**CHAPTER 1** 

#### CONTROL OF GASEOUS EMISSIONS



#### APTI COURSE 415

#### **COURSE INTRODUCTION**

#### **CONTROL OF GASEOUS EMISSIONS**



#### WELCOME

This course introduces general instruction for the control of gaseous emissions.

- Course Topics Covered
  - 10 topics introduce the benefits and risks of controlling or not controlling gaseous emissions.
- Course Completion Requirements
  - Chapter Assessments

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#### **CHAPTER 1**

#### **CONTROL OF GASEOUS EMISSIONS**



#### INTRODUCTION

#### This lesson introduces gaseous contaminants.

- Primary contaminants
  - Emitted directly from the stack and/or process equipment
- Secondary Contaminants
  - Formed due to reactions between primary pollutants in the atmosphere or between a primary pollutant and naturally occurring compounds in the atmosphere



### **LEARNING OBJECTIVES**

At the end of this training, you will be able to:

- Identify primary and secondary gaseous contaminants.
- Recognize regulations that govern gaseous contaminants.
- Identify the environmental impacts of gaseous contaminants.

## EXAMPLES OF PRIMARY GASEOUS CONTAMINANTS

- Primary Gaseous Contaminants
  - Sulfur dioxide and sulfuric acid vapor
  - Nitric 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 reduced sulfur compounds (mercaptans, sulfides)
  - Ammonia

# EXAMPLES OF SECONDARY GASEOUS CONTAMINANTS

- Secondary Gaseous Contaminants
  - Nitrogen dioxide (NO<sub>2</sub>)
  - Ozone (O<sub>3</sub>) and other photochemical oxidants
  - Sulfuric acid  $(H_2SO_4)$

### **SULFUR DIOXIDE**

This topic introduces the following important information:

- Sulfur dioxide is a colorless gas
  - Formed during the combustion of sulfur containing fuel
  - Coal
  - No. 6 oil
  - Sulfur containing industrial waste gases
- Reacts with clouds and fog to yield sulfuric acid, inorganic sulfate compounds, and organic sulfate compounds

### SULFURIC ACID VAPOR

This topic introduces the following important information:

- During the combustion of sulfur containing fuels, approximately 95% of the sulfur is converted to sulfur dioxide, while .5% to 2% is converted to sulfur trioxide
- At temperatures below 600°F (300°C), sulfur trioxide reacts with water to form sulfuric acid

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

### **NITRIC OXIDE AND NITROGEN DIOXIDE**

- Collectively referred to as NO<sub>x</sub>
- NO<sub>x</sub> formation is the result of:
  - Thermal fixation of atmospheric  $N_2$ (thermal  $NO_x$ )
  - Oxidation of organic nitrogen compounds in the fuel (fuel NO<sub>x</sub>)
  - Reaction with partially oxidized compounds within the flame (prompt NO<sub>x</sub>)
- Nitric Oxide (NO) –odorless gas that is insoluble in water
- Nitrogen Dioxide (NO<sub>2</sub>) –moderately soluble in water, has a distinct reddish-brown color

### **CARBON MONOXIDE**

- Carbon Monoxide (CO)
  - Results from the incomplete combustion of fuel and other organic compounds
  - Difficult to oxidize
    - Requires temperatures of >1800°F (1000°C)
- Chemical asphyxiant
- Colorless, odorless and insoluble in water

# OTHER PARTIALLY OXIDIZED ORGANIC COMPOUNDS(POCS)

- Partially Oxidized Organic Compounds refer to a broad range of species formed during the combustion process:
  - Polyaromatic compounds
  - Unsaturated compounds
  - Aldehydes
  - Organic acids

### **VOLATILE ORGANIC COMPOUNDS (VOCS)**

- VOCs are organic compounds that can volatilize and participate in photochemical reactions upon release to the atmosphere
- Most organic compounds are classified as VOCs
- Dominant source is the vaporization of organic compounds used as solvents in industrial processes
- Categorized as
  - Contained
  - Fugitive



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# TABLE 1-1. ORGANIC COMPOUNDS NOTCLASSIFIED AS VOCS

#### (DUE TO LACK OF PHOTOCHEMICAL REACTIVITY)

- 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)
- 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 Siloxanes (VMS)
- Acetone

### HAZARDOUS AIR POLLUTANTS (HAPS)

#### **VOC Emissions**

 Dominant Source of VOC emissions is the vaporization of organic compounds used as industrial solvents.

#### Hazardous Air Pollutants (HAPs)

- Approximately 200 specific organic compounds have known adverse health effects.
- They are regulated and classified as HAPs (Section 112(b) of the Clean Air Act.
- Subject to Maximum Achievable Control Technology (MACT) standards

### TABLE 1-2. ORGANIC HAP COMPOUNDS

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

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# HYDROGEN CHLORIDE AND HYDROGEN FLUORIDE

- Inorganic acid gases that are released from processes such as
  - Waste incinerators
  - Fossil fuel-fired boilers
  - Chemical reactors
  - Ore roasting operations
- Emitted from combustion processes burning chloride and fluoride organic compound and a variety of mineral ore processing operations

 Essentially 100% of the chlorine and fluorine in the fuel is released as HCl and HF

# HYDROGEN SULFIDE AND TOTAL REDUCED SULFUR COMPOUNDS

- Hydrogen Sulfide, H<sub>2</sub>S: emitted from metallurgical, petroleum, and petrochemical processes and from sour natural gas wells; strong rotten egg odor
- Total Reduced Sulfur compounds (TRSs): emitted primarily from Kraft pulp mills
  - Methyl Mercaptan, CH<sub>3</sub>SH
  - Dimethyl Sulfide, (CH<sub>3</sub>)2S
  - Dimethyl Disulfide,  $(CH_3)_2S_2$

# OZONE AND OTHER PHOTOCHEMICAL OXIDANTS

- Ozone forms in the troposphere because of photochemical reactions with NO<sub>x</sub>, VOCs, and CO
- Ozone control is based on the control of precursor compounds
- Reducing ground level ozone concentrations does NOT have an adverse effect on ozone levels in the stratosphere

### FIGURE 1-1. POLLUTANT CONCENTRATION PROFILES



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### MERCURY

- Methylmercury (CH<sub>3</sub>Hg<sup>+</sup>) is of most concern
  - Formed from other forms of mercury by microbial action in sediments and soils
  - Bioaccumulates in the aquatic food chain
- Anthropogenic mercury enters the atmosphere through the combustion of coal and other fossil fuels

#### **OTHER SOURCES OF MERCURY EMISSIONS**

- Certain chlor-alkali chlorine manufacturing processes
- Mining operations
- Metal refining
- Products that contain elemental mercury
  - Batteries
  - Lamps
  - Thermometers

### **MERCURY REDUCTION EFFORTS**

- Focused on large point source emissions from chloralkali facilities and combustion sources including
  - Power plants
  - Industrial boilers
  - Hazardous waste and medical incinerators
- Between 1990 and 1999, mercury emissions were reduced by half

# GREENHOUSE GASES AND EMISSION SOURCES

- Carbon Dioxide (CO<sub>2</sub>)
  - Combustion of fossil fuels, solid waste, and trees and other wood products
- Methane (CH<sub>4</sub>)
  - Production and transportation of fossil fuels, livestock and other agricultural activities, and organic waste decay
- Nitrous Oxide (N<sub>2</sub>O)
  - Combustion of fossil fuels
- Fluorinated Gases
  - Industrial processes

### **GLOBAL WARMING POTENTIAL**

- The impact of greenhouse gases is measured by the Global Warming Potential (GWP)
- GWP is based on the impact and average atmospheric lifetime of greenhouse gases

Gas	Atmospheric Lifetime (Years)	100-Year GWP	
Carbon Dioxide*	50-200	1	
Methane	12±3	21	
Nitrous oxide	120	310	
Fluorinated gases as a group	1.5-209	140-11,700	

\*Used as a reference point

## EMISSION RATES AND SOURCES OF GASEOUS CONTAMINANTS

The gaseous pollutants emphasized in this course include:

- Sulfur Dioxide (SO<sub>2</sub>)
- Nitrogen Oxides (NO<sub>x</sub>)
- Organic compounds (including VOCs).

### FIGURE 1-2. SO<sub>2</sub>, NO<sub>X</sub>, AND VOC EMISSIONS HISTORY



Reduction: 1970 to 2007 SO<sub>2</sub> 59%, NO<sub>x</sub>37%, VOC 47%

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### FIGURE 1-3. ESTIMATED GREENHOUSE GAS EMISSIONS



15% increase from 1990 to 2006

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### **EMISSION SOURCE CATEGORIES: SO<sub>2</sub>**

Table 1-4. SO<sub>2</sub> emissions by source category, 1970 and 2008.

Source Category	1970		2008	
	Thousands of Short Tons	Percent of Total	Thousands of Short Tons	Percent of Total
Fuel combustion, electric utilities	17,398	56	7552	66
Fuel combustion, industrial	4568	15	1670	14
Fuel combustion, other	1490	5	578	5

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### **EMISSION SOURCE CATEGORIES: SO<sub>2</sub>**

Table 1-4. SO<sub>2</sub> emissions by source category, 1970 and 2008.

Source Category	1970		2008	
	Thousands	Percent of	Thousands of	Percent of
	of Short	Total	Short Tons	Total
	Tons			
Chemical and allied	591	2	255	2
products				
Metals processing	4775	15	203	2
Petroleum and	881	3	206	2
related industries				
Other industrial	846	3	329	3
processes				
Highway vehicles	273	1	64	1
Off-highway	278	1	456	4
vehicles				
Other	118	0	116	1
Total	31,218	101	11,429	100

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### **EMISSION SOURCE CATEGORIES: NO<sub>2</sub>**

Table 1-5. NO<sub>x</sub> emissions by source category, 1970 and 2008.

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

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### **EMISSION SOURCE CATEGORIES: VOC**

Table 1-6. VOC emissions by	y source category, 1970 and 2008.
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Source Category	ory 1970		2008	
	Thousands of Short Tons	Percent of Total	Thousands of Short Tons	Percent of Total
Fuel combustion, electric utilities	30	0	50	0
Fuel combustion, industrial	150	0	130	1
Fuel combustion, other	541	2	1269	8
Chemicals manufacture	1341	4	228	1

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### **EMISSION SOURCE CATEGORIES: VOC**

#### Table 1-6. VOC emissions by source category, 1970 and 2008.

Source Category	1970		2008	
	Thousands of	Percent of	Thousands of	Percent of
	Short Tons	Total	Short Tons	Total
Petroleum industry	1194	3	561	4
Solvent utilization	7174	21	4226	27
Storage and transport	1954	6	1303	8
Waste disposal &	1984	6	374	2
recycling				
Highway vehicles	16,910	47	3418	21
Off-highway vehicles	1616	5	2586	16
Other	1765	5	1782	11
Total	34,659	99	15,927	99

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### **MERCURY EMISSIONS**

- In 1990, municipal solid waste incinerators, coal-fired electric utility boilers, and medical waste incinerators each contributed 25% of the total mercury emissions
- Largely eliminated from municipal waste and medical waste incinerators by 1999
- By 1999 coal-fired utility boilers contributed about 40% of the total estimated emissions of 115 short tons

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### **POLLUTION CONTROL**

- This section introduces pollution control regulations and standards:
  - National Ambient Air Quality Standards
  - New Source Performance Standards
  - National Emission Standards for Hazardous Air Pollutants
## **GASEOUS CONTAMINANT REGULATIONS**

- From 1950 through 1970, gaseous pollutant control regulations were enacted by state and local agencies for contaminants such as SO<sub>2</sub>, VOCs, and HF
- The environmental awareness that began to increase during the 1950s and 1960s culminated in the enactment of the Clean Air Act of 1970 (CAA)
- The CAA of 1970 introduced
  - National Ambient Air Quality Standards (NAAQS)
  - New Source Performance Standards (NSPS)

## NATIONAL AMBIENT AIR QUALITY STANDARDS (NAAQS)

- Apply to sulfur dioxide, nitrogen oxides, photochemical oxidants, and carbon monoxide
- Primary standards are more restrictive and are designed to protect human health
- Secondary standards are intended to reduce adverse material effects, such as crop damage and building soiling
- Individual states are responsible for developing control strategies (SIP) to satisfy the NAAQS

## NEW SOURCE PERFORMANCE STANDARDS (NSPS)

- Individual states implement control strategies for NAAQS, as part of State Implementation Plans (SIP)
- Nationwide application that apply to all new and substantially modified sources
- Sources subject to these regulation are required to install air pollution control systems that represent the "best demonstrated technology" for the category

## NATIONAL EMISSION STANDARDS FOR HAZARDOUS AIR POLLUTANTS (NESHAPS)

- Applies to toxic or hazardous chemicals
- Regulations developed for 188 specific compounds and classes of compounds
- Sources subject to NESHAPs must limit emission levels to be consistent with Maximum Achievable Control Technology (MACT)
  - MACT requirements based on best performing source technology

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## **NEW SOURCE REVIEW (NSR)**

- New sources or major modification to existing sources are required to undergo review before receiving a pre-construction permit
- If NAAQS are satisfied
  - Permit is based on Prevention of Significant
     Deterioration (PSD) requirements
- If NAAQS are not satisfied
  - New emissions must be offset with emission reductions from other sources and to satisfy Lowest Achievable Emissions Rate (LAER)

# TABLE 1-7. NSPS FOR FOSSIL FUEL-FIREDELECTRIC POWER GENERATING FACILITIES

Table 1-7. New source performance standards for fossil fuel-fired electric powergenerating facilities						
Category	Fuel Type	Emission Limit	Reduction			
			Requirement			
Particulate	Solid	0.015 lb <sub>m</sub> /10 <sup>6</sup> Btu <sup>A</sup>	99.9%			
Matter						
SO <sub>2</sub>	Liquid	1.4 lb <sub>m</sub> /MWh	95%			
SO <sub>2</sub>	Coal Refuse	1.4 lb <sub>m</sub> /MWh	94%			
		<0.6 lb <sub>m</sub> /10 <sup>6</sup> Btu	70%			
NO <sub>x</sub>	Solid	0.5 lb <sub>m</sub> /10 <sup>6</sup> Btu	65%			
NO <sub>X</sub>	Liquid	0.3 lb <sub>m</sub> /10 <sup>6</sup> Btu	30%			
NO <sub>x</sub>	Gas	0.2 lb <sub>m</sub> /10 <sup>6</sup> Btu	20%			
NO <sub>x</sub>		1.0 lb <sub>m</sub> /MWh				
NO <sub>x</sub>	Liquid Backup Fuel <sup>B</sup>	1.5 lb <sub>m</sub> /MWh				
A: The owner/operator of a facility with a PM Continuous Emission Monitoring System						

(CEMS) may elect to comply with an alternate  $0.14 \text{ lb}_{m}$ /MWh standard.



## TABLE 1-8. NAAQS

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



## FIGURE 1-4. POPULATION LIVING IN COUNTIES WITH AIR QUALITY CONCENTRATIONS ABOUT NAAQS LEVELS (2007)



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#### **SUMMARY**

- This lesson provided an overview of the following:
- Differences between primary and secondary gaseous pollutants.
- Emission rates and sources of gaseous pollutants.
- Air quality regulations pertaining to gaseous emissions.

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## SUMMARY (CONTINUED)

- Gaseous contaminants continue to be regulated as individual categories of sources.
- However, it is important to recognize that many categories of gaseous contaminants interact in the atmosphere to generate other gaseous pollutants and to form particulate matter.
- Accordingly, their environmental impact must be evaluated collectively.

CHAPTER 2 CONTROL TECHNIQUES FOR GASEOUS CONTAMINANTS



## APTI COURSE 415

#### **CHAPTER 2**

## CONTROL TECHNIQUES FOR GASEOUS CONTAMINANTS





This lesson introduces gas stream characteristics:

Characteristics of gas streams that affect the selection and design of gaseous control



## **LEARNING OBJECTIVES**

At the end of this training, you will be able to:

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

#### **IMPORTANT GAS STREAM PROPERTIES**

- The selection and design of a gaseous contaminant control system relies on specific information about the gas stream including
  - Flow rate
  - Temperature
  - Pressure
  - Contaminant concentration
  - Contaminant ignition characteristics
  - Oxygen concentration

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## **GAS STREAM PROPERTIES**

- Information concerning the gas flow rate, temperature, and pressure are needed to physically size the collector
- Most control devices operate efficiently over a relatively narrow temperature range
- Knowledge of minimum, average, and maximum flow rate, temperature, and pressure is valuable, but frequently not available
- Particulate matter can have a severe impact on the efficiency and reliability of the collector



## **EXPLOSION LIMITS**

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

## **EXPLOSIVE LIMIT CONCENTRATIONS**

- Lower Explosive Limit (LEL)
  - Contaminant concentrations below the LEL means there is insufficient contaminant for an explosion
- Upper Explosive Limit (UEL)
  - Contaminant concentrations above the UEL means there is insufficient oxygen for the oxidation of the compounds present
- Normally operate at no more than 25% of LEL



## TABLE 2-1. LEL AND UEL AT ROOM TEMPERATURE AND AMBIENT OXYGEN CONCENTRATION

	Lower Explosive	Upper Explosive	
Compound	Limit, % by	Limit, % by	
	Volume	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	

Continued...



## TABLE 2-1. LEL AND UEL AT ROOM TEMPERATURE AND AMBIENT OXYGEN CONCENTRATION (CONTINUED)

Compound	Lower Explosive Limit, % by Volume <sup>1</sup>	Upper Explosive Limit, % by Volume <sup>1</sup>
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

Source: National Institute for Occupational Safety and Health (June 1997) 1. Convert percent by volume to ppm by multiplying 10,000 (e.g., 2% = 20,000 ppm)



### **ADDITIONAL LEL AND UEL CONSIDERATIONS**

- A gas stream having contaminants with a large explosive range requires extreme caution in control system design and operation
- Additional LEL and UEL concentrations for specific compounds can be found in Material Data Safety Sheets or other references

## ESTIMATING LEL AND UEL: THE JONES METHOD

(Eq. 2-1)  
(Eq. 2-2)  

$$C_m H_x O_y + ZO_2 \rightarrow mCO_2 + \frac{x}{2} H_2 O$$
  
 $LEL, \% = \frac{0.55 (100)}{(4.76m + 1.19x + 1 - 2.38y)}$ 

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

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(Eq. 2-3)

## **LEL OF MIXTURES**

- Laboratory measurement using mixture composition of interest.
- Estimation of mixture LEL (two methods)
  - Assume that LEL of all contaminants equal to lowest LEL of any single contaminant –most conservative approach
  - Use Le Chatelier equations based on weighted average of LEL of each component

#### 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?

Note: Base your answer on the compound having the lowest LEL.



## **PROBLEM 2-1: SOLUTION**

LEL Limits from Table 2-1:

- Acetone, LEL = 25,000 ppm
- Benzene, LEL = 12,000 ppm
- Toluene, LEL = 11,000 ppm
- <u>The lowest LEL limit is 11,000 (toluene)</u>.
   25% of 11,000 ppm = **2,750 ppm**
- <u>Total contaminant concentration</u> = 1,000 ppm + 2,000 ppm + 500 ppm = **3,500 ppm**
- Answer: No. Total concentration exceeds 25% LEL value.



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#### **LECHATELIER EQUATIONS**

LEL<sub>mixture</sub>, % = 
$$\frac{100}{\sum(y_i/LEL_i)}$$
 Eq. 2-4

UEL<sub>mixture</sub>, % = 
$$\frac{100}{\sum(y_i/UEL_i)}$$
 Eq. 2-5

## y<sub>i</sub> = concentration of component i on a combustible-only basis

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#### PROBLEM 2-2

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

LeChatelier Equation 2-4 Eq. 2-4 LEL<sub>mixture</sub>,  $\% = \frac{100}{\sum(y_i/\text{LEL}_i)}$ 



#### **PROBLEM 2-2: SOLUTION**

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



LEL <sub>mixture</sub> = 
$$\frac{1}{11.43 + 47.62 + 12.99} = 0.014 = 14000$$
 ppm

25% of the LEL = 0.25 (14000) = 3500 ppm

Using this approach the gas mixture concentration is just equal to 25% of the LEL Air Pollution Training Institute | APTI

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## **SOURCES OF IGNITION**

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

## PROBLEMS IN MONITORING LEL CONCENTRATIONS

- Oxygen levels are less than 10%.
- 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.

## POTENTIALLY EXPLOSIVE MATERIALS NOT MONITORED BY LEL METERS

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

## GASEOUS CONTAMINANT CONTROL TECHNOLOGIES

This section introduces:

- The six major technologies used to control gaseous contaminants
- The uses and limitations of these gaseous control technologies.

## **TYPES OF CONTROL TECHNIQUES**

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

#### **Absorption**

- Involves the transfer of contaminant from the gas to a liquid phase
- Two types
  - Simple dissolution
  - Irreversible chemical reaction
- Used for removal of acid gas compounds and water soluble organic compounds
- Biological oxidation involves a surface that contains viable microorganisms



## HENRY'S LAW: EQUATION 2-6

- y\* = Hx
- y\* = Mole fraction of contaminant in gas phase in equilibrium with liquid
- H = Henry's Law constant
- x = Mole fraction of contaminant in liquid phase

### **APPLICABILITY OF ABSORBERS**

- Simple dissolution
  - Limited by the solubility of contaminant in solvent
- Irreversible chemical reactions
  - Limited by the ability to capture and retain the contaminant in solution for a long enough time
- Biological oxidation systems
  - Compatibility of the contaminants with the microorganisms
## IMPORTANT FACTORS AFFECTING ABSORPTION

- Concentration dependence
- Gas temperature dependence
- Multiple contaminant removal
- Particulate matter limitations



#### **ADSORPTION**

- Involves the transfer of contaminant from the gas to the surface of a solid adsorbent
- Two types:
  - <u>Physical</u>: weakly held to the adsorbent surface by intermolecular cohesion, normally reversible, used for organic compounds
  - <u>Chemical</u>: involves a chemical reaction which is not easily reversed, used for mercury vapors and acid gases

#### **APPLICABILITY OF ADSORPTION PROCESSES**

- Molecular weights between 50 and 200
- Other considerations
  - Boiling point
  - Empirical adsorption correlation coefficients (Yaws)
- Chemical adsorption may provide high efficiency control of a variety of acid gases

## IMPORTANT FACTORS AFFECTING ADSORPTION

- Concentration dependence
- Temperature dependence
- Multiple contaminant limitations
- Particulate matter limitations



#### OXIDATION

- Destruction of contaminant
- Three categories
  - Thermal oxidizers
  - Catalytic oxidizers
  - Flares
- Thermal and catalytic oxidizers are used for sources such as surface coaters, gasoline storage and distribution terminals, and organic chemical plants
- Flares are primarily used to treat emergency vent gases in organic chemical plants and petroleum refineries



#### **APPLICABILITY OF OXIDIZERS**

- Applicable to essentially all organic compounds.
- Thermal oxidation
  - Extremely high operating temperature
  - Supplemental energy required
- Catalytic oxidation
  - Lower operating temperature
  - Concern with catalyst poisoning
  - Consult with catalyst suppliers and catalytic oxidizer manufacturers
  - Flares
    - Used as emergency controls for a wide variety of organic compounds
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#### **FACTORS AFFECTING OXIDATION SYSTEMS**

- Concentration dependence
  - High efficiency destruction of a variety of organic compounds without concern of the inlet concentrations
- Gas temperature dependence
  - Gas stream is preheated before it reaches the system and supplemental energy often required to achieve temperature
- Multiple contaminant capability
  - Capable of treating a large number of compounds
- Particulate matter limitations

#### **CHEMICAL REDUCTION SYSTEMS**

- Used primarily for the destruction of NO<sub>x</sub> compounds emitted from combustion processes
- Includes
  - Selective Noncatalytic Reduction (SNCR)
  - Selective Catalytic Reduction (SCR)
- For both systems, a chemically reduced form of nitrogen, ammonia, or urea is injected into the gas stream
- SCR processes operate at 550 °F to 750 °F while SNCR processes operate at 1600 °F to 2000°F

#### **APPLICABILITY OF REDUCTION SYSTEMS**

#### SNCR

- Needs sufficient space to install injection nozzles
- Injection must occur where combustion gases are in the required temperature range (1600 °F to 2000 °F)
- NO $_{\rm x}$  destruction efficiencies in the range of 20% to 60%

#### **APPLICABILITY OF REDUCTION SYSTEMS**

SCR

- Injection must occur where combustion gases are in the required temperature range (550 °F to 750 °F)
- Needs sufficient space for the moderately large reaction vessel
- High particulate matter levels can create problems in gas flow through the catalyst bed or with masking of the catalyst surfaces
- $NO_x$  destruction efficiencies in the range of 60% to >90%

#### **FACTORS AFFECTING REDUCTION SYSTEMS**

- Concentration dependence
  - Highest efficiencies for NO<sub>x</sub> levels between 100 and 1000 ppm
- Gas temperature dependence
  - SNCR and SCR processes operate in narrow temperature ranges
- Multiple contaminant capability
  - Effective for the reduction of NO and NO<sub>2</sub>
- Particulate matter limitations
  - NSCR systems not normally sensitive to particulates
  - SCR systems subject to flow alterations and masking
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#### **CONDENSATION SYSTEMS**

- Conversion of contaminant(s) from gas to liquid phase
- Used exclusively for the recovery of organic compounds present at moderate-to-high concentrations
- Three categories
  - Water-based direct and indirect condensers (40°F to 80°F); Most Common
  - Refrigeration condensers (-50°F to -150°F)
  - Cryogenic condensers (-100°F to -320°F)



#### **APPLICABILITY OF CONDENSATION SYSTEMS**

 Determined by the concentration and vapor pressure of the contaminant(s) being controlled



## FACTORS AFFECTING CONDENSATION SYSTEMS

- Concentration dependence
  - Generally limited to high concentrations of high value organic contaminants
- Gas temperature dependence
  - Operates at low temperatures
- Multiple contaminant capability
  - May be used for simultaneous removal of multiple organic compounds
  - Separation and recovery of pure components may be difficult and expensive
- Particulate matter limitations
  - Reduction in heat transfer effectiveness may require particulate matter removal prior to the condenser

#### **SUMMARY OF CONTROL TECHNIQUES**

- A number of potentially explosive gases and vapors are collected in gaseous contaminant control systems
- The explosive range of such gases is bounded by the lower explosive limit (LEL) and the upper explosive limit (UEL)
- To control gaseous contaminants there are six major control techniques...

Continued . . .

## TABLE 2-2: SUMMARY OF CONTROL TECHNIQUES

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

Continued . . .

## TABLE 2-2: SUMMARY OF CONTROL TECHNIQUES (CONTINUED)

Table 2-2. Summary of the General Applicability of Gaseous Contaminant Techniques					
Control Technique	General Applicability	Typical Concentration Range	Typical Gas Temperature Range	Applicable for Control of Multiple Contaminants?	Applicable for Control of Gas Streams with Particulate Matter?
Oxidation	Organic Compounds	< 1 ppm to 25% of LEL <sup>a</sup>	600°F to 2000°F <sup>d</sup>	Yes	Pretreatment Often Required
Reduction	NO and NO <sub>2</sub>	< 100 ppm to 1,000 ppmª	550°F to 2000°F <sup>e</sup>	Yes <sup>i</sup>	Yes
Condensation	Organic Compounds	> 100 ppmª	-320°F to 80°F <sup>f</sup>	Yes <sup>g,h</sup>	Pretreatment Often Required

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#### **CHAPTER SUMMARY**

This chapter covered the following topics:

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

CHAPTER 3 AIR POLLUTION CONTROL SYSTEMS

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#### **CHAPTER 3**

#### **AIR POLLUTION CONTROL SYSTEMS**



#### **EVALUATING THE INDUSTRIAL PROCESS**

- Changes in the process equipment can have a major impact on control device efficiency
- Changes in the air pollution control device can affect the ability of the process hoods to capture 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 efficiency of the air pollution control equipment and the release of fugitive emissions from the process equipment

#### **FLOWCHARTS**

- This section introduces:
  - The basics of a system flowchart



#### FIGURE 3-1. MATERIAL STREAM SYMBOLS



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#### TABLE 3-1 CODES FOR UTILITY STREAMS

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

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#### FIGURE 3-3. IDENTIFICATION OF EMISSION POINTS





Stack

Major equipment

Fan

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#### FIGURE 3-3. IDENTIFICATION OF EMISSION POINTS



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#### FIGURE 3-4. MINOR COMPONENT SYMBOLS



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#### FIGURE 3-5. INSTRUMENT SYMBOLS



Direct reading instrument Panel mounted instrument Panel mounted instrument with continuous recorder

# TABLE 3-4. MATERIALS OFCONSTRUCTION SYMBOLS

CS	Carbon steel
SS	Stainless steel
FRP	Fiberglass reinforced plastic
RL	Rubber lined
N	Nickel alloy
WD	Wood

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#### **BASIC FLOWCHARTING TECHNIQUES**

- Flowcharts for air pollution control studies should be relatively simple
  - Shouldn't be so cluttered that it is difficult to include present system operating conditions
  - Small enough to be carried easily while walking around the facility

#### FIGURE 3-6. EXAMPLE FLOWCHART OF A WASTE SOLVENT SYSTEM



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#### 

#### FIGURE 3-7. EXAMPLE FLOWCHART OF AN ASPHALT PLANT





#### PROBLEM 3-1

- A regulatory agency is conducting an inspection of a soil remediation unit at a hazardous waste site
- The site is an abandoned chemical plant where several nonvolatile carcinogens are present in old lagoons
- The plant uses a rotary kiln for destruction of the carcinogens and two side-by-side pulse jet fabric filter units for control of particulate matter generated in the kiln

#### PROBLEM 3-1 (CONTINUED)

- Determine the following:
  - Is the operating data for the system consistent and logical?
  - Do any important discrepancies exist between the current and baseline data?
  - What areas of the facility should be emphasized during the inspection?
  - What health and safety issues should be considered during the inspection?

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#### FIGURE 3-8. EXAMPLE FLOWCHART FOR PROBLEM 3-1



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# TABLE 3-5. BASELINE DATA FOR THEHAZARDOUS 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

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#### PROBLEM 3-1: SOLUTION PART A

- There should be logical trends in:
- Gas temperature: Should be maximum leaving the kiln and decrease throughout the system.
- Gas static pressures: Should be minimum entering the fan and increase to just below atmospheric leaving the kiln.
- Gas oxygen concentrations (combustion sources)
- Other parameters along the direction of gas flow

# FIGURE 3-9. STATIC PRESSURE AND TEMPERATURE PROFILE



General trends in both static pressure and temperature appear to be logical.

**SEDA**

## PROBLEM 3-1: SOLUTION PART B

Compare the present and the site specific baseline data to the extent possible

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		

<u>Possible problem</u>: Large differences in temperatures at the evaporative cooler inlet and across the baghouse. <u>Possible cause</u>: Air inleakage in duct B and/or in the baghouse or malfunctioning temperature gauges. Inleakage could adversely affect kiln operation and baghouse particulate collection.



Continued...

## PROBLEM 3-1: SOLUTION PART B

Table 3-7. Gas static pressure profile for the hazardous waste incinerator (in. W.C.)				
	Present	Baseline		
Kiln hood	-0.1	-0.1		
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		

<u>Possible problem</u>:  $\Delta P$  between evaporative cooler inlet and baghouse outlet considerably lower now than baseline. <u>Possible cause:</u> Air inleakage due to torn or worn bags or holes in baghouse housing. But be aware that  $\Delta P$  in a baghouse changes with time. Torn bags would decrease particulate collection efficiency.

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Continued...

## PROBLEM 3-1: SOLUTION PART C

- Determine the areas that should be emphasized during equipment performance evaluation
  - Check for air infiltration in Duct B
  - Check for fugitive emissions from rotary kiln
  - Investigate the reason for the temperature drop across the pulse jet baghouses
  - Check for air inleakage across the pulse jet baghouse

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Continued...

# FIGURE 3-10. EXAMPLE FLOWCHART FOR PROBLEM 3-2



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# TABLE 3-8. STATIC PRESSURES AND STATICPRESSURE DROPS (IN. W.C.)

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

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### TABLE 3-9. GAS TEMPERATURES (°F)

	Present	Baseline
Incinerator secondary chamber	1860	1835
Duct B	200	197
Fan inlet	143	142
Stack	148	147

All temperatures are in close agreement.

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#### **PROBLEM 3-2: SOLUTION**

Part A

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Since static pressures are close, it is reasonable to suspect a malfunctioning  $\Delta P$  gauge.

Continued...

#### **PROBLEM 3-2: SOLUTION**

#### Part B

No reason to suspect fugitive emissions at the emergency bypass stack. Pressures both upstream and downstream of the bypass stack are negative so air inleakage is possible, but not leakage of fugitive emissions.



Continued...

#### Hoods

- This section introduces:
  - The variables that contribute to hood efficiency



#### Hoods

- In processes that are open to the surroundings, pollutants are prevented from escaping by the use of a hood
- Hoods are an integral part of the process equipment
- Pollutants not captured by a hood are considered fugitive emissions
  - Because of this, evaluation of the operation of a hood is important

# FIGURE 3-13. ROLE OF HOODS IN AN INDUSTRIAL PROCESS



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### PROBLEM 3-3

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

# EQUATIONS 3-1 AND 3-2: FUGITIVE AND STACK EMISSIONS

Emissions Fugitive emissions = Process emissions – captured by hood

Emissions Stack emissions = captured  $\times \frac{100\% - \eta}{100\%}$ 

> Where:  $\eta =$ Collection efficiency (%)

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#### **PROBLEM 3-3: SOLUTION**

1. Calculate fugitive emissions.EmissionsFugitive emissions = Process emissions -captured<br/>by hood

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

# 2. Calculate stack emissions. Emissions Stack emissions = captured $\times \frac{100\% - \eta}{100\%}$

$$= (95\,\text{lb}_{\rm m}/\text{hr})\frac{100\% - 95\%}{100\%}$$

$$= 4.75 \ lb_{\rm m}/hr$$

#### **PROBLEM 3-3: SOLUTION**

#### 3. Calculate total emissions

Total emissions = Hood emissions + Stack emissions =  $5 \text{ lb}_{\text{m}}/\text{hr} + 4.75 \text{ lb}_{\text{m}}/\text{hr} = 9.75 \text{ lb}_{\text{m}}/\text{hr}$ 



#### PROBLEM 3-4

Calculate the stack and fugitive emissions if...

- the process equipment generates 100 lbm/hr of VOCs,
- the hood capture efficiency is 90%,
- and the collection efficiency of the air pollution control device is 95%.

#### **PROBLEM 3-4: SOLUTION**

1. Calculate fugitive emissions.

Fugitive emissions =  $100 \text{ lb}_{\text{m}}/\text{hr} - 90 \text{ lb}_{\text{m}}/\text{hr} = 10 \text{ lb}_{\text{m}}/\text{hr}$ 

2. Calculate stack emissions.

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

 $= 4.5 \text{ lb}_{\text{m}}/\text{hr}$ 

3. Calculate total emissions.

Total emissions =  $10 \text{ lb}_{\text{m}}/\text{hr} + 4.5 \text{ lb}_{\text{m}}/\text{hr} = 14.5 \text{ lb}_{\text{m}}/\text{hr}$ 

#### **HOOD OPERATING PRINCIPLES**

- Hoods are generally designed to operate under negative (sub-atmospheric) pressure
- Since air from all directions moves toward the lowpressure hood, the hood must be as close as possible to the process equipment

#### FIGURE 3-14. HOOD CAPTURE VELOCITIES



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# EQUATION 3-3: VOLUMETRIC FLOW AND CAPTURE VELOCITY

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

Where:

- Q = volumetric air flow rate (ACFM)
- X = distance from hood face to point of contaminant release (ft)

 $v_h$  = hood capture velocity at distance X (ft/min)

 $A_h$  = area of hood opening (ft<sup>2</sup>)

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## PROBLEM 3-5

 Calculate the required volumetric flow rate and capture velocity for the following distances from the hood face (X):

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

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

- Assume that the recommended capture velocity for the pollutant is 300 fpm entering a 16-inch diameter hood.
- Assume that X is the farthest distance from the hood face to the released contaminant.



### **PROBLEM 3-5 SOLUTION: PART A**

1. Calculate the area of the hood opening.

$$A = \frac{\pi D^2}{4} = \frac{3.14(16 \text{ in .})^2}{4}$$

 $= 201 \text{ in.}^2$ 

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

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

= 3,580 *ACFM* 

#### **PROBLEM 3-5 SOLUTION: PART B**

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

$$Q = v_{h} (10X^{2} + A_{h})$$
  
=  $\frac{300 \text{ ft}}{\text{min}} \left[ 10(2 \text{ ft})^{2} + (201 \text{ in}.^{2}) \left( \frac{1 \text{ ft}^{2}}{144 \text{ in}.^{2}} \right) \right]$   
= 12,585 *ACFM*

Doubling the distance results in an almost four-fold increase in volumetric flow rate.

# HOOD DESIGNS FOR IMPROVED PERFORMANCE

- Side baffles or flanges
- Used to restrict the flow of clean air into the hood



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# HOOD DESIGNS FOR IMPROVED PERFORMANCE

- Push-pull hood
- A high velocity clean air stream is "pushed' across the area of pollutant generation into a "pull" hood



FIGURE 3-17. HOOD DESIGN FOR PROTECTION OF PLANT PERSONNEL



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# MONITORING HOOD CAPTURE EFFECTIVENESS

- Hood performance should be monitored on a regular basis to include:
  - Visible emission observations
  - Confirmation that the hood has not been moved away from the point of pollutant generation
  - Checking for damage or removal of side baffles and other equipment necessary to maintain good operation
- Hood static pressure should also be monitored to ensure the appropriate gas flow rate is being maintained

# EQUATION 3-4 AND 3-5: HOOD STATIC PRESSURE AND VELOCITY PRESSURE

$$\mathbf{SP}_{\mathbf{h}} = -(\mathbf{VP}_{\mathbf{d}}) - \mathbf{h}_{\mathbf{e}}$$

Where:

 $SP_{h} = Hood static pressure (in. W.C.)$   $VP_{d} = Duct velocity pressure (in. W.C.)$   $h_{c} = Overall hood entry loss (in. W.C.)$   $h_{e} = (F_{h})(VP_{d})$ 

Where:

 $F_h$  = Hood entry loss coefficient (dimensionless)

 $SP_{h} = -(VP_{d}) - (F_{h})(VP_{d}) = -(VP_{d})(1+F_{h})$ 

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# FIGURES 3-18: HOOD ENTRY LOSS COEFFICIENT



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#### **EQUATION 3-7: VELOCITY PRESSURE**

$$VP_{d} = \left(\frac{V}{4,005}\right)^{2} \left(\frac{\rho_{Actual}}{\rho_{Standard}}\right)$$

Where:

 $\begin{array}{ll} VP_d &= Velocity \ pressure \ of \ duct \ (in. \ W.C.) \\ v &= Gas \ velocity \ (ft/min) \\ \rho_{Actual} &= Density \ at \ actual \ conditions \ (lb_m/ft^3) \\ \rho_{Standard} &= Density \ at \ standard \ conditions \ (lb_m/ft^3) \end{array}$ 

Note that this is a dimensional equation and the specified units of v must be used. Any consistent units for  $\rho$  may be used since the ratio is dimensionless.

# FIGURE 3-19. RELATIONSHIP BETWEEN HOOD STATIC PRESSURE AND FLOW RATE



A flanged hood with  $F_h = 0.49$  and  $\rho_{actual} = \rho_{standard}$  has been assumed in preparing this figure.

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## PROBLEM 3-6

- A hood serving a paint dipping operation has a static pressure of -1.10 in. W.C.
- Estimate the gas flow rate under the following conditions:
  - A. At present operating conditions
  - B. At baseline levels
- Use the following data:
  - Hood F<sub>h</sub>= 0.93
  - Baseline air temperature= 68°F
  - Duct inside diameter= 2 ft
  - Baseline hood static pressure= -1.70 in. W.C.

#### **PROBLEM 3-6: SOLUTION PART A-3**

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

 $SP_h = -(VP_d) - h_e$ Calculate the value from the hood entry loss, h<sub>e</sub>, as  $h_e = (F_h)(VP_d) = (0.93)(VP_d)$ follows.  $SP_h = -VP_d - (0.93)(VP_d) = -1.93(VP_d)$ Given  $SP_h = -1.10$  in. W.C. -1.1 in. W.C. =  $-1.93(VP_d)$  $VP_d = \frac{-1.1 \text{ in. W.C.}}{1.02} = 0.57 \text{ in. W.C.}$ 

#### **PROBLEM 3-6 SOLUTION: PART A**

Step 2. Calculate the gas velocity using a variation of Equation 3-7 at 68°F,  $\rho_{Actual} = 0.075 \ lb_m/ft3$ .

$$\mathbf{v} = \mathbf{4},005\sqrt{VP}$$

$$v = 4,005\sqrt{0.57}$$

 $v = 3,024 \text{ ft} / \min$ 

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# **PROBLEM 3-6 SOLUTION: PART A**

Step 3. Calculate the gas flow rate:

Flow rate = Velocity × Area of duct Area of duct =  $\frac{\pi D^2}{4}$ =  $\frac{3.14(2 \text{ ft})^2}{4}$ = 3.14 ft<sup>2</sup>

Flow rate = 3,024 ft/min  $\times 3.14$  ft<sup>2</sup> = 9,495 ACFM

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# **PROBLEM 3-6 SOLUTION: PART B**

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

$$\begin{split} SP_{h} &= -(VP_{d}) - h_{e} \\ SP_{h} &= -(VP_{d}) - (0.93)(VP_{d}) \\ &= -(VP_{d}) - 0.93 VP_{d} = -1.93(VP_{d}) \\ \text{Given SP}_{h} &= -1.7 \text{ in. W.C.:} \\ &-1.7 \text{ in. W.C.} = -1.93(VP_{d}) \\ &VP_{d} &= 0.88 \text{ in. W.C.} \end{split}$$

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### **PROBLEM 3-6 SOLUTION: PART B**

Step 2. Calculate the gas velocity using a variation of Equation 19 at standard conditions,  $\rho_{Actual} = 0.075 \text{ lb}_m/\text{ft3}$ .

$$\mathbf{v} = \mathbf{4}, \mathbf{005}\sqrt{\mathbf{VP}}_d$$

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

v = 3,757 ft/min

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## **PROBLEM 3-6 SOLUTION: PART B**

Step 3. Calculate the gas flow rate: Flow rate = Velocity x Area of duct = 3,757 ft/min (3.14 ft<sup>2</sup>) = 11,797 ACFM

Gas velocity and volumetric flow rate have decreased by about 20%.



# **TRANSPORT VELOCITY**

- Hood systems must maintain a minimum transport velocity in the ducts to prevent particulate matter from settling and accumulating
- A build up of particulate matter will increase flow resistance and result in a decrease in hood capture efficiency

# TABLE 3-10. COMMONLY RECOMMENDEDTRANSPORT VELOCITIES

Type of Pollutant	Transport Velocity
Gases	~1000-2000 ft/min
Light particulate loading	~3000-3500 ft/min
Normal particulate loading	~3500-4500 ft/min

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# PROBLEM 3-7

- A duct system transporting a very light dust requires 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?

# **PROBLEM 3-7 SOLUTION**

Step 1. Calculate the duct area.

# $Ductarea = \frac{Gas \ volume \ tricflow \ rate}{Minimum \ transport \ velocity}$

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

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

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# **PROBLEM 3-7 SOLUTION**

2. Calculate the duct diameter.

Duct diameter =  $\frac{\pi D^2}{4}$  $D^2 = \frac{4(0.349 \text{ ft}^2)}{3.14}$ = 8 in.

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### **F**ANS

- This section introduces:
- The variables that contribute to fan performance



### FANS

- Fans are used to control the gas flow rate from the point of pollutant generation, through the air pollution control devices, and out through the stack to the atmosphere
- There are two main types of fans:
  - Axial
  - Centrifugal (normally used in air pollution control systems)

## FIGURES 3-20 AND 3-21: FAN TYPES







# **CATEGORIES OF FAN DRIVES**

- Direct drive
  - The fan wheel is linked directly to the shaft of the motor
- Belt drive
  - Connected to the drive motor by a belt mounted on sheaves connected to the motor and fan wheel shafts
- Variable drive
  - Use hydraulic or magnetic coupling that allow the operator to control the fan wheel speed independent of the motor speed

# FIGURE 3-22. CENTRIFUGAL FAN AND MOTOR SHEAVES



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### **EQUATION 3-8: FAN ROTATIONAL SPEED**

 $RPM_{(FAN)} = RPM_{(MOTOR)} \frac{D_{(MOTOR)}}{D_{(FAN)}}$ 

#### Where:

 $RPM_{(FAN)} = Fan speed (revolutions/min)$   $RPM_{(MOTOR)} = Motor speed (revolutions/min)$   $D_{(FAN)} = Fan sheave diameter (in.)$   $D_{(MOTOR)} = Motor sheave diameter (in.)$ 

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# FIGURE 3-23. TYPES OF FAN WHEELS



A. Forward curved



B. Backward curved



C. Radial



# THE FIRST FAN LAW

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

$$Q_2 = Q_1 \left(\frac{RPM_2}{RPM_1}\right)$$

Where:

 $Q_1$  = baseline air flow rate  $Q_2$  = present air flow rate  $RPM_1$  = baseline fan wheel rotational speed  $RPM_2$  = present fan wheel rotational speed



# FIGURE 3-25. FAN STATIC PRESSURE RISE



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# THE SECOND FAN LAW

 The Second Fan Law (Equation 3-10) states that the Fan ΔSP is proportional to the square of the fan speed

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

#### Where:

 $\Delta SP_1$  = baseline fan static pressure rise (in. W.C.)  $\Delta SP_2$  = present fan static pressure rise (in. W.C.) RPM<sub>1</sub> = baseline fan wheel rotational speed RPM<sub>2</sub> = present fan wheel rotational speed



# FIGURE 3-26. TOTAL SYSTEM STATIC PRESSURE DROP



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# FIGURE 3-27. SYSTEM CHARACTERISTIC CURVE



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# FIGURE 3-28. FAN STATIC PRESSURE RISE



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# FIGURE 3-29. PORTION OF A TYPICAL MULTI-RATING TABLE

194 LS							X	2	Inlet diameter: 11" O.D. Wheel diameter: 19½" Outlet area: .660 sq. ft. inside Wheel circumference: 5.01 ft												
		2*SP		4"SP		6"SP		8"SP		10"SP		12"SP		14"SP		16"SP		18"SP		Τ	
ÇFM	ov	RPM	BHP	RPM	внр	RPM	BHP	RPM	BHP	RPM	BHP	RPM	BHP	RPM	BHP	RPM	BHP	RPM	внр	F	
660 792 924 1056	1000 1200 1400 1600	995 1008 1023 1042	0.48 0.55 0.62 0.71	1392 1398 1405 1418	1.01 1.11 1.23 1.35	1698 1703 1708 1716	1.60 1.75 1.90 2.07	1960 1962 1965 1971	2.27 2.45 2.64 2.84	2191 2192 2194 2197	2.98 3.20 3.43 3.67	2399 2398 2401 2401	3.74 3.99 4.27 4.53	2592 2588 2589 2593	4.55 4.83 5.14 5.46	2769 2767 2766 2769	5.38 5.71 6.05 6.42	2938 2936 2932 2935	6.27 6.65 7.01 7.41	1.46.4	
1188 1320 1452 1584	1800 2000 2200 2400	1061 1084 1109 1136	0.80 0.90 1.01 1.13	1431 1447 1465 1485	1.49 1.64 1.80 1.98	1726 1739 1753 1769	2.24 2.44 2.65 2.87	1980 1987 1999 2012	3.06 3.29 3.541 3.80	2203 2209 2221 2229	3.92 4.19 4.49 4.78	2407 2414 2422 2431	4.83 5.15 5.47 5.82	2593 2600 2607 2612	5.78 6.13 6.50 6.87	2771 2773 2778 2786	6.79 7.16 7.55 7.98	2936 2940 2943 2949	Ĩ		
1716 1980 2244 2508	2600 3000 3400 3800	1162 1223 1290 1361	1.26 1.56 1.91 2.33	1505 1554 1606 1661	2.16 2.58 3.04 3.56	1784 1824 1867 1917	3.10 3.62 4.19 4.84	2025 2059 2098 2141	4.08 4.70 5.38 6.12	2242 2272 2305 2345	5.11 5.82 6.59 7.44	2441 2464 2495 2531	6.18 6.95 7.83 8.78	2623 2644 2671 2703	7.28 8.14 9.09 10.1	2791 2815 2838 2866	9.381 10.4 11.5	2956 2973 2995 30			
2772 3036 3300 3564 3828	4200 4600 5000 5400 5800	1439 1519 1603 1691 1781	2.83 3.40 4.07 4.84 5.73	1723 1788 1855 1929 2005	4.16 4.84 5.58 6.45 7.41	1958 2025 2086 2148 2214	5.54 6.32 7.20 8.14 9.18	2189 2239 2294 2350 2409	6.95 7.85 8.83 9.88 11.0	2387 2432 2483 2536 2591	8.37 9.36 10.5 11.6 12.9	2569 2611 2660 2708 2759	9.80 10.9 12.1 13.4 14.8	2740 2780 2825 2869 2917	11.3 12.5 13.8 15.2 16.7	2900 2937 2978 3024 3069	12.8 14.1 15.5 17.0 18				



# FIGURE 3-31. FAN CHARACTERISTIC CURVE



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# FIGURE 3-32. CHANGES IN THE SYSTEM RESISTANCE CURVE



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# FACTORS THAT AFFECT THE SYSTEM CHARACTERISTIC CURVE

- Air pollution control system cleaning cycles
- Gradually increasing air infiltration between maintenance cycles
- The opening and closing of dampers on individual process sources ducted into the overall ventilation system

# FIGURE 3-33. CHANGES IN THE FAN SPEED



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# FIGURE 3-34. CHANGES IN THE INLET DAMPER POSITION



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# FIGURE 3-35. PORTION OF A VENTILATION SYSTEM (PROBLEM 3-8)





# PROBLEM 3-8

- 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.

### **PROBLEM 3-8: SOLUTION**



$$SP_{@High Flow} = SP_{@Low Flow}(2.25)$$

= -16.5 in. W.C. (2.25)

= - 37.13 in. W.C.

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# THE THIRD FAN LAW

 The Third Fan Law (Equation 3-12) states that the brake horsepower is proportional to the cube of the fan rotational speed

$$\mathbf{BHP}_{2} = \mathbf{BHP}_{1} \left( \frac{\mathbf{RPM}_{2}}{\mathbf{RPM}_{1}} \right)^{3}$$

 $BHP_1$  = baseline brake horsepower  $BHP_2$  = present brake horsepower  $RPM_1$  = baseline fan wheel rotational speed  $RPM_2$  = present fan wheel rotational speed

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### **EQUATION 3-11: BRAKE HORSEPOWER**

# $BHP = \frac{I \ x \ E \ x \ 1.73 \ x \ Eff \ x \ PF}{745}$

Where:

BHP= Brake horsepower (total power consumed by the fan)

I = Fan motor current (amps)

E = Voltage (volts)

Eff = Efficiency expressed as decimal

PF = Power factor

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# FIGURE 3-36. EXAMPLE OF A BRAKE HORSEPOWER CURVE



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# EQUATION 3-15: MOTOR CURRENT AND GAS DENSITY

$$\mathbf{I}_{\text{STP}} = \mathbf{I}_{\text{Actual}} \left( \frac{\rho_{\text{STP}}}{\rho_{\text{Actual}}} \right)$$

Where:

 $I_{STP}$  = Fan motor current at standard conditions (Amperes)  $I_{Actual}$  = Fan motor current at actual conditions (Amperes)  $r_{STP}$  = Gas density at standard conditions ( $Ib_m/ft^3$ )  $r_{Actual}$  = Gas density at actual conditions ( $Ib_m/ft^3$ )

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### EQUATIONS 3-13 AND 3-14: GAS DENSITY

Ideal Gas Law

$$\rho = \left(\frac{\mathbf{PM}}{\mathbf{RT}}\right)$$

$$\frac{\rho_2}{\rho_1} = \left(\frac{P_2}{P_1}\right) \left(\frac{T_1}{T_2}\right)$$

Where:

 $\rho$  = gas density, Ib<sub>m</sub>/ft<sup>3</sup>

P = pressure, atm

 $M = molecular weight of gas, lb_m/lb mole$ 

T = absolute temperature, R

 $R = gas constant = 0.7302 ft^3 atm/lb mole R$
#### **PROCESS START-UP CONSIDERATIONS**

 During process start-up the gas temperature is normally low and the gas density is high. In order to avoid burning out the fan motor, it is often necessary to start with low gas flow rate and increase the rate gradually as the gas temperature increases.

#### PROBLEM 3-9

- A fan motor is operating at 80 amps and the air 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?

#### PROBLEM 3-9

- A number of potentially explosive gases and vapors are collected in gaseous contaminant control systems
- The explosive range of such gases is bounded by the lower explosive limit (LEL) and the upper explosive limit (UEL)
- To control gaseous contaminants there are six major control techniques...

#### **PROBLEM 3-9: SOLUTION**

Step 1. Calculate the gas density at actual conditions: 1a. Convert pressure from inches of water to psia.

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

=14.34 psia



#### **PROBLEM 3-9: SOLUTION**

Step 1b. Calculate the gas volume at actual conditions using the Ideal Gas Law equation.

$$V = \frac{nRT}{P}$$
$$= \left(\frac{10.73\text{psiax ft}^3}{^\circ\text{R x lb mole}}\right) \frac{(460^\circ\text{F} + 300^\circ\text{F})}{14.34\text{psia}}$$
$$= 568.7 \text{ ft}^3/\text{lb mole}$$

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#### **PROBLEM 3-9: SOLUTION**

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

 $=\frac{29\,lb_{\rm m}}{568.7\,{\rm ft}^3}$ 

 $= 0.051 \, \text{lb}_{\text{m}}/\text{ft}^3$ 

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#### **PROBLEM 3-9 SOLUTION**

Step 2. Calculate the gas density at standard conditions:a. Calculate the gas volume at standard conditions using the Ideal Gas Law.

$$\mathbf{V} = \left(\frac{10.73 \text{ps} \text{ ia x ft}^3}{^\circ \text{R x lb mole}}\right) \frac{(460^\circ \text{F} + 68^\circ \text{F})}{14.7 \text{ps} \text{ ia}}$$

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



#### **PROBLEM 3-9 SOLUTION**

Step 2b. Calculate gas density at standard conditions.

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

 $=\frac{29 \, \text{lb}_{\text{m}}}{385.4 \, \text{ft}^3}$ 

 $=0.075 \, \text{lb}_{\text{m}}/\text{ft}^3$ 

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#### **PROBLEM 3-9 SOLUTION**

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

$$s_{\text{TP}} = I_{\text{Actual}} \left( \frac{\rho_{\text{STP}}}{\rho_{\text{Actual}}} \right)$$
$$= 80 \text{ amps} \left( \frac{0.075 \text{ lb}_{\text{m}}/\text{ft}^3}{0.051 \text{ lb}_{\text{m}}/\text{ft}^3} \right)$$
$$= 80 \text{ amps} \left( 1.47 \right)$$

=118 amps

#### **REVIEW OF FAN LAWS**

Capacity varies directly with speed.

$$\frac{Q_2}{Q_1} = \left(\frac{RPM_2}{RPM_1}\right)$$

Pressure is related to the square of the fan speed.

$$\frac{\mathrm{SP}_2}{\mathrm{SP}_1} = \left(\frac{\mathrm{RPM}_2}{\mathrm{RPM}_1}\right)^2$$

Horsepower is related to the cube of the fan speed.

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

#### **SUMMARY**

This lesson covered the following topics:

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

Continued . . .





## SUMMARY (CONTINUED)

- Fan performance is important because it influences pollutant capture efficiency at the point of pollutant generation.
- The fan characteristic curve is determined by the fan wheel design, fan wheel housing configuration, fan speed, damper positions, and inlet and outlet duct configurations.
- The system operating point is the intersection of the fan characteristic curve and the system resistance curve.

Continued . . .

## SUMMARY (CONTINUED)

- Changes in gas flow rate can be caused by changes in the system resistance curve, fan speed, or damper positions.
- Changes in the gas flow rate are qualitatively indicated by changes in the fan motor current. As current increases, gas flow rate increases.
- Fan motor currents are also a function of gas density. Current should be corrected to standard conditions when comparing operating conditions at two significantly different gas temperatures.

Continued . . .



#### CHAPTER 4 ADSORPTION

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#### **CHAPTER 4**

## ADSORPTION : TRANSFER OF POLLUTANTS FROM A GAS TO A SOLID



#### **O**VERVIEW

- This section will introduce:
  - Adsorbents
  - Characteristics of Adsorbents
  - Adsorption Systems



#### INTRODUCTION

- Adsorption processes have been used since the 1950s
- Nonregenerative
  - Adsorbent bed is discarded as it approaches saturation with the contaminant
- Regenerative
  - Adsorbent is treated and placed back in service

#### **LEARNING OBJECTIVES**

At the end of this training, you will be able to:

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

#### **Adsorbents**

- Adsorbent is a bed or layer of highly porous material through which the gas stream passes during adsorption
- Adsorbate is the compound to be removed by the adsorbent

#### FIGURE 4-1. THE ADSORPTION PROCESS





#### **Types of Adsorbents**

- Most Common
  - Activated Carbon --the workhorse
  - -Zeolites
  - -Polymers
- Other
  - Silica Gel
  - -Activated Alumina



### **ACTIVATED CARBON**

- Feedstock
  - Wood
  - Coal
  - Coconut
  - Nutshells
  - Petroleum Products

## **ACTIVATION PROCESS**

- Feedstock is pyrolyzed
- Heating the material to a temperature high enough to drive off all volatile material in the absence of air
- The carbon left over is then selectively oxidized or "activated" by reaction with steam, air, or CO<sub>2</sub> at high temperatures

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#### ZEOLITES

- Remove moisture from exhaust streams
- Separate hydrocarbons in refining processes
- Remove nitrogen oxides from air pollution sources



#### FIGURE 4-2. STRUCTURE OF ZEOLITES





## **SYNTHETIC POLYMERS**

- Very high adsorption capacities for selected organic compounds
- Regenerated more rapidly than activated carbon adsorbents
- Mainly used to control organic compounds and reactive compounds
- Significantly more expensive than activated carbon and zeolites

## FIGURE 4-3. SYNTHETIC POLYMER STRUCTURE



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## **OTHER ADSORBENTS**

- Silica Gel
  - Primarily used to remove moisture from exhaust streams
  - Ineffective at temperatures above 500°F (260°C)
- Activated Alumina
  - Primarily used for drying gases
  - Not typically used in air pollution applications

# TABLE 4-1. PHYSICAL PROPERTIES OF MAJORTYPES OF ADSORBENTS

Adsorbent <sup>2</sup>	Internal Porosity (%)	Surface Area (m²/g)	Pore Volume (cm <sup>3</sup> /g)	Bulk Dry Density (g/cm <sup>3</sup> )	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 <sup>2</sup>		1080-1100	0.94-1.16	0.34-0.40	

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#### **NONREGENERATIVE ADSORPTION SYSTEMS**

- Usually consist of thin adsorbent beds, ranging in thickness from 0.5 to 4 inches (1 to 10 cm)
- Used mainly as air purification devices for small air flow streams
- Can be flat, cylindrical, or pleated

## FIGURE 4-4. THIN-BED ADSORBER – NINE CELL SYSTEM



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#### FIGURE 4-5. NONREGENRATIVE ADSORBERS



## FIGURE 4-6. NONREGENERATIVE CANISTER ADSORBER

Thick bed systems also used in some cases.





## FIGURE 4-7. FLOWCHART OF A SIMPLE, NONREGENERATIVE ADSORBER SYSTEM



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#### **REGENERATIVE ADSORPTION SYSTEMS**

- Types
  - Fixed Beds
  - Moving Beds
  - Fluidized Beds
- The choice of a particular system depends on the pollutants to be controlled and the recovery equipment

### FIXED BED DESIGNS

- Commonly used to control a variety of organic vapors
- Often regenerated by low-pressure steam
- Continuous operation requires multiple beds


## FIGURE 4-8. TWO-BED ADSORPTION SYSTEM



## FIGURE 4-9. MULTI-BED, FIXED-BED ADSORPTION SYSTEM



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## FIGURE 4-10. HORIZONTAL ADSORBER VESSEL



#### FIGURE 4-11. CARBON FIBER SYSTEM



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## **MOVING BED DESIGNS**

- Uses a carbon bed more effectively than a fixedbed system
- Rotary Wheel Zeolite Adsorber
- Rotary Carbon Fiber Adsorber



## FIGURE 4-12. ROTARY WHEEL ZEOLITE ADSORBER



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## FIGURE 4-13A. ROTOR FOR CARBON FIBER SYSTEM

Cleaned air



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## FIGURE 4-13B. CARBON FIBER ROTOR SYSTEM



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## FLUIDIZED BED ADSORBERS

- Uses the motion of the solvent-laden gas stream to entrain adsorbent material
- Organic contaminants can be concentrated by a factor of 10 to 50 because adsorption and desorption processes are physically separate



## FIGURE 4-14. FLUIDIZED BED ADSORBER/REGENERATOR



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## FIGURE 4-15. FLUIDIZED BED ADSORBER



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## **OPERATING PRINCIPLES**

- This section will introduce:
  - Adsorption Steps
  - Adsorption Forces
  - Adsorption-Capacity Relationships



## FIGURE 4-16. ADSORPTION STEPS



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## **ADSORPTION FORCES**

- Physical
  - Electrostatic in nature
  - Also referred to as van der Waals' adsorption
  - Occurs from three different effects
    - Orientation
    - Dispersion
    - Induction

## FIGURE 4-17. PHYSICAL FORCES





## **ADSORPTION FORCES**

- Chemical (Chemisorption)
  - The gas is held to the surface of the adsorbate by the formation of a chemical bond
  - Chemical bond normally sufficiently strong to prevent regeneration
  - Adorbents used can be either pure substances or chemicals deposited on an inert carrier material

# TABLE 4-2. CHARACTERISTICS OFCHEMISORPTION AND PHYSICAL ADSORPTION

Chemisorption	Physical Adsorption
Releases high heat, 10Kcal/gm mole	Releases low heat, 0.1K cal/gm mole
Forms a chemical compound	Adsorbate retained by electrostatic forces
Desorption difficult	Desorption possible
Adsorbate recovery impossible	Adsorbate recovery possible



## **ADSORPTION CAPACITY**

- Equilibrium capacity is the maximum amount of vapor that can be adsorbed at a given set of operating conditions
- Adsorption equilibrium data may be presented in three forms:
  - Isotherm (most commonly used)
  - Isostere
  - Isobar
- The three forms are interdependent. Given one, the other two can be determined.

#### **I**SOTHERM

- Most common and useful method of presenting equilibrium data
- A plot of the adsorbent capacity versus the partial pressure of the adsorbate at a constant temperature



# FIGURE 4-18. ADSORPTION ISOTHERM: CARBON TETRACHLORIDE ON A SPECIFIC ACTIVATED CARBON



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## PROBLEM 4-1

- A dry cleaning process exhausts a 15,000 SCFM air stream containing 680 ppm carbon tetrachloride.
- Given Figure 4-18, and assuming that the exhaust stream is at approximately 140F and 14.7 psia, determine the saturation capacity of the activated carbon.

#### **PROBLEM 4-1 SOLUTION**

Step 1. In the gas phase, the mole fraction (y) is equal to the ppm divided by 106.

y = 680 ppm= 0.00068

The partial pressure is the product of the mole fraction and the total pressure.

P\* = yP= (0.00068)(14.7 psia) = 0.01 psia

Step 2. From Figure 4-18, at a partial pressure of 0.01 psia and a temperature of 140°F, the carbon capacity is read as approximately 45%.

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#### ISOSTERE

- A plot of the natural log of the pressure versus the reciprocal of absolute temperature at a constant amount of vapor adsorbed
- The slope of the isostere corresponds to the differential heat of adsorption

## FIGURE 4-19. ADSORPTION ISOSTERES: H2S ON 13X MOLECULAR SIEVE



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#### **I**SOBAR

 Plot of the amount of vapor adsorbed versus temperature at a constant partial pressure of the adsorbate

## FIGURE 4-20. ADSORPTION ISOBAR: BENZENE ON SPECIFIC ACTIVATED CARBON



## **ADSORPTION SYSTEM PERFORMANCE**

- This section will introduce:
  - Applicability
  - Working Capacity
  - Factors Affecting Adsorption System
    - Performance
  - Regeneration Methods

## **APPLICABILITY**

- Nonregenerative
  - Organic compounds with molecular weights >50 and/or boiling points >20°C
  - Service life equivalent to as much as 50% of the saturation capacity

## **APPLICABILITY**

- Regenerative
  - Organic compounds with molecular weights >50 and <200 or boiling points >20°C and <175°C</li>
  - Limited concentrations of reactive 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					
Buty Acetate	259 (126.1)	116.2	No	Yes	7.60
Ethyl Acetate	171 (77.2)	88.1	Yes	Yes	2.50

#### Continued...

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## TABLE 4-3 (CONTINUED)

Organic Compound	Boiling Point °F(°C)	Molecular Weight	Solubility in Water	Flammable Liquid	Lower Explosive Limit, % Vol.
Halogenated				Contract of the	
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

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# TABLE 4-4. ORGANIC COMPOUNDS NOT USUALLY SUITABLE FOR CARBON ADSORPTION4

Reactive Compounds	High Boilers
Organic acids	Plasticizers
Aldehydes	Resins
Monomers (some)	Long Chain HCs (+C <sub>14</sub> )
Ketones (some)	Glycols, Phenols, Amines



## **ADSORPTION CAPACITY**

- Breakthrough capacity
  - The capacity of the bed at the time where unadsorbed vapor begins to be emitted
- Saturation (equilibrium) capacity
  - The maximum amount of vapor that can be adsorbed per unit weight of carbon at a given set of conditions
- Working capacity
  - A fraction of the saturation capacity, often in the range of .1 to .5

## PROBLEM 4-2

- A dry cleaning process exhausts a 15,000 SCFM air stream containing 680 ppm carbon tetrachloride.
- Based on Figure 4-18 and gas stream conditions of 140°F and 14.7 psia, estimate the amount of carbon required if the adsorber operates on a 4hour cycle.
- Note: Saturation capacity of the activated carbon is 45% by weight. The molecular weight of CCl₄is 154.
- Use a working capacity of 25% of the saturation capacity.



#### **PROBLEM 4-2: SOLUTION**

## Step 1. Compute the flow rate of $CCl_{a}$ . $Q_{CC14} = 15,000 \text{ SCFM} \times 0.00068 = 10.2 \text{ SCFM CCl}_4$ 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 4-hour cycle, there are $4 \times 245 = 980 \text{ lb}_{\text{m}} \text{ CCl}_{4}$

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

required.  $980lb_m CCl_4 \times \left(\frac{100lb_m carbon}{45lb_m CCl_4}\right) = 2,178lb_m activated carbon$ 

Estimate actual activated carbon requirement by multiplying the amount needed at saturation by four (working capacity of 25% of the saturation capacity).

 $4 \times 2,178 = 8,712 \ lb_m$  carbon per four-hour cycle, per adsorber.

## FACTORS AFFECTING ADSORPTION SYSTEM PERFORMANCE

- Temperature
- Pressure
- Gas Velocity
- Humidity
- Bed Depth
- Contaminants


#### TEMPERATURE

 The capacity of an adsorbent decreases as the temperature of the system increases





 Adsorber temperatures are kept below 130°F (54°C) to ensure adequate bed capacities



#### **PRESSURE AND GAS VELOCITY**

- Pressure
  - Capacity increases with an increase in pressure
- Gas Velocity
  - Capacity decreases with an increase in velocity
  - Systems are designed for a maximum gas velocity of 100 ft/min to achieve 90% or more capture efficiency
  - A lower limit of 20 ft/min is maintained to avoid flow problems

#### 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 surface area of each bed if the gas velocity must be maintained below 100 feet per minute?

#### **PROBLEM 4-3: SOLUTION**

#### Step 1. Calculate the absolute static pressure.

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

Step 2. Calculate the gas flow rate in ACFM.

$$ACFM = 9,000 SCFM \left(\frac{460^{\circ}R + 100^{\circ}F}{528^{\circ}R}\right) \left(\frac{407 \text{ in.W.C.}}{416 \text{ in.W.C.}}\right) = 9,339 ACFM$$

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

Velocity = 
$$\left(\frac{\text{Gas flow rate in ACFM}}{\text{Area}}\right)$$
  
100 ft/min =  $\left(\frac{9,340 \text{ ACFM}}{\text{Area}}\right)$   
A rea = 93.4 ft<sup>2</sup>

## HUMIDITY AND BED DEPTH

- Humidity
  - At high relative humidity, water molecules compete for adsorption sites, thereby reducing the capacity and efficiency of the system
- Bed Depth
  - The minimum depth is based primarily on the length of the mass transfer zone (MTZ)
  - MTZ is related to the rate of adsorption at fixed conditions

#### FIGURE 4-22. MASS TRANSFER ZONE



Time

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## **TYPES OF ADSORPTION SYSTEMS**

- Breakthrough Point
  - When the leading edge of the MTZ reaches the outlet of the bed
- MTZ length depends on six separate factors:
  - adsorbent particle size
  - gas velocity
  - Adsorbate concentration
  - fluid properties of the gas stream
  - temperature of the system
  - pressure of the system

# EQUATION 4-1. ESTIMATING THE LENGTH OF THE MTZ

$$MTZ = \frac{1}{1 - X_s} D\left(1 - \frac{C_B}{C_s}\right)$$

Where:

C<sub>s</sub>

MTZ = Length of MTZ, meters

- X<sub>s</sub> = Degree of saturation in the MTZ, % (usually assumed to be 50%)
- **D** = Bed depth, meters
- **C**<sub>B</sub> = Breakthrough capacity, %
  - = Saturation capacity, %



# EQUATION 4-2. ESTIMATING BREAKTHROUGH CAPACITY

• Equation 4-1 can be rearranged to solve for breakthrough capacity

# $C_{B} = \frac{(X_{S})(C_{S})(MTZ) + C_{S}(D - MTZ)}{D}$



#### **BED DEPTH**

• Often determined by the maximum allowable static pressure drop across the bed.



#### FIGURE 4-23. PRESSURE DROP



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## **ADSORBENT REGENERATION METHODS**

- Adsorbent regeneration is mandatory to maintain continuous operation
- Regeneration is accomplished by reversing the adsorption process
- Four methods:
  - Thermal Swing
  - Pressure Swing
  - Inert Purge Gas Stripping
  - Displacement

## **THERMAL SWING – STEAM STRIPPING**

- Most common desorption technique
  - Simple
  - Relatively inexpensive if source of low pressure steam is available
- Advantages
  - Effective desorption without damaging carbon
  - Condensed steam and adsorbate can be separated by decantation or distillation
  - Concentrated source of heat that is effective in raising temperature quickly

## **STEAM STRIPPING DISADVANTAGES**

- Aqueous effluent can pose a water pollution problem
- Some organic compounds may hydrolyze or form corrosive solutions in the presence of water
- A hot, wet carbon bed will not effectively remove organic vapors (bed must be dried and cooled prior to next adsorption cycle)

#### **PRESSURE SWING – VACUUM DESORPTION**

- Primary advantage is the times for heating and cooling the bed are
- Primary disadvantages are its high operating and construction costs



#### **PROBLEM 4-4**

- A solvent degreaser is designed to recover toluene from an 8,000 ACFM air stream at 80°F (26.7°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.

## PROBLEM 4-4 (CONTINUED)

- Given the adsorption isotherm for toluene (Figure 4-24), 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:
  - The molecular weight of toluene = 92.1
  - -The density of activated carbon = (30 lb<sub>m</sub>/ft<sup>3</sup>)

#### FIGURE 4-24. TOLUENE ISOTHERM



Partial pressure, psia

#### **PROBLEM 4-4: SOLUTION**

Step 1. Calculate the toluene flow rate.

 $(8,000 A CFM) \frac{528^{\circ} R}{540^{\circ} R} = 7,820 S CFM$ 

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

The mass flow rate of toluene is: (0.0487 lb mole/min)(92.1 lb<sub>m</sub>/lb mol) = 4.49 lb<sub>m</sub>/min

Continued...

#### **PROBLEM 4-4: SOLUTION (CONTINUED)**

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

$$P^* = yP = \left(\frac{2,400}{1,000,000}\right) 14.7 \text{ psia} = 0.0353 \text{ psia}$$

Use Figure 4-24 to estimate the saturation capacity at P\* = 0.0353 and T = 80°F.

Capacity  $\approx$  45 wt % or 45 lb<sub>m</sub>/100 lb<sub>m</sub> carbon

Continued...

## **PROBLEM 4-4: SOLUTION (CONTINUED)**

Step 3. Determine the amount of carbon at saturation for a 4 hour cycle.

$$= \left(4.49 \frac{\text{lb}_{\text{m}} \text{ toluene}}{\text{min}}\right) \left(\frac{60 \text{ min}}{\text{hr}}\right) \left(\frac{100 \text{ lb}_{\text{m}} \text{ carbon}}{45 \text{ lb}_{\text{m}} \text{ toluene}}\right) \left(4 \frac{\text{hr}}{\text{cycle}}\right)$$

= 2,390  $lb_m$  of carbon (at saturation) Therefore, the working charge is: = (4)(2,390  $lb_m$  of carbon) = 9,680  $lb_m$  of carbon for a 4-hour cycle

[Answer 1]

The required surface area is:

 $A = \frac{Q}{MaximumVelocity} = \frac{8,000ac f/min}{100 ft/min} = 80 ft^{2}$ [Answer 2]

#### Continued...

## **PROBLEM 4-4 SOLUTION (CONTINUED)**

#### **Step 4: Estimate the bed depth.**

At a carbon density of 30 lbm/ft3, the bed depth would be:

*Vol.* carbon = 9,680  $lb_m$  carbon/(30  $lb_m/ft3$ ) = 320  $ft^3$ 

 $Bed Depth = 320 \, ft^3 / 80 \, ft^2 = 4 \, ft$ 

[Answer 3]

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## **PROBLEM 4-4: SOLUTION (CONTINUED)**

It is quite possible that the 4 ft bed depth will cause the total pressure drop to be too large. Let us calculate the required bed depth if the velocity was reduced from 80 ft/min to 60 ft/min.

 $A = \frac{Q}{MaximumVelocity} = \frac{8,000ac f/min}{60 ft/min} = 133 ft^{2}$ The bed depth for this modified approach would be:

 $320 \text{ ft}^3/133 \text{ ft}^2 = 2.4 \text{ ft}$ 

The pressure drop would be reduced both because the pressure drop per foot of packing would be smaller and because the of the reduced bed depth.

# FACTORS THAT CONTRIBUTE TO PREMATURE ORGANIC BREAKTHROUGH

- 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

# FIGURE 4-25. FLOWCHART OF A THREE-BED ADSORBER WITH INSTRUMENTATION



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## **OUTLET VOC CONCENTRATION MONITOR**

- Most direct measure of adsorber performance
- Draws a sample of gas stream from the outlet of each bed on a frequent basis
- Common types include:
  - Flame ionization detectors
  - Photoionization detectors
  - Gas-chromatographs

# FIGURE 4-26. CALIBRATION GAS INJECTION LOCATIONS



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# POTENTIAL VOC OUTLET MONITOR 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

## **PORTABLE VOC DETECTORS**

- Types
  - Flame ionization Detectors
  - Catalytic oxidation Detectors
  - Photoionization Detectors
- Samples should be obtained from a positive pressure portion of the outlet duct near the end of the adsorption cycle when using portable VOC detectors

## **ADDITIONAL MONITORING CONSIDERATIONS**

- Lower Explosive Limit Inlet Monitor
- Gas Inlet Temperature
- Adsorber Vessel Bed Static Pressure Drop
- Gas Flow Rate
- Hood Static Pressure

#### **SUMMARY**

- Adsorption systems are used for a wide variety of organic compounds. Most of the systems used for air pollution control use physical adsorption techniques. Physical adsorption can be reversed during desorption to recover the organic compound or to generate a low volume, high concentration gas stream for subsequent oxidation.
- Common adsorbents include activated carbon, zeolites (molecular sieves), and polymers. All adsorbents have high a high surface area.

#### Continued . . .

#### **SUMMARY**

This lesson covered the following topics:

- Several types of adsorption systems used for various organic compounds.
- Principles of operation that apply to adsorption, and common adsorbants.
- Factors that affect the performance of an adsorption system.
- Areas of an adsorption system that require monitoring.

Continued...

# SUMMARY (CONTINUED)

#### **Conclusions**

- Contaminants having molecular weights between about 50 and 200 are good candidates for adsorption. These compounds generally have boiling temperatures between about 70°F and 350°F.
- The size of an adsorption system depends, in part, on the temperature and inlet organic vapor concentration of the inlet gas stream. Adsorbers are usually designed for inlet gas temperatures less than approximately 120°F.
- The inlet organic vapor concentrations can vary from as low as 10 ppm to up to approximately 25% of the LEL. Adsorber removal efficiencies are usually in the range of 90% to 98%.

CHAPTER 5



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#### **CHAPTER 5**

#### **ABSORPTION**





#### This lesson introduces:

- Absorbers in air pollution control applications
  - Use aqueous scrubbing liquids to remove gases and vapors
  - Transfers a gaseous contaminant from the gas phase to the liquid phase
- Two classifications of Absorbers
  - Straight dissolution of absorbate into absorbent
  - Dissolution accompanied by irreversible chemical reaction


# **LEARNING OBJECTIVES**

At the end of this training, you will be able to:

- Identify various types of absorbers.
- Identify the principles of operation that influence the efficiency of absorbers.
- Determine the capability and sizing parameters of an absorber system.
- Identify the instrumentation requirements for an absorber system.

# **TYPES AND COMPONENTS OF ABSORBERS**

- This section will introduce:
  - Types of absorbers
  - Components common to most absorption systems

# **TYPES OF ABSORBERS**

- Spray Tower Absorbers
- Packed Bed Absorbers
- Tray Tower Absorbers
- Venturi and Ejector Absorbers
- Biofiltration Beds

# **SPRAY TOWER ABSORBERS**

- Simplest devices used for gas absorption
- Flow is typically countercurrent
  - Contaminant gas enters near the bottom and flows upward
  - Liquid enters near the top and flows downward
- Range in size from 5 to 100,000 ACFM

# FIGURE 5-1. SPRAY TOWER SCRUBBER



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# **FLOW ARRANGEMENTS**

- Spray chambers can also operate
  - Cross-current: Gas flow is perpendicular to the liquid flow
  - Co-current: Gas and liquid flow in the same direction
- Both arrangements allow for higher gas stream velocities but are not as efficient as countercurrent units

# FIGURE 5-2. FULL-CONE SPRAY NOZZLE



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# COMPARISON

- Quantity of liquid (liquid-to-gas ratio) is key to gas absorption.
- Contaminant capture efficiency
- Advantages / components
  - Spray-tower absorbers
  - Mist eliminators



# PACKED BED ABSORBERS

- The most common absorbers used for gas removal
- Absorbing liquid is dispersed over packing material
- Classified according to the relative direction of gas-to-liquid flow

# **TYPES OF PACKED BED ABSORBERS**

- Counter-current flow tower
  - Most common
  - Gas stream enters at bottom and flows up through packing material, liquid flows downward
  - Most dilute gas contacts least saturated liquid at the top of the tower
  - Most concentrated gas contacts liquid that is closest to saturation at the bottom of the tower
  - Driving force for mass transfer relatively constant throughout the tower

# FIGURE 5-3. COUNTER-CURRENT PACKED TOWER



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# **TYPES OF PACKED BED ABSORBERS**

- Cross-flow absorber
  - Gas stream flows horizontally through the packed bed, which is irrigated by the scrubbing liquid flowing down through the packing material

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# FIGURE 5-4. FLOWCHART OF CROSS-FLOW SCRUBBER



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# PACKING MATERIAL

- Provides a large surface area for mass transfer
- Size normally range from 1 to 4 inches
- Materials –plastic, metal, ceramic
- Selection considerations include:
  - Cost
  - Low-pressure drop
  - Corrosion resistance
  - Structural strength
  - Weight
  - Design flexibility

# FIGURE 5-5. TYPES OF PACKING







Raschig™ ring

Pall ring

#### Berl saddle



Intalox saddle



#### Tellerette™

# LIQUID DISTRIBUTION

- Liquid should be distributed over the entire upper surface of the packed bed
- Liquid flows downward by the force of gravity
- Liquid tends to flow toward the tower wall where the void spaces are greater than in the center (channeling)
- Re-distribution section may be required when packed height exceeds about 10 feet

#### FIGURE 5-6. TYPES OF LIQUID DISTRIBUTORS



(a) Trough and weir type

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(b) Perforated pipe

# **TRAY TOWER ABSORBERS**

- Vertical column with one or more trays mounted horizontally
- Liquid enters at the top and travels across each tray where mass transfer occurs, gas enters at the bottom and travels to the top through openings in each tray
- Types of trays include:
  - Bubble Cap
  - Sieve
  - Impingement Trays
  - Float Valve ™ Trays

# FIGURE 5-7. BUBBLE CAP TRAY



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# FIGURE 5-8. GAS-LIQUID CONTACT IN A DISK-AND-DONUT SIEVE TRAY



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# VENTURIS

- Consists of:
  - Converging section for the acceleration of gas stream
  - A means to introduce the liquid absorbent stream
  - Gas-liquid contacting throat
  - Diverging section for decelerating the gas stream and atomized liquid droplets

# FIGURE 5-9. VENTURI ABSORBER



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# **EJECTOR ABSORBERS**

- Liquid is added to the ejector through a high pressure spray nozzle operating at more than 80 psig
- Liquid creates an aspiration effect that pulls the gas through the vessel and eliminates the need for a blower
- Used in acid production facilities and also for some types of emergency scrubbers



#### FIGURE 5-10. EJECTOR ABSORBERS



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# **BIOFILTRATION BEDS**

- Use aerobic microorganisms in a packed bed to consume organic compounds
- Requires gas stream to be humidified to approx.
  95% relative humidity
- Bed temperature is maintained between 68°F and 105°F (20°C and 40°C)

# FIGURE 5-11. BIOLOGICAL OXIDATION SYSTEM



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# COMMON ABSORPTION SYSTEM COMPONENTS

- Mist Eliminators
  - Used to remove entrained droplets from the gas stream prior to discharge of the effluent to the stack
- Common Types
  - Cyclonic vessels
  - Chevrons
  - Radial vanes
  - Mesh pads

# FIGURE 5-12. CHEVRON MIST ELIMINATOR



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# FIGURE 5-13. RADIAL VANE MIST ELIMINATOR



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# FIGURE 5-14. MESH PAD MIST ELIMINATOR



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# **ABSORPTION SYSTEMS COMPONENTS**

- Pumps and Piping Systems
  - Centrifugal pumps are commonly used
  - Piping system generally consists of a number of components
    - Suction pipe
    - Strainer
    - Suction side check valve
    - Discharge control valve

### INSTRUMENTATION

Gas Temperature

•Absorber inlet

Absorber outlet

Liquid Flow Rate

Recirculation liquid streamPurge liquid stream

Liquid Pressure

Recirculation pump dischargeAbsorber liquid distribution headers

Liquid pH

Recirculation liquid tankRecirculation liquid stream

Static Pressure Drop

Absorber vessel

Mist eliminator

# **OPERATING PRINCIPLES**

- Adsorbent is a bed or layer of highly porous material through which the gas stream passes during adsorption
- Adsorbate is the compound to be removed by the adsorbent

# FIGURE 5-15. TWO-FILM THEORY OF ABSORPTION



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# **EQUILIBRIUM CONDITIONS**

- When the gas film and liquid film are in equilibrium, no additional contaminant removal can occur
- Two ways to avoid equilibrium conditions:
  - 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

# TABLE 5-1. EQUILIBRIUM PARTIAL PRESSURE OFAMMONIA OVER AQUEOUS SOLUTIONS, MM HG

Wt. NH <sub>3</sub> per 100 wts. H <sub>2</sub> O	0°C	10°C	20°C	30∘C	40°C	50°C	60°C
20.0	64	103.5	166	260	395	596	834
15.0	42.7	70.1	114	179	273	405	583
10.0	25.1	41.8	69.6	110	167	247	361
7.5	17.7	29.9	50	79.7	120	179	261
5.0	11.2	19.1	31.7	51	76.5	115	165
4.0		16.1	24.9	40.1	60.8	91.1	129.2
3.0		11.3	18.2	29.6	45	67.1	94.3
2.5			15.0	24.4			77.0
2.0			12.0	19.3			61.0
1.6				15.3			48.7
1.2				11.5			36.3
1.0							30.2
0.5							


### FIGURE 5-16. SOLUBILITY OF NH<sub>3</sub> IN H<sub>2</sub>0



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#### **EQUATION 5-1: HENRY'S LAW**

 $(Eq. 5.1) P_A = H_p X_A$ 

Where:

- p<sub>A</sub>= Partial pressure of contaminant in gas phase at equilibrium
- H<sub>p</sub>= Henry's Law constant when the gas concentration is expressed in partial

pressure

x<sub>A</sub> = Mole fraction of contaminant dissolved in the liquid phase at equilibrium

## EQUATION 5-2: ALTERNATE FORM OF HENRY'S LAW

 $(Eq. 5.2) y_A = H_y x_A$ 

#### Where:

- y<sub>A</sub> = Mole fraction of the contaminant in the gas phase at equilibrium
- H<sub>y</sub>= Henry's Law constant when the gas concentration is expressed in mole fraction
   x<sub>A</sub> = Mole fraction of contaminant dissolved in the liquid phase at equilibrium

#### PROBLEM 5-1

 Use the NH<sub>3</sub>-H<sub>2</sub>O data in Table 5-1 to show that Henry's Law is valid at low concentrations of NH<sub>3</sub>and calculate H<sub>p</sub> and H<sub>y</sub> at 20°C in this low concentration range.

#### **PROBLEM 5-1 SOLUTION**

Step 1. From equation. 5-1, Hp=  $PA/x_A$ . The mass concentration data from Figure 5-1 must be converted to  $x_A$ , the mole fraction of  $NH_3$  in the liquid.

 $x_A = (mol A)/(mol A + mol H_2O)$ =  $(m_A/M_A)/[(m_A/M_A) + (m_{H2O}/M_{H2O})]$ 

Use the first data entry from Table 5-1 as an example:  $m_A = 20$ ,  $m_{H2O} = 100$ ,  $M_A = 17$ , and  $M_{H2O} = 18$ .

 $x_A = (20/17)/[(20/17) + (100/18)] = 0.1755$ 

**Continued...** 

Step 2. Converting the remaining mass concentration data in the same manner leads to the following table of  $x_A - P_A - H_p$ .

× <sub>A</sub>	P <sub>A</sub>	H <sub>p</sub>
0.175	166	949
0.137	114	832
0.095	69.6	732
0.0735	50	680
0.0503	31.7	630
0.0401	24.9	621
0.0301	18.2	605
0.0258	15.0	581
0.0208	12.0	576

The last three entries, for  $x_A$  less than 0.0301 are effectively constant at an average value of  $H_p$ = 587. This value can be accepted to be approximately correct at low concentrations.

Step 3. In deriving equation 5-2:

Hy = Hp/P Hy = 587/760 Hy = 0 .772



The final values with units are:

 $H_p = 584 \text{ mmHg/mole fraction NH}_3 \text{ in liquid, and}$ 

H<sub>y</sub>= 0.772 mole fraction NH<sub>3</sub>in gas/mole fraction NH<sub>3</sub>in liquid

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#### **CAPABILITY AND SIZING**

This section will introduce:

- Two Systems: Empirical Model and Pilot Scale
- Evaluation Guidance
  - Gaseous Pollutant Removal Capability
  - Absorber Sizing
  - Packed Tower Absorber Diameter and Height
  - Tray Tower Absorber Diameter and Height
  - Mist Eliminator Evaluation
  - Alkali Requirements

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#### SITE SPECIFIC DATA TO CONSIDER

- 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

#### **GENERAL APPROACHES**

- Empirical Model Approach
  - Most absorber manufacturers have incorporated empirical data from prior installations
    - Liquid to gas ratios required
    - > Height of bed or number of trays for removal efficiency
    - > Diameter of the absorber
- Pilot Scale Tests
  - Conducted when there is uncertainty of application
  - Conducted preferably on the specific source to be controlled
  - Costly and time consuming

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#### **Absorber Sizing**

- Liquid-to-Gas Ratio
  - Must be sufficient liquid to avoid mass transfer equilibrium
  - Must provide good gas-liquid contact within the absorber

## FIGURE 5-17. DEFINITION OF THE LIQUID-TO-GAS RATIO



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## FIGURE 5-18. MATERIAL BALANCE FOR **COUNTERCURRENT FLOW ABSORBER**



(Eq. 5-3)

Moles contaminant in = Moles of contaminant out

$$G_{m1}y_1 + L_{m2}x_2 = G_{m2}y_2 + L_{m1}x_1$$

#### **EQUATIONS 5-4 AND 5-5: MOLE RATIOS**

(Eq. 5-4) 
$$Y = \frac{y}{1-y}$$
  
Y = moles contaminant/moles contaminant free gas  
y = mole fraction contaminant in gas  
1- y = mole fraction contaminant free gas

(Eq. 5-5) 
$$X = \frac{x}{1-x}$$

X = moles contaminant/moles contaminant free liquid x = mole fraction contaminant liquid 1-x = mole fraction contaminant free liquid

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#### **MOLE RATIOS (CONTINUED)**

- When x and y are small, x ≈ X and y ≈ Y
- For example, when y = 0.03
   Y = y/(1 y) = 0.03/0.97 = 0.0309
- This is normally the case in air pollution control problems

## EQUATIONS 5-6 TO 5-10: MATERIAL BALANCES

(Eq. 5-6) Total mole balance  $G_{m1}+L_{m2}=G_{m2}+L_{m1}$ 

- (Eq. 5-7) Contaminant mole balance  $G_{m1}Y_1 + L_{m2}X_2 = G_{m2}Y_2 + L_{m1}X_1$ 
  - Dilute solutions  $G_{m1} = G_{m2} = G_m \quad and \quad L_{m1} = L_{m2} = L_m$ 
    - Rearranging

(Eq. 5-10)

(Eq. 5-8)

(Eq. 5-9)

$$\begin{split} G_{m}(Y_{1}-Y_{2}) &= L_{m}(X_{1}-X_{2}) \\ H_{m}(X_{1}-X_{2}) & \text{The equation of a straight} \\ & \text{line on a Y-X diagram,} \\ Y_{1}-Y_{2} &= \frac{L_{m}}{G_{m}}(X_{1}-X_{2}) & \text{slope = } L_{m}/G_{m} \end{split}$$

# FIGURE 5-19. DIAGRAM SHOWING THE EQUILIBRIUM AND OPERATING LINES



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#### FIGURE 5-20. LIQUID-TO-GAS RATIO



X, mole fraction of solute in liquid phase

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#### PROBLEM 5-2

- Calculate (L<sub>m</sub>/G<sub>m</sub>)<sub>min</sub> for the removal of 90% of the NH<sub>3</sub> from a 85.0 m<sup>3</sup>/min (3000 ACFM) feed gas containing 3% NH<sub>3</sub> and 97% air.
- The inlet liquid is pure H<sub>2</sub>O and the temperature and pressure are 293 K and 1 atm, respectively.

Use the results from Problem 5-1.

#### **PROBLEM 5-2: SOLUTION**

#### Step 1. Sketch and label a drawing of the system.



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Step 2. At the minimum, liquid rates  $Y_1$  and  $X_1$  will be in equilibrium. The liquid will be saturated with  $NH_3$ .

 $Y_1 = H_y X_1$  (Remember that  $y_1 = Y_1$  and  $x_1 = X_1$  for dilute systems)  $H_y = 0.768 \frac{\text{mole fraction NH}_3 \text{in air}}{\text{mole fraction NH}_3 \text{in water}}$  (from Problem 5-1)  $0.03 = 0.768 X_1$  $X_1 = 0.0391$  mole fraction

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Continued...

Step 3. The minimum liquid-to-gas ratio from Equation 5-9:

$$\mathbf{Y}_1 - \mathbf{Y}_2 = \frac{\mathbf{L}_m}{\mathbf{G}_m} \left( \mathbf{X}_1 - \mathbf{X}_2 \right)$$

$$\left(\frac{\mathbf{L}_{\mathbf{m}}}{\mathbf{G}_{\mathbf{m}}}\right)_{\mathbf{min}} = \frac{\mathbf{Y}_{1} - \mathbf{Y}_{2}}{\mathbf{X}_{1} - \mathbf{X}_{2}}$$

$$\left(\frac{\mathbf{L}_{m}}{\mathbf{G}_{m}}\right)_{\min} = \frac{0.03 - 0.003}{0.0391 - 0}$$

 $(L_m/G_m)_{min} = 0.6905 \text{ gmol water/gmol air}$ 

Continued...

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Step 4. Convert m<sup>3</sup> of air to gram moles, then compute the minimum required liquid flow rate. At 293 K and 1 atm, the molar volume of an ideal gas (air) can be calculated as follows:

PV = nRT

$$\frac{V}{n} = \frac{RT}{p} = \frac{\left(0.08206 \frac{L*atm}{gmol*K}\right) 293K}{(1 atm \left(1000 \frac{L}{m^3}\right)} = 0.024 \frac{m^3}{gmol}$$

$$G_{m} = 85.0 \frac{m^{3}}{min} \left( \frac{gmol}{0.024 m^{3}} \right) = 3,542 \frac{gmol air}{min}$$

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Continued...

$$\begin{aligned} (L_{m})_{min} &= \left(0.6905 \frac{gmol H_{2} \odot}{gmol air}\right) *G_{m} \\ (L_{m})_{min} &= (0.6905) * (3542) = 2,446 \frac{gmol H_{2} \odot}{min} \\ L_{min} &= \left(2,446 \frac{gmol H_{2} \odot}{min}\right) * \left(18 \frac{gH_{2} \odot}{gmol H_{2} \odot}\right) = 44,024 \frac{gH_{2} \odot}{min} \\ L_{min} &= \left(44,024 \frac{gH_{2} \odot}{min}\right) * \left(\frac{11b}{453.6g}\right) * \left(\frac{1gal}{8.341b H_{2} \odot}\right) \\ L_{min} &= 11.6 \frac{gal H_{2} \odot}{min} \end{aligned}$$

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Continued...

Step 4. Figure 5-22 illustrates the graphical solution to the problem. Multiply the slope of the minimum line by 1.5 to get the slope of the actual operating line.

- L = 1.5 L<sub>min</sub> = 1.5(2447g mol/min) = 3670g mol/min, or
- L = 1.5(44,227 g/min) = 66340 g/min, or
- L = 1.5(11.7gal/min) = 17.6gal/min



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Continued...

#### **EQUATION 5-11: ABSORPTION FACTOR**

 $AF = \frac{L_2}{mG_1}$ 

#### Where:

- **AF** = **Absorption** factor
- L<sub>2</sub> = Molar flow rate of liquid
- m = Slope of the equilibrium line on a mole fraction basis = H<sub>v</sub>
- $G_1 = Molar$  flow rate of gas

#### PACKED TOWER ABSORBER DIAMETER

- Gas velocity at which liquid droplets become entrained in the exiting gas stream is the main parameter that determines the diameter of a packed column
- Loading point is reached when the liquid flowing down over the packing begins to be held in the void spaces between the packing
- Flooding occurs when the liquid forms a layer over the top of the packing material where no more liquid can flow down

# FIGURE 5-23. GENERALIZED SHERWOOD FLOODING AND PRESSURE DROP CORRELATION



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#### **EQUATION 5-12**



Where:

- L = Mass velocity of liquid stream, lb/sec·ft<sup>2</sup>
- **G** = Mass velocity of gas stream, lb/sec·ft<sup>2</sup>
- $\rho_g = Gas density, lb/ft^3$
- $\rho_1$  = Liquid density, lb/ft<sup>3</sup>



#### **EQUATION 5-13**

**Ordinate** = **G**\* = 
$$\left(\frac{\epsilon \rho_{g} \rho_{1} \mathbf{g}_{c}}{\mathbf{F}_{p} \phi \boldsymbol{\mu}^{0.2}}\right)^{0.5}$$

#### Where:

3

 $\rho_{g}$ 

 $\rho_l$ 

g

Fp

ø

 $\mu_l$ 

- $G^*$  = gas mass velocity at flooding,  $lb_m/ft^2$ ·sec
  - = Ordinate of Sherwood Correlation (Figure 5-23)
    - = Density of gas, lb<sub>m</sub>/ft<sup>3</sup>
    - = Density of liquid, lb<sub>m</sub>/ft<sup>3</sup>
    - = Gravitational acceleration (32.2  $lb_m \cdot ft/lb_f \cdot sec^2$ )
    - = Packing factor (Table 5-3), dimensionless
    - = specific gravity of absorbent, dimensionless
    - = Viscosity of liquid, cP



#### EQUATIONS 5-14 THROUGH 5-17

**Operate at some fraction of G\*** 

$$\mathbf{G}_{\mathrm{op}} = \mathbf{G}^* \mathbf{f}$$

Where:

 $G_{op}$  = Actual gas flow rate per unit area ( $lb_m/ft^2 \cdot sec$ )

f = Coefficient, typically 0.75

Step 5. Calculate the packed bed diameter based on the actual gas mass velocity.

 $TowerArea = \frac{Total volumetric gas flow rate}{Gas flow rate per unit area}$ 

Tower Diameter =  $\left[\frac{4*\text{TowerArea}}{\pi}\right]^{0.5}$ 

Tower Diameter = 1.13 (Tower Area)<sup>0.5</sup>

#### TABLE 5-2. PACKING DATA

Packing	Size, (in.)	Weight, (lb <sub>m</sub> /ft³)	Surface Area, (ft²/ft³)	Void Fraction, (%)	Packing Factor, F <sub>p</sub> (ft²/ft³)
Raschig™ Rings (Ceramic.	1.0 1.5 2.0	44 42 38	58 36 28	70 72 75	155 95 65
Porcelain)	3.0	34	19	77	37
Raschig™ Rings (Steel)	1.0x1/32 2.0x1/16	40 38	63 31	92 92	115 57
Berl™ Saddles (Ceramic Porcelain)	1.0 2.0	48 38	79 32	68 75	110 45
Intalox™ Saddles (Ceramic)	1.0 2.0	44 42	78 36	77 79	98 40

Note: Data for guide purposes only. Packing factor for the specific application should be obtained from the manufacturer or from other sources.

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#### TABLE 5-2. PACKING DATA (CONTINUED)

Packing	Size, (in.)	Weight, (lb <sub>m</sub> /ft <sup>3</sup> )	Surface Area, (ft²/ft³)	Void Fraction, (%)	Packing Factor, F <sub>p</sub> (ft²/ft³)
Intalox™	1.0	44	78	77	98
Saddles (Ceramic)	2.0	42	36	79	40
Intalox <sup>TM</sup>	1.0	6.0	63	91	30
Saddles	2.0	3.8	33	93	20
(Plastic)	3.0	3.3	27	94	15
Pall™Rings	1.0	5.5	63	90	52
(Plastic)	2.0	4.5	31	92	25
Pall™Rings (Metal)	1.5 x 0.03	24	39	95	28
Tellerette™	1.0	7.5	55	87	40
	2.0	3.9	38	93	20
	3.0	5.0	30	92	15

Note: Data for guide purposes only. Packing factor for the specific application should be obtained from the manufacturer or from other sources.

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#### 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<sup>™</sup> saddles.

Continued...

Step 1. Calculate the value of the abscissa in Figure 5-23.

G <sub>m</sub>	= 3,540 g mole/min
L	= 3,670 g mole/min

from Problem 5-2

Convert gas molar flow to a mass flow, assuming molecular weight of the gas to be 29 g/g mole (air).

G = (3,540 g moles/min)(29 g/g mole)= 102,700 g/min (1 lb<sub>m</sub>/454 g)

 $= 226 \text{ lb}_{\text{m}}/\text{min}$ 

Continued...


# ADSORPTION PROBLEM 5-3: SOLUTION (CONTINUED)

Step 1. (Continued) :

L = (3,670 g mole/min)(18 g/g mole)=  $(66,060 \text{ g/min})(1 \text{ lb}_m/454 \text{ g})$ =  $146 \text{ lb}_m/\text{min}$ 

The densities of air and water at 293K are:  $\rho_1 = 62.4 \text{ lb}_m/\text{ft}^3$  $\rho_g = 0.074 \text{ lb}_m/\text{ft}^3$ 

Calculate the abscissa using Equation 5-11.

Abscissa=
$$\left(\frac{\mathbf{L}}{\mathbf{G}}\right)\left(\frac{\mathbf{\rho}_{g}}{\mathbf{\rho}_{1}}\right)^{0.5}$$
  
= $\left(\frac{146}{226}\right)\left(\frac{0.074}{62.4}\right)^{0.5}$ = 0.0222

# **PROBLEM 5-3 SOLUTION: (CONTINUED)**

**Step 2. Determine the ordinate in Figure 5-25** 

At an abscissa of 0.0222, the ordinate is 0.1.



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# **PROBLEM 5-3: SOLUTION (CONTINUED)**

Step 3. Calculate the gas flow rate per unit area at flooding.

$$\mathbf{G}^{*} = \left(\frac{\boldsymbol{\epsilon} \boldsymbol{\rho}_{\mathrm{g}} \boldsymbol{\rho}_{\mathrm{l}} \mathbf{g}_{\mathrm{c}}}{\mathbf{F}_{\mathrm{p}} \boldsymbol{\phi} \boldsymbol{\mu}^{0.2}}\right)^{0.5}$$

For water,  $\phi = 1.0$  and the liquid viscosity equals 1 cP.

From Table 5-2, for 2-inch Intalox<sup>TM</sup> saddles:  $F_p = 40 \text{ ft}^2/\text{ft}^3$  $g_c = 32.2 \text{ ft } \text{lb}_m/\text{lb}_f \cdot \sec^2$ 

$$G^{*} = \left[\frac{\left(0.3\right)\left(0.074\frac{lb_{m}}{ft^{3}}\right)\left(62.4\frac{lb_{m}}{ft^{3}}\right)\left(32.2\frac{ft*lb_{m}}{lb_{f}*s^{2}}\right)}{\left(40\frac{ft^{2}}{ft^{3}}\right)\left(1.0\right)\left(1cP\right)^{0.2}}\right]^{0.5} = 1.056$$

 $G^* = 1.056 \text{ lb}_m/\text{ft}^{2*}\text{s}$  at flooding

# **PROBLEM 5-3: SOLUTION (CONTINUED)**

Step 4. Calculate the actual gas flow rate per unit area.

 $G_{op} = 0.75 (0.61) = 0.457 \text{ lb}_{\text{m}}/\text{ft}^2 \text{ sec}$ 

Step 5. Calculate the tower diameter.

Tower Area = gas flow rate/ $G_{op}$ 

Tower Area = 
$$\frac{\left(226\frac{\text{lb}_{m}}{\text{min}}\right)\left(\frac{1\text{min}}{60\text{s}}\right)}{\left(0.792\frac{\text{lb}_{m}}{\text{ft}^{2} * \text{s}}\right)} = 4.76\text{ft}^{2}$$

Tower Diameter= $1.13 * A^{0.5} = 1.13 * (4.76 \text{ ft}^2)^{0.5} = 2.46 \text{ ft}$ 

### **PROBLEM 5-3: SOLUTION (CONTINUED)**

Pressure Drop: Use Figure 5-25 once again. The new value of the ordinate based on the actual mass flow rate is:

$$(\varepsilon_{\text{new}}/\varepsilon_{\text{old}}) = (G_{\text{act}}/G_{\text{flood}})^2$$

 $\varepsilon_{\text{new}} = 0.1(0.457/0.61)^2 = 0.056$ 

Use the original abscissa value of 0.0222 and estimate: ΔP ≈ 1 in W.C./ft packed height

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# PACKED TOWER ABSORBER HEIGHT

- Refers to the height of packing material needed to accomplish the required contaminant removal
- The more difficult the separation the larger the required packed height



## **EQUATION 5-18**

$$Z = \frac{G}{K_g a} \int_{Y_2}^{Y_1} \frac{dY}{(1-Y)(Y-Y^*)}$$

Where:  $K_g = Overall gas film coefficient (lb mole/sec•ft<sup>2</sup>)$ Z = Height of packing, ft

- G = Molar flow rate of gas per unit cross-sectional area (lb mole/ft<sup>2</sup>•sec)
- a = Interfacial contact area per unit packing volume, ft<sup>2</sup>/ft<sup>3</sup>
- Y = Mole ratio of contaminant to contaminant-free gas
- Y\* = Mole ratio of contaminant to contaminant-free gas at equilibrium

# EQUATIONS 5-19 AND 5-20

#### Z = (HTU)(NTU)

Where:

HTU = Height of a transfer unit, ft

NTU = Number of transfer units

$$Z = N_{OG} H_{OG} = N_{OL} H_{OL}$$

N<sub>og</sub> = Number of transfer units based on overall gas film coefficient

H<sub>OG</sub> = Height of a transfer unit based on overall gas film coefficient, ft

N<sub>OL</sub> = Number of transfer units based on overall liquid film coefficient

H<sub>OL</sub> = Height of a transfer unit based on overall liquid film coefficient, ft

# FIGURE 5-24. HEIGHT OF A TRANSFER UNIT, AMMONIA AND WATER SYSTEM



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# EQUATION 5-21: NUMBER OF TRANSFER UNITS

Lm

$$N_{OG} = \frac{\ln \left[ \frac{(Y_1 - m X_2)}{(Y_2 - m X_2)} \left( 1 - \frac{m G_m}{L_m} \right) + \left( \frac{m G_m}{L_m} \right) \right]}{1 - \frac{m G_m}{L_m}}$$

Where:

- Y<sub>1</sub> = Mole ratio of contaminant to contaminant-free gas entering the absorber
- m = Slope of the equilibrium line (= Henry's constant)
- X<sub>2</sub> = Mole ratio of contaminant to contaminant-free liquid entering the absorber in the liquid
- Y<sub>2</sub> = Mole ratio of contaminant to contaminant-free gas exiting the absorber
- **G**<sub>m</sub> = Molar flow rate of gas, lb mole/hr
- **L**<sub>m</sub> = Molar flow rate of liquid, lb mole/hr

# EQUATION 5-22: NUMBER OF TRANSFER UNITS

- Simplification when the slope of the equilibrium line approaches zero (m = 0)
- an irreversible chemical reaction occurs
- the contaminant is extremely soluble

$$N_{OG} = \ln\left(\frac{Y_1}{Y_2}\right)$$

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## FIGURE 5-25. COLBURN DIAGRAM



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#### **PROBLEM 5-4**

Continue Problems 5-1 through 5-3 by estimating the required packed height.

In order to calculate HOG, use the correlation for 1.5-inch Raschig rings in Figure 5-24 as a substitute for the 2-inch Intalox saddles specified in the earlier examples.

# PROBLEM 5-4 (CONTINUED)

Use data from previous problems:

m = 0.768 mole ratio  $NH_3$ in air/mole ratio  $NH_3$ in water

 $G = 226 \text{ lb}_{m}/\text{min}$ 

 $L = 146 \text{ lb}_{m}/\text{min}$ 

X2= 0 (no recirculated liquid)

Y1= 0.03

Y2= 0.003

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#### **PROBLEM 5-4: SOLUTION**

#### **Step 1. Compute the NOG from Equation 5-21.**

 $G_m = (226 \text{ lb}_m/\text{min})(\text{lb mole}/29 \text{ lb}_m) = 7.79 \text{ lb mole}/\text{min}$  $L_m = (146 \text{lb}_m/\text{min})(\text{lb mole}/18 \text{ lb}_m) = 8.11 \text{ lb mole}/\text{min}$ 



 $N_{OG} = 4.65$ 

#### **PROBLEM 5-4: SOLUTION (CONTINUED)**

Step 3. Obtain  $H_{OG}$  from Figure 5-25 L' = (146lb<sub>m</sub>/min)(60 min/hr)(1/5.84 ft<sup>2</sup>) = 1500 lb<sub>m</sub>/hr ft<sup>2</sup>  $H_{OG}$  = 1.6 ft

Step 4. The total packing height is:  $Z = (H_{OG})(N_{OG})$  = (1.6 ft)(4.65) = 7.44 ftTotal Pressure Drop:  $\Delta P_{tot} = (1 \text{ in. W.C./ft})(7.44 \text{ ft}) \approx 7.44 \text{ in W.C.}$ 

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# TRAY TOWER ABSORBER DIAMETER AND HEIGHT

- Liquid and gas concentrations at the top of the tower are designated X<sub>a</sub> and Y<sub>a</sub>
- Liquid and gas concentrations at the bottom of the tower are designated X<sub>b</sub> and Y<sub>b</sub>
- Trays are numbered from 1 at the top to n at the bottom and gas and liquid concentrations are subscripted according to the tray from which each originates

# FIGURE 5-26. SCHEMATIC DIAGRAM OF A TRAY TOWER ABSORBER



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## **EQUATION 5-23: MINIMUM DIAMETER**

Sized to prevent entrainment of liquid droplets to the tray above when the gas velocity is too large

$$\mathbf{d} = \boldsymbol{\psi} (\mathbf{Q} \sqrt{\boldsymbol{\rho}_{\mathrm{g}}})^{0.5}$$

Where:

 $\Psi$  = Empirical correlation, ft<sup>0.25</sup>·min<sup>0.5</sup>/lb<sup>0.25</sup>

Q = Volumetric gas flow rate, ft<sup>3</sup>/min

 $\rho_g = \text{Gas density}, \text{lb}_m/\text{ft}^3$ 

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# TABLE 5-3. TRAY SPACING PARAMETERS, $\Psi$

Tray	Metric <sup>1</sup>	English <sup>2</sup>
Bubble Cap	0.0162	0.1386
Sieve	0.0140	0.1198
Valve	0.0125	0.1069

Note:

- 1. <u>Metric (expressed in m<sup>0.25</sup> . hr<sup>0.5</sup>/kg<sup>0.25</sup>)</u> for use with Q (expressed in m<sup>3</sup>/hr) and  $r_q$ (expressed in kg/m<sup>3</sup>).
- English (expressed in ft<sup>0.25</sup>min<sup>0.5</sup>/lb<sup>0.25</sup>) for use with Q in ACFM and r<sub>g</sub> expressed in lb/ft<sup>3</sup>

Directly applicable when tray spacing is 24 inches and liquid specific gravity is 1.05. For other values a correction factor must be used.

# FIGURE 5-27. TRAY SPACING CORRECTION FACTOR



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# **TRAY SPACING**

- Trays are spaced far enough apart to allow the gas and liquid phases to separate before reaching the plate above and for easy maintenance and cleaning
- Trays are normally spaced 45 to 70 cm (18 to 18 inches) apart

# 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 1030 kg/m<sup>3</sup>

## **PROBLEM 5-5: SOLUTION**

From Problem 5-2: Gas flow rate = Q = 85 m<sup>3</sup>/min Density =  $\rho_g = \left(\frac{\text{gm mole}}{0.024 \text{ m}^3}\right) \left(\frac{29 \text{ gm}}{\text{gm mole}}\right) = 1.21 \text{kg/m}^3$ 

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<sup>3</sup>/hr:

 $Q = (85 \text{ m}^3/\text{min})(60 \text{ min/hr}) = 5,100 \text{ m}^3/\text{hr}$ 

Continued...

# **PROBLEM 5-5: SOLUTION (CONTINUED)**

**Step 1. Substitute these values into Equation 5-22 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 m

Step 2. Correct the minimum diameter for a tray spacing of 0.53 m. From Figure 5-27, read a correction factor of 1.06.

Therefore, the minimum diameter is d = 1.21 (1.06) = 1.28 m (4.20 ft)

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# FIGURE 5-28. GRAPHIC DETERMINATION OF THE NUMBER OF IDEAL PLATES



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#### **EQUATION 5-24: NUMBER OF IDEAL PLATES**

$$N_{OG} = \frac{\ln \left[ \frac{(Y_1 - m X_2)}{(Y_2 - m X_2)} \left( 1 - \frac{m G_m}{L_m} \right) + \left( \frac{m G_m}{L_m} \right) \right]}{\ln \left( \frac{L_m}{m G_m} \right)}$$

Equation is applicable when both the operating and equilibrium lines are straight, a situation often encountered in air pollution control problems.

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# **THREE TYPES OF EFFICIENCIES**

- The overall efficiency
  - Is applied equally to all trays within the column
  - The ratio of the number of theoretical to the actual number of trays
- Other two efficiencies
  - The Murphree efficiency and local efficiency are tray specific
  - Estimation is complex and of questionable reliability

# PROBLEM 5-6

- Calculate the number of theoretical trays required for the NH<sub>3</sub>absorber in Problem 5-5.
- Estimate the total height of the absorber if the trays are spaced at 0.53m intervals, and assume an overall tray efficiency of 40%.

#### **PROBLEM 5-6: SOLUTION**

From Problem 5-5 and the previous examples, the following data are obtained.

 $Y_1 = 0.03$   $Y_2 = 0.003$   $X_2 = 0.0Lm = 3680 \text{ g mole } H_2O/\text{min}$   $G_m = 3540 \text{ g mole air/min}$  $m = H_v = 0.772$ 

#### Continued...

# **PROBLEM 5-6 SOLUTION (CONTINUED)**

Step 1. The number of theoretical plates from Equation 5-23 is:

$$N_{OG} = \frac{\ln\left[\frac{(Y_1 - m X_2)}{(Y_2 - m X_2)}\left(1 - \frac{m G_m}{L_m}\right) + \left(\frac{m G_m}{L_m}\right)\right]}{\ln\left(\frac{L_m}{m G_m}\right)}$$

$$N_{OG} = \frac{\ln\left[\frac{(0.03 - 0)}{(0.003 - 0)}\left(1 - \frac{(0.772)(3540)}{3680}\right) + \left(\frac{(0.772)(3540)}{3680}\right)\right]}{\ln\left(\frac{3680}{(0.772)(3540)}\right)}$$

N<sub>OG</sub> = 4.1 theoretical plates

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#### Continued...

# **PROBLEM 5-6 SOLUTION (CONTINUED)**

Step 2. Assuming that the overall plate efficiency is 40%, the actual number of trays is:

Actual plates = 4.1/0.40 ≈ 10.3 trays

**Step 3. The height of the tower is given by:** 

 $Z = N_p x$  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 = 10.3 trays (0.53 m/tray) + 0.53 m

Z = 6.0 meters = 17.2 ft

# TABLE 5-4. GAS VELOCITIES THROUGH MISTELIMINATORS1

Mist Eliminator Type	Orientation	Maximum Gas Velocity, ft/sec
Zigzag <sup>2</sup>	Horizontal	15 – 20
Zigzag <sup>2</sup>	Vertical	12 – 15
Mesh Pad	Horizontal	15 – 23
Mesh Pad	Vertical	10 – 15
Woven Pad <sup>3</sup>	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

# EQUATION 5-25: MIST ELIMINATOR ALLOWABLE VELOCITY

Velocity = 
$$\frac{\text{Gas flow rate, ft}^3/\text{min.}}{\text{Mist Eliminator area, ft}^2} \times \left(\frac{\text{min.}}{60 \text{ sec.}}\right)$$



# **ALKALI REQUIREMENTS**

- Absorption systems may require an alkali addition system if the gas stream is acidic
- Sulfur dioxide (SO<sub>2</sub>), hydrogen chloride (HCl), and hydrogen fluoride (HF) are the most common acid gases
- Calcium hydroxide is the most common alkali material used to neutralize acid gases

Reaction 5-1  $-SO_2 + Ca(OH)_2 + 0.5 O_2 \rightarrow (CaSO_4) + H_2O$ Reaction 5-2  $-2HCI + Ca(OH)_2 \rightarrow 2Ca^+ + 2CI^- + 2H_2O$ Reaction 5-3  $-2HF + Ca(OH)_2 \rightarrow 2Ca^+ + 2F^- + 2H_2O$ 

# PROBLEM 5-7

- Calculate the amount of calcium hydroxide (lime) needed to neutralize the HCl absorbed from a gas stream having 50 ppm HCland a flow rate of 10,000 SCFM.
- Assume an HCl removal efficiency of 95%.
### **PROBLEM 5-7: SOLUTION**

$$HCl = 10,000 \text{ SCFM}\left(\frac{\text{lb mole}}{385.4 \text{ SCF}}\right) \left(\frac{0.00005 \text{ lb mole HCl}}{\text{lb mole total}}\right) \left(\frac{95\% \text{ Efficiency}}{100\%}\right)$$

HCl = 0.00123 lb mole HCl/min

$$Ca(OH)_{2} req' d = \left(\frac{1 lb mole Ca(OH)_{2}}{2 lb mole HCl}\right) \left(\frac{0.00123 lb mole HCl}{min}\right)$$

# $=\frac{0.00061\text{ fb} \text{ mole} \text{Ca(OH)}_2}{\text{min}}$

Ca(OH)<sub>2</sub> req'd = 0.00062 lb mole/min (74 lb/lb mole)

= 0.0455 lb/min

= 2.73 lb/hr

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- This section will introduce:
- Standard Absorbers Instrumentation
- Biofiltration Systems Instrumentation



# MOST COMMON PROBLEMS AFFECTING ABSORBERS

- Inadequate recirculation liquid flow
- Poor gas-liquid contact
- Inadequate alkali feed rates to neutralize dissolved acids
- Excessive liquid temperatures
- Corrosion

# FIGURE 5-29. PERFORMANCE MONITORING INSTRUMENTS



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- Mist Eliminator Static Pressure Drop
- Excellent indicator of the physical condition of the mist eliminator
- The pressure drops across mist eliminators usually vary from 0.5 to 2 in. W.C. (0.1 to 0.5 kPa)
- $\Delta P$  higher than baseline  $\rightarrow$  Solids buildup
- $\Delta P$  lower than baseline  $\rightarrow$  Mist eliminator damage

- Liquid Flow Rate
- Large decreases can result in inadequate gas-liquid contact
- Large increases may result in flooding
- Instruments used to monitor liquid flow rates
  - Magnetic flow meters
  - Ultrasonic flow meters
  - Orifice meters
  - Swinging vane meters
- Indirect indicators
  - Change in recirculation pump discharge pressure
  - Change in spray nozzle header supply pressure



- Outlet Gas Temperature
  - Should be within 5°F to 10°F (2.7°C to 5.5°C) above the adiabatic saturation temperature
  - Larger deviation from adiabatic gas temperature may indicate significant gas-liquid maldistribution



## FIGURE 5-30. PSYCHROMETRIC CHART

#### Used to evaluate adiabatic saturation temperature



# CONDITIONS THAT COULD CREATE GAS-LIQUID MALDISTRIBUTION

- 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
  - Channeling due to plugging in the bed
  - Collapse of one or more beds

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# CONDITIONS THAT COULD CREATE GAS-LIQUID MALDISTRIBUTION

- Tray Towers
  - Sloped, bowed, or warped trays
  - Gas short-circuiting through incompletely filled liquid downcomers
  - Sloped overflow weirs on one or more trays
  - Solids accumulation in localized portions of the trays
- Venturis
  - Inadequate distribution of liquid across the inlet to the throat
  - Gas maldistribution entering the converging area of the throat



# CONDITIONS THAT COULD CREATE GAS-LIQUID MALDISTRIBUTION

- Ejectors
  - Inadequate distribution of liquid across the ejector inlet
  - Erosion of the ejector nozzle



- Column Static Pressure Drop
- ΔP above baseline may indicate plugging in packed beds or impingement trays or increased process gas flow rate
- ΔP below baseline may indicate reduction in process gas flow rate or gas bypassing through downcomer in tray column or collapsed bed in packed columns
- Change in gas flow rate can be evaluated by checking the process operating rate and the fan motor current

- Recirculation Liquid pH
- pH levels above 9 indicate the potential for precipitation of calcium and magnesium compounds
- pH levels below 5 indicate that insufficient alkali is being added to neutralize the acidic gases and increase the risk of corrosion

# **BIOFILTRATION SYSTEMS**

- Inlet Gas Temperature
- Inlet temperature significantly above 105°F (41°C) may be harmful to microorganisms and indicate a problem in the humidification system
- Inlet Gas Relative Humidity
- Relative humidity in excess of 95% is needed to avoid drying the bed and killing the microorganisms
- Recirculated Liquid pH
- The pH should be in the range of 6 to 8



# FIGURE 5-31. FLOWCHART OF A TYPICAL BIOFILTRATION OXIDATION SYSTEM



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### **SUMMARY**

This chapter covered the following topics:

- Various types and components of absorbers.
- Operating principles that influence the efficiency of absorbers.
- Capability and sizing parameters of an absorber system.
- Instrumentation requirements for an absorber system.

#### CHAPTER 6 OXIDATION SYSTEMS

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#### **CHAPTER 6**

#### **OXIDATION SYSTEMS**



### **OVERVIEW OF OXIDATION PROCESSES**

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



#### **RECUPERATIVE AND REGENERATIVE**

- Terms referring to the type of heat exchanger used in the oxidation system.
- Recuperative: Heat is transferred through a metal surface in a tubular or plate heat exchanger.
- Regenerative: Heat is transferred using two or more packed beds that alternately store and release heat.

## **LEARNING OBJECTIVES**

At the end of this training, you will be able to:

- Distinguish between the various types of oxidation systems.
- Identify the principles of operation for oxidation systems.
- Determine the factors that influence the capability and sizing of an oxidation system.
- Identify the operating parameters that need to be evaluated in an oxidation system.

## **TYPES AND COMPONENTS OF OXIDIZERS**

- This section will introduce:
  - High Temperature, Gas Phase Oxidation
    Systems
  - Catalytic Oxidation Systems



# FIGURE 6-1. THE EFFECTS OF TIME AND TEMPERATURE



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# FIGURE 6-2. THERMAL OXIDIZER USING MULTIJET BURNERS AND BAFFLES6



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### **RECUPERATIVE THERMAL OXIDIZERS**

- A refractory-lined chamber equipped with one or more gas or oil-fired burners
- A contaminant-laden gas stream is mixed with the hot combustion gases from the burner flame
- The feed gas is preheated using the hot oxidizer product gas
- Heat recovery in range of 40% to 65%

# FIGURE 6-3. DOUBLE PASS RECUPERATIVE HEAT EXCHANGER



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# FIGURE 6-4. FLOWCHART OF A RECUPERATIVE HEAT EXCHANGER



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- Temperature monitors
  - Oxidizer Inlet
  - Oxidizer outlet
  - Exhaust to atmosphere
- Composition monitor
  - Contaminated feed gas <25% of LEL</li>
- Static pressure
  - Measure flow resistance through recuperator (not always used)

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## **REGENERATIVE THERMAL OXIDIZERS**

- Much higher heat recovery efficiencies than recuperative units, as high as 95%
- Inlet gas stream is passed through a large packed bed containing preheated ceramic packing
- Product gas preheats a second bed containing ceramic packing
- Flow directions are switched periodically
- At least two beds are required, three beds are commonly used

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# FIGURE 6-5. REGENERATIVE THERMAL OXIDIZER





## FIGURE 6-6. FLAMELESS THERMAL OXIDIZER



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# PROCESS BOILERS USED FOR THERMAL OXIDATION

- Most plants equipped with one or more process boilers
- Combustion chamber temperatures in excess of 1800°F
- Flue gas residence times in excess of 1 to 2 seconds
- Oxidizer feed gas should be only small fraction of normal boiler flow
- Operating schedules of boiler and oxidizer feed gas must match

### FIGURE 6-7. OIL-FIRED BURNER



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### **FLARES USED FOR THERMAL OXIDATION**

- Used for the destruction of intermittent or emergency emissions of combustible gases
- Feed composition may exceed UEL
- Have destruction efficiencies exceeding 98%
- Can be elevated or at ground level

# SAFETY AND OPERATIONAL PROBLEMS OF FLARES

- Thermal radiation
- Light
- Noise
- Smoke
- Energy consumption

# FIGURE 6-8. STEAM-ASSISTED ELEVATED FLARE SYSTEM



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# FIGURE 6-9. SMOKELESS FLARE TIP OF AN ELEVATED FLARE



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#### FIGURE 6-10. ENCLOSED GROUND FLARE



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### **CATALYTIC OXIDATION SYSTEMS**

- A waste gas is passed through a catalyst bed, which causes the oxidation reactions to proceed at a much lower temperature than in gas phase thermal oxidation
- Operating temperature range of 600°F to 850°F
- Designed with either regenerative or recuperative heat exchangers

#### **ADVANTAGES AND DISADVANTAGES**

- Advantages
  - Lower temperatures

Reduced supplemental fuel requirements
(in some cases may only be required during start-up)

- Disadvantages
  - Cost of the catalyst
  - Performance problems related to physical and chemical deterioration of catalyst activity

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# FIGURE 6-11. CUTAWAY OF A CATALYTIC OXIDIZER



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#### FIGURE 6-12. CATALYST BED HONEYCOMBS



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# FIGURE 6-13. CROSS-SECTION OF A CATALYST ON A HONEYCOMB





# FOULING (OR MASKING)

- Reduction of catalyst activity through blockage of access to active sites, may be reversible
  - particulate matter
  - oil droplets
  - sulfur compounds
  - halogens

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### **COMMON TYPES OF CATALYST MATERIALS**

- Noble Metals
  - Platinum
  - Palladium
  - Rhodium
- Metal Oxides
  - Chromium oxide
  - Magnesium oxide
  - Cobalt oxide
- Active catalyst typically supported on inert material such as alumina
- Metal oxides used when halogens are present



## **CATALYST POISONS**

- Fast Acting Poisons
  - Phosphorus
  - Bismuth
  - Arsenic
  - Antimony
  - Lead
  - Mercury
- Slow Acting Poisons
  - Iron
  - Lead
  - Tin

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- Silicones
- Often irreversible

## **CATALYST SERVICE LIFE**

- All catalysts deteriorate with normal use
- High temperatures can accelerate catalyst deactivation
- The average service life is 2 to 5 years
- Lower operating temperatures generally result in a longer service life



### **OPERATING PRINCIPLES**

- This section will introduce:
  - Operating principles of high temperature, gas phase oxidation systems and catalytic oxidation systems



#### **COMBUSTION PRODUCTS AND GAS VOLUMES**

- In all high temperature combustion processes, a complex set chemical reactions occur simultaneously
- Objective is to oxidize all carbon to CO<sub>2</sub>, hydrogen to H<sub>2</sub>O, and sulfur to SO<sub>2</sub>
- Represent the set of simultaneous reactions by the single generalized reaction

**Reaction 6-1** 

$$C_{x}H_{y}S_{z}O_{w} + \left(x + \frac{y}{4} + z - \frac{w}{2}\right)O_{2} \longrightarrow xCO_{2} + \left(\frac{y}{2}\right)H_{2}O + zSO_{2}$$

### MINOR COMPONENTS IN WASTE GAS

- Sulfur
- $\geq$  98% converted to SO<sub>2</sub> (as shown)
- Small amount of SO<sub>3</sub> may be formed
- Chlorine –converted to HCl
- Fluorine –converted to HF
- Nitrogen (in waste gas) –may be converted to N<sub>2</sub>, NO, or NO<sub>2</sub>
- Cl, F, N (in waste gas) normally neglected in material balance calculations

### **COMPOSITION OF AIR**

- Oxygen is almost always supplied by air
- Air composition: 21% O<sub>2</sub>

79% N<sub>2</sub>

 Neglect minor components in material balance calculations

### TABLE 6-1: AUTO IGNITION TEMPERATURES

 Most oxidizers operate at temperatures 200°F to 300°F above the auto-ignition temperature of the most difficult to oxidize compound

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		

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#### **TURBULENCE**

- Mixing of the burner fuel with air is needed to ensure complete combustion
- The organic-containing waste gases must be thoroughly mixed with the burner combustion gases



#### **COMBUSTION AIR REQUIREMENTS**

- To achieve complete combustion of the fuel, a sufficient supply of oxygen must be present in the burner flame to convert all of the carbon present in both the waste gas and supplemental fuel to CO<sub>2</sub>
- As an example, consider that the waste gas contains benzene (C<sub>6</sub>H<sub>6</sub>) and that natural gas (represented by CH<sub>4</sub>) is the supplemental fuel

**Reaction 6-2** 

 $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O_2$ 

#### LEAN AND RICH

- Rich there is insufficient O<sub>2</sub> available for complete oxidation. Partially oxidized products (e.g., CO) will be formed and flame temperature will be reduced
- Lean the amount of O<sub>2</sub> exceeds the amount required for complete oxidation. Residence time and flame temperature will be reduced because of the presence of large amounts of N<sub>2</sub>
- Normal operation –10% to 30% excess air

#### **EQUATION 6-1: RESIDENCE TIME**

Usually between 0.3 and 2 seconds

(Eq. 6-1) 
$$t = \frac{V}{O}$$

Where:

t=Residence time, sec

V=Chamber volume, ft<sup>3</sup>

Q=Actual gas volumetric flow rate at combustion conditions, ft<sup>3</sup>/sec

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## PROBLEM 6-1

- Emissions from a paint baking oven are controlled by a thermal oxidizer. The cylindrical unit has a diameter of 5 feet and a length of 12 feet, with all combustion air supplied by an auxiliary source.
- The exhaust from the oven is 8,000 SCFM. The oxidizer uses 300 SCFM of natural gas and operates at a temperature of 1,400°F.
- What is the residence time in the combustion chamber? Assume that the fuel is 100% methane, and that the burner is operated at 125% of the stoichiometric requirement.

#### **PROBLEM 6-1: SOLUTION**

Draw a box diagram to represent the problem



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#### **PROBLEM 6-1: SOLUTION**

**Step 1. Write the combustion reaction.** 

## $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

Stoichiometric oxygen requirement is two moles of oxygen for every mole of methane

Continued...



Step 2. Calculate the total amount of O<sub>2</sub> at stoichiometric conditions.

$$300 \operatorname{SCFM}\left(\frac{\operatorname{lb}\operatorname{mole}\operatorname{CH}_{4}}{385.4 \operatorname{ft}^{3}}\right) = 0.778 \frac{\operatorname{lb}\operatorname{mole}\operatorname{CH}_{4}}{\operatorname{min}}$$

Stoichiometric  $O_2 = 2 \times (lb mole CH_4)$ 

 $\frac{2 \text{ lb mole } O_2}{\text{ lb mole } CH_4} \left( 0.778 \frac{\text{ lb mole } CH_4}{\text{ min}} \right) = 1.56 \frac{\text{ lb mole } O_2}{\text{ min}}$ 

Continued...

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**Step 4. Calculate the total flue gas flow rate.** 

Total flue gas flow rate =

Exhaust		Products		Nitrogen and
gas heated	+	of combustion	+	excess oxyger
(a)		(b)		(c)

a. Exhaust gas heated = 8,000 SCFM

b. Products of combustion =  $CO_2 + H_2O$ 

$$CO_2 = 1 \frac{\text{lb mole CO}_2}{\text{lb mole CH}_4} \left( 0.778 \frac{\text{lb mole CH}_4}{\text{min}} \right) = 0.778 \text{ lb mole CO}_2/\text{min}$$

 $\mathbf{H}_{2}\mathbf{O} = 2\frac{\mathbf{lb \ mole \ H}_{2}\mathbf{O}}{\mathbf{lb \ mole \ CH}_{4}} \left(0.778\frac{\mathbf{lb \ mole \ CH}_{4}}{\mathbf{min}}\right) = 1.56 \, \mathbf{lb \ mole \ H}_{2}\mathbf{O}$ 

 $CO_2 + H_2O = 2.34 lb mole/min$ 

$$2.34 \frac{\text{lb mole}}{\text{min}} \left( \frac{385.4 \text{ SCF}}{\text{lb mole}} \right) = 902 \text{ SCFM}$$

Continued...

#### c. Nitrogen and excess oxygen = total $N_2 + O_2$ remaining

= 7.34 lb mole N<sub>2</sub>/min + 0.39 lb mole O<sub>2</sub>/min = 7.73 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

 $7.73 \frac{\text{lb mole}}{\text{min}} \left( \frac{385.4 \text{ SCF}}{\text{lb mole}} \right) = 2,980 \text{ SCFM}$ 

Total flue gas = 8,000 SCFM + 902 SCFM + 2,980 SCFM = 11,880 ACFM

#### Step 5. Convert the flue gas flow rate to actual conditions.

TotalACFM = 11,880 SCFM +  $\frac{1,400 + 460^{\circ}R}{528^{\circ}R}$  = 41,850 ACFM

Continued...

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Step 6. Calculate the volume of the combustion chamber. Combustion chamber volume  $= \pi (r)^2 L = 3.14(2.5ft)^2 12ft$  $= 235.5 ft^2$ 

#### Step 7. Calculate the residence time.

 $=\frac{\text{chamber volume}}{\text{volumetric flow rate}} = \frac{235.5 \text{ ft}^3}{41,850 \text{ ACF/min}} = 0.00562 \text{ minutes}$ 

$$= 0.00562 \min\left(\frac{60 \operatorname{sec}}{\min}\right) = 0.337 \operatorname{sec}$$

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### PROBLEM 6-2

- What would be the residence time for the thermal oxidizer described in Problem 6-1— if all of the combustion air were supplied by the waste gas stream?
- Assume that the waste gas stream has an oxygen concentration of 16%, a carbon dioxide concentration of 1%, a moisture concentration of 1%, and a nitrogen concentration of 82% (volume).

#### **PROBLEM 6-2: SOLUTION**

Step 1. Determine if there is sufficient oxygen in the waste gas stream.

$$O_2 = 8,000 \text{ SCFM} \left( \frac{\text{lb mole gas}}{385.4 \text{ SCF}} \right) \left( \frac{0.16 \text{ lb mole } O_2}{\text{lb mole gas}} \right)$$
$$= 3.32 \text{ lb mole } O_2/\text{min}$$

#### Sufficient O<sub>2</sub> is available

Continued...



#### Step 2. Calculate the gas flow rate.

#### Flue gas flow rate

(Waste gas stream - reacted oxygen) + (Products of combustion) Waste gas stream

= 
$$8,000 \operatorname{SCFM}\left(\frac{\operatorname{lb mole}}{385.4 \operatorname{SCF}}\right)$$

= 20.76 lb mole/min

Waste gas stream - reacted O<sub>2</sub>

=(20.76 - 1.56)

= 19.20 lb mole/min

Products of combustion (see Problem 6-1)

 $= (\mathrm{CO}_2 + \mathrm{H}_2\mathrm{O})$ 

= 2.34 lb mole/min

#### Flue gas

= (19.20 lb mole/min + 2.34 lb mole/min)

= 21.54 lb mole/min

Step 3. Calculate total volumetric flow rate.

Vol.Flow rate = 21.54 lb mol/min  $\left(\frac{385.4 \text{ SCF}}{\text{lb mol}}\right) \left(\frac{1,400+459.7^{\circ} \text{ R}}{527.7^{\circ} \text{ R}}\right)$ 

Vol. Flow rate = 29,256 ACFM

Step 4. Calculate residence time.

Residence time  $= \frac{\text{Chamber volume}}{\text{Volumetric flow rate}}$   $= \frac{235.6 \text{ ft}^3}{29,256 \text{ ft}^3/\text{min}} = 0.00805 \text{ minutes}$ 

$$= 0.00805 \min\left(\frac{60 \sec}{\min}\right) = 0.483 \sec^2$$

#### **INLET ORGANIC VAPOR CONCENTRATION**

- Thermal oxidizers and boilers usually operate at organic vapor concentrations below 25% of the LEL
- Because of this the risk of flashback from the oxidizer to the process equipment is minimized



### **CATALYTIC OXIDATION SYSTEMS**

- The temperature is set at a level at which the controlling factor is the rate of mass transfer of oxygen and organic compounds to and from the catalyst surface
- The temperature depends on the compounds present in the waste gas stream and the characteristics of the catalyst bed

# FIGURE 6-14. IMPORTANCE OF TEMPERATURE IN CATALYTIC SYSTEMS



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# FIGURE 6-15. DESTRUCTION EFFICIENCY CURVES 6



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## **CAPABILITY AND SIZING**

- This section will introduce:
  - Destruction Efficiency
  - Acid Gas Emissions


### **DESTRUCTION EFFICIENCY**

- There are two primary means for estimating the organic compound destruction efficiency of oxidation systems:
  - Empirical evaluation based on previous applications
  - Pilot plant tests

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#### **EQUATION 6-2: FUEL REQUIREMENTS**

- The supplemental fuel requirement is one of the main parameters of concern in oxidation systems
- From the 1<sup>st</sup> Law of Thermodynamics:

(Eq. 6-2) Heat in = Heat out + Heat loss



## FIGURE 6-16. HEAT BALANCE AROUND AN OXIDIZER6



#### **AVAILABLE HEAT AND ENTHALPY**

- Available Heat –that portion of the energy liberated by oxidation that is available to heat the waste gas to the outlet temperature.
- Enthalpy –a thermodynamic term that establishes the energy content of a compound or stream relative to reference conditions (for out purposes: H = 0 at T<sub>ref</sub>= 60°F).
- Available heat will be read from a graph while enthalpy will be obtained from tables or estimated from specific heat data.

## FIGURE 6-16B. AVAILABLE HEAT OF COMMON FUELS



Source: North American Combustion Handbook, 1965

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# TABLE 6-2A. ENTHALPIES OF COMBUSTIONGASES, BTU/SCF

Gas Temp (°F)	<b>O</b> <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O	Air
60	0.00	0.00	0.00	0.00	0.00
100	0.74	0.74	0.39	0.36	0.74
200	2.61	2.58	0.94	0.85	2.58
300	4.50	4.42	3.39	2.98	4.42
400	6.43	6.27	5.98	5.14	6.29
500	8.40	8.14	8.69	7.33	8.17
600	10.40	10.01	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

Continued

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# TABLE 6-2A. ENTHALPIES OF COMBUSTION GASES, BTU/SCF (CONTINUED)

Gas Temp (°F)	<b>O</b> <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O	Air
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

Continued

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# TABLE 6-2B. ENTHALPIES OF COMBUSTIONGASES, BTU/LBM

Gas Temp (°F)	0 <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O	Air
60	0.0	0.0	0.0	0.0	0.0
100	8.8	6.4	5.8	17.8	9.6
200	30.9	34.8	29.3	62.7	33.6
300	53.4	59.8	51.3	108.2	57.8
400	76.2	84.9	74.9	154.3	82.1
500	99.5	110.1	99.1	201.0	106.7
600	123.2	135.6	124.5	248.7	131.6
700	147.2	161.4	150.2	297.1	156.7
800	171.7	187.4	176.8	346.4	182.2

Continued



# TABLE 6-2B. ENTHALPIES OF COMBUSTION GASES, BTU/LB<sub>M</sub> (CONTINUED)

Gas Temp (°F)	<b>O</b> <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O	Air
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

# ENTHALPY ESTIMATION FROM SPECIFIC HEAT EQUATIONS 6-3 AND 6-4

(Eq. 6-3)  $H = C_{p}(T - T_{o})$ Where: H = enthalpy (Btu/lb<sub>m</sub>) C<sub>p</sub> = mean specific heat between T and T<sub>o</sub> (Btu/lb<sub>m</sub>°F) T = temperature of the component (°F)  $T_{o}$  = reference temperature (°F) (Eq. 6-4)  $\Delta H = C_{p2}(T_2 - T_0) - C_{p1}(T_1 - T_0)$ Where: ΔH = change in enthalpy (Btu)  $C_{p2}$  = mean specific heat between  $T_o$  and  $T_2$ 

 $C_{p1}$  = mean specific heat between  $T_o$  and  $T_1$ 

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#### EQUATIONS 6-5 AND 6-6

 To simplify this calculation, an average specific heat value, C<sub>p</sub> between T<sub>1</sub> and T<sub>2</sub>, can be used. This reduces Equation 6-4 to:

(Eq. 6-5)  $\Delta H = C_p (T_2 - T_1)$ 

The total heat rate required is given by:

(Eq. 6-6)  $q = m\Delta H = mC_p(T_2 - T_1)$ 

Where: q=total heat rate (Btu/hr) m=mass flow rate of waste gases (lb<sub>m</sub>/hr)

## 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.

#### EXAMPLE 6-3

Draw the picture



We will assume that the composition of the exhaust gas is the same as that of air and that no supplemental air will be added.

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#### **PROBLEM 6-3: 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.

$$m = \left(\frac{288,000 \text{ SCF}}{\text{hr}}\right) \left(\frac{10 \text{ mole}}{385.4 \text{ SCF}}\right) \left(\frac{29 \text{ lb}_{\text{m}}}{10 \text{ mole}}\right) = 21,700 \text{ lb}_{\text{m}}/\text{hr}$$

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Step 3. The heat rate can be determined by using two methods.

Using the enthalpy values in Table 6-2b: H for air at 1,200°F = 287.2 Btu/lb<sub>m</sub> H for air at 90°F is obtained by interpolating = 9.6 - [9.6 (10/40)] = 7.2 Btu/lb<sub>m</sub> q = m ΔH= m(H<sub>air @1,200</sub> - H<sub>air @ 90</sub>)

> =  $(21,700 \text{ lb}_{\text{m}}/\text{hr})(287.2 - 7.2 \text{ Btu/lb}_{\text{m}})$ = (0.070,000 Ptu/h)

= 6,070,000 Btu/hr

This is the energy needed to heat the exhaust gas from 90°F to 1200°F

Continued...

Using mean specific heat, Equation 6:

For air  $C_p = 0.26 \text{ Btu/lb}_m^\circ F$ 

 $q = m C_p \Delta T$ 

= (21,700 Btu/hr)(0.26 Btu/lb<sub>m</sub> °F)(1,200-90)°F

= 6,260,000 Btu/hr

The previous method is more accurate since the C<sub>p</sub> value used is only an approximation.

Continued...

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Step 4. To compute the amount of natural gas required from the heating rate, the available heat of the fuel (HA) must be computed.

From Figure 16b, for natural gas at 1200°F

 $H_{A} \approx 690 \text{ Btu/SCF}$  $Q_{gas} = q/H_{A}$ 

= <u>6,070,000 Btu/hr</u> 690 Btu/SCF

= 8,780 SCF natural gas/hr

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## ACID GAS EMISSIONS

- For waste gases containing:
  - Sulfur
  - Chlorine
  - Fluorine
  - Bromine
- Emission rates should be calculated to determine if an absorption system is required after the oxidizer.



### 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.

#### **PROBLEM 6-4: SOLUTION**

**Step 1. Write the combustion reactions.** 

$$C_{6}H_{6} + 7.5O_{2} \longrightarrow 6CO_{2} + 3H_{2}O$$
$$CCI_{4} + 2H_{2}O \xrightarrow{O_{2}} CO_{2} + 4HCI$$
$$CH_{4} + 2O_{2} \longrightarrow CO_{2} + 2H_{2}O$$

Continued



#### PROBLEM 6-4



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#### **PROBLEM 6-4: SOLUTION**

**Step 2. Calculate the total amount of O2 required 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<sub>2</sub> = 2 × (lb mole CH<sub>4</sub>)  $\frac{2 \text{ lb mole O}_2}{\text{lb mole CH}_4} \left( 0.778 \frac{\text{lb mole CH}_4}{\text{min}} \right) = 1.56 \text{ lb mole O}_2/\text{min}$ 

Step 3. Calculate air sent to the burner (125% of stoichiometric requirement).

$$=1.25 \left(\frac{1.56 \,\mathrm{lb}\,\mathrm{mol}\,\mathrm{O}_2}{\mathrm{min}}\right) = 1.95 \,\mathrm{lb}\,\mathrm{mol}\,\mathrm{O}_2/\mathrm{min}$$
  

$$\mathrm{Fotal}\,\mathrm{N}_2 = \frac{0.79 \,\mathrm{lb}\,\mathrm{mol}\,\mathrm{N}_2}{0.21 \,\mathrm{lb}\,\mathrm{mol}\,\mathrm{O}_2} \left(1.95 \,\frac{\mathrm{lb}\,\mathrm{mol}\,\mathrm{O}_2}{\mathrm{min}}\right)$$

= 7.34 lb mol N<sub>2</sub>/min

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#### Step 4. Calculate the total flue gas flow rate.

Flue gas = Exhaust + Products + Excess oxygen flow rate gas heated of combustion & nitrogen **(B) (A) (C)** A. Exhaust gas heated = 5,000 SCFM – (benzene + carbon tetrachloride) oxidized  $C_6H_6 = 5000 \text{ SCFM}\left(\frac{0.0005 \text{ lb mole } C_6H_6}{\text{ lb mole total}}\right) = 2.5 \text{ SCFM}$  $\text{CCl}_4 = 5000 \text{ SCFM} \left( \frac{0.00012 \text{ lb mole CCL}_4}{\text{lb mole total}} \right) = 0.6 \text{ SCFM}$ Exhaust gas heated = 5,000 SCFM - (2.5 SCFM + 0.6 SCFM) = 4,996.9 SCFMExhaust gas heated =  $(4996.9 \text{ SCFM}) \left(\frac{\text{lb mole}}{385.4 \text{ SCF}}\right) = 12.97 \text{ lb mole/min}$ 

#### Continued ...

Step 4. Calculate the total flue gas flow rate (continued). B. Products of combustion =  $CO_2 + H_2O + HCI$ 

<u>First:</u> determine the total amount of  $CO_2$  produced from all sources.  $CO_2$  as a product of the natural gas/methane (CH<sub>4</sub>) combustion:

$$\operatorname{CO}_{2} = \left(0.778 \frac{\operatorname{lb}\operatorname{mol}\operatorname{CH}_{4}}{\operatorname{min}}\right) \left(\frac{11 \operatorname{b}\operatorname{mol}\operatorname{CO}_{2}}{1 \operatorname{b}\operatorname{mol}\operatorname{CH}_{4}}\right) = 0.778 \frac{\operatorname{lb}\operatorname{mol}\operatorname{CO}_{2}}{\operatorname{min}}$$

Plus the  $CO_2$  as a product of the benzene ( $C_6H_6$ ) combustion:

$$CO_2 = 2.5 \text{ SCFMC}_6H_6 \left(\frac{\text{lb mol}}{385.4 \text{ SCF}}\right) \left(\frac{6 \text{ lb mol} \text{ CO}_2}{\text{lb mol} \text{ C}_6 \text{H}_6}\right) = 0.039 \frac{\text{lb mol} \text{ CO}_2}{\text{min}}$$

Plus the CO<sub>2</sub> as a product of the carbon tetrachloride (CCl<sub>4</sub>) combustion: CO<sub>2</sub> = 0.6 SCFM CCl<sub>4</sub>  $\left(\frac{\text{lb mol}}{385.4 \text{ SCF}}\right) \left(\frac{\text{lb molCO}_2}{\text{lb molCCl}_4}\right) = 0.002 \frac{\text{lb molCO}_2}{\text{min}}$ 

Gives the total  $CO_2$  formed due to combustion: 0.778 + 0.039 + 0.002 lb mol  $CO_2/min = 0.819$  lb mol  $CO_2/min$ 

Continued...

Step 4. Calculate the total flue gas flow rate (continued). B. Products of combustion =  $CO_2 + H_2O + HCI$  (continued)

<u>Second</u>: determine total amount of  $H_2O$  produced from all sources.  $H_2O$  as a product of the natural gas/methane (CH<sub>4</sub>) combustion:

$$H_2O = \left(\frac{2 \text{lb} \text{mol} \text{H}_2O}{\text{lb} \text{mol} \text{CH}_4}\right) \left(0.778 \frac{\text{lb} \text{mol} \text{CH}_4}{\text{min}}\right) = 1.56 \frac{\text{lb} \text{mol} \text{H}_2O}{\text{min}}$$

Plus the  $H_2O$  as a product of the benzene ( $C_6H_6$ ) combustion:

$$H_2O = 2.5 \text{ SCFM } C_6H_6 \left(\frac{\text{lb mol}}{385.4 \text{ SCF}}\right) \left(\frac{3 \text{lb mol} H_2O}{\text{lb mol} C_6H_6}\right) = 0.019 \frac{\text{lb mol} H_2O}{\text{min}}$$

Gives the total H<sub>2</sub>O formed due to combustion:

 $1.56 \text{ lb mol/min} + 0.019 \text{ lb mol/min} = 1.58 \text{ lb mol } H_2O/\text{min}$ 

**<u>Third</u>**: determine the amount of HCl produced from carbon tetrachloride (CCl<sub>4</sub>) combustion:

$$HCl = 0.6 \text{ SCFM } CCl_4 \left(\frac{lb mol}{385.4 \text{ SCF}}\right) \left(\frac{4 lb mol HCl}{lb mol CCl_4}\right) = 0.00623 \frac{lb mol HCl}{min}$$

**Finally,** the total products of combustion =  $CO_2 + H_2O + HCl = 0.819 + 1.58 + 0.00623 = 2.41$  lb mol/min

Step 4. Calculate the total flue gas flow rate (continued). C. Nitrogen and excess oxygen = Total  $N_2 + O_2$  remaining

Amount of oxygen stoichiometric consumed in = required = 1.56 lb mole O<sub>2</sub>/min burning methane

Amount of oxygen consumed in burning benzene: = 5,000 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<sub>2</sub>/min

Amount of oxygen needed for carbon tetrachloride  $\approx 0$ 

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

Step 4. Calculate the total flue gas flow rate (continued).

Flue gas = Exhaust + Products + Excess oxygen flow rate gas heated of combustion & nitrogen (A) (B) (C)

> = 12.97 lb mole/min + 2.41 lb mole/min + 7.68 lb mole/min = 23.06 lb mole/min



#### **Step 5. Calculate the lb mole of HCl formed per minute.**

 $HCl = 5,000 \text{ SCFM}\left(\frac{\text{lb mol total}}{385.4 \text{ SCF}}\right)\left(\frac{0.000120 \text{ lb mol CCl}_4}{\text{lb mol total}}\right)\left(\frac{4 \text{ lb mol HCl}}{\text{lb mol CCl}_4}\right)$ 

= 0.00623 lb mol HCl/min

Step 6. Calculate the HCl concentration.

$$= \left(\frac{0.00623 \text{ lb mol HCl}}{23.06 \text{ lb mol total}}\right) \left(10^6 \text{ ppm}\right) = 270 \text{ ppm}$$

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#### INSTRUMENTATION

- This section will introduce:
  - Instrumentation considerations for high temperature, gas phase oxidation and catalytic oxidation systems



# PROBLEMS DETECTED BY OXIDIZER INSTRUMENTATION

- 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 6-18. FLOWCHART OF A THERMAL OXIDIZER SYSTEM



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# GAS TEMPERATURE AND VOC CONCENTRATION

- The most important operating parameter used to evaluate the operation of thermal oxidizers is the gas outlet temperature (T<sub>3</sub>), which should be 200°F -300°F above the auto-ignition of the most difficult to oxidize compound.
- Monitoring VOC concentration of outlet gas provides qualitative indication of composition.
   Monitor should be downstream of the secondary heat exchanger so that the temperature is relatively low

## **OTHER INSTRUMENTS**

- Static pressure to determine satisfactory performance of hood.
- Temperature indicators around the primary heat exchanger provide indication of fouling or other causes of performance deterioration.
- LEL monitor (not shown) should be included on the gas inlet stream.

# FIGURE 6-19. FLOWCHART OF A CATALYTIC OXIDIZER SYSTEM



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# GAS TEMPERATURE AND VOC CONCENTRATION

- The inlet and outlet gas temperatures (T<sub>1</sub> and T<sub>2</sub>) of the catalyst bed provide useful indirect indicators of system performance
- VOC monitor on exhaust gas (not shown) should be included to determine satisfactory catalyst performance



## **OTHER INSTRUMENTS**

- Static pressure monitor to determine proper operation of the hood
- LEL monitor on the inlet gas to determine safe operating conditions
- ΔP across the catalyst bed could indicate build-up of particulate matter and loss of catalytic activity
#### **SUMMARY**

This chapter covered the following topics:

- Types of oxidation systems.
- Principles of operation for oxidation systems.
- Factors that influence the capability and sizing of an oxidation system.
- Operating parameters to evaluate in an oxidation system.

# SUMMARY (CONTINUED)

#### **Conclusions**

- Oxidizers can achieve high efficiency destruction of a wide variety of organic compounds.
- Thermal oxidizers must operate at temperatures 200°F to 300°F above the auto-ignition temperature of the most difficult-to-oxidize organic compound present as a major constituent of the gas stream.
- Catalytic oxidizers operate at a temperature range of 550°F to 750°F at the inlet of the catalyst bed. The catalyst must be protected from fouling, masking, and poisoning.
- The fuel requirements of the thermal and catalytic oxidizers depend on the efficiency of the heat exchanger and on the concentration of organic compounds present in the gas stream.

# CHAPTER 7 CONDENSER SYSTEMS

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#### **CHAPTER 7**

#### **CONDENSER SYSTEMS**



#### INTRODUCTION

- The concentration of organic compounds in a gas stream can be reduced by condensation at low gas temperatures
- Condensation control systems can be divided into two general categories based on operating temperatures:
  - Conventional (operate in the 40°F to 80°F range)
  - Refrigeration/cryogenic (operate in the -50°F to -150°F range)

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#### **LEARNING OBJECTIVES**

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

- Recognize the various types of condenser systems.
- Identify the principles of operation for condenser systems.
- Determine the factors that influence the capability and sizing of a condenser system.

## **TYPES OF SYSTEMS**

- This section will introduce:
  - Conventional systems
  - Refrigeration systems
  - Cryogenic systems

### **CONVENTIONAL SYSTEMS**

- Simple, relatively inexpensive
- Normally use water or air to cool and condense the VOC
- Fall into two basic categories
  - Direct Contact Condensers
  - Surface Condensers

### **DIRECT CONTACT CONDENSERS**

- Examples include spray towers and water jet ejectors
- They bring the coolant into direct contact with the vapors
- If the vapor is soluble in the coolant, absorption also occurs

#### FIGURE 7-1. DIRECT CONTACT CONDENSER





#### FIGURE 7-2. EJECTOR CONDENSER



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### SURFACE CONDENSERS

- Usually in the form of shell-and-tube heat exchangers
- Consist of a cylindrical shell into which the gas stream flows while coolant flows through small tubes inside the shell
- VOCs contact the cool surface of the small tubes, condense, and are collected

#### FIGURE 7-3. SINGLE PASS CONDENSER



# FIGURE 7-4. 1-2 SHELL-AND-TUBE CONDENSER



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#### SURFACE CONDENSER CONCERNS

- Temperature variances between the gas stream and coolant cause the tubes to expand and contract
- Floating head construction is used to avoid resultant of stress damage

## **AIR CONDENSERS**

- Used in situations where water is not available or treatment of the water stream is very expensive
- Larger than water condensers because of reduced heat transfer efficiency
- Extended surface air condensers may be used to increase efficiency by conserving space and reducing equipment cost
- When using extended surfaces the air flows on the outside while VOC-containing gas flows on the inside of the tubes

#### FIGURE 7-5. EXTENDED SURFACE TUBES





Traverse fins

Longitudinal fins

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#### **REFRIGERATION SYSTEMS**

- Increased VOC condensation as a result of lower operating temperatures than a conventional system
- The most common refrigerants are chlorofluorocarbons (CFCs)

#### FIGURE 7-6. BASIC REFRIGERATION CYCLE



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# FIGURE 7-7. TWO-STAGE REFRIGERATION SYSTEM FOR ORGANIC VAPOR RECOVERY





#### **CRYOGENIC CONDENSERS**

- Use liquefied gases such as nitrogen or carbon dioxide to cool the waste gas stream
- Temperature ranges from -100°F to -320°F
- There are three general types:
  - Indirect contact, single heat exchanger
  - Indirect contact, dual heat exchanger
  - Direct contact

# INDIRECT CONTACT – SINGLE HEAT EXCHANGER SYSTEMS

- Uses a shell-and-tube heat exchanger
- Liquefied nitrogen is the most commonly used liquefied gas
- The liquefied nitrogen flows through the tubes while the waste gas passes through the shell
- Organic compounds may accumulate as frost on the exterior of the tubes, reducing heat transfer efficiency and increasing static pressure drop

# FIGURE 7-8. SINGLE HEAT EXCHANGER, INDIRECT CONTACT CRYOGENIC SYSTEM



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# INDIRECT CONTACT – DUAL HEAT EXCHANGER SYSTEMS

- Does not have the same frost buildup problem that the single heat exchanger system has
- The capacity is limited by the size of the heat exchanger
- Applicable to gas streams less than 5,000 ACFM

# FIGURE 7-9. DUAL HEAT EXCHANGE CRYOGENIC SYSTEM



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#### **DIRECT CONTACT SYSTEMS**

- Liquid nitrogen is dispersed using spray nozzles
- The outlet gas stream includes the uncondensed compounds from the inlet gas stream and the vaporized nitrogen
- Must operate at lower temperatures than an indirect contact condenser to achieve the same VOC removal efficiency since the vaporized nitrogen reduces the partial pressure of the VOC

## FIGURE 7-10. DIRECT CONTACT CRYOGENIC SYSTEM



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#### **OPERATING PRINCIPLES**

- This section will introduce:
  - The principles of operating a condenser



#### CONDENSATION

- Condensation can occur by reducing the gas temperature, increasing the gas pressure, or a combination of both
- Temperature reduction is used in practice
- The volume of the VOC-laden gas stream and the average kinetic energy of the gas molecules are reduced as the temperature is reduced

#### **CONDENSATION**

- At the dew point temperature the partial pressure of the VOC is equal to the vapor pressure of the compound
- The gas is said to be saturated
- Condensation begins at the dew point temperature and increases at the temperature is lowered

# FIGURE 7-11. VAPOR PRESSURES AND ORGANIC COMPOUNDS



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#### 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 included in Figure 7-11.

#### **PROBLEM 7-1: SOLUTION**

Step 1. Determine the outlet concentration of toluene by assuming that the outlet gas stream is in equilibrium (saturated) with toluene. From Figure 7-11 Outlet partial pressure @ -100 F = 0.015 mm Hg (very approximate)

Step 2. Convert the outlet concentration to ppm. Outlet concentration =  $\left(\frac{0.015 \text{ mm Hg}}{760 \text{ mm Hg}}\right) 10^6 \text{ ppm} = 19.7 \text{ ppm}$ 

Step 3. Calculate the removal efficiency.  $\eta = \frac{(\text{In} - \text{Out})}{\text{In}} (100\%) = \frac{10,000 - 19.7}{10,000} (100\%) = 99.8\%$ 

### **CAPABILITY AND SIZING**

- This section will introduce:
  - Condensation Efficiency
  - Sizing of Conventional Condensers



# EQUATION 7-1: THE ANTOINE EQUATION FOR CALCULATING VAPOR PRESSURE



Where:	P* = vapor pressure in mm Hg
	t = gas temperature in °C
	A, B, C = specific constants for each compound



#### PROBLEM 7-2

 What is the vapor pressure of ortho-xylene at a temperature of -50°F? Use the Antoine constants found in Table 7-1.
## TABLE 7-1. ANTOINE CONSTANTS

Table 7-1. Antoine Constants				
Compound	Range (°C)	Α	В	С
Acetaldehyde	-0.2 to 34.4	8.00552	1600.017	291.809
Acetic acid	29.8 to 126.5	7.38782	1533.313	222.309
Acetone	-12.9 to 55.3	7.11714	1210.595	229.664
Ammonia	-83 to 60	7.55466	1002.711	247.885
Benzene	14.5 to 80.9	6.89272	1203.531	219.888
n-Butane	-78.0 to -0.3	6.82485	943.453	239.711
i-Butane	-85.1 to -11.6	6.78866	899.617	241.942
1-Butene	-77.5 to -3.7	6.53101	810.261	228.066
Butyric acid	20.0 to 150.0	8.71019	2433.014	255.189
Carbon tetrachloride	14.1 to 76.0	6.87926	1212.021	226.409
Chlorobenzene	62.0 to 131.7	6.97808	1431.063	217.55
Chlorobenzene	0 to 42	7.106	1500.000	224.000

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Continued...

Table 7-1. Antoine Constants				
Compound	Range (°C)	Α	В	С
Chloroform	-10.4 to 60.3	6.95465	1170.966	226.232
Cyclohexane	19.9 to 81.6	6.84941	1206.001	223.148
n-Decane	94.5 to 175.1	6.95707	1503.568	194.056
1,1-Dichloroethane	-38.8 to 17.6	6.97702	1174.022	229.06
1,2-Dichloroethane	-30.8 to 99.4	7.0253	1271.254	222.927
Dichloromethane	-40.0 to 40	7.40916	1325.938	252.615
Diethyl ether	-60.8 to 19.9	6.92032	1064.066	228.799
Dimethyl ether	-78.2 to -24.9	6.97603	889.264	241.957
Dimethylamine	-71.8 to 6.9	7.08212	960.242	221.667
Ethanol	19.6 to 93.4	8.1122	1592.864	226.184
Ethanolamine	65.4 to 170.9	7.4568	1577.67	173.368
Ethyl acetate	15.6 to 75.8	7.10179	1244.951	217.881

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Table 7-1. Antoine Constants				
Compound	Range (°C)	Α	В	С
Formaldehyde	-109.4 to - 22.3	7.19578	970.595	244.124
Glycerol	183.3 to 260.4	6.16501	1036.056	28.097
n-Heptane	25.9 to 99.3	6.90253	1267.828	216.823
i-Heptane	18.5 to 90.9	6.87689	1238.122	219.783
1-Heptene	21.6 to 94.5	6.91381	1265.12	220.051
n-Hexane	13.0 to 68.5	6.88555	1175.817	224.867
i-Hexane	12.8 to 61.1	6.86839	1151.401	228.477
1-Hexene	15.9 to 64.3	6.8688	1154.646	226.046
Hydrogen Cyanide	-16.4 to 46.2	7.52823	1329.49	260.418
Methanol	14.9 to 83.7	8.08097	1582.271	239.726
Methyl acetate	1.8 to 55.8	7.06524	1157.63	219.726
Methyl chloride	-75.0 to 5.0	7.09349	948.582	249.336

Continued...

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Table 7-1. Antoine Constants				
Compound	Range (°C)	Α	В	С
Nitrobenzene	134.1 to 210.6	7.11562	1746.586	201.783
Nitromethane	55.7 to 136.4	7.28166	1446.937	227.6
n-Nonane	70.3 to 151.8	6.93764	1430.459	201.808
1-Nonane	66.6 to 147.9	6.95777	1437.862	205.814
n-Octane	52.9 to 126.6	6.91874	1351.756	209.10
i-Octane	41.7 to 118.5	6.88814	1319.529	211.625
1-Octene	44.9 to 122.2	6.93637	1355.779	213.022
n-Pentane	13.3 to 36.8	6.84471	1060.793	231.541
i-Pentane	16.3 to 28.6	6.73457	992.019	229.564
1-Pentanol	74.7 to 156.0	7.18246	1287.625	161.33
1-Pentene	12.8 to 30.7	6.84268	1043.206	233.344
1-Propanol	60.2 to 104.6	7.74416	1437.686	198.463

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Continued...

Table 7-1. Antoine Constants				
Compound	Range (°C)	Α	В	С
Propionic acid	72.4 to 128.3	7.71423	1733.418	217.724
Propylene oxide	-24.2 to 34.8	7.01443	1086.369	228.594
Styrene	29.9 to 144.8	7.06623	1507.434	214.985
Toluene	35.3 to 111.5	6.95805	1346.773	219.693
1,1,1-Trichloroethane	-5.4 to 16.9	8.64344	2136.621	302.769
1,1,2-Trichloroethane	50 to 113.7	6.95185	1314.41	209.197
Trichloroethylene	17.8 to 86.5	6.51827	1018.603	192.731
Water	0 to 60	8.10765	1750.286	235.000
m-Xylene	59.2 to 140.0	7.00646	1460.183	214.827
o-Xylene	63.5 to 145.4	7.00154	1476.393	213.872
p-Xylene	58.3 to 139.3	6.9882	1451.792	215.111

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Continued...

#### **PROBLEM 7-2: SOLUTION**

**Step 1. Convert the temperature to C.** 

°C = (°F-32)/1.8 = -45.6 °C

**Step 2. Calculate the vapor pressure using the Antoine Equation.** 

For ortho-xylene, A = 7.00154, B = 1476.393, C = 213.872

$$\frac{B}{C+t} = \frac{1476.393}{213.872-45.6} = 8.774$$

 $\log_{10}(P) = 7.002 - 8.774 = -1.772$ 

P = 0.0169 mm Hg

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## COOLANT FLOW RATE FOR DIRECT CONTACT CONDENSERS

#### Heat In = Heat Out

Heat required to reduce vapors to the final temperature

Heat required + to condense =

vapors

Heat to be removed by the coolant

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#### **EQUATION 7-2**

#### (Eq. 7-2)

 $q = m_G C_{pG} (T_{Ginitial} - T_{Gfinal}) + m_C \Delta H_v = L C_{pL} (T_{Linitial} - T_{Lfinal})$ 

#### Where:

- q = Heat transfer rate (Btu/hr)
- $m_G = Mass flow rate of vapor (lb_m/hr)$
- $m_{\rm C}$  = Mass flow rate of condensate (lb<sub>m</sub>/hr)
- L = Mass flow rate of liquid coolant (lb<sub>m</sub>/hr)
- $C_p$  = Average specific heat of a gas or liquid (Btu/lb<sub>m</sub> °F)
- T = Temperature of streams:

G for gas and L for liquid coolant (°F)

 $\Delta H_v$  = Heat of condensation or vaporization, (Btu/lb<sub>m</sub>)

#### SURFACE AREA OF SURFACE CONDENSERS

- The rate of heat transfer depends on:
  - Total cooling surface area available
  - Resistance to heat transfer
  - Mean temperature difference between condensing vapor and coolant

#### **EQUATION 7-3: RATE OF HEAT TRANSFER**

 $(Eq. 7-3) q = U A \Delta T_m$ 

- Where: q = heat transfer rate (Btu/hr) U = overall heat transfer coefficient (Btu/°F ·ft<sup>2</sup>·hr) A = heat transfer surface area (ft<sup>2</sup>)
  - $\Delta T_m$  = mean temperature difference (°F)



#### FIGURE 7-12. HEAT TRANSFER RESISTANCES



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# TABLE 7-1. TYPICAL OVERALL HEAT TRANSFERCOEFFICIENTS IN TUBULAR HEAT EXCHANGERS (USEONLY FOR ROUGH ESTIMATIONS)

Condensing Material (Shell Side)	Cooling Liquid	U, Btu/°F ● ft²-hr
Organic solvent vapor with high percent of noncondensable gases	Water	20 - 60
High boiling hydrocarbon vapor (vacuum)	Water	20 - 50
Low boiling hydrocarbon vapor	Water	80 - 200
Hydrocarbon vapor and steam	Water	80 - 100
Steam	Feedwater	400 - 1000
Water	Water	200 - 250

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#### **MEAN TEMPERATURE DIFFERENCE**

- The temperature difference between the hot gas and the coolant varies throughout the length of an indirect heat exchanger, therefore a mean temperature difference must be used
- The log mean temperature difference can be used for special cases:
  - Co-current flow
  - Countercurrent flow
  - The temperature of one of the fluids is constant

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## FIGURE 7-13. TEMPERATURE PROFILES IN A HEAT EXCHANGER



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## EQUATION 7-4: LOG MEAN TEMPERATURE DIFFERENCE

(Eq. 7-4) 
$$\Delta T_{\rm lm} = \frac{\Delta T_1 - \Delta T_2}{\ln \left(\frac{\Delta T_1}{\Delta T_2}\right)}$$

Where:  $\Delta T_{lm} = \log$  mean temperature difference

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#### **EQUATION 7-5: SURFACE AREA**

(Eq. 7-5)

$$A = \frac{q}{U\Delta T_{lm}}$$

Where:

- A = Surface area of a shell-and-tube condenser  $(ft^2)$
- q = Heat transfer rate (Btu/hr)
- U = Overall heat transfer coefficient ( $Btu/{}^{\circ}F \cdot ft^{2} \cdot hr$ )

 $\Delta T_{lm}$  = Log mean temperature (°F)

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#### PROBLEM 7-3

- A vapor stream of pure acetone at 120°C and 14.7 psia is fed to a condenser.
- The acetone exits the condenser as a subcooled liquid at 30°C.
- A single-pass countercurrent flow indirect contact condenser is used.

Continued...



## PROBLEM 7-3 (CONTINUED)

- The cooling liquid is water, which enters at a temperature of 20°C and exits at 40°C.
- The acetone feed rate is 10kg/min.
- Calculate the required cooling water flow rate and estimate the required area of the exchanger.

## PROBLEM 7-3 (CONTINUED)

The following data are available for acetone

- Condensation temperature at 14.7 psia: 56°C
- Heat capacity of vapor: C<sub>p</sub> = 0.084 kJ/mol K
- Heat capacity of liquid: C<sub>p</sub> = 0.13 kJ/mol K
- Heat of condensation:  $\Delta H_v = 25.1 \text{ kJ/mol}$
- Molecular weight: M = 58.1 g/mol

## PROBLEM 7-3 (CONTINUED)

The following data is available for water

- Heat capacity of liquid: C<sub>p</sub> = 0.0754 kJ/mol K = 4.19 kJ/kg K
- Heat Transfer Coefficients:
- Cooling Superheated Acetone Vapor: U = 40 Btu/hr ft<sup>2</sup> °F
- Condensing Acetone: U = 100 Btu/hr ft<sup>2</sup> °F
- Subcooling Acetone Liquid: U = 50 Btu/hr ft<sup>2</sup> °F
- Conversion Factor: 1 Btu/hr ft<sup>2</sup> °F = 0.34 kJ/min m<sup>2</sup>K

#### **PROBLEM 7-3: SOLUTION**

Step 1. Calculate the molar flow rate of acetone.

Molar flow rate m = (10kg/min)/58.1kg/kmol = 0.172 kmol/min = 172 mol/min

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Continued...

Step 2. Calculate the total amount of heat that must be removed from the acetone.

 $q = m[CpG(120 - 56) + \Delta Hv + C_{pL}(56 - 30)]$ = 172[0.084(64) + 25.1 + 0.13(26)] = 172[5.4 + 25.1 + 3.4] = 5.83 x 10<sup>3</sup>kJ/min

Continued...



Step 3. Calculate the flow rate of water needed to absorb the total amount of heat to be removed from Step 2.

> q =  $mC_{pL}(40^{\circ}C - 20^{\circ}C) \Delta T(K) = \Delta T(^{\circ}C)$ 5.83 x10<sup>3</sup>kJ/min = m(4.19 kJ/kg K)(20 K) m = (5.83 x103 kJ/min)/(4.19 kJ/kg K)(20 K) = 69.6 kg/min

> > Continued...

To calculate the area of the exchanger, divide it into three parts.

Step 4. Calculate the area of the de-superheater.

Removal of superheat:

 $q = mC_{pG}(120 - 56)$ 

= 172(0.084)(64)

= 0.93 x 103 kJ/min

Water temp change over de-superheater  $\Delta T_{H2O} = q/m C_p$ = 0.93 x103/69.6(4.19) = 3.2 K

Continued...

#### **Step 4 continued.**

Log mean temperature difference  $\Delta T_{Im} = (\Delta T_2 - \Delta T_1)/ln(\Delta T_2/\Delta T_1)$  = [(120 - 40) - (56 - 36.8)]/ln[(120 - 40)/(56 - 36.8)] = (80 - 19.2)/ln(80/19.2) = 42.8 KArea A = q/U $\Delta T_{Im}$  $= (0.93 \times 10^3)/(40)(0.34)(42.8)$   $= 1.6m^2$ 

Continued...

#### **Step 5: Calculate the area of the condenser.**

Acetone condensation:

 $q = m\Delta Hv = 172(25.1)$ 

 $= 4.32 \times 10^{3} \text{kJ/min}$ 

Water temperature change over condenser ΔT<sub>H2O</sub>= q/mC<sup>p</sup> = 4.32 x 10<sup>3</sup>/69.6(4.19) = 14.8 K

Continued...

#### **Step 5 continued.**

Log mean temperature difference  $\Delta T_{Im} = [(56 - 36.8) - (56 - 22)]/ln[(56 - 36.8)/(56 - 22)]$  = (19.2 - 34)/ln(19.2 - 34) = 26.2 KArea A = q/U $\Delta T_{Im}$   $= (4.32 \text{ x}10^3)/(100)(0.34)(26.2)$  $= 4.84 \text{ m}_2$ 

Continued...

#### **PROBLEM 7-3: SOLUTION**

#### Step 6: Calculate the area of the subcooler.

Subcooling liquid  $q = mC_{pL}(56 - 30)$  = 172(0.13)(26) $= 0.58 \times 10^{3} kJ/min$ 

Water temp change over subcooler  $\Delta T_{H2O} = q/mC_p$   $= 0.58 \times 10^3/(69.6)(4.19)$  = 2 K

Continued...

#### **Step 6 continued.**

```
Log mean temperature difference

\Delta T_{lm} = [(56 - 22) - (30 - 20)]/ln[(56 - 22)/(30 - 20)]

= 19.7 K

Area

A = q/U\Delta T_{lm}

= (0.58 x103)/(50)(0.34)(19.7)

= 1.7 m<sup>2</sup>
```

Continued...

Step 7: Check overall  $H_2O$  temperature change.  $\Delta T = \Delta T_1 + \Delta T_2 + \Delta T_3$ 

= 3.2 + 14.8 + 2

= 20

Step 8. Calculate the total area.

$$A = A_1 + A_2 + A_3$$
  
= 1.6 + 4.84 + 1.7  
= 8.14 m<sup>2</sup>

Continued...

## **GRAPHICAL SOLUTION**

#### Temperature as a function of surface area





#### **SUMMARY**

This chapter covered the following topics:

- The various types of condenser systems.
- Operating principles for condenser systems.
- Factors that influence the capability and sizing of a condenser system.

## SUMMARY (CONTINUED)

#### **Conclusions**

- Condensers remove organic compounds by cooling the gas stream. The concentration of organic vapor is reduced to a level equal to the vapor pressure of the compound at the exit gas temperature.
- Direct and indirect condensers using water as a cooling material reduce the gas temperature to approximately 40°F.
- Refrigeration and cryogenic systems can reduce the gas temperatures to levels from -50°F to -320°F.



## CHAPTER 8 NITROGEN OXIDES CONTROL

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#### **CHAPTER 8**

#### **NITROGEN OXIDES CONTROL**



#### INTRODUCTION

This chapter provides an overview of:

- Mechanisms that Create Nitrogen Oxides
  - Thermal Fixation
  - Fuel Nitrogen (NO<sub>x</sub>)
  - Prompt Nitrogen (NO<sub>x</sub>)
- Sources of Nitrogen Oxides
- Methods for controlling Nitrogen Oxides


## **LEARNING OBJECTIVES**

At the end of this Chapter, you'll be able to:

- Recognize the mechanisms that create nitrogen oxides.
- Identify sources of nitrogen oxides.
- Identify the types and components for controlling nitrogen oxide.

## **NITROGEN OXIDES FORMATION**

- This section of the course, will introduce:
  - Conventional systems
  - Refrigeration systems
  - Cryogenic systems



# THERMAL FORMATION MECHANISMS FOR NITROGEN OXIDES

Factors affecting the quantity of NO<sub>x</sub> formed by thermal fixation:

- (1) Flame temperature,
- (2) Residence time of the combustion gases in the peak temperature zone of the flame,
- (3) Amount of oxygen present in the peak temperature zone of the flame.

Reaction 8-1  $N_2 + O_2 \leftrightarrow 2 \text{ NO}$ 

Reaction 8-2 NO +  $\frac{1}{2}$  O<sub>2</sub>  $\leftrightarrow$  NO<sub>2</sub>

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## FUEL NO<sub>X</sub> FORMATION MECHANISMS

- Forms from organic nitrogen compounds in the fuel (i.e., nitrates, amines).
- A portion of organic nitrogen is oxidized to NO<sub>x</sub> in peak temperature zones.
- A portion of organic nitrogen is reduced to N<sub>2</sub>in char.

# **PROMPT NO<sub>X</sub>**

- Forms due to free radical reactions in the burner flame.
- Formation reactions not dependent on the peak gas temperature.
- Generates less than 10 ppm NO<sub>x</sub>in most systems.

## PROBLEM 8-1

What are the total NO<sub>x</sub> emissions in pounds per hour from an industrial boiler emitting 475 ppm NO and 25 ppm NO<sub>2</sub> in a flue gas stream of 100,000 SCFM?





## **PROBLEM 8-1: SOLUTION**

### **Emission rate of NO<sub>x</sub>**

 $= \left(\frac{500 \text{ ppm}}{10^6 \text{ ppm total}}\right) \left(\frac{100,000 \text{ SCF}}{\text{min}}\right) \left(\frac{10 \text{ mole}}{385.4 \text{ SCF}}\right) \left(\frac{46 \text{ lb NO}_2}{10 \text{ mole NO}_2}\right)$ 

=  $5.97 \text{ lb}_{\text{m}}/\text{min No}_{\text{x}} \text{ as NO}_{2}$ 

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## **SOURCES OF NITROGEN OXIDES**

This section covers the following topics

- Pulverized coal-fired boilers
- Oil-and gas-fired boilers
- Gas turbines
- Municipal waste incinerators
- Coal-and wood-fired spreader stoker boilers

## **PULVERIZED COAL-FIRED BOILERS**

Economical for large industrial and utility power stations.

- Coal is pulverized prior to combustion to a size range that is at least 70% less than 200 mesh.
- Combustion occurs in a large refractory-lined furnace with boiler tubes for steam generation.

Designs based on the arrangement of the burners:

- Front-fired
- Opposed (front and back walls)
- Tangential (four corners)

## FIGURE 8-1. PULVERIZED COAL-FIRED BOILER



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# PULVERIZED COAL-FIRED BOILERS (CONTINUED)

A variety of combustion modification techniques have been demonstrated:

- Low excess air combustion
- Off stoichiometric combustion
- Flue gas recirculation
- Low NO<sub>x</sub> burners
- Gas reburning

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## **OIL AND GAS-FIRED BOILERS**

The primary differences between oil- and gas-fired boilers and pulverized coal boilers are:

- Geometry of the furnace area
- Size of the furnace volume
- Type of burners

Combustion modifications appropriate for oil-fired boilers are similar to pulverized coal-fired boilers:

- Low excess air operation
- Off-stoichiometric firing
- Flue gas recirculation
- Gas reburning

## **GAS TURBINE APPLICATIONS**

- Peaking service
- Cogeneration systems
- Gas compressor stations
- Emergency service

## FIGURE 8-3. SIMPLE CYCLE GAS TURBINE



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## FIGURE 8-4. SIMPLE CYCLE GAS TURBINE



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## FIGURE 8-5. TYPICAL COMBUSTOR



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## FIGURE 8-6. MUNICIPAL WASTE INCINERATOR



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# FIGURE 8-7. COAL OR WOOD-FIRED SPREADER STOKER BOILER



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# TYPES AND COMPONENTS OF NO<sub>X</sub> CONTROL TECHNIQUES

This section introduces the following combustion modification topics :

- Low Excess Air Combustion
- Off-Stoichiometric Combustion
- Burners Out-of-Service
- Flue Gas Recirculation
- Low NOx Burners
- Gas Reburning in Fossil Fuel-Fired Boilers
- Fuel Switching
- Selective Non-Catalytic Reduction
- Selective Catalytic Reduction (SCR)

# **NO<sub>X</sub> CONTROL TECHNIQUES**

- Combustion modifications
- Add-on control systems
- Fuel switching



## **COMBUSTION MODIFICATIONS**

- Low excess air combustion
- Off-stoichiometric combustion
- Flue gas recirculation
- Low NO<sub>x</sub>burners
- Gas reburning

## REACTIONS 8-3 THROUGH 8-5:LOW EXCESS AIR COMBUSTION

Reaction 1  $C + O_2 \rightarrow CO_2$ Reaction 2  $2H + \frac{1}{2}O_2 \rightarrow H_2O$ Reaction 3  $S + O_2 \rightarrow SO_2$ 



## 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 quantity of air needed to complete combustion and the total effluent gas stream at this condition?

#### Coal Ultimate Analysis

Carbon, C	65.0%
Hydrogen, H	8.0%
Oxygen, N	7.5%
Sulfur, S	1.0%
Nitrogen, N	1.2%
Water, H <sub>2</sub> O	4.0%
Ash	13.3%
TOTAL	100%

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# PROBLEM 8-2: SOLUTION DATA SUMMARY TABLE

Step 1. Summarize the material balances for fuel, combustion air and combustion products.

a	b	c	d	e	f	g
Material	Composition	Input Weight, Ib/hr	Input, Ib mole/hr	Consumed, Ib mole/hr	Formed, Ib mole/hr	Flue Gas, Ib mole/hr, (columns d - e + f)
Fuel	•	2,000,000	•			
С	65.0%	1,300,000	108,000	108,000	0	0
Н	8.0%	160,000	160,000	160,000	0	0
0	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 <sub>2</sub>	20.9%		146,000	146,000	0	0
N <sub>2</sub>	79.1%		552,000	0	0	552,000
Combustion Products						
CO <sub>2</sub>				0	108,000	108,000
H <sub>2</sub> O				0	80,000	80,000
SO <sub>2</sub>				0	625	625
NO <sub>2</sub>				0	1,700	1,700

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Step 2. Calculate the input quantity of each fuel constituent by dividing the weight by the molecular weight.

С	= (1,300,000 lb/hr)/(12 lb/lb mol)
н	= (160,000 lb/hr)/(1 lb/lb mol)
0	= (150,000 lb/hr)/(16 lb/lb mol)
S	= (20,000 lb/hr)/(32 lb/lb mol)
N	= (24,000 lb/hr)/(14 lb/lb mol)
H <sub>2</sub> O	= (80,000 lb/hr)/(18 lb/lb mol)

= 108,000 lb mol/hr

- = 160,000 lb mol/hr
- = 9,400 lb mol/hr
- = 625 lb mol/hr
- = 1,700 lb mol/hr
- = 4,400 lb mol/hr

Continued...

Step 3. Calculate the oxygen requirement using the lb mol/hr data and the stiochiometry of the combustion reactions.

$$O_2 = CO_2 + 1/2 H_2O + SO_2 - O_2 \text{ (fuel)}$$

$$O_2 = 108,000 + 1/2 \left(\frac{160,000}{2}\right) + 625 + 1,700 - \left(\frac{9,400}{2}\right)$$

$$= 146,000 \text{ lb mole/hr}$$

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.



Step 6. Calculate the amount of combustion gases formed based on the stoichiometry of the reactions.

CO2	= 1 (lb mol C/hr)= 108,000 lb mol/hr
H <sub>2</sub> O	= 1/2 (lb mol H/hr)= 80,000 lb mol/hr
SO2	= 1(lb mol S/hr)= 625 lb mol/hr
NO <sub>2</sub>	= 1 (lb mol N/hr) = 1,700 lb mol/hr

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Step 7.Calculate the lb mole of material leaving the combustion process (combustion products, combustion air, and unburned constituents of fuel).

Effluent gas = Fuel + Combustion + Remaining + Combustion stream products + Remaining + Combustion air nitrogen

Effluent gas stream = 4,400 + (108,000 + 80,000 + 625 + 1,700) + 0 + 552,000

Effluent gas stream = 747,000 lb mole/hr

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## PROBLEM 8-3

What is the oxygen concentration (%) and total gas flow rate (lb mol/hour) if the boiler addressed in Problem 8-2 is fired at an excess air rate of 40%?

# PROBLEM 8-3 SOLUTION: DATA SUMMARY TABLE

Step 1. Summarize the material balances for fuel, combustion air and combustion products.

a	b	с	d	e	f	g
Material	Composition	Input Weight, Ib/hr	Input, Ib mole/hr	Consumed, Ib mole/hr	Formed, Ib mole/hr	Flue Gas, Ib mole/hr (columns d – e + f)
Fuel 2,000,000						
С	65.0%	1,300,000	108,000	108,000	0	0
Н	8.0%	160,000	160,000	160,000	0	0
0	7.5%	150,000	9,400	9,400	0	0
S	1.0%	20,000	625	625	0	0
Ν	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 <sub>2</sub>	20.9%		206,000	146,000	0	60,000
N <sub>2</sub>	79.0%		779,000	0	0	779,000
Combustion Products						
CO <sub>2</sub>				0	108,000	108,000
H <sub>2</sub> O				0	80,000	80,000
SO <sub>2</sub>				0	625	625
NO <sub>2</sub>				0	1,700	1,700

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Step 2. Calculate the input quantity of each fuel constituent by dividing the weight by the molecular weight.

С	= (1,300,000 lb/hr)/(12 lb/lb mol)
н	= (160,000 lb/hr)/(1 lb/lb mol)
0	= (150,000 lb/hr)/(16 lb/lb mol)
S	= (20,000 lb/hr)/(32 lb/lb mol)
N	= (24,000 lb/hr)/(14 lb/lb mol)
H <sub>2</sub> O	= (80,000 lb/hr)/(18 lb/lb mol)

- = 108,000 lb mol/hr
- = 160,000 lb mol/hr
- = 9,400 lb mol/hr
- = 625 lb mol/hr
- = 1,700 lb mol/hr
- = 4,400 lb mol/hr

Step 3. Calculate the oxygen requirement using the lb mol/hr data and the stiochiometry of the combustion reactions.

 $O_{2} = (140\% / 100\%)[CO_{2}+1/2 H_{2}O + SO_{2} + NO_{2}] - O_{2} \text{ (Fuel)}$ = 1.40 [108,000 + 1/2 H<sub>2</sub>O + SO<sub>2</sub> + NO<sub>2</sub>] -  $\frac{9,400}{2}$ 

= 206,000 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 lb mole/hr (0.79/0.209)

= 779,000 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.

Step 6. Calculate the amount of combustion gases formed based on the stoichiometry of the reactions.

- $CO_2 = 1 (lb mol C/hr)$
- $H_2O = 1/2$  (lb mol H/hr)
- $SO_2 = 1(lb mol S/hr)$
- $NO_2 = 1(lb mol N/hr)$

- = 108,000 lb mol/hr
- = 80,000 lb mol/hr
- = 625 lb mol/hr
- = 1,700 lb mol/hr

Step 7. Calculate the volumetric flow rate leaving the combustion process (combustion products, combustion air, and unburned constituents of fuel).

Total effluent = 4,400 + (108,000 + 80,000 + 625 + 1,700) + 60,000 + 779,000

Total effluent = 1,034, 000 lb mol/hr


# FIGURE 8-8. STAGED COMBUSTION USING OVERFIRE AIR PORTS



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# FIGURE 8-10. BIASED FIRING



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# FIGURE 8-11. BURNERS OUT-OF-SERVICE



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# FIGURE 8-12. FLUE GAS RECIRCULATION (FGR)



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# FIGURE 8-13. EXAMPLE OF A CONTROLLED FLOW SPLIT FLAME LOW NO<sub>X</sub> BURNER



# FIGURE 8-14. EXAMPLE OF A DUAL REGISTER LOW NO<sub>x</sub> BURNER



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# GAS REBURNING IN FOSSIL FUEL-FIRED BOILERS

- Gas or other low NO<sub>x</sub> fuel replaces fossil fuel in boiler.
- Fossil fuels burned slightly fuel-rich.
- Overfire air used to complete combustion.



# FIGURE 8-15. GAS REBURNING





# **GAS TURBINE COMBUSTORS**

- Lean, pre-mixed combustors
  - Common dry combustor
  - Burn at lower peak gas temperatures



# WATER OR STEAM INJECTION

#### Rich/quench/lean combustors

- Reduces peak gas temperatures
- Increases flue gas volumes
- Reduces gas turbine thermal efficiency



# **FUEL SWITCHING**

- Reduced coal nitrogen content
- Fuel substitution
- Gas co-firing



# SELECTIVE NON-CATALYTIC REDUCTION (SNCR) REACTIONS 8-6 AND 8-7

In SNCR systems , ammonia  $(NH_3)$  or urea is injected into a very hot gas zone where thermal reactions leading to the chemical reduction of nitrogen oxides can occur.

The ammonia or urea reduces the NO to  $N_2$ 

Reaction 8-6 4  $NH_3 + 4 NO + O_2 \rightarrow 4 N_2 + 6H_2O$ 

Reaction 8-7 2NO + NH,CONH, + 0.5 O,  $\rightarrow$  2N, + 2 H,O + CO,

# FIGURE 8-16. TEMPERATURE SENSITIVITY OF SNCR REACTIONS



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### FIGURE 8-17. AMMONIA SLIP EMISSIONS



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# FIGURE 8-18. BOILER WITH SNCR INJECTION NOZZLES



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# FIGURE 8-19. SELECTIVE CATALYTIC REDUCTION (SCR) CONFIGURATION



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## **REACTIONS 8-10 AND 8-11**

The composite reactions involved in SCR nitrogen oxides reduction are shown in Reactions 8-10 and 8-11.

Reaction 8-10

 $4 \text{ NO} + 4 \text{ NH}_3 + \text{ O}_2 \rightarrow 4 \text{ N}_2 + 6 \text{ H}_2\text{ O}$ 

Reaction 8-11  $2 \operatorname{NO}_2 + \operatorname{NH}_2\operatorname{CONH}_2 \rightarrow 2\operatorname{N}_2 + 2 \operatorname{H2O}$  $+ \operatorname{CO}_2 + \frac{1}{2} \operatorname{O}_2$ 

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# **CAPABILITY AND SIZING**

This section introduces:

- Nitrogen Oxides Emissions Reduction Efficiencies
- Ammonia Or Urea Feed Requirements



# TABLE 8-1. GENERAL RANGE OF NOXSUPPRESSION EFFICIENCIES

Control Technique	Typical Applications	NO <sub>X</sub> Reduction Efficiencies, %
Combustion Modifications		
Low Excess Air	Coal-Fired Boilers, Municipal Waste Incinerators	15-30%
Off-Stoichiometric Combustion	Coal-, Oil-, Gas-Fired Boilers	15-50%
Flue Gas Recirculation	Coal-, Oil- Gas-Fired Boilers	15-50%
Low NO <sub>X</sub> Burners	Coal-, Oil-, Gas-Fired Boilers	25-40%
Gas Reburning	Coal-, Oil-, Gas-Fired Boilers	30-70%
Lean Combustors	Gas-Fired Turbines	>90%
Water/Steam Injection	Gas-Fired Turbines	60-75%
Flue Gas Treatment		
SNCR	Coal-Fired Boilers, Municipal Waste Incinerators	20-60%
SCR	Coal-Fired Boilers, Gas Turbines	60-90%
Fuel Switching		
Low Nitrogen Coal	Coal-Fired Boilers	No Data
Co-Firing	Coal-Fired Boilers	No Data

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### **AMMONIA OR UREA FEED REQUIREMENTS**

- Set by the stoichiometry of the reactions
- Usually set at slightly less than the stoichiometric amount to minimize ammonia slip
- One-half mole of urea is needed for every mole of NO that must be reduced.

# PROBLEM 8-4

- Calculate the ammonia feed rate needed to achieve a 30% reduction in the NO<sub>x</sub> rate of an SNCR system.
- The boiler flue gas flow rate is 100,000 SCFM, and the present NO<sub>x</sub> emissions rate is 200 ppm. The NO<sub>x</sub> emissions limitation is equivalent to 100 ppm.

### **PROBLEM 8-4: SOLUTION**

#### Step 1. Calculate the pound moles of gas.

 $\frac{100,000 \text{ SCF}}{\text{min}} \frac{\text{lb mole}}{385.4 \text{ SCF}} = 259.5 \text{ lb mole gas/min}$ 

Step 2. Calculate the pound moles of  $NO_{\chi}$  at 200 ppm.

 $\left(\frac{0.0002 \text{ lb mole NO}_{X}}{\text{lb mole gas}}\right)\left(\frac{259.5 \text{ lb mole gas}}{\text{min}}\right) = 0.0519 \text{ lb mole NO}_{X}/\text{min}$ 

Pound moles of NO<sub>x</sub> reacted =0.5(0.0519 lb mol/min)=0.0.26 lb mol/min

Pound moles of ammonia =  $\frac{11b \text{ mol NH}_3}{11b \text{ mol NO}_x} \times 0.0261b \text{ mol/min}$ Pound moles of ammonia = 0.0261b mol/min

Ammonia feed rate =  $0.026 \text{ lb mol} / \text{min x} (17 \text{ lb}_m / \text{lb mol NH}_3)$ =  $0.44 \text{ lb}_m / \text{min} = 633.6 \text{ lb}_m / \text{day}$ 

### **EVALUATING PERFORMANCE**

This section covers the following topics:

- Continuous Emission Monitors
- No<sub>2</sub> And Nh<sub>3</sub> Visible Emissions
- Oxygen Concentrations
- Carbon Monoxide Concentrations
- SCR and SNCR Reagent Feed Rates and Injection Conditions
- Gas Turbine Steam or Water Steam Injection



### INSTRUMENTATION

- NO<sub>2</sub> And NH<sub>3</sub> Visible Emissions
  - No plume if NO<sub>x</sub> control systems work properly
- Oxygen Concentrations should be reviewed to :
  - Determine if air infiltration or burner operational problems increase NO<sub>x</sub>

# **CARBON MONOXIDE CONCENTRATIONS**

- SCR and SNCR reagent feed rates and injection conditions
- Gas temperatures
- Gas static pressure drop
- Gas turbine water or steam injection rates

# FIGURE 8-20. STATIC PRESSURE DROP VERSUS PROCESS OPERATING RATE



# GAS TURBINE STEAM OR WATER STEAM INJECTION

- The gas turbine electrical and steam output is monitored on a continuous basis at the system control panel. The steam injection or water rates are usually monitored continuously.
- Boiler Flyash Loss-On-Ignition (LOI)
  - The boiler flyash combustible levels are often monitored by means of the loss-on-ignition or "LOI."

**SUMMARY** 

This training provided the resources that will enable students to:

- Recognize the mechanisms that create nitrogen oxides.
- Identify sources of nitrogen oxides.
- Identify the types and components for controlling nitrogen oxide.

Continued...



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# SUMMARY (CONTINUED)

#### **Conclusions**

- Add-on control techniques in common use include selective catalytic reduction and selective noncatalytic reduction systems. Both use a reagent that chemically reduces NO<sub>x</sub> to N<sub>2</sub>.
- SNCR systems operate in a very narrow temperature range of 1600°F to 2000°F. Below this temperature range, high ammonia slip emission occur. Above this temperature range, the ammonia or urea reagents are converted to NO<sub>x</sub>. SCR systems use a catalyst to complete the NO<sub>x</sub> reduction reactions in the temperature range of 500°F to 750°F. In these systems, the condition of the catalyst is very important.

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# CHAPTER 9 SULFUR OXIDES CONTROL

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### **CHAPTER 9**

### **SULFUR OXIDES CONTROL**



### INTRODUCTION

- Sources of Sulfur Oxides
- Concerns about SO<sub>2</sub> emissions

   Clean Air Act Amendments of 1990 (Title IV)
- Emissions and monitoring requirements

# **LEARNING OBJECTIVES**

At the end of this Chapter, you'll be able to:

- Recognize operating principles for sulfur dioxides control.
- Identify appropriate evaluation and test methods for controlling sulfur dioxide.
- Identify appropriate evaluation and test methods when using fuel sulfur sampling systems.
- Recognize appropriate methods and evaluation for dry and wet scrubbing systems.

# TYPES AND COMPONENTS OF SULFUR OXIDES CONTROL SYSTEMS

Sulfur oxides are formed from the sulfur compounds entering with the fuel. In coal, the sulfur compounds include pyrites, sulfates, and organic sulfur compounds.

Reaction 9-1  $S + O_2 \rightarrow SO_2$ Reaction 9-2  $S + 1.5 O_2 \rightarrow SO_3$ Reaction 9-3  $SO_3 + H_2O \rightarrow H_2SO_4$ 



# PROBLEM 9-1

- What is the emission rate of sulfur dioxide if 100 tons of coal are 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.



### **PROBLEM 9-1: SOLUTION**

#### Step 1. Calculate the amount of sulfur in the coal.

#### Pounds of fuel sulfur

 $= \frac{100 \text{ tons}}{\text{hour}} \frac{2,000 \text{ lb}_{\text{m}}}{\text{ton}} \frac{2 \text{ lb}_{\text{m}} \text{ S}}{100 \text{ lb}_{\text{m}} \text{ coal}}$ = 4,000 lb<sub>m</sub> S/hour

#### Step 2. Convert sulfur quantity to pound moles per hour.

#### Pound moles of sulfur/hour

 $= \frac{4,000 \text{ lb}_{\text{m}}}{\text{hr}} \frac{\text{lb mole S}}{32 \text{ lb}_{\text{m}}}$ = 125 lb mole S/hr
### **PROBLEM 9-1: SOLUTION (CONTINUED)**

Step 3. Convert sulfur pound moles to SO<sub>2</sub> pound moles.

Pound moles of sulfur converted to  $SO_2$ =  $\frac{125 \text{ lb mole S}}{\text{hr}} \times \frac{0.94 \text{ lb S converted}}{\text{lb S total}} \times \frac{1 \text{ lb mole S}O_2}{\text{lb mole S}}$ = 117.5 lb mole  $SO_2/\text{hour}$ 

Step 4. Convert SO<sub>2</sub> pound moles to pound mass. Pounds of SO<sub>2</sub> emitted per hour

 $=\frac{117.51 \text{ b} \text{ mole SO}_2}{\text{hour}} \frac{641 \text{ b} \text{m SO}_2}{1 \text{ b} \text{ mole SO}_2}$ 

= 7,520 lb<sub>m</sub> SO<sub>2</sub>/hour

### FIGURE 9-1. CONVERSION OF FUEL SULFUR



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### **SULFUR OXIDES CONTROL TECHNIQUES**

- Low sulfur fuel firing
- Flue gas desulfurization
- Dry scrubbing
- Fluidized bed combustion
- Fuel treatment

### 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 Btu/pound to a low sulfur coal having a sulfur content of 1.0% and a heating value of 8,500 Btu/pound.
- Assuming that 94% of the sulfur in the coal exists as SO<sub>2</sub>, what is the percent reduction in sulfur dioxide emissions due to this fuel conversion?

### **PROBLEM 9-2: SOLUTION**

Step 1. Calculate the boiler sulfur dioxide emissions for the high sulfur fuel.

As indicated in Problem 9-1, 2 pounds of sulfur dioxide form for every pound of sulfur escaping the combustion chamber. Choose a boiler firing rate of 100 MMBtu.

 $SO_{2}(lb/hour) = \left(\frac{2 lb_{m} S}{100 lb_{m} coal}\right) \left(\frac{0.94 lb_{m} S Converted}{lb_{m} S Total}\right) \left(\frac{2 lb_{m} SO_{2}}{lb_{m} S}\right) \left(\frac{lb_{m} coal}{13,500 Btu}\right) 100 \times 10^{6} Btu/hr$ 

 $SO_2(lbm/hour) = 279 lb SO_2/hour$ 

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### **PROBLEM 9-2: SOLUTION (CONTINUED)**

**Step 2.** Calculate the boiler sulfur dioxide emissions from the low sulfur fuel.

 $SO_{2}(lb/hour) = \left(\frac{1 \text{ lbm S}}{100 \text{ lbm coal}}\right) \left(\frac{0.94 \text{ lbm S Converted}}{\text{ lbm S Total}}\right) \left(\frac{2 \text{ lbm SO}_{2}}{\text{ lbm S}}\right) \left(\frac{1 \text{ lbm coal}}{8,500 \text{ Btu}}\right) 100 \text{ x } 10^{6} \text{ Btu/hr}$ 

= 221 lb<sub>m</sub> SO<sub>2</sub>/hour

Step 3. Calculate the percent reduction. Reduction  $=\left(\frac{279-221}{279}\right)100\% = |20.8\%$ 

# TABLE 9-1. COMMON TYPES OF FGDPROCESSES FOR BOILERS

Type of SO <sub>2</sub> Control System	1989 (%)	2010 (%)
Wet Scrubbers, Nonregenerative (Throw-away)		
Lime <sup>1</sup>	23.6	18.4
Limstone <sup>1</sup>	50.6	45.5
Dual Alkali	3.4	2.3
Sodium Carbonate	4.0	3.3
Regenerative (Saleable Product)		
Magnesium Oxide	1.4	1.0
Wellman Lord	3.1	2.1
Lime/Limestone	4.0	4.7

<sup>1</sup>This includes systems that use alkaline flyash for part of the alkali feed requirement.

### FIGURE 9-2. SIMPLIFIED FLOWCHART OF A LIME SCRUBBING SYSTEM



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### FIGURE 9-3. DUAL ALKALI SCRUBBER SYSTEM



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### FIGURE 9-4. SIMPLIFIED FLOWCHART OF THE MAGNESIUM OXIDE PROCESS



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### **DRY SCRUBBER PROCESSES**

- Spray dryer absorption
  - Rotary atomizer systems
  - Air-assisted atomizing nozzle systems
- Dry injection absorption
  - Without recycle
  - With recycle
- Combination spray dryer and dry injection systems

### FIGURE 9-5. SIMPLIFIED FLOWCHART OF A SPRAY DRYER TYPE DRY SCRUBBER



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### FIGURE 9-6. DRY INJECTION DRY SCRUBBER FLOWCHART



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### FIGURE 9-7. COMBINATION SPRAY DRYER AND DRY INJECTION UNITS



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### **OTHER SULFUR OXIDE CONTROL TECHNIQUES**

- Fluidized Bed Combustion
- Fuel Treatment
  - Coal gasification
  - Coal liquefaction
  - Coal cleaning

### **OPERATING PRINCIPLES**

Three basic steps in the removal of sulfur dioxide from combustion process flue gas

- Absorption of SO<sub>2</sub> into water droplets
- Reaction of the dissolved sulfur dioxide (as sulfurous) with alkaline species
- Precipitation and removal of solid reaction products



### FIGURE 9-8. ABSORPTION OF SO<sub>2</sub> INTO WATER



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### FIGURE 9-9. ABSORPTION OF SO<sub>2</sub> IN ALKALINE SLURRY



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CHEMICAL REACTIONS IN SOLUTION AND PRECIPITATION OF REACTION PRODUCTS

**Absorption Reactions** 

 Reaction 9-4
  $SO_2(g) \rightarrow SO_2(l)$  

 Reaction 9-5
  $SO_2(l) + H_2O \rightarrow H_2SO_3(l)$  

 Reaction 9-6
  $H_2SO_3(l) \rightarrow HSO_3^{-1}(l) + H^+$  

 Reaction 9-7
  $HSO_3^{-1}(l) \rightarrow SO_3^{-2}(l) + H^+(l)$  

 Reaction 9-8
  $SO_3^{-2}(l) + 0.5 O_2 \rightarrow SO_4^{-2}(l)$ 

Note: (g) = gas phase (l) = liquid phase (s) = solid phase

### **REACTIONS 9-9 THROUGH 9-15**

#### **Limestone Reactions**

- 9-9  $CaCO_3(s) \rightarrow CaCO_3(l)$
- $CaCO_3(l) \rightarrow Ca^{+2} + CO_3^{-2}$ 9-10
- $CO_3^{-2} + H^+ \rightarrow HCO_3^{-1}$ 9-11
- $SO_3^{-2} + H^+ \rightarrow HSO_3^{-1}$ 9-12
- $SO_3^{-2} + 0.5 O_2(l) \rightarrow SO_4^{-2}$ 9-13

- $Ca^{+2} + SO_3^{-2} + 0.5 H_2O \rightarrow CaSO_3 \cdot \frac{1}{2}H_2O(s)$

 $Ca^{+2} + SO_4^{-2} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O(s)$ 

- 9-14

9-15

### **REACTIONS 9-16 THROUGH 9-21**

Lime Reactions

- 9-16  $CaO(s) + H_2O \rightarrow Ca(OH)$ , (l)
- 9-17  $Ca(OH)_{2}(l) \rightarrow Ca^{+2} + 2 OH^{-1}$
- 9-18  $OH^{-1} + H^+ \rightarrow H_2O$
- 9-19  $SO_3^{-2} + H^+ \rightarrow HSO_3^{-1}$
- 9-20  $Ca^{+2} + SO_3^{-2} + 0.5 H_2O \rightarrow CaSO_3 \cdot \frac{1}{2}H_2O(s)$
- 9-21  $Ca^{+2} + SO_4^{-2} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O(s)$

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### 9-26 2NaOH + SO<sub>3</sub> $\rightarrow$ Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O 9-27 Na<sub>2</sub>SO<sub>3</sub> + 0.5 O<sub>2</sub> $\rightarrow$ Na<sub>2</sub>SO<sub>4</sub>

9-25  $Na_2SO_3 + SO_2 + H_2O \rightarrow 2 NaHSO_3$ 

9-24 2NaOH + SO<sub>2</sub>  $\rightarrow$  Na<sub>2</sub>SO<sub>3</sub> + H<sub>2</sub>O

9-23  $NaHCO_3 + SO_2 \rightarrow NaHSO_3 + CO_2(g)$ 

9-22  $2NaCO_3 + SO_2 + H_2O \rightarrow Na_2SO_3 + 2NaHCO_3$ 

**Absorber Loop Reactions** 

### DUAL ALKALI SCRUBBING REACTIONS 9-22 THROUGH 9-27

### **REACTIONS 9-28 AND 9-29**

**Regeneration Loop Reactions** 

9-28 2NaHSO<sub>3</sub>(l) + Ca(OH)<sub>2</sub>  $\rightarrow$  Na<sub>2</sub>SO<sub>3</sub> + CaSO<sub>3</sub>·2H<sub>2</sub>O(s)

9-29  $Na_2SO_4 + Ca(OH)_2 \rightarrow 2NaOH + CaSO_4$ 

### REACTIONS 9-30 THROUGH 9-33

Magnesium Oxide Scrubbing

- 9-30  $Mg(OH)_2 + 5 H_2O + SO_2 \rightarrow MgSO_3 \cdot 6H_2O$
- 9-31  $MgSO_3 \cdot 6H_2O + SO_2 \rightarrow Mg(HSO_3)_2 + 5H_2O$
- 9-32  $Mg(HSO_3)_2 + MgO \rightarrow 2MgSO_3 + H_2O$
- 9-33  $2MgSO_3 + O_2 + 7H_2O \rightarrow 2MgSO_4 \cdot 7H_2O$

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### **REACTIONS 9-34 THROUGH 9-38**

#### Cake dryer

- 9-34  $MgSO_3 \cdot 6H_2O \longrightarrow MgSO_3 + 6H_2O$
- 9-35  $MgSO_4 \cdot 7H_2O \longrightarrow MgSO_4 + 7H_2O$

#### **MgO Regeneration in Calciner**

- 9-36  $MgSO_3 \longrightarrow MgO + SO_2$
- 9-37  $C + \frac{1}{2}O_2 \longrightarrow CO$
- 9-38  $CO + MgSO_4 \longrightarrow CO_2 + MgO + SO_2$

### WELLMAN-LORD REACTIONS 9-39 THROUGH 9-42

Wellman-Lord Process

9-39  $SO_2 + Na_2SO_3 + H_2O \rightarrow 2NaHSO_3$ 9-40  $Na_2SO_3 + \frac{1}{2}O_2 \rightarrow Na_2SO_4$ 9-41  $Na_2CO_3 + 2NaHSO_3 \rightarrow 2Na_2SO_3 + CO_2 + H_2O$ 9-42  $2NaHSO_3 \rightarrow Na_2SO_3 + H_2O + SO_2$ 

### **REACTIONS 9-43 AND 9-44**

**Dry Scrubbing** 

9-43  $Ca(OH)_2 + 2 HCl \rightarrow CaCl_2 + 2 H_2O$ 9-44  $Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O$ 

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### FIGURE 9-11. EFFECT OF ALKALI STOICHIOMETRIC RATION ON REMOVAL EFFICIENCY



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### **CAPABILITY AND SIZING**

There are three general approaches to evaluating the capability of a sulfur dioxide control system

- Empirical evaluation
- Pilot scale tests
- Computerized performance models

### FUEL SULFUR SAMPLING SYSTEMS

- 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

### ALKALI REQUIREMENTS REACTIONS 9-45 THROUGH 9-47

Alkali Requirements

9-45  $SO_2 + Ca(OH)_2 + 0.5 O_2 \rightarrow (CaSO_4)_s + H_2O$ 9-46  $2HCl + Ca(OH)_2 \rightarrow 2Ca^+ + 2 Cl^- + 2H_2O$ 9-47  $2HF + Ca(OH)_2 \rightarrow 2Ca^+ + 2 F^- + 2H_2O$ 





- 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%.

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### **PROBLEM 9-3: SOLUTION**

Step 1. Calculate the quantity of HCl absorbed in the scrubbing liquid.

 $HCl = 10,000 \text{ SCFM}\left(\frac{\text{lb mole}}{385.4 \text{ SCF}}\right) \left(\frac{0.00005 \text{ lb mole HCl}}{\text{lb mole total}}\right) \left(\frac{95\% \text{ Efficiency}}{100\%}\right)$ 

HCl = 0.00123lb mole HCl/minute

Step 2. Calculate the amount of Ca(OH)<sub>2</sub> required.

 $= \left(\frac{1 \text{ lb mole Ca(OH)}_2}{2 \text{ lb mole HCl}}\right) \left(\frac{0.0024 \text{ lb mole HCl}}{\text{min}}\right) = \frac{74 \text{ lb}_{\text{m}} \text{ mole Ca(OH)}_2}{\text{ lb mole Ca(OH)}_2}$ 

= 0.0456 lbm Ca(OH)  $_2/min = 2.74$  lbm Ca(OH)  $_2/hr$ 

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### **CONTINUOUS EMISSION MONITORS**

- Performance Evaluation Analyzers
- Instrumentation
- Techniques
  - SO<sub>2</sub>

• 0<sub>2</sub>



### **REACTIONS 9-48 AND 9-49**

**Performance Evaluation** 

**9-48**  $SO_2 + \eta hv \rightarrow SO_2 \rightarrow SO_2 + hv''$ 

210 nm Excited

240-410 nm Molecule

**9-49**  $SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H + 2e^{-}$ 

E 0 =0.17 V 298

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### **EQUATION 9-1**

## (Eq 9-1) $S = \frac{\delta^2}{4} \left[ -cl \frac{d^2 \alpha}{d\lambda^2} I \right]$

Where:

S = oscillating signal monitored by the analyzer

 $\delta$  = scanning distance

c = gas concentration

I = light path length through the gas

 $\alpha$  = wavelength-dependent molecular absorption coefficient

 $\lambda$  = wavelength

I = intensity of the light leaving the probe
#### INSTRUMENTATION

- Flue gas oxygen content
- Mist eliminator static pressure drop
- pH
- Alkali feed rate
- Inlet and outlet gas temperature
- Dry and Wet Scrubbing

#### **SUMMARY**

This chapter covered the following topics:

- Recognize operating principles for sulfur dioxides control.
- Identify appropriate evaluation and test methods for controlling sulfur dioxide.
- Identify appropriate evaluation and test methods when using fuel sulfur sampling systems.
- Recognize appropriate methods and evaluation for dry and wet scrubbing systems.

Continued...

#### SUMMARY (CONTINUED)

#### **Conclusions**

- The majority of the sulfur entering with fuel into combustion systems is converted to sulfur dioxide.
- There are no combustion modifications that minimize the rate of sulfur dioxide generation.
   However, the reduction of fuel sulfur levels has a direct and proportional impact on the sulfur dioxide emissions.

Continued...

#### SUMMARY (CONTINUED)

#### **Conclusions**

- Add-on control systems are used to remove sulfur dioxide from the gas stream. The main categories of control systems include non-regenerative wet scrubbing systems, regenerative wet scrubbing systems, and dry scrubbing systems.
- Most add-on control systems provide removal efficiencies of 75% to more than 90%. In wet scrubbing systems, alkali is injected into the gas stream to maintain the necessary sulfur dioxide absorption rates.

CHAPTER 10 CONTROL TECHNIQUES FOR GASEOUS CONTAMINANTS



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#### **CHAPTER 10**

#### CONTROL TECHNIQUES FOR GREENHOUSE GAS EMISSIONS





This lesson introduces :

- Pollution control measures
- Technologies
- Resources to reduce Greenhouse Gas Emissions



#### **LEARNING OBJECTIVES**

At the end of this training, you will be able to:

- Understand the definition of GHG and the main industrial sources of GHG emissions
- Identify the main GHG control techniques and strategies
- Identify additional GHG emission control and reduction resources

#### **GHG EMISSION SOURCES**

United Nations Framework Convention on Climate Change

- Gases with Global Warming Potential (GWP) -
  - Carbon Dioxide (CO<sub>2</sub>)
  - Methane (CH<sub>4</sub>)
  - Nitrous Oxide  $(N_2O)$
  - Select Hydrofluorocarbons (HFCs)
  - Select Perfluorocarbons (PFCs)
  - Sulfur Hexafluoride (SF<sub>6</sub>)



#### FIGURE 10-1: CONTRIBUTION OF GHG TO TOTAL U.S. EMISSIONS



Results are per the EPA's national greenhouse gas inventory.

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#### FIGURE 10-2: ANNUAL PERCENT CHANGE IN U.S. GREENHOUSE GAS EMISSIONS



1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010

Results illustrate trends in total U.S. emissions since 1990.

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#### FIGURE 10-3: EMISSIONS ALLOCATED TO ECONOMIC SECTORS



Results illustrate trends in total U.S. emissions between 1990 and 2010.

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#### FIGURE 10-4: EMISSIONS WITH ELECTRICITY DISTRIBUTED TO ECONOMIC SECTORS



Emissions from Industry generally declined between 1990-2010.

#### FIGURE 10-5: U.S. GREENHOUSE GAS EMISSIONS AND SINKS BY CHAPTER/IPCC SECTOR



Land use, land-use change, and forestry activities offset approximately 15 percent of total U.S. CO<sub>2</sub> emissions.

#### **GHG EMISSIONS FROM INDUSTRIAL SOURCES**

This section provides an overview of the processes, factors effecting emissions, and efficiency improvement opportunities of the following industrial GHG emission sources:

- Coal Fired Electric Generating Units (EGUs)
- Large Industrial/Commercial/Institutional Boilers
- Pulp and Paper
- Cement
- Iron and Steel Industry
- Refineries
- Nitric Acid Plants



#### **GHG EMISSIONS FROM COAL-FIRED EGUS**

#### **Combustion Process**

- Integrated Gasification Combined Cycle (IGCC)
- Electric Generating Unit (EGU)
- Fluidized Bed Combustion (FBC)

#### **Emission Reduction**

• Selective Noncatalytic Reduction (SNCR)



## FACTORS IMPACTING COAL-FIRED EGU CO<sub>2</sub> EMISSIONS

- Type of Coal Burned
- Heat Generated is determined by
  - Carbon
  - Hydrogen
  - Oxygen
  - Sulfur
- Ratio of Carbon and Heat

# TABLE 10-1: CO2 EMISSION FACTORS FOR COAL BY COAL RANK



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## IMPACT OF COAL-FIRED EGU EFFICIENCY ON CO<sub>2</sub> EMISSIONS

- Thermal Efficiency
- Electric Energy Output
- Calculating Efficiency
  - Higher heating value (HHV)
  - Lower heating value (LHV)
  - Parasitic load
  - Net output

HHV is typically used in the U.S. to express the efficiency of steam electric power plants.

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#### **EFFICIENCY IMPROVEMENT OPPORTUNITIES**

- Incremental-step methods for:
  - New EGUs
  - Older EGUs
- EGU improvements are incorporated during planning and engineering phases of a new EGU project:
  - EGU design
  - Equipment selection
  - Cost decisions

#### **GHG EMISSIONS FROM ICI BOILERS**

- Types and Uses
  - Industrial (Manufacturing, Processing, Mining, etc.)
  - Commercial (Hotels, Motels, Restaurants, etc.)
  - Institutional (Hospitals, Government Buildings, Schools, etc.)
- ICI boilers can use a number of different fuels
  - including coal (bituminous, sub bituminous, anthracite, lignite),
  - fuel oil, natural gas, biomass (wood residue, bagasse),
  - liquefied petroleum
- Coal -highest CO<sub>2</sub> emission factor (93.98 kg CO<sub>2</sub>/MMBtu)
- Natural gas lowest CO<sub>2</sub> emissions (53.06 kg CO<sub>2</sub>/MMBtu)

#### FIGURE 10-6. SCHEMATIC OF AN INDUSTRIAL BOILER SYSTEM



This combustion operation produces CO<sub>2</sub> emissions and is the focus of the emission reduction techniques presented in this chapter

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### FACTORS IMPACTING EMISSIONS FROM ICI BOILERS

- GHG emissions are similar to those of the EGUs.
  - These units also combust fossil fuels to generate steam.
  - The primary difference: they do not use the steam to run a turbine and generate electricity for the grid.
  - Biggest factor for GHG emissions, is the type of fuel used.
- The most common ICI boiler designs are:
  - Pulverized coal (PC) boilers
  - Fluidized bed combustors (FBC)
  - Stoker boilers
  - Watertube boilers
  - Firetube boilers

#### **EFFICIENCY OPPORTUNITIES FOR ICI BOILERS**

- As boilers deteriorate, this results in:
  - Higher heat rates,
  - Increased CO<sub>2</sub> emissions,
  - Increased operating costs
  - Reduced reliability; and
  - Reduced output (in some cases)
- Replace or Repair?
  - Rehabilitation may focus on life extension and reliability or the efficiency of the original design efficiency.
  - Efficiency can be improved by retrofitting combustion control technologies such as: heat recovery systems, control technology, and upgrading burners.

### GHG EMISSIONS FROM PULP AND PAPER MANUFACTURING

- The U.S. pulp and paper industry --largest self-generator of electricity in the U.S. manufacturing sector.
- Combined heat and power (CHP) generate the electricity and process heat to power:
  - Steam and gas Turbines
  - Power Boilers
  - Recovery Furnaces
  - Chemical Recovery Combustion Units
    - Generates electricity, steam, process heat
- Biomass Energy Recovery "On-site fuels"
  - Black Liquor and Hog Fuel (i.e., wood and bark)
  - Power over half of the industry's systems

#### FLOW DIAGRAM OF THE PULP AND PAPER MANUFACTURING PROCESS



#### Six main process areas:

- (1) Wood preparation;
- (2) Pulping;
- (3) Bleaching;
- (4) Chemical recovery;
- (5) Pulp drying
- (6) Papermaking.

#### PULP AND PAPER GHG EMISSION SOURCES

- GHG emissions from pulp and paper mill operations can be attributed to:
  - Combustion of on-site fuels
    - Natural gas, fuel, biomass-based materials, purchased electricity, and coal
  - Non- energy-related emission sources, such as by-product CO<sub>2</sub> emissions from the lime kiln chemical reactions and CH<sub>4</sub> emissions from wastewater treatment.

## TABLE 10-2. NATIONWIDE GHG EMISSIONS FROM PULPAND PAPER MANUFACTURING (DIRECT EMISSIONS)

Table 10-2. Nationwide GHG Emissions from Pulp and Paper Manufacturing

<b>Emission Source</b>	Million metric tons of CO <sub>2</sub> e per year <sub>1</sub>	Million short tons of CO <sub>2</sub> e per year
Direct Emi	ssions	
Direct emissions associated with fuel combustion (excluding biomass $CO_2$ )	57.7	63.6
Wastewater treatment plant $CH_4$ releases	0.4	0.4
Forest products industry landfills <sup>3</sup>	2.2	2.4
Use of carbonate make-up chemicals and fluegas desulfurization chemicals	0.39 <sup>3</sup>	0.4 <sup>3</sup>
Secondary pulp and paper manufacturing operations (i.e., converting primary products into final products)	2.5	2.8
Direct emissions of $CO_2$ from biomass fuel combustion (biogenic) <sup>4</sup>	113	125
Process-related $CO_2$ including $CO_2$ emitted from lime kilns (biogenic) <sup>4</sup>	Unavailable <sup>5</sup>	Unavailable <sup>5</sup>

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## TABLE 10-2. NATIONWIDE GHG EMISSIONS FROM PULPAