed and operated absorption systems usually work very well; however, a variety of operating problems can occur in essentially any absorber. The most common problems affecting absorbers used for air pollution control include the following:

- Inadequate recirculation liquid flow
- Poor gas-liquid contact
- Inadequate alkali feed rates to neutralize acids
- Excessive liquid temperatures
- Corrosion

The system shown in Figure 5-28 is a three-tray impingement tray absorber with a mesh-pad mist eliminator. A recirculation tank and alkali feed equipment are included in the system. This system is used simply to illustrate the types of instruments that might be present on a large population of conventional absorption systems. These instruments might be required as part of a periodic monitoring program (e.g., Compliance Assurance Monitoring [CAM]), or as part of an operating permit.
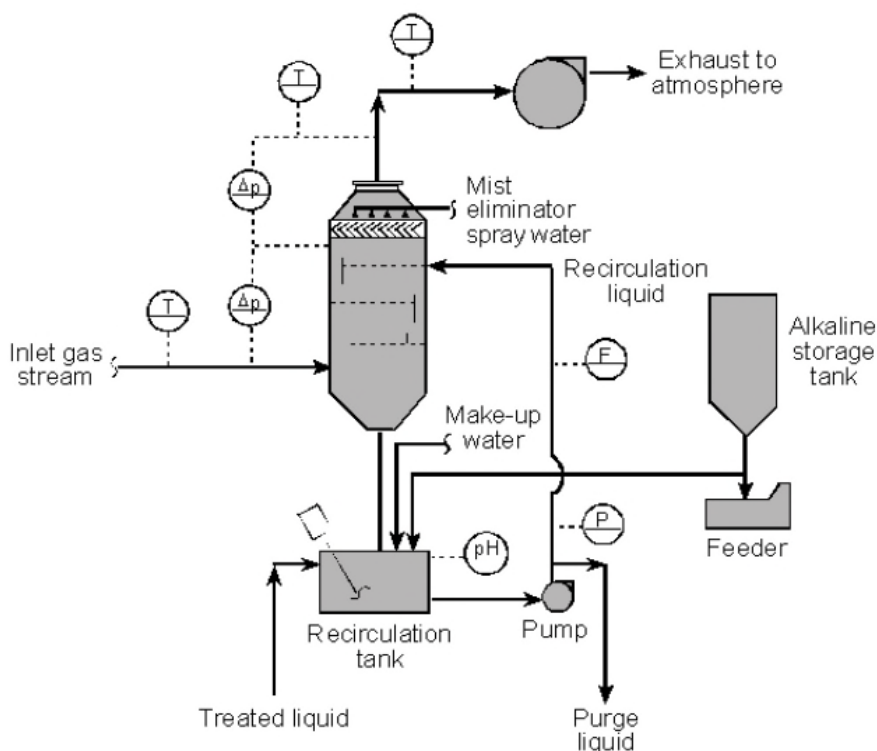
Figure 5-28. Performance monitoring instruments on an example absorber system.

The instrumentation provided in this example system measures inlet gas temperature, outlet gas temperature, recirculation liquid flow rate, liquid header pressure, pump discharge pressure, liquid pH, tray static pressure drop, and mist eliminator static pressure drop. This set of

instruments is relatively typical for many absorber systems, but the liquid flow rate monitor is rarely included on small-scale systems.

No outlet concentration monitor has been included, because these instruments are difficult to use on saturated gas streams such as those found in absorbers. It is difficult to extract a gas sample and remove the condensed water without inadvertently removing some of the contaminant that has penetrated the scrubber. Furthermore, there are no commercially available concentration monitors for many of the gaseous contaminants of interest in absorption; therefore, less direct indicators of performance are used.

Mist Eliminator Static Pressure Drop

The static pressure drop across the mist eliminator provides an excellent indicator of the physical condition of the mist eliminator. The static pressure drop is strictly a function of the geometry of the mist eliminator, the gas flow rate through the mist eliminator, and the gas density. Accordingly, the static pressure drop should be relatively constant. Increases from the baseline level are probably indicative of solids buildup. The pressure drops across mist eliminators usually vary from 0.5 to 2 in. W.C. (0.1 to 0.5 kPa), but some commercial designs have pressure drops as high as 4 in. W.C. (1.0 kPa). Accumulation of solids can increase mist eliminator pressure drops by more than 1 in. W.C. (0.25 kPa).

If high-pressure drop occurs, it may be necessary to activate the cleaning system more frequently or for a longer operating time. Mist eliminator washing usually lasts from several minutes to more than 15 minutes.

Mist eliminator static pressure drop well below the baseline range suggests that the mist eliminator has been damaged. Structural failure of the mist eliminator is possible because of the forces that can be imposed on the surface when it is significantly blinded. For example, a 6-foot-diameter mist eliminator immediately upstream of a fan with an inlet static pressure of -10 in. W.C. (2.5 kPa) can create a force of over 1400 pounds-force on the surface. Corrosion-related weakening of the supporting frame of the mist eliminator could cause the entire unit to break into parts and be pulled toward the fan. Units constructed of FRP and other synthetic materials can suffer adhesive failure if there is a gas temperature spike, causing part of the mist eliminator to break away. The gaps left in the mist eliminator have a very low static pressure drop, and most of the gas stream channels through this area. Accordingly, the effectiveness of the unit is compromised.

Liquid Flow Rate

Liquid flow rate monitors on the recirculation line leading back to the absorber (Figure 5-29) provide an indirect indication of absorber performance. Large decreases in the liquid flow rate can result in inadequate gas-liquid contact. Large increases may result in the absorber approaching flooding conditions.

There are a variety of instruments used to monitor liquid flow rates, including:

1. Magnetic flow meters
2. Ultrasonic flow meters
3. Orifice meters
4. Swinging vane meters

The magnetic flow meters are usually used on moderate-to-large systems, and the other types are common on moderate-to-small systems. All of these units are vulnerable to high suspended-solids levels in the recirculation liquid. Solids can precipitate inside the pipe and blind the sensors of magnetic flow meters and ultrasonic meters. Suspended solids can erode orifice plates and block the movement of swinging vane meters.

Indirect indicators of liquid flow rate are useful in absorber systems that have vulnerable liquid flow meters because of the high suspended-solids levels. Indirect indications of decreases in the liquid flow rate include (1) a decrease in the recirculation pump discharge pressure and (2) an increase in the pressure in headers supplying spray nozzles at the top of the absorber vessel. Increased pressure in the spray nozzle supply header is usually due to a plugged nozzle orifice or header itself.

Outlet Gas Temperature

Another indirect indicator of reduced liquid flow is the outlet gas temperature, which can increase from normal levels because of poor gas-liquid contact, caused in part by low liquid flow rates. A temperature monitor in the outlet duct of the scrubber vessel is especially useful. The outlet gas stream temperature should be close to the adiabatic saturation temperature because of the relatively long contact time between the gas and liquid streams. The adiabatic saturation temperature is the temperature that is reached as heat is transferred from the gas to the liquid phase due to the vaporization of liquid. The term *adiabatic* means that heat transfer occurs only between the liquid and gas streams, and there is no net heat transfer into or out of the absorber. While this is not precisely the case, most large absorbers closely approximate adiabatic operation.

The adiabatic saturation temperature is estimated using a psychrometric chart, such as Figure 5-29. The inlet gas dry bulb temperature and dew point establish a point on the psychrometric chart representing inlet gas conditions. Adiabatic operation is represented by the dashed line running parallel to the wet bulb temperature lines. The dashed line intersects the saturation line at the adiabatic saturation temperature. The outlet absorber gas temperature should be close to this value when the absorber is operating properly.
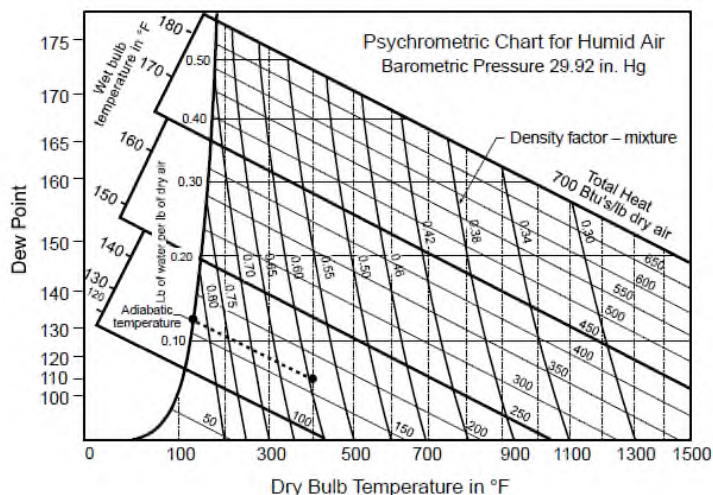
Figure 5-29. Psychrometric chart.

Conditions That Could Create Gas-Liquid Maldistribution

Absorber outlet gas temperatures more than 5°F to 10°F (2.8°C to 5.5°C) above the adiabatic saturation temperature are sometimes associated with poor gas-liquid distribution or inadequate recirculation liquid flow. Some of the conditions that could create poor gas-liquid distribution in the various types of absorbers are listed below.

Spray Towers

- Plugging of one or more spray nozzles
- Plugging of nozzle supply headers
- Uneven distribution of the gas stream entering the vessel

Packed-Bed

- Inadequate liquid distribution at the top and/or inadequate redistribution between beds
- Channeling due to plugging in the bed
- Collapse of one or more beds

Tray Towers

- Sloped, bowed, or warped trays
- Gas short-circuiting through incompletely filled liquid downcomers
- Sloped overflow weirs on one or more trays
- Solids accumulation in localized portions of the trays

Venturis

- Inadequate distribution of liquid across the inlet to the throat
- Uneven gas distribution entering the converging area of the throat

Ejectors

- Inadequate distribution of liquid across the ejector section
- Erosion of the ejector nozzle

Column Static Pressure Drop

The absorber static pressure drop provides a useful indication of plugging in packed beds or impingement trays. Static pressure drops above baseline levels are usually caused by partial plugging.

A change in the gas flow rate through the system can be evaluated by checking the process operating rate and the fan motor currents. A decrease in the fan motor current is usually associated with a decrease in the gas flow rate through the absorber system.

Recirculation Liquid pH

Variations in the recirculation liquid pH levels are useful in evaluating absorber performance. The pH is usually monitored in the recirculation tank where alkali is added to the system or in the recirculation line leading back to the inlet of the absorber.

pH levels above 9 indicate the potential for the precipitation of calcium and magnesium compounds. These precipitates can cause plugging of spray nozzles, distributors, packed beds, and trays. Furthermore, the precipitates can accumulate as a layer inside the recirculation lines and restrict liquid flow. The decrease in liquid flow is not always apparent because of the adverse impact of the solids on the liquid flow rate monitors.

pH levels below approximately 5 indicate that insufficient alkali is being added to neutralize the acid gases being absorbed. Low removal efficiencies are probable because of the liquid stream's potential for saturation. When the pH is lower than 5, severe corrosion of metal components is possible. Corrosion is especially rapid when the low pH conditions occur in systems with high dissolved chloride or fluoride concentrations.

BIOFILTRATION SYSTEMS

A schematic flowchart of a biofiltration system is shown in Figure 5-30. Permanent instrumentation on these systems may be limited, in which case portable instruments will be important in evaluating their performance.
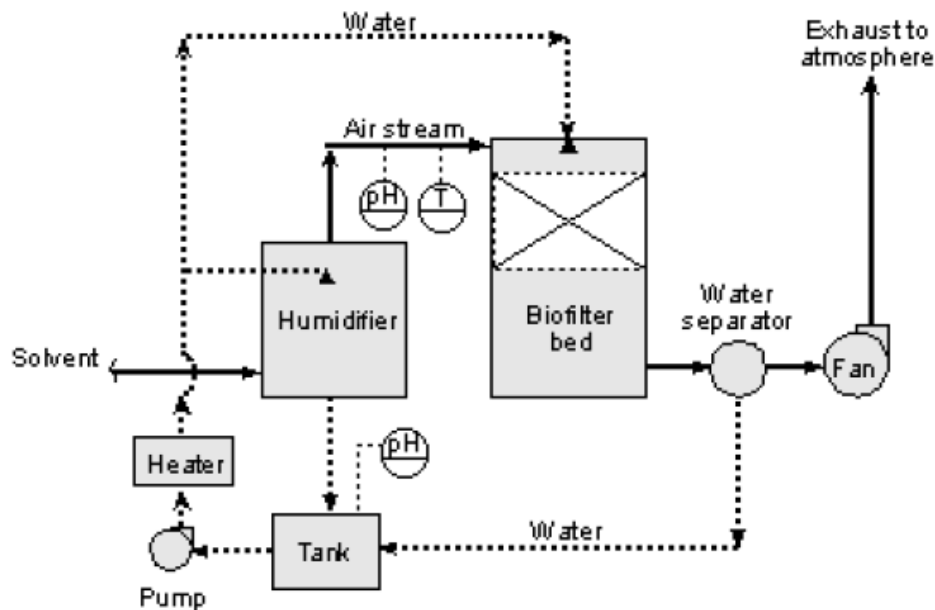
Figure 5-30. Flowchart of a typical biofiltration oxidation system.

Inlet Gas Temperature

Instrumentation can be limited to simply an inlet temperature monitor. Good control of inlet gas temperature is necessary to avoid destroying the microorganisms. Inlet temperature significantly above 105°F (41°C) may indicate a failure in the humidification system.

Inlet Gas Relative Humidity

The relative humidity of the inlet gas stream can be measured using portable instruments, including a simple wet bulb–dry bulb thermometer and battery-powered instruments. Relative humidity in excess of 95% is needed to maintain the necessary water layer over the packing material, which is needed for the microorganisms to be active.

Outlet VOC Concentration

Portable VOC analyzers provide the only direct means of evaluating the ability of the microorganisms to metabolize the organic compounds present in the gas stream. These instruments must be capable of operating in the 10 ppm to 500 ppm concentration range.

High outlet concentrations could occur because of low bed temperature, toxicity of one or more organics in the waste gas stream to the microorganisms, or death of the microorganisms because of excessive temperature and/or loss of moisture in the bed.

Recirculated Liquid pH

The pH of the recirculated water can be measured with a portable pH monitor or even pH paper. Low pH levels indicate the acidification resulting from the presence of sulfur-, chlorine- and/or fluorine-containing materials in the gas stream. The pH should be in the range of 6 to 8.

5.6 SUMMARY

CONTROL TECHNIQUES FOR GASEOUS CONTAMINANTS

This chapter covered the following topics:

- Various types and components of absorbers.
- Operating principles that influence the efficiency of absorbers.
- Capability and sizing parameters of an absorber system.
- Instrumentation requirements for an absorber system.

5.7 REVIEW EXERCISES

MULTIPLE CHOICE QUESTIONS

Select the best response(s) for each of the following multiple-choice questions.

1. The gas stream temperature at the scrubber inlet has increased significantly. If the other operating conditions (i.e., liquid flow rate) stay the same, how will this change affect the control efficiency of the absorber system?

    a) It will increase
    b) It will decrease
    c) It will remain unchanged
    d) No way to predict

2. Sulfur dioxide absorbed in a packed bed reacts with alkali dissolved in the scrubbing liquid. Does the Henry's Law equilibrium constant limit sulfur dioxide absorption in this system?

    a) Yes
    b) No
    c) Only if the temperature is too high
    d) Only if the temperature is too low

3. What type of spray nozzle is used in most spray-tower absorbers?

    a) Full cone
    b) Hollow cone
    c) Fan
    d) Two-fluid atomizing

4. What is the typical liquid-to-gas ratio in spray-tower absorbers?

    a) 5 to 50 gallons/ACF
    b) 50 to 200 gallons/ACF
    c) 1 to 5 gallons/1,000 ACF
    d) 5 to 50 gallons/1,000 ACF

5. What is the typical liquid-to-gas ratio in a Venturi absorber?

    a) 20 to 100 gallons/ACF
    b) 100 to 500 gallons/ACF
    c) 1 to 20 gallons/1,000 ACF
    d) 20 to 50 gallons/1,000 ACF

6. What is the primary purpose of the packing material in a packed-bed scrubber?

    a) To provide liquid surface area for mass transfer
    b) To provide liquid sheet impaction targets
    c) To decrease the gas stream velocity
    d) None of the above

7. What factors affect the performance of spray-tower, packed-bed, tray-tower, and Venturi absorbers? Select all answers that apply.

    a) Gas velocity
    b) Gas-liquid distribution
    c) Gas-droplet-size distribution
    d) All of the above

8. What is the purpose of the mist eliminator? Select all that apply.

    a) To protect the fan from accumulation of solids
    b) To minimize the emission of droplets containing solids
    c) To capture droplets ranging in size from 10 micrometers to 1,000 micrometers
    d) To capture droplets ranging in size from 1 to 10 micrometers

9. What is the typical gas velocity approaching chevron, radial-blade, and mesh-pad mist eliminators?

    a) 1 to 5 feet per minute
    b) 5 to 15 feet per minute
    c) 1 to 5 feet per second
    d) 5 to 15 feet per second

10. What is the typical pH range in an absorber system?

    a) 1 to 5
    b) 5 to 9
    c) 9 to 14
    d) None of the above

11. What is the purpose of adding alkali to the recirculating liquid in an absorber system? Select all that apply.

    a) To protect the absorber materials of construction from corrosion
    b) To optimize absorption of acid gases
    c) To optimize droplet size distribution
    d) To optimize settling rates of suspended solids in clarifiers used to treat the purge stream

Operating Principles of Absorbers

12. A gas is more soluble when _____ .

a) the absorbent is cold
b) the absorbent is hot
c) solubility is independent of absorbent temperature
d) the liquid surface tension is low

13. Henry's Law usually applies when the gas phase concentration of the pollutant is
_____.

a) low
b) high
c) Henry's Law is independent of the gas phase concentration.
d) Impossible to say

14. The Henry's Law constant for compound A is 40, while the value for compound B is 0.4.
Which compound is more soluble?

a) Compound A
b) Compound B
c) Both are equally soluble
d) More information is required

15. A pollutant dissolving into an aqueous absorbent reacts rapidly upon entering the liquid.
What factors influence the determination of the necessary liquid-to-gas ratio for this absorber?

a) Equilibrium of the gas phase pollutant and the dissolved form of the pollutant
b) Adequacy of gas-liquid contact (hydraulic considerations)
c) Both a and b
d) None of the above

16. When does Henry's Law not apply to absorption processes? Select all that apply.

a) When the gas concentration is high
b) When the gas concentration is low
c) When there is substantial heat released during dissolution
d) None of the above

Capability and Sizing of Absorbers

17. Which factors can cause poor gas-liquid distribution in a packed-bed absorber?

a. Inadequate liquid distribution at the top and/or inadequate redistribution between beds in the vertical tower
b. Channeling due to plugging in the bed
c. Collapse of one or more beds
d. All of the above

18. A vertical spray-tower absorber has a gas flow rate of 6,000 ACFM. The absorber diameter is 3.5 feet. What is the average velocity through the absorber? Is this velocity within the normal range for a chevron-type (zigzag) mist eliminator?

19. An exhaust stream of 3000 SCFM contains 3% NH_3 by volume. The operator plans to reduce the NH_3 content by 90% by scrubbing with water (no alkaline additives). What is the required liquid flow rate at 1.5 times the minimum liquid-to-gas ratio? Use the following data to solve the problem.

$$\text{Henry's Law constant} = 0.768 \frac{\text{mole fraction } NH_3 \text{ in gas}}{\text{mole fraction } NH_3 \text{ in liquid}}$$

Liquid density = 62.4 lb_m/ft^3
7.48 gal H_2O = 1.00 ft^3
Gas density = 0.0732 lb_m/ft^3
Gas temperature = 20°C

5.8 REVIEW EXERCISES: SOLUTIONS

This Student Guide includes separate exercises and solutions, which allow students to check their work.

MULTIPLE CHOICE ANSWERS

1. The gas stream temperature at the scrubber inlet has increased significantly. If the other operating conditions (i.e., liquid flow rate) stay the same, how will this change affect the control efficiency of the absorber system?

    a) It will increase
    b) It will decrease
    c) It will remain unchanged
    d) No way to predict

2. Sulfur dioxide absorbed in a packed bed reacts with alkali dissolved in the scrubbing liquid. Does the Henry's Law equilibrium constant limit sulfur dioxide absorption in this system?

    a) Yes
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    c) 1 to 20 gallons/1,000 ACF
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   a) To provide liquid surface area for mass transfer
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   c) To decrease the gas stream velocity
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   a) Gas velocity
   b) Gas-liquid distribution
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    b) 5 to 9
    c) 9 to 14
    d) None of the above

11. What is the purpose of adding alkali to the recirculating liquid in an absorber system? Select all that apply.

    a) To protect the absorber materials of construction from corrosion
    b) To optimize absorption of acid gases
    c) To optimize droplet size distribution
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      b) the absorbent is hot
      c) solubility is independent of absorbent temperature
      d) the liquid surface tension is low

13. Henry's Law usually applies when the gas phase concentration of the pollutant is
_____.

      a) **low**
      b) high
      c) Henry's Law is independent of the gas phase concentration.
      d) Impossible to say

14. The Henry's Law constant for compound A is 40, while the value for compound B is 0.4.
Which compound is more soluble?

      a) Compound A
      b) **Compound B**
      c) Both are equally soluble
      d) More information is required

15. A pollutant dissolving into an aqueous absorbent reacts rapidly upon entering the liquid.
What factors influence the determination of the necessary liquid-to-gas ratio for this absorber?

      a) Equilibrium of the gas phase pollutant and the dissolved form of the pollutant
      b) **Adequacy of gas-liquid contact (hydraulic considerations)**
      c) Both a and b
      d) None of the above

16. When does Henry's Law not apply to absorption processes? Select all that apply.

      a) **When the gas concentration is high**
      b) When the gas concentration is low
      c) **When there is substantial heat released during dissolution**
      d) None of the above

Capability and Sizing of Absorbers

17. Which factors can cause poor gas-liquid distribution in a packed-bed absorber?

      a) Inadequate liquid distribution at the top and/or inadequate redistribution between
         beds in the vertical tower
      b) Channeling due to plugging in the bed
      c) Collapse of one or more beds
      d) **All of the above**

18. A vertical spray-tower absorber has a gas flow rate of 6,000 ACFM. The absorber diameter is
3.5 feet. What is the average velocity through the absorber? Is this velocity within the normal
range for a chevron-type (zigzag) mist eliminator?

SOLUTION:

Calculate the average velocity.

$$\text{Area} = \frac{\pi D^2}{4} = \left(\frac{\pi(3.5\,\text{ft})^2}{4} \right) = 9.6\,\text{ft}^2$$

$$\text{Velocity} = \text{Gas flow rate/area} = \left(\frac{6{,}000\,\text{ft}^3/\text{min}}{9.6\,\text{ft}^2} \right)\left(\frac{\text{min}}{60\,\text{sec}} \right) = 10.4\,\text{ft/sec}$$

The velocity is within the normal range.

19. An exhaust stream of 3000 SCFM contains 3% NH_3 by volume. The operator plans to reduce the NH_3 content by 90% by scrubbing with water (no alkaline additives). What is the required liquid flow rate at 1.5 times the minimum liquid-to-gas ratio? Use the following data to solve the problem.

$$\text{Henry's Law constant} = 0.768\,\frac{\text{mole fraction } NH_3 \text{ in gas}}{\text{mole fraction } NH_3 \text{ in liquid}}$$

Liquid density = 62.4 lb_m/ft^3
7.48 gal H_2O = 1.00 ft^3
Gas density = 0.0732 lb_m/ft^3
Gas temperature = 20°C

SOLUTION:

Calculate the equilibrium concentration of NH_3 in water.

$$y^* = H^*x$$
$$Y_1 = H_y^*X_1$$

$$0.03\,\text{mol fraction } NH_3 \text{ in gas} = \left(0.768\,\frac{\text{mole fraction } NH_3 \text{ in gas}}{\text{mole fraction } NH_3 \text{ in liquid}} \right) x$$

$$x = 0.0391 \text{ mole fraction } NH_3 \text{ in exit liquid}$$

Calculate $(L_m/G_m)_{min}$ using Equation 5-16, then solve for L_m.

$$Y_1 - Y_2 = \left(\frac{L_m}{G_m} \right)(X_1 - X_2)$$

$$G_m = 3000\,\text{SCFM} * \left(\frac{0.0732\,lb_m}{ft^3} \right)\left(\frac{lb\,mol}{29\,lb_m} \right) = 7.57\,\frac{lb\,mol\,gas}{min}$$

$$(L_m)_{min} = \frac{G_m(Y_1 - Y_2)}{(X_1 - X_2)} = \frac{\left(7.57\frac{lbmol}{min}\right)(0.03 - 0.003)}{(0.0391 - 0)} = 5.23\frac{lb\,mol}{min}$$

$$L_{op} = 1.5*(L_m)_{min} = 1.5*\left(5.23\frac{lb\,mol}{min}\right) = 7.85\frac{lb\,mol}{min}$$

$$L_{op} = \left(7.85\frac{lb\,mol}{min}\right)\left(\frac{18\,lb_m\,H_2O}{lb\,mol}\right)\left(\frac{ft^3}{62.4\,lb_m}\right)\left(\frac{7.48\,gal}{ft^3}\right) = 16.9\frac{gal\,H_2O}{min}$$

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6.0 OXIDATION

6.1 OVERVIEW

PURPOSE

Oxidation systems are used to destroy organic compounds classified as volatile organic compounds (VOCs) and/or air toxic compounds. At sufficiently high temperatures and adequate residence times, essentially all organic compounds can be oxidized to form carbon dioxide and water vapor. The oxidation products of organic compounds containing chlorine, fluorine, or sulfur are HCl, HF, Cl_2 or SO_2.

Oxidation air pollution control systems are based on mature technology that has been used successfully for more than 40 years. However, there have been a number of developments that have increased the types of commercially available oxidizer systems. Oxidizer systems for VOC and air toxic compound control can be categorized into two main groups and a number of subgroups:

High-Temperature, Gas-Phase Oxidation Processes

- Recuperative thermal oxidizers
- Regenerative thermal oxidizers
- Process boilers used for thermal oxidation
- Flares used for thermal oxidation

Catalytic Oxidation Processes

- Recuperative catalytic oxidizers
- Regenerative catalytic oxidizers

High-temperature, gas-phase oxidation processes use temperatures in the range of 1,000°F to 2,000°F (540°C to 1,100°C). Thermal oxidizers and process boilers handle gas streams with inlet organic vapor concentrations less than 25% to 50% of their Lower Explosive Limit (LEL). (Refer to Chapter 2 for discussion on explosive limits.) Flares are used for the combustion of organic vapor waste streams that have concentrations greater than 100% of the Upper Explosive Limit (UEL). Catalytic oxidation processes operate at temperatures ranging from 400°F to 1,000°F (200°C to 540°C) and are designed for gases containing less than 25% of the LEL.

The terms *recuperator* and *regenerator* refer to the type of heat exchanger used to increase system efficiency. A recuperator is a tubular or plate heat exchanger where heat is transferred

through the metal surface. A regenerator uses a set of refractory packed beds that store heat. Both types reduce the amount of supplement fuel needed to oxidize the contaminants in the combustion chamber. With sufficiently high organic concentration, the energy released during oxidation may be sufficient to maintain the necessary temperature without the addition of supplemental fuel.

LEARNING OBJECTIVES

At the conclusion of this training, students will be able to:

- Distinguish between the various types of oxidation systems.
- Identify the principles of operation for oxidation systems.
- Determine the factors that influence the capability and sizing of an oxidation system.
- Identify the operating parameters that need to be evaluated in an oxidation system.

6.2 TYPES AND COMPONENTS OF OXIDIZER SYSTEMS

HIGH-TEMPERATURE, GAS-PHASE OXIDATION SYSTEMS

This section describes the characteristics of the four main categories of high-temperature, gas-phase oxidation processes.

- Recuperative thermal oxidizers
- Regenerative thermal oxidizers
- Boilers
- Flares

The emphasis is on the design and performance characteristics that determine their applicability to various types of air pollution sources.

All four of these process types use very high gas temperatures to oxidize the organic pollutants to carbon dioxide, water, and other combustion products. These processes usually operate at gas temperatures ranging from 1,000°F to more than 2,000°F (540°C to 1,100°C), and should be at least 200°F to 300°F (95°C to 150°C) above the auto-ignition temperature of the most difficult-to-oxidize organic compound in the gas stream.[1]

A proper oxidizer design is achieved by considering the three ―T's of combustion—time, temperature, and turbulence. Large residence times, high temperatures, and highly turbulent flow all contribute to the complete destruction (i.e., oxidation) of the organic pollutant. Figure 6-1 shows the interplay between time and temperature for a hypothetical compound. With a residence time of 1 sec, 100% destruction can be achieved at a temperature of about 1200°F (650°C). However, with a residence time of 0.01 sec, a temperature of about 1500°F (815°C) is required.
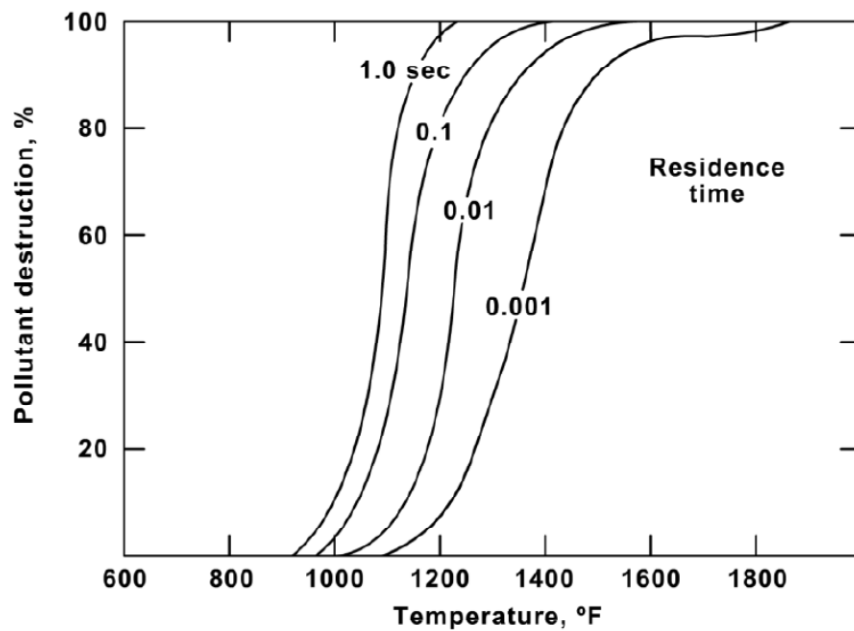
Figure 6-1. The effects of time and temperature on pollutant destruction efficiency.

Turbulent flow is needed to ensure that the oxidizer feed is well-mixed with the products from the supplemental fuel burners and that none of the pollutants are allowed to bypass the zone of maximum temperature. As shown in Figure 6-2, mixing can be promoted by the proper use of baffles within the oxidization chamber.
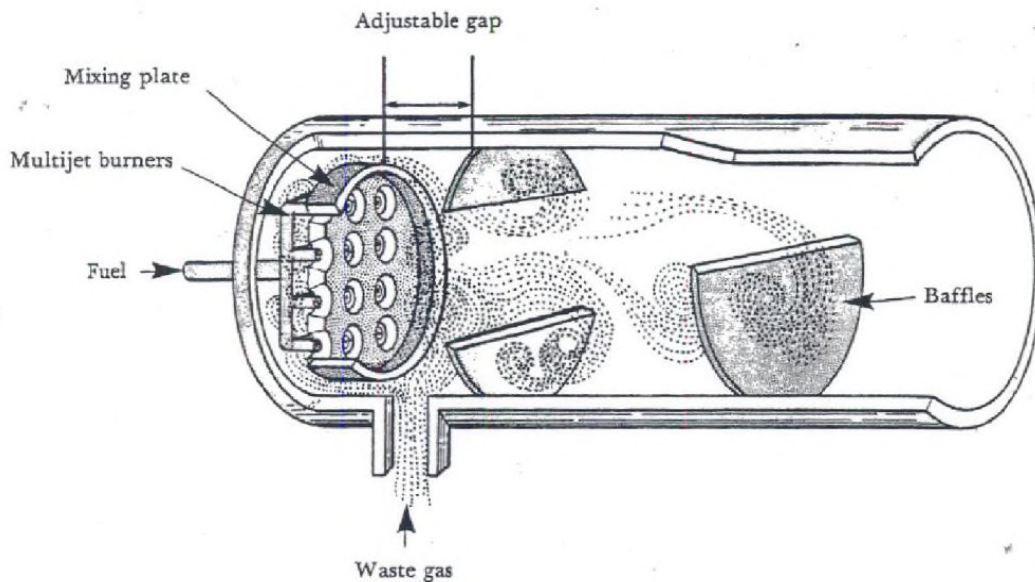
Figure 6-2. Thermal oxidizer using multi-jet burners and baffles to promote mixing.

Recuperative Thermal Oxidizers

A recuperative thermal oxidizer consists of a refractory-lined chamber equipped with one or more gas- or oil-fired burners. As shown in Figure 6-3, the contaminant-laden gas stream is mixed with the hot combustion gases from the burner flame in order to achieve the desired operating temperature. The contaminated gas stream does not necessarily pass through the burner itself.
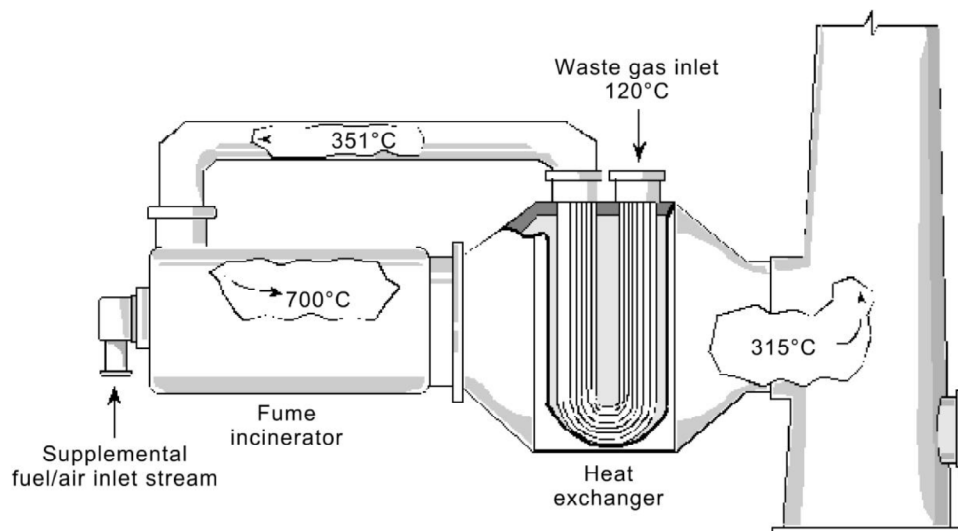
Figure 6-3. Oxidizer equipped with a double-pass recuperative heat exchanger.

The combustion chamber is sized to provide sufficient residence time to complete the oxidation reactions, typically from approximately 0.3 to more than 2 seconds. The time needed for high-efficiency destruction is strongly dependent on the operating temperature and the mixing within the chamber.

The unit depicted in Figure 6-3 includes a recuperative heat exchanger (recuperator) to recover a portion of the sensible heat generated by the combustion of the burner fuel and by the oxidation of the organic vapors in the gas stream. A recuperator is a tubular or plate-type heat exchanger. The hot gas stream passes on one side of the tube bank, and the cold inlet gas stream passes on the other side. Heat recoveries range from approximately 40% to 65% of the total heat released in the combustion chamber. Typical temperatures at key locations in the system are included.

Because of the presence of the recuperative heat exchanger, particulate matter in the inlet gas stream must be minimized to prevent fouling the surface of the tubes and reducing heat-transfer efficiency. Some recuperative units include clean-out ports and access hatches to facilitate cleaning.

Thermal oxidizers are relatively heavy units because of the refractory lining required to protect the metal shell from the high temperatures within the chamber. Because of their weight, thermal oxidizers are often placed on the ground rather than on roofs or other elevated areas.

A simplified flowchart of a recuperative thermal oxidizer system is shown in Figure 6-4. The instrumentation used to evaluate the performance of the oxidizer includes temperature monitors on the incinerator products (before and after the recuperator) and the solvent-laden gas exiting the recuperator, and the inlet LEL concentration monitor. Recuperative and regenerative thermal oxidizers are usually designed for inlet concentrations less than 25% of the LEL, but in some cases, the oxidizers have been operated with concentrations as high as 50% of the LEL. Because of

safety-related LEL limits, the inlet concentrations of thermal oxidizers are usually in the 1,000 to 10,000 ppm range.
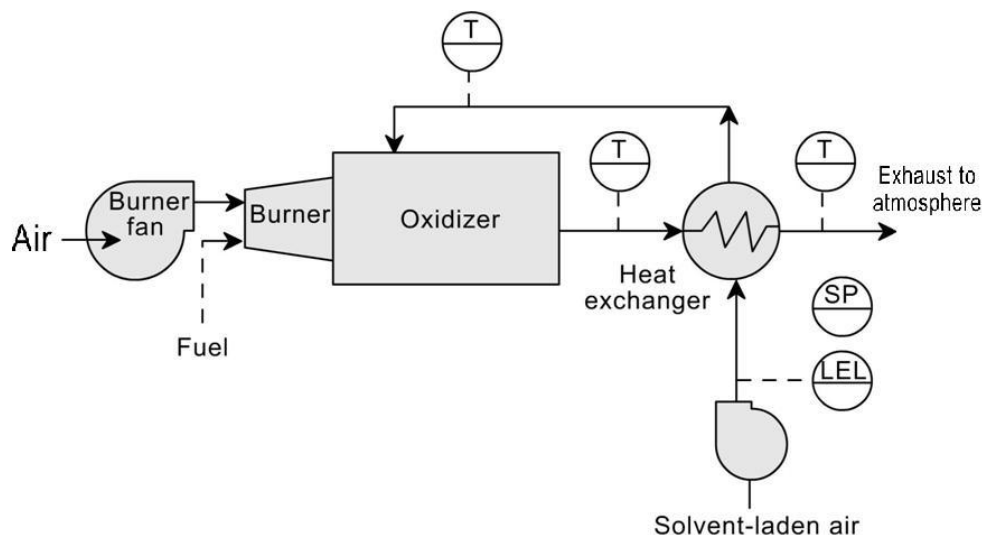
Figure 6-4. Flowchart of a recuperative heat exchanger.

The burner normally operates continuously unless the organic vapor concentration in the inlet gas stream is sufficiently high to maintain the desired temperature without supplemental fuel. The outlet temperature monitor downstream of the heat exchanger is used to shut down the burner (pilot flame remains on) in the event of excessively high gas temperatures.

A burner master controller is used to maintain proper air-fuel ratios. A pilot flame igniter system and a flame scanner system (not shown on Figure 6-2) ensure that the burner operates safely. These types of oxidizers usually do not have flashback protection devices, because flashback through the gas handling system is not a major safety concern with the low organic vapor concentrations of the inlet gas stream. The LEL monitor on the inlet gas stream is used to activate the atmospheric discharge vent and to shut down the entire process that generates the organic-vapor-containing gas stream if the concentrations exceed the safe level.

The static pressure gauge, while rarely present in recuperative thermal oxidizers, can be used to monitor the gas flow resistance through the recuperator.

Regenerative Thermal Oxidizers

Regenerative thermal oxidizers have heat recovery efficiencies as high as 95%, much higher than recuperative units.[2] Because of the high inlet gas temperatures created by the heat recovery, burner fuel is required only if the organic vapor concentrations in the gas stream are very low. At moderate-to-high concentrations, the heating value of the organic contaminants is sufficient to maintain the necessary temperatures in the combustion chamber.

High-efficiency heat recovery is achieved by passing the inlet gas stream through a large packed bed containing ceramic packing that has been previously preheated by passing the outlet gases from the combustion chamber through the bed. At least two beds are required, and gas flow dampers are used to switch the inlet and outlet gas streams to the appropriate beds.

Three beds are commonly used in a regenerative system. One of the beds is used to preheat the inlet gas stream, the second is used to transfer the heat of combustion from the treated gas stream, and the third is in a purge cycle. Without a purge cycle, emission spikes would occur as a portion of the untreated gas stream would be released immediately after each flow reversal.[2]

An example of a commercial system is shown in Figure 6-5. This unit has three parallel beds with an overhead refractory-lined combustion chamber equipped with two gas-fired burners.

Another type of regenerative thermal oxidizer, a ―flameless oxidizer, is shown in Figure 6-6. In this case, the burner is used only for preheating the packed ceramic bed prior to the introduction of organic vapor.[3] The contaminated gas stream enters a gas distribution chamber near the bottom of the unit and is mixed with air. The ceramic bed temperature is maintained above the auto-ignition temperature of the most difficult-to-oxidize compound being treated. One of the advantages of this type of combustion system is the low NO_x generation rate due to the limited peak gas temperatures in the packed bed.

Packed-bed (flameless) oxidizer systems are not used for gas streams containing organometallic or organophosphorus compounds, as these contaminants can form particulate matter that accumulates in the packed bed.
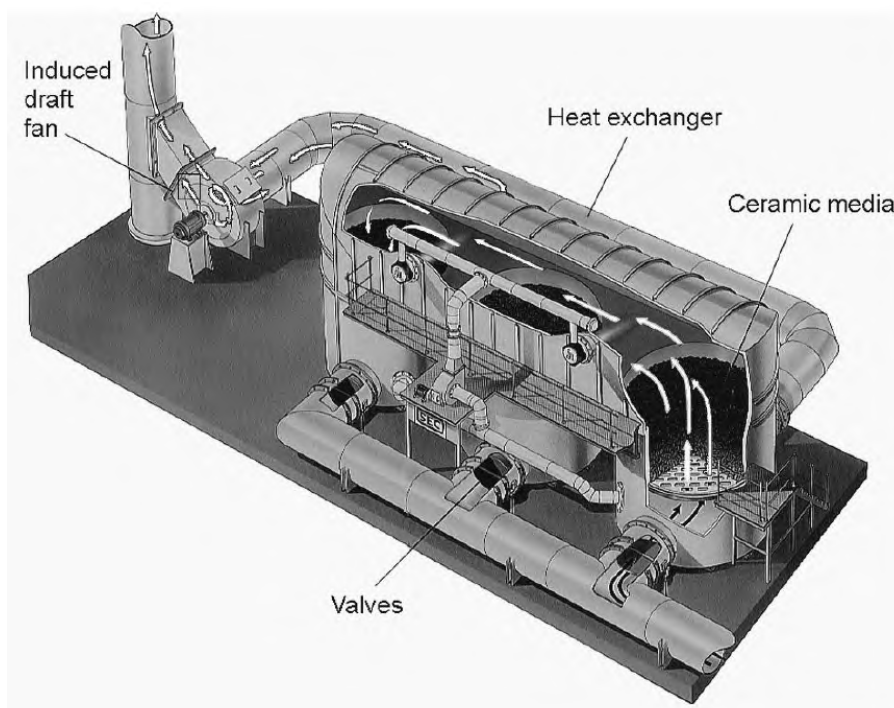
Figure 6-5. Regenerative thermal oxidizer.
(Reprinted courtesy of Smith Engineering Co., Ontario, CA.)
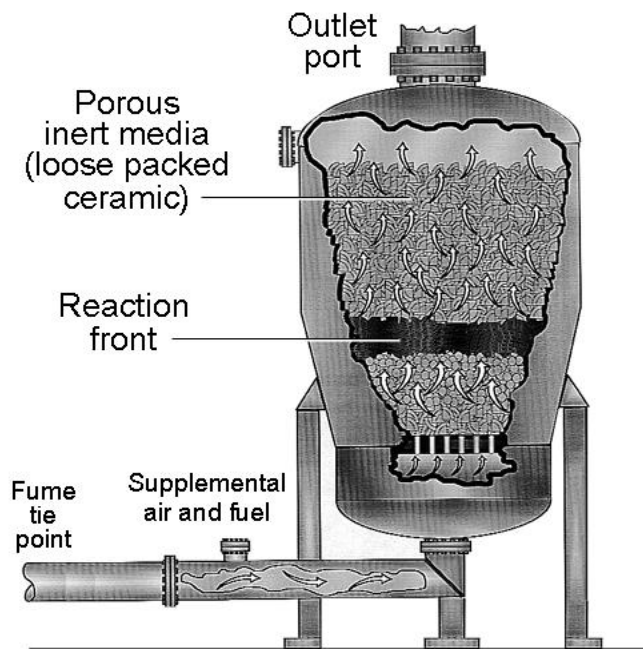
Figure 6-6. Flameless thermal oxidizer.
(Reprinted courtesy of Thermatrix, Inc., San Jose, CA.)

All of the regenerative units are vulnerable to particulate matter in the inlet gas stream that can plug the packed bed and increase the static pressure drop. Therefore, regenerative units are used only on sources with very low particulate loadings (i.e., < 0.015 gr/ACF) or on sources where it is safe and practical to remove the particulate matter upstream of the oxidizer.

Regardless of the type of thermal oxidizer used, the oxidation of halogenated compounds results in the formation of compounds such as hydrochloric acid (HCl) and hydrofluoric acid (HF), which are regulated air toxic compounds. Accordingly, it is necessary to include absorbers downstream of the oxidizer in order to reduce the emission of these compounds.

Process Boilers Used for Thermal Oxidation

An alternative to installing a thermal oxidizer is to burn the waste gases in an existing plant or process boiler, thus avoiding the capital cost of new equipment. Process and plant boilers are normally designed to operate with combustion chamber temperatures in excess of 1,800°F (980°C) and with flue gas residence times in excess of 1 to 2 seconds, conditions similar to those of thermal oxidizers.

The waste gas stream is usually injected into the boiler at an elevation close to the main burners and overfire air nozzles (Figure 6-7). In some cases, the waste gas stream may be used as part of the combustion air supply for the burners in the boiler. Regardless of the injection location, the temperatures in this area are well above the auto-ignition temperatures of most organic compounds. Oxidation must be completed before the combustion products pass through the furnace area and reach the main heat exchange surfaces (convective superheaters, reheaters and economizers) where the gas temperature drops quickly.
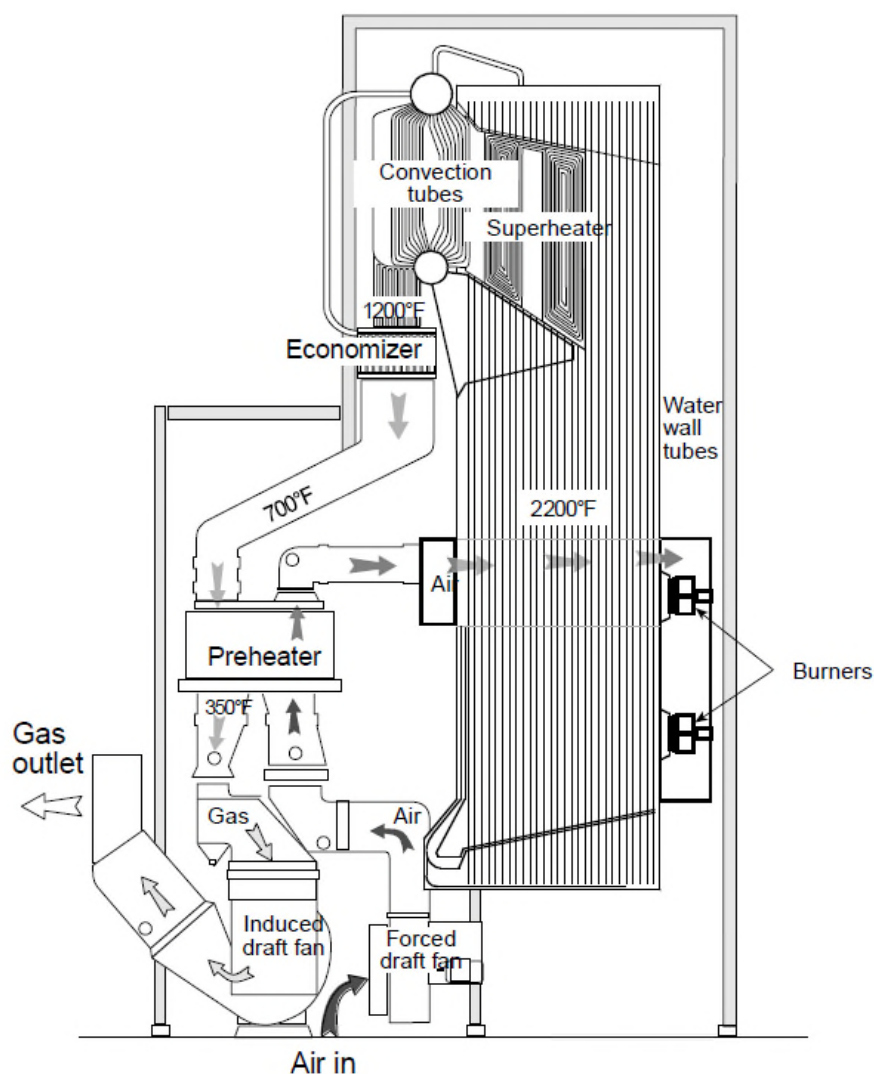
Figure 6-7. Oil-fired boiler.

The flow rate of the organic-contaminated stream must not overwhelm the gas-handling capability of the boiler-induced draft fans. The volume of combustion gas generated by the oxidation of the waste gas stream should be only a small fraction of the total combustion gas flow rate of the unit to avoid exceeding the allowable gas velocities and gas temperatures throughout the boiler.

The combustion of the organic vapor in the waste stream must not create high-temperature zones in the furnace areas of boilers with temperature-sensitive selective noncatalytic reduction systems (SNCR) for NO_x control. SNCR systems are discussed in a later chapter (Chapter 8).

The operating schedules of the boiler and the process generating the gas stream are one of the main constraints to using a boiler for organic vapor oxidation. The boiler must operate within a normal load range of approximately 40% to 100% of design load in order have the necessary temperatures for organic vapor combustion. If the boiler firing rate varies greatly, it may be necessary to operate auxiliary burners in the boiler to maintain the temperatures necessary for oxidization.

Another factor limiting the usefulness of process boilers is the long ducts often needed to transport the organic--containing gas stream from the process area to the boiler area. Ducts can be expensive, and some of the organic vapor may condense and accumulate in the ducts.

Flares Used for Thermal Oxidation

Flaring is used for the destruction of intermittent or emergency emissions of combustible gases from industrial sources that otherwise would create safety and health hazards at or near the plant. As such, they are more properly classified as safety devices instead of pollution-control devices. Flares are used mainly at oil refineries and chemical plants that handle large volumes of combustible gases, and can have organic compound destruction efficiencies exceeding 98%.[4]

Flares, which are simply burners designed to handle varying rates of fuel while burning smokelessly, may be elevated or at ground level. Flares are elevated to eliminate potential fire hazards at ground level. Ground-level flares must be completely enclosed to conceal the flame. Either type of flare must be capable of operating over a wide range of waste gas flow rates in order to handle all plant emergencies. The range of waste gas flows within which a flare can operate and still burn efficiently is referred to as the *turndown ratio*. Flares are expected to handle turndown ratios of up to 1,000:1, while most industrial boilers seldom handle more than a 10:1 turndown ratio.

Safety and Operational Problems

the flares are designed to eliminate waste gas stream disposal problems, they can present safety and operational problems of their own.

- **Thermal radiation.** Heat given off to the surrounding area may be unacceptable.
- **Light.** Luminescence from the flame may be a nuisance if the plant is located in an urban area.
- **Noise.** Jet venturis are used for mixing at the flare tip. They can cause excessive noise levels in nearby neighborhoods.
- **Smoke.** Incomplete combustion can result in toxic or obnoxious emissions.
- **Energy consumption.** Flares waste energy because of (1) the need to maintain a constant pilot flame and (2) the loss of the heating value of the chemicals burned.

Flares are usually used for waste gas streams having organic vapor concentrations above the lower explosive limit. The heat content of the organic compounds in the waste gas stream must usually be in the range of 100 Btu/SCF to 150 Btu/SCF to sustain efficient combustion; otherwise supplemental fuel must be added. This type of system is referred to as a *fired* or *endothermic* flare.

Elevated Flares

A typical elevated flare is composed of a system that first collects the waste gases and then passes the gases through a knockout drum to remove any liquids. Flame arrestors are placed between the knockout drum and the flare stack to prevent flashback of flames into the collection system. The elevated flare stack (Figure 6-8) is essentially a hollow pipe that may extend to heights exceeding 150 feet. The diameter of the flare stack determines the volume of waste gases that can be handled.
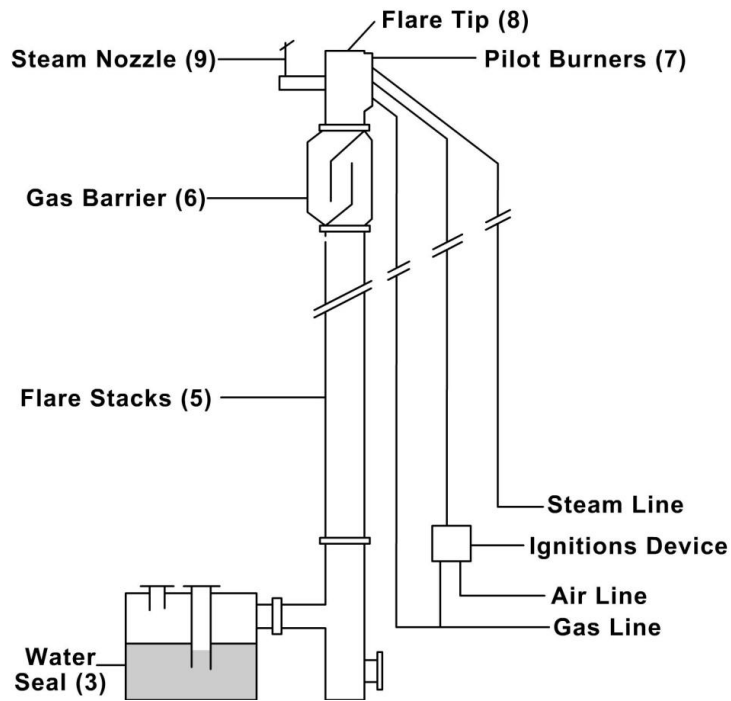
Figure 6-8. Steam-assisted Elevated Flare System.

The smokeless flare tip using steam injection shown in Figure 6-9 is at the top of the stack. It is comprised of the burners and a system to mix the air and fuel.
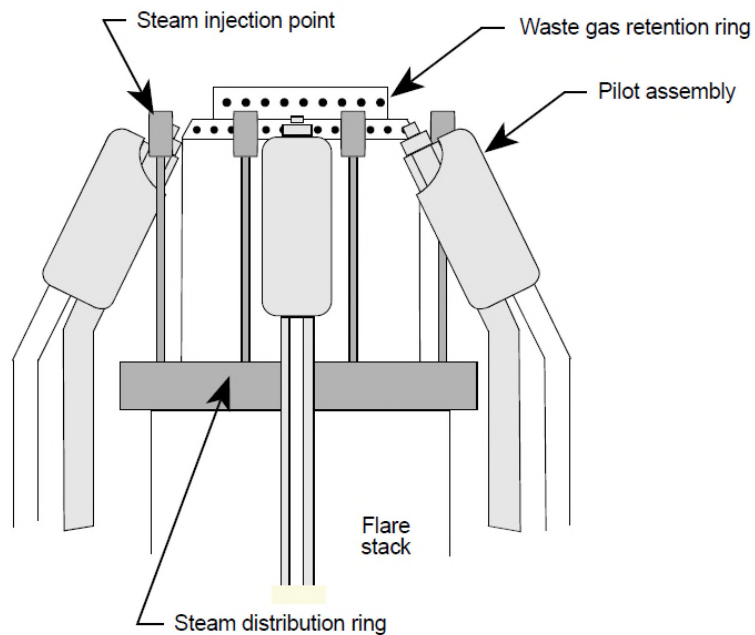
Figure 6-9. Smokeless flare tip of an elevated flare.

A number of flare tip designs provide good mixing characteristics over a wide range of waste gas flow rates while maintaining excellent flame-holding capabilities. Steam jets have proven to be one of the most effective ways to mix air and waste gases. In addition to increasing turbulence, the steam reacts with the gases to produce oxygenated intermediate compounds that burn readily at lower temperatures and reduce polymerization of organic compounds in the waste gas stream. For these reasons, steam injection is used for waste gases that are difficult to burn. Compounds with a hydrogen-to-carbon weight ratio less than 0.3, which includes most organics, are difficult to burn and usually require steam injection.[1] Steam requirements range between 0.05 and 0.3 kg of steam per kg of waste gas.[5] The steam is automatically injected at a rate proportional to the flow rate of the waste gases.

Shields are often used on elevated flares to protect the flame from atmospheric conditions. These shields also help reduce noise and visibility problems associated with flares.

Enclosed Ground Flares Used for Thermal Oxidation

A number of ground flares are available commercially. The term *ground flare* refers to locating the flare tip at or near ground level. Most ground flares consist of multiple burners enclosed within a refractory shell that encloses the flame to eliminate noise, luminescence, and safety hazards. The waste gas is introduced through a jet or venturi to provide turbulent mixing, and a stack is still required for the proper release of the combustion gases. Figure 6-10 shows a ground flare that has two chambers.
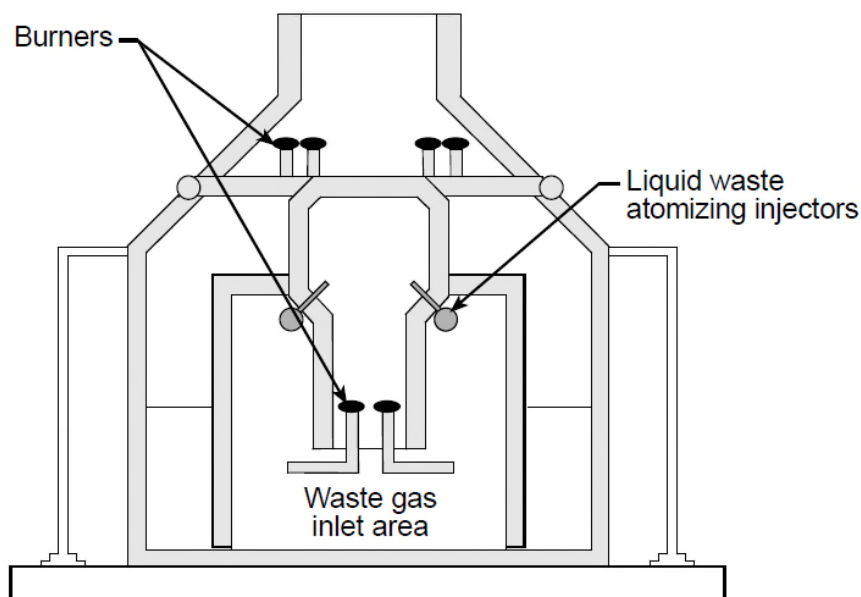
Figure 6-10. Enclosed ground flare.

The size of a ground flare is directly proportional to the volume of vapors it must handle. Ground flares can require more than twice the steam injection rates as elevated flares. Some plants have incorporated both designs: a ground flare used for normal or intermittent operation, and a large elevated flare used only to control emergency releases of large quantities of gases.

CATALYTIC OXIDATION SYSTEMS

Catalytic oxidation systems are designed with both regenerative and recuperative heat exchangers to minimize fuel consumption. The advantages and limitations of the recuperators and regenerators are identical to those of thermal oxidizers. Accordingly, this section emphasizes only the characteristics of catalytic oxidation.

A catalyst is a substance that accelerates a chemical reaction without undergoing a change itself. In catalytic oxidation, a waste gas is passed through a catalyst bed. The catalyst causes the oxidation reactions to proceed at a much lower temperature than is possible in gas-phase thermal oxidation. A catalytic oxidizer operating in the 600°F to 850°F (315°C to 450°C) range can achieve the same efficiency as a thermal oxidizer operating between 1,000°F and 2,000°F (540°C and 1,100°C). Because of the lower operating temperatures, it is often possible for catalytic oxidizers to operate without supplemental fuel except during start-up.

Advantages and Disadvantages

Catalytic oxidizers, which can achieve organic compound destruction efficiencies of more than 95%,[6] can be used with inlet organic concentrations ranging from approximately 100 ppm to more than 10,000 ppm. The upper concentration limit depends on the lowest LEL for the compounds present in the gas stream. The principle advantages of catalytic oxidizers over thermal oxidizers are the lower temperatures and the reduced supplemental fuel requirements. In addition, because of the low operating temperatures, refractory-lined combustion chambers are usually not needed, which reduces the weight of the unit.

The primary disadvantages of catalytic oxidizers are the cost of the catalyst and performance problems related to the physical and chemical deterioration of catalyst activity. Some chemicals react irreversibly with the catalyst, while other materials mask the catalyst surface. Both problems result in the need to regenerate or replace the catalyst at frequent intervals.

Catalytic units have start-up times similar to thermal units. The time needed to heat the catalyst bed is approximately equal to the time necessary to preheat the refractory of a thermal oxidizer. Accordingly, both types of oxidizers are subject to emission problems from processes that have frequent start-up/shut-down cycles.

Operation

A cutaway of a conventional catalytic oxidizer is shown in Figure 6-11. The inlet gas stream passes through a recuperative-type heat exchanger to recover a portion of the sensible heat from the hot exhaust gases. The preheated gas stream then enters a chamber where it is distributed across the inlet face of the catalyst bed. If the inlet gas temperature and concentration are too low to sustain the catalytic reactions, a preheat burner is used to raise the temperature to the range of 500°F to 900°F (260 °C to 480°C).[6] The preheat burner is also operated during start-up.
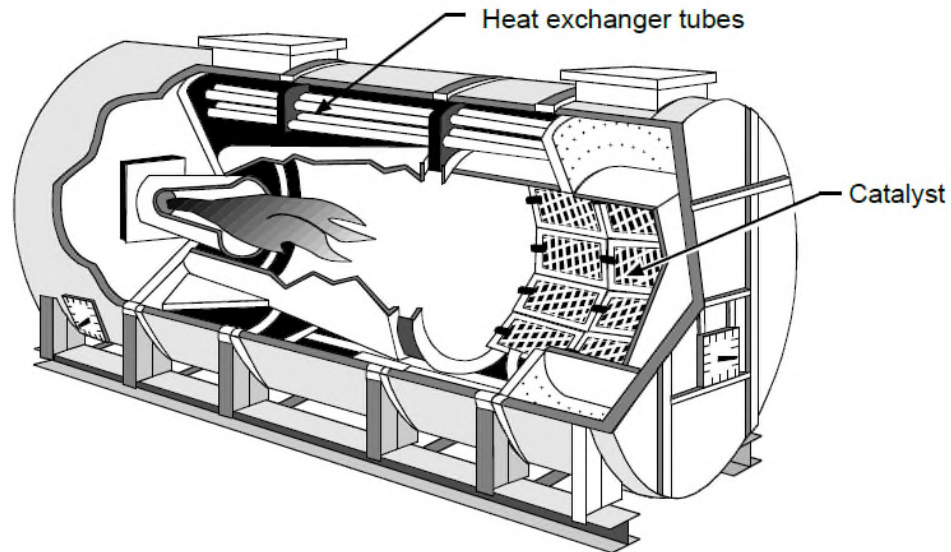
Figure 6-11. Cutaway of a catalytic oxidizer.

The exothermic combustion reactions that occur as the gas stream passes through the catalyst bed increase the gas temperature by 50°F to 300°F (10°C to 150°C), depending on organic concentration. The gas stream then passes through the hot-gas-side of the recuperative heat exchanger and is exhausted to the atmosphere.

The active catalyst is deposited onto the surface of a carrier, such as alumina, that is bonded to a support structure. The support material is arranged in a matrix shape to provide high geometric surface area, low pressure drop, and uniform flow of the waste gas through the catalyst bed. Structures that provide these characteristics are honeycomb matrices (Figure 6-12), grids, or mesh-pads.
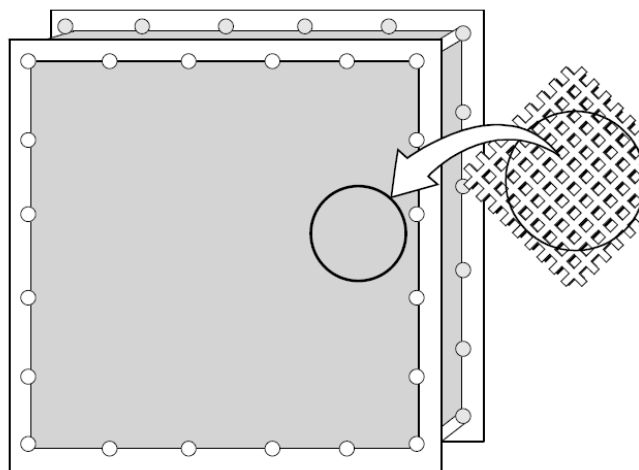
Figure 6-12. Catalyst bed honeycombs.

A close-up cross-section view of a honeycomb-type catalyst is shown in Figure 6-13. The walls of

the honeycomb are metallic. The catalyst (e.g., active precious metal site) is precipitated uniformly over the entire surface of the carrier to maximize the surface area available for the catalytic reactions.
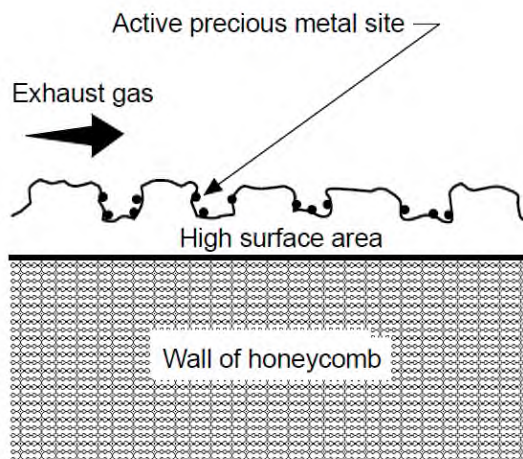
Figure 6-13. Close-up cross-section of a catalyst on a honeycomb.
(Reprinted courtesy of Engelhard Corporation, Ontario, CA.)

The geometry of a honeycomb catalyst bed is described in terms of the cell (gas-passage) density. Typical values range from 100 to 600 cells per square inch.[6] The catalyst surface area is proportional to the number of cells per square inch.

The operation of the catalytic oxidizer is often described in terms of the space velocity which has units of reciprocal time (time^{-1}). The space velocity is calculated by dividing the gas flow rate entering the bed (actual volumetric flow rate) by the volume of the bed. Normal values are between 20,000 hour^{-1} and 100,000 hour^{-1}. High space velocities correspond to high gas volumetric flow rates and/or low catalyst quantities. At a given operating temperature, decreasing space velocity results in increased residence time and provides increased destruction (oxidation) efficiency.[7] The catalyst bed is the main contributor to the static pressure drop across the oxidizer. Normal static pressure drops are between 2 and 8 in. W.C. (0.5 and 2.0 kPa).

Catalytic oxidizers usually cannot be used on waste gas streams containing high concentrations of particulate matter. The particulate matter deposits on the surface of the catalyst and blocks the access of the organic compounds. Oil droplets can also block access to the catalyst bed unless they are vaporized in the preheat section. By periodically cleaning and washing the catalyst, much of the activity can be restored. Blocking access to the catalyst surface in this manner is referred to as *fouling*.

Masking and Fouling

Masking and fouling problems can sometimes be minimized by using a fluidized bed arrangement. In this type of system, the catalyst is prepared as small spherical particles supported on a grid. The catalyst particles are fluidized by the upward flow of gas. Particle-to-particle abrasion continually cleans the catalyst surfaces to minimize the effect of masking. One disadvantage of this type of system is the need to collect and dispose of the fine particulate matter generated by physical attrition in the fluidized bed.

Common Types of Catalyst Material

The active catalyst material typically consists of:

Noble metals

- Platinum (Pt)
- Palladium (Pd)
- Rhodium (Rh)

Metal oxides

- Chromium oxide
- Manganese oxide
- Cobalt oxide

The metal oxides are used when halogenated compounds are present, because the chlorine and fluorine will deactivate the noble metal catalysts

Catalyst Poisoning

Certain metals react irreversibly with or alloy to the catalyst, thereby making it inactive. Deactivation in this manner is called *catalyst poisoning*. Catalyst poisons can be divided into two categories:

Fast-Acting Poisons

- Phosphorus (P)
- Bismuth (Bi)
- Arsenic (As)
- Antimony (Sb)
- Mercury (Hg)

Slow-Acting Poisons

- Iron (Fe)
- Lead (Pb)
- Tin (Sn)
- Silicon (Si)

Catalysts are more tolerant of the slow-acting poisons, particularly at temperatures below 1,000°F (540°C). At sufficiently high temperatures (i.e., 1,000°F and above), even copper and iron are capable of alloying to noble metals such as platinum, thereby reducing their activity.

Sulfur and halogen compounds act as masking agents and thereby inhibit the oxidation reactions. Their interaction with the catalyst is reversible, and once the halogen or sulfur compound is removed, catalyst activity is restored.

Catalyst Service Life

All catalysts deteriorate with normal use. Gradual loss of the catalyst material can occur from

erosion, attrition, and vaporization. High temperatures can also accelerate catalyst deactivation through the process referred to as *thermal aging*. This is caused by the sintering or densification of the catalyst support material, which results in the loss of active catalyst surface area.

The average service life of a catalyst is two to five years, with low operating temperatures generally resulting in a longer service life.

6.3 OPERATING PRINCIPLES

OPERATING PRINCIPLES

The operating principles for high-temperature, gas-phase oxidation systems and catalytic systems are discussed in this section. This material provides a basis for the later information presented concerning the capability and sizing of new oxidizer systems.

HIGH-TEMPERATURE, GAS-PHASE OXIDATION SYSTEMS

Combustion Products and Gas Volumes

In all high-temperature combustion processes, a complex set of several hundred to several thousand chemical reactions occur simultaneously. The result of these reactions is represented by the following generalized stoichiometric reaction. The main reaction products are carbon dioxide and water vapor.

Reaction 6-1
$$C_xH_yS_zO_w + \left(x + \frac{y}{4} + z - \frac{w}{2}\right)O_2 \rightarrow xCO_2 + \left(\frac{y}{2}\right)H_2O + zSO_2$$
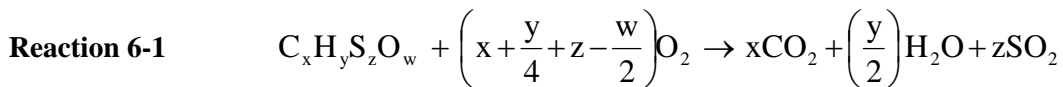
Usually, sulfur dioxide (SO_2) is the dominant reaction product formed from sulfur present in the fuel or waste stream. However, 0.5% to 2% of the total sulfur can also form sulfur trioxide (SO_3), which ultimately forms vapor phase sulfuric acid (H_2SO_4) once the gas stream cools below approximately 600 °F (315 °C). To estimate the oxygen requirement, it is assumed that all of the sulfur forms sulfur dioxide. The reactions involving the formation of nitrogen oxides (NO_x) are ignored when making material balance calculations involving the total volume of reaction products and the amount of oxygen needed. If chlorine or fluorine atoms are present in the organic compound being burned, hydrochloric acid (HCl) and hydrofluoric acid (HF) will usually be formed. However, if the compounds being burned have only a limited number of hydrogen atoms per molecule, chlorine gas (Cl_2) can also form in the combustion chamber.[1]

Nitrogen atoms in the organic compounds (e.g., cyanides or amines) being oxidized can form nitrogen oxides (NO and NO_2), or they can be chemically reduced to molecular nitrogen (N_2). The quantity of nitrogen oxides formed from the organic wastes is usually small compared to the nitrogen oxides formed in the burner flame of the thermal oxidizer. Nitrogen oxides are also generally neglected when making material balance calculations.

The concentrations of the pollutants generated by thermal oxidation can be calculated by using the stoichiometry of the combustion reactions and information concerning the quantity of supplemental fuel being burned in the unit.

The combustion reactions go to completion if the following conditions exist:

- The gas temperature is sufficiently high.
- The combustible materials and the air are well-mixed (turbulence).
- There is sufficient oxygen (air).
- The residence time within the combustion chamber is relatively long.

Temperature

The necessary gas temperature is based primarily on the auto-ignition temperature of the most difficult-to-oxidize organic compound contained in the waste stream.[1] The auto-ignition temperature of various fuels and compounds can be found in combustion handbooks such as the *North American Combustion Handbook*.[8] Table 6-1 provides a list of the auto-ignition temperatures of some common organic compounds present in waste gas streams.

Table 6-1. Auto-ignition temperatures.	
Compound	**Auto-Ignition Temperature (°F)**
Acetone	870
Acetonitrile	970
Isopropyl Alcohol (IPA)	780
Methanol	878
Methyl Ethyl Ketone (MEK)	759
Toluene	896
Xylene	867

Most oxidizers operate at temperatures 200°F to 300°F (95°C to 150°C) above the auto-ignition temperature of the organic compound being burned. Thermal destruction of most organic compounds occurs between 1,100°F and 1,200°F (590°C and 650°C). Therefore, most thermal oxidizers operate at 1,300°F to 1,600°F (700°C to 870°C).

Turbulence

Proper mixing is important in combustion processes for two reasons. First, mixing the burner fuel with air ensures complete combustion of the fuel. Second, thoroughly mixing the organic-containing waste gases with the burner combustion gases ensures that the entire waste gas stream reaches the necessary combustion temperatures.

A number of methods are available to improve the mixing of the air and combustion streams, including the use of refractory baffles, swirl-fired burners, or baffle plates. It is difficult to obtain complete mixing. Unless properly designed, many of these mixing devices may create "dead spots" and reduce operating temperatures. Inserting obstructions to increase turbulence may not be sufficient.

Combustion Air Requirements

The combustion air requirements for the supplemental fuel burner used in thermal oxidizers must be taken into account when sizing the burner system and the combustion chamber. To achieve

complete combustion of the fuel (e.g., natural gas, propane, No. 2 oil), a sufficient supply of oxygen must be present in the burner flame to convert all of the carbon to CO_2. This quantity of oxygen is referred to as the *stoichiometric* (or theoretical) *amount*. The stoichiometric amount of oxygen is determined from a balanced chemical equation summarizing the oxidation reactions. For example, 1 mole of methane (the major component of natural gas) requires 2 moles of oxygen for complete combustion (Reaction 6-2).

Reaction 6-2 $\qquad\qquad\qquad CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

If a sub-stoichiometric amount of oxygen is available (not enough oxygen to completely oxidize the fuel), the mixture is referred to as *fuel-rich*. Incomplete combustion occurs under these conditions. This reduces the peak flame temperature and results in the formation of CO and other partially-oxidized compounds.

If more than the stoichiometric amount of oxygen is supplied, the mixture is referred to as *lean*. The unreacted oxygen and nitrogen entering with the combustion air carry away a portion of the heat released by the combustion reactions, and the peak flame temperature is reduced. The high oxygen levels in the flame can also contribute to generating nitrogen oxides.

In order to maximize the flame temperature and minimize pollutant generation, the burner should be operated with a slight excess of oxygen, i.e., slightly lean. Burners firing natural gas, propane, and No. 2 oil usually operate with excess air rates in the range of 10% to 30%. This means that the combustion air supplied to the burner has 1.1 to 1.3 times the amount of the necessary oxygen based on the balanced stoichiometric reactions of the fuel. In Problem 6-1 below, the calculated (stoichiometric) oxygen requirement is 1.56 pound moles per minute. Because the burner was operating at a 25% excess air rate, the total amount of oxygen supplied to the burner was 1.25 times this amount, or 1.95 pound moles per minute. This additional oxygen is needed simply to ensure complete combustion and to account for the non-ideal factors, such as incomplete mixing, that affect fuel combustion.

At high excess air rates, the total flow rate of the combustion products is high. This is due primarily to the large amount of nitrogen that enters with the oxygen, and, in part, to the excess oxygen that is part of the flue gas stream. Nitrogen comprises approximately 79% of ambient air. Therefore, when the oxygen requirement increases, a large quantity of nitrogen enters with the combustion air and is included in the exhaust gas stream. In Problem 6-1, the combustion air supply to the burner included 7.34 pound moles per minute of nitrogen, all of which exits with the combustion products. The residence time of the combustion products in the combustion chamber is reduced because of the additional quantity of nitrogen present. Therefore, the fuel-firing rate must be increased slightly to account for the heat lost with the additional nitrogen.

The reduction in combustion chamber residence time associated with high excess air levels can be minimized by using oxygen present in the waste gas stream. Most waste streams have oxygen concentrations between 16% and 20.9%, so that by using this source of oxygen, the combustion air rate to the burner can be reduced, and the residence time can be increased.

Residence Time

The residence time needed to complete the oxidation reactions in the combustion chamber depends both on the rate of the reactions at the prevailing temperature and on the mixing of the waste stream and the hot combustion gases from the supplemental burner or burners. Residence times are usually between 0.3 and 2 seconds.

The residence time of gases in the combustion chamber may be calculated as the ratio of the volume of the refractory-lined combustion chamber and the volumetric flow rate of combustion products through the chamber.

(Eq. 6-1) $$t = \frac{V}{Q}$$

Where: t = residence time (sec)
                V = chamber volume (ft^3)
                Q = actual gas volumetric flow rate at combustion conditions (ft^3/sec)

Q is the total flow of hot gases in the combustion chamber. Adjustments to the flow rate must include any outside air added for combustion. Problem 6-1 illustrates how to determine residence time from the volumetric flow rate of gases.

PROBLEM 6-1

A thermal oxidizer controls emissions from a paint-baking oven. The cylindrical unit has a diameter of 5 feet and a length of 12 feet, with all combustion air supplied by an auxiliary source. The exhaust from the oven is 8,000 SCFM. The oxidizer uses 300 SCFM of natural gas and operates at a temperature of 1,400°F. What is the residence time in the combustion chamber? Assume that the fuel is 100% methane and that the burner is operated at 125% of the stoichiometric requirement.

SOLUTION

Step 1. Write the combustion reaction.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
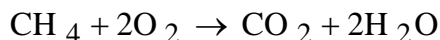
The stoichiometric oxygen requirement is two moles of oxygen for every mole of methane burned to completion, this is consistent with the coefficients noted in Reaction 6-1.

Step 2. Calculate the total amount of O_2 at stoichiometric conditions.

The molar flow rate of the natural gas fuel can be calculated as follows:

$$300 \text{ SCFM} \left(\frac{\text{lb mol CH}_4}{385.4 \text{ ft}^3} \right) = 0.778 \ \frac{\text{lb mol CH}_4}{\text{min}}$$

Stoichiometric $O_2 = 2 \times$ (lb mole CH_4)

$$\frac{2 \, \text{lb mol O}_2}{\text{lb mol CH}_4} \left(0.778 \, \frac{\text{lb mol CH}_4}{\text{min}} \right) = 1.56 \, \frac{\text{lb mol O}_2}{\text{min}}$$

Step 3. Calculate air sent to burner (125% of stoichiometric requirement).

Total O_2 requirement = $1.25 \times$ (stoichiometric requirement)

$$= 1.25 \left(1.56 \, \frac{\text{lb mol O}_2}{\text{min}} \right) = 1.95 \, \frac{\text{lb mol O}_2}{\text{min}}$$

$$\text{Total N}_2 \ = \frac{0.79 \, \text{lb mol N}_2}{0.21 \, \text{lb mol O}_2} \left(1.95 \, \frac{\text{lb mol O}_2}{\text{min}} \right)$$

= 7.34 lb mol N_2/min

Step 4. Calculate the total flue gas flow rate.

Total flue gas flow rate = Exhaust gas heated (a) + Products of combustion (b) + Nitrogen and excess oxygen (c)

  a. Exhaust gas heated = 8,000 SCFM
  b. Products of combustion = CO_2 + H_2O

$$CO_2 = 1 \frac{\text{lb mol CO}_2}{\text{lb mol CH}_4} \left(0.778 \, \frac{\text{lb mol CH}_4}{\text{min}} \right) = 0.778 \, \text{lb mol CO}_2/\text{min}$$

$$H_2O = 2 \frac{\text{lb mol H}_2\text{O}}{\text{lb mol CH}_4} \left(0.778 \, \frac{\text{lb mol CH}_4}{\text{min}} \right) = 1.56 \, \text{lb mol H}_2\text{O}/\text{min}$$

$$CO_2 + H_2O = 2.34 \, \text{lb mol/min}$$

$$2.34 \frac{\text{lb mol}}{\text{min}} \left(\frac{385.4 \, \text{SCF}}{\text{lb mol}} \right) = 900 \, \text{SCFM}$$

  c. Nitrogen and excess oxygen = total N_2 + O_2 remaining

Amount of oxygen consumed = stoichiometric required

  = 1.56 lb mol/min

Amount of oxygen remaining = total - consumed

  = 1.95 lb mol/min - 1.56 lb mol/min
  = 0.39 lb mol/min

Amount of Nitrogen and excess oxygen

$$= 7.34 \text{ lb mol N}_2/\text{min} + 0.39 \text{ lb mol O}_2/\text{min} = 7.73 \text{ lb mol/min}$$

$$7.73 \frac{\text{lb mol}}{\text{min}} \left(\frac{385.4 \text{ SCF}}{\text{lb mol}} \right) = 2,979 \text{ SCFM}$$

Total flue gas flow rate = 8,000 SCFM + 900 SCFM + 2,979 SCFM

$$= 11,879 \text{ SCFM}$$

Step 5. Convert the flue gas flow rate to actual conditions.

Using the Ideal Gas Law, for the case of constant pressure and moles:

$$PV = nRT \rightarrow \frac{P_1 V_1}{T_1} = nR = \frac{P_2 V_2}{T_2} \rightarrow V_{actual} = \frac{V_{std} T_{actual}}{T_{std}}$$

$$\text{Total ACFM} = 11,887 \text{ SCFM} \left(\frac{1,400 + 460 \,^\circ R}{68 + 460 \,^\circ R} \right) = 41,864 \text{ ACFM}$$

Step 6. Calculate the volume of the combustion chamber.

$$\text{Combustion Chamber Vol.} = \pi(r)^2 L = 3.14 \, (2.5 \text{ ft})^2 \, 12 \text{ ft} = 235.6 \text{ ft}^3$$

Step 7. Calculate the residence time.

$$\text{Residence Time} = \frac{\text{Chamber Volume}}{\text{Volumetric flow rate}} = \frac{235.6 \text{ft}^3}{41,864 \text{ ACF/min}} = 0.00563 \text{ minutes}$$

$$= 0.00563 \text{ min} \left(\frac{60 \sec}{\min} \right) = 0.338 \text{ seconds}$$

The residence time of the combustion gas in the thermal oxidizer described in Problem 6-1 is 0.338 seconds.

PROBLEM 6-2

What would be the residence time for the thermal oxidizer described in Problem 6-1 if all of the combustion air is supplied by the waste gas stream? Assume that the waste gas stream has an oxygen concentration of 16%, a carbon dioxide concentration of 1%, a moisture concentration of 1%, and a nitrogen concentration of 82% (volume).

SOLUTION

Step 1. Determine if there is sufficient oxygen in the waste gas stream.

$$O_2 = 8,000\,SCFM \left(\frac{lb\,mol\,gas}{385.4\,SCF} \right) \left(\frac{0.16\,lb\,mol\,O_2}{lb\,mol\,gas} \right)$$

$$= 3.32 \text{ lb mol } O_2/min$$

This is more than the 1.56 lb mol O_2/min calculated in Problem 6-1. Therefore, there is sufficient O_2. (However, there may be flame-stability limits that are more restrictive than the simple stoichiometric requirements used in this example.)

Step 2. Calculate flue gas flow rate.

Flue gas = (Waste gas stream - reacted oxygen) + (Products of combustion)

$$Waste\,gas\,stream = 8,000\,SCFM \left(\frac{lb\,mol}{385.4\,SCF} \right) = 20.76\,lb\,mol/min$$

Waste gas stream - reacted O_2 = (20.76 - 1.56) = 19.20 lb mol/min

Products of combustion = ($CO_2 + H_2O$) = 2.34 lb mol/min (from Problem 6-1, step 4)

Flue gas = (19.20 lb mol/min + 2.34 lb mol/min) = 21.54 lb mol/min

Step 3. Calculate total volumetric flow rate (ACFM).

$$Vol.\,Flow\ rate = 21.54\,lb\,mol/min \left(\frac{385.4\,SCF}{lb\,mol} \right) \left(\frac{1,400 + 460°\,R}{68 + 460°\,R} \right)$$

$$Vol.\ Flow\,rate = 29,256 \text{ ACFM}$$

Step 4. Calculate residence time.

$$Residence\,time = \frac{Chamber\ Volume}{Volumetric\,flow\,rate}$$

$$= \frac{235.6\,ft^3}{29,256\,ft^3/min} = 0.00805 \text{ minutes}$$

$$= 0.00805\,min \left(\frac{60\,sec}{min} \right) = 0.483 \text{ sec}$$

This is substantially longer than the 0.338-second residence time calculated in Problem 6-1. It illustrates the change that results when the waste gas stream is used as the source of oxygen instead of having a separate combustion air supply for the burner.

Despite the apparent advantage, thermal oxidizers often use a separate air supply rather than obtaining all or part of the needed oxygen from the waste gas stream. One of the main problems with using the waste gas stream is that nonvolatile organic compounds or particulate matter in the waste gas stream may potentially foul the burner. There can also be variations in the waste gas stream composition that affect the ability to maintain a stable flame, especially when the oxygen concentration drops below approximately 16%.

Inlet Organic Vapor Concentration

Thermal oxidizers and boilers usually operate at organic vapor concentrations below 25% of the LEL. Since combustion does not occur readily in this range, the waste gas stream can be transported safely to the combustion device, and the risk of flashback from the oxidizer to the process equipment is minimized. The VOC inlet concentration is usually determined by an LEL detector, which determines the approximate total concentration of oxidizable organic compounds. However, explosive limits are not absolute values that apply at all temperatures, pressures, and other conditions. At high temperatures, there is sufficient energy to overcome the activation energy for the organic molecules to begin oxidation, and the exothermic energy released by the oxidation reaction is not quickly lost to the surrounding molecules.

CATALYTIC OXIDATION SYSTEMS

The general factors that control the rate of catalytic oxidation are illustrated in Figure 6-14. At low temperatures, the rate of oxidation is limited by the kinetics of the oxidation reactions, while at high temperatures the rate is limited by the rate of mass transfer. The temperature of the catalytic oxidizer is set at a level at which the controlling factor is the rate of mass transfer of oxygen and organic compounds to and from the catalyst surface.
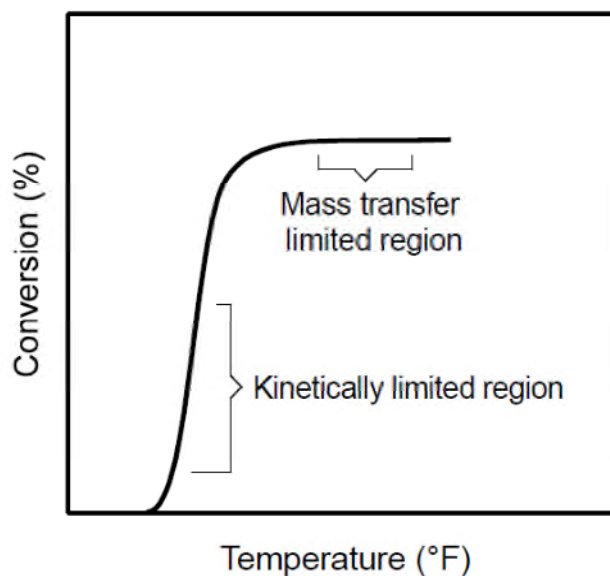
Figure 6-14. Importance of temperature in catalytic systems.
(Reprinted courtesy of Engelhard Corporation, Ontario, CA.)

The temperature necessary for catalytic oxidation depends on the compounds present in the waste gas stream and the characteristics of the catalyst bed. An example of destruction efficiency curves for typical compounds is shown in Figure 6-15.
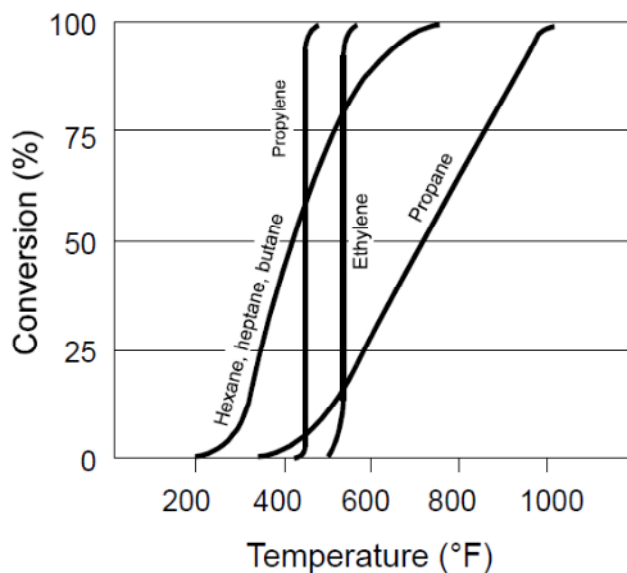
Figure 6-15. Destruction efficiency curves for selected organic compounds.
(Reprinted courtesy of Engelhard Corporation, Ontario, CA.)

The minimum operating temperature is the left side of the destruction efficiency temperature curve where the controlling factor is the mass transfer rate, i.e., about 600°F for ethylene but about 1000°F for propane. It is not necessary to operate the supplemental fuel burner when the waste gas contains moderate to high concentrations of organics. The heat released during catalytic oxidation and recovered in the recuperative heat exchanger is sufficient to maintain the required oxidation temperature. Accordingly, catalytic oxidizers are generally more energy-efficient than high-temperature flame oxidizers.

6.4 CAPABILITY AND SIZING

DESTRUCTION EFFICIENCY

There are two primary means for estimating the organic compound destruction efficiency of high-temperature, gas-phase oxidation systems and catalytic oxidation systems: (1) empirical evaluation based on previous applications and (2) pilot plant tests.

Most units are selected based on empirical data available to the oxidizer manufacturer and/or the facility owner. The destruction efficiency data determined by testing procedures, such as the U.S.

EPA reference methods, provide useful databases for evaluating the capability of new units. Destruction efficiency data from other units must be evaluated on a compound-specific basis to predict the differences in the oxidation rates.

Pilot plant tests can be conducted when there is insufficient data on a specific compound or group of compounds in the waste gas stream. These tests involve the treatment of a 100 to 2,000 ACFM slipstream from the operating process unit for approximately one to four weeks. One or more reference method tests are usually conducted as part of these test programs. One of the advantages of the pilot plant tests is that data directly relevant to the process equipment is obtained prior to the design of the full-scale system. The primary disadvantage of the pilot tests is the cost. However, an improperly conducted pilot test can also give erroneous results. For example, the condensation of nonvolatile organic vapor in the slipstream duct upstream of the pilot oxidizer can give lower-than-actual emission rates. Also, short-term tests may not fully reveal long-term problems that could affect catalyst beds.

Fuel Requirements

The supplemental fuel requirement is one of the main parameters of concern in oxidation systems. If insufficient supplemental fuel is supplied or if combustion is not complete, the oxidizer temperature will not be sufficiently high to destroy all the organic contaminants. The supplemental fuel requirement can be estimated based on a simple heat balance around the unit coupled with information on the waste gas stream. Figure 6-16 shows a simplified oxidation system that serves as the basis for the heat balance.

From the 1st Law of Thermodynamics:

(Eq. 6-2)   Heat in = Heat out + Heat loss
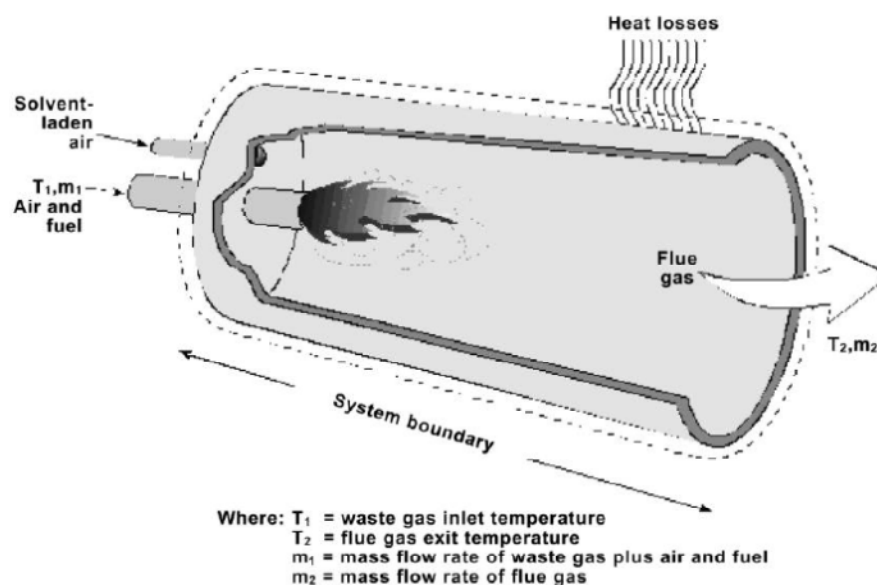
Figure 6-16. Heat balance around an oxidizer.

Available Heat and Enthalpy

Energy is supplied by the combustion of the waste organics and the supplemental fuel. Some of this energy is used to heat the products of combustion (CO_2, H_2O, excess O_2, combustion air N_2) to the outlet gas temperature. The remainder of the energy generated by the burner is used to heat the waste gas stream to the outlet gas temperature. This quantity of heat that remains is called the available heat. The available heat is highest at low oxidizer temperatures (because less of the total heat is needed to heat the combustion products) and decreases as the oxidizer temperature increases. This is illustrated in Figure 6-16b.
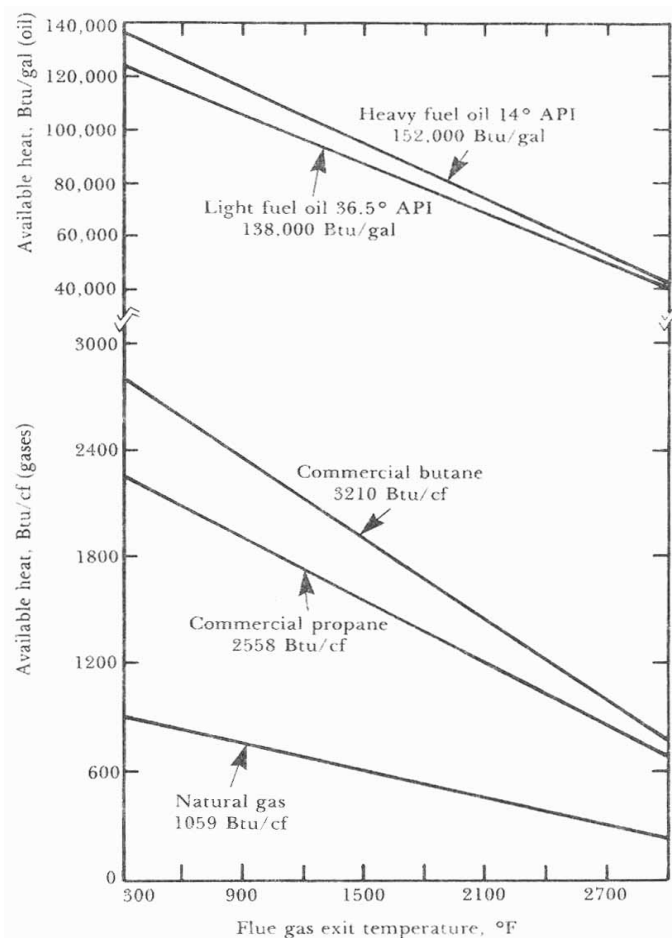
Figure 6-16b. Available heat of common fuels.

The available heat approaches the gross heating value (also known as the higher heating value) of the fuel at 60°F (16°C) if the products of combustion are also at 60°F.

When the available heat value is used to evaluate oxidizers, it is not necessary to take separate account of the heat lost with the combustion products, because this is automatically included in the available heat value for the temperature being evaluated. However, there are cases where it is more convenient to use the gross heating value and then take into account the heat loss associated with the combustion products and the waste gases separately.

In order to calculate the heat that exits the oxidizer with the waste gas stream, the enthalpies of the inlet and outlet waste gas streams must be determined. *Enthalpy* is a thermodynamic term whose numerical value can be read from tables such as those below. Table 6-2a presents the enthalpies of combustion gases in units of Btu/SCF, while Table 6-2b presents the same data in units of Btu/lb$_m$. Enthalpy is a relative term that is compared to some reference temperature. 60°F is chosen as the reference temperature in these tables, and the enthalpy of all components is arbitrarily set to be zero at that temperature. It is important to note, particularly for H_2O, that the tabulated values apply only to gases. Thus, if for some reason liquid H_2O is injected into the oxidizer, it would also be necessary to include the latent heat of vaporization of water in the calculation. The latent heat of vaporization represents the heat required to evaporate a liquid at its boiling temperature.

Table 6-2a. Enthalpies of combustion gases, Btu/SCF.					
Gas Temp. (°F)	**O$_2$**	**N$_2$**	**CO$_2$**	**H$_2$O**	**Air**
60	0.00	0.00	0.00	0.00	0.00
100	0.74	0.74	0.39	0.36	0.74
200	2.61	2.58	0.94	0.85	2.58
300	4.50	4.42	3.39	2.98	4.42
400	6.43	6.27	5.98	5.14	6.29
500	8.40	8.14	8.69	7.33	8.17
600	10.40	10.02	14.44	11.81	10.07
700	12.43	11.93	17.45	14.11	12.00
800	14.49	13.85	20.54	16.45	13.95
900	16.59	15.80	23.70	18.84	15.92
1000	18.71	17.77	26.92	21.27	17.92
1100	20.85	19.78	30.21	23.74	19.94
1200	23.02	21.79	33.55	26.26	21.98
1300	25.20	23.84	36.93	28.82	24.05
1400	27.40	25.90	40.36	31.42	26.13
1500	29.62	27.98	43.85	34.08	28.24
2000	40.90	38.65	61.71	47.91	38.99
2500	52.43	49.67	80.15	62.60	50.07

Table 6-2b. Enthalpies of combustion gases, Btu/lbm.					
Gas Temp. (°F)	**O$_2$**	**N$_2$**	**CO$_2$**	**H$_2$O**	**Air**
60	0.0	0.0	0.0	0.0	0.0
100	8.8	6.4	5.8	17.8	9.6
200	30.9	34.8	29.3	62.7	33.6
300	53.4	59.8	51.3	108.2	57.8
400	76.2	84.9	74.9	154.3	82.1
500	99.5	110.1	99.1	201.0	106.7
600	123.2	135.6	124.5	248.7	131.6
700	147.2	161.4	150.2	297.1	156.7
800	171.7	187.4	176.8	346.4	182.2
900	196.5	213.8	204.1	396.7	211.4
1000	221.6	240.5	231.9	447.7	234.1

Table 6-2b. Enthalpies of combustion gases, Btu/lbm (cont'd).					
Gas Temp. (°F)	O_2	N_2	CO_2	H_2O	Air
1100	247.0	267.5	260.2	499.7	260.5
1200	272.7	294.9	289.0	552.9	287.2
1300	298.5	326.1	318.0	606.8	314.2
1400	324.6	350.5	347.6	661.3	341.5
1500	350.8	378.7	377.6	717.6	369.0
2000	484.5	523.0	531.4	1003.1	509.5
2500	621.0	672.3	690.2	1318.1	654.3

Source of Tables 6-2a and 6-2b: U.S. EPA, Air Pollution Engineering Manual, 2nd ed., 1973.

In addition to using tables such as those above, the enthalpy of the combustion gas component at the outlet temperature, T, can also be computed from Equation 6-3.

(Eq. 6-3) $\qquad H = C_p(T - T_o)$

Where: $\qquad$ H $\quad$ = $\quad$ enthalpy (Btu/lb$_m$)
$\qquad\qquad\qquad$ C_p $\quad$ = $\quad$ specific heat at temperature T (Btu/lb$_m$ °F)
$\qquad\qquad\qquad$ T $\quad$ = $\quad$ temperature of the component (°F)
$\qquad\qquad\qquad$ T_o $\quad$ = $\quad$ reference temperature (°F)

The change in enthalpy of a component between the oxidizer's entering and exit temperatures is obtained by subtracting the enthalpy of the component entering the oxidizer from that of the component exiting, which is also the amount of heat that must be supplied by the fuel. Using Equation 6-3, the enthalpy entering at T_1 is subtracted from the enthalpy exiting at T_2, giving:

(Eq. 6-4) $\qquad \Delta H = C_{p2}(T_2 - T_o) - C_{p1}(T_1 - T_o)$

Where: $\qquad$ ΔH $\quad$ = $\quad$ change in enthalpy (Btu/lb$_m$)
$\qquad\qquad\qquad$ C_{p2} $\quad$ = $\quad$ average specific heat between T_o and T_2
$\qquad\qquad\qquad$ C_{p1} $\quad$ = $\quad$ average specific heat between T_o and T_1

To simplify this calculation, an average specific heat value, C_p between T_1 and T_2, can be used. This reduces Equation 6-4 to:

(Eq. 6-5) $\qquad\qquad\qquad \Delta H = C_p(T_2 - T_1)$

The specific heat varies with the temperature and composition of the gas stream. Therefore, Equation 6-5 is used to obtain an approximate value. For most incineration systems, the waste gases are considered to be essentially air, for which an average specific heat value, C_p, is 0.26 Btu/lb$_m$ °F (1086 J/kg °C) for typical temperature ranges normally encountered in high-temperature, gas-phase oxidation systems.

Equation 6-5 depicts the amount of heat required to increase unit mass of gas from T_1 to T_2. The

total heat requirement is then determined by multiplying both sides of Equation 6-5 by the mass flow rate (m) of the waste gas stream. The total heat rate required is given by:

(Eq. 6-6) $$q = m\Delta H = mC_p\left(T_2 - T_1\right)$$

Where: q   =   total heat rate (Btu/hr)
                 m   =   mass flow rate of waste gases (lb_m/hr)

Equation 6-6 can be used to compute the heat rate required to raise the gas temperature from T_1 to T_2. Problem 6-3 illustrates the use of Equation 6-6 and Table 6-2.

These equations are simple heat balances, equating heat in to heat out. They do not account for any heat losses in the system. Heat losses from refractory or ducting are usually accounted for by assuming that a fixed percent of the total theoretical heat input with the fuel is lost. For example, if an oxidizer is required to supply heat at the rate of 1 x 10^6 Btu/hr, and there is a 10% heat loss from the combustion chamber, the total heat rate would have to be 1.1 x 10^6 Btu/hr to account for the losses. Heat is also lost to the system from the latent heat associated with vaporization of water or organic liquid droplets entrained in the waste gas stream.

Problem 6-3 illustrates a method that can be used to roughly estimate the fuel requirement for an oxidizer.

PROBLEM 6-3

The exhaust from a meat smokehouse contains obnoxious odors and fumes. The company plans to oxidize the 5,000 ACFM exhaust stream. What quantity of natural gas is required to raise the waste gas stream from a temperature of 90°F to the required temperature of 1,200°F? The gross heating value of natural gas is 1,059 Btu/SCF. The exhaust gas can be considered to be air. Assume no heat losses.

SOLUTION

Step 1. All calculations are based on a 1-hour time period. First, the volume of waste gas must be corrected to standard conditions (68 °F and 1 atm).

$$G = \frac{5,000\ \text{ACF}}{\text{min}}\left(\frac{68 + 460\,^\circ R}{90 + 460\,^\circ R}\right)\left(\frac{60\ \text{min}}{\text{hr}}\right) = 287,993\ \text{ft}^3/\text{hr}$$

Step 2. The volumetric flow rate is then converted to a mass flow rate by multiplying by the density.

$$m = \left(\frac{287,993\,\text{SCF}}{\text{hr}}\right)\left(\frac{\text{lb mol}}{385.4\,\text{SCF}}\right)\left(\frac{29\,lb_m}{\text{lb mol}}\right) = 21,670\,lb_m/\text{hr}$$

Recall that the average molecular weight of air is 29 lb_m/lb mol.

Step 3. The heat rate can be determined by two methods.

a. By using the enthalpy values in Table 6-2b:

H for air at 1,200°F = 287.2 Btu/lb$_m$

H for air at 90°F is obtained by interpolating:
= 9.6 – [9.6*(10/40)] = 7.2 Btu/lb$_m$

$$q = m\Delta H = m\left(H_{air@1,200} - H_{air@90}\right)$$

= (21,670 lb$_m$/hr)(287.2 – 7.2 Btu/lb$_m$)
= 6,067,600 Btu/hr or 6.07 x 10^6 Btu/hr

b. By using Equation 6-6:

For air Cp = 0.26 Btu/lb$_m$ °F:

$$q = mC_p\Delta T$$

= (21,670 lb$_m$/hr)(0.26 Btu/lb$_m$)(1,200 – 90°F)
= 6,253,962 Btu/hr or 6.25 x 10^6 Btu/hr

This value (b) is less accurate because it was calculated using an average value for Cp.

Step 4. To compute the amount of natural gas required from the heating rate, the available heat of the fuel (H_A) must be computed using Figure 6-16b.

In Figure 6-16b, the flue gas temperature is located on the x-axis (1,200°F). Read up from this point to the line for natural gas with a heating value of 1,059 Btu/SCF. The heat available is read from the y-axis as approximately 690 Btu/SCF.

The amount of natural gas needed is:

$$Q_{gas} = \frac{q}{H_A} = \frac{6,067,600 \text{ Btu/hr}}{690 \text{ Btu/SCF}} = 8,794 \text{ SCF}$$

ACID GAS EMISSIONS

The oxidation of halogenated organic compounds generates compounds such as HCl and HF. The emission rates of these compounds must be calculated to determine if an absorption system is needed after the oxidizer. The calculation is a straightforward application of the combustion stoichiometry in the oxidizer. Problem 6-4 illustrates these procedures.

PROBLEM 6-4

A thermal oxidizer is treating a 5,000 SCFM gas stream containing 500 ppm benzene (C_6H_6) and 120 ppm carbon tetrachloride (CCl_4). The oxidizer uses 300 SCFM of natural gas and operates at a temperature of 1,400°F with externally supplied combustion air. What is the concentration of HCl formed in the oxidizer's effluent gas stream? Assume that the oxidizer fuel is 100% methane (CH_4), and that the burner is operated at 125% of the stoichiometric requirement.

SOLUTION

Step 1. Write the combustion reactions.

$$C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O$$

$$CCl_4 + 2H_2O \xrightarrow{\ O_2\ } CO_2 + 4HCl$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
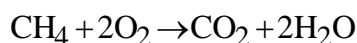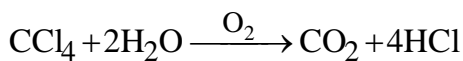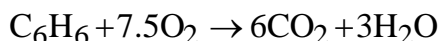
Step 2. Calculate the required amount of O_2 at stoichiometric conditions.

$$300 \text{ SCFM} \frac{\text{lb mol CH}_4}{385.4 \text{ SCF}} = 0.778 \text{ lb mol CH}_4/\text{min}$$

Stoichiometric O_2 = 2 x (lb mole CH_4)

$$\frac{2 \text{ lb mol O}_2}{\text{lb mol CH}_4}\left(0.778 \frac{\text{lb mol CH}_4}{\text{min}}\right) = 1.56 \text{ mol O}_2/\text{min}$$

Step 3. Calculate air sent to the burner (125% of stoichiometric requirement).

Total O_2 requirement for methane fuel = 1.25*(stoichiometric requirement)

$$= 1.25\left(\frac{1.56 \text{ lb mol O}_2}{\text{min}}\right) = 1.95 \text{ lb mol O}_2/\text{min}$$

$$\text{Total N}_2 = \frac{0.79 \text{ lb mol N}_2}{0.21 \text{ lb mol O}_2}\left(1.95\frac{\text{lb mol O}_2}{\text{min}}\right)$$

$$= 7.34 \text{ lb mol N}_2/\text{min}$$

Step 4. Calculate the total flue gas flow rate:

Flue gas flow rate = Exhaust gas heated (a) + Products of combustion (b) + Excess oxygen & nitrogen (c)

a. *Exhaust gas heated = 5,000 SCFM – benzene and carbon tetrachloride oxidized*

$$C_6H_6 = 5,000 \text{ SCFM}\left(\frac{0.000500 \text{ lb mol } C_6H_6}{\text{lb mol total}}\right)=2.5 \text{ SCFM}$$

$$CCl_4 = 5,000 \text{ SCFM}\left(\frac{0.000120 \text{ lb mol } CCl_4}{\text{lb mol total}}\right)= 0.6 \text{ SCFM}$$

Exhaust gas heated = 5,000 SCFM – (2.5 SCFM + 0.6 SCFM)
= 4,996.9 SCFM (could have neglected change with negligible error)

$$\text{Exhaust gas heated} = (4,996.9 \text{ SCFM})\left(\frac{\text{lb mol}}{385.4 \text{SCF}}\right)$$

=12.97 lb mol/min

b. *Products of combustion = CO$_2$ + H$_2$O + HCl*

First determine the total amount of CO$_2$ produced from all sources.

CO$_2$ as a product of the natural gas/methane (CH$_4$) combustion:

$$CO_2 =\left(0.778 \frac{\text{lb mol } CH_4}{\text{min}}\right)\left(\frac{1 \text{ lb mol } CO_2}{\text{lb mol } CH_4}\right)=0.778 \frac{\text{lb mol } CO_2}{\text{min}}$$

Plus the CO$_2$ as a product of the benzene (C$_6$H$_6$) combustion:

$$CO_2 = 2.5 \text{ SCFM } C_6H_6\left(\frac{\text{lb mol}}{385.4 \text{SCF}}\right)\left(\frac{6 \text{ lb mol } CO_2}{\text{lb mol } C_6H_6}\right)=0.039\frac{\text{lb mol } CO_2}{\text{min}}$$

Plus the CO$_2$ as a product of the carbon tetrachloride (CCl$_4$) combustion:

$$CO_2 = 0.6 \text{ SCFM } CCl_4\left(\frac{\text{lb mol}}{385.4 \text{ SCF}}\right)\left(\frac{\text{lb mol } CO_2}{\text{lb mol } CCl_4}\right)=0.002\frac{\text{lb mol } CO_2}{\text{min}}$$

Gives the total CO$_2$ formed due to combustion:
0.778 + 0.039 + 0.002 lb mol CO$_2$/min = 0.819 lb mol CO$_2$/min

Second determine total amount of H$_2$O produced from all sources.

H$_2$O as a product of the natural gas/methane (CH$_4$) combustion:

$$H_2O = \left(\frac{2\,lb\,mol\,H_2O}{lb\,mol\,CH_4}\right)\left(0.778\frac{lb\,mol\,CH_4}{min}\right) = 1.56\frac{lb\,mol\,H_2O}{min}$$

Plus the H$_2$O as a product of the benzene (C$_6$H$_6$) combustion:

$$H_2O = 2.5\,SCFM\,C_6H_6\left(\frac{lb\,mol}{385.4\,SCF}\right)\left(\frac{3\,lb\,mol\,H_2O}{lb\,mol\,C_6H_6}\right) = 0.019\frac{lb\,mol\,H_2O}{min}$$

Gives the total H$_2$O formed due to combustion:
1.56 lb mol/min + 0.019 lb mol/min = 1.58 lb mol H$_2$O/min

Third determine the amount of HCl produced from carbon tetrachloride (CCl$_4$) combustion:

$$HCl = 0.6\,SCFM\,\,CCl_4\left(\frac{lb\,mol}{385.4\,SCF}\right)\left(\frac{4\,lb\,mol\,HCl}{lb\,mol\,CCl_4}\right) = 0.00623\frac{lb\,mol\,HCl}{min}$$

Finally, the total products of combustion = CO$_2$ + H$_2$O + HCl = 0.819 + 1.58 + 0.00623 = 2.41 lb mol/min

c. Nitrogen and excess oxygen = Total N$_2$ + O$_2$ remaining

Amount of oxygen consumed in combustion of methane = stoichiometric requirement = 1.56 lb mol O$_2$/min

Amount of oxygen consumed in combustion of benzene:

$$O_2 = 2.5\,SCFM\,C_6H_6\left(\frac{lb\,mol}{385.4\,SCF}\right)\left(\frac{7.5\,lb\,mol\,O_2}{lb\,mol\,C_6H_6}\right) = 0.0487\frac{lb\,mol\,O_2}{min}$$

Amount of oxygen needed for carbon tetrachloride = 0 (no net oxygen consumption)

Amount of oxygen remaining = total – consumed
= 1.95 lb mol/min – (1.56 lb mol/min + 0.0487 lb mol/min)
= 0.34 lb mol/min

Excess oxygen and nitrogen = 0.34 lb mol O$_2$/min + 7.34 lb mol N$_2$/min
= 7.68 lb mol total/min

Flue gas flow rate = Exhaust gas heated (a) + Products of combustion (b) + Excess oxygen & nitrogen (c)

= 12.97 lb mol/min + 2.41 lb mol/min + 7.68 lb mol/min
= 23.06 lb mol/min

Step 5. Calculate the lb mol of HCl formed per minute.

$$HCl = 5,000 \text{ SCFM}\left(\frac{\text{lb mol total}}{385.4 \text{SCF}}\right)\left(\frac{0.000120 \text{lb mol CCl}_4}{\text{lb mol total}}\right)\left(\frac{4 \text{lb mol HCl}}{\text{lb mol CCl}_4}\right)$$
$$= 0.00623 \text{ lb mol HCl/min}$$

Note that this was already calculated in the third section of Step 4, (b) above.

Step 6. Calculate the HCl concentration.

$$=\left(\frac{0.00623 \text{ lb mol HCl}}{23.06 \text{lb mol total}}\right)\left(10^6 \text{ ppm}\right)=270 \text{ ppm}$$

6.5 OPERATING PARAMETERS AND INSTRUMENTATION

HIGH-TEMPERATURE, GAS-PHASE OXIDATION SYSTEMS

The thermal oxidizer system flowchart shown in Figure 6-17 includes the instrumentation commonly used to evaluate performance. These instruments are used to detect the onset of one or more of the following performance problems:

- Low gas temperatures
- Burner combustion problems
- Short-circuiting through the heat exchanger
- Reduced pollutant destruction due to restricted gas flow through the oxidizer
- Fouling and/or plugging of the heat exchanger
- Generation of additional pollutants in the oxidizer
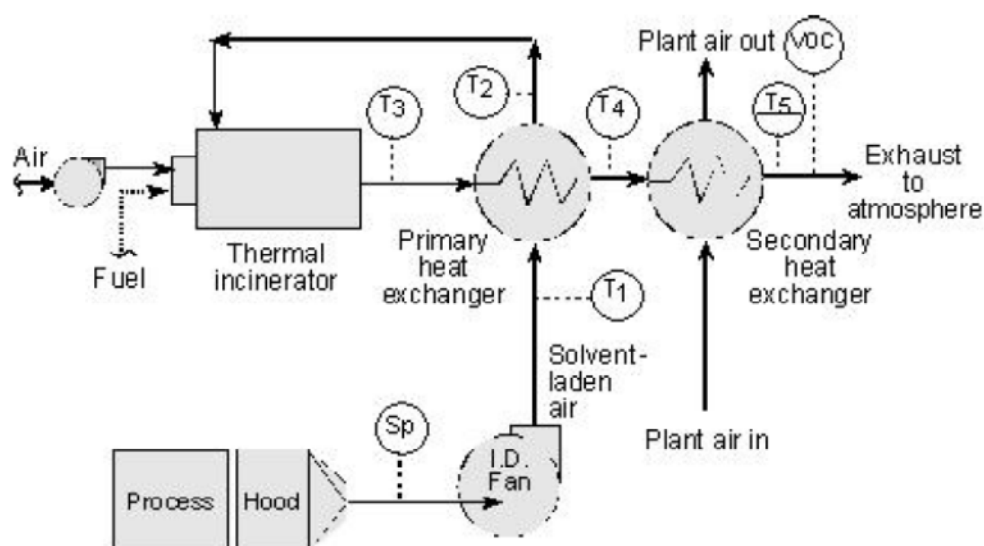
Figure 6-17. Flowchart of a thermal oxidizer system.

Gas Temperatures

The most important operating parameter used to evaluate the operation of thermal oxidizers is the outlet gas temperature (T_3). As stated earlier, this temperature should be 200°F to 300°F (95°C to 150°C) above the auto-ignition temperature of the most difficult-to-oxidize compound in the waste gas stream.

The outlet gas temperature should be monitored carefully during start-up of the unit. The combustion chamber should be preheated before introducing the waste gas stream to ensure that the gas temperatures will be sufficiently high. This preheat period also allows the oxidizer components, such as the refractory lining, to thermally expand at acceptable rates. For these reasons, thermal oxidizers do not usually go from cold off-line conditions to full on-line waste gas oxidation service on an immediate basis.

The inlet gas stream temperature increase across the recuperative or regenerative heat exchanger (T_2 – T_1) provides a useful indicator of its physical condition. The accumulation of particulate matter on either side of the unit reduces the heat transfer efficiency, resulting in increased fuel requirements. The temperature of the exhaust to the atmosphere (T_5) should be monitored to ensure that it is well above the dew point temperature of the exhaust gas to prevent moisture condensation and the formation of artificial rain in the vicinity of the exhaust stack.

VOC Concentration

The outlet VOC concentration can be measured using portable VOC analyzers. The normal monitoring location is downstream of the secondary heat exchanger (Figure 6-18) so that the temperature is relatively low.

The VOC concentration measured by the portable instruments provides only a qualitative indication of the outlet concentration since the instruments respond differently to each organic compound. There is also some inevitable uncertainty regarding (1) the presence of partial oxidation products in

the burner flame and (2) the incomplete combustion of the waste gas stream organic compounds.

Furthermore, thermal oxidizers often handle waste gas streams containing numerous organic compounds, and it is impractical to calibrate portable VOC analyzers for the exact mixture. Nevertheless, these instruments provide a very useful qualitative indicator of performance. High outlet VOC concentrations could be due to low combustion chamber temperatures or the short-circuiting of inlet gas through the heat exchanger.

CATALYTIC OXIDATION SYSTEMS

The instrumentation used with catalytic oxidizers is somewhat more extensive than that used for thermal oxidizers because of the presence of the vulnerable catalyst. Figure 6-18 illustrates the type of instrumentation used to support performance evaluation of catalytic oxidizers.
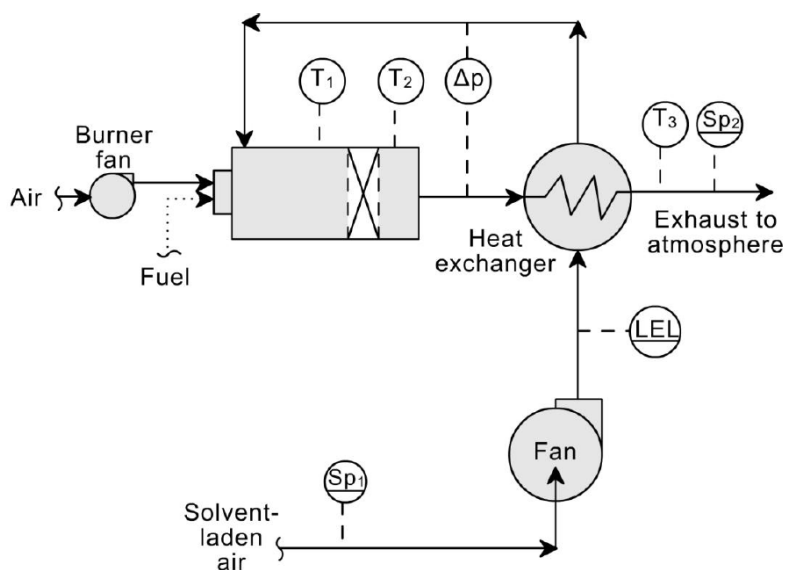
Figure 6-18. Flowchart of a catalytic oxidizer system.

Gas Temperatures

The inlet and outlet gas temperatures (Figure 6-18) of the catalyst bed (T_1 and T_2, respectively) provide useful indirect indicators of the performance of the system. The inlet gas temperature should be above the minimum level necessary for high-efficiency destruction of the organic compounds being treated. During routine operation, the bed outlet temperature should be 50°F to 200°F (10°C to 95°C) higher than the inlet temperature, because the oxidation reactions are exothermic. If the catalyst bed has become fouled, masked, or poisoned, the gas temperature increase across the bed will not be as high as baseline levels.

The gas temperature rise across the catalyst bed is also related to the concentration of organic vapor in the waste gas stream. A decrease in the inlet VOC concentration will also cause a decrease in the temperature rise across the catalyst bed. Accordingly, changes in the inlet VOC concentration should be evaluated along with the temperature data. The inlet VOC concentration is usually monitored by an LEL detector. During start-up periods, the oxidizer should be preheated to the operating temperature using the supplemental burner. If the organic vapor–laden waste gas stream is

directed to the oxidizer before it is hot, many of the organics will not be destroyed, and contaminants could condense on the catalyst surfaces.

High oxidizer outlet gas temperatures (T_2) can damage the recuperative heat exchanger. In extreme cases, it is also possible to volatilize a portion of the catalyst. Accordingly, this outlet temperature should be monitored. High outlet temperatures can be caused by short-term, high-concentration surges of organics in the waste gas stream or may be due to the ignition of carbonaceous deposits on a portion of the catalyst bed.

Outlet VOC Concentration

A portable VOC analyzer can be used to qualitatively monitor the outlet organic concentration from the oxidizer. Outlet concentrations considerably higher than baseline levels indicate the need to evaluate the catalyst activity.

6.6 SUMMARY

OXIDATION

This lesson provided the following information:

- Types of oxidation systems.
- Principles of operation for oxidation systems.
- Factors that influence the capability and sizing of an oxidation system.
- Operating parameters to evaluate in an oxidation system.

6.7 REVIEW EXERCISES

INSTRUCTIONS

Select the best response(s) for each of the following multiple-choice questions.

MULTIPLE CHOICE QUESTIONS

Types and Components of Oxidizer Systems

1. A recuperative heat exchanger is composed of _____.

    a)   packed beds of ceramic material
    b)   tube banks
    c)   rotating cylinder with heat exchange baskets
    d)   None of the above

2. Regenerative heat exchangers are capable of heat recoveries up to ____ efficiency.

    a)   40% to 65%
    b)   65% to 90%
    c)   90% to 95%
    d)   95% to 99%

3. Recuperative heat exchangers are capable of heat recoveries up to ____ efficiency.

    a)   40% to 65%
    b)   65% to 90%
    c)   90% to 95%
    d)   95% to 99%

4. Regenerative heat exchangers are vulnerable to _____ .

    a)   plugging due to particulate matter
    b)   poisoning due to phosphorus
    c)   deactivation due to sulfur compounds
    d)   None of the above

5. What type of air pollution control system is generally used to collect acid gases formed during the oxidation of halogenated organic compounds?

    a)   Absorbers
    b)   Adsorbers
    c)   Condensers
    d)   None of the above

6. What is the typical operating temperature range (bed inlet) of a catalytic oxidizer?

    a)   200°F to 500°F
    b)   500°F to 900°F
    c)   900°F to 1400°F
    d)   1400°F

7. What is the typical operating temperature range (bed inlet) of a thermal oxidizer?

    a)   200°F to 800°F
    b)   800°F to 1200°F
    c)   1200°F to 1800°F
    d)   >1800°F

8. When is the burner operated in a catalytic oxidizer? Select all that apply.

    a)   During start-up and shutdown
    b)   When the concentration of the contaminant is too low to provide sufficient heat for the oxidation reactions in the catalyst bed
    c)   When the heat exchanger has too low of an efficiency to increase inlet gas temperature sufficiently for the necessary oxidation temperature
    d)   All of the time

9. When is the burner operated in a thermal oxidizer? Select all that apply.

    a)   During start-up and shutdown
    b)   When the concentration of the contaminant is too low to provide sufficient heat for the oxidation reactions in the oxidizer chamber
    c)   When the heat exchanger has too low of an efficiency to increase inlet gas temperature sufficiently for the necessary oxidation temperature
    d)   All of the time

10. What is the typical inlet contaminant concentration for thermal and catalytic oxidizers?

    a)   < 5% of the LEL of the gas mixture
    b)   < 25% of the LEL of the gas mixture
    c)   < 50% of the LEL of the gas mixture
    d)   < 75% of the LEL of the gas mixture

Operating Principles of Oxidizer Systems

11. What is the typical operating temperature of a thermal oxidizer?

   a) The average auto-ignition temperature of the gas mixture
   b) 200°F to 300°F above the average auto-ignition temperature of the gas mixture
   c) The auto-ignition temperature of the most difficult-to-oxidize major gas stream contaminant
   d) 200°F to 300°F above the auto-ignition temperature of the most difficult-to-oxidize major gas stream contaminant

12. What is the typical residence time for gas streams in the combustion chamber of a thermal oxidizer?

   a) Up to 0.3 seconds
   b) 0.3 to 2 seconds
   c) 2 to 5 seconds
   d) Greater than 5 seconds

13. What are some of the consequences of a high-temperature gas surge in a catalytic oxidizer? Select all that apply.

   a) The catalyst could volatilize and be lost to the gas stream
   b) A recuperative heat exchanger could warp and develop leaks
   c) The catalyst could sinter
   d) There are no consequences of high-temperature surges

Capability and Sizing of Oxidizer Systems

14. How many lb moles of combustion air are needed to burn 1 SCF of methane (CH_4) if the burner operates with 15% excess air?

15. The preheated waste gas stream of 4,000 ACFM enters a thermal oxidizer. The waste gas stream temperature is 1,000°F, and the pressure is +6 in W.C. How much natural gas is needed to incinerate this gas stream at a temperature of 1,500°F?

6.8 REVIEW EXERCISES: SOLUTIONS

This Student Guide includes separate exercises and solutions, which allow students to check their work.

MULTIPLE CHOICE ANSWERS

Types and Components of Oxidizer Systems

1. A recuperative heat exchanger is composed of _____.

    a) packed beds of ceramic material
    b) tube banks
    c) rotating cylinder with heat exchange baskets
    d) None of the above

2. Regenerative heat exchangers are capable of heat recoveries up to ____ efficiency.

    a) 40% to 65%
    b) 65% to 90%
    c) 90% to 95%
    d) 95% to 99%

3. Recuperative heat exchangers are capable of heat recoveries up to ____ efficiency.

    a) 40% to 65%
    b) 65% to 90%
    c) 90% to 95%
    d) 95% to 99%

4. Regenerative heat exchangers are vulnerable to _____ .

    a) plugging due to particulate matter
    b) poisoning due to phosphorus
    c) deactivation due to sulfur compounds
    d) None of the above

5. What type of air pollution control system is generally used to collect acid gases formed during the oxidation of halogenated organic compounds?

    a) Absorbers
    b) Adsorbers
    c) Condensers
    d) None of the above

6. What is the typical operating temperature range (bed inlet) of a catalytic oxidizer?

    a) 200°F to 500°F
    b) 500°F to 900°F
    c) 900°F to 1400°F
    d) 1400°F

7. What is the typical operating temperature range (bed inlet) of a thermal oxidizer?

    a) 200°F to 800°F
    b) 800°F to 1200°F
    c) 1200°F to 1800°F
    d) >1800°F

8. When is the burner operated in a catalytic oxidizer? Select all that apply.

    a) During start-up and shutdown
    b) When the concentration of the contaminant is too low to provide sufficient heat for the oxidation reactions in the catalyst bed
    c) When the heat exchanger has too low of an efficiency to increase inlet gas temperature sufficiently for the necessary oxidation temperature
    d) All of the time

9. When is the burner operated in a thermal oxidizer? Select all that apply.

    a) During start-up and shutdown
    b) When the concentration of the contaminant is too low to provide sufficient heat for the oxidation reactions in the oxidizer chamber
    c) When the heat exchanger has too low of an efficiency to increase inlet gas temperature sufficiently for the necessary oxidation temperature
    d) All of the time

10. What is the typical inlet contaminant concentration for thermal and catalytic oxidizers?

    a) < 5% of the LEL of the gas mixture
    b) < 25% of the LEL of the gas mixture
    c) < 50% of the LEL of the gas mixture
    d) < 75% of the LEL of the gas mixture

Operating Principles of Oxidizer Systems

11. What is the typical operating temperature of a thermal oxidizer?

   a) The average auto-ignition temperature of the gas mixture
   b) 200°F to 300°F above the average auto-ignition temperature of the gas mixture
   c) The auto-ignition temperature of the most difficult-to-oxidize major gas stream contaminant
   d) 200°F to 300°F above the auto-ignition temperature of the most difficult-to-oxidize major gas stream contaminant

12. What is the typical residence time for gas streams in the combustion chamber of a thermal oxidizer?

   a) Up to 0.3 seconds
   b) 0.3 to 2 seconds
   c) 2 to 5 seconds
   d) Greater than 5 seconds

13. What are some of the consequences of a high-temperature gas surge in a catalytic oxidizer? Select all that apply.

   a) The catalyst could volatilize and be lost to the gas stream
   b) A recuperative heat exchanger could warp and develop leaks
   c) The catalyst could sinter
   d) There are no consequences of high-temperature surges

Capability and Sizing of Oxidizer Systems

14. How many lb moles of combustion air are needed to burn 1 SCF of methane (CH_4) if the burner operates with 15% excess air?

SOLUTION

Step 1. Calculate the lb mole of CH_4 burned.

$$\text{Pound mol of methane} = \left(\frac{1.0 \text{ lb mol}}{385.4 \text{SCF}} \right) 1.0 \text{ SCF CH}_4 = 0.00259 \text{ lb molCH}_4$$

Step 2. Write the combustion reaction.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
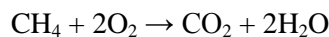
Step 3. Calculate the O_2 and N_2 required.

$$\text{lb mol O}_2 \text{ needed} = 0.00259 \text{ lb mol CH}_4 \left(\frac{2 \text{ lb mol O}_2}{1 \text{ lb mol CH}_4} \right)$$
$$= 0.00519 \text{ lb mol O}_2$$

At 15% excess air, lb mol of O_2 = 1.15 (0.00519 lb mol O_2)
= 0.0060 lb mol O_2

$$\text{lb mol N}_2 \text{ fed} = \left(\frac{0.79 \text{ lb mol N}_2}{0.21 \text{ lb mol O}_2} \right) 0.00601 \text{ lb mol O}_2$$

$$= 0.0226 \text{ lb mol N}_2$$

Therefore, at 15% stoichiometric excess 0.006 lb mol O_2 and 0.0226 lb mol N_2 (or 0.0286 lb mol total) of combustion air are needed.

15. The preheated waste gas stream of 4,000 ACFM enters a thermal oxidizer. The waste gas stream temperature is 1,000°F, and the pressure is +6 in W.C. How much natural gas is needed to incinerate this gas stream at a temperature of 1,500°F?

SOLUTION:

Step 1. Determine the enthalpy change for 1 SCF of air based on data in Table 6-2a.

Enthalpy of air @ 1,000 F = 17.92 Btu/SCF
Enthalpy of air @ 1,500 F = 28.24 Btu/SCF

Change in enthalpy = 28.24 Btu/SCF – 17.92 Btu/SCF
= 10.32 Btu/SCF

Step 2. Convert the gas flow rate to SCFM.

$$PV = nRT \rightarrow \frac{P_1 V_1}{T_1} = nR = \frac{P_2 V_2}{T_2} \rightarrow V_{std} = \frac{V_{actual} T_{std} P_{actual}}{T_{actual} P_{std}}$$

$$\text{SCFM} = 4,000 \text{ ACFM} \left(\frac{68 + 460 \, ^\circ R}{1,000 + 460 \, ^\circ R} \right) \left(\frac{407 + 6 \text{ in. W.C.}}{407 \text{ in W.C.}} \right) = 1,467 \text{ SCFM}$$

Step 3. Calculate the total change in enthalpy of the gas stream heated to 1,500°F.

(1,467 SCF/min)(10.32 Btu/SCF) = 15,140 Btu/min

Step 4. Calculate the natural gas requirement using the available heat at 1,500 F (data in Figure 6-16b).

$$\left(15{,}140\,\frac{\text{Btu}}{\text{min}}\right)\left(\frac{\text{SCF of natural gas}}{600\,\text{Btu available heat}}\right) = 25.2\ \text{SCF/min of natural gas}$$

6.9 REFERENCES

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7.0 CONDENSATION

7.1 OVERVIEW

INTRODUCTION TO CONDENSATION

The concentration of organic compounds (VOC and air toxic compounds) in a gas stream can be reduced by condensation at low gas temperatures. Condensation begins at the dew point, the temperature at which the partial pressure becomes equal to the VOC vapor pressure and the gas is said to be saturated. The gas remains saturated as the temperature is further reduced and increasing amounts of VOC are condensed.

Condensation control systems can be divided into two general categories according to the operating temperatures that can be achieved. Conventional condensers operate in the 40°F to 80°F (4°C to 27°C) range using chilled water. Refrigeration and cryogenic systems operate in the range of -50°F to -150°F (-45°C to -65°C). In extreme cases, cryogenic units using liquid nitrogen can operate at temperatures as low as -320°F (-195°C). Because of the lower temperatures possible in refrigeration and cryogenic units, the removal efficiency is much higher than in conventional condensers; however, these units are considerably more complicated and expensive.

Condensation systems are usually applied to industrial sources where there is a significant economic value to the recovered VOCs. Usually only one or two VOCs are present in the inlet gas, since separating pure materials from a multi-component condensate is difficult. The gas streams treated in condensation systems should have low particulate loadings.

LEARNING OBJECTIVES

At the conclusion of this training, students will be able to:

- Recognize the various types of condenser systems.
- Identify the principles of operation for condenser systems.
- Determine the factors that influence the capability and sizing of a condenser system.

7.2 TYPES OF SYSTEMS

CONVENTIONAL SYSTEMS

Conventional condensers are simple, relatively inexpensive devices that normally use water or air to cool and condense the VOC. Because these devices are usually not capable of reaching very low temperatures (below 40°F or 4°C), high removal efficiencies are obtained only for organic vapors that condense in the temperature range of 40°F to 80°F (4°C to 27 °C). Conventional condensers fall into two basic categories: (1) direct contact condensers and (2) surface condensers. In a direct contact condenser, the coolant and gas stream are in physical contact. In a surface condenser, the coolant is separated from the gas stream by heat transfer surfaces. The coolant, the condensate, and the permanent gases leave by separate exits. Surface condensers are commonly called shell-and-tube heat exchangers or indirect condensers.

Direct Contact Condensers

Contact condensers are simple devices such as spray towers or water jet ejectors. These devices bring the coolant, usually water, into direct contact with the vapors as illustrated in Figure 7-1. If the vapor is soluble in the coolant, absorption also occurs, increasing the amount of contaminant that can be removed at the given conditions.
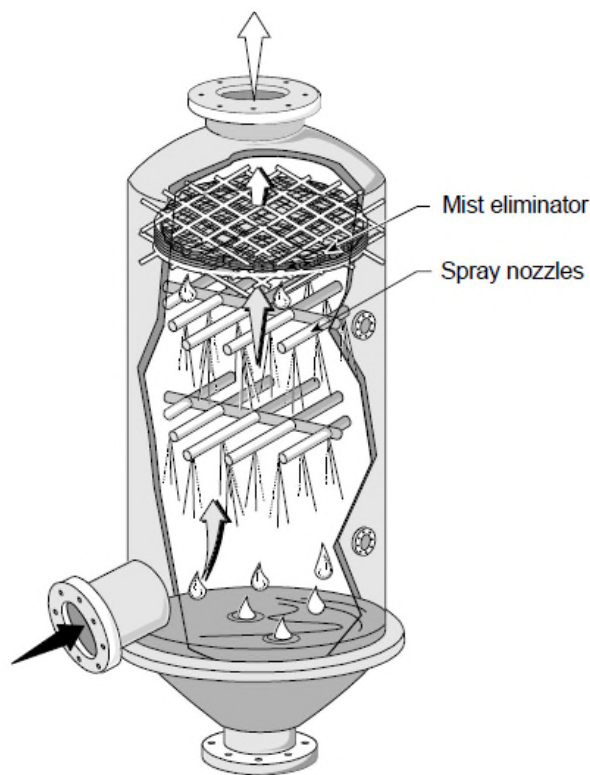
Figure 7-1. Direct contact condenser.

An ejector is a type of contact condenser. Ejectors use high-pressure liquid sprays to create suction for moving the VOC-laden gas stream and, therefore, do not need fans for gas movement. The coolant liquid is sprayed into the throat of the ejector, and organic vapors

condense while passing through. Absorption can also occur if the organic compound is soluble in the coolant fluid. An ejector condenser is illustrated in Figure 7-2.
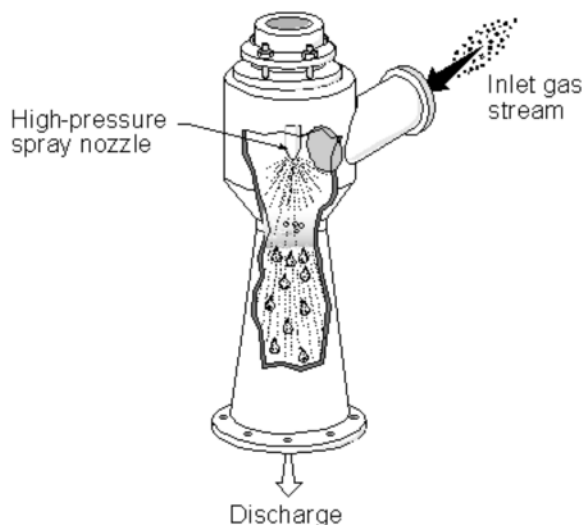
Figure 7- 2. Ejector condenser.

The main advantages of contact condensers are their flexibility and low cost. The main disadvantage is the mixing of the water and the condensed VOC, which increases wastewater treatment costs and/or VOC recovery costs, particularly if the VOC is miscible in H_2O.

Surface Condensers

Surface condensers are usually in the form of shell-and-tube heat exchangers as shown in Figure 7-3. These devices consist of a cylindrical shell into which the gas stream flows while the coolant flows through numerous small tubes inside the shell. VOCs encounter the cool surface of the tubes, condense, and are collected. Permanent plus uncondensed VOCs exit the condenser and are emitted to the atmosphere.
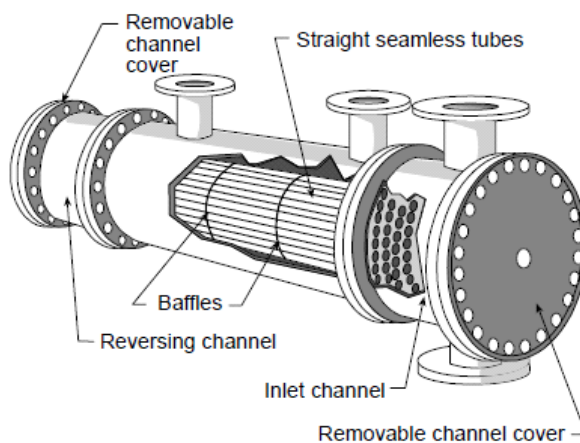
Figure 7-3. Single-pass condenser.

The system shown in Figure 7-3 is known as a single-pass condenser since both the coolant and gas streams flow in a single direction between entry and exit. This simple condenser is not usually used since improved heat transfer can be achieved with more complex systems that provide multiple passes, shorter tube lengths, and higher gas velocities. Figure 7-4 illustrates a 1-2 condenser. The first digit refers to the number of passes the gas makes on the shell side, while the second digit indicates the number of tube-side passes made by the coolant liquid. The addition of shell-side baffles increases the distance that the gas travels and the gas velocity. This design gives improved performance over the single-pass exchanger. A 2-4 heat exchanger (not shown) results in still higher gas velocities and better heat transfer than the 1-2 exchanger. However, adding more passes does have disadvantages: the exchanger construction is more complicated, friction losses are increased because of the higher velocities, and exit and entrance losses are multiplied.
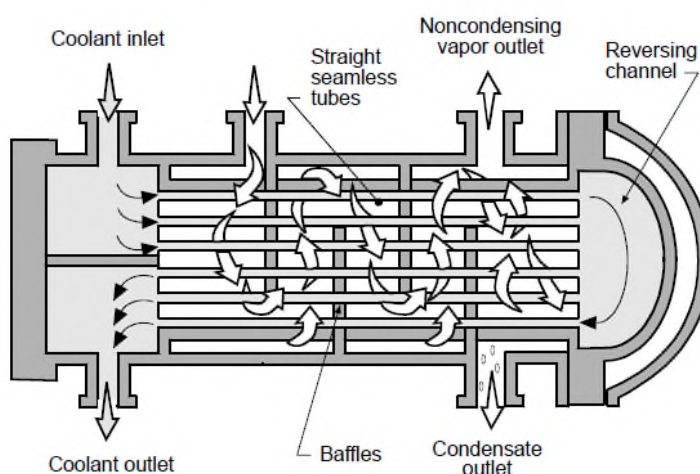
Figure 7-4. 1-2 pass shell-and-tube condenser.

Condensation applications normally involve large temperature differences between the gas and coolant. These temperature variances cause the tubes to expand or contract, and may cause the tubes to buckle or pull loose from the shell, destroying the condenser. Floating head construction is commonly used to avoid condenser expansion/contraction stress damage. In a floating head condenser, one end of the tube bundle is mounted so that, while sealed from the shell to prevent leakage, it is structurally independent and allows the tubes to expand and contract within the shell.

Air Condensers

Air condensers can be used in situations where water is not available, or treatment of the water stream is very expensive. Because of reduced heat transfer efficiency, condensers using air must be considerably larger than those using water.

Extended-surface air condensers may be used to increase the efficiency by conserving space and reducing equipment cost. In these units, the outside area of the tube is multiplied or extended by adding fins or disks, as shown in Figure 7-5, which illustrates two types of finned tubes. In extended-surface condensers, the VOC condenses inside the tubes while air flows around the outside in contact with the extended surfaces.

Traverse fins   Longitudinal fins
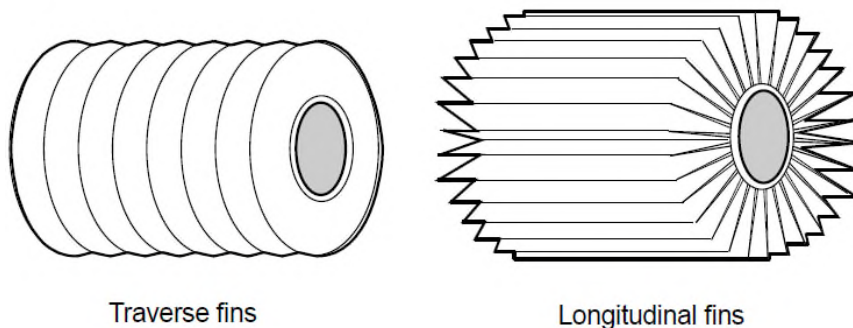
Figure 7-5. Extended surface tubes.

REFRIGERATION SYSTEMS

Refrigeration systems achieve low operating temperatures and are capable of increased VOC condensation. A simplified schematic of a refrigeration system is illustrated in Figure 7-6. Heat is removed from the VOC-laden gas stream in the evaporator section, causing condensation of a portion of VOC. The condensate and exhaust gas exit as separate streams. Heat removed from the gas stream is added to the refrigerant liquid, causing the refrigerant to vaporize. The refrigerant vapor leaving the evaporator section is then compressed to form a high-temperature, high-pressure vapor stream that is subsequently condensed in an air condenser. The refrigerant liquid then passes through an expansion valve where the pressure is reduced to the level necessary for the evaporator. The overall operation is basically the same as a home air conditioning system. The most common refrigerants used are chlorofluorocarbons (CFCs).
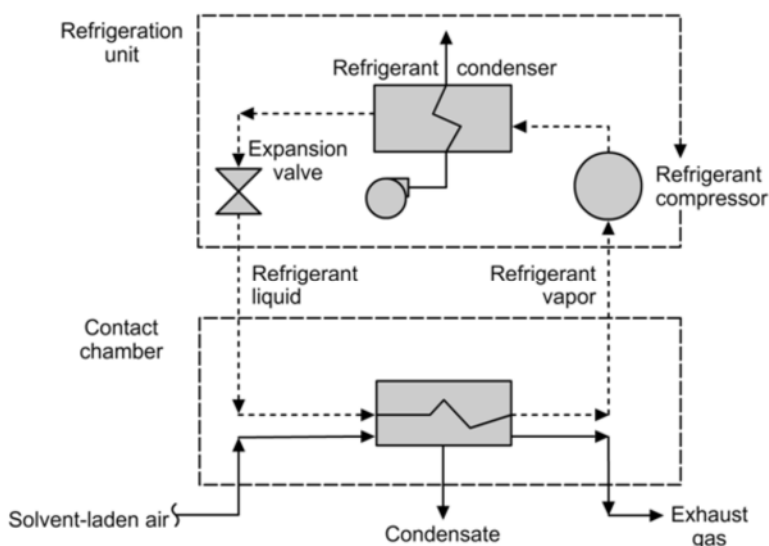
Figure 7-6. Basic refrigeration cycle.

A two-stage refrigeration system for VOC recovery from a gas stream that also contains appreciable amounts of water vapor is shown in Figure 7-7. The inlet gas stream enters a pre-condenser where it is cooled to approximately 40°F (4°C) in order to condense most of the water. The vapor pressure of water at 40°F is 0.12 psi, which corresponds to a water level of approximately 0.005 lb_m H_2O per lb_m air. By removing water vapor in the first stage, frost buildup on the heat exchange surfaces of the main chamber is minimized.
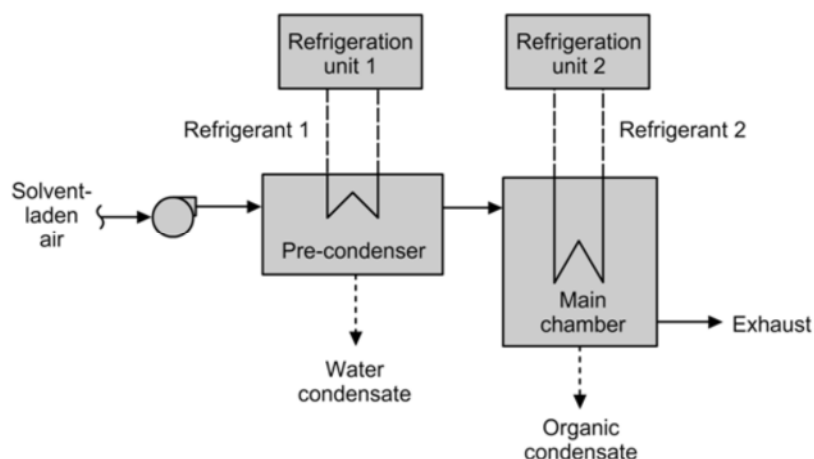
Figure 7-7. Simplified flowchart of a two-stage refrigeration system for organic vapor recovery.

The second stage (main chamber) operates at a lower temperature, ranging perhaps between -50°F to -150°F (-45°C to -100°C). Coolant for this chamber is supplied by a separate compressor system. Cascade-type systems are often used when extremely low temperatures are needed. The individual chambers are interconnected so that one unit can be used to expel the heat removed from another unit. Different coolants can be used in the various interconnected refrigeration units.

The treated gas stream leaving the main chamber is vented to the atmosphere. The condensate from the main chamber is collected in a storage tank and processed to remove water or other contaminants that would affect its reuse. The high water content condensate from the pre-condenser chamber is usually treated in a wastewater treatment system.

CRYOGENIC SYSTEMS

Cryogenic control systems use liquefied gases, such as nitrogen or carbon dioxide, to cool the waste gas streams to temperatures approaching the freezing point of the solvents. The extremely cold temperatures ranging from -100°F to -320°F (-70°C to -200°C) condense much larger amounts of VOCs. These systems are relatively simple because no refrigeration system is required, and the liquefied gas used for VOC control is simply vented to the atmosphere. Cryogenic systems do require a facility to receive and store the liquefied gas. There are three general types of cryogenic systems.

1. Indirect contact–single heat exchangers
2. Indirect contact–dual heat exchangers
3. Direct contact

Cryogenic systems are used primarily for single-component gas streams. To be economical, the

organic vapor concentration must be greater than 500 ppm. As is the case with most condensation systems, cryogenic units are not tolerant of particulate matter that can accumulate on heat exchange surfaces.

Indirect Contact–Single Heat Exchanger Systems

A shell-and-tube heat exchanger is used for heat exchange between a liquefied gas and the VOC-containing gas stream. Liquefied nitrogen (N_2) at a temperature of -320°F (-200°C) is the most commonly used liquefied gas.[1,2,3] The liquefied N_2 gas flows through the tubes of the heat exchanger while the waste gas passes through the shell side. A flowchart of an indirect contact–single heat exchanger system is shown in Figure 7-8.
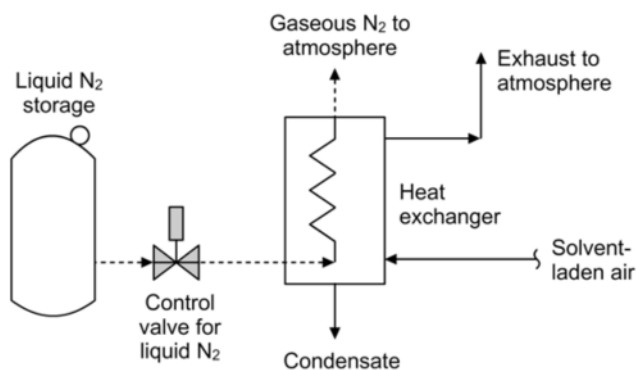
Figure 7-8. Single heat exchanger, indirect contact cryogenic system for organic vapor recovery.

Because of the extremely cold temperatures on the surface of the N_2 containing tubes, it is possible for the organic compounds to accumulate as frost on the exterior surfaces of the tubes.[1,2,3] These layers can reduce heat transfer efficiency significantly and increase heat exchanger–static pressure drop.

To avoid this problem, it may be necessary to operate a parallel set of heat exchangers. One heat exchanger can be in a heat/defrost cycle while the other is in service for VOC condensation. Cryogenic system shell-and-tube heat exchangers are not well-suited for large gas flow rates and are used primarily for small systems.

Indirect Contact–Dual Heat Exchanger Systems

The freezing problem inherent in an indirect contact–single heat exchange system can be avoided by the more complex dual system. As shown in Figure 7-9, the liquefied N_2 used in heat exchanger 1 cools a heat transfer fluid that, in turn, is used in heat exchanger 2 to condense VOC from the solvent-laden air.
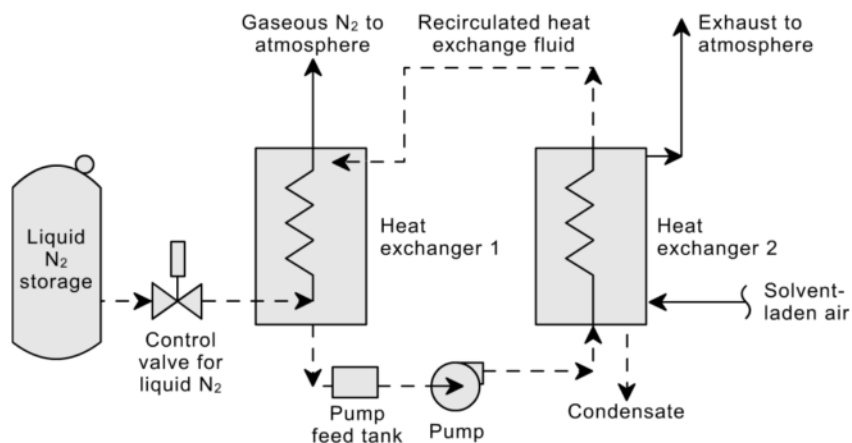
Figure 7-9. Dual heat exchange cryogenic system for organic vapor recovery.

The flow rate of the heat exchange fluid is controlled to maintain a VOC stream temperature just above the freezing point of the organic compound. This reduces the frequency of defrosting necessary to maintain adequate heat exchange efficiency, although occasional defrosting may still be needed because of the presence of moisture in the VOC-laden gas stream. The capacity of the dual heat exchanger system is limited by the size of the heat exchanger. Dual heat exchanger systems are generally applicable to gas streamers less than 5,000 ACFM.

Direct Contact Systems

In direct contact systems, the VOC-laden gas stream comes into direct contact with a spray of liquid N_2 droplets. These systems avoid the frost buildup problem because there are no surfaces at extremely cold temperatures. The outlet gas temperature is controlled by the flow rate of liquefied gas. A typical flowchart is shown in Figure 7-10.
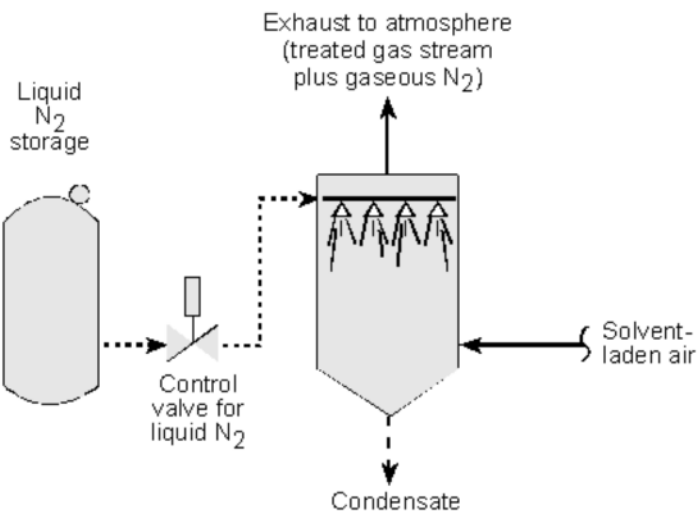
Figure 7-10. Direct contact cryogenic system for organic vapor recovery.

The liquid N_2 is dispersed using spray nozzles in the upper areas of the contacting chamber.

The chamber is insulated to maintain the lowest possible gas temperatures. Heaters are included on the exterior sides of the chamber walls for the occasional removal of frost from the interior surfaces.

The outlet gas stream exhausted to the atmosphere includes the uncondensed compounds from the inlet gas stream and the vaporized nitrogen. The increased gas flow rate from the direct contact systems has a slight impact on its ability to remove organic vapor. The additional N_2 serves as a diluent and reduces the partial pressure of the VOC. Thus, a direct contact cryogenic condenser must operate at a lower temperature than an indirect contact condenser in order to achieve the same VOC removal efficiency.

The liquefied gas requirements for direct contact systems vary with the inlet concentration of the gas stream. At organic vapor concentrations less than 10,000 ppm, the liquefied gas requirement can be more than 20 pounds per pound of organic. As the concentration exceeds 100,000 ppm, the liquefied gas requirement drops to less than 5 pounds per pound of organic.[1,2] For this reason, cryogenic systems are used primarily for vapor recovery applications in which the organic vapors are at high concentrations.

7.3 OPERATING PRINCIPLES

CONDENSATION

Condensation can be caused by reducing the gas temperature, increasing the gas pressure, or a combination of both. Since it is not economical to compress the large volumes of gas encountered in air pollution applications, temperature reduction is used.

As the temperature of the VOC-laden stream is reduced, both the volume occupied by the gas and the average kinetic energy of the gas molecules are reduced. Ultimately, the weak attractive forces (van der Waals' forces) between the molecules cause condensation to begin at the dew point temperature, where the partial pressure of the VOC is equal to the vapor pressure of the compound. As condensation begins, the partial pressure of the VOC decreases and further reductions in temperature are needed so that the vapor pressure of the VOC remains equal to the vapor pressure ion.

The gas stream leaving the condensation system will have a reduced VOC partial pressure. Because the condensate and the vapor are assumed to be in equilibrium, this outlet stream partial pressure will be equal to the vapor pressure of the organic compound. The reduction in vapor pressure with decreasing temperature is illustrated for a number of common VOCs in Figure 7-11.
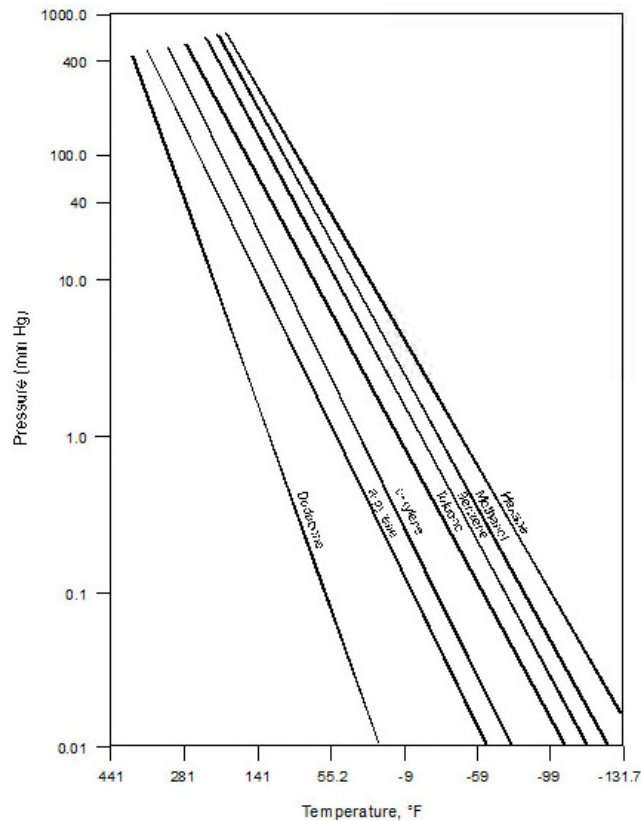
Figure 7-11. Vapor pressures of organic compounds.[4]

Problem 7-1 illustrates how the extent of VOC removal depends on the outlet temperature.

PROBLEM 7-1

What is the maximum toluene removal efficiency possible in a refrigeration-type indirect contact condenser operating at -100°F and 760 mm Hg if the inlet concentration is 10,000 ppm? Use the toluene vapor pressure data provided in Figure 7-11.

SOLUTION

Step 1. Determine the outlet concentration of toluene by assuming that the outlet gas stream is in equilibrium with the toluene condensate. From Figure 7-11.

Outlet partial pressure @ -100 °F = 0.015 mm Hg (very approximate)

Step 2. Calculate the outlet concentration of toluene assuming saturation.

y = P* /P = 0.015mm Hg/760mm Hg = 0.0000197

Multiply by 10^6 to convert to ppm: $0.0000197(10^6)$ = 19.7 ppm

Step 3. Calculate the removal efficiency.

$$\eta = \frac{\text{In} - \text{Out}}{\text{In}}(100\%) = \frac{10{,}000 - 19.7}{10{,}000}(100\%) = 99.8\%$$

Temperature is the only process variable that governs the effectiveness of a condenser. At the operating pressure of the system, the outlet temperature from the condenser determines the maximum removal efficiency. Condensers cannot be used in series like adsorbers or absorbers to further reduce outlet concentration unless the outlet temperature of the second condenser is lower than the previous one.

7.4 CAPABILITY AND SIZING

EFFICIENCY

The partial pressure of an organic compound leaving a condenser is assumed to be equal to the vapor pressure of that compound at the outlet gas temperature. Accordingly, the efficiency of a condenser can be estimated based on vapor pressure data for the specific compounds being removed. Vapor pressures for various organic compounds are often calculated using the Antoine Equation (Equation 7-1).

(Eq. 7-1) $$\log_{10}(P^*) = A - \left[\frac{B}{C + T}\right]$$

Where: P*   = vapor pressure in mm Hg
          T   = gas temperature in °C
          A, B, C = specific constants for each compound

Antoine constants for a number of compounds are tabulated in Table 7-1 and in standard reference texts such as *Chemical Properties Handbook* (1999), *Lange's Handbook* (1956), and *Hydrocarbon Processing.*

PROBLEM 7-2

What is the vapor pressure of ortho-xylene at a temperature of 150°F?

SOLUTION

Step 1. Convert the temperature to °C.

°C = (°F - 32)/1.8 = (150 – 32)/1.8 = 65.6°C

Step 2. Calculate the vapor pressure using the Antoine equation.

$$\log_{10}(P^*) = A - \left[\frac{B}{C + T}\right] = 7.00154 - \left[\frac{1476.393}{213.872 + 65.6}\right] = 1.719$$

$$P^* = 10^{1.719} = 52.360 \, mm \, Hg$$

Table 7-1. Antoine constants.				
Compound	**Range (°C)**	**A**	**B**	**C**
Acetaldehyde	-0.2 to 34.4	8.00552	1600.017	291.809
Acetic acid	29.8 to 126.5	7.38782	1533.313	222.309
Acetone	-12.9 to 55.3	7.11714	1210.595	229.664
Ammonia	-83 to 60	7.55466	1002.711	247.885
Benzene	14.5 to 80.9	6.89272	1203.531	219.888
n-Butane	-78.0 to -0.3	6.82485	943.453	239.711
i-Butane	-85.1 to -11.6	6.78866	899.617	241.942
1-Butene	-77.5 to -3.7	6.53101	810.261	228.066
Butyric acid	20.0 to 150.0	8.71019	2433.014	255.189
Carbon tetrachloride	14.1 to 76.0	6.87926	1212.021	226.409
Chlorobenzene	62.0 to 131.7	6.97808	1431.063	217.55
Chlorobenzene	0 to 42	7.106	1500.000	224.000
Chloroform	-10.4 to 60.3	6.95465	1170.966	226.232
Cyclohexane	19.9 to 81.6	6.84941	1206.001	223.148
n-Decane	94.5 to 175.1	6.95707	1503.568	194.056
1,1-Dichloroethane	-38.8 to 17.6	6.97702	1174.022	229.06
1,2-Dichloroethane	-30.8 to 99.4	7.0253	1271.254	222.927
Dichloromethane	-40.0 to 40	7.40916	1325.938	252.615
Diethyl ether	-60.8 to 19.9	6.92032	1064.066	228.799
Dimethyl ether	-78.2 to -24.9	6.97603	889.264	241.957
Dimethylamine	-71.8 to 6.9	7.08212	960.242	221.667
Ethanol	19.6 to 93.4	8.1122	1592.864	226.184
Ethanolamine	65.4 to 170.9	7.4568	1577.67	173.368
Ethyl acetate	15.6 to 75.8	7.10179	1244.951	217.881
Ethyl acetate	-20 to 150	7.09808	1238.71	217.000
Ethyl chloride	-55.9 to 12.5	6.98647	1030.007	238.612
Ethylbenzene	56.5 to 137.1	6.9565	1423.543	213.091
Ethylene oxide	0.3 to 31.8	8.69016	2005.779	334.765
Formaldehyde	-109.4 to -22.3	7.19578	970.595	244.124
Glycerol	183.3 to 260.4	6.16501	1036.056	28.097
n-Heptane	25.9 to 99.3	6.90253	1267.828	216.823
i-Heptane	18.5 to 90.9	6.87689	1238.122	219.783
1-Heptene	21.6 to 94.5	6.91381	1265.12	220.051
n-Hexane	13.0 to 68.5	6.88555	1175.817	224.867
i-Hexane	12.8 to 61.1	6.86839	1151.401	228.477
1-Hexene	15.9 to 64.3	6.8688	1154.646	226.046
Hydrogen Cyanide	-16.4 to 46.2	7.52823	1329.49	260.418
Methanol	14.9 to 83.7	8.08097	1582.271	239.726
Methyl acetate	1.8 to 55.8	7.06524	1157.63	219.726
Methyl chloride	-75.0 to 5.0	7.09349	948.582	249.336

Compound	Range (°C)	A	B	C
Methyl ethyl ketone	42.8 to 88.4	7.06356	1261.339	221.969
Nitrobenzene	134.1 to 210.6	7.11562	1746.586	201.783
Nitromethane	55.7 to 136.4	7.28166	1446.937	227.6
n-Nonane	70.3 to 151.8	6.93764	1430.459	201.808
1-Nonane	66.6 to 147.9	6.95777	1437.862	205.814
n-Octane	52.9 to 126.6	6.91874	1351.756	209.10
i-Octane	41.7 to 118.5	6.88814	1319.529	211.625
1-Octene	44.9 to 122.2	6.93637	1355.779	213.022
n-Pentane	13.3 to 36.8	6.84471	1060.793	231.541
i-Pentane	16.3 to 28.6	6.73457	992.019	229.564
1-Pentanol	74.7 to 156.0	7.18246	1287.625	161.33
1-Pentene	12.8 to 30.7	6.84268	1043.206	233.344
1-Propanol	60.2 to 104.6	7.74416	1437.686	198.463
2-Propanol	52.3 to 89.3	7.74021	1359.517	197.527
Propionic acid	72.4 to 128.3	7.71423	1733.418	217.724
Propylene oxide	-24.2 to 34.8	7.01443	1086.369	228.594
Styrene	29.9 to 144.8	7.06623	1507.434	214.985
Toluene	35.3 to 111.5	6.95805	1346.773	219.693
1,1,1-Trichloroethane	-5.4 to 16.9	8.64344	2136.621	302.769
1,1,2-Trichloroethane	50 to 113.7	6.95185	1314.41	209.197
Trichloroethylene	17.8 to 86.5	6.51827	1018.603	192.731
Water	0 to 60	8.10765	1750.286	235.000
m-Xylene	59.2 to 140.0	7.00646	1460.183	214.827
o-Xylene	63.5 to 145.4	7.00154	1476.393	213.872
p-Xylene	58.3 to 139.3	6.9882	1451.792	215.111

SIZING OF CONVENTIONAL CONDENSERS

Coolant Flow Rate for Direct Contact Condensers

The first step in analyzing any heat transfer process is to set up a heat balance relationship. For a condensation system, the heat balance can be expressed as:

Heat in = Heat out

| Heat required to reduce vapors to the final temperature | + | Heat required to condense vapors | = | Heat needed to be removed by the coolant |

This heat balance for an indirect contact condenser is written in equation form as:

(Eq. 7-2) $\quad q = m_G C_{pG} (T_{Ginitial} - T_{Gfinal}) + m_C \Delta H_v = L C_{pL}(T_{Linitial} - T_{Lfinal})$

Where:
- q = heat transfer rate (Btu/hr)
- m_G = mass flow rate of gas (lb$_m$/hr)
- m_C = mass flow rate of condensate (lb$_m$/hr)
- L = mass flow rate of liquid coolant (lb$_m$/hr)
- C_p = average specific heat of a gas or liquid (Btu/lb$_m$ °F)
- T = temperature of streams: G for gas and L for liquid coolant (°F)
- ΔH_v = heat of condensation or vaporization (Btu/lb$_m$)

In Equation 7-2, the mass flow rate (m_G) and inlet temperature of the gas stream ($T_{Ginitial}$) are set by the process exhaust stream. The temperature of the coolant entering the condenser ($T_{Linitial}$) is also set. The average specific heats (C_p) of both streams and the heat of condensation (ΔH_v) can be obtained from chemistry handbooks. The final gas temperature (T_{Gfinal}) can be calculated based on the required fractional VOC condensation. Only the amount of coolant (L) and its outlet temperature are left to be determined. If either one of these terms is set by process restrictions (i.e., only x pounds per hour of coolant are available, or the outlet temperature of coolant must be below a set temperature), then the other term can be solved for directly. Equation 7-2 may also be written in terms of molar flow rates in which case the specific heats and heat of condensation must also be on a molar basis.

Equation 7-2 has a number of limitations and should be used only for rough estimates. The specific heat of a substance is dependent on temperature, and the temperature throughout the condenser is constantly changing. The C_p of water varies only slightly between 32°F and 212°F (0°C to 100°C), and Cp = 1 Btu/lb$_m$ °F is generally accurate enough for air pollution control work. When the concentration of VOC is small, the gas flow rate (m_G) is effectively constant. However, for high VOC concentration, m_G may decrease significantly as condensation increases.

Surface Area of Surface Condensers

In a surface (indirect) condenser, heat is transferred from the vapor stream to the coolant through a heat exchange surface. The rate of heat transfer depends on three factors: (1) total cooling surface available, (2) resistance to heat transfer, and (3) mean temperature difference between condensing vapor and coolant. This can be expressed mathematically by:

(Eq. 7-3) $\quad\quad q = U A \Delta T_m$

Where:
- q = heat transfer rate (Btu/hr)
- U = overall heat transfer coefficient (Btu/°F·ft²·hr)
- A = heat transfer surface area (ft²)
- ΔT_m = mean temperature difference (°F)

The overall heat transfer coefficient (U) is a measure of the total resistance that heat experiences while being transferred from the hot body to the cold body. In a shell-and-tube condenser, cold water flows through the tubes, causing vapor to condense on the outside surface of the tube wall.

Heat, which is always transferred from high to low temperature, is transferred from the vapor to the coolant. Figure 7-12 shows the typical contributions to heat transfer resistance in a shell-and-tube condenser.

Resistances (Figure 7-12) are associated with the condensate, any scale or dirt on the outside of the tube (outside fouling), the tube itself, with any scale or dirt on the inside of the tube (inside fouling), and with the cooling liquid. Each of these resistances must be combined to obtain an overall heat transfer coefficient. The overall heat transfer coefficients shown in Table 7-2 can be used for preliminary estimating purposes.
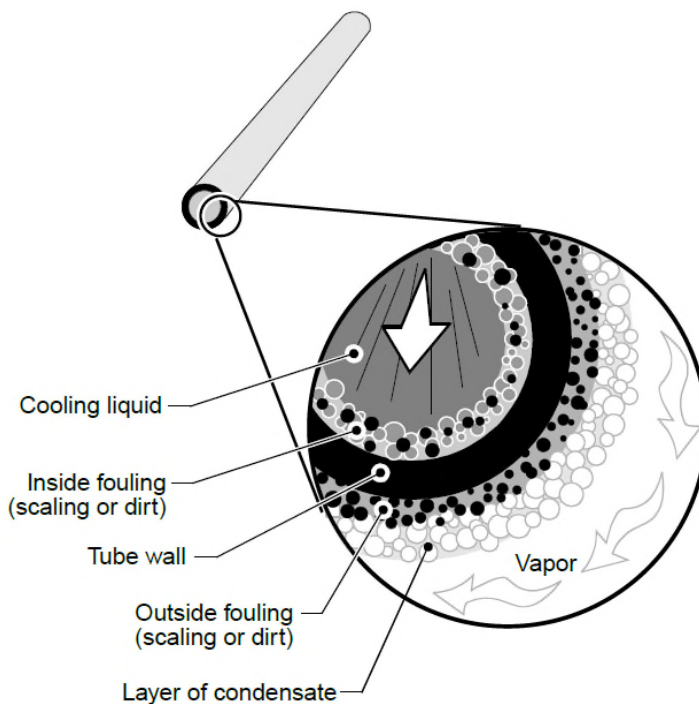
Figure 7-12. Heat transfer resistances.

Table 7-2. Typical overall heat transfer coefficients in tubular heat exchangers.		
Condensing Material (shell side)	**Cooling Liquid**	**U, Btu/ °F ft² hr**
Organic solvent vapor with high percent of noncondensable gases	Water	20 - 60
High-boiling hydrocarbon vapor (vacuum)	Water	20 - 50
Low-boiling hydrocarbon vapor	Water	80 - 200
Hydrocarbon vapor and steam	Water	80 - 100
Steam	Feedwater	400 – 1,000
Water	Water	200 - 250

Mean Temperature Difference

In an indirect heat exchanger, the temperature difference between the hot gas and the coolant usually varies throughout the length of the exchanger; therefore, a mean temperature difference (ΔT_m) must be used. The log mean temperature difference can be used for the special cases when the flow of both streams is completely co-current, completely countercurrent, or the temperature of one of the fluids remains constant (as is the case in condensing a pure liquid). The temperature profiles for these three conditions are illustrated in Figure 7-13.
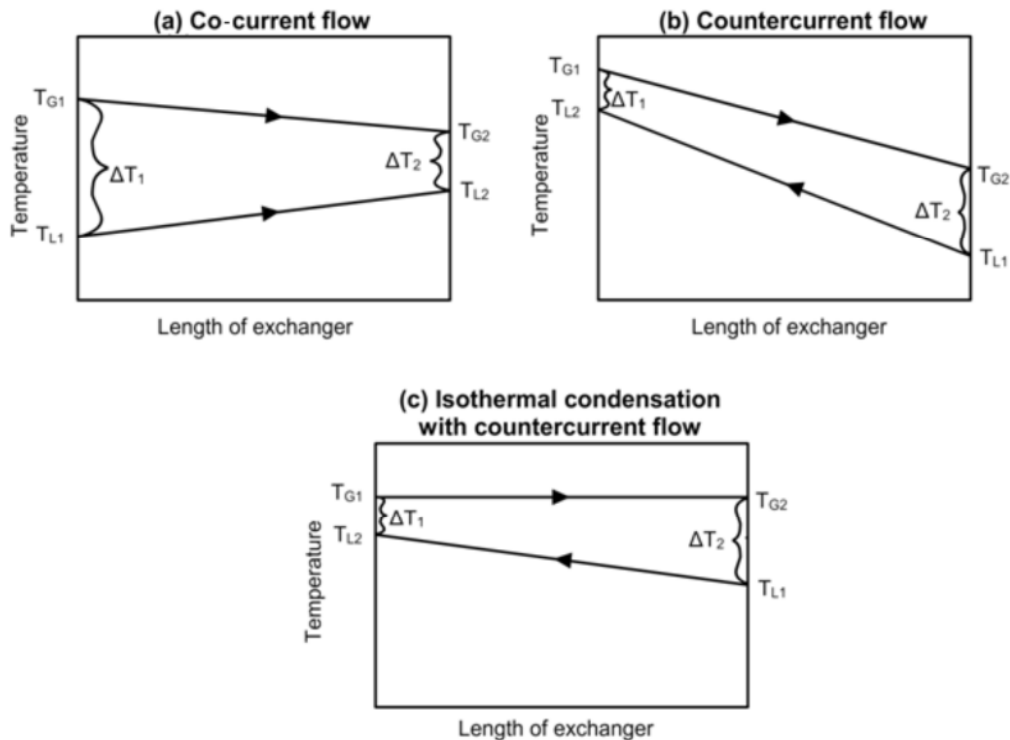
Figure 7-13. Temperature profiles in a heat exchanger for co-current flow, countercurrent flow, and isothermal condensation with countercurrent flow.

The log mean temperature for countercurrent flow can be expressed as:

$$\textbf{(Eq. 7-4)} \qquad \Delta T_{lm} = \frac{\Delta T_1 - \Delta T_2}{\ln\left(\Delta T_1 / \Delta T_2\right)}$$

Where: ΔT_{lm} = log mean temperature difference

In co-current flow (Figure 7-13a), the temperature difference is a maximum at the inlet of the exchanger where the inlet gas temperature is a maximum and inlet coolant is a minimum. The temperature difference then decreases continually from the inlet to the outlet of the exchanger. In countercurrent flow (Figure 7-13b), the temperature difference is reasonably constant

throughout the exchanger. The exit gas is opposite the inlet coolant liquid, and both temperatures are at their minimum values. At the other end of the exchanger, the inlet gas is opposite the outlet coolant, where both temperatures are at their maximum values. When the inlet gas is pure, the gas temperature does not change once the dew point temperature is reached, as condensation occurs isothermally.

The value calculated from Equation 7-4 is valid for single-pass heat exchangers. For multiple-pass exchangers, a correction factor for the log mean temperature must be included. Values of the correction factor may be found in most heat transfer textbooks. No correction factor is needed for the special case of isothermal condensation when there is a single component vapor and the gas temperature is equal to the dew point temperature.

In order to size a condenser, Equation 7-5 must be rearranged to solve for the surface area.

(Eq. 7-5)
$$A = \frac{q}{U \Delta T_{lm}}$$

Where:

A = surface area of a shell-and-tube condenser (ft^2)

q = heat transfer rate (Btu/hr)

U = overall heat transfer coefficient (Btu/°F·ft^2·hr)

ΔT_{lm} = log mean temperature difference (°F)

If the incoming vapor stream is above its dew point (superheated), it must first be cooled to its dew point before condensation begins. It is generally considered conservative to size the condenser as if the entire heat load (de-superheating and condensing) were transferred to the condensate.[3] In general, the condensate must be subcooled to ensure that it will not re-vaporize. This is accomplished by maintaining a condensate level that covers the bottom tubes in the condenser, a condition known as *flooding*.

Equation 7-5 gives the surface area required to cool the inlet gas and condense the VOC, but does not include subcooling. The area required for the subcooling section, which is generally small compared to the area for condensation, can be treated separately, and the total condenser area can be considered to be the sum of the areas required for condensing and subcooling.

Condensation from a gas containing multiple VOCs is a considerably more difficult problem and several cases may be encountered. In one case, all the components may condense at the final gas temperature. In other cases, some components may condense while others may not. Multicomponent condensation is always nonisothermal. Sensible heat removal or addition must be provided for both the liquid and vapor streams. The composition of both phases changes continually, all of which complicates the design.

In nearly all condensation applications related to air pollution control, the gas to be treated will contain one or more condensable VOCs and noncondensable gas components. Noncondensable gases offer resistance to the rate of condensation in terms of both heat and mass transfer, because the condensable vapor must diffuse to the cool surface. Air is usually the contaminant vapor, but other gases that do not condense or dissolve in the liquid can also affect heat transfer.

Problem 7-3 illustrates the design procedure for the special case in which the gas stream consists

of pure acetone. In choosing a heat transfer coefficient, the smallest value should be used to allow as much overdesign as possible.

PROBLEM 7-3

This is a special case in which a vapor stream of pure acetone at 120°C and 14.7 psia is fed to a condenser. The acetone exits the condenser as a subcooled liquid at 30°C. A single-pass, countercurrent-flow, indirect contact condenser is used. The cooling liquid is water that enters at a temperature of 20°C and exits at 40°C. The acetone feed rate is 10 kg/min. Calculate the required cooling water flow rate and estimate the required area of the exchanger. The following data for acetone and water are available:

For acetone:
Condensation temperature at 14.7 psia: 56°C
Heat capacity of vapor: $C_p = 0.084$ kJ/mol K
Heat capacity of liquid: $C_p = 0.13$ kJ/mol K
Heat of condensation: $\Delta H_v = 25.1$ kJ/mol
Molecular weight: M = 58.1kg/kmol

For water:
Heat capacity of liquid: $C_p = 0.0754$ kJ/mol K = 4.19 kJ/kg K

Heat transfer coefficients:
Cooling superheated acetone vapor: U = 40 Btu/hr ft² °F
Condensing acetone: U = 100 Btu/hr ft² °F
Subcooling acetone liquid: U = 50 Btu/hr ft² °F
Conversion factor: 1 Btu/hr ft² °F = 0.34 kJ/min m² K

SOLUTION

Step 1. Calculate the molar flow rate of acetone.

Molar flow rate, m = (10kg/min)/58.1kg/kmol
= 0.172 kmol/min
= 172 mole/min

Step 2. Calculate the total amount of heat that must be removed from the acetone in three steps: a) cooling the superheated vapor from 120 °C to the saturation temperature of 56 °C; b) condensing the acetone isothermally at 56 °C; c) subcooling the liquid acetone from 56 °C to 30 °C.

$$q = m \, [C_{pG}(120 - 56) + \Delta H_v + C_{pL}(56 - 30)]$$
$$= 172 \, [0.084(64) + 25.1 + 0.13(26)]$$
$$= 172 \, [5.4 + 25.1 + 3.4]$$
$$= 5.83 \times 10^3 \text{ kJ/min}$$

Step 3. Calculate the flow rate of water needed to absorb the total amount of heat to be

removed from Step 2.

$$q = mC_{pL}(40K - 20K)$$
$$5.83 \times 10^3 \text{ kJ/min} = m(4.19 \text{ kJ/kg K})(20 \text{ K})$$
$$m = (5.83 \times 10^3 \text{ kJ/min})/(4.19 \text{ kJ/kg K})(20 \text{ K})$$
$$= 69.6 \text{ kg/min}$$

Step 4. Calculate the area of the de-superheater.

Removal of superheat:
$$q = mC_{pG}(120 - 56)$$
$$= 172(0.084)(120 - 56)$$
$$= 0.93 \times 10^3 \text{ kJ/min}$$

Water temperature change over de-superheater:
$$\Delta T_{H2O} = q/m\,C_p$$
$$= 0.93 \times 10^3/69.6(4.19)$$
$$= 3.2 \text{ K}$$

Log mean temperature difference:
$$\Delta T_{lm} = (\Delta T_1 - \Delta T_2)/\ln(\Delta T_1/\Delta T_2)$$
$$= [(120 - 40) - (56 - 36.8)]/\ln[(120 - 40)/(56 - 36.8)]$$
$$= (80 - 19.2)/\ln(80/19.2) = 42.8 \text{ K}$$

Area:
$$A = q/U\Delta T_{lm}$$
$$= (0.93 \times 10^3)/(40)(0.34)(42.8)$$
$$= 1.6 \text{m}^2$$

Step 5: Calculate the area required for condensation.

Acetone condensation:
$$q = m\Delta H_v = 172(25.1) = 4.32 \times 10^3 \text{ kJ/min}$$

Water temperature change over condenser:
$$\Delta T_{H2O} = q/mC_p$$
$$= 4.32 \times 10^3/69.6(4.19)$$

$$= 14.8 \text{ K}$$

Log mean temperature difference:

$$\Delta T_{lm} = [(56 - 36.8) - (56 - 22)]/\ln[(56\text{-}36.8)/(56 - 22)]$$
$$= (19.2 - 34)/\ln(19.2 \ / 34)$$
$$= 26.2 \text{ K}$$

Area:

$$A = q/U\Delta T_{lm}$$
$$= (4.32 \text{ x}10^3)/(100)(0.34)(26.2)$$
$$= 4.84 \text{ m}^2$$

Step 6: Calculate the area of the subcooler.

$$q = mC_{pL}(56\ \text{-}30)$$
$$= 172(0.13)(56 - 30)$$
$$= 0.58 \text{ x } 10^3 \text{ kJ/min}$$

Water temperature change over subcooler:

$$\Delta T_{H2O} = q/mCp$$
$$= 0.58 \text{ x } 10^3/(69.6)(4.19)$$
$$= 2 \text{ K}$$

Log mean temperature difference:

$$\Delta T_{lm} = [(56 \text{ -}22) - (30 - 20)]/\ln[(56 - 22)/(30 - 20)]$$
$$= 19.7 \text{ K}$$

Area:

$$A = q/U\Delta T_{lm}$$
$$= (0.58 \text{ x}10^3)/(50)(0.34)(19.7)$$
$$= 1.7 \text{ m}^2$$

Step 7: Check overall H₂O temperature change.

$$\Delta T = \Delta T_1 + \Delta T_2 + \Delta T_3$$
$$= 3.2 \text{ K} + 14.8 \text{ K} + 2 \text{ K}$$
$$= 20 \text{ K}$$

Step 8: Calculate the total area.

$$A = A_1 + A_2 + A_3$$
$$= 1.6 + 4.84 + 1.7$$
$$= 8.14 \text{ m}^2$$
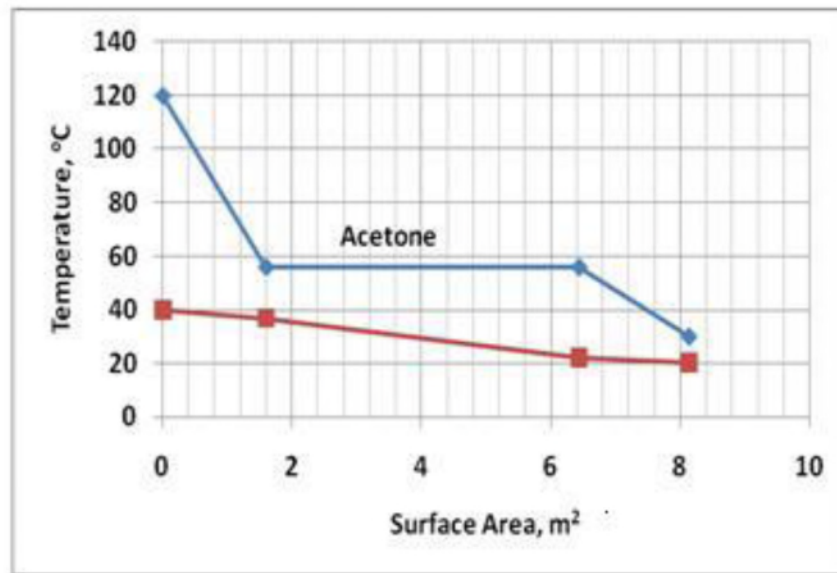
Figure 7-14. Graphical representation of Problem 7-3.

7.5 SUMMARY

CONDENSATION

This chapter covered the following topics:

- The various types of condenser systems.
- Operating principles for condenser systems.
- Factors that influence the capability and sizing of a condenser system.

7.6 REVIEW EXERCISES

INSTRUCTIONS

Select the best response(s) for each of the following multiple-choice questions.

MULTIPLE CHOICE QUESTIONS

Types and Components of Condensers

1. A shell-and-tube condenser using chilled water usually reduces the gas stream temperature to _____.

   a) 80°F to 150°F
   b) 40°F to 80°F
   c) < -100°F
   d) None of the above

2. A refrigeration condenser system usually reduces the gas stream temperature to _____.

   a) < 40°F
   b) < -50°F
   c) < -320°F
   d) None of the above

3. A precondenser is often used in refrigeration and cryogenic systems to_____.

   a) prevent frost buildup on the heat exchanger surfaces of the main contacting chamber
   b) minimize water-organic condensate separation problems
   c) remove the organics prior to the removal of water vapor and other contaminants at high concentration
   d) Answers a and b

4. A cryogenic condenser system usually reduces the gas stream temperature to _____.

   a) -40°F to 80°F
   b) -50°F to -100°F
   c) -50°F to -320°F
   d) None of the above

Operating Principles of Condensers

5. The gas stream exiting a condensation system has an organic vapor partial pressure
_____.

    a) equal to the vapor pressure of the compound at the exit gas temperature
    b) equal to 10% of the partial pressure of the organic compound in the inlet gas stream
    c) approximately 10% of the vapor pressure of the compound at the exit gas temperature
    d) equal to the vapor pressure of water

6. Condensation systems are generally used for_____.

    a) low-concentration, multicomponent organic vapors
    b) high-concentration, multicomponent organic vapors
    c) low-concentration, single-component organic vapor
    d) high-concentration, single-component organic vapor

Capability and Sizing of Condensers

7. Use the Antoine Equation to calculate the vapor pressure of ethyl acetate at 40°F, given the Antoine Constants A= 7.09808, B = 1238.71, and C = 217.00.

8. What is the outlet concentration of ethyl acetate exiting from a surface condenser operating at 40°F?

7.7 REVIEW EXERCISES: SOLUTIONS

This Student Guide includes separate exercises and solutions, which allow students to check their work.

MULTIPLE CHOICE ANSWERS

Types and Components of Condensers

1. A shell-and-tube condenser using chilled water usually reduces the gas stream temperature to _____.

   a) 80°F to 150°F
   b) 40°F to 80°F
   c) < -100°F
   d) None of the above

2. A refrigeration condenser system usually reduces the gas stream temperature to _____.

   a) < 40°F
   b) < -50°F
   c) < -320°F
   d) None of the above

3. A precondenser is often used in refrigeration and cryogenic systems to_____.

   a) prevent frost buildup on the heat exchanger surfaces of the main contacting chamber
   b) minimize water-organic condensate separation problems
   c) remove the organics prior to the removal of water vapor and other contaminants at high concentration
   d) Answers a and b

4. A cryogenic condenser system usually reduces the gas stream temperature to _____.

   a) -40°F to 80°F
   b) -50°F to -100°F
   c) -50°F to -320°F
   d) None of the above

Operating Principles of Condensers

5. The gas stream exiting a condensation system has an organic vapor partial pressure
_____.

   a) **equal to the vapor pressure of the compound at the exit gas temperature**
   b) equal to 10% of the partial pressure of the organic compound in the inlet gas stream
   c) approximately 10% of the vapor pressure of the compound at the exit gas temperature
   d) equal to the vapor pressure of water

6. Condensation systems are generally used for_____.

   a) low-concentration, multicomponent organic vapors
   b) high-concentration, multicomponent organic vapors
   c) low-concentration, single-component organic vapor
   d) **high-concentration, single-component organic vapor**

Capability and Sizing of Condensers

7. Use the Antoine equation to calculate the vapor pressure of ethyl acetate at 40°F, given the Antoine constants A= 7.09808, B = 1238.71, and C = 217.00.

SOLUTION

Step 1. Convert the temperature to °C.

°C = (°F - 32)/1.8 = (40 – 32)/1.8 = 4.4°C

Step 2. Calculate the log10 P using the Antoine equation (Equation 7-1).

$$\log_{10} P* = 7.09808 - \left[\frac{1238.71}{217.00 + 4.4} \right] = 1.50318$$

Step 3. Calculate the vapor pressure.

$P* = 10^{1.50} = 31.86$ mm Hg

8. What is the outlet concentration of ethyl acetate exiting from a surface condenser operating at 40°F?

SOLUTION

Use the vapor pressure for ethyl acetate at 40°F calculated in Exercise 7.

P* = 31.86

$$\frac{P^*}{P} = \frac{31.86 \text{ mm Hg}}{760 \text{ mm Hg}} = 0.042 = 41,921.1 \, \text{ppm}$$

7.8 REFERENCES

1   Barbour, W., et al. OAQPS Control Cost Manual, 4th ed., Supplement 2; EPA 450/3-90-006b; October 1992.

2   Bell, K.J.; Ghaly, M.A. An Approximate Generalized Design Method for Multicompartment/Partial Condensers; American Institute of Chemical Engineers Symposium Series; American Institute of Chemical Engineers: New York, 1972; Vol. 69, No. 131, pp 72-79.

3   Henzler, G.W.; Sameshima, G.T. Cryogenic Vapor Recovery of VOC Emissions; Paper 93-TP-51.02, presented at the 86th Annual Meeting and Exhibition of the Air & Waste Management Association, Denver, CO, June 13-18, 1993; Liquid Carbonic Industries Corporation: Northville, MI, 1993.

4   Perry, J.H., Ed. Chemical Engineers Handbook, 5th ed.; McGraw Hill: New York, 1973.

5.   Spencer, R.J. Cryogenic Condensation and Recovery of VOCs; Paper 92-114.10, presented at the 85th Annual Meeting & Exhibition of the Air & Waste Management Association, Kansas City, MO, June 21-16, 1992; Liquid Carbonic Corporation: Chicago, 1992.

8.0 CONTROL TECHNIQUES FOR NITROGEN OXIDES

8.1 OVERVIEW

INTRODUCTION

Nitrogen oxides (NO_x) are formed during the combustion of fuel in the presence of air. NO_x is a generic term for mono-nitrogen oxides NO and NO_2 (nitric oxide and nitrogen dioxide). At elevated temperatures, nitrogen from the air and the fuel reacts with oxygen to form nitrogen oxides. NO_x emissions are formed by three complex chemical processes occurring during combustion of fuel in the presence of air.

At elevated temperatures, NO_x emissions are formed by:

- thermal fixation of molecular nitrogen in the combustion air,
- oxidation of nitrogen contained in the fuel, and
- formation of "prompt" nitrogen due to the presence of partially oxidized organic species present within the flame.

These three separate reaction mechanisms are usually referenced by the abbreviated terms: "thermal," "fuel," and "prompt" NO_x.

The complex sets of reactions responsible for nitrogen oxides generation are very sensitive to high oxygen concentrations and high gas temperatures in the combustion zone. Nitrogen oxides emissions are highest during high boiler or incinerator loads because the highest gas temperatures occur under these conditions.

Approximately 90 to 95% of the nitrogen oxides generated in combustion processes are in the form of nitric oxide (NO). Once in the atmosphere, the NO reacts in a variety of photochemical and thermal reactions to form NO_2. Accordingly, the total mass emissions of nitrogen oxides from the unit are usually expressed in the form of NO_2.

LEARNING OBJECTIVES

At the conclusion of this training, students will be able to:
- Recognize the mechanisms that create nitrogen oxides.
- Identify sources of nitrogen oxides.
- Identify the types and components for controlling nitrogen oxide.

8.2 NITROGEN OXIDES FORMATION

THERMAL NO$_X$ FORMATION MECHANISMS

When fossil fuels are burned with air in a combustion process, some of the oxygen (O_2) and nitrogen (N_2) combine to form nitric oxide (NO) and nitrogen dioxide (NO_2) in the high temperature zones of the burner flame. There are a large number of reactions involved in the formation of nitric oxide, and the overall reaction process is approximated by a set of reactions termed the Zeldovich Mechanism. The result of these simultaneous and interacting chemical reactions is indicated by Reaction 8-1.

Reaction 8-1 $$N_2 + O_2 \leftrightarrow 2\,NO$$
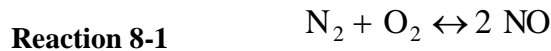
While this is a reversible process, the rate of NO decomposition back to molecular nitrogen and oxygen is extremely slow. Instead, the NO reacts with more oxygen to form NO_2. This oxidation process is also the result of a large number of simultaneous thermal and free radical reactions that occur in the high temperature area of the combustion process. Summary Reaction 8-2 shows the net result of these reactions.

$$NO + \frac{1}{2}\,O_2 \leftrightarrow NO_2$$
Reaction 8-2
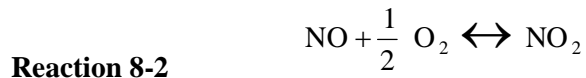
The main factors affecting the quantity of NO$_x$ formed by thermal fixation are (1) the flame temperature, (2) the residence time of the combustion gases in the peak temperature zone of the flame, and (3) the amount of oxygen present in the peak temperature zone of the flame.

In some combustion processes, peak flame temperatures can exceed 2,500°F (1,371°C). At these high temperatures, NO is formed in great abundance (sometimes greater than 1,000 ppm). The residence time existing at this peak temperature is usually too short for an appreciable fraction (usually less than 5%) of the NO to be oxidized to NO_2.

The formation of thermal NO$_x$ can be reduced in three ways:

- reduction of the oxygen concentration in the maximum temperature zone,
- reduction of the peak flame temperature, and/or
- reduction of the residence time of the combustion gases at the peak temperature.[2]

These are accomplished by various combustion modification techniques such as the use of low excess air, staged combustion, reduced air preheat, or flue gas recirculation.

FUEL NOₓ FORMATION MECHANISMS

The oxidation of nitrogen compounds contained in fossil fuel can create appreciable concentrations of NO and NO_2. The concentration of NOx developed from the fuel nitrogen is partially dependent on the nitrogen content of the fuel. However, this relationship is neither linear nor simple.

In fuels such as coal and heavy oil that are high in nitrogen content, approximately 20-60% of the fuel-bound nitrogen is oxidized.[2] The concentrations can vary from as low as 1.5 to 2%. As the nitrogen content of the fuel increases, the fraction of the fuel nitrogen converted to NOx often decreases. The rate of NOx formation due to fuel nitrogen is strongly affected by the local oxygen concentration present in the flame and by the mixing rate of the fuel and air. Thus, as with thermal NOx, fuel NO is dominated by the local combustion conditions.

One way to reduce fuel NO_x emissions is to reduce the nitrogen content in the fuel. This is not always possible, and, therefore, combustion modification techniques are used to reduce NO_x emissions. These include combining the use of low excess air firing, low NO_x burner designs, staged combustion, and/or high air preheat (secondary air preheat).

PROMPT NOₓ FORMATION MECHANISMS

NO_x can also form due to the reaction of molecular nitrogen with free radicals such as HCN, NH, and N present in the burner flame.[3] These reactions are not sensitive to the peak gas temperature. Therefore, combustion modifications do not have a strong influence on the NO_x formed by this mechanism.

CALCULATING NITROGEN OXIDES EMISSIONS

Most stationary source combustion processes emit approximately 95% of the total NO_x in the form of NO with the remainder being NO_2 (see Figure 8-1). However, due to the relatively rapid and complete conversion of NO to NO_2 in the atmosphere, the total emissions are calculated as if the emissions were entirely in the form of nitrogen dioxide.
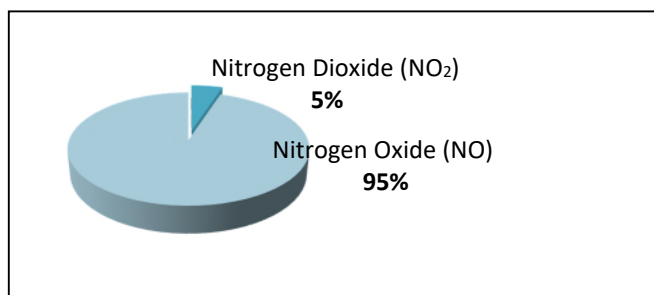
Figure 8-1. Distribution of Nitrogen Oxides Emissions.

8.3 SOURCES OF NITROGEN OXIDES

This section provides an introduction to some of the major combustion processes that require NO$_x$ control techniques. An understanding of the basic operation of these units is necessary since modification of combustion conditions is one of the main NO$_x$ control approaches.

PULVERIZED COAL-FIRED BOILERS

Pulverized boilers are economical primarily for large industrial and utility power stations. The coal is pulverized prior to combustion to a size range that is at least 70% less than 200 mesh. In this size range, the coal can be burned entirely in suspension in the flame of the coal burner. Combustion occurs in a large refractory-lined furnace with boiler tubes for steam generation.

There are a wide variety of designs based on the arrangement of the burners.

- Front-fired
- Opposed (front and back walls)
- Tangential (four corners)

The arrangement of the burners has an impact on the generation of NO$_x$ due to the differences in the maximum gas temperatures generated in the burner flames. As shown in Figure 8-2, each boiler has a number of separate coal burners.
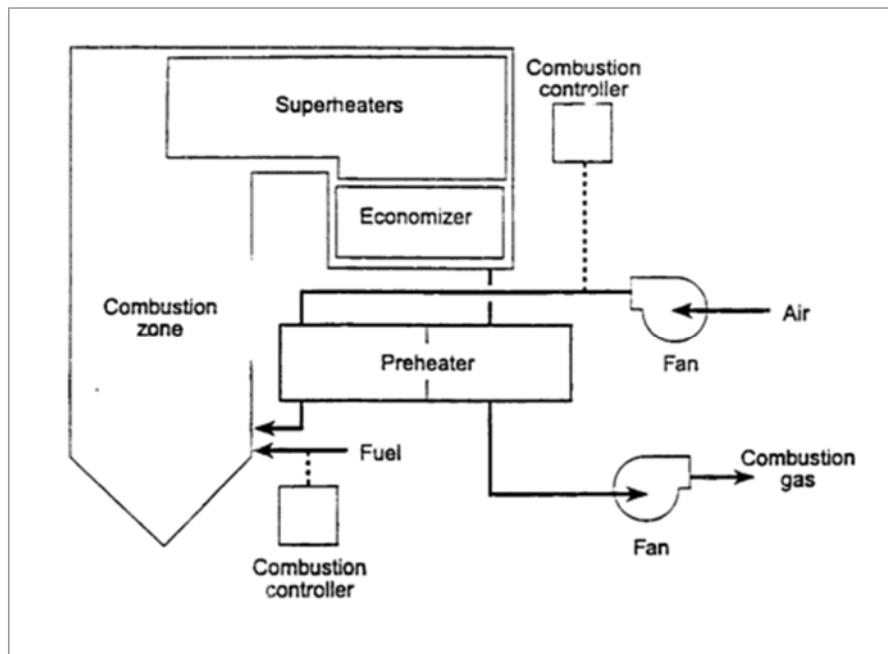
Figure 8-2. Pulverized coal-fired boiler.

Combustion air is supplied by forced draft fans. The air is heated in either rotary or tube-type air preheaters and injected into the pulverizers to suspend the fuel. The combustion air and coal particles are transported to each of the burners. Air flow to each of the burners is controlled by a set of air registers.

Fossil fuel-fired boilers have heat recovery systems to convert the thermal energy in the gas stream into steam. The steam is generated in boiler tubes that usually line the entire combustion zone and are arranged in tube banks throughout the upper portions of the boiler or incinerator. These tubes are connected to a set of large drums inside the unit that distribute the water and the partially heated steam to the appropriate areas of the system. The layout and functions of each of the tube sections and the drums are beyond the scope of this course, due in part to the diversity of boiler designs. However, the basic functions of some of the most common heat exchange areas are summarized in the following list.

- Superheater - heats steam to temperatures and pressures well above saturation levels in order to operate the first pass of the steam turbine
- Reheater - heats steam released from the first stage of the turbine to increase the steam pressures and temperatures to the levels necessary for the later stages of the turbine
- Economizer - heats feedwater returning from the condensers for the purpose of energy recovery
- Air Preheater - heats combustion air from the forced draft fan prior to the burners for the purpose of energy recovery

Typical combustion product gas stream ("flue gas") temperatures for gases entering the superheater and reheater areas are usually in the range of 1,800°F to 2,200°F (982°C to 1204°C). The peak combustion gas stream temperatures in the burner flames can be more than 3,000°F (1649°C). Flue gas temperatures leaving the air preheater are usually in the range of 250°F to 350°F (121°C to 177°C).

A significant fraction of the ash in the coal is removed from the bottom of the boiler furnace and is termed "bottom ash." When the ash fusion temperature is relatively high, this ash is entirely in solid form. Units that remove ash in this form are called "dry bottom." Pulverized coal-fired boilers designed for low ash fusion that remove the bottom ash in the molten state are termed "wet bottom."

Considerable progress has been achieved since 1970 in the reduction of NO_x emissions from pulverized coal-fired boilers. A variety of combustion modification techniques have been demonstrated.

- Low excess air combustion
- Off stoichiometric combustion
- Flue gas recirculation
- Low NO_x burners
- Gas reburning

The operating principles and general NO_x reduction efficiencies for these combustion modifications are discussed later.

OIL-AND GAS-FIRED BOILERS

A large industrial or utility scale oil- or gas-fired boiler is very similar to a pulverized coal boiler. There is an array of burners mounted in a boiler tube lined furnace area. Heat exchange and heat recovery equipment are used to generate steam and to reduce the flue gas temperatures.

The primary differences between oil- and gas-fired boilers and pulverized coal boilers are the geometry of the furnace area, the size of the furnace volume, and the type of burners. Essentially all of the small quantities of ash (oil-fired only) entering with the fuel are emitted as flyash. The flyash from oil-fired units usually has a quite different composition than that generated in coal-fired boilers. Gas-fired units have negligible ash emissions.

There are two main types of oil used in large installations. No. 6 oil is a residual oil with a relatively high sulfur and ash content. No. 2 oil, kerosene, has a low sulfur and ash content. Combustion modifications appropriate for oil-fired boilers are similar to those used for pulverized coal-fired boilers: low excess air operation, off-stoichiometric firing, flue gas recirculation, and gas reburning.

GAS TURBINE APPLICATIONS

Gas turbines burn natural gas, distillate oil, and other fuels to generate electricity and steam and are used for a variety of quite different applications. The options available for minimizing pollutant emissions vary for these different applications.

Peaking Service

Units used primarily for satisfying peak electrical demand often operate a relatively small number of hours per year. Exhaust gases from these units are often discharged directly to the atmosphere and are difficult to control due to the limited operating time and the high temperatures in the flue gas stream.

Cogeneration Systems

These units are relatively large and operate on a relatively stable load. Accordingly, they are amenable to advanced pollutant control techniques. To a certain extent, the increased number of cogeneration units is due to the Public Utilities Regulatory Policies Act, which mandated that utilities must purchase excess electrical power generated at these stations.

Gas Compressor Stations

Gas turbines at pipeline compressor stations are used to provide electrical power for the compressor at the remote pipeline station. These are relatively small units.

Emergency Service

Gas turbines can be used to provide power for emergency pumps and electrical power. These units are usually not subject to air pollution control requirements.

Figure 8-3 is a schematic of a simple cycle type gas turbine. The fuel is burned in a parallel set of combustion chambers. Exhaust gases at temperatures of 900°F to 1,000°F (482°C to 538°C) are exhausted directly to the atmosphere.
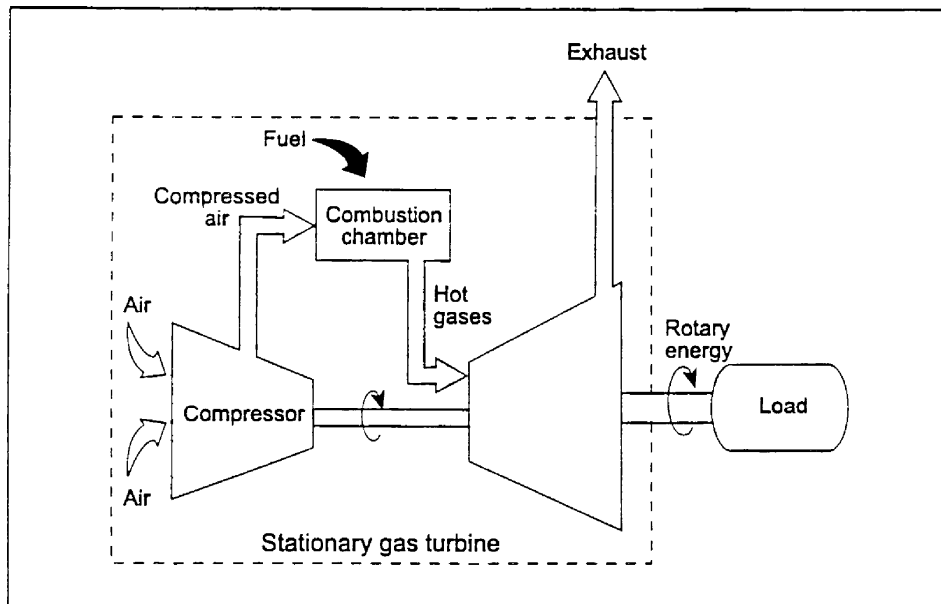
Figure 8-3. Simple cycle gas turbine.

This type of arrangement is used in some old installations intended for peaking service. It has a relatively low thermal efficiency due to the loss of the sensible heat in the hot exhaust gases. Simple cycle turbines may also include a heat recovery steam generator to produce low pressure steam.

A simplified schematic of a combined cycle gas turbine system is shown in Figure 8-4. The waste heat boiler section is a conventional boiler tube heat exchanger. This boiler generates steam that can be used to generate electrical power and can also be exported for process use or space heating. The facility is termed a cogeneration unit when both electrical power and steam are generated.

Combined cycle turbines can be equipped with a duct burner to increase the gas temperature of the exhaust gases entering the waste heat boiler. The duct burners generally use natural gas as a fuel. They increase the gas temperature to more than 1,800°F (982°C) so that more steam can be generated. Oxygen in the turbine exhaust gas stream is used for combustion of the natural gas in the duct burner.

A conventional combustor for a gas turbine is shown in Figure 8-5. A number of these combustors are used on the gas turbine to generate the high temperature, high pressure exhaust gases necessary for the turbine located downstream. The combustion air is supplied under pressure from the upstream compressor.

Conventional combustors use a diffusion-type flame. The air and fuel are mixed in proportions that are very close to the stoichiometric level. Accordingly the peak gas temperatures are very high. Typical NO_x concentrations at full load average 175 ppm, and some units exceed 400 ppm.
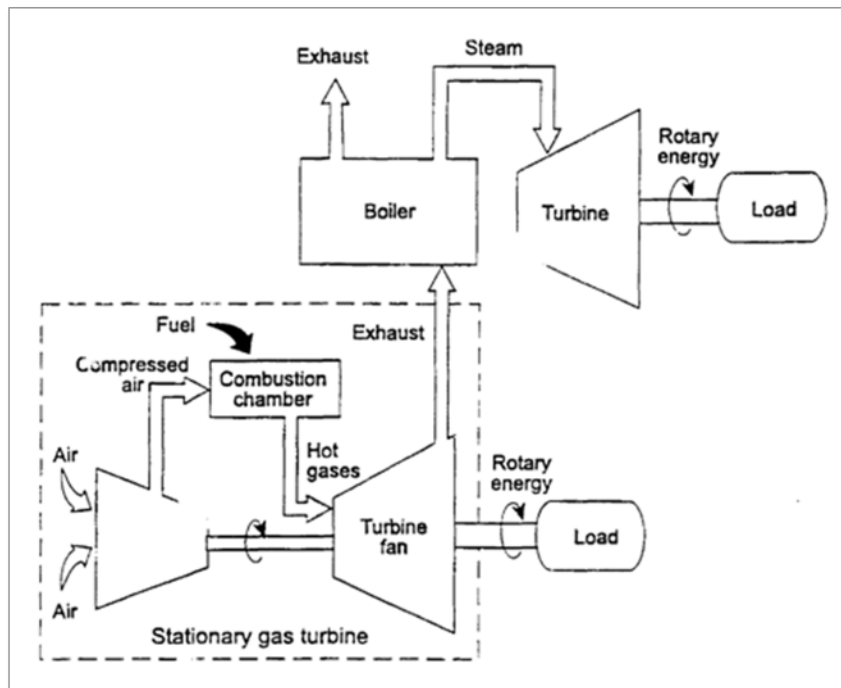
Figure 8-4. Combined cycle gas turbine

Conventional gas turbines use water or steam injection to minimize NO_x emissions. They dilute the combustion uses and thereby reduce the peak temperatures. The water vapor also reduces the retention time of the combustion gases in the reaction zone. Both factors act to reduce the NO_x formation rate. However, water or steam injection can increase carbon monoxide emissions by decreasing the oxidation rates.
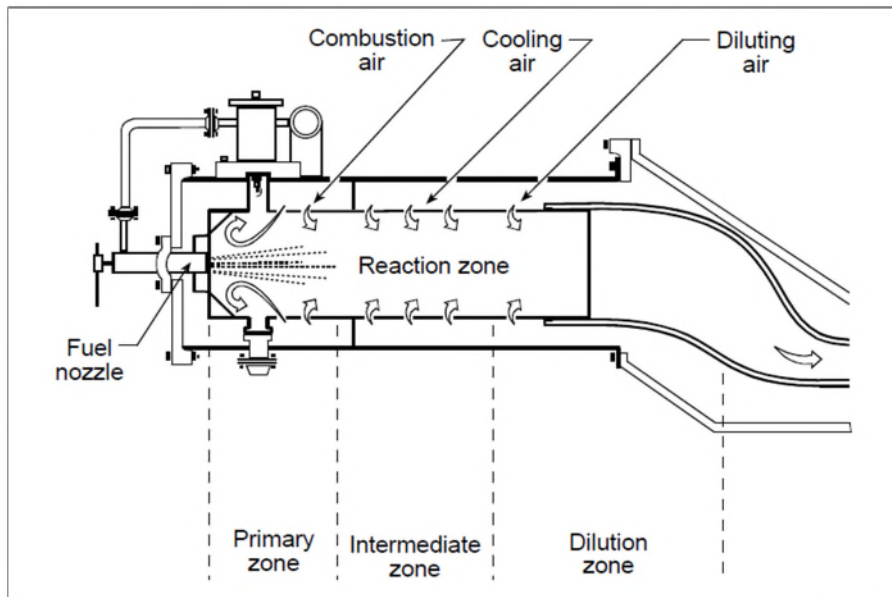
Figure 8-5. Typical combustor.

There have been substantial advances in gas turbine design and air pollution control techniques in recent years. New combustion chamber designs have been commercialized to allow low NO_x concentrations without the use of steam injection into the combustion chambers. These are termed "dry" systems.

The conventional "wet" systems that suppress NO_x formation by water or steam injection have been enhanced by the addition of Selective Catalytic Reduction (SCR) systems. The SCR systems can reduce the NO_x emissions by 80-90%. Slight ammonia emissions, termed ammonia slip, can be created by the SCR system. Catalytic reduction systems have been developed to reduce carbon monoxide emissions. These various NO_x control techniques are discussed later.

MUNICIPAL WASTE INCINERATORS

The sloped, reciprocating grate waste incinerator shown in Figure 8-7 is a common type of municipal waste incinerator. The wastes move through the unit due to the slope of the grate and the reciprocating (back-and-forth) movement of the grate sections. Wastes are deposited on the upper sections of the grate from a chute that is loaded by an overhead crane. There are at least four undergrate plenums used to adjust the underfire air rates to the different rates of combustion in the incinerator. Low air flow rates are used in the first zone (drying and ignition) and in the last zone (ash burnout). As indicated in Figure 8-6, the air flow rates are adjusted using dampers in the air supply ducts to the plenums. Ash and residue are discharged from the grate into an ashpit. The ash is quenched and continually removed by a conveyor.
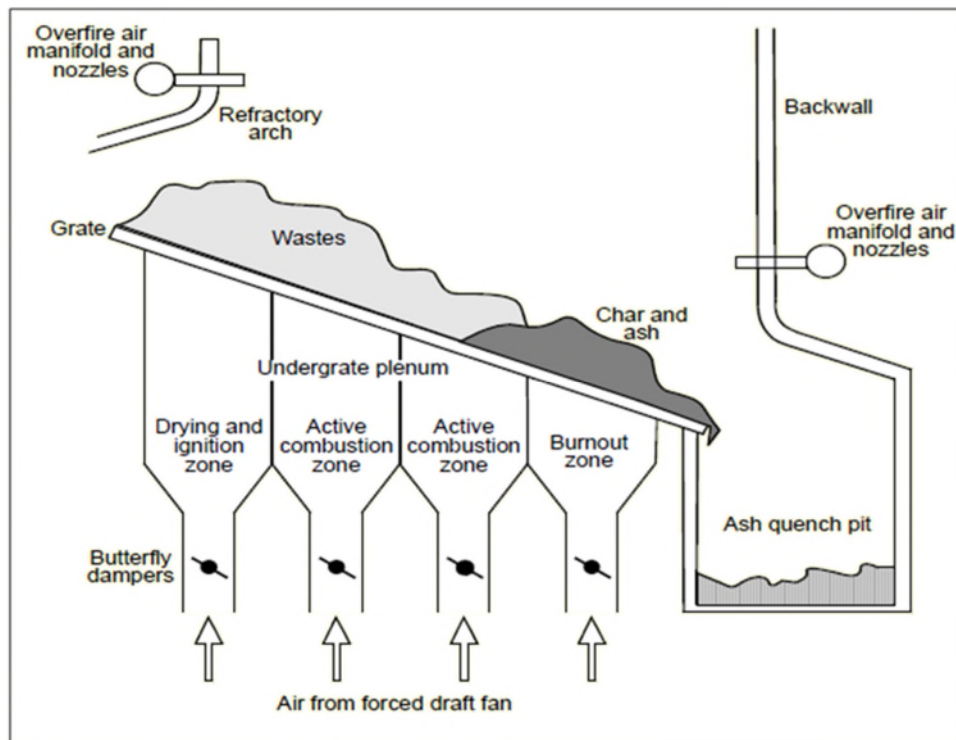
Figure 8-6. Municipal waste incinerator.

Waste nitrogen levels can be high and can vary substantially on a seasonal basis. Yard waste and other vegetation are the primary nitrogen containing materials entering the incinerator feed stream.

Due to the differences in the combustion process, many of the combustion modifications used successfully on fossil fuel-fired boilers and gas turbines are not directly applicable to waste incinerators. For example, low NO_x burners can only be used for the supplemental heat burners that are used for start-up and for short term periods when the incinerator furnace temperatures are low. Other conventional combustion modification such as flue gas recirculation and off-stoichiametric combustion are also difficult to apply to waste incinerators. Accordingly, NO_x is usually controlled by add-on control systems.

COAL-AND WOOD-FIRED SPREADER STOKER BOILERS

These boilers are relatively large and have steam capacities ranging from 40,000 to more than 400,000 pounds of steam per hour. They can change load rapidly and are often used in process operations where there are rapidly changing steam demands due to cyclic operations.

Coal or wood is fed from fuel bunkers into mechanical feeders at the front of the boiler. There are usually between two and six independent feeders. The fuel is flung outward and distributed uniformly on a grate that moves toward the front of the boiler. Combustion air is introduced through a single undergrate air plenum and a set of overfire air nozzles on the front and back walls of the boiler. A sketch of a spreader stoker is provided in Figure 8-8.
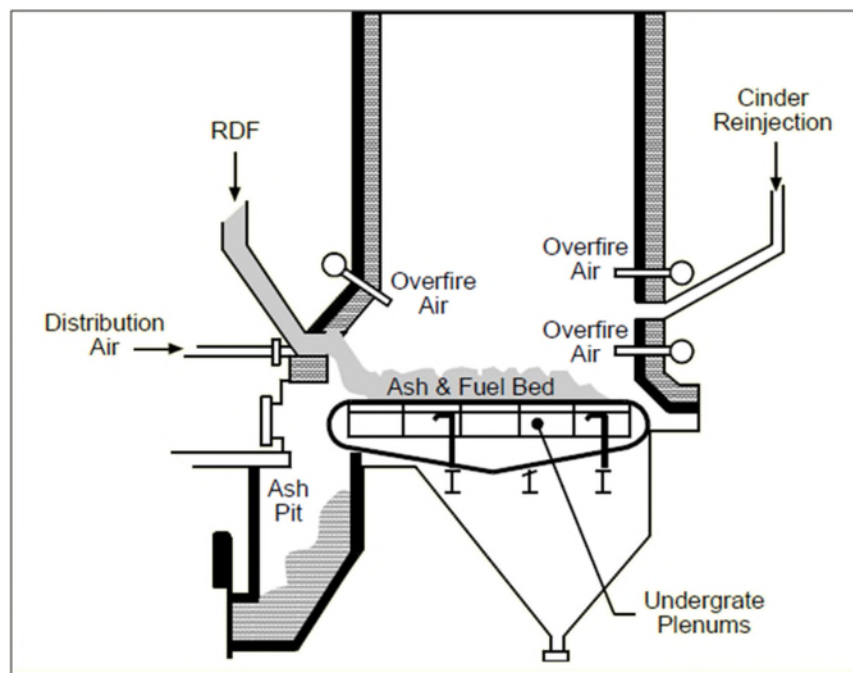
Figure 8-7. Coal or wood-fired spreader stoker boiler.

Approximately 30% of the fuel or waste is burned while the particles are in suspension during feeding. The remainder of the fuel burns on the bed. Overfire air ports are usually located at

several elevations on the back wall and on at least one elevation on the front wall. These ports provide air for combustion of the fuel being burned in suspension and for combustion of volatile matter released from the coal or wood burning on the grates.

Due to the characteristics of the combustion process, it is also difficult to suppress NO_x formation using the types of combustion modifications applied to pulverized coal-, oil-, or gas-fired boilers. NO_x control, if required, will usually have to be achieved by means of add-on control systems such as selective non-catalytic reduction (SNCR) and SCR units.

8.4 TYPES AND COMPONENTS OF NO$_X$ CONTROL TECHNIQUES

NO$_X$ CONTROL TECHNIQUES

The techniques used to minimize NO_x emission from stationary source combustion processes can be divided into three categories: (1) combustion modifications, (2) control systems, and (3) fuel switching: Combustion modifications prevent the emission of NO_x by creating conditions that inhibit the NO_x formation reactions or that cause the NO_x formed to be reduced back to molecular nitrogen, while the gasses remain in the high temperature furnace area. The add-on control systems inject an ammonia or urea reagent to chemically reduce the NO_x to molecular nitrogen in an area of the combustion process downstream of the furnace. Fuel switching involves the use of a fuel that inherently has low NO_x generating rates due to its combustion characteristics or fuel nitrogen characteristics.

Combustion Modifications

All of the combustion modifications attempt to suppress the formation of NO_x by controlling the peak flame temperatures, oxygen concentrations, and residence times in the active combustion zones. In essence, the distribution of the air and fuel is modified to reduce the rate of formation reactions and to create conditions that preclude these reactions.

There are practical limits to essentially all of the combustion modification techniques for suppressing NO_x formation. These limits include carbon monoxide formation, increased combustible levels in the ash, boiler tube fouling, and corrosion.[3]

Low Excess Air Combustion

In a combustion system, a certain amount of excess air is required to ensure complete combustion of the fuel. The more efficient the burners are for air and fuel mixing, the less excess air is needed.

The level of excess air in an industrial or utility boiler will usually range from 3% to as high as 100%, depending on the type of fossil fuel and the boiler operating load. Gas-fired boilers can operate with excess air levels as low as 3-5% when the unit is near full load. Oil-fired units typically operate at excess air rates of 5-20%, depending on the type of oil and the load conditions. Pulverized coal-fired boilers operate at excess air rates of 20-50%. Obviously, the ability to utilize low excess air firing depends on the fuel characteristics. In essence, gas-fired boilers and most oil-fired boilers inherently use low excess air firing. In the case of pulverized

coal-fired boilers, the ability to decrease excess air levels depends on the burner design characteristics, the variability of the coal quality, and the variability of the load.

Low excess operation is not readily adapted to processes such as waste incinerators and spreader stoker boilers. In these cases, high excess air levels are needed for proper fuel burning on the grates. Low excess air firing practices reduce NO_x emissions by reducing the oxygen concentrations in the portion of the burner flame where gas temperatures are at a maximum. This inhibits the sets of reactions responsible for both thermal and fuel NO_x. This method is easy to implement and actually slightly increases the efficiency of the furnace. However, there are problems with this combustion modification. Very low excess air firing can produce increased particulate and CO emissions, and fouling and slagging of boiler tube surfaces can occur if excess air levels are too low.

Low excess air firing practices are used in conjunction with other NO_x combustion modification techniques. However, there are definite limits to the minimum excess air levels in these cases since minimum quantities of combustion air are needed for proper operation of low NO_x burners and other techniques based primarily on off-stoichiometric combustion.3

NOx reductions averaging between 16% and 20% can be achieved on gas- and oil-fired utility boilers when the excess air is reduced to a level between 2% and 7%.[4] NO_x reductions averaging around 20% can be achieved on coal-fired utility boilers if the excess air is reduced to the 20% leve1.[4] Reactions 8-3 through 8-5 are reaction equations for low excess air combustion to be used in the problems below.

Reaction 8-3 $\qquad C + O_2 \rightarrow CO_2$

Reaction 8-4 $\qquad 2H + \dfrac{1}{2} O_2 \rightarrow H_2O$

Reaction 8-5 $\qquad S + O_2 \rightarrow SO_2$
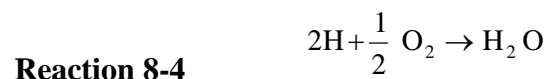
Off-Stoichiometric Combustion

During off-stoichiometric combustion, air and fuel mixtures are combusted in two separate zones. In one zone, the fuel is fired with less than a stoichiometric amount of air. This creates a fuel-rich local zone in the region of the primary flame. The second zone is an air-rich zone where the remainder of the combustion air is introduced to complete the combustion of the fuel. The heat in the primary flame zone is not as intense as with normal firing because combustion is incomplete. The air mixed with the fuel is sub-stoichiometric in the NO forming region of the flame, thus creating a low NO condition.

Staged combustion reduces NOx emissions by a combination of several factors. First, a lack of available oxygen for NO_x formation **in** the fuel-rich stage is due to off-stoichiometric firing. Second, the flame temperature may be lower in the first stage than in single stage combustion. Third, the peak temperature in the second stage (air-rich) is lower. Staged

combustion is an effective technique for controlling both thermal and fuel NO_x due to its ability to control the mixing of fuel with combustion air. The NO_x reduction effectiveness depends on good burner operation to prevent convective boiler tube fouling, unburned hydrocarbon emissions, and poor ignition characteristics that occasionally occur at excessively fuel-rich boiler operations Fire-side boiler tube corrosion may occur when burning some coals or heavy oils under staged combustion conditions.

Figure 8-8 illustrates how staged combustion may be accomplished by using overfire air ports (often abbreviated OFA). These are separate air injection nozzles located above the burners. The burners are operated fuel-rich and the overfire air ports maintain the remainder of the combustion.
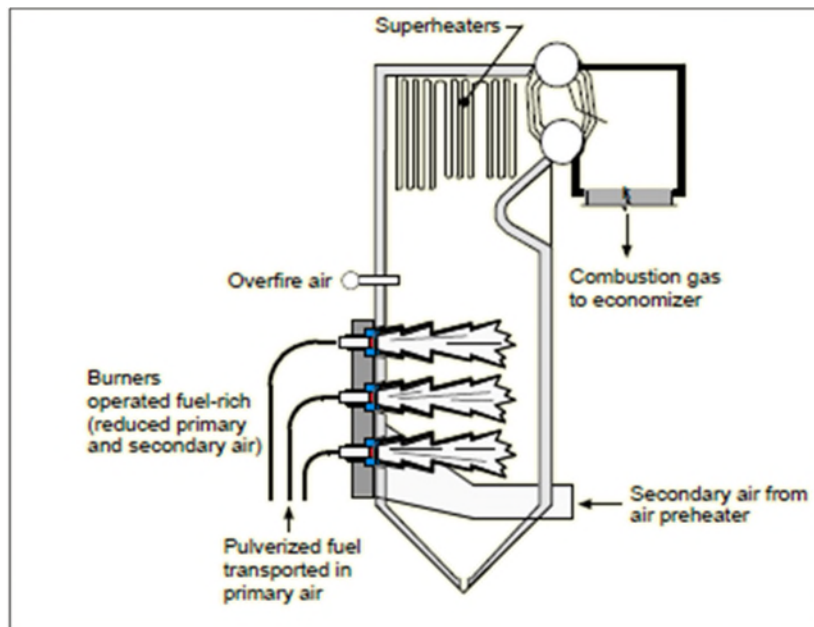
Figure 8-8. Off-stochiometric combustion using overfire air ports.

Flue Gas Recirculation

Flue gas recirculation (FGR) has been used to reduce thermal NO_x emissions from large coal-, oil-, and gas-fired boilers. A portion (10-30%) of the flue gas exhaust is recycled back into the main combustion chamber by removing it from the stack and breeching and mixing it with the secondary air entering the windbox (Figure 8-9). In order for FGR to be effective in reducing NO_x emissions, the gas must enter directly into the combustion zone. This recirculated gas lowers the flame temperature and dilutes the oxygen content of the combustion air, thus lowering NO_x emissions.
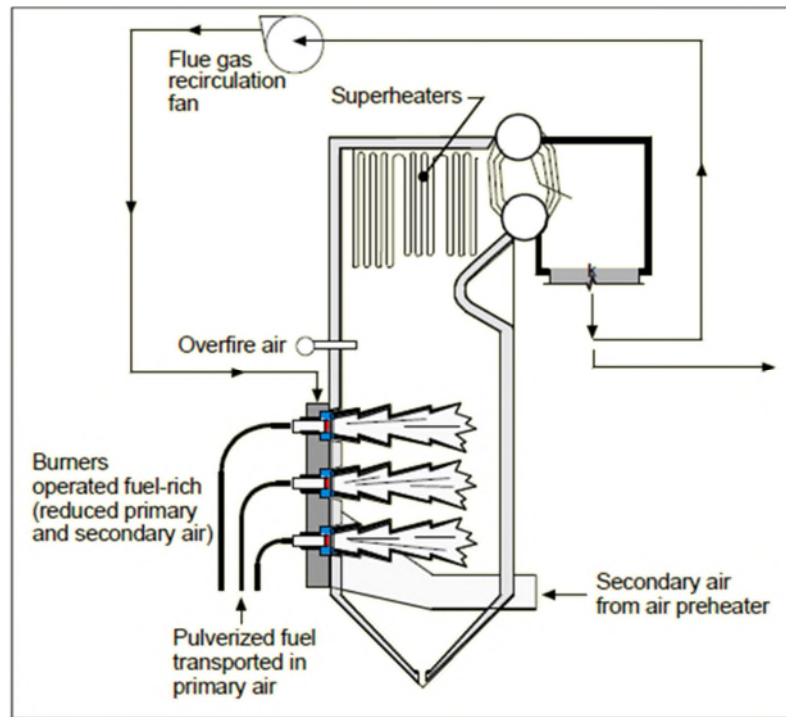
Figure 8-9. Flue gas recirculation (FGR).

Some operational problems can occur using FGR. Possible flame instability, loss of heat exchanger efficiency, and condensation of partially oxidized compounds on internal heat transfer surfaces limit the usefulness of gas recirculation.

FGR requires greater capital expenditures than for low excess air and staged combustion modifications. High temperature fans (forced or induced draft), ducts, and large spaces are required for recirculating the gas.

NO_x reduction of approximately 40-50% is possible with recirculation of 20-30% of the exhaust gas in gas- and oil-fired boilers. At high rates of recirculation (approximately 30%), the flame can become unstable. thus increasing carbon monoxide and partially oxidized organic compound emissions.

Low NO$_x$ Burners

Low NO_x burners have been developed by a large number of manufacturers to reduce NO_x emissions. Burners control mixing of fuel and air in a pattern that keep flame temperature low and dissipates the heat quickly.

Some burners are designed to control the flame shape in order to minimize the reaction of nitrogen and oxygen at peak flame temperatures. Other designs have fuel-rich and air-rich regions to reduce flame temperature and oxygen availability.

The Dual Register Low NO_x burner is shown in Figure 8-10. The mixture of pulverized coal and primary air is controlled to slightly delay combustion of the fuel. The remainder of the combustion air (secondary air) is introduced through two concentric air zones that surround

the coal nozzle.
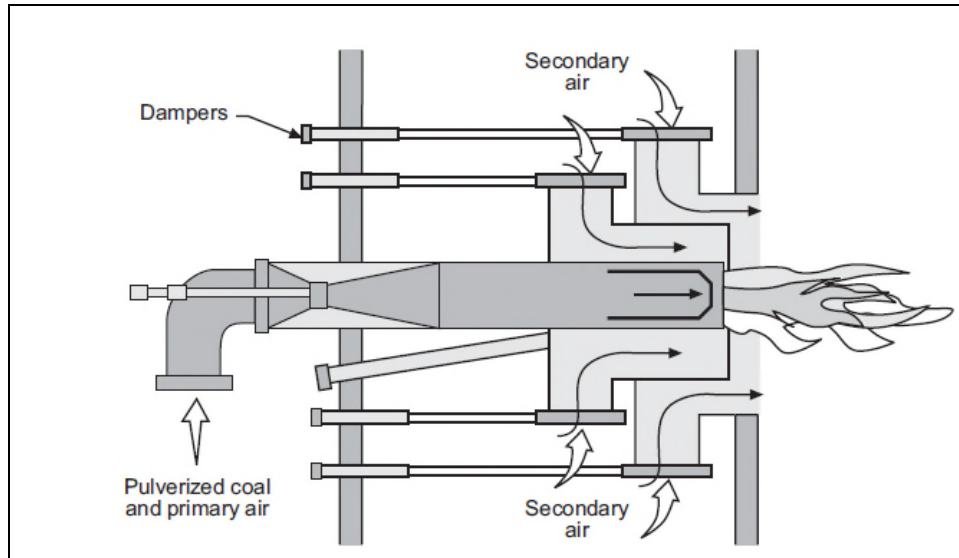
Figure 8-90. Example of a dual register low NO$_x$ burner.

The flame produced by a low NO$_x$ burner is elongated compared to the short intense flame produced in a conventional burner. The peak flame temperature is reduced, thus lowering thermal NO$_x$ emissions, and the oxygen available in the flame is lower, thus reducing fuel NO$_x$ emissions.

First generation low NO$_x$ burners demonstrated NO$_x$ reduction efficiencies of 35-45%.[6] Continued improvements in the technology have produced current generation ultra low NO$_x$ burners that have efficiencies approaching 80% and outlet concentrations less than 10 ppm.

Recent improvements in flame scanners may allow improved performance of Low-NO$_x$ burners and other combustion modification techniques in the future. Previously, these scanners were used to rapidly shut down fuel flow to a burner in the event that the flame was extinguished. Scanners are also being developed to monitor the average flame intensity, flame ignition point, stability at the ignition point, and size of the fuel stream.' This data can be used to optimize the burner performance and to identify burners that are not operating properly.

Gas Reburning in Fossil Fuel-Fired Boilers

Gas reburning involves the use of separate gas-fired burners in the upper portions of the combustion chamber (Figure 8-11). Approximately 10-15% of the fuel demand of the boiler is supplied by these gas-fired burners rather than the pulverized coal burners.[1] The gas burners are operated slightly fuel-rich so that conditions favorable for reducing NO$_x$ formed in the lower array of coal burner flames are possible.[1] The fuel/air stoichiometry is an important operating parameter, and it is usually 0.9 to 1.0.[3] Additional combustion air is supplied above the gas burners so that combustion of the fuel can be completed. Accordingly, gas reburning systems incorporate off-stoichiometric firing practices.
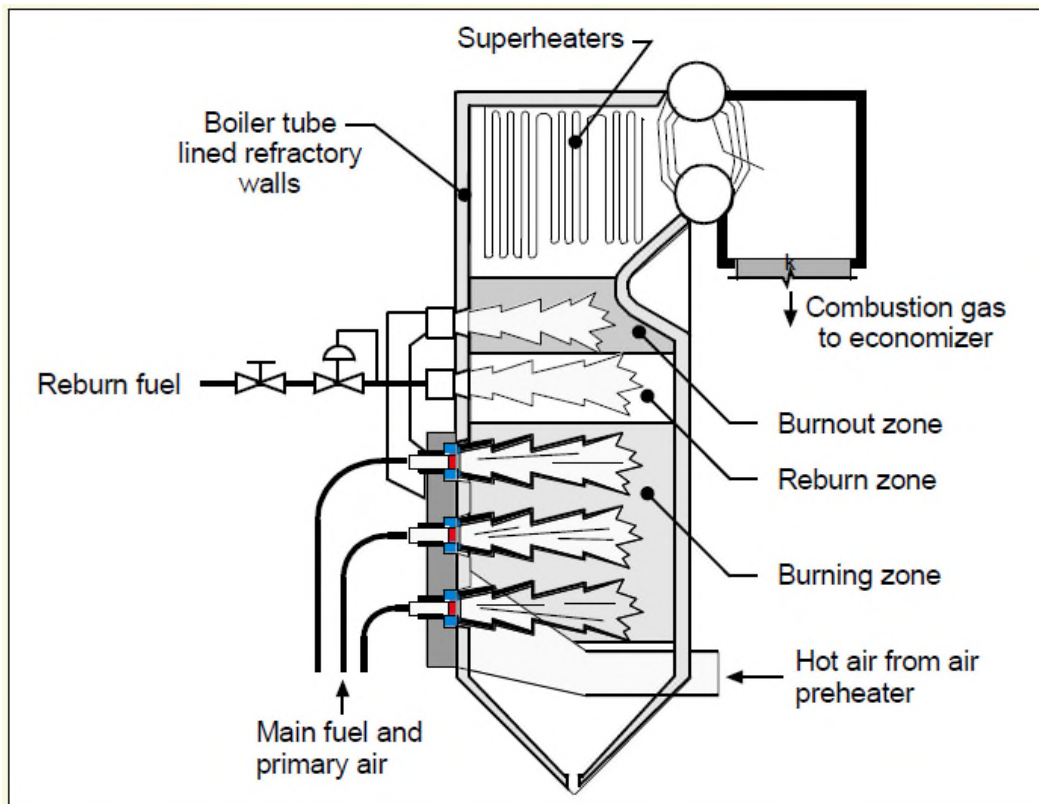
Figure 8-101. Gas Reburning.

Gas Reburning in Fossil Fuel-Fired Boilers

Gas reburning involves the use of separate gas-fired burners in the upper portions of the combustion chamber (Figure 8-13). Approximately 10-15% of the fuel demand of the boiler is supplied by these gas-fired burners rather than the pulverized coal burners.[1] The gas burners are operated slightly fuel-rich so that conditions favorable for reducing NO_x formed in the lower array of coal burner flames are possible.[1] The fuel/air stoichiometry is an important operating parameter, and it is usually 0.9 to 1.0.[3] Additional combustion air is supplied above the gas burners so that combustion of the fuel can be completed. Accordingly, gas reburning systems incorporate off-stoichiometric firing practices.

All types of coal-fired units can utilize gas reburning. However, there must be sufficient room above the elevation of the main coal burners to install the gas burners and the overfire air ports.[11]

NO_x reductions of 50-70% at full boiler load have been demonstrated with gas reburning on coal- and oil-fired boilers.[10,11]

Other Combustion Modification Techniques

Other combustion modifications that can reduce NO_x emissions from combustion sources include reduced air preheat and load reduction. Reduced air preheat and load reduction are used sparingly in large boilers due to the energy penalty involved and the relatively low emission reduction.

GAS TURBINE COMBUSTORS

Lean, Pre-Mixed

The most common type of dry combustor is the lean, pre-mixed design. These operate with a very lean fuel-air mixture to minimize NO_x formation. Lean mixtures burn at lower peak gas temperatures than the conventional diffusion burners that operate at an air-fuel stoichiometric ratio close to 1.0.

The combustion air and the fuel are mixed prior to injection into the combustion zone. This reduces localized high concentrations that contribute to thermal NO_x formation .[8]

A conventional diffusional burner-type pilot flame is used to ensure that the lean mixture does not "black-out."[8] At very low load, the pilot burner is used instead of the premix burner to maintain gas turbine load. Due to the near-stoichiometric firing conditions of the pilot burner, the NO_x concentrations are higher at low load than at high load:[8]

Rich/Quench/Lean Combustors

These systems have three separate stages for combustion of the fuel. The first stage is operated fuel-rich so that the temperature is low and the partially oxidized organic compounds reduce NO_x formed in this area. The combustion reactions are then quenched with air or water in the second stage. Oxidation is completed in the third stage under lean conditions to prevent high gas temperatures and the associated NO_x formation.

Water or Steam Injection into Gas Turbines

Water or steam injection reduces the peak temperatures in the gas turbine combustion gases and thereby reduces the quantity of thermal NO_x formed. Water is slightly more effective than steam because of its higher heat capacity. However, due to water quality factors, steam has replaced water in most installations.
The quantity of steam used varies from 1.07 to 2 pounds per pound of fuel. This usually results in NOx emissions of less than 42 ppm for natural gas-fired turbines and 65 ppm for fuel oil-fired turbines. Some turbine designs operate at less than 25 ppm (natural gas firing) when using water or steam injection.' The fuel firing rate is usually increased slightly to maintain the necessary turbine inlet temperatures. Accordingly, the energy output of the turbine is increased several percent the to the water or steam injection. The overall thermal efficiency of the turbine is reduced several percent due to energy losses associated with heating diluent water vapor. Water or steam injection increases the turbine exhaust gas stream moisture content to 10-30% by volume.

Gas turbines used primarily for peaking service often use water or steam injection as the only means of minimizing NO_x emissions. In systems that run more frequently, the water or steam injection is used in conjunction with a catalytic reduction system.

FUEL SWITCHING

In coal-fired boilers, NO_x emissions can be reduced by fuel switching. There are three different approaches: (1) conversion to a coal supply with a low nitrogen content or a coal with fuel nitrogen in a chemical form less likely to form NO_x, (2) firing the boiler with natural gas instead of coal during time periods when ambient ozone levels are high, and (3) gas co-firing.

Coal Nitrogen Content

Nitrogen levels in coal supplies vary from less than 0.5% to more than 2% by weight. Conversion from a high nitrogen content to a low nitrogen content can reduce NO_x slightly. However, the emission reduction is not usually proportional the change in the coal nitrogen content. The fraction of the fuel nitrogen converted to NO usually increases as the fuel nitrogen content decreases.

Fuel Substitution

Coal-fired boilers with the capability to burn natural gas in addition to coal can use natural gas during time periods when ambient ozone levels are high. For example, natural gas can be used during very hot summer periods when metropolitan ozone levels are high[3] and dispersion conditions are poor. Natural gas is often available to boiler operators during this time period since it is not needed for residential space heating. Natural gas inherently has a lower NO_x generation rate than coal.

Gas Co-Firing

Gas co-firing involves the simultaneous combustion of coal and gas. Gas burners must usually be installed on conventional stoker and pulverized coal-fired boilers in order to co-fire natural gas. The gas replaces a portion of the coal used in the boiler.[9] In the case of stoker-fired units, the natural gas burners also improve the ability of the boiler to respond to rapid load changes:[9]

SELECTIVE NON-CATALYTIC REDUCTION (SNCR)

In selective non-catalytic reduction systems (SNCR), ammonia (NH3) or urea is injected into a very hot gas zone where thermal reactions leading to the chemical reduction of nitrogen oxides can occur (see Figure 8-12). The ammonia or urea reduces the NO to N_2 (Reactions 8-6 and 8-7).

Reaction 8-6 $4 NH_3 + 4 NO + O_2 \rightarrow 4 N2 + 6H_2O$

Reaction 8-7 $2NO + NH_2CONH_2 + O.5 O_2 \rightarrow 2N_2 + 2 H_2O + CO_2$
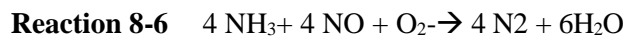
The reaction processes represented by Reactions 8-6 and 8-7 are very temperature dependent. In a boiler, this conversion takes place successfully at an approximate temperature range of 1,600°F to 2,000°F[3], (871°C to 1093°C). Figure 8-13 shows the relationship of NO_x reduction to N_2 (i.e., NO_x reduction efficiency) as a function of the flue gas temperature.
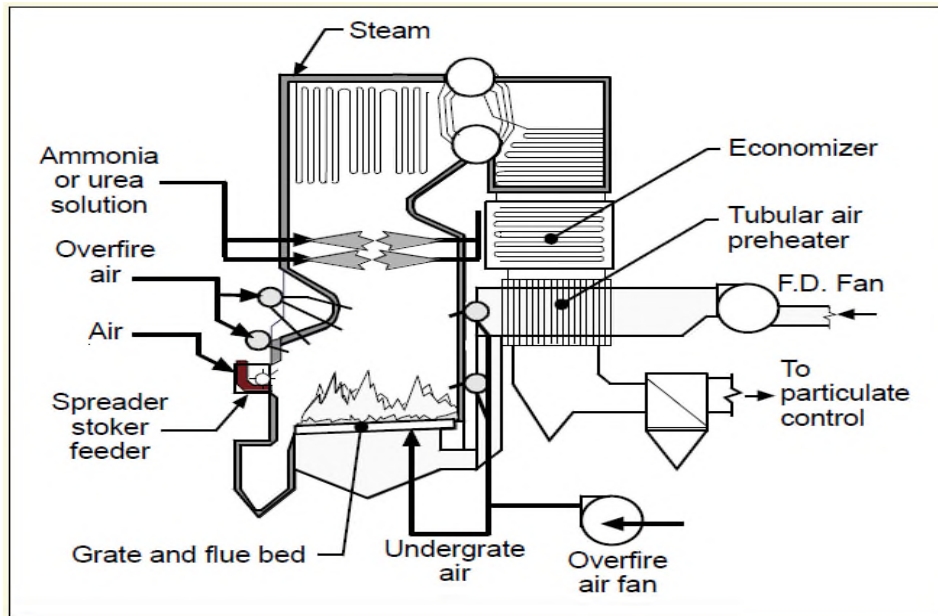
Figure 8-12. SNCR system components.
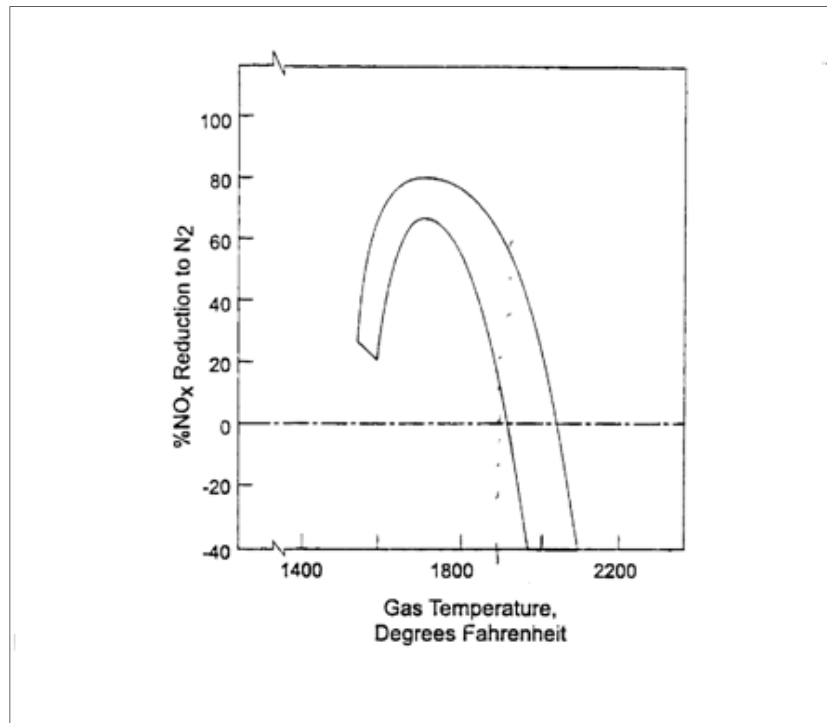
Figure 8-113. Temperature sensitivity of SNCR reactions.

At temperatures above 2,000°F (1093°C), the ammonia or urea is oxidized to form additional NO_x. At temperatures below 1,600°F (871°C), the ammonia passes through the boiler unreacted. The impact of ammonia slip of operating below 1,600°F (871°C) is indicated in Figure 8-14.
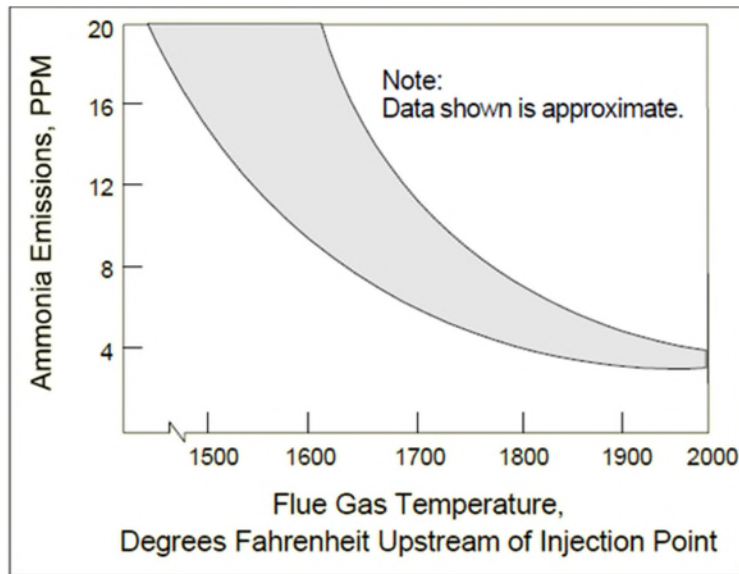
Figure 8-124. Ammonia slip emissions.

Ammonia emissions are generally referred to as ammonia "slip." Ammonia concentrations greater than 10 ppm can be objectionable since ammonia is a toxic air pollutant and can form a light scattering particulate plume by reacting with chloride and/or sulfate compounds.

These SNCR reactions also depend on the ammonia and NO_x concentrations in the system. As can be seen from summary Reaction 8-6, four moles of NH_3 are needed to reduce 4 moles of NO_x (stoichiometric ratio of 1:1). Injection of ammonia at a higher stoichiometric ratio increases the NO_x conversion efficiency. However, this also substantially increases the ammonia emission rate. The normal ammonia injection rate is set at a stoichiometric ratio approaching 0.90:1.00 to minimize ammonia slip. In the case of urea, the stoichiometric ratio is set at approximately 0.45:1.00 due to the ratios of reactants needed for the reaction processes summarized in Reaction 8-7. The typical NO_x reduction efficiencies range from 20-60%6 at the normal stoichiometric injection levels (ammonia and urea) and operating temperatures.

In order to achieve these efficiencies, the reactant must be injected into the portion of the boiler or incinerator near the point where the peak efficiency temperature (1,600°-2,000°F, 871°C to 1093°C) occurs (as shown in Figures 8-12 and 8-15). The location of this optimum point varies due to changes in the operating rate of the combustion process and due to fluctuations in the heating value and composition of the wastes being burned. Accordingly, a set of separate injection nozzles is usually needed. The ammonia or urea reactant is automatically directed to the set of nozzles at the temperature most favorable for NO_x reduction.
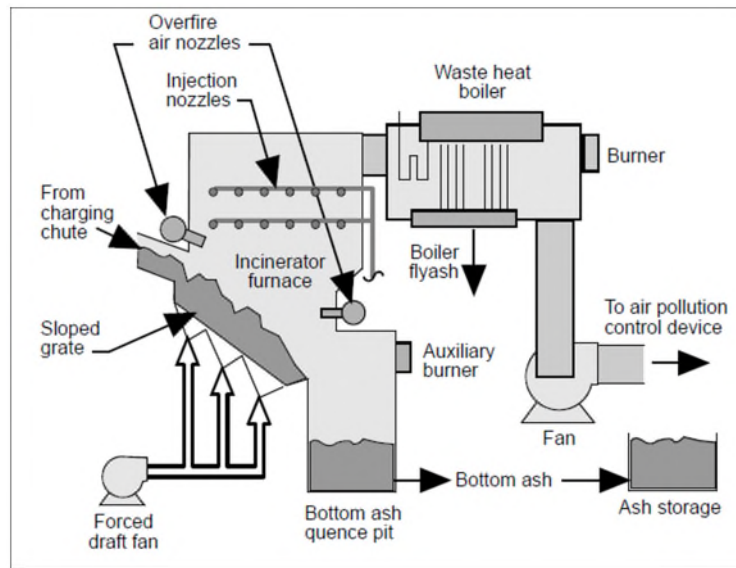
Figure 8-135. Boiler with SNCR injection nozzles.

Proper distribution of the reagent(s) is very important for achieving the desired efficiencies.' The ammonia or urea reactant must be injected through a set of nozzles to achieve uniform distribution. When anhydrous ammonia is used, the ammonia gas must be mixed with air or steam to serve as a carrier gas stream. The presence of the carrier gas dilutes the ammonia below the explosive range and facilitates mixing in the flue gas stream because of the increased flue gas velocities and flow rates at the nozzles.

This ammonia-air mixture is injected at various points in the convection and superheater sections of the boiler. Multipoint injection grids are used (to inject ammonia) to compensate for varying temperatures in the convection and superheater sections. Temperature differences result from changing electric loads to the generator.

When aqueous solutions of ammonia or urea are used, the water serves as the carrier stream. In these cases, it is important to achieve complete atomization of the droplets since the evaporation rate of the droplets is inversely related to the droplet size. If the droplets evaporate too slowly, the ammonia could be released from the droplets in an area that is too cold for the NO_x reactions to proceed. The ammonia slip rate can be influenced significantly by the droplet size distribution.[13] NO_x emissions from oil-, gas-, and coal-fired boilers and from waste incinerators can be reduced more than 20-60% by using ammonia or urea injection.

Under some conditions, SNCR systems can generate N_2O,[3] which is classified as a greenhouse gas. Systems operating with urea are more vulnerable to N_2O formation.

One variation of the SNCR process is the two stage $DeNO_x{}^{Tm}$ system that uses methanol with urea. A urea-methanol mixture is injected through the first set of nozzles while an aqueous methanol stream is injected in a downstream set of nozzles.

This system uses a relatively high urea-NO_x stoichiometric ratio of 0.70:1.00 and then controls the ammonia slip by methanol injection.[14] Methanol and other oxygenated compounds may extend the effective temperature range for NO_x reduction down to 1,400°F[13] (760°C).

SELECTIVE CATALYTIC REDUCTION (SCR)

In an SCR system (see Figure 8-16), the hot exhaust stream from the combustion process is cooled to a temperature range of 550 to 800°F (288°C to 427°C) in the heat exchange areas of the boiler. Ammonia-containing air or steam is injected through a series of nozzles arranged in a grid to facilitate uniform mixing prior to the catalyst bed. The ammonia reduces the nitrogen oxides on the catalyst surface. The effluent gas stream contains the unreacted NO_x and small quantities of unreacted ammonia. The overall efficiency usually ranges from 80% to more than 90%.[6] The outlet NO_x concentrations in some gas turbine systems are less than 4 ppm corrected to 15% oxygen.
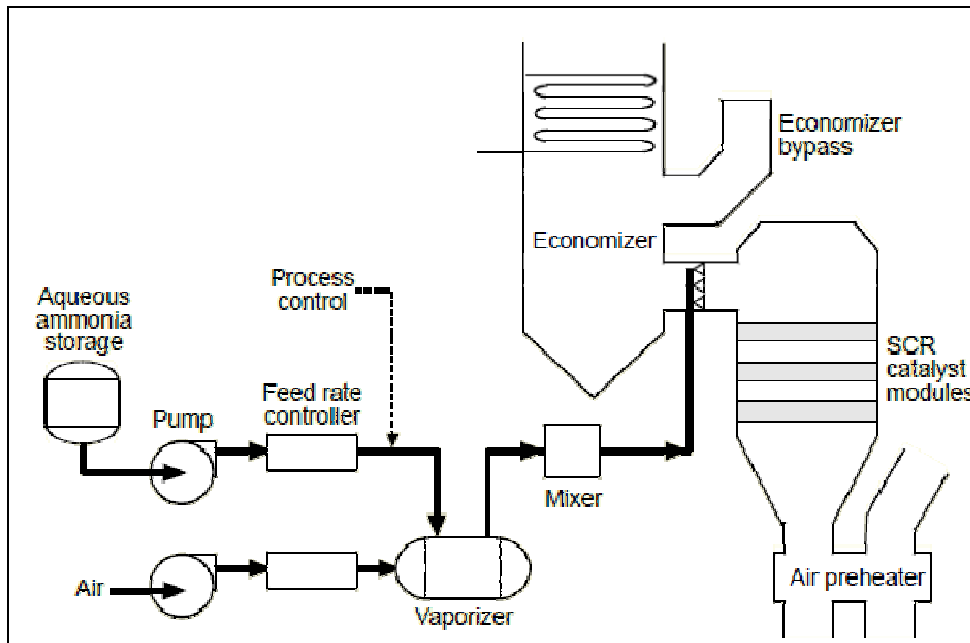
Figure 8-146. SCR configuration.

The necessary temperature range for the SCR system depends on the type of catalysts. Most of the systems operate in the range of 550 to 750°F (288°C to 399°C).[15] At temperatures exceeding approximately 670°F (354°C), the oxidation of ammonia begins to become significant.[16] At low temperatures, ammonium bisulfate formation causes scaling and corrosion problems.

Typical catalysts include vanadium pentoxide, titanium dioxide, noble metals, and tungsten trioxide.[3] Zeolites, which can also be used, may be capable of operating at as high as 1,100°F (593°C).[3] Each of the catalysts has a relatively narrow temperature "window." Variations of as little as plus or minus 50°F (28°C) from the optimum temperature could have an impact on the NO_x reduction efficiency.[15]

Ammonia slip from the SCR system is usually less than 3 to 5 ppm.[15] The emission of ammonia increases during load changes due to the instability of the temperature in the catalyst bed. Ammonia slip can also increase at low loads because of the low gas temperature.

The ammonia is injected at stoichiometric ratios of approximately 0.85:1.00[15] to 0.90:1.00.[6]

This means that the pound-moles of ammonia injected are approximately equal to the pound-moles of NO_x being generated. The composite reactions involved in SCR nitrogen oxides reduction are shown in Reactions 8-10 and 8-11.

Reaction 8-10 $4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6 H_2O$

Reaction 8-11 $2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6 H_2O$
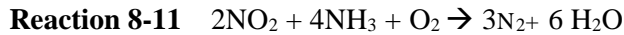
In some systems, the rate of ammonia feed is controlled by an NO_x continuous emission monitor upstream of the SCR bed. In other systems, the NO_x monitor is installed downstream of the catalyst bed. The ammonia is usually stored as a pressurized liquid. It is vaporized and metered into a dilution carrier gas stream to keep the ammonia concentration below the explosive range and to facilitate mixing into the gas stream. The ammonia concentration of the gas stream injected upstream of the SCR bed is usually 3-5% by volume. Aqueous ammonia can be used instead of ammonia gas when there is concern about ammonia gas releases from the storage area.

Sulfur trioxide can react with unreacted ammonia in the SCR effluent gas stream. Ammonium bisulfate and ammonium sulfate can form due to these reactions. Ammonium bisulfate is corrosive and can also foul the blades of gas turbines. To avoid problems with ammonium bisulfate, the SCR system must operate above the temperature where this compound forms.

The catalyst must be selected to minimize the conversion of sulfur dioxide to sulfur trioxide. In addition to forming ammonium bisulfate, the sulfur trioxide can react with water vapor to form sulfuric acid, which condenses and corrodes downstream equipment. Most SCR catalysts limit sulfur trioxide formation while maintaining high efficiency NO_x reduction.

The catalyst beds are usually constructed in a honeycomb type block.[3,16] The beds may be mounted in either a horizontal or vertical position. However, vertically oriented downflow designs are usually used in coal-fired boiler applications to minimize flyash deposition in the catalyst.[17]

There are a variety of problems that can affect the performance of the catalyst bed. These include poisons such as phosphorus, lead, and arsenic that can irreversibly affect catalyst activity.'

The catalyst surface can be masked by particulate or chemicals adsorbing on the surface. Particulate matter can also blind the catalyst bed. At high gas temperatures, the catalyst bed can sinter and thereby reduce the accessibility of the catalyst to the nitrogen oxide-containing gas stream.

In addition to their use for NO_x reduction, SCR-type systems can be used for the destruction of carbon monoxide generated by water or steam injection into conventional gas turbines. Precious metal catalysts deposited in a honeycomb arrangement can be used to reduce CO emissions by more than 90%." The typical operating temperatures range from 500°F (260°C) to more than 1,200°F (649°C).[18]

8.5 CAPABILITY AND SIZING

The capabilities of NO_x control systems are highly variable due to the diversity of the combustion sources and to the rapid development of this technology. This section presents an overview of the control efficiencies and emissions that have been reported on these systems. However, this information should be used only to determine the generally achievable efficiency range. Specific units may have NO_x reduction efficiencies above or below these levels.

There are very few well established sizing criteria for catalyst beds, reagent injection grids, and other important factors. Accordingly, a proposed system must be evaluated primarily by comparison with data recently obtained from a similar control system installed on a similar combustion process.

NITROGEN OXIDES EMISSIONS REDUCTION EFFICIENCIES

Table 8-1 presents a summary of the general ranges in NO_x reduction efficiencies possible with the control techniques discussed previously. It should be noted that the actual reduction efficiencies obtained at a specific site depend on the adequacy of the system design and operation.

Table 8-1. General range of NO_x suppression efficiencies.		
Control Technique	**Typical Applications**	**NO_x Reduction Efficiencies, %**
Combustion Modifications		
Low Excess Air	Coal-Fired Boilers, Municipal Waste Incinerators	15-30% [17]
Staged Combustion	Coal-, Oil-, and Gas-Fired Boilers	30-40%. 15-50% [17]
Flue Gas Recirculation	Coal-, Oil- and Gas-Fired Boilers	15-50% [17]
Low NOx Burners	Coal-, Oil-, and Gas-Fired	25-60% [17]
Gas Rebuming	Coal-, Oil-, and Gas-Fired	30-70% [17]
Lean Combustors	Gas-Fired Turbines	> 90%
Water/Steam Injection	Gas-Fired Turbines	60-75%
Flue Gas Treatment		
SNCR	Coal-Fired Boilers, Municipal Waste Incinerators	20-60 % [4,17]
SCR	Coal-Fired Boilers, Gas Turbines	80-90%
Fuel Switching		
Low Nitrogen Coal	Coal-Fired Boilers	No Data
Co-Firing	Coal-Fired Boilers	No Data

8.6 EVALUATING PERFORMANCE

CONTINUOUS EMISSION MONITORING DATA

Nitrogen oxides continuous emission monitors (CEMs) provide a direct indication of the performance of the NO_x control techniques being used. Chemiluminescent analyzers are the most common type of NO_x monitors presently used in CEM systems. Other major components of the CEM system include the sample acquisition and conditioning equipment, the calibration equipment, and the data acquisition system. The operating principles of NO_x CEMs are described in detail in U.S. EPA, APTI Course 474.

To ensure that the NO_x emission data are accurate and representative, the CEM system should be installed in accordance with U.S. EPA specifications in 40 CFR Part 60. The CEM system should be routinely calibrated and tested in accordance with Appendix F of Part 60. The NO_x data should be recorded and reduced in accordance with Reference Method 19.

Before reviewing the NO_x CEM data, it is helpful to confirm that the instrument is functioning properly. The following list of inspection points provides a qualitative indication of the performance of an extractive type CEM system:

Analyzer and Data Acquisition System

- Daily zero and span checks
- Fault lamps on the analyzer panel and/or codes on the data acquisition system
- Data acquisition system operation

Extractive Sample Conditioning System

- Inlet sample line temperature
- Condenser temperature
- Sample gas flow rate
- Sample pressure
- Dilution gas flow rate (if applicable) Calibration Gas Cylinder

- Pressure and concentration

Stack/Breeching Sampling Location

- Upstream air infiltration into stack or breeching
- Sample line insulation temperature
- Visible probe corrosion
- Location of audit gas injection

Alternative inspection points may be necessary for other types of CEM systems. Some of these inspection steps are described briefly in this section. More detailed information concerning the inspection and evaluation of the CEM systems is provided in APTI Course 474. The first set of inspection points involves a basic inspection of the analyzer and the sample gas conditioning system. These are usually at a convenient ground level location. The inspection checks primarily concern the daily quality assurance procedures conducted by plant personnel.

The zero and span checks are required on a daily basis to check for instrument drift. These checks are required by 40 CFR 60.13. They are normally initiated automatically but can also be performed manually. The zero and span drift values (as indicated by the data acquisition system) should be compared against the allowable drift specifications included in Performance Specification 2 (SO_2 and NO_x CEMs).

Most CEM systems have fault lamps that indicate if there are any mechanical or electrical problems that could be affecting the accuracy of the emissions data. In addition to these fault lamps on the front panels of the instruments, there may also be warning codes or symbols included on the data acquisition system records. All fault lamps and other warning codes should be noted. Generally, these indicate that the CEM system is not working properly. Instrument adjustments are required when the drift exceeds the allowed limits (two times the drift specifications) for five consecutive daily periods. The CEM system is considered "out-of-control" if the drift exceeds four times the drift specification at any time in the Performance Specification Test.

The gas cylinders used for the daily zero and span checks should be checked. The indicated concentrations should be compared against the values used in the zero and span checks. The pressures should be above approximately 150 psig since some changes in concentration are possible at less than this pressure. Compressed gas samples older than 6 months may have suffered some concentration changes.

Sample lines for extractive-type CEM systems must be kept heated from the stack or breeching to the condenser. The outer temperature of the insulation surrounding the sample lines should be felt to confirm that the heaters are working. It should feel moderately warm to the back of the hand. If the sample line has been cold for an extended time period, it is possible that corrosion, solids buildup, and/or pollutant absorption are occurring. It should be noted that extractive systems with dilution probes are not kept hot since the sample gas stream is diluted before moisture can condense.

Localized conditions that could affect the accuracy of extractive-type CEM systems should also be checked if there are indications that the CEM system is not working properly. Some of these localized problems include air infiltration upstream of the sampling port and corrosion-related air infiltration into the probe itself. The location of audit gas injection into the probe should also be determined.

The condenser liquid bath temperatures should be in the range of 35° to 45 °F (1.7°C to 7.2°C). Inadequate removal of water vapor can create the potential for analyzer damage. It can also affect the accuracy of the emission concentration measurement since the instrument **is no** longer receiving a "dry" sample gas. The presence of water causes a lower-than-actual concentration value.

The sample gas flow rates to each of the gaseous pollutant analyzers should be checked against the minimum flow requirements stated in the instrument manufacturer's specifications. Inadequate sample gas flow rates or significant changes in the sample gas flow rates can affect the accuracy of the CEM data.

In addition to the qualitative checks, the quarterly accuracy tests of the CEM system required by 40 CFR Part 60 Appendix F should be reviewed. Only instruments that are operating in compliance with 40 CFR Part 60 should be used to evaluate the performance of the NO_x control

system.

NO₂ AND NH₃ VISIBLE EMISSIONS

There should be no visible NO_2 "plume" or NH_3-related plume if the NO_x control system(s) is working properly. At high concentrations, NO_2 can form its dimer compound, N_2O_4, which has a reddish-brown color and is often associated with photochemical smog. The appearance of this color is a strong indication that stack emissions are high. It should be noted that this color is not classified as "opacity" since the ambient light is being absorbed by the dimer compound rather than being scattered by particulate matter.

Ammonia slip from the NO_x control system can result in the formation of ammonia chloride, ammonium bisulfate, and ammonium sulfate. These compounds can nucleate homogeneously and heterogeneously downstream of the NO_x control systems. Plume opacities from 20% to more than 80% can occur even when the ammonia slip levels are in the range of 10 to 20 ppm. These ammonia-related plumes usually have a bluish-white color due to the particle size distribution of the nucleated ammonia compounds. These plumes are most prevalent during cold weather and/or high humidity periods since these conditions favor particle nucleation.

OXYGEN CONCENTRATIONS

Most combustion systems limit oxygen concentrations in order to avoid localized high concentrations in the peak temperature zones where thermal NO_x can form. However, air infiltration into the combustion system can increase to substantial levels due in part to the frequent thermal expansion and contraction of the combustion system durinᵍ start-up, shut down, and operating rate changes. The oxygen entering with the infiltrating air can increase the thermal NO_x formation rates.

Improperly adjusted burners can have oxygen levels above the intended levels causing high NO_x formation rates due to the availability of the oxygen in the peak temperature zones. Oxygen concentration data should be reviewed *to* determine if factors such as air infiltration or burner operational problems may be increasing NO_x formation rates. In reviewing this data, it is important to note that the normal oxygen concentrations are a function of the combustion system operating rate. The oxygen concentrations are at a minimum at full load and increase slightly as the load is decreased due to the need for higher excess air rates at low load. Accordingly, the present oxygen concentration data should be compared against baseline data for the combustion system operating rate (load) at the time that the oxygen data is obtained.

In reviewing the oxygen concentration data, it is also important to note that the oxygen concentrations are often not spatially uniform at the measurement location. Problems caused by air infiltration or burner adjustment can create stratified gas streams with substantial differences in oxygen concentrations. Oxygen monitors sampling gas at only one or two locations in the duct or breeching may not accurately characterize the variations in the oxygen concentration across the gas stream. Accordingly, the entire breeching or duct should be traversed with an oxygen monitor whenever there are concerns about oxygen concentrations in the flue gas stream.

CARBON MONOXIDE CONCENTRATIONS

Carbon monoxide concentrations can be monitored by CEMs. As in the case with the NO_x

monitor, it is important to check the adequacy of the instrument quality assurance procedures and operating conditions prior to using the data.

High carbon monoxide concentrations indicate that the combustion conditions have been upset. This could be due in part to overly aggressive attempts to reduce NO_x emissions.

INSTRUMENTATION

SCR and SNCR Reagent Feed Rates and Injection Conditions

The feed rates of anhydrous ammonia (gas), aqueous ammonia (liquid), and urea (liquid) are monitored by conventional liquid or gas flow rate monitors. The feed rate should be recorded and compared with the design values for the combustion system operating rate. Low values indicate that the stoichiometric ratio between the reducing agent (e.g., ammonia) and the NO_x is too low. Therefore, the NO_x concentrations in the stack could be high. High values indicate that excessive quantities of the reducing agent are being added, and there may be excessive "slip" emissions.

In addition to checking the average reagent feed rates, the CEM data should be evaluated to ensure that the feed rate control system can keep up with the normal fluctuations in the NO_x concentrations formed in the combustion system. The reagent feed rate should be modulated to maintain a constant stoichiometric feed rate during these variations. There should not be a long time delay between a change in the NO_x emission levels and a change in the reagent feed rate.

Proper distribution of the reducing agent (e.g., aqueous ammonia) is very important. This is partially dependent on the pressures in the supply headers feeding the nozzles. It is also dependent on the flow rates of the carrier streams such as preheated air for anhydrous ammonia and water for aqueous ammonia. These data should also be recorded when evaluating performance of the NO_x control system.

Gas Temperature Data

Both the SCR and SNCR systems have limited gas temperature operating ranges. In the case of SCR systems, the gas temperatures at the inlet to the catalyst bed should be monitored. This data can be compared against the required temperature range for the type of catalyst being used. Low gas temperatures indicate the potential for incomplete NO_x reduction in the catalyst and the formation of corrosive ammonium bisulfate. High gas temperatures indicate the potential for damage to the catalyst. The sensitivity of SCR performance to high and low gas temperatures increases with the age of the catalyst.

In the case of SNCR systems, the gas temperature at the point of reagent injection should be monitored to be in the range of 1,600 to 1,900°F (871 to 1,038°C). Low gas temperatures at the injection point indicate the potential for high ammonia slip emissions. At high gas temperatures, the conversion of NO_x ceases, and the reducing agent can be oxidized to form additional NO_x Accordingly, at high gas temperatures, the emissions of NO_x can be higher than the concentrations that would exist without reagent injection.

Gas Static Pressure Drop

The static pressure drop across the SCR catalyst bed should be monitored. After correcting this data for changes in the gas flow rate, monitoring provides an indication of the physical condition

of the catalyst bed. The static pressure drop is related to the square of the gas flow rate. Since gas flow rate data are usually not available, the process operating rate (e.g., boiler) can be used as an indirect measure of the gas flow rate. The general relationship between the static pressure drop and the process operating rate is illustrated in Figure 8-17. Static pressures above the normal range may indicate particulate buildup within the catalyst bed.
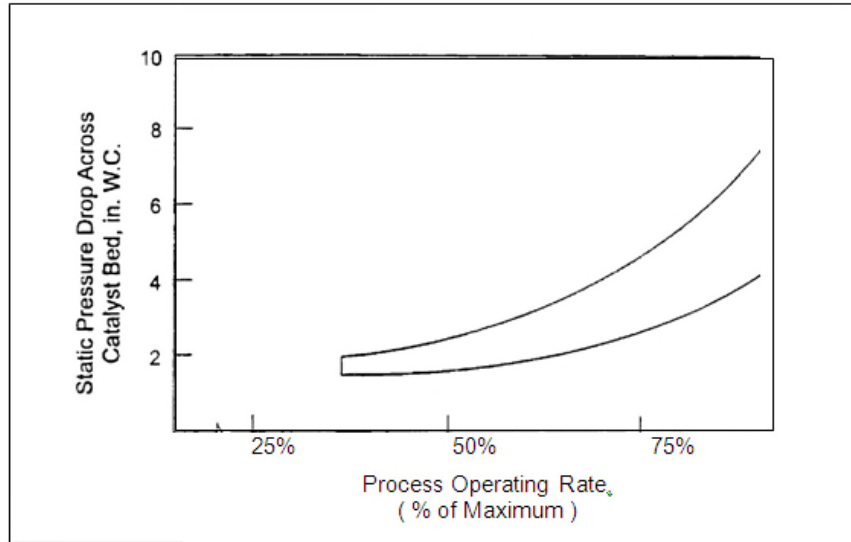
Figure 8-157. Static pressure drop versus process operating rate.

Gas Turbine Steam or Water Flow Rates

The gas turbine electrical and steam output is monitored on a continuous basis at the system control panel. The steam injection or water rates are usually monitored continuously. Due to Subpart GG (NSPS) requirements, the steam/fuel ratio or water/fuel ratio is usually calculated automatically and recorded. The NSPS requirements also include routine measurement of the fuel nitrogen content.

8.7 SUMMARY

CONTROL TECHNIQUES FOR NITROGEN OXIDES

This training provided the resources that will enable students to:

- Recognize the mechanisms that create nitrogen oxides.
- Identify sources of nitrogen oxides.
- Identify the types and components for controlling nitrogen oxide.

8.8 REVIEW EXERCISES

INSTRUCTIONS

Select the best response(s) for each of the following multiple-choice questions.

MULTIPLE CHOICE QUESTIONS

1. What category of stationary sources has the highest emissions of NO_X in the U.S.?

    a. Utility and industrial boilers
    b. Metallurgical furnaces
    c. Cement kilns
    d. Industrial furnaces

2. What factors strongly influence the rate of thermal NO_X formation?

    a. Peak gas temperatures
    b. Peak gas oxygen concentrations
    c. Residence time of the combustion products in the area of peak gas temperature   and peak oxygen concentration
    d. Nitrogen content of the fuel
    e. All of the above

3. What is the normal gas temperature leaving the economizer of a pulverized coal-fired boiler?

    a. 1800°F to 2000°F
    b. 1400°F to 1800°F
    c. 700°F to 1400°F
    d. 500°F to 700°F
    e. 250°F to 500°F
    f. 100°F to 250°F

4. How many separate burners are generally used in a large pulverized coal-fired boiler?

    a. 1
    b. 2 to 5
    c. 5 to 10
    d. 10 to 100
    e. 100 to 500
    f. 500 to 1000
    g. More than 1000

5. What are the typical combustion gas temperatures in the combustion zone before entering the superheater area of pulverized coal boilers, oil and gas-fired boilers, and wood spreader stoker boilers?

    a. 1800°F to 2200°F
    b. 1400°F to 1800°F
    c. 700°F to 1400°F
    d. 500°F to 700°F
    e. 250°F to 500°F
    f. 100°F to 250°F

Types and Components of NO_X Control Systems

6. What factors limit the effectiveness of combustion modifications to suppress NO_X formation?

    a. Carbon monoxide formation
    b. Increased combustible levels in flyash
    c. Boiler tube fouling
    d. N_2O formation
    e. All of the above

7. What is the fundamental principle underlying all off-stoichiometric combustion practices?

    a. Burn as much as possible of the fuel under fuel rich conditions where the peak gas temperature and the peak oxygen concentrations are at a minimum
    b. Generate CO to serve as a reducing agent for NO_X compounds
    c. Minimize the average oxygen level in the combustion zone
    d. All of the above

8. What factors influence the excess air rate in a boiler?

    a. Fuel/air ratio set by the boiler controller
    b. Air infiltration into the boiler
    c. Air infiltration into the air preheater
    d. All of the above

9. Does the excess air levels increase or decrease as boiler load increases?

    a. Increases
    b. Decreases
    c. None of the above

10. What is the primary objective of fuel gas recirculation systems?

    a. Burn as much as possible of the fuel under fuel rich conditions where the peak gas temperature and the peak oxygen concentrations are at a minimum
    b. Generate CO to serve as a reducing agent for NO_X compounds
    c. Minimize the peak oxygen level in the combustion zone

Operating Principles of NO_X Control Systems

11. The inlet gas temperature to an SCR system on a boiler operating at low load has dropped to 500°F. The normal inlet gas temperature at low load is 585°F. What will happen to the ammonia concentration in the gas turbine exhaust?

    a. It will increase substantially
    b.   It will not change from baseline levels at this load
    c. It will decrease

12. The inlet gas temperature to an SCR system on a gas turbine operating at high load has increased to 850°F. The normal inlet gas temperature at high load is 585°F. What will probably happen to the NO_X concentration in the gas turbine exhaust?

    a. It will increase to a level equal to 100% of the inlet concentration
    b. It will not change from baseline levels at this load
    c. It will decrease to less than 50% of the baseline levels because of the increased reaction rates at this temperature

13. What factors can contribute to ammonia slip in a SNCR system?

    a. Excess ammonia feed rates
    b. Injection of ammonia in a portion of the boiler that is too cold
    c. Injection of aqueous ammonia in the form of large droplets
    d. All of the above
    e. Answers a and b

14. What is the typical ammonia stoichiometry in SCR systems
    a. 1.0 to 1.25 mole of reagent per mole of NO_X
    b.   0.85 to 0.9 mole of reagent per mole of NO_X
    c. 1.9 to 2.0 mole of reagent per mole of NO_X
    d. None of the above

Capability and Sizing of NO$_X$ Control Systems

15. What is the typical NO$_X$ suppression efficiency of Low NO$_X$ burners?

    a. 10% to 20%
    b. 25% to 40%
    c. 40% to 60%
    d. 60% to 80%
    e. 80% to 95%

16. What is the typical NOX reduction efficiency of SNCR Systems?

    a. 10% to 20%
    b.   20% to 60%
    c. 60% to 90%
    d. 90% to 98%

17. What is the typical NO$_X$ reduction efficiency of SCR Systems?

    a. 10% to 20%
    b. 20% to 60%
    c. 60% to 90%
    d.   90% to 98%

8.9 REVIEW EXERCISES: SOLUTIONS

This Student Guide includes separate exercises and solutions, which allow students to check their work.

MULTIPLE CHOICE ANSWERS

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    a. Utility and industrial boilers
    b. Metallurgical furnaces
    c. Cement kilns
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    c. Air infiltration into the air preheater
    d. All of the above

9. Does the excess air levels increase or decrease as boiler load increases?

    a. Increases
    b. **Decreases**
    c. None of the above

10. What is the primary objective of fuel gas recirculation systems?

    a. Burn as much as possible of the fuel under fuel rich conditions where the peak gas temperature and the peak oxygen concentrations are at a minimum

    b. Generate CO to serve as a reducing agent for NO_X compounds

    c. Minimize the peak oxygen level in the combustion zone

Operating Principles of NO_X Control Systems

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9.0 SULFUR OXIDES CONTROL

9.1 OVERVIEW

SOURCES OF SULFUR OXIDES

More than 18 million metric tons of sulfur oxides (SO_X) are emitted into the atmosphere each year from manmade sources. The sulfur oxides include sulfur dioxide (SO_2), sulfur trioxide (SO_3), and sulfuric acid (H_2SO_4). Approximately 98 to 99% of the SO, emissions are in the form of SO_2. These emissions can cause health problems and contribute to global acid rain.

More than two-thirds of all anthropogenic SO_X emissions result from fossil fuel combustion in utility and industrial boilers. Coal and No. 6 fuel-oil boilers are responsible for most of the utility and industrial boiler SO_X emissions because these fuels have moderate-to-high fuel sulfur levels. The largest noncombustion sources are copper smelters, followed by petroleum refining operations. Other small SO_X sources include residential, commercial, and institutional heating furnaces and mobile sources.[1]

The NSPS for boilers larger than 25 MMBtu heat input (40 CFR Part 60, Subpart Da) limit SO_2 emissions to 1.2 pounds per MMBtu. Many state and local agencies promulgated regulations that limit the sulfur content of the oil or coal used in the boilers. While these regulations are effective in minimizing the emissions from a specific facility, they do not limit the total emissions of sulfur oxides. New boilers and other new SO_2 sources can add to the emissions from existing sources and thereby increase total emissions to the atmosphere.

Due, in part, to concerns about the impact of nationwide emissions of SO_2 on acid rain, Title IV of the Clean Air Act Amendments of 1990 included absolute caps on utility SO_2 emissions. These limits were imposed in two steps: Phase I and II. Phase I applied to 110 specifically identified units that have a generating capacity greater than 100 megawatts and a 1985 emission rate exceeding 2.5 pounds per MMBtu. Phase II applied to all fossil-fuel fired boilers (utility and industrial). In both cases, SO_2 emission allowances are allocated. Many existing utility and industrial boilers must use a low sulfur fuel or an SO_2 control device in order to stay within the allocated emission limit. Owners of new boiler facilities must either purchase emission allowances from other sources that significantly exceed emission limits or reduce SO_2 emissions at their existing facilities. Compliance with the Phase I requirements had to be achieved by January 1, 1995 while the Phase II requirements had to be achieved by January 1, 2000. As part of these Clean Air Act requirements, owners of affected sources must monitor their SO_2 emissions using continuous emission monitors and gas flow rate monitors so that the actual emissions of SO_2 can be tracked accurately. The emission allocations and monitoring requirements included in Title IV of the Clean Air Act are intended to reduce the total SO_2 emissions from utility and industrial boilers by 10 million tons from the 1980 levels.

LEARNING OBJECTIVES

At the conclusion of this training students will be able to:

- Recognize operating principles for sulfur dioxides control.
- Identify appropriate evaluation and test methods for controlling sulfur dioxide.
- Identify appropriate evaluation and test methods when using fuel sulfur sampling systems.
- Recognize appropriate methods and evaluation for dry and wet scrubbing systems.

9.2 SULFUR OXIDES FORMATION

Sulfur oxides are formed from the sulfur compounds entering with the fuel. In the case of coal, the sulfur compounds include pyrites, sulfates, and organic sulfur compounds. Approximately 94-95% of the sulfur compounds are converted to SO_2 in burner flames as indicated in summary Reaction 9-1. Another 0.5-2% of the fuel sulfur is converted to sulfur trioxide (SO_3). Once the fuel gas stream is cooled below approximately 600°F (316°C), the SO_3 adds a water molecule to form vapor phase sulfuric acid as indicated in summary Reaction 9-3.

Reaction 9-1 $\quad\quad\quad S + O_2 \rightarrow SO_2$

Reaction 9-2 $\quad\quad\quad S + 1.5\,O_2 \rightarrow SO_3$

Reaction 9-3 $\quad\quad\quad SO_3 + H_2O \rightarrow H_2SO_4$

Reactions 9-1 and 9-2 summarize the result of a complex set of simultaneous reactions occurring in the burner flames and in the high temperature furnace area. These reactions are useful for indicating the overall stoichiometry of the oxidation reactions. In the case of SO_2, one mole is formed for every mole of fuel sulfur reacting by means of summary Reaction 9-1. Due to the differences in molecular weights of sulfur and SO_2, the emission rate of sulfur dioxide in terms of pounds per hour is exactly twice the quantity of fuel sulfur reacting by means of Reaction 9-1. This is illustrated in Problem 9-1.

9.3 CONTROL OF SULFUR OXIDES

Sulfur dioxide emissions from fossil-fuel-fired combustion sources can be reduced by five techniques.

Low sulfur fuel

Flue gas desulfurization

Dry scrubbing

Fluidized bed combustion

Fuel treatment

Fuel treatment and flue gas desulfurization are the most common techniques presently being used to comply with the Clean Air Act Title IV requirements.
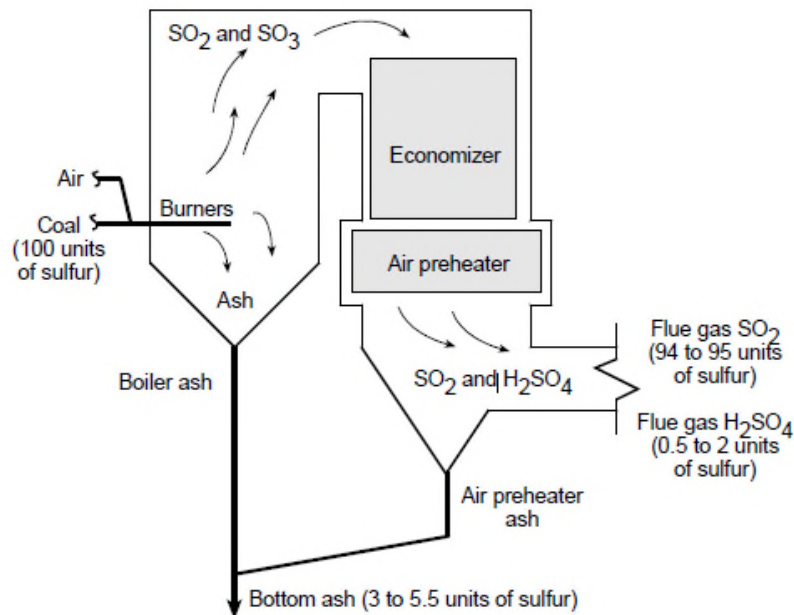
Figure 9-1. Conversion of fuel sulfur.

LOW SULFUR FUELS

One of the most straightforward ways to reduce SO_2 emissions from combustion sources is by burning a low sulfur-containing fuel. In the case of coal-fired boilers, this could involve using low sulfur coal, low sulfur fuel oil, or natural gas instead of a high sulfur coal. The use of low sulfur coal (most western U.S. coals and some eastern U.S. coals) can reduce SO_2 by more than 80%. Low sulfur coal has been used to meet Federal NSPS air pollution regulations. Low sulfur coal usually contains less than 0.6-1% sulfur; high sulfur coal contains between 2% and 5% sulfur. Low sulfur coal is more expensive and less available in the eastern U.S. than high sulfur coal.

When comparing the sulfur contents of fuel supplies, it is important to evaluate the heating value of the coal as well as the sulfur content on a weight percent basis. For example a change from 2% sulfur coal to 1% sulfur coal does not necessarily mean that the sulfur dioxide emissions will be cut in half. The heating value of the fuel must be taken into account along with the sulfur

content when evaluating the potential benefits of a low sulfur fuel. Many low sulfur coal supplies have a lower heating value as expressed in terms of Btus per pound of coal. Therefore, more of the low heating value fuel is needed to produce a given amount of energy. When a plant switches to a low heating value, low sulfur coal, it must fire more fuel than with its original high sulfur, high heating value fuel. The difference in heating value partially offsets the benefits of the low sulfur fuel.

While the conversion to low sulfur fuels has often been a successful control option, it is not universally applicable to all coal-fired boilers. Each boiler system is designed for a narrow range of coal characteristics. The available low sulfur coals can have properties, such as a heat content, volatile content, ash fusion temperature, or grindability, that are not appropriate for the specific unit.

In addition to completely changing the type of fuel being burned, it is possible to substitute a portion of the heating demand supplied by a high sulfur fuel with a fuel such as natural gas or No. 2 oil, which has low fuel sulfur levels.

FLUE GAS DESULFURIZATION

Flue gas desulfurization (FGD) is the most common technology used for controlling sulfur oxides emissions from combustion sources. FGD technology is also used to reduce SO_2 emissions from copper smelters. In this method, SO_2 gaseous emissions are usually removed by a post-combustion absorption process. FGD scrubbing processes can be either "wet" or "dry."

Wet scrubbing processes use a liquid absorbent to absorb the SO_2 gases. Wet scrubbing can be further categorized into nonregenerative and regenerative processes. Nonregenerative processes produce a sludge that must be disposed of properly. These are sometimes referred to as throwaway FGD processes. Regenerative processes generate a salable product **in** addition to removing SO_2 Regenerated products include elemental sulfur, sulfuric acid, or gypsum. Dry scrubbing processes use a dry spray to absorb SO_2 gas and form dry particles that are collected in a baghouse or electrostatic precipitator.

More than 50 different FGD processes have been developed. Of these, there are eight dominant systems that will continue to be used in the foreseeable future. They are summarized in Table 9-1. This section will address these processes, which are used most commonly in the U.S. for coal- and oil-fired utility boilers, coal-fired industrial boilers, and waste incinerators.

Table 9-1. Common types of FGD processes for boilers.[5]		
Type of SO$_2$ Control System	**1989**	**2010**
Wet Scrubbers, Nonregenerative (Throw-away)		
Lime*	23.6	18.4
Limestone*	50.6	45.5
Dual Alkali	3.4	2.3
Sodium Carbonate	4.0	3.3
Regenerative (Saleable Product)		
Magnesium Oxide	1.4	1.0
Wellman Lord	3.1	2.1
Lime/Limestone	4.0	4.7
Citrate/Undecided	0.0	8.1

*includes systems that use flyash for part of the alkali feed.

Nonregenerative FGD Processes

Nonregenerative FGD processes generate a sludge or waste product as a result of SO_2 emission control. The sludge must be disposed of in a pond or landfill. The three most common nonregenerative processes used on both utility and industrial boilers are lime scrubbing, limestone scrubbing, and dual alkali scrubbing. The use of lime and limestone scrubbing expected to increase in the future due to the Title IV requirements in the Clean Air Act Amendments of 1990. Sodium carbonate scrubbing is used primarily for industrial boilers due to relative simplicity. Non regenerable wet scrubbers remove greater than 90% of SO_2 emissions.

Lime Scrubbing

Lime scrubbing uses an alkaline slurry prepared directly from calcium hydroxide [Ca(OH)$_2$] or by slaking lime (CaO) to form calcium hydroxide. The alkaline slurry containing calcium hydroxide is sprayed in a scrubbing vessel and reacts with the SO$_2$ absorbed into the slurry droplets. Calcium sulfite (Ca.SO$_3$) and calcium sulfate (CaSO$_4$) salts are formed **in** the reaction and are removed as solids. The solids produced can be stabilized to produce an inert fill material or can be stored indefinitely as sludge in ponds. A simplified flowchart of a lime scrubbing system is shown in Figure 9-2.
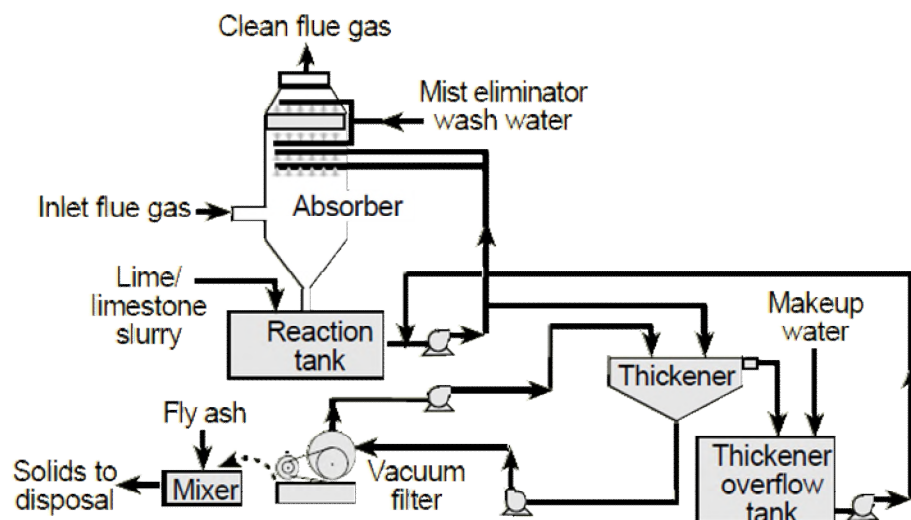
Figure 9-2. Simplified flowchart of a lime scrubbing system.

The equipment components necessary for a lime scrubbing system can be divided into four separate groups.

Scrubbing or absorption: scrubbers, holding tanks, liquid spray nozzles, and pumps.

Lime handling and slurry preparation: lime unloading and storage equipment, lime processing, and slurry preparation equipment.

Sludge processing: sludge clarifiers for dewatering, sludge pumps and handling equipment, and sludge solidifying equipment.

Flue gas handling: inlet and outlet ductwork, dampers, fans, and reheaters.

Individual lime scrubbing systems vary depending on the engineering firm, equipment vendor, and owner requirements.

Limestone Scrubbing

Limestone scrubbing uses an alkaline slurry prepared from limestone (CaCO$_3$) The equipment necessary for SO$_2$ absorption is the same as for lime scrubbing except in the slurry preparation. The limestone feed is reduced in size by crushing it in a ball mill and then sending it to a size classifier. Pieces larger than

200 mesh are sent back to the ball mill for recrushing. Limestone is mixed with water in a slurry supply tank. Even with these slurry preparation differences, the lime and limestone processes are so similar that an FGD system can be set up to use either material to absorb SO_2 gas.

Dual Alkali Scrubbing

Dual alkali scrubbing is a nonregenerative FGD process that uses two different alkalis to remove SO_2 from combustion exhaust gas. These two different alkalis are used in two separate liquid recirculation loops: one for absorption of the sulfur dioxide and one for the regeneration of the scrubbing liquid. A typical dual alkali system is shown in Figure 9-3.
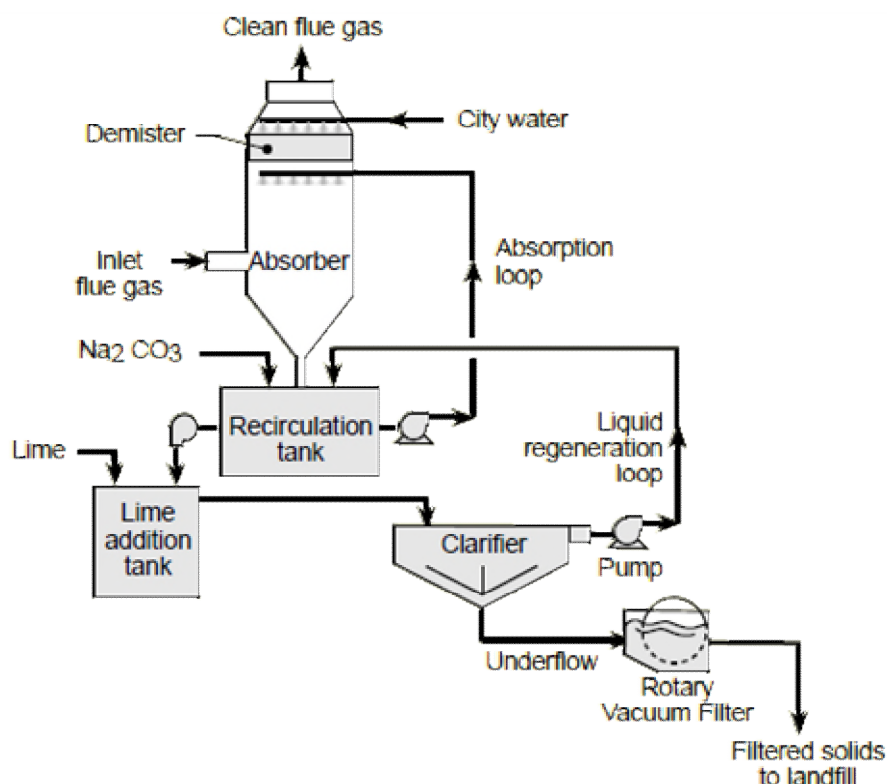
Figure 9-3. Dual alkali scrubber system.

Sodium sulfite (Na_2SO_3) scrubbing liquid is used in the main scrubbing circuit. Sodium sulfite and the reaction products with sulfur dioxide are very soluble. Therefore, chemical precipitation in the scrubbing circuit is not a problem. Makeup sodium carbonate is added to a recirculation tank in the main recirculation loop in order to maintain the necessary levels of SO_2 reaction. The dissolved solids levels in the recirculation liquor are usually very high, ranging from 10-30% by weight. At these dissolved solids levels, the liquid is classified as an electrolyte.

A portion of the dual alkali scrubbing liquid is treated in a regeneration loop. Calcium hydroxide is mixed into a recirculation tank to convert sodium bisulfite ($NaHSO_3$) to sodium sulfite (Na_2SO_3). Calcium sulfite and calcium sulfate are formed and removed in a rotary vacuum filter.

Most dual alkali systems have a particulate control device upstream of the main scrubber vessel. This is needed to remove calcium- and magnesium-containing fly ash particles that could create chemical scaling conditions in the main scrubbing loop.

Regenerative Wet FGD Processes

Regenerative FGD processes are wet scrubbing processes that remove SO_2 from the flue gas and generate some salable product. Regenerated products include elemental sulfur, sulfuric acid, or gypsum. Regenerative processes used on industrial and utility boilers include magnesium oxide, Wellman-Lord, and citrate. In 1980, approximately 3.1% of all operating and committed FGD systems in the U.S. used the Wellman-Lord process, 1.4% used the magnesium process, and less than 1% used the citrate process. Very few new units have been installed since this time. Due to the installation of new nonregenerative lime and limestone scrubbing systems, the fraction of the scrubbing market served by regenerative wet FGD systems is now lower than in 1981. The major disadvantages of the regenerative systems include high capital costs and problems selling the materials generated. The major advantage of the regenerative processes as opposed to the nonregenerative processes is the elimination of the sludge disposal problems.

Wellman-Lord

In the Wellman-Lord process, sulfur dioxide is absorbed by an aqueous sodium sulfite solution to form sodium bisulfite. The sodium bisulfite-containing scrubbing liquid is sent to an evaporator- crystallizer where sodium sulfite and concentrated SO_2 gas are produced. The sodium sulfite is recycled to the absorber, and the SO_2 is converted to either sulfuric acid or elemental sulfur. Sodium carbonate must be added to the scrubbing liquid to make up for the sodium sulfite that is inadvertently oxidized to sodium sulfate. A particulate control device is used upstream of the absorber vessel to minimize problems associated with particulate in the scrubber liquid.

Dry Scrubbing

Dry scrubbing is basically a two-step chemical process. The flue gas leaving the boiler or incinerator is contacted with a stream of alkali, usually calcium hydroxide. The reaction products are collected in a high efficiency particulate control device such as a pulse jet baghouse, a reverse air baghouse, or an electrostatic precipitator.

There are a number of different processes that are termed dry scrubbers.

>   Spray dryer absorption
>   Rotary atomizer systems
>
>   Compressed air assisted atomizing nozzle systems
>
>
>   Dry injection absorption
>   Without recycle
>   With recycle
>
>   Combination spray dryer and dry injection systems

Spray Dryer Units

A flowchart of a spray dryer absorber is shown in Figure 9-4. In this system, the inlet gas stream is split, with one-half entering at the top and moving downward and the other half entering near the middle and moving toward the atomizer.
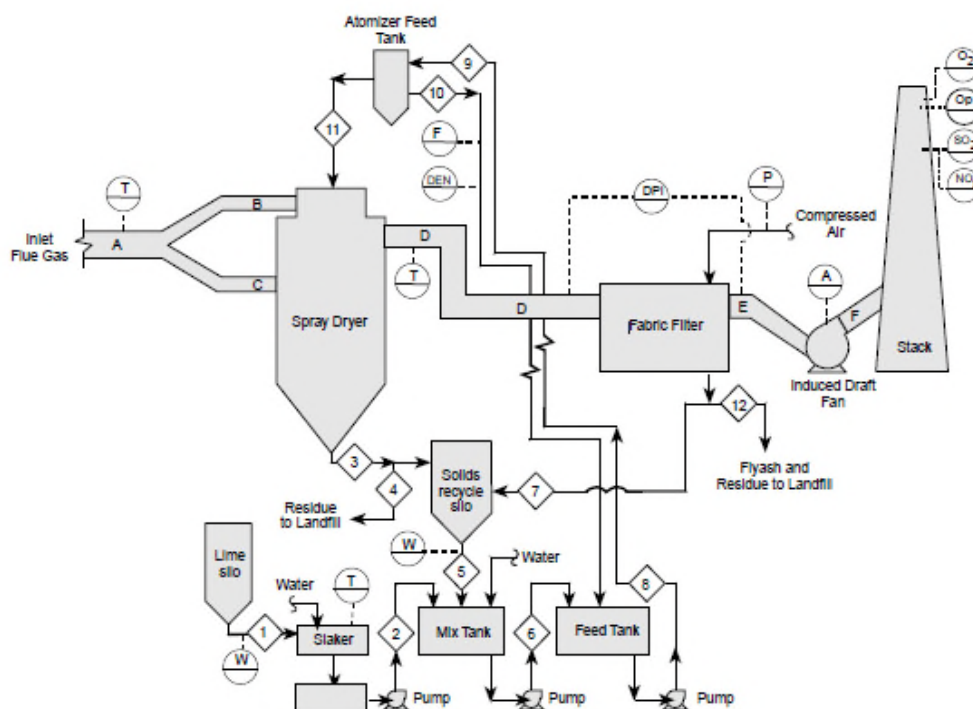
Figure 9-4. Simplified flowchart of a spray dryer type dry scrubber.

In other commercial systems, the entire gas stream enters from the top. In this type of dry scrubber, the alkali reagent is prepared as a slurry containing 5-20% by weight solids.[3,4,5] The slurry is atomized in a large absorber vessel having a gas residence time of 6 to 20 seconds.[3,4]

There are two major types of atomizers: rotary atomizers and compressed air assisted atomizing nozzles. The rotary atomizers operate at 10,000 to 17,000 rpm. A thin film of slurry is fed to the top of the rotating atomizer disk to achieve droplet sizes in the range of 100 microns. The spray pattern produced is inherently broad due to the geometry of the disk. This requires a large diameter spray dryer vessel. A single rotary atomizer is used for each spray dryer vessel. However, facilities typically maintain a spare in the event of maintenance problems.

The compressed air nozzles operate at air pressures of 60 to 90 psig and slurry pressures up to 40 psig. Multiple nozzles are used in a single-spray dryer. The spray dryer vessel designed for nozzles is taller and thinner than rotary atomizer dryers due to the geometry of the spray pattern of the nozzles. This type of atomizer can operate over wider variations of the gas flow rate than the rotary atomizer. However, nozzle atomizers do not have the slurry feed rate turndown capability of the rotary units.

The alkaline material generally used in spray dryer absorbers is pebble lime. This material must be slaked in order to prepare a reactive slurry. Slaking is the addition of water to convert the calcium oxide to calcium hydroxide. Proper slaking conditions are important to ensure that the resulting calcium hydroxide slurry has the proper particle size distribution and that the particles have not been coated due

to the precipitation of contaminants in the slaking water.
Recycle of the solids collected particulate control device is used in some systems. The locations of the possible recycle streams are shown in Figure 9-4. Recycle maximizes the utilization of the alkali and thereby reduces operating costs.

Dry Injection Units

This type of dry scrubber uses finely divided calcium hydroxide for the adsorption of acid gases. The reagent feed has particle sizes that are 90% through 325 mesh,[6] which is approximately the consistency of talcum powder. The alkali particle size distribution is important since removal efficiency is related to the amount of surface area available.

The calcium hydroxide feed rate for dry injection systems is three to four times the stoichiometric quantities.[67] This is much higher than the requirements for the spray dryer absorber type systems discussed earlier and is the main disadvantage of the dry injection systems. Their main advantage is that they are less expensive to build. A diagram of a dry injection system is shown in Figure 9-5. It consists of a calcium hydroxide feeding system, a gas-to-gas heat exchanger, a solids recycle contactor, and a fabric filter.
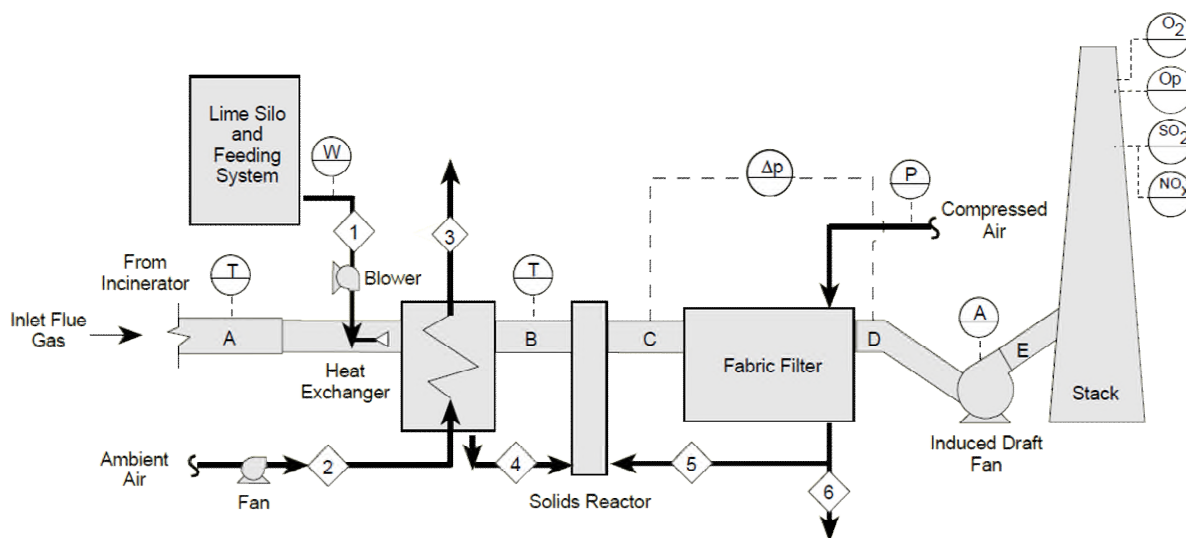
Figure 9-5. Dry injection dry scrubber flowchart.

The calcium hydroxide from the storage hopper is volumetrically fed to a blower. This fluidizes the alkali particles and transports them to the distribution nozzle in the system inlet duct. The gas-to-gas heat exchanger is designed to reduce the inlet temperature from the 400°F to 500°F (204°C to 260°C) range down to 250°F (121°C). This lower temperature is needed to achieve adequate adsorption of the acid gases.

The system shown in Figure 9-6 has a solids reactor for redistributing the fabric filter solids back into the flue gas stream. This is a rotating drum that breaks up flyash-alkali solids agglomerates and

exposes fresh alkali surfaces for adsorption. Only a portion of these baghouse solids are recycled.

Combination Spray Dryer and Dry Injection Units

A flowchart for a combination system is shown in Figure 9-6. This is very similar to the conventional spray dryer system except that a nozzle for dry injection of solids is included downstream of the spray dryer vessel.
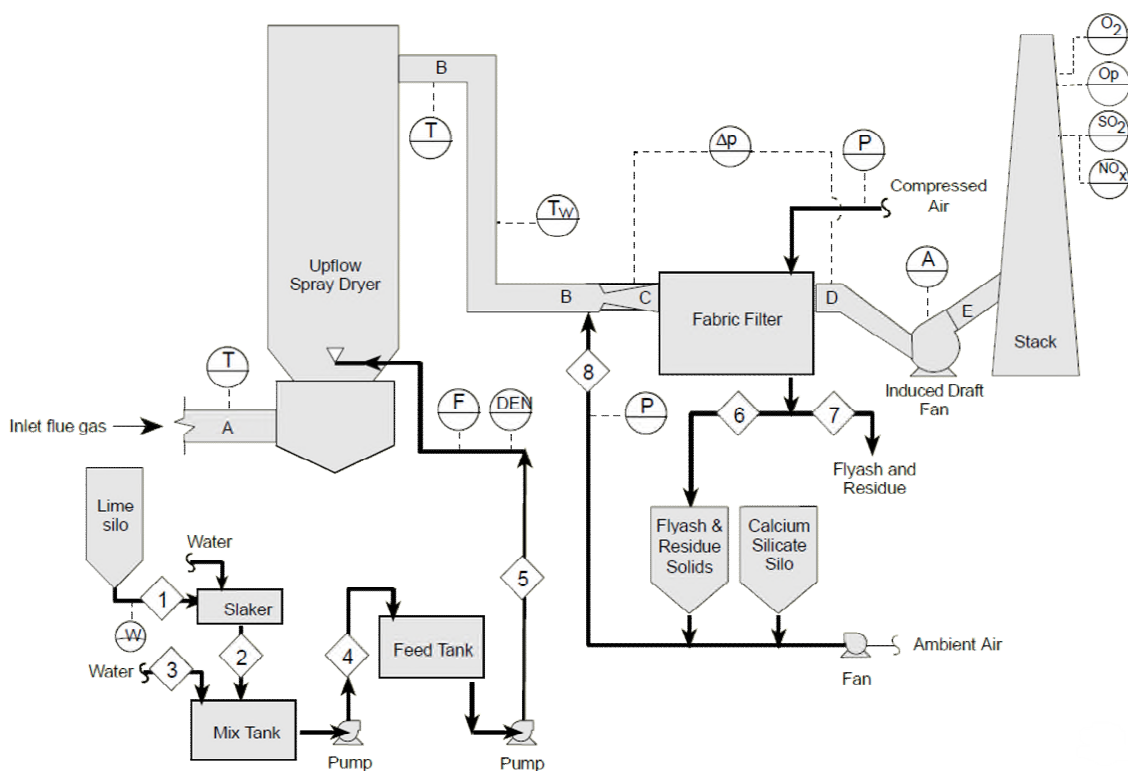
Figure 9-6. Flowchart of dry scrubber using a spray absorber vessel and dry injection recycle stream.

OTHER SULFUR OXIDE CONTROL TECHNIQUES

Fluidized Bed Combustion

A fluidized bed boiler utilizing an alkali such as limestone can reduce sulfur oxides emissions. In this type of boiler, a grid supports a bed of coal and limestone (or dolomite) in the firebox of the boiler. Combustion air is forced upward through the grid, suspending the coal and limestone bed in a fluid-like motion. Natural gas is used to ignite the pulverized coal. Once the coal is ignited, the gas is turned off. The sulfur in the coal is oxidized to SO_2 and consequently combined with the limestone to form calcium sulfate ($CaSO_4$). The $CaSO_4$ and flyash particulate matter are usually collected in a baghouse or an electrostatic precipitator.

Fluidized bed boilers usually require a calcium-to-sulfur stoichiometric ratio of 2.0:1.0 to 4.0:1.0 due to the limited amount of calcium oxide surface area available.[8] This lime feed requirement is considerably above that required for wet scrubber type systems and spray atomization type dry

scrubbers. This disadvantage is partially offset by the relative simplicity of this sulfur dioxide control approach and the inherently low NO_x generation rate of fluidized bed boilers.

Fuel Treatment

Coal Gasification

Over 70 different processes have been developed for producing a combustible gas from coal. Three basic steps are common to all coal gasification processes: pretreatment, gasification, and gas cleaning. Coal pretreatment involves coal pulverizing and washing. The pulverized coal is gasified in a reactor with limited oxygen producing either a low, medium, or high Btu gas by applying heat and pressure or by using a catalyst to break down the components of the coal.' The gas produced contains carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), water (H_2O), methane (CH_4), and contaminants such as hydrogen sulfide and char. Low and medium Btu gas contains more CO and H2 than high Btu gas which has a higher CH_4 content. Methane gas produces more heat when burned. During gasification, the sulfur content in the coal is converted to H_2S which is then converted to elemental sulfur by partial oxidation and catalytic conversion. The synthetic gas produced is sulfur-free and can be burned without releasing harmful pollutants.

Coal Liquefaction

A process for changing coal into synthetic oil is called coal liquefaction. Coal liquefaction is similar to coal gasification. Two basic approaches are used for liquefaction. One involves using a gasifier to convert coal to carbon monoxide, hydrogen, and methane. This is followed by condensation to convert the gases to oils. The second approach uses a solvent or slurry to liquefy pulverized coal and then processes this liquid into a heavy fuel oil. Some processes produce both a synthetic gas and synthetic oil.

Hydrogen is used to convert sulfur in the coal to hydrogen sulfide gas. Hydrogen sulfide is partially oxidized to form elemental sulfur and water. More than 85% of the sulfur is removed from coal by liquefaction.[1]

Coal Cleaning

There are two types of coal cleaning: (1) physical coal cleaning and (2) chemical cleaning. Physical coal cleaning is used to remove the inorganic (mainly pyritic) sulfur compounds present in the coal. Chemical coal cleaning is used to reduce organic sulfur compounds.

Physical coal cleaning is a well-established technology that has been used for more than 50 years to reduce the sulfur and ash content of high sulfur coal supplies. Physical coal cleaning utilizes the differences in density of both the coal and the sulfur-bearing impurities in the coal. The coal is crushed, washed, and then separated by settling processes using cyclones, air classifiers or magnetic separators. Approximately 40-90% of the pyrite sulfur content can be removed by physical coal cleaning.' Its effectiveness depends on the size of pyritic sulfur particles and the amount of pyritic sulfur contained in the coal.

Chemical coal cleaning methods that reduce the organically bound sulfur are currently under development. In microwave desulfurization, the coal is crushed and then heated for 30 to 60 seconds by exposure to microwaves. Mineral sulfur selectively absorbs this radiation forming hydrogen sulfide gas (H_2S). The H_2S is usually reduced to elemental sulfur by the Claus process. Another microwave process adds calcium hydroxide [$Ca(OH)_2$] to crushed coal. The organic sulfur converts to calcium

sulfite (CaSO$_3$) when exposed to this radiation. The coal is washed with water to remove the CaSO$_3$ and other impurities. As much as 70% of the sulfur can be removed by the microwave process.[1]

Hydrothermal desulfurization, developed by Battelle Laboratories in Columbus, Ohio, is being refined through experiments sponsored by EPA's Office of Research and Development (ORD). Coal is crushed and mixed with a solution of sodium and calcium hydroxides [NaOH and Ca(OH)$_2$]. When this mixture is heated to 500°F (260°C) in a pressurized vessel, most of the pyritic sulfur and 20-50% of the organic sulfur are converted to sodium and calcium sulfites.[1] The coal is rinsed to remove the sulfites, and the water is processed to recycle the sodium and calcium hydroxides. This process is an expensive but effective method of removing sulfur from coal.

9.4 OPERATING PRINCIPLES

NONREGENERATIVE AND REGENERATIVE WET SCRUBBERS

There are three basic steps in the removal of sulfur dioxide from combustion process flue gas:

- Absorption of SO$_2$ into water droplets
- Reaction of the dissolved sulfur dioxide (as sulfurous) with alkaline species
- Precipitation and removal of solid reaction products

Absorption

Absorption of SO$_2$ into water droplets is illustrated in Figure 9-8. This is a very pH dependent process due to the formation of sulfurous acid in solution. The pH in the liquid decreases during absorption until the rate of absorption into the liquid and the rate of stripping of SO$_2$ out of the liquid are equal. At this equilibrium point, the removal efficiency of the FGD system for sulfur dioxide reaches zero.
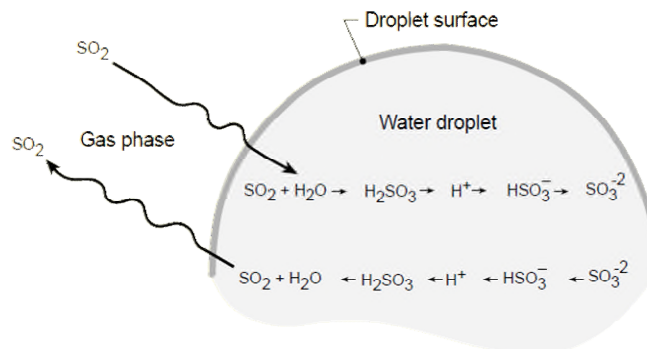
Figure 9-4. Absorption of SO$_2$ into water.

The extent to which this mass transfer equilibrium limits the removal efficiency of the scrubber is indicated by the sulfur dioxide equilibrium vapor pressure curve as a function of liquid pH. At pH levels below approximately 5.0, the equilibrium vapor pressure is above the normal concentrations of sulfur dioxide in the flue gas stream. Therefore, mass transfer to the liquid stops. In order to avoid this problem, the scrubbers are operated at pH levels above 5.5 and usually in the range of 6.0 to 6.5. These pH levels are maintained by the continual addition of alkali, which neutralizes the sulfurous acid and forms dissolved sulfite and sulfate compounds

as indicated in Figure 9-9. These chemical reactions in the liquid phase prevent the stripping of sulfurous acid molecules back to the gas phase. Accordingly, there is no significant equilibrium limit to the absorption in the >5.5 pH range.
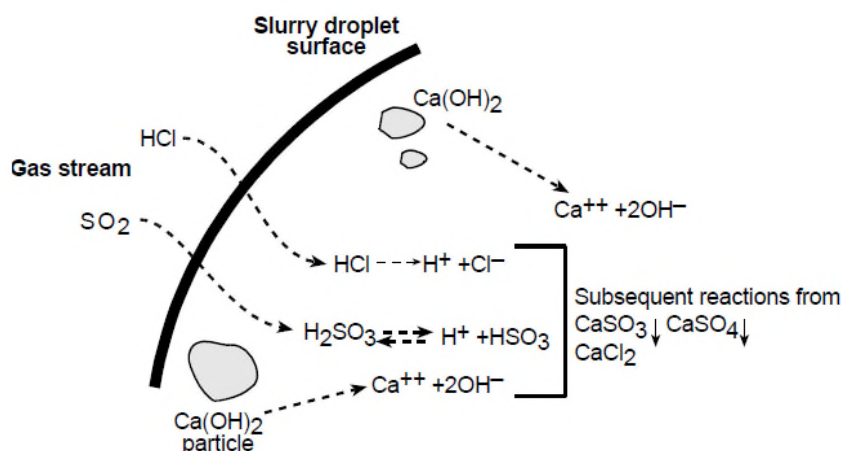
Figure 9-5. Absorption of SO_2 in alkaline slurry.

There are several additives that have proven useful for improving the absorption step. These include organic acids such as adipic acid and dibasic acid.[9] At concentrations of 800 to 3,000 ppm in the scrubbing liquid, these acids enhance SO_2 and improve the utilization of alkali. Magnesium hydroxide [$Mg(OH)_2$] may also be used to improve absorption and to improve the quality of the sludge generated in the process.

In addition to the pH level, the mass transfer of sulfur dioxide to the slurry droplets (or sheets of slurry liquid) depends on the extent of contact between the gas and liquid streams. Most lime and limestone systems use either an open spray tower design or a spray tower with a sieve-type tray in order to ensure high mass transfer rates. It is necessary to operate with liquid-to-gas ratios in the range of 20 to 100 gallons of slurry per 1,000 ACFM of flue gas. The size of the absorber vessel is based on the mass transfer rates achieved at the desired liquid-to-gas ratios. These mass transfer rates are determined empirically in pilot scale and demonstration scale test programs.

The absorption process is also affected by the temperature of the scrubbing liquid. However, the liquid temperature does not vary significantly in most boiler applications. The scrubbers usually operate at the adiabatic saturation temperature of the gas stream, which enters at temperatures of 250°F to 400°F (121°C to 204°C), and at a moisture content of 6-10% by volume. At these conditions, the scrubber operating temperatures are usually in the range of 120°F to 140°F (49 to 60°C). Higher temperatures would reduce the initial absorption step and cause water losses due to vaporization.

Chemical Reactions in Solution and Precipitation of Reaction Products

A number of chemical reactions take place in the scrubbing liquid. SO_2 is absorbed in the water and forms sulfite (SO^2), and sulfate (SO_4^{-2}) ions as indicated in Reactions 9-4 to 9-8.

Absorption Reactions

Reaction 9-4 $SO_2(g) \rightarrow SO_2(l)$

Reaction 9-5 $SO_2(l) + H_2O \rightarrow H_2SO_3(l)$

Reaction 9-6 $H_2SO_3(l) \rightarrow HSO_3^{-1}(l) + H^+$

Reaction 9-7 $HSO_3^{-1}(l) \rightarrow SO_3^{-2}(l) + H^+(l)$

Reaction 9-8 $SO_3^{-2}(l) + 0.5\ O_2 \rightarrow SO_4^{-2}(l)$

Note: (g)   gas phase

(l)   liquid phase

(s)   solid phase

Limestone dissolves in the slurry to form carbonate and bicarbonate species. The carbonate ion can react with the hydroxyl ion to increase the liquid pH. The dissolved calcium ions are free to react with the sulfite and sulfate ions to produce calcium sulfite and sulfate. These materials begin to precipitate out of solution when they exceed their solubility product limits.

Limestone Reactions

Reaction 9-9 $CaCO_3(s) \rightarrow CaCO_3(l)$

Reaction 9-10 $CaCO_3(l) \rightarrow Ca^{+2} + CO_3^{-2}$

Reaction 9-11 $CO_3^{-2} + H^+ \rightarrow HCO_3^{-1}$

Reaction 9-12 $SO_3^{-2} + H \rightarrow HSO_3^{-1}$

Reaction 9-13 $SO_3^{-2} + 0.5\ O_2 \rightarrow SO4^{-2}$

Reaction 9-14 $Ca^{+2} + SO_3^{-2} + 0.5\ H_2O \rightarrow CaSO_3 \cdot \frac{1}{2}H_2O(s)$

Reaction 9-15 $Ca^{+2} + SO_4^{-2} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O(s)$

Lime (CaO) is slaked with water (Reaction 9-16) to produce a slurry of calcium hydroxide {Ca(OH)$_2$. The calcium hydroxide/water slurry contains dissolved calcium and hydroxyl ion species that can react as shown in Reactions 9-16 to 9-21.

Lime Reactions

Reaction 9-16 $CaO(s) + H_2O \rightarrow Ca(OH)_2\ (1)$

Reaction 9-17 $Ca(OH)_2(1) \rightarrow Ca^{+2} + 2\ OH^{-1}$

Reaction 9-18 $OH^{-1} + H^+ \rightarrow H_2O$

Reaction 9-19 $SO_3^{-2} + H^+ \rightarrow HSO_3^{-1}$

Reaction 9-20 $Ca^{+2} + SO_3^{-2} + 0.5\ H_2O \rightarrow CaSO_3 \cdot \frac{1}{2}H_2O(s)$

Reaction 9-21 $Ca^{+2} + SO_4^{-2} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O(s)$

It is apparent from these reactions that a stoichiometric ratio of 1:1 must be maintained between the moles of lime and the moles of sulfur dioxide to be removed. Actually, larger quantities of lime are needed since the lime used **in** FGD systems is not a pure chemical and since the contact between the liquid and gas streams is not ideal. Actual stoichiometric ratios vary from 1.1 to 2:1.

Some FGD systems utilize forced oxidation in order to convert most of the sulfite to sulfate in accordance with Reaction 9-13. This improves the ability to handle the sludge that is formed in the clarifier and the vacuum filter. In other systems, oxidation is suppressed in order to minimize the conversion of sulfite to sulfate. Usually, it is not desirable to have a mixture with significant quantities of both calcium sulfite and calcium sulfate.

Dual Alkali Reactions

After reacting in the absorber, spent scrubbing liquor is bled to a reactor tank for regeneration. Sodium bisulfite and sodium sulfate are inactive salts and do not absorb SO_2. Actually, it is the hydroxide ion (OH), sulfite ion (SO_3) and carbonate ion (CO_3) that react with dissolved SO_1. Sodium bisulfite and sodium sulfate are reacted with lime or limestone to produce a calcium sludge and a regenerated sodium solution. Reactions 9-22 to 9-29 occur in the absorption loop and the scrubbing liquid regeneration loop.

Absorber loop:

Reaction 9-22 $2Na_2CO_3 + SO_2 + H_2O \rightarrow Na_2SO_3 + 2NaHCO_3$

Reaction 9-23 $NaHCO_3 + SO_2 \rightarrow NaHSO_3 + CO_2(^g)$

Reaction 9-24 $2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$

Reaction 9-25 $Na_2SO_3 + SO_2 + H_2O \rightarrow 2\,NaHSO_3$

Reaction 9-26 $2NaOH + SO_3 \rightarrow Na_2SO_4 + H_2O$

Reaction 9-27 $Na_2SO_3 + 0.5\,O_2 \rightarrow Na_2SO_4$

Regeneration loop:

Reaction 9-28 $2NaHSO_3(1) + Ca(OH)_2 \rightarrow Na_2SO_3 + CaSO_3 \cdot 2H_2O(s)$

Reaction 9-29 $Na_2SO_4 + Ca(OH)_2 \rightarrow 2NaOH + CaSO_4$
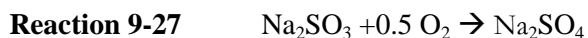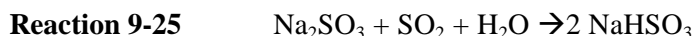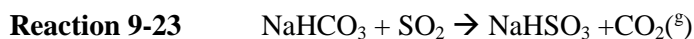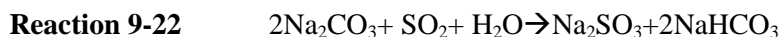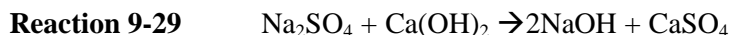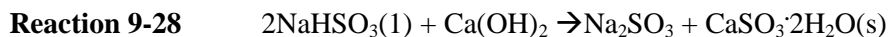
From the reactor, the slurry is pumped either to a clarifier or thickener where precipitated solids (sludge) are separated from the scrubbing liquor. These solids are dewatered by a vacuum filter and occasionally stabilized with a chemical or a lime and flyash mixture. Unstabilized sludge is

discarded in a settling pond. Stabilized sludge is discarded in a proper landfill. Some sodium sulfate is unreacted (lost) in the regeneration step. Additional sodium is added to the regenerated solution in the form of soda ash or caustic soda. This regenerated absorbent is then ready to be used again.

Wellman-Lord Reactions

The main absorption reaction in the Wellman-Lord process is the conversion of sodium sulfite to sodium bisulfite. Reaction 9-39 shown for the Wellman-Lord process is essentially identical to Reaction 9-25 for the dual alkali process and Reaction 9-31 for the magnesium oxide process.

Reaction 9-39 $SO_2 + Na_2SO_3 + H_2O \rightarrow 2NaHSO_3$

Some oxidation occurs in the absorber forming sodium sulfate as indicated in Reaction 9-40. Additional sodium sulfite can be generated to replace the amount lost due to Reaction 9-30 by adding sodium carbonate to the scrubbing liquid. This reacts with sodium bisulfite as shown in Reaction 9-41.

Reaction 9-40 $Na_2SO_3 + \frac{1}{2}O_2 \rightarrow Na_2SO_4$

Reaction 9-41 $Na_2CO_3 + 2NaHSO_3 \rightarrow 2Na_2SO_3 + CO_2 + H_2O$
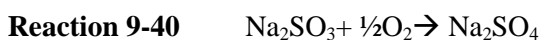
In the evaporator/crystallizer, sodium sulfite is regenerated, and a concentrated stream of sulfur dioxide gas is released as indicated in Reaction 9-42. The sulfur dioxide is then oxidized to form sulfuric acid or reduced to form elemental sulfur.

Reaction 9-42 $2NaHSO_3 \rightarrow Na_2SO_3 + H_2O + SO_2$

DRY SCRUBBING

Dry scrubbers use both absorption and adsorption mass transfer techniques for the removal of the acid gases. In absorption, acid gases first diffuse into the slurry droplet. The molecules dissociate and react, thereby preventing the acid gas molecules from going back into the gas phase. Adsorption occurs due to [p]hysical and chemical bonding of the acid gas molecules on the surfaces of the alkali particles. More alkali is generally needed for this type of mass transfer step. For spray dryer type systems, it is important that all of the slurry deposits evaporate to dryness prior to approaching the absorber vessel walls and prior to exiting the absorber with the gas stream. Any atomizer problems that result in larger slurry droplet size populations can cause this problem. Also, operation at lower than intended gas inlet temperatures can interfere with droplet drying.

The effectiveness of acid gas removal is partially dependent on spray dryer effluent gas temperature "approach-to-saturation." This is the difference between the extant gas temperature and the moisture dew point of the gas stream leaving the spray dryer vessel. In the case of fossil-fuel fired boilers, the approach-to-saturation must be within 15°F to 40°F (8°C to 22°C) in order to achieve the necessary SO_2 removal efficiencies due to the difficulty in collecting sulfur dioxide. In municipal waste incinerators, the "approach-to-saturation" is approximately 90°F to 180°F[3,6,7] (50°C to 100°C). However, this range is difficult to measure on a routine basis due to the unreliability of the wet bulb temperature measurements. Accordingly, the spray dryer outlet

gas temperature is often used as an indication of the "approach-to-saturation." If this value has increased substantially, it is possible that the acid gas removal efficiency has decreased.
The feed rate of alkali also affects the removal efficiency for acid gases. As indicated in Figure 9-11, the efficiency increases substantially for spray dryer systems as the ratio of alkali-to-acid gas increases above approximately a 1.5:1 to 2:1 stoichiometric ratio. This means that there must be approximately 1.5 to 2 times the molecules of calcium necessary to react with the hydrogen chloride and sulfur dioxide in the gas stream in accordance with the following composite reactions:

Reaction 9-43 $\quad Ca(OH)_2 + 2\ HCl \rightarrow CaCl_2 + 2\ H_2O$

Reaction 9-44 $\quad Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O$
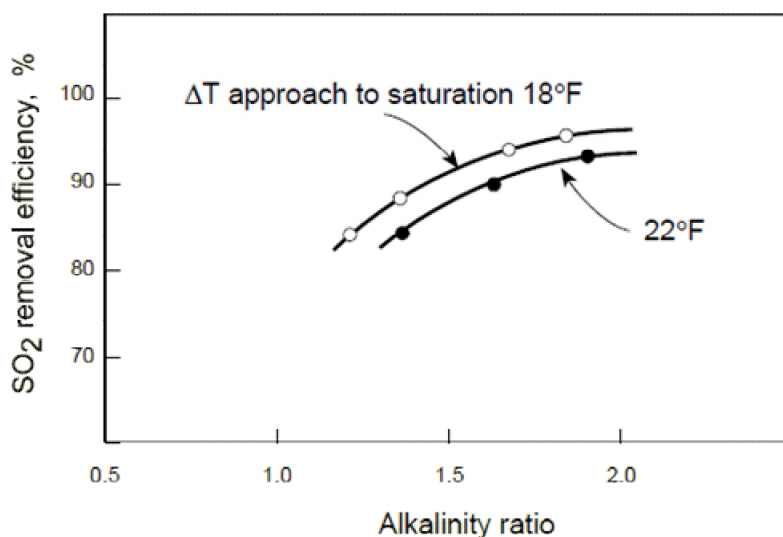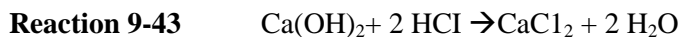
Figure 9-11. Effect of alkali stoichiometric ration on removal efficiency.

Gas temperature and alkali feed rates are also important for the dry injection type systems. The alkali stoichiometric requirements are several times greater than those, shown in Figure 9-11 for spray dryer type systems. This is due to the absence of the absorption mass transfer mechanism when operating with a dry powder rather than an evaporating slurry droplet.

9.5 SULFUR OXIDES CONTROL SYSTEMS CAPABILITY AND SIZING

EVALUATING A SULFUR DIOXIDE CONTROL SYSTEM

There are three general approaches to evaluating the capability of a sulfur dioxide control system: (1) empirical evaluations based on previously installed scrubbers on similar sources and

previous research programs, (2) pilot scale tests, and (3) theoretical performance models. Empirical data and information are most often used for selecting and designing sulfur dioxide control systems. These are appropriate due to the general similarity of fossil-fuel-fired boilers and waste incinerators with respect to sulfur dioxide control. Pilot scale tests are rarely performed due to the difficulty of making and transporting small scale scrubber vessels (e.g., spray atomization vessels), alkali reagent feed systems, and purge liquor treatment systems. Theoretical performance models can be used by the equipment manufacturers to supplement empirical information. However, these are not usually available to regulatory agency personnel for evaluating permit applications for new sulfur dioxide control systems.

Empirical Evaluation

Most FGD and dry scrubber manufacturers have extensive data bases describing the performance of their various commercial brands of systems on different types of fossil fuel fired boilers, waste incinerators, and other sulfur dioxide sources. This data is useful for determining whether or not a given type of system will be able to meet the performance requirements specified by the source owner. Site-specific information is considered along with this historical performance data to determine if a system would be appropriate.

- Average and maximum gas flow rates
- Average and maximum sulfur dioxide concentrations
- Average and maximum particulate concentrations
- Particulate matter composition
- Concentrations of corrosive gases and vapors in the inlet gas stream
- Availability of make-up water
- Purge liquid treatment and disposal requirements
- Sludge treatment and disposal requirements
- Source operating schedule

Area available for scrubber and wastewater treatment equipment Essentially all of the information included in this list can be determined for both new and existing sources. In the case of sulfur dioxide control systems, there are very few site-specific difficult-to-measure variables that could affect the ability of the system to meet the sulfur dioxide removal efficiency requirements and emission limitations. Most of the uncertainty that does exist concerns the particle size distribution in the gas stream leaving the particulate control system upstream of the SO_2 system and the concentrations of condensable vapor entering the SO_2 system. This site-specific information is used in conjunction with the historical data base to determine if the scrubber is applicable to the process. The data also provide a basis for designing the scrubber system components, determining the need for redundant scrubber modules and pumps, determining the need for stack gas reheating, and estimatin^g the necessary recirculation liquid flow rates and alkali feed rates.

The empirical data from previously installed control systems similar to the proposed control system is usually used as a basis for evaluating the capability of the proposed system to meet the regulatory requirements.

Pilot Scale Tests

Pilot scale tests are rarely performed due to the adequacy of the empirical approach and to the costs involved in pilot testing. In order to obtain representative results, it would be necessary to include an alkaline slurry preparation system that performs in a manner similar to the full scale system. It is

also be necessary to design a small scale absorber vessel or dry scrubbing vessel with the same mass transfer characteristics of the full scale units. The disposal of the sludge or solids generated during the pilot test may also be difficult. For these reasons, pilot scale testing is rarely performed for the purpose of designing a specific system. Pilot testing is used by equipment manufacturers to develop improved scrubbing system components and to optimize performance characteristics of their systems. However, this data may not be directly relevant to new systems being permitted.

Computerized Performance Models

Sophisticated performance models have been developed to help source operators maintain adequate recirculation liquid "chemistry" in the scrubbing system. These are very useful for avoiding scaling problems, corrosion problems, and SO_2 control problems due to shifts in the concentrations of important species in the recirculation liquid. However, these models are not intended for use in designing new sulfur dioxide control systems or for estimating the sulfur dioxide removal efficiency of proposed systems.

FUEL SULFUR SAMPLING SYSTEMS

For some industrial sources choosing to use low sulfur fuels for compliance with SO_2 emission limits, there is a need to routinely monitor the sulfur content of the fuel supply. There are several techniques available for obtaining small samples (usually 1 to 2 pounds) for the laboratory analyzes.

- Cyclonic samplers built into burner pipes from the pulverizer to the burners of pulverized coal fired boilers.
- Grab samples taken from the belts conveying coal to the boiler bunkers
- Grab samples taken from one or more bunkers on the boiler
- Grab samples taken during unloading of rail cars delivering coal to the plant

Because of the moderate-to-high variability of coal properties, there can be significant spatial variability in the coat sulfur levels. It is sometimes difficult to obtain a 1 to 2 pound sample from a coal stream of 50 to 500 tons of coal per hour. In addition to the spatial variability, the coal sulfur content of the coal can vary moderately over time due to differences in the parts of the coal mine being worked at a specific time.

Because of the spatial and temporal variations, the overall sulfur content of the fuel should be determined based on a statistically valid sample acquired over time rather than one individual measurement. To the maximum extent possible, the ASTM procedures concerning the representativeness of the sampling procedures should be followed in acquiring these fuel samples.

ALKALI REQUIREMENTS

Sulfur oxides control systems must include an alkali addition system to maintain proper absorption. The alkali requirements are usually calculated based on the quantities of acidic gases captured and the molar ratios necessary for reactions such as 9-45, 9-46, and 9-47.

Reaction 9-45 $SO_2 + Ca(OH)_2 + 0.5\ O2 \rightarrow CaSO_4 + H_2O$

Reaction 9-46 $2HCl + Ca(OH)_2 \rightarrow Ca^+ + 2\ Cl\text{-} + 2H_2O$

Reaction 9-47   2HF + Ca(OH)2$\rightarrow$ Ca ++2 F-+ 2H$_2$O
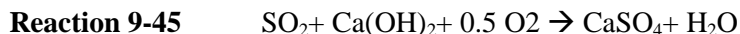
9.6 SO$_2$ CONTINUOUS EMISSION MONITORING

PERFORMANCE EVALUATION

Sulfur dioxide continuous emission monitors (CEMs) provide a direct indication of the performance of the control system. Common sulfur dioxide continuous analyzers include nondispersive infrared (NDIR) spectroscopy, gas filter correlation (GFC), nondispersive ultraviolet (NDUV) photometer-differential absorption, fluorescence, polargraphic, polarographic and second derivative spectroscopy units. A NDIR, ultraviolet, or fluorescence analyzer must be used for Reference Method (RM) testing according to 40 CFR Appendix A, Method 6C. NDIR is the most widely used type of analyzer for CEM systems.

The NDIR spectroscopy instrument measures the light absorbed by heteroatomic pollutant molecules such as SO$_2$, NO, CO, HCl, CO2, and hydrocarbons. Infrared light is emitted from a radiation source and transmitted through two cells, a reference cell and a sample cell, in parallel. The reference cell contains a gas that does not absorb the infrared light at the wavelength specific to the gaseous target compound. The sample cell contains the flue gas sample. A detector measures the energy difference of the light exiting the two cells at the wavelength of the target pollutant. This energy difference can then be related to the gas concentration.

Another type of NDIR technique is GFC. In addition to determination of SO$_2$ this method is currently applied to NO, CO$_2$, CO, NH$_3$, H$_2$O, HCl and hydrocarbon measurement. GFC differs from NDIR spectroscopy in that all of the reference signal energy is absorbed for the target gas compound. The infrared light emitted from a source passes through a rotating filter wheel. Half the filter contains a neutral gas allowing the light of interest to pass through. The other half of the filter contains the target gas, which absorbs nearly all of the light at the wavelength specific to the target pollutant. After exiting the filter wheel the light passes through a modulator to create an alternating signal. The alternating signal enters the sample cell where it reflects through a series of mirrors to increase the path length and improve the sensitivity of the instrument. The difference of the alternated light signals is measured to provide the gas concentration.

NDUV photometer-differential absorption takes advantage of the light in the UV region of the spectrum. An UV source emits light that passes through the sample gas before reaching the photomultiplier detection tube. The detector measures the light at two wavelengths. One wavelength is the absorption band of the molecule of interest (e.g., 280 nm for SO$_2$). The other wavelength provides reference signal at a wavelength not absorbed by the target gas. Differential absorption is used to relate the ratio of the two wavelength signals to the gas concentration.

Fluorescence is a photoluminescence process for determination of SO$_2$ in which emission of light is created by an excited molecule. UV light is emitted in a continuous or pulsating manner through the gas sample where the SO$_2$ molecules absorb a portion of the UV light. The SO$_2$ molecules become excited for 10^{-8} to 10^{-4} seconds before dropping to a lower energy state. By reverting to a lower energy state the molecules emit light of a longer wavelength than was

absorbed.

Reaction 9-48 $SO_2 + \eta \; h\nu \rightarrow SO_2 \rightarrow SO_2 + h\nu''$

                        210 nm   excited
                                    molecule
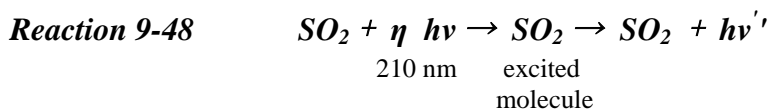
The emitted light from the SO_2 molecules is sent through a band-pass filter to filter out light wavelength that may cause interference before reaching the photomultiplier tube or other detection device.

Polarographic instruments (electrochemical transducers) utilize a transducer to measure the current produced from a chemical reaction involving the target pollutant. A chemical reaction takes place in an electrochemical cell where a selective semipermeable membrane causes the pollutant to diffuse to an electrolytic solution. The change in current is then measured as the oxidation or reduction reaction takes place. This reaction for SO_2 is shown below.

Reaction 9-49 $SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H+ 2e^-$

                        $E_0 = 0.17 \; V$
                        $_{298}$
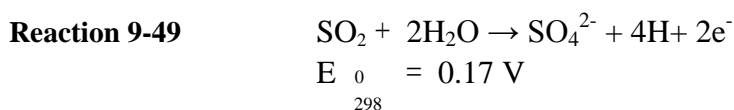
Second derivative spectroscopy is an in-situ method used for determining SO_2 concentrations. UV light is sent down a probe into the stack. The light enters a measurement chamber before being reflected back out the probe. A diffraction grating is located in a transceiver to measure the light. An oscillating lens moves the reflected light across the diffraction grating to scan a band of wavelengths centered on the pollutant absorption peak wavelength. Since the absorption peak of SO_2 is 218.5 nm, the range is 217.8 to 219.2 $_{nm}$ is commonly used for measurement. An oscillating signal produces a frequency that is twice the scanning frequency. The signal of the higher frequency is proportional to the second derivative of the intensity of the light entering the probe (shown in Equation 9-1). This signal is also proportional to the concentration of the gas.

Equation 9-1 $$S = \frac{\delta^2}{4}\left[-cl\frac{d^2\alpha}{d\lambda^2}I \right]$$

Where: S = oscillating signal monitored by the analyzer
              δ = scanning distance
              c = gas concentration
              l = light path length through the gas
              α = wavelength-dependent molecular absorption coefficient
              λ = wavelength
              I = intensity of the light leaving the probe

Some other in-situ CEM methods for SO_2 determination include GFC, band-pass filters, diffraction grating, and diode array detectors.

For those CEMs using an extracted gas sample, the SO_2 monitoring system generally consists of the probe, filter, conditioning system, and pump. Flue gas is continuously extracted from the stack at a constant flow rate using a pump. The flue gas enters a probe situated at an appropriate location inside the stack, passes through a filter and remains heated until reaching the conditioning system. The conditioning system, consisting of either a condensation device or

permeation tubes, removes the moisture and reduces the temperature of the sample. After the extractive system transports and conditions the sample gas, the sample is sent to analyzers. The analyzer outputs are then conveyed to a data acquisition system (DAS). Gas cylinders with known gas concentrations are used during calibration to prove the CEM system is void of leaks and the DAS is recording accurate values.

To ensure that the SO_2 emission data are accurate and representative, the CEM system should be installed in accordance with U.S. EPA specifications in 40 CFR Part 60. The CEM system should be routinely calibrated and tested in accordance with Appendix F of Part 60. Furthermore, the SO_2 data should be recorded and reduced in accordance with 40 CFR Part 60, Reference Method 6C and 19. The CEM system should have the instruments and/or data to confirm proper operation of the sulfur dioxide monitor.

Analyzer and Data Acquisition System

- Daily zero and span check recording
- Fault lamps on the analyzer panel and/or warning codes on the data acquisition system
- Data acquisition system warning codes
- Sample Conditioning System (Extractive Systems Only)
- Inlet sample line temperature
- Condenser temperature
- Sample gas flow rate
- Sample pressure
- Dilution gas flow rate (if applicable)

The installation and operation of the sulfur dioxide CEMs are similar to those discussed in Chapter 8 concerning NO_X continuous emission monitors. More detailed information concerning CEM systems is provided in APTI Course 474.

INSTRUMENTATION

Flue Gas Oxygen Content

The flue gas oxygen data are necessary in order to correct the SO_2 and NO_X data to a pounds per million Btu heat input basis. This is required due to the format of the NSPS, which is applicable to many utility and industrial boilers. For this reason, an oxygen monitor is usually installed in the stack at a location close to the CEM or CEM extractive probe.

The flue gas oxygen concentration is an important operating variable. Increased boiler excess air levels and/or increased air infiltration provide additional oxygen in the scrubbing liquor that can cause increased oxidation of sulfite to sulfate. Calcium sulfate precipitation can cause scaling-related operating problems in systems designed for sulfites.

Mist Eliminator Static Pressure Drop

All absorber vessels used on wet scrubbing systems must have a mist eliminator to remove droplets formed in the scrubber. The static pressure drop across the mist eliminator is usually in the range of 1 to 4 in. W.C. (0.25 kPa to 1.0 kPa) depending on the design of the mist eliminator and the gas velocity through the unit. An increase in the static pressure drop above the baseline range indicates solids buildup.

The static pressure drop data indicate that conditions have shifted significantly. This usually means that more aggressive cleaning of the mist eliminator is needed to remove the solids blocking part of the unit. If these solids are not removed, droplet reentrainment conditions could occur.

For large scale systems, the mist eliminator static pressure drop is usually monitored using a differential pressure (DP) transducer connected to the upper and lower ends of the mist eliminator section. The DP transmitter converts the static pressure data into an electrical signal that is transmitted to the control panel for the scrubber system. The static pressure taps on both sides of the mist eliminator should be readily accessible for the cleaning of accumulated sludge.

pH (Wet Scrubbing System)

The pH of the recirculation liquid used for SO_2 scrubbing is an important operating parameter. If the pH drops below approximately 5.5, the removal efficiency begins to drop due to absorption equilibrium limits. When the pH levels are above 5.5, there is sufficient alkali to react with the dissolved sulfur dioxide species and prevent mass transfer back to the gas phase. pH levels above approximately 8 can create scaling problems due to the precipitation of calcium and magnesium carbonates. Accordingly, the normal pH range for lime and limestone scrubbers varies from 5.5 to 8.

The pH is monitored by one or more instruments in the recirculation liquid system. In-line (pipe mounted) instruments can be used on the liquid return to the absorber vessel. pH instruments can also be located in the recirculation tanks or absorber sumps. In both these areas, the pH instruments can be vulnerable to scaling (solids buildup over the sensors) and to breakage. It is usually necessary to check

Alkali Feed Rates (Wet and Dry Scrubbing Systems)

The alkali feed rate to the absorber, spray dryer, or dry contractor is part of the primary data set that should be used to evaluate the performance of the sulfur dioxide control system. If the performance of the system is good (as indicated by the SO_2 CEM), these feed rate data also become part of a baseline data set. For absorbers and dry scrubber spray dryers, the rate of alkali slurry feed is usually monitored by a magnetic flow meter. Most systems also have a slurry density meter to monitor the slurry solids concentrations.

For dry injection-type dry scrubbers, the alkali feed rate is determined by a weight belt feeder between the storage hopper and the blower, which is used to inject the calcium hydroxide into the inlet duct.

Inlet and Outlet Gas Temperatures (Dry and Wet Scrubbing Systems

Dry Scrubbing Systems. The dry scrubber system inlet temperature is important for several reasons. In the case of spray dryer type systems, it affects the capability to evaporate the slurry droplets to dryness. Inlet temperatures that are too low can create sludge build-up problems in the outlet of the spray dryer vessel.

For dry injection systems, the inlet temperature affects the ability to cool the gas stream to the 250°F (121°C) level necessary for proper adsorption to the acid gases. Inlet temperatures

substantially above normal could create problems, especially if gas flow rates are also high. For these reasons, the inlet gas temperature during the performance evaluation should be recorded from the monitor in the control room. The operating records should also be checked to confirm that this temperature has consistently been maintained above the minimum at all times with the exception of startup and shutdown periods.

The spray dryer outlet gas temperature should be recorded in the primary data set since this is an indirect indicator of acid gas removal. Efficiency of absorption increases as this outlet temperature decreases. This is due partially to the longer time available for absorption of the acid gases into the water layers surrounding the drying particles. The limit is the saturation temperature. To prevent incomplete drying and sludge accumulation **in** the spray dryers, operators must keep the wet bulb temperature 50°F to 150°F (28°C to 83°C) above this saturation temperature. Unfortunately, the wet bulb temperature is difficult to measure under the conditions prevailing in the outlet ducts of spray dryers. Therefore, a standard thermocouple is often used. This measures the dry bulb temperature and serves as an indirect indicator of the actual "approach-to-saturation" in the spray dryer. Lower dry bulb temperatures are associated with more efficient acid gas removal.

Wet Scrubbing Systems. In the case of wet scrubbing systems, the inlet gas temperature is important only with respect to the materials of construction in the absorber vessel. If the inlet gas temperature is significantly higher than normal, damage could occur to the corrosion resistant liners and other non-metal components in the absorber vessel.

The outlet gas temperature is a useful indicator of severe gas-liquid maldistribution. The existence of this problem is indicated by absorber outlet gas temperatures 5°F to 10°F (3°C to 6°C) above the adiabatic saturation temperature.

9.7 SUMMARY

AIR SULFUR OXIDES SUMMARY

This chapter covered the following topics:

- Recognize operating principles for sulfur dioxides control.
- Identify appropriate evaluation and test methods for controlling sulfur dioxide.
- Identify appropriate evaluation and test methods when using fuel sulfur sampling systems.
- Recognize appropriate methods and evaluation for dry and wet scrubbing systems.

CONCLUSIONS

- The majority of the sulfur entering with fuel into combustion systems is converted to sulfur dioxide.
- There are no combustion modifications that minimize the rate of sulfur dioxide generation. However, the reduction of fuel sulfur levels has a direct and proportional impact on the sulfur dioxide emissions.
- Add-on control systems are used to remove sulfur dioxide from the gas stream. The main categories of control systems include nonregenerative wet scrubbing systems, regenerative wet scrubbing systems, and dry scrubbing systems.

- Most add-on control systems provide removal efficiencies of 75% to more than 90%.
- In wet scrubbing systems, alkali is injected into the gas stream to maintain the necessary sulfur dioxide absorption rates.

9.8 REVIEW EXERCISES

INSTRUCTIONS

Select the best response(s) for each of the following multiple-choice questions.

MULTIPLE CHOICE QUESTIONS

Sulfur Oxides Control System Types and Components

1. The calculated fuel sulfur input to the boiler is 100 pound moles per hour. What is the sulfur dioxide emission rate if 94% of the input sulfur is converted to sulfur dioxide. Select all that apply.

    a.   94 pound moles of sulfur dioxide per hour
    b. 188 pound moles of sulfur dioxide per hour
    c. 100 pound moles of sulfur dioxide per hour
    d. 6,016 pounds per hour
    e. 12,012 pounds per hour

2. Does the Henry's Law absorption limit affect the amount of sulfur dioxide that can be absorbed in a wet scrubbing type system?

    a. Yes
    b. No

3. What fraction of the sulfur entering with coal is usually converted into SO_2?

    a. 10% to 50%
    b. 50% to 75%
    c. 75% to 90%
    d. 90% to 94%
    e. 94% to 95%

4. What combustion modification techniques can be used to minimize the formation of sulfur dioxide in a coal-fired boiler?

    a. Low excess air operation
    b. Flue gas recirculation
    c. Off-stoichiometric combustion
    d. None of the above

Sulfur Oxides Control System Operating Principles

5. What is the normal pH range for the recirculation liquid in a lime- or limestone-type wet scrubbing system?

   a. 1 to 4
   b. 4 to 5.5
   c. 5.5 to 8
   d. 8 to 10
   e. 10 to 14

6. What is the normal stoichiometric ratio between the sulfur dioxide and the calcium hydroxide in lime scrubbers?

   a. 0.5:1 to 1.0:1
   b. 1.0:1 to 1.1:1
   c. 1.1:1 to 2.0:1
   d. 2.0:1 to 3.5:1

7. What is the normal stoichiometric ratio between the sulfur dioxide and the calcium hydroxide in a dry injection system?

   a. 0.5:1 to 1.0:1
   b. 1.0:1 to 1.1:1
   c. 1.1:1 to 2.0:1
   d. 2.0:1 to 3.0:1
   e. 3.0:1 to 4.0:1

Sulfur Oxides Control Systems Capability and Sizing

8. What is the typical sulfur dioxide removal efficiency in a nonregenerable wet scrubber?

   a. 99.5%
   b. 99%
   c. > 90%
   d. > 75%

9. What factors affect the accuracy of fuel sulfur measurements? Select all that apply.

   a. Spatial variability of the sulfur in the coal feed stream
   b. Temporal variability of the sulfur in the coal feed stream
   c. Laboratory analyses of the fuel sample
   d. None of the above

Sulfur Oxides Continuous Emission Monitoring

10. Which of the following techniques are used for SO_2 CEM systems? Select all that apply.

    a. Gas filter correlation (GFC)
    b. Flame ionization detector (FID)
    c. Nondispersive ultraviolet (NDUV)
    d. Fluorescence
    e. None of the above

9.9 REVIEW EXERCISE: SOLUTIONS

MULTIPLE CHOICE QUESTIONS

Sulfur Oxides Control System Types and Components

1. The calculated fuel sulfur input to the boiler is 100 pound moles per hour. What is the sulfur dioxide emission rate if 94% of the input sulfur is converted to sulfur dioxide. Select all that apply.

    a. **94 pound moles of sulfur dioxide per hour**
    b. 188 pound moles of sulfur dioxide per hour
    c. 100 pound moles of sulfur dioxide per hour
    d. **6,016 pounds per hour**
    e. 12,012 pounds per hour

2. Does the Henry's Law absorption limit affect the amount of sulfur dioxide that can be absorbed in a wet scrubbing type system?

    a. Yes
    b. **No**

3. What fraction of the sulfur entering with coal is usually converted into SO_2?

    a. 10% to 50%
    b. 50% to 75%
    c. 75% to 90%
    d. 90% to 94%
    e. 94% to 95%

4. What combustion modification techniques can be used to minimize the formation of sulfur dioxide in a coal-fired boiler?

    a. Low excess air operation
    b. Flue gas recirculation
    c. Off-stoichiometric combustion
    d. None of the above

Sulfur Oxides Control System Operating Principles

5. What is the normal pH range for the recirculation liquid in a lime- or limestone-type wet scrubbing system?

    a. 1 to 4
    b. 4 to 5.5
    c. 5.5 to 8
    d. 8 to 10
    e. 10 to 14

6. What is the normal stoichiometric ratio between the sulfur dioxide and the calcium hydroxide in lime scrubbers?

    a. 0.5:1 to 1.0:1
    b. 1.0:1 to 1.1:1
    c. 1.1:1 to 2.0:1
    d. 2.0:1 to 3.5:1

7. What is the normal stoichiometric ratio between the sulfur dioxide and the calcium hydroxide in a dry injection system?

    a. 0.5:1 to 1.0:1
    b. 1.0:1 to 1.1:1
    c. 1.1:1 to 2.0:1
    d. 2.0:1 to 3.0:1
    e. 3.0:1 to 4.0:1

Sulfur Oxides Control Systems Capability and Sizing

9. What is the typical sulfur dioxide removal efficiency in a nonregenerable wet scrubber?

    a. 99.5%
    b. 99%
    c. > 90%
    d. > 75%

10. What factors affect the accuracy of fuel sulfur measurements? Select all that apply.

    a. Spatial variability of the sulfur in the coal feed stream
    b. Temporal variability of the sulfur in the coal feed stream
    c. Laboratory analyses of the fuel sample
    d. None of the above

Sulfur Oxides Continuous Emission Monitoring

11. Which of the following techniques are used for SO_2 CEM systems? Select all that apply.

   a. Gas filter correlation (GFC)
   b. Flame ionization detector (FID)
   c. Nondispersive ultraviolet (NDUV)
   d. Fluorescence
   e. None of the above

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CHAPTER 10

10.0 CONTROL TECHNIQUES FOR GREENHOUSE GAS EMISSIONS

10.1 OVERVIEW

PURPOSE

The purpose of this chapter is to discuss the pollution control measures, technologies, and resources available to reduce greenhouse gas (GHG) emissions from stationary sources.

Note that some of the control techniques for N_2O emissions refer to those processes that were introduced in Chapter 8 of this course, *'Control Techniques for Nitrogen Oxides'*.

LEARNING OBJECTIVES

At the conclusion of this training, students will be able to:

- Understand the definition of GHG and the main industrial sources of GHG emissions.
- Identify the main GHG control techniques and strategies.
- Identify additional GHG emission control and reduction resources.

INTRODUCTION TO GREENHOUSE GAS EMISSIONS

The Earth's climate is determined by the balance between energy received from the sun and energy emitted back to space from the Earth and its atmosphere. Certain gases in the atmosphere, such as carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), water vapor, and others, trap some of the outgoing energy, retaining heat in the Earth's atmosphere. These are called "greenhouse gases" (GHGs). The best understood GHGs emitted by human activities are CO_2, CH_4, N_2O, and certain fluorinated compounds.

Changes in GHG emissions are influenced by many long-term factors, including population and economic growth, land use, energy prices, technological changes, and inter-annual temperatures. On an annual basis, combustion of fossil fuels, which accounts for most GHG emissions in the U.S., generally fluctuates in response to changes in general economic conditions, energy prices, weather, and the availability of non-fossil alternatives (U.S. EPA, 2011).

This chapter uses data and analysis from the Inventory of U.S. Greenhouse Gas Emissions and Sinks (U.S. EPA, 2012), an assessment of the anthropogenic sources and sinks of GHG emissions for the U.S. and its territories for the 1990-2010 period. The inventory constitutes estimates derived from direct measurements, aggregated national statistics, and validated models in most source categories. An extensive discussion of the methods for determining the emissions or uptake

from each source type and the uncertainties inherent in the calculations is available in U.S. EPA (2011) and its Annexes 2, 3, 4 and 7. http://www.epa.gov/climatechange/ghgemissions/ The introduction provided here is expressed in terms of CO_2 equivalents, meaning that emissions of different gases are weighted by their "global warming potential" (GWP). A GWP is a measure of how much a given mass of GHG is estimated to contribute to radiative forcing which in turn contributes to global warming over a selected period of time, relative to one another. Each gas's GWP is determined by comparing the radiative forcing associated with emissions of that gas versus the radiative forcing associated with emissions of the same mass of CO_2, for which the GWP is set at 1. EPA is mandated to use the GWPs documented in the Intergovernmental Panel on Climate Changes Second Assessment Report (IPCC, 1996), which characterize GWPs for a 100-year time to measure the effect of the gas on radiative forcing over 100 years. Annex 6.1 of the U.S. GHG inventory includes extensive information on GWPs and how they relate to emission estimates (U.S. EPA, 2011).

This chapter focuses on the six types of GHGs currently covered by agreements under the United Nations Framework Convention on Climate Change. These compounds are CO_2, CH_4, N_2O, selected hydrofluorocarbons (HFCs), selected perfluorocarbons (PFCs), and sulfur hexafluoride (SF_6). This indicator does not include emission estimates for substances such as chlorofluorocarbons (CFCs), methyl bromide, sulfates, black carbon, and organic carbon. These substances are excluded primarily because either their emissions have not been quantified in the U.S. GHG inventory or they have different kinds of effects on climate and therefore cannot be compared directly with the six types of GHGs included in the inventory. Combined, these excluded substances might account for a considerable portion of climate change, or offset climate change to some degree, but their omission cannot be scientifically quantified in comparable terms.

Emission data is presented in units of teragrams of CO_2 equivalents (Tg CO_2e). These units are conventionally used in GHG inventories prepared worldwide. For reference, one teragram (Tg) is equal to one million metric tons.

10.2 GREENHOUSE GAS EMISSION SOURCES

OVERVIEW

The EPA develops the national greenhouse gas inventory each year to track the national trend in emissions and removals since 1990. The national greenhouse gas inventory is submitted to the United Nations in accordance with the Framework Convention on Climate Change . In preparing the annual emissions inventory report, the EPA collaborates with hundreds of experts representing more than a dozen U.S. government agencies, academic institutions, industry associations, consultants and environmental organizations.

Figure 10-1 illustrates the relative contribution of the direct greenhouse gases to total U.S. emissions for the period 1990-2010. The primary greenhouse gas emitted by human activities in the United States was carbon dioxide (CO_2), representing approximately 83% of total greenhouse gas emissions. The largest source of CO_2, and of overall greenhouse gas emissions, was the combustion of fossil fuels. Methane emissions, which accounted for 10% of U.S. greenhouse gas emissions in 2009, resulted primarily from natural gas systems, enteric fermentation in livestock and decomposition of wastes in landfills. Agricultural soil management and mobile source fossil fuel combustion were the major sources of nitrous oxide emissions. Hydrofluorocarbons that substitute for ozone depleting substances and SF_6 emitted from electrical transmission and

distribution equipment were the primary sources of fluorinated gas emissions. To compare and combine emissions of different greenhouse gases into a national total, EPA uses global warming potentials (GWPs). GWPs compare the radiative forcing or ability to trap heat of one metric ton of a greenhouse gas to a metric ton of CO_2.
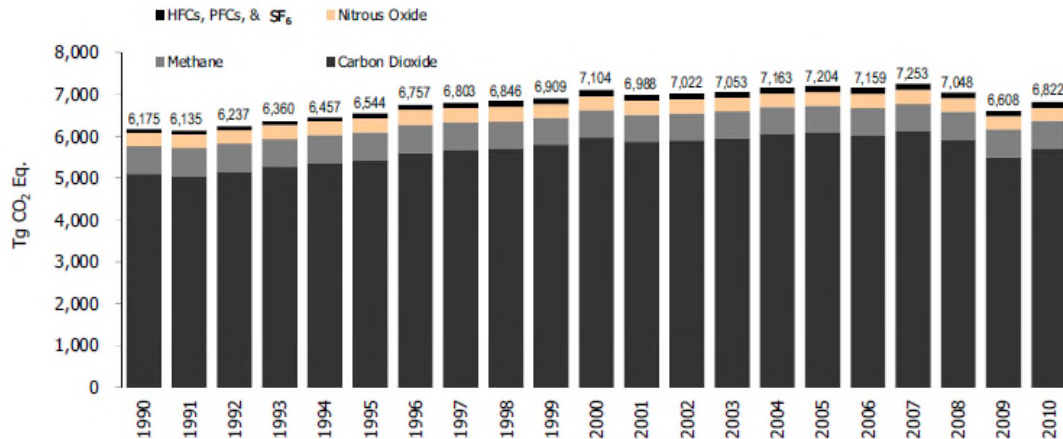
Figure 10-1. Contribution of GHG to total U.S. emissions.
Source: Inventory of U.S. Greenhouse Gas Emissions and Sinks,1990-2010.

In 2010, total U.S. greenhouse gas emissions were 6,821.8 Tg or million metric tons CO_2 Eq. Total U.S. emissions have increased by 10.5% from 1990 to 2010, and emissions increased from 2009 to 2010 by 3.2 % (213.5 Tg CO_2 e.). The increase from 2009 to 2010 was primarily due to an increase in economic output resulting in an increase in energy consumption across all sectors, and much warmer summer conditions resulting in an increase in electricity demand for air conditioning that was generated primarily by combusting coal and natural gas. Since 1990, U.S. emissions have increased at an average annual rate of 0.5%. Figure 10-1 and Figure 10-2 illustrate the overall trends in total U.S. emissions by gas, annual changes, and absolute change since 1990.
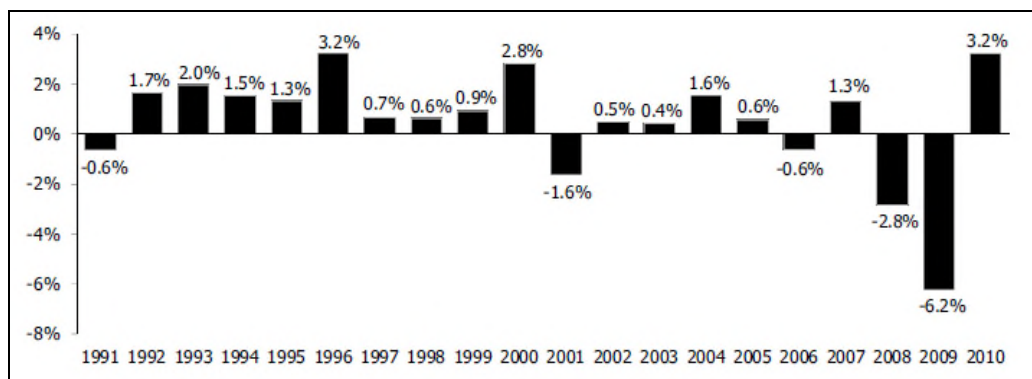
Figure 10-2. Annual percent change in U.S. greenhouse gas emissions.
Source: Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2010.

The U.S. greenhouse gas inventory also presents emissions by more commonly used economic categories: agriculture, commercial, electricity generation, industry, residential and transportation. Using this categorization, emissions from electricity generation accounted for the largest portion of

U.S. greenhouse gas emissions in 2010. Transportation activities accounted for the second largest portion, and emissions from industry made up the third largest portion. The agriculture, commercial and residential economic sectors, listed in descending order of their contribution, together account for the remaining U.S. greenhouse gas emissions. Figure 10-3 shows the trend in emissions by sector from 1990 to 2010.
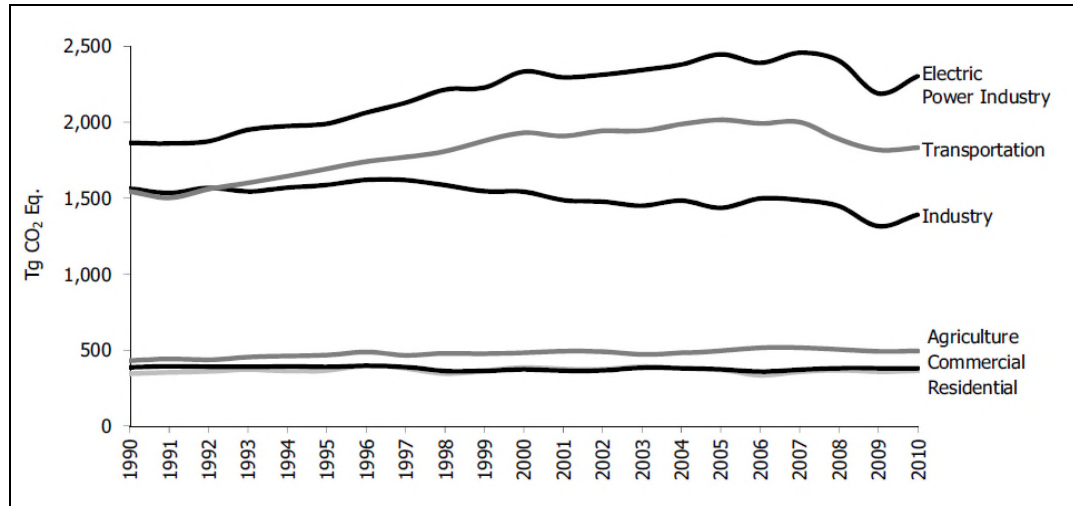
Figure 10-3. Emissions allocated to economic sectors
Source: Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2010,

Electricity, though produced at power plants, is ultimately consumed in the other economic sectors. When emissions from electricity are distributed among these sectors, the industrial sector accounts for the largest share of U.S. greenhouse gas emissions, about 34% of U.S. greenhouse gas emissions in 2010. Transportation remains the second largest contributor to GHG emissions (about 27%). Emissions from the residential and commercial sectors increase substantially due to their relatively large share of electricity consumption (e.g., lighting, appliances, etc.), with agriculture consuming little electricity. In contrast to electricity generation and transportation, emissions from industry have in general declined over the past decade. The long-term decline in these emissions has been due to structural changes in the U.S. economy (i.e., shifts from a manufacturing-based to a service-based economy), fuel switching, and efficiency improvements.
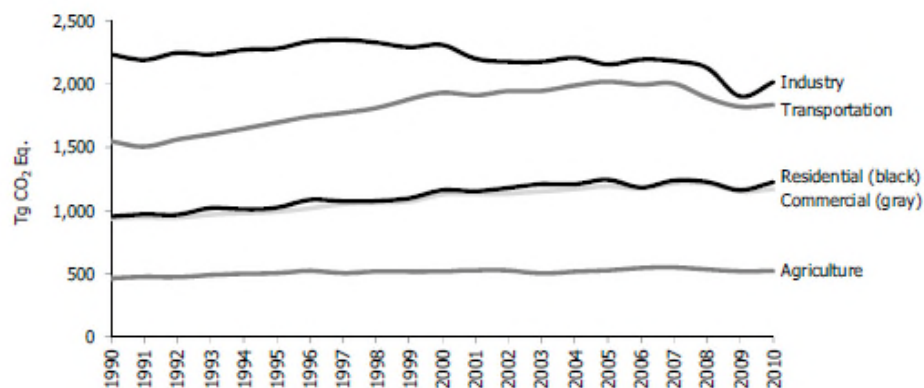
Figure 10-4. Emissions with electricity distributed to economic sectors.
Source: Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2010.

Land use, land-use change, and forestry activities in the United States result in a net removal of CO_2 from the atmosphere. This sector is responsible for offsetting approximately 15% of total U.S. CO_2 emissions, as represented in Figure 10-5.
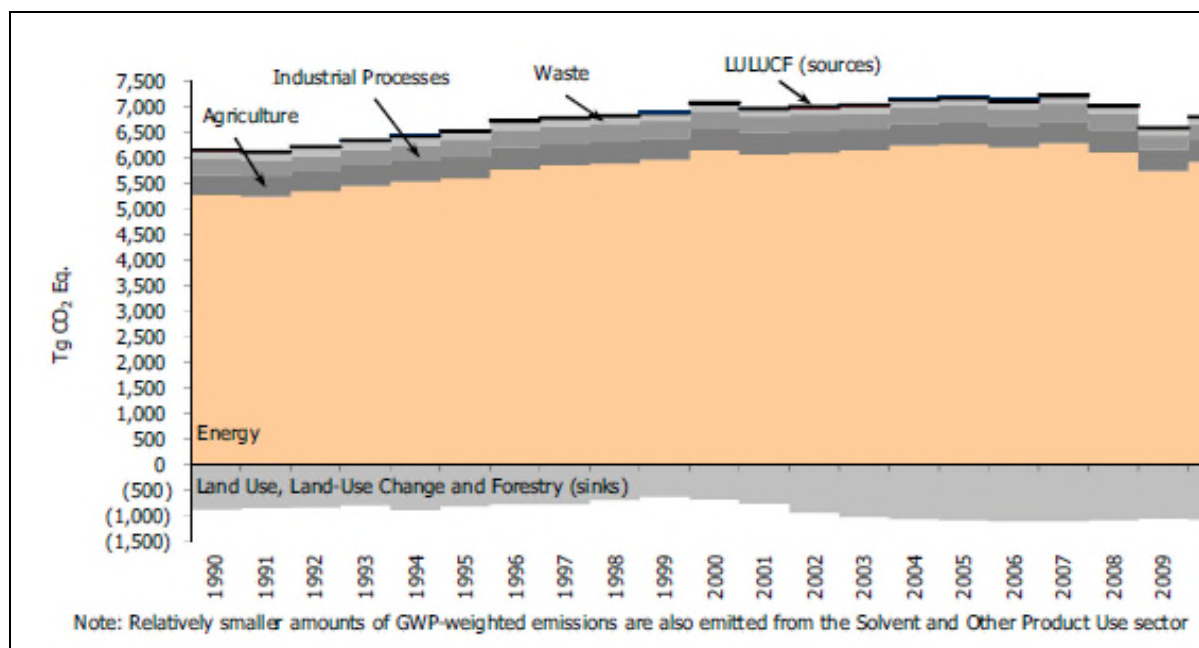
Figure 10-5. U.S. greenhouse gas emissions and sinks by Chapter/IPCC Sector.

Source: Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2010.

10.3 GHG EMISSIONS FROM INDUSTRIAL SOURCES

OVERVIEW OF GHG EMISSION SOURCES

This section includes an overview of the main industrial sectors, and the specific aspects of the related processes, and other factors that contribute to the national GHG emissions that were presented in the previous section of this chapter.

The following industrial sectors are described in this overview:

- Coal-Fired Electric Generating Units (EGUs)
- Large Industrial/Commercial/Institutional Boilers
- Pulp and Paper Manufacturing
- Cement Manufacturing
- Iron and Steel Industry
- Petroleum Refineries
- Nitric Acid Plants

Section 10.5 'GHG Emission Controls and Reductions' will introduce the emission reduction potential, energy savings, costs, and feasibility of control options available for each sector identified in the bulleted list above. The information presented in this training utilizes the research that is available in the EPA GHG Control Measures White Papers, which were published in October 2010.

10.3.1   GHG Emissions from Coal-Fired EGUs

Description of the Process

Coal is the most abundant fossil fuel in the United States and is predominately used for electric power generation. In 2008, approximately 49% of the net electricity generated in the U.S. was produced by coal (U.S. EIA 2010). Historically, electric utilities have burned solid coal in steam generating units. However, coal can also be first gasified and then burned as a gaseous fuel. The integration of coal gasification technologies with the combined cycle electric generation process is called an integrated gasification combined cycle (IGCC) system or a "coal gasification facility". The term "electric generating unit" or "EGU" is used to mean a solid fuel-fired steam generating unit that serves a generator that produces electricity for sale to the electric grid.

An EGU can be classified as either dry or wet bottom, depending on the ash removal technique used. To improve the overall thermal conversion efficiency of the Rankine cycle, the majority of EGUs include a series of heat recovery sections. The flue gas exhausted from the boiler passes through particulate matter (PM) and other air emissions control equipment before being vented to the atmosphere through a stack.

The principal chemical constituents of coal are carbon, hydrogen, oxygen, nitrogen, sulfur, moisture, and incombustible mineral matter (i.e., ash). When coal is burned, the carbon and hydrogen are oxidized to form the primary combustion products of CO_2 and water. Other combustion products such as NO_X, SO_2, CO, and PM are formed in varying amounts. The principal GHGs that enter the atmosphere because of human activities are CO_2, nitrous oxide (N_2O), methane (CH_4), hydrofluorocarbons (HFC's), perfluorocarbons (PCF's), and sulfur hexafluoride (SF_6). Of these, CO_2 is by far the most abundant GHG emitted from power production by coal utilization. To optimize overall efficiency for a given EGU, the unit is operated under conditions such that nearly all of the fuel carbon is converted to CO_2 during the combustion process. Methane is emitted during the mining and transport of coal but is not a significant by-product of EGU coal combustion. Fluorinated gases are not formed by coal combustion. Sulfur hexafluoride might be used at the power plant switchyard, but the switchyard is not typically considered part of the EGU.

Formation of N_2O during the combustion process results from a complex series of reactions and its formation is dependent upon many factors. However, the formation of N_2O is minimized when combustion temperatures are kept high and excess air is kept to a minimum. Pulverized Coal-fired EGUs are typically operated at these conditions and are not significant sources of N_2O emissions. However, Fluidized Bed Combustion (FBC) EGUs can have measurable N_2O emissions, resulting from the lower combustion temperatures and the use of selective noncatalytic reduction (SNCR) to reduce NO_X emissions. Operating factors impacting N_2O formation include combustion temperature, excess air, and sorbent feed rate[1]. The N_2O formation resulting from SNCR depends upon the reagent used, the amount of reagent injected, and the injection temperature[2].

FACTORS IMPACTING COAL-FIRED EGU CO₂ EMISSIONS

The level of CO_2 emissions that can potentially be released from a given coal-fired EGU depends on the type of coal burned (i.e., the coal rank), the overall efficiency of the power generation process, and use of air pollution control devices. The amount of heat released by coal combustion depends on the amounts of carbon, hydrogen, and oxygen present in the coal and, to a lesser extent, on the sulfur content. Hence, the ratio of carbon to heat content depends on these heat-producing components of coal, and these components vary by coal rank. Table 10-1 presents a comparison of the CO_2 emissions for the average heating values of U.S. coals. The values presented in the table are arithmetic averages and assume complete combustion. Based on these averages, in general anthracite emits the largest amount of CO_2 per million Btu (MMBtu), followed by lignite, subbituminous coal, and bituminous coal. However, for a given coal rank there is variation in the CO_2 emission factor depending on the coal bed from which the coal is mined.

Table 10-1. CO₂ Emission factors for coal by coal rank.		
Coal Rank	**CO₂ Emissions per Unit of Heat Input (lbs CO₂/MMBtu)**	
	U.S. Average	**Range Across States with Coal Rank Deposits**
Anthracite	22	227.
Bituminous	20	201.3 to 211.6
Subbituminous	21	207.1 to 214.0
Lignite	21	211.7 to 220.6

Source: U.S. EIA (Hong, R. and E. Slatick, 1994).

In addition to the lower CO_2 emissions rate per unit of heat input (lbs CO_2/MMBtu), due to the inherent moisture in subbituminous and lignite coals, all else being equal a bituminous coal-fired boiler is more efficient than a corresponding boiler burning subbituminous or lignite coal. Therefore, switching from a low to a high-rank coal will tend to lower GHG emissions from the utility stack. However, overall GHG emissions might not be lowered by switching to bituminous coal. All coal mining operations release coal bed methane to the atmosphere during the mining process. Some bituminous coal reserves release significant amounts of methane, which could, in theory, offset GHG savings. Additional factors when considering overall GHG emissions include the fuel needs to mine, process, and transport the coal.

IMPACT OF COAL-FIRED EGU EFFICIENCY ON CO₂ EMISSIONS

As the thermal efficiency of a coal-fired EGU is increased, less coal is burned per kilowatt-hour (kWh) generated, and there is a corresponding decrease in CO_2 and other air emissions. There is no standardized procedure for continuous on-line measurement of coal-fired EGU thermal efficiency (Peltier, 2010).

The electric energy output as a fraction of the fuel energy input expressed in percentage is a commonly-used practice for reporting the efficiency of a coal-fired EGU. The greater the output of electric energy for a given amount of fuel energy input, the higher the efficiency for the electric

generation process. Heat rate is another common way to express efficiency. Heat rate is expressed as the number of Btu or kJ required to generate a kWh of electricity. Lower heat rates are associated with more efficient power generating plants. Although the same basic formula is used to calculate efficiency for coal-fired EGUs, there are different methodologies for measuring the appropriate parameters. For example, the varying accuracy of the different methodologies can cause discrepancies in the measurement the heating value of the coal burned.

Calculating Efficiency

Efficiency can be calculated using the higher heating value (HHV) or the lower heating value (LHV) determined for the fuel. The HHV is the heating value directly determined by calorimetric measurement of the fuel in the laboratory. The LHV is calculated using a formula to account for the moisture in the fuel (i.e., subtract the energy required to vaporize the water in the coal and is thus not available to produce steam) and is a smaller value than the HHV. Consequently, the HHV efficiency for a given EGU is always lower than the corresponding LHV efficiency, because the reported heat input is larger. For bituminous coals the HHV efficiency value is typically about 2 percentage points lower than the corresponding LHV efficiency. For higher moisture subbituminous coals and lignites, the HHV efficiency is approximately 3 to 5 percentage points lower than the corresponding LHV efficiency (depending on moisture content). In engineering practice, HHV is typically used in the U.S. to express the efficiency of steam electric power plants while in Europe the practice is to use LHV.

Similarly, the electric energy output for an EGU can be expressed as either of two measured values. One value relates to the amount of total electric power generated by the EGU, or "gross output." However, a portion of this electricity must be used by the EGU facility to operate the unit, including pumps, fans, electric motors, and pollution control equipment. This in-facility electrical load, often referred to as the "parasitic load," reduces the amount of power that can be delivered to the transmission grid for distribution and sale to customers. Consequently, electric energy output is also expressed in terms of "net output," which reflects the EGU gross output minus its parasitic load.

More information about efficiency improvements is provided in *Section 10.5.1 'Emission Controls for Coal-fired EGUs'*

10.3.2   GHG EMISSIONS FROM LARGE INDUSTRIAL/COMMERCIAL/ INSTITUTIONAL BOILERS

Description of Typical Boiler Types and Uses

Industrial boilers include those used in manufacturing, processing, mining, and refining or any other industry to provide steam, hot water, and/or electricity. They are used for heating with hot water or steam in industrial process applications. **Commercial boilers** include boilers used in commercial establishments such as hotels/motels, restaurants, stores, and laundries to provide steam and/or hot water. **Institutional boilers** are use in those establishments such as medical centers, universities, schools, government buildings, and military installations to provide steam, hot water, and/or electricity. Institutional boiler systems are used for heating with hot water or steam. A majority of these are located at educational facilities.

ICI boilers can use a number of different fuels including coal (bituminous, sub bituminous, anthracite, lignite), fuel oil, natural gas, biomass (wood residue, bagasse), liquefied petroleum gas (LPG), and a variety of process gases and waste materials. Each of these fuels has different combustion characteristics and produces distinct GHG emissions. Coal is the highest CO_2 producer

in ICI boilers with an average emission factor of 93.98 kg CO_2/million British thermal units (MMBtu); natural gas has the lowest emissions of CO_2 from ICI boilers with an average emission factor of 53.06 kg CO_2/MMBtu. (EPA, 2008).

Figure 10-6 presents a process flow diagram of a typical industrial boiler system. Combustion for heat generation begins in the boiler burner system and the heat is transferred to the water in the boiler. The boiler produces steam and hot water for industrial process applications. Many boilers use an economizer to preheat the process water before it is fed to the boiler using waste heat from the exhaust gas. This combustion operation produces CO_2 emissions and is the focus of the emission reduction techniques presented in this chapter.
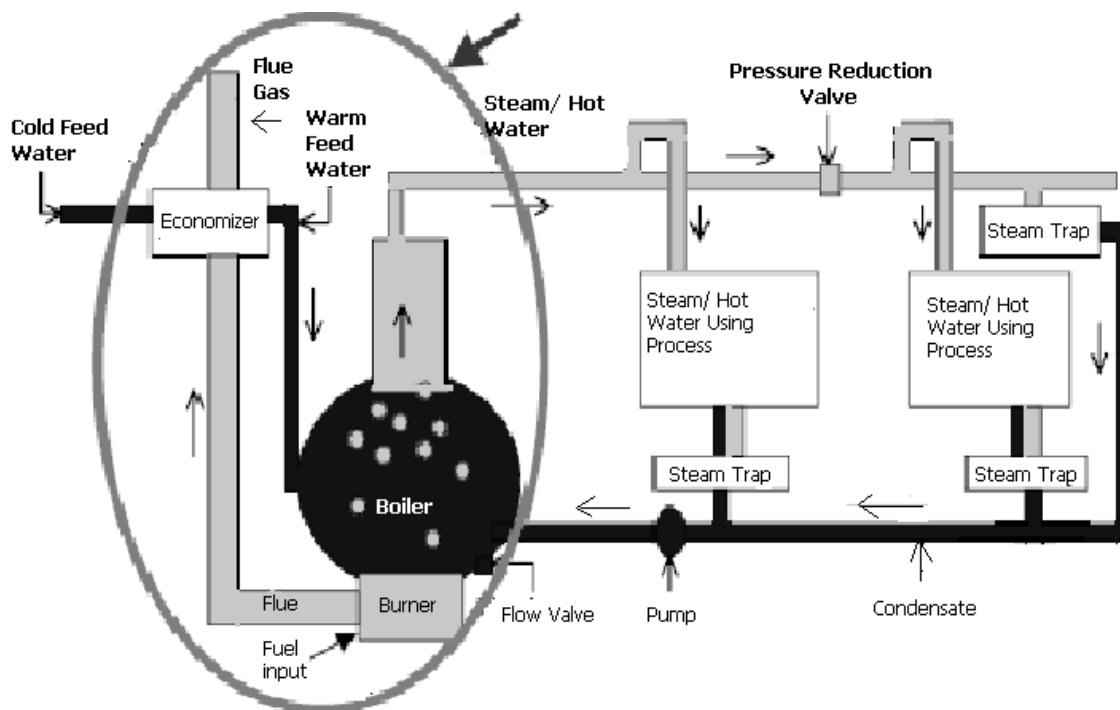
Figure 10-6. Schematic of an industrial boiler system.
Source: EPA, 2008.

FACTORS IMPACTING EMISSIONS FROM ICI BOILERS

The nature of the GHG emissions associated with industrial boilers, are similar to those of the EGUs. These units also combust fossil fuels to generate steam. The primary difference is that these do not use the steam to run a turbine and generate electricity for the grid. The biggest factor influencing the GHG emissions for these boilers is the type of fuel used.

The most common ICI boiler designs are:

- Pulverized coal (PC) boilers
- Fluidized bed combustors (FBC)
- Stoker boilers
- Watertube boilers
- Firetube boilers

Pulverized coal (PC) boilers — An efficient alternative to stokers for burning coal. Coal particles are blown into the boiler through a burner, and burned in suspension in the furnace. Typically, the bottom ash exits the boiler in solid or molten form. (dry bottom vs. wet bottom) (EEA, 2005).

Fluidized bed combustors (FBC) — Combustion takes place in suspension, like the PC boiler, but instead of individual burners controlling the air/fuel mixing, fuel and a mixture of inert material are kept suspended above the bed by an upward flow of combustion air through the fuel bed. This fluidization improves mixing of fuel and air, and allows for higher residence times in the furnace (the retention time of the fuel in the bed). FBC are inherently suited for various fuels, including low-grade fuels such as petroleum coke, coal refuse, municipal waste, and biomass materials.

Stoker boilers— Stoker boilers have been around the longest. In stoker boilers, the fuel is combusted in relatively thin layers on top of a "grate." Stoker boilers are typically characterized according to the way fuel is transported to the grate. The most common type is the spreader stoker, where the fuel is "spread" above the grate, allowing the fines to combust in suspension while the heavier pieces fall to the grate and combust. As with PC boilers, heat is transferred from the fire and combustion gases to watertubes on the walls of the boiler. Stokers can burn a variety of solid fuels, including coal and various wood and waste fuels.

Large, or Small Watertube — In watertube boilers, the fuel is combusted in a central chamber (furnace, bed, or grate) and the combustion gas transfers heat energy, through radiation and convection, to the water circulating in the metal tubes.

- Small watertube boilers are sized under 10 MMBtu/hr and, hence, are mostly oil- and gas-fired boilers.
- Large watertube boilers range generally from 10 to 10,000 million Btu per hour (MMBtu/hr).

Firetube — Firetube units are typically the smallest boilers, with most units less than 10 MMBtu/hr in capacity. Almost all firetube boilers burn oil, gas, or both. The "fire" and the water trade places-- the water is stored in the main body of the boiler, while the combustion gases flow through one or several metal tubes within the body of the boiler. Heat is transferred to the water by conduction from the firetube(s) to the surrounding water. Characterized by the number of "passes" the firetubes make through the boiler water. Increasing the number of passes increases overall efficiency. The advantages of firetube boilers are their simplicity and low cost.

ENERGY EFFICIENCY OPPORTUNITIES FOR ICI BOILERS

Over time, boilers deteriorate. This deterioration results in higher heat rates, increased CO_2 emissions, and operating costs; as well as reduced reliability; and in some cases, reduced output. After a few years of neglect, it may reach the point where significant investment is required to rehabilitate the plant and bring it as close as possible to the design performance.

Rehabilitation may focus on life extension and reliability or the efficiency of the original design efficiency. Efficiency can be improved by retrofitting combustion control technologies such as: heat recovery systems, control technology, and upgrading burners.

More information about efficiency improvements for ICI boilers is included in Section 10.5.2

'Emission Controls for Industrial, Commercial, and Institutional Boilers.'

10.3.3   GHG EMISSIONS FROM PULP AND PAPER MANUFACTURING

The U.S. pulp and paper industry is the largest self-generator of electricity in the U.S. manufacturing sector, with pulp and paper mills using on-site power boilers to generate steam, electricity, and process heat needed for mill processes. Steam is the largest end use of energy in the pulp and paper industry, with more than 1,026 TBtu used in 2002.

Recovery furnaces and other types of chemical recovery combustion units—used at pulp mills primarily to recover pulping process chemicals—also produce steam, electricity, and process heat for the mill. The need to keep up with significant mill demands for process steam and electricity, the high annual operating hours, and the presence of on-site generated fuels (i.e., wood waste and black liquor) has made combined heat and power (CHP) systems an operationally and financially attractive option for many mills around the country.

Major industrial CHP "prime mover" technologies include steam turbines, gas turbines, reciprocating engines, and fuel cells. Of these, steam and gas turbines dominate in U.S. pulp and paper mill applications. Traditional boilers, recovery furnaces, and steam turbine systems are by far the most common, and account for nearly 70% of current installed CHP capacity at pulp and paper mills. Around half of these boiler-based systems are fired by on-site fuels (i.e., by black liquor and hog fuel), and the other half are fired by purchased fuels (i.e., by coal, natural gas, and other fuels). These systems generally produce much more steam than electricity and, as a result, do not typically generate enough electricity to meet a mill's total electricity demand.

Biomass Energy Recovery

Two biomass by-products of the pulp and paper manufacturing process, black liquor and hog fuel (i.e., wood and bark), meet over half of the industry's annual energy requirements. The American Forest and Paper Association (AF&PA) estimates that biomass comprises 64% of total fuel use by AF&PA members' pulp and paper facilities. (AF&PA 2008) The use of these by-products as fuels significantly reduces the industry's dependence on purchased fossil fuels and electricity, with the added benefits of reduced raw material costs (i.e., avoided pulping chemical purchases) and reduced waste generation. Natural gas and coal comprise the majority of the remaining fuel used by the industry. (Kramer 2009) Incidental amounts of pulping vent gases and pulping by-products (tall oil and turpentine) are also used.

Pulp and Paper Manufacturing Processes

The manufacturing of paper or paperboard can be divided into six main process areas, which are discussed further in the sections below: (1) wood preparation; (2) pulping; (3) bleaching; (4) chemical recovery; (5) pulp drying (non-integrated mills only); and (6) papermaking. Figure 10-7 below presents a flow diagram of the pulp and paper manufacturing process. Some pulp and paper mills may also include converting operations (e.g., coating, box making, etc.); however, these operations are usually performed at separate facilities.
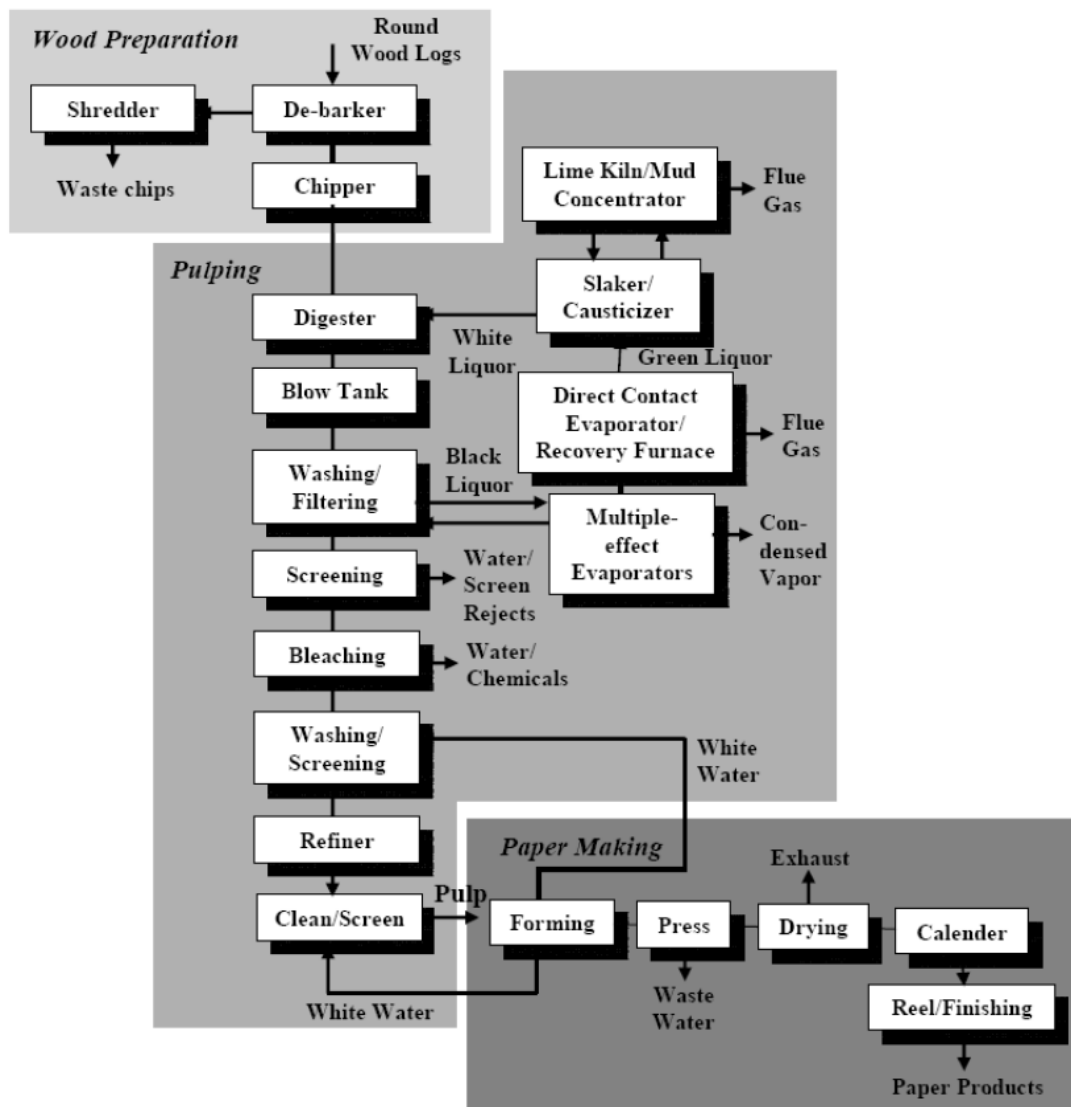
Figure 10-7. Flow diagram of the pulp and paper manufacturing process.
Source: Staudt 2010.

PULP AND PAPER GHG EMISSION SOURCES

Natural gas, fuel oil, biomass-based materials, purchased electricity, and coal are the major energy-related GHG emission sources for U.S. pulp and paper mills. When biomass-derived GHG emissions are not counted, the remaining four energy sources accounted for an estimated 80% or more of the industry's energy related GHG emissions in 2002. Thus, a primary option to reduce GHG emissions is to improve energy efficiency.

The GHG emissions associated with the pulp and paper mill operations can be attributed to: (1) the combustion of on-site fuels; and (2) non-energy-related emission sources, such as by-product CO_2 emissions from the lime kiln chemical reactions and CH_4 emissions from wastewater treatment. These emissions are emitted directly from the pulp and paper plant site. In addition, indirect emissions of GHG are associated with the off-site generation of steam and electricity that

are purchased by or transferred to the mill. Table 10-2 shows the relative magnitude of nationwide GHG emissions (in million metric tonnes of CO_2e per year [MTonne CO_2e/yr] and million short tons of CO_2e per year [Mton CO_2e/yr]) from stationary sources in the pulp and paper manufacturing sector.

Table 10-2. Nationwide GHG emissions from pulp and paper manufacturing.		
Emission Source	**Million metric tons of CO_2e per year[1]**	**Million short tons of CO_2e per year**
Direct Emissions		
Direct emissions associated with fuel combustion (excluding biomass CO_2)	57.7	63.6
Wastewater treatment plant CH_4 releases	0.4	0.4
Forest products industry landfills[3]	2.2	2.4
Use of carbonate make-up chemicals and fluegas desulfurization chemicals	0.39[3]	0.4[3]
Secondary pulp and paper manufacturing operations (i.e., converting primary products into final products)	2.5	2.8
Direct emissions of CO_2 from biomass fuel combustion (biogenic)[4]	113	125
Process-related CO_2 including CO_2 emitted from lime kilns (biogenic)[4]	*Unavailable[5]*	*Unavailable[5]*
Indirect Emissions		
Electricity purchases by pulp and paper mills	25.4	28
Electricity purchases by secondary manufacturing operations (i.e., converting primary products into final products)	8.9	9.8
Steam purchases	*Unavailable[5]*	*Unavailable[5]*

1. Except for make-up chemicals, nationwide CO_2e MTonne/yr totals are from National Council for Air and Stream Improvement (NCASI) Special Report No. 08-05, The Greenhouse Gas and Carbon Profile of the U.S. Forest Products Sector, September 2008; the Mton CO_2e/yr values are representative of year 2004.
2. Total includes emissions from wood products industry landfills (but it is expected that pulp and paper landfills are the dominant portion of the total).
3. Nationwide CO_2e MTonne/yr totals associated with carbonate makeup chemical use are from memorandum from Reid Miner, NCASI, to Becky Nicholson, RTI International, Calculations Documenting the Greenhouse Gas Emissions from the Pulp and Paper Industry, May 21, 2008; the Mton CO_2e/yr values are representative of years 1995 ($CaCO_3$) and 1999 (Na_2CO_3).
4. Historically, in voluntary GHG reporting, biogenic emissions at pulp and paper mills were considered "other emissions" and were not reported consistently across the industry. EPA's final GHG mandatory reporting rule (MRR) does require reporting of biogenic emissions (40 CFR Part 98).
5. Information on emissions of process-related CO_2 (including CO_2 emitted from lime kilns) and indirect emissions from steam purchases was not available in the literature reviewed. However, this information is required to be reported under subpart AA of EPA's final GHG MRR (40 CFR Part 98).

Secondary manufacturing facilities are not engaged in manufacturing primary pulp or paper products, but instead convert paper products into other products (e.g., paperboard into containers, coated/laminated papers). Some converting operations may operate small fossil fuel- fired package boilers. Direct and indirect emissions from secondary manufacturing operations are included in Table 10-2 above, along with emissions from primary manufacturing operations.

Table 10-3 lists the stationary direct GHG emission sources found in the pulp and paper manufacturing industry. GHG emissions associated with mobile sources and machinery are not discussed in this chapter. Almost all direct GHG emissions from pulp and paper manufacturing are the result of fuel combustion, and CO_2 emissions from stationary fuel combustion represent the majority of GHG emissions from pulp and paper mills on-site.

Mill projects might also involve indirect emissions of GHG associated with energy consumption by pulp and paper processing equipment, such as new or modified digesters, brownstock washers, bleach plant equipment, paper machines, and various other pulp and paper mill equipment. Emissions related to energy consumption depend on the type and source of the energy (e.g., electrical energy and/or process heat/steam generated on-site or from an outside source).

A number of tools are available to assist with estimating GHG emissions for the pulp and paper industry. Notably, EPA's GHG MRR (40 CFR part 98) contains equations and emission factors for stationary combustion (Subpart C), pulp and paper manufacturing (Subpart AA), industrial landfills (Subpart TT), and industrial wastewater treatment (Subpart II). The calculation procedures in the GHG MRR regulatory text are further described in technical support documents (TSDs) related to each subpart. These GHG MRR subparts and TSDs were compiled considering various GHG inventory and calculation protocols.

Table 10-3. Direct GHG emission sources at pulp, paper, and paperboard facilities.		
Emission Source	**Types of pulp and paper mills where emissions sources typically are located**	**Type of GHG Emissions**
Fossil fuel- and/or biomass- fired boilers	All types of pulp and paper mills	Fossil CO_2, CH_4, N_2O Biogenic CO_2, CH_4, N_2O
Thermal oxidizers and regenerative thermal oxidizers (RTOs)	Kraft pulp mills for NCG control and semi-chemical pulp mills (for combustion unit control)	Fossil CO_2, CH_4, N_2O
Direct-fired dryers	Gas-fired dryers at some pulp and paper mills	Fossil CO_2, CH_4, N_2O
Combustion turbines	All types of pulp and paper mills	Fossil CO_2, CH_4, N_2O
Chemical recovery furnaces –kraft & soda	Kraft and soda pulp mills	Fossil CO_2, CH_4, N_2O Biogenic CO_2, CH_4, N_2O
Chemical recovery furnaces –sulfite	Sulfite pulp mills	Fossil CO_2, CH_4, N_2O Biogenic CO_2, CH_4, N_2O
Chemical recovery combustion units – stand-alone semi- chemical	Stand-alone semi-chemical pulp mills	Fossil CO_2, CH_4, N_2O Biogenic CO_2, CH_4, N_2O
Kraft and soda lime kilns	Kraft and soda pulp mills	Fossil CO_2, CH_4, N_2O Process biogenic CO_2

Makeup chemicals (CaCO$_3$, Na$_2$CO$_3$)	Kraft and soda pulp mills	Process CO$_2$
Flue gas desulfurization systems	Mills that operate coal-fired boilers required to limit SO$_2$ emissions	Process CO$_2$
Anaerobic wastewater treatment	Chemical pulp mills (kraft, mostly)	Biogenic CO$_2$, CH$_4$
On-site landfills	All types of pulp and paper mills	Biogenic CO$_2$, CH$_4$

1. Except for make-up chemicals, nationwide CO$_2$e MTonne/yr totals are from National Council for Air and Stream Improvement (NCASI) Special Report No. 08-05, The Greenhouse Gas and Carbon Profile of the U.S. Forest Products Sector, September 2008; the Mton CO$_2$e/yr values are representative of year 2004.
2. Total includes emissions from wood products industry landfills (but it is expected that pulp and paper landfills are the dominant portion of the total).
3. Nationwide CO$_2$e MTonne/yr totals associated with carbonate makeup chemical use are from memorandum from Reid Miner, NCASI, to Becky Nicholson, RTI International, Calculations Documenting the Greenhouse Gas Emissions from the Pulp and Paper Industry, May 21, 2008; the Mton CO$_2$e/yr values are representative of years 1995 (CaCO$_3$) and 1999 (Na$_2$CO$_3$).
4. Historically, in voluntary GHG reporting, biogenic emissions at pulp and paper mills were considered "other emissions" and were not reported consistently across the industry. EPA's final GHG mandatory reporting rule (MRR) does require reporting of biogenic emissions (40 CFR Part 98).
5. Information on emissions of process-related CO$_2$ (including CO$_2$ emitted from lime kilns) and indirect emissions from steam purchases was not available in the literature reviewed. However, this information is required to be reported under subpart AA of EPA's final GHG MRR (40 CFR Part 98).

10.3.4   GHG EMISSIONS FROM CEMENT MANUFACTURING

Cement is a finely ground powder which, when mixed with water, forms a hardening paste of calcium silicate hydrates and calcium aluminate hydrates. Cement is used in mortar (to bind together bricks or stones) and concrete (bulk rock-like building material made from cement, aggregate, sand, and water). By modifying the raw material mix and the temperatures utilized in manufacturing, compositional variations can be achieved to produce cements with different properties. In the U.S., the different varieties of cement are denoted per the American Society for Testing and Materials (ASTM) Specification C-150.

Process-related CO$_2$ Emissions

Process-related CO$_2$ emissions from cement production are the second largest source of industrial CO$_2$ emissions in the United States[3]. (EPA, 2008) The cement production process comprises the following two steps: (i) clinker production and (ii) finish grinding. Essentially all GHG emissions from cement manufacturing are CO$_2$ emissions from clinker production. There are no CO$_2$ emissions from the finish grinding process, during which clinker is ground finely with gypsum and other materials to produce cement. However, indirect CO$_2$ emissions are associated with the electric power consumed by plant equipment such as the grinders.

Figure 10-8 presents a diagram of the cement manufacturing process using a rotary kiln and cyclone preheater configuration. The schematic for a rotary kiln and precalciner configuration is very similar to that shown below, with a calciner vessel located between the rotary kiln and cyclone preheater. Combustion for heat generation may occur in the riser to the preheater, in the calciner

and/or in the kiln. These combustion processes are one of two primary sources of GHG emissions, the second being the calcinations reaction that occurs in the kiln. These GHG sources are the focus of the control measures presented here.

Figure 10-8. Diagram for cement manufacturing preheater process.
Source: Cembureau 1999.

TOTAL COMBUSTION AND PROCESS-RELATED GHG EMISSIONS

Total combustion and process-related GHG emissions from 2006 cement production, including methane (CH_4) and nitrous oxide (N_2O) emissions from fossil fuel combustion based on plant-specific characteristics were estimated to be 95.5 tons (86.8 million metric tons) of CO_2e (MTonne CO_2e) (EPA, 2007b). This is equivalent to 0.98 tons of CO_2e per ton of clinker, of which 0.46 tons are attributable to fuel combustion.

Combustion emissions include CO_2, N_2O and CH_4 emissions that result from the combustion of carbon-based fuels in the cement kiln and other onsite combustion equipment. The cement kiln is the most significant of these combustion units and typically is fueled with coal. Other fossil fuels are generally too expensive to be used for kiln fuel; however carbon-based waste materials (e.g., solvents, oils, and waste tires) are commonly combusted in the kilns to dispose of the waste, and make use of their energy content. The other sources of CO_2 emissions stemming from cement manufacturing operations include transportation equipment used in the mining and transport of raw and finished materials and the fuels required for operating the process. The direct CO_2 emission intensity of fuels depends on the carbon content of the fuel which varies by type of fuel and further may vary within a given fuel type. The emission intensity of coals, for example, will vary depending on its geologic source. Table 10-4 shows the CO_2 emission intensity in pounds per million British Thermal Units (lb/MMBtu) for fuels combusted at cement kilns in the United States.

Table 10-4. CO_2 emission intensity (lb/MMBtu).					
Natural Gas	Heavy Fuel Oil	Western Sub- bituminous Coal[1]	Tires	Eastern Bituminous Coal[2]	Petroleum Coke
105.02	169.32	186.83	187.44	199.52	212.56

1 Origin - Rosemont Powder River Basin
2 Origin - Logan, West Virginia
Source: Staudt, 2008a

10.3.5   GHG EMISSIONS FROM IRON AND STEEL INDUSTRY

Steel is an alloy made by combining iron and another element, usually carbon. When carbon is used, its content in the steel is between 0.2% and 2.1% by weight, depending on the grade. When iron is smelted from its ore by commercial processes, it contains more carbon than is desirable. To become steel, it must be melted and reprocessed to reduce the carbon to the correct amount, at which point other elements can be added.

The GHG emissions are generated as (1) process emissions, in which raw materials and combustion both may contribute to CO_2 emissions; (2) emissions from combustion sources alone; and (3) indirect emissions from consumption of electricity (primarily in EAFs and in finishing operations such as rolling mills at both integrated and EAF plants).

PROCESS-RELATED GHG EMISSIONS

The production of steel at an integrated iron and steel plant is accomplished using several interrelated processes. The major processes are (1) coke production, (2) sinter production, (3) iron production, (4) raw steel production, (5) ladle metallurgy, (6) continuous casting, (7) hot and cold rolling, and (8) finished product preparation.

The operations for secondary steelmaking, where ferrous scrap is recycled by melting and refining in electric arc furnaces (EAFs) include (4) through (8) above. The interrelation of these operations is shown in a general flow diagram of the iron and steel industry in Figure 10-9.

Additional Process Terminology/ Background

Coke Production (Coke) - is the carbon product formed by thermal distillation of coal at high temperatures in the absence of air in coke oven batteries. Coke is used in the blast furnace to provide a reducing atmosphere and is also a source of fuel. Most coke in the U.S. is produced in by-product recovery coke oven batteries, which recover tar, light oil, ammonia, and coke ovengas (COG) from the vapors generated in the ovens. Approximately one-third of the cleaned COG is used to fuel the coke ovens, and the balance is used in other combustion units at the steel plant. The four newest coke plants use non-recovery coke oven batteries that burn the by-products rather than recover them. The new non-recovery coke plants capture the waste heat from combustion to generate steam and electricity. The primary GHG emission point at coke plants is the battery's combustion stack.

Sinter Production (Sintering) **-** is a process that recovers the raw material value of many waste materials generated at iron and steel plants that would otherwise be landfilled or stockpiled. Feed material to the sintering process includes ore fines, coke, reverts (including blast furnace dust, mill scale, and other by-products of steelmaking), recycled hot and cold fines from the sintering process, and trim materials (e.g., limestone, calcite fines, and other supplemental materials needed to produce a sinter product with prescribed chemistry and tonnage). The sinter feed materials are fused together by a flame fueled by natural gas and/or COG plus the ignition of coal and coke fines in the sinter feed. The product is a hard-fused material called sinter that is suitable for charging to the blast furnace.

The primary emissions point of interest for the sinter plant is the stack that discharges the exhaust gases after gas cleaning. The CO_2 is formed from the fuel combustion (COG or natural gas) and from carbon in the feed materials, including limestone, coke fines, and other carbonaceous materials.

Iron Production- Iron is produced in **blast furnaces** by the reduction of iron-bearing materials with a hot gas. The large, refractory-lined furnace is charged through its top with iron ore pellets (taconite), sinter, flux (limestone and dolomite), and coke, which provides the fuel and forms a reducing atmosphere in the furnace. Many modern blast furnaces also inject pulverized coal or other sources of carbon to reduce the quantity of coke required. Iron oxides, coke, coal, and fluxes react with the heated blast air injected near the bottom of the furnace to form molten reduced iron, carbon monoxide (CO), and slag. The molten iron and slag collect in the hearth at the base of the furnace and are periodically removed from the furnace ("tapping"). The blast furnace gas (BFG) is collected at the top of the furnace and is recovered for use as fuel in the blast furnace stoves and other parts of the steel plant.

The vast majority of GHGs (CO_2) are emitted from the blast furnaces' stove stacks where the combustion gases from the stoves are discharged. The carbon in the CO_2 exhaust comes mostly from the coke and coal used as fuel. A small amount of emissions may also occur from flares, leaks in the ductwork for conveying the gas, and from blast furnace emergency venting.

Steelmaking Routes: Integrated Route and Electric Arc Funace Route.
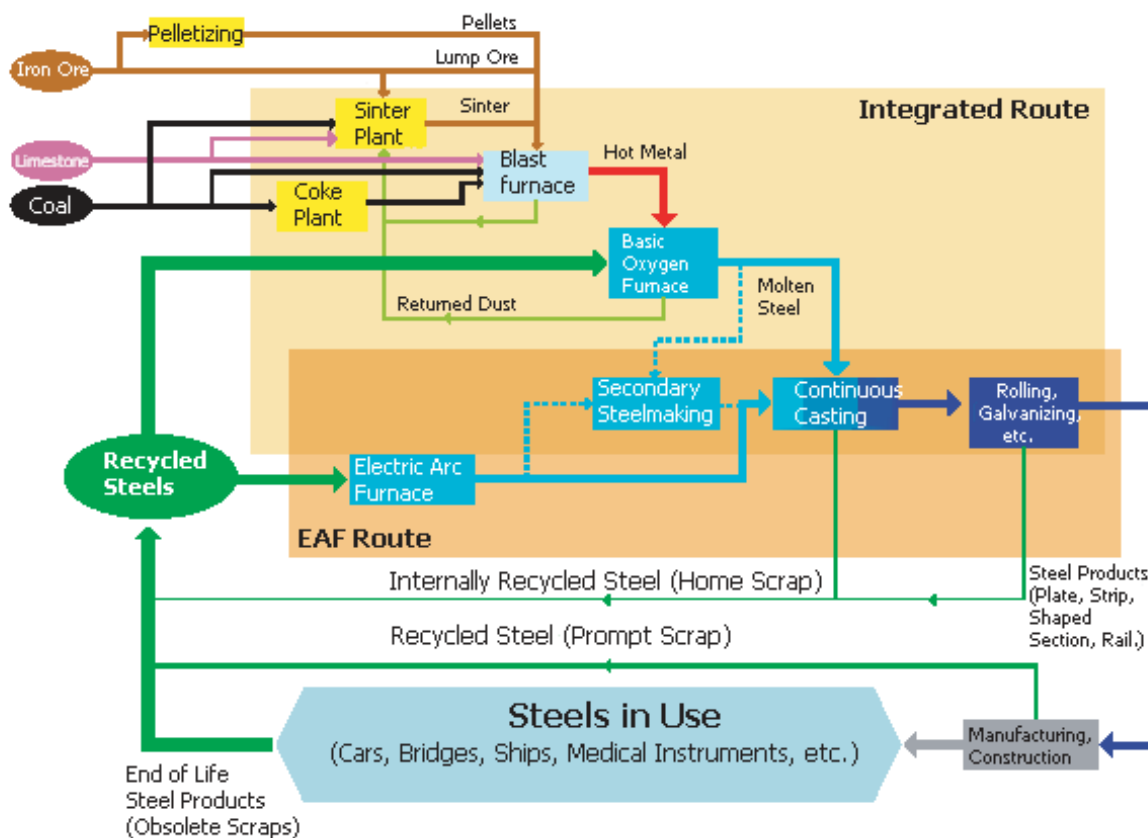
Figure 10-9. General flow diagram of the iron and steel industry.
Source: GHG Control Measures White Papers (EPA 2010).

FACTORS IMPACTING GHG EMISSIONS IN IRON AND STEEL MANUFACTURING

For integrated steelmaking, the primary sources of GHG emissions are blast furnace stoves (43%), miscellaneous combustion sources burning natural gas and process gases (30%), other process units (15%), and indirect emissions from electricity usage (12 %). For EAF steelmaking, the primary sources of GHG emissions include indirect emissions from electricity usage (50%), combustion of natural gas in miscellaneous combustion units (40%) and steel production in the EAF (10%). Table 10- 5 provides preliminary estimates of GHG emissions from various iron and steel operations (based primarily on emissions factors and 2007 production rates). Blast furnaces and non-recovery coke plants are the largest emitters on a per process basis. Note that due to the economic downturn, lower production rates, GHG emissions were lower for 2008-2009.

Table 10-5. Estimates of GHG emissions from iron and steel manufacturing.						
Type of Facility	Number of Facilities	Emissions (million tonnes of CO_2/yr)				
		Process Units	Miscellaneous Combustion Units	Indirect Emissions (Electricity)	Facility Total	Average per Plant
Coke and EAF						
By-product coke (standalone)	9	2.8	2.7		5.5	0.6
Nonrecovery coke	3	3.0			3.0	1.0
EAF facilities	92	4.8	18.6	22.8	46.2	0.5
Integrated Iron and Steel Plants:						
By-product coke (co-located)	6	1.2			1.2	0.2
Blast furnace	17	23.9			23.9	1.4
BOF	18	4.4			4.4	0.2
Sinter plant	5	2.7			2.7	0.5
Totals						
All Integrated Iron and Steel	18	32.2	16.8	6.5	55.5	3.1
All Facilities	130	42.8	38.0	29.3	110.1	0.8

Note: yr = year.

10.3.6   GHG Emissions from Petroleum Refining

Description of the Process

Petroleum refineries produce liquefied petroleum gases (LPG), motor gasoline, jet fuels, kerosene, distillate fuel oils, residual fuel oils, lubricants, asphalt (bitumen), and other products through distillation of crude oil or through redistillation, cracking, or reforming of unfinished petroleum derivatives. There are three basic types of refineries: topping refineries, hydroskimming refineries, and upgrading refineries (also referred to as "conversion" or "complex" refineries).

Topping refineries have a crude distillation column and produce naphtha and other intermediate products, but not gasoline. There are only a few topping refineries in the U.S., predominately in Alaska. Hydroskimming refineries have mild conversion units such as hydrotreating units and/or reforming units to produce finished gasoline products, but they do not upgrade heavier components of the crude oil that exit near the bottom of the crude distillation column. Some topping/hydroskimming refineries specialize in processing heavy crude oils to produce asphalt. There are eight operating asphalt plants and approximately 20 other hydroskimming refineries operating in the United States as of January 2006 (Energy Information Administration [EIA], 2006). The vast majority (approximately 75 to 80%) of the approximately 150 domestic refineries are upgrading/conversion refineries.

Upgrading/conversion refineries have cracking or coking operations to convert long-chain, high molecular weight hydrocarbons ("heavy distillates") into smaller hydrocarbons that can be used to produce gasoline product ("light distillates") and other higher value products and petrochemical feedstocks.

GHG EMISSIONS FROM PETROLEUM REFINING

The petroleum refining industry is the nation's second-highest industrial consumer of energy (U.S. DOE, 2007). Nearly all of the energy consumed is fossil fuel for combustion; therefore, the petroleum refining industry is a significant source of GHG emissions. In addition to the combustion-related sources (e.g., process heaters and boilers), there are certain processes, such as fluid catalytic cracking units (FCCU), hydrogen production units, and sulfur recovery plants, which have significant process emissions of CO_2.

Methane emissions from a typical petroleum refinery arise from process equipment leaks, crude oil storage tanks, asphalt blowing, delayed coking units, and blow down systems. Asphalt blowing and flaring of waste gas contributes to the overall CO_2 and CH_4 emissions at the refinery. Based on a bottom-up, refinery-specific analysis (adapted from Coburn, 2007, and U.S. EPA, 2008), GHG emissions from petroleum refineries were estimated to be 214-million metric tons of CO_2e, based on production rates in 2005. Figure 10-10 provides a breakdown of the nationwide emissions projected for different parts of the petroleum refineries based on this bottom-up analysis.
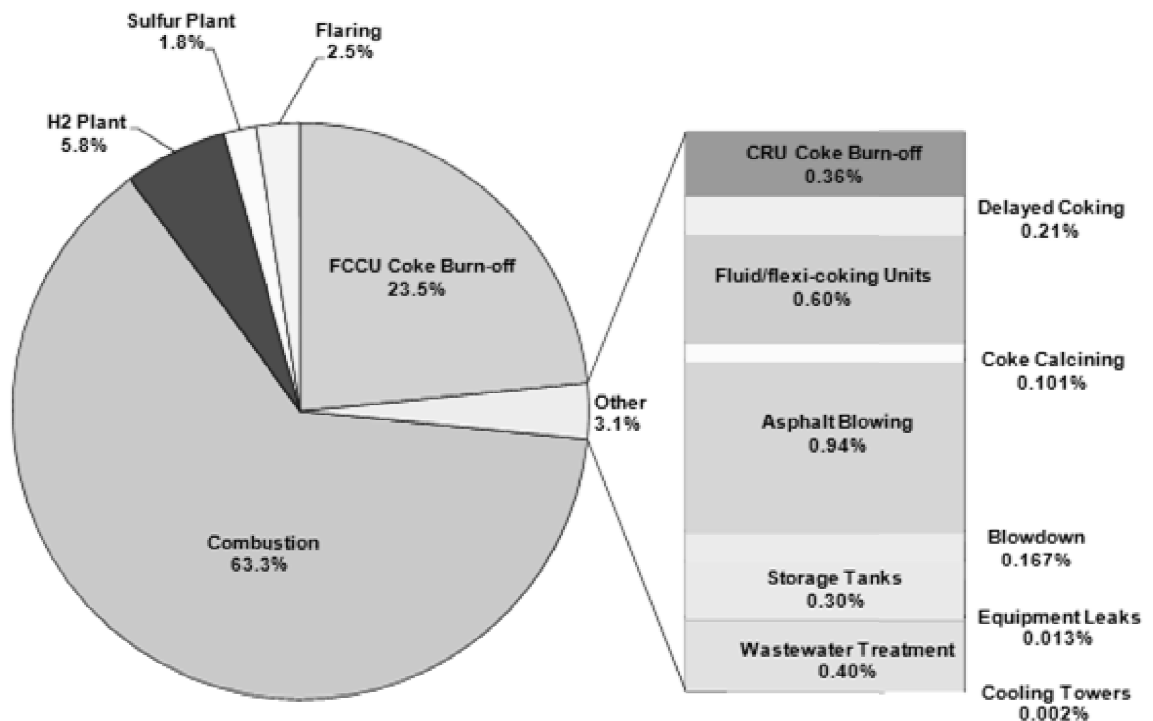
Figure 10-10. Contribution of different emission sources to the nationwide CO_2 equivalent GHG emissions from petroleum refineries.
Source: GHG Control Measures White Papers (EPA 2010).

Figure 10-11 presents what GHGs are emitted by refineries. CO_2 is the predominant GHG emitted by petroleum refineries, accounting for almost 98% of all GHG emissions at petroleum refineries. Methane emissions are 4.7-million metric tons CO_2e and account for 2.25% of the petroleum refinery emissions nationwide. Note that the relative magnitude of CO_2 and CH_4 emissions is dependent on the types of process units and other characteristics of the refinery.

Facilities that do not have catalytic cracking units and hydrogen plants will tend to have a higher fraction of their total GHG emissions released as CH_4.
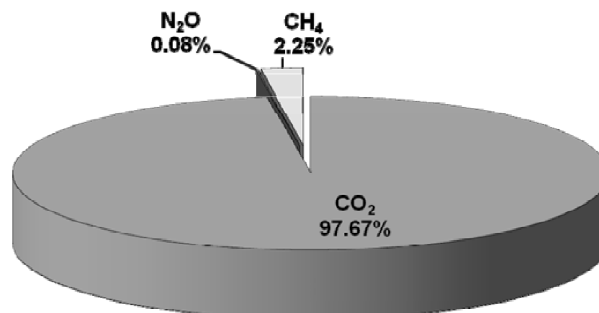
Figure 10-11. GHG emissions from petroleum refineries.
Source: GHG Control Measures White Papers (EPA 2010).

ENERGY EFFICIENCY IMPROVEMENTS

In 2001, the domestic petroleum refining industry consumed an estimated 3,369 trillion British Thermal Units (TBtu). One report estimated the CO_2 emissions from this energy consumption to be about 222 million tonnes, which accounts for about 11.6% of industrial CO_2 emissions in the United States (Worrell and Galitsky, 2005). The EIA provides on-site fuel consumption data as well as electricity and steam purchases (EIA, 2009). These data were used to estimate the CO_2 emissions resulting from this fuel consumption using the emission factors from the Intergovernmental Panel on Climate Change (IPCC) (2006), and converted to appropriate units (Coburn, 2007).

Figure 10-12 presents the projected CO_2 emissions from the direct, on-site fuel consumption, as well as the indirect, off-site electricity and steam purchases. From Coburn (2007), the on-site annual CO_2 emissions from fuel combustion were 190 million tonnes in 2005 and the overall CO_2 emissions from energy consumption (including purchased steam and electricity) were 216 million tonnes in 2005, which agrees well with the estimate of Worrell (2005). As also seen in Figure 10-12, catalyst coke consumption dropped 10 % from 2006 to 2008. Much of the resulting CO_2 emission reductions were offset by increased electricity and steam purchases. As nearly all catalytic cracking units recover the latent heat from the catalyst coke burn-off exhaust to produce steam and/or electricity, the decrease in catalyst coke consumption does not translate into an equivalent net GHG emissions reduction when indirect CO_2 emissions from electricity and steam purchases are considered.
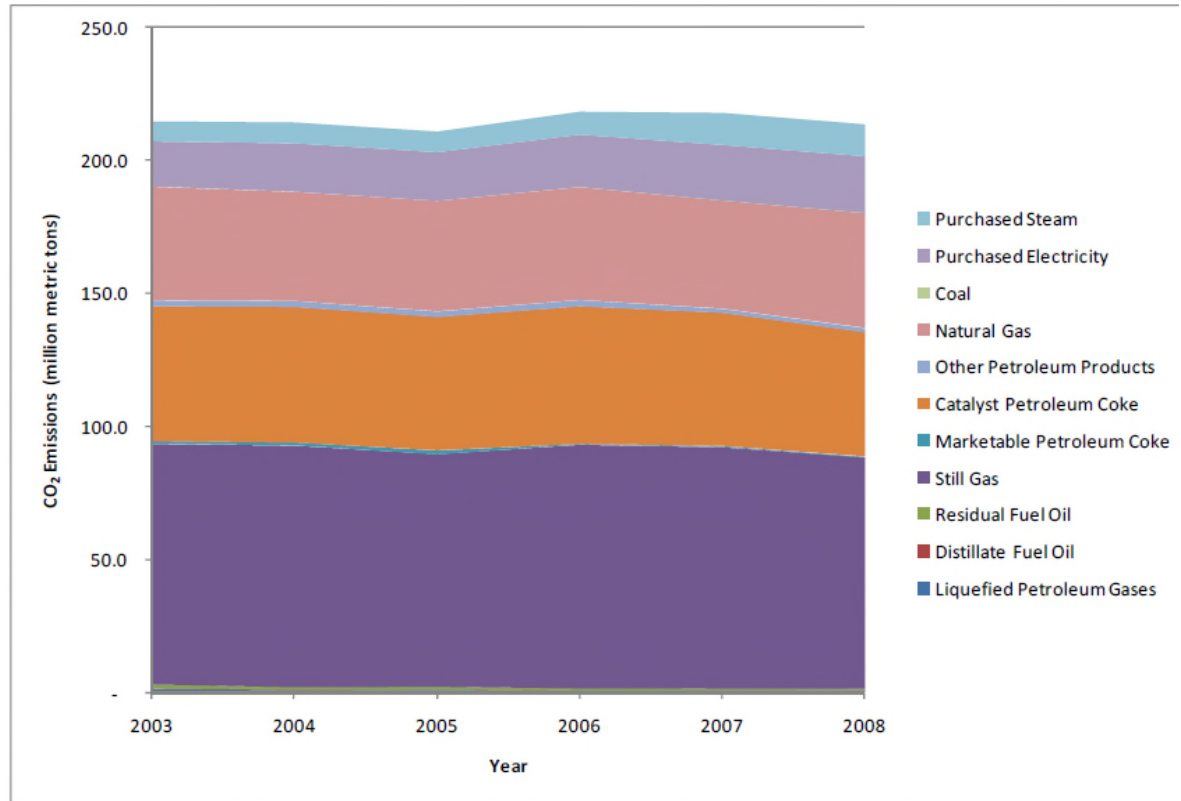
Figure 10-12. Direct CO_2 emissions from fuel consumption and indirect CO_2 emissions from electricity and steam purchases at U.S. petroleum refineries from 2003 to 2008.
Source: GHG Control Measures White Papers (EPA 2010).

10.3.7   GHG Emissions From Nitric Acid Plants

There are two different nitric acid production methods: weak nitric acid and high-strength nitric acid. The first method utilizes oxidation, condensation, and absorption to produce nitric acid at concentrations between 30 and 70% nitric acid. High-strength acid (90% or greater nitric acid) can be produced from dehydrating, bleaching, condensing, and absorption of the weak nitric acid. The basic process technology for producing nitric acid has not changed significantly over time. Most U.S. plants were built between 1960 and 2000. There are presently 40 active weak nitric acid production plants and one high-strength nitric acid production plant.

N$_2$O Emissions and Nitric Acid Production Process

N$_2$O emissions from nitric acid are a byproduct of the process stream and therefore characterized as "industrial process" emissions. Ammonia oxidation is the source of N$_2$O emissions from nitric acid production. The amount of N$_2$O formed depends on combustion conditions in the oxidizing unit, catalyst compositions, catalyst age, and burner design.

Note: The GWP value of N$_2$O is approximately 300, therefore, reducing 1 lb or 1 ton of N$_2$O is equivalent to reducing 300 lbs, or 300 tons of CO_2.

Reactions 10-1 through 10-3 show the formation of N_2O at nitric acid plants.(EPA, 2009). More details on N_2O formation are contained in Perez-Ramirez, J. et al, 2003.

Reaction 10-1 $\qquad 2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O$

Reaction 10-2 $\qquad 2NH_3 + 8NO \rightarrow 5N_2O + 3H_2O$

Reaction 10-3 $\qquad 4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O$
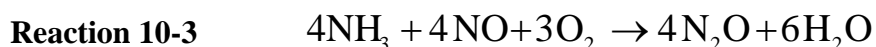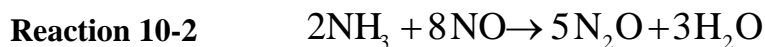
The default values that were used in the Technical Support Document (TSD) for the proposed GHG Reporting Rule are shown in Table 10-6. These values are from the IPCC Guidelines for National Greenhouse Gas Inventories (2006). In determining uncontrolled N_2O emissions from nitric acid plants for the GHG inventory, EPA used 9 kg N_2O/metric ton HNO_3. (U.S. EPA April, 2010) The low and high values represent the uncertainty bounds of the default factors provided by IPCC.

Table 10-6. Default N_2O emission factors.				
Production Process	**Approximate Pressure (atm)**	**N_2O Emissions (kg N_2O/metric ton Nitric Acid)**		
		Low	**Average**	**High**
Plants with NSCR		1.9	2.0	2.1
Plants with process-integrated or tailgas N_2O destruction		2.25	2.5	2.75
Atmospheric pressure (low pressure)	1	4.5	5.0	5.5
Medium pressure plants	4-8	5.6	7	8.4
High Pressure plants	8-14	5.4	9	12.6

Source: IPCC 2006 Guidelines for National GHG Inventories

In addition, uncontrolled N_2O emission factors are available from Clean Development Mechanism (CDM) projects. A summary of the uncontrolled N_2O emission tests from these projects is contained in Table 10-7. The uncontrolled default N_2O emissions factor used for nitric acid plants from the IPCC guidelines for the U.S GHG inventory (9 kg N_2O/metric ton HNO_3) is very close to the average uncontrolled N_2O emission rate of 8.9 kg N_2O/metric ton of HNO_3 from the CDM projects.

Table 10-7. Uncontrolled N_2O emissions – CDM projects.			
Type of Control	**Number of Test Reports**	**Range (kg N_2O /metric ton HNO_3; lb N_2O /T)**	**Average (kg N_2O /metric ton HNO_3; lb N_2O /T)**
Secondary	38	4.0 - 19;8.1 – 38	8.5; 17.1
Tertiary	11	6.2 – 15.7; 12.4 –31.4;	10; 20.0
Primary	49	4.0 – 19; 8.1 - 38	8.9; 17.8

In the U.S., N_2O emissions contributed approximately 4.6% of total GHG emissions in 2008 in terms of the CO_2e. The nitric acid production process is the third largest source of N_2O emissions in the US, comprising 6% of total N_2O emissions or 19 million metric tons (tonnes) of CO_2e (EPA 2010 Inventory).

10.4 EFFICIENCY IMPROVEMENTS ACROSS INDUSTRIAL SECTORS

OVERVIEW

Each of the industrial sectors mentioned in this chapter, can benefit from technologies and processes that use energy more efficiently. Some of the resources and means to improve efficiency apply to all sectors.

Some of these efficiency measures include using these methods and/or resources:

- Alternative and Renewable Energy Sources
- EPA's Energy Star™ Program Incentives
- Energy Management Systems (EnMSs)
- Benchmarking/ Energy Performance Indicators (EPI)
- Carbon Capture and Storage (CCS)

Primary controls emphasize the following:

1. Improved energy efficiency by burning less fuel, or by conserving the resources of electrical generation process—this reduces the required energy for a process, which can lead to reductions in GHG emissions.
2. Separating the CO_2 for long-term storage using Carbon Capture and Storage technology.

ALTERNATIVE AND RENEWABLE SOURCES

Though it is not covered extensively in this chapter, it should be clear that where possible, alternative and renewable energy sources such as solar, wind, geothermal, nuclear, and biomass technologies can improve energy efficiency and can reduce the GHG emissions that are normally released from traditional combustion energy generation processes, (such as coal, petroleum-based fuels, and natural gas combustion, etc.).

EPA ENERGY STAR PROGRAM

The U.S. EPA's Energy Star™ Program works with hundreds of U.S. manufacturers and has seen that companies and sites with stronger energy management programs gain greater improvements in energy efficiency than those that lack procedures and management practices focused on continuous improvement of energy performance.

Energy Management Systems (EnMSs)

For nearly 10 years, the U.S. EPA's Energy Star™ Program has promoted an Energy Management Systems (EnMSs) framework to manage energy and promote continuous improvement. EnMSs establish assessments, planning, and evaluation procedures, which are critical for actually realizing and sustaining the potential energy efficiency gains of new technologies or operational changes. The EnMS facilitates improvement with specific processes to assist with the following:

- Team development;
- Planning and evaluation;
- Tracking and measurement;
- Communication and employee engagement; and
- Evaluation and corrective measures.

In recent years, interest in EnMSs has grown, as industries recognize it as a tool to improve their commitment to increasing energy efficiency. EnMS has become a tool to build effective energy programs that generate results.

BENCHMARKING/ ENERGY PERFORMANCE INDICATORS (EPI)

Specific industrial plants can measure their improvements in energy efficiency either against themselves or against the performance of the entire industry. This type of plant energy benchmarking is typically done at a whole-facility, or site, level in order to capture the synergies of different technologies, operating practices, and operating conditions. Benchmarking enables companies to set informed and competitive goals for plant energy improvement and also helps companies prioritize investment to improve the performance of lowest performing processes while learning from the approaches used by the best performing processes.

When benchmarking is conducted across an industrial sector, a benchmark can be established that defines best-in-class energy performance. The U.S. EPA's Energy Star™ Program has developed benchmarking tools that establish best in class for specific industrial sectors. These tools, known as Plant Energy Performance Indicators (EPI) are established for specific industrial sectors and are available for free at *http://www.energystar.gov/industrybenchmarkingtools.* Using several basic plant specific inputs, the EPIs calculate a plant's energy performance providing a score from 0-100. EPA defines the average plant within the industry nationally at the score of 50; energy-efficient plants score 75 or better. Energy Star™ offers recognition for sites that score in the top quartile of energy efficiency for their sector using the EPI.

CARBON CAPTURE AND STORAGE (CSS)

Carbon capture and storage (CCS) involves the separation and capture of CO_2 from flue gas, or other process exhaust stream. It also requires pressurization of the captured CO_2, transportation via pipeline if necessary, and injection and long-term geologic storage. Several different technologies,

at varying stages of development, may be considered for the CO_2 separation and capture. Some have been demonstrated at the slip-stream or pilot-scale, while many others are still at the bench-top or laboratory stage of development.

Development of commercially viable processes for capturing CO_2 from EGUs is being funded by U.S. DOE, electric utility companies, and other organizations. These processes typically use solvents, solid sorbents, and membrane-based technologies for separating and capturing CO_2. Amine-based solvent systems are in commercial use for scrubbing CO_2 from industrial flue gases and process gases. However, solvents have yet to be applied to removing the large volumes of CO_2 that would be required for a coal-fired EGU. Solid sorbents can be used to capture CO_2 through chemical adsorption, physical adsorption, or a combination of the two effects. Membrane-based capture uses permeable or semi-permeable materials that allow for the selective transport/separation of CO_2. Oxy-combustion uses high-purity oxygen (O_2) instead of air to combust coal, producing a highly concentrated CO_2 stream that does not require a separation/capture step.

Once the CO_2 is captured, it is transported, if necessary, and stored. Geologic formations such as oil and gas reservoirs, unmineable coal seams, and underground saline formations are potential options for long-term storage. Basalt formations and organic rich shales are also being investigated for potential use as storage. Beneficial reuse (e.g., enhanced oil recovery or carbonation) is a potential alternative to strict storage that provides potential revenue to offset a portion of the CCS costs.

Task Force on Carbon Capture and Storage

In 2010, an Interagency Task Force on Carbon Capture and Storage was established to develop a comprehensive and coordinated federal strategy to speed the commercial development and deployment of CCS technologies. The Task Force is specifically charged with proposing a plan to overcome the barriers to the widespread, cost-effective deployment of CCS within 10 years, with a goal of bringing 5 to 10 commercial demonstration projects online by 2016. As part of its work, the Task Force prepared a report that summarizes the state of CCS and identified technical and non-technical barriers to implementation. For additional information on the Task Force and its findings on CCS, go to the website listed here:
http://www.epa.gov/climatechange/policy/ccs_task_force.html.

Note that this technology and the resources provided here, are available as resources and tools for those industrial processes that produce carbon emissions. Please refer to the information available in the Task Force report, to learn about the development status of CCS technologies and their applicability to the industries outlined in this chapter.

10.5 GHG EMISSION CONTROLS FOR INDUSTRIAL SECTORS

CONTROLS FOR EACH SECTOR

The GHG control techniques and strategies presented in this section apply to the main GHG contributors from the industrial sectors, which were identified as the stationary industrial contributors to GHG emissions.

The content of this section includes basic technical information, which may be useful in a Best Available Control Technology (BACT) analysis, but does not define BACT for each sector. Where possible, the information presented includes emission reduction potential, energy savings, costs, and feasibility of options available.

10.5.1   EMISSION CONTROLS FOR COAL-FIRED EGUS

Energy Efficiency and Emission Control Technologies for Coal-Fired EGUs

When the efficiency of the power generation process is increased, less coal is burned to produce the same amount of electricity. This provides the benefits of lower fuel costs and reduced air pollutant emissions (including CO_2). A number of energy efficiency technologies are available for application to both existing and new coal-fired EGU projects that can provide incremental step improvements to the overall thermal efficiency. The energy efficiency technologies with the potential to achieve the greatest improvements in electric power generation efficiency involve EGU design, equipment selection, and cost decisions that are typically incorporated during the planning and engineering design phases for a new EGU project.

These designs may implement any of the following process modifications:

- *EGU thermodynamic cycle* – Using supercritical, or ultra-critical steam cycles.
- *EGU coal rank and quality* – Burning higher quality coals (EGUs using higher quality coals tend to be more efficient).
- *EGU plant size* – varying *equipment* size; to reduce electricity requirements.
- *EGU cooling system* – The *temperature* of the cooling water entering the condenser can have impacts on steam turbine performance.
- *EGU geographic location* – re-locating processes to improve efficiency. At higher elevations, air pressure is lower and *less* oxygen is available for combustion per unit volume of ambient air than at lower elevations. Cooler ambient temperatures theoretically could increase the overall EGU efficiency by increasing the draft pressure of the boiler flue gases and the condenser vacuum, and by increasing the efficiency of a condenser recirculating cooling system.
- *EGU load generation flexibility requirements* – Operating an EGU as a base load unit is more efficient than operating an EGU as a load cycling unit to respond to fluctuations in customer electricity demand.
- *EGU equipment manufacturers* – The efficiency specifications of major EGU components

such as *boilers*, turbines, and electrical generators provided by equipment manufacturers can affect EGU efficiency.

- *EGU plant components* – EGUs using the optimum number of feed water heaters, high-efficiency electric motors, variable speed drives, better materials for heat exchangers, etc. tend to be more efficient.

Because of these factors, coal-fired EGUs that are identical in design but operated by different utility companies in different locations may have different efficiencies. Thus, the level of effectiveness of a given GHG control technology used to improve the efficiency at one coal- fired EGU facility may not necessarily directly transfer to a coal-fired EGU facility at a different location.

Results of Implementing EGU Efficiency Technologies

Numerous efficiency improvements have been applied to coal-fired EGUs to increase thermal efficiency of power production (NETL, 2008, Sargent & Lundy, 2009; U.S. DOE, 2009; U.S. DOE, 2010). One specific example is the NETL study, which conducted a literature review of published articles and technical papers identifying potential efficiency improvement techniques applicable to existing coal-fired EGUs. Efficiency improvements can be expressed in different formats; they may be reported as an absolute change in overall efficiency (e.g., a change from 40% to 42% represents a 2% absolute increase). They may also be presented as the relative change in efficiency (e.g., a change from 40% to 42% is a relative change in efficiency and fuel use of 5%). The relative change in efficiency is the most consistent approach, since it corresponds to the same change in heat rate.

A summary of the findings from the NETL study is presented in Table 10-8. The efficiency percentages were converted to a common basis so that all of the data could be compared. All of these improvements could not necessarily be implemented at each coal-fired EGU because of site-specific factors.

Table 10-8. Existing coal-fired EGU efficiency improvements reported for actual efficiency improvement projects.		
Efficiency Improvement Technology	**EGU Efficiency**	**Reported Efficiency Increase**
Combustion Control Optimization	Combustion controls adjust coal and air flow to optimize steam production for the steam turbine/generator set. However, combustion control for a coal-fired EGU is complex and impacts a number of important operating parameters including combustion efficiency, steam temperature, furnace slagging and fouling, and NO_x formation. The technologies include instruments that measure carbon levels in ash, coal flow rates, air flow rates, CO levels, oxygen levels, slag deposits, and burner metrics as well as advanced coal nozzles and plasma assisted coal combustion.	0.15 to 0.84%
Cooling System Heat Loss Recovery	Recover a portion of the heat loss from the warm cooling water exiting the steam condenser prior to its circulation thorough a cooling tower or discharge to a water body. The identified technologies include replacing the cooling tower fill (heat transfer surface) and tuning the cooling tower and condenser.	0.2 to 1%

Efficiency Improvement Technology	EGU Efficiency	Reported Efficiency Increase
Flue Gas Heat Recovery	Flue gas exit temperature from the air preheater can range from 250 to 350°F depending on the acid dew point temperature of the flue gas, which is dependent on the concentration of vapor phase sulfuric acid and moisture. For power plants equipped with wet FGD systems, the flue gas is further cooled to approximately 125°F as it is sprayed with the FGD reagent slurry. However, it may be possible to recover some of this lost energy in the flue gas to preheat boiler feedwater via use of a condensing heat exchanger.	0.3 to 1.5%
Low-Rank Coal Drying	Subbituminous and lignite coals contain relatively large amounts of moisture (15 to 40%) compared to bituminous coal (less than 10%). A significant amount of the heat released during combustion of low-rank coals is used to evaporate this moisture, rather than generate steam for the turbine. As a result, boiler efficiency is typically lower for plants burning low-rank coal. The technologies include using waste heat from the flue gas and/or cooling water systems to dry low-rank coal prior to combustion.	0.1 to 1.7%
Scotblower Optimization	Sootblowers intermittently inject high velocity jets of steam or air to clean coal ash deposits from boiler tube surfaces in order to maintain adequate heat transfer. Proper control of the timing and intensity of individual sootblowers is important to maintain steam temperature and boiler efficiency. The identified technologies include intelligent or neural-network sootblowing (i.e., sootblowing in response to real-time conditions in the boiler) and detonation sootblowing.	0.1 to 0.65%
Steam Turbine Design	There are recoverable energy losses that result from the mechanical design or physical condition of the steam turbine. For example, steam turbine manufacturers have improved the design of turbine blades and steam seals that can increase both efficiency and output (i.e., steam turbine dense pack technology).	0.84 to 2.6

SUMMARY OF CONTROLS FOR COAL-FIRED EGUS

There is no one best available coal-fired EGU technology universally applicable to all EGU projects. The coal-fired EGU technology alternatives most suitable for a given project must be evaluated on a site-specific basis. An evaluation for a new facility would include the use of carbon capture and storage and the most efficient technologies (e.g., ultra-supercritical steam conditions, IGCC, pressurized fluidized bed), double steam reheat, coal drying, FGD technology, and CHP.

Additional information about these methods is available on the EPA website, in the GHG Control Measures White Papers pertaining to Electric Generating Units (EGUs). See *http://www.epa.gov/nsr/ghgpermitting.html* for more specific guidance and information.

10.5.2 EMISSION CONTROLS FOR INDUSTRIAL, COMMERCIAL, AND INSTITUTIONAL BOILERS

Energy Efficiency Improvements and controls for ICI Boilers

The following efficiency measures are common from the perspective of applicability, availability, and owner/operator experience. Some options that may require project or site reconfiguration and process modifications, such as combined heat and power (CHP) and repowering, are also included in this section. Additional costs and complexities would need to be considered with these options. Options will vary for each unit and multiple options may be applied to save energy.

The options listed here, are summarized below:

1. Operating and Maintenance (O&M) Practices
2. Air Preheat and Economizers
3. Turbulators for Firetube Boilers
4. Boiler Insulation
5. Minimization of Air filtration
6. Boiler Blowdown Heat Exchanger
7. Condensate Return System
8. Refractory Material Selection
9. Minimization of Gas-side Heat Transfer Surface Deposits
10. Steam Line Maintenance

1. ***Operating and Maintenance (O&M) Practices*** – O&M practices have a significant impact on plant performance, including efficiency, reliability, and operating costs. Boiler efficiency decreases over time. This rate of deterioration can be curbed by good O&M practices. Additional GHG reductions can be achieved through energy improvements in the steam/hot water distribution system, the boiler auxiliaries, or in process efficiency improvements. (U.S. EPA, 2008) These methods may also include: new/upgraded burners, improved combustion measures.

2. ***Air Preheaters (APH) and Economizers*** – Air preheaters are widely used in large boiler applications. However, there use has been limited in the ICI sector, due to recent NOx regulations. (The high temperatures of combustion promote NOx formation.) Many gas and liquid fuel boilers do not have APH. Economizers are favored in these cases, as they do not adversely impact the combustion air temperature and the resulting NOx formation. Economizers are tubular heat transfer surfaces used to preheat boiler feedwater before it enters the steam drum or furnace surfaces. Economizers also reduce the potential of thermal shock and strong water temperature fluctuations as the feedwater enters the drum or waterwalls.

3. ***Turbulators for Firetube Boilers*** – In firetube boilers, the hot combustion gases travel across the boiler heat-exchange surfaces several times. Each time this occurs is commonly called a "pass" and boilers are typically categorized by the number of "passes."

   In simple terms, turbulators help to regain the heat transfer characteristics of a turbulent flow regime by creating "turbulence" within the tubes. Physically, turbulators are simple devices (baffles, blades, coiled wire) that are inserted in the gas tubes to "break-up" the laminar boundary layer, resulting in the increased convective heat transfer. The result is that the flue gas exits at a lower temperature, and boiler efficiency is improved. For firetube boilers,

turbulators are a cheaper alternative to economizers and APHs (Ganapathy, 2003).

4. ***Boiler Insulation*** – Insulation is any material that is employed to restrict the transfer of heat energy. It can generally be categorized as either mass or reflective type depending on whether it is aimed at reducing conductive or radiative heat transmission, respectively. Properly applied insulation can result in large savings in energy losses depending on type, thickness, and condition of the existing insulation. Bare surface temperature in boilers range from saturation temperature on exposed tube surfaces to air and gas temperatures on duct surfaces. Radiation losses tend to increase with decreasing load and can be as high as 7% for small units or larger units operating at reduced loads.

5. ***Minimization of Air Infiltration*** – This occurs as a result of the large temperature difference between the hot combustion gases and ambient air temperature, which creates a negative pressure in the furnace. This is often called "stack effect" or "thermal head." This negative pressure also occurs in balanced draft systems where an induced draft fan is used. Indicators of excessive air leakage include: high O_2 levels measured at the outlet of the boiler, as well as fuel consumption and gas temperatures. Depending on the severity and source of the leaks, the solution can be as simple as routine maintenance (e.g., adjust door seals), or requiring more thorough fixes during planned outages (e.g., repair boiler casing cracks).

6. ***Boiler Blowdown Heat Exchanger*** – Blowdown is required to maintain water quality. Depending on site-specific conditions and make-up water quality, blowdown rates may vary greatly. Unfortunately, the blowdown still contains energy, which could otherwise be used instead of being wasted. This waste heat can be recovered with a heat exchanger, a flash tank, or flash tank in combination with a heat exchanger. The resulting low-pressure steam is most typically used in deaerators. Cooling the blowdown has the additional advantage of reducing the temperature of the liquids released into the sewer system.

7. ***Condensate Return System*** – Hot condensate that is not returned to the boiler represents a corresponding loss of energy. A return condensate system must be a function of the specific boiler and water/condensate quality, but essentially involves a new distribution line configuration. Overall cost savings accrue from the fuel savings due to the efficiency improvement, plus the value of the reduction in the cost of make-up water, sewage disposal, and water treatment chemicals.

8. ***Refractory Material Selection*** –The refractory bricks lining the combustion zone of the boiler protect the outer shell from the high combustion temperatures, as well as chemical and mechanical stresses. The choice of refractory materials is highly dependent on fuels, raw materials, and operating conditions, consideration should be given to refractory materials that provide the highest insulating capacity and have the longest life.

9. ***Minimization of Gas-Side Heat Transfer Surface Deposits*** –To minimize deposition problems (slagging and fouling), it is important to operate the boiler within the parameters for which it was designed. This imposes a number of operational issues, such as fuel quality restrictions and firing rates, among others. However, systems firing ash-laden fuels also include "cleaning" systems (soot blowers that typically use compressed air or steam) to periodically remove the unavoidable deposition on the boiler walls and tubes. In addition, many units utilize "fuel treatment" to mitigate the deposition propensity of the ash and products of combustion. Many such products are available and typically modify the characteristics of the ash (e.g., the temperature–viscosity relationship) to minimize deposition.

10. *Steam Line Maintenance* – Energy audits and maintenance procedures should highlight common maintenance items such as uninsulated steam distribution and condensate return lines and other fittings. Ensuring that all steam/condensate lines are properly insulated will yield measurable efficiency gains. Common practice suggests that surfaces over 120°F (steam and condensate return piping, fittings) should be insulated. Insulating jackets are available for valves, traps, flanges and other fittings. Leaky steam traps should be fixed as they represent another potentially significant source of wasted energy

SUMMARY OF MEASURES TO REDUCE GHG EMISSIONS FROM ICI BOILERS

Table 10-9 summarizes the GHG emission reduction measures for existing ICI boilers. Where available, the table includes emission reduction potential, energy savings, costs, and feasibility of each measure. Generally, efficiency gains are a function of the difference between the new and old technologies or processes and are expressed in percent.

Table 10-9. ICI boilers – summary of greenhouse gas emission reduction measures.					
GHG Measure	Applicability	Efficiency Improvement (percentage pt)	CO$_2$ Reduction (%)	Capital Costs	Notes/Issues
Energy Efficiency Improvements					
Replace/ Upgrade Burners	All, except for Stoker-type boilers and fluidized bed boilers	Up to 4-5%.	Up to ~ 6%.	$2,500 – 5,100 per MMBtu/hr	Site-specific considerations (retrofit ability) and economic factors may affect the installation of burners
Tuning	All	CO from 1000-2000 to < 200 ppm Unburned carbon (UBC) from 20-30% to 10-15%	Up to ~3%	Up to $3000	Manual tuning with parametric testing
Optimization	All	0.5% – 3.0%	Up to ~ 4%	$100,000	Neural network-based
Instrumentation & Controls	All, especially at large plants	0.5% – 3.0% (in addition to optimization)	Up to ~ 4%	>$1million	System integration, calibration, and maintenance
Economizer	Units with capacity over 25,000 pounds of steam per hour;	40°F decrease in flue gas temp. equals 1% improvement	Relates to efficiency Gain in boiler	$2.3 million (For 650 MMBtu/hr)	Larger units; must consider pressure Loss, steam Conditions

GHG Measure	Applicability	Efficiency Improvement (percentage pt)	CO_2 Reduction (%)	Capital Costs	Notes/Issues
Air Preheater	Units with capacity over 25,000 pounds of steam per hour	A 300°F decrease in gas temperature represents about 6% improvement	~ 1% per 40°F temperature decrease	$200,000 – 250,000 (for 10MMBtu/hr)	Used in large boiler applications, not widely used in ICIs due to increase in NO_X
Create turbulent flow within firetubes	Single or two pass firetube boilers	1% efficiency gain for 40°F reduction in flue gas temperature 100°F -150°F temperature decrease potential	~ 1% per 40°F temperature decrease up to ~ 4%	$10 – 15 per tube	Widely accepted with older boilers;
Insulation	All, most suitable for surface temperatures above 120°F	Dependent on surface temperature	Up to 7%		Radiation losses increase with decreasing load
Reduce air leakages	All	1.5 – 3% potential (Effect similar to reducing excess air)	Up to ~ 4%	Site-specific (None to cost of maintenance Program)	Requires routine maintenance procedures
Capture energy from boiler blowdown	Most suitable for units w/ continuous boiler blowdown exceeding 5% of steam rate	Site-specific depending on steam conditions Up to ~ 7%	Up to ~ 8% See efficiency comment	NA	Water quality is important
Condensate return system	All; However, larger units more economical to retrofit	Site-specific - depends on condensate temperature and % recovery	Same as efficiency improvement, ratio of Btu/hr saved from condensate to Btu/hr input	$75,000	Energy savings is the energy contained in the return condensate, condensate quality affects use
Reduce slagging and fouling of heat transfer surfaces	Watertube boilers	1% to 3% Site-specific; fuel quality/operating condition have large impact	Up to ~ 4%	$50,000 to $125,000	Downtime/economic factors, regain lost capacity
Insulating jackets	Surfaces over 120°F		Same as efficiency improvement	Depends on length/type of insulation required for implementation	No deployment barriers
Reduce steam trap leaks	All			None to cost of maintenance program	No deployment barriers

GHG Measure	Applicability	Efficiency Improvement (percentage pt)	CO$_2$ Reduction (%)	Capital Costs	Notes/Issues
Post-Combustion					
Carbon capture and storage					Demonstrated at the slip-stream or pilot-scale
Alternative fuels –biomass	All fossil fuels				Less caloric content than fossil fuel
Other Measures					
Co-firing	Coal-fired and oil-fired boilers	Reduction up to 2% for biomass co-firing	20-30% reduction with gas co-firing		Negative impact of boiler efficiency
Fuel switching	Coal-fired and oil-fired boilers		20-35% reduction switching from coal to oil; 20-35% reduction switching from coal to natural gas		Change in hardware to accommodate 100% fuel switch
Combined heat and power	All	Overall efficiency improves from 30-50% to 70-80%		$1,000-2,500/kW	High capital investment

OTHER MEASURES TO REDUCE GHG EMISSIONS FROM BOILERS

The following measures are commonly used to reduce GHG emissions:

1. Alternative Fuels – Biomass

2. Co-firing

3. Fuel Switching (Coal-fired and Oil-fired Systems)

Alternative Fuels – Biomass

The potential on-site reduction in CO$_2$ emissions that may be realized by switching from a traditional fossil fuel to a biomass fuel is based on the specific emission factor for the fuel as related to its caloric value. Pure biomass fuels include animal meal, waste wood products and sawdust, and sewage sludge. It may also be possible to use biomass materials that are specifically cultivated for fuel use, such as wood, grasses, green algae, and other quick-growing species.

There are a number of issues related to the use of biomass fuels:

- Caloric Value - Most organic materials have a caloric content less than traditional fossil fuels.

- Trace compounds - The biomass fuel, particularly waste products, may contain trace elements such as heavy metals or may contain compounds that are detrimental such as chlorine. These substances could result in other air emission issues.
- Waste regulations - The regulation of wastes that may be used for fuel, or the types of units that the material may be utilized in, affects the use of those wastes as fuel. For example, if there are no impediments to landfilling the waste, then there may be little of the waste available for fuel use.
- Social acceptance - The use of waste fuels in a given area may be driven by social acceptance of burning the fuel in the community.
- Agricultural areas - For crops grown for biomass purposes, sufficient agricultural areas in proximity to the industrial boiler are required.

Co-firing

"Co-firing" refers to the case of burning more than one fuel in one boiler. As such, gas ("gas co-firing") could be burned in a boiler designed for oil or coal. Also, biomass (in solid form) could be co-fired in a boiler designed for coal. Finally, liquid or gas biofuels may be co-fired in all types of boilers.

Biomass may include switchgrass, sawdust, wood wastes, municipal solid wastes, non- recyclable paper, pulp mill sludge, chicken manure and other waste fuels. Typically, biomass has been limited to a maximum of 20% of the total plant input, and in most cases, between 3 and 12%. However, the pulp and paper industry has decades of experience co-firing up to 50% biomass with coal (DOE, 2004). Boilers could be designed specifically to accommodate biomass combustion or existing boilers could be modified; the industry has experience with both.

Gas co-firing involves modification of the combustion system to accommodate the introduction of natural gas or biomass-derived gas. The co-fired fuel is injected directly into the combustion zone. In case of biomass co-firing in boilers burning coal, the techniques can be classified either as *direct* or *indirect*.

Direct firing involves mixing of the biomass before the pulverizers ("co-milling" or blending) or direct injection (separate feed system for the biomass fuel). Indirect firing consists of separate boilers for the primary fuel and for biomass linked by a common connection to the steam cycle (may share the same steam generator and steam turbine).

From the five model plants identified for industrial applications, the models burning solid fuels (PC, circulating fluidized bed, and stoker) are clearly suitable to co-fire natural gas, biofuels, and (solid) biomass. The watertube and firetube boilers burning oil can accommodate biofuels and natural gas.

Co-firing of natural gas or biofuels does not present any technical issues which cannot be addressed through appropriate design. In most cases, the issues associated with these fuels relate to economic attractiveness, availability of biofuels, and availability of natural gas at the plant site.

In the case of biomass co-firing, retrofits face a number of issues, mainly related to the key characteristics of biomass compared to coal:

- Biomass has lower density; hence it is bulkier and affects the fuel handling equipment (pulverizers, fuel transport and fuel feed systems).
- High moisture content, above 40%, increases the time required for complete combustion and affect boiler efficiency.
- Biomass is more volatile than coal; biomass contains up to 80% volatile matter (on a dry-weight basis) compared to a maximum of 45% for coal; hence it is easier to self- ignite.
- High alkali biomass may contribute to formation of alkali sulfates, which make it easier to clean the boiler heating surface through sootblowing.
- Biomass degrades over time, which means that it cannot be stored for long periods of time.
- Biomass may contain high concentration of chloride, causing corrosion, especially if sulfur is also present in the fuel (either in the biomass or the coal).

However, all these issues can be addressed through appropriate design and operation. The same issues are being faced by new plants, but in this case, it is easier to adjust the initial design to accommodate co-firing.

The impact on efficiency of co-firing gas in existing boilers is expected to be minor (less than 0.5 percentage point). Depending on the composition of the co-fired fuel vs. the fuel, it is replacing; fuel with high concentrations of H_2 and moisture would have an adverse impact on plant efficiency. The impact of biomass co-firing in coal-fired boilers could result in a reduction of up to 2 percentage points in boiler efficiency and up to 1 percentage point in plant efficiency. With regards to CO_2 emission reductions:

- Gas co-firing has a beneficial impact in the case where it replaces coal; this is mainly because the carbon content of the coal is higher than gas; a 20-30% reduction in CO_2 is typical.
- Estimating the impact of biofuels on CO_2 emissions requires a process-specific assessment.

Other impacts due to biomass co-firing:
- Usually there are no impacts on plant output and reliability, assuming the right precautions are taken in designing and operating the facility.
- SO_2 and mercury are reduced proportionally to the biomass or gas input because these fuels contain less sulfur or mercury.
- NO_X emissions reduction is usually greater than the percentage of biomass or gas heat input.
- If the co-firing system is designed to be also a "reburning" system (introduction of fuel above the primary combustion zone), NO_X reduction of up to 30% could be achieved.

There is significant industry experience in co-firing in all types of boilers (PC, FBC, cyclone and stokers) ranging from 1 to 700 megawatt (MW). The pulp and paper industry has been co-firing for decades. In the 1990s, many power plants demonstrated this option in Europe, Japan, and the United States, and then proceeded to use it commercially.

The most common issues and barriers associated with co-firing are:
- Availability of natural gas on site; if it is not available, it may be too costly to extend a gas pipeline to reach the site. However, this is expected to affect a very small number of facilities, as the natural gas distribution in the U.S. is well-developed and reaches most locations.
- Price of the co-fired fuel; natural gas is highly affected by oil and gas market conditions.

- Biofuels depends on the production process, the price of the biomass feedstock and potential regulatory incentives (tax breaks, etc.). Finally, biomass is site-specific, may vary significantly, and may increase in cost after the co-firing project is implemented.
- Availability and logistics for biomass collection and transportation.

Fuel Switching

Fuel switching refers to a change in the plant hardware to accommodate complete (100%) replacement of one fuel with another fuel. Fuel switching from a coal-, fuel oil-, or diesel-fired boiler to a natural gas-fired boiler can result in decreased emissions (U.S. EPA 2008). Considering that the focus of this chapter is to identify CO_2 reducing options, the following fuel switching options are of interest:

- Coal could be switched to oil, natural gas or coal-derived gas; and
- Oil could be switched to natural gas or coal-derived gas.

Fuel Switching in Coal-fired Systems

Switching from coal to another fuel is feasible and has been put into practice in several cases. Economics and other issues are most often the reason such switching is not taking place. Switching from coal to oil is feasible and has occurred in the U.S., especially in the 1960s when oil was inexpensive. If such a change would be desirable, the required hardware changes include:

- Construction of oil storage; if there is existing oil storage, it may not be adequate and a larger storage capacity would need to be provided.
- Replacement or modification of the burners.
- If the same output of electricity or steam is required, additional hardware modifications may be required. While such changes are site-specific, coal-fired boilers are usually larger than oil-fired; the cross sectional area of a coal-fired boiler is about 20% larger and the boiler is about 33% taller than an oil-fired boiler (Llinares and Smith, 1980). As a result, burning oil in a larger furnace most likely would not produce the same amount of steam, or steam with the same temperatures. If the output conditions need to be maintained, more extensive boiler modifications would be required.

Switching from coal to natural gas presents similar issues as a switch to oil. The cross sectional area of a coal-fired boiler is about 50% larger and the boiler is about 60% taller than a gas-fired boiler (Richards, 1978). The only differences between switching to natural gas and to oil are:

- The extent of the boiler modifications, which is design-specific.
- There is no need for natural gas storage, as gas is usually provided directly from a gas pipeline. However, there are plants which may not have access to natural gas and may need to invest in bringing a gas pipeline into the plant.
- Switching from coal to coal-derived fuels is also practical, but its viability requires very site-specific assessment. First, the potential for CO_2 reduction depends on the coal-derived gas production process and needs to consider all the emissions released throughout the fuel chain (including coal mining, coal transport, conversion from coal to gas-derived fuel and utilization in the industrial boiler). In terms of an existing industrial boiler accommodating the coal-derived gas, the considerations are similar as those required for a switch to natural gas.

- Switching from coal to biofuels (of either gas or liquid form) would involve similar considerations as the switch from coal to oil and natural gas. Switching from coal to biomass requires:

    o Replacement of the fuel storage, handling and feed system; some equipment from the coal system may also be usable for biomass. Space is not likely to be a constraint, because the space available for storage and handling of the coal is likely to be adequate for biomass.
    o Depending on the boiler design, some modifications may be required to maintain plant output conditions. Biomass firing typically occurs in either stoker or fluidized bed boilers. This requires a site-specific assessment.

Fuel Switching in Oil-fired Systems

Switching from oil to natural gas would involve:

- Making sure that a natural gas supply is available; if a gas pipeline is not available at the plant site, a pipeline extension may be required.
- Replacement or modification of the burners.
- Some modifications of the boiler are likely to be required to maintain the same output of electricity or steam. However, the boiler modifications are generally not expected to be as extensive as in the case of coal to gas switching.

Switching from oil to coal-derived gas or biofuels (in gaseous form) is similar to natural gas. The only difference is that CO_2 emissions would need to consider all CO_2 emissions released throughout the fuel chain (including coal mining, coal transport, conversion from coal to gas-derived fuel, and utilization in the industrial boiler). Switching from oil to liquid biofuels is the easiest option in terms of required modifications to the plant hardware and potential impacts on plant performance. However, the CO_2 emissions would need to consider all fuel-chain impacts.

Switching from oil to biomass entails similar modifications as in the case of a coal to biomass switch. Some differences are noteworthy:

- In some sites, space to accommodate the biomass may be an issue; oil-firing facilities only require an oil storage tank, while biomass would require significant storage area, as well as space for drying and crushing prior to being fed into the boiler.
- Oil-fired boilers are compact relative to biomass-firing boilers; hence, it is likely that the boiler would not be able to maintain the plant output even after significant modifications.

The EPA GHG Emission Control White Paper for Large Industrial/Commercial/Institutional Boilers, which is a primary source for this chapter, emphasizes that it is generally assumed that an oil to biomass switch is not attractive.

Fuel Switching in Other Systems

Switching of PC plants to any of the fuels mentioned above is feasible and the industry has relevant experience (switching from coal to oil occurred in the 1960s, and from coal to gas in the 1980s and 1990s). Switching to coal-derived gas or biofuels has similarities with switching to natural gas and oil, respectively. In addition, there is adequate experience in boiler modifications to accommodate biomass.

Switching of FBC to oil, gas, coal-derived gas, or biofuels is not feasible, as the circulating fluidized bed requires solid materials to 'build up the bed." FBC are suitable candidates to switch to biomass.

It is theoretically and practically viable to switch stoker boilers to burn oil, gas, coal- derived gas, or biofuels. However, the overall design of stokers results in significantly lower efficiency than other prime movers (e.g., gas turbines and diesel engines), which can burn these fuels more efficiently. Stokers can easily accommodate biomass fuels.

Watertube and firetube boilers that use oil and natural gas, are suitable only for clean liquid or gaseous fuels. As a result, an oil-fired boiler could be switched to gas or coal-derived gas or biofuel. In addition to the burners which would need to be replaced, some additional modifications may be needed depending on the design of the existing boiler and the properties of the fuels. Gas-fired boilers would have less of an incentive to switch to coal-derived gas or biofuels, unless the price differential is adequate to justify the investment in the design modifications.

Plant efficiency improvements depend greatly on the existing plant design and design modifications implemented as part of the fuel switching project. However, the efficiency changes due to design modifications are expected to be much smaller than the impact of the fuel composition.

In addition to CO_2 emission impacts, switching to another fuel may have an impact on the other pollutants (particulates, SO_2, NO_X, and mercury). Switching from coal or oil to other fuels reduces particulates and, in most cases (natural gas, biofuels and biomass), SO_2 emissions; the exact percentage SO_2 reduction depends on the sulfur content of the coal or oil. NO_X emissions depend on the design of the boiler, but some NO_X reduction is expected as a result of fuel switching.

Specific information about implementing these methods is available on the EPA website, in the GHG Control Measures White Papers pertaining to ICI Boilers. See *http://www.epa.gov/nsr/ghgpermitting.html* for guidance.

10.5.3   EMISSION CONTROLS FOR PULP AND PAPER MANUFACTURING

Energy Efficiency Improvements and controls

The control measures for pulp and paper production are general to the following process areas:

- Power Boilers
- Chemical Recovery Furnaces, Combustion Units, Turbines
- Combined Heat and Power (CHP) Systems
- Steam Systems

Power Boilers - The control technologies, energy efficiency measures, and fuel switching options for power boilers used in pulp and paper making are similar to those that were presented for in the previous section; 10.5.2 Emission Controls for Industrial, Commercial, and Institutional Boilers.
The boiler energy efficiency measures that are presently available focus primarily on improved maintenance and process control to reduce heat loss, and improve heat recovery.

Chemical Recovery Furnaces, Combustion Units and Turbines

- **Black liquor concentrators** are used to increase the solids content of black liquor prior to combustion in a recovery furnace; increased solid content means less water must be evaporated in the recovery furnace, which can increase the efficiency of steam generation substantially. There are two primary types in use today: submerged tube concentrators and falling film concentrators. (Kramer 2009). One study estimated that, for a 1,000 ton per day pulp mill, increasing the solids content in black liquor from 66 to 80% would lead to fuel savings of 30 MMBtu per hour (hr), or about $550,000. Capital costs of the high solids concentrator would include concentrator bodies, piping for liquor and steam supplies, and pumps. (Kramer 2009).

- **Using composite alloy tubes for recovery furnaces**. Recovery furnaces consist of tubes that circulate pressurized water to permit steam generation. Replacing carbon steel tubes with composite alloy tubes in the recovery furnace supports the use of black liquor with higher dry solids content, which increases the thermal efficiency of the recovery furnace. They've been installed in more than 18 kraft recovery furnaces in the U.S., leading to a cumulative energy savings of 4.6 TBtu since their commercialization in 1996. (Kramer 2009)

Combined Heat and Power (CHP) Systems - CHP systems are significantly more efficient than standard power plants, because they take advantage of waste heat that is usually lost in central power generating systems and also reduce electricity transmission losses. Thus, society also benefits from CHP in the form of reduced grid demand, reduced air pollution, and reduced GHG emissions.

Despite the benefits of CHP systems, and their widespread use in the U.S. pulp and paper industry (currently 225 of the 386 mills have some form of CHP system in place, representing approximately 12,000 megawatts [MW] of electric generating capacity [ICF 2010]), much potential for CHP remains. Examples of CHP technology include power boilers and chemical recovery furnaces (e.g., at kraft pulp mills). There are significant remaining opportunities to add CHP capacity, based on evaluation of steam requirements met by boilers and by CHP in the paper industry. In addition, there are opportunities to repower existing CHP plants, making them larger and more efficient. If natural gas is available, existing steam turbine CHP systems can be replaced by newer, more efficient combustion turbines; existing simple cycle combustion turbine CHP systems can be converted to combined cycle operation by adding steam turbines for additional power.

Steam Systems - Energy efficiency measures related to steam distribution systems and reduced electrical consumption can result in small incremental reductions in boiler demand.

SUMMARY OF MEASURES AND ENERGY EFFICIENCY IMPROVEMENTS FOR DIRECT EMISSION SOURCES

The control measures and energy efficiency options that are currently available for pulp and paper mill processes are listed in Table 10-10 and discussed in further detail in the sections below.

Table 10-10. List of control measures and energy efficiency options.	
Boilers	
Burner Replacement	Boiler Maintenance
Boiler Process Control	Condensate return
Reduction of Flue Gas Quantities	Minimizing boiler blow down
Reduction of excess air	Blow down steam recovery
Improved boiler insulation	Flue gas heat recovery
Chemical Recovery Furnaces	
Boiler control measures and energy efficiency options (See above)	Recovery furnace deposition monitoring
Black liquor solids concentration	Quaternary air injection
Improved composite tubes for recovery furnaces	
Turbines	
Boiler/steam turbine CHP	Replacement of pressure reducing valves
Simple cycle gas turbine CHP	Steam injected gas turbines
Combined cycle CHP	Regular performance monitoring and maintenance
Natural-Gas Fired Dryers and Thermal Oxidizers	
Energy efficiency turbine CHP	Use of thermal oxidizers employing heat recovery (e.g., regenerative or recuperative thermal oxidizers)
Use of existing combustion processes (e.g., power boilers or lime kilns) over a separate thermal oxidizer	
Kraft and Soda Lime Kilns	
Piping of stack gas to adjacent PCC plant	Lime kiln modifications (e.g., high-efficiency filters, higher efficiency refractory insulation brick)
Lime kiln oxygen enrichment	Lime kiln ESP
Makeup Chemicals	
Practices to ensure good chemical recovery rates in the pulping and chemical recovery processes	Addition of Na and Ca in forms that do not contain carbon (e.g., Na_2SO_4, NaOH, CaO)
Flue Gas Desulfurization (FGD) Systems	
Use of sorbents other than carbonates	Use of lower-emitting FGD systems
Wastewater Treatment	
Use of mechanical clarifiers or aerobic	Minimization of potential for formation of

biological treatment systems (instead of anaerobic treatment systems)	anaerobic zones in wastewater treatment systems (e.g., through placement of aerators where practical)
On-site Landfills	
Dewatering and burning of wastewater treatment plant residuals in on-site boiler	Capture and control of landfill gas by burning it in onsite combustion device (e.g., boilers) for energy recovery and solid waste management

Additional information about these methods is available on the EPA website, in the GHG Control Measures White Papers pertaining to the Pulp and Paper Industry. See *http://www.epa.gov/nsr/ghgpermitting.html* for more specific guidance and information.

For additional information, refer to the *2006 Intergovernmental Panel on Climate Change (IPCC) Guidelines for National Greenhouse Gas Inventories* available at *www.ipcc-nggip.iges.or.jp/public/2006gl/index.html* and industry-specific guidance for the pulp and paper sector entitled *Calculation Tools for Estimating Greenhouse Gas Emissions from Pulp and Paper Mills*, which was developed by the National Council for Air and Stream Improvement (NCASI) for the International Council of Forest and Paper Associations (ICFPA) and accepted by the World Resources Institute (WRI) and the World Business Council for Sustainable Development (WBCSD) (available at *http://www.ghgprotocol.org/calculation-tools/pulp-and-paper*). It should be noted that these protocols use different emission factors for estimating GHG emissions and are broader in scope than the MRR (e.g., include mobile sources).

10.5.4   EMISSION CONTROLS FOR CEMENT MANUFACTURING

Cement manufacturing, like many of the industrial processes discussed in this chapter, requires a lot of energy. Therefore, when considering the best emission and efficiency controls to reduce GHG emissions, improved energy efficiency is a primary focus. Table 10-10 below, provides an extensive list of the control technologies available for implementation in cement production.

The data provides useful information and guidance for selecting and/or recommending emission controls for many different processes and equipment. The reductions, along with the potential energy savings are provided so that they can be compared alongside any required capital expenditures. The control technologies are applied to the following process improvements:

- Raw Materials Preparation
- Clinker Production
- Finish Grinding
- Facility Operations
- Raw Materials Substitution
- Carbon Capture
- Other Control Methods

Because the primary GHG emitted by the cement industry is CO_2, the control technologies and measures presented here focus on this pollutant. In general, emissions of CO_2 from the cement manufacturing sector can be reduced by:

- Improving the energy efficiency of the process;
- Shifting to a more energy efficient process (e.g., from wet and long dry to preheater/precalciner process);
- Replacing high carbon fuels with low carbon fuels;
- Applying lower clinker/cement ratio (increasing the ratio additives/cement): to blended cements; and
- Removing CO_2 from the flue gases.

SUMMARY OF CONTROL MEASURES OF CEMENT PRODUCTION

Table 10-11 summarizes CO_2 control measures for cement production. Where available, the table includes the emission reduction potential, energy savings, costs, and feasibility of each measure.

For many of the control technologies and/or measures described in the EPA's White Paper for controlling GHG emissions from the Portland Cement Industry CO_2 emission reductions are not explicitly provided. Energy efficiency improvements lead to reduced fuel consumption in the kiln system, and/or reduce electricity demand. Thus, where CO_2 emission reductions are not provided, these reductions can be calculated from the reduction of fuel used by the kiln system. For facilities that produce their own electricity, emission reductions that result from reduced electricity usage can be calculated from the reduced amount of fuel consumed at their power plant (if fuel combustion rather than waste heat is used for this purpose).

Table 10-11. Portland Cement Manufacturing Sector- summary of greenhouse gas controls [a,b.]							
Control Technology	**Emission Reduction**	**Energy Savings**	**Capital Costs**	**Operating Costs**	**Applicability**	**In Practice?**	**Other factors**
Energy Efficiency Improvements in Raw Material Preparation							
Switch from pneumatic to mechanical raw material transport	Calculated from energy savings	2.9 kWh/ton cement	$4.1/annual ton cement capacity	NA	New and Existing Facilities with LD, PH, PH/PC kilns	Yes	
Use of belt conveyors and bucket elevators instead of pneumatics	Calculated from energy savings	2.5 kWh/ton cement	$3.43/ton cement capacity	Reduction of $0.17/ton cement	New and Existing Facilities	Yes	
Convert raw meal blending silo to gravity-type homogenizing	Calculated from energy savings	1.4-3.5 kWh/ton cement	$5.0/ton cement capacity (silo retrofit)	NA	New and Existing Facilities	Yes	
Improvements in raw material blending	Calculated from energy savings	1.0 kWh/ton cement	$2.5/ton cement capacity	Increase of $0.02/ton cement	New and Existing Facilities with LD, PH, PH/PC kilns	Yes	May increase production by up to 5%
Replace ball mills with high efficiency roller mills	Calculated from energy savings	9-11 kWh/ton cement	$7.6/ton cement capacity	NA	New and Existing Facilities	Yes	

Control Technology	Emission Reduction	Energy Savings	Capital Costs	Operating Costs	Applicability	In Practice?	Other factors
Replace ball mills with vertical roller mills	14-22 lb CO_2/ton cement	11-15 kWh/ton cement	$33/ton cement capacity	Reduction of $0.17/ton cement	New and Existing Facilities	Yes	
Replace ball mills with vertical roller mills	14-22 lb CO_2/ton cement	11-15 kWh/ton cement	$33/ton cement capacity	Reduction of $0.17/ton cement	New and Existing Facilities	Yes	
High Efficiency Classifiers	4-6 lb CO_2/ton cement	3.8-5.2 kWh/ton cement	$3/annual ton cement capacity	NA	New and Existing Facilities	Yes	May increase grinding mill capacity
Roller mill for fuel (coal) preparation instead of impact or tube mill	Calculated from energy savings	7-10 kWh/ton coal	Cost of roller mill is higher than impact or tube mill	Reduction of as much as 20- 50%	New and Existing Facilities	Yes	
Energy Efficiency Improvements in Clinker Production							
Process control and management systems	7-33 lb CO_2/ton cement and 1.3 lb CO_2/ton cement from electricity usage reduction	2.5-5% or 42-167 MJ/ton cement and electricity savings of 1 kWh/ton cement	$0.3/annual ton cement capacity	NA	New and Existing Facilities. All kilns.	Yes	
Replacement of kiln seals	Calculated from energy savings	0.4% or 0.01 MMBtu/ ton cement	NA	NA	New and Existing Facilities. All kilns.	Yes	
Kiln combustion System improvements	Calculated from energy savings	2-10% reduction in fuel usage	$0.8/annual ton cement capacity	NA	New and Existing Facilities. All kilns	Yes	May result in up to 10% increase in kiln output
Fluxes and mineralizers to reduce energy demand	9-30 lb CO_2/ton cement and 0-2 lb/ton cement from electricity usage reduction	42-150 MJ/ton cement	NA	Fuel savings may be offset by cost of fluxes and mineralizers	New and Existing Facilities. All kilns.	Yes	
Kiln/preheater insulation (internal)	Calculated from energy savings	0.1-0.31 MMBtu/ton cement	$0.21/annual ton cement capacity	NA	New and Existing PH and PH/PC kilns	Yes	
Refractory material selection	Calculated from energy savings	49,800 Btu/ton cement	$0.50/ton cement capacity	NA	All kilns	Yes	
Replacement of planetary and travelling grate cooler with reciprocating grate cooler	Reduction of 17-52 lbCO_2/ton cement, but increase of 2-6 lb/ton cement from increased electricity use	Reduce energy consumption by 8% or 84-251 MJ/ton cement; increase electricity use by 1-5 kWh/ton	NA	NA	New and Existing kilns with capacity > 500 tonnes/day	Yes	

		cement					
Heat recovery for power – cogeneration	Calculated from energy savings	Produce 7-20 kWh/ton cement	$2-4/annual ton cement capacity	$0.2-0.3/ annual ton cement capacity	LD kilns	Yes	
Suspension preheater low pressure drop cyclones	Up to 2 lb CO_2/ton cement	0.5-0.6 kWh/ton cement per 50 mm water column pressure reduction	$2.5-2.9/annual ton cement capacity	NA	New and retrofitting PH and PH/PC kilns		May result in up to 3% production increase
Multistage preheater	Calculated from energy savings	0.4 MMBtu/ Ton cement	$12.8-34/annual ton cement capacity	NA	New and retrofitting PH and PH/PC kilns	Yes	May increase kiln capacity by up to 50%
Conversion from long dry kiln to preheater/ precalciner kiln	50-460 lb CO_2/ton cement	1.1MMBtu/ton cement	$7.9-96/ annual ton cement capacity	Decrease by $0.08/ton cement	LD kilns	Yes	Actual values are highly site-specific
Kiln drive efficiency improvements	Calculated from energy savings	0.5 kWh/ton cement	Increased by about 6%	Reduced power cost for kiln drive by 2-8%	New and Existing Facilities.	Yes	
Adjustable speed drive for kiln fan	Calculated from energy savings	5 kWh/ton cement	NA	NA	New and Existing Facilities.	Yes	
Oxygen enrichment	18-37 lb CO_2/ton cement; however, this may be completely offset by increased electricity consumption	NA	NA	NA	All Kilns	Yes	May increase production by 3-7%. May increase NOx emissions.
Mid kiln firing	Calculated from the emission factor of tires compared to fuel being replaced	NA	NA	NA	Existing Wet, LD kilns	Yes	Burning tires may result in lower emissions
Air mixing technology	Calculated from fuel reduction	Improves combustion efficiency reducing fuel use	$520,000	Increases electricity usage by 0.23 kWh/ton cement	TBD	Yes	Likely reduces CO, NO_x, and SO_2 emissions
Preheater riser duct firing	--	--	--	--	Ph and PH/PC Kilns		

				Energy Efficiency Improvements in Finish Grinding			
Control Technology	**Emission Reduction**	**Energy Savings**	**Capital Costs**	**Operating Costs**	**Applicability**	**In Practice?**	**Other factors**
Improved ball mill	Calculated from energy savings	6-25 kWh/ton cement	$2.3-7.3/annual ton cement capacity; or $35/ton cement capacity for a vertical roller mill	May reduce by 30-40%, but vertical roller mill may increase costs by $0.17/ton Cement	Existing and New Facilities. All kilns.	Yes	
High efficiency classifiers	Calculated from energy savings	1.7-2.3 kWh/ton cement, but could be as high as 6 kWh/ton cement	$2/annual ton cement	$0.045/ton cement	Existing and New Facilities. All kilns.	Yes	May increase production by up to 25%
				Energy Efficiency Improvements in Facility Operations			
High efficiency motors	Calculated from energy savings	5%, or about 5 kWh/ton clinker	$0.67/ton cement	No change	Existing and New Facilities. All kilns.	Yes	
Variable speed drives	3-10 lb CO_2/ton cement	3-8 kWh/ton cement	NA	NA	Existing and New Facilities. All kilns.	Yes	Capital and operating cost savings are highly site-specific
High efficiency fans	Calculated from energy savings	0.9 kWh/ton cement	$0.46/ton cement	NA	Existing and New Facilities. All kilns.	Yes	
Optimization of compressed air systems	Calculated from energy savings	Up to 20%	NA	NA	Existing and New Facilities. All kilns.	Yes	
Lighting system Efficiency improvements	Calculated from energy savings	12-50% depending on specific changes made	NA	NA	Existing and New Facilities. All kilns.	Yes	
				Raw Material Substitution			
Decarbonated feedstocks (steel slag or fly ash)	0.02-0.51 ton CO_2/ton material	1.12 MMBtu/ton cement; or 0.07-1.59 MMBtu/ton material	$0.75/ton cement for steel slag fed into kiln without grinding	Increased by $0.08/ton cement for steel slag fed into kiln without grinding	All Facilities	Yes	Energy savings may be offset by 0.08 MBtu/ton to dry feedstock

Calcereous oil shale	0.009 lb CO_2/ton cement	0.07 MMBtu/ton cement	$1/ton cement when replacing 8% of raw meal	Increase by $0.08/ton cement when replacing 8% of raw meal	All Facilities	Yes		
Blended Cements								
Cementitious Materials	200-860 lb CO_2/ton cement for cement with 30-70% blast furnace slag	380-1710MJ /ton cement for cement with 30- 70% blast furnace slag	NA	NA	All Facilities	Yes		
Pozzolanic materials	100-280 lb CO_2/ton cement	200-500 MJ/ton cement	NA	NA	All Facilities	Yes		
Carbon Capture								
Calera process	90%, but varies with specific application	Parasitic load of 10-20 of the power plant	$950/kW for coal-fired power plant	NA	TBD	Pilot testing	Pilot testing is on power pl	
Oxy-combustion	1000-1600 lb CO_2/ton cement, but increased electricity usage could generate 110-150 CO_2/ton cement	Overall energy requirements decrease by 75- 84 MJ/ton cement, but electricity requirements increase by 92-96 kWh/ton cement	NA	NA	TBD	No	No installatio ns at cement plants;ma ny technical issues to overcome	
Post-combustion solvent capture and stripping	Up to 95%	NA	NA	NA	TBD	Yes, but not at cement plants		
Post-combustion membranes	Up to 80%	NA	NA	NA	TBD	No, currently in research stage		
Superheated CaO	Up to 43%	NA	NA	NA	TBD	No, currently in research stage		
Other Control Measures								
Fuel switching	18% for switching from coal to heavy oil; 40% for switching from coal to natural gas	NA	NA	NA	All Facilities	Yes	Does not affect emissions from calcinatio ns reaction	
Alternative fuels – biomass	Depends on emission factor	NA	NA	NA	All Facilities	Certain biomass		

	of biomass compared to fuel being replaced					materials have been used	
Hybrid solar plants	Equivalent to emissions that would have been generated	NA	NA	NA	TBD	No, currently in research stage	
Syngas coproduction	Up to 650 lb CO_2/ton cement	NA	NA	NA	TBD	No, but has been applied to smaller streams	
Power plant/cement plant carbonate looping	830-1300 lb CO_2/ton cement	NA	NA	NA	TBD	No, currently in research stage	

The Portland Cement Association (PCA, 2008) provides a discussion on most of the efficiency measures presented in this section, particularly addressing technical feasibility. Staudt (2009) provides a means of estimating the capital costs for the energy efficiency measures using the following equation:

Capital Costs ($2008) = Scale-Up Factor x (tons/yr cement capacity)$^{0.6}$

Additional information about these methods is available on the EPA website, in the GHG Control Measures White Papers pertaining to the Cement Industry. See *http://www.epa.gov/nsr/ghgpermitting.html* for more specific guidance and information.

10.5.5 EMISSION CONTROLS FOR THE IRON AND STEEL INDUSTRY

Energy Efficiencies for Integrated Iron and Steel Production

New initiatives for the iron and steel industries are included in the EPA Emission Control White Paper for Iron and Steel Production. The targets provide a list of opportunities for improvements and process controls to increased electrical energy, improve transfer efficiency, reduce tap-to-tap times, and increase the percentage of power-on time. The following list provides a small sample of the potential energy improvements.

Processes	**Estimated Potential Energy Savings**
Preventive Maintenance -	0.21 MMBtu/ton (0.24 GJ/tonne)
Facility Modifications	0.06 MMBtu/ton (0.07 GJ/tonne)
Coal Moisture Control and Dry Quenching	0.22 MMBtu/ton (0.26 GJ/tonne)
Pulverized coal and natural gas injection -	1.34 MMBtu/ton (1.56 GJ/tonne)
Casting/hot rolling	0.93 MMBtu/ton (1.08 GJ/tonne)

These process-related opportunities were noted by the American Iron and Steel Institute (AISI). (EPA, 2007a). The results of this study are summarized in Table 10-12 below.

Efficiencies for Electric Arc Furnace (EAF) Steelmaking

Implementing process controls can optimize operations and significantly reduce electricity consumption. By monitoring the furnace exhaust gas flow rate and composition, the use of chemical energy in the furnace can be enhanced. Detailed investigation of the post-combustion of off-gases can be controlled online. Benefits of this practice include reduced electricity consumption, shorter power-on times, increased productivity, a decrease in production costs, a reduction of electrode consumption, reduced natural gas, oxygen and carbon consumption, and a reduction of refractory wear. It has been demonstrated that, if oxygen injected for post-combustion is continuously controlled by real-time data acquisition of CO and CO_2 concentrations in off-gases, a 50% increase in recovery rate of chemical energy in fumes can be achieved compared to operation based on predefined set-points.

Long Term Opportunities to Reduce CO_2 Emissions

A way to decrease CO_2 emissions from the blast furnaces ironmaking process is using hydrogen bearing materials such as steam, natural gas and waste plastics to substitute coke and coal. Apart from CO_2 emission reductions due to energy efficiency of resource utilization, there are several emerging technologies to mitigate emissions. However, none are currently commercially available or used at commercial scale. Development of these technologies may take decades.

The global steel industry collaborates in the ULCOS project to find opportunities to dramatically reduce CO_2 emissions from iron and steelmaking. ULCOS is a consortium of 48 European companies and organizations from 15 European countries that have launched a cooperative R&D initiative to enable drastic reduction in CO_2 emissions from steel production. The aim of the ULCOS program is to reduce the CO_2 emissions by at least 50%. ULCOS has selected four process concepts that could lead to a reduction of CO_2 emissions by more than half compared to current best practice.

The following are the four breakthrough technologies identified:

- Top gas recycling blast furnace with carbon capture and storage (CCS);
- HIsarna with CCS;
- Advanced direct reduction with CCS; and
- Electrolysis.

Traditionally, carbon from fossil fuels is used in the steel industry to provide the chemical function of reducing oxide ores. This function could also be performed using hydrogen or carbon-free electricity, or wood:

- Hydrogen reduction of iron ore has steam as a gas product instead of CO_2.
- Hydrogen can be produced from natural gas, by electrolysis of seawater, etc. Limitations are not technical, as technologies in the area of pre-reduction are very mature, and are related to the volatile issue of resource depletion in the longer term. Research projects are underway in different countries. In the U.S. the AISI, U.S. DOE, and the University of Utah investigate a process called Hydrogen Flash Smelting.
- The concept of using wood to make iron in a charcoal blast furnace is presently being applied in Brazil.
- Electrolysis, which leads directly to final products, is to be compared to a whole conventional mill, which has an energy consumption of 15 to 20 GJ/t liquid steel,

- HIsarna is a technology based on bath-smelting. It combines coal preheating and partial pyrolysis in a reactor, a melting cyclone for ore melting and a smelter vessel for final ore reduction and iron production. It requires significantly less coal usage and thus reduces the amount of CO_2 emissions. Furthermore, it is a flexible process that allows partial substitution of coal by biomass, natural gas or even hydrogen.

Emerging Technologies

According to AISI, the greatest potential for reducing the energy intensity of steelmaking lies with development of new transformational technologies and processes. Examples of such transformational R&D efforts (applicable both to integrated and EAF steelmaking) include the following: (1) molten oxide electrolysis (under development at MIT); (2) ironmaking by flash smelting using hydrogen (under development at the University of Utah); and (3) the paired straight hearth (PSH) furnace (under development at McMaster University in Ontario, Canada). AISI lists the following additional areas as important R&D opportunities for EAF steelmaking:
improved processes for low-grade scrap recovery, and sensible heat recovery from slag, fumes, and off-gases (EPA, 2007a).

The R&D opportunities noted in the DOE study (EPA, 2007a) include increasing the efficiency of melting processes (0.4 MMBtu/ton or 0.47 GJ/tonne), integration of refining functions and reductions of heat losses prior to casting (0.35 MMBtu/ton or 0.41 GJ/tonne), economical heat capture from EAF waste gas (0.26 MMBtu/ton or 0.30 GJ/tonne), purification and upgrading to scrap, and effective use of slag and dust. Casting and rolling opportunities (applicable both to integrated and EAF steelmaking) include the reduction of heat losses from cast products prior to rolling and/or reheating (0.75 MMBtu/ton or 0.87 GJ/tonne) and thin-strip casting (0.5–0.7 MMBtu/ton [0.3-0.8 GJ/tonne]) (EPA, 2007a).

The GHG control measures for integrated iron and steel plants are included in Table 10-12, and Table 10-13 provides the measures for EAF steelmaking. Most of the information in the tables and the descriptions of the options in the next section were taken from a study by Worrell et al. (1999) that was conducted for the EPA and DOE and subsequently updated (Worrell et al., 2009) in a study for the EPA's Climate Protection Partnerships Division as part of the Energy Star™ Program. The two tables include the emission reduction potential, energy savings, costs, and feasibility of each measure when such information was available.

The energy efficiency improvement options are provided by the Department of Energy (DOE) (EPA, 2007a), and they are technically available but may not be economically viable in all situations. Note that casting, hot rolling, and other finishing processes at EAF facilities are similar to those described for integrated iron and steel plants.

DOE estimates that a reduction of 5.1 MMBtu/ton (5.9 GJ/tonne) (27%) is possible for integrated mills (half from existing technologies and half from research and development [R&D]). A reduction of 2.7 MMBtu/ton (3.1 GJ/tonne) (53%) is possible for EAFs (two-thirds from existing technologies) (DOE, 2005).

According to the American Iron and Steel Institute (AISI), with improvements in blast furnace efficiency are possible through optimized blast injection technologies and better sensors and process controls.

Table 10-12. Energy efficiency technologies and measures applied to integrated steel production in the U.S.

Option	Emission Reduction (kg of CO$_2$/tonne of product)	Fuel Savings (GJ/tonne of product)	Electricity Savings (GJ/tonne of product)	Annual Operating Costs ($/tonne of product)	Retrofit Capital Costs ($/tonne of product)	Payback Time (years)
Iron Ore Preparation (Sintering)						
Sinter plant heat recovery	57.2	0.55	0.0	0.0	4.7	2.8
Emission optimized sintering						
Reduction of air leakage	2.0	0.0	0.0	0.0	0.14	1.3
Increasing bed depth	9.9	0.09	0.0	0.0	0.0	0.0
Improved process control	5.0	0.05	0.0	0.0	0.21	1.4
Use of waste fuels (e.g., lubricants) in sintering plant	19.5	0.18	0.0	0.0	0.29	0.5
Improve charging method						
Improve ignition oven efficiency						
Cokemaking						
Coal moisture control	6.7	0.30	0.0	0.0	76.6	>50
Programmed heating	3.8	0.17	0.0	0.0	0.37	0.7
VSD COG compressor	0.12	0.0	0.0	0.0	0.47	21.2
Coke dry quenching	27.5	1.2	0.0	0.78	109.5	35.7
Additional use of COG						
Single chamber system						
Non-recovery coke ovens						
Ironmaking - Blast Furnace						
Pulverized coal injection to 130 kg/ton iron	47.0	0.77	0.0	-3.1	11.0	2.0
Pulverized coal injection to 225 kg/ton iron	34.7	0.57	0.0	-1.6	8.1	2.4
Injection of natural gas to 140 kg/ton iron	54.9	0.90	0.0	-3.1	7.8	1.3
Injection of oil						
Injection of COG and BOF gas						<1.0
Charging carbon composite agglomerates						
Top pressure recovery turbines (wet type)	17.6	0.0	0.11	0.0	31.3	29.8
Recovery of BFG	4.0	0.07	0.0	0.0	0.47	2.3
Hot-blast stove automation	22.6	0.37	0.0	0.0	0.47	0.4
Recuperator hot-blast stove	4.9	0.08	0.0	0.0	2.2	8.7
Improvement of combustion in hot stove						
Improved blast furnace control systems	24.4	0.40	0.0	0.0	0.56	0.4
Blast furnace gas recycling						
Slag heat recovery						
Steelmaking - Basic Oxygen Furnace (BOF)						
BOF gas plus sensible heat	46.0	0.92	0.0	0.0	34.4	11.9
VSD on ventilation fans	0.51	0.0	0.003	0.0	0.31	9.9
Improvement of process monitoring and control						
Programmed and efficient ladle heating						
Casting						
Efficient caster ladle/tundish heating	1.1	0.02	0.0	0.0	0.09	1.3

Option	Emission Reduction (kg of CO_2/tonne of product)	Fuel Savings (GJ/tonne of product)	Electricity Savings (GJ/tonne of product)	Annual Operating Costs ($/tonne of product)	Retrofit Capital Costs ($/tonne of product)	Payback Time (years)
Near net shape casting - thin slab	728.8	3.5	0.64	-54.8	234.9	3.3
Near net shape casting - strip				25% less		
General Measures for Rolling Mills						
Energy efficient drives	1.6	0.0	0.01	0.0	0.30	3.2
Gate communicated turn-off inverters						
Install lubrication system			0.016			
Hot Rolling						
Proper reheating temperature						
Avoiding overload of reheat furnaces						
Hot charging	30.2	0.60	0.0	-2.1	23.5	5.9
Process control in hot strip mill	15.1	0.30	0.0	0.0	1.1	1.2
Recuperative burners	35.2	0.70	0.0	0.0	3.9	1.8
Flameless burners	60%	60%				
Insulation of furnaces	8.0	0.16	0.0	0.0	15.6	31.0
Walking beam furnace			25%			
Controlling oxygen levels and VSDs on combustion air fans	16.6	0.33	0.0	0.0	0.79	0.8
Heat recovery to the product		50%		32%		
Waste heat recovery (cooling water)	1.9	0.03	0.0	0.11	1.3	> 50

Option	Emission Reduction (kg of CO_2/tonne of product)	Fuel Savings (GJ/tonne of product)	Electricity Savings (GJ/tonne of product)	Annual Operating Costs ($/tonne of product)	Retrofit Capital Costs ($/tonne of product)	Payback Time (years)
Cold Rolling and Finishing						
Heat recovery on the annealing line	17.5	0.30	0.02	0.0	4.2	4.0
Reduced steam use (pickling line)	9.9	0.19	0.0	0.0	4.4	7.3
Automated monitoring and targeting system	35.3	0.0	0.21	0.0	1.7	0.8
Inter-electrode insulation in electrolytic pickling line						
Continuous annealing						
General						
Preventive maintenance	35.7	0.43	0.02	0.03	0.02	
Energy monitoring and management system	9.5	0.11	0.01	0.0	0.23	0.5
Combined heat and power/cogeneration	82.1	0.03	0.35	0.0	22.7	6.1
High-efficiency motors						
VSD—flue gas control, pumps, and fans	1.5	0.0	0.02	0.0	2.0	10.7

Table 10-13. Energy efficiency technologies and measures applied to integrated steel production in the U.S.

Option	Emissions Reduction (kg CO_2/tonne of product)	Fuel Savings (GJ/tonne of product)	Electricity Savings (GJ/tonne of product)	Annual Operating Costs ($/tonne of product)	Retrofit Capital Costs ($/tonne of product)	Payback Time (years)
Steelmaking - Electric Arc Furnace						
Improved process control (neural network)	17.6	0.0	0.11	-1.6	1.5	0.5
Adjustable speed drives (ASDs)			0.05		2.0	2–3
Transformer efficiency—ultra-high power transformers	10.0	0.0	0.06	0.0	4.3	5.2
Bottom stirring/stirring gas injection	11.7	0.0	0.07	-3.1	0.94	0.2
Foamy slag practice	10.6	0.0	0.07	-2.8	15.6	4.2
Oxy-fuel burners	23.5	0.0	0.14	-6.2	7.5	0.9
Post-combustion of the flue gases						
DC arc furnace	52.9	0.0	0.32	-3.9	6.1	0.7
Scrap preheating—tunnel furnace (Consteel)	35.2	0.0	0.22	-3.0	7.8	1.3
Scrap preheating, post-combustion—shaft furnace (Fuchs)	35.3	-0.70	0.43	-6.2	9.4	1.0
Engineered refractories			0.036			
Airtight operation			0.36			
Contiarc furnace			0.72			
Flue gas monitoring and control	8.8	0.0	0.05	0.0	3.1	4.3
Eccentric bottom tapping on existing furnace	8.8	0.0	0.05	0.0	5.0	6.8
Twin-shell DC with scrap preheating	11.1	0.0	0.07	-1.7	9.4	3.5
Casting						
Efficient caster ladle/tundish heating	1.1	0.02	0.0	0.0	0.09	1.3
Near net shape casting - thin slab	265.3	3.2	0.64	-54.8	234.8	3.3
Near net shape casting - strip				25% less		
Hot Rolling						
Proper reheating temperature						
Avoiding overload of reheat furnaces						
Energy efficient drives in the rolling mill	1.6	0.0	0.01	0.0	0.30	5.9
Process control in hot strip mill	15.1	0.30	0.0	0.0	1.1	1.2
Recuperative burners	35.2	0.70	0.0	0.0	3.9	1.8
Flameless burners	60%	60%				
Insulation of furnaces	8.1	0.16	0.0	0.0	15.7	31.0
Walking beam furnace			25%			
Controlling oxygen levels and VSDs on combustion air fans	16.6	0.33	0.0	0.0	0.79	0.8
Heat recovery to the product		50%		32%		
Flameless burners	60%	60%				
Insulation of furnaces	8.1	0.16	0.0	0.0	15.7	31.0
Walking beam furnace			25%			
Controlling oxygen levels and VSDs on combustion air fans	16.6	0.33	0.0	0.0	0.79	0.8
Heat recovery to the product		50%		32%		

Option	Emission Reduction (kg of CO₂/tonne of product)	Fuel Savings (GJ/tonne of product)	Electricity Savings (GJ/tonne of product)	Annual Operating Costs ($/tonne of product)	Retrofit Capital Costs ($/tonne of product)	Payback Time (years)
General						
Preventive maintenance	15.0	0.09	0.05	0.03	0.02	
Energy monitoring and management systems	3.7	0.02	0.01	0.0	0.23	0.9

Note: DC = direct current; VSD = variable-speed drive.

SUMMARY OF CONTROL MEASURES IN IRON AND STEEL MANUFACTURING

There are several important caveats associated with the estimated costs and savings presented in these tables that require caution in extrapolating the estimates in $/ton to specific iron and steel plants. For many of the measures, the costs and savings are based on the experience of a single plant or an individual application of the measure, or in some cases, best estimates based on the available information.

The actual costs could be quite different when applying the measures to other individual plants because of the numerous site-specific differences among plants that affect costs. In addition, some measures may not be applicable to certain plants because of the process configuration, product type or quality constraints, or the fact that the measure or a similar one has already been applied. Some equipment modifications may incur significant retrofit costs that are not included in the estimates. The calculation of cost effectiveness introduces additional uncertainty because of the additional variability and uncertainty associated with potential reductions in GHG emissions.The choice of which measures might be the most appropriate to implement at a given facility should be based on a detailed analysis by the facility's engineering or energy manager to assess site-specific costs, savings, and emission reductions.

Additional information about these opportunities to improve energy efficiency at EAF steelmaking facilities and integrated iron and steel plants are available on the EPA website, in the GHG Control Measures White Papers pertaining to the Iron and Steel Industry. See *http://www.epa.gov/nsr/ghgpermitting.html* for more specific guidance and information.

10.5.6   EMISSION CONTROLS FOR PETROLEUM REFINING

For a refinery, emissions intensity is influenced by a number of factors, including energy efficiency, fuel use, feed composition, and products. While refineries all refine crude oil to make a range of common products (e.g., gasoline, diesel, fuel oils, liquefied petroleum gases), they often vary in size and the number of processing units that are operating.

For example, refineries with more simple configurations may not be able to process certain fractions into more energy intensive products. Likewise, refineries that process heavy sour crudes may require more energy intensive processing. Benchmarking approaches have been used in the refining industry for many years to improve efficiency and productivity. The European Union evaluated and concluded that the Solomon's complexity weighted barrel approach should be used to benchmark refineries as part of their methodology for allocating emission allowances in the European Union Emissions Trading System (Ecofys, 2009).

Energy Efficiency Improvements in Petroleum Refining Facility Operations

Most refineries already employ some energy management systems (EnMSs). At existing facilities, only a limited number of processes or energy streams may be monitored and managed. Opportunities should be evaluated for expanding the coverage of monitoring systems throughout the plant. New facilities should include a comprehensive energy management program (Worrell and Galitsky, 2005).

Process control systems are available for essentially all industrial processes. These control systems are typically designed to primarily improve productivity, product quality, and efficiency of a process. However, each of these improvements will lead to increased energy efficiency as well. Process control systems also reduce downtime, maintenance costs, and processing time, and increase resource efficiency and emission control (Worrell and Galitsky, 2005). Table 10-14 summarizes the GHG reduction measures that are currently available for the petroleum refining industry.

Table 10-14. Summary of GHG reduction measures for the petroleum refining industry.

GHG Control Measure	Description	Efficiency Improvement/ GHG emission reduction	Retrofit Capital Costs ($/unit of CO2e)	Pay-back time (years)	In Practice?	Other Factors
Energy Efficiency Programs and Systems						
Energy Efficiency Initiatives and Improvements	Benchmark GHG performance and implement energy management systems to improve energy efficiency, such as: ▪ improve process monitoring and control systems ▪ use high efficiency motors ▪ use variable speed drives ▪ optimize compressed air systems ▪ implement lighting system efficiency improvements	4-17% of electricity consumption		1-2 years	Yes	
Stationary Combustion Sources						
Steam Generating Boilers						
Systems Approach to Steam Generation	Analyze steam needs and energy recovery options, including: ▪ minimize steam generation at excess pressure or volume ▪ use turbo or steam expanders when excesses are unavoidable ▪ schedule boilers based on efficiency				Yes	
Boiler Feed Water Preparation	Replace a hot lime water softener with a reverse osmosis membrane treatment system to remove hardness and reduce alkalinity of boiler feed.	70-90% reduction in blowdown steam loss; up to 10% reduction in GHG emissions		2-5 years	Yes	

GHG Control Measure	Description	Efficiency Improvement/ GHG emission reduction	Retrofit Capital Costs ($/unit of CO₂e)	Pay-back time (years)	In Practice?	Other Factors
Improved Process Control	Oxygen monitors and intake air flow monitors can be used to optimize the fuel/air mixture and limit excess air.	1-3% of boiler emissions		6 - 18 mos	Yes	Low excess air levels may increase CO emissions
Improved Insulation	Insulation (or improved insulation) of boilers and distribution pipes.	3-13% of boiler emissions		6 - 18 mos	Yes	
Improved Maintenance	All boilers should be maintained according to a maintenance program. In particular, the burners and condensate return system should be properly adjusted and worn components replaced. Additionally, fouling on the fireside of the boiler and scaling on the waterside should be controlled.	1-10% of boiler emissions			Yes	
Recover Heat from Process Flue Gas	Flue gases throughout the refinery may have sufficient heat content to make it economical to recover the heat. Typically, this is accomplished using an economizer to preheat the boiler feed water.	2-4% of boiler emissions		2 years	Yes	
Recover Steam from Blowdown	Install a steam recover system to recovery blowdown steam for low pressure steam needs (e.g., space heating and feed water preheating).	1 –3%		1 - 3 years	Yes	

GHG Control Measure	Description	Efficiency Improvement/ GHG emission reduction	Retrofit Capital Costs ($/unit of CO_2e)	Pay-back time (years)	In Practice?	Other Factors
Reduce Standby Losses	Reduce or eliminate steam production at standby by modifying the burner, combustion air supply, and boiler feedwater supply, and using automatic control systems to reduce the time needed to reach full boiler capacity.	Up to 85% reduction in standby losses (but likely a small fraction of facility total boiler emissions)		1.5 years	Yes	
Improve and Maintain Steam Traps	Implement a maintenance plan that includes regular inspection and maintenance of steam traps to prevent steam lost through malfunctioning steam traps.	1-10% of boiler emissions			Yes	
Install Steam Condensate Return Lines	Reuse of the steam condensate reduces the amount of feed water needed and reduces the amount of energy needed to produce steam since the condensate is preheated.	1-10% of steam energy use		1-2 years	Yes	
Process Heaters						
Combustion Air Controls-Limitations on Excess air	Oxygen monitors and intake air flow monitors can be used to optimize the fuel/air mixture and limit excess air.	1-3%		6-18 mos	Yes	

GHG Control Measure	Description	Efficiency Improvement/ GHG emission reduction	Retrofit Capital Costs ($/unit of CO_2e)	Pay-back time (years)	In Practice?	Other Factors
Heat Recovery: Air Preheater	Air preheater package consists of a compact air-to-air heat exchanger installed at grade level through which the hot stack gases from the convective section exchange heat with the incoming combustion air. If the original heater is natural draft, a retrofit requires conversion to mechanical draft.	10-15% over units with no preheat.			Yes	May increase NO_x emissions
Combined Heat and Power						
Combined Heat and Power	Use internally generated fuels or natural gas for power (electricity) production using a gas turbine and generate steam from waste heat of combustion exhaust to achieve greater energy efficiencies			5 years	Yes	
Carbon Capture						
Oxy-combustion	Use pure oxygen in large combustion sources to reduce flue gas volumes and increase CO_2 concentrations to improve capture efficiency and costs				No	
Post-combustion Solvent Capture	Use solvent scrubbing, typically using monoethanolamine (MEA) as the solvent, for separation of CO_2 in post-combustion exhaust streams				Yes	

GHG Control Measure	Description	Efficiency Improvement/ GHG emission reduction	Retrofit Capital Costs ($/unit of CO_2e)	Pay-back time (years)	In Practice ?	Other Factors
Post-combustion membranes	Use membrane technology to separate or adsorb CO_2 in an exhaust stream		$55-63		No	
Fuel Gas System and Flares						
Fuel Gas System						
Compressor Selection	Use dry seal rather than wet seal compressors; use rod packing for reciprocating compressors				Yes	
Leak Detection and Repair	Use organic vapor analyzer or optical sensing technologies to identify leaks in natural gas lines, fuel gas lines, and other lines with high methane concentrations and repair the leaks as soon as possible.	80-90% of leak emissions; <0.1% refinery-wide			Yes	
Sulfur Scrubbing System	Evaluate different sulfur scrubbing technologies or solvents for energy efficiency				Yes	
Flares						
Flare Gas Recovery	Install flare gas recovery compressor system to recover flare gas to the fuel gas system			1 yr	Yes	

GHG Control Measure	Description	Efficiency Improvement/ GHG emission reduction	Retrofit Capital Costs ($/unit of CO_2e)	Pay-back time (years)	In Practice?	Other Factors
Proper Flare Operation	Maintain combustion efficiency of flare by controlling heating content of flare gas and steam- or air-assist rates				Yes	
Refrigerated Condensers	Use refrigerated condensers to increase product recovery and reduce excess fuel gas production				Yes	
Cracking Units						
Fluid Catalytic Cracking Units						
Power/Waste Heat Recovery	Install or upgrade power recovery or waste heat boilers to recover latent heat from the FCCU regenerator exhaust				Yes	
High-Efficiency Regenerators	Use specially designed FCCU regenerators for high efficiency, complete combustion of catalyst coke deposits				Yes	
Hydrocracking Units						
Power/Waste Heat Recovery	Install or upgrade power recovery.Power can be recovered from the pressure difference between the reactor and fractionation stages			2.5 years	Yes	

GHG Control Measure	Description	Efficiency Improvement/ GHG emission reduction	Retrofit Capital Costs ($/unit of CO_2e)	Pay-back time (years)	In Practice?	Other Factors
Hydrogen Recovery	Use hydrogen recovery compressor and back-up compressor to ensure recovery of hydrogen in process off-gas				Yes	
Coking Units						
Fluid Coking Units						
Power/Waste Heat Recovery	Install or upgrade power recovery or waste heat boilers to recover latent heat from the fluid coking unit exhaust				Yes	
Flexicoking Units						
Delayed Coking Units						
Steam Blowdown System	Use low back-pressure blowdown system and recycle hot blowdown system water for steam generation				Yes	
Steam Vent	Lower pressure and temperature of coke drum to 2 to 5 psig and 230°F to minimize direct venting emissions	50 to 80% reduction in direct steam vent CH_4 emissions			Yes	

GHG Control Measure	Description	Efficiency Improvement/ GHG emission reduction	Retrofit Capital Costs ($/unit of CO_2e)	Pay-back time (years)	In Practice?	Other Factors
Catalytic Reforming Units						
Sulfur Recovery Units						
Sulfur Recovery System Selection	Evaluate energy and CO_2 intensity in selection of sulfur recovery unit and tail gas treatment system and a variety of different tail gas treatment units including Claus, SuperClaus® and EuroClaus®, SCOT, Beavon/amine, Beavon/Stretford, Cansolv®, LoCat®, and Wellman-Lord				Yes	
Hydrogen Production Units						
Hydrogen Production Optimization	Implement a comprehensive assessment of hydrogen needs and consider using additional catalytic reforming units to produce H_2				Yes	
Combustion Airand Feed/Steam Preheat	Use heat recovery systems to preheat the feed/steam and combustion air temperature	5% of total energy consumption for H_2 production			Yes	

GHG Control Measure	Description	Efficiency Improvement/ GHG emission reduction	Retrofit Capital Costs ($/unit of CO_2e)	Pay-back time (years)	In Practice?	Other Factors
Cogeneration	Use cogeneration of hydrogen and electricity: hot exhaust from a gas turbine is transferred to the reformer furnace; the reformer convection section is also used as a heat recovery steam generator (HRSG) in a cogeneration design; steam raised in the convection section can be put through either a topping or condensing turbine for additional power generation				Yes	
Hydrogen Purification	Evaluate hydrogen purification processes (e.g., pressure-swing adsorption, membrane separation, and cryogenic separation) for overall energy intensity and potential CO_2 recovery.				Yes	
Hydrotreating Units						
Hydrotreater Design	Use energy efficient hydrotreater designs and new catalyst to increase sulfur removal.				Yes	
Crude Desalting and Distillation Units						
Desalter Design	Alternative designs for the desalter, such as multi-stage units and combinations of AC and DC fields, may increase efficiency and reduce energy consumption.				Yes	

GHG Control Measure	Description	Efficiency Improvement/ GHG emission reduction	Retrofit Capital Costs ($/unit of CO_2e)	Pay-back time (years)	In Practice?	Other Factors
Progressive Distillation Design	Progressive distillation process uses as series of distillation towers working at different temperatures to avoid superheating lighter fractions of the crude oil.	30% reduction in crude heater emissions; 5% or more refinery-wide			Yes	
Storage Tanks						
Vapor Recovery or Control for Unstabilized Crude Oil Tanks	Consider use of a vapor recovery or control system for crude oil storage tanks that receive crude oil that has been stored under pressure ("unstabilized" crude oil)	90-95% reduction in CH_4 from these tanks			Yes	
Heated Storage	Insulate heated storage tanks				Yes	

Additional detail regarding these GHG reduction measures are provided in Section 4, Energy Programs and Management Systems, and Section 5, GHG Reduction Measures by Source, of the EPA GHG Control Measures White Paper for Refineries.
See *http://www.epa.gov/nsr/ghgpermitting.html* for more specific guidance and information.

10.5.7 EMISSION CONTROLS FOR NITRIC ACID PLANTS

Three types of controls exist for N_2O at nitric acid plants based on the location of the control within the nitric acid production process: (Durilla, 2009)

Primary – reduces the amount of N_2O formed in the ammonia oxidation step. This can be done by modifying the catalyst used in the oxidation process and/or modifying the operating conditions of this process.

Secondary – reduces N_2O immediately after it is formed in the ammonia oxidation step.

Tertiary – reduces N_2O by installing a catalytic reactor either upstream or downstream of the tailgas expansion unit following ammonia oxidation.

The most commonly applied controls are secondary and tertiary controls. These control technologies employ abatement or decomposition control techniques. These technologies

are capable of and typically achieve greater than 80% reduction of N_2O emissions. A 2006 EPA economic report constructed marginal abatement curves to be used for modeling the cost of emissions reductions of non-CO_2 greenhouse gases globally in the 2010 to 2020 timeframe (U.S. EPA, June 2006). In the nitric acid sector, the report utilized engineering reports to characterize catalytic reduction methods developed by several companies. The capital costs for control technology ranged from $2 to $6 per ton of carbon equivalent removed. Operating costs ranged from $0.14 to $1.91 per ton carbon equivalent removed (U.S. EPA; June 2006).

SUMMARY OF CONTROL MEASURES FOR NITRIC ACID PRODUCTION

Table 10-15 summarizes the GHG control measures for nitric acid plants. Where available, the table includes the emission reduction potential, energy savings, costs, and feasibility of each measure.

Table 10-15. Summary of GHG control measures in the nitric acid production industry.

Pollutant	Control Technology	Emission Reduction (%)	Energy Savings	Capital Costs ($/ton CO_2e)	Operating Costs ($/ton CO_2e)	Demonstrated in Practice
N_2O	Primary	30 - 85	None	NA	Na	Yes
N_2O	Secondary	70 -90	None	NA	0.12 – 0.97	Yes
N_2O	NSCR	> 80	None	6.27	0.14 – 0.22	Yes
N_2O	Other Tertiary Controls	>80	None	2.18 – 3.55	0.14 – 1.91	Yes

Sources: EPA 2006; European Commission August 2007

Primary Controls– Suppression of N_2O Formation

One primary control is the extension of the NH_3 oxidation reactor. Yara has developed and patented a technology that consists of an "empty" reaction chamber of approximately 10 ft in length between the platinum catalyst and the first heat exchanger. This allows an additional residence time of 1 to 3 seconds. Reductions are estimated to be 70% to 85% (4 to 6 lb N_2O/ton 100% acid or about 400 ppm). This technique is applicable to new plants with low additional investments. For existing plants, costs are much higher as a new reactor may be required along with other plant modifications. (European Commission, August 2007).

Another primary control is modifying the ammonia oxidation gauzes. These catalysts can be improved platinum catalysts. A few plants have shown a 30 -40 % N_2O reduction. Alternative oxidation catalysts (not platinum based) can achieve 80 – 90% reduction but lower NO is produced. (European Commission, August 2007). Data from 14 European units with improved oxidation catalyst showed a range of 3.6 –9.7 kg N_2O/tonne (7.2 – 19.4 lb N_2O/ton). The average was 6.2 kg N_2O/tonne (12.4 lb N_2O/ton). (European Commission, February 2008).

Secondary Control - Catalytic N₂O Decomposition in the Oxidation Reactor

For this control, a catalyst is located immediately downstream of the NH_3 oxidation step. Using this catalyst, N_2O is decomposed to N_2 and O_2 almost instantly. Four companies (Yara, BASF, Johnson Matthey, and Hereaus) have developed selective catalysts for the removal of N_2O. The catalyst is contained in the ammonia burner and is termed "selective" as it promotes the decomposition of N_2O to N_2 and O_2, as shown in Reaction 10-7. No major modification of the ammonia oxidation reactor is typically required and the installation of this catalyst has shown no effect on ammonia conversion. The placement of the catalyst in the ammonia burner allows for reduction of N_2O emissions by increasing the residence time of the gas in the burner. The average lifetime for the pellet catalyst is 4 years (ICAC, 2009). Up to 90% reduction is possible (ICAC, 2009) and rates of 130 to 400 ppm of N_2O are achievable. Yara's system (Figure 10-13) was first installed in 2002 and is presently operating in 17 plants. The plants applying the secondary controls range in size from 200 to 2,650 million tonne per day.
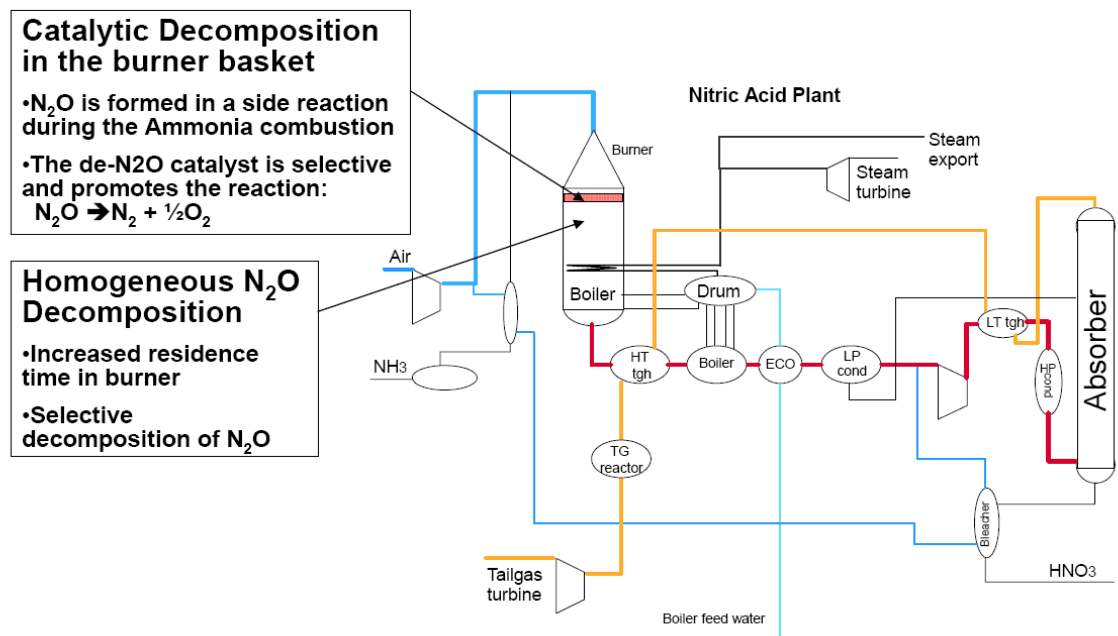
Reaction 10-7 $2N_2O \rightarrow 2N_2 + O_2$

Figure 10-13. Yara secondary N_2O control from nitric acid production
Source: ICAC, 2009.

One reference states this control has the lowest capital cost as minimal modifications are required to the reactor for the ammonia oxidation catalyst. There are no additional operating costs. A total of 53 process lines at nitric acid plants worldwide have implemented this technology. Three facilities have installed this technology in the United States. A recent article discussed a secondary catalyst being installed at El Dorado's Nitrogen LP's Baytown, Texas plant (Industrial GHG, 6/17/10).The project began operating around July 2010. The facility has applied to obtain GHG emission credits under the Climate Action Reserve program. Also, Terra Industries has installed secondary catalysts in Yazoo City, Mississippi and Claremore, Oklahoma under this program.

Emission test results from use of secondary controls were available from 2 sources – European Commission (February 2008) and emissions monitoring reports from CDM projects.These results are summarized in Table 10-14. For the CDM projects, 30 of the 37 test results had efficiencies greater or equal to 70%. Twenty three of 37 test results had efficiencies greater or equal to 80%.The CDM projects include 2 units with percent reductions (9, 39%) much lower than the other 30 units tested. Table 10-16 shows the data on secondary controls from these CDM projects. As shown here, many secondary catalysts achieve less than 3 lb of N_2O/ton of 100% nitric acid.

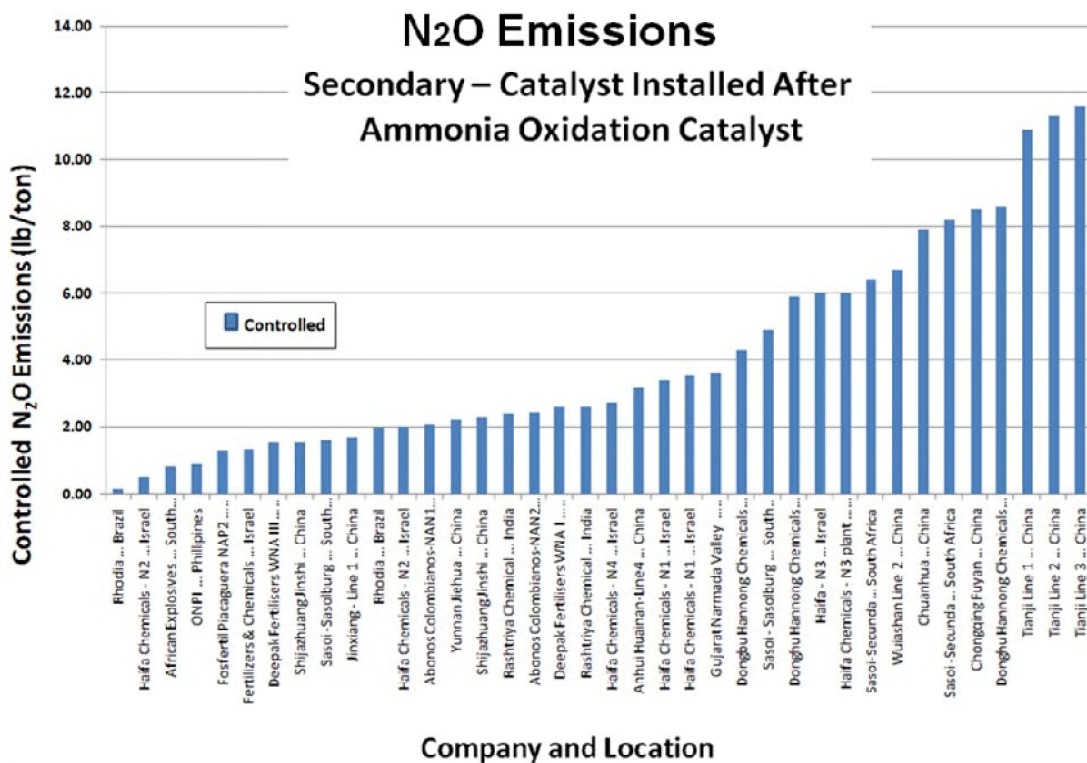| Table 10-16. N_2O emission test results – secondary controls.					
Source	Units tested	Range (lb N_2O/ton)	Average (lb N_2O/ton)	% Reduction Range	% Reduction Average
EC	8	1.8 – 5.0	3.2	Unknown	Unknown
EC*	4*	3.0 – 3.8*	3.4*	Unknown	Unknown
CDM Projects	30 (37 test periods)	0.15 – 11.6	4.1	9 – 98	76

With Improved oxidation catalyst

Figure 10-14. N_2O emissions from secondary controls – CDM projects.

Source: GHG Control Measures White Papers (EPA 2010).

Tertiary Controls –Catalytic Reduction

Note that Nonselective Catalytic Reduction (NSCR) and Selective Catalytic Reduction (SCR) methods are introduced in Chapter 8: Control Techniques for Nitrogen Oxides. You may refer students to Chapter 8 for specific information regarding these methods.

Nonselective Catalytic Reduction (NSCR)

Nonselective Catalytic Reduction (NSCR) is a common control technology utilized at nitric acid production facilities to reduce NO_x emissions where a reagent fuel, such as natural gas, propane, butane, or ammonia plant purge gas (mainly H_2) is used as a reagent to reduce NO_X, and N_2O over a catalyst to produce N_2 and water. Similar to a three-way catalytic converter, reductions of NO_x and N_2O occur while other emissions are oxidized. Catalysts for NSCR are usually based on platinum, vanadium pentoxide, iron oxide or titanium.

Catalyst supports are typically made of alumina pellets or a ceramic honeycomb substrate. NSCR has a N_2O reduction efficiency of 80-95% (European Commission, August 2007). As far as selection of a NO_x control, NSCR is typically used at plants that have the capability to preheat tailgas to 200-450º C and requires a greater reagent input than SCR (RTI, 2009). As stated earlier, 14 process trains in the U.S. use NSCR. These facilities have installed NSCR to control NO_X emissions and as an additional benefit NSCR reduces N_2O emissions. The one U.S. plant with NSCR with emission test data was at 0.43 lb N_2O/ton. In numerous nitric acid plants outside of the

US, NSCR/catalytic reduction is used in conjunction with SCR.

One NSCR manufacturer, Süd-Chemie, has a unit (EnviCat$^{®}$ HNO$_3$) that works best when the tailgas temperature is greater than 400°C. This unit is a direct disintegration process with the catalyst positioned close to the reactor. Hydrocarbons are required in the tailgas stream to provide efficient control. Both N$_2$O and NO$_X$ react with the hydrocarbons to break down the compounds to nitrogen and oxygen. (Süd-Chemie, n.d.).

Süd-Chemie along with Uhde have developed a process referred to as EnviNOx® process. More details are shown in Figures 10-15 and 10-16. There are two variants of the EnviNO$_x$® process depending on the tail gas temperature. Variant 1 is discussed under the next section – catalytic decomposition. Variant 2 is suitable for lower tail gas temperatures ranging from 300 to 520°C.

The low temperature variant (Variant 2) utilizes hydrocarbons, such as natural gas, to drive catalytic reduction. The reaction vessel is positioned upstream of the tailgas expander (turbine). Ammonia is mixed with the tailgas that contains both N$_2$O and NO$_x$. The mixture passes through a single catalyst bed where parallel reduction of the pollutants takes place. A vanadium-free catalyst is used to convert N$_2$O and NO$_x$ to nitrogen, oxygen, and water. This particular catalyst also removes the ammonia that was added to drive the reaction between the catalyst and N$_2$O, thus preventing ammonia leakage. Conversion rates greater than 98% have been achieved with the EnviCat® N$_2$O system right below the platinum gauze (Süd-Chemie, n.d.). The addition of hydrocarbons to drive this reaction is not thought to produce significant CO$_2$ emissions when compared to the reduction of N$_2$O in the unit (Uhde, 2005). This process utilizes a tailgas reactor positioned directly upstream of the tailgas expander (turbine).
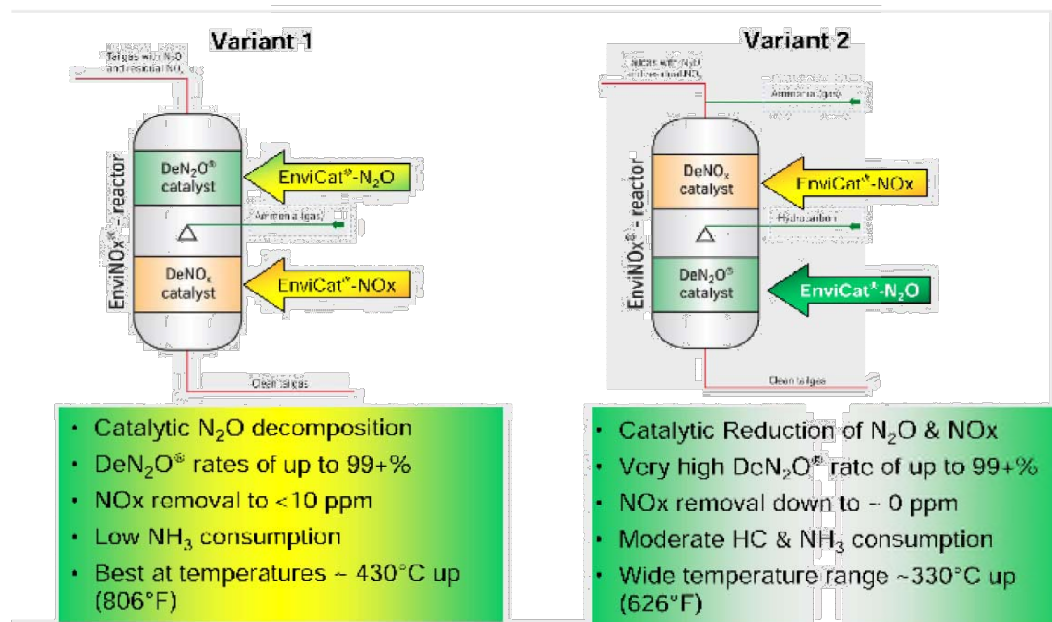

Figure 10-15. Uhde combination N$_2$O and NO$_X$ control for nitric acid production plants.
Source: ICAC, 2009.

Figure 10-16. Uhde EnviNO$_X$® reactor in Linz, Austria.
Source: ICAC, 2009.

Tertiary Controls – Catalytic Decomposition

Decomposition technology, which can be high temperature or low temperature, does not require any additional reducing agents or additives, and no undesirable byproducts are formed from the reaction. The basis of decomposition technology is to simply decompose N_2O to form nitrogen and oxygen (ICAC, 2009). A catalyst is used to drive the decomposition. This catalyst is stable in the presence of NO_X and ammonia, allowing placement either upstream or downstream of the SCR used to reduce NO_X (ICAC, 2009). Decomposition can remove up to 99% of the N_2O in the process stream.

As mentioned above, Uhde along with Süd-Chemie have developed a process referred to as EnviNO$_X$®. More details are shown in Figures 10-13 and 10-14. There are two variants of the EnviNO$_X$® process depending on the tail gas temperature. Variant 1 is discussed under this section – catalytic decomposition. Variant 1 is good for higher tail gas temperatures ranging from 425 to 520°C. For these temperatures, EnviNO$_X$® is a two-stage process. In the first stage, N_2O is decomposed to oxygen and nitrogen in a catalyst bed. The resulting tailgas is then mixed with ammonia and enters a second catalyst bed where NO_X is reduced to water vapor and nitrogen. The N_2O is further removed in this catalyst bed. (Uhde, 2005 and ThyssenKrupp, 2005).

Another decomposition technology is the Shell N_2O Abatement Technology (C-NAT). A pellet catalyst (manufactured by CRI, a wholly own affiliate of Shell), is contained within a lateral flow

reactor. The tailgas is forced laterally through the packed-bed design to achieve more efficient utilization of the catalyst surface area than traditional catalyst design. This technology works best at temperatures between 450°C and 650°C but can operate as low as 300°C. The Shell C-NAT system can achieve greater than 98% reduction of N_2O (CRI, 2009; ICAC, 2009).

Another decomposition technology is the BASF NO_X CAT ™ ZN_2O Catalyst. This technology removes both NO_X and N_2O at temperatures from 300-600°C. In this process ammonia is injected into a catalyst bed that consists of an SCR catalyst (e.g., Vandium/Titanium) and the NO_XCAT™ $Z\, N_2O$ reduction catalyst. (ICAC, 2009).

Emission test results for tertiary controls were obtained from 2 sources – European Commission (February 2008) and monitoring reports from CDM projects. These results are summarized in Table 10-17. Also, the results from the CDM projects and 1 U.S. plant using NSCR are shown in Figure 10-17. Most controls achieve less than 1.0 lb of N_2O per ton of 100% acid.

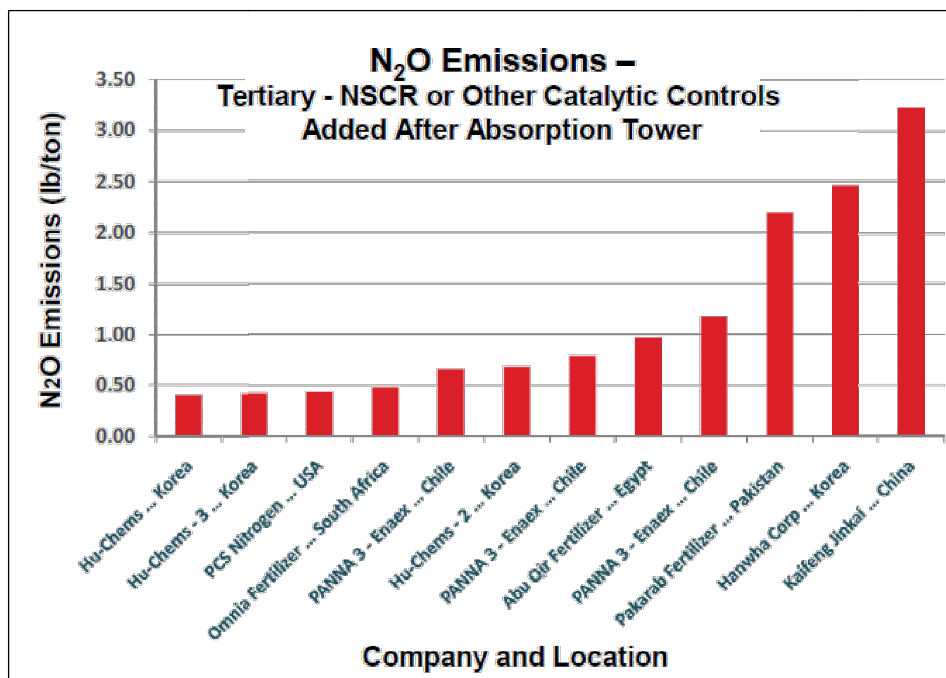| Table 10-17. N_2O emission test results – tertiary controls.					
Source	Units tested	Range (lb N_2O/ton)	Average (lb N_2O/ton)	% Reduction Range	% Reduction Average
EC	7	0.02 – 0.48	0.18	Unknown	Unknown
CDM Projects	11	0.41 – 2.2	1.2	88 - 98	94

Figure 10-17. N_2O emissions from tertiary controls.
Source: GHG Control Measures White Papers (EPA 2010).

ENERGY EFFICIENCY IMPROVEMENTS TO REDUCE OTHER GHG EMISSIONS (RTI, 2009)

Energy Recovery

Nitric acid production is a net exporter of energy. Therefore, energy recovery is a valuable resource for these facilities. External sources of fuel can be minimized through recovery of energy from the production process.

There are two exothermic reactions, oxidation and absorption, that produce more energy than the total production process consumes. Single and dual-pressure plants are used within the US. For new plants, dual-pressure is the most predominant design. However, there is not a substantial difference in the total energy required or recovered from the two designs. The energy requirements of controls should also be considered.

Background

NO_x is another regulated/controlled pollutant, which can have an impact on energy efficiency and recovery. When considering NO_x controls, SCR units require less energy than NSCR units because they operate at lower temperatures. As shown earlier NSCR has the additional benefit of controlling N_2O. The overall energy recovery is dependent on the design of the facility. Approximately 1,660 Btu/lb of 100% nitric acid (Btu/lb) is produced from the catalytic reactor. The absorption tower produces approximately 370 Btu/lb. All of this energy is potentially available for recovery. Additionally, the expansion unit has the potential to recover 80% of the mechanical energy used, or approximately 325 Btu/lb. This provides for an overall amount of energy available for recovery of approximately 1,955 Btu/lb. The potential CO_2 equivalent emissions that are avoided by this level of steam energy recovery are 0.26 tonnes CO_2e per ton of 100% nitric acid. An additional 0.77 tonnes CO_2e per ton 100% nitric acid is avoided through electric energy production. However, the actual levels of energy recovery, due to economic and practical considerations, are around 50-65% of the theoretical values. Therefore, between 969 and 1,217 Btu/lb is available for recovery. This equates to an offset of 0.12 to 0.5 tonnes CO_2e/ton HNO_3.

Steam production is the most common form of energy recovery for process lines in nitric acid production. Heat from the process is typically recovered and used to generate a large portion of the steam needed elsewhere in the plant. During startup, natural gas is used to augment this steam when nitric acid production is at levels below those needed to recover enough steam for the rest of the facility. Although not widely practiced currently at nitric acid production facilities, bottoming cycle combined heat and power (CHP) could also be used for energy recovery at nitric acid plants. With this type of CHP system, steam would be generated from heat recovery at a higher pressure than is needed in the other processes and run through a steam turbine generator before being sent to the processes at the required pressure. The power generated could be used within the plant, offsetting power purchases from the grid. This would not result in direct CO_2 reductions at the facility from the power produced, but indirect reductions from displacing grid power. The level of reduction is a function of the CO_2 intensity of the displaced external power production.

Energy Efficiency

There are energy efficiency measures that can be implemented at nitric acid plants. These areas include building lighting and HVAC, motors, compressed air and pumps. Energy Star™ has not prepared an Energy Guide specific to nitric acid plants. A general guide "Managing Your Energy" is available.

Additional information about these opportunities to improve energy efficiency at EAF steelmaking facilities and integrated iron and steel plants are available on the EPA website, in the GHG Control Measures White Papers pertaining to Nitric Acid Plants. See *http://www.epa.gov/nsr/ghgpermitting.html* for more specific guidance and information.

10.6 ADDITIONAL RESOURCES FOR GHG EMISSION CONTROL

Additional information and resources for this chapter are available at the EPA's Greenhouse Gas Permitting website. *http://www.epa.gov/nsr/ghgpermitting.html.* The industrial sectors described in this course are represented in a series of technical "white papers" which provide additional results, historical data, and process information. This chapter provides some a summary of available information on control techniques and measures to reduce GHG emissions from specific industrial sectors.

The following resources provide additional information regarding identifying, controlling, and mitigating greenhouse gas from many types of operations.

- ***Resources for Estimating GHG Emissions***
  http://www.epa.gov/nsr/ghgresources.html
- ***Clean Air Act Permitting for Greenhouse Gases***
  http://www.epa.gov/nsr/ghgpermitting.html
  This website provides access to important guidance and tools for implementing GHG permitting requirements.
- ***BACT/RACT/LAER Clearinghouse (RBLC)***
  http://cfpub.epa.gov/RBLC/

  The RBLC data base contains case-specific information on the "Best Available" air pollution technologies that have been required to reduce the emission of air pollutants from stationary sources (e.g., power plants, steel mills, chemical plants, etc.). This information has been provided by State and local permitting agencies.

  Data in the Clearinghouse is not limited to just sources subject to these requirements. Noteworthy prevention and control technology decisions are included in the RBLC even if they are not related to RACT, BACT, or LAER decisions.

  Refer to the EPA permitting website for additional resources regarding BACT analysis.

10.7 SUMMARY

This chapter covered the control techniques and measures to reduce GHG emissions from specific industrial sectors. This information provides basic technical information, which may be useful in a BACT analysis, but does not define BACT for each sector.

The chapter covered the following topics:

- The definition of GHG and the primary sources of GHG emissions.
- The main GHG control techniques and strategies for these industries: Electric Generating Units (EGUs), Large Industrial/Commercial/Institutional Boilers, Pulp and Paper Manufacturing, Cement Manufacturing, Iron and Steel Industry, Petroleum Refineries, and Nitric Acid Plants.
- Additional GHG emission control and reduction resources.

10.8 REVIEW EXERCISES

INSTRUCTIONS

Select the best response(s) for each of the following multiple-choice questions.

MULTIPLE CHOICE QUESTIONS

1. What was the change in total U.S. Emissions between 2009 and 2010?

    a) Total emissions dropped 1.3%
    b) Total emissions increased 3.2%
    c) Total emissions dropped by 0.5%

2. To optimize overall efficiency for an EGU, the unit is operated under conditions that enable
    _____ to be converted to CO_2 during combustion.

    a) natural gas
    b) fluorinated gases
    c) fuel carbon
    d) coal

3. Which of the following boiler types is the most efficient alternative to stokers for burning coal?

    a) Pulverized coal (PC) boilers
    b) Fluidized bed-combustors (FBC)
    c) Watertube boilers
    d) Firetube boilers

4. Which of the following is the largest end use of energy in the pulp and paper industry?

    a) Electricity
    b) Steam
    c) Chemical purchases

5. Which of the following control methods are used to reduce GHG emissions in Cement
    Manufacturing? Select all that apply.

    a) Shifting from wet/long dry to preheater/precalciner processing
    b) Selective catalytic reduction (NSCR)
    c) Removing CO_2 from flue-gases
    d) Applying a lower cement/clinker ratio

6. The vast majority of GHGs (CO_2) are emitted from which aspect(s) of the iron production process? Select
    all that apply.

    a) Sinterfeed materials
    b) Coke oven battery's combustion stack
    c) Combustion of coke, and coal
    d) Blast furnace's stove stacks

7. Label the 1) Primary, 2) Secondary, and 3)Tertiary technologies for GHG Control in Nitric Acid
    Production on the lines below.

a) _____ reduces N_2O by installing a catalytic reactor either upstream or downstream of the tailgas expansion unit following ammonia oxidation.

b) _____ reduces N_2O immediately after it is formed in the ammonia oxidation step.

a) _____ reduces the amount of N_2O formed in the ammonia oxidation step. This can be done by modifying the catalyst used in the oxidation process and/or modifying the operating conditions of this process.

8. *True or False:* Nearly all of the energy consumed in Petroleum refining is fossil fuel for combustion.
   a) True
   b) False

9. Which of the following is identified in this chapter as the source of indirect emissions of CO_2, N_2O and CH_4 at nitric acid plants?

   a) Ammonia oxidation
   b) Burner design
   c) Steam powered compressor startup

10. Which of the following is the best source(s) for up-to-date information about GHG permitting

    a) www.epa.gov
    b) RACT/BACT/LAER Clearinghouse, or the RBLC
    c) Trade magazines

10.9 REVIEW EXERCISE: SOLUTIONS

MULTIPLE CHOICE ANSWER

1. What was the change in total U.S. Emissions between 2009 and 2010?

   a) Total emissions dropped 1.3%
   b) Total emissions increased 3.2%
   c) Total emissions dropped by 0.5%

The increase is attributed to an increase in energy consumption across all sectors with much warmer summer temperatures (requiring additional A/C demand which is produced with coal combustion and natural gas. Since 1990, U.S. emissions have increased at 0.5% annually.

2. To optimize overall efficiency for an EGU, the unit is operated under conditions that enable _____to be converted to CO_2 during combustion.
   a) natural gas
   b) fluorinated gases
   c) fuel carbon
   d) coal

3. Which of the following boiler types is the most efficient alternative to stokers for burning coal?

   a) Pulverized coal (PC) boilers
   b) Fluidized bed-combustors (FBC)
   c) Watertube boilers
   d) Firetube boilers

4. Which of the following is the largest end use of energy in the pulp and paper industry?
   a) Electricity
   b) Steam
   c) Chemical purchases

5. Which of the following control methods are used to reduce GHG emissions in Cement Manufacturing? Select all that apply.

   a) Shifting from wet/long dry to preheater/precalciner processing
   b) Selective catalytic reduction (NSCR)
   c) Removing CO_2 from flue-gases
   d) Applying a lower cement/clinker ratio

6. The vast majority of GHGs (CO_2) are emitted from which aspect(s) of the iron production process? Select all that apply.
   a) Sinterfeed materials
   b) Coke oven battery's combustion stack
   c) Combustion of coke, and coal
   d) Blast furnace's stove stacks

7. Label the 1) Primary, 2) Secondary, and 3)Tertiary technologies for GHG Control in Nitric Acid Production on the lines below.

a) **3) Tertiary** – reduces N_2O by installing a catalytic reactor either upstream or downstream of the tailgas expansion unit following ammonia oxidation.

b) **2) Secondary** – reduces N_2O immediately after it is formed in the ammonia oxidation step.

c) **1) Primary** – reduces the amount of N_2O formed in the ammonia oxidation step. This can be done by modifying the catalyst used in the oxidation process and/or modifying the operating conditions of this process.

8. *True or False:* Nearly all of the energy consumed in Petroleum refining is fossil fuel for combustion.
   a) **True**
   b) False

9. Which of the following is identified in this chapter as the source of indirect emissions of CO_2, N_2O and CH_4 at nitric acid plants?
   a) Ammonia oxidation
   b) Burner design
   c) **Steam powered compressor startup**

10. Which of the following is the best source(s) for up-to-date information about GHG permitting
    a) *www.epa.gov*
    b) **RACT/BACT/LAER Clearinghouse, or the RBLC**
    c) Trade magazines

The website *www.epa.gov* is the one stop source for GHG permitting information. The RACT/BACT/LAER Clearinghouse (RBLC) provides access to information and decisions about pollution control measures required by air pollution emission permits issued for GHG by permitting agencies. Information is accessible to all permitting agencies working on similar projects. The expanded RBLC includes GHG control and test data, and a GHG message board for permitting authorities.

10.10   REFERENCES

1.   GHG White Paper (1) – Electric Generating Units [October 2010]

2.   GHG White Paper (2) – Large Industrial/Commercial/Institutional Boilers [October 2010]

3.   GHG White Paper (3) – Pulp & Paper Industry [October 2010]

4.   GHG White Paper (4) – Portland Cement Industry [October 2010]

5.   GHG White Paper (5) – Iron & Steel Industry [October 2010]

6.   GHG White Paper (6) – Petroleum Refining Industry [October 2010]

7.   GHG White Paper (7) – Nitric Acid Production [December 2010]

8.   Supporting information: EPA New Source Review website - Clean Air Act Permitting for Greenhouse Gases *http://www.epa.gov/nsr/ghgpermitting.html*

9.   Supporting information: EPA Climate Change- Greenhouse Gas Emissions website – 2012 U.S. Greenhouse Gas Inventory Report *http://www.epa.gov/climatechange/emissions.htm*

APPENDIX

BASIC CONCEPTS

GAS TEMPERATURE

There are several scales available for measuring temperature, all of them entirely arbitrary. The two that have come into common use are the Farenheit scale and the Celsius or Centigrade scale. As shown in Figure A-1, the Fahrenheit scale sets 32°F as the freezing temperature of water and divides the scale between the freezing and boiling points into 180 degree units, making 212°F the boiling temperature of water. The Celsius scale sets 0°C as the freezing temperature of water and divides the scale between the freezing and boiling points into 100 degree units, making 100°C the boiling temperature of water. The following relationships convert one scale to another:

$$°F = 1.8°C + 32 \qquad\qquad (A\text{-}1)$$

$$°C = \frac{°F - 32}{1.8} \qquad\qquad (A\text{-}2)$$
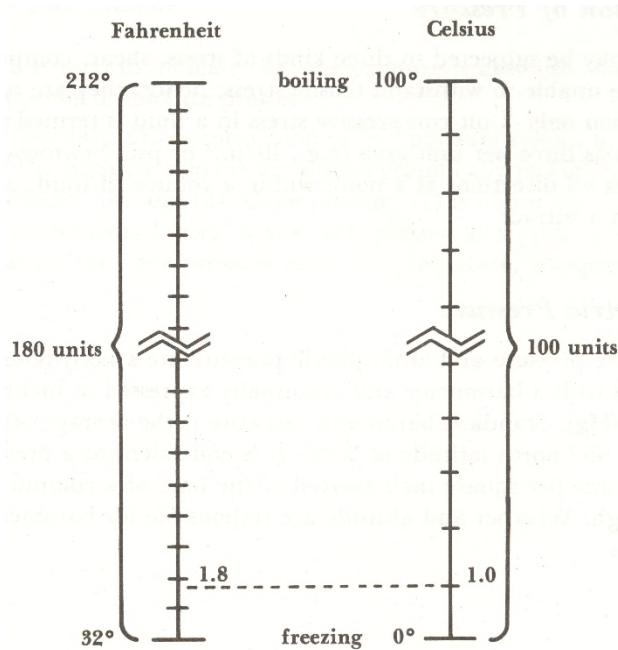
Figure A-1. Comparison of Fahrenheit and Celsius temperature scales

ABSOLUTE TEMPERATURE

Although these two scales are very serviceable, their use causes difficulties when forming temperature ratios or when taking roots and powers of negative temperatures. What is needed in these situations is a temperature scale that has zero as its lowest value. These scales are referred to as *absolute temperature* scales. Experiments with perfect gases have shown that, under constant pressure, for each change in Farenheit degree below 32°F the volume of gas changes 1/491.69. Similarly, for each Celsius degree the volume changes 1/273.16. Therefore, if this change in volume per temperature degree is constant, the volume of gas would, theoretically, become zero at 491.69 Farenheit degrees below 32°F, or at -459.69°F. On the Celsius scale, this condition occurs at 273.16 Celsius degrees below 0°C, or at a temperature of -273.16°C.

Absolute temperatures determined by using Farenheit units are expressed as degrees Rankine (°R); those determined by using Celsius units are expressed as Kelvin (K). The following approximate relationships convert one scale to the other:

$$°R = °F + 460 \qquad\qquad (A\text{-}3)$$

$$K = °C + 273 \qquad\qquad (A\text{-}4)$$

STANDARD TEMPERATURE

One particular temperature of interest is *standard temperature*. Unfortunately, there is no common temperature that is recognized by all groups. Even USEPA has two standard temperatures, one for air monitoring and one for all other applications. The standard temperatures used by various groups are listed in Table A-1.

Table A-1. Standard Temperatures	
Group	T_{std}
USEPA (General)	68°F (20°C)
USEPA (Air monitoring)	77°F (25°C)
Industrial hygiene	70°F (21.1°C)
Combustion	60°F (15.6°C)
Science	32°F (0°C)

In this course, the USEPA standard temperature of 68°F will be used.

EXAMPLE A-1

The gas temperature in the stack of a wet scrubber system is 130°F. What is the absolute temperature in Rankine and Kelvin?

SOLUTION:

Absolute Temperature, $°R = 460°R + 130°F = 590°R$

Absolute Temperature, $K = \dfrac{590\,°R}{1.8} = 327.8\,K$

GAS PRESSURE

A body may be subjected to three kinds of stress: shear, compression and tension. Fluids are unable to withstand tensile stress; hence, they are subject only to shear and compression. Unit compressive stress in a fluid is termed *pressure* and is expressed as force per unit area (e.g., lb_f/in^2 and Newtons/m^2). Pressure is equal in all directions at a point within a volume for fluid and acts perpendicular to a surface.

BAROMETRIC PRESSURE

Barometric pressure and atmospheric pressure are synonymous. These pressures are measured with a barometer and are usually expressed as inches or millimeters of mercury (Hg). Standard barometric pressure is agreed to by all groups and is the average atmospheric pressure at sea level, 45°N latitude and at 35°F. It is equivalent to a pressure of 14.696 pounds force per square inch exerted at the base of a column of mercury 29.92 inches high. Other equivalents to standard pressure are listed in Table A-2. Weather and altitude are responsible for barometric pressure variations.

Table A-2. Standard Pressure	
Units	**Value**
Atmosphere (atm)	1
Pounds force per square inch (psi)	14.70
Inches of mercury (in Hg)	29.92
Millimeters of mercury (mm Hg)	760
Feet of water column (ft WC)	33.92
Inches of water column (in WC)	407
Kilopascals (kPa)	101.3
Millibars (mb)	1013

GAUGE PRESSURE

The pressure inside an air pollution control system is termed the *gauge or static pressure* and is measured relative to the prevailing atmospheric pressure, as shown in Figure A-2. If the system pressure is greater than atmospheric, the gauge pressure is expressed as a positive value. If smaller, the gauge pressure is expressed as negative. The term *vacuum* designates a negative gauge pressure. Gauge or static pressures in air pollution systems are usually expressed in inches of water column (in WC).

ABSOLUTE PRESSURE

The gauge pressures commonly used in reference to air pollution control systems share an attribute that caused difficulties in the use of normal temperature scales—they can have negative values. As a result, calculations involving pressure ratios and roots and powers of pressure must use *absolute pressure*. Absolute pressure is the algebraic sum of the atmospheric pressure and the gauge pressure:
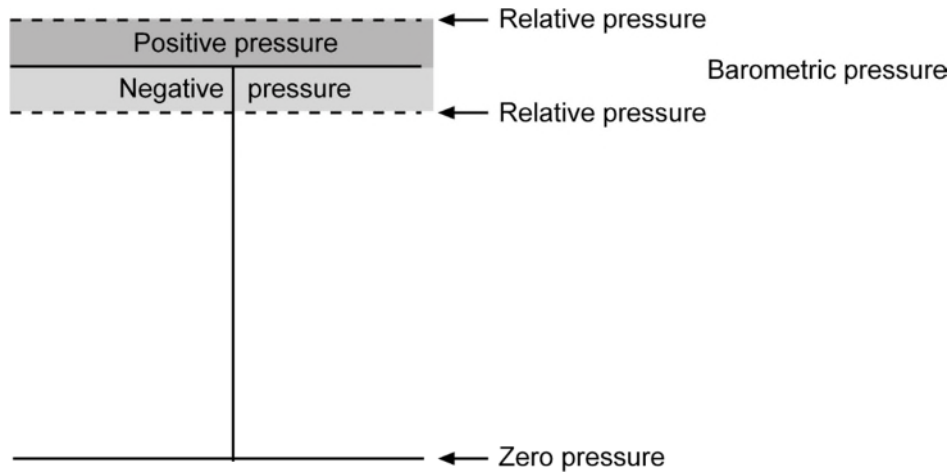
$$P = P_b + p_g \qquad\qquad (A-5)$$

Figure A-2. Definition of positive and negative gauge pressures

where

P = absolute pressure
P_b = barometric or atmospheric pressure
P_g = gauge pressure

EXAMPLE A-2

An air pollution control device has an inlet static pressure of –25 in WC. What is the absolute static pressure at the inlet of the air pollution control device if the barometric pressure at the time is 29.85 in Hg?

SOLUTION:

Convert the barometric pressure units to in WC:

$$P_b = 29.85\,\text{in Hg}\left(\frac{407\,\text{in WC}}{29.92\,\text{in Hg}}\right) = 406\,\text{in WC}$$

Add the barometric and gauge (static) pressures:

P = 406 in WC + (-25 in WC) = 381 in WC

MOLECULAR WEIGHT AND THE MOLE

The molecular weight of a compound is simply the sum of the atomic weights of all the atoms in the molecule. The atomic weight of an atom is based on an arbitrary scale of the relative masses of the elements, usually based on a carbon value of 12. The chemical identity of an atom is determined by the number of protons in its nucleus and is called the atomic number. Values of atomic number and atomic weight can be found in a Periodic Table of Elements.

Mixtures of molecules do not have a true molecular weight; however, they do have an apparent molecular weight that can be calculated from the composition of the mixture:

$$MW_{mixture} = \sum_{i=1}^{n} \chi_i MW_i \qquad \text{(A-6)}$$

where χ_i is the mole fraction of component i and MW_i is its molecular weight. Many times, properties of a contaminated gas can be approximated by the properties of air, itself a mixture of molecules. The apparent molecular weight of air is 28.95, or approximately 29.

A mole is a mass of material that contains a certain number of molecules. Moles can be expressed in terms of any mass unit; thus, e.g., there are gram-moles, kilogram-moles, ounce-moles, pound-moles and ton-moles. The relationship between the different types of moles is the same as the relationship between the corresponding mass units. Thus, there are 1,000 gram-moles in a kilogram-mole, 453.6 gram-moles in a pound-mole, 16 ounce-moles in a pound-mole and 2,000 pound-moles in a ton-mole.

The gram-mole is the mass of material that contains Avogadro's number of molecules, approximately 6.023 x 10^{23}. The mass of a mole is numerically equal to the molecular weight. For oxygen, which has a molecular weight of 32, there are 32 grams per gram-mole, 32 kilograms per kilogram-mole, and 32 pounds per-pound mole. However, only the gram-mole contains Avogadro's number of molecules. The kilogram-mole contains 1,000 times Avogadro's number of molecules, and the pound-mole contains 453.6 times.

EQUATION OF STATE

Equations of state relate the pressure, volume and temperature properties of a pure substance or mixture by semi-theoretical or empirical relationships. Over the range of temperature and pressure usually encountered in air pollution control systems, these values may be related by the ideal or perfect gas law:

$$PV = nRT \qquad \text{(A-7)}$$

where
     P = absolute pressure
     V = gas volume
     n = number of moles
     R = constant
     T = absolute temperature

Here, R is referred to as the universal gas constant, and its value depends on the units of the other terms in the equation. Values of R include:

10.73 psia·ft³/lb-mole·°R
0.73 atm·ft³/lb-mole·°R
82.06 atm·cm³/g-mole·K
8.31 x 10^3 kPa·m³/kg-mole·K

VOLUME CORRECTION

A useful relationship may be developed from the ideal gas law by noting that PV/T = nR, and that, for a given number of moles of a gas, nR is a constant. Thus, at two different conditions for the same gas, we may write:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \qquad\qquad (A\text{-}8)$$

or

$$V_1 = V_2 \left(\frac{P_2}{P_1} \right) \left(\frac{T_1}{T_2} \right) \qquad\qquad (A\text{-}9)$$

Equation 1-9 allows volumes (or volume rates) to be corrected from one set of temperature and pressure conditions to another. One common calculation is to convert volumetric flow rate from actual conditions to standard conditions, or vice versa:

$$SCFM = ACFM \left(\frac{P_{actual}}{P_{std}} \right) \left(\frac{T_{std}}{T_{actual}} \right) \qquad\qquad (A\text{-}10)$$

$$ACFM = SCFM \left(\frac{P_{std}}{P_{actual}} \right) \left(\frac{T_{actual}}{T_{std}} \right) \qquad\qquad (A\text{-}11)$$

EXAMPLE A-3

A particulate control system consists of a hood, ductwork, fabric filter, fan, and stack. The total gas flow entering the fabric filter is 8,640 scfm. The gas temperature in the inlet duct is 320°F and the static pressure is –10 in WC. The barometric pressure is 28.30 in Hg. If the inlet duct has inside dimensions of 3 feet by 4 feet, what is the velocity into the fabric filter?

SOLUTION:

Velocity must be calculated from the actual volumetric flow rate.

Convert the static pressure to absolute pressure:

$$P = 28.30 \, in \, Hg \left(\frac{407 \, in \, WC}{29.92 \, in \, Hg} \right) + \left(-10 \, in \, WC \right) = 375 \, in \, WC$$

Convert the gas temperature to absolute temperature:

$$T_{actual} = 320°F + 460° = 780°R$$

Convert the inlet flow rate to actual conditions:

$$Q_{actual} = 8,640 \, scfm \left(\frac{780 \, ^\circ R}{528 \, ^\circ R} \right) \left(\frac{407 \, in \, WC}{375 \, in \, WC} \right) = 13,853 \, acfm$$

Calculate the velocity:

$$V = \frac{13,853 \dfrac{ft^3}{min}}{(3 \, ft)(4 \, ft)} = 1,154 \frac{ft}{min}$$

MOLAR VOLUME

The ideal gas law may also be rearranged to calculate the volume occupied by a mole of gas, called the *molar volume*:

$$\frac{V}{n} = \frac{RT}{P} \qquad\qquad (A\text{-}12)$$

EXAMPLE A-4

What is the molar volume of an ideal gas at 68°F and 1 atm? At 200°F and 1 atm?

SOLUTION:

At 68°F and 1 atm:

$$\frac{V}{n} = \frac{RT}{P} = \frac{\left(0.73 \dfrac{atm \cdot ft^3}{lb - mole \, ^\circ R} \right)(528 \, ^\circ R)}{(1 \, atm)} = 385.4 \frac{ft^3}{lb - mole}$$

At 200°F and 1 atm:

$$\frac{V}{n} = \frac{RT}{P} = \frac{\left(0.73 \dfrac{atm \cdot ft^3}{lb - mole \, ^\circ R} \right)(660 \, ^\circ R)}{(1 \, atm)} = 481.8 \frac{ft^3}{lb - mole}$$

or

$$\frac{V}{n} = 385.4 \left(\frac{660 \, ^\circ R}{528 \, ^\circ R} \right) = 481.8 \frac{ft^3}{lb - mole}$$

GAS DENSITY

Finally, we may use the ideal gas law to estimate gas density. Density is the ratio of the mass of a material to the volume that material occupies. For accurate values, gas densities should be determined from reference texts. However, an estimate of the gas density can be determined from the ideal gas law. Recognizing that the number of moles is given by mass (m) divided by molecular weight (MW), the ideal gas law may be written:

$$PV = \left(\frac{m}{MW} \right) RT \qquad \text{(A-13)}$$

The gas density ($\square$) can then be estimated from:

$$\rho = \frac{m}{V} = \frac{P \cdot MW}{RT} \qquad \text{(A-14)}$$

Density can also be estimated from the molecular weight and molar volume:

$$\rho = \left(\frac{MW}{385.4} \right) \left(\frac{528}{T} \right) \left(\frac{P}{29.92} \right) \qquad \text{(A-15)}$$

where

P = absolute pressure (in. Hg)
T = absolute temperature (°R)

DALTON'S LAW OF PARTIAL PRESSURE

AND

AMAGAT'S LAW OF PARTIAL VOLUME

When non-reacting gases or vapors are present as a mixture in a given space, the pressure exerted by a component of the gas mixture at a given temperature is the same as it would exert if it filled the whole space alone. The pressure exerted by one component of a gas mixture is called its partial pressure. The total pressure of the gas mixture is the sum of the partial pressures.

According to Amagat's law of partial volume, the total volume of a non-reacting mixture of gases at constant temperature and pressure should be equal to the sum of the individual partial volumes of the constituent gases.

A useful concept from these and the ideal gas law is pressure fraction = volume fraction = mole fraction:

$$\frac{p_i}{P_T} = \frac{n_i}{n_T} = \frac{v_i}{V_T} \qquad \text{(A-16)}$$

For example, if a mixture of air is 21% oxygen and 79% nitrogen by volume at 1 atm and 0°C, then this mixture contains 0.21 mole fraction oxygen and 0.79 mole fraction nitrogen. Also, the partial pressure of oxygen is equal to 0.21 atm and the partial pressure of nitrogen is 0.79 atm at 0°C.

GAS-LIQUID RELATIONSHIPS

Raoult's Law states that the partial pressure of a component over a solution is the product of the vapor pressure of that component and the mole fraction of that component. Raoult's Law is expressed as:

$$p_A = p_A°X_A \qquad \text{(A-17)}$$

where

p_A = partial pressure of A, atm
$p_A°$ = vapor pressure of A, atm
X_A = mole fraction of A in the liquid

Raoult's Law applies over the entire concentration range from 0 to 1.0, but is applicable only if the solution behaves in an ideal manner. Unfortunately few solutions behave ideally. A special case of Raoult's Law is Henry's Law. Henry's Law states that the concentration of a gas dissolved in solution is directly proportional to its partial pressure at a constant temperature.

$$p_A = \mathcal{H}X_A \qquad \text{(A-18)}$$

where

$\mathcal{H}$ = Henry's Law constant, atm/mole fraction

Henry's Law applies only if a plot of the partial pressure versus the mole fraction of component A is a straight line (discussed in more detail in Chapter 5, Absorption). This relationship holds true for most solutions in the dilute concentration range. The value and concentration range over which Henry's Law constant applies can be found by experiment.

Other forms of Henry's Law include:

$$Y_A = \mathcal{H}'X_A \qquad \text{(A-19)}$$

where

Y_A = mole fraction of A in the gas
$\mathcal{H}'$ = Henry's Law constant, mole fraction in the gas/mole fraction in the liquid

and

$$X_A = \mathcal{H}''Y_A \qquad \text{(A-20)}$$

where

$\mathcal{H}''$ = Henry's Law constant, mole fraction in liquid/mole fraction in gas

This latter form is more useful for performing stripping calculations.

SPECIFIC HEAT

The specific heat of a gas is the amount of heat required to change the temperature of a unit-mass of gas one temperature-degree. Units of specific heat are calories/g• °C or Btu/lb•°F, depending upon the dimensional system used.

Heat may be added while the volume or pressure of the gas remains constant. Hence, there may be two values of specific heat: the specific heat at constant volume (C_v) and the specific heat at constant pressure (C_p).

Because the heat energy added at constant pressure is used in raising the temperature and doing work against the pressure as expansion takes place, C_p is greater than C_v. The most commonly encountered heat capacity is C_p, and unless otherwise noted will be the value used in this manual when referring to specific heat. Since C_p varies with temperature, an average specific heat between two temperature values is often used.

REVIEW EXERCISES

1. You are given the velocity of a liquid stream in units of ft/min and you need the velocity in units of ft/sec. Should you:

    (a) Divide by 12
    (b) Multiply by 60
    (c) Multiply by 12
    (d) Divide by 60

2. In the SI system, the basic unit of force is the Newton (N) and the basic unit of mass is the kilogram (kg). Under what conditions are the SI units of force and mass numerically equal?

    (a) Never
    (b) On the moon
    (c) At sea level
    (d) Always

3. Unless otherwise specified, you may assume that the composition of a gas mixture is expressed in which of the following units?

    (a) ppm
    (b) lb_m/ft^3
    (c) mole fraction
    (d) mass fraction

4. The static pressure of a gas stream entering a fan is -25 in. W.C. and the barometric pressure is 410 in. W.C. What is the absolute pressure of the gas stream?

    (a) 407 in. W.C.
    (b) 385 in. W.C.
    (c) 435 in. W.C.
    (d) Impossible to tell

5. The daily high temperature is predicted to be 75°F. What is the expected temperature in K?

    (a) 75 K
    (b) 297 K
    (c) 273 K
    (d) 535 K

6. Under which set of the following temperatures and pressures can you be certain that the actual volumetric flow rate will be greater than the standard volumetric flow rate?

    (a) $T_{act} > T_{std}$, $P_{act} < P_{std}$

    (b) $T_{act} < T_{std}$, $P_{act} > P_{std}$

    (c) $T_{act} = T_{std}$, $P_{act} > P_{std}$

    (d) $T_{act} = T_{std}$, $P_{act} = P_{std}$

7. The temperature, pressure, volume, and number of moles are expressed in °R, atm, m^3, and g-moles, respectively. What should be the units of the gas constant R?

    (a) $[(\text{g-mole})(°R)]/[(m^3)(\text{atm})]$

    (b) $[(\text{psia})(ft^3)]/[(\text{lb-mole})(°F)]$

    (c) $[(m^3)(\text{atm})]/[(\text{g-mole})(°R)]$

    (d) There is no gas constant having the proper units

REVIEW EXERCISE SOLUTIONS

1. You are given the velocity of a liquid stream in units of ft/min and you need the velocity in units of ft/sec. Should you

    (d) Divide by 60

$$\left(\frac{x\,ft}{min}\right)\left(\frac{min}{60\,sec}\right)$$

2. In the SI system, the basic unit of force in the Newton (N) and the basic unit of mass is the kilogram (kg). Under what conditions are the SI units of force and mass numerically equal?

    (a) Never

3. Unless otherwise specified, you may assume that the composition of a gas mixture is expressed in which of the following units?

    (c) Mole fraction

4. The static pressure of a gas stream entering a fan is -25 in. W.C. and the barometric pressure is 410 in. W.C. What is the absolute pressure of the gas stream?

    (b) 385 in. W.C.

$$P = P_b + P_g = 410 + (-25) = 385 \text{ in. W.C.}$$

5. The daily high temperature is predicted to be 75°F. What is the expected temperature in K?

    (b) 297 K

6. Under which set of the following temperatures and pressures can you be certain that the actual volumetric flow rate will be greater than the standard volumetric flow rate?

    (a) $T_{act} > T_{std}$, $P_{act} < P_{std}$

    Higher temperature causes the volumetric flow rate to increase. Lower pressure causes the volumetric flow rate to increase.

7. The temperature, pressure, volume, and number of moles are expressed in °R, atm, m^3, and g-moles, respectively. What should be the units of the gas constant R?

    (c) $[(m^3)(atm)]/[(g\text{-}mole)(°R)]_f$

$$R \; [=] \; \frac{PV}{nT} \; [=] \; \frac{(atm)(m^3)}{(g\text{-}mole)(°R)}$$

CONVERSION FACTORS

Length
1 in = 2.54 cm
1 m = 3.281 ft
1 ft = 0.3048 m

Mass
1 lb_m = 453.6 g
1 lb_m = 7,000 grains
1 kg = 2.205 lb_m

Pressure
1 atm = 101,325 Pa
1 atm = 760 mm Hg
1 atm = 14.7 psia

Force
1 N = 1 kg·m/sec^2
1 N = 0.225 lb_f
1 dyne = 1 g·cm/sec^2
1 N = 1 x 10^5 dynes

Energy
1 cal = 4.18 J
1 J = 9.486 x 10^{-4} Btu
1 Btu = 252.2 cal

Power
1 watt = 1 J/sec
1 watt = 3.414 Btu/hr
1 watt = 1.341 x 10^{-3} hp
1 hp = 33,479 Btu/hr

Density
1 kg/m^3 = 0.0624 lb_m/ft^3
1 kg/m^3 = 1 x 10^{-3} g/cm^3

Absolute viscosity
1 Pa·sec = 1 kg/m·sec = 1,000 cp
1 cp = 6.72 x 10^{-4} lb_m/ft·sec

Kinematic viscosity
1 m^2/sec = 3.875 x 10^4 ft^2/hr

Area
1 m^2 = 10.764 ft^2
1 cm^2 = 0.155 in^2
1 m^2 = 1.196 yd^2

Volume
1 m^3 = 35.31 ft^3
1 cm^3 = 0.061 in^3
1 m^3 = 264.2 gal
1 ft^3 = 28.317 liters
1 m^3 = 1 x 10^3 liters
1 ft^3 = 7.48 gal

Volumetric flow
1 m^3/sec = 35.31 ft^3/sec
1 ft^3/min = 1.7 m^3/hr
1 gpm = 0.227 m^3/hr

Velocity
1 m/sec = 3.28 ft/sec
1 m/sec = 196.85 ft/min
1 mph = 0.447 m/sec

Geometry
Area of circle = $\pi r^2 = \pi d^2/4$
Circumference of circle = $2\pi r = \pi d$
Surface area of sphere = $4\pi r^2 = \pi d^2$
Surface area of cylinder = $2\pi rh = \pi dh$
Volume of sphere = $4\pi r^3/3 = \pi d^3/6$

CONSTANTS AND USEFUL INFORMATION

Gas constants

$R = 82.06$ atm·cm^3/g-mole·K
$R = 8.31$ x 10^3 kPa·m^3/kg-mole·K
$R = 10.73$ psia·ft^3/lb-mole·°R
$R = 0.73$ atm·ft^3/lb-mole·°R

Acceleration of gravity

$g = 32.17$ ft/sec^2 = 980.7 cm/sec^2 = 9.8 m/sec^2

Newton's conversion constant

$g_c = 32.17$ lb$_m$·ft/lb$_f$·sec^2

Molar volume

1 lb-mole = 385.4 ft^3 at 20°C and 1 atm
1 g-mole = 24.1 liters at 20°C and 1 atm

Specific heat

C_p for water = 1 Btu/lb$_m$·°F = 1 cal/g·°C (at 20°C and 1 atm)
C_p for air = 0.244 Btu/lb$_m$·°F = 0.244 cal/g·°C (average over 0-2,000°F)

Absolute viscosity

Viscosity of water = 1 cp = 0.01 g/cm·sec = 6.72 x 10^{-4} lb$_m$/ft·sec (at 20°C and 1 atm)
Viscosity of air = 1.8 x 10^{-4} g/cm·sec = 1.21 x 10^{-5} lb$_m$/ft·sec (at 20°C and 1 atm)

Density

Density of water = 1 g/cm^3 = 62.4 lb$_m$/ft^3 (at 20°C and 1 atm)
Density of air = 1.2 x 10^{-3} g/cm^3 = 7.47 x 10^{-2} lb$_m$/ft^3 (at 20°C and 1 atm)

ATOMIC WEIGHTS OF THE ELEMENTS

Element	Atomic Mass	Element	Atomic Mass	Element	Atomic Mass
Actinium	227.028	Hafnium	178.49	Promethium	145
Aluminum	26.981539	Hassium	265	Protactinium	231.0359
Americium	243	Helium	4.002602	Radium	226.025
Antimony	121.757	Holmium	164.93032	Radon	222
Argon	39.948	Hydrogen	1.00794	Rhenium	186.207
Arsenic	74.92159	Indium	114.82	Rhodium	102.9055
Astatine	210	Iodine	126.90447	Rubidium	85.4678
Barium	137.327	Iridium	192.22	Ruthenium	101.07
Berkelium	247	Iron	55.847	Rutherfordium	261
Beryllium	9.012182	Krypton	83.8	Samarium	150.36
Bismuth	208.98037	Lanthanum	138.9055	Scandium	44.95591
Bohrium	262	Lawrencium	262	Seaborgium	263
Boron	10.811	Lead	207.2	Selenium	78.96
Bromine	79.904	Lithium	6.941	Silicon	28.0855
Cadmium	112.411	Lutetium	174.967	Silver	107.8682
Calcium	40.078	Magnesium	24.305	Sodium	22.989768
Californium	251	Manganese	54.93805	Strontium	87.62
Carbon	12.011	Meitnerium	266	Sulfur	32.066
Cerium	140.115	Mendelevium	258	Tantalum	180.9479
Cesium	132.90543	Mercury	200.59	Technetium	98
Chlorine	35.4527	Molybdenum	95.94	Tellurium	127.6
Chromium	51.9961	Neodymium	144.24	Terbium	158.92534
Cobalt	58.9332	Neon	20.1797	Thallium	204.3833
Copper	63.546	Neptunium	237.048	Thorium	232.0381
Curium	247	Nickel	58.6934	Thulium	168.93421
Dubnium	262	Niobium	92.90638	Tin	118.71
Dysprosium	162.5	Nitrogen	14.00674	Titanium	47.88
Einsteinium	252	Nobelium	259	Tungsten	183.85
Erbium	167.26	Osmium	190.2	Uranium	238.0289
Europium	151.965	Oxygen	15.9994	Vanadium	50.9415
Fermium	257	Palladium	106.42	Xenon	131.29
Fluorine	18.9984032	Phosphorus	30.973762	Ytterbium	173.04
Francium	223	Platinum	195.08	Yttrium	88.90585
Gadolinium	157.25	Plutonium	244	Zinc	65.39
Gallium	69.723	Polonium	209	Zirconium	91.224
Germanium	72.61	Potassium	39.0983		
Gold	196.96654	Praseodymium	140.90765		