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Air

Control of Gaseous Emissions

Student Manual

APTI Course 415
Third Edition

Author

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Air Control Techniques, P.C.

Developed by

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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
EPA	-	environmental protection agency
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

ACRONYM		**DEFINITION**
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

Chapter 1

Introduction

The control of gaseous contaminants from industrial sources in the United States began with efforts to recover useful raw materials and products entrained in gas streams. Some of the control techniques in use today for high efficiency control of pollutants had their origin in the 1940s and 1950s as low-to-moderate efficiency collectors used strictly for process control. Starting in the 1950s and 1960s, control equipment for gaseous contaminants were 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.

1.1 INTRODUCTION TO GASEOUS CONTAMINANTS

Gaseous contaminants can be divided into two main categories: (1) primary and (2) secondary pollutants. Primary pollutants are compounds that are emitted directly from the stack and/or process equipment of the source. Typical examples of primary pollutants include sulfur dioxide 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. The most well recognized category of secondary pollutants includes ozone and other photochemical oxidants formed because of sunlight initiated reactions of nitrogen oxides, organic compounds, and carbon monoxide. A summary of the main categories of gaseous contaminants is provided in the following list.

Primary Gaseous Contaminants

- Sulfur dioxide and sulfuric acid vapor
- Nitrogen oxide and nitrogen dioxide
- Carbon monoxide and partially oxidized organic compounds
- Volatile organic compounds and other organic compounds
- Hydrogen chloride and hydrogen fluoride
- Hydrogen sulfide and other total reduced sulfur compounds (mercaptans, sulfides)
- Ammonia

Secondary Gaseous Contaminants

- Nitrogen dioxide
- Ozone and other photochemical oxidants
- Sulfuric acid

There is not a sharp dividing line between primary and secondary gaseous contaminants. For example, nitrogen dioxide and sulfuric acid are in both groups. Essentially all primary gaseous contaminants can participate in atmospheric reactions to form secondary reaction products.

1.1.1 Sulfur Dioxide and Sulfuric Acid Vapor

Sulfur dioxide is a colorless gas having the chemical formula SO_2. It is formed primarily during the combustion of a sulfur-containing fuel such as coal, No. 6 oil, or sulfur-containing industrial waste gases. Once released to the atmosphere, sulfur dioxide reacts slowly because of photochemically initiated reactions and reactions with cloud and fog droplets, at rates of between approximately 0.1% and 3% per hour. These atmospheric reactions yield sulfuric acid, inorganic sulfate compounds, and organic sulfate compounds. A major fraction of the sulfur dioxide is 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. Sulfur dioxide is moderately soluble in water and aqueous liquids. It has strong irritant properties due, in part, to its solubility and tendency to form sulfurous acid following absorption in water.

During the combustion of sulfur-containing fuels, approximately 94% to 95% of the sulfur is converted to sulfur dioxide. Generally 0.5% to 2% of the fuel sulfur is converted to sulfur trioxide, SO_3. Sulfur trioxide remains in the vapor state until temperatures decrease below approximately 600°F (300°C). At this temperature, sulfur trioxide reacts with water as indicated in Reaction 1-1.

$$SO_3 + H_2O \rightarrow H_2SO_4 \qquad \text{Reaction 1-1}$$

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

1.1.2 Nitrogen Oxide and Nitrogen Dioxide

These two compounds are formed during the combustion of all fuels. They can also be released from nitric acid plants and other types of industrial processes involving the generation and/or use of nitric acid.

There are two primary reaction processes responsible for emissions of these compounds from combustion sources: (1) high temperature thermal oxidation and (2) oxidation of fuel nitrogen compounds. The high temperature oxidation reactions involve the conversion of atmospheric nitrogen (N_2) to nitric oxide (NO) and nitrogen dioxide (NO_2) in portions of the burner flame having temperatures exceeding 2500°F (1400°C) and high localized oxygen concentrations. The conversion of fuel nitrogen simply involves the oxidation of a portion of the nitrogen compounds often present in fossil fuels.

NO and NO_2 are collectively termed “nitrogen oxides” or “NO_x”. This term does not include nitrous oxide (N_2O), which is emitted in very small quantities from some types of stationary sources.

Nitric oxide is an odorless gas that is insoluble in water. Nitrogen dioxide is moderately soluble in aqueous liquids 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 dimmer compound (N_2O_4). Both compounds, particularly NO_2, are associated with adverse effects on the respiratory tract. NO_2 has been regulated since 1971 as one of the seven criterial 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. In fact, at the present time, all regions of the country are attaining 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 nitrogen oxides to secondary reaction products. In fact, NO_2 is the main chemical compound responsible for the absorption of the ultraviolet light responsible for driving photochemical reactions.

1.1.3 Carbon Monoxide and Other Partially Oxidized Organic Compounds

Carbon monoxide is a partially oxidized compound that results from incomplete combustion of fuels and organic compounds. It forms when either the gas temperature or the gas oxygen concentration is insufficient to provide complete oxidation of carbon monoxide to carbon dioxide as shown in Reaction 1-2.

$$CO + 0.5\ O_2 \rightarrow CO_2 \qquad \text{Reaction 1-2}$$

Carbon monoxide is a very stable, difficult-to-oxidize compound. This reaction process summarized by Reaction 1-2 is very slow at gas temperatures less than approximately 1800°F (1000°C). It is more difficult to complete the oxidation of CO to CO_2 than to complete the oxidation of any partially oxidized organic compound.

Carbon monoxide is colorless, odorless and is insoluble in water. It is a chemical asphixant 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.

1.1.4 Volatile Organic Compounds or Other Organic Compounds

Volatile organic compounds (VOCs) are organic compounds that can volatilize in industrial processes and participate in photochemical reactions once the gas stream is 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)
Trichlorofluoromethane (CFC-11)
Dichlorodifluoromethane (CFC-12)
Chlorodifluoromethane (CFC-22)
Trifluoromethane (FC-23)
1,2-dichloro 1,1,2,2-tetrafluoroethane (CFC-114)
Chloropentafluoroethane (CFC-115)
1,1,1-trifluoro 2,2-difluoroethane (HCFC-123)
1,1,1,2-tetrafluoroethane (HCFC-134a)
(Continued)

Table 1-1. **(Continued)** **Organic Compounds <u>Not</u> Classified as VOCs**
1,1-dichlorofluoroethane (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)
Cyclic, branched or linear completely fluorinated alkanes
Cyclic, branched, or linear completely fluorinated ethers with no unsaturations
Cyclic, branched, or linear completely fluorinated tertiary amines with no unsaturations
Sulfur containing perfluorocarbons with no unsaturations and with sulfur bonds only to carbon and fluorine
Perchloroethylene (addition proposed by U.S. EPA)
Perchloroethylene (tetrachloroethylene)
Parachlorobenzotrifluoride (PCBTF)
Volatile Methyl Siloxane (VMS)
Acetone

The dominant source of VOC emissions is the vaporization of organic compounds used as solvents in industrial processes. These sources include, but are not limited to, surface coating, painting, gasoline distribution, and synthetic organic chemical manufacturing.

There are two main categories of volatile organic compound emissions: (1) contained and (2) fugitive.

Contained emissions are those VOCs that are captured in hoods, penetrate through the air pollution control systems, and released from the stack.

Fugitive emissions consist of the numerous small leaks from pumps, valves and other process equipment handling VOC-containing liquids, and gases that escape industrial process hoods. Course 415 addresses only the fugitive emissions that escape industrial process hoods. The control of fugitive VOC emissions from pumps, flanges, valves and other process equipment is addressed in U.S. EPA Air Pollution Training Institute Course 417 titled, "Industrial Process Fugitive Emissions."

Many specific organic compounds have known adverse health effects and are regulated as toxic air pollutants. These compounds are listed in Title III of the Clean Air Act Amendments of 1990 (CAAA of 1990). Sources of toxic air pollutants are subject to Maximum Achievable Control Technology (MACT) standards promulgated by the U.S. Environmental Protection Agency (EPA). A partial list of the organic compounds listed as hazardous air pollutants (HAPs) in Title III are presented in Table 1-2.

Table 1-2.
Examples of Organic HAPs

Compound	CAS Number	Compound	CAS Number
Acetaldehyde	75070	Methylene chloride	75092
Acetonitrile	75058	Methyl ethyl ketone	78933
Acrolein	107028	Methyl isocyanate	624839
Acrylonitrile	107131	Naphthalene	91203
Aniline	62533	Nitrobenzene	98953
Benzene	71432	Phenol	108952
13, Butadiene	106990	Phosgene	75445
Carbon disulfide	75150	Phthalic anhydride	85449
Chlorobenzene	108907	Styrene	100425
Chloroform	67663	Tetrachloroethylene	127184
Ethyl benzene	100414	Toluene	108883
Ethylene oxide	75218	2,4 Toluene diisocyanate	584849
Ethylene glycol	107211	1,2,4 Trichlorobenzene	120821
Formaldehyde	50000	Trichloroethylene	79016
Hexane	110543	Xylenes	95476
Methanol	67561		

A copy of the complete list of HAPs included in Title III is available on the EPA website (www.epa.gov/Hn/uatw/orig189.html).

1.1.5 Hydrogen Chloride and Hydrogen Fluoride

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

Both hydrogen chloride and hydrogen fluoride are extremely soluble in aqueous liquids. Because of their acidic properties, they are strong irritants. Both compounds have significant adverse health effects at elevated concentrations. They are both regulated as toxic air pollutants under Title III of the CAAA of 1990.

The concentrations of hydrogen chloride and hydrogen fluoride formed during waste incineration and fossil fuel combustion are directly related to the chloride and fluoride concentration of the waste or fuel being fired. Essentially all of the chloride and fluoride atoms in the fuel or waste being burned convert to HCl or HF as long as sufficient hydrogen atoms are present from hydrocarbons or water vapor in the gas stream. Very little of the chloride or fluoride ions remain in the ash of combustion processes. All of the chlorides and fluorides are released in the early stages of combustion and eventually react with a hydrogen atom to form hydrogen chloride or hydrogen fluoride.

1.1.6 Hydrogen Sulfide and Other Total Reduced Sulfur Compounds

Hydrogen sulfide (H_2S) is emitted from a number of metallurgical, petroleum, and petrochemical processes. Fugitive emission of hydrogen sulfide can occur from sour gas wells and certain petrochemical processes. It is a highly toxic gas due to its chemical asphixant characteristics. Despite its strong rotten eggs odor, it is often difficult to detect at high concentrations due to rapid olefactory fatigue. Hydrogen sulfide is highly soluble in water and can be easily oxidized to form sulfur dioxide.

Total reduced sulfur (TRS) compounds are emitted primarily from kraft pulp mills. The specific sources of TRS compounds at kraft pulp mills include the chemical recovery boiler, digesters, brown stock washers, smelt dissolve tanks, and a variety of small sources. TRS compounds consist primarily of the following four chemicals.

- Hydrogen sulfide, H_2S
- Methyl mercaptan, CH_3SH
- Dimethyl sulfide, $(CH_2)_2S$
- Dimethyl disulfide, $(CH_3)_2S_2$

All four compounds 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 reaction processes that eventually yield sulfur dioxide as the main reaction product. TRS compounds are usually controlled by oxidation.

1.1.7 Ammonia

Ammonia (NH_3) is a common raw material used in a large number of synthetic organic chemical manufacturing processes. However, the emissions of ammonia are usually quite small. The overall emission of ammonia to the atmosphere is well below the natural emissions that are due to microbial activity. Ammonia is not considered a toxic compound at the levels generated by anthropogenic or natural emissions. It is not regulated under Title III of the CAAA.

Ammonia is of interest in Course 415 primarily because it is a reactant in two main types of nitrogen oxides control systems. A small fraction of the ammonia feed in these NO_X control systems can be emitted to the atmosphere. These emissions are regulated in some states.

1.1.8 Ozone and Other Photochemical Oxidants

Ozone (O_3) is an oxidant that forms in the troposphere because of the photochemically initiated reactions of nitrogen oxides, volatile organic compounds, and carbon monoxide. Course 415 does not explicitly cover the control of ozone because it is a secondary pollutant. The control techniques information relevant to ozone control concerns precursor compounds such as nitrogen oxide, volatile organic compounds, and carbon monoxide.

The general cycle of pollutant concentrations created by the photochemical reactions is illustrated by the pollutant cycles in Figure 1-1. The reactions begin quickly in the mid-to-late morning following the increase in concentrations of nitrogen oxides, organic compounds, and carbon monoxide caused, in part, by motor vehicles. Nitric oxide is rapidly converted to nitrogen dioxide because of the photochemically initiated reactions. The formation of nitrogen dioxide further stimulates the photochemical "smog" forming reactions because nitrogen dioxide is very efficient in absorbing light in the ultraviolet portion of the sun's spectrum.

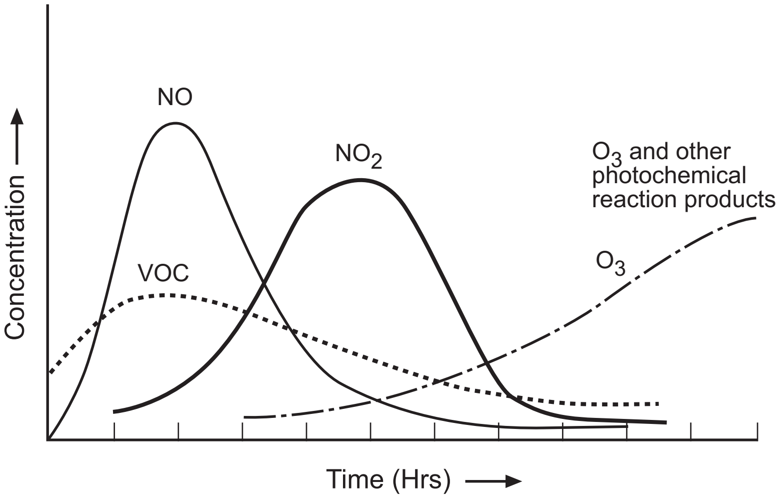

Figure 1-1. Pollutant concentration profiles due to photochemical reactions

As the reactions proceed further, the nitrogen dioxide concentration peaks and then decreases as it is consumed to form particulate matter and vapor phase nitrates. As the nitrogen dioxide 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 that scatter light.

The formation of high ambient levels of ozone is highest during “ozone season,” a period that is usually defined as May through September. The intensity of sunlight for the photochemically initiated reactions is highest during this time period. The air temperatures available for thermal reactions associated with the photochemical reactions also contributes to the high levels of ozone and photochemical oxidant formation during the summer months.

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 nitrogen oxides emitted from natural biological activity. The photochemical reactions are similar to those in polluted urban areas. However, the concentrations of rural ozone are limited by the very low concentrations of nitrogen oxides that are usually available.

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 compounds such as chlorinated and fluorinated organic compounds and nitrous oxide; compounds that are not especially reactive at 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 nitrogen oxides emitted into the troposphere to minimize ground level 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.

1.2 SOURCES OF GASEOUS CONTAMINANTS

The gaseous contaminants emphasized in this course include sulfur dioxide, nitrogen oxides, and organic compounds (including VOCs). Emission inventory data are summarized in the following charts indicating the major source categories of interest in gaseous contaminant control.

The 1997 emission inventory data for sulfur dioxide are summarized in Figure 1-2. These indicate that 81% of the total sulfur dioxide emissions are due to the combustion of sulfur-containing fuels in utility and industrial boilers; therefore, sulfur dioxide control efforts focus on these two major source categories. Industrial sources, such as driers, kilns, industrial furnaces, and metallurgical furnaces, emit considerably lower emissions than fossil-fuel fired boilers. Accordingly, information concerning sulfur dioxide control is oriented primarily to coal and oil-fired utility and industrial boilers.

The 1997 emission inventory data for nitrogen oxides also indicate the importance of fuel combustion sources. As shown in Figure 1-3, utility and industrial boilers are responsible for 40% of the total NO_x emissions. Industrial furnaces, such as metallurgical processes, driers, and kilns (shown as other fuel combustion), are responsible for approximately 5% of the total nationwide emissions. These other sources will probably be included in the scope of future stationary source control requirements to reduce NO_x emissions. For that reason, these additional sources will be considered along with utility and industrial boilers in the material presented concerning NO_x control.

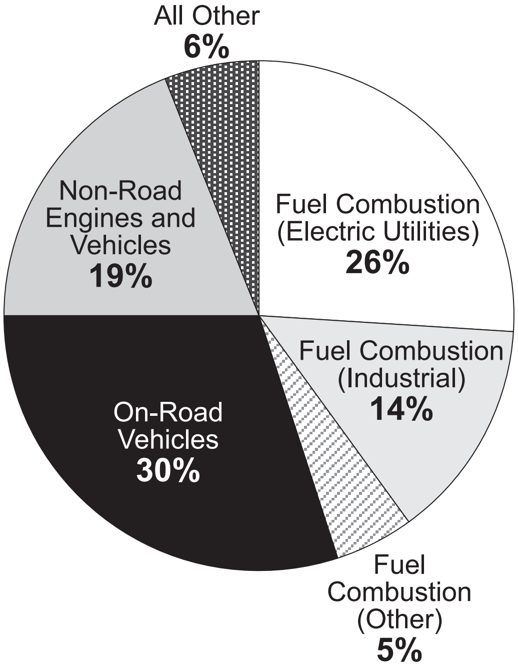

Figure 1-2. Emission inventory for sulfur dioxide[1]

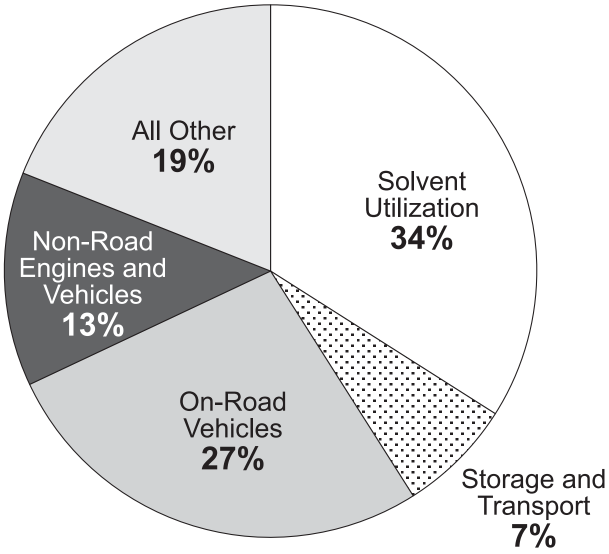

Figure 1-3. Emission inventory for nitrogen oxides[1]

Emissions of volatile organic compounds are summarized in Figure 1-4. These data indicate that 60% of the total emissions are from stationary sources and that solvent utilization is the largest single category of these stationary source emissions. This category includes but is not limited to the following categories of industrial sources:

- Metal surface coating
- Furniture coating
- Miscellaneous metal parts surface coating
- Printing and graphic arts
- Synthetic organic chemical manufacturing
- Petroleum refining
- Paint manufacturing
- Automobile manufacturing

Other important stationary sources of VOCs include the storage and distribution of fuels. A wide variety of control techniques have been developed for VOC and other organic compound control due to the diversity in the industries generating these contaminants.

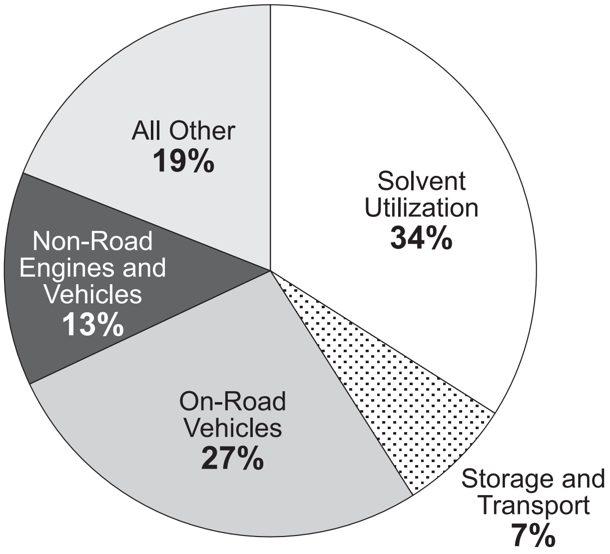

Figure 1-4. Emission inventory for volatile organic compounds[1]

The EPA emission data indicate that transportation sources, such as automobiles, trucks, trains and planes, are responsible for 49% of the total NO_x emissions and 75% of the carbon monoxide[1]. Reduction of CO and NO_x emissions from these sources will be an important component of the overall control strategies in the future; however, Course 415 is restricted to stationary sources controls.

1.3 GASEOUS CONTAMINANT REGULATIONS

From 1950 through 1970, gaseous contaminant control requirements were enacted by state and local agencies for contaminants such as sulfur dioxide, volatile organic compounds, and hydrogen fluoride. These regulations were aimed at alleviating localized health and welfare effects relating to these emissions. The environmental awareness that began to increase during the 1950s and 1960s culminated in the enactment of the Clean Air Act Amendments of 1970. These amendments considerably strengthened the Federal program and were associated with the formation of the U.S. EPA from a variety of agencies sharing environmental responsibility before this time. The 1970 amendments substantially increased the pace of gaseous contaminant control.

In 1971, the newly formed EPA promulgated primary and secondary NAAQS for sulfur dioxide, nitrogen oxides, photochemical oxidants, and carbon monoxide. These standards were based on the available ambient monitoring and health/welfare effects research data. All areas of the country were divided into Air Quality Control Regions, and all areas having measured ambient concentrations that exceeded the NAAQS levels were labeled as nonattainment areas for the specific gaseous contaminant. Nonattainment areas were required to devise a set of emission regulations and other procedures that would reduce ambient levels of particulate matter below the NAAQS specified limits.

The NAAQS for each gaseous contaminant included both primary and secondary limits. The primary standards were more restrictive and were designed to protect health. The secondary standards were intended to reduce adverse material effects, such as crop damage and building soiling, of the gaseous contaminants. Control strategies for the achievement of the NAAQS were developed and adopted as part of the State Implementation Plan (SIP) required by the Clean Air Act Amendments of 1970. These control strategies were designed by each state and local regulatory agency having areas above the

NAAQS limits. Gaseous contaminant emission regulations were adopted by many state and local agencies to ensure that these emissions would be reduced.

These gaseous contaminant emission limitations took many regulatory forms, many of which are still in effect today. Sulfur dioxide emissions were limited by placing a maximum sulfur content restriction (e.g., ≤ 1% sulfur by weight) for the fuel being burned. Mass emission limitations for sulfur oxides and nitrogen oxides were based on the pounds of emission per million heat input basis (e.g., 0.1 lb NO_X/MM Btu) or strictly on a concentration basis (e.g., 500 ppm) were established. Emissions of volatile organic compounds were restricted based on the total mass per unit time (e.g., pounds per hour) or a VOC content per unit of coating.

Fugitive emission 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. Regulation types include but are not limited to (1) required work practices, (2) leak detection and repair programs, and (3) hood capture efficiency requirements.

All of the regulation types discussed above apply to existing sources included within the scope of the SIPs. Substantial differences in the stringency of the regulations existed from jurisdiction to jurisdiction, depending on the contaminant control strategy believed necessary and advantageous to achieve the NAAQS. The Clean Air Act of 1970 (CAA of 1970) also stipulated emission limitations that would apply to new (and substantially modified) sources on a nationwide basis. The purpose of these regulations was to ensure continued reductions in the contaminant emissions as new sources replaced existing sources. These new standards were titled “New Source Performance Standards” (NSPS). These were stringent standards adopted by EPA on a source category-by-category basis. Sources subject to these regulations are required to install air pollution control systems that represent the “best demonstrated technology” for that particular type of industrial source. The first set of NSPS standards (often termed Group I) included emission limitations for sulfur dioxide and nitrogen oxides for large combustion sources. EPA has included continuous monitoring requirements in many of the new and revised NSPS standards applicable to sulfur dioxide and nitrogen oxides emissions.

The CAA of 1970 authorized the promulgation of especially stringent regulations for pollutants that are considered highly toxic or hazardous. EPA was charged with the responsibility of identifying these pollutants and developing appropriate regulations to protect human health. This set of regulations is titled 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 contaminants. The CAAA of 1990 require a major revision and expansion of these requirements. Title III provisions of the CAAA of 1990 require that regulations be developed for 188 specific pollutants and categories of pollutants. This list includes many compounds and elements that are generally in a gaseous form. These regulations were adopted on a source category-by-category basis starting in 1991. Sources subject to the regulation will be required to install MACT as defined by EPA for that source category. These regulations will be a major driving force for gaseous contaminant control in the future.

In 1997, EPA added a new NAAQS applicable to particulate matter equal to or less than 2.5 μm (termed $PM_{2.5}$). EPA concluded that the $PM_{2.5}$ NAAQS were needed due to 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 a relevant issue in Course 415 because atmospheric chemistry research indicates that the atmospheric conversion of sulfur dioxide, nitrogen oxides, volatile organic compounds, and carbon monoxide have a significant role in the formation of $PM_{2.5}$ particles. The $PM_{2.5}$ regulations will continue to be a driver for gaseous contaminant control in the future.

Review Exercises

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%
   e. 100%

2. What factors influence the formation of NO_x in a boiler?
   a. Temperatures
   b. Oxygen concentrations
   c. Fuel nitrogen content
   d. All of the above
   e. a and b

3. What categories of air pollutants are responsible for the formation of photochemical smog? Select all that apply.
   a. Volatile organic compounds
   b. Nitrogen oxides
   c. Sulfur dioxide
   d. Ammonia
   e. TRS compounds
   f. Carbon monoxide

4. Ozone is a ______________ air pollutant.
   a. primary
   b. secondary

5. What category of sources is most responsible for VOC emissions?
   a. Transportation (automobiles, trucks, planes)
   b. Fuel handling and distribution
   c. Solvent utilization
   d. Fuel combustion
   e. None of the above

6. What category of sources is most responsible for sulfur dioxide emissions?
   a. Utility and industrial boilers
   b. Industrial processes
   c. Transportation
   d. None of the above

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

   a. Transportation (automobiles, trucks, planes)
   b. Fuel handling and distribution
   c. Solvent utilization
   d. Fuel combustion (electric utilities)
   e. None of the above

8. When were National Ambient Air Quality Standards initiated for sulfur dioxide?
   a. 1961
   b. 1970
   c. 1977
   d. 1990

9. What type of regulations 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

Review 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?

   d. 94% to 95%

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

   d. All of the above

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

   a. Volatile organic compounds
   b. Nitrogen oxides
   f. Carbon monoxide

4. Ozone is a ______________ air pollutant.

   b. secondary

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

   c. Solvent utilization

6. What category of sources is most responsible for sulfur dioxide emissions?

   a. Utility and industrial boilers

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

   a. Transportation (automobiles, trucks, planes)

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

   b. 1970

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

   c. Maximum Achievable Control Technology Standards (MACTS)

10. Why are VOC emissions controlled?

    a. To achieve the ozone NAAQS

References

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

Chapter 2
Control Techniques for Gaseous Contaminants

This chapter provides an introduction to the types of control techniques that can be used to remove gaseous contaminants from industrial gas streams. The appropriateness of a given technique depends, in part, on the chemical and physical characteristics of the specific gas and vapor phase compounds present in the gas stream. Data concerning some of the chemical compounds are summarized in this chapter. Fundamental characteristics of gases and vapors are covered more comprehensively in a web-based course titled "*Basic Concepts in Environmental Sciences*" (OL2000), prepared by N.C. State University and Air Control Techniques, P.C. References to data tabulations concerning other compounds are also provided at the end of this chapter.

Several gas stream characteristics must be taken into account in the selection and design of a gaseous control system. These characteristics are introduced briefly in this chapter and are discussed in more detail in subsequent chapters concerning each major control technique.

2.1 GAS STREAM CHARACTERISTICS

2.1.1 Important Gas Stream Properties

The selection and design of a gaseous contaminant control system must be based on some specific information concerning the gas stream to be treated. The following is a partial list of the information that is often useful.

- Gas stream particulate matter characteristics
- Gas stream average and peak flow rates
- Gas stream average and peak temperatures
- Gas stream particulate matter average and peak concentrations
- Gas stream minimum, average, and maximum oxygen concentrations
- Contaminant average and peak concentrations
- Contaminant ignition characteristics

Information concerning the gas flow rates and temperatures are needed to physically size the collector for the expected process operating conditions. Because most gaseous contaminant control systems have a relatively narrow range of optimal gas velocities, information concerning the average and peak gas flow rates must be as accurate as possible.

2.1.2 Particulate Matter

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

Information concerning the oxygen concentration and ignitability of the gases and vapors is needed to determine the allowable contaminant concentrations. Many of the organic and inorganic compounds collected can be ignited if the contaminant concentrations, oxygen concentrations, and gas temperatures are in the hazardous range. These potentially explosive conditions must be anticipated and conscientiously avoided in the design of a control system.

2.1.3 Explosive Limit Concentrations

A large number of potentially explosive gases and vapors are collected in gaseous contaminant control systems. A partial list of these compounds relevant to this course is as follows:

- Organic compounds
- Carbon monoxide
- Ammonia
- Hydrogen (sometimes present with organic compounds)
- Hydrogen sulfide

One of the main factors that must be considered in designing a gaseous contaminant control system is the concentration range at which one or more of the contaminants can be ignited.

Evaluating Contaminant Concentrations Relative to the Explosive Limit Concentrations

The explosive range is bounded 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. At contaminant concentrations above the UEL, there is insufficient oxygen for the oxidation of the compounds present. Theoretically, a gaseous control system could be designed for contaminant concentrations below the LEL or above the UEL. However, almost all systems (with the exception of certain types of flares) are designed for concentrations below the LEL. Because of the uncertainties in the LEL calculations 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 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 3,000 ppm. The 25% LEL safety limit usually restricts the maximum contaminant concentration in the gas stream to be treated to less than 10,000 ppm.

Table 2-1. LEL and UEL at Room Temperature and Ambient Oxygen Concentration[1]

Compound	Lower Explosive Limit, % by Volume*	Upper Explosive Limit, % 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	2.0	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 % by volume to ppm, multiply by 10,000 (2% by volume is equivalent to 20,000 ppm).

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

The LEL and UEL concentrations for specific compounds of interest 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 representative of the specific condition being evaluated. Some of the published LEL and UEL data were measured under gas temperature, pressure, and oxygen concentrations different from the specific application being designed. Furthermore, the evaluation of references used in compiling the LEL and UEL tables often demonstrates that a few of the tests used in measuring the values 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 that is 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 standard empirical equations used to estimate LEL and UEL concentrations. These equations provide a useful screening tool to initially estimate the LEL and UEL concentrations. These values can then be further evaluated and confirmed using modern analytical techniques. One of the available estimation techniques is the Jones method summarized in Equations 2-1 through 2-3.

$$C_mH_xO_y + O_2 \rightarrow m\,CO_2 + \frac{x}{2}H_2O \tag{2-1}$$

$$\text{LEL, \%} = \frac{0.55(100)}{(4.76m + 1.19x + 1 - 2.38y)} \tag{2-2}$$

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

An industrial process being controlled usually generates a gas stream 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 this is illustrated in Problem 2-1.

Problem 2-1

A gas stream contains acetone at 1,000 ppm, benzene at 2,000 ppm, and toluene 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 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

The lowest LEL limit is 11,000 ppm (toluene).

25% of 11,000 ppm = 2,750 ppm

The total contaminant concentration = 1,000 ppm + 2,000 ppm + 500 ppm = 3,500 ppm

Answer: No. The total concentration exceeds the 25% LEL value.

An alternative, less conservative approach for determining the concentration limits for gas mixtures in air is 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.

$$\text{LEL}_{\text{mixture}}, \% = \frac{100}{\sum \frac{y_i}{\text{LEL}_i}} \qquad (2\text{-}4)$$

$$\text{UEL}_{\text{mixture}}, \% = \frac{100}{\sum \frac{y_i}{\text{UEL}_i}} \qquad (2\text{-}5)$$

Where:
y_i = proportion of component i in the fuel mixture without air (volume %)

The use of the Le Chatelier approach is illustrated in Problem 2-2.

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

$$\text{LEL}_{\text{Mixture}} = \frac{100}{\left[\left(\frac{\left(\frac{1{,}000}{3{,}500}\right)100}{\left(\frac{25{,}000}{1{,}000{,}000}\right)}\right)+\left(\frac{\left(\frac{2{,}000}{3{,}500}\right)100}{\left(\frac{12{,}000}{1{,}000{,}000}\right)}\right)+\left(\frac{\left(\frac{500}{3{,}500}\right)100}{\left(\frac{11{,}000}{1{,}000{,}000}\right)}\right)\right]}$$

$$\text{LEL}_{\text{Mixture}} = \frac{100}{1{,}143+4{,}762+1{,}299} = 0.014\%$$

25% of the LEL = 0.25 (14,000) = 3,500 ppm

Using this approach, the gas mixture is below the 25% LEL safety limit. This is considerably different from the result in Problem 2-1.

Sources of Ignition

The removal of sources of ignition from the system does not provide a satisfactory solution to a contaminant ignitability 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. This is because the ignition energy requirement to ignite the gas mixture is extremely small. A number of subtle conditions can create sources of ignition in the system.

- Static electricity due to movement of the gas stream through a bed
- Static electricity due to particle impaction of isolated metal components in the ductwork or collector
- 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 the sources of ignition on a long-term basis.

Monitoring Contaminant Concentrations

There are a variety of fixed monitoring instruments and portable instruments available for directly measuring LEL levels in an existing gas stream. The instruments are very 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 approaches the 25% level, the control system and associated process equipment can be deenergized, and the problem can be corrected safely. The LEL readings can be in error when one or more of the following conditions exist.

- Oxygen levels are low.
- Oxygen levels are greater than 21%.
- Acid gases are present in the gas stream and might have damaged the sensor.
- The gas stream absolute pressures are either very high or very low.
- The gas stream contains combustible particles and/or fibers.

The oxygen levels are important because the instruments use combustion air in the sample gas stream to measure the concentration relative to the 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 20.9% because oxygen rich environments are inherently more ignitable.

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

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.

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. These materials are most hazardous when the size distribution is small because this condition provides a high surface area for oxidation reactions. Unfortunately, the LEL monitors cannot detect the presence of these materials in the gas stream entering a gaseous contaminant control system.

2.2 GASEOUS CONTAMINANT CONTROL TECHNIQUES

Five major techniques are used commercially for the capture and/or destruction of gaseous contaminants.

- Adsorption onto solid surfaces
- Absorption into liquids
- Biological oxidation to form nontoxic compounds
- Oxidation to form nontoxic compounds
- Chemical reduction to form nontoxic compounds
- Condensation of vapors to form liquids

This section provides a general introduction to the uses and limitations of these gaseous contaminant control techniques.

2.2.1 Adsorption

Adsorption involves the interaction between gaseous contaminants and 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.

There are two types of adsorption mechanisms: (1) physical, and (2) chemical. The basic difference between physical and chemical adsorption is the manner in which the gas or vapor molecule is held to the adsorbent surface.

In physical adsorption, the gas or vapor molecule is weakly held to the solid surface by intermolecular cohesion. Physical adsorption is easily reversed by the application of heat or by reducing the pressure surrounding the adsorbing material. In chemical adsorption, a chemical reaction occurs between the adsorbent and the gaseous contaminant. This reaction is not easily reversed.

Physical adsorption is commonly used for the capture and concentration of organic compounds. Chemical adsorption is frequently used for the control of acid gases such as hydrogen chloride, hydrogen fluoride, and hydrogen sulfide. Chemical adsorption is also used for the control of mercury vapor.

General Applicability

Physical adsorption systems are used primarily for the control of organic compounds. Adsorption systems have been 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 affecting the suitability of an organic compound for collection by physical adsorption is the strength of the adhesive forces holding 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. For example, methane with a molecular weight of 16 has almost negligible adhesion to most adsorbents and can not be controlled by this technique. Most organic compounds with molecular weights greater than 50 and less than 200 are collected with high efficiency. Compounds with molecular weights greater than 200 can be collected with very high efficiency; however, the adhesion forces are often too large to overcome in normal regeneration type systems. In fact, the presence of the high molecular weight compounds as trace contaminants in gas streams containing other organic compounds is one of the major limits to the applicability of physical adsorption systems.

In addition to molecular weight, the applicability of physical adsorption systems is often evaluated based on boiling point data and other physical parameters such as the empirical adsorption correlation coefficients summarized by Yaws. Overall, these general applicability relationships indicate that physical adsorption is a viable control technique for a diverse set of organic compounds. The development of new types of adsorbents and improved properties of existing adsorbents is partly responsible for the increasing applicability of the physical adsorption systems.

Chemical adsorption systems have a high efficiency control of a variety of acid gases, including hydrogen sulfide, hydrogen chloride, and hydrogen sulfide. There are now increasing applications for the control of vapor phase mercury using chemical adsorption systems.

Concentration Dependence

Both physical and chemical adsorption systems are most efficient at high contaminant concentrations. This is caused by the concentration driving force available to cause diffusion of the contaminant to the surface of the adsorbent. The concentration dependence of adsorption processes does not necessarily mean that they cannot work well at low concentrations (e.g., such as 1 to 100 ppm levels). However at these low concentrations, relatively large quantities of adsorbent are needed to ensure efficient collection.

Despite the importance of concentration, these types of control systems are applicable to concentrations ranging from trace levels associated with some odor sources to levels approaching 25% of the lower explosive limit (i.e., organic compounds and hydrogen sulfide). There are also some adsorption systems operating on gasoline recovery systems at concentrations that are well above the UEL levels.

Gas temperature Dependence

Essentially all adsorption processes work best when the gas temperature is low. In physical adsorption, the gas temperature is usually maintained at levels less than approximately 120°F. As new adsorbents are being 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, precooling is often needed. Chemical adsorption can be conducted at higher temperatures due to the strength of the chemical bond formed during adsorption. Many chemical adsorption processes operate in the 100°F to 400°F range.

Multiple Contaminant Compound Limitations

Physical adsorption systems used for the recovery and reuse of solvents are usually limited to gas streams with one to three organic compounds. The cost of separation of more than three compounds is often prohibitive. Systems that are not designed for the recovery of solvents are not limited by the number of organic compounds in the industrial gas stream to be treated.

Particulate Matter Limitations

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

2.2.2 Absorption and Biofiltration

Gaseous contaminants that are soluble in aqueous liquids can be removed in absorbers. This 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, organic acids). The contaminant gas or vapor is absorbed from the gas stream as it comes into contact with the liquid. The rate of pollutant capture increases as the contact between the liquid and the pollutant-laden gas increases. Therefore, factors such as (1) turbulent mixing of the pollutant-containing gas stream and the liquid, and (2) increased surface area of the aqueous liquid promote absorption.

Once the contaminant enters the liquid phase, it can simply dissolve, or it can react with other chemicals also in the liquid. The behavior of the contaminant at this point creates the two fundamentally different absorption processes.

Simple dissolution systems are limited by the solubility of the contaminant in the liquid at the prevailing temperature of the liquid. These types of systems are often used for the removal of soluble organic compounds.

Irreversible chemical reaction type 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. These types of absorption systems are often used for acid gases.

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

General Applicability – 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 a slightly soluble gas that can be dissolved into a liquid is proportional to the partial pressure (concentration) of the gas and the Henry' Law Constant. One of the most common forms of the equation for Henry's Law is given in Equation 2-6.

$$y^* = Hx \qquad \text{Equation 2-6}$$

Where:

y^* = Mole fraction of pollutant 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 pollutant in the liquid phase

Equation 2-6 is the equation of a straight line that starts at the origin and has 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 only by the ability to capture and retain the contaminant in solution sufficiently long to complete the necessary reactions. It is also important to maintain the proper mixtures of dissolved and suspended materials in the liquid to ensure that there is no significant build-up of material that exceeds its solubility limits and precipitates in spray nozzles or other wetted portions of the absorption vessel.

The primary factor affecting the applicability of a biological oxidation system is the compatibility of the mixture of contaminant compounds with the microorganisms. Most organic compounds present at moderate-to-low concentrations can be controlled. However, there are a few organics that are toxic to the microorganisms and, therefore, cannot be effectively treated. There are also gas stream contaminants that modify the pH levels thereby reducing the microorganism population.

The applicability of biological systems for a specific application can be determined by contacting one or more suppliers of this equipment. These organizations will need a reasonably complete summary of the contaminants present in the gas stream in order to evaluate the feasibility of this type of control system.

Concentration Dependence

Essentially all absorbers operate at their highest contaminant removal efficiency when the concentrations are high because this maximizes the driving forces for mass transfer into the liquid phase. Absorption processes retain high efficiencies even when the contaminant concentrations are in the low range (i.e., less than 100 ppm). In the case of low concentration applications, the absorbers must be designed to have highly effective gas-liquid contact to maximize mass transfer conditions. Biological systems are generally designed for moderate-to-low concentrations.

Gas Temperature Dependence

All absorption processes operate best when the gas and liquid temperatures are low. Gas and vapor phase contaminants are most soluble under cold conditions. In most cases, the cooling provided by the evaporation of water present as part of the recirculated absorber stream liquid is sufficient to reduce the gas temperature for proper absorption. When the gas stream temperatures are very hot, a precooler such as a presaturation 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. In most cases, the necessary gas temperatures are less than 110°F. If the inlet gas stream is higher than this level, cooling with water sprays or a similar technique is needed to protect the microorganisms. One of the advantages of cooling water sprays is the increased gas stream relative humidity reduces the vulnerability of the biofiltration bed to drying.

Multiple Contaminant Removal

Absorption processes can usually remove multiple contaminants effectively. The primary issue raised by the presence of multiple contaminants is the need for a sophisticated separation process if it is necessary to recover each of the contaminants individually. However, in most absorption processes, the collected contaminants are 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 depends on the type of absorption vessel used for gas-liquid contact. Most absorption vessels are well suited for removal of particulate matter with aerodynamic diameters greater than approximately 3 micrometers. The removal of particulate matter will not usually impair the removal efficiency for gaseous materials. However, in a few cases, the particulate matter could include soluble materials that dissolve and affect the tendencies of the systems to have solids precipitate from solution. The accumulation of precipitated solids could affect the adequacy of gas-liquid contact and/or mist removal. The absorption of particulate matter could also add materials to the wastewater stream that require pretreatment and removal prior to discharge. For these reasons, it is helpful to have the maximum possible information available concerning the particulate matter characteristics when selecting and designing an absorption system.

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

2.2.3 Oxidation

Oxidizers can be used for the destruction of a wide variety of organic compounds. There are 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 synthetic organic chemical plants. Flares are used primarily to treat emergency vent gases in synthetic organic chemical plants and petroleum refiners. The majority of thermal and catalytic oxidizers operate at contaminant concentrations that are 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 effluent gas stream. Accordingly, they are used when economic recovery of the compounds is impractical.

General Applicability

Oxidizers can be used to treat essentially any organic compound that can be economical oxidized. With respect to thermal oxidizers, the practicality of treatment depends on both the necessary operating temperature and the concentration or organic compounds. In most thermal oxidizers, the heating value of the organic compounds available in the gas stream provide a major fraction of the total energy input necessary for combustion. The necessary operating temperatures are usually 200°F to 300°F above the autoignition temperature of the organic compound of concern. If there is more than one organic compound present as a major constituent, thermal oxidizers operate at a temperature that is 200°F to 300°F above the autoignition temperature of the most difficult to oxidize compound. Chemistry/physics reference texts and organic chemical properties tests provide compound specific data concerning the autoignition temperatures. Most thermal oxidizers operate at gas temperatures ranging from 1200°F to more than 1800°F.

With catalytic oxidizers, the suitability of this control technique is determined based on control efficiency data provided by catalyst suppliers and catalytic oxidizer manufacturers. The necessary operating temperature and the destruction capability for specific compounds varies for each of the numerous types of catalysts that are in commercial service. As in the case with thermal oxidizers, the overall fuel requirements depend, in part, on the concentration of organic contaminants in the gas stream and the efficiency of the heat exchanger used ahead of the catalytic oxidizer. Catalytic oxidizers can not be used on systems that have high concentrations of materials that could interfere with the surface of the catalyst (often termed masking agents) or that could poison the catalyst. More information concerning these types of materials is in this course.

Flares serve as emergency vent controls for a wide variety of organic compounds. They can be used for essentially all compounds that can be oxidized. To improve destruction efficiencies in the short time periods available provided later at peak gas stream temperatures, flares often include steam injection to improve mixing and to accelerate oxidation reactions.

Concentration Dependence

Oxidation systems can provide high efficiency destruction of a wide variety of organic compounds regardless of the inlet concentration(s) of the contaminants present in the gas stream. The energy requirement(s) needed to maintain the necessary operating temperatures decrease rapidly as the contaminant concentration increases.

Gas Temperature Dependence

Essentially all oxidation systems require preheating of the gas stream to achieve the necessary oxidation temperatures. Accordingly, these systems are not very dependent on the actual temperature of the process gas stream being treated.

Multiple Contaminant Control

All oxidation systems are capable of treating gas streams with a large number of compounds in the gas mixture.

Particulate Matter Control Limitations

Oxidation systems are capable of treating gaseous contaminants present in particulate matter laden gas streams. In fact, in some applications the oxidizer serves to destroy organic constituents in the particulate matter. However, the particulate matter can deposit in the recuperative heat exchanger and the regenerative beds and, thereby, partially plug the system. Particulate matter can also accumulate in catalyst beds. The accumulated material in heat exchange equipment 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.

2.2.4 Reduction Systems

Reduction systems are used primarily for the destruction of NOx compounds emitted from combustion processes. These systems include selective noncatalytic reduction systems (SNCR) and selective catalytic reduction systems (SCR). In both types of systems, a chemically reduced form of nitrogen is injected into the gas stream to react with the oxidized nitrogen compounds, namely NO and NO_2. The reactions between the reduced and oxidized forms of nitrogen result in molecular N_2, the major constituent of clean air.

There are two main reduced nitrogen compounds used in SNCR and SCR systems. Ammonia (NH_3) can be used in either the anhydrous form (compressed gas) or in an aqueous form. Urea ($CO(NH_2)_2$) is available in the liquid form. Both compounds are fed to the combustion system in a diluted air or liquid stream to provide optimum conditions for reagent distribution in the gas stream. In the case of ammonia systems, dilution is also needed to remain below the LEL for ammonia-air mixtures.

General Applicability

SNCR systems operate in the very high and very narrow gas temperature range of 1600°F to 2000°F (870ºC to 1100ºC). There must be a part of the combustion system at this temperature that has sufficient space for the ammonia or urea injection nozzles. This space is not always available on existing boilers and gas turbines installed long before SNCR was available in commercial service. 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 (often termed "ammonia slip"). Injection of ammonia or urea into a portion of the gas stream that is too hot will result in oxidation of the reduced nitrogen compounds 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%.

SCR systems use one or more catalyst beds mounted in reaction vessels. As the gas stream passes through the catalyst bed, the reduced nitrogen compound react with NO_X and oxygen to yield molecular nitrogen. SCR systems can be used effectively on combustion systems with sufficient space for the moderately large reaction vessel in an area close to the existing boiler equipment. Boilers with high fuel sulfur levels can create a vulnerability to the unintentional conversion of sulfur dioxide to sulfuric acid and the formation of very sticky ammonium bisulfate and ammonium sulfate deposits in downstream boiler equipment. High particulate matter levels can also create problems in gas flow through the catalyst bed or with masking of the catalyst surfaces. As in the case with all catalyst systems, SCR systems must be designed to withstand potential catalyst poison present as part of the particulate matter or injected into the gas stream due to maintenance work. When operated with properly distributed reagent in the normal operating range of 550°F to 750°F (290ºC to 400ºC), SCR achieves NOx reduction efficiencies ranging from 60 to more than 90%.

Concentration Dependence

SNCR and SCR systems achieve the high efficiencies when the inlet NO_X levels are high (i.e., 500 to 1,000 ppm). However, both types of systems have worked well even when the concentrations are in the 100 to 200 ppm levels.

Gas Temperature Dependence

Both types of chemical reduction systems are very sensitive to gas temperature. For proper operation, the gas temperatures must be in a relatively narrow design range. Furthermore, the spatial distribution of the gas temperatures at the points of reagent injection must be relatively uniform to ensure that the entire gas stream being treated is in the necessary range.

Multiple Contaminant Capability

SNCR and SCR systems are believed to be effective for NO and NO_2. It is important to note that in the majority of combustion systems, 90% to 95% of the NO_X in the gas stream is present as NO, and the remaining is present as NO_2.

Particulate Matter Limitations

SNCR systems are not sensitive to the particulate matter concentrations except in extreme circumstances when solid deposition on the injection nozzles disrupts proper reagent spray patterns. This is rarely a problem.

In SCR systems, the catalyst bed must be properly designed to withstand the anticipated particulate matter loadings. If the particulate matter contains metals that cause poisoning of the catalyst, the NO_X removal efficiency can be reduced if the catalyst is not replaced on a moderately frequent basis.

2.2.5 Condensation

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)
- Refrigeration condensers (–50°F to –150°F)
- Cryogenic condensers (–100°F to –320°F)

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

General Applicability

The applicability of condensation systems is evaluated using vapor pressure data for the contaminants being controlled. Condensation systems reduce the contaminant concentration in the gas stream to a concentration equivalent to the vapor pressure of the compound at the operating temperature of the condenser. Accordingly, vapor pressure data provided in standard physical chemistry and chemical properties texts can be used to determine if the vapor pressures are sufficiently low to provide the necessary extent of control. Procedures for estimating the vapor pressure are discussed later in this course.

Concentration Dependence

Condensation systems are used primarily for the control of high concentrations of organic contaminants.

Gas Temperature Dependence

Condensations operate at cold temperatures. If the inlet gas stream is hot, pre-cooling is necessary to allow for efficient condensation of the organic compounds.

Multiple Contaminant Control Limitations

Condensers can be used for the simultaneous control of a wide variety of organic compounds present in the gas stream. However, in systems handling mixtures of organics, the cost of separation and recovery of the condensed compounds can be high. Most condensers operate on systems with only a single contaminant compound or a mixture of compounds that does not usually require separation (i.e., gasoline).

Particulate Matter Limitations

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

2.2.6 Summary of Control Techniques

Table 2-2 summaries the general properties and characteristics of the main control techniques used for the control of gaseous contaminants. Essentially all of the control techniques have a maximum control efficiency when the inlet concentrations are high. All of the techniques are also sensitive to the gas stream temperature. Absorption, adsorption, biological treatment, and condensation work best at cold temperatures. Oxidation and reduction systems operate in narrowly limited high temperature ranges.

Table 2-2. Summary of the General Applicability of Gaseous Contaminant Control 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 Gas and Organic Compounds	< 1 ppm to > 100,000 ppm[1]	< 150°F[2]	Yes [7]	Yes
Adsorption	Acid Gases and Organic Compounds	< 1 ppm to 25% of LEL[1]	< 130°F[2]	Yes [7, 8]	Pretreatment Often Required
Biological Treatment	Organic Compounds	< 1 ppm to ~1,000 ppm	<110°F[3]	Yes	Pretreatment Often Required
Oxidation	Organic Compounds	< 1 ppm to 25% of LEL[1]	600°F to 2,000°F[4]	Yes	Pretreatment Often Required
Reduction	NO and NO_2	< 100 ppm to 1,000 ppm[1]	550°F to 2,000°F[5]	Yes [9]	Yes
Condensation	Organic Compounds	> 100 ppm[1]	-320°F to 80°F[6]	Yes [7, 8]	Pretreatment Often Required

Notes:
1. Maximum removal efficiency usually occurs at maximum contaminant inlet concentration
2. Gas stream precooling needed in some applications to reduce operating temperatures
3. Gas stream precooling and humidification needed in some applications to reduce operating temperatures and to increase gas stream humidity.
4. Catalytic system operate in the 500°F to 1,000°F range. Thermal oxidizers and flares operate in the 1200°F to 2000°F range.
5. SCR system operate in the 550°F to 750°F range. SNCR system operate in the 1600°F to 1900°F range.
6. 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.
7. Multiple compound separation and recovery can be difficult in some applications
8. Generally used for systems having one to three organic compounds in the gas stream
9. Used for control of nitric oxide (NO) and nitrogen dioxide (NO_2)

All of these data are intended to provide only a general indication of the most common operating characteristics. Specific systems can be designed to operate at high efficiency outside to the ranges described in Table 2-2.

It is important to note that Course 415 is limited by practical constraints to the six major control techniques summarized in this section. There are a number of additional techniques in commercial service that can also be used for high efficiency treatment of gaseous contaminants. There are also a number of research and development programs in progress concerning new gaseous control systems. Course 415 is not intended to serve as a comprehensive summary of all of the possible control techniques that could be used for gaseous contaminant control.

Review Exercises

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
   e. 100% to 300% 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. None of the above

4. Physical adsorption is more effective when the gas temperature is _______________.
   a. High
   b. Low

5. The capacity of an adsorbent for a gaseous contaminant (grams per 100 grams of adsorbent) increases with _______________. Select all that apply.
   a. Reduced gas temperature
   b. Decreased contaminant concentration
   c. Decreased gas pressure

6. In simple dissolution, the mass transfer of a gaseous contaminant to the liquid stream is limited by_______________. Select all that apply.
   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.

Review Answers

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

   b. 25% of the LEL

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

   d. All of the above

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

   a. Physical adsorption

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

   b. Low

5. The capacity of an adsorbent for a gaseous contaminant (grams per 100 grams of adsorbent) increases with ______________. Select all that apply.

   a. Reduced gas temperature

6. In simple dissolution, the mass transfer of a gaseous contaminant to the liquid stream is limited by______________. Select all that apply.

   a. Solubility equilibrium

7. The vapor pressure of an organic compound as a function of temperature can be estimated using _____________.

   c. Antonie Equation

8. Thermal oxidizers usually operate at gas temperatures that are ______________.

   b. 200°F to 300°F above the auto-ignition temperature of the most difficult to oxidize major constituent.

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

   d. Between 400°F and 800°F.

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3. Himmelblau, D. *Basic Principles and Calculations in Chemical Engineering*. Prentice Hall, Inc. Englewood Cliffs, New Jersey. 1962.
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Chapter 3

Air Pollution Control Systems

Industrial process systems consist of the process equipment, which 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 you to the preparation and use of industrial source system flowcharts. Flowcharts provide an important tool for evaluating the overall system.

Some reasons for understanding and evaluating the entire industrial process as a whole are given below.

- 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.

3.1 FLOWCHARTS

Flowcharts are a useful tool when you want to evaluate the performance of an entire system because they provide a means for organizing and presenting operating data. More specifically, flowcharts can be used for the following purposes:

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

As discussed later (see lesson on Flowchart Diagrams) an expanded block diagram flowchart has been adopted for use in this Course. Major components such as baghouses are shown as a simple block rather than a complex sketch resembling the actual baghouse. A set of conventional instrument symbols 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 any of the specific information included within this course. The form is basically "self contained."

3.1.1 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.

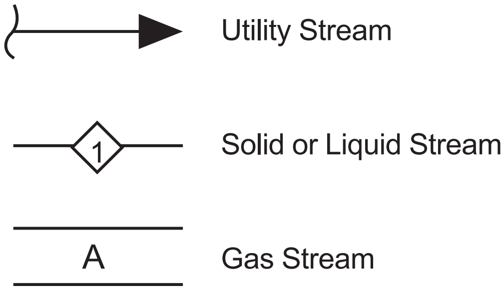


Figure 3-1. Material stream symbols

Gas flow streams are shown as two parallel lines spaced slightly apart and therefore appear larger than other streams. This size difference is important so that the inspector can quickly scan the flowchart and differentiate between gas and liquid material 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 material streams for which operating data will not be necessary are unnumbered. These types of streams are often called *utility streams* for a couple of reasons. They provide necessary materials to the system being shown 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 the 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 so that it is easy to pick out the major equipment items from the gas handling ductwork and other streams leaving these units as shown in Figure 3-2.

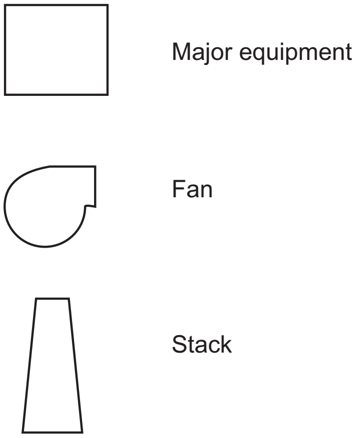


Figure 3-2. Major equipment symbols

The items treated as major equipment depend on the overall complexity of the system being drawn and on individual preferences. These decisions are determined based primarily on the types of data and observations that are possible and the level of detail that is necessary to evaluate the performance of the overall system.

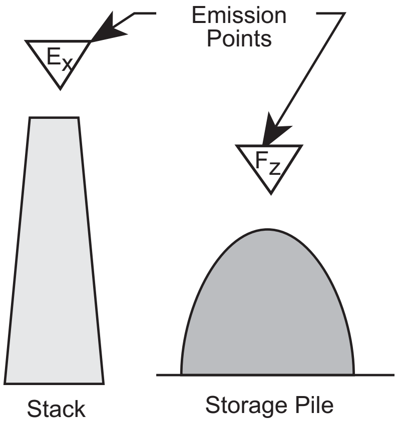


Figure 3-3. Identification of emission points

The stack (or emission discharge point) is obviously important due to the visible emission observations and the presence of continuous emission monitors and stack sampling ports in some systems. The emission points, which should be subject to Method 9 or Method 22 visible emission observations, are identified by a set of inverted triangles immediately above the source as shown in Figure 3-3. These are numbered whenever there is any possibility of confusing 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. Typical identification numbers E_1, E_2, ... E_n are 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.

Minor Components of Systems

A number of relatively small components in air pollution control systems should be shown on the block-diagram-type flowcharts in order to clarify how the system operates. A partial list of these minor equipment components is provided in Table 3-2.

Table 3-2. Minor Components

Fabric Filters	Wet Scrubbers
• Bypass dampers	• Pumps
• Relief dampers	• Nozzles
• Outlet dampers	• Manual valves
• Reverse air fans	• Automatic valves

Carbon adsorbers and Oxidizers

- Indirect heat exchangers
- Fans

Symbols for the minor components listed in Table 3- 2 are shown in Figure 3-4. Note that all of these symbols are relatively simple and quick to draw.

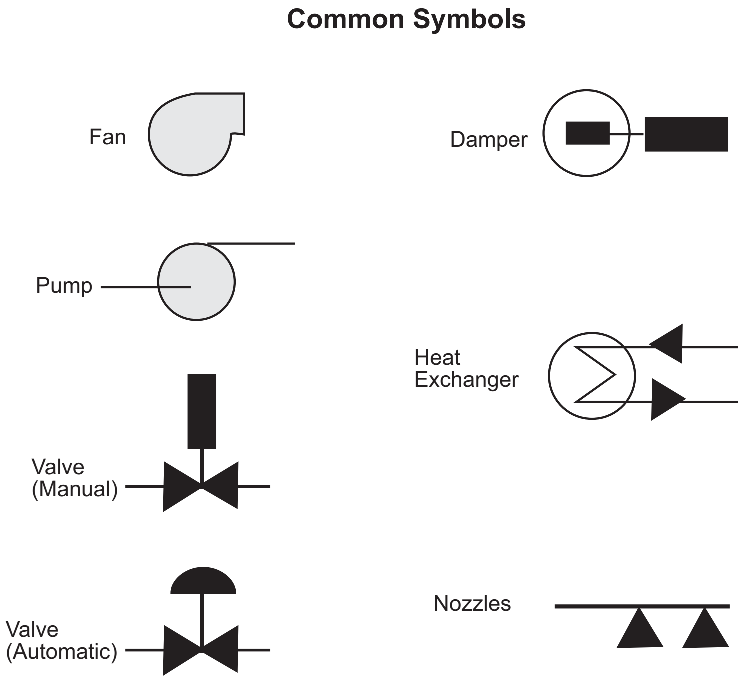


Figure 3-4. Minor component symbols Instruments

Instruments

The presence of an instrument or a sampling port is indicated by a small circle connected to a stream line by a short dashed line as shown in Figure 3-5.

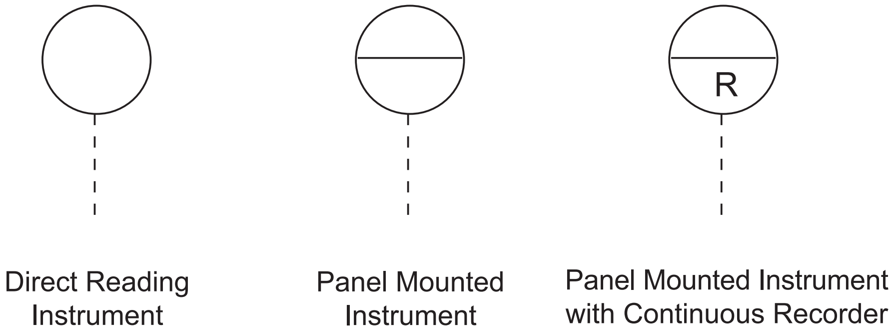


Figure 3-5. Gauge symbols

The type of instrument is indicated using the symbols listed in Table 3-3.

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 indicating 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 in the control room) are indicated using a line horizontally 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 there has been or may be a serious corrosion problem that could affect either system performance or safety. On a single-page-format-type of flowchart, it is impractical to specify the exact types of material and protective coatings on each vulnerable component because there are several hundred combinations of materials and coatings in common use. However, the general type of material in certain selected 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. A small 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.

3.1.2 Diagrams

Basic Flowcharting Techniques

Flowcharts can serve many purposes and therefore many levels of sophistication in flowchart preparation exist. Some of 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 more than 500 separate items shown on it. Conversely, a simple block diagram used as a field sketch may have only 3 to 5 symbols on the drawing.

Flowcharts for air pollution control studies should be relatively simple. Generally, you need more equipment detail than shown on a simple block diagram, but far less information than provided by the standard P & I drawing. The flowcharts should not be so cluttered with system design details that it is difficult to include present system operating conditions to help identify health and safety risks and performance problems. Since these are primarily "working" drawings, they must be small enough to be carried easily while walking around the facility. The flowcharts should not also 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. In this type of flowchart, only the system components directly relevant to the study are included. Major components such as baghouses are shown as a simple block rather than a complex sketch resembling the actual baghouse. Most minor components and material flow streams are omitted to avoid cluttering the drawing.

The size of 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.

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.

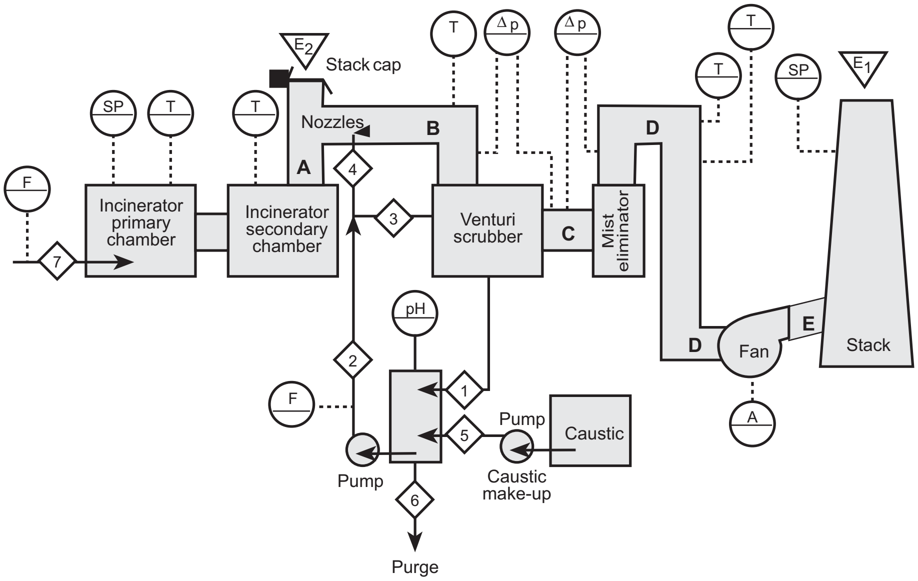


Figure 3-6. Example flowchart of a waste solvent system

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.

Another flowchart example is shown in Figure 3-7. This is a simple wet scrubber system serving a recycle operation in a hot mix asphalt plant. Most of the plant is not shown since the scrubber only controls the particulate 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 and with a slightly different form of cross hatching so that it is easy to differentiate between the pond and the major equipment items.

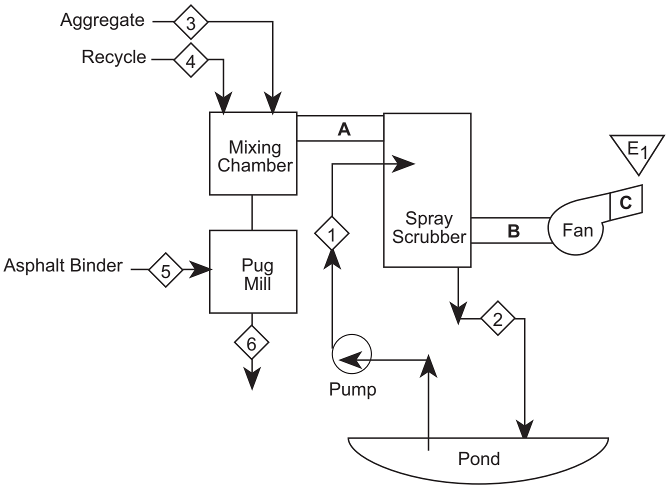


Figure 3-7. Example flowchart of an asphalt plant

It should be noted that the symbols for the major pieces of equipment and the symbols for 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 stack 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 a tool for organizing relevant data and determining what needs further investigation.

Follow these steps when evaluating the overall system:

1. Determine whether or not the operating data is consistent and logical.
2. Compare current data against site-specific baseline data.
3. Determine specific areas that may need emphasis during the inspection.
4. 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. This 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 filters for control of particulate matter 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?

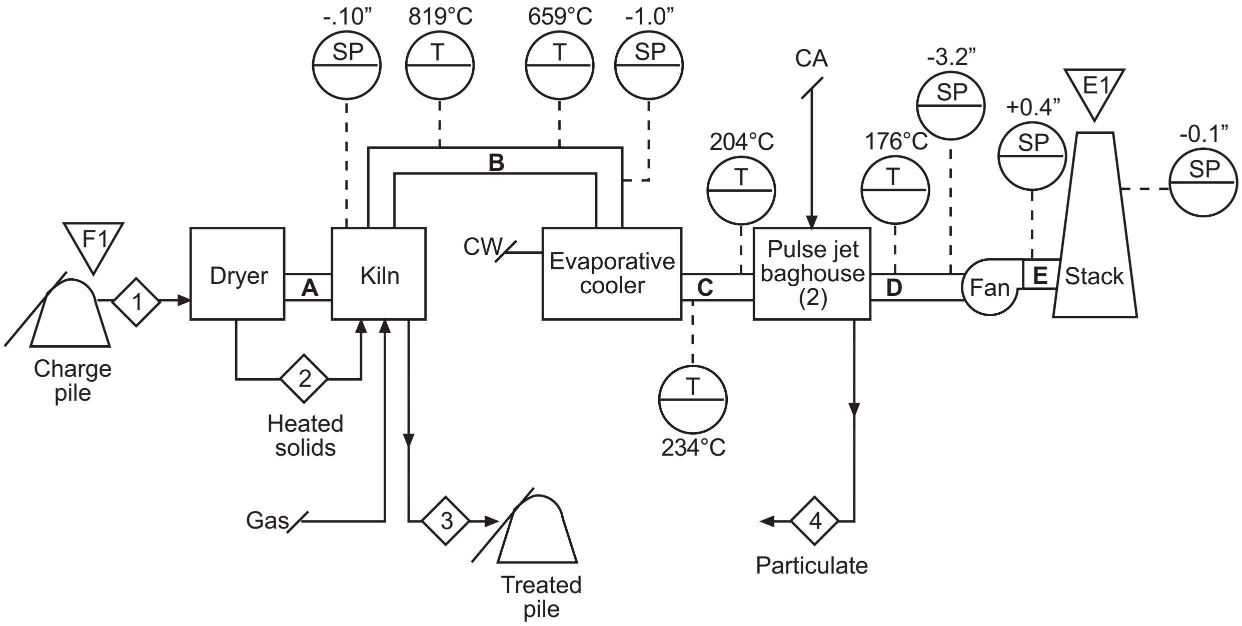


Figure 3-8. Example flowchart of a hazardous waste incinerator and pulse jet baghouse system

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 is 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.

For this example, the gas temperature and static pressure data 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

The gas temperature and static pressure trends through the system are both logical. The gas temperatures are at a maximum at the discharge of the combustion source, and they decrease throughout the system. The gas temperature at the fan outlet is not provided for this example. Note that sometimes gas temperature at the fan outlet is *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 pressures become progressively more negative as the gas approaches the fan. After the fan, the static pressure of the system significantly increases, as expected. Since the set of plant instruments provides consistent and logical profiles through the system, they are probably relatively accurate.

Solution:

Part B

Compare the current data against the site-specific baseline data to the extent that it is available.

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

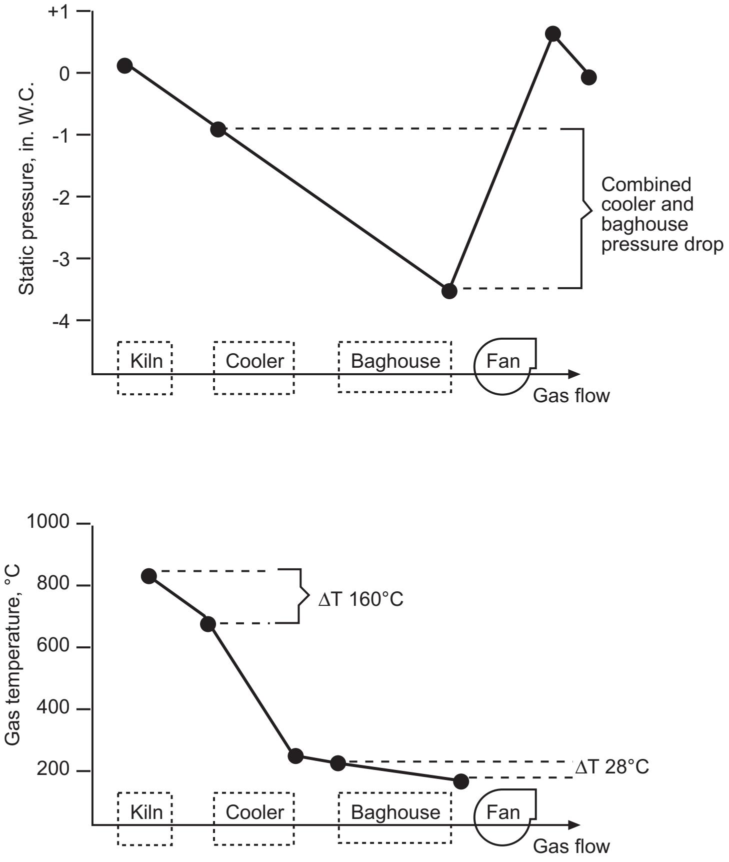


Figure 3-9. Static pressure and temperature profile for present data

a. Evaluate the temperature data for Duct B using Figure 3-9 and 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 relatively new. The baseline data indicates that the previous temperature drop was 25°C due to radiative and convective heat losses from the refractory-lined duct. The significantly higher temperature drop presently occurring across this short section of ductwork indicates that air infiltration is probably happening. This air infiltration could reduce the amount of combustion being pulled from the kiln and thereby cause fugitive emissions from the kiln. 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 using Figure 3-9 and Table 3-6.

The primary function of this portable plant is to incinerate the contaminated soil. It is apparent from the flowchart that the most useful single parameter for evaluating the destruction efficiency of the rotary kiln system 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 is important primarily because it protects the temperature-sensitive Nomex® bags used in the downstream pulse jet baghouses. It is clear from the flowchart that presently there is a gas temperature drop of 425°C across the evaporative cooler. This fact combined with an observed 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 flowchart data indicates there is a severe temperature drop across the baghouse (28°C). This should be included in the field evaluation.

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

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

The pressure readings are in agreement for the baseline data and the present data.

b. 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 is 4.1 in. W.C. compared with a present pressure drop reading of 2.2 in. W.C. Pressure drops across evaporative coolers tend to remain constant. However, the pressure drop across baghouses can vary due to changes in emission loading or a malfunction. Emission loading is directly related to a pressure drop increase. A decrease in pressure drop may result from air inleakage at the bag connention points. Air inleakage can also occur due to worn or torn bags.

c. 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 is also in agreement.

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 reasons for temperature drop of the pulse jet baghouses.
4. Check for air inleakage across the pulse jet baghouse

Solution:

Part D

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

The pulse jet baghouse should be one of the main areas evaluated during the field portion of the inspection. However, this work must be conducted carefully in order to minimize safety hazards. The roof of the unit should be avoided because it is an uninsulated metal surface at 176°C (349°F). The soles of safety shoes could begin to melt and thereby cause a fall. Furthermore, there is a slight possibility of falling through the roof of the baghouse. The gas temperature drop of 28°C across the baghouse indicates severe air infiltration that may be caused by corrosion. If so, the roof may have been weakened. Corrosion is very likely in this process due to the formation of hydrochloric acid and water vapor in the kiln.

The waste being burned in this portable plant includes 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 baghouse.
2. Remain aware that chemicals in process are possible carcinogens. Avoid areas where inhalation or absorption may become dangerous.

Problem 3-2

A company is routinely 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.

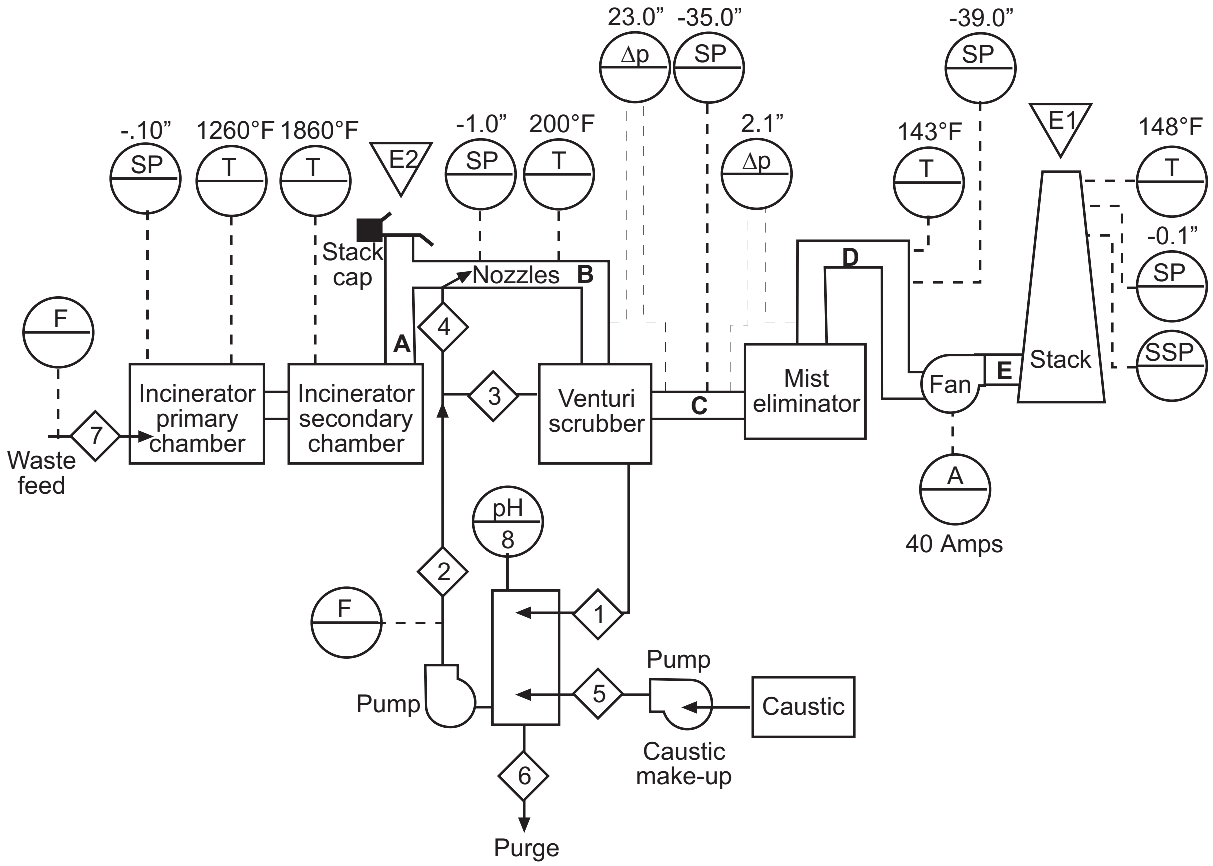


Figure 3-10. Example flowchart of a hazardous waste incinerator and venturi scrubber system

Table 3-8. Static Pressures and Static Pressure Drops (in. W.C.)

	Present	Baseline
Static Pressures		
Incinerator primary chamber	-0.10	-0.12
Duct B	-1.0	-1.10
Mist eliminator inlet	-35.0	-38.0
Fan Inlet (Duct D)	-39.0	-40.0
Stack	-0.1	-0.1
Static Pressure Drop		
Venturi scrubber	23.0	36.0
Mist eliminator	2.1	1.6

Table 3-9. Gas Temperatures (°F)

	Present	Baseline
Incinerator secondary	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 pressures, gas temperatures, and other relevant parameters.

The static pressure and pressure drop data 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. The present mist eliminator inlet static pressure and fan inlet static pressure data suggest that the static pressure drop across the venturi scrubber should be higher than indicated by the gauge. It is quite possible that the venturi scrubber pressure drop gauge is malfunctioning and that the actual static pressure drop is relatively similar to the baseline value of 36 in. W.C.

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. Untreated combustion gas could not escape through gaps in the stack seal.

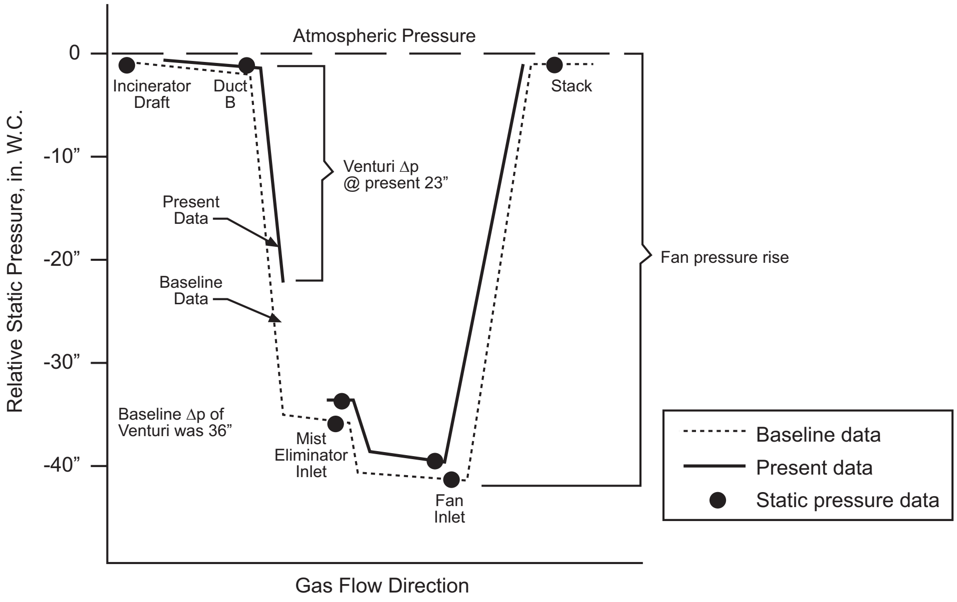


Figure 3-11. Static pressure profiles

Flowcharts Summary

A flowchart of the process system can be used to:

- Identify changes in control device performance due to process changes
- 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.

3.2 GAS PRESSURE, GAS TEMPERATURE, AND GAS FLOW RATE

Gas pressure, gas temperature, and gas flow rate data are used in essentially all projects concerning the performance of a particulate control device.

Gas Pressure

The pressures of the gas streams throughout the particulate control system are very important. Throughout this course, gas pressure data will be used to evaluate operating conditions.

The total pressure of a gas stream is the sum of the static pressure and velocity pressure of the gas stream as indicated in Equation 3-1. Velocity pressure is exerted only in gas streams that are in motion. This part of the total pressure is of concern only during emission tests and gas flow rate measurements and is not routinely monitored by plant personnel.

$$\text{Total Pressure} = \text{Static Pressure} + \text{Velocity Pressure} \tag{3-1}$$

The term *static pressure* is used to describe the pressure exerted by gases in all directions. This pressure is related to the number of gas molecules in a given volume and at a given temperature. If the number of molecules in the space increases, the pressure increases. An increase in the gas temperature increases the kinetic energy of the molecules, and the static pressure increases. All gas streams exert a static pressure. The static pressure exerted by ambient air is termed either *atmospheric* or *barometric pressure*. The latter term is often used since atmospheric pressure is measured by a barometer.

When fans used in industrial systems create gas static pressures above the prevailing atmospheric pressure, the condition is termed *positive pressure*. When the fans create a gas static pressure below the prevailing atmospheric pressure, *negative pressure* exists. Both positive and negative pressures are considered relative terms since the static pressure is being described in a form that is compared to the atmospheric pressure. The atmospheric pressure is an absolute term since it is directly related to the number of molecules and their kinetic energy.

$$\text{SP(absolute)} = \text{SP (barometric)} + \text{SP(relative)} \tag{3-2}$$

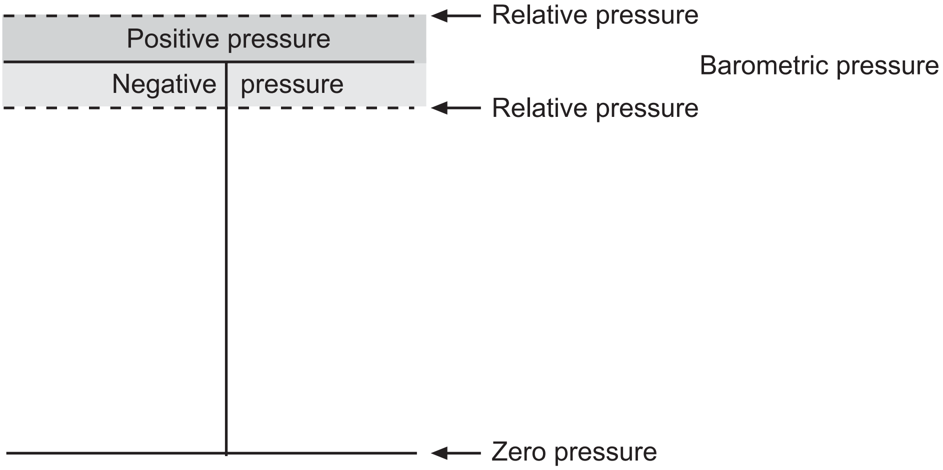


Figure 3-12. Definition of positive and negative pressure

Standard atmospheric pressure is defined as 14.7 pounds per square inch (psi). This is the average pressure that exists at sea level at 45° latitude. On a mountain, the atmospheric pressure is lower than 14.7 psi since the column of air above the measuring point is smaller. When weather systems pass over, there are slight variations in the atmospheric pressure that are slightly above or slightly below 14.7 psi. Nevertheless, the value of 14.7 psi will be used as a "standard."

The absolute and relative air pressures can be expressed in a number of units which are listed in Table 3-10. The values of the atmospheric pressure under standard conditions are listed in the second column.

Table 3-10. Units of Pressure

Units	**Value at Standard Conditions**
psi	14.70
in. Hg	29.92
mm Hg	760.00
ft W.C.	33.92
in. W.C.	407.00

The most useful of these units is 407 inches of water (in. W.C.). This format is most convenient due to the magnitudes of the positive and negative relative pressures commonly found in industrial source systems. For example, the normal positive pressure gas streams are generally from +1 to +20 in. W.C., which is equivalent to the awkward values of +0.036 to +0.722 psi or +0.0735 to +1.47 inches of mercury (in. Hg). The normal negative pressures range from -0.20 to -60 in. W.C. which are equivalent to -0.0072 to -2.17 psi. Generally, the inches of water units for pressure are most convenient. Furthermore, gauges often used in air pollution control, and industrial ventilation systems indicate relative pressure directly in inches of water.

Problem 3-3

An air pollution control device has an inlet static pressure (relative) of –25 in. W.C. 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 to in. W.C.

$$\text{SP (barometric)} = \left(\frac{407 \text{ in. W.C.}}{29.92 \text{ in Hg.}}\right) 29.85 \text{ in. Hg.} = 406 \text{ in. W.C.}$$

$$\text{SP (absolute)} = \text{SP (barometric)} + \text{SP (relative)}$$

$$\text{SP (absolute)} = \text{SP (406 in. W.C.)} + \text{SP (-25 in. W.C.)} = 381 \text{ in. W.C.}$$

Generally, the inches of water units for pressure are most convenient. Furthermore, gauges often used in air pollution control, and industrial ventilation systems indicate relative pressure directly in inches of water.

Gas Temperature

Gas temperature can be expressed using both absolute and relative scales. The absolute scales start at absolute zero. These include the Kelvin scale for the centimeter-gram-second system (cgs) of measurements and the Rankine scale for the American engineering system of measurements.

The commonly used Celsius and Fahrenheit temperature units are relative scales. Both of these have arbitrary values that apply to the freezing and boiling points of water at standard conditions. When recording temperature values, it is important to note the units as well as the values. Many of the calculations performed in this course and in later APTI courses will require the conversion of the relative temperatures to absolute temperatures. The relationships between these various temperature scales are indicated by Equation 3-3 through Equation 3-9.

$$\rho °F = \rho °R \tag{3-3}$$

$$\rho °C = \rho °K \tag{3-4}$$

$$°R = 460 + °F \tag{3-5}$$

$$°K = 273 + °C \tag{3-6}$$

$$°F = 32 + 1.8 (°C) \tag{3-7}$$

$$°C = (°F-32)/1.8 \tag{3-8}$$

$$\rho °R = 1.8 (\rho °K) \tag{3-9}$$

Problem 3-4

The gas temperature in the stack of a wet scrubber system is 130°F. What is the absolute temperature in degrees Rankine and degrees Kelvin?

Solution:

Absolute Temperature, °R = 460°R + 130°F=590°R

Absolute Temperature, °K = 590°R/1.8 = 327.8°K

Gas Flow Rate

The gas flow rate can be expressed either in terms of standard cubic feet per minute (SCFM) or actual cubic feet per minute (ACFM).

The SCFM value is directly related to the number of gas molecules being handled per minute. It is the measure of the total quantity of gas being handled. It is also the volume that this amount of gas occupies at standard temperature (20°C or 68°F) and pressure (14.7 psi or 407 in. W.C.). Quantities in standard cubic feet per minute can be handled, added, and subtracted as necessary to describe the industrial source system. For example, if 1000 SCFM enter an air pollution control device, and none is reacted or lost, then 1000 SCFM exit the control device. If there is a negative pressure control device which is suffering air inleakage of 125 SCFM, and the inlet gas flow rate is 2000 SCFM, then the outlet gas flow rate is 2125 SCFM. The SCFM quantity can be calculated directly from the ideal gas law as indicated in Equation 3-10 and 3-11.

$$n = x / MW_{Avg.} \tag{3-10}$$

$$V = (n)(R)(T)/P \tag{3-11}$$

Where:

n = number of pound mole

x = pounds of gas per minute

MW_{Avg} = average molecular weight (usually between 28 and 30 for air and combuston gases)

V = gas volume in SCFM

R = universal gas constant (10.73 (psi)(cf)/(lb×moles)(°R))

T = absolute temperature (°R)

P = absolute pressure (psi)

It is possible to convert between SCFM and ACFM values using the ideal gas law relationship. This has been expressed in the form of simple ratios shown in Equations 3-12 and 3-13.

$$ACFM = SCFM\left(\frac{T_{ACTUAL}}{T_{STP}}\right)\left(\frac{P_{STPL}}{P_{ACTUAL}}\right) \tag{3-12}$$

$$SCFM = ACFM\left(\frac{T_{STP}}{T_{ACTUAL}}\right)\left(\frac{P_{ACTUAL}}{P_{STP}}\right) \tag{3-13}$$

Where:

T_{Actual} = gas temperature at actual conditions (°R)

T_{STP} = gas temperature at standard conditions (°R)

P_{Actual} = gas pressure at actual conditions (in. W.C.)

P_{STP} = gas pressure at standard conditions (in. W.C.)

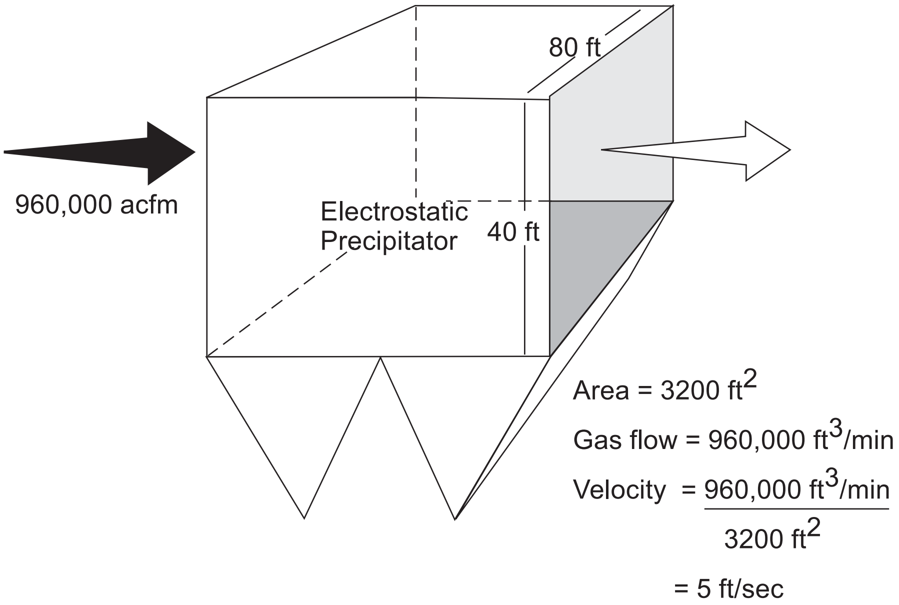


Figure 3-13. Example gas velocity calculation using ACFM

The SCFM form for gas flow rate is used whenever it is necessary to describe the *quantity* of gas. However, this form is not very useful when evaluating the gas flow characteristics inside the ductwork, air pollution control devices, and process equipment. When it is necessary to evaluate gas velocities and other flow conditions, the gas flow rate is expressed in terms of ACFM. This is the total *volume* of gas passing through the area of concern in one minute. The usefulness of the ACFM form is illustrated by the example shown in Figure 3-18. In this case, the velocity of 5 ft/sec through the electrostatic precipitator is calculated simply by dividing the gas flow rate in ACFM by the cross sectional area of the precipitator. The gas flow rates must be expressed in ACFM whenever *velocity* is calculated.

Problem 3-5

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 and the total gas flow rate entering the fan downstream of the fabric filter is 11,340 SCFM. What is the rate of air infiltration into the fabric filter and the ductwork between the fabric filter and the fan?

Solution:

Prepare a material balance around the fabric filter and its outlet ductwork using SCFM.

Gas flow into the fabric filter and outlet ductwork= 8,640 SCFM + air infiltration

Gas flow out of the fabric filter and outlet ductwork = 11,340 SCFM

Gas flow in = Gas flow out

8,640 SCFM + air infiltration = 11, 340 SCFM

Air infiltration = 2,700 SCFM

Problem 3-6

The same system described in Problem 3-5 has a rectangular fabric filter inlet duct with inside dimensions of 3 feet by 4 feet. What is the velocity into the fabric filter? The gas temperature in the inlet duct is 320°F, the relative static pressure is –10 in. W.C. and the barometric pressure is 28.3 in. Hg.

Solution:

Convert the relative pressure to absolute pressure

$$\text{SP (absolute)} = \left(\frac{407\,\text{in. W.C.}}{29.92\,\text{in. Hg.}}\right) 28.3\,\text{in. Hg.} + (-10\,\text{in. W.C.}) = 375\,\text{in. W.C.)}$$

Convert the relative gas temperature to absolute temperature

$$T_{\text{actual}} = 460°\text{R} + 320°\text{F} = 780°\text{R}$$

Convert the fabric filter inlet flow rate to ACFM

$$\text{ACFM} = \text{SCFM}\left(\frac{T_{\text{ACTUAL}}}{T_{\text{STP}}}\right)\left(\frac{P_{\text{STPL}}}{P_{\text{ACTUAL}}}\right)$$

$$\text{ACFM} = 8{,}640\,\text{SCFM}\left(\frac{780°\text{R}}{528°\text{R}}\right)\left(\frac{407\,\text{in. W.C.}}{375\,\text{in. W.C.}}\right) = 13{,}853\,\text{ACFM}$$

Calculate the velocity

$$\text{Velocity} = \frac{\text{Gas flow rate (ACFM)}}{\text{Area (ft}^2)} = \frac{13{,}853\,\text{ft}^3/\text{min}}{12\,\text{ft}^2} = 1{,}154\,\text{ft/min}$$

3.3 HOODS

The pollutants generated or released in process equipment must be captured so that they can be transported to the air pollution control device. Pollutant capture occurs in hoods.

Hoods are normally 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 3-14. Stationary hood in an industrial process

If hoods do not capture pollutants generated by process equipment, the pollutants 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. The EPA defines fugitive emissions as “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.”[3]

$$\text{Fugitive emissions} = \text{Total emissions} - \text{Emissions captured by hood} \tag{3-14}$$

$$\text{Stack emissions} = \text{Emissions captured by hood} \times \left(\frac{100\% - \eta}{100\%}\right) \tag{3-15}$$

Where:

η = collection efficiency (%)

The importance of hood performance is illustrated by Problems 3-7 and 3-8, which are based on the simplified industrial process shown in Figure 3-15. This system consists of a process unit that generates pollutants, several hoods surrounding the process equipment, the ductwork, an air pollution control device, a fan, and a stack.

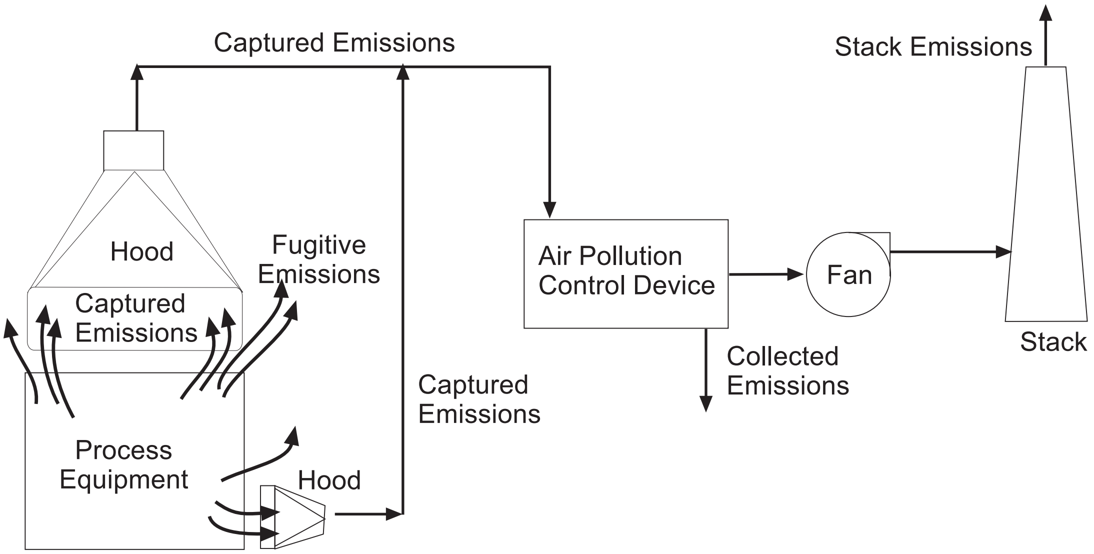


Figure 3-15. Role of hoods in an industrial process

Problem 3-7

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

$$= 100\ lb_m/hr - 95\ lb_m/hr = 5\ lb_m/hr$$

2. Calculate stack emissions.

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

Where:

η = collection efficiency (%)

$$\text{Stack emissions} = (95\ lb_m/hr)\frac{(100\% - 95\%)}{100\%}$$

$$= 4.75\ lb_m/hr$$

The capture of fugitive emissions is the key step in an air pollution control system. It is crucial that all the fugitive emissions are captured and transported to the air pollution control device. Problem 3 shows that even with hood capture efficiencies approaching 100%, fugitive emissions can be higher than emissions leaving the stack.

Problem 3-8

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:

Fugitive emissions = 100 lb_m/hr-90 lb_m/hr = 10 lb_m/hr

$$\text{Stack emissions} = \frac{(100\% - 95\%)}{100\%}(90\,\text{lb}_\text{m}/\text{hr}) = 4.5\,\text{lb}_\text{m}/\text{hr}$$

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 fugitive and stack emissions released into the atmosphere.

Unfortunately, it is not always possible to see the fugitive emissions. Gaseous and vapor emissions such as carbon monoxide, sulfur dioxide, hydrogen chloride, and nitric oxide are not visible. Even particulate emissions may be hard to see under the following circumstances:

- If there are numerous small fugitive sites
- If there is one major site that cannot be seen from normal areas accessible to personnel
- If the particulate matter is not in the size range that causes light scattering

Techniques for monitoring hood capture effectiveness are important because the quantities of fugitive emissions can be high, and these emissions are often hard to see.

3.3.1 Hood Operating Principles

Hoods are generally designed to operate under negative 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. 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 3-16 illustrates how quickly the gas velocity decreases as distance from the hood increases.

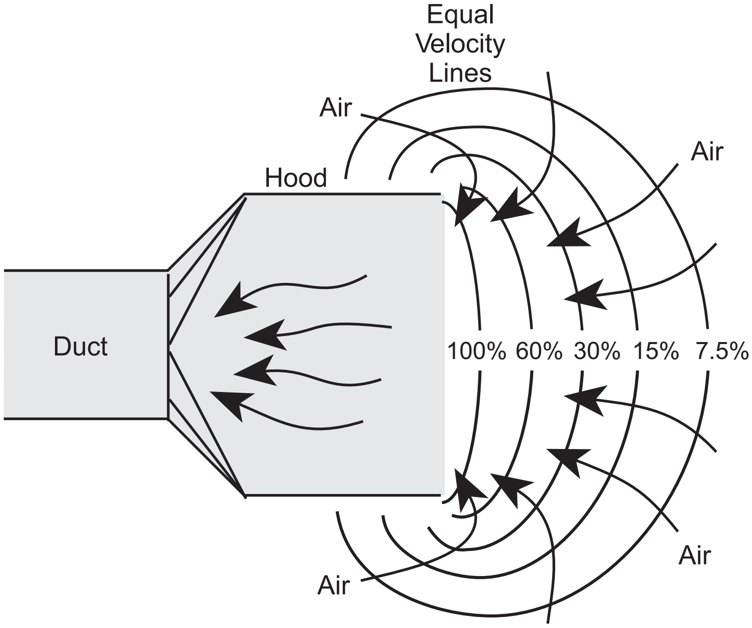


Figure 3-16. Hood capture velocities

Figure 3-16 indicates that the hood has very little influence on gas flow except in the area very close to the hood entrance. In order to ensure good capture of the pollutant-laden gas streams, the hood must be close to the emission source. 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.*[1] The following examples show conditions that would help determine what part of the capture velocity range for a particular operation should be used, low end of the capture velocity vs. upper end of the capture velocity range.[1]

- The surrounding air currents

  Minimal room air currents vs. disturbing room air currents
- The level of toxicity of the pollutant to be captured

  Nuisance values only vs. high toxicity
- The amount of pollutant

  Intermittent (low production) vs. high production (heavy use)
- Area of the hood opening

  Large hood (large air mass in motion) vs. small hood (local control only)

The following flow/capture velocity equation for a freely suspended hood without a flange demonstrates the importance of the proximity of the hood to the source.

$$Q = v_h(10X^2+A_h) \tag{3-16}$$

Where:

Q = volumetric flow rate (ACFM)
X = distance from hood face to farthest point of contaminant release (ft)
v_h = hood capture velocity at distance X (ft/min)
A_h = area of hood opening (ft^2)

It should be noted that the correlation between distance, gas flow rate, and capture velocity should be used for *estimation purposes only* because the vacuum from a hood does not create equal velocity lines or points. Equation 3-16 is also limited to the distance (X) being less than or equal to 1.5 hood diameters.[1]

Problem 3-9

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

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

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

Solution:

Part A.

$$Q = v_h(10X^2+A_h)$$

1. Calculate the area of the hood opening.

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

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

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

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

$$= 3{,}419\text{ ACFM}$$

Solution:

Part B.

$$Q = v_h\,(10X_2 + A_h)$$

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

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

$$= 12{,}419\text{ ACFM}$$

The volumetric flow rate requirements increased approximately four times when the distance between the hood and the contaminant source doubled.

The 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. 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.

Side baffles or **flanges** can be used to block the movement of clean air into the hood. The possible beneficial effect of side baffles on the gas velocities near the hood entrance is shown in Figure 3-17.

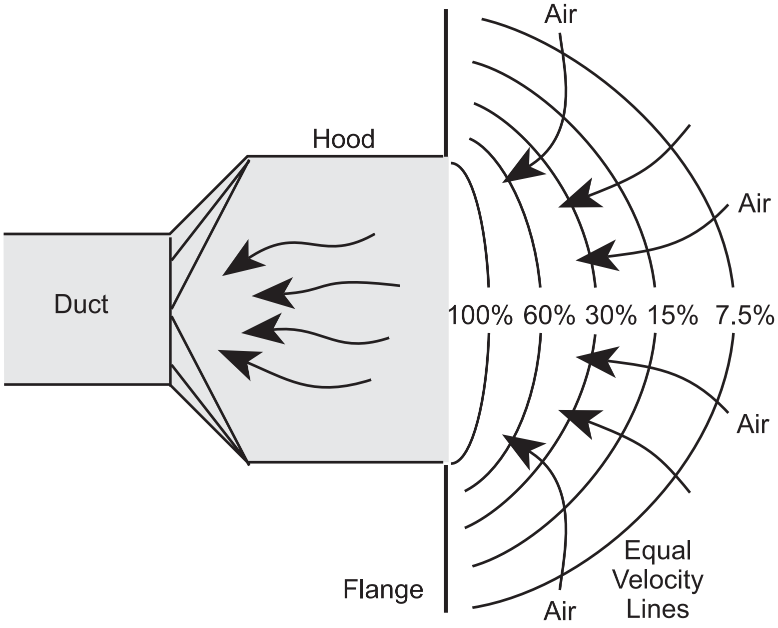


Figure 3-17. Beneficial effect of side baffles on hood capture velocities

Hood capture is greatly improved when the enclosure comprised of the hood and the side baffles can encompass the point of pollutant generation. These side baffles can be in the form of metal sheets, strips of fabric or plastic, or any other materials that block the movement of clean air into the low-pressure area of the hood. In addition to reducing the unintentional capture of clean air, these side baffles prevent cross drafts, which can prevent the intended movement of the pollutant-laden gas into the hood. The recommended width of a flange for most situations should be equal to the square root of the hood area.

Some process equipment inherently creates an entirely enclosed area for pollutant-laden gas capture. For example, coal-fired boilers generate pollutants in an enclosed furnace area that is maintained at a slightly negative static pressure of -0.05 to -0.25 in. W.C. In this case, the boiler walls serve as the hood.

Another hood design that is used to improve capture effectiveness is called the **push-pull hood**. As shown in Figure 3-18, a high-velocity clean air stream is blown across the area of pollutant generation into the hood on the opposite side.

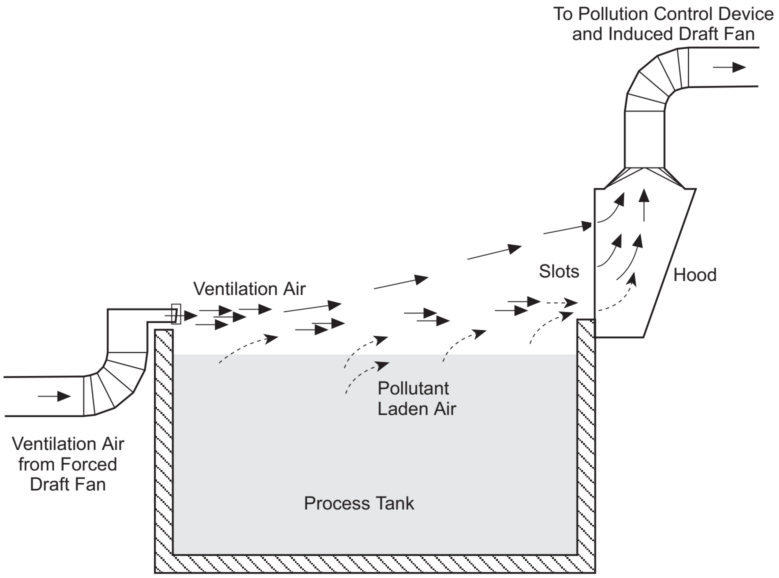


Figure 3-18. Push-pull hood

The high-velocity gas stream does not inherently disperse rapidly. Therefore, it flows toward the hood and is captured. The hood also effectively captures the pollutant-laden gas that is trapped in this strong cross draft. 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 may not be appropriate for tanks and other processes handling materials where the cross draft could significantly increase the quantities vaporized. Push-pull hoods can provide very high capture efficiencies where they are applicable.

3.3.2 Monitoring Hood Capture Effectiveness

There are several effective ways to confirm that the hood capture effectiveness has not decreased since it was installed or 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 be 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* is simply the static pressure in the duct immediately downstream from the hood. This static pressure 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. As indicated in Equation 3-17, the hood static pressure is determined by (1) the velocity pressure in the duct from the hood and (2) the hood entry loss. The loss of pressure caused by airflow moving into a system is referred to as entry loss.

$$SP_h = -(VP_d) - h_e \tag{3-17}$$

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.)

$h_e = (F_h)\ (VP_d)$

Where:

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

The hood entry loss term is calculated using the coefficient of entry, F_h, which is tabulated in standard texts concerning hoods and ventilation systems.

$$SP_h = -(VP)-(F_h)\ (VP_d) \tag{3-19}$$

Where:

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

The velocity pressure term in Equation 3-18 is due to the energy necessary to accelerate the air from zero velocity to the velocity in the duct.

When air enters a duct under suction, the airflow converges as shown in Figures 3-19 through 3-21. The area where air converges upon entering a duct is referred to as *vena contracta*. After passing through the vena contracta, the air flow expands to fill the duct. As the air expands, some of the velocity pressure converts to static pressure. The vena contracta is dependent on the hood geometry, which determines the resistance to airflow entering the hood.

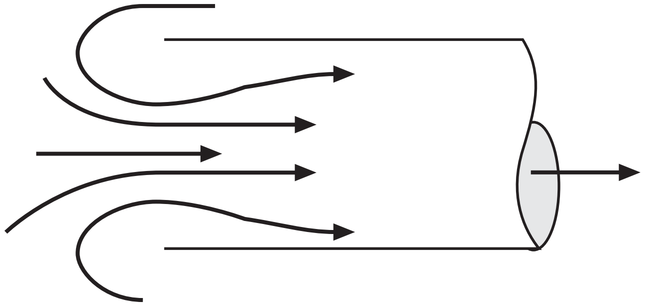


Figure 3-19. Plain duct end with a hood entry loss coefficient of 0.93

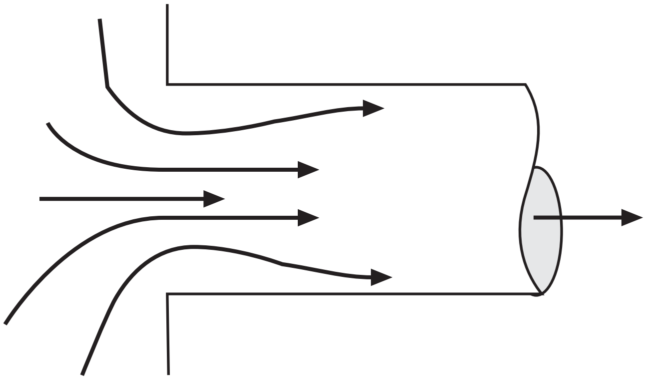


Figure 3-20. Flanged opening with a hood entry loss coefficient of 0.49

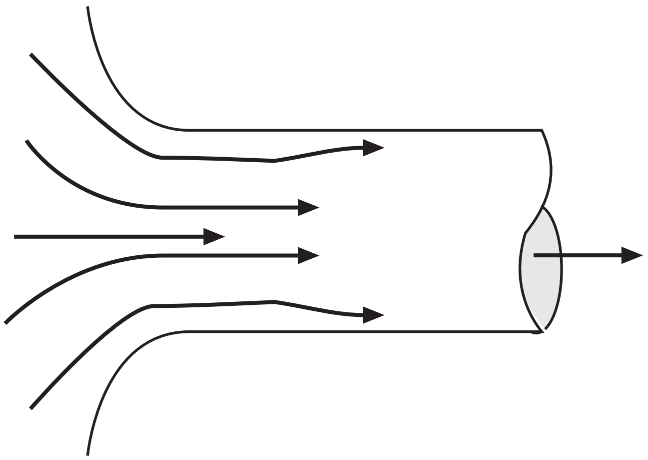


Figure 3-21. Bell-mouth inlet with a hood entry loss coefficient of 0.04

The velocity pressure is related to (1) the square of the velocity of the gas stream in the duct and (2) the gas density. The velocity pressure is calculated using Equation 3-20.

$$VP_d = \left(\frac{v}{4005}\right)^2 \frac{\rho_{Actual}}{\rho_{Standard}} \tag{3-20}$$

Where:

VP_d = velocity pressure 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)

$$VP_d = \left(\frac{v}{4005}\right)^2 \frac{\rho_{Actual}\ lb_m / ft_3}{0.075\ lb_m / ft_3}$$

As the gas flow rate into the hood increases, the hood static pressure increases (see Figure 3-22). In this figure, a hood with an entry loss coefficient (F_h) of 0.49 has 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.

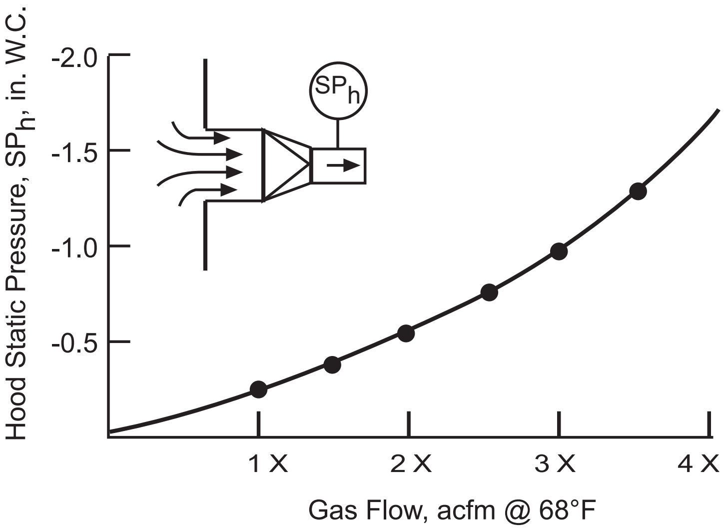


Figure 3- 22. Relationship between hood static pressure and flow rate

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 velocities at the hood entrance.

Problem 3-10

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. Estimate the gas flow rate under the following two conditions:

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.

Step 1. Calculate the gas velocity and flow rate at present conditions.

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

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

Calculate the value for the hood entry loss, h_e, 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.

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

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

2. Calculate the gas velocity using a variation of Equation 3-19 at standard conditions ($\rho_{Actual} = 0.075\ lb_m/ft^3$.)

$$v = 4005\sqrt{VP}$$

$$v = 4005\sqrt{0.57}$$

$v = 3.024$ ft/min

3. Calculate the gas flow rate as follows:

Flow rate = Velocity × Area of duct

$$\begin{aligned}\text{Area of duct} &= \frac{\pi D^2}{4}\\ &= \frac{3.14(2\text{ft})^2}{4}\\ &= 3.14\,\text{ft}^2\end{aligned}$$

Flow rate = 3,024 ft/min (3.14 ft^2) = 9,495 ACFM

Solution:

Part B.

Step 1. Calculate the gas flow rate at baseline conditions.

1. Calculate the velocity pressure using the following.

$$\begin{aligned}SP_h &= -(VP_d) - h_e\\ &= -(VP_d) - (0.93)(VP_d)\\ &= -(VP_d) - 0.93\,VP_d = 1.93(VP_d)\end{aligned}$$

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

$-\ 1.7$ in. W.C. $= -\ 1.93\ (VP_d)$

$VP_d = 0.88$ in. W.C.

2. Calculate the gas velocity using a variation of Equation 3-19 at standard conditions

$\rho_{Actual} = 0.075\ lb_m/ft^3$

$$\begin{aligned} v &= 4005\sqrt{VP} \\ &= 4005\sqrt{0.88} \\ v &= 3{,}757 \text{ ft/min} \end{aligned}$$

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

$$\begin{aligned} \text{Flow rate} &= \text{Velocity} \times \text{Area} \\ &= 3.757 \text{ ft/min} \times \left(3.14 \text{ ft}^2\right) \\ &= 11{,}797 \text{ ACFM} \end{aligned}$$

The change in hood static pressure from -1.7 in. W.C. to -1.1 in. W.C. indicates a drop in the gas flow rate from 11,797 ACFM to 9,495 ACFM. This is a 20% decrease in the gas flow rate.

Flow / Capture Velocity Equation

The flow / capture velocity equation that was used in Problem 3-9 can be modified to determine the gas flow rate with different hood designs. A hood with a wide flange would use the following equation:

$$Q = v_h\,(0.75)\,(10X^2 + A_h) \tag{3-21}$$

Using the information given in Problem 3-9 (Part A)

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

$$\begin{aligned} Q &= \frac{300 \text{ ft}}{\text{min}}(0.75)\left[10(1 \text{ ft})^2 + \left(201 \text{ in.}^2\right)\left(\frac{1 \text{ ft}^2}{144 \text{ in.}^2}\right)\right] \\ &= 2{,}564 \text{ ACFM} \end{aligned}$$

The volumetric flow requirements decreased by approximately 25% when a flanged hood was used.

Transport Velocity

When the contaminant is captured by the hood system and enters the ductwork, a minimum transport velocity must be maintained to keep the contaminant from settling out of the gas flow stream and building up deposits in the ductwork. The minimum transport velocity is particularly important when handling particulate-laden gas streams. If the minimum transport velocity is not maintained in the ductwork, then the particulate matter will settle out in the ductwork due to decreased flow rate. This will lead to decreased hood capture efficiencies and increased fugitive emissions. Systems with heavy particulate-laden gas streams should have clean-out ports installed to remove particulate that has settled out.

$$v = \frac{Q}{A} \tag{3-22}$$

Where:

v = gas velocity (ft/min)

Q = volumetric gas flow rate (ACFM)

A = cross-sectional area of duct or equipment (ft^2)

The proper duct diameter is a key element when addressing minimum transport velocity. If a section of ductwork has a larger than necessary diameter, then settling out will most likely occur. 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. The amount of abrasion that occurs is dependent upon several factors: the duct velocity, the amount and type of particulate in the gas stream, and the construction of the ductwork.

Minimum transport velocities for different types of particulate matter can be obtained from standard texts concerning hoods and ventilation systems. Examples of transport velocities are listed below.

Table 3-11. Commonly Recommended Transport Velocity

Type of Pollutant	Transport Velocity
Gaseous Gases	~1000–2000 ft/min
Light Particulate Loading	~3000–3500 ft/min
Normal Particulate Loading	~3500–4500 ft/min

Problem 3-11

Transport Velocity

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:

1. Calculate the duct area.

$$Duct\ \text{area} = \frac{\text{Gas flow rate, actual}}{Gas\ \text{velocity}}$$

$$= \frac{978\ \text{ft}^3/\text{min}}{2800\ \text{ft/min}}$$

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

2. Calculate the duct diameter.

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

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

$$= 8\ \text{in.}$$

Summary

Hoods are the first component of the air pollution control system and are of critical importance. If they fail to capture the pollutant, the overall collection efficiency of the system is reduced. Pollutants not captured by hoods become fugitive emissions. Many factors affect a hood's capture efficiency; however, one of the key factors is the distance between the pollutant source and the hood.

The geometry of a hood opening 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 condition provides a good indicator if the system has developed any problems.

Maintaining a system's minimum transport velocity is necessary to ensure that all of the captured pollutant reaches the air pollution control device and to prevent build-up of the pollutants in the ductwork.

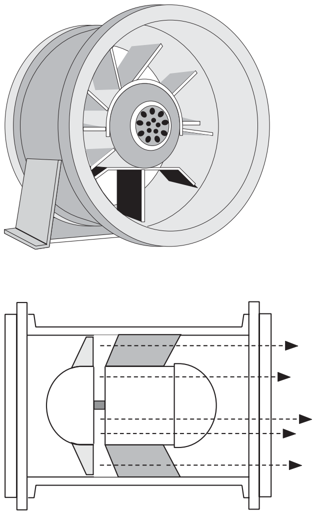
3.4 FANS

Fans are the heart of the system. They control the gas flow rate at the point of pollutant generation in the process equipment and through the air pollution control devices. Fans provide the necessary energy for the gas stream to overcome the resistance to gas flow caused by the ductwork and air pollution control devices. Data concerning fan performance is important during inspections and all other technical evaluations of system performance.

3.4.1 Types of Fans and Fan Components

There are two main types of fans: axial and centrifugal. Most fans used in air pollution control systems are centrifugal fans.

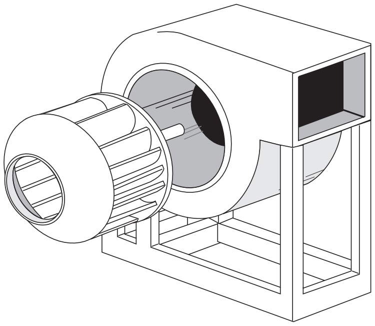
An axial fan is shown in Figure 3-23. The term, axial, refers to the use of a set of fan blades mounted on a rotating shaft. A standard house ventilation fan is an axial fan.



A. Axial Fan

Figure 3-23. Axial fans

A centrifugal fan has a fan wheel composed of a number of fan blades mounted around a hub. As shown in Figure 3-24, the hub 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.



B. Centrifugal Fan

Figure 3-24. Centrifugal fan components

Centrifugal fans can generate high-pressure rises in the gas stream. Accordingly, they are well-suited for industrial processes and air pollution control systems. The remainder of this section concerns centrifugal fans.

The major components of a typical centrifugal fan include the fan wheel, fan housing, drive mechanism, and inlet dampers 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. The types of 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. This means that the fan wheel speed is identical to the motor rotational speed. With this type of fan drive, the fan speed cannot be varied.

Belt driven fans use multiple belts which rotate in a set of sheaves mounted on the motor shaft and the fan wheel shaft. This type of drive mechanism is illustrated in Figure 3-25.

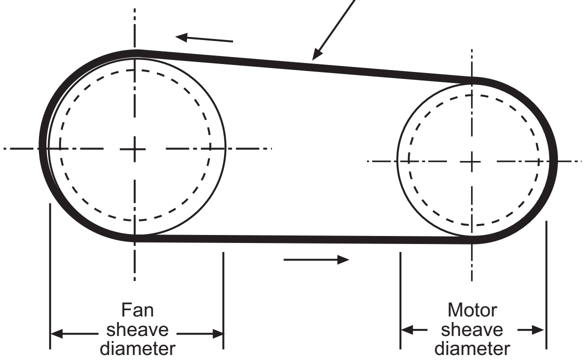


Figure 3-25. Centrifugal fan and motor sheaves

The belts transmit the mechanical energy from the motor to the fan. The fan wheel speed is simply the ratio of the fan wheel sheave diameter to the motor sheave diameter as indicated in Equation 3-23.

$$RPM_{(Fan)} = RPM_{(Motor)} \frac{D_{(Motor)}}{D_{(Fan)}} \tag{3-23}$$

Where:

$RPM_{(Fan)}$ = fan speed (Revolutions Per Minute)
$RPM_{(Motor)}$ = motor speed (Revolutions Per Minute)
$D_{(Fan)}$ = diameter of fan sheave (inches)
$D_{(Motor)}$ = diameter of motor sheave (inches)

Fan wheel speeds in belt-driven arrangements are fixed unless the belts slip. Belt slippage normally reduces fan wheel speed several hundred rpm and creates a noticeable squeal. If it is necessary to change the fan wheel speed in a belt-driven arrangement, the motor and/or fan wheel sheaves must be replaced with units having different diameters. 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.

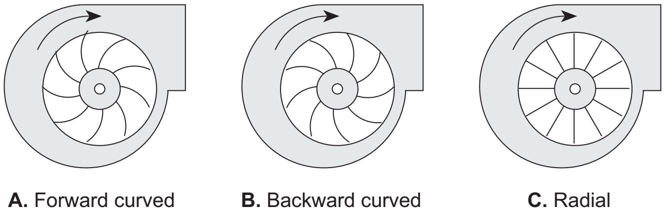
Variable speed fans use hydraulic or magnetic couplings that allow operator control of the fan wheel speed independent of the motor speed. The fan speed controls are often integrated into automated systems to maintain the desired fan performance over a variety of process operating conditions.
Fan dampers are used to control gas flow into and out of the centrifugal fan. These dampers can be on the inlet side and/or on the outlet side of the fan. Dampers on the outlet side simply impose a flow resistance that is used to control gas flow. Dampers on the inlet side are designed to control gas flow and to change 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. The fan blades on the hub can be forward-curved, backward-curved, or radial.

Forward-curved fans (Figure 3-26a) use blades that curve toward the direction of rotation of the fan wheel. These are especially sensitive to particulate and are not used extensively in air pollution control systems.

Backward-curved fan blades (Figure 3-26b) use a straight plate, a curved plate, or a curved airfoil. These types of fan wheels are used in fans designed to handle gas streams with relatively low particulate loadings because they are prone to solids build-up. Backward-curved fans are more energy efficient than radial blade fans.

Radial blades are fan wheel blades that extend straight out from the hub. A radial blade fan wheel, as shown in (Figure 3-26c), is often used on particulate-laden gas streams because it is the least sensitive to solids build-up on the blades.



A. Forward curved **B.** Backward curved **C.** Radial

Figure 3-26. Types of fan wheels

3.4.2 Centrifugal Fan Operating Principles

A basic understanding of fan operating principles is necessary to evaluate the performance of an industrial ventilation system. 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- 27, can operate over a modest range of speeds.

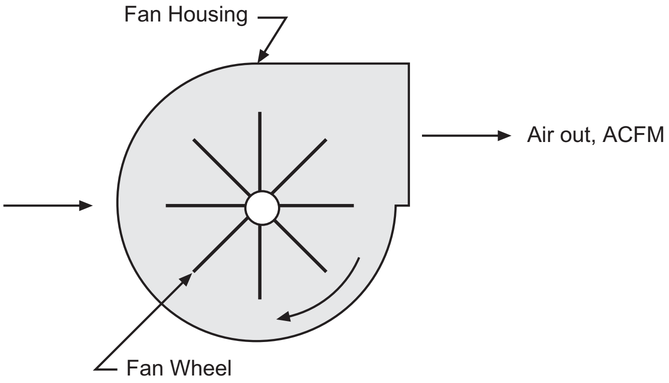


Figure 3-27. Centrifugal fan with radial blade

The flow rate of air moving through the fan depends on the fan wheel rotational speed. As the speed increases, the air flow rate increases as indicated in the example data in Table 3-12.

Table 3-12. Relationship Between Fan Speed and Air Flow Rate

Fan Wheel Speed	Air Flow Rate, ACFM
800	16,000
900	18,000
1000	20,000
1100	22,000
1200	24,000

It is important to recognize that a 10% decrease in fan speed results in a 10% decrease in the air flow rate through the ventilation system. This relationship is expressed as one of the major fan laws shown below as Equation 3-24.

$$Q_2 = Q_1(RPM_2/RPM_1) \qquad (3\text{-}24)$$

Where:

Q_1 = baseline air flow rate (ACFM)
Q_2 = present air flow rate (ACFM)
RPM_1 = baseline fan wheel rotational speed (Revolutions Per Minute)
RPM_2 = present fan wheel rotational speed (Revolutions Per Minute)

The rate of air flow through a fan is always expressed in terms of ACFM. This is helpful because this value does not change regardless of the air density. In this respect, a fan is much like a shovel. It moves a specific amount of air per minute regardless of whether the air is dense cold air or light hot air.

The air stream moving through the fan has a static pressure rise due to the mechanical energy expended by the rotating fan wheel. As indicated in Figure 3-28, the static pressure at the outlet is always higher than the static pressure at the inlet. For the purposes of this course, the static pressure rise across the fan is denoted Fan ΔSP.

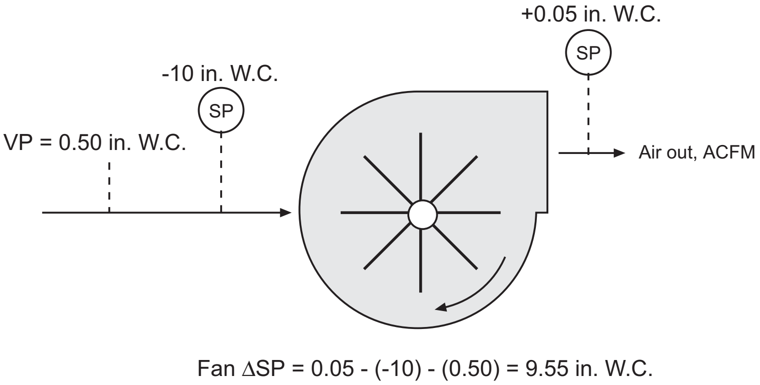


Figure 3-28. Fan static pressure rise

The Fan ΔSP is related to the square of the fan speed as indicated in the second fan law shown below as Equation 3-25. The fan static pressure rise is usually expressed in units of inches of water column (in. W.C.).

$$\text{Fan } \Delta SP_2 = \text{Fan } \Delta SP_1(RPM_2/RPM_1)^2 \quad (3\text{-}25)$$

Where:

ΔSP_1 = baseline fan static pressure rise (in. W.C.)
ΔSP_2 = present fan static pressure rise (in. W.C.)
RPM_1 = baseline fan wheel rotational speed (Revolutions Per Minute)
RPM_2 = present fan wheel rotational speed (Revolutions Per Minute)

The static pressure rise across the fan increase rapidly as the fan speed is increased. This is illustrated using example data shown in Table 3-13.

Table 3-13. Relationship Between Fan Speed and Fan Static Pressure Rise

Fan Wheel Speed	Fan ΔSP In. W.C.
800	5
900	5.6
1000	6.3
1100	6.9
1200	7.5

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

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 hood, ductwork, and air pollution control system air flow velocities.

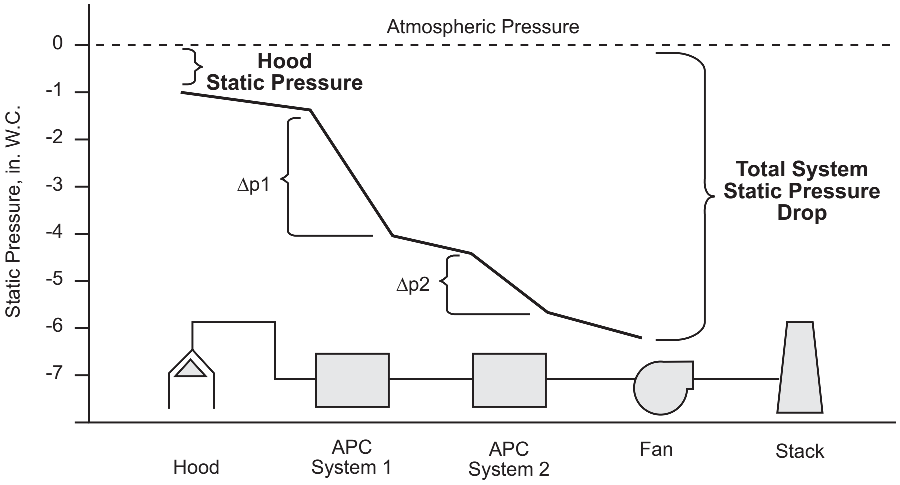


Figure 3-29. Total system static pressure drop

The changes in the air stream static pressure from the point of entry into the hood to the point of discharge from the stack are illustrated in Figure 3-29. This static pressure profile of the system is useful in illustrating the necessary fan static pressure rise.

The designer of a system, such as the one shown at the bottom of Figure 3-29, 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 overall static pressure drop across each component of the overall system is related to the square of the air flow rate. This is illustrated in Figure 3-30.

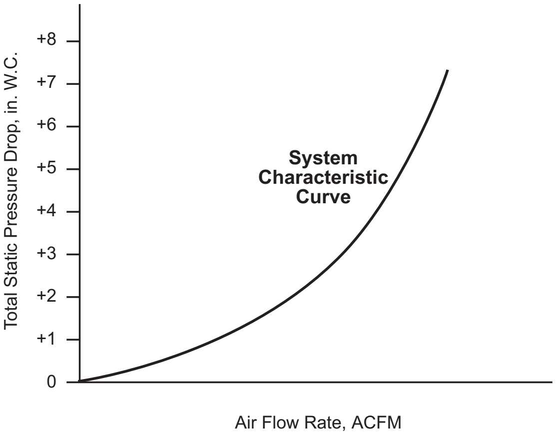


Figure 3-30. System characteristic curve

This general relationship between total system static pressure drop and air flow rate is term the system characteristic curve. For example, if the designer of the system needed 12,000 ACFM to achieve the necessary velocities in the system, he or she would know that the total static pressure drop across the system would be 10 in. W.C. Therefore, a fan would have to be found to generate an air flow of 12,000 ACFM at a fan static pressure rise of at least 10 in. W.C.

The use of the fan allows the air static pressure to be increased from the low level exiting the last air pollution control system, to a static pressure close to, or even slightly above ambient absolute pressure levels. This is illustrated in Figure 3-31 which is simply the completed version of the static pressure profile chart shown in Figure 3-29.

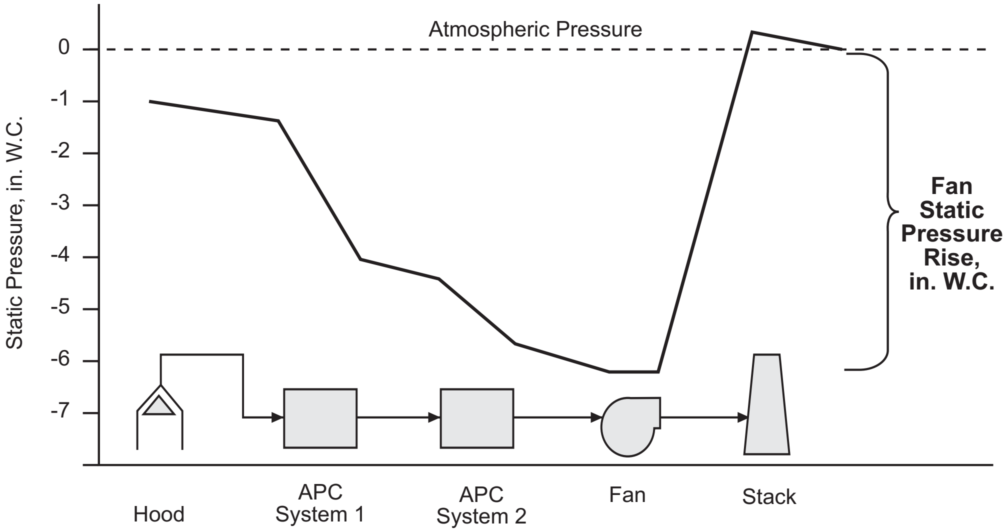
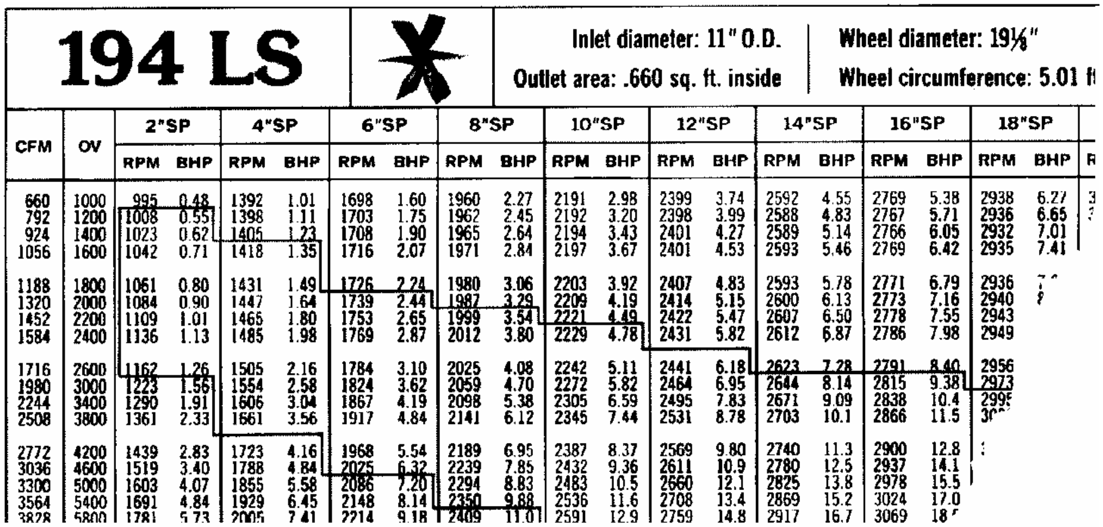


Figure 3-31. Fan static pressure rise profile

An appropriate fan is selected based on fan manufacturer's performance data. Usually, these data are provided in terms of multi-ratings tables published for each specific fan model and size. Based on these data it is possible to select a fan model, the specific model size, and the fan speed necessary to achieve the air flow rates and static pressure rise conditions necessary for the overall air pollution control system. An excerpt from a multi-rating table for a centrifugal fan is shown below in Figure 3-32.



194 LS

Inlet diameter: 11" O.D. | **Wheel diameter: 19⅛"**

Outlet area: .660 sq. ft. inside | **Wheel circumference: 5.01 f**

CFM	OV	2"SP		4"SP		6"SP		8"SP		10"SP		12"SP		14"SP		16"SP		18"SP	
		RPM	BHP	RPM	BHP	RPM	BHP	RPM	BHP	RPM	BHP	RPM	BHP	RPM	BHP	RPM	BHP	RPM	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	[illegible]
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	[illegible]
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	[illegible]	
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	[illegible]	
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	[illegible]	
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	2869	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	[illegible]		

Figure 3-32. 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 3-33 for the specific fan rotational speed chosen. As long as the overall system remains in good condition and the fan remains in good condition, the system will operate at the point shown in Figure 3-33. This is termed the *operating point*.

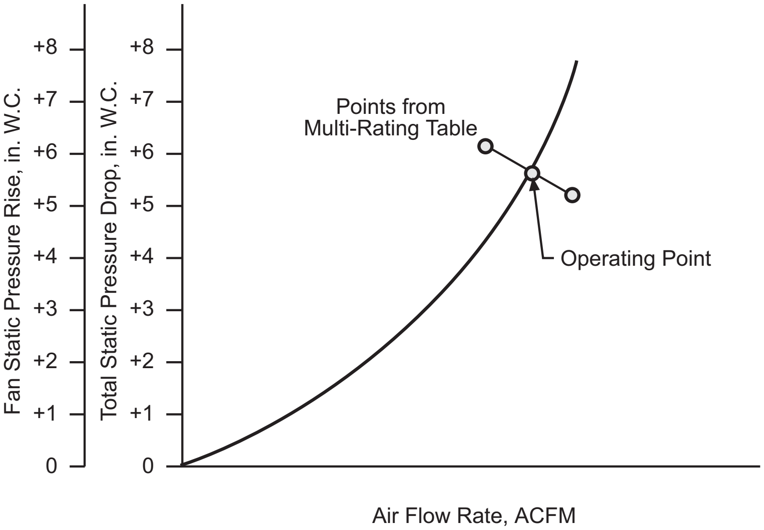


Figure 3-33. Operating point

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 3-33, it is convenient to simply delete the total system static pressure drop axis.

Figure 3-34 illustrates an example fan curve for a given fan speed. The multi-rating data used to select the fan represented a subset of the total data set that defines this fan curve. There is a specific fan curve for each fan model, model size, and speed. The intersection of the fan curve and the system characteristic curve is illustrated as Point A. This is the point that was determined previously by the system designer selecting the fan.

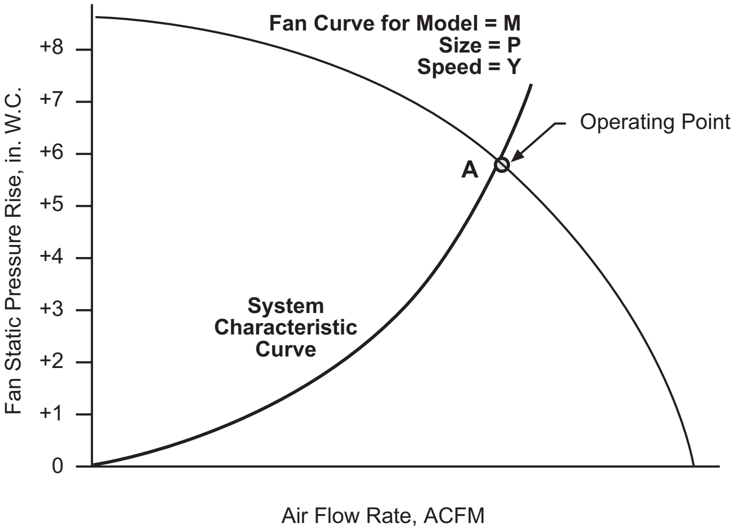


Figure 3-34. Fan characteristic curve

Air pollution control systems and other types of industrial ventilation systems, however, do not necessarily remain exactly at the conditions anticipated by the system designer and the fan manufacturer. A number of normal operating changes and operating problems can cause changes in the overall system air flow rates and the static pressure rises across the fan. The extent of the air flow and static pressure rise changes depend on the fan's performance conditions and the system characteristic curve. Some of these changes are illustrated in Figures 3-35 through 3-37.

If the gas flow resistance increases due to the build-up of dust in an air pollution control device or because a damper is closed, the system characteristic curve will shift upwards as indicated in Figure 3-35. With this increased gas flow resistance there will be a new operating point, labeled "B" in Figure 3-35. At this new operating point, the fan static pressure rise will be slightly higher while the air flow rate will be slightly lower.

If the air flow resistance decreases due to changes in an air pollution control device or opening of a damper, the system characteristic curve will shift downwards. This results in a new operating point (labeled "C") that has a slightly reduced fan static pressure and increased air flow rate.

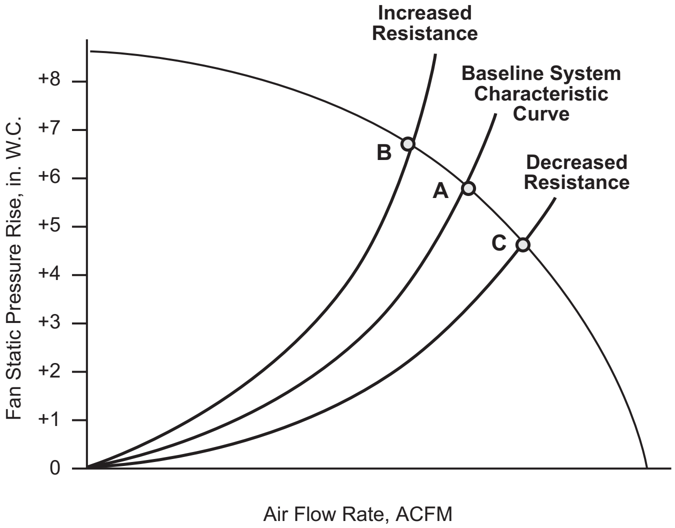


Figure 3-35. Changes in the system resistance curve

Some changes in the system characteristic curve are normal 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 individual 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 air flow rates.

When changes in the system characteristic curve are outside of the anticipated range, operators often have the option of modifying the fan to increase its capability. Most fans on industrial systems are selected to operate at a speed near the middle of its safe operating range. Slight increases in the fan speed can improve air flow rates and static pressure rises without exceeding the safe operating speed limits. The impact of a slight increase in the fan speed is illustrated in Figure 3-36.

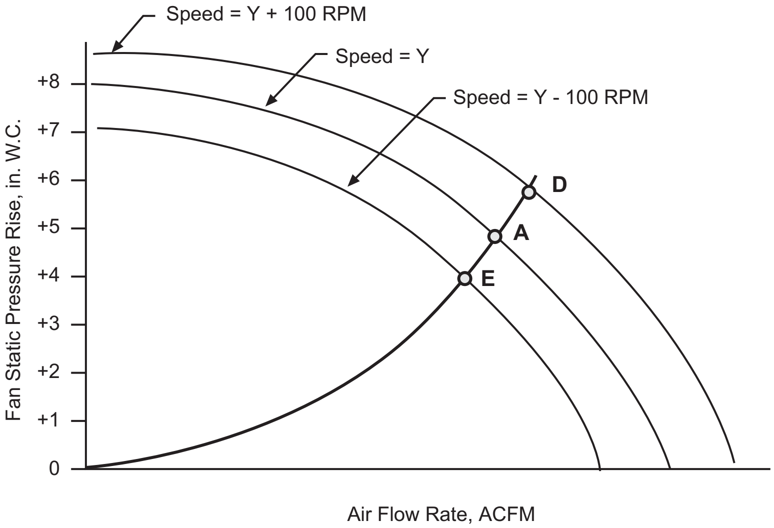


Figure 3-36. Changes in the fan speed

It is apparent that the 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 conditions represented by operating point "A." Not all fans can be easily adjusted to change the fan speed. For example, direct drive fans where the fan wheel shaft is directly driven by the fan motor operate only at the motor rotation speed and can not 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.

Some inadvertent reductions in fan speed are possible for belt driven fans. If the drive belts become slightly loose, they can slip as they move across the sheaves. This often results in a decreased air flow rate of 100 to 200 rpm. The decrease in the air flow rate is directly proportional to the decrease in the fan speed.

The operating point of a system can also be changed due to the opening and closing of a fan inlet damper. This is a special damper mounted immediately ahead of the fan and this damper changes how air enters fan wheel. Changes caused by the opening and closing of a fan inlet damper are illustrated in Figure 3-37. It is apparent that the operating point changes to lower air flow rates and fan static pressure rises as the inlet damper is closed.

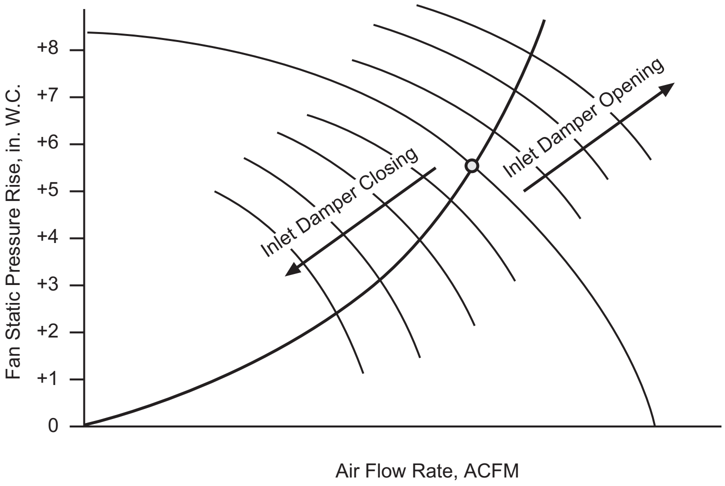


Figure 3-37. Changes in the inlet damper position

The fan inlet damper is often used to ensure safe opening of a fan that operates with air streams at elevated gas temperatures. During start-up when the air is cold, the fan inlet damper is kept partially closed to minimize the quantity of heavy cold air moved through the system. As the air heats and becomes less dense, the fan inlet damper opens to increase the air flow rate and fan static pressure rise. This approach minimizes the electrical power demand on the fan motor. Starting with the fan inlet dampers wide open would often exceed the safe current levels for the motor and thereby result in burnout of the motor windings. It is very important to avoid overloading fan motor currents.

Problem 3-12

A portion of a ventilation system is shown in Figure 3-38. 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.

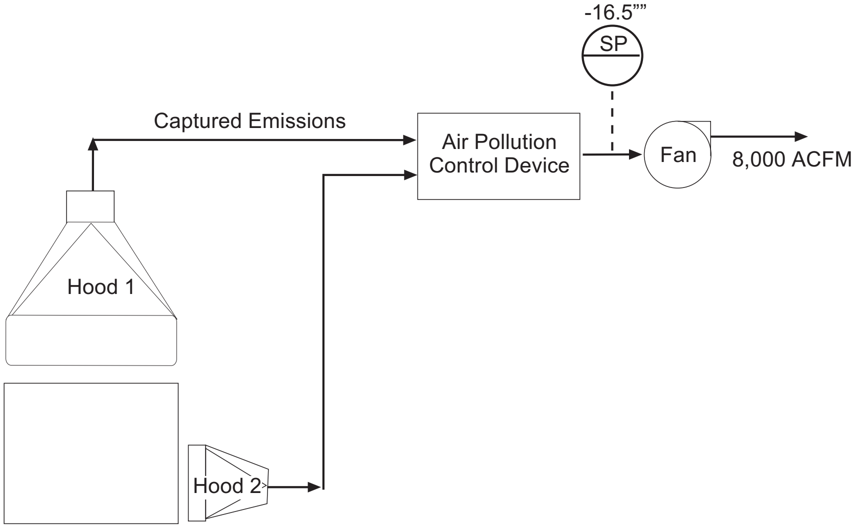


Figure 3-38. Portion of a ventilation system

Solution:

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

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

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 3-12 illustrates that an increase in the gas flow rate of 50% more than doubled the static pressure drop across the system. The static pressure drop for a set of hoods, ductwork, and air pollution control devices can be calculated using the "velocity pressure" methods described in the (ACGIH Industrial Ventilation Manual, 23rd edition). This calculation method takes into account the energy losses throughout the ventilation system. A partial list of these energy losses include the following:

- Turbulence at the hood inlet

- Acceleration of the gas from zero velocity to the velocity of the duct
- Frictional losses on the surfaces of the duct
- Turbulence losses at duct expansions and contractions
- Static pressure drop across the air pollution control device

Decreased system resistance can also be a problem. In this situation, the system operating point shifts to the right to a position of higher gas flow rate and lower static pressure rise. While this change would favor improved hood capture, it could reduce the collection efficiency of the air pollution control device. High gas velocities through certain types of air pollution control systems such as fabric filters, electrostatic precipitators, carbon bed adsorber, and catalytic oxidizers can reduce efficiency slightly.

It is helpful to be able to determine when the system characteristic curve has shifted. The most direct way to check the fan performance is to measure the gas flow rate. However, this is time consuming. The fan motor current data provides an indirect, but nevertheless very useful, indication of gas flow changes from the baseline conditions. An increase in fan motor current is generally associated with an increase in the gas flow rate. Decreases in fan current occur when the gas flow rate drops. 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 3-39. The fan motor current is directly proportional to the brake horsepower as indicated by Equation 3-26, which applies to three-phase motor.

$$\mathrm{BHP} = \frac{1 \times \mathrm{E} \times 1.73 \times \mathrm{Eff} \times \mathrm{P.F.}}{745} \tag{3-26}$$

Where:

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

While the shape of the horsepower curve varies for different types of fan wheels, the general relationship applies to all centrifugal fans in their normal operating range. As the horsepower increases, the gas flow rate increases.

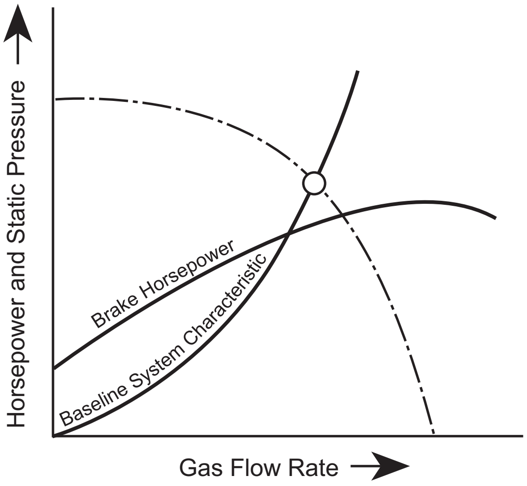


Figure 3-39. Example of a brake horsepower curve

The fan motor current is related directly to brake horsepower as indicated by Equation 3-26. Therefore, it provides a good indicator of changes in the gas flow rate. When the fan motor current has increased, the brake horsepower has probably increased, and, therefore, the gas flow rate has probably increased. However, the extent of the change cannot be determined from the simple relationship due to the nonlinearity of the brake horsepower curve and the variations in the power factor.

The brake horsepower is related to the cube of the fan speed as indicated in the third fan law shown below as Equation 3-27.

$$BHP_2 = BHP_1(RPM_2/RPM_1)^3 \tag{3-27}$$

Where:

BHP_1 = baseline brake horsepower (BHP)
BHP_2 = present brake horsepower (BHP)
RPM_1 = baseline fan wheel rotational speed (Revolutions Per Minute)
RPM_2 = present fan wheel rotational 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.

3.4.3 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 operating point moves a constant volume of air. While the volume is constant, the weight of the air being moved may not be constant. The density of the gas being handled by the fan is a strong function of the gas temperature. At high gas temperatures, the gas has a low density, and the gas is relatively light. When the gas temperature is cold, for example at ambient temperature, the gas is dense, and its weight is substantial.

Table 3-14. Gas Densities at Different Gas Temperatures

Gas Temperature °F	**Gas Density[1] lb_m/ft^3**	**Gas Temperature °F**	**Gas Density[1] lbm/ft^3**
32	0.081	600	0.037
60	0.076	700	0.034
68	0.075	800	0.032
70	0.075	900	0.029
100	0.071	1000	0.027
150	0.065	1200	0.024
200	0.060	1400	0.021
250	0.056	1600	0.019
300	0.052	1800	0.018
400	0.046	2000	0.016
500	0.041	2500	0.013

1. Gas density at standard pressure of 407 in. W.C. and zero moisture level

In addition to gas temperature, gas density is also a function of the absolute gas pressure. The absolute pressure can be taken into account using Equation 3-28.

$$\rho_{\text{Actual}} = \rho_{\text{STP}}\left(\rho_{\text{Actual}} / \rho_{\text{STP}}\right) \tag{3-28}$$

Where:

ρ_{Actual} = gas density at actual conditions ($\text{lb}_m/\text{ ft}^3$)

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

P_{STP} = gas pressure at standard conditions (in. W.C.)

P_{Actual} = gas pressure at actual conditions (in. W.C.)

The gas density has a direct effect on the fan motor current. The current will be high when the gas stream is cold such as the times when the process is starting up. 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 this, the fan inlet or outlet dampers are usually partially closed during start-up to restrict the amount of "dense" air being handled. As the process heats up and the gas stream becomes less dense, the dampers can be opened to permit normal gas flow rates.

When using the fan motor current as an indicator of gas flow rate, it is important to correct the motor currents at the actual conditions back to standard conditions. This correction can be performed using Equation 3-9.

$$I_{\text{STP}} = I_{\text{Actual}}\left(\rho_{\text{STP}} / \rho_{\text{Actual}}\right) \tag{3-29}$$

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

Problem 3-13

A fan motor is operating at 80 amps and the gas flow 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 mole of gas. Assume 1 lb mole of gas has a mass of 29 pounds.

1. Convert pressure from inches of water to psia.

$$\begin{aligned}\text{psia} &= \frac{\left(407\text{ in. W.C.} - 10\text{ in. W.C.}\right)}{407\text{ in. W.C.}} \times \left(14.7\text{psia}\right)\\ &= 14.34\text{ psia}\end{aligned}$$

2. Calculate the gas volume at actual conditions using the ideal gas law equation.

$$V = nRT/P$$

$$V = \left[\frac{10.73\ \text{psia} \bullet \text{ft}^3}{°\text{R} \bullet \text{lb mole}}\right]\frac{(460°\text{F} + 300°\text{F})}{14.34\text{psia}}$$

$$= 568.7\ \text{ft}^3/\text{lb mole}$$

3. Calculate the gas density, ρ.

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

$$\text{Mass} = 29\ \text{lb}_m/\text{lb mole}$$

$$\text{Volume} = 568.7\ \text{ft}^3/\text{lb mole (at actual conditions)}$$

$$\rho = \frac{29\ \text{lb}_m}{568.7\ \text{ft}^3}$$

$$= 0.051\ \text{lb}_m/\text{ft}^3$$

Step 2. Calculate the gas density at standard conditions.

1. Calculate the gas volume at standard conditions using the ideal gas law.

$$V = \left[\frac{10.73\ \text{psia} \bullet \text{ft}^3}{°\text{R} \bullet \text{lb mole}}\right]\frac{(460°\text{F} + 68°\text{F})}{14.7\ \text{psia}}$$

$$= 385.4\ \text{ft}^3/\text{lb mole}$$

2. Calculate the gas density, ρ.

$$\rho = 29\ \text{lb}_m/385.4\ \text{ft}^3 = 0.075\ \text{lb}_m / \text{ft}^3$$

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

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

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

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

$$= 118\ \text{amps}$$

Note 1: The problem could have been solved quickly by using tabulated values of the gas density. However, this approach also reduces the risk of a gas density error caused by not taking into account the effect of pressure changes.

> Note 2: The gas composition in Problem 3-13 could be taken into account by calculating the weighted average molecular weights of the constituents rather than assuming 29 pounds per pound mole, which is close to the value for air. This correction is important when the gas stream has a high concentration of compounds such as carbon dioxide or water, which have molecular weights that are much different than air.

The gas temperature and gas 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 temperature of a gas may increase, decrease, or remain constant when a pressure change occurs. When the gas flow reaches the fan, the gas flow changes from negative to positive pressure. This increase in pressure can cause the temperature to increase slightly.

Summary

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 dampers and/or outlet dampers.

The intersection of the fan characteristic curve and the system characteristic curve is called the operating point for the fan. The factors that affect the fan characteristic curve are the type of fan wheel and blade, the fan wheel rotational speed, and the shape of the fan housing. The system characteristic curve takes into account the energy losses throughout the ventilation system. These curves are helpful indicators in determining if a change in the system has occurred. A change in the system can also be detected through the fan motor current data that corresponds with the gas flow rate, however not linearly.

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

A fan will move a constant volume of air; however the amount of work required to move the gas flow is dependent on the density of the gas. Two factors that affect density are temperature and pressure. The gas flow density has a direct effect on the fan motor current.

Review Exercises

Use the drawing shown below to answer questions 1-3.

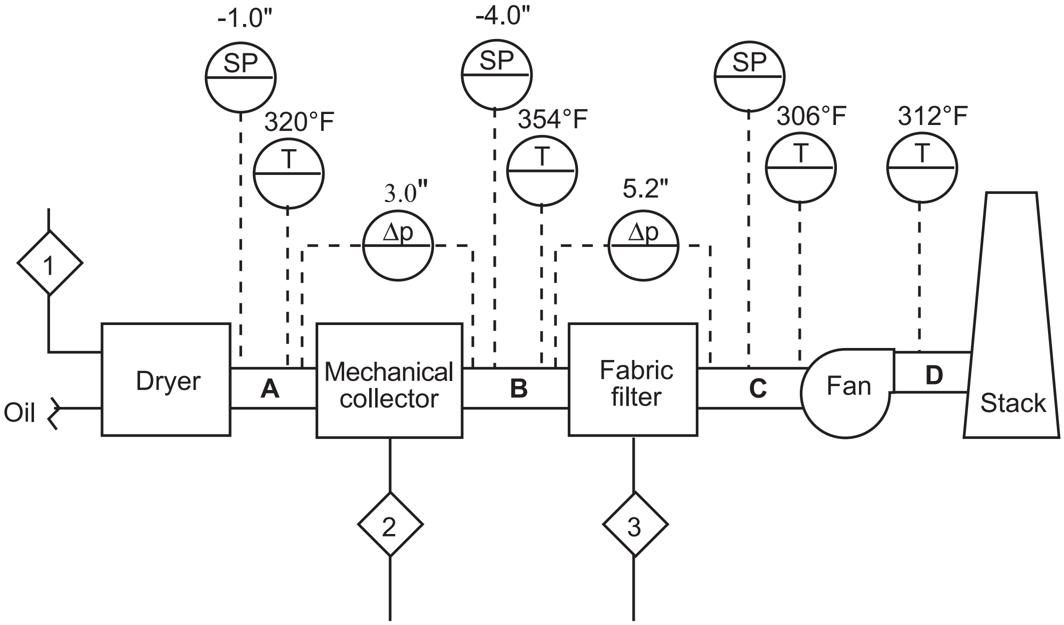


Figure 3-40. Example flowchart

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 gas temperature is 350°F and the gas pressure is –32 in. W.C. The gas flow rate in Duct B is 4,000 ACFM, the gas temperature is 400°F, and the gas pressure is –35 in. W.C. Calculate the total gas flow rate in a combined Duct C 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 2000 ACFM. The equation for a flanged hood is:

$$Q = (0.75)\, v_h \left[10(X)^2 + A_h\right]$$

   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 is moving 1,000 cubic feet of air per minute at a temperature of 450°F and a fan inlet pressure of -15 inches of water. What will the actual air flow rate be if the gas temperature decreases to 68°F, the inlet pressure remains unchanged, and the fan rotational speed remains the same?
   a. The air flow rate will increase to 1,5800 ACFM.
   b. The air flow rate will decrease to 580 ACFM.
   c. The air flow rate will remain at 1000 ACFM.

10. A centrifugal fan is operating with a motor current of 120 amps. The gas density entering the fan during normal operation 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 are no gas density changes 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 collection efficiency of 95%. If the process served by this system is generating 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. 11.2 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. Using the fan laws determine the new RPM, brake horsepower, and static pressure when the volumetric 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.

    The system characteristic curve will shift up, the volumetric flow rate will increase, and the hood static pressure will decrease.

Review Answers

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

   d. They all appear logical.

   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.)

   c. -9.2 in. W.C.

   Solution:

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

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

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

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

   The temperatures should decrease as the gas moves through the system since no significant source of heat 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. Other wise the temperature trend appears logical.

4. The gas flow rate is duct A is 5,000 SCFM, the gas temperature is 350°F and the gas pressure is –32 in.W.C.. The gas flow rate in duct B is 4,000 ACFM, the gas temperature is 400°F, and the gas pressure is –35 in. W.C. Calculate the total gas flow rate in a combined duct C 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

$$\mathrm{SP} = \left(\frac{407\ \text{in. W.C.}}{29.92\ \text{in. Hg.}}\right) 29.15\ \text{in.H.G.} + (-32\ \text{in. W.C.})$$

$$= 364.5\ \text{in. W.C.}$$

   Convert the flow in duct B to SCFM

$$\mathrm{SCFM} = 4000\ \mathrm{ACFM}\left(\frac{528°\mathrm{R}}{460°\mathrm{R} + 400°\mathrm{F}}\right)\left(\frac{407\ \text{in. W.C.}}{364.5\ \text{in. W.C.}}\right)$$

$$= 2{,}742\ \mathrm{SCFM}$$

   Flow in Duct C = Flow in Duct A + Flow in Duct B =5,000 SCFM + 2,740 SCFM = 7,740 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.

   b. -1.15 in. W.C.

   Solution:

   To calculate the hood static pressure (SP_h), use the following equation:

$$SP_h = -VP_d - h_e$$

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

      At standard conditions, $\rho_{Actual} = 0.075\ lb_m/ft^3$.

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

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

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

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

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

$$VP_d = 0.77$$

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

$$h_e = F_h(VP)$$

      Given: $F_h = 0.49$

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

$$= 0.38\ in.\ W.C.$$

   3. Calculate the hood static pressure (SP_h).

$$SP_h = -0.77\ in.\ W.C. - 0.38\ in.\ W.C.$$

$$= -1.15\ in.\ W.C.$$

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 2000 ACFM. The equation for a flanged hood is:

$$\mathrm{Q} = (0.75)\,\mathrm{v_h}\left[10(\mathrm{X})^2 + \mathrm{A_h}\right]$$

   d. 11 inches

Solution:

1. Solve for X using the following equation.

$$Q = (0.75)\,\mathrm{v_h}\left[10(X)^2 + A_h\right]$$

$$\frac{2000\,\mathrm{ACF}}{\mathrm{min}} = \left(\frac{0.75}{1}\right)\left(\frac{300\,\mathrm{ft}}{\mathrm{min}}\right)\left[10(\mathrm{X\,ft})^2 + \left(\frac{72\,\mathrm{in}^2}{1} \times \frac{1}{144\,\mathrm{in}^2}\right)\right]$$

$$2000\,\mathrm{ACFM} = \left(\frac{225\,\mathrm{ft}}{\mathrm{min}}\right)\left[10(\mathrm{X\,ft})^2 + 0.5\mathrm{ft}^2\right]$$

$$8.89\,\mathrm{ft}^2 = 10(\mathrm{X\,ft})^2 + 0.5\mathrm{ft}^2$$

$$8.39\,\mathrm{ft}^2 = 10(\mathrm{X\,ft})^2$$

$$0.839\,\mathrm{ft}^2 = (\mathrm{X\,ft})^2$$

$$X = 0.916\,\mathrm{ft} \times \frac{12\,\mathrm{in.}}{1\,\mathrm{ft}} = 11\,\mathrm{in.}$$

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

   Motor rotational speed, $\mathrm{RPM_{Motor}}$ = 1778 RPM
   Motor sheave diameter, $\mathrm{D_{Motor}}$ = 8 in.
   Fan sheave diameter, $\mathrm{D_{Fan}}$ = 14 in.
   d. 1016 $\mathrm{RPM_{fan}}$

Solution:

Calculate the fan speed ($\mathrm{RPM_{fan}}$) using the following equation.

$$\mathrm{RPM_{Fan}} = \mathrm{RPM_{Motor}} \times \frac{\mathrm{D_{Motor}}}{\mathrm{D_{Fan}}}$$

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

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).

   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 is moving 1,000 cubic feet of air per minute at a temperature of 450°F and a fan inlet pressure of -15 inches of water. What will the actual air flow rate be if the gas temperature decreases to 68°F, the inlet pressure remains unchanged, and the fan rotational speed remains the same?

   c. The air flow rate will remain at 1000 ACFM

   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 during normal operation 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.

    b. 200 amps

    Solution:

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

$$= 120\text{ amps}\frac{\left(0.075\text{ lb}_m/\text{ft}^3\right)}{\left(0.045\text{ lb}_m/\text{ft}^3\right)} = 200\text{ amps}$$

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 are no gas density changes associated with the increased gas flow rate.

    a. -3.07 in W.C.

    Solution:

$$\frac{SP_{@\text{ High flow}}}{SP_{@\text{ Low flow}}} = \frac{(8{,}000\text{ ACFM})^2}{(5{,}000\text{ ACFM})^2} = 2.56$$

Given: $SP_{@\text{ Low flow}}$ = -1.2 in. W.C.

$SP_{@\text{ High flow}}$ = -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 collection efficiency of 95%. If the process served by this system is generating 140 pounds of pollutant per hour, calculate the fugitive emissions and the stack emissions.

    c. 11.20 lb_m/hr Fugitive emissions and 6.44 lb_m/hr Stack emissions

    Solution:

$$\text{Fugitive emissions} = (140\ \text{lb}_\text{m}/\text{hr})\frac{(100\% - 92\%)}{100\%} = 11.2\ \text{lb}_\text{m}/\text{hr}$$

$$\text{Capture emissions} = 140\ \text{lb}_\text{m}/\text{hr} - 11.20\ \text{lb}_\text{m}/\text{hr} = 128.8\ \text{lb}_\text{m}/\text{hr}$$

$$\text{Stack emissions} = (128.8\ \text{lb}_\text{m}/\text{hr})\frac{(100\% - 95\%)}{100\%} = 6.4\ \text{lb}_\text{m}/\text{hr}$$

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. Using the fan laws determine the new RPM, brake horsepower, and static pressure when the volumetric increases to 22,500.

    d. 450 RPM, 17.1BHP, -3.2 in. W.C.

    Solution:

New fan speed:

$$\frac{Q_2}{Q_1} = \frac{\text{RPM}_2}{\text{RPM}_1}$$

$$\frac{22{,}500\ \text{ACFM}}{20{,}000\ \text{ACFM}} = \frac{\text{RPM}_2}{400\ \text{RPM}}$$

$$\text{RPM}_2 = 450\ \text{RPM}$$

Brake horsepower:

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

$$\frac{\text{BHP}_2}{12\ \text{BHP}} = \frac{91{,}125{,}000}{64{,}000{,}000}$$

$$\text{BHP}_2 = 17.1\ \text{BHP}$$

Static pressure:

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

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

$$SP_2 = -3.2\,\text{in. W.C.}$$

14. What would happen to a fan's desired operating point 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.

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

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

References

1. American Conference of Governmental Industrial Hygienists, *Industrial Ventilation - A Manual of Recommended Practice*, 23rd Edition, 1998.
2. Cengel, Yunus A., Boles, Michael A., *Thermodynamics An Engineering Approach*. McGraw-Hill Publishing. 19893
3. Code of Federal Regulations, 40 Part 60, Method 22, July 1, 1997

Chapter 4
Adsorption

Adsorption processes have been used since the 1950s for the high efficiency removal of a wide variety of organic vapors and several types of inorganic gases. 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.

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 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 uneconomical to discard the absorbent. 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. Adsorber systems that operate continuously must have (1) multiple, fixed beds of adsorbent, (2) fluidized bed contactors with separate 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 being used as preconcentrators for thermal or catalytic oxidizer systems. The high concentration, low gas 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 has expanded 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 time 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. The onset of these problems can usually be identified by shifts in the operating conditions and by increases in the stack contaminant concentrations.

4.1 TYPES AND COMPONENTS OF ADSORPTION SYSTEMS

4.1.1 Adsorbents

During adsorption, vapor phase compounds in the gas stream pass through a bed or layer of highly porous material called the *adsorbent*. The vapor phase compounds, termed the *adsorbate*, diffuse to the surface of the adsorbent and are retained because of weak attractive forces. Adsorption occurs on the internal surfaces of the materials as shown in Figure 4-1.

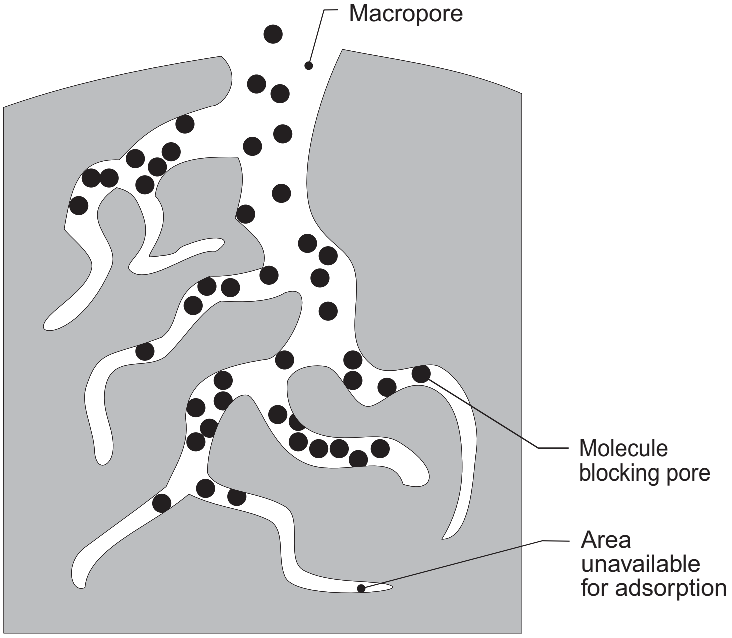


Figure 4-1. Vapor adsorbed into pores of adsorbent

Types of Adsorbents

The most common types of adsorbents are activated carbons, zeolites (molecular sieves), and synthetic polymers. Other types of adsorbents include silica gel and activated alumina.

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. First, the feedstock is carbonized. This involves heating the material in the absence of air to a temperature high enough (e.g., 1,100°F (590°C)), to drive off all volatile material. Carbon and small quantities of ash are all that is left. 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 x 6 and 4 x 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 gm/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/gm.

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.

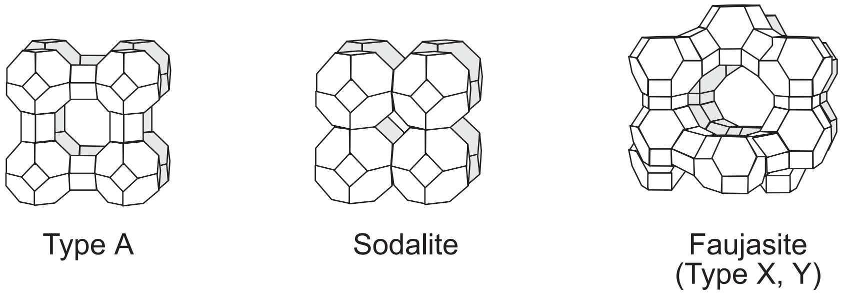


Figure 4-2. Sketches of zeolites[3]
(Reprinted by permission of Chemical Engineering Progress,
American Institute of Chemical Engineers)

The main uses of molecular sieves have been to remove moisture from exhaust streams, to separate hydrocarbons in refining processes, and to remove nitrogen oxides compounds from air pollution sources. Because of the development of new synthetic zeolites, their applications are expanding into the VOC control field. The surface areas of molecular sieves range from 590 to 700 m^2/gm.

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/gm.[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 desorbed more rapidly than activated carbon adsorbents. They can be desorbed with 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 monomers that can undergo various chemical reactions on the surfaces of activated carbon.

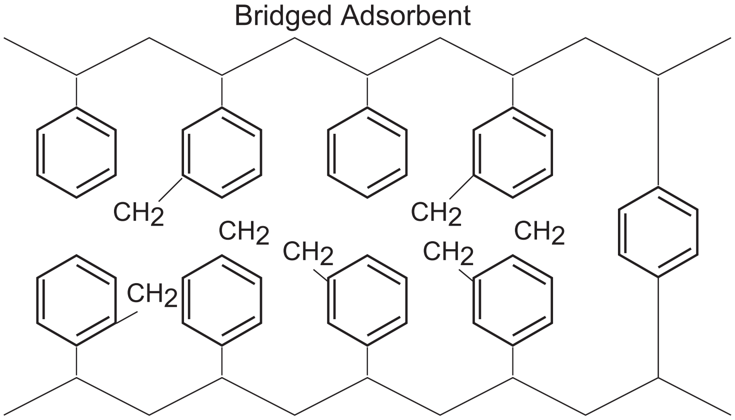


Figure 4-3. Example synthetic polymer
(Reprinted courtesy of Dow Chemical, Inc.; Midland, Michigan)

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/gm. 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). Aluminum oxides are manufactured by heating alumina in an inert atmosphere to produce a porous aluminum oxide pellet. Aluminum oxides are not commonly used in air pollution applications. They are used primarily for drying gases, especially under high pressures, and as support material in catalytic reactions. A prime example of the latter is the depositing of alumina with platinum or palladium for use in catalytic incineration. The surface area of activated alumina adsorbents can range from 2 to 300 m^2/gm.

4.1.2 Characteristics of Adsorbents

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[2]	**Internal Porosity, (%)**	**Surface Area, (m^2/gm)**	**Pore Volume, (cm^3/gm)**	**Bulk Dry Density, (gm/cm^3)**	**Mean Pore Diameter, (Å)**
Activated Carbon	55-75	600-1600	0.80-1.20	0.35-0.50	1500-2000
Activated Alumina	30-40	200-300	0.29-0.37	0.90-1.00	1800-2000
Zeolites (Molecular Sieves)	40-55	600-700	0.27-0.38	0.80	300-900
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]
2. Data on silica gels not available.

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. 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 are openings whose diameters are 10-100 Angstroms (Å, Angstrom = 1.0 x 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.

Most gaseous air pollutant molecules are in the 400 to 900 Angstrom size range. If a large portion of an adsorbent's surface area is in pores smaller than 400 Angstroms, many contaminant molecules will be unable to reach these sites.

The large pores serve mainly as passageways to the smaller micropore areas where the adsorption forces are strongest. These forces are strongest in pores that are smaller than approximately twice the size of the contaminant molecule. These strong adsorption forces result from the overlapping attraction of the closely spaced walls.

Capillary condensation occurs when multilayers 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.

4.1.3 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 air flow 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 up to two years for trace concentrations or intermittent operations.[7] Nonregenerative adsorption systems are used mainly as air purification devices for small air flow 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.

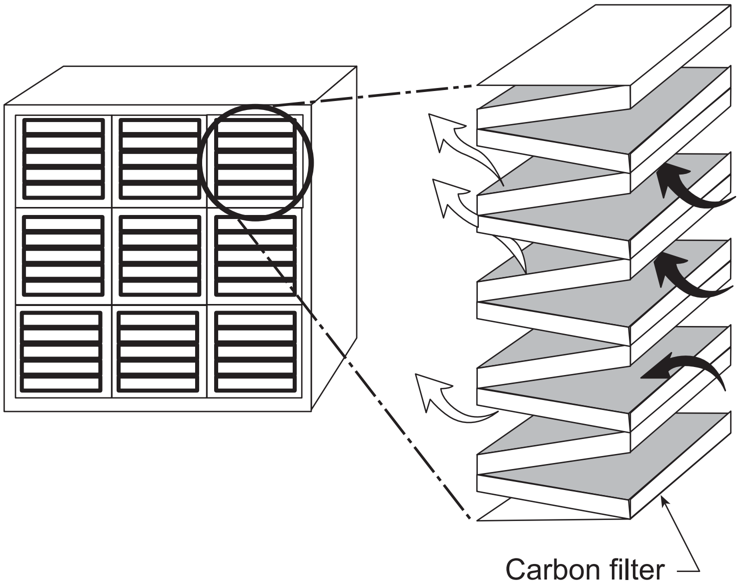
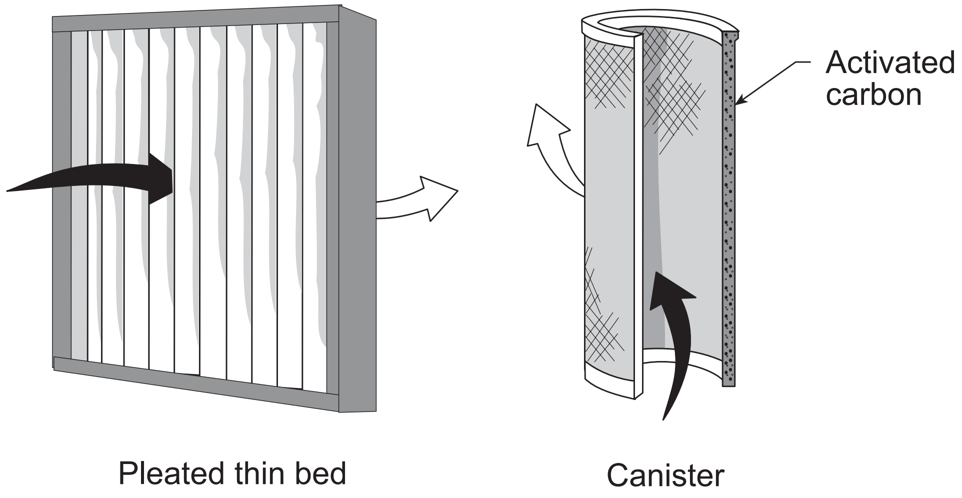


Figure 4-4. Thin-bed adsorber — nine cell system

The pleated cell adsorber (Figure 4-5) is one continuous retainer of activated carbon, rather than individual panels. The cylindrical canisters (Figure 4-5) are usually small units designed to handle low flow rates of approximately 25 ACFM (0.7 m^3/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 m^3/min), while pleated beds are limited to flow rates of 1,000 ACFM (28 m^3/min).



Figures 4-5. Nonregenerative adsorbers

Thick bed nonregenerative systems are also available. One system that can be used is essentially a 55-gallon drum. The bottom is filled with gravel to support a bed of activated carbon weighing approximately 150 lb_m (70 kg). A typical unit is shown in Figure 4-6. These units are used to treat small flow rates of 100 ACFM (2.8 m^3/min) from laboratory hoods, chemical storage tank vents, or chemical reactors.

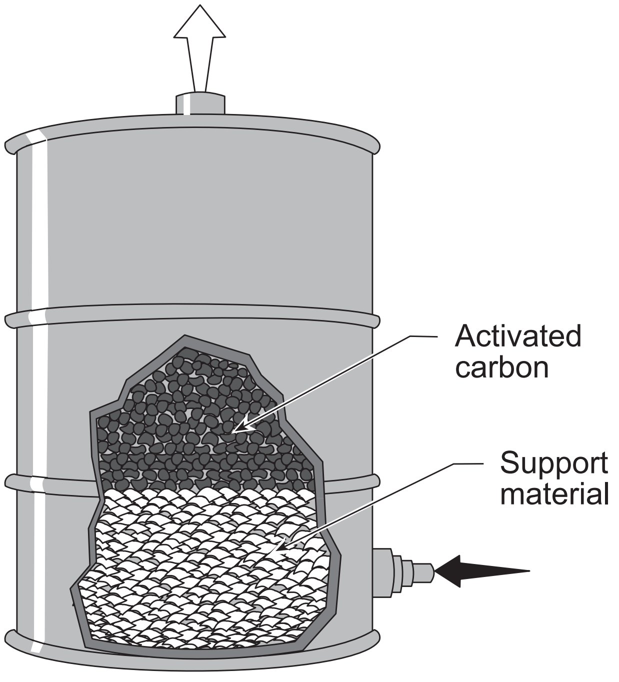


Figure 4-6. Nonregenerative canister adsorber

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

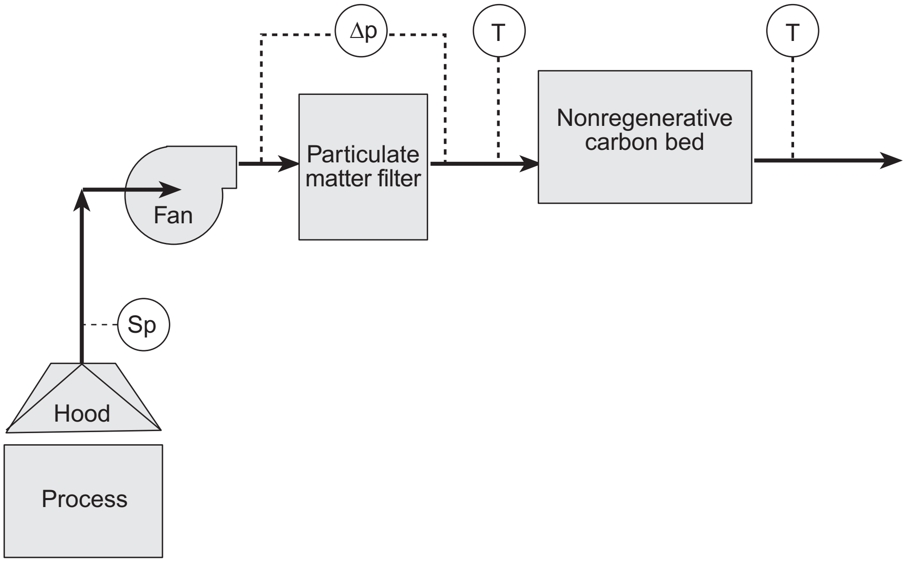


Figure 4-7. Flowchart of a simple, nonregenerative adsorber

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 indicates that the service life of the activated carbon may 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.

Some of the nonregenerative units have particulate matter filters 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. 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 - Fixed Bed Designs

Large regenerative adsorption systems can be categorized as *fixed*, *moving*, or *fluidized* beds. The name refers to the manner in which the vapor 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 carbon beds are a common adsorption system for controlling air pollutants. These systems are used to control a variety of organic vapors and are often regenerated by low-pressure steam. They are best used for solvents that are immiscible with water. The organic compounds may be recovered by condensing the exhaust from the regeneration step and separating the water and the solvent.

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 three-bed adsorption system is shown in Figure 4-8.

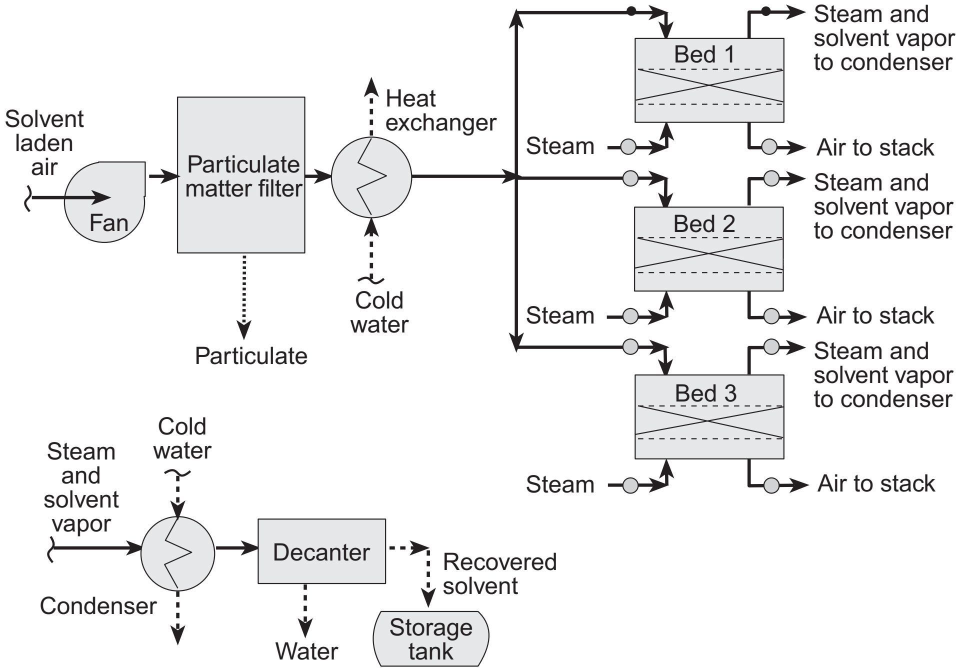


Figure 4-8. Multi-bed, fixed-bed type adsorption system

The SLA stream is first pretreated to remove any solid particles that could plug the carbon bed and, thereby, 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 40°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. Gas flow is usually passed downward through the fixed carbon bed. Upward flow through the bed is avoided to eliminate the risk of entraining carbon particles in the exhaust stream.

During desorption, the bed is isolated from the solvent laden airflow. Steam is then injected to remove the adsorbed vapors. The steam and desorbed vapors are then usually sent to a recovery system. If the solvents are immiscible in water, condensing the exhaust and decanting the solvent can separate them. If the solvents are miscible in water, distillation may be required. Before the adsorber bed is returned to service, the activated carbon should be cooled and dried. This prevents an initially poor collection efficiency of organic vapors caused by the carbon bed being "hot" and "wet."

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) with 100 ft/min being a maximum normal flow rate. 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 4-9.

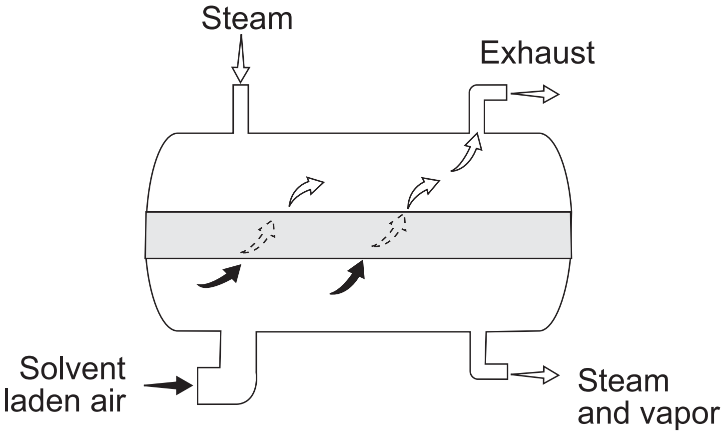


Figure 4-9. Cutaway sketch of horizontal adsorber vessel

Adsorbers of this type are manufactured as a package system capable of handling flow rates up to 400,000 ACFM (11,500 m^3/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. A flowchart for a "multi-pass" system is shown in Figure 4-10. This approach is also called *series/parallel*.

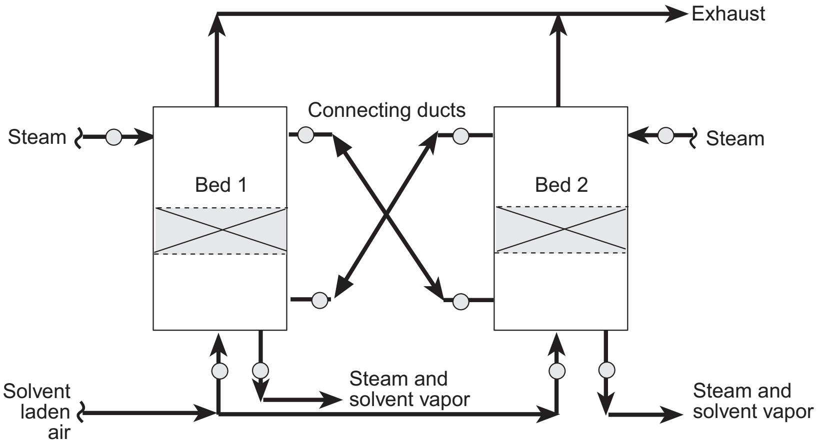


Figure 4-10. Series/parallel fixed-bed system

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 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 those for the conventional deep bed, carbon pellet designs. A flowchart of a two bed, carbon fiber adsorber is shown in Figure 4-11.

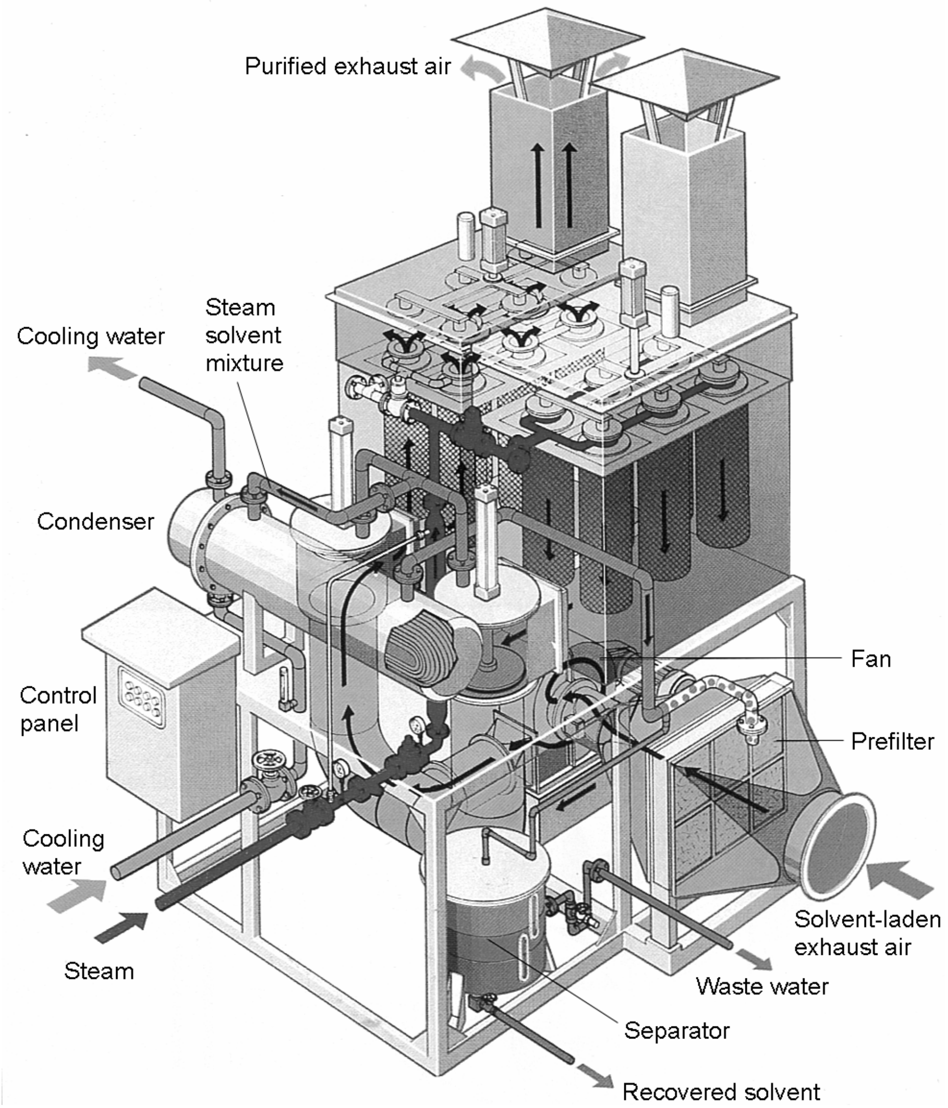


Figure 4-11. Carbon fiber system
(Reprinted courtesy of Durr Industries, Inc.; Plymouth, Michigan)

Regenerative Adsorption Systems – Moving Bed Designs

Moving bed systems can use a carbon bed more effectively than a fixed-bed system. In moving bed systems, 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, such as the unit shown in Figure 4-12. The zeolite adsorbent is mounted in a vertical 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 stream that is concentrated approximately a factor of 10 to 15 over the inlet level. The desorbed stream had 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%

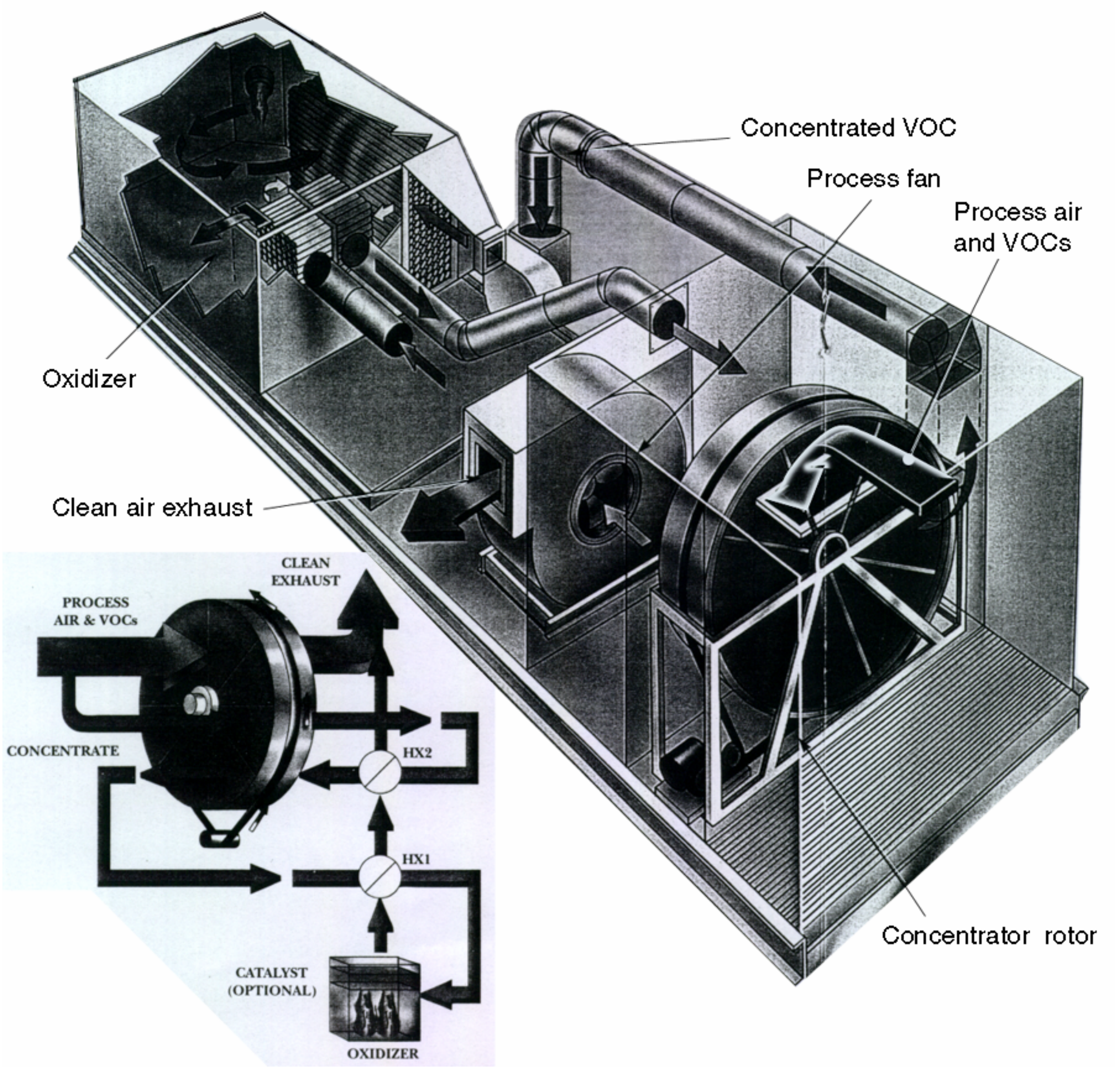


Figure 4-12. Rotary wheel zeolite adsorber

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 absorbent 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.

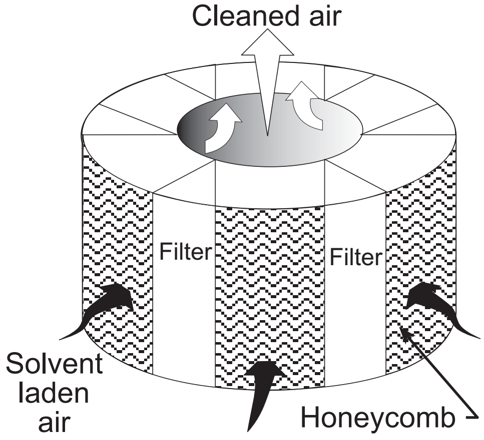


Figure 4-13a. Rotor for carbon fiber system

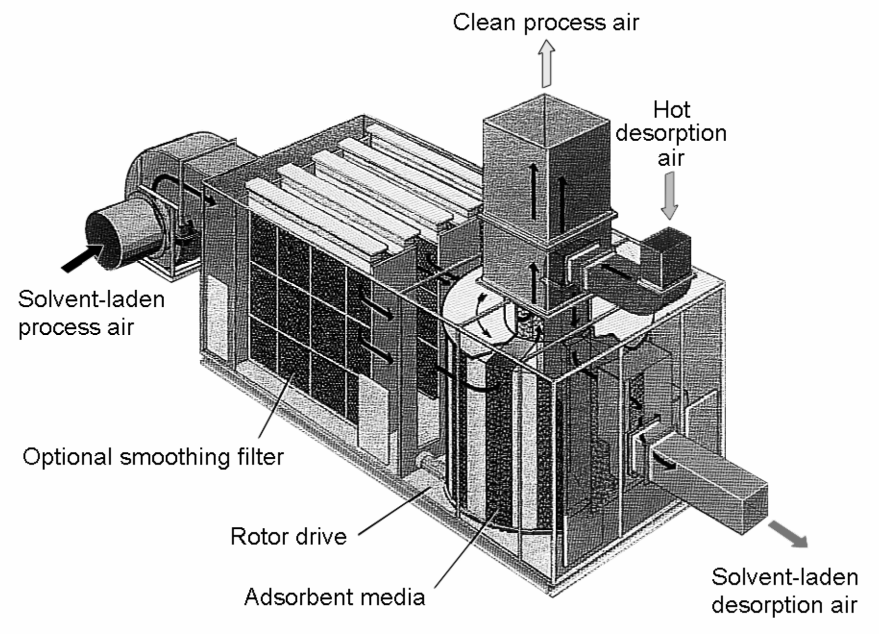


Figure 4-13b. Rotor system
(Reprinted courtesy of Durr Industries, Inc.; Plymouth, Michigan)

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 uses the motion of the solvent-laden air stream to entrain adsorbent material and thereby facilitate good gas-adsorbent contact. Figure 4-14 shows a fluidized bed system. The solvent-laden air stream is introduced at the bottom of the vessel and passes upward through a set of two to six beds. The movement of the gas stream fluidizes the adsorbent. The adsorbent flows down through the vessel from tray to tray until it reaches the desorption section. The adsorbent is pneumatically conveyed to a desorption vessel for regeneration. Regeneration is accomplished by indirect contact with steam or with hot air from a thermal or catalytic incinerator (as shown in Figure 4-14). The desorbed adsorbent is then conveyed back to the top of the adsorption vessel. Because the adsorption and desorption processes are physically separate, organic contaminants can be concentrated by a factor of 10 to 50.

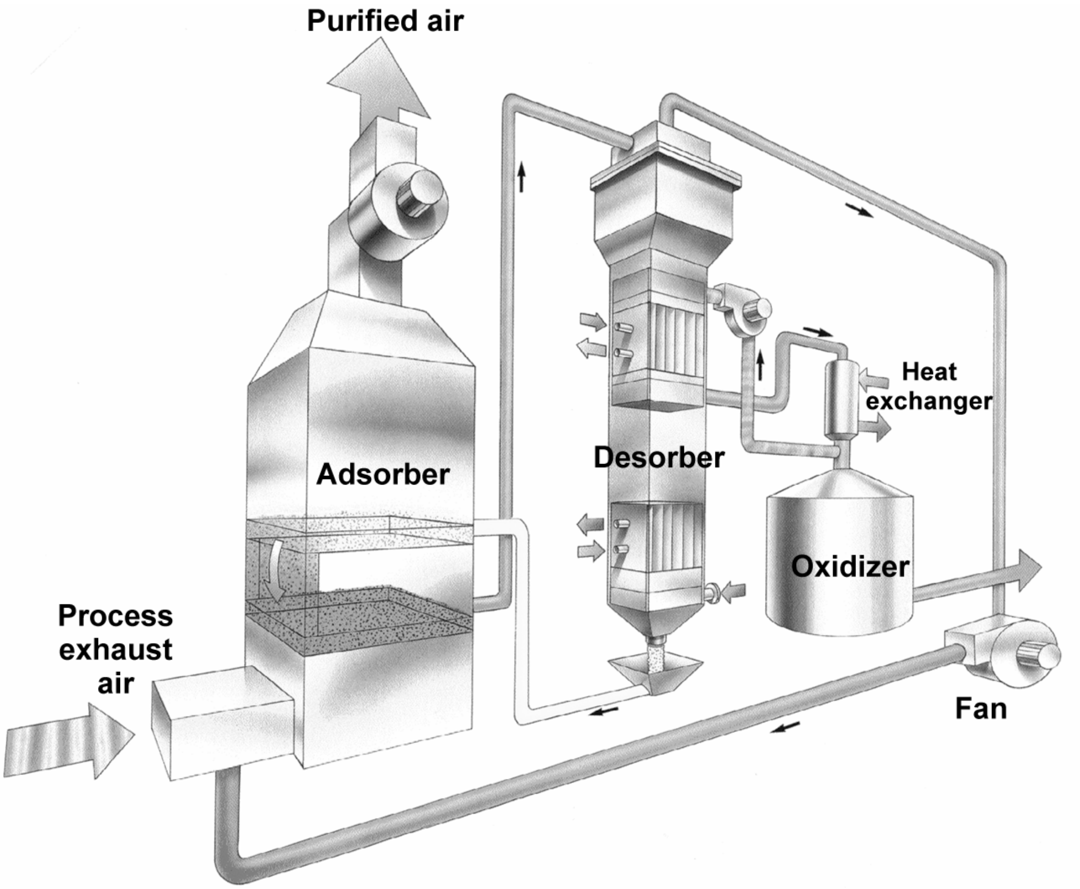


Figure 4-14. Fluidized bed adsorber
(Reprinted courtesy of Weatherly, Inc.; Atlanta, Georgia)

As with the moving bed, the fluidized bed also provides continuous operation and more efficient utilization of the adsorbent. These systems can be used with either polymeric adsorbents or activated carbon adsorbents. With activated carbon, it is necessary to use a form 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.

4.2 OPERATING PRINCIPLES

4.2.1 Adsorption Steps

Adsorption occurs in a series of three steps. In the first step, the contaminant diffuses from the bulk gas stream to the external surface of the adsorbent material. In the second step, the contaminant molecule migrates from the relatively small area of the external surface (a few square meters per gram) to 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 adheres to the surface in the pore. Figure 4-15 illustrates this overall diffusion and adsorption process.

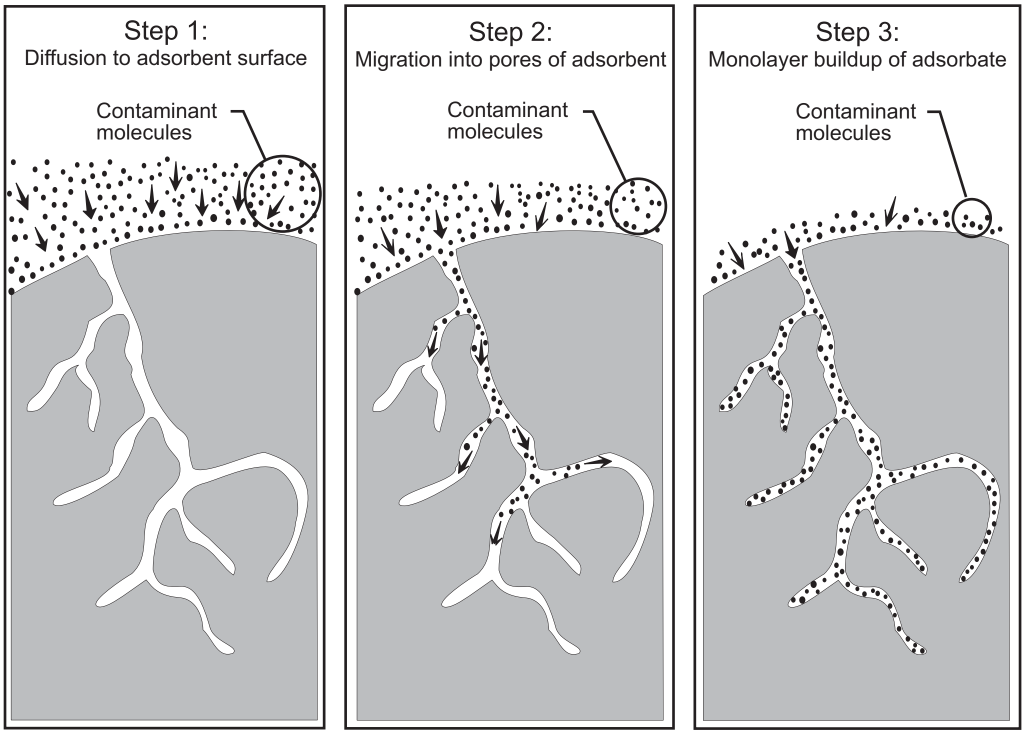


Figure 4-15. Adsorption steps

Steps 1 and 2 are diffusional processes that 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 occurs more rapidly than steps 1 and 2.

4.2.2 Adsorption Forces

The adsorption process is classified as either *physical* or *chemical*. The basic difference between physical and chemical adsorption is the manner 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 chemical bond is formed between the gas molecule and adsorbent. Chemical adsorption is not easily reversed.

Physical Adsorption

The forces active in physical adsorption 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 multilayers 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. This separation of positive and negative charges 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 occur from three different effects: orientation, dispersion, or induction (Figure 4-16). For polar molecules, attraction to each other occurs because of the *orientation effect* that describes the attraction occurring between the dipoles of two polar molecules. The negative area of one is attracted to the positive area 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).

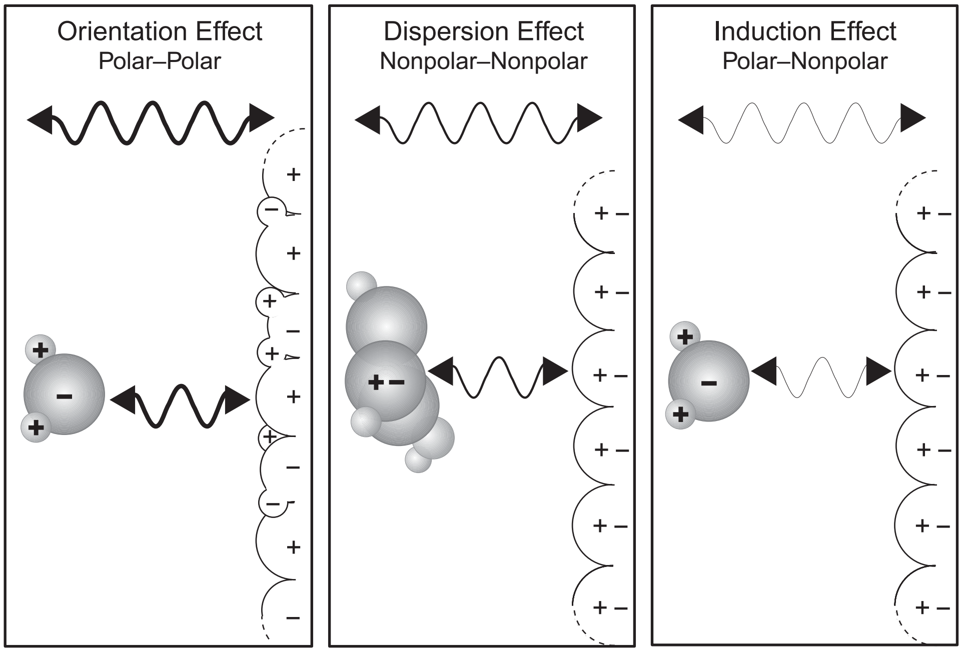


Figure 4-16. Physical forces causing adsorption

The adsorption of a nonpolar gas molecule onto a nonpolar surface is accounted for by the *dispersion effect*. The dispersion 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 or polarize 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, very 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 the 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. In adsorption, molecules are transferred from the gas to the surface of a solid. The fast-moving gas molecules lose kinetic energy to the solid adsorbent in the form of heat.

In chemisorption, the heat of adsorption is comparable to the heat evolved from a chemical reaction, usually over 10 Kcal/gm moles. The heat given off by physical adsorption is much lower, approximately 0.1 Kcal/gm mole, which is comparable to the heat of condensation. Additional general differences between physical adsorption and chemisorption make physical adsorption more desirable for air pollution control.

Molecules that are adsorbed by chemisorption are very difficult (and, in some cases, impossible) to remove from the adsorbent bed. Either increasing the operating temperature or reducing the pressure of the adsorbent bed can usually remove physically adsorbed molecules.

For industrial purposes, specific solids that enhance the rate of adsorption are chosen. Chemisorption is a highly selective process. A gas molecule must be capable of forming a chemical bond with the adsorbent surface for chemisorption to occur.

Chemisorption stops when all the reactive sites on the surface of the adsorbent have reacted, forming only a monolayer of adsorbate molecules on the surface. While the physical adsorption rate decreases with increasing temperature, the chemisorption rate increases with increasing temperature.

Table 4-2 displays the main reasons why chemisorption is not used extensively in air pollution control systems. 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/gm mole	Releases low heat, 0.1 Kcal/gm mole
Forms a chemical compound	Gas retained by dipolar interaction
Desorption difficult	Desorption easy
Adsorbate recovery impossible	Adsorbate recovery easy

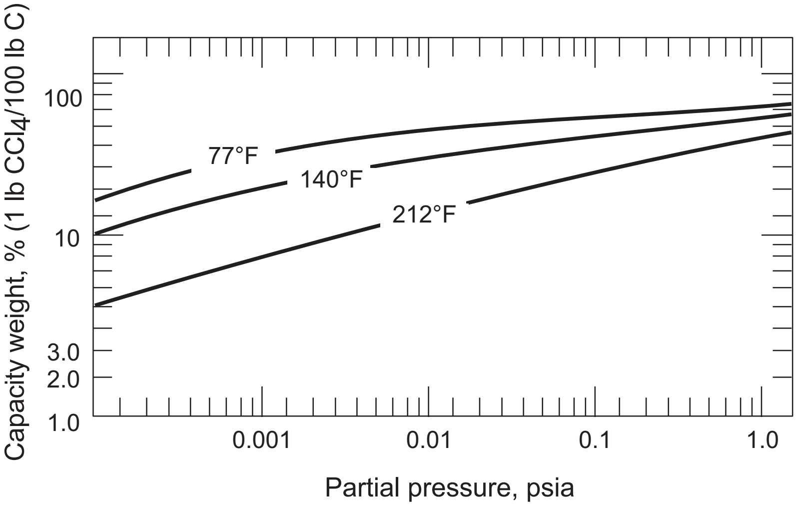
4.2.3 Adsorption-Capacity Relationships

Most available data on adsorption systems are determined at equilibrium 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. The equilibrium capacity determines the maximum amount of vapor that can be adsorbed at a given set of operating conditions. Although a number of variables affect adsorption, gas temperature and pressure are the two most important in determining adsorption capacity for a given system.

Three types of equilibrium graphs are used to describe adsorption capacity: isotherm at constant temperature, isobar at constant pressure, and isostere at constant amount of vapor adsorbed.

Isotherm

The most common and useful adsorption equilibrium data graph is the adsorption isotherm. The isotherm is a plot of the adsorbent capacity versus the partial pressure of the adsorbate at a constant temperature. Adsorbent capacity is usually given as pounds of adsorbate per 100 pounds of adsorbent. Figure 4-17 is an example of an adsorption isotherm for carbon tetrachloride on activated carbon. Graphs 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 that can 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 adsorbates-adsorbent systems and are valid over limited concentration ranges.



Source: Adapted from Technical Bulletin, Calgon Corp.

Figure 4-17. Adsorption isotherm for carbon tetrachloride 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. Given Figure 4-17, 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 percent by volume.

$$Y = \% \text{ volume} = 680 \text{ ppm} = 0.00068$$

Obtaining the partial pressure:

$$p = YP = (0.00068)(14.7 \text{ psia}) = 0.010 \text{ psia}$$

Step 2. From Figure 4-17, at a partial pressure of 0.01 psia and a temperature of 140°F, the carbon capacity is read as approximately 30%.

This means that, at saturation, 30 pounds of vapor are removed per 100 pounds of carbon in the adsorber (30 gm of vapor/100 gm of carbon).

It must be noted that, in practical applications, adsorbers use more carbon than is predicted at saturation to ensure that uncaptured vapors are not being 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 4-18 shows an adsorption isostere graph for the adsorption of H_2S gas onto molecular sieves. The isostere 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.

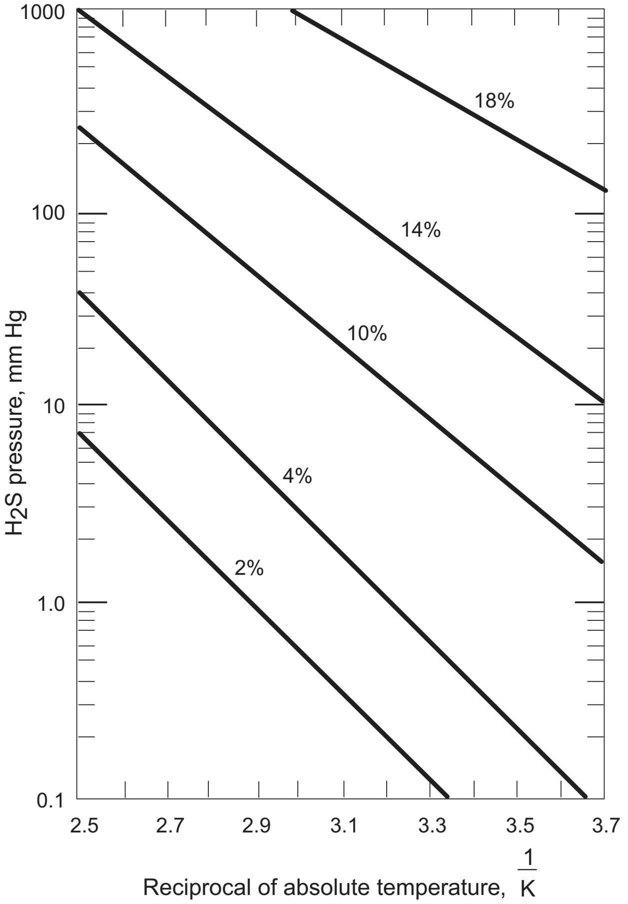


Figure 4-18. Adsorption isosteres of H_2S on 13X molecular sieve loading in % weight

Isobar

The isobar is a plot of the amount of vapor adsorbed versus temperature at a constant pressure. Figure 4-19 shows an isobar line for the adsorption of benzene vapors on activated carbon.

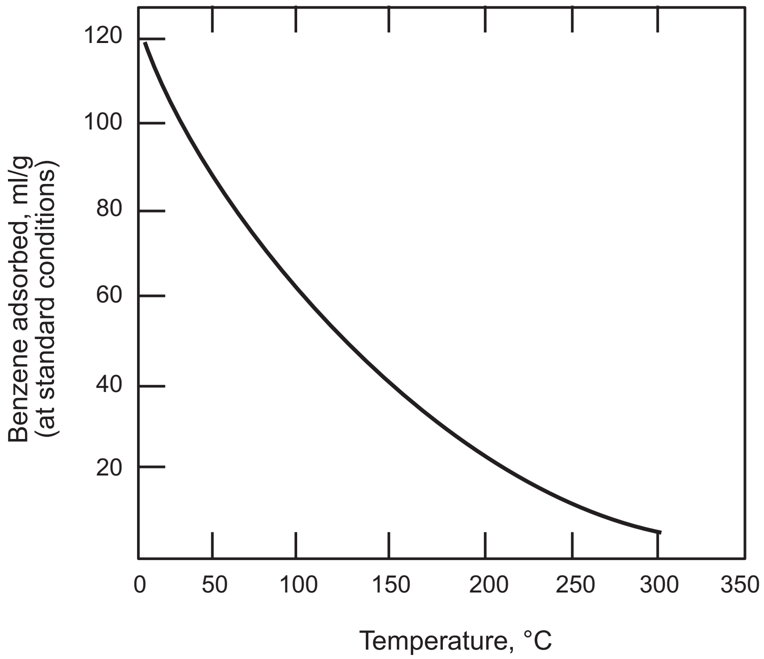


Figure 4-19. Adsorption isobar for benzene on carbon
(benzene at 10.0 mm Hg)

Note that the amount adsorbed decreases with increasing temperature. This is always the case for physical adsorption. Because these three relationships were developed at equilibrium conditions, they depend on each other. By determining one, such as the isotherm, the other two relationships can be determined for a given system. In the design of an air pollution control system, the adsorption isotherm is by far the most commonly used equilibrium relationship.

4.3 CAPABILITY AND SIZING

4.3.1 Applicability

Nonregenerative Systems

Nonregenerative systems are applicable to a wide variety of small, low concentration organic vapor sources. Organic compounds with an affinity for organic vapor can be removed in the nonregenerative units. 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 removed. 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 a much higher adsorbent utilization than is practical in regenerative systems. Accordingly, nonregenerative units can have a relatively long service life despite the limited quantities 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 high affinity for the adsorbent that it is impractical to attempt 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.

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	1.50
Naptha	288 (142)	-	No	Yes	0.92
Mineral Spirits	381 (194)	-	No	Yes	<1.00
Stoddard Solvent	379 (193)	-	No	Yes	1.10
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 Ketone	174 (78.9)	72.1	Yes	Yes	1.80
Methyl 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

There are practical limits to carbon adsorber applicability. The types of organic compounds that are usually not suitable for these systems are listed in Table 4-4.

Table 4-4. Organic Compounds Not Usually Suitable for Carbon Adsorption	
Reactive Compounds	**High Boilers**
Organic acids	Plasticizers
Aldehydes	Resins
Monomers (some)	Long Chain HCs (+C_{14})
Ketones (some)	Glycols, Phenols, Amines

4.3.2 Adsorption Capacity

In adsorption systems, three important terms are used to describe the capacity of the adsorbent bed as measured in pounds of vapor per pound of adsorbent. *Breakthrough capacity* is defined as the capacity of the bed at which unreacted vapor begins to be emitted. *Saturation 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 the actual amount of adsorbent used in an adsorber. The working capacity is a fraction of the saturation capacity. Working capacity can range from 0.1 to 0.5 of the saturation capacity for activated carbon systems. Smaller capacities increase the amount of carbon required. The designer selects this fraction for individual systems by balancing the cost of carbon and adsorber operation versus preventing breakthrough, allowing for an adequate cycle time.

It is uneconomical to desorb all the vapor from the adsorber bed. The small amount of residual vapor left on the bed is referred to as the *heel*. This 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 twice the amount required at saturation.

Problem 4-2

A dry cleaning process exhausts a 15,000 SCFM air stream containing 680 ppm carbon tetrachloride. Based on Figure 4-17 and gas stream conditions of 140°F and 14.7 psia, estimate the amount of carbon that would be required if the adsorber were to operate on a four-hour cycle. Note that saturation capacity of the activated carbon is 30% by weight. The molecular weight of CCl_4 is 154. Use a working capacity of 25% of the saturation capacity.

Solution:

It is known that the activated carbon used will remove 30 pounds of vapor for every 100 pounds of activated carbon at saturation conditions.

Step 1. Compute the flow rate of CCl_4.

$$Q_{CCl_{14}} = 15{,}000\,\text{SCFM} \times 0.00068 = 10.2\,\text{SCFM}\ \ CCl_4$$

Converting to pounds per hour:

$$\frac{10.2\ \text{ft}^3}{\text{min}} \times \frac{\text{lb mole}}{385.4\ \text{ft}^3} \times \frac{154\ \text{lb}_\text{m}}{\text{lb mole}} \times \frac{60\ \text{min}}{\text{hour}} = 245\ \text{lb}_\text{m}\ \text{CCl}_4/\text{hour}$$

For a four-hour cycle

$4 \times 245 = 980\ \text{lb}_\text{m}\ \text{CCl}_4$

Step 2. The amount of activated carbon (at saturation) required

$$980\ \text{lb}_\text{m}\ \text{CCL}_4 \times \frac{100\ \text{lb}_\text{m}\ \text{carbon}}{30\ \text{lb}_\text{m}\ \text{CCL}_4} = 3270\ \text{lb}_\text{m}\ \text{activated carbon}$$

The actual amount of activated carbon required can be estimated by multiplying the amount needed at saturation by four.

$4 \times 3270 = 13{,}100\ \text{lb}_\text{m}$ carbons per four-hour cycle per adsorber.

Note: This gives only a rough estimate of the amount of carbon needed. Actual working capacity may be 25% to 75% of the saturation capacity.

A number of factors or system variables influence the performance of an adsorption system. These variables and their effects on the adsorption process are discussed in the following section.

Temperature

For physical adsorption processes, the capacity of an adsorbent decreases as the temperature of the system increases. Figure 4-20 illustrates this concept. 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.

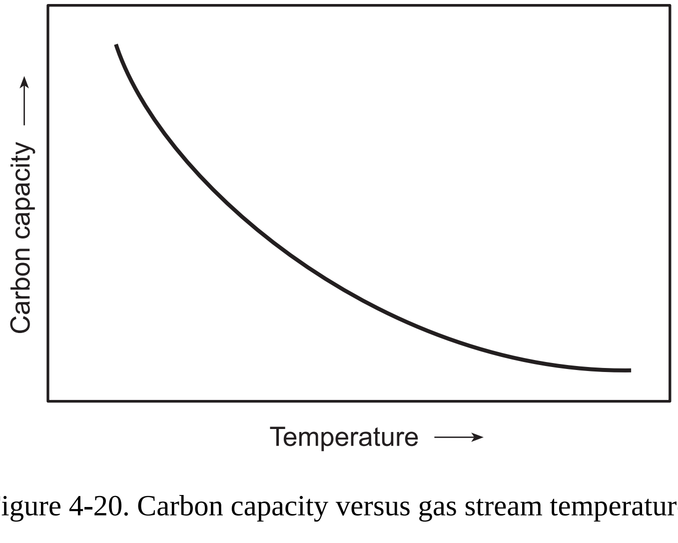


Figure 4-20. Carbon capacity versus gas stream temperature

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 airflow through the bed. At higher concentrations (e.g., 5,000 ppm), the bed can accumulate considerable heat that, if not removed, can cause the adsorber efficiency to decrease rapidly. 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. The partial pressure of a vapor is proportional to the total pressure of the system. Any increase in pressure will increase the adsorption capacity of a system. 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 determines the contact or residence time between the contaminant stream and adsorbent. The residence time directly affects capture efficiency. The slower the contaminant stream flows through the adsorbent bed, the greater 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 airflow 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 a function of the cross-sectional area of the adsorber for a given volume of contaminant gas. By specifying a minimum velocity through the adsorber, the minimum 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.

$$\text{SP}_{\text{absolute}} = (4\text{ in. W.C.}) + 30.3\text{ in.Hg.}\left(\frac{407\text{ in. W.C.}}{29.92\text{ in.Hg.}}\right) = 416\text{ in. W.C.}$$

Step 2. Calculate the gas flow rate in ACFM.

$$\text{ACFM} = 9{,}000\text{ SCFM}\left(\frac{460°\text{R} + 100°\text{F}}{528°\text{R}}\right)\left(\frac{407\text{ in. W.C.}}{416\text{ in. W.C.}}\right) = 9{,}340\text{ ACFM}$$

Step 3. Calculate the minimum cross-sectional area of the bed to maintain a maximum of 100 ft/min.

$$\text{Velocity} = \left(\frac{\text{Gas flow rate in ACFM}}{\text{Area}}\right)$$

$$100\text{ ft/min} = \left(\frac{9{,}340\text{ ACFM}}{\text{Area}}\right)$$

$$\text{Area} = 93.4\text{ ft}^2$$

Increasing the gas flow rate through the absorber increases the pressure drop. Within the above stated maximum and minimum flow rates, the allowable pressure drop usually dictates the required tower cross-sectional 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 strong attractions for each other rather than the adsorbent. At high relative humidity, over 50%, the number of water molecules increases to the extent that they begin to compete with the hydrocarbon molecules for active adsorption sites. This reduces the capacity and the efficiency of the adsorption system.

Exhaust streams with humidities greater than 50% may require installation of additional equipment to remove some of the moisture. Coolers to remove 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 gas removal due to the rate that VOC compounds are adsorbed in the bed. 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 is related to the rate of adsorption. This 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 4-21. The actual length of the MTZ remains fairly constant throughout the adsorption step. While the MTZ is above the bed outlet, the effluent concentration at c_2 remains very low because there is still an unsaturated section of the bed.

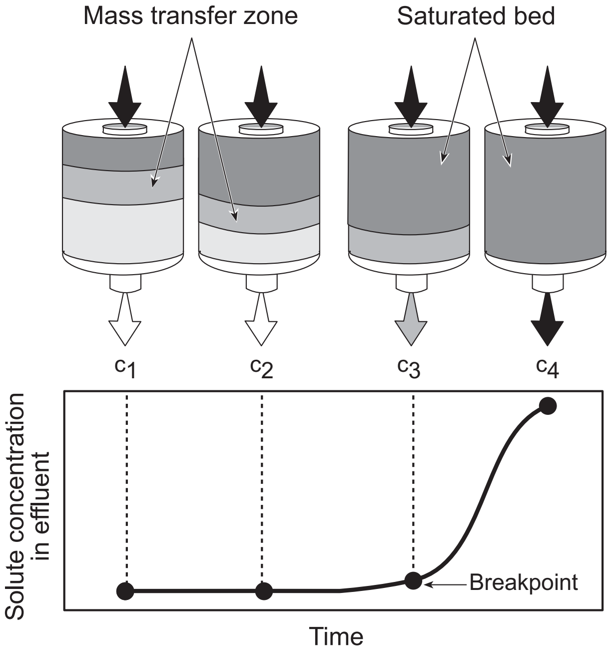


Figure 4-21. Mass transfer zone

When the lower portion of the MTZ reaches the bottom of the bed, the concentration of contaminant in the effluent suddenly begins to rise. This is referred to as the breakthrough point where untreated vapors are being exhausted from the adsorber. If the contaminated air stream is not switched to a fresh bed, the concentration of contaminant in the outlet will quickly rise until it equals the initial concentration, illustrated at point c_4.

If the adsorber bed depth is shorter than the required MTZ, breakthrough will occur immediately, rendering the system ineffective. Estimating the MTZ is important to determine the minimum bed depth.

Computing 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 depth.

$$\mathrm{MTZ} = \frac{1}{1-X_s} D \left(1 - \frac{C_B}{C_S}\right) \tag{4-1}$$

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 (%)

The above equilibrium equation is used mainly as a check to ensure that the proposed bed depth is longer than the MTZ. Actual bed depths are usually many 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.

$$C_B = \frac{(X_S)(C_S)(\mathrm{MTZ}) + C_S(D - \mathrm{MTZ})}{D} \tag{4-2}$$

The minimum bed depth is often determined based on empirical factors due to the difficulty in accurately calculating the MTZ for a specific industrial application. Designers use bed depths well above the estimated minimum values to take into account site-specific differences in gas stream characteristics and the adequacy of gas distribution across the beds.

Often the adsorbent bed is sized to the maximum length allowed by the maximum static pressure drop across the bed. Data on the pressure drop per meter of bed depth for typical carbons are presented in Figure 4-22.[16] The pressure drop per meter of bed depth is plotted versus the gas flow rate 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 (1.5 kPa per meter) of bed depth. Therefore, if the 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).

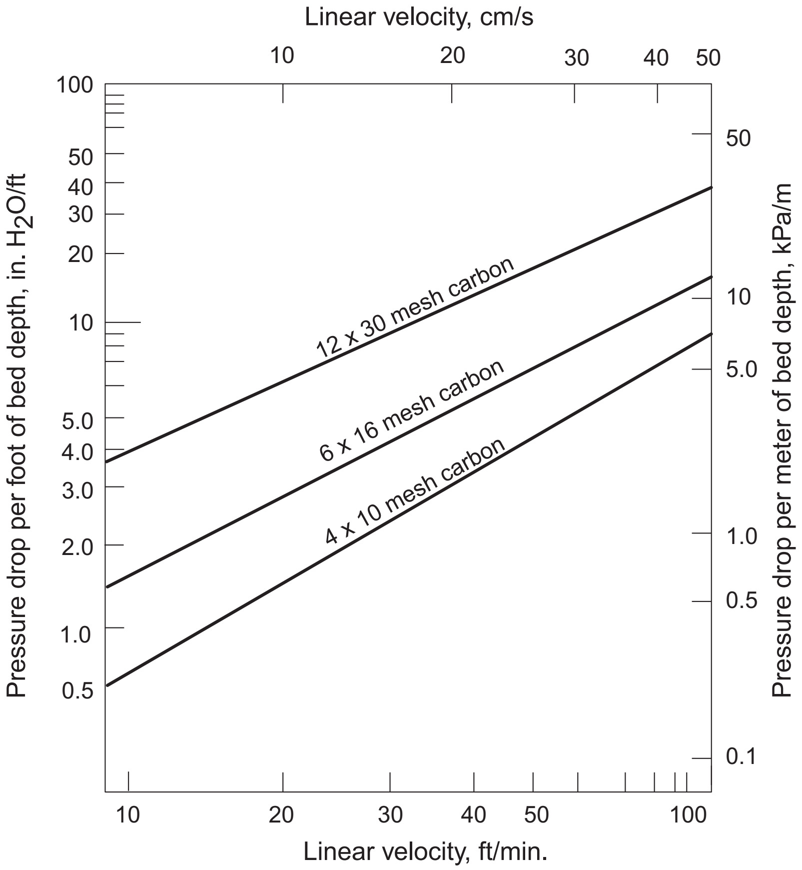


Figure 4-22. Pressure drop versus gas flow rate through a deep bed granular carbon

Contaminants

Particulate matter, organic compounds that have high boiling points, and entrained liquid droplets can also reduce adsorber efficiency if present in the air stream.

Dust or lint greater than 3 micrometers in size that is not filtered can cover the surface of the adsorbent. This greatly reduces the surface area of the adsorbent available to the gas molecule 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 particulate matter removal device.

For activated carbon systems, high boiling point organic compounds, usually in excess of 500°F (260°C), can also be contaminants. High boiling point (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 as particulate matter: the liquid covers the surface, blinding the bed. If the liquid is the same as the adsorbate, high heats of adsorption occur. This is especially a problem in activated carbon systems where 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.

4.3.3 Adsorbent 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 to a lower level. 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 an example of thermal swing regeneration.

Pressure Swing
The pressure is lowered at a constant temperature to reduce the adsorbent capacity.

Inert Purge Gas Stripping
The stripping action is caused by an inert gas that reduces the partial pressure of the contaminant in the gas phase, reversing the concentration gradient. Molecules migrate from the surface into the gas stream.

Displacement Cycle
The adsorbates are displaced by a preferentially adsorbed material. 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.[7]

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.

- At high pressure, the temperature of the steam, 230°F (110°C), is high enough to desorb most solvents of interest without damaging the carbon or the desorbed vapors.
- Steam readily condenses in the adsorber bed, releasing its (the steam's) heat of condensation and aiding in desorption.
- Many organic compounds can be easily separated and recovered from the effluent stream by condensation or 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 concentrated source of heat than hot air so it is very effective in raising the temperature of the adsorber bed quickly.

The amount of steam required for regeneration depends on 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 the entire adsorbed vapor from the bed. Acceptable working capacities can be achieved by using less steam and leaving a small portion of adsorbate in the bed. During the initial heating period, no vapors are desorbed because a fixed amount of steam is first required to raise the temperature of the cold bed to the desorption temperature. After this initial period, a substantial amount of adsorbate vapor is released 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.[18] In these systems, 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 effluent from the condenser can pose a water pollution problem unless the condensate is sent to a wastewater treatment facility.
- Some organic compounds are subject to hydrolysis and/or other reactions with water that may produce corrosive substances. 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 may 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 no time is required to initially heat up or cool the carbon bed. This adiabatic pressure swing allows the bed to be in the adsorbing cycle longer. Units may also be sized smaller 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. In addition, the desorbed vapors can be recovered directly without 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. In pressure/vacuum systems, the adsorber vessel and valving must be constructed of materials capable of withstanding vacuums of 28 in Hg. A vacuum producing 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. Vacuum systems operating cyclically may require more operating attention than other regeneration systems. To be effective, pressure regeneration systems must be designed 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 80°F (27°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 4-23), and the additional operational data, 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 = $(30\ \text{lb}_m/\text{ft}^3)$

Solution:

Step 1. First calculate the toluene flow rate.

$$(8{,}000\ \text{ACFM})\frac{528^\circ\ \text{R}}{540^\circ\ \text{R}} = 7{,}820\ \text{SCFM}$$

$$(7{,}820\ \text{SCFM})\left(\frac{\text{lb moles total}}{385.4\ \text{scf}}\right)\left(\frac{0.0024\ \text{lb moles toluene}}{\text{lb moles total}}\right) = 0.0487\ \text{lb moles toluene/min}$$

The flow rate of toluene is:

$(0.0487\ \text{lb mole/min})(92.1\ \text{lb}_m/\text{lb mole}) = 4.49\ \text{lb}_m/\text{min}$

Step 2. To determine the saturation capacity of the carbon, calculate the partial pressure of toluene at the adsorption conditions.

$$p = YP = \left(\frac{2400\ \text{ppm}}{1{,}000{,}000}\right)(14.7\ \text{psia}) = 0.0353\ \text{psia}$$

From Figure 4-23, the saturation capacity of the carbon is 38% or 38 pounds toluene per 100 pounds of carbon at 0.0353 psia.

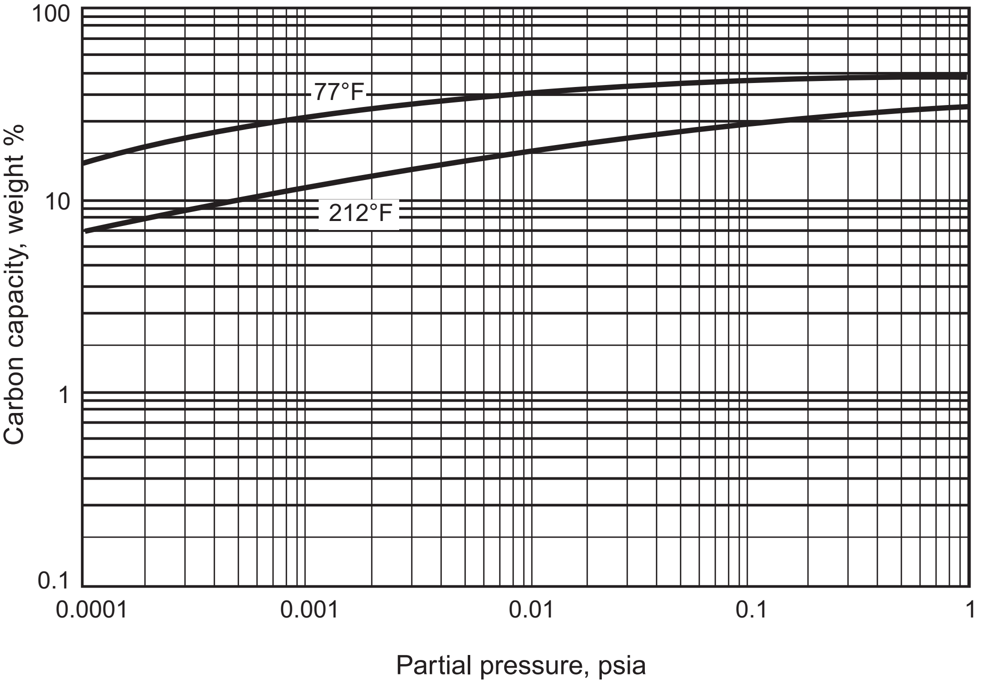


Figure 4-23. Toluene isotherm

Step 3. The amount of carbon at saturation for a 4-hour cycle is:

$$\left(4.49\,\frac{\text{lb}_m\ \text{toluene}}{\text{min}}\right)\left(\frac{60\ \text{min}}{\text{hr}}\right)\left(\frac{100\ \text{lb}_m\ \text{carbon}}{38\ \text{lb}_m\ \text{toluene}}\right)\left(4\,\frac{\text{hr}}{\text{cycle}}\right)$$

$= 2{,}840\ \text{lb}_m$ of carbon (at saturation)

The working charge of carbon can be estimated by multiplying the saturation capacity by four. Therefore, the working charge is: $(4)(2{,}840\ \text{lb}_m$ of carbon)

$= 11{,}400\ \text{lb}_m$ of carbon for a 4 hour cycle

The square feet of superficial surface area is the surface area set by the maximum velocity of 100 ft/min through the adsorber.

The required surface area is:

$$A = \frac{Q}{\text{Maximum Velocity}} = \frac{8{,}000\ \text{ACF/min}}{100\ \text{ft/min}} = 80\ \text{ft}^2$$

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 = 11,400 lb_m carbon/(30 $\text{lb}_m/\text{ft}^{3)}$ = 380 ft^3

Bed Depth = 380 ft^3/80 ft^2 = 4.75 ft

This is too deep and would result in excessively high-pressure drop. It would be preferable to use a larger vessel and a lower gas velocity. The required surface area is recalculated below using an average velocity of 60 ft/min rather than the 100 ft/min value used earlier in this problem.

$$A = \frac{Q}{\text{Maximum Velocity}} = \frac{8{,}000\ \text{acf/min}}{60\ \text{ft/min}} = 133\ \text{ft}^2$$

The bed depth for this modified approach would be:

380 ft^3/133 ft^2 = 2.9 ft

4.3.4 Instrumentation

The factors that contribute to organic vapor 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
- 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. These techniques are relatively similar for all types of fixed-bed systems. However, 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 4-24. This shows three adsorber beds in series. The SLA stream from the process equipment passes through a particulate matter filter and an indirect heat exchanger. The treated SLA stream is then discharged by the centrifugal fan into the tops of the on-line adsorber vessels. 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.

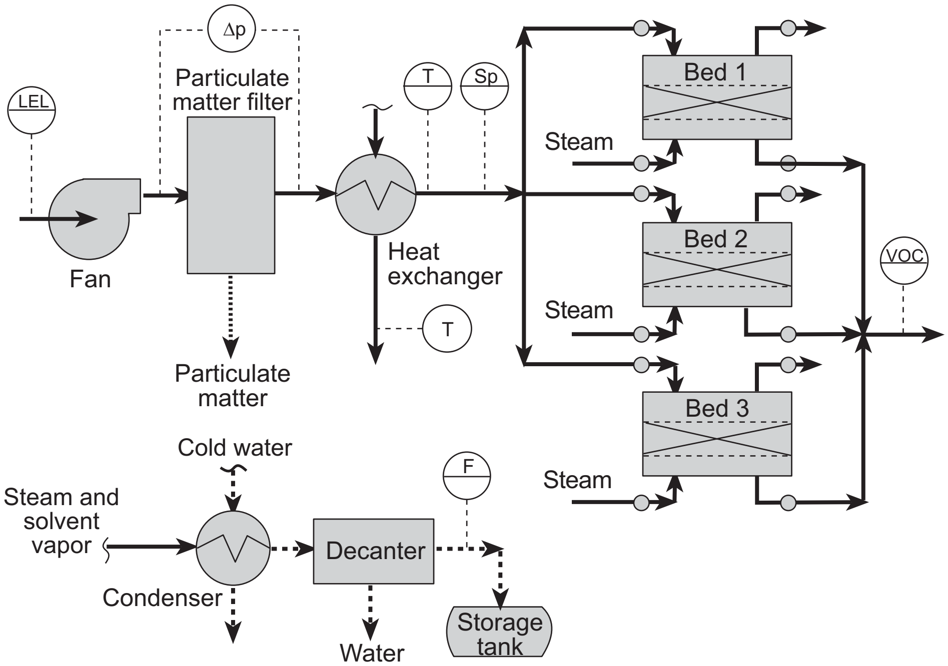


Figure 4-24. Flowchart of a three-bed (deep bed) absorber

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 Organic Vapor Concentration Monitor

The most direct measure of the performance of the adsorber is provided by the outlet organic vapor concentration monitor. This instrument draws a sample gas stream from the outlet of each bed on a frequent basis. The most common types of instruments include photoionization and flame ionization detectors (FID) analyzers. The outlet concentrations are determined and recorded on a single data acquisition system (DAS) or strip chart recorder at the control panel for the adsorber system.

Using the outlet concentration monitor, the outlet concentration of each bed should be determined just prior to desorption. If breakthrough is occurring, the outlet concentration can be high.

It should be noted that the instruments provide an accurate indication of the outlet concentration only when they are calibrated for the specific type of 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, the instrument reading is only a qualitative indicator of performance; however, instrument readings above the baseline levels for the unit are a clear indication of adsorber performance problems.

The adequacy of the organic vapor concentration data should be checked routinely. The instruments should be calibrated on a daily basis using gas cylinders. Calibration gas from a cylinder is usually injected near the sample port on each adsorber bed (Figure 4-27) 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. A partial list of these sample line problems follows.

- 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 are corrected for calibration drift and zero drift by computerized data acquisition systems.

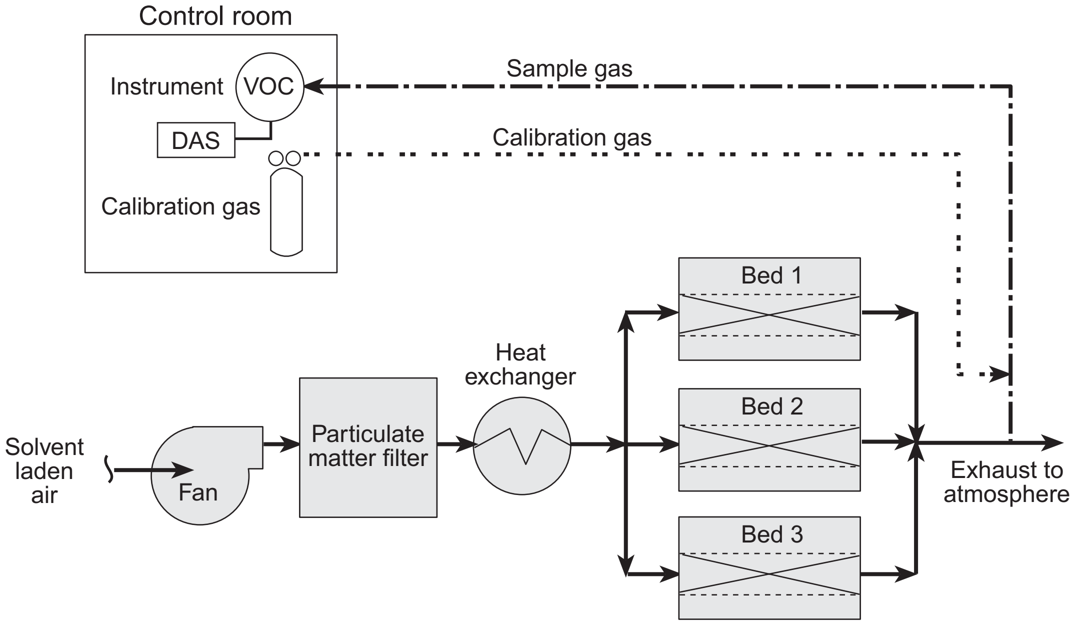


Figure 4-25. Calibration gas injection locations to check for sample line tubing problems

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 of portable VOC analyzers include (1) flame ionization detectors, (2) catalytic combustion analyzers, and (3) photoionization detectors (PID). All of these are battery-powered instruments that can be used to obtain a small gas sample and provides 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.

The FID analyzer 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 compounds (highly oxygenated or halogenated, such as formaldehyde and carbon tetrachloride).

The catalytic combustion instrument 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.

A PID analyzer 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 analyzer 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 analyzers 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 evaluation, however, because these same compounds have 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 on-line cycle of the adsorber, just before desorption. At this time, the outlet VOC concentration is at a maximum. The measurements must not be conducted when the adsorber is in the cool down-purge cycle just prior to returning to adsorption service. During this period, water droplets and high gas stream humidity are present in the gas stream, and the moisture can damage the sensors of all three types of instruments.

VOC Inlet Concentration

Adsorbers designed to operate at 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 concentrations could lead to organic vapor breakthrough unless desorption frequency is increased.

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 removal efficiency in the adsorbent bed leading to organic vapor breakthrough. The present inlet gas temperatures and the inlet temperatures during the last several months should be evaluated for significant increases above baseline values. Furthermore, gas inlet temperatures above 100°F may be associated with emission problems.

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 levels of the pressure drop 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. Because of the mal-distributed gas flow through the bed, adsorption efficiency is decreased. A decrease in the static pressure drop is also indicative of increased emissions. Decreased pressure drop is usually due to 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 longer-than-anticipated mass transfer zones. Breakthrough can occur if the mass transfer zone 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 associated with the system. Fugitive emissions of organic vapor 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 currents, decreased hood static pressures, decreased static pressure drop across the adsorber vessels, and/or decreased static pressure drop across the particulate matter prefilter.

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.

Review Exercises

Types and Components of Adsorption Systems

1. What types of adsorbents are often used in adsorption systems? Select all that apply.
   a. Activated carbon
   b. Calcium carbonate
   c. Zeolites
   d. Polymeric materials
   e. Carbon fiber

2. What is the primary purpose for using a preconcentrator 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
   e. All of the above

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

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
   e. 125% 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. Pluggage of the inlet side of the bed
   b. Increased channeling of the solvent laden air through the bed
   c. Increased static pressure drop

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
   e. 200°F
   f. 300°F
   g. 400°F
   h. 500°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%
   e. 99.5% to 99.99%

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 air temperature.

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.

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.

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.

13. Can the adsorption isotherm shown in Figure 4-19 be used for sizing an absorber 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 both 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.

Capability and Sizing of Adsorption Systems

15. Using Figure 4-23, 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 Problem 16, 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 25% 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 Problem 17 have areas of 180 ft^2 each? If necessary, 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 in solving the problem.

18. What is the approximate static pressure drop across the carbon bed based on the data shown in Figure 4-22? Use the data for 4 x 10 mesh carbon.

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

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. Measure the bed static pressure drop
    c. Measure 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.

Review Answers

Types and Components of Adsorption Systems

1. What types of adsorbents are often used in adsorption systems? Select all that apply.

   a. Activated carbon
   c. Zeolites
   d. Polymeric materials
   e. Carbon fiber

2. What is the primary purpose for using a preconcentrator adsorption system?

   c. Reduce the gas stream volume and increase the VOC concentration in an incinerator inlet gas stream

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

4. What is the adsorber bed inlet concentration limit for VOC-containing gas streams?

   a. 25% of the LEL (Note – 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. Pluggage of the inlet side of the bed
   b. Increased channeling of the solvent laden air through the bed
   c. Increased static pressure drop

6. What is the normal maximum gas temperature used in VOC adsorption systems?

   c. 130°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

8. What is the typical VOC removal efficiency of a properly designed and operated adsorption system?

   c. 90% to 98%

9. Is an activated carbon adsorber system applicable to the removal of methane and ethane from a gas stream?

   b. No

   Methane and ethane have molecular weights below 50.

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.

11. How does the saturation capacity of an activated carbon bed change when the temperature of the solvent laden air increases?

    b. It decreases.

12. How does the saturation capacity of an activated carbon bed change when the humidity of the solvent laden air increases?

    b. It decreases.

13. Can the adsorption isotherm shown in Figure 4-19 be used for sizing an absorber using a different commercial activated carbon product?

    b. No

14. Why are high molecular weight compounds (> molecular weight of 200) difficult to handle in a regenerative adsorber system?

    b. They have too high an affinity and cannot be efficiently desorbed.

Capability and Sizing of Adsorption Systems

15. Using Figure 4-23, what is the saturation capacity of activated carbon for toluene at a temperature of 77°F and a toluene concentration of 600 ppm?

    Step 1. In the gas phase, the mole fraction (Y) is equal to the percent by volume.

    $Y = \% \text{ volume} = 600 \text{ ppm} = 0.0006$

    Obtaining the partial pressure:

    $p = YP = (0.0006)(14.7 \text{ psia}) = 0.0088 \text{ psia}$

    Step 2. From Figure 4-23, at a partial pressure of 0.0088 psia and a temperature of 77°F, the carbon saturation capacity is read as 33%.

16. Based on the saturation capacity determined in Problem 16, 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, desorption requires exactly one hour, and that two beds are in service during all operating times. Assume that the working capacity is 25% of the saturation capacity.

Step 1. First calculate the toluene flow rate per bed.

$$(15{,}000\ \text{SCFM})\left(\frac{\text{lb mole total}}{385.4\ \text{SCF}}\right)\left(\frac{0.0006\ \text{lb mole toluene}}{\text{lb mole total}}\right) = 0.0234\ \text{lb mole toluene/min}$$

The flow rate of toluene is:

$(0.0234\ \text{lb moles/min})(92.1\ \text{lb}_m/\text{lb mole}) = 2.16\ \text{lb}_m/\text{min}$

From Problem 16, the saturation capacity of the activated carbon is 33% or 33 pounds toluene per 100 pounds of carbon at 0.0088 psia.

Step 2. The amount of carbon at saturation for a 3-hour cycle is:

$$\left(\frac{2.16\ \text{lb}_m}{\text{min}}\right)\left(\frac{100\ \text{lb}_m\ \text{carbon}}{33\ \text{lb}_m\ \text{toluene}}\right)\left(\frac{60\ \text{min.}}{\text{hr}}\right)\left(\frac{3\ \text{hours}}{\text{cycle}}\right) = 1{,}160\ \text{lb}_m\ \text{carbon per bed}$$

The working charge of carbon can be estimated by multiplying the saturation capacity by 4. Therefore, the working charge is calculated as:

$(4)(1{,}160\ \text{lb}_m\ \text{of carbon}) = 4{,}640\ \text{lb}_m$ of carbon for a 3-hour cycle

17. Is the superficial velocity within the normal range for activated carbon fixed bed systems if the three beds evaluated in Problem 17 have 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.

Step 1. Calculate the absolute static pressure.

$$\text{SP}_{\text{absolute}} = (6\ \text{in. W.C.}) + 29.65\ \text{in. Hg}\left(\frac{407\ \text{in. W.C.}}{29.92\ \text{in. Hg.}}\right) = 409\ \text{in. W.C.}$$

Step 2. Calculate the gas flow rate in ACFM.

$$= \left(\frac{15{,}000\ \text{SCFM}}{\text{Bed}}\right)\left(\frac{460°\text{R} + 77°\text{F}}{528°\text{R}}\right)\left(\frac{407\ \text{in.W.C.}}{409\ \text{in.W.C.}}\right) = 15{,}200\ \text{ACFM}$$

Step 3. Determine the superficial velocity through bed.

Velocity = Flow Rate/Area = $(15{,}200\ \text{ft}^3/\text{min})/180\ \text{ft}^2 = 84.4\ \text{ft/min}$

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 Question 17? The bed contains 4 x 10 mesh carbon having a density of 30 lb_m/ft^3.

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 = 4,460 lb_m carbon/(30 $\text{lb}_m/\text{ft}^{3)}$ = 155 ft^3

Bed depth = 155 ft^3/180 ft^2 = 0.86 ft

Step 2. Calculate the static pressure drop.

From Problem 18, linear velocity = 84, therefore from Figure 4-22 the pressure drop per foot of bed depth is approximately 7 in. W.C./ft.

Static pressure drop = 0.86 ft (7.0 in. W.C./foot of bed) = 6.0 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?

    a. Increased

20. Which techniques are used to determine the adsorption isotherms that are used to size adsorbent beds?

    b. Laboratory tests with the specific type or brand of adsorbent

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

22. What is the primary purpose of measuring the hood static pressure?

    c. Identify possible increases in fugitive emissions from process equipment.

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.

24. What is the primary purpose of installing a solvent laden air temperature gauge at the inlet of the adsorption beds?

    b. Detect increased gas temperatures that could require increased desorption frequency.

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Chapter 5
Absorption

Absorbers used for air pollution control use aqueous scrubbing liquids to remove gases and vapors. Absorber design has benefited substantially from the extensive development of these types of systems for process applications (non-pollution control) 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 that generate acid gases because of the combustion of sulfur-containing and/or halogenated compounds.

Absorption refers to the transfer of a gaseous component from the gas phase to a liquid phase. 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. The absorption of gases into liquids is shown conceptually in Figure 5-1.

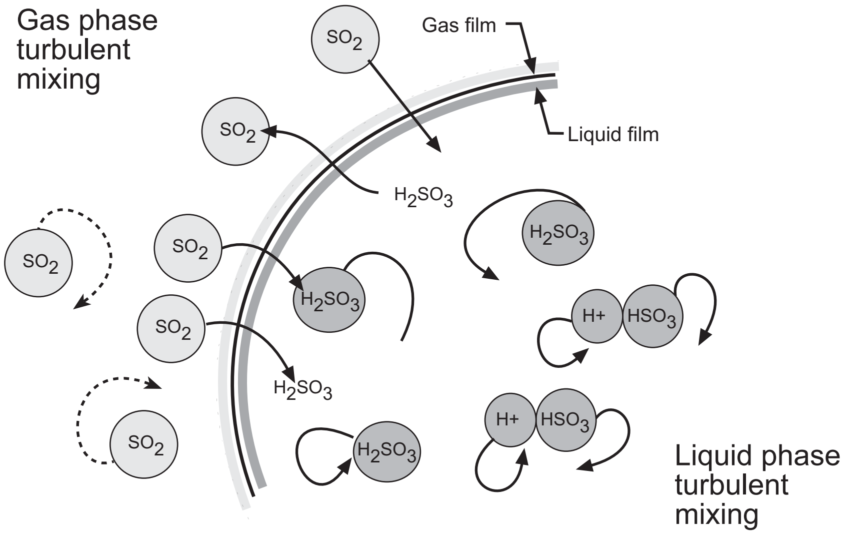


Figure 5-1. Conceptual sketch of absorption into droplets

The gaseous contaminant being absorbed must be at least slightly soluble in the scrubbing liquid, termed the *absorbent*. Mass transfer to the liquid continues until the liquid approaches saturation. At saturation, equilibrium is established between the mass transfer rate of the contaminant into the liquid and the mass transfer rate of the dissolved species back into the gas phase. Accordingly, the solubility of the contaminant 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. The use of reactants is very common in absorbers used for air pollution control.

5.1 TYPES AND COMPONENTS OF ABSORBERS

5.1.1 Types of Absorbers

Spray Tower Absorbers

Spray towers are the simplest devices used for gas absorption. They consist of an open vessel and a set of liquid spray nozzles to distribute the scrubbing liquid (absorbent). Typically, the contaminant gas stream enters the bottom of the tower and passes upward through the vessel. The flow of the liquid and gas streams in opposite directions is referred to as counter-current flow. Figure 5-2 is a typical co-current flow-type spray tower absorber. Spray towers range in size from 5 to 100,000 ACFM (0.14 to 2,800 m^3/min).

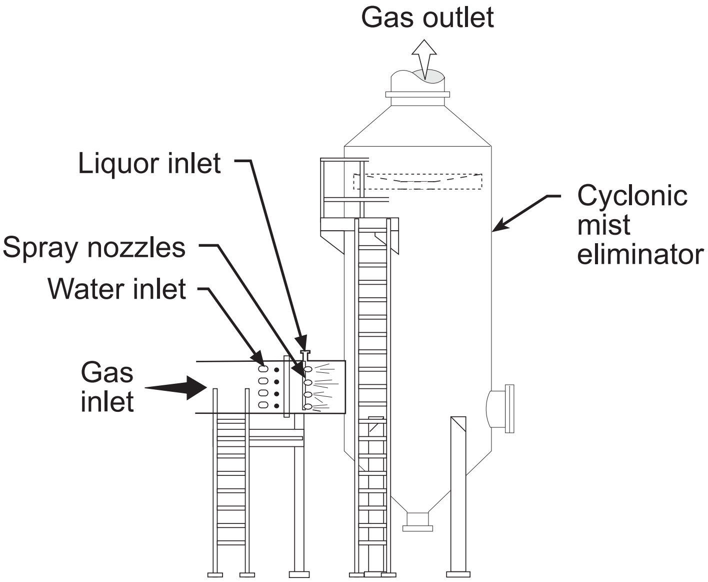


Figure 5-2. Co-current gas flow spray tower scrubber

Spray chambers can operate in cross-current or co-current flow arrangements when there is limited space in an industrial facility. In cross-current absorbers, the gas flow is perpendicular to the liquid flow. In co-current absorbers, the gas and liquid flow in the same direction. Because the gas stream does not "push" against the liquid stream as in counter-current flow, higher gas stream velocities can be used. With higher gas stream velocities, that the size of the unit can be reduced. However, cross-current or co-current spray towers are not usually as efficient as counter-current units. The counter-current flow exposes the most dilute portion of the contaminant gas stream to the freshest liquid in the absorber vessel.

One of the main components of spray tower absorbers is the spray nozzle. Various types of full cone nozzles are often used. A full cone nozzle generates a spray pattern that completely fills the target area as shown in Figure 5-3. The spray angle is a function of the liquid pressure in the supply header.

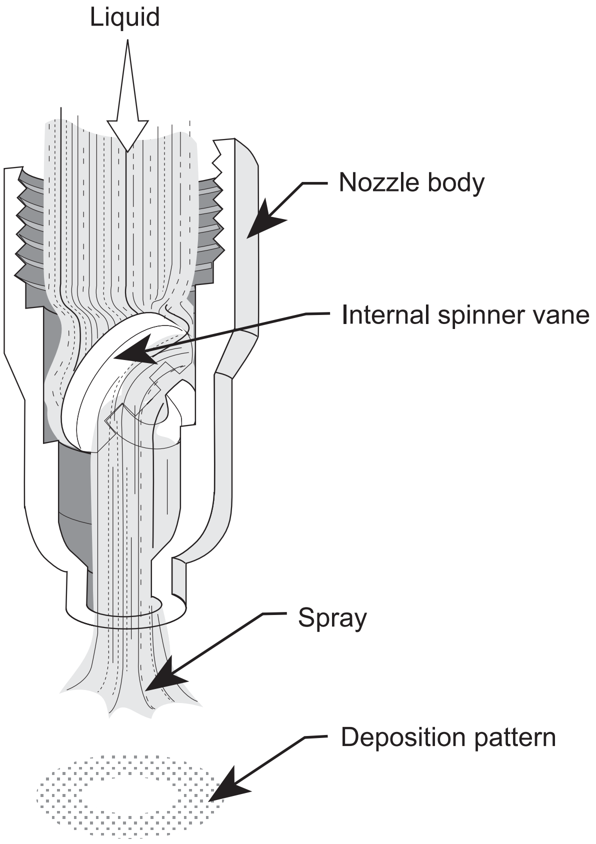


Figure 5-3. Full cone nozzle

The quantity of liquid used in the spray tower absorber is important. This is characterized by the liquid-to-gas ratio, which is defined as the gallons per minute of recirculated scrubbing liquor divided by the gas flow at the stack in units of 1,000 ACFM.

Typical liquid-to-gas ratios (L/G) for spray tower absorbers can vary from 5 to more than 50 gallons per 1,000 ACF. The necessary liquid-to-gas ratio is determined partially by the solubility of the gaseous contaminant and partially by the mass transfer requirements in the spray tower vessel. Figure 5-4 illustrates how the SO_2 removal is affected by the L/G ratio. Figure 5-4 was developed for SO_2 removal in a spray tower using limestone on a 4,000 ACFM (110 m^3/min), 30-megawatt test unit.

Because of the limited contact between the liquid droplets and the gas stream, spray tower absorbers can have very limited capability for removing pollutants. They 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.

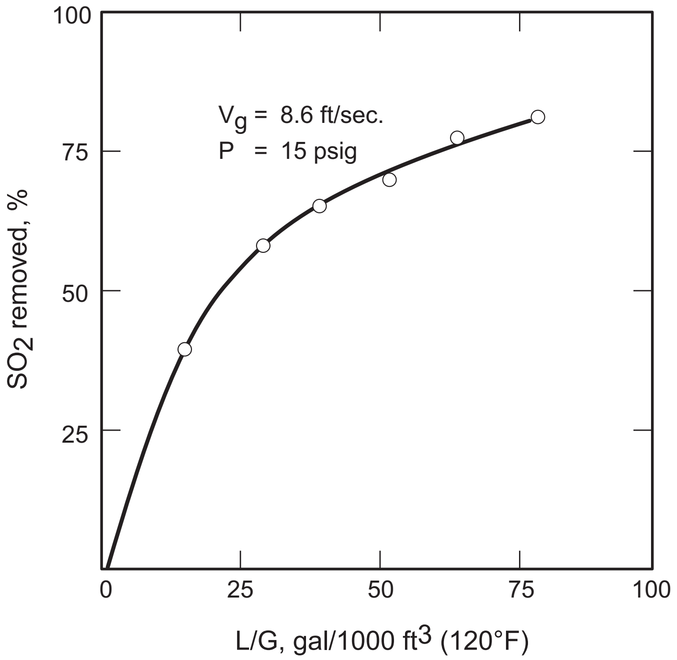


Figure 5-4. Spray tower efficiency

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 used in spray tower scrubbers can add a 0.3 to 4 in. W.C. (0.075 to 1.0 kPa) to the total gas phase static pressure drop. A mist eliminator is used to prevent droplets from exiting the absorber vessel.

Packed Bed Absorbers

Packed bed absorbers are the most common absorbers used for gas removal. Packed columns disperse the scrubbing liquid over 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 counter-current flow tower shown in Figure 5-5. The gas stream being treated enters the bottom of the tower and flows upward through the bed of packing material.

Liquid is introduced at the top of the packed bed by sprays or weirs and flows downward over the packing material, resulting in the highest theoretically achievable efficiency. The most dilute gas is put into contact with the least saturated absorbing liquor. Accordingly, the maximum concentration difference between the gas phase contaminants and the dissolved concentration of the contaminant in the liquid is at the top of the packed bed. This concentration difference provides a driving force for continued absorption.

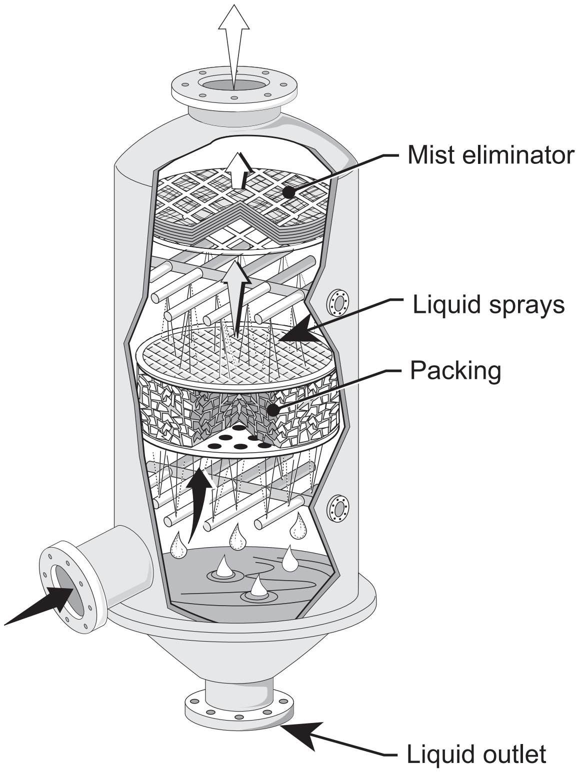


Figure 5-5. Counter-current packed tower

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 5-6. Inlet sprays aimed at the face of the bed (not shown in Figure 5-6) may also be included. The leading face of the packed bed is often slanted in the direction of the in-coming gas stream as shown in Figure 5-6. This ensures complete wetting of the packing by allowing the liquid at the front face of the packing enough time to drop to the bottom before being pushed back by the entering gas.

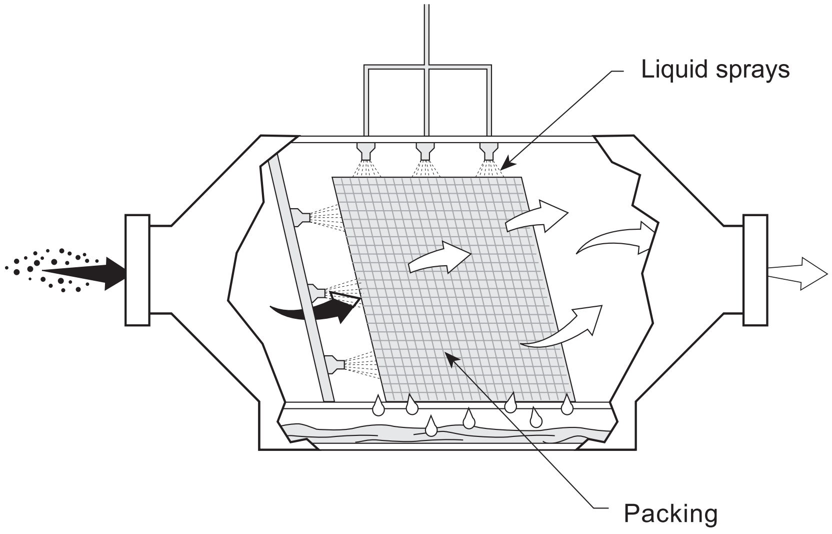


Figure 5-6. Flowchart of cross-flow scrubber

Cross-flow absorbers require complex design procedures because concentration gradients exist in two directions in the liquid: 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. per meter of packing) 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 exhaust 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. 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 packing material provides a large surface area for mass transfer. Figure 5-7 illustrates some of the most commonly used packings. These packings are usually mde 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™ rings or 1-inch (2.5-centimeter) Tellerettes™. The overall dimensions of packing materials normally range from 1 to 4 inches (2.5- to 10.1-centimeter).

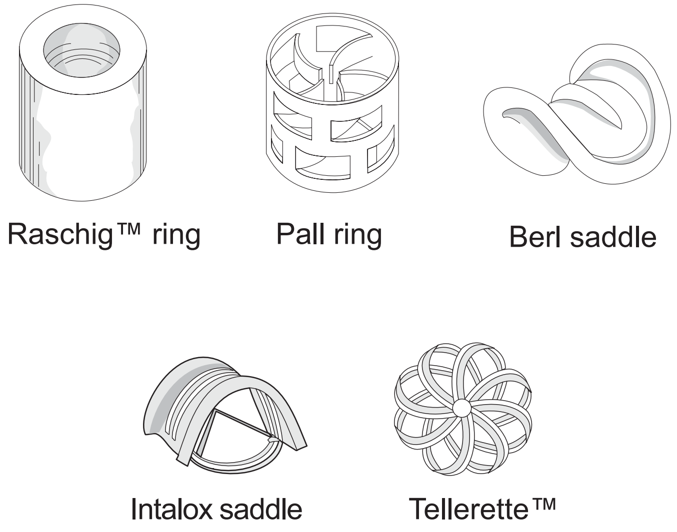


Figure 5-7. Types of packing

The specific packing selected depends on the nature of 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.

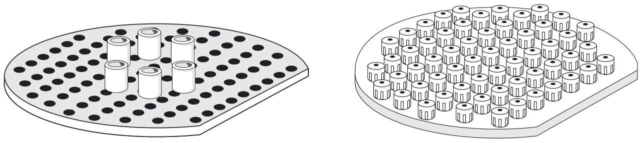
- **Cost.** Plastic packings are generally cheaper than metal, with ceramic being the most expensive.

- **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 or stacked as structured material. Randomly packed towers provide a higher surface area (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.

Liquid Distribution. One of the requirements for efficient absorption is good gas-liquid contact throughout the entire packed bed. The performance of the liquid distributors in the absorber is important to achieve good gas-liquid contact.

Liquid should be distributed over the entire upper surface of the packed bed. This is commonly achieved by weirs or feed tube arrangements as shown in Figure 5-8. Arrays of spray nozzles are also used. However, distributors similar to the units are more flexible with respect to variations in the liquid recirculation rate.


(a) Riser orifice (b) Notched riser

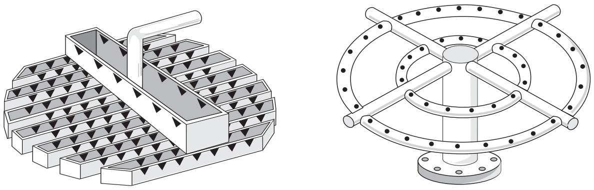

(c) Trough and weir type (d) Perforated pipe

Figure 5-8. 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 (channels). It is necessary to redirect the liquid from the tower wall back to the center of the column. Liquid redistributors are used to funnel the liquid back over the entire surface of packing. Redistributors are usually placed at intervals of no more than 10 feet (3.1 meters), or 5 tower diameters, whichever is smaller.[1]

Uniform distribution of the inlet gas stream is also very 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 plates. Liquid enters at the top of the tower and travels across each tray, 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 5-9 illustrates a typical tray tower unit.

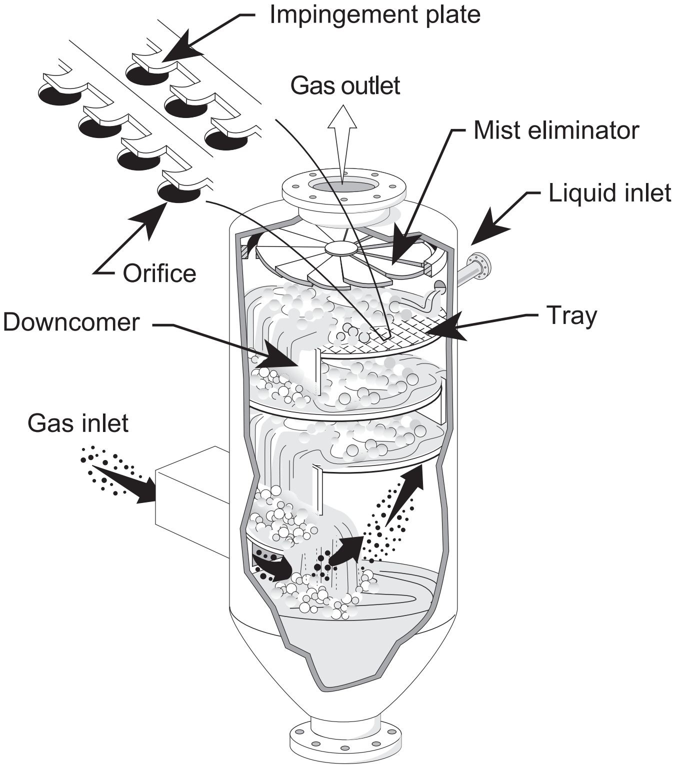


Figure 5-9. Impingement tray

The function of the trays is to disperse the liquid into droplets and the gas into bubbles, thereby creating large gas-liquid interface areas for mass transfer. A variety of different tray designs are used for air pollution control. The most common types are impingement trays and sieve trays.

Impingement Trays. The gas stream passes through orifices in the impingement tray that are usually 3/16 in. (0.48 cm) in diameter. Due to high gas velocities, the liquid passing across the tray is atomized. Small impingement targets above each orifice are used to enhance gas-liquid contact immediately above the tray. 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. Most impingement tray absorbers have two to three trays in series.

Sieve Trays. The orifices in sieve tray absorbers range from 0.25 to 1 in. (0.64 to 2.5 cm) in diameter. Because of these relatively large openings, the sieve trays are less prone to solids accumulation and pluggage of the orifices than the impingement tray units that have smaller orifices. Mass transfer in sieve tray absorbers occurs because of mass transfer from gas bubbles to the liquid layer and from the bulk gas stream to liquid droplets formed above the orifices.

Bubble Cap Trays. The gas stream enters the liquid layer through bubble caps mounted on the trays. This type of unit can handle wide ranges of gas and liquid rates without adversely affecting efficiency. Because bubble caps are liquid tight, this type of tray can use very low liquid rates.

Float Valve™ Trays. The gas stream flows up through small holes in the tray and lifts up 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 opening for gas flow proportional to the gas flow rate through the absorber.

High removal efficiencies are possible because of the good gas-liquor contact that can be achieved on a tray. The use of several trays in series also ensures that gas-liquid maldistribution 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 is moved 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 is shown in Figure 5-10. It consists of a converging section for the acceleration of the approaching gas stream, a means to introduce the recirculated liquid stream, a gas-liquid contacting throat, and a diverging section for decelerating the gas stream and atomized liquid droplets.

Some venturis have a side-mounted baffle type adjustable throat mechanism to adjust the velocity of the gas stream passing through the throat. 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 determined based primarily on the particle size distribution of the incoming gas stream and the applicable particulate matter removal requirements. The static pressure drop 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 are effective for the impaction of particles into atomized droplets because there is very limited time for gaseous absorption. In fact, at normal venturi throat velocities, the gas stream and the liquid droplets are in close contact for time periods of less than 0.002 seconds.

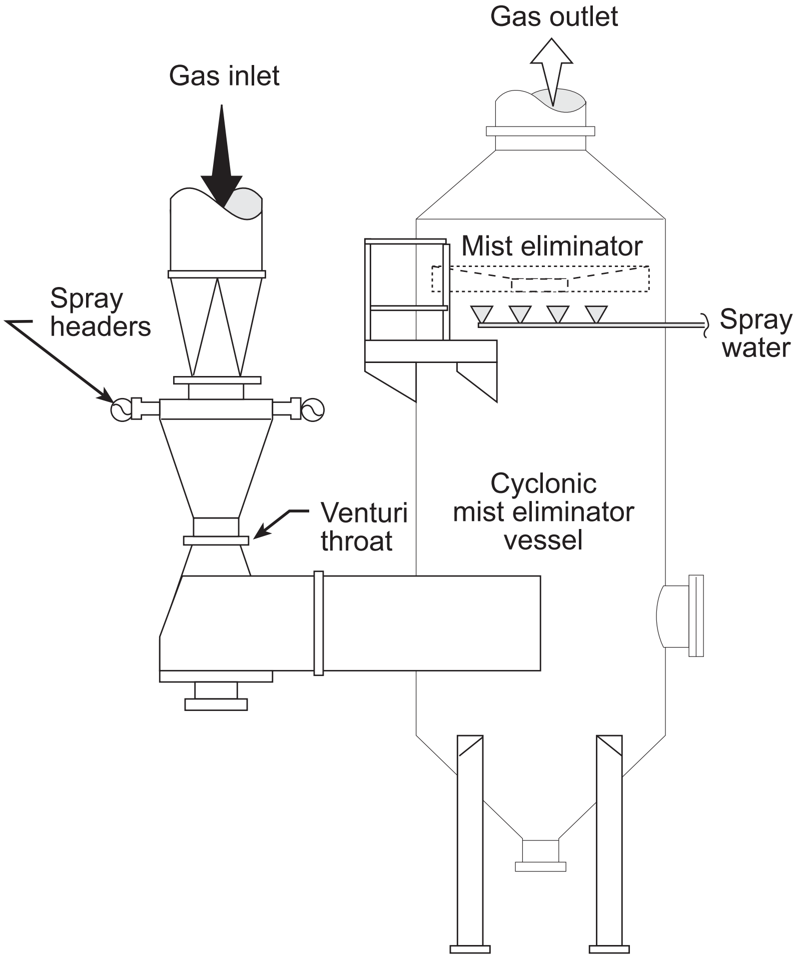


Figure 5-10. Venturi absorber

To overcome the short residence time, some venturi systems used primarily for gaseous absorption operate at high L/G ratios. These can range from 20 to 100 gallons per 1,000 ACF (2.7 to 13 liters per m^3 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 ACFM (0.5 to 2.7 liters per m^3).

Ejector Absorbers. An ejector absorber uses a high pressure spray nozzle operating at more than 80 psig. The liquid stream is aimed at the throat section. The movement of the liquid creates an aspiration effect that pulls the gas stream through the absorber vessel. This 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 interface area for absorption of gases. Mass transfer is aided by the highly turbulent conditions around the droplets. However, mass transfer is limited by the relatively short contact time between the droplets and the gas stream.

Ejector venturis 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.

Ejector venturis can be designed for relatively small gas flow rates. They are often used in series in acid production facilities. For example, the set of ejectors shown in Figure 5-11 is used to concentrate hydrochloric acid. The scrubbing liquid passes from ejector to ejector in a direction opposite that of the gas stream. Therefore, the most concentrated acid stream is exposed to the inlet gas stream where the hydrochloric acid concentration is the highest. In this unit, a packed bed absorber is used as a “polishing” stage to meet air pollution control requirements.

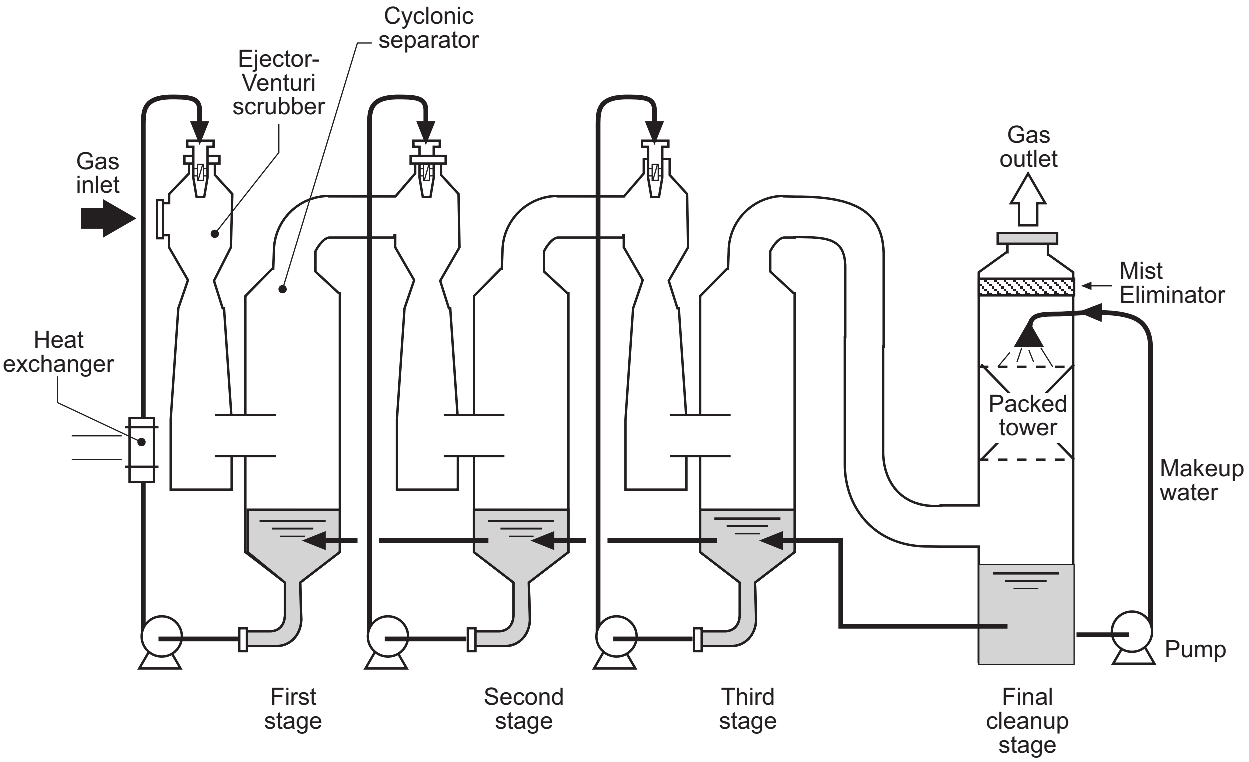


Figure 5-11. Ejector absorber

Ejector absorbers are also used for some types of emergency scrubbers. These scrubbers are often required for treating 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 5-12.

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 or beds 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 40.6°C).[3,4] High temperature excursions can kill the organisms. 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.

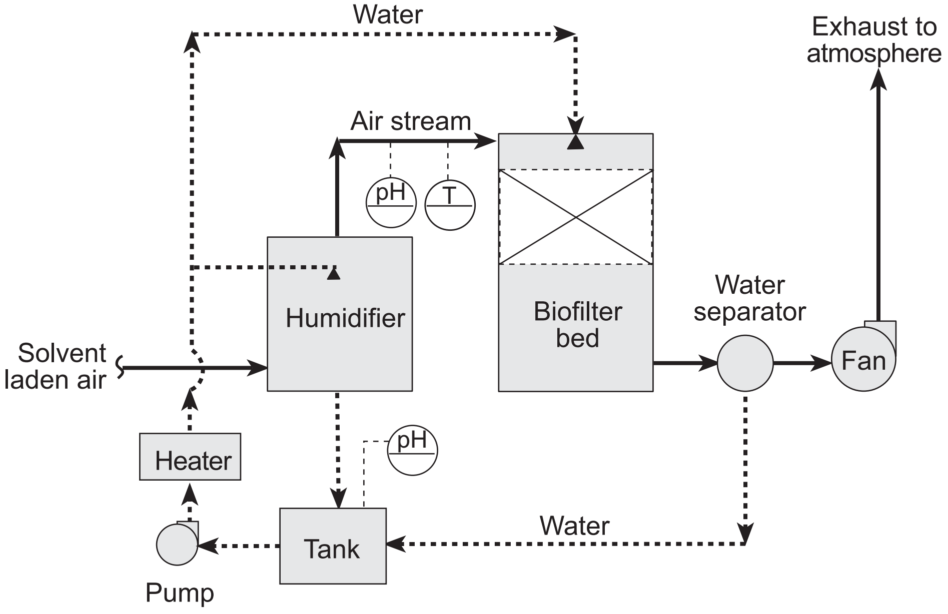


Figure 5-12. Biological oxidation system[5] (Modified)

The organic vapor contaminants passing through the bed must be soluble in order to enter the water layers surrounding the packing material. Once in the water layers, the compounds must be biodegradable. The rates at which organic compounds are consumed vary substantially. This must be taken into account when sizing the unit for a specific organic compound.

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 6 to 8 where the organisms are viable.[2]

The packed beds are usually approximately 3 feet (0.9 m) in height and have gas flow static pressure drops between 4 and 12 in. W.C. (1 and 4 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.

5.1.2 Components Common to Most Absorption Systems

Mist Eliminators

Most absorption systems generate liquid droplets that are entrained in the gas stream leaving the treatment area. It is necessary to remove these entrained droplets prior to the induced draft fan (if present) and prior to discharge of the effluent from the stack. 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. Some of the large droplets quickly settle out of the gas stream. However, 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 5-10), chevrons (Figure 5-13), radial vanes (Figure 5-14), and mesh pads (Figure 5-15).

The cyclonic vessels have a tangential inlet and operate like a conventional large diameter cyclone. 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.

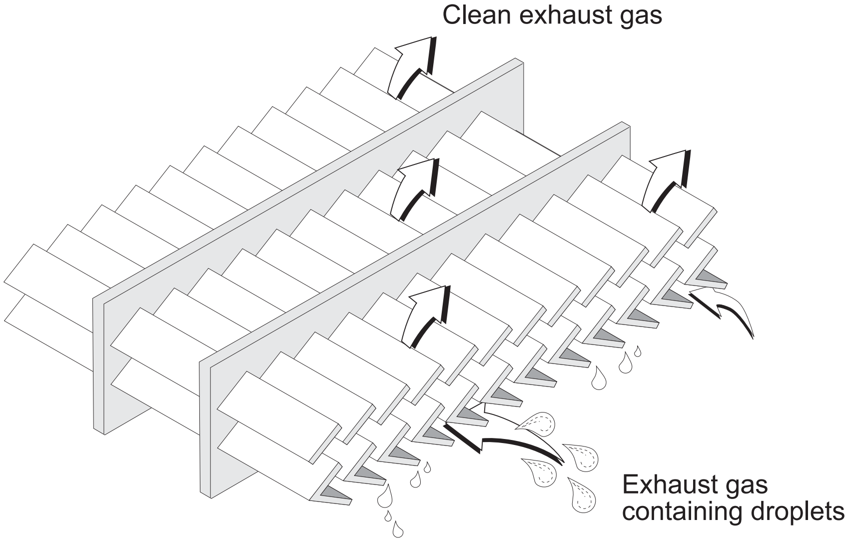


Figure 5-13. Chevron mist eliminator

Chevrons are simply zig-zig baffles that force the gas to turn sharply several times while passing through the mist eliminator. Water droplets are collected on the chevron blades and drain downward. These are generally limited to gas velocities of less than approximately 20 ft/sec (6 m/sec). At high 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 velocities in the portion of the mist eliminator that is 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, such as the one shown in Figure 5-14, 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.

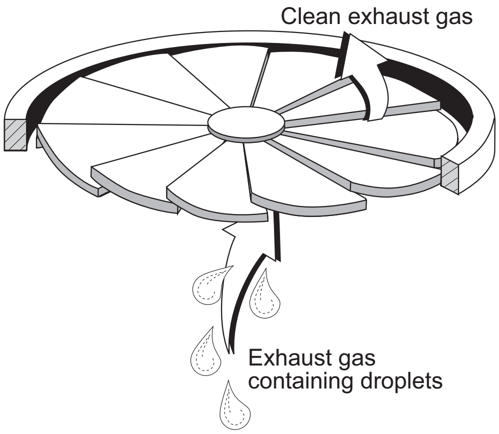


Figure 5-14. Radial vane mist eliminator

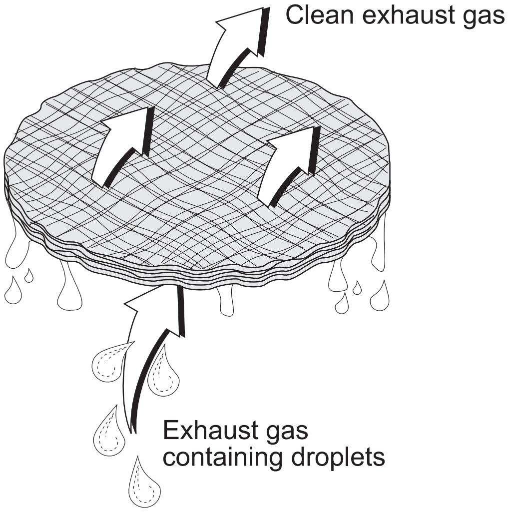


Figure 5-15. Mesh pad mist eliminator

Mesh pads are randomly interlaced metal fibers. The pads can be up to 6 inches thick. As with the chevrons, there is a maximum gas velocity above which reentrainment is possible. This maximum gas velocity depends on the density of the mesh (usually 5 - 9 lb_m/ft^3), on the materials of construction, and on the gas density. The maximum velocity is usually in the range of 12 ft/sec (3.7 m/sec).

Woven pads have complex, interlaced synthetic fibers that serve as impaction targets. Mist eliminators composed of these materials are often layered. The inlet side layers are open weaves capable of removing large quantities of large diameter materials without overloading. The middle and outlet side layers have more compact weaves that have high removal efficiencies for the small 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.

Both the mesh pads and woven pad mist eliminators usually have clean water spray systems to remove solids. Blinding of these mist eliminators 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. (0.13 to 1.0 kPa). Static pressure drop gauges are useful for monitoring the pressure drop and providing and early warning of solids accumulation.

Pumps and Piping Systems

Centrifugal pumps are the most common type of pump 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 may consist of a number of components, including the suction pipe, strainer, suction side check valve, discharge 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 system components and to monitor performance. A partial list of the parameters and common monitoring locations that are needed 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 could damage absorber system materials of construction. 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 gas temperatures, emergency flush systems are often included in absorption systems to protect the system during an emergency shutdown. The inlet gas temperature monitors also provide an indication of temperature increases that could impair absorption efficiency.

The outlet gas temperature gauges 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. The absorber outlet temperature data are also useful for evaluating absorber performance.

Liquid flow monitors are used to indicate that the flow rates remain in the intended operating range. These instruments 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 rate must be maintained at rates 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 van 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 (acid gas removal applications). It is usually advantageous to maintain the pH at levels between 5 and 9. At low pH levels, the materials are vulnerable to corrosion. At high levels, calcium and magnesium compounds can precipitate out of solution and create scale deposits 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 sensed 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. These data are used to indicate the need for cleaning sprays.

5.2 OPERATING PRINCIPLES

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.

5.2.1 Mechanisms of Absorption

The gaseous contaminant (termed the *solute*) in the bulk gas stream passing through the absorber is transported by turbulent mixing action to a gas film immediately adjacent to the liquid interface (Figure 5-16). The contaminant then diffuses through this thin gas film, across the interface and then through the liquid film adjacent to the interface. The dissolved contaminant is then mixed into the bulk liquid droplet interface. Finally, the pollutant diffuses into the bulk portion of the liquid droplet or sheet because of turbulent mixing within the liquid.

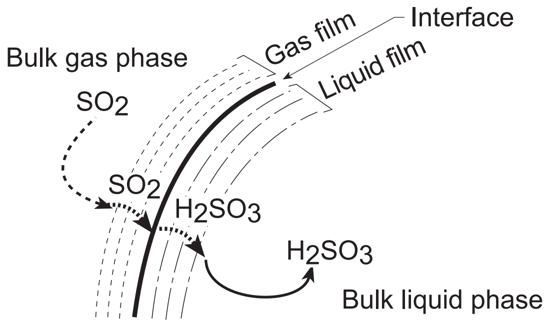


Figure 5-16. Two-film theory of absorption

If the dissolved form of the pollutant does not react, it can move in the direction opposite to the liquid phase; therefore, mass transfer goes in both directions. When the dissolved contaminant species reaches its saturation limit, the rates of mass transfer are equal in both directions. This is termed equilibrium. No additional contaminant removal occurs once equilibrium is established. Accordingly, it is important to design and operate absorbers so that equilibrium 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.

Solubility is a function of the temperature of the liquid. Solubility of gases increases as the liquid temperature decreases. Gas phase pressure can also influence solubility. However, this is not a major variable in absorbers used for air pollution control since they operate at close to atmospheric pressure.

The solubility of a specific gas in a given liquid is defined at a designated temperature. For example, Table 5-1 presents data concerning the solubility of SO_2 gas in water at various temperatures (atmospheric pressure). The units used to express the solubility are often the partial pressure of the contaminant in millimeters of mercury versus the quantity of the contaminant dissolved in the liquid in grams of per 100 grams of liquid. The data in Table 5-1 were taken from the *International Critical Tables*.

Table 5-1. Partial Pressure of SO_2 (mm Hg) Above Aqueous Solutions

gm SO_2 per 100 gm H_2O	10°C	20°C	30°C	40°C	50°C	60°C	70°C
0.0	0	0	0	0	0	0	0
0.5	21	29	42	60	83	111	144
1.0	42	59	85	120	164	217	281
1.5	64	90	129	181	247	328	426
2.0	86	123	176	245	333	444	581
2.5	108	157	224	311	421	562	739
3.0	130	191	273	378	511	682	897
3.5	153	227	324	447	603	804	-
4.0	176	264	376	518	698	-	-
4.5	199	300	428	588	793	-	-
5.0	223	338	482	661	-	-	-

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 SO_2 and water system given in Table 5-1 are plotted in Figure 5-17.

Figure 5-17 illustrates the temperature dependence of the absorption process. At a constant mole fraction of solute in the gas (y), the mole fraction of SO_2 in the liquid (x) increases as the liquid temperature decreases.

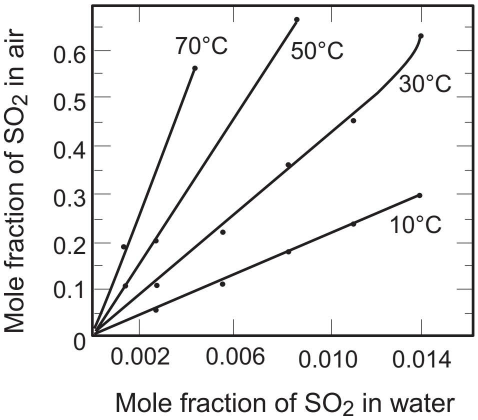


Figure 5-17. SO_2 water system

Under certain conditions, the relationship between the gas phase concentration and the liquid phase concentration of the contaminant at equilibrium can be expressed by Henry's law.

$$p^* = Hx \tag{5.1}$$

Where:

p^* = partial pressure of contaminant in gas phase at equilibrium
H = Henry's law constant
x = mole fraction of contaminant dissolved in the liquid phase at equilibrium

Henry's law can be written in a more useful form by dividing both sides of Equation 5-1 by the total pressure, P, of the system. The left side of the equation becomes the partial pressure divided by the total pressure, which equals the mole fraction in the gas phase, y*. It is important to express the contaminant concentrations in mole fraction as indicated in Equation 5-2.

$$y^* = Hx \tag{5.2}$$

Where:

y^* = mole fraction of the contaminant in the gas phase at equilibrium
H = Henry's law constant
x = mole fraction of contaminant dissolved in the liquid phase at equilibrium
(Note: *H* is now dependent on the total pressure.)

Equation 5-2 is the equation of a straight line where the slope (m) is equal to H. Henry's law can be used to predict solubility only in the range in which the equilibrium line is straight. This is the case when the contaminant concentrations are very dilute as in many air pollution control applications. For example, an exhaust stream that contains a 1,000-ppm SO_2 concentration corresponds to a mole fraction of SO_2 in the gas phase of only 0.001. Figure 5-18 demonstrates that the equilibrium lines for SO_2 in aqueous solutions are still straight at this low concentration of SO_2.

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 HF or 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.

Henry's law constants for the solubility of several gases in water are listed in Table 5-2. The smaller the Henry's law constant, the more soluble the gaseous compound is in the liquid. Table 5-2 indicates that SO_2 is approximately 50 times more soluble in water than CO_2.

Table 5-2. Henry's Law Constants for Gases in Water ATM/Mole Fraction

Gas	20°C	30°C
N_2	80,400	92,400
CO	53,600	62,000
H_2S	48,300	60,900
O_2	40,100	47,500
NO	26,400	31,000
CO_2	1,420	1,860
SO_2	29	43

The following problem illustrates how to develop an equilibrium diagram from solubility data.

Problem 5-1

Given the following data for the solubility of SO_2 in pure water at 303°K (30°C) and 101.3 kPa (760 mm Hg), plot the equilibrium diagram and determine if Henry's law applies.

Concentration SO_2 (gm SO_2 per 100 gm H_2O)	p^*SO_2 (SO_2 partial pressure)
0.5	6 kPa (42 mm Hg)
1.0	11.6 kPa (85 mm Hg)
1.5	18.3 kPa (129 mm Hg)
2.0	24.3 kPa (176 mm Hg)
2.5	30.0 kPa (224 mm Hg)
3.0	36.4 kPa (273 mm Hg)

Solution:

Step 1. The data must first be converted to mole fraction units.

The mole fraction in the gas phase at equilibrium, y*, is obtained by dividing the partial pressure of SO_2 by the total pressure of the system. For the first entry of the data table:

$$y^* = \frac{p^*_{SO2}}{P} = 6 \text{ kPa}/101.3 \text{ kPa} = 0.0592$$

The mole fraction in the liquid phase, x, is obtained by dividing the moles of SO_2 in solution by the total moles of liquid.

$$x = \frac{\text{mole } SO_2 \text{ in solution}}{\text{mole } SO_2 \text{ in solution} + \text{mole } H_2O}$$

mole of H_2O = 100 grams H_2O/18 grams H_2O per gram mole = 5.55

For the first entry of the data table in the problem:

$$x = \frac{\left(\frac{0.5}{64}\right)}{\left(\frac{0.5}{64}\right) + 5.55} = 0.0078/(0.0078 + 5.55) = 0.0014$$

Step 2. Completing the following table for Problem 5-1.

c_{SO2} (gm SO_2/100 gm H_2O)	**P^*SO_2 (kPa)**	**y^***	**x**
0.5	6.0	0.059	0.0014
1.0	11.6	0.115	0.0028
1.5	18.3	0.181	0.0042
2.0	24.3	0.24	0.0056
2.5	30.0	0.296	0.0070
3.0	36.4	0.359	0.0084

The above data are plotted in Figure 5-18. Henry's law applies in the given concentration range with Henry's law constant equal to 43 mole fraction SO_2 in air/mole fraction SO_2 water.

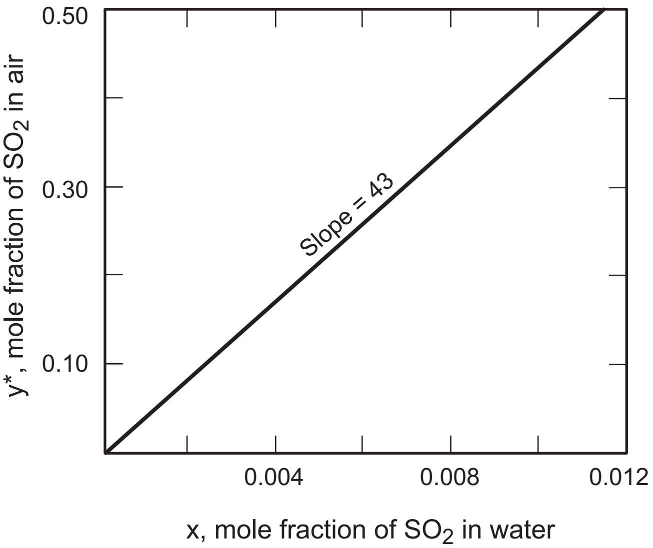


Figure 5-18. SO_2 absorption data

The straight relationship shown in the above graph clearly indicates that Henry's law applies over the concentration range evaluated. Accordingly, it could be used to determine the SO_2 removal efficiency that is theoretically possible if equilibrium were reached.

5.2.2 Contaminant Reactions

The equilibrium limit for absorption is eliminated when the dissolved contaminant reacts with other dissolved materials to form new compounds that cannot diffuse from the liquid to the gas phase. In air pollution control systems used for acid gases, the most common reactants are alkali compounds. When alkali compounds such as soda ash, caustic, and limestone are dissolved in the scrubbing liquid, the dissolved acid gas species are neutralized as indicated in Reactions 5-1 through 5-6.

$H_2SO_3 + OH^- \rightarrow HSO_3^- + H_2O$ Reaction 5-1

$HSO_3 + OH^- \rightarrow SO_3^{-2} + H2O$ Reaction 5-2

$SO_3^{-2} + Ca^{+2} \rightarrow CaSO_3$ Reaction 5-3

$SO_3^{-2} + 0.5\ O_2 \rightarrow SO_4^{-2}$ Reaction 5-4

$SO_4^{-2} + Ca^{+2} \rightarrow CaSO_4$ Reaction 5-5

$HCl + OH^- \rightarrow Cl^- + H_2O$ Reaction 5-6

Reactions 5-1 through 5-6 proceed when there are sufficient hydroxyl ions because of the dissociation of the alkali added to the scrubbing liquor. The presence of sufficient hydroxyl ions is indicated by the liquid pH. Usually, absorbers that depend on the neutralization reactions operate at pH levels between 5.0 and 9.0. There is a high pH limit because the dissolved calcium ions and/or magnesium ions, which often enter as part of the alkali, can precipitate as solid calcium carbonate (limestone) or magnesium carbonate at high pH levels. A pH meter in the recirculation liquid line or recirculation liquid tank is often used to control the alkali feed rate and maintain the pH in the necessary range.

When the dissolved contaminants are reacted in the absorbing liquid, the equilibrium line limit to absorption is eliminated. This is similar to a Henry's law constant of essentially 0.0 (horizontal line).

This does not mean that there are no limits to absorption. The solubility of the products of the neutralization reactions (or other reactions) must be taken into account when determining the necessary scrubbing liquid flow rate. For example, in the acid gas neutralization reactions shown above, the solubility of calcium sulfite ($CaSO_3$) and calcium sulfate ($CaSO_4$) must be considered. If they reach their solubility limits, they can precipitate as solids in absorber packing, piping, and recirculation tanks.

5.2.3 Biofiltration

After absorption into the thin water layers surrounding the packing, the microorganisms metabolize the dissolved organic compounds. The rate of destruction of the organic compounds is independent of the concentration in the waste gas stream. The rate of destruction (or consumption) is usually measured in terms of the grams of pollutant per unit volume per hour. This rate depends on the type of pollutant and the prevailing temperature.

5.3 CAPABILITY AND SIZING

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.

5.3.1 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.

Empirical Model Approach

Most absorber manufacturers have extensive databases describing the performance of their commercial brands of 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 be used to confirm that a specific type of absorber is appropriate for the proposed application and to determine the necessary absorber operating parameters. It can also be used to determine the absorber liquid-to-gas ratio, the alkali requirements, the make-up liquid requirements, the purge liquid flow rate requirements, and the basic sizing parameters such as the absorber diameter and absorber height.

Most absorber manufacturers have incorporated the empirical data from prior installations into mass transfer rate models. These models (1) calculate the liquid-to-gas ratios required at the minimum and average gas temperatures, (2) calculate the number of beds or trays needed for the required removal efficiency, and (3) calculate 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 capability and overall performance capability.

The primary disadvantage of this approach is that occasionally the data provided to the manufacturers are inaccurate or incomplete. For example, some sources have intermittent process operating conditions that can generate high particulate matter loadings that could plug a packed bed or an impingement tray scrubber. In some cases, the gas flow rates estimated for a new process source are less than the actual flow rates generated once the source is completed. Some types of absorbers cannot maintain high removal efficiencies at gas flow rates much 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 an absorber. These tests are conducted preferably 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 this approach 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 series of tests can be conducted relatively quickly to identify the optimal operating conditions. These tests include the liquid-to-gas ratio, the recirculation liquor pH, and the recirculation liquid purge rate. The main disadvantage is that the tests are 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.

5.3.2 Absorber Sizing

Liquid-to-Gas Ratios

The liquid-to-gas ratio is defined as the quantity of recirculation liquid used in the absorber divided by the outlet gas flow rate. This definition is illustrated in Figure 5-19. The liquid-to-gas ratio (L/G) is usually expressed in units of gallons (inlet) per 1,000 ACF (outlet).

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-liquor contact within the absorber. The combinations of factors that influence gas-liquor contact are sometimes referred to as “hydraulic” factors.

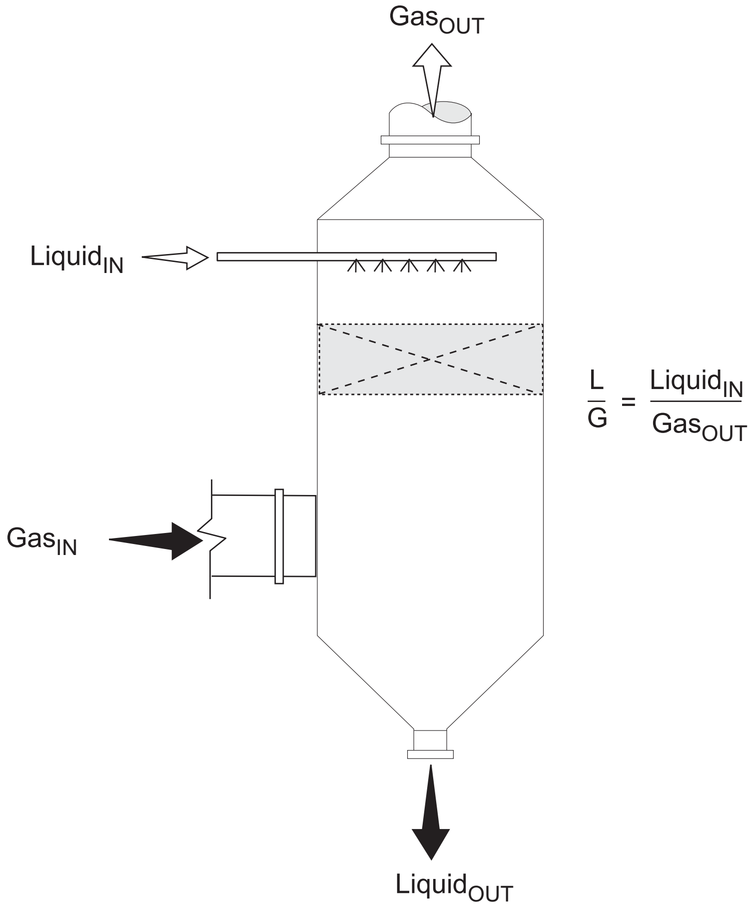
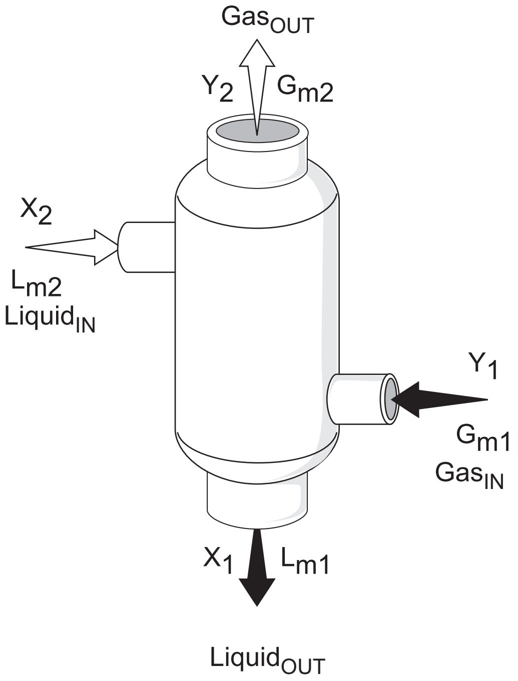


Figure 5-19. Definition of the liquid-to-gas ratio

An approximate estimate of the necessary liquid-to-gas ratio 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 5-20 illustrates a typical counter-current flow absorber for which a material balance is drawn. The contaminant compound is the material that is balanced in these calculations.



$$G_{m1}Y_1 + L_{m2}X_2 = G_{m2}Y_2 + L_{m1}X_1$$

Figure 5-20. Material balance for countercurrent flow absorber

Terms used in Figure 5-20:

G_m = gas flow molar rate (gm moles/hr)
Y = mole fraction of contaminant in gas stream
L_m = liquid molar flow rate (gm moles/hr)
X = mole fraction of the contaminant in pure liquid

These approximate calculations are usually done on a contaminant-free basis to make the material balance calculations easier. The contaminant-free basis is defined in Equations 5-3 and 5-4.

$$Y = \frac{y}{1-y} \tag{5-3}$$

$$X = \frac{x}{1-x} \tag{5-4}$$

In air pollution control systems, the percent of pollutant transferred, y and x, is generally small. Therefore, from Equations 5-3 and 5-4, Y = y, and X = x. In this section, it is assumed that X and Y are always equal to x and y, respectively. If y (inlet gas concentration) is larger than a few percent by volume, this assumption is invalid and will cause errors in the material balance calculations.

An overall balance across the absorber in Figure 5-20 yields the following equation:

$$(\text{gm moles/hr})_{\text{in}} = (\text{gm moles/hr})_{\text{out}}$$

$$G_m(\text{inlet}) + L_m(\text{inlet}) = G_m(\text{outlet}) + L_m(\text{outlet}) \tag{5-5}$$

For convenience, the top of the absorber is designated as point 2, and the bottom is designated as point 1. This changes Equation 5-5 to Equation 5-6.

$$G_{m1} + L_{m2} = G_{m2} + L_{m1} \tag{5-6}$$

In this same manner, a material balance is obtained for the contaminant to be removed.

$$G_{m1} Y_1 + L_{m2} X_2 = G_{m2} Y_2 + L_{m1} X_1 \tag{5-7}$$

Equation 5-7 can be simplified by assuming that as the gas and liquid streams flow through the absorber, their total mass does not change appreciably (i.e., $G_{m1} = G_{m2}$ and $L_{m1} = L_{m2}$). This is justifiable for most air pollution control systems because the mass flow rate of contaminant is very small compared to the liquid and gas mass flow rates. For example, a 10,000 SCFM exhaust stream containing 1,000 ppm SO_2 would be only 0.1% SO_2 by volume or 10 SCFM. If the absorber were 100% efficient, the gas mass flow rate would change from 10,000 SCFM at G_{m1} to 9,990 at G_{m2}. The transfer of a quantity this small is negligible in an overall material balance. Therefore, Equation 5-7 can be reduced to the following:

$$G_m(Y_1 - Y_2) = L_m(X_1 - X_2) \tag{5-8}$$

Rearranging Equation 5-8 yields Equation 5-9.

$$Y_1 - Y_2 = \frac{L_m}{G_m}\left(X_1 - X_2\right) \tag{5-9}$$

Equation 5-9 is the equation of a straight line. When this line is plotted on an equilibrium diagram, it is referred to as an operating line. This line defines operating conditions within the absorber: the material going in and the material coming out. An equilibrium diagram with a typical operating line plotted on it is shown in Figure 5-21. The slope of the operating line is the liquid mass flow rate divided by the gas molar flow rate. Accordingly, the slope of the line is the liquid-to-gas ratio.

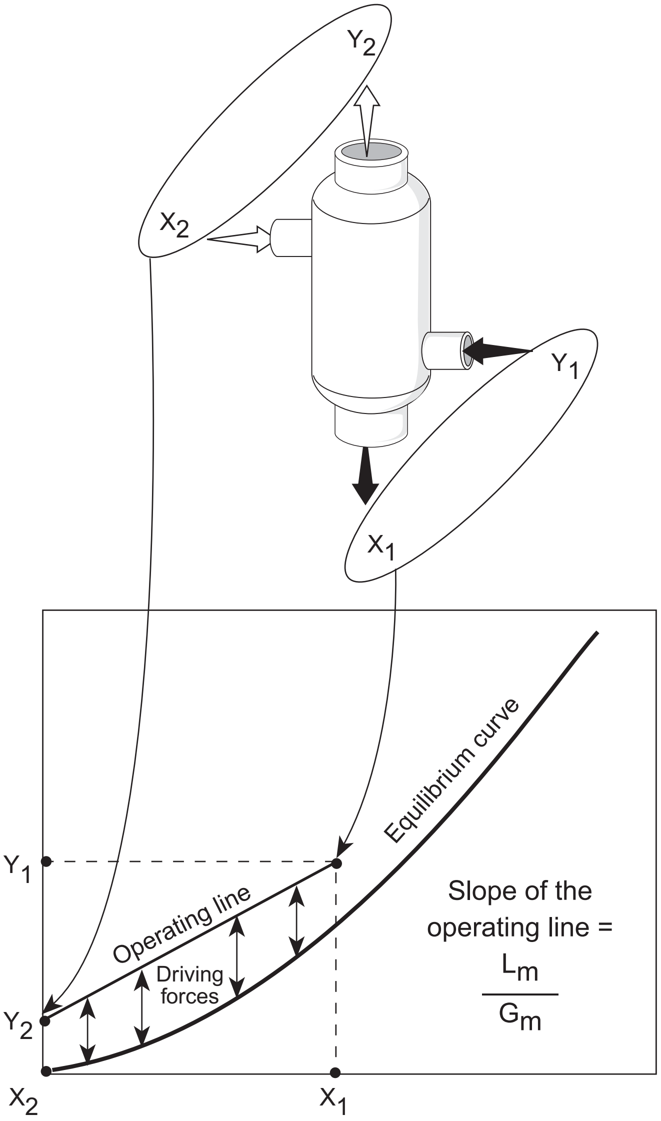


Figure 5-21. Operating line diagram

In the design of most absorption columns, the quantity of gas to be treated (G_m) and the inlet contaminant concentration (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. By plotting these data on an equilibrium diagram, the minimum amount of liquid required to achieve the required outlet concentration (Y_2) can be determined.

Figure 5-22a is a typical equilibrium diagram with operating points plotted for a counter-current flow absorber. At the minimum liquid rate, the inlet gas concentration of contaminant (Y_1) is in equilibrium with the outlet liquid concentration of contaminant (X_{max}). The liquid leaving the absorber is saturated with the contaminant and can no longer dissolve contaminants unless additional liquid is added.

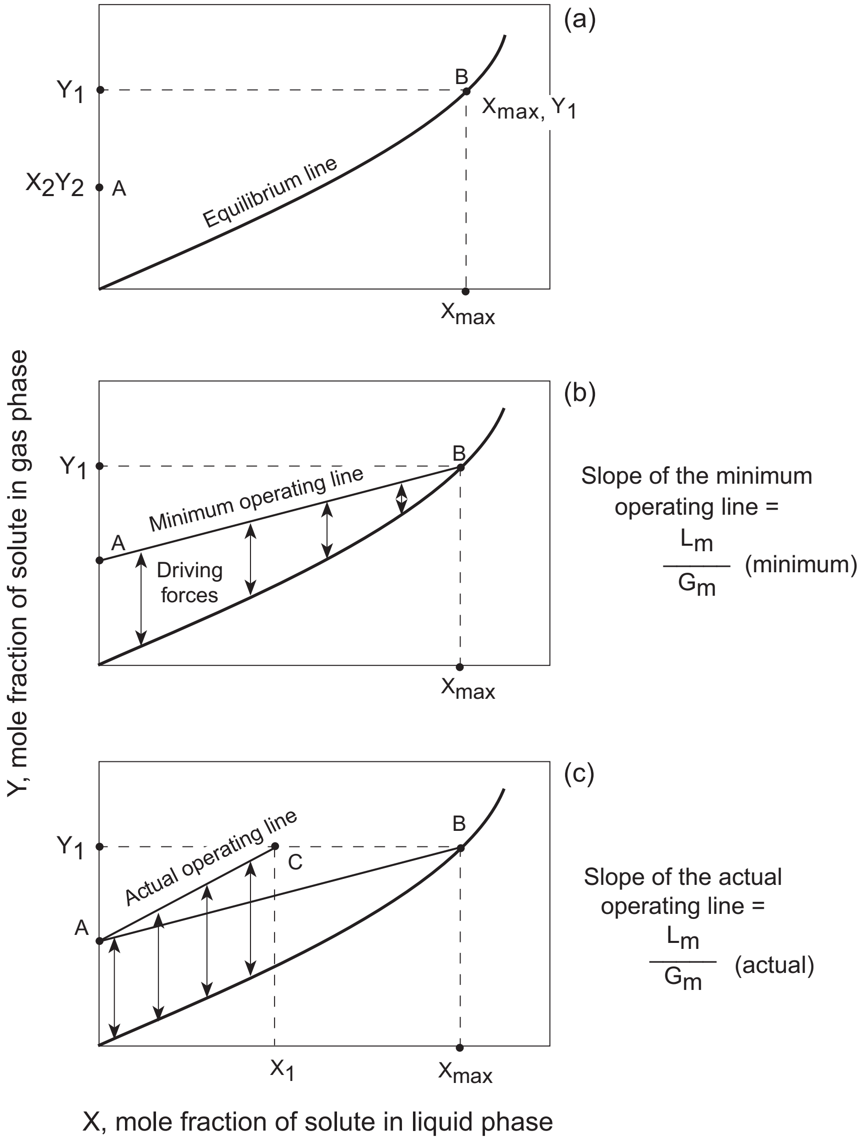


Figure 5-22. Liquid-to-gas ratio

This condition is represented by point B on the equilibrium curve. The slope of the line drawn between point A and point B represents the operating conditions at minimum flow rate in Figure 5-22b. The driving force for mass transfer decreases to zero at point B. The slope of line AB (L_m/G_m) may be determined graphically or from the equation for a straight line. By knowing the slope 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 25% to 100% greater than the minimum. Typical absorber operation would be at 50% greater than the minimum liquid flow rate (i.e., 1.5 times the minimum liquid-to-gas ratio). Setting the liquid rate in this way assumes that the gas flow rate set by the process does not change appreciably. Line AC in Figure 5-22c is drawn at a slope of 1.5 times the minimum L_m/G_m. Line AC is referred to as the operating line because it describes the absorber operating conditions.

The following problem illustrates how to compute the minimum liquid rate required to achieve desired removal efficiency.

Problem 5-2

Using the data and results from Problem 5-1, compute the minimum liquid rate of pure water required to remove 90% of the SO_2 from a gas stream of 85.0 m^3/min (3,000 ACFM) containing 3% SO_2 by volume (gal/min). The temperature is 293°K, and the pressure is 101.3 kPa.

Solution:

Step 1. Sketch and label a drawing of the system. Figure 5-23 shows the pertinent parameters for this problem.

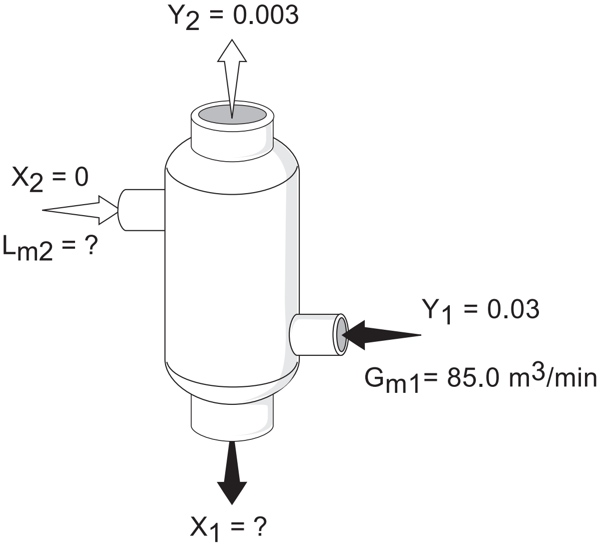


Figure 5-23. Absorber operating conditions in Problem 5-2

Step 2. At the minimum, liquid rate Y_1 and X_1 will be in equilibrium. The liquid will be saturated with SO_2.

$$Y_1 = H\,X_1$$

$$H = 43\frac{\text{mole fraction SO}_2\text{ in air}}{\text{mole fraction SO}_2\text{ in water}}$$ (from Problem 5-1)

$$0.03 = 43\,X_1$$

$$X_1 = 0.000698 \text{ mole fraction}$$

Step 3. The minimum liquid-to-gas ratio from Equation 5-9 is:

$$Y_1 - Y_2 = \frac{L_m}{G_m}(X_1 - X_2)$$

$$\frac{L_m}{G_m} = \frac{Y_1 - Y_2}{X_1 - X_2}$$

$$\frac{L_m}{G_m} = \frac{0.03 - 0.003}{0.000698 - 0}$$

L_m/G_m = 38.7 gm moles water/gm moles air

Step 4. Convert m^3 of air to gram moles, then compute the minimum required liquid flow rate.

At 0°C and 101.3 kPa, there are 0.0224 m^3/gm moles (359 ft^3/lb mole) of an ideal gas.

At 20°C, 0.0244 m^3/gm mole (293°K/273°K) = 0.024 m^3/gm mole

$$G_m = 85.0\frac{m^3}{min}\left(\frac{gm\ mole}{0.024\ m^3}\right)$$

$$= 3{,}540\frac{gm\ mole\ air}{min}$$

L_m/G_m = 38.7 gm moles water/gm mole air (at minimum)

L_m = (38.7)(3,540) = 137,000 gm mole water/min in mass units

L = 137,000 gm moles H_2O/min (18 gm/gm mole H_2O)

= 2,470,000 gm/min

$$L = 2{,}470{,}000\ \text{gm/min}\left(\frac{1\ lb_m}{453.6\ gm}\right)\left(\frac{1\ ft^3}{62.4\ lb_m}\right)\left(7.48\frac{gal}{ft^3}\right)$$

L = 653 gal/min

Step 5. Figure 5-24 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).

38.7 x 1.5 = 58.1

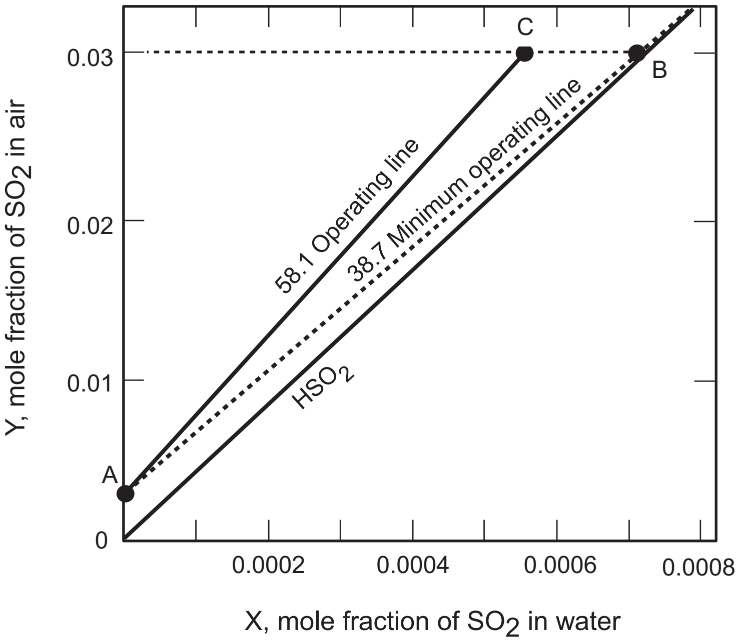


Figure 5-24. Liquid-to-gas ratio in Problem 5-2

The evaluation technique shown 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 to 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 5-10).

$$AF = \frac{L_2}{mG_1} \tag{5-10}$$

Where:

AF = absorption factor
L_2 = moles of liquid entering the scrubber
m = slope of the equilibrium line on a mole fraction basis
G_1 = moles of gas entering the scrubber

This is simply the ratio of the slope of the equilibrium line and the slope of the actual operating line.

5.3.3 Packed Tower Absorber Diameter and Height

Packed Tower Absorber Diameter

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.

The main parameter that affects the size 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. By decreasing the diameter of the column, the gas flow rate through the column increases. If the gas flow rate 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-to-liquid flow ratio is termed the loading point. The pressure drop over the column begins to increase, and the degree of mixing between the phases decreases. A further increase in gas velocity 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. The pressure drop increases substantially, and mixing between the phases is minimal. 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.

Normal practice is to size a packed column diameter to operate at a certain percent of the flooding velocity. A typical operating range for the gas velocity through the columns is 50% to 75% of the flooding velocity. 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. One version of the flooding and pressure drop relationship in a packed tower is the generalized Sherwood flooding and pressure drop correlation shown in Figure 5-25.

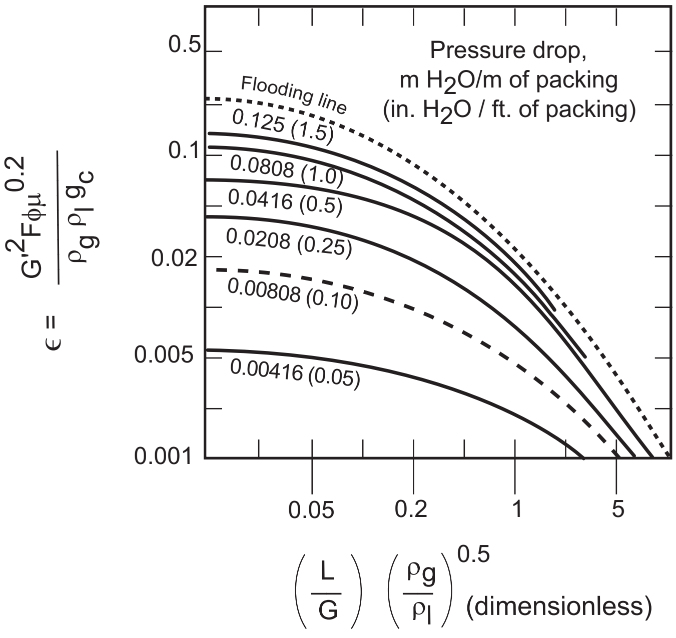


Figure 5-25. Generalized Sherwood flooding and pressure drop correlation

This correlation is based on the physical properties of the gas and liquid streams and on the tower packing characteristics. The procedure to determine the tower diameter is summarized in the following set of calculations.

Step 1. Calculate the value of the abscissa (horizontal axis) of Figure 5-25 using Equation 5-11.

$$\text{Abscissa} = \left(\frac{L}{G}\right)\left(\frac{\rho_g}{\rho_l}\right)^{0.5} \tag{5-11}$$

Where:

L = mass flow rate of liquid stream
G = mass flow rate of gas stream
ρ_g = gas density
ρ_l = liquid density

Step 2. Calculate the flooding pressure drop using the Equation 5-12 derived by Kister and Gill.[6] The packing factors should be obtained from the manufacturer of the packing or from the book by Strigle.[7]

$$\Delta P_{flood} = 0.115\ F_p^{0.7} \tag{5-12}$$

Where:

F_p = packing factor (dimensionless)

Step 3. From the point on the abscissa, move vertically up to the flooding line and read the ordinate ε at the flooding pressure drop calculated in Equation 5-12.

Step 4. Calculate the gas flow rate at flooding using Equation 5-13.

$$G^* = \left(\frac{\varepsilon \rho_g \rho_l g_c}{F_p \phi \mu^{0.2}} \right)^{0.5} \tag{5-13}$$

Where:

G^* = mass flow rate of gas per unit cross sectional area at flooding ($lb_m/ft^2 \cdot sec$)
ε = ordinate of Sherwood Correlation (Figure 5-25)
ρ_g = density of gas (lb_m/ft^3)
ρ_l = density of liquid (lb_m/ft^3)
g_c = gravitational acceleration (32.2 $lb_m \cdot ft/lb_f \cdot sec^2$)
F_p = packing factor (Table 5-3) (dimensionless)
ϕ = specific gravity of absorbent (dimensionless)
μ_l = viscosity of liquid ($lb_m/ft \cdot sec$)

Step 5. Calculate the actual gas flow rate per unit area as a fraction of the gas flow rate at flooding (Equation 5-14).

$$G_{op} = G^* f \tag{5-14}$$

Where:

G_{op} = Actual gas flow rate per unit area ($lb_m/ft^3 \bullet sec$)
f = coefficient (0.75)

Step 6. Calculate the packed bed diameter based on the actual gas flow rate per unit area in the system.

$$\text{Tower Area} = \frac{\text{Total gas flow rate}}{\text{Gas flow rate per unit area}} \tag{5-15}$$

$$\text{Tower Diameter} = \frac{(4 \times \text{Tower Area})^{0.5}}{\pi} \tag{5-16}$$

$$\text{Tower Diameter} = 1.13\ A^{0.5} \tag{5-17}$$

Table 5-3. Packing Data[1]

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)	1.5x0.03	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

1. 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 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™ saddles.

Solution:

Step 1. Calculate the value of the abscissa in Figure 5-25.

From Problem 5-2:

G_m = 3,540 gm mole/min
L = 2,470 kg/min

Convert gas molar flow to a mass flow, assuming molecular weight of the gas to be 29 gm/gm mole.

$$G = (3{,}540 \text{ gm mole/min})(29 \text{ gm/gm mole})$$
$$= 102{,}700 \text{ gm/min} = 102.7 \text{ kg/min}$$

Adjusting the liquid flow to 1.5 time the minimum:

$$L = 1.5\,(2{,}470 \text{ kg/min}) = 3{,}710 \text{ kg/min}$$

The densities of air and water at 293K are:

$\rho_l = 1{,}000 \text{ kg/m}^3$

$\rho_g = 1.17 \text{ kg/m}^3$

Calculate the abscissa using Equation 5-11.

$$\text{Abscissa} = \left(\frac{L}{G}\right)\left(\frac{\rho_g}{\rho_l}\right)^{0.5}$$

$$= \left(\frac{3{,}710}{102.7}\right)\left(\frac{1.17}{1{,}000}\right)^{0.5} = 1.24$$

Step 2. Determine the flooding pressure drop using Equation 5-12 and the packing factor (F_p) data in Table 5-3.

$$\Delta P_{\text{flood}} = 0.115\, F_p^{0.7} = 0.115\,(40)^{0.7} = 1.52$$

Step 3. Determine the ordinate in Figure 5-25.

At an abscissa of 1.52, the ordinate is 0.019.

Step 4. Calculate the gas flow rate per unit area at flooding.

$$G^* = \left(\frac{\varepsilon\, \rho_g\, \rho_l\, g_c}{F_p\, \phi\, \mu_l^{0.2}}\right)^{0.5}$$

For water, $\phi = 1.0$, and the liquid viscosity is equal to 0.0008 Pa·sec.

From Table 5-3, for two inch Intalox™ saddles,

$F_p = 40 \text{ ft}^2/\text{ft}^3$ or $131 \text{ m}^2/\text{m}^3$

$g_c = 9.82 \text{ kg/m}^3 \bullet \text{sec}$

$$G^* = \left(\frac{(0.019)(1.17)(1000)(9.82)}{131(1.0)(0.0008^{0.2})}\right)^{0.5}$$

$G^* = 2.63 \text{ kg/m}^3 \bullet \text{sec}$ at flooding

Step 5. Calculate the actual gas flow rate per unit area.

$$G_{op} = 0.75\,(2.63) = 1.97 \text{ kg/m}^3 \bullet \text{sec}$$

Step 6. Calculate the tower diameter.

Tower Area = Gas Flow Rate/G_{op}

$$\frac{(102.7\ \text{kg/min})(\text{min/60 sec})}{1.97\ \text{kg/m}^2 \bullet \text{sec}} = 0.87\text{m}^2$$

Tower Diameter = 1.13 $A^{0.5}$ = 1.05 m

Packed Tower Absorber Height

The height of a packed tower absorber refers to the depth of packing material needed to accomplish the required removal efficiency. The more difficult the separation, the larger the packing height required. For example, a much larger packing height would be required to remove SO_2 than to remove Cl_2 from an exhaust stream using water as the absorbent. This is 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 are used to predict the required packing height. These equations are based on diffusion principles. The general form of the design equation for a gas phase controlled resistance (common in air pollution systems) is given in Equation 5-18.

$$Z = \frac{G^*}{K_g a P} \int_{Y_2}^{Y_1} \frac{dY}{(1-Y)(Y-Y^*)} \quad (5\text{-}18)$$

Where:

Z = height of packing (m)
K_g = overall gas film coefficient (gm moles/hr•m^2•Pa)
G* = mass flow rate of gas per unit cross sectional area at flooding (lb_m/ft^2•sec)
a = interfacial contact area (m^2)
P = pressure of the system (kPa)
Y = mole fraction pollutant
Y* = mole fraction pollutant at equilibrium

In analyzing Equation 5-18, the term $G^*/K_g aP$ has the dimension of length and is defined 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 5-18 can be simplified to Equation 5-19.

$$Z = (HTU)(NTU) \quad (5\text{-}19)$$

Where:

HTU = height of a transfer unit (m)
NTU = number of transfer units

The concept of a transfer unit comes from the operation of tray tower absorbers. Discrete stages (trays) of separation occur in tray tower units. 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 are based on either the gas or liquid phase. Equation 5-19 is modified to yield Equation 5-20.

$$Z = N_{OG} H_{OG} = N_{OL} N_{OL} \tag{5-20}$$

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 (m)
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 (m)

Values for the height of a transfer unit used in designing absorption systems 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 graphs that can be used to estimate the height of a transfer unit. These graphs do not provide the accuracy of pilot plant data, but they are less expensive and easier to use. Figure 5-26 gives a typical example of a graph for the ammonia-water system. In this figure, the superficial gas flow rate is plotted versus the H_{OG} with the superficial liquid rate as a parameter. It is also common to plot liquid rate versus the H_{OG} and have the gas rate as a parameter. In applying these data, it is important that the process conditions be similar to the conditions at which the HTU was measured.

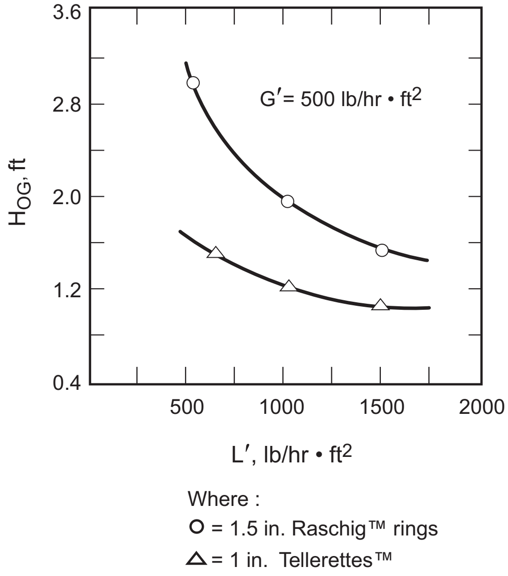


Figure 5-26. Height of a transfer unit, ammonia and water system

When no experimental data are available, or if only a preliminary estimate of absorber efficiency is needed, there are generalized correlations available to predict the height of a transfer unit. The correlations for predicting the H_{OG} or the H_{OL} are empirical in nature and are a function 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 from a variety of methods. When the pollutant concentration is low, and the equilibrium line is straight, Equation 5-21 can be used to determine the number of transfer units (N_{OG}) based on the gas phase resistance. Equation 5-21 can be derived from the integral portion of Equation 5-18.

$$N_{OG} = \frac{\ln\left[\frac{(Y_1 - mX_2)}{(Y_2 - mX_2)}\left(1 - \frac{mG_m}{L_m}\right) + \left(\frac{mG_m}{L_m}\right)\right]}{1 - \frac{mG_m}{L_m}} \qquad (5\text{-}21)$$

Where:

Y_1 = mole fraction of pollutant in entering gas
m = slope of the equilibrium line
X_2 = mole fraction of pollutant entering the absorber in the liquid
Y_2 = mole fraction of pollutant in exiting gas
G_m = molar flow rate of gas (kg mole/hr)
L_m = molar flow rate of liquid (kg mole/hr)

Equation 5-21 may be solved directly or graphically by using the Colburn diagram presented in Figure 5-27. The Colburn Diagram is a plot of the N_{OG} versus $\ln[(Y_1 - mX_2)/(Y_2 - mX_2)]$ at various values of (mG_m/L_m). Figure 5-26 is used by first computing the value of $\ln[(Y_1 - mX_2)/(Y_2 - mX_2)]$, reading up the graph to the line corresponding to (mG_m/L_m), and then reading across to obtain the N_{OG}.

Equation 5-21 can be further simplified for situations where (1) a chemical reaction occurs, (2) the pollutant is extremely soluble, or (3) the operating line is straight (low concentrations of solute in the inlet gas). In these cases, the pollutant exhibits almost no partial pressure, and, therefore, the slope of the equilibrium line approaches zero (m = 0). For any of these cases (very soluble or reactive pollutants), Equation 5-21 reduces to Equation 5-22.

$$N_{OG} = \ln\left(\frac{Y_1}{Y_2}\right) \qquad (5\text{-}22)$$

The number of transfer units depends only on the inlet and outlet concentration of the pollutant. For example, if the conditions in Equation 5-22 are met, 2.3 transfer units are required to achieve 90% removal of any pollutant. Equation 5-22 only applies when the equilibrium line is straight (low concentrations) and the slope approaches zero (very soluble or reactive pollutants). Problem 5-4 illustrates the use of Equation 5-22.

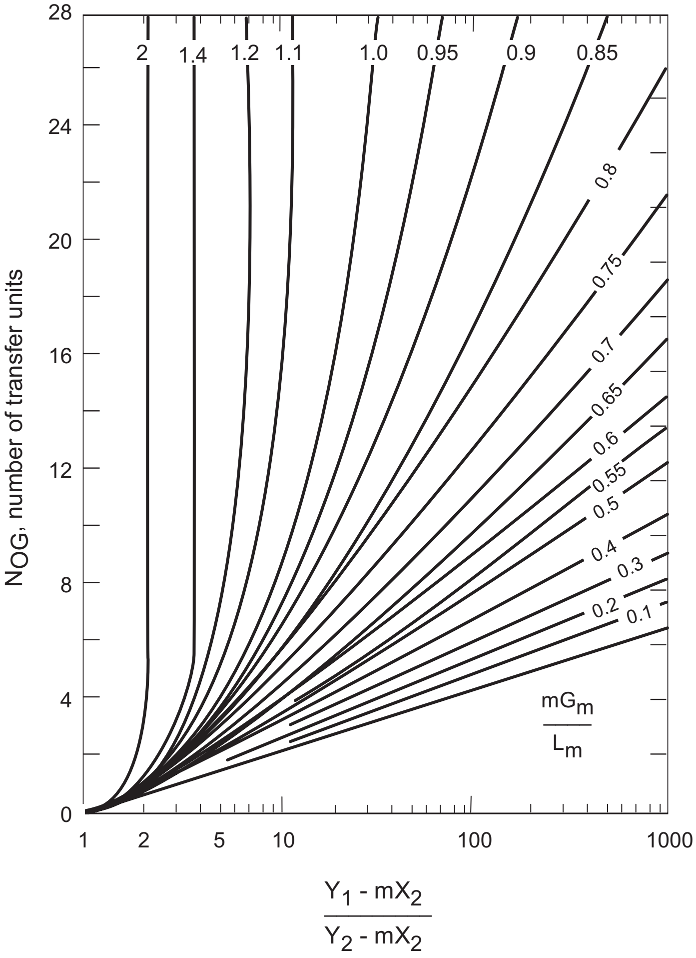


Figure 5-27. Colburn diagram

Problem 5-4

From pilot plant studies of the absorption system in Problem 5-2, it was determined that the H_{OG} for the SO_2-water system is 0.829 m. Calculate the total height of packing required to achieve 90% removal.

Solution:

Step 1.Use data from previous problems.

m = 43 kg moles in water/kg mole in air
G_m = 3.4 kg mole air/min
L_m = (3,710 kg/min)(kg mole H_2O/18 kg) = 206 kg mole/min
X_2 = 0 (no recirculated liquid)
Y_1 = 0.03
Y_2 = 0.003

Step 2. Compute the N_{OG} from Equation 5-21.

$$N_{OG} = \frac{\ln\left[\frac{(Y_1 - mX_2)}{(Y_2 - mX_2)}\left(1 - \frac{mG_m}{L_m}\right) + \left(\frac{mG_m}{L_m}\right)\right]}{1 - \frac{mG_m}{L_m}}$$

$$N_{OG} = \frac{\ln\left[\frac{(0.03)}{(0.003)}\left(1 - \frac{(43)(3.5)}{206}\right) + \left(\frac{(43)(3.5)}{206}\right)\right]}{1 - \frac{(43)(3.5)}{206}}$$

$N_{OG} = 4.57$

Step. 3. The total packing height is:

$Z = (H_{OG})(N_{OG}) = (0.892)(4.57) = 4.1$ m

5.3.4 Tray Tower Absorber Diameter and Height

In a tray tower absorber, the liquid enters at the top of the tower, passes over the top trays, and then down over each lower tray until it reaches the bottom. 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 or stage process.

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 by using the gas velocity through the tower. If the gas velocity is too great, liquid droplets are entrained, causing a condition known as priming. Priming occurs when the gas velocity through the tower is so great that it causes liquid on one tray to foam and rise to the tray above. Priming reduces absorber efficiency by inhibiting gas and liquid contact. For the purpose of determining tower diameter, priming in a tray tower is analogous to the flooding point in a packed tower: it determines the minimum acceptable diameter. The actual diameter should be larger. Equation 5-23 expresses the smallest allowable diameter for a tray tower absorber.

$$d = \psi\left(Q\sqrt{\rho_g}\right)^{0.5} \tag{5-23}$$

Where:

Ψ = Empirical correlation ($ft^{0.25}\cdot min^{0.5}/lb^{0.25}$)

Q = Volumetric gas flow rate (ft^3/min)

ρ_g = Gas density (lb_m/ft^3)

The term Ψ is an empirical correlation and is a function of both the tray spacing and the densities of the gas and liquid streams. Values for Ψ in Table 5-4 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 5-4. Tray Spacing Parameters[11]

Tray	Metric[1]	English[2]
Bubble Cap	0.0162	0.1386
Sieve	0.0140	0.1198
Valve	0.0125	0.1069

[1] Metric expressed in $m^{0.25} \cdot hr^{0.5}/kg^{0.25}$ for use with Q expressed in m^3/hr, and ρ_g expressed in kg/m^3

[2] English expressed in $ft^{0.25} \cdot min^{0.5}/lb^{0.25}$ for use with Q in ACFM, and ρ_g expressed in lb/ft^3

Depending on operating conditions, trays are spaced at a minimum distance between plates to allow the gas and liquid phases to separate before reaching the plate above. Trays should be spaced to allow for easy maintenance and cleaning. They are normally spaced 45 cm to 70 cm (18 to 28 in) apart. If Table 5-4 is being used for tray spacing different than 61 cm (24 in.), a correction factor must be used. Figure 5-28 is used to determine the correction factor that is multiplied by the estimated diameter.

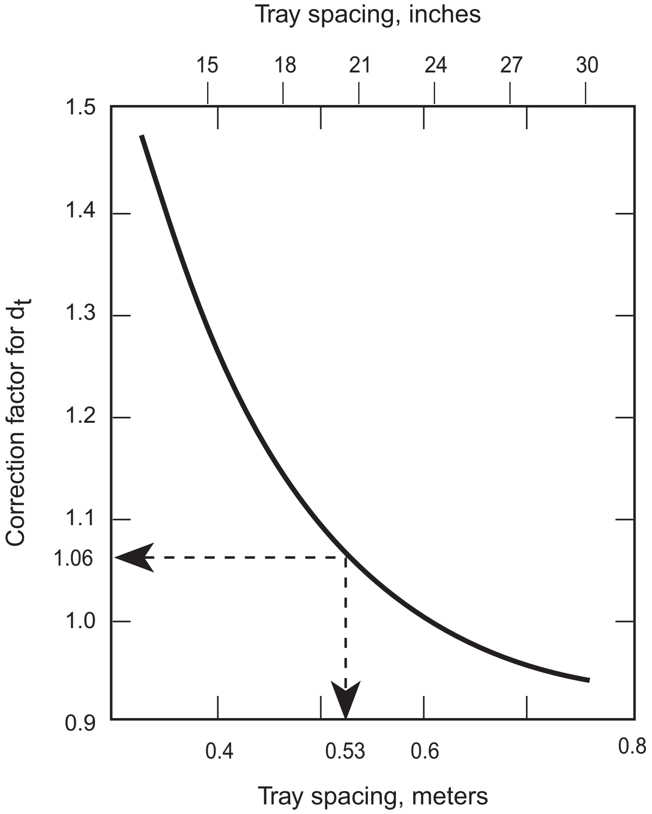


Figure 5-28. Tray spacing correction factor

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. Use a liquid density of 1.03 kg/m^3.

Solution:

From Problem 5-2:

Gas flow rate = Q = 85.0 m^3/min

Density = ρ_g = $\left(\frac{\text{gm mole}}{0.024\ \text{m}^3}\right)\left(\frac{29\ \text{gm}}{\text{gm mole}}\right) = 1.21\ \text{kg/m}^3$

From Table 5-2 for a bubble cap tray:

$\Psi = 0.0162\ \text{m}^{0.25}\cdot\text{hr}^{0.50}/\text{kg}^{0.25}$

Before Equation 5-22 can be used, Q must be converted to m^3/hr.

Q = (85.0 m^3/min)(60 min/hr) = 5,100 m^3/hr

Step 1. Substituting these values into Equation 5-23 for a minimum diameter,

$$d = \psi(Q\sqrt{\rho_g})^{0.5}$$

$$d = (0.0162)[5{,}100\ (1.21)^{0.5}]^{0.5} = 1.21\ \text{m}$$

Correct this diameter for a tray spacing of 0.53 m.

Step 2. From Figure 5-28, read a correction factor of 1.06.

Therefore, the minimum diameter is

d = 1.21 (1.06) = 1.28 meters (4.20 feet)

Note: This estimated diameter is the minimum acceptable diameter based on the conditions. In practice, a larger diameter is usually chosen.

Height of Tray Tower Absorbers

There are several methods used to determine the number of ideal plates or trays required for a given removal efficiency. These methods can become quite complicated. One method used is a graphical technique.

The number of ideal plates is obtained by drawing "steps" on an operating diagram. This procedure is illustrated in Figure 5-29. This method can be rather time consuming, and inaccuracies can result at both ends of the graph.

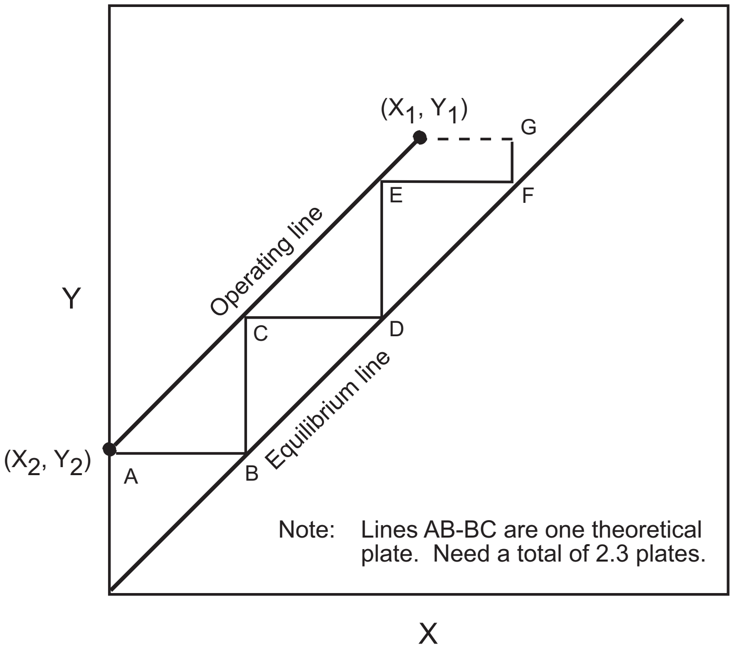


Figure 5-29. Graphic determination of the number of theoretical plates

Equation 5-24 is a simplified method of estimating the number of plates. It can only be used if both the equilibrium and operating lines for the system are straight. This is a valid assumption for most air pollution control systems. Equation 5-24, taken from Reference 7, is very similar to Equation 5-21 for computing the N_{OG} of a packed tower.

$$N_{OG} = \frac{\ln\left[\frac{(Y_1 - mX_2)}{(Y_2 - mX_2)}\left(1 - \frac{mG_m}{L_m}\right) + \left(\frac{mG_m}{L_m}\right)\right]}{\ln\left(\frac{L_m}{mG_m}\right)} \qquad (5\text{-}24)$$

Equation 5-24 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 are used to describe absorption efficiency for a plate tower: (1) an overall efficiency, which is concerned with the entire column, (2) Murphree efficiency, which is applicable to a single tray, and (3) local efficiency, which pertains to a specific location on a tray. A number of methods are available to predict these plate efficiencies, but these methods are complex, and values predicted by two different methods for a given system can vary by as much as 80%.

The simplest of the tray efficiency concepts, the overall efficiency, is the ratio of the number of theoretical plates to the number of actual plates. Because overall tray efficiency is an oversimplification of the process, reliable values are difficult to obtain. 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 absorber in Problem 5-5. Use the same conditions as in Problem 5-4. 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.

$Y_1 = 0.03$

$Y_2 = 0.003$

$X_2 = 0$

$L_m = 206$ kg mole H_2O/min

$G_m = 3.5$ kg mole air/min

Step. 1. The number of theoretical plates from Equation 5-27 is:

$$N_{OG} = \frac{\ln\left[\frac{(Y_1 - mX_2)}{(Y_2 - mX_2)}\left(1 - \frac{mG_m}{L_m})\right) + \left(\frac{mG_m}{L_m}\right)\right]}{\ln\left(\frac{L_m}{mG_m}\right)}$$

$$N_{OG} = \frac{\ln\left[\frac{(0.03 - 0)}{(0.003 - 0)}\left(1 - \frac{(43)(3.5)}{206}\right) + \left(\frac{(43)(3.5)}{206}\right)\right]}{\ln\left(\frac{206}{(43)(3.5)}\right)}$$

$N_{OG} = 3.92$ theoretical plates

Step 2. Assuming that the overall plate efficiency is 40%, the actual number of trays is:

Actual plates = 3.92/0.40 = 9.8 or 10 trays

Step 3. The height of the tower is give by:

$Z = N_p \times$ tray spacing + 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 trays (0.53 m/tray) + 0.53 m

Z = 5.83 meters

This height of the tray tower absorber calculated in Problem 5-6 is higher than that predicted 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.

5.3.5 Mist Eliminator Evaluation

There are definite limits to the gas velocity through the mist eliminator. 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 5-5.

Table 5-5. Gas Velocities Through Mist Eliminators[1]

Mist Eliminator Type	Orientation	Maximum Gas Velocity (ft/sec)
Zigzag[2]	Horizontal	15 - 20
Zigzag[2]	Vertical	12 - 15
Mesh Pad	Horizontal	15 - 23
Mesh Pad	Vertical	10 - 15
Woven Pad[3]	Vertical	7 - 15
Tube Bank	Horizontal	18 - 23
Tube Bank	Vertical	12 - 16

1. Source, Reference 12
2. Termed chevron in remainder of manual
3. Source, Reference 13

The actual maximum velocities that apply to the specific type of mist eliminator should be determined from the manufacturers' specification sheets. These data can then be used to confirm that the mist eliminator is located in an area with gas velocities below the maximum levels. The average gas velocity through the mist eliminator can be calculated simply by dividing the actual gas flow rate by the area of the mist eliminator, as shown in Equation 5-25.

$$\text{Velocity} = \frac{\text{Gas flow rate, ft}^3\text{/min}}{\text{Mist Eliminator area, ft}^2}\left(\frac{\text{min}}{60\,\text{sec}}\right) \tag{5-25}$$

5.3.6 Alkali Requirements

Absorption systems sometimes need an alkali addition system if they are treating gas streams that have acidic gases. The most common acidic gases are sulfur dioxide, hydrogen chloride, and hydrogen fluoride. Carbon dioxide, which is formed in all combustion processes involving fossil fuels, wood fuels, and waste fuels, is also acidic. The alkali requirements are usually calculated based on the quantities of acidic gases captured and the molar ratios necessary for reactions such as 5-7, 5-8, and 5-9.

$SO_2 + Ca(OH)_2 + 0.5\ O_2 \longrightarrow (CaSO_4)_s + H_2O$ Reaction 5-7

$2HCl + Ca(OH)_2 \longrightarrow 2Ca^+ + 2\ Cl^- + 2H_2O$ Reaction 5-8

$2HF + Ca(OH)_2 \longrightarrow 2Ca^+ + 2\ F^- + 2H_2O$ Reaction 5-9

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 removal efficiency of 98%.

Solution:

The quantity of HCl absorbed in the scrubbing liquid is calculated as follows.

$$\mathrm{HCl} = 10{,}000\,\mathrm{SCFM}\left(\frac{\mathrm{lb\,mole}}{385.4\,\mathrm{SCF}}\right)\left(\frac{0.00005\,\mathrm{lb\,mole\,HCl}}{\mathrm{lb\,mole\,total}}\right)\left(\frac{95\%\ \mathrm{Efficiency}}{100\%}\right)$$

HCl = 0.00123 lb mole HCl/min

$$\mathrm{Ca(OH)_2\ req'd} = \left(\frac{1\,\mathrm{lb\,mole\,Ca(OH)_2}}{2\,\mathrm{lb\,mole\,HCl}}\right)\left(\frac{0.00123\,\mathrm{lb\,mole\,HCl}}{\mathrm{min}}\right) = \frac{0.000615\,\mathrm{lb\,mole\,Ca(OH)_2}}{\mathrm{min}}$$

$Ca(OH)_2$ req = 0.00062 lb mole/min (74 lb/lb mole) = -0.0455 lb/min = 2.73 lb/hour

The alkali feed system should be designed to provide sufficient alkali during times of peak acidic 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 severe pH excursions to values less than approximately 5. At these levels, the rate of corrosion begins to accelerate, especially in the presence of chlorides and fluorides.

5.3.7 Instrumentation – Standard 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 dissolved acids
- Excessive liquid temperatures
- Corrosion

The example absorber system flowchart shown in Figure 5-30 illustrates the instruments that can be installed to identify the onset of these problems. These instruments might be required as part of a periodic monitoring program (e.g., Compliance Assurance Monitor (CAM)), or as part of an operating permit.

The system shown in Figure 5-30 is a three-tray impingement tray scrubber 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.

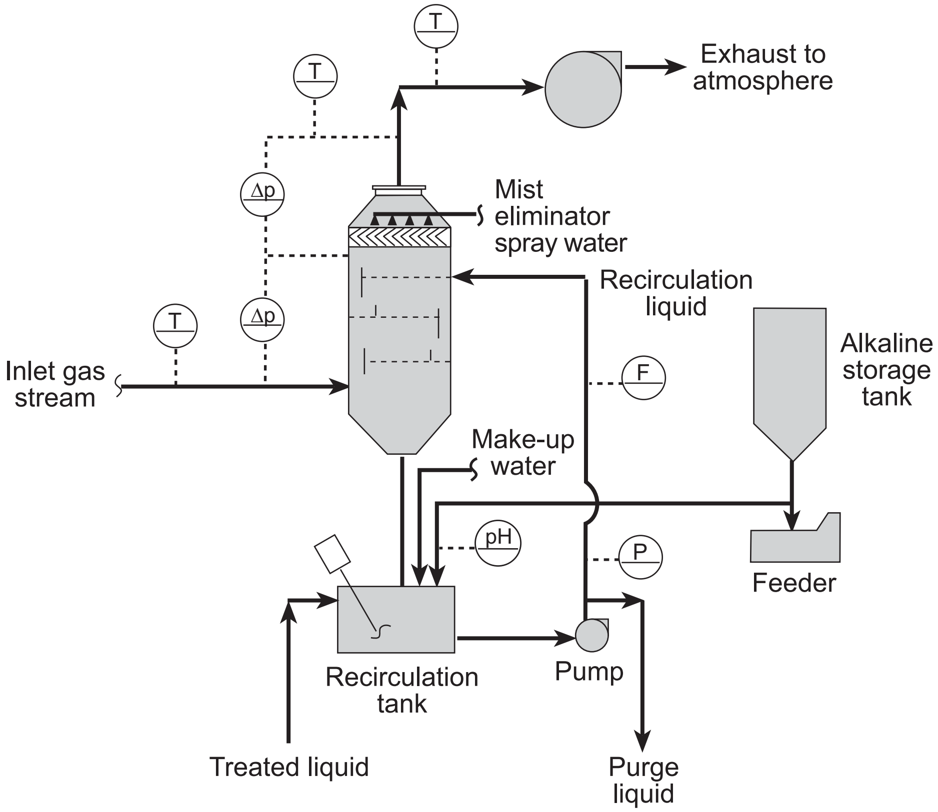


Figure 5-30. Performance monitoring instruments on an example absorber system

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-by-tray static pressure drops, 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 very difficult to use on absorbers. The gas stream is usually close to saturation at the outlet of the absorber. It is hard to extract a gas stream 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 a relatively constant value. Deviations from the baseline level indicate buildup of solids. 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). Solids accumulations can increase mist eliminator pressure drops by more than 1 in. W.C. (0.25 kPa).

If high-pressure drop is occurring, 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 drops well below the baseline range suggest that part of the mist eliminator has fallen apart or otherwise 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. can create a force of over 1,400 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. Some units constructed of FRP and other synthetic materials can suffer adhesive failure if there is a gas temperature spike. This can cause 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 5-30) provide a direct indication of changes in the liquid flow rate. Large decreases in the liquid flow rate can impair performance by causing saturation conditions or by causing inadequate gas-liquid contact.

There are a variety of instruments used to monitor liquid flow rates. These include (1) magnetic flow meters, (2) ultrasonic flow meters, (3) orifice meters, and (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 and dissolved solids levels in the recirculation liquid. Solids can precipitate as a layer inside the pipe and blind the sensors of magnetic flow meters and ultrasonic meters. High-suspended solids levels can erode orifice plates and block the movement of swinging vane meters.

Other indicators of liquid flow rate are useful in absorber systems that have vulnerable liquid flow meters because of the high suspended and dissolved 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 a nozzle supply header is usually because of plugging of the nozzle orifices or the header itself.

Another indirect indicator of reduced liquid flow is the outlet gas temperature. The outlet temperature can increase from normal levels because of the poor gas-liquid contact caused in part by low liquid flow rates. The interpretation of outlet gas temperature data is discussed further in the section concerning the variety of operating problems that contribute to poor gas-liquid contact.

Outlet Gas Temperature

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 stream and the liquid. The adiabatic saturation temperature is the temperature that is reached as heat is transferred from the gas phase to the liquid phase due to the vaporization of liquid. The term *adiabatic* simply means that there is no net heat transfer in or out of the absorber when gas-liquid contact occurs. While this is not precisely the case, adiabatic conditions can be assumed for absorber vessels in order to simplify the determination of the adiabatic saturation temperature.

The adiabatic saturation temperature is estimated using a procedure illustrated in the psychrometric chart in Figure 5-31. The starting point in the procedure is a point on the psychrometric chart defined by the inlet gas stream dry bulb temperature and absolute humidity (generally estimated based on information concerning the process). From the point established by these two conditions, go parallel to an adiabatic saturation line until reaching the 100% relative humidity line. The adiabatic saturation temperature is indicated on the psychrometric chart.

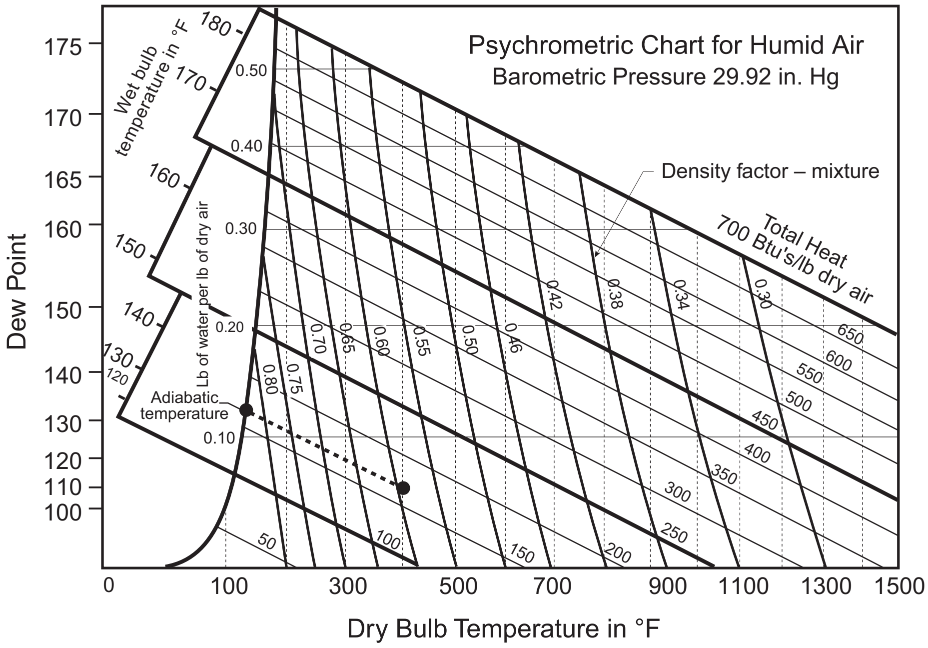


Figure 5-31. Psychrometric chart

Absorber outlet gas temperatures more than 5°F to 10°F (2.7°C to 5.5°C) above the adiabatic saturation temperature are sometimes associated with significant gas-liquid maldistribution or inadequate recirculation liquid flow. Some of the conditions that could create gas-liquid maldistribution in the various types of absorbers are listed below.

Spray Towers

- Plugging of one or more spray nozzles
- Plugging of nozzle supply headers
- Maldistribution of the gas stream entering the vessel

Packed Bed

- Inadequate liquid distribution at the top and/or inadequate redistribution between beds in the vertical tower
- Channeling due to plugging in the bed
- Collapse of one or more beds

Tray Towers

- Sloped, bowed, or warped trays
- Gas short-circuiting up incompletely full 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

- Gas maldistribution entering the converging area of the throat

Ejectors

- Inadequate distribution of liquid across the ejector section
- Erosion of the ejector nozzle

Static Pressure Drop

The absorber static pressure drop provides a useful indication of pluggage of packed beds or impingement trays. Static pressure drops above the baseline levels for the unit are usually caused by partial pluggage.

A change in the overall gas flow rate through the system can be evaluated by checking the process operating rate and the fan motor currents, if monitored. A decrease in the fan motor current is usually associated with a drop in the gas flow rate through the absorber system.

Recirculation Liquor pH

Data concerning the variations in the recirculation liquid pH levels are very 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 that are occasionally above 9 indicate the potential for precipitation of calcium and magnesium compounds. These deposits can cause severe plugging of spray nozzles, distributors, packed beds, and trays. Furthermore, they 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 provided to neutralize the acidic gases being absorbed. Low removal efficiencies are probable because of the potential for saturation of the liquid stream.

When the pH is lower than 5, severe corrosion of metallic components is possible. Corrosion is especially rapid when the low pH conditions occur in systems with high dissolved chloride or fluoride concentrations.

5.3.8 Instrumentation – Biofiltration Systems

A flowchart of a biofiltration system is shown in Figure 5-33. The instrumentation on these systems may be limited. Therefore, portable instruments may be important in evaluating their performance.

Inlet Gas Temperature

The instrumentation can be limited to simply an inlet temperature monitor. Inlet temperatures significantly above 105°F (41°C) indicate a failure in the humidification system, which threatens the microorganisms.

Inlet Gas Relative Humidity

The relative humidity of the inlet gas stream can be measured qualitatively using portable instruments including relatively simple wet bulb-dry bulb thermometers and battery powered instruments. Relative humidity in excess of 95% is needed to maintain the necessary water layers over the packing material.

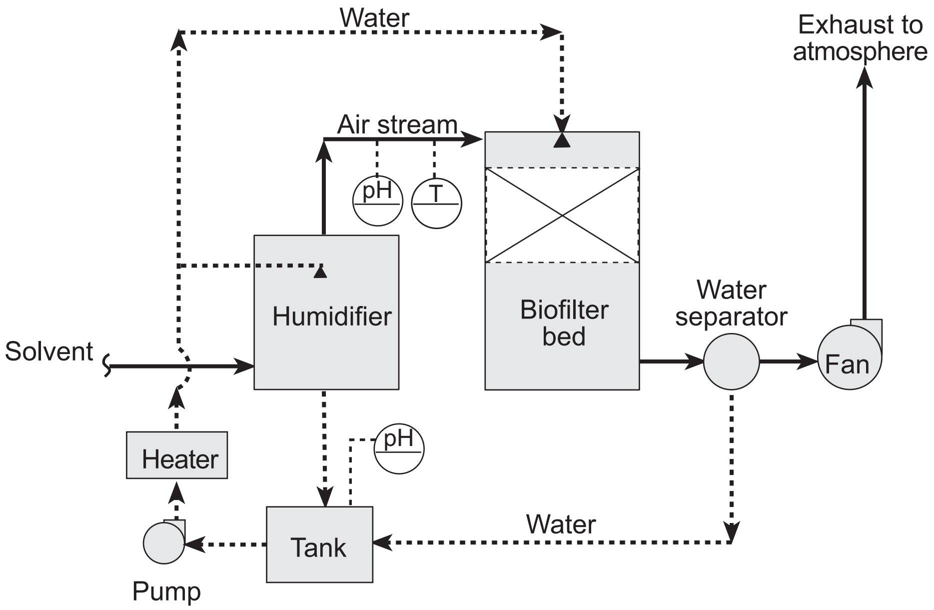


Figure 5-32. Flowchart of a typical biofiltration oxidation system

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 be because of low gas temperatures in the bed, toxicity of one or more organics in the waste gas stream, or death of the microorganisms because of loss of moisture in the bed.

Recirculated Liquid pH

The pH of the water that drains from the bed and is recirculated can be measured with pH paper or a portable pH monitor. Low pH levels indicate the acidification of the bed because of the presence of sulfur- and chlorine-containing materials in the gas stream being treated. The pH should be in the range of 6 to 8.

REVIEW PROBLEMS

Types and Components of Absorbers

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.

2. Sulfur dioxide absorbed in a packed bed is reacting 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. It depends.

3. What type of spray nozzles is used in most spray tower absorbers?
   a. Full cone
   b. Hollow cone
   c. Fan
   d. High pressure liquid atomizing
   e. Two fluid atomizing

4. What is the typical liquid-to-gas ratio in spray tower and venturi absorbers?
   a. 1 to 5 gallons/ACF
   b. 5 to 50 gallons/ACF
   c. 50 to 200 gallons/ACF
   d. 1 to 5 gallons/1000 ACF
   e. 5 to 50 gallons/1000 ACF

5. What is the typical liquid-to-gas ratio in a venturi absorber?
   a. 1 to 20 gallons/ACF
   b. 20 to 100 gallons/ACF
   c. 100 to 500 gallons/ACF
   d. 1 to 20 gallons/1000 ACF
   e. 20 to 50 gallons/1000 ACF

6. What is the primary purpose of the packing material in a packed bed scrubber?
   a. Provide liquid surface area for mass transfer.
   b. Provide liquid sheet impaction targets.
   c. Decrease the gas stream velocity.
   d. None of the above.

7. What is one of the most important factors affecting the performance of spray tower, packed bed, tray tower, and venturi absorbers?
   a. Gas velocity
   b. Gas-liquid distribution
   c. Gas droplet size distribution
   d. None of the above.

8. What is the purpose(s) of the mist eliminator? Select all that apply.
   a. Protect the fan from accumulation of solids.
   b. Minimize the emission of solids containing droplets.
   c. Capture droplets ranging in size from 10 micrometers to 1000 micrometers.
   d. 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. Protect the absorber materials of construction from corrosion.
    b. Optimize absorption of acid gases.
    c. Optimize surface tension.
    d. Optimize droplet size distribution.
    e. 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.

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.

14. A 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. 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 are correct.
    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 gas-liquid maldistribution 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 3,000 SCFM contains 3% SO_2 by volume. The operator plans to reduce the SO_2 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.

$$\text{Henry's law constant} = 43\,\frac{\text{mole fraction } SO_2 \text{ in gas}}{\text{mole fraction } SO_2 \text{ in liquid}}$$

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 = 30°C

REVIEW ANSWERS

Types and Components of Absorbers

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?
    b. It will decrease.

2. Sulfur dioxide absorbed in a packed bed is reacting with alkali dissolved in the scrubbing liquid. Does the Henry's Law Equilibrium Constant limit sulfur dioxide absorption in this system?
    b. No

3. What type of spray nozzles is used in most spray tower absorbers?
    a. Full cone

4. What is the typical liquid-to-gas ratio in spray tower and venturi absorbers?
    c. 5 to 50 gallons/1000 ACF

5. What is the typical liquid-to-gas ratio in venturi absorbers?
    e. 20 to 50 gallons/1000 ACF

6. What is the primary purpose of the packing material in a packed bed scrubber?
    a. Provide liquid surface area for mass transfer.

7. What is one of the most important factors affecting the performance of spray tower, packed bed, tray tower, and venturi absorbers?
    b. Gas-liquid distribution

8. What is the purpose(s) of the mist eliminator? Select all that apply.
    a. Protect the fan from accumulation of solids.
    b. Minimize the emission of solids containing droplets.
    c. Capture droplets ranging in size from 10 micrometers to 1000 micrometers.

9. What is the typical gas velocity approaching chevron, radial blade, and mesh pad mist eliminators?
    d. 5 to 15 feet per second

10. What is the typical pH range in an absorber system?
    b. 5 to 9

11. What is the purpose of adding alkali to the recirculating liquid in an absorber system? Select all that apply.
    a. Protect the absorber materials of construction from corrosion.
    b. Optimize absorption of acid gases.

Operating Principles of Absorbers

12. A gas is more soluble when ___________________ .
    a. the absorbent is cold

13. Henry's law usually applies when the gas phase concentration of the pollutant is___________ .
    a. low

14. A Henry's law constant for compound A is 40, while the value for compound B is 0.4. Which compound is more soluble?
    b. Compound B

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?
    b. Adequacy of gas-liquid contact (hydraulic considerations)

16. When does Henry's Law not apply to absorption processes?
    a. When the gas concentration is high
    c. When there is substantial heat released during dissolution

Capability and Sizing of Absorbers

17. Which factors can cause gas-liquid maldistribution in a packed bed absorber?
    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?
    a. yes

Solution:

Calculate the average velocity.

$$\text{Area} = \left(\frac{3.14\,(3.5\text{ ft})^2}{4}\right) = 9.6\text{ ft}^2$$

$$\text{Velocity} = \text{Gas flow rate/area} = \left(\frac{6{,}000\text{ ft}^3/\text{min}}{9.6\text{ ft}^2}\right)\left(\frac{\text{min}}{60\text{ sec}}\right) = 10.4\text{ ft/sec.}$$

This is within the normal range for a Chevron type mist eliminator.

19. An exhaust stream of 3,000 SCFM contains 0.3% SO_2 by volume. The operator plans to reduce the SO_2 content by 90% by scrubbing with water (no alkaline additives). What is the required liquid flow rate (gal/min) at 1.5 times the minimum liquid-to-gas ratio? Use the following data to solve the problem.

$$\text{Henry's law constant} = 43\left(\frac{\text{mole fraction SO}_2\text{ in gas}}{\text{mole fraction SO}_2\text{ in liquid}}\right)$$

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 = 30°C

Solution:

Step. 1. Calculate the amount of SO_2 o be absorbed.

$$3{,}000\,\text{SCFM}\left(\frac{\text{lb mole flue gas}}{385.4\,\text{SCF}}\right)\left(\frac{0.003\,\text{lb mole SO}_2}{\text{lb mole flue gas}}\right)\left(\frac{0.9\,\text{lb mole SO}_2\text{ absorbed}}{\text{lb mole SO}_2\text{ in flue gas}}\right)$$

$$= 0.021\,\text{lb mole SO}_2\text{ absorbed/min}$$

Step. 2. Calculate the equilibrium concentration of SO_2 in water.

$$y^* = Hx$$

$$0.03\text{ mole fraction SO}_2\text{ in gas} = \left(43\,\frac{\text{mole fraction SO}_2\text{ in gas}}{\text{mole fraction SO}_2\text{ in liquid}}\right)x$$

$$x = 0.000698\text{ mole fraction SO}_2\text{ in liquid}$$

Step. 3. Calculate the required liquid flow rate.

$$\frac{0.021\,\text{lb mole SO}_2\text{/min}}{0.000698\,\text{lb mole SO}_2\text{/lb mole water}} = 30.1\,\text{lb mole H}_2\text{O/min}$$

$$\left(\frac{30.1\,\text{lb mole water}}{\text{min}}\right)\left(\frac{18\,\text{lb}_\text{m}}{\text{lb mole}}\right)1.5\,\text{safety factor} = 813\,\text{lb}_\text{m}\ \text{H}_2\text{O/min}$$

$$\left(\frac{813\,\text{lb}_\text{m}\ \text{H}_2\text{O}}{\text{min}}\right)\left(\frac{\text{ft}^3}{62.4\,\text{lb}_\text{m}\ \text{H}_2\text{O}}\right)\left(\frac{7.48\,\text{gal H}_2\text{O}}{\text{ft}^3}\right) = 97.5\,\text{gal H}_2\text{O/min}$$

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Chapter 6
Oxidation

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. Organic compounds containing chlorine, fluorine, or sulfur also form 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 since 1985 that have increased the types of commercially available oxidizer systems. Oxidizer systems for VOC and air toxic compound control can now be categorized into two main groups and a number of subgroups, according to the types of oxidation reactions utilized.

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 organic vapor concentrations less than 25% to 50% of their Lower Explosive Limit (LEL). (Refer to Section 2.1.3 for discussion on explosive limits.) Flares are used for 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). These oxidizers are designed for gases with less than 25% of the LEL.

The terms *recuperator* and *regenerator* refer to the type of heat exchanger used in the oxidizer system. A recuperator is a tubular or plate heat exchanger where heat is transferred through the metal surface. A regenerator is a set of refractory packed beds that store heat. Both types of heat exchangers reduce the amount of supplement fuel needed to oxidize the contaminants in the combustion chamber. If the concentration of organic compounds is sufficiently high, the exothermic oxidation of these compounds in the combustion chamber may be sufficient to maintain the necessary temperature in the oxidizer without any supplemental fuel during steady state operation.

6.1 TYPES AND COMPONENTS OF OXIDIZER SYSTEMS

6.1.1 High Temperature, Gas Phase Oxidation Systems

This section describes the characteristics of the four main categories of high temperature, gas phase oxidation processes.

1. Recuperative thermal oxidizers
2. Regenerative thermal oxidizers
3. Flares
4. Boilers

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 convert combustible material to carbon dioxide, water, and other combustion products. The contaminant-laden gas stream is heated 200°F to 300°F (150°C to 260°C) above the auto ignition temperature of the most difficult to oxidize organic compound in the gas stream.[1] These processes usually operate at gas temperatures ranging from 1,000°F to more than 2,000°F (540°C to 1,100°C).

Recuperative Thermal Oxidizers

A recuperative thermal oxidizer consists of a refractory-lined chamber equipped with one or more of gas- or oil-fired burners. As shown in Figure 6-1, 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.

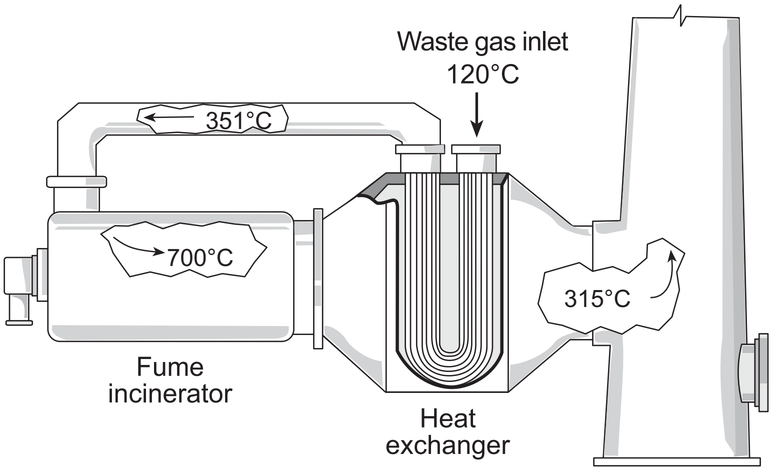


Figure 6-1. Double pass recuperative heat exchanger

The combustion chamber is sized to provide sufficient residence time to complete the oxidation reactions. The residence times of the combustion products in the combustion chamber vary 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 6-1 includes a recuperative heat exchanger (recuperator) to recover a portion of the sensible heat generated by combustion of the burner fuel and by 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.

Because of the presence of the recuperative heat exchanger, the particulate matter concentrations in the inlet gas stream must be minimized. The particulate matter can foul the surfaces of the tubes and thereby reduce the thermal efficiency of the unit. Some recuperative units include clean-out ports and access hatches to facilitate cleaning.

Thermal oxidizers are relatively heavy units because of the refractory lining of the combustion chamber. This lining is needed 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 6-2. The instrumentation used to evaluate the performance of the oxidizer includes the outlet temperature monitor (hot gas into the recuperator), the recuperator gas outlet temperature monitor, and the inlet VOC concentration monitor. Recuperative and regenerative thermal oxidizers are usually designed for inlet concentrations less than 25%. In some cases, the oxidizers have been allowed to operate 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.

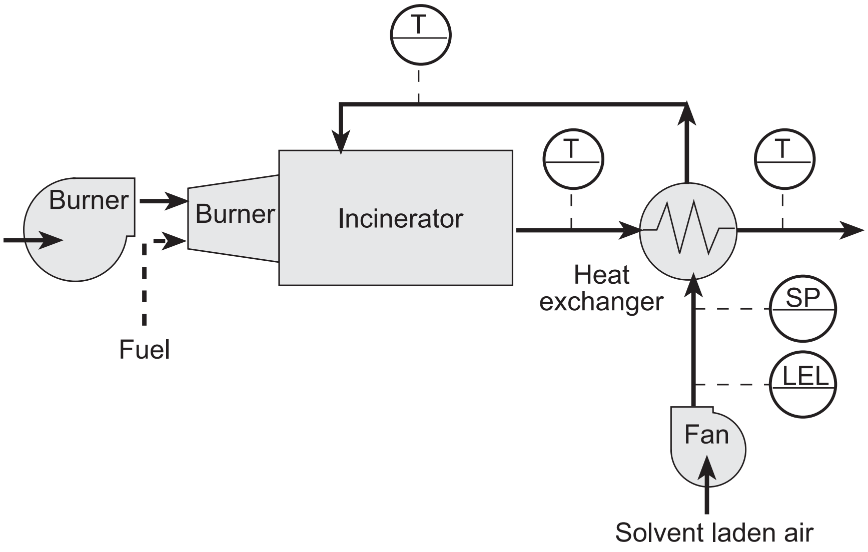


Figure 6-2. Flowchart of a recuperative heat exchanger

The burner normally operates continuously unless the organic vapor concentration in the inlet gas stream is high. 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. There is a pilot flame igniter system and a flame scanner system (not shown on Figure 6-2) to ensure safe operation of the burner.

Because of the low organic vapor concentrations of the inlet gas stream, flashback through the gas handling system is not a major safety concern. Accordingly, these types of oxidizers usually do not have flashback protective devices. 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 is rarely present in recuperative thermal oxidizers. This instrument can be used to monitor the gas flow resistance through the recuperator.

Regenerative Thermal Oxidizers

Regenerative thermal oxidizers have much higher heat recovery efficiencies than recuperative units. Heat recovery efficiencies as high as 95% are possible.[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 compound 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 composed of ceramic packing. This packing is preheated by passing the outlet gases from the combustion chamber through the bed prior to exposure to the inlet gas stream. A set of gas flow dampers is used to switch the inlet and outlet gas streams to the appropriate beds.

It is common to use at least three beds in a regenerative system. One of the beds is used to preheat the inlet gas stream, one is used to transfer the heat of combustion from the treated gas stream, and one is in a purge cycle. The purge cycle is needed to prevent emission spikes each time the gas flow is reversed through the regenerative beds. Without a purge cycle, a portion of the untreated gas stream would be released immediately after the flow is reversed.[2]

An example of a commercial system is shown in Figure 6-3. 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 6-4. 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. These contaminants can form particulate matter that accumulates in the packed bed.

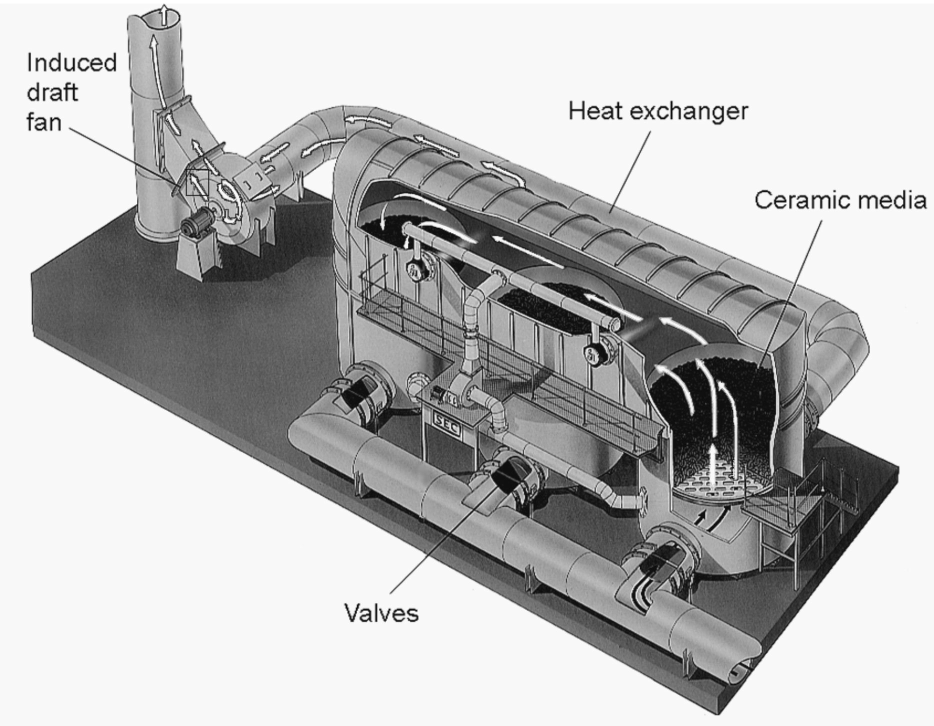


Figure 6-3. Regenerative thermal oxidizer
(Reprinted courtesy of Smith Engineering Co.; Ontario, California)

All of the regenerative units are vulnerable to particulate matter in the inlet gas stream. Particulate matter can severely plug the packed bed and thereby increase the static pressure drop. Therefore, regenerative units are used only on sources with very low particulate matter 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.

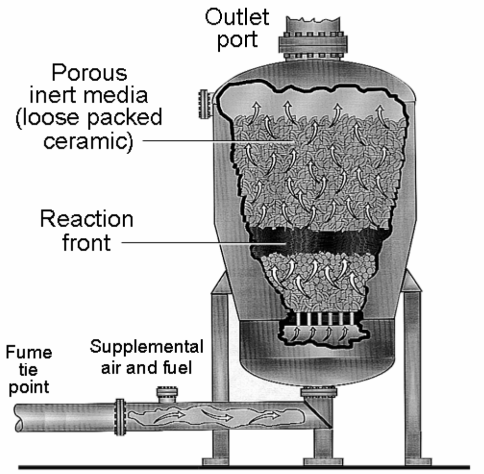


Figure 6-4. Flameless thermal oxidizer
(Reprinted courtesy of Thermatrix, Inc.; San Jose, California)

Regardless of the type of thermal oxidizer used, the oxidation of halogenated compounds results in the formation of compounds such as hydrochloric acid and hydrofluoric acid. These 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. This avoids 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. These conditions are 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 6-5). Alternatively, 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, economizers) because the gas temperature drops quickly because of heat transfer in these areas.

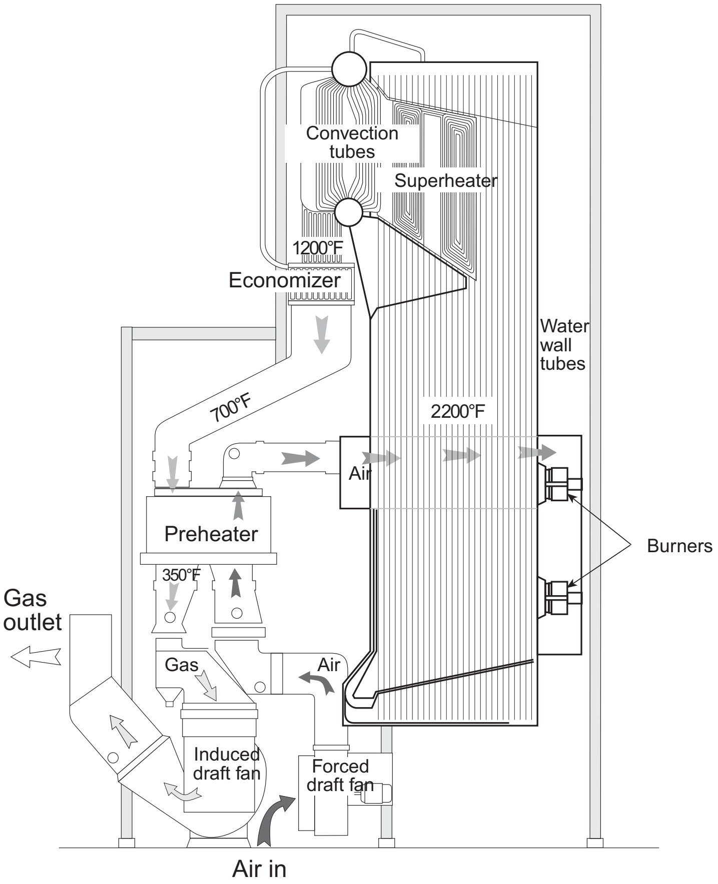


Figure 6-5. Oil-fired boiler

The flow rate of the organic vapor contaminated air stream must not overwhelm the gas handling capability of the boiler induced draft fans. The volume of combustion gas generated by oxidation of the waste gas stream should be only a small fraction of the total combustion gas flow rate of the unit. The maximum gas velocities and gas temperatures throughout the boiler will be exceeded if the volume of additional gas is large.

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 Chapter 8.

Figure 6-5 illustrates a typical front wall fired oil-fired boiler. Combustion of organic vapor is completed prior to the gas stream reaching the heat exchange tube banks at the top of the boiler.

The operating schedules of the boiler and the process generating the gas stream are one of the main constraints to the use of a boiler for organic vapor oxidation. The boiler must be operating 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 vapor containing gas stream from the process area over to the boiler area. These ducts can be expensive. Furthermore, some of the organic vapor can condense and accumulate in the ducts.

Flares Used for Thermal Oxidation

Direct combustion or flaring is used for the disposal of intermittent or emergency emissions of combustible gases from industrial sources. Using flares to prevent direct venting of these emissions can eliminate safety and health hazards at or near the plant. Flares are used mainly at oil refineries and chemical plants that handle large volumes of combustible gases. They can have organic compound destruction efficiencies exceeding 98%.[4]

Flares are simply burners designed to handle varying rates of fuel while burning smokelessly. In general, flares can be classified as either elevated or 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. Most industrial boilers seldom handle more than a 10:1 turndown ratio.

Although 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 excess 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 upper 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. Fuel must be added to the waste gas if it is too dilute for a flare. 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 flare stack 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. The flare tip is at the top of the stack. It is comprised of the burners and a system to mix the air and fuel. The smokeless flare tip of a typical elevated flare is shown in Figure 6-6.

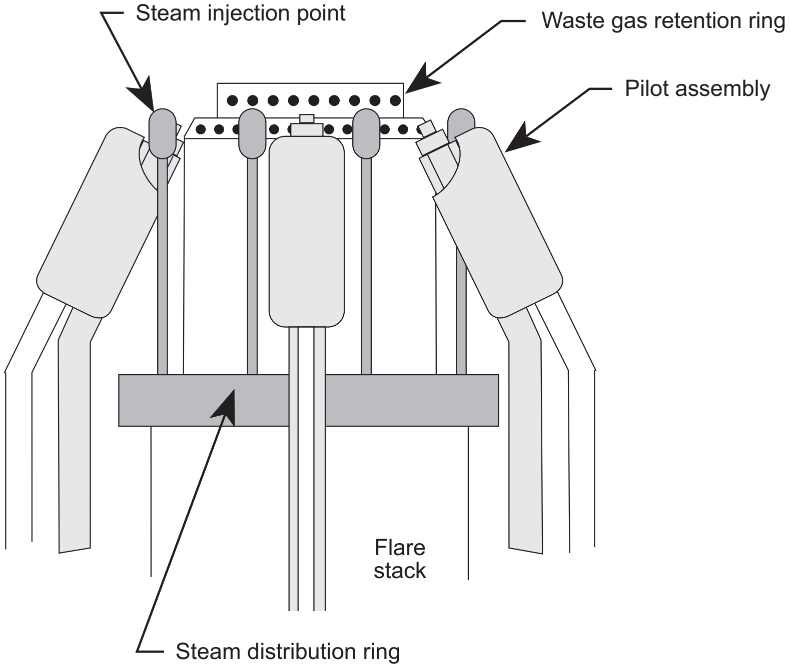


Figure 6-6. Smokeless flare tip of an elevated flare

Smokeless combustion is accomplished by proper design of the flare tip. Smokeless flares require a system that allows for complete mixing of waste gases and air. A number of flare tip designs provide good mixing characteristics over a wide range of waste gas flow values while maintaining excellent flame holding capabilities. Steam jets have proven to be one of the most effective ways to mix air and waste gases. An example of a flare tip designed for steam injection is illustrated in Figure 6-6. In addition to increasing turbulence, steam injection reduces the partial pressure of the waste gas, thus reducing polymerization reactions. The steam also reacts with the gases to produce oxygenated compounds that burn readily at lower temperatures and reduce polymerization of organic compounds in the waste gas stream. For these reasons, steam is used for waste gases that are difficult to burn. The difficulty of combustion can be approximated by the hydrogen-to-carbon weight ratio in the organic compound. Compounds with a hydrocarbon-to-carbon ratio less than 0.3 (most organics) 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 proportionally to the flow rate of the waste gases.

Shields are 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

There are a number of different commercially available ground flares. 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. The term ground flare refers to locating the flare tip at or near ground level. The flare system still requires a stack for proper release of the effluent gases. Figure 6-7 shows a ground flare that has two chambers.

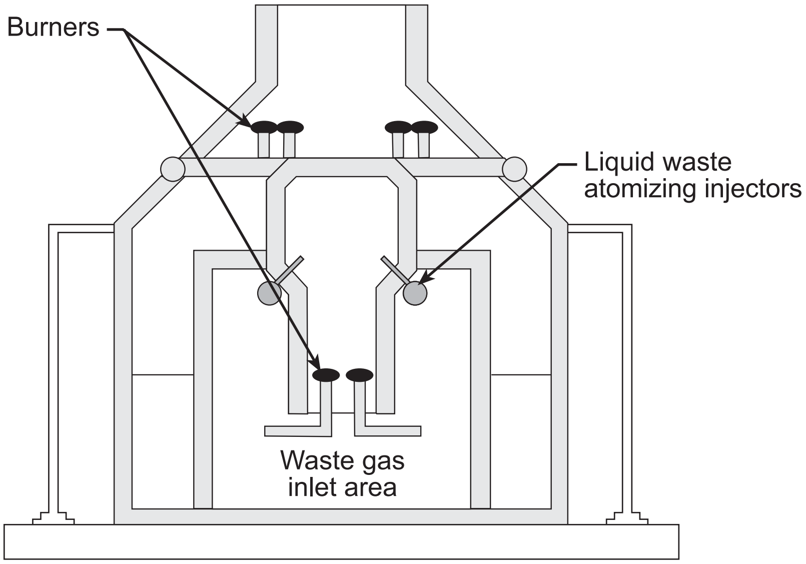


Figure 6-7. Enclosed ground flare

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.

6.1.2 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 will emphasize 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 layer of catalyst known as the bed. The catalyst causes the oxidation reaction to proceed at a much lower temperature than is possible in gas phase thermal oxidation. A catalytic oxidizer operating in a 600°F to 850°F (320°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.

Catalytic oxidizers can achieve organic compound destruction efficiencies of more than 95%.[6] This type of oxidation system can be used for inlet 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 advantage of catalytic oxidizers over thermal oxidizers is that catalytic oxidation reactions occur at considerably lower temperatures than thermal oxidation reactions. The supplemental fuel requirements are low, especially when the contaminated gas stream has a high organic vapor content that serves as a “fuel.” Because of the low gas temperatures, refractory-lined combustion chambers are usually not needed. This reduces the weight of the unit.

The primary disadvantages of catalytic oxidizers are the cost of the expensive catalysts and the performance problems related to physical and chemical deterioration of the catalyst bed. Chemicals that react irreversibly with the catalyst can result in the need to replace the catalyst bed. Materials that mask the catalyst surface can result in the need to clean the catalyst elements.

Catalytic units have “heat-up” times similar to thermal units. The time needed to heat the catalyst bed is approximately equal to that necessary to preheat the refractory of a thermal oxidizer. Accordingly, the catalytic units are also subject to emission problems from processes that have frequent start-up/shut-down cycles.

A cutaway of a conventional catalytic oxidizer is shown in Figure 6-8. 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 gas stream then enters a preheat chamber where the inlet gas is distributed across the inlet face of the catalyst bed. If the inlet gas temperature is too low for the catalytic reactions, a preheat burner is used to raise the temperature. In many cases, the necessary minimum temperature is in the range of 500°F to 900°F (260°C to 480°C).[6] The preheat burner is operated mainly during start-up and during periods when the inlet organic vapor concentration is very low.

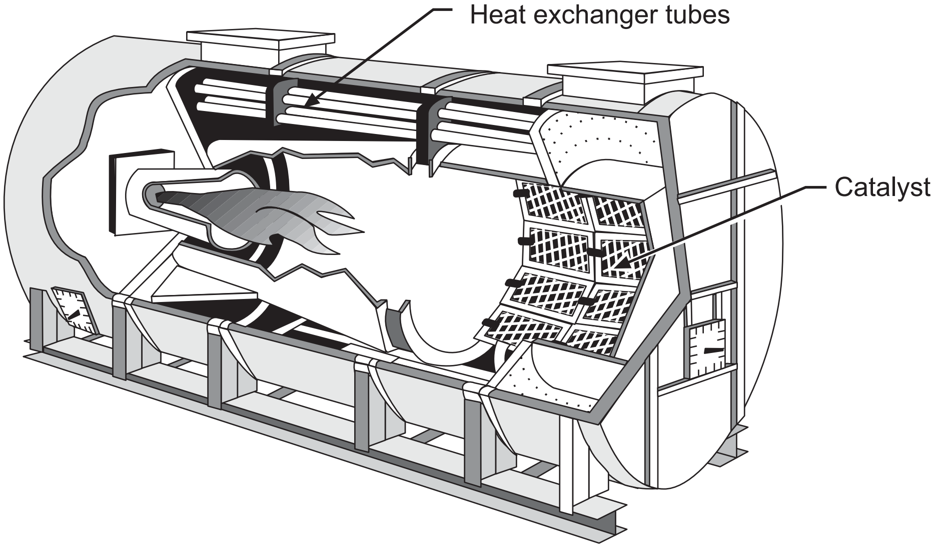


Figure 6-8. Cutaway of a catalytic oxidizer

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). The gas stream then passes through the hot gas side of the recuperative heat exchanger and is exhausted to the atmosphere.

The catalysts are deposited onto the surfaces 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, uniform flow of the waste gas through the catalyst bed, and a structurally stable surface.

Structures providing these characteristics are honeycomb matrices, grids, or mesh pads. Figure 6-9 shows a typical honeycomb module.

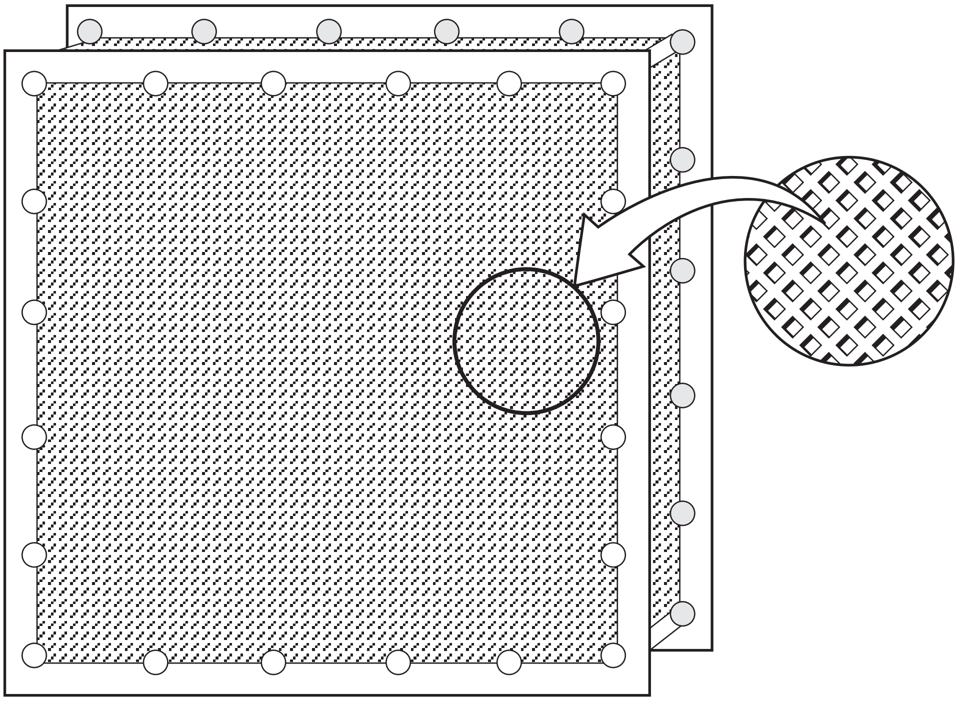


Figure 6-9. Catalyst bed honeycombs

A close-up cross-section view of a honeycomb type catalyst is shown in Figure 6-10. The walls of the honeycomb are metallic. The catalyst is precipitated uniformly over the entire surface of the carrier to maximize the surface area available for the catalytic reactions.

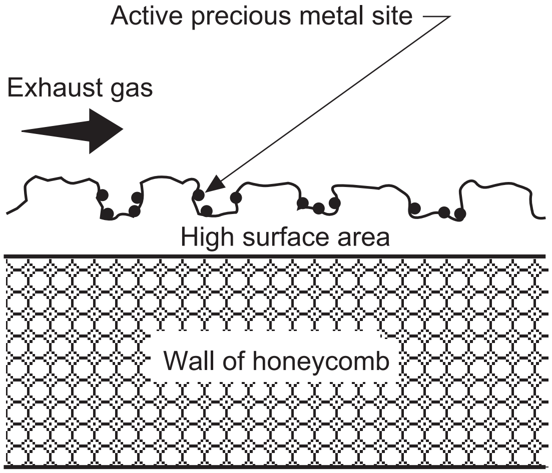


Figure 6-10. Close-up cross-section of a catalyst on a honeycomb
(Reprinted courtesy of Engelhard Corporation; Ontario, California)

The surface area of a honeycomb catalyst bed is described in terms of the number of cells (gas passages) per square inch. 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 quantity of catalyst is often described in terms of the space velocity. This is simply the reciprocal of the residence time of the gas stream passing through the catalyst bed. The space velocity can be calculated by dividing the gas flow rate entering the bed (in actual flow rate) by the volume of the bed. Normal values are between 20,000 hour^{-1} to 100,000 hour.^{-1} High space velocities indicate low catalyst quantities. At a given operating temperature, decreasing space velocities provide increased destruction efficiencies.[7]

Typical catalytic compounds include (1) noble metals such as platinum, palladium and rhodium, and (2) metal oxides such as chromium oxide, manganese oxide, and cobalt oxide. The metallic oxides are used for halogenated compounds because the chlorine and fluorine can deactivate the noble metal catalysts.

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.). A fan is used to overcome this gas flow resistance, the heat exchanger gas flow resistance, and the hood/ventilation system gas flow resistance.

Catalytic oxidizers usually cannot be used effectively on waste gas streams containing high concentrations of particulate matter. Particulate matter that deposits on the surface of the catalyst blocks the access of the organic compounds. Coating the catalyst surface in this manner is referred to as fouling the catalyst. Oil droplets can also foul the catalyst bed unless they are vaporized in the preheat section. By periodically cleaning and washing the catalyst, more than 90% of its activity can be restored.

Masking and fouling problems in catalytic oxidizers can sometimes be minimized by using a fluidized bed arrangement. In this type of system, the catalyst is prepared as spherical particles supported on a grid. Space is provided so that the catalyst containing particles can move freely because of the action of the gas stream passing through the bed. In this type of system, particle-to-particle abrasion continually cleans the catalyst containing surfaces to minimize the effect of masking. One of the disadvantages 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.

Certain metals can 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: (1) fast acting poisons, which include phosphorus, bismuth, arsenic, antimony, and mercury, and (2) slow acting poisons, which include iron, lead, tin, and silicones. 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), 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. Once the halogen or sulfur compound is removed, catalyst activity is restored to normal.

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. Loss of activity because of high temperature is known as thermal aging. This results in very rapid loss of catalyst activity and is caused primarily by the sintering of the catalyst support material. Conceptually, sintering involves the merging of the support material ridges. As this occurs, some of the precipitated catalyst is trapped below the surface of the support material and is, therefore, no longer involved in catalytic reactions. High temperature excursions can also cause volatilization of the catalyst from the carrier material and damage to the recuperative heat exchanger.

The average life of a catalyst is 2 to 5 years. As a general rule, the service life of a catalyst is higher for units that operate at low temperature.

6.2 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.

6.2.1 High Temperature, Gas Phase Oxidation Systems

Combustion Products and Gas Volumes

In all high temperature combustion processes, there is a complex set of several hundred to several thousand chemical reactions occurring simultaneously. The result of these reactions is represented by the following generalized reaction. The main reaction products are carbon dioxide and water vapor.

$$C_xH_y\,S_z\,O_w + (x + y/4 + z - w/2)O_2 + 0.79/0.21(x + y/4 + z - w/2)\,N_2 \rightarrow$$

$$(x)CO_2 + (y/2)H_2O + (z)SO_2 + (0.79/0.21)(x + y/4 + z - w/2)\,N_2 \qquad \text{Reaction 6-1}$$

Usually, sulfur dioxide is the dominant reaction product of the sulfur in the fuel or waste stream compounds. However, 0.5% to 2% of the total sulfur can also form sulfur trioxide, which ultimately forms vapor phase sulfuric acid once the gas stream cools below approximately 600°F (320°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 are ignored when calculating the total volume of the 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 can also form in the combustion chamber.[1]

Nitrogen atoms in the organic compounds (i.e. cyanides or amines) being oxidized can form nitrogen oxides (NO and NO_2), or they can be chemically reduced to form molecular nitrogen. The quantity of nitrogen oxides formed because of the organic compound wastes is usually small compared to the nitrogen oxides formed in the burner flame of the thermal oxidizer.

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 (temperature).
- The combustible materials and the oxygen are well mixed (turbulence).
- There is sufficient oxygen (air).
- The residence time of the combustible gases is relatively long (time).

Temperatures

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 being oxidized.[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 (90°C to 150°C) above the auto-ignition temperature for 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 of the burner fuel with air is needed to ensure complete combustion of the fuel. Second, the organic compound-containing waste gases must be thoroughly mixed with the burner combustion gases to ensure that the entire waste gas stream reaches the necessary combustion temperatures.

A number of methods are available to improve mixing of the air and combustion streams. Some of these include 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 heat 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).

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \qquad \text{Reaction 6-2}$$

If an insufficient amount of oxygen is supplied (there is not enough oxygen to combine with all the fuel), the mixture is referred to as fuel rich. Incomplete combustion occurs under these conditions. This reduces the peak flame temperature and creates carbonaceous emissions.

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. Accordingly, the peak flame temperature is reduced. The high oxygen levels in the flame can also contribute to nitrogen oxides generation.

In order to maximize the flame temperature and minimize pollutant generation, it is advantageous to operate the burner relatively close to the stoichiometric limit. 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 chemical reaction of the fuel. In Problem 6-1, the calculated oxygen requirement was 1.56-pound mole 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 mole per minute. This additional oxygen is needed simply to account for the non-ideal factors that affect combustion of the fuel in the burner.

At high excess air rates, the gas flow rate of the combustion products is high. This is due, in part, to the unreacted oxygen that is part of the flue gas stream. However, the major component of the effluent gas stream is the additional nitrogen entering with the combustion air. 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 mole per minute of nitrogen. All of the nitrogen exited 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 combustion chamber residence time problem 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%. By using this source of oxygen, the combustion air rates 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 partly on the rate of the reactions at the prevailing temperature and partly 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 from a simple ratio of the volume of the refractory-lined combustion chamber and the volumetric flow rate of combustion products through the chamber.

$$q = V/Q \qquad (6\text{-}1)$$

Where:

q = residence time (sec)
V = chamber volume (ft^3)
Q = 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 shows the determination of 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 being operated at 125% of the stoichiometric requirement.

Solution:

Step 1. Write the combustion reaction.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

Stoichiometric oxygen requirement is two moles of oxygen for every mole of methane burned to completion.

Step 2. Calculate the total amount of O_2 at stoichiometric conditions.

$$300\,\text{SCFM}\left(\frac{\text{lb mole CH}_4}{385.4}\right) = 0.778\,\frac{\text{lb mole CH}_4}{\text{min}}$$

Stoichiometric O_2 = 2 × (lb mole CH_4)

$$\frac{2\text{ lb mole O}_2}{\text{lb mole CH}_4}\left(0.778\,\frac{\text{lb mole CH}_4}{\text{min}}\right) = 1.56\,\frac{\text{lb mole O}_2}{\text{min}}$$

Step 3. Calculate air sent to burner (125% of stoichiometric requirement).

Total O_2 requirement = 1.25 × (stoichiometric requirement)

$$= 1.25\left(1.56\,\frac{\text{lb mole O}_2}{\text{min}}\right) = 1.95\,\frac{\text{lb mole O}_2}{\text{min}}$$

$$\text{Total N}_2 = \frac{0.79\,\text{lb mole N}_2}{0.209\,\text{lb mole O}_2}\left(1.95\,\frac{\text{lb mole O}_2}{\text{min}}\right)$$

= 7.37 lb mole 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

$$CO_2 = 1\ \frac{\text{lb mole } CO_2}{\text{lb mole } CH_4}\left(0.778\frac{\text{lb mole } CH_4}{\text{min}}\right) = 0.778 \text{ lb mole } CO_2\text{/min}$$

$$H_2O = 2\ \frac{\text{lb mole } H_2O}{\text{lb mole } CH_4}\left(0.778\frac{\text{lb mole } CH_4}{\text{min}}\right) = 1.56 \text{ lb mole } H_2O$$

$CO_2 + H_2O$ = 2.34 lb mole/min

$$2.34\ \frac{\text{lb mole}}{\text{min}}\left(\frac{385.4\ \text{SCF}}{\text{lb mole}}\right) = 902\ \text{SCFM}$$

c. Nitrogen and excess oxygen = total $N_2 + O_2$ remaining

= 7.37 lb mole N_2/min + 0.39 lb mole O_2/min = 7.76 lb mole/min

Amount of oxygen consumed = stoichiometric required = 1.56 lb mole/min

Amount of oxygen remaining = total – consumed = 1.95 lb mole/min - 1.56 lb mole/min

= 0.39 lb mole/min

$$7.73\ \frac{\text{lb mole}}{\text{min}}\left(\frac{385.4\ \text{SCF}}{\text{lb mole}}\right) = 2{,}990\ \text{SCFM}$$

Total flue gas flow rate = 8,000 SCFM + 902 SCFM + 2,990 SCFM = 11,900 SCFM

Step 5. Convert the flue gas flow rate to actual conditions.

$$\text{Total ACFM} = 11{,}900\ \text{SCFM}\left(\frac{1{,}400 + 460\ ^\circ\text{R}}{528\ ^\circ\text{R}}\right) = 41{,}900\ \text{ACFM}$$

Step 6. Calculate the volume of the combustion chamber.

Combustion Chamber Vol. = $\pi\ (r)^2\ L = 3.14\ (2.5\ \text{ft})^2\ 12\ \text{ft}$

= 235.5 ft^3

Step 7. Calculate the residence time.

$$\text{Residence Time} = \frac{\text{chamber volume}}{\text{volumetric flow rate}} = \frac{235.5\ \text{ft}^3}{41{,}900\ \text{ACF/min}} = 0.00562\ \text{minutes}$$

$$= 0.00562\ \text{min}\left(\frac{60\ \text{sec}}{\text{min}}\right)\left(\frac{1{,}000\ \text{millisec}}{\text{sec}}\right) = 337\ \text{milliseconds}$$

The residence time of the combustion gas in the thermal oxidizer described in Problem 6-1 is 0.337 milliseconds.

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 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.

$$O_2 = 8{,}000\ \text{SCFM}\left(\frac{\text{lb mole gas}}{385.4\ \text{SCF}}\right)\left(\frac{0.16\ \text{lb mole O}_2}{\text{lb mole gas}}\right)$$

$= 3.32$ lb mole O_2/min

This is more than the 1.56 lb mole 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)

$$\text{Waste gas stream} = 8000\,\text{SCFM}\left(\frac{\text{lb mole}}{385.4\,\text{SCF}}\right) = 20.76\,\text{lb mole/min}$$

Waste gas stream - reacted O_2 = (20.76 - 1.56) = 19.20 lb mole/min

Products of combustion = (CO_2 + H_2O) = 2.34 lb mole/min (from Problem 6-1, step 4)

Flue gas = (19.20 lb mole/min + 2.34 lb mole/min) = 21.54 lb mole/min

Step 3. Calculate total volumetric flow rate (ACFM).

$$\text{Vol. Flow rate} = (21.54\ \text{lb mole/min})\left(\frac{385.4\ \text{SCF}}{\text{lb mole}}\right)\left(\frac{1{,}400 + 460^\circ\text{R}}{528^\circ\text{R}}\right)$$

Vol. Flow rate = 29,240 ACFM

Step 4. Calculate residence time.

$$\text{Residence time} = \frac{\text{chamber volume}}{\text{volumetric flow rate}}$$

$$= \frac{235.5\ \text{ft}^3}{29{,}240\ \text{ft}^3/\text{min}} = 0.008054\ \text{minutes}$$

$$= 0.008054\ \text{min}\left(\frac{60\ \text{sec}}{\text{min}}\right)\left(\frac{1000\ \text{millisec}}{\text{sec}}\right) = 483\ \text{milliseconds}$$

Residence time = 483 milliseconds

This is substantially longer than the 337-millisecond residence time calculated in Problem 6-1. This 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 advantages, 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 as a source of air is fouling of the burner because of nonvolatile organic compounds or particulate matter in the waste gas stream. 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. Combustion does not occur readily in this range. Therefore, the waste gas stream can be transported safely to the combustion device. The risk of flashback from the oxidizer to the process equipment is minimized in this concentration range. The VOC inlet concentration is usually determined by an LEL detector. An LEL detector determines the approximate total concentration of oxidizable organic compounds.

Table 2-1 (Section 2.1.3) provides LEL and UEL values for some selected compounds at room temperature and ambient pressure.

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. Thermal oxidizers operate by heating the waste gas stream to this point called the auto-ignition temperature.

6.2.2 Catalytic Oxidation Systems

The general factors that control the rate of catalytic oxidation are illustrated in Figure 6-11. The temperature of the catalytic oxidizer is set at a level at which the controlling factor is the mass transfer of oxygen and organic compounds to and from the catalyst surface.

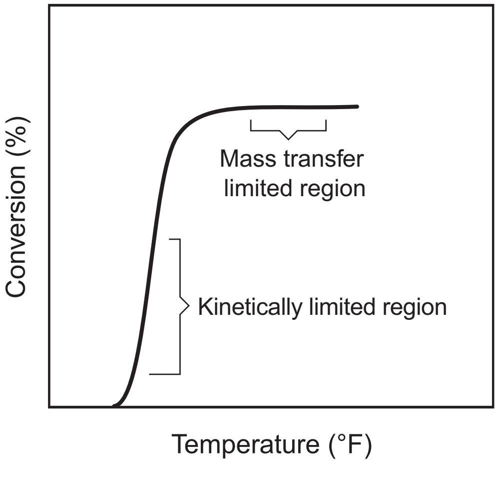


Figure 6-11. Importance of temperature in catalytic systems
(Reprinted courtesy of Engelhard Corporation; Ontario, California)

The temperature necessary for catalytic oxidation varies for the different organic compounds in the waste gas stream and the characteristics of the catalyst bed. An example of destruction efficiency curves are shown in Figure 6-12

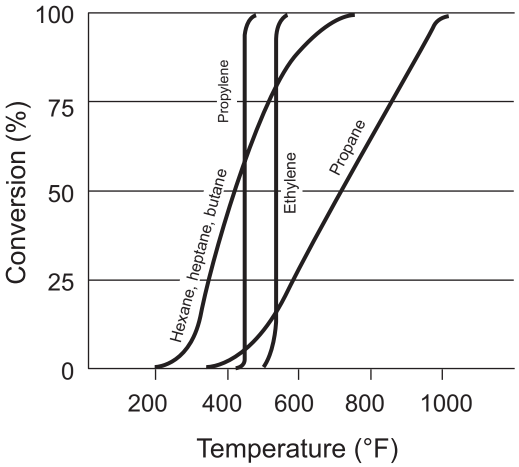


Figure 6-12. Destruction efficiency curves for selected organic compounds
(Reprinted courtesy of Engelhard Corporation; Ontario, California.)

The minimum operating temperature is the left side of the destruction efficiency-temperature curve where the controlling factor is the mass transfer rate. Catalytic oxidizers with moderate-to-high organic vapor concentration in the waste gas stream do not need to operate the preheat chamber burner in order to maintain these temperatures. The heat released during catalytic oxidation and recovered in the recuperative heat exchanger is sufficient to maintain these relatively low gas temperatures. Accordingly, catalytic oxidizers can use the available heat content in the waste gas stream.

6.3 CAPABILITY AND SIZING

6.3.1 Destruction Efficiency

There are two primary means of 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 U.S. EPA Reference Methods, provide useful data bases for evaluating the capability of new units. The 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 a duration of 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.

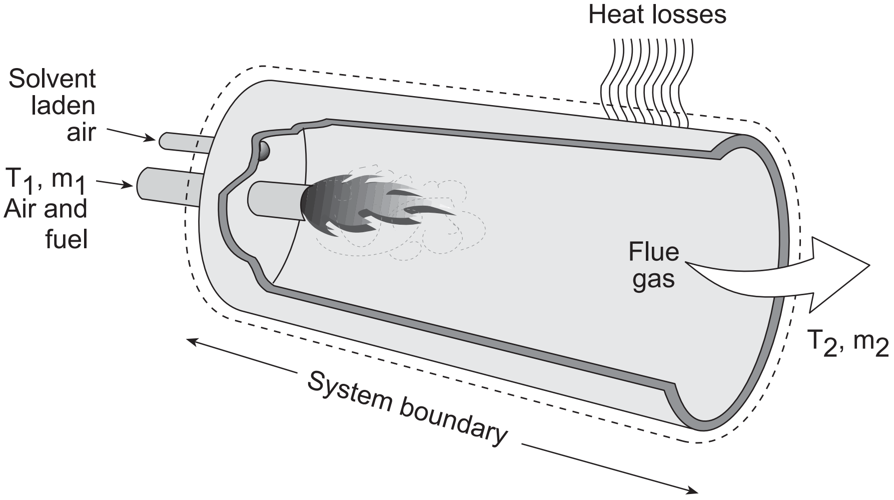
Fuel Requirements

The supplemental fuel requirement is one of the main parameters of concern in oxidation systems. If the burner is not sized properly, the oxidizer will not operate at the temperature needed for full combustion.

The supplemental fuel requirement can be estimated based on a simple heat balance of the unit and information concerning the waste gas stream. The first step in estimating the fuel requirement is to perform a heat balance around the oxidation system. Figure 6-13 shows a simplified oxidation system illustrating the heat entering and leaving the oxidizer.

From the 1st Law of Thermodynamics:

$$\text{Heat in} = \text{Heat out} + \text{Heat loss} \tag{6-2}$$



Where: T_1 = waste gas inlet temperature
T_2 = incinerator temperature
m_1 = mass flow rate of waste gas plus air and fuel
m_2 = mass flow rate of flue gas

Figure 6-13. Heat balance around an oxidizer

Heat is supplied by the burner. Some of the heat released 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 heat generated by the burner is released and can be used to heat the waste gas stream. 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 used to heat the combustion products. The available heat decreases as the oxidizer temperature increases. This is illustrated in Figure 6-14.

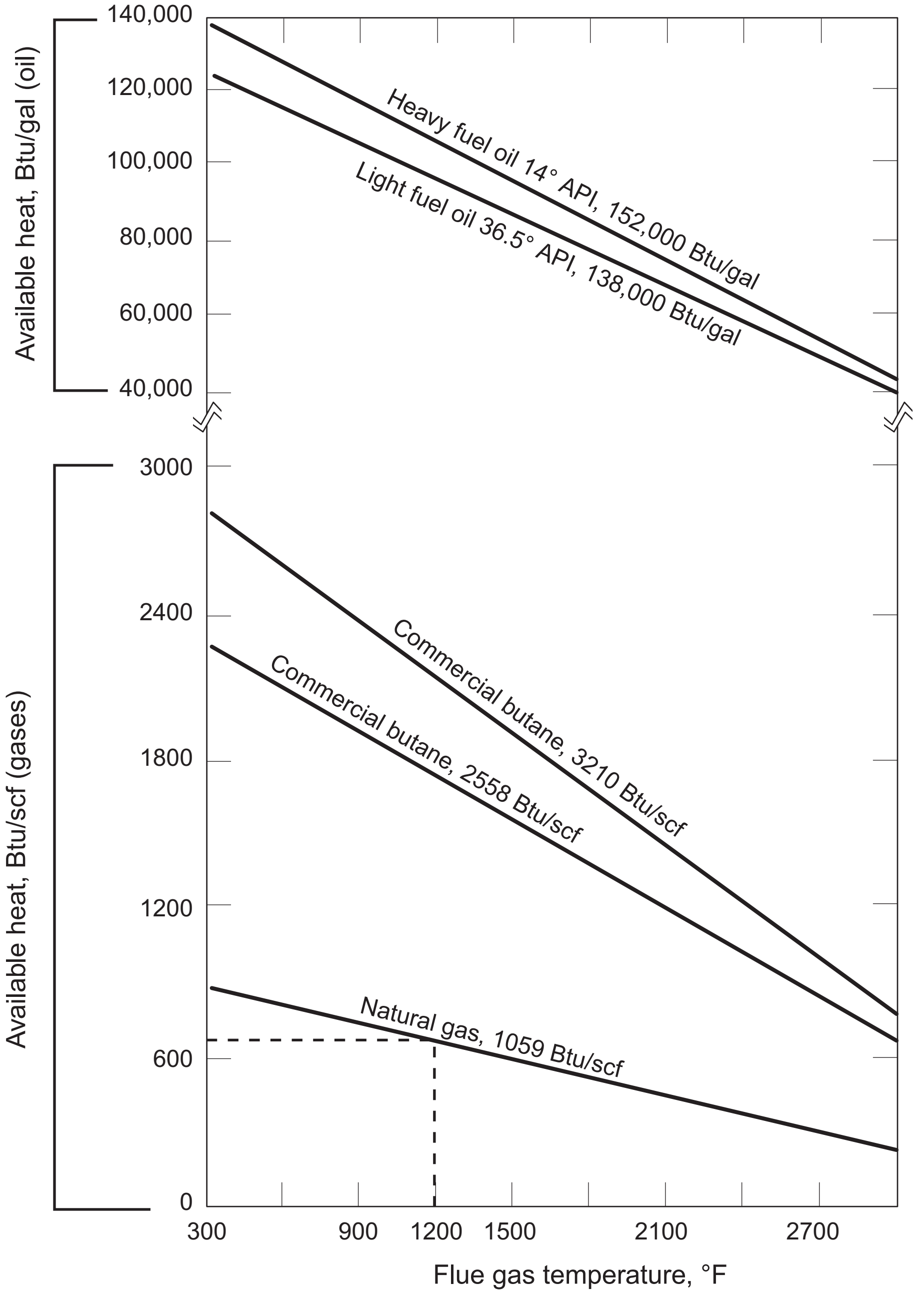


Figure 6-14. Available heat of common fuels
(Reprinted courtesy of North American Combustion Handbook, 1965)

The available heat approaches the gross heating value of the fuel at 60°F (16°C) if the products of combustion are also at 60°F. The gross heating value is equal to the total heat released and is termed the total or higher heating value.

The available heating value is usually used to evaluate oxidizers. When the available heat value is used, it is not necessary to take into account the heat lost with the combustion products because this is already 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.

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 that includes the sensible heat and latent heat of a material. The sensible heat of the compounds of interest in combustion system heat balances are summarized in Table 6-2. Note that the latent heat of vaporization for water is not included in the table. The latent heat of vaporization represents the amount of energy required to evaporate a liquid at its boiling temperature.

Table 6-2a. Sensible Heat of Gases, Btu/SCF

Gas Temp. (°F)	O_2	N_2	CO_2	H_2O	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. Sensible Heat of Gases, Btu/lb$_m$					
Gas Temp. (°F)	**O_2**	**N_2**	**CO_2**	**H_2O**	**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
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 b: U.S. EPA,
Air Pollution Engineering Manual, Second Edition, 1973

Enthalpy is a relative term that is compared at a reference temperature. The enthalpy of a substance is arbitrarily taken as zero at a specified reference temperature. A value of 68°F (20°C) has been used as the reference temperature throughout this chapter.

The enthalpy of the waste gas stream at the outlet temperature, T, can be computed from Equation 6-3 as well as found by using tables such as Table 6-2.

$$H = C_p(T-T_o) \qquad (6\text{-}3)$$

Where:

H = enthalpy (Btu/lb$_m$)
C_p = specific heat at temperature T (Btu/lb$_m$ °F)
T = temperature of the substance (°F)
T_o = reference temperature (°F)

Subtracting the enthalpy of the waste stream exiting the oxidizer from the waste gas stream entering the oxidizer gives the heat that must be supplied by the fuel. This is referred to as a change in enthalpy or heat content. Using Equation 6-3, the enthalpy entering (T_1) is subtracted from the enthalpy exiting (T_2), giving:

$$\Delta H = C_{p2}(T_2 - T_o) - C_{p1}(T_1 - T_o) \tag{6-4}$$

Where:

ΔH = change in enthalpy (Btus)

To simplify this calculation, an average specific heat value (C_p) can be used over the temperature range involved. This reduces Equation 6-4 to:

$$\Delta H = C_p (T_2 - T_1) \tag{6-5}$$

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 air, 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 raise a set quantity of gas from T_1 to T_2. This data is used to calculate the total amount of heat that must be added. The heat requirement is determined by multiplying either side of Equation 6-5 by the mass flow rate (m) of the waste gas stream. The heat rate required is given by:

$$q = m\Delta H = m\, C_p \left(T_1 - T_2\right) \tag{6-6}$$

Where:

q = heat rate (Btu/hr)
m = mass flow rate of 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 1×10^6 Btu/hr, and there is a 10% heat loss from the combustion chamber, the total heat rate would have to be 1.1×10^6 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 smoke house 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. 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).

$$G = \frac{5{,}000\ \text{ACF}}{\text{min}}\left(\frac{460^\circ\text{R}+68}{460^\circ\text{R}+90}\right)\left(\frac{60\ \text{min}}{\text{hr}}\right) = 288{,}000\ \text{ft}^3/\text{hr}$$

Step 2. The volumetric flow rate is then converted to a mass flow rate by multiplying by the density.

$$m = \left(\frac{288{,}000\,\text{SCF}}{\text{hr}}\right)\left(\frac{\text{lb mole}}{385.4\ \text{SCF}}\right)\left(\frac{29\,\text{lb}_\text{m}}{\text{hr}}\right) = 21{,}700\,\text{lb}_\text{m}/\text{hr}$$

Step 3. The heat rate can be determined by two methods.

a. By using the enthalpy values in Table 6-2:
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 ΔH= m($H_{air\ @1,200}$ - $H_{air\ @\ 90}$)
= (21,700 lb_m/hr)(287.2- 7.2 Btu/lb_m)
= 6,070,000 Btu/hr

b. By using Equation 6-6:
For air C_p = 0.26 Btu/lb_m°F
q = m C_p ΔT
= (21,700 Btu/hr)(0.26 Btu/lb_m)(1,200-90°F)
= 6,260,000 Btu/hr

This value is not as accurate because it was calculated using an average value for C_p.

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 6-14.

In Figure 6-14, 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:

$$Q_{gas} = q/H_A = \frac{6{,}070{,}000\ \text{Btu/hr}}{690\ \text{Btu/SCF}}$$

Q_{gas} = 8,780 SCF natural gas/hr

6.3.3 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 straight-forward 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 and 120 ppm carbon tetrachloride. The oxidizer uses 300 SCFM of natural gas and operates at a temperature of 1,400°F. What is the concentration of HCl formed in the oxidizer effluent gas stream? Assume that the oxidizer fuel is 100% methane, and that the burner is being 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 total amount of O_2 at stoichiometric conditions.

$$300\ \text{SCFM}\ \frac{\text{lb mole CH}_4}{385.4\ \text{SCF}} = 0.778\ \text{lb mole CH}_4\text{/min}$$

Stoichiometric O_2 = 2 ×(lb mole CH_4)

$$\frac{2\ \text{lb mole O}_2}{\text{lb mole CH}_4}\left(0.778\ \frac{\text{lb mole CH}_4}{\text{min}}\right) = 1.56\ \text{lb mole O}_2\text{/min}$$

Step 3. Calculate air sent to the burner (125% of stoichiometric requirement).

Total O_2 requirement for methane fuel = 1.25 × (stoichiometric requirement)

$$= 1.25\left(\frac{1.56\,\text{lb mole O}_2}{\text{min}}\right) = 1.95\,\text{lb mole O}_2\text{/min}$$

$$\text{Total N}_2 = \frac{0.79\ \text{lb mole N}_2}{0.21\ \text{lb mole O}_2}\left(1.95\ \frac{\text{lb mole O}_2}{\text{min}}\right)$$

= 7.34 lb mole N_2/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

$$C_6H_6 = 5000 \text{ SCFM} \left(\frac{0.000500 \text{ lb moleC}_6H_6}{\text{lb mole total}} \right) = 2.5 \text{ SCFM}$$

$$CCI_4 = 5000 \text{ SCFM} \left(\frac{0.000120 \text{ lb mole CCI}_4}{\text{lb mole total}} \right) = 0.6 \text{ SCFM}$$

Exhaust gas heated = 5,000 SCFM – (2.5 SCFM + 0.6 SCFM) = 4,996.9 SCFM

$$\text{Exhausted gas heated} = (4{,}996.9 \text{ SCFM}) \left(\frac{\text{lb mole}}{385.4 \text{ SCF}} \right) = 12.97 \text{ lb mole/min}$$

B. Products of combustion = CO_2 + H_2O + HCl

$$CO_2 = \left(0.778 \frac{\text{lb mole CH}_4}{\text{min}} \right) \left(\frac{1 \text{ lb mole CO}_2}{\text{lb mole CH}_4} \right) +$$

$$(5{,}000 \text{ SCFM}) \left(\frac{\text{lb mole total}}{385.4 \text{ SCF}} \right) \left(\frac{0.000500 \text{ lb mole C}_6H_6}{\text{lb mole total}} \right) \left(\frac{6 \text{ lb mole CO}_2}{\text{lb mole C}_6H_6} \right) +$$

$$(5{,}000 \text{ SCFM}) \left(\frac{\text{lb mole total}}{385.4 \text{ SCF}} \right) \left(\frac{0.000120 \text{ lb mole CCI}_4}{\text{lb mole total}} \right) \left(\frac{\text{lb mole CO}_2}{\text{lb mole CCl}_4} \right)$$

$$= (0.778 + 0.039 + 0.002) \text{ lb mole CO}_2\text{/min} = 0.819 \text{ lb mole CO}_2\text{/min}$$

$$H_2O = \left(\frac{2 \text{ lb mole H}_2O}{\text{lb mole CH}_4} \right) \left(0.778 \frac{\text{lb mole CH}_4}{\text{min}} \right) +$$

$$(5{,}000 \text{ SCFM}) \left(\frac{\text{lb mole total}}{385.4 \text{ SCF}} \right) \left(\frac{0.000500 \text{ lb mole C}_6H_6}{\text{lb mole total}} \right) \left(\frac{3 \text{ lb mole H}_2O}{\text{lb mole C}_6H_6} \right)$$

1.56 lb mole/min + 0.019 lb mole/min = 1.58 lb mole H_2O/min

$$HCI = 5{,}000 \text{ SCFM} \left(\frac{\text{lb mole total}}{385.4 \text{ SCF}} \right) \left(\frac{0.00012 \text{ lb mole CCl}_4}{\text{lb mole total}} \right) \left(\frac{4 \text{ lb mole HCl}}{\text{lb mole CCl}_4} \right)$$

$$= 0.00623 \ \frac{\text{lb mole HCl}}{\text{min}}$$

Products of combustion = CO_2+H_2O +HCI = 0.820+1.58 +0.00623 = 2.41 lb mole/min

C. Nitrogen and excess oxygen = Total N_2 + O_2 remaining

Amount of oxygen consumed in burning methane = stoichiometric required = 1.56 lb mole O_2/min

Amount of oxygen consumed in burning benzene :

$$= 5{,}000\ \text{SCFM}\left(\frac{\text{lb mole total}}{385.4\ \text{SCF}}\right)\left(\frac{0.000500\ \text{lb mole}\ C_6H_6}{\text{lb mole total}}\right)\left(\frac{7.5\ \text{lb mole}\ O_2}{\text{lb mole}\ C_6H_6}\right)$$

= 0.0487 lb mole O_2/min

Amount of oxygen needed for carbon tetrachloride = 0 (no net oxygen consumption)

Amount of oxygen remaining = total - consumed

= 1.95 lb mole/min – (1.56 lb mole/min + 0.0487 lb mole/min)

= 0.34 lb mole/min

Excess oxygen and nitrogen = 0.34 lb mole/min + 7.34 lb mole/min = 7.68 lb mole/min

$$\text{Flue gas flow rate} = \underset{(A)}{\begin{matrix}\text{Exhaust gas}\\ \text{Heated}\end{matrix}} + \underset{(B)}{\begin{matrix}\text{Products}\\ \text{of combustion}\end{matrix}} + \underset{(C)}{\begin{matrix}\text{Excess oxygen}\\ \text{\& nitrogen}\end{matrix}}$$

= 12.97 lb mole/min + 2.41 lb mole/min + 7.68 lb mole/min

= 23.06 lb mole/min

Step 4. Calculate the lb mole of HCl formed per minute.

$$(5{,}000\ \text{SCFM})\left(\frac{\text{lb mole total}}{385.4\ \text{SCF}}\right)\left(\frac{0.00012\ \text{lb mole}\ CCl_4}{\text{lb mole total}}\right)\left(\frac{4\ \text{lb mole HCl}}{\text{lb mole}\ CCl_4}\right)$$

= 0.00623 lb mole/min

Step 5. Calculate the HCl concentration.

$$= \left(\frac{0.00623\ \text{lb mole HCl}}{23.06\ \text{lb mole total}}\right)(10^6\ \text{ppm}) = 270\ \text{ppm}$$

6.3.4 Instrumentation — High Temperature, Gas Phase Oxidation Systems

The thermal oxidizer system flowchart shown in Figure 6-15 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 capture due to restricted gas flow rate through the oxidizer
- Fouling and/or plugging of the heat exchanger
- Generation of additional pollutants in the oxidizer

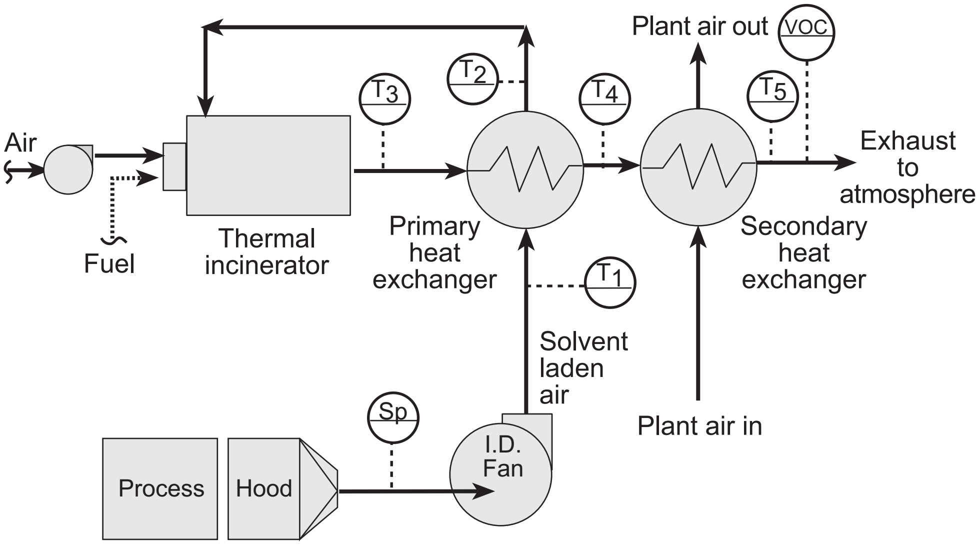


Figure 6-15. Flowchart of a thermal oxidizer system

Gas Temperatures

The most important operating parameter used to evaluate the operation of thermal oxidizer is the gas outlet temperature. As stated earlier, this temperature should be 200°F to 300°F (90°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. It is usually necessary to preheat the combustion chamber before introducing the waste gas stream to ensure that the gas temperatures will be sufficiently high. This preheat period is also necessary to allow 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 provides a useful indicator of its physical condition. The accumulation of particulate matter on either side of the units reduces the heat transfer efficiency, resulting in increased fuel requirements.

Outlet VOC Concentration

The outlet VOC concentration can be measured using portable VOC analyzers. The normal monitoring location is downstream of the primary heat exchanger (Figure 6-15) so that the temperature is relatively low.

The VOC concentrations measured by the portable instruments provide only a qualitative indication of the outlet concentration. 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 having numerous organic compounds, and it is impractical to calibrate portable VOC analyzers for the exact mixture of these compounds. Nevertheless, these instruments provide a very useful qualitative indicator of performance.

High outlet VOC concentrations could be due to low combustion chamber temperatures or short-circuiting of inlet gas through the heat exchanger.

6.3.5 Instrumentation – Catalytic Oxidation Systems

The monitoring of catalytic oxidizers is relatively similar to that for thermal oxidizers. However, the presence of a vulnerable catalyst bed increases the scope of the performance evaluation. Figure 6-16 illustrates the type of instrumentation used to support performance evaluation of catalytic oxidizers.

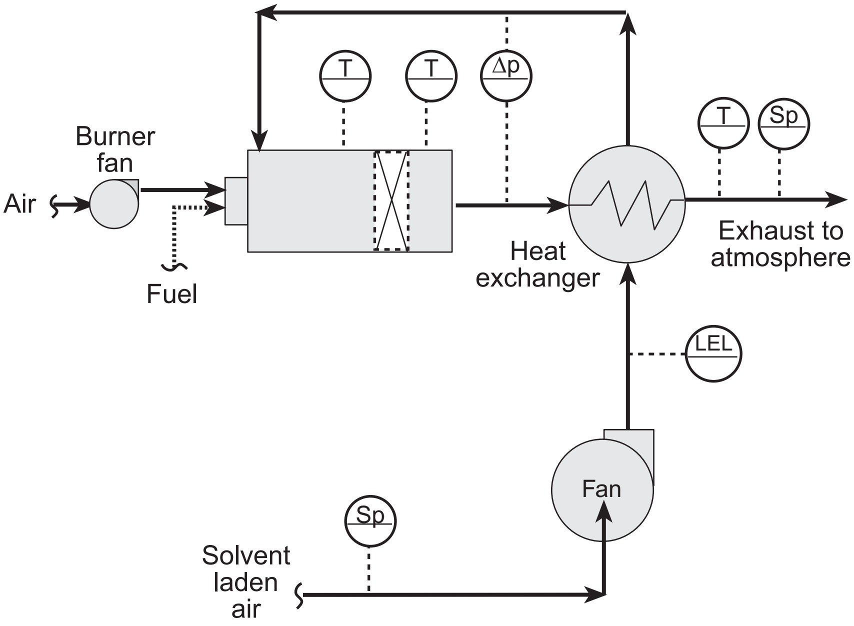


Figure 6-16. Flowchart of a catalytic oxidizer system

Gas Temperatures

The inlet and outlet gas temperatures (Figure 6-16) of the catalyst bed 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 start-up periods, the oxidizer should be preheated using the supplemental burner. Waste gas should not be sent to the oxidizer until the outlet of the catalyst bed has reached the necessary temperature. If the organic vapor-laden waste gas stream is directed to the oxidizer before it is hot, most of the organics will not be destroyed, and contaminants could condense on the catalyst surfaces.

During routine operation, the bed outlet temperature should be 50°F to 200°F (30°C to 110°C) higher than the inlet temperature. The increase in gas temperature across the catalyst bed is because of the oxidation of the organic compounds in the waste gas stream. If the catalyst bed has become fouled, masked, or poisoned, the gas temperature increase across the bed will not be as high as its 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.

High outlet gas temperatures from the oxidizer can damage the recuperative heat exchanger. In extreme cases, it is also possible to volatilize a portion of the catalyst. Accordingly, the outlet temperature should be monitored to detect high temperature excursions. These can be caused by short term, high concentration surges of organic vapor in the waste gas stream or can be because of 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 organic compound emissions from the oxidizer. It is used downstream of the heat exchanger to detect short-circuiting emissions through the heat exchanger (inlet gas duct to outlet gas duct).

These instruments are especially useful in detecting problems affecting the catalyst bed. Outlet concentrations that are considerably higher than baseline levels indicate the need to evaluate the catalyst activity.

Review Exercises

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
   e. Greater than 1400°F

7. What is the typical operating temperature range 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 operation 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 to 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
    e. < 100% of the LEL of the gas mixture
    f. Between 100% and 250% 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. 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 required to burn 1 SCF of methane (CH_4) if the burner operating with 15% excess air?

15. The preheated waste gas stream of 4,000 ACFM is entering a thermal oxidizer. The waste gas stream temperature is 1000°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. Use an oxygen concentration of 20.9% oxygen and 79.1% nitrogen in solving the problem.

Review Answers

Types and Components of Oxidizer Systems

1. A recuperative heat exchanger is composed of ________________.
   b. tube banks

2. Regenerative heat exchangers are capable of heat recoveries up to ____ efficiency.
   c. 90% to 95%

3. Recuperative heat exchangers are capable of heat recoveries up to ____ efficiency.
   a. 40% to 65%

4. Regenerative heat exchangers are vulnerable to __________________ .
   a. plugging due to particulate matter

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

6. What is the typical operating temperature range (bed inlet) of a catalytic oxidizer?
   b. 500% to 900°F

7. What is the typical operating temperature range of a thermal oxidizer?
   c. 1200°F to 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

9. When is the burner operation 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

10. What is the typical inlet contaminant concentration to thermal and catalytic oxidizers?
    b. < 25% of the LEL of the gas mixture

Operating Principles of Oxidizer Systems

11. What is the typical operating temperature of a thermal oxidizer?
    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?
    b. 0.3 to 2 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

Capability and Sizing of Oxidizer Systems

14. How many lb moles of combustion air are required to burn 1 SCF of methane (CH4) if the burner is operating with 15% excess air?

Solution:

Step 1. Calculate the lb mole of CH_4 burned.

$$\text{Pound mole of methane} = \left(\frac{1.0\ \text{lb mole}}{385.4\ \text{SCF}}\right) 1.0\ \text{SCF}\ \text{CH}_4 = 0.00259\ \text{lb mole}\ \text{CH}_4$$

Step 2. Write the combustion reaction.

$$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$$

Step 3. Calculate the O_2 and N_2 required.

$$\begin{aligned}\text{Pound mole of } \text{O}_2 \text{ needed} &= \left(0.00259\ \text{lb mole CH}_4\right)\left(\frac{2\ \text{lb mole O}_2}{1\ \text{lb mole CH}_4}\right)\\ &= 0.000519\ \text{lb mole O}_2\end{aligned}$$

At 15% excess air, lb mole of air = 1.15 (0.00519 lb mole O_2) = 0.0060 lb mole O_2

$$\begin{aligned}\text{Pound mole N}_2 \text{ needed} &= \left(\frac{0.79\ \text{lb mole N}_2}{0.21\ \text{lb mole O}_2}\right)\left(0.0060\ \text{lb mole O}_2\right)\\ &= 0.0226\ \text{lb mole N}_2\end{aligned}$$

Step 4. Calculate air needed for 15% excess air.

$$\begin{aligned}\text{Air needed} &= 0.0060 + 0.0226\\ &= 0.0286\ \text{lb mole air}\end{aligned}$$

15. The preheated waste gas stream of 4,000 ACFM is entering a thermal oxidizer. The waste gas stream temperature is 1000°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? Use an oxygen concentration of 20.9 % oxygen and 79.1% nitrogen in solving the problem.

Solution

Step 1. Determine the enthalpy change for 1 SCF of air based on data in Table 6-2a.

Enthalpy of air @ 1000°F = 17.92 Btu/SCF

Enthalpy of air @ 1500°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.

$$\text{SCFM} = 4000\ \text{ACFM}\left(\frac{528°\text{R}}{1000°\text{F} + 460°\text{R}}\right)\left(\frac{407 + 6\ \text{in. W.C.}}{407\ \text{in. W.C.}}\right) = 1470\ \text{SCFM}$$

Step 3. Calculate the total change in enthalpy of the gas stream heated to 1500°F.

(1470 SCF/min)(10.32 Btu/SCF) = 15,170 Btu/min

Step 4. Calculate the natural gas requirement using the available heat at 1500°F

(Data in Figure 6-14)

$$\left(15{,}170\,\frac{\text{Btu}}{\text{min}}\right)\left(\frac{\text{SCF of gas}}{600\ \text{Btu available heat}}\right) = 25.3\ \text{SCF/min of gas}$$

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Chapter 7
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 continues until the partial pressure (concentration) of the organic compound in the gas stream is reduced to a concentration equivalent to the vapor pressure of that compound at the operating temperature of the condensation control system. The gas stream leaving the control device is at the vapor pressure limit.

The 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 25°C) range using chilled water. Refrigeration and cryogenic systems operate in a range from -50°F to -150°F (-45°C to -100°C). In some cases, cryogenic units can operate as low as -320°F (-200°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 organic compounds. There are usually only one or two organic compounds in the gas stream to be treated since it would be difficult to separate a large number of compounds from the condensate. The gas streams treated in condensation systems usually have low particulate loadings.

7.1 TYPES OF SYSTEMS

7.1.1 Conventional Systems

Conventional condensers are simple, relatively inexpensive devices that normally use water or air to cool and condense a vapor stream. Because these devices are usually not capable of reaching very low temperatures (below 40°F, 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 25°C).

Conventional condensers fall into two basic categories: (1) direct contact condensers and (2) surface condensers. In a contact condenser, the coolant and vapor stream are physically mixed. They leave the condenser as a single exhaust stream. In a surface condenser, the coolant is separated from the vapors by tubular heat transfer surfaces. The coolant and condensed vapors 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.

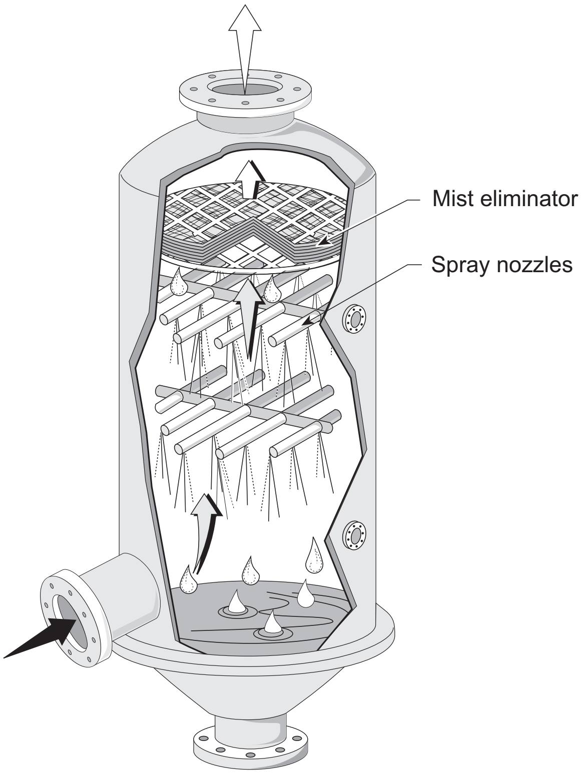


Figure 7-1. Direct contact condenser

An ejector is a type of contact condenser. Ejectors use high pressure liquid sprays to create suction for moving the organic vapor-laden gas stream and, therefore, do not need centrifugal 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.

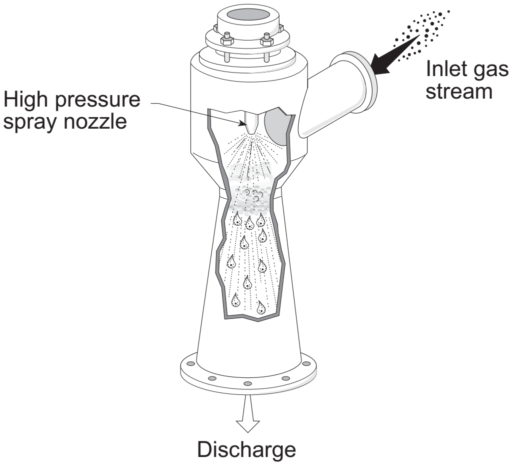


Figure 7-2. Ejector condenser

The main advantages of contact condensers are their flexibility and low cost. The main disadvantage is the mixing of the water and the condensed organic, which increases wastewater treatment costs or organic recovery costs.

Surface Condensers

Surface condensers are usually in the form of shell-and-tube heat exchangers. These devices consist of a circular or oval cylindrical shell into which the vapor stream flows. The coolant flows through numerous small tubes inside the shell. Vapors contact the cool surface of the tubes, condense, and are collected. Noncondensed vapors exit the condenser and are emitted. Figure 7-3 is a diagram of a single-pass exchanger.

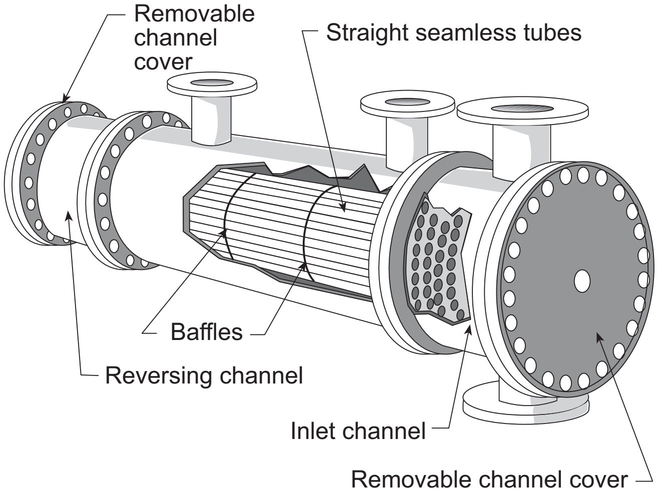


Figure 7-3. Single pass condenser

The coolant stream flows through the parallel tubes while the organic vapor-laden stream passes between the outer shell and the tubes. The unit is termed “single pass” because the organic vapor gas stream makes a single pass on the shell side of the exchanger. The single pass exchanger is not generally used because it requires a large number of tubes and low gas velocities through the exchanger to provide adequate heat transfer. Improved heat transfer can be achieved by using a multipass system, shorter tube lengths, and higher gas velocities through the exchanger.

Figure 7-4 illustrates a 1-2 multipass heat exchanger. The first digit refers to the number of passes the vapor makes on the shell side, and the second digit indicates the number of tube side passes made by the coolant liquid. This design gives improved performance over the single-pass exchanger. A 2-4 heat exchanger (not shown) is capable of higher gas velocities and better heat transfer than the 1-2 exchanger shown in Figure 7-4. 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.

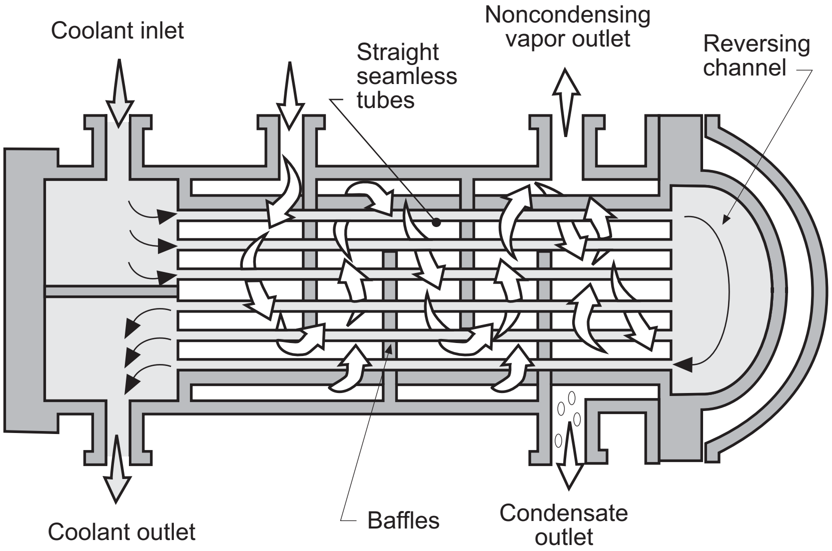


Figure 7-4. Multipass shell-and-tube condenser

Condensation applications normally require large temperature differentials between the vapor and the coolant. These temperature variances can cause the tubes to expand or contract, eventually causing the tubes to buckle or pull loose from the shell, destroying the condenser. Floating head construction is commonly used to avoid condenser expansion stress damage. In a floating head, one end of the tube bundle is mounted so that it is structurally independent from the shell, allowing the tubes to expand and contract within the shell.

Air condensers can be used in situations where water is not available, or treatment of the water stream is very expensive. Because of the limited heat capacity of air, condensers using air must be considerably larger than those using water.

Heat exchangers with extended surfaces can be used to conserve space and reduce equipment cost. In these units, the outside area of the tube is multiplied or extended by adding fins or disks. Figure 7-5 illustrates two types of finned tubes. In extended surface condensers, the vapor is condensed inside the tube while air flows around the outside, contacting the extended surfaces.

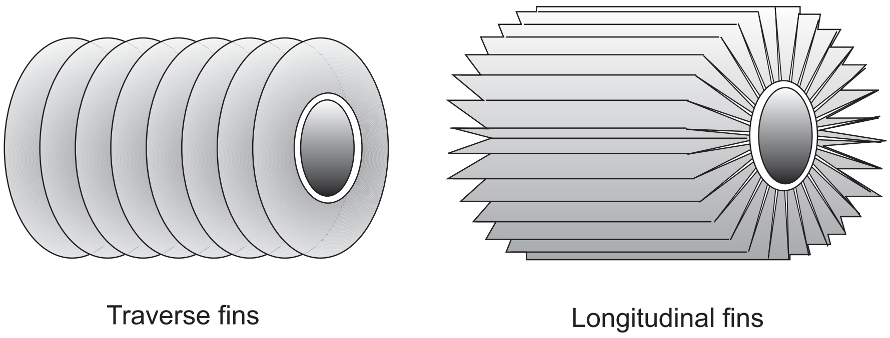


Figure 7-5. Extended surface tubes

7.1.2 Refrigeration Systems

Refrigeration systems achieve low operating temperatures by using coolants and compressors. A simplified schematic of a refrigeration system is illustrated in Figure 7-6. Heat is absorbed from the organic vapor-laden stream in the evaporator section. This heat vaporizes the coolant liquid. The coolant vapor leaving the evaporator section is then compressed to form a vapor stream at high pressure and temperature. The superheated vapor stream is condensed to expel heat from the coolant. The coolant liquid passes through an expansion valve to reduce the pressure to the level necessary for the evaporator.

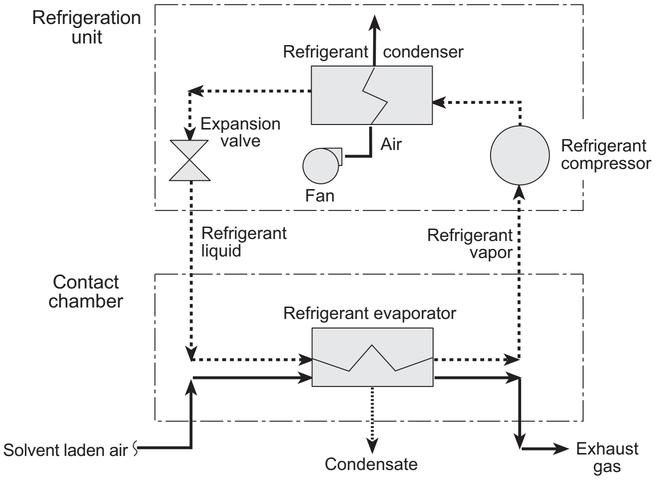


Figure 7-6. Basic refrigeration cycle

The most common coolants used in refrigeration systems are chlorofluorocarbons (CFCs). These types of coolants are changing in response to the Clean Air Act Amendments of 1990.

A typical refrigeration system for organic vapor recovery is shown in Figure 7-7. The inlet gas stream enters a pre-condenser where it is copied to approximately 40°F (4°C) in order to reduce water to levels of approximately 0.02 pounds of water per pound of dry air. By removing water vapor in the pre-condenser chamber, frost buildup on the heat exchange surfaces of the main chamber are minimized.

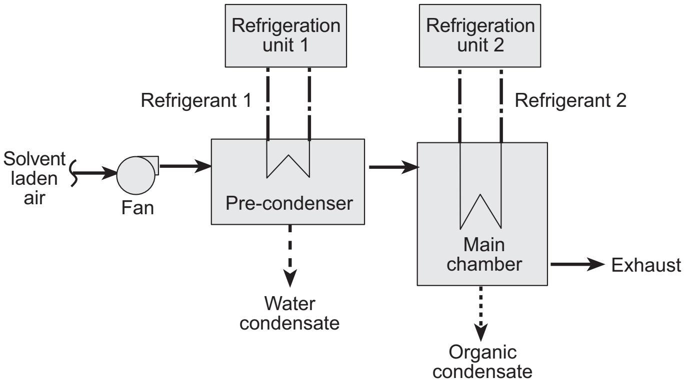


Figure 7-7. Simplified flowchart of a refrigeration system for organic vapor recovery

The main contacting chamber operates at temperatures ranging from -50°F to -150°F (-45°C to -100°C). Coolant for this chamber is supplied by a separate compressor system. Because of the very low temperatures in this chamber, cascade type systems are often used. They 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.

7.1.3 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 extreme cold temperatures ranging from -100°F to -320°F (-70°C to -200°C) condense and collect much lower VOC concentrations than refrigeration condensers. 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 to a liquefied gas from the waste 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.

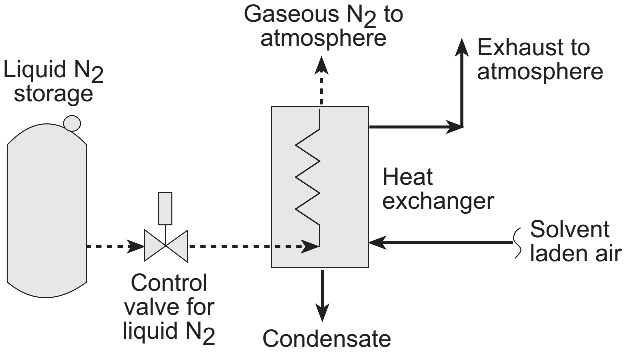


Figure 7-8. Single heat exchanger, indirect contact cryogenic system for organic vapor recovery

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 control.

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 a single heat exchange (indirect) system can be avoided by the more complex dual system. As shown in Figure 7-9, the liquefied gas is used in a cascade type arrangement to cool a heat transfer fluid that, in turn, is used in the heat exchanger for the organic vapor-laden gas handling system.

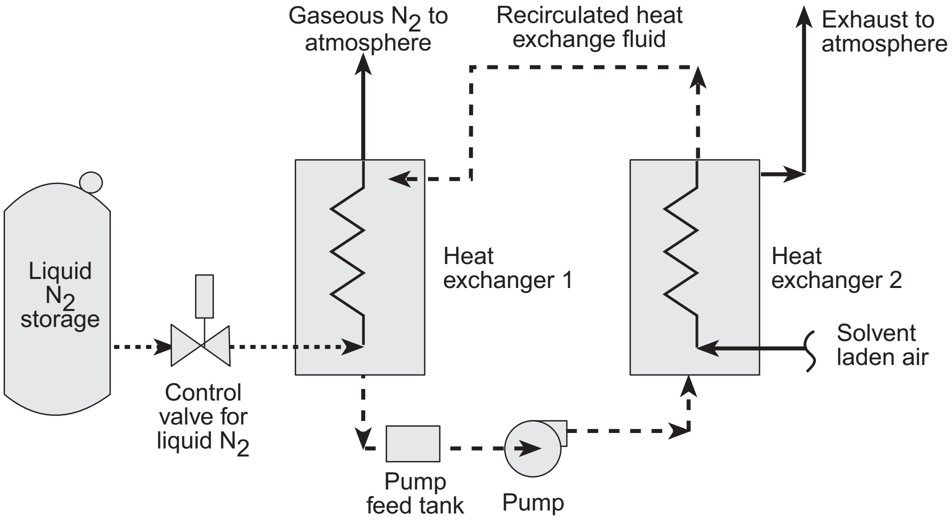


Figure 7-9. Dual heat exchange cryogenic system for organic vapor recovery

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. Occasional defrosting is still 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 is contacted 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.

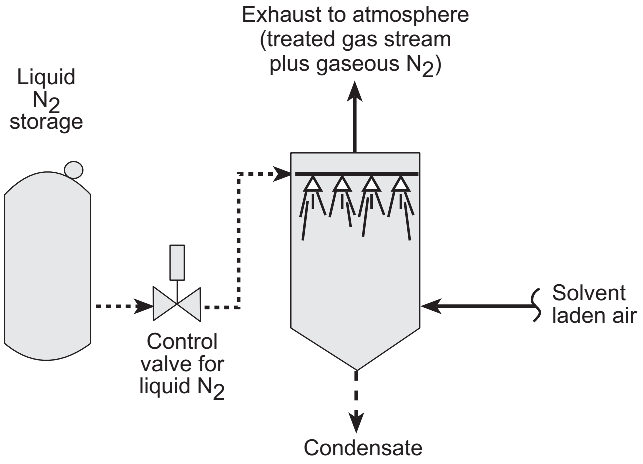


Figure 7-10. Direct contact cryogenic system for organic vapor recovery

The liquefied gas is dispersed using spray nozzles in the upper areas of the contacting chamber. The chamber is insulated to maintain gas temperatures as cold as possible. 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 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 the capability to remove organic vapor. This is because the outlet stream from any condensation system has organic compounds at concentrations equivalent to the vapor pressures of the compounds at the operating temperature. In other words, the outlet gas streams are saturated with the organic compounds at the operating temperature. By increasing the total quantity of gas exiting the system, direct contact type units have more gas that is saturated with the organic compounds.

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 where the organic vapors are at high concentrations.

7.2 OPERATING PRINCIPLES

Condensation can be caused by reducing the gas temperature, increasing the gas pressure, or a combination of both changes. In air pollution control systems, organic compounds are removed by reducing the gas temperature. Because of the large gas volumes involved, it is not economical to operate condensers based on pressure increases (compression).

As the temperature of the organic vapor-laden stream is cooled, the average kinetic energy of the gas molecules is reduced along with the volume that they occupy. Ultimately, the gas molecules are slowed down and crowded together so closely that the weak attractive forces (van der Waals' forces) between the molecules cause them to condense to a liquid. This is called the dewpoint temperature. At this point, the partial pressure of the organic compound is equal to the vapor pressure of the compound.

Once the gas temperature reaches the dewpoint temperature, the organic compound begins to condense. From that point on, the gas-liquid mixture follows the vapor pressure line. If the mixture is cooled, the partial pressure of the organic vapor will decrease as the volume of condensate increases (Figure 7-11).

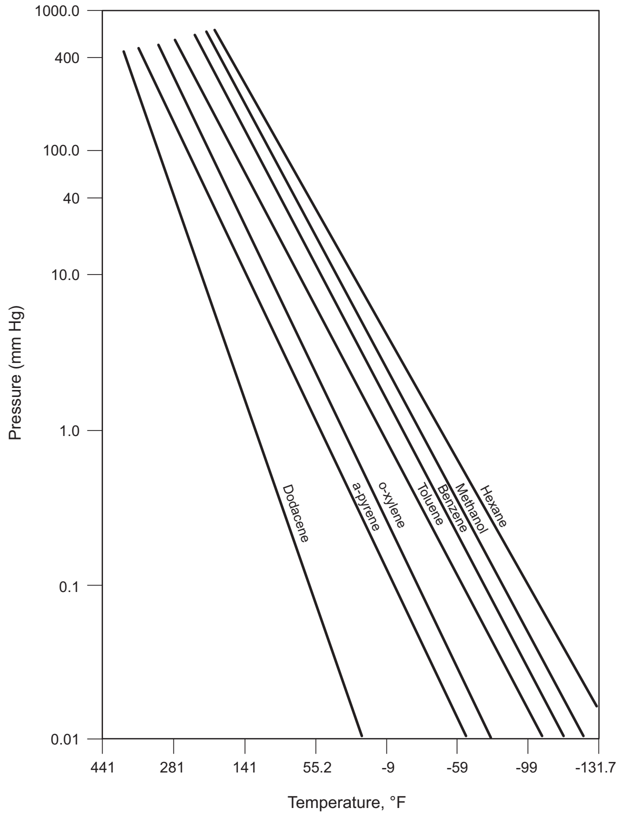


Figure 7-11. Vapor pressures of organic compounds[4]

The gas stream leaving the condensation system will have a reduced partial pressure of the organic compound. 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 extent of organic vapor removal depends on the outlet temperature as illustrated in Problem 7-1.

Problem 7-1

What is the maximum toluene removal efficiency possible in a refrigeration-type condenser operating at -100°F 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. (Figure 7-11)

Outlet partial pressure @ -100°F = 0.015 mm Hg

Step 2. Convert the outlet concentration to ppm.

Outlet concentration = (0.015 mm Hg/760 mm Hg)(10^6 ppm) = 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; therefore, condensers cannot be used in the same manner as other gaseous pollutant control devices. For example, 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.

7.3 CAPABILITY AND SIZING

7.3.1 Efficiency

The organic vapor removal efficiency of a condensation system depends on the outlet gas temperature. 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 pressure data for various organic compounds are often expressed using the Antoine Equation (Equation 7-1).

$$\log_{10}(P) = A - \left[\frac{B}{C + t}\right] \tag{7-1}$$

Where:

P = vapor pressure in mm Hg
t = gas temperature in °C
A,B,C = specific constants for each compound

The vapor pressure of an organic compound can be estimated using the Antoine Equation constants tabulated 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 -50°F?

***Solution*:**

Step 1. Convert the temperature to °C.

$^\circ\text{C} = (^\circ\text{F}-32)/1.8 = -45.6^\circ\text{C}$

Step 2. Calculate the vapor pressure using the Antoine Equation.

For ortho-xylene, A = 6.999, B = 1474.679, C = 213.69

$$\frac{B}{C + t} = \frac{1474.679}{213.69 - 45.6} = 8.77$$

$\log_{10}(P) = 6.999 - 8.77 = -1.77$

$P = 0.017$ mm Hg

The efficiency of the unit can be calculated using the estimated partial pressure of the outlet gas stream (vapor pressure at outlet temperature) and the inlet concentration of the organic vapor. It is helpful to convert the data to a ppm basis using Equation 7-2 prior to calculating the efficiency.

$$y = \left(\frac{p_i}{P_t}\right)10^6 \qquad (7\text{-}2)$$

Where:

y = mole fraction (ppm)
p_i = partial pressure of compound *i*
P_t = total pressure of gas stream

7.3.2 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 dew point.	+	Heat required to condense Vapors.	=	Heat needed to be removed by The coolant.

This heat balance is written in equation form as:

$$q = mC_p\,(T_G - T_{\text{dew point}}) + mH_v = LC_p(T_{L2} - T_{L1}) \qquad (7\text{-}3)$$

Where:

q = heat transfer rate (Btu/hr)
m = mass flow rate of vapor (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)
H_v = heat of condensation or vaporization (Btu/lb_m)

In Equation 7-3, the mass flow rate (m) and inlet temperature of the vapor stream (T_G) are set by the process exhaust stream. The temperature of the coolant entering the condenser (T_L) is also set. The average specific heats (C_p) of both streams, the heat of condensation (H_v), and the dew point temperature can be obtained from chemistry handbooks. 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 7-3 is applicable for direct contact condensers and should be used only to obtain rough estimates. Equation 7-3 has a number of limitations. 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 slightly between 32°F to 212°F (0°C to 100°C), however 1 Btu/lb_m °F is generally accurate enough for air pollution control work. The dew point of a substance is also dependent on its concentration in the gas phase, and because m is constantly changing (vapors being condensed), the dew point temperature is constantly changing. Finally, no provision is made for cooling vapors below their dew point. An additional term would have to be added to the left side of Equation 7-3 to account for this amount of cooling.

Surface Area of Surface Condensers

In a surface condenser or heat exchanger, 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:

$$q = U\,A\,\Delta T_m \tag{7-4}$$

Where:

q = heat transferred (Btu/hr)
U = overall heat transfer coefficient (Btu/°F $\cdot$ft$^2\cdot$hr)
A = heat transfer surface area (ft^2)
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 a hot body to a 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 is transferred from the vapor to the coolant. The ideal situation for heat transfer is when heat is transferred from the vapor to the coolant without any heat loss (heat resistance). Figure 7-12 shows the typical heat resistance components occurring during heat transfer in a shell-and-tube condenser.

Each time heat moves through a different medium, it encounters a different and additional heat resistance. These heat resistances (Figure 7-12) occur through the condensate, through any scale or dirt on the outside of the tube (outside fouling), through the tube itself, and through the film on the inside of the tube (inside fouling). Each of these resistances is individual heat transfer coefficients and must be added together to obtain an overall heat transfer coefficient. The overall heat transfer coefficients shown in Table 7-1 can be used for preliminary estimating purposes.

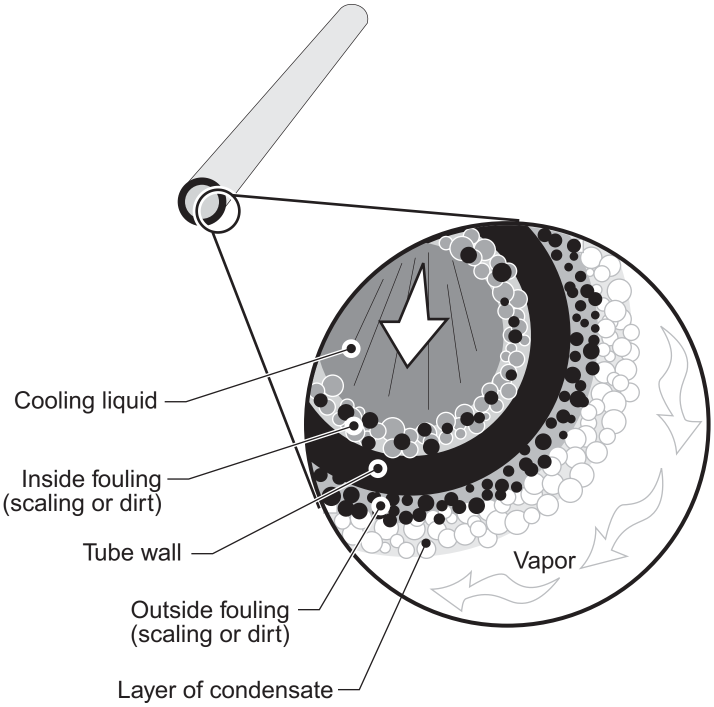


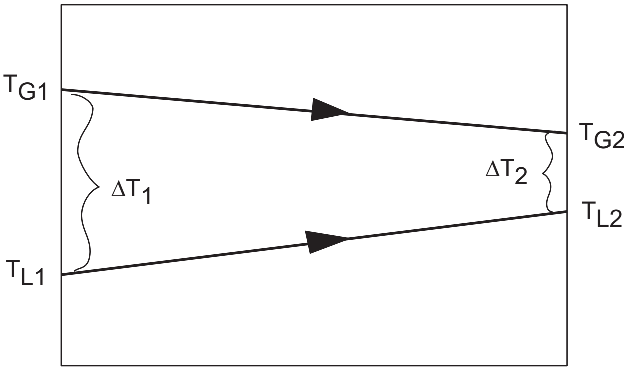
Figure 7-12. Heat transfer resistances

Table 7-1. Typical Overall Heat Transfer Coefficients in Tubular Heat Exchangers

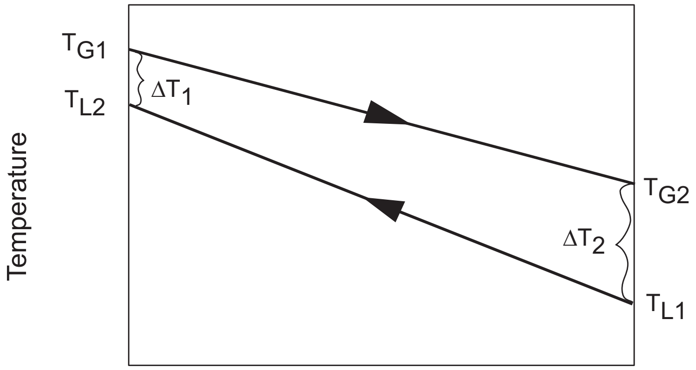
Condensing Material (shell side)	Cooling Liquid	U Btu/°F ·ft^2·hr
Organic solvent vapor with high percent of noncondensable gases	Water	20 - 60
High boiling hydrocarbon vapor (vacuum)	Water	20 - 50
Low boiling hydrocarbon vapor	Water	80 - 200
Hydrocarbon vapor and steam	Water	80 - 100
Steam	Feedwater	400 - 1000
Water	Water	200 - 250

In a surface heat exchanger, the temperature difference between the hot vapor 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, the flow of both streams is 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.

(a) Cocurrent flow



(b) Countercurrent flow



(c) Isothermal condensation with countercurrent flow

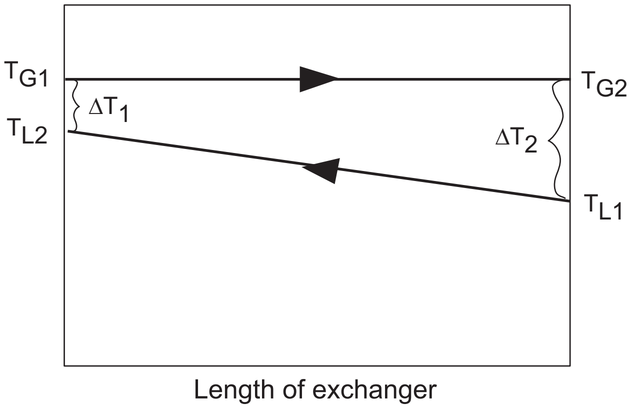


Figure 7-13. Temperature profiles in a heat exchanger for countercurrent flow, co-current flow, and isothermal condensation with countercurrent flow

The log mean temperature for contercurrent flow can be expressed as:

$$\Delta T_{lm} = \frac{\Delta T_1 - \Delta T_2}{\ln\left(\Delta T_1 / \Delta T_2 \right)} \tag{7-5}$$

Where:

ΔT_{lm} = log mean temperature

The value calculated for Equation 7-5 is used for single pass heat exchangers or condensers. For multiple pass exchangers, a correction factor for the log mean temperature must be included. No correction factor is needed for the special case of isothermal condensation (no change in temperature) 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 7-4 must be rearranged to solve for the surface area.

$$A = \frac{q}{U\Delta T_{lm}} \tag{7-6}$$

Where:

A = surface area of a shell-and-tube condenser (ft^2)
q = heat transfer rate (Btu/hr)
U = overall heat transfer coefficient ($Btu/°F \cdot ft^2 \cdot hr$)

Equation 7-6 is valid only for isothermal condensation of a single component. This implies that the pollutant is a pure vapor stream comprised of only one specific hydrocarbon, such as benzene, and not a mixture of hydrocarbons. Nearly all air pollution control applications involve multicomponent mixtures, which complicates the design procedure for a condenser.

If the incoming vapor stream is above its dew point (superheated), it must first be cooled to its dew point. It is generally considered conservative to size the condenser as if the entire heat load (desuperheating and condensing) were transferred to the condensate.[3] In this case, the heat load, q, is computed by using the left side of Equation 7-6. The dew point temperature of the gas is used in calculating the log mean temperature.

Solving for the surface area, A, will give the size of the condenser necessary to cool the vapor to the dew point and condense it. This method will not include the heat removal required for subcooling. The liquid must be subcooled to ensure that vapor will not volatilize readily from the condensate. The liquid is subcooled by maintaining a liquid level that covers some of the bottom tubes in the condenser. This condition is called *flooding*.

The single phase (liquid) subcooling section can be treated separately to give an area that is added to the area needed for condensation. The heat balance and surface area are determined on the basis of cooling the liquid from its dew point temperature to the subcooled outlet temperature.

Different situations can occur when trying to condense vapors containing more than one component. In one case, all the components will condense at the coolant temperature. In another case, a few of the components may condense, while the other components will not condense as pure components but are very soluble in the condensate. There are also mixtures where one or more of the components will not condense and will be insoluble in the liquid condensate.

Characteristics common to all three conditions can affect condenser design. Multicomponent condensation is always nonisothermal. Both liquid and vapor sensible heat removal must be provided. The composition of both phases is continually changing.[5] This complicates the design of multicomponent condensers. In order to design the condenser, temperature and condensation profiles and diffusion coefficients must be evaluated at various points in the condenser.

In nearly all condensation applications related to air pollution control, the gas to be treated is a mixture of condensable and noncondensable vapors. 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.

For preliminary estimates of condenser size, the procedure in Problem 7-3 for single component condensation can be used for condensing multicomponents. In choosing a heat transfer coefficient, the smallest value should be used to allow as much over design as possible.

Problem 7-3

In a rendering plant, tallow is obtained by removing the moisture from animal matter in a cooker. Exhaust gases from the cooker contain mostly steam; however, the entrained vapors are highly odorous and must be controlled. Condensers are normally used to remove most of the moisture prior to incineration, scrubbing, or carbon adsorption.

The exhaust flow rate from the continuous rendering cooker is 20,000 ACFM at 250°F. The exhaust gases are 95% moisture with the remaining portion consisting of air and obnoxious organic vapors. The exhaust stream is sent first to a shell-and-tube condenser to remove the moisture and then to a carbon absorption unit. If the coolant water enters at 60°F and leaves at 120°F, estimate the required surface area of the condenser. The condenser is a horizontal, countercurrent flow system with the bottom few tubes flooded to provide subcooling.

***Solution*:**

Step 1. Compute the pounds of steam condensed per minute.

20,000 ACFM x 0.95 = 19,000 ACFM steam

19,000 ACFM [528°R/(460°R + 250)] = 14,130 SCFM

14,130 SCFM (lb moles/385.4 SCF) =36.66 lb mole min

m = (36.66 lb mole/min)(18 lb/lb mole)

= 660 lb_m/min of steam to be condensed

Step 2. Solve the heat balance to determine q for cooling the superheated steam and condensing only.

$$q = \begin{matrix}\text{heat needed to cool}\\ \text{steam to condensation}\\ \text{temperature}\end{matrix} + \begin{matrix}\text{heat of}\\ \text{condensation}\end{matrix}$$

$$q = m\, C_p\, \Delta T + m\, H_v$$

The average specific heat (C_p) of steam @ 250°F = 0.45 Btu/lb_m °F (from reference text)

The heat of vaporization of steam (H_v) @ 212°F = 970.3 Btu/lb_m

Substituting into the equation:

q = (660 lb/min)(0.45 Btu/lb°F)(250°F-212°F) +

(660 lb/min)(970.3 Btu/lb)

q = 11,300 Btu/min + 640,400 Btu/min = 651,700 Btu/min

Step 3. For a countercurrent condenser, the log mean temperature is given by Equation 7-5.

$$\Delta T_{lm} = \frac{(T_{G1} - T_{L2}) - (T_{G2} - T_{L1})}{\ln\left(\frac{T_{G1} - T_{L2}}{T_{G1} - T_{L1}}\right)}$$

Remember that the desuperheater-condenser section is designed using the saturation temperature to calculate the log mean temperature difference.

$$\Delta T_{lm} = \frac{(212 - 120) - (212 - 60)}{\ln\left(\frac{212 - 120}{212 - 60}\right)}$$

ΔT_{lm} = 119.5°F

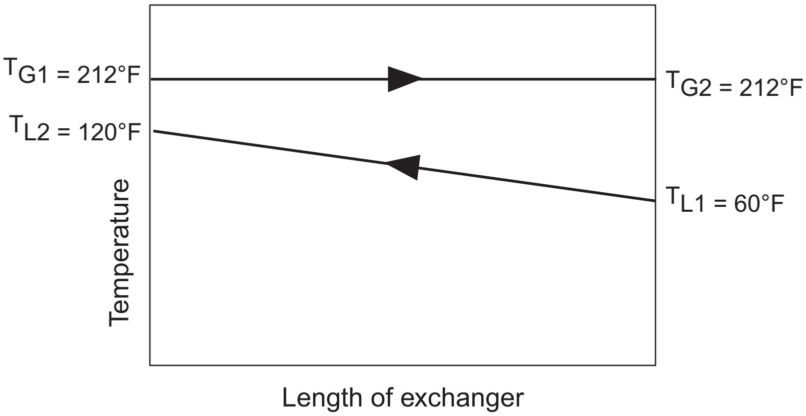


Figure 7-14. Temperature profile

Step 4. Estimate the surface area for this part of the condenser.

The overall heat transfer coefficient, U, is assumed to be 100 Btu/°F•ft^2•hr based on data in Table 7 -1 (steam and hydrocarbon vapors).

Substituting the appropriate values into Equation 7-6:

$$A = \frac{(651{,}700 \text{ Btu/min})(60 \text{ min/hr})}{(100 \text{ Btu/°F} \bullet \text{ft}^2 \text{ hr})(119.5 \text{ °F})} = 3{,}272 \text{ ft}^2$$

Step 5. Estimate the area required for subcoding.

Allow for subcooling of the water (212°F to 160°F). (160°F is an assumed safe margin.) Refiguring the heat balance for cooling the water:

$q = m\ C_p\ \Delta T$

Where:

m = 660 lb_m/min (assuming all the steam is condensed)

q = (660 lb_m/min)(1 Btu/lb °F)(212°F -160°F) = 34,300 Btu/min

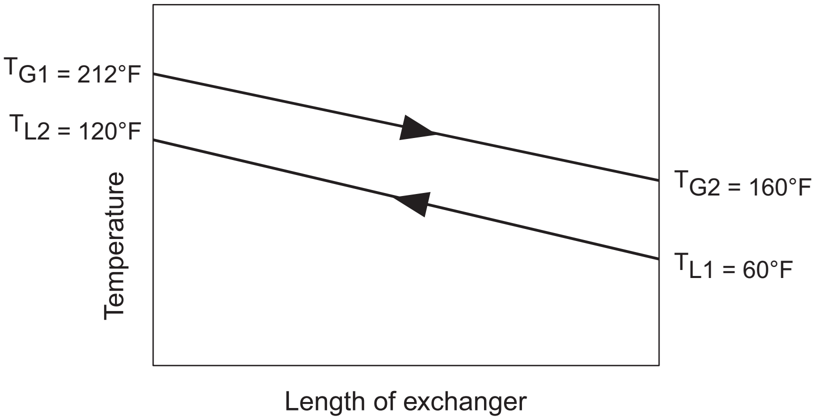


Figure 7-15. Temperature profile, Problem 7-3

$$\Delta T_{lm} = \frac{(212-120)-(160-60)}{\ln\left(\dfrac{212-120}{160-60}\right)}$$

$\Delta T_{lm} = 96°F$

$A = q / U\ \Delta T_{lm}$

U for cooling water with a water coolant is 200 Btu/°F•ft²•hr.

$$\boldsymbol{A} = \frac{34{,}300\ \text{Btu/min}}{\left(200\ \text{Btu/}^\circ\text{F} \bullet \text{ft}^2 \bullet \text{hr}\right)\left(96^\circ\ \text{F}\right)}$$

$A = 1.79\ ft^2$ or $2\ ft^2$

Step 5. The total area needed is as follows.

$A = 3{,}272 + 2 = 3{,}274\ ft^2$

As illustrated by this example, the area for subcooling is usually very small compared to the area required for condensing.

Review Exercises

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 build-up 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
   e. Answers a, b, and c

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 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

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= 7.098, B = 1238.71, and C = 217.

8. What is the maximum ethyl acetate removal efficiency in a direct contact condensation system operating at 40°F if the inlet concentration is 500 ppm?

Review Answers

Types and Components of Condensers

1. A shell-and-tube condenser using chilled water usually reduces the gas stream temperature to _____.
   b. 40°F to 80°F

2. A refrigeration condenser system usually reduces the gas stream temperature to _________.
   b. < –50°F

3. A precondenser is often used in refrigeration and cryogenic systems to_________.
   a. prevent frost build-up on the heat exchanger surfaces of the main contacting chamber.

4. A cryogenic condenser system usually reduces the gas stream temperature to _________.
   c. < –50°F to –320°F

Operating Principles of Condensers

5. The gas stream exiting a condensation system has an organic vapor __________.
   a. equal to the vapor pressure of the compound at the exit gas temperature.

6. Condensation systems are generally used for__________.
   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= 7.098, B = 1238.71, and C = 217.

   Solution:

   Step 1. Convert the temperature to °C.

   °C = (°F-32)/1.8 = 4.4°C

   Step 2. Calculate the $\log_{10}$ P using the Antoine Equation (Equation 7-1).

   $$\log_{10} P = 7.098 - \left[\frac{1238.71}{217 + 4.4}\right] = 1.50$$

   Step 3. Calculate the vapor pressure.

   $P = 10^{1.50} = 31.8$ mm Hg

8. What is the maximum ethyl acetate removal efficiency in a direct contact condensation system operating at 40°F if the inlet concentration is 500 ppm?

Solution:

Step 1. Use the vapor pressure for ethyl acetate at 40°F calculated in Review Exercise 7.

Out = 31.8

Step 2. Determine the removal efficiency.

$$\eta = \left(\frac{\text{in - out}}{\text{in}}\right)100\% = \left(\frac{500 - 31.8}{500}\right)(100) = 93.6\%$$

References

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2. Bell, K.J. and M.A. Ghaly. *An Approximate Generalized Design Method For Multicompartment/Partial Condensers.* American Institute of Chemical Engineers Symposium Series. 1972, Vol. 69, No. 131, pp. 72-79.

3. Henzler, G.W. and 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 Colo. Northville, MI: Liquid Carbonic Industries Corporation. June 13-18, 1993.

4. Perry, J.H., Ed. *Chemical Engineers Handbook*, 5th ed. New York: McGraw Hill. 1973.

5. Spencer, Robert 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. Chicago IL: Liquid Carbonic Corporation. June 21-16, 1992.

Chapter 8
Nitrogen Oxides Control

More than 20 million tons of nitrogen oxides are emitted into the atmosphere each year as a result of burning fossil fuels.[1] These emissions can create local ambient levels that are 10 to 100 times greater than the NO_X emitted by natural sources.[1] Controlling NO_X is important because of their involvement in the formation of ozone and other photochemical smog compounds that have harmful effects on public health.

Stringent NO_X controls are required by several quite different portions of the CAAA of 1990. Title IV acid rain requirements limit NO_X emissions from essentially all utility boilers as of January 1, 2000. Title I NAAQS limit NO_X emissions from some existing fuel burning sources and process sources in ozone nonattainment areas.

In the past, NO_X control efforts have focused primarily on combustion system modifications that limit the formation of emissions. These design modifications have been very successful for many sources, such as gas turbines and gas-and oil-fired boilers. There has also been an increased need for add-on NO_X controls for certain types of sources. Accordingly, a variety of add-on control devices and systems have been developed for use in addition to combustion system modifications.

8.1 INTRODUCTION TO NO_X FORMATION AND EMISSION SOURCES

8.1.1 Formation of Nitrogen Oxides in Stationary Sources

NO_X emissions are formed by three complex chemical processes occurring during combustion: (1) thermal fixation of molecular nitrogen, (2) oxidation of organically bound nitrogen contained in the fuel, and (3) formation of NO_X due to the presence of partially oxidized organic species present within the flame. These three separate reaction mechanisms are usually referenced to respectively as: *thermal*, *fuel*, and *prompt* NO_X.

Thermal 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 and nitrogen dioxide 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. Reaction 8-1 indicates the result of these simultaneous and interacting chemical reactions.

$$N_2 + O_2 \leftrightarrow 2\ NO \qquad \text{Reaction 8-1}$$

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.

$$NO + \tfrac{1}{2}\ O_2 \leftrightarrow NO_2 \qquad \text{Reaction 8-2}$$

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 (1,370°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: (1) reduction of the oxygen concentration in the maximum temperature zone, (2) reduction of the peak flame temperature, and/or (3) 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. This will be discussed later in this chapter.

Fuel NO_X Formation

The oxidation of nitrogen compounds contained in fossil fuels can create appreciable concentrations of NO and NO_2. The concentration of NO_X 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% to 60% of the fuel-bound nitrogen is oxidized.[2] The concentrations can vary from less than 0.5% to more than 2%. As the nitrogen content of the fuel increases, the *fraction* of the fuel nitrogen converted to NO_X often *decreases*. The rate of NO_X formation because of 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 NO_X, fuel NO_X 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; 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) discussed later in this chapter.

Prompt NO_X Formation

NO_X can also form because of 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.

8.1.2 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. However, because of 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. This is illustrated in Problem 8-1.

Problem 8-1

What are the total NO_X emissions in pounds per hour from an industrial boiler emitting 475 ppm NO and 25 ppm NO_2 in a flue gas stream of 100,000 SCFM?

Solution:

$$\text{Emission rate of } NO_x = \left(\frac{500 \text{ ppm}}{10^6 \text{ ppm total}}\right)\left(\frac{100{,}000 \text{ SCF}}{\text{min}}\right)\left(\frac{\text{lb mole}}{385.4 \text{ SCF}}\right)\left(\frac{46 \text{ lb } NO_2}{\text{lb mole } NO_2}\right)$$

$$= 5.97 \text{ lb}_m/\text{min } NO_X \text{ as } NO_2$$

It should be noted that the molecular weight of NO_2 (MW = 46), rather than the molecular weight of NO (MW=28), is used for calculating the total emissions on a nitrogen dioxide basis. All of the emission regulations are based on NO_2, primarily because the NAAQS concern NO_2 rather than NO.

8.1.3 NO_X Emission Sources

It is apparent that utility and industrial combustion systems are very important sources of NO_X. Control techniques have been developed primarily for this broad category of sources. Some basic information concerning the characteristics of these sources is needed for later discussions concerning NO_X control techniques.

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 that can be divided into three general categories of units based on the arrangement of the burners.

- Front-fired
- Opposed-fired (front and back walls)
- Tangentially-fired (four corners)

The arrangement of the burners has an impact on the generation of NO_X because of the differences in the maximum gas temperatures generated in the burner flames. Large utility and industrial pulverized coal boilers usually have between 10 to more than 100 separate coal burners.

Figure 8-1 is a simplified schematic of a typical pulverized caol-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.

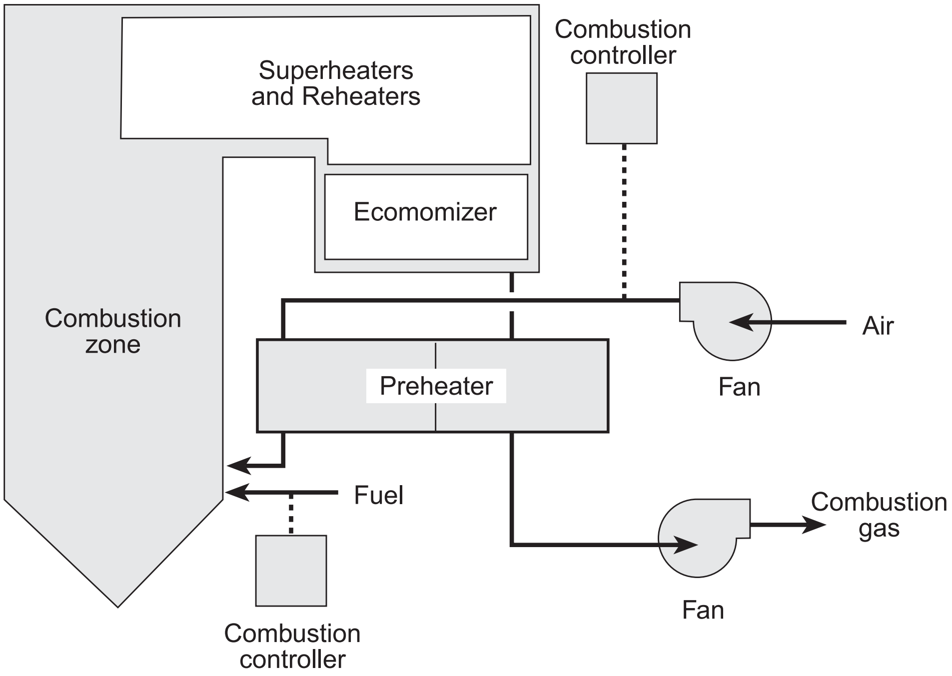

Figure 8-1. Pulverized coal-fired boiler

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. *APTI Course 427: Combustion Source Evaluation* provides a more comprehensive discussion of boiler designs. However, the basic functions of some of the most common heat exchange areas shown in Figure 8-1 are summarized below.

- 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 are indicated on Figure 8-2. The peak combustion gas stream temperatures in the burner flames can be more than 3,000°F (1650°C). Gases entering the superheater and reheater areas are usually in the range of 1,800°F to 2,200°F (980°C to 1200°C). The normal gas temperature leaving the econimizer is 500°F to 700°F (260°C to 370°C). Flue gas temperatures leaving the air preheater are usually in the range of 250°F to 350°F (120°C to 180°C).

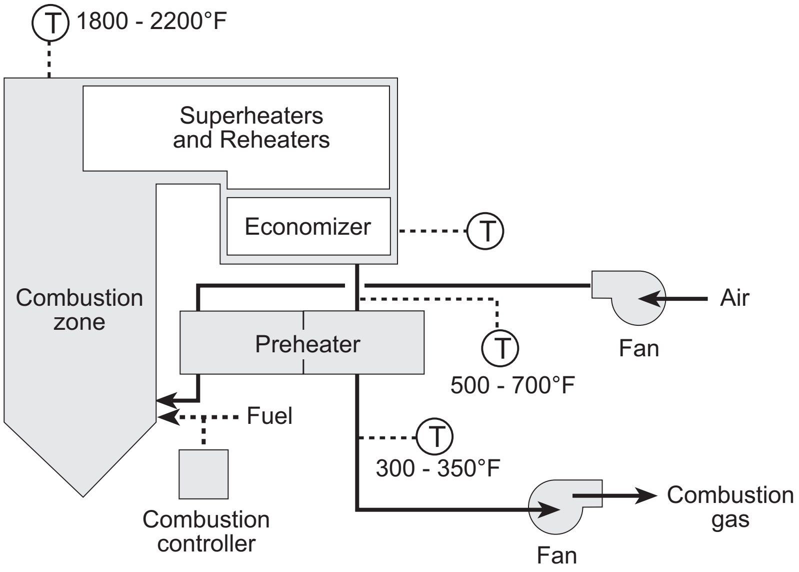

Figure 8-2. Typical gas temperatures in a pulverized coal-fired boiler

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 coals 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 are 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, low NO_X burners, and gas reburning.

Gas Turbines

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 because of 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 because of 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. Fuel is burned in a parallel set of combustion chambers. Exhaust gases at temperatures of 900°F to 1,000°F (480°C to 540°C) are exhausted directly to the atmosphere.

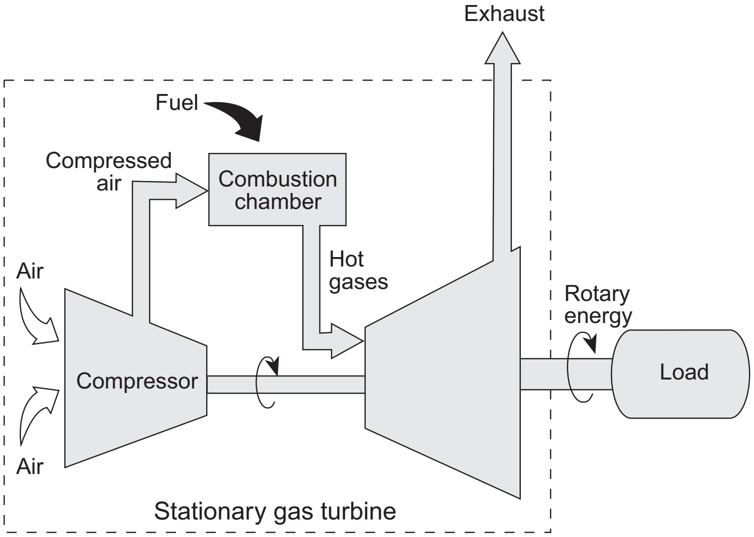

Figure 8-3. Simple cycle gas turbine

This type of arrangement is used in some old installations intended for peaking service. It has a relatively low thermal efficiency because of 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.

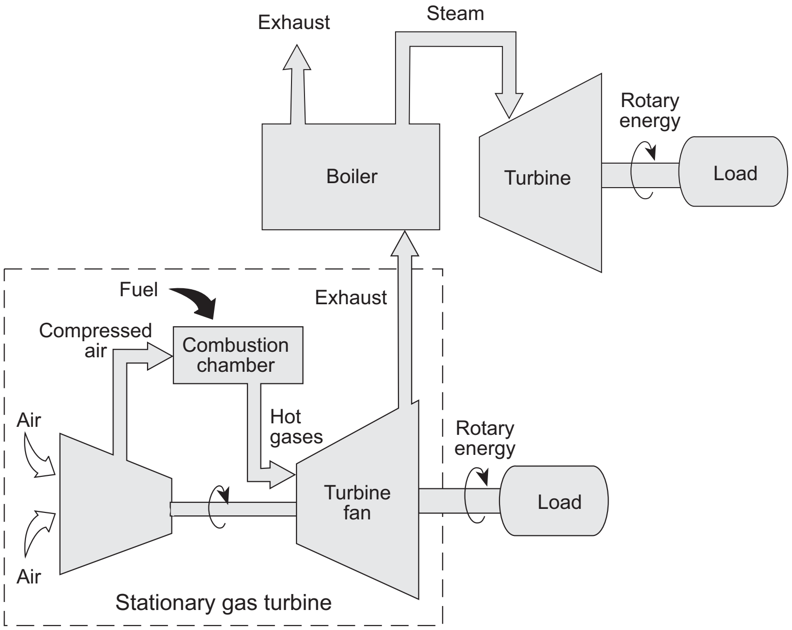

Figure 8-4. Combined cycle gas turbine

Combined cycle turbines can be equipped with a duct burner to increase the gas temperature of the exhaust gases entering the waste heat boiler. Duct burners generally use natural gas as a fuel. They increase the gas temperature to more than 1,800°F (980°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. Combustion air is supplied under pressure from the upstream compressor.

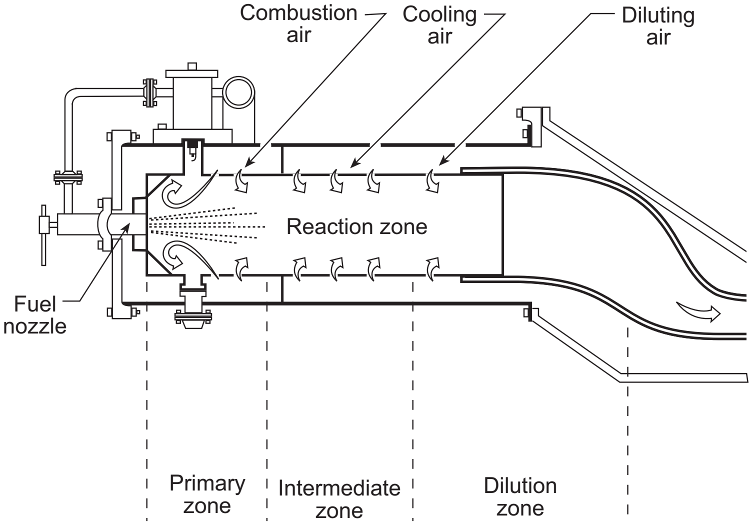

Figure 8-5. Typical combustor

Conventional combustors use a diffusion-type flame. 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.

Conventional gas turbines use water or steam injection to minimize NO_X emissions. They dilute the combustion gases and thereby reduce the peak temperatures. The heat capacity of water reduces the peak combustion gas temperatures. 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.

There have been substantial advances in gas turbine design and air pollution control techniques in the past ten 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 60% to 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 8-6 is a common type of municipal waste incinerator. The wastes move through the unit because of 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 ash pit. The ash is quenched and continually removed by a conveyor.

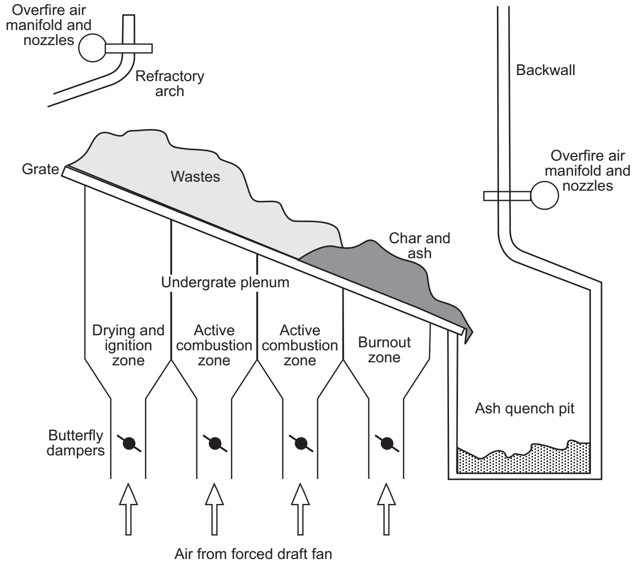

Figure 8-6. Municipal waste incinerator

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.

Because of 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-stoichiometric 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 because of 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. 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 boiler is provided in Figure 8-7.

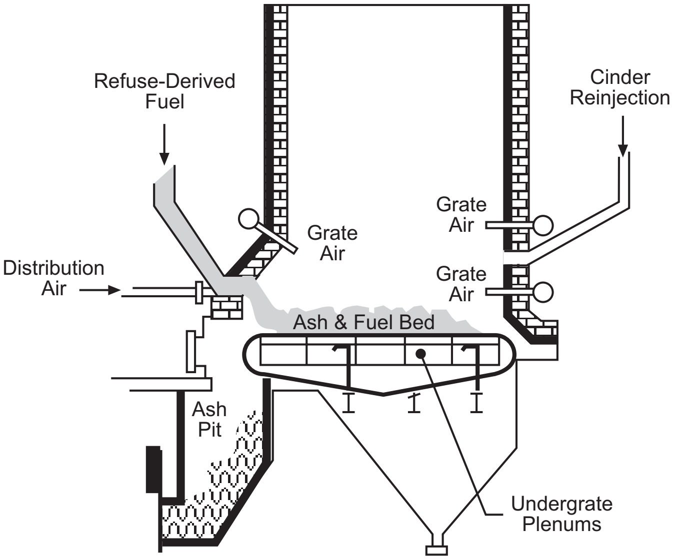

Figure 8-7. Coal- or wood-fired spreader stoker boiler

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.

Overgrate 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.

Because of 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 SNCR and SCR units.

8.2 TYPES AND COMPONENTS OF NO_X CONTROL SYSTEMS

The techniques used to minimize NO_X emissions from stationary source combustion processes can be divided into three categories: (1) combustion modifications, (2) add-on 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 gases 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 because of its combustion characteristics or fuel nitrogen characteristics.

8.2.1 Boiler Combustion Modifications

The initial efforts to control nitrogen oxides in utility and industrial boilers concerned combustion modifications. There are changes to the fuel firing equipment and operating conditions to suppress the formation of nitrogen oxides. There are five major categories of combustion modification techniques.

- Low excess air combustion
- Off-stoichiometric combustion
- Flue gas recirculation
- Low NO_X burners
- Gas reburning

The fundamental objective of all five categories of techniques is to suppress NO_X formation by minimizing the residence peak temperatures, peak oxygen concentration, and the time of the combustion products in a peak temperature-peak oxygen concentration combustion zone. These changes have a direct impact on the thermal NO_X formation rates. In addition, these combustion modifications also have a beneficial impact on fuel NO_X formation rates.

Low Excess Air Combustion

The amount of air needed to complete combustion can be accurately calculated based on the amount of fuel being fired and the ultimate analysis of the fuel. The ultimate analysis provides the total quantity of carbon, hydrogen, oxygen, nitrogen, sulfur, chlorine, ash, and moisture in the fuel. The amount of oxygen needed for combustion can then be calculated based on the following stoichiometric relationships.

$$C + O_2 \rightarrow CO_2 \qquad \text{Reaction 8-3}$$

$$2H + \frac{1}{2}O_2 \rightarrow H_2O \qquad \text{Reaction 8-4}$$

$$S + O_2 \rightarrow SO_2 \qquad \text{Reaction 8-5}$$

In calculating the total oxygen required, the amount of oxygen already present in the fuel is subtracted because this oxygen will contribute to the conversion of the fuel to its final reaction products; CO_2, H_2O, and SO_2. The calculation of the total air requirement is illustrated in Problem 8-2.

Problem 8-2

A coal has the ultimate analysis indicated. Based on a total fuel firing rate of 1,000 tons per hour, what is the minimum quanitity of air needed to complete combustion? What is the total effluent gas stream at this condition?

Coal Ultimate Analyses			
Carbon, C	65.0%	Nitrogen, N	1.2%
Hydrogen, H	8.0%	Water, H_2O	4.0%
Oxygen, O	7.5%	Ash	13.3%

Sulfur, S	1.0%	Total	100.0%

Solution:

Step 1. Compile a table to summarize the material balances for fuel, combustion air and combustion products.

Table 8-1. Data Summary

a	b	c	d	e	f	g
Material	**Composition**	**Input Weight, lbs/hr**	**Input, lbs moles/hr**	**Consumed, lb moles/hr**	**Formed, lb moles/hr**	**Flue Gas, lb moles/hr columns (d-e+f)**
Fuel		2,000,000				
C	65.0%	1,300,000	108,000	108,000	0	0
H	8.0%	160,000	160,000	160,000	0	0
O	7.5%	150,000	9,400	9,400	0	0
S	1.0%	20,000	625	625	0	0
N	1.2%	24,000	1,700	1,700	0	0
Water	4.0%	80,000	4,400	0	0	4,400
Ash	13.3%	266,000	N/A	N/A	0	N/A
Combustion Air						
O_2	20.9%		146,000	146,000	0	0
N_2	79.1%		552,000	0	0	552,000
Combustion Products						
CO_2				0	108,000	108,000
H_2O				0	80,000	80,000
SO_2				0	625	625
NO_2				0	1700	1700

Step 2. Calculate the input quantities of the fuel constituents by dividing the weights by the molecular weights.

C = (1,300,000 lb/hr)/(12 lb/lb mole) = 108,000 lb mole/hr

H = (160,000 lb/hr)/(1 lb/lb mole) = 160,000 lb mole/hr

O = (150,000 lb/hr)/(16 lb/lb mole) = 9,400 lb mole/hr

S = (20,000 lb/hr)/(32 lb/lb mole) = 625 lb mole/hr

N = (24,000 lb/hr)/(14 lb/lb mole) = 1,700 lb mole/hr

H_2O = (80,000 lb/hr)/(18 lb/lb mole) = 4,400 lb mole/hr

Step 3. Calculate the oxygen requirement using the lb mole/hr data and the stoichiometry of the combustion reactions.

$O_2 = CO_2 + 1/2\ H_2O + SO_2 + NO_2 - O_2$ (Fuel)

$$O_2 = 108{,}000 + 1/2\left(\frac{160{,}000}{2}\right) + 625 + 1{,}700 - \left(\frac{9400}{2}\right) = 146{,}000 \text{ lb mole/hr}$$

Step 4. Calculate the nitrogen present in the combustion air by using the ratio 79% N_2 and 20.9% O_2.

$N_2 = O_2$ (0.79/0.209) = 146,000 lb mole/hr (0.79/0.209) = 552,000 lb mole/hr

Step 5. Complete column e by entering the molar quantities that are consumed in the combustion reaction. In combustion calculations, it is assumed that the reactions go to completion.

> Note: Only the water and ash from the fuel remain. Because the excess air level is zero, none of the oxygen remains.

Step 6. Calculate the amount of combustion gases formed (column f) based on the stoichiometry of the reactions.

CO_2 = 1 (lb mole C/hr) = 108,000 lb mole/hr

H_2O = 1/2 (lb mole H/hr) = 80,000 lb mole/hr

SO_2 = 1(lb mole S/hr) = 625 lb mole/hr

NO_2 = 1(lb mole N/hr) = 1,700 lb mole/hr

Step 7. Calculate the lb moles of material leaving the combustion process (combustion products, combustion air, and unburned constituents of fuel).

Total effluent gas stream = fuel moisture + combustion products + remaining oxygen + combustion air nitrogen

Total effluent gas stream = 4,400 + (108,000 + 80,000 + 625 + 1700) + 0 + 552,000

Total effluent gas stream = 747,000 lb mole/hr.

In Problem 8-2, the oxygen concentration in the effluent gas stream (combustion products) is zero. All of the oxygen available in the fuel and provided as part of the combustion air stream is consumed in the oxidation reactions at stoichiometric conditions. If combustion systems were perfect, this would be a very desirable operating condition. However, the mixing of fuel and air in the burner and in the combustion chamber in general is never perfect. To allow for the inherently non-ideal conditions, boilers are designed to operate with a slight excess air level. The excess air is expressed as a percentage of the theoretical air calculated for complete combustion. For example, a 40% excess air level means that the amount of air provided is 140% of the total theoretical air requirement. This is illustrated in Problem 8-3.

Problem 8-3

What is the oxygen concentration (%) and total gas flow rate (lb moles per hour) if the boiler addressed in Problem 8-2 is fired at an excess air rate of 40%?

Solution:

Step 1. Compile a table to summarize the material balances for fuel, combustion air and combustion products. The quantity and composition of the fuel is identical to Table 8-1.

Table 8-2. Data Summary

a	b	c	d	e	f	g

Material	Composition	Input Weight, lbs/hr	Input, lbs moles/hr	Consumed, lb moles/hr	Formed, lb moles/hr	Flue Gas, lb moles/hr columns (d-e+f)
Fuel		2,000,000				
C	65.0%	1,300,000	108,000	108,000	0	0
H	8.0%	160,000	160,000	160,000	0	0
O	7.5%	150,000	9,400	9,400	0	0
S	1.0%	20,000	625	625	0	0
N	1.2%	24,000	1,700	1,700	0	0
Water	4.0%	80,000	4,400	0	0	4,400
Ash	13.3%	266,000	N/A	N/A	0	N/A
Combustion Air						
O_2	20.9%		206,000	146,000	0	60,000
N_2	79.0%		779,000	0	0	779,000
Combustion Products						
CO_2				0	108,000	108,000
H_2O				0	80,000	80,000
SO_2				0	625	625
NO_2				0	1700	1700

Step 2. Calculate the input quantities of the fuel constituents (column e) as performed in Step 2 of Problem 8-2.

Step 3. Calculate the oxygen requirement using the lb mole/hr data and the stiochiometry of the combustion reactions.

$$O_2 = (140\%/100\%)[CO_2+1/2\ H_2O + SO_{2+}\ NO_2]– O_2\ (\text{Fuel})$$

$$O_2 = 1.40\ [108{,}000 + 1/2\ \left(\frac{160{,}000}{2}\right) + 625+ 1700] - \left(\frac{9400}{2}\right) = 206{,}000 \text{ lb mole/hr}$$

Step 4. Calculate the nitrogen present in the combustion air by using the ratio 79% N_2 and 20.9% O_2.

$$N_2 = O_2\,(0.79/0.209) = 206{,}000 \text{ lb mole/hr } (0.79/0.209) = 779{,}000 \text{ lb mole/hr}$$

Step 5. Complete column e by entering the molar quantities that are consumed in the combustion reaction. In combustion calculations, it is assumed that the reactions go to completion.

Note: Only the water and ash from the fuel remain. From Step 3 of Problem 8-2 we know 146,000 lb mole/hr of O_2 will be consumed under stoichiometric conditions.

Step 6. Calculate the amount of combuston gases formed based on the stoichiometry of the reactions as performed in Step 6 of Problem 8-2.

Step 7. Calculate the volumetric flow rate leaving the combustion process (combustion products, combustion air, and unburned constituents of fuel).

Total effluent gas stream = fuel moisture + combustion products + remaining oxygen + combustion air nitrogen

Total effluent gas stream = 4,400 + (108,000 + 80,000 + 625 + 1700) + 60,000 + 779,000

Total effluent gas stream = 1,034,000 lb mole/hr.

It is apparent from Problem 8-2 and 8-3 that lowering the excess air rate reduces the total gas flow. An excess air rate of 25% will result in 924,000 lb mole/hr of effluent gas for the situation in the preceeding examples. Therefore, an excess air rate reduction from 40% to 25% results in an 11% reducion of effluent gas flow. Considering that the flue gases have significant enthalpy (heat energy) levels, the reduced gas flow rate reduces the amount of heat lost from the boiler and thereby improves the thermal efficiency of the unit.

There are definite limitations to low excess air operation. Very low excess air firing can produce increased particulate and CO emissions, and fouling and slagging of boiler tube surfaces can occur. This is indicated by the general performance curve shown as Figure 8-8.

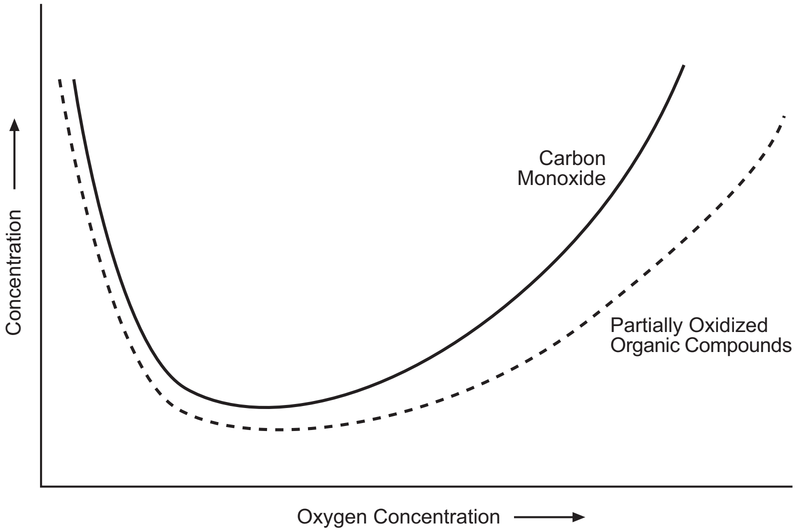

Figure 8-8. General relationship between oxygen levels in the flue gas and the formation of partially oxidized organic compounds and carbon monoxide.

NO_X 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% level.[4]

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% to 5% when the unit is near full load. Oil-fired units typically operate at excess air rates of 5% to 20%, depending on the type of oil and the load conditions. Pulverized coal-fired boilers operate at excess air rates of 20% to 50%. Obviously, the ability to use 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 air 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. Low excess air firing practices is easy to implement and actually slightly increases the efficiency of the furnace.

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 (Figure 8-9). 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_X forming region of the flame, thus creating a low NO_X condition.

Staged combustion reduces NO_X emissions by a combination of several factors. First, a lack of available oxygen for NO_X formation in the fuel-rich stage is because of 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 because of 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 can occur when burning some coals or heavy oils under staged combustion conditions.

Staged combustion can 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.

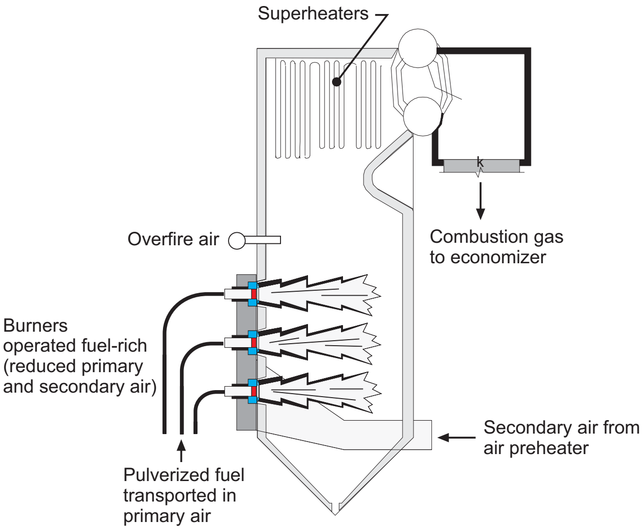

Figure 8-9. Off-stoichiometric combustion

In some boilers, a number of the burners are operated fuel-rich, and others are operated air-rich in a staggered configuration called biased firing (Figure 8-10). When some burners are operated on air only, this modification is called burners-out-of-service (sometimes abbreviated BOOS) as seen in Figure 8-11.

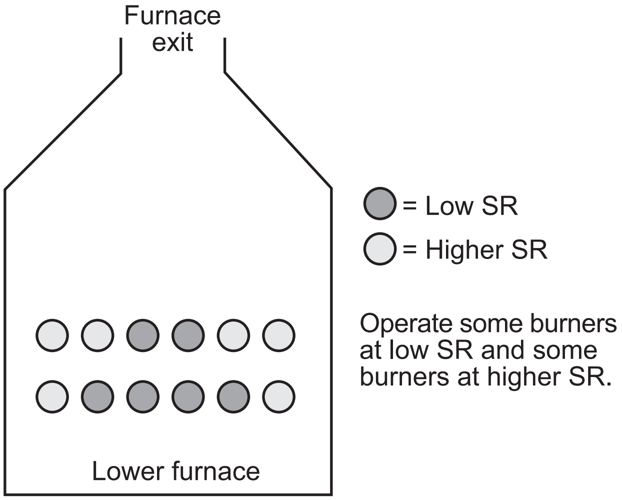

Figure 8-10. Burner firing conditions using biased firing approach
(Note: SR = stoichiometric ratio)

On existing boilers, a steam load reduction will result with burners-out-of-service if the active fuel burners do not have the capacity to supply fuel for a full load. Most utility boilers installed since 1971 have been designed with over fire air ports so that all fuel burners are active during the staged combustion operation.[4] Using staged combustion modifications on oil- and gas- fired boilers reduces NO_X emissions by approximately 30% to 40%.[4] Modifying existing coal boilers has reduced NO_X emissions 30% to 50%.[1]

Staged combustion can also be accomplished by careful control of air and fuel mixing in the burner. Low NO_X burners, discussed later in this chapter, use this basic approach in order to suppress NO_X formation.

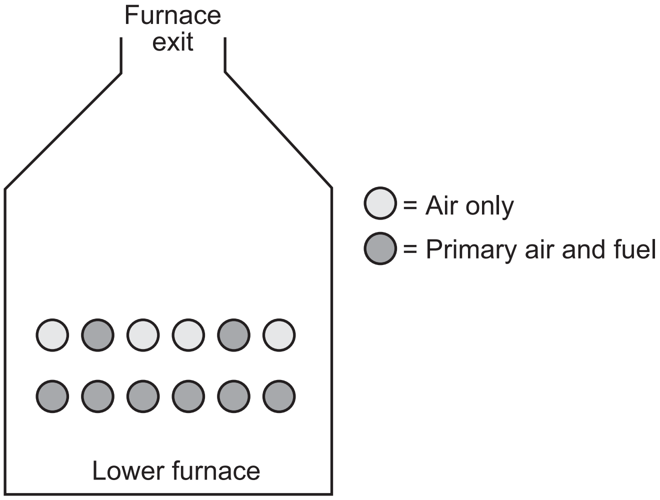

Figure 8-11. Burner firing conditions using
burners-out-of-service approach

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% to 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 8-12). 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.

Some operational problems can occur using flue gas recirculation. 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.[4]

Flue gas recirculation 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.

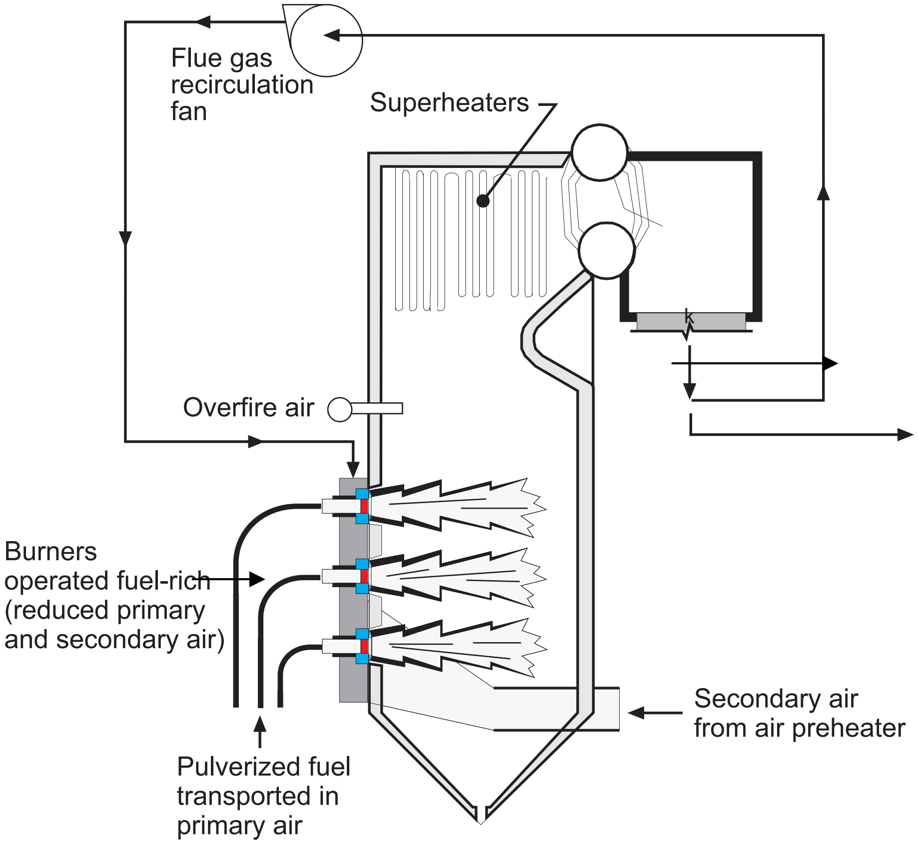

Figure 8-12. Flue gas recirculation

NO_X reduction of approximately 40% to 50% is possible with recirculation of 20% to 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 keeps 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 8-13. 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.

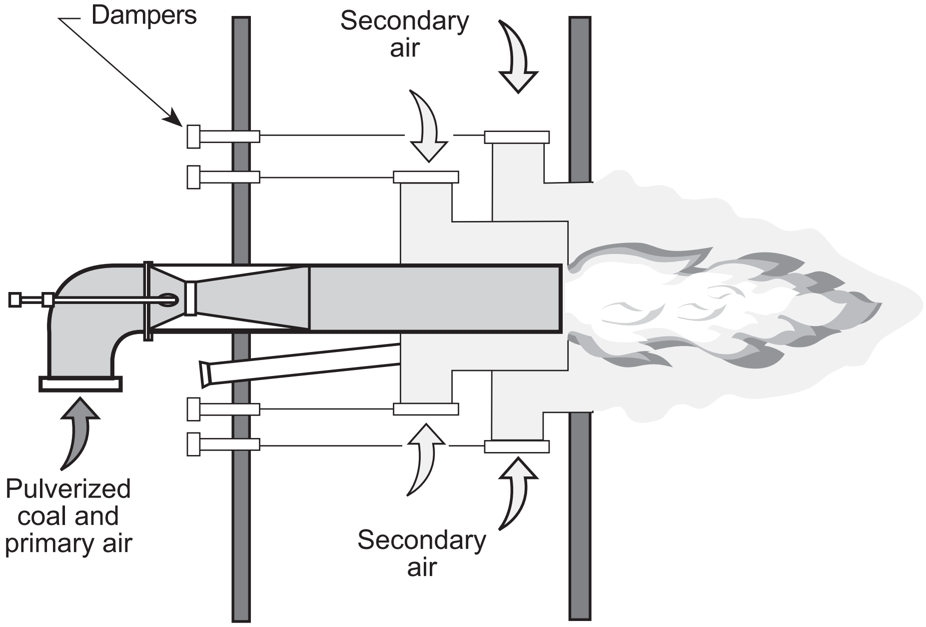

Figure 8-13. Example of a dual register low NO_X burner

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.

Most low NO_X burners have demonstrated NO_X reduction efficiencies of 25% to 40%.[6] However, manufacturers have documented efficiencies on a number of units higher than 60%.[5]

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.[7] These data can be used to optimize the burner performance and to identify burners that are not operating properly.

Gas Reburning

Gas reburning involves the use of separate gas-fired burners in the upper portions of the combustion chamber. Approximately 10% to 15% of the fuel demand of the boiler is supplied by these gas-fired burners rather than the pulverized coal burners.[10] 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.[10] The air/fuel ratio 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.

A schematic diagram of a gas reburning system is shown in Figure 8-14.

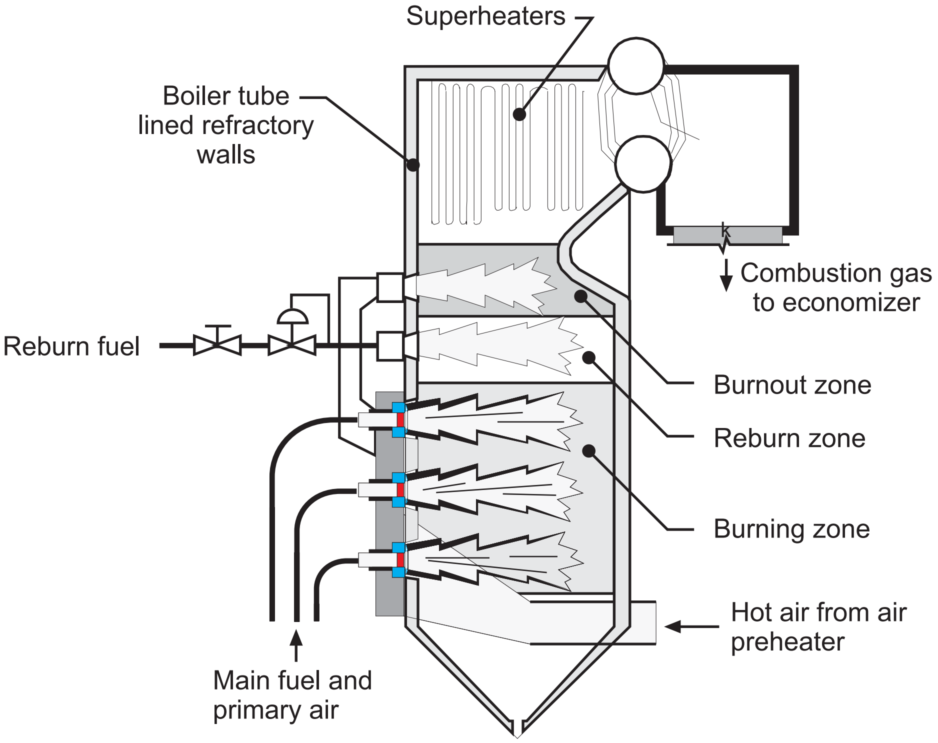

Figure 8-14. Gas reburning system

All types of coal-fired units can use 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% to 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 because of the energy penalty involved and the relatively low emission reduction.

8.2.2 Gas Turbine Combustion Modifications

Lean, Pre-Mixed Gas Turbine Combustors

The most common type of dry combustor used in gas turbines 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. Because of 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. In the second stage, combustion reactions are 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

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. Because of 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 NO_X 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.[9] 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 because of the water or steam injection. The overall thermal efficiency of the turbine is reduced several percent because of energy losses associated with heating diluent water vapor. Water or steam injection increases the turbine exhaust gas stream moisture content to 10% to 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.

8.2.3 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 to the change in the coal nitrogen content. The fraction of the fuel nitrogen converted to NO_X 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 because 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.[19] In stoker-fired units, the natural gas burners also improve the ability of the boiler to respond to rapid load changes.[19]

8.2.4 Flue Gas Treatment

Selective Non-Catalytic Reduction

These systems are used to control NO_X emissions from boilers and waste incinerators. A selective non-catalytic reduction (SNCR) system uses either ammonia or urea to react with NO_X in a complex set of high temperature homogeneous gas phase reactions. The product of the reactions between ammonia and urea with NO_X is molecular nitrogen, N_2 and water, H_2O. In both ammonia and urea systems, small quantities of ammonia can remain in the gas stream after the reactions are completed. These emissions are termed "ammonia slip."

The SNCR equipment is both simple and compact. There is a set of high pressure spray nozzles mounted in a high temperature zone of the boiler as shown in Figure 8-15. These nozzles are slightly above the elevation of the upper most row of burners in the boiler. It is important that the ammonia or urea be injected into a portion of the boiler when the combustion gas temperature is in the range of 1600°F to 2000°F. (870°C to 1100°C)

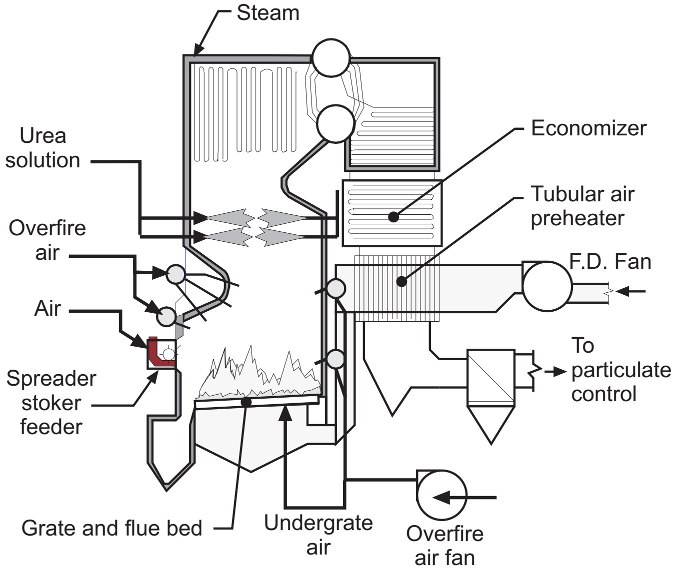

Figure 8-15. SNCR system components

Urea is stored as a liquid and is often diluted immediately prior to use. The flow rates to each of the sets of nozzes are controlled individually to ensure optimum gas-liquid distribution.

Ammonia can be used in either an anhydrous or aqueous form. The aqueous ammonia storage and feeding systems are similar to those used for urea. The ammonia is diluted prior to use, and the flow rate to each set of nozzles is controlled individually. In anhydrous ammonia injection systems, the ammonia is stored in pressurized storage tanks and fed as a gas. The ammonia stream is diluted with air so that the ammonia concentration at the injection point is well below the LEL of ammonia.

In both ammonia and urea injection systems, NO_X reduction effectiveness depends on the adequacy of the gas temperature range at the area of injection. If the gas stream is in the 1600°F to 2000°F temperature range, NO_X reductions of up to 60% are possible. If some of the ammonia or urea reagent is injected in portions of the combustion gas stream that are too cold, high ammonia slip emissions can occur. Injection of reagents in portions of the gas stream that are above 2000°F can result in the oxidation of the nitrogen in the reagents to form additional NO_X.

SNCR system designers use two complete set of nozzles at two different elevations of the boiler to ensure that the reagent can be injected at a point where gas temperatures are optimal. Operators can select the set of nozzles to be used based, in part, on the operating load of the boiler.

When properly designed and operated, SNCR systems are capable of sustained NO_X reductions in the range of 20% to 60%. To minimize reagent costs, SNCR systems are applied after all reasonable combustion modifications have been installed in the boiler to minimize the NO_X formation rates.

Selective Catalytic Reduction Systems

An SCR system uses a catalyst impregnated bed to reduce NO_X emissions. Because of the affect of the catalyst, the chemical reduction reaction between ammonia and NO_X occurs at much lower temperatures than those required for SNCR systems. Most SCR systems operate in the range of 550°F to 750°F (290°C to 400°C). This is a very convenient temperature range because these gas temperatures exist at the exit of the feedwater economizers in the boiler (Figure 8-16). The gas stream can be withdrawn from the boiler at this point, passed through a series of catalyst beds, and returned to the boiler upstream of the air preheater.

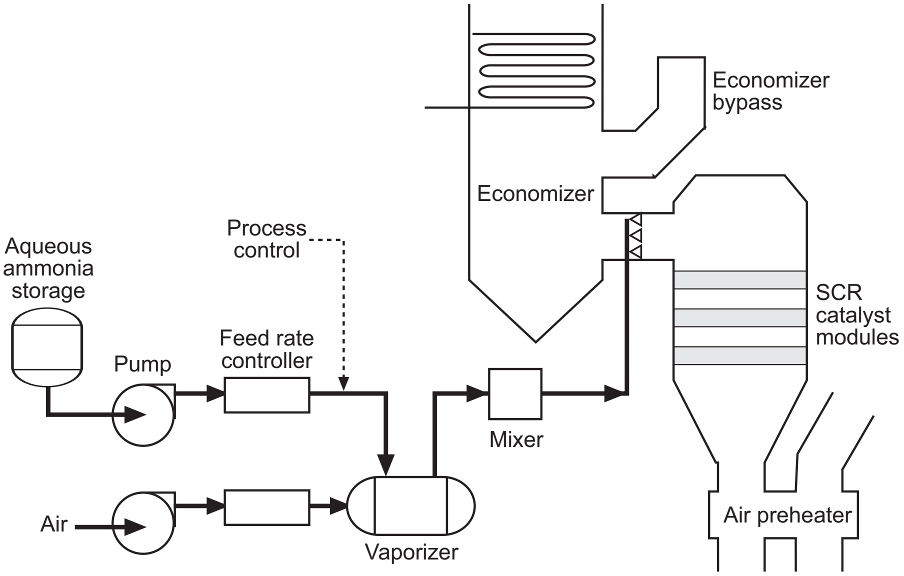

Figure 8-16. Schematic of an SCR system

The catalyst used in SCR systems is an extruded honeycomb with a geometry similar to the types of catalysts used for VOC control (Chapter 6). However, in SCR systems, the catalyst material is distributed throughout the entire catalyst support material rather than simply being deposited on the surface. The catalysts developed for boilers having high particulate matter concentrations have large cells to facilitate particle movement through the cells.

Catalyst modules are often designed with sufficient space for three or more separate catalyst beds in series. Initially two beds can provide the necessary NO_X removal. As the catalyst deteriorates over time, the operator can install the third bed to maintain NO_X destruction efficiencies.

Ammonia is injected into the gas stream upstream of the catalyst bed vessel. A set of injection nozzles is used to ensure that the reagent-gas distribution is optimal. Both anhydrous and aqueous ammonia can be used as the reagent. The storage and supply systems for ammonia in SCR systems are very similar to those used for SNCR systems.

When properly designed and operated, SCR systems are capable of sustained NO_X reductions in the range of 60% to 90%. However, to minimize reagent costs, SCR systems are applied after all reasonable combustion modifications have been installed in the boiler to minimize the NO_X formation rates.

8.3 OPERATING PRINCIPLES OF FLUE GAS TREATMENT SYSTEMS

NO_X can be reduced to molecular nitrogen in add-on systems (i.e., SCR and SNCR) located downstream of the furnace area of the combustion process. There are a number of different process systems for SCR and SNCR control techniques.

In addition to these treatment systems, there are a large number of other processes being developed. These approaches involve innovative techniques for chemically reducing, absorbing, or adsorbing NO_X downstream of the combustion chamber. These are not discussed in this manual because they have not yet reached widespread commercial use.

8.3.1 Selective Non-catalytic Reduction

As described in Section 8.2.4, ammonia or urea is injected into the post-combustion zone of the boiler. The ammonia reacts with NO_X to reduce the oxides to molecular nitrogen and water. There are several commonly used commercial names for these processes. SNCR systems using ammonia are usually termed “Thermal De-NO_X®”,[12] while those using urea are usually termed “NO_XOUT,®”[13] “DeNO_X”, “advanced urea injection” [12] or “Two-Stage DeNO_X®.”

The stoichiometry of the overall reaction processes is shown in Reactions 8-6 and 8-7. The actual set of reactions responsible for the chemical reduction of NO is considerably more complicated than indicated by these summary reactions.

$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$ Reaction 8-6

$2NO + NH_2CONH_2 + 0.5\ O_2 \rightarrow 2N_2 + 2\ H_2O + CO_2$ Reaction 8-7

$4NO_2 + 4NH_3 \rightarrow 4N_2 + 6H_2O + O_2$ Reaction 8-8

$2\ NO_2 + NH_2CONH_2 \rightarrow 2N_2 + 2\ H_2O + CO_2 + 1/2\ O_2$ Reaction 8-9

The reaction processes represented by Reactions 8-6 through 8-9 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] (870°C to 1100°C), as indicated in Figure 8-17. At temperatures above 2,000°F, the ammonia or urea is oxidized to form additional NO_X. At temperatures below 1,600°F, the ammonia passes through the boiler unreacted. The impact of operating below 1,600°F is indicated in Figure 8-18.

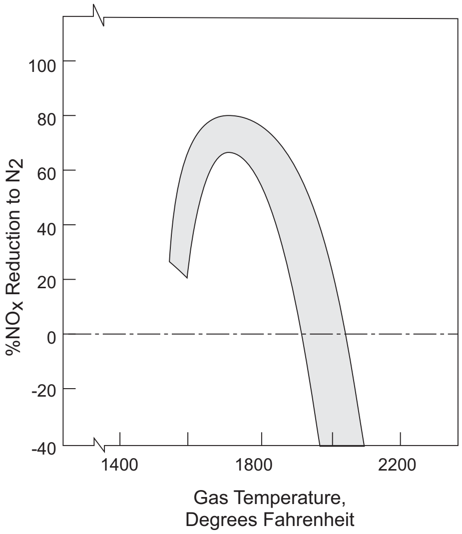

Figure 8-17. Temperature sensitivity of SNCR reactions

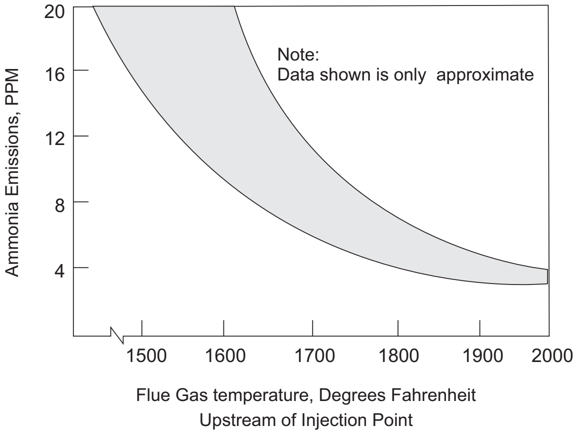

Figure 8-18. Ammonia slip emissions at cold injection temperatures

Ammonia slip concentrations greater than 10 ppm can be objectionable because ammonia 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 four moles of NO (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 a maximum of 0.9:1.0 to minimize ammonia slip. In the case of urea, the stoichiometric ratio is set at approximately 0.5:1.0 because of the ratios of reactants needed for the reaction processes summarized in Reaction 8-7. The typical NO_X reduction efficiencies range from 20% to 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 (Figure 8-17) near the point where the peak efficiency temperature ranging from 1,600°F to 2,000°F occurs. The location of this optimum point varies because of changes in the operating rate of the combustion process and because of fluctuations in the heating value and composition of the wastes being burned. Accordingly, a set of separate injection nozzles as shown in Figure 8-19 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.

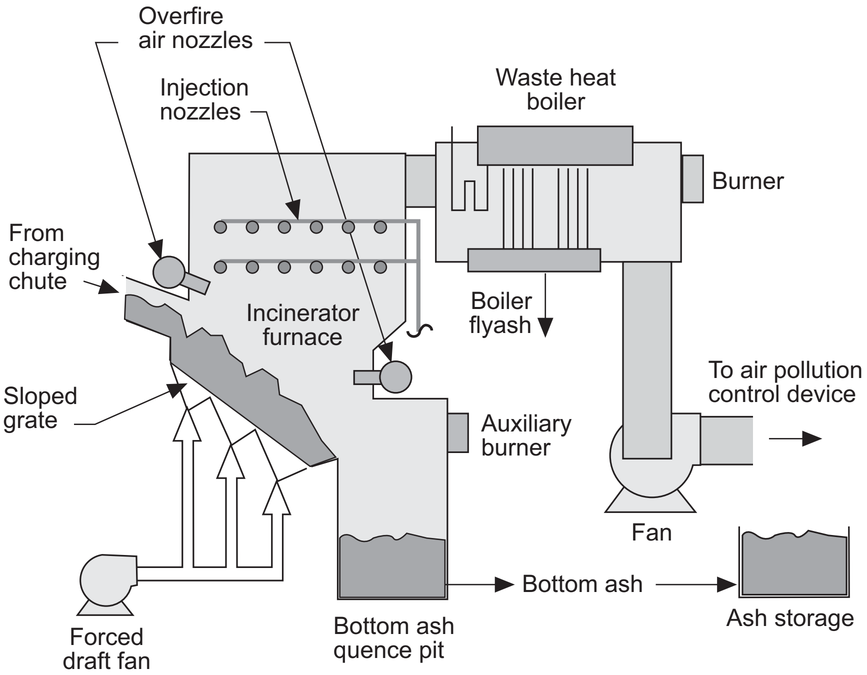

Figure 8-19. Sets of reactant injection nozzles in a boiler

Proper distribution of the reagent(s) is very important for achieving the desired efficiencies.[6] 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 because 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% to 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 $DeNO_X$™ 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 0.7:1.0 and then controls the ammonia slip by methanol injection.[14] Methanol and other oxygenated compounds can extend the effective temperature range for NO_X reduction down to 1,400°F (760°C) [13].

8.3.2 Selective Catalytic Reduction

In an SCR system, the hot exhaust stream from the combustion process is cooled to a temperature range of 550°F to 750°F (290°C to 400°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 ranges from 60% to more than 90%.[6] The outlet NO_X concentrations in some gas turbine systems are less than 4 ppm corrected to 15% oxygen.

The necessary temperature range for the SCR system depends on the type of catalysts. Most of the systems operate in the range of 550°F to 750°F.[15] At temperatures exceeding approximately 670°F (350°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, can be capable of operating at as high as 1,100°F (590°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 because of 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.

$$4\ NO + 4\ NH_3 + O_2 \rightarrow 4\ N_2 + 6\ H_2O \qquad \text{Reaction 8-10}$$

$$2\ NO_2 + 4\ NH_3 + O_2 \rightarrow 3\ N_2 + 6\ H_2O \qquad \text{Reaction 8-11}$$

In some systems, the rate of ammonia feed is controlled according to measurements taken upstream of the SCR bed by a NO_X continuous emission monitor. 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% to 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 ammonia slip in the SCR effluent gas stream. Ammonium bisulfate and ammonium sulfate can form because of 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.

Catalyst beds are usually constructed in a honeycomb type block.[3,16] The beds may be mounted in either a horizontal or vertical position. 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.[3] The catalyst surface can be masked by particulate matter 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%.[17] Typical operating temperatures range from 500°F (260°C) to more than 1,200°F (650°C).[18]

8.4 CAPABILITY AND SIZING OF NO_X CONTROL SYSTEMS

The capabilities of NO_X control systems are highly variable because of the diversity of the combustion sources and to the rapid development of this technology. This section presents an overview of the control efficiencies and emission rates that have been reported on these systems. 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. This section is limited to a basic review of the feed rates of ammonia or urea reagent needed based on the stoichiometry of the overall reactions.

8.4.1 Nitrogen Oxides Emission Reduction Efficiency

Table 8-4 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 8-3. General Range of NO_X Suppression Efficiencies		
Control Technique	**Typical Applications**	**NO_X Reduction Efficiencies, %**
Combustion Modifications		
Low Excess Air	Coal-Fired Boilers, Mun.Waste Incinerators	15-30%[17]
Off-Stoichiometric Combustion	Coal-, Oil-, and Gas-Fired Boilers	15-50%[17]
Flue Gas Recirculation	Coal-, Oil- and Gas-Fired Boilers	15-50%[17]
Low NO_X Burners	Coal-, Oil-, and Gas-Fired Boilers	25-40%[17]
Gas Reburning	Coal-, Oil-, and Gas-Fired Boilers	30-70%[1,17]
Lean Combustors	Gas-Fired Turbines	> 90%
Water/Steam Injection	Gas-Fired Turbines	60-75%
Flue Gas Treatment		
SNCR	Coal-Fired Boilers, Mun.Waste Incinerators	20-60%[4,17]
SCR	Coal-Fired Boilers, Gas Turbines	60-90%[6]
Fuel Switching		
Low Nitrogen Coal	Coal-Fired Boilers	No Data
Co-Firing	Coal-Fired Boilers	No Data

8.4.2 Ammonia or Urea Feed Requirements

The ammonia or urea feed requirements of a nitrogen oxides control system can be estimated based on the stoichiometry of the conversion reactions and the necessary outlet concentration. In the case of ammonia, a stoichiometry of 1.0:1.0 is often used. This means that a mole of ammonia is needed for every mole of NO_X that must be reduced in order to achieve the emission limitation. For urea, the stoichiometry of the conversion reactions is 0.5:1.0. This means that one-half mole of urea is needed for every mole of NO_X that must be reduced. The calculations are illustrated in Problem 8-5.

Problem 8-5

Calculate the ammonia feed rate needed to achieve a 30% reduction in the NO_X rate of an SNCR system. The boiler flue gas flow rate is 100,000 SCFM, and the present NO_X emissions rate is 200 ppm. The NO_X emissions limitation is equivalent to 100 ppm.

Solution:

Step 1. Calculate the pound moles of gas

$$\left(\frac{100{,}000\,\text{scf}}{\text{min}}\right)\left(\frac{\text{lb mole}}{385.4\,\text{scf}}\right) = 259.5 \text{ lb mole gas/min}$$

Step 2. Calculate the pound mole of NO_X at 200 ppm.

$$\left(\frac{0.0002\ \text{lb mole NO}_x}{\text{lb mole gas}}\right)\left(\frac{259.5\ \text{lb mole gas}}{\text{min}}\right) = 0.0519\ \text{lb mole NO}_X/\text{min}$$

Step 3. Calculate the pound moles of NH_3 required.

Pound mole of NO_X reacted = 0.3 (0.0519 lb mole NO_X/min) = 0.016 lb mole NO_X/min

$$\text{Pound mole of ammonia} = \frac{1\ \text{lb mole NH}_3}{1\ \text{lb mole NO}_x} \times 0.016\ \text{lb mole NO}_X/\text{min}$$

Pound mole of ammonia = 0.016 lb mole NH_3/min

Step 4. Determine the amount of NH_3 feed rate.

Ammonia feed rate = 0.016 lb mole NO_X/min (17 lb_m/lb mole NH_3) = 0.26 lb_m/min = 381 lb_m/day

8.4.3 NO_X Continuous Emission Monitoring

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 7E and 19.

The NO_X CEM system should have the capability to compile the following data necessary to confirm proper system operation.

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 Instrumentation

- Inlet sample line temperature
- Condenser temperature
- Sample gas flow rate
- Sample pressure
- Dilution gas flow rate (if applicable)

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.

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.

Sample lines for extractive-type CEM systems must be kept heated from the stack or breeching to the condenser. 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 because the sample gas stream is diluted before moisture can condense.

The condenser liquid bath temperatures should be in the range of 35°F 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 because the instrument is no longer receiving a “dry” sample gas. The presence of water causes a lower-than-actual concentration value.

8.4.4 Carbon Monoxide Continuous Emission Monitors

Carbon monoxide (CO) concentrations can be monitored by CEMs. Non-dispersive infrared (NDIR) type instruments are usually used for CO monitoring. These extract a sample gas stream in a manner similar to that described for NO_X monitors. The installation and design requirements for CO CEMs is also similar to NO_X monitors. The applicable design specification for CO CEMs is in EPA Performance Specification 4.

The use of CO CEMs provides a means to detect high carbon monoxide concentrations caused by combustion upsets and/or overly aggressive attempts to reduce NO_X emissions. CO instruments are useful because they often provide an early warning concerning conditions that could cause increased emissions of partially oxidized organic compounds. The poor combustion conditions that cause CO formation can also contribute to fireside fouling of heat exchange surfaces in the boiler or incinerator.

8.4.5 Oxygen Concentration Monitors

Most combustion systems limit oxygen concentrations in order to avoid localized high concentrations in the peak temperature zones where thermal where thermal and fuel 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 because of the availability of the oxygen in the peak temperature zones.

Oxygen concentrations should be monitored so that the operator can determine if factors such as air infiltration or burner operational problems could be increasing NO_X formation rates. In reviewing these 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 during full load and increase slightly as the load is decreased because of the need for higher excess air rates during 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 might not accurately characterize the variations in the oxygen concentration across the gas stream. Accordingly, to the extent possible, the the entire breeching or duct should be sampled with an oxygen monitor.

8.4.6 Instrumentation

SCR and SNCR Reagent Feed Rates and Injection Conditions. The feed rates of anhydrous ammonia, aqueous ammonia, and aqueous urea 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.

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 monitored and recorded to help operators routinely evaluate the performance of the NO_X control system.

Gas Temperatures. As previously discussed, both the SCR and SNCR systems have limited gas temperature operating ranges. In 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.

Low gas temperatures (<1600°F) at the injection point indicate the potential for high ammonia slip emissions. At high gas temperatures (>2000°F), 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 these 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. Because 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. Static pressures above the normal range may indicate particulate buildup within the catalyst bed.

Gas Turbine Steam or Water Flow Rates. The gas turbine electrical and steam output are monitored on a continuous basis at the system control panel. The steam injection or water rates are usually monitored continuously. Because of 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.

Review Exercises

Introduction to NO_X Control

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 NO_X 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%

.

Review Answers

Introduction to NO_X Control

1. What category of stationary sources has the highest emissions of NO_X in the U.S.?

   a. Utility and industrial boilers

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

3. What is the normal gas temperature leaving the economizer of a pulverized coal-fired boiler?

   d. 500°F to 700°F

4. How many separate burners are generally used in a large pulverized coal-fired boiler?

   d. 10 to 100

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

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

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

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

9. Does the excess air levels increase or decrease as boiler load increases?

   b. Decreases

10. What is the primary objective of fuel gas recirculation systems?

   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.

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.

13. What factors can contribute to ammonia slip in a SNCR system?

    d. All of the above

14. What is the typical ammonia stoichiometry in SCR systems

    b. 0.85 to 0.9 mole of reagent per mole of NO_X

Capability and Sizing of NO_X Control Systems

15. What is the typical NO_X suppression efficiency of Low NO_X burners?

    b. 25% to 40%

16. What is the typical NO_X reduction efficiency of SNCR Systems?

    b. 20% to 60%

17. What is the typical NO_X reduction efficiency of SCR Systems?

    d. 60% to 90%

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Chapter 9
Sulfur Oxides Control

More than 18 million metric tons of sulfur oxides (SO_X) are emitted into the atmosphere each year from man-made sources. Sulfur oxides include sulfur dioxide (SO_2) and sulfuric acid (H_2SO_4). Approximately 98% to 99% of the SO_X emissions are in the form of SO_2. These emissions can cause health problems and contribute to 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.

9.1 TYPES AND COMPONENTS OF SULFUR OXIDES CONTROL SYSTEMS

9.1.1 Sulfur Oxides Formation Mechanisms

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% to 95% of the sulfur compounds are converted to SO_2 in burner flames as indicated in summary Reaction 9-1. Another 0.5% to 2% of the fuel sulfur is converted to sulfur trioxide (SO_3). Once the fuel gas stream is cooled below approximately 600°F (320°C), the SO_3 adds a water molecule to form vapor phase sulfuric acid as indicated in summary Reaction 9-3.

$S + O_2 \rightarrow SO_2$ Reaction 9-1

$S + 1.5\ O_2 \rightarrow SO_3$ Reaction 9-2

$SO_3 + H_2O \rightarrow H_2SO_4$ Reaction 9-3

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. Because of 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.

Problem 9-1

What is the emission rate of sulfur dioxide if 100 tons of coal is being burned per hour, and the fuel sulfur content is 2 % by weight? Assume that 94% of the fuel sulfur reacts by means of Reaction 9-1.

***Solution*:**

Step 1. Calculate the amount of sulfur in the coal.

$$\text{Pounds of fuel sulfur} = \left(\frac{100\text{ tons}}{\text{hour}}\right)\left(\frac{2{,}000\text{ lb}_m}{\text{ton}}\right)\left(\frac{2\text{ lb}_m\text{ S}}{100\text{ lb}_m\text{ coal}}\right)$$

$= 4{,}000\ \text{lb}_m$ S/hour

Step 2. Convert sulfur quantity to pound moles per hour.

$$\text{Pound mole of sulfur per hour} = \left(\frac{4{,}000\ \text{lb}_m\text{ S}}{\text{hr}}\right)\left(\frac{\text{lb mole S}}{32\ \text{lb}_m\text{ S}}\right)$$

= 125 lb mole S/hour

Step 3. Convert sulfur pound mole to SO_2 pound mole.

$$\text{Pound mole S converted to SO}_2 = \left(\frac{125\text{ lb mole S}}{\text{hr}}\right)\left(\frac{0.94\text{ lb S converted}}{\text{lb S total}}\right)\left(\frac{1\text{ lb mole SO}_2}{1\text{ lb mole S}}\right)$$

= 117.5 lb mole SO_2/hour

Step 4. Convert SO_2 pound mole to pound mass.

$$\text{Pound of SO}_2\text{ emitted per hour} = \left(\frac{117.5\text{ lb mole of SO}_2}{\text{hr}}\right)\left(\frac{64\text{ lb}_m\text{ SO}_2}{\text{lb mole SO}_2}\right)$$

$= 7{,}520\ \text{lb}_m$ moles SO_2/hour

As indicated in Figure 9-1, the remaining 3% to 5.5% of the sulfur that is not converted to sulfur dioxide or sulfur trioxide leaves the boiler with the bottom ash. Changes in the boiler oxygen levels and burner characteristics do not significantly influence the fraction of the fuel sulfur leaving with the ash; however, these operational changes may influence the fraction of fuel sulfur converted to sulfur trioxide.

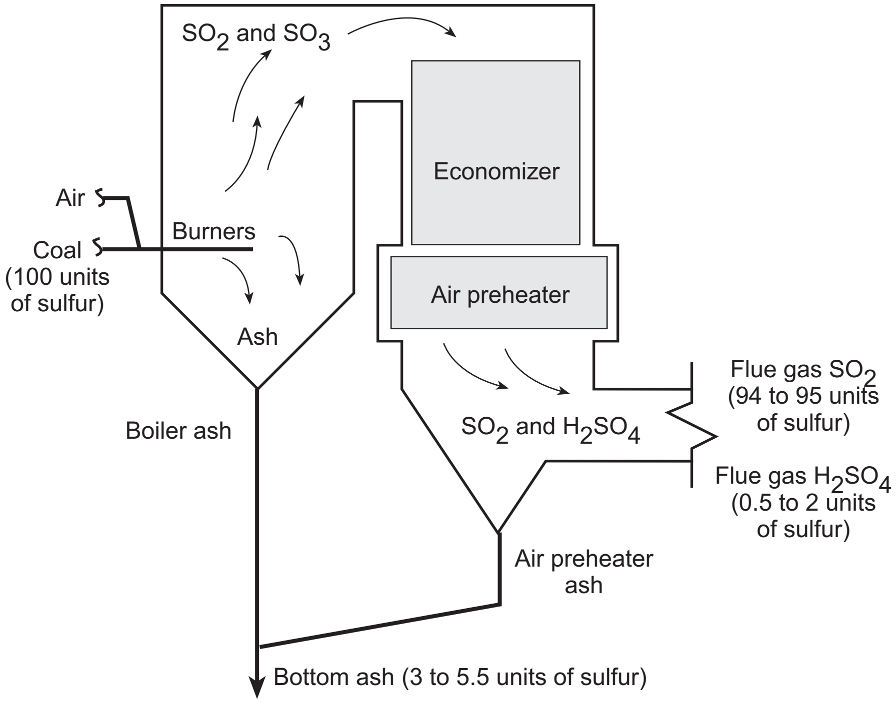

Figure 9-1. Conversion of fuel sulfur

Sulfur dioxide emissions from fossil-fuel-fired combustion sources can be reduced by five techniques.

- Low sulfur fuel firing
- 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.

9.1.2 Low Sulfur Fuel Firing

One of the most straightforward ways to reduce SO_2 emissions from combustion sources is by burning a low sulfur-containing fuel. In 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 (i.e. 1.2 lb_m/10 MMBtu) air pollution regulations. Low sulfur coal usually contains between 0.4% to 1% sulfur; high sulfur coal contains between 1% to 5% sulfur.

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 as illustrated in Problem 9-2.

Problem 9-2

A boiler is converting from a coal supply having a sulfur content of 2.0% by weight and a heating value of 13,500 Btus per pound to a low sulfur coal having a sulfur content of 1.0% and a heating value of 8,500 Btu/pound. Assuming 94% of the fuel sulfur reacts according to Reaction 9-1, what is the percent reduction in sulfur dioxide emissions due to this fuel conversion?

***Solution*:**

Step 1. Calculate the boiler sulfur dioxide emissions for the high sulfur fuel.

As indicated in Problem 9-1, two pounds of sulfur dioxide form for every pound of sulfur escaping the combustion chamber. Choose a boiler firing rate of 100 MM Btu/hr.

$$SO_2\,\text{(lb/hour)} = \left(\frac{2\ lb_m\ S}{100\ lb_m\ coal}\right)\left(\frac{0.94\ lb\ S\ converted}{lb\ \ S\ total}\right)\left(\frac{2\ lb_m\ SO_2}{lb_m\ S}\right)\left(\frac{lb_m\ coal}{13{,}500\ \ Btu}\right)100\ \ x\ 10^6\,Btu/hr$$

$$SO_2\,\text{(lb/hour)} = 279\ lb_m\ SO_2/hour$$

Step 2. Calculate the boiler sulfur dioxide emissions form the low sulfur fuel.

$$SO_2\ \text{(lb/hour)} = \left(\frac{1\,lb_m\ S}{100\,lb_m\ coal}\right)\left(\frac{0.94\,lb\,S\,converted}{lb\,S\,total}\right)\left(\frac{2\ lb_m\ SO_2}{lb_m\ S}\right)\left(\frac{lb_m\ coal}{8{,}500\,Btu}\right)100\,x\,10^6\ Btu/hr$$

$$SO_2\ \text{(lb/hour)} = 221\,lb\,SO_2/hour$$

Step 3. Calculate the percent reduction

$$\text{Reduction} = \left(\frac{279\ -\ 221}{279}\right)100\% = 20.8\%$$

While this example has extreme differences in the fuel quality, it does illustrate the importance of evaluating the fuel's heating value along with the sulfur content. The calculated sulfur dioxide reduction is considerably lower than the 50% reduction that would be estimated based only on the fuel sulfur content.

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 sometimes 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 have low fuel sulfur levels.

9.1.3 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_X. Regenerated products include elemental sulfur, sulfuric acid, or gypsum.

Dry scrubbing processes use a dry or wet 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. Estimated Use of 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 (Salable Product)		
Magnesium Oxide	1.4%	1.0%
Wellman Lord	3.1%	2.1%
Lime/Limestone	4.0%	4.7%

* This includes systems that use alkaline flyash for part of the alkali feed reuirement.

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 is expected to increase in the future due to the Title IV requirements in the CAAA of 1990. Sodium carbonate scrubbing is used primarily for industrial boilers due to its 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). Slaking is the addition of water to convert calcium oxide to calcium hydroxide. Calcium hydroxide is added at a 1.0:1 to 1.1:1 stoichiometric ratio to SO_2. 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 ($CaSO_3$) and calcium sulfate ($CaSO_4$) salts are formed in the reaction and are removed as solids. The solids generated can be stabilized to produce an inert landfill material or can be stored indefinitely as sludge in ponds. A simplified flowchart of a lime scrubbing system is shown in Figure 9-2.

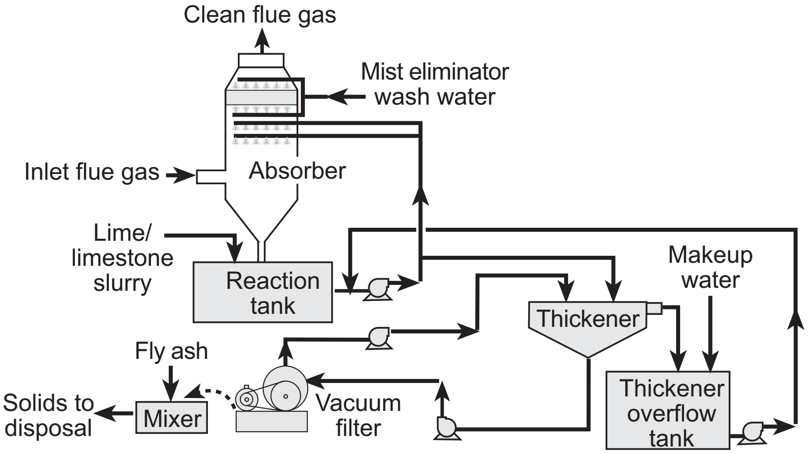

Figure 9-2. Simplified flowchart of a lime scrubbing system

The equipment components necessary for a lime scrubbing system can be divided into four separate groups.

1. **Scrubbing or absorption:** scrubbers, holding tanks, liquid spray nozzles, and pumps
2. **Lime handling and slurry preparation:** lime unloading and storage equipment, lime processing, and slurry preparation equipment
3. **Sludge processing:** sludge clarifiers for dewatering, sludge pumps and handling equipment, and sludge solidifying equipment
4. **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.

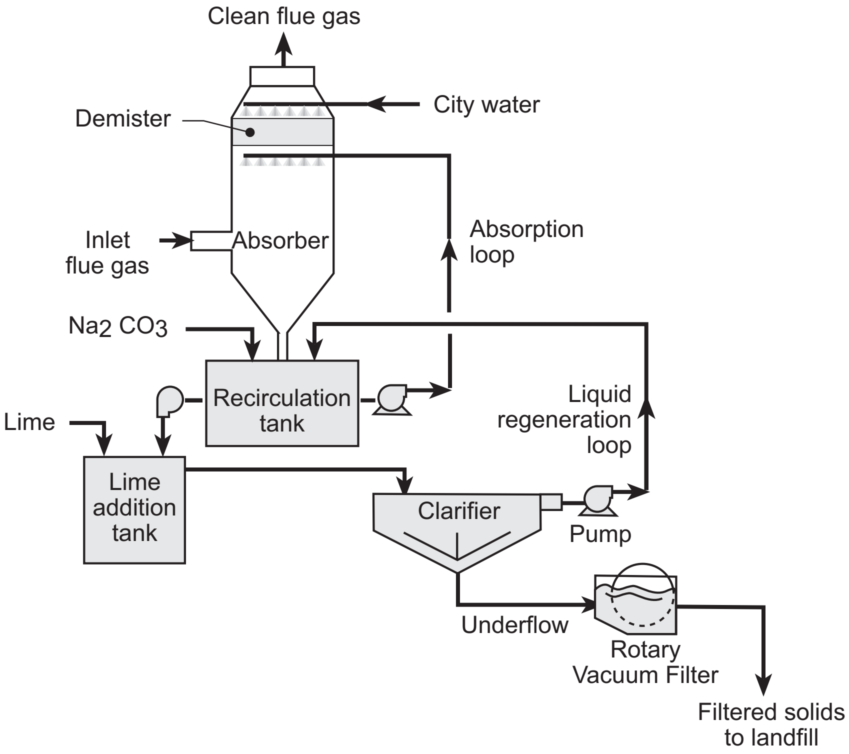

Figure 9-3. Dual alkali scrubber system

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% to 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. Calcium sulfite and calcium sulfate are formed and removed in a rotary vacuum filter.

Most dual alkali systems have a particulate matter control device upstream of the main scrubber vessel. This is needed to remove calcium and magnesium containing flyash particles that could create chemical scaling conditions in the main scrubbing loop.

Sodium Carbonate Scrubbing. These systems are similar to dual alkali scrubbers with respect to the use of highly soluble sodium compounds for reacting with dissolved sulfite and sulfate compounds. In these systems, sodium carbonate or sodium hydroxide (NaOH) is added to the liquid recirculation tank at a rate controlled by the liquid pH and the dissolved solids content. The dissolved solids levels can be between 15% and 30% by weight and can be considered to be electrolytes rather than aqueous streams. A portion of the recirculation stream is sent to a pond or wastewater treatment facility to minimize flyash levels and sulfate concentrations in the liquid.

Because of the simplicity of these systems, they require very little plant area. Process control is also relatively easy because the system is not very vulnerable to solids precipitation due to upsets in the liquid chemistry. However, the cost of the sodium based reagents is higher than the cost of calcium based materials such as lime or limestone. There can also be problems associated with the high sodium content purge liquid.

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. Because of 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.

Magnesium Oxide Process. Magnesium oxide (MgO) slurry absorbs SO_2 and forms magnesium sulfite ($MgSO_3$). Magnesium sulfite solids are separated from the scrubbing liquor in a centrifuge and dried to remove moisture. The mixture is calcined to regenerate magnesium oxide and produce concentrated SO_2 gas for production of sulfuric acid or elemental sulfur. Prior to entering the absorber, particulate matter is removed from boiler exhaust by a precipitator or wet scrubber. A simplified flowchart of a process is shown in Figure 9-4.

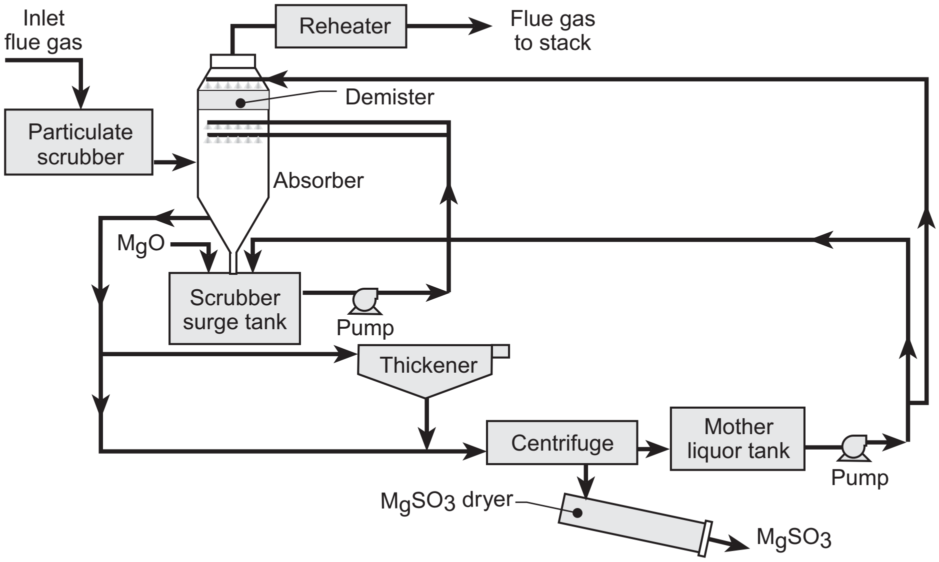

Figure 9-4. Simplified flowchart of the magnesium oxide process

Wellman-Lord. 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 matter control device is used upstream of the absorber vessel to minimize problems associated with particulate matter in the scrubber liquid.

Citrate Process. The citrate process uses sodium citrate and citric acid as buffering agents to attain a higher solubility of the SO_2 in an aqueous absorbent solution. The absorption of SO_2 is pH dependent, increasing with higher pH (more alkaline). SO_2 forms H_2SO_3 when absorbed by water, resulting in decreasing pH levels. This creates a more acidic condition that inhibits additional absorption of SO_2 gas. Higher amounts of SO_2 can be absorbed by using a buffering agent to prevent a pH drop.

Particulate matter is removed from the flue gas by an electrostatic precipitator. Chlorides and sulfuric acid mist are removed from the flue gas by a small venturi scrubber before entering the packed tower.

SO_2 is absorbed by a solution of sodium citrate, citric acid, and sodium thiosulfate to produce sodium sulfite. SO_2 removal efficiency is approximately 90%.[2] The solution (containing absorbed SO_2) is reacted with hydrogen sulfide gas (H_2S) in a closed vessel to precipitate elemental sulfur and regenerate citrate solution. The elemental sulfur precipitate is concentrated by air flotation into a sulfur slurry that is separated from the regenerated solution. The sulfur slurry is heated to form liquid sulfur, and the solution is decanted. Hydrogen sulfide gas (used in regeneration) is either obtained as a byproduct of petroleum refining or produced on-site by reacting recovered sulfur with natural gas and steam.

The citrate process is expensive compared to lime and limestone scrubbing. Because the size of the absorption, regeneration, and floatation equipment is large, retrofitting the system into an existing boiler facility is difficult. These disadvantages have limited the application of citrate processes for sulfur dioxide control.

9.1.4 Dry Scrubbing

Dry scrubbing is basically a two step chemical process. (1) The flue gas leaving the boiler or incinerator is contacted with a stream of alkali, usually calcium hydroxide. (2) The reaction products are collected in a high efficiency particulate matter 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 9-5. 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.

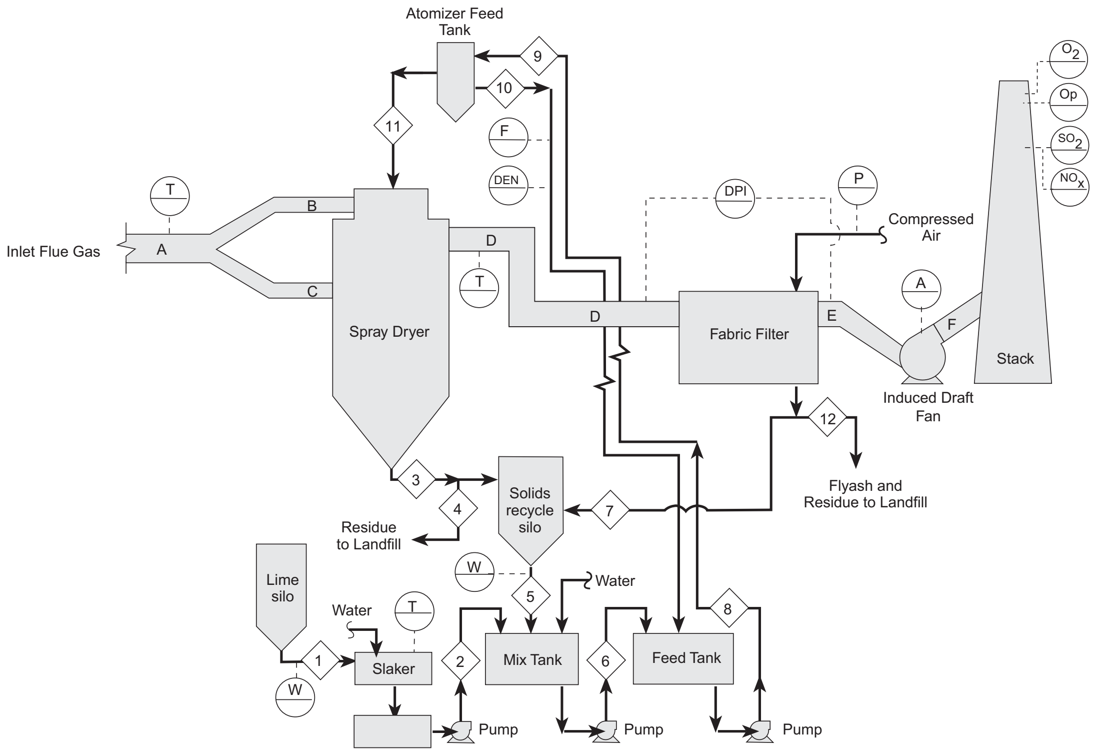

Figure 9-5. Simplified flowchart of a spray dryer-type dry scrubber

In other commercial systems, all of the gas stream enters from the top. In this type of dry scrubber, the alkali reagent is prepared as a slurry containing 5% to 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: (1) rotary atomizers and (2) compressed air assisted atomizing nozzles. The rotary atomizers operate at 10,000 rpm 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 micrometers. 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. The plants maintain a spare in the event of maintenance problems.

Compressed air nozzles operate at air pressures of 60 psig 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 because of 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. Nozzle atomizers do not have the slurry feed rate turndown capability of the rotary units.

Alkaline material generally used in spray dryer absorbers is pebble lime. This material must be slaked in order to prepare a reactive slurry. 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 because of the precipitation of contaminants in the slaking water.

Recycle of the solids collected in particulate matter control device is used in some systems. Locations of the possible recycle streams are shown in Figure 9-5. Recycle maximizes the utilization of the alkali and thereby reduces operating costs.

Dry Injection Units

Dry injection systems are also referred to as *dry injection-type scrubber* and *injection-type dry scrubber*. This type of dry scrubber uses finely divided calcium hydroxide for the adsorption of acid gases. The reagent feed has particle sizes that pass through 325 mesh with 90% efficiency,[6] which is approximately the consistency of talcum powder. The alkali particle size distribution is important because removal efficiency is related to the amount of surface area available.

The calcium hydroxide feed rate for dry injection systems is 3 to 4 times the stoichiometric quantities.[6,7] This is much higher than the requirements for the spray dryer-type absorber 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 9-6. It consists of a calcium hydroxide feed system, a gas-to-gas heat exchanger, a solids recycle contactor, and a fabric filter.

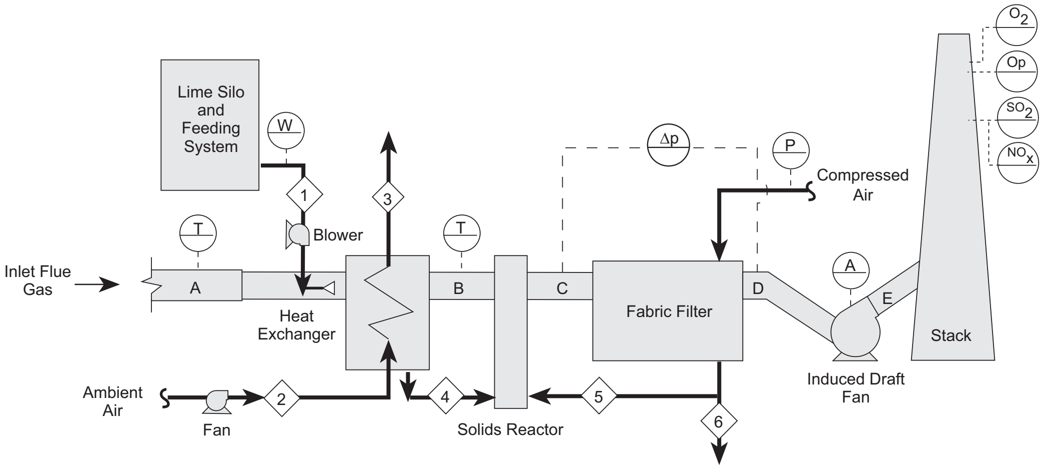

Figure 9-6. Dry injection dry scrubber flowchart

The calcium hydroxide from the storage hopper is fed volumetrically 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 (200°C to 260°C) range down to 250°F (120°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 9-7. 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.

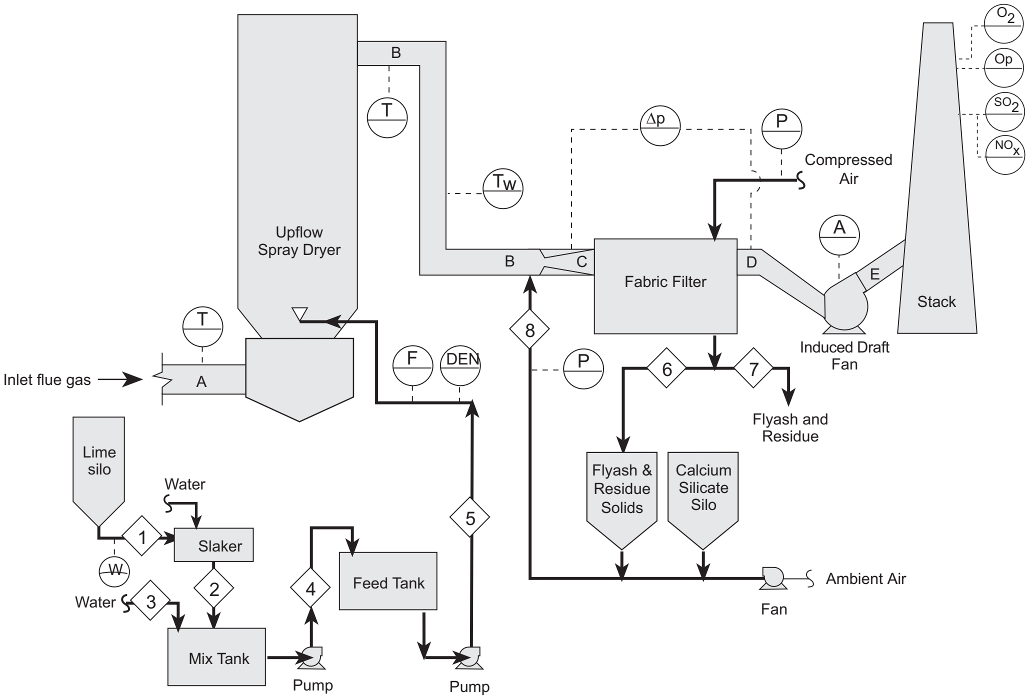

Figure 9-7. Flowchart of a dry scrubber using both a spray absorber vessel and a dry injection recycle stream

9.1.5 Fluidized Bed Combustion

A fluidized bed boiler using 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 because of 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.

9.1.6 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 gas with a low, medium, or high heating value by applying heat and pressure or by using a catalyst to break down the components of the coal.[1] The gas produced contains carbon monoxide, molecular hydrogen, carbon dioxide, water, methane, and contaminants such as hydrogen sulfide and char. Low and medium Btu gas contains more CO and H_2 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. (1) using a gasifier to convert coal to carbon monoxide, hydrogen, and methane. This is followed by condensation to convert the gases to oils. (2) Using 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 and (2) chemical. 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 uses 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% to 90% of the pyrite sulfur content can be removed by physical coal cleaning.[1] 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 H_2S gas. 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 $CaSO_3$ 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. When this mixture is heated to 500°F (260°C) in a pressurized vessel, most of the pyritic sulfur and 20% to 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.

9.2 OPERATING PRINCIPLES

9.2.1 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 because of 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.

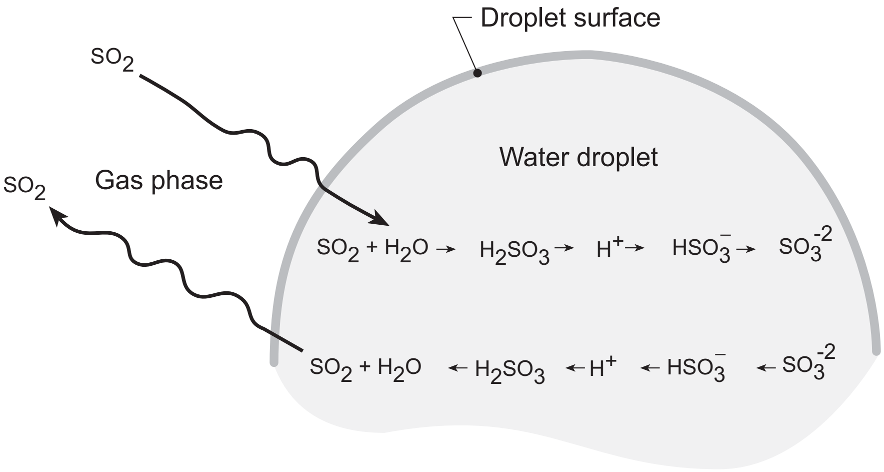

Figure 9-8. Absorption of SO_2 into water

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.

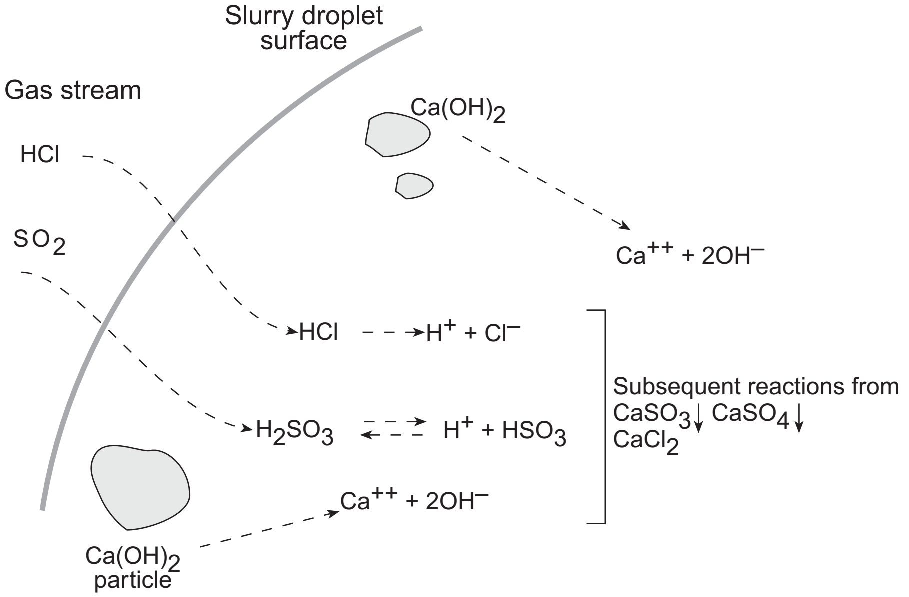

Figure 9-9. Absorption of SO_2 in an alkaline slurry

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 ACF 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 temperature of the scrubbing liquid also affects the absorption process; 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 (120°C to 200°C), and at a moisture content of 6% to 10% by volume. At these conditions, the scrubber operating temperatures are usually in the range of 120°F to 140°F (50°C to 60°C). Higher temperatures would reduce the initial absorption step and cause water losses because of 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^{-2}) and sulfate (SO_4^{-2}) ions as indicated in Reactions 9-4 to 9-8.

Absorption Reactions

$SO_2(g) \rightarrow SO_2(l)$ Reaction 9-4

$SO_2(l) + H_2O \rightarrow H_2SO_3(l)$ Reaction 9-5

$H_2SO_3(l) \rightarrow HSO_3^{-1}(l) + H^+$ Reaction 9-6

$HSO_3^{-1}(l) \rightarrow SO_3^{-2}(l) + H^+(l)$ Reaction 9-7

$SO_3^{-2}(l) + 0.5\ O_2 \rightarrow SO_4^{-2}(l)$ Reaction 9-8

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

$CaCO_3(s) \rightarrow CaCO_3(l)$ Reaction 9-9
$CaCO_3(l) \rightarrow Ca^{+2} + CO_3^{-2}$ Reaction 9-10
$CO_3^{-2} + H^+ \rightarrow HCO_3^{-1}$ Reaction 9-11
$SO_3^{-2} + H^+ \rightarrow HSO_3^{-1}$ Reaction 9-12
$SO_3^{-2} + 0.5\ O_2(l) \rightarrow SO_4^{-2}$ Reaction 9-13
$Ca^{+2} + SO_3^{-2} + 0.5\ H_2O \rightarrow CaSO_3 \cdot \frac{1}{2}H_2O(s)$ Reaction 9-14
$Ca^{+2} + SO_4^{-2} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O(s)$ Reaction 9-15

Lime is slaked with water (Reaction 9-16) to produce a slurry of calcium hydroxide. 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

$CaO(s) + H_2O \rightarrow Ca(OH)_2\ (l)$ Reaction 9-16
$Ca(OH)_2(l) \rightarrow Ca^{+2} + 2\ OH^{-1}$ Reaction 9-17
$OH^{-1} + H^+ \rightarrow H_2O$ Reaction 9-18
$SO_3^{-2} + H^+ \rightarrow HSO_3^{-1}$ Reaction 9-19
$Ca^{+2} + SO_3^{-2} + 0.5\ H_2O \rightarrow CaSO_3 \cdot \frac{1}{2}H_2O(s)$ Reaction 9-20
$Ca^{+2} + SO_4^{-2} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O(s)$ Reaction 9-21

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 because lime used in FGD systems is not a pure chemical and because contact between the liquid and gas streams is not ideal. Actual stoichiometric ratios vary from 1.1 to 2:1.

Some FGD systems use 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. It is usually not desirable to have a mixture with significant quantities of both calcium sulfite and calcium sulfate.

9.2.2. Dual Alkali Scrubbing

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_2. 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 Reactions

$2NaCO_3 + SO_2 + H_2O \rightarrow Na_2SO_3 + 2NaHCO_3$ Reaction 9-22

$NaHCO_3 + SO_2 \rightarrow NaHSO_3 + CO_2(g)$ Reaction 9-23

$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$ Reaction 9-24

$Na_2SO_3 + SO_2 + H_2O \rightarrow 2\ NaHSO_3$ Reaction 9-25

$2NaOH + SO_3 \rightarrow Na_2SO_4 + H_2O$ Reaction 9-26

$Na_2SO_3 + 0.5\ O_2 \rightarrow Na_2SO_4$ Reaction 9-27

Regeneration Loop Reactions

$2NaHSO_3(l) + Ca(OH)_2 \rightarrow Na_2SO_3 + CaSO_3 \bullet 2H_2O(s)$ Reaction 9-28

$Na_2SO_4 + Ca(OH)_2 \rightarrow 2NaOH + CaSO_4$ Reaction 9-29

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.

9.2.3 Magnesium Oxide Scrubbing

Magnesium oxide slurry is sprayed and absorbs SO_2 according to Reactions 9-30 to 9-33.

$Mg(OH)_2 + 5\ H_2O + SO_2 \rightarrow MgSO_3 \bullet 6H_2O$ Reaction 9-30

$MgSO_3 \bullet 6H_2O + SO_2 \rightarrow Mg(HSO_3)_2 + 5H_2O$ Reaction 9-31

$Mg(HSO_3)_2 + MgO \rightarrow 2MgSO_3 + H_2O$ Reaction 9-32

$2MgSO_3 + O_2 + 7H_2O \rightarrow 2MgSO_4 \bullet 7H_2O$ Reaction 9-33

The aqueous slurry used for scrubbing contains the hydrated crystals of MgO, $MgSO_3$ and $MgSO_4$. A continuous side stream of this recycled slurry is sent to a centrifuge where partial dewatering produces a moist cake. The liquid removed from the crystals is returned to the main slurry stream. The moist cake is dried at 305°F to 450°F (152°C to 232°C) in a direct contact or rotary bed dryer. The dried cake is then sent to a calciner where coke is burned at very high temperatures, 1,250°F to 1,350°F (680°C to 730°C) to regenerate magnesium oxide crystals according to the following reactions.

Cake dryer

$MgSO_3 \bullet 6H_2O \longrightarrow MgSO_3 + 6H_2O$ Reaction 9-34

$MgSO_4 \bullet 7H_2O \longrightarrow MgSO_4 + 7H_2O$ Reaction 9-35

MgO Regeneration in Calciner

$MgSO_3 \longrightarrow MgO + SO_2$ Reaction 9-36

$C + \frac{1}{2}O_2 \longrightarrow CO$ Reaction 9-37

$CO + MgSO_4 \longrightarrow CO_2 + MgO + SO_2$ Reaction 9-38

9.2.4 Wellman-Lord

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 6-31 for the magnesium oxide process.

$SO_2 + Na_2SO_3 + H_2O \rightarrow 2NaHSO_3$ Reaction 9-39

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 because of Reaction 9-30 by adding sodium carbonate to the scrubbing liquid. This reacts with sodium bisulfite as shown in Reaction 9-41.

$Na_2SO_3 + \frac{1}{2}O_2 \rightarrow Na_2SO_4$ Reaction 9-40

$Na_2CO_3 + 2NaHSO_3 \rightarrow 2Na_2SO_3 + CO_2 + H_2O$ Reaction 9-41

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.

$2NaHSO_3 \rightarrow Na_2SO_3 + H_2O + SO_2$ Reaction 9-42

9.2.5 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 because of physical 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 extent gas temperature and the moisture dewpoint of the gas stream leaving the spray dryer vessel. In 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[8] because of 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 because of 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 9-10, 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.

$Ca(OH)_2 + 2\ HCl \rightarrow CaCl_2 + 2\ H_2O$ Reaction 9-43

$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O$ Reaction 9-44

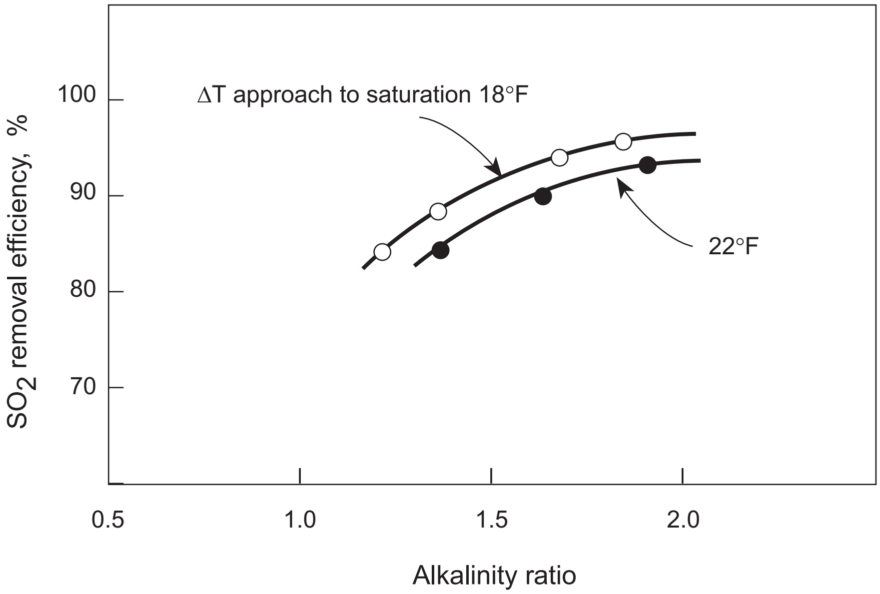

Figure 9-10. Effect of alkali stoichiometric ratio on removal efficiency

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 9-10 for spray dryer-type systems. This is because of the absence of the absorption mass transfer mechanism when operating with a dry powder rather than an evaporating slurry droplet.

9.3 SULFUR OXIDES CONTROL SYSTEMS CAPABILITY AND SIZING

9.3.1 Sulfur Dioxide Removal Efficiency

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 because of the general similarity of fossil-fuel-fired boilers and waste incinerators with respect to sulfur dioxide control. Pilot scale tests are rarely performed because of 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. These data are 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 matter 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 waste water treatment equipment

Essentially all of the information included in this list can be determined for both new and existing sources. In 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 matter 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 estimating the necessary recirculation liquid flow rates and alkali feed rates.

The empirical data from previously installed control systems similar to the proposed control system are 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 generally not performed because of 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 necessary to design a small scale absorber vessel or dry scrubbing vessel with the same mass transfer characteristics of the full scale units. Disposal of the sludge or solids generated during the pilot test could 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, these 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 because of shifts in the concentrations of important species in the recirculation liquid. 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.

9.3.2 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.

9.3.3 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 9-47, 9-48, and 9-49.

$SO_2 + Ca(OH)_2 + 0.5\ O_2 \rightarrow (CaSO_4)_s + H_2O$ Reaction 9-47

$2HCl + Ca(OH)_2 \rightarrow 2Ca^+ + 2\ Cl^- + 2H_2O$ Reaction 9-48

$2HF + Ca(OH)_2 \rightarrow 2Ca^+ + 2\ F^- + 2H_2O$ Reaction 9-49

Problem 9-3

Calculate the amount of calcium hydroxide (slaked 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 removal efficiency of 98%.

***Solution*:**

Step 1. Calculate the quantity of HCl absorbed in the srubbing liquid.

$$\mathrm{HCl} = 10{,}000\,\mathrm{SCFM}\left(\frac{\mathrm{lb\ mole}}{385.4\,\mathrm{SCF}}\right)\left(\frac{0.00005\,\mathrm{lb\ mole\ HCl}}{\mathrm{lb\ mole\ total}}\right)\left(\frac{95\%\ \mathrm{efficiency}}{100\%}\right)$$

HCl = 0.00123 lb mole HCl/minute

Step 2. Calculate the amount of $Ca(OH)_2$ required.

$$\mathrm{Ca(OH)_2\ req'd} = \left(\frac{1\,\mathrm{lb\ mole\ Ca(OH)_2}}{2\,\mathrm{lb\ mole\ HCl}}\right)\left(\frac{0.0024\,\mathrm{lb\ mole\ HCI}}{\mathrm{min}}\right) = \left(\frac{74\,\mathrm{lb_m\ Ca(OH)_2}}{\mathrm{lb\ mole\ Ca(OH)_2}}\right)$$

$Ca(OH)_2$ req = 0.0456 lb_m $Ca(OH)_2$/min = 2.74 lbm $Ca(OH)_2$/hr

The alkali feed system should be designed to provide sufficient alkali during times of peak acidic 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 severe pH excursions to values less than approximately 5. At these levels, the rate of corrosion begins to accelerate, especially in the presence of chlorides and fluorides.

9.3.4 SO_2Continuous Emission Monitoring

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 (Section 5.1.10). 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, CO_2, 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_2O, 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.

$$SO_2 + \eta \underset{210\,\text{nm}}{hv} \rightarrow \underset{\substack{\text{excited}\\ \text{molecule}}}{SO_2^*} \rightarrow SO_2 + \underset{240\text{-}410\,\text{nm}}{hv'} \qquad \text{Reaction 9-45}$$

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.

$$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$$

Reaction 9-46

$$E^0_{298} = 0.17\ V$$

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.

$$S = \frac{\delta^2}{4}\left[-cl\frac{d^2\alpha}{d\lambda^2}I\right] \qquad (9\text{-}1)$$

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.

9.3.5 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 and calibrate the pH monitors on a daily basis. Redundant pH monitors are usually installed to minimize the operational problems caused by the failure or drift of a single instrument.

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 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 (120°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 because 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.

Review Exercises

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. Based on the data provided, what is the approximate reduction in SO_2 emissions if a plant switches from Fuel A to Fuel B?

Type SO_2 Emission	**Fuel A**	**Fuel B**
Ash Content	15%	21%
Volatile Content	30%	39%
Sulfur Content	1.5%	0.75%
Moisture Content	6%	17%
Heating Value	11,500 Btu/lb	8,100 Btu/lb

4. 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%

5. 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

6. 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

7. 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

8. 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

Review Answers

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
   d. 6,016 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?

   b. No

3. Based on the data provided, what is the approximate reduction in SO_2 emissions if a plant switches from Fuel A to Fuel B?

Type SO_2 Emission	Fuel A	Fuel B
Ash Content	15%	21%
Volatile Content	30%	39%
Sulfur Content	1.5%	0.75%
Moisture Content	6%	17%
Heating Value	11,500 Btu/lb	8,100 Btu/lb

Solution

Step 1. Calculate the boiler sulfur dioxide emissions for the high sulfur fuel. Choose a boiler firing rate of 100 x 10^6 Btu/hour as the boiler firing rate.

$$SO_2\,(\text{lb}_m/\text{hr}) = \left(\frac{1.5\ \text{lb}_m\ \text{S}}{100\ \text{lb}_m\ \text{coal}}\right)\left(\frac{0.94\ \text{lb}_m\ \text{S converted}}{\text{lb}_m\ \text{S total}}\right)\left(\frac{2\ \text{lb}_m\ SO_2}{\text{lb}_m\ \text{S}}\right)\left(\frac{\text{lb}_m\ \text{coal}}{11{,}500\ \text{Btu}}\right)100\ \text{x}\ 10^6\ \text{Btu/hr}$$

$$SO_2\,(\text{lb}_m/\text{hr}) = 245\ \text{lb}_m\ SO_2/\text{hr}$$

As indicated in Problem 9-1, two pounds of sulfur dioxide form for every pound of sulfur escaping the combustion chamber.

Also, the above calculation assumes that 94% of the sulfur in the fuel forms sulfur dioxide.

Step 2. Calculate the boiler sulfur dioxide emissions for the low sulfur fuel

$$SO_2\,(\text{lb/hr}) = \left(\frac{0.75\ \text{lb}_m\ \text{S}}{100\ \text{lb}_m\ \text{coal}}\right)\left(\frac{0.94\ \text{lb}_m\ \text{S converted}}{\text{lb}_m\ \text{S total}}\right)\left(\frac{2\ \text{lb}_m\ SO_2}{\text{lb}_m\ \text{S}}\right)\left(\frac{\text{lb}_m\ \text{coal}}{8{,}100\ \text{Btu}}\right)100\ \text{x}\ 10^6\ \text{Btu/hr}$$

$$SO_2\ (\text{lb}_m/\text{hr}) = 174\ \text{lb}_m\ SO_2/\text{hr}$$

Step 3. Calculate the percent reduction.

$$\text{Reduction} = \left(\frac{245-174}{245}\right)100\% = 29\%$$

4. What fraction of the sulfur entering with coal is usually converted into SO_2?

   e. 94% to 95%

5. What combustion modification techniques can be used to minimize the formation of sulfur dioxide in a coal-fired boiler?

   d. None of the above

Sulfur Oxides Control System Operating Principles

6. What is the normal pH range for the recirculation liquid in a lime- or limestone-type wet scrubbing system?

   c. 5.5 to 8

7. What is the normal stoichiometric ratio between the sulfur dioxide and the calcium hydroxide in lime scrubbers?

   b. 1.0:1 to 1.1:1

8. What is the normal stoichiometric ratio between the sulfur dioxide and the calcium hydroxide in a injection type dry scrubbers?

   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?

   c. > 90%

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

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)
    c. Nondispersive ultraviolet (NDUV)
    d. Fluoresence

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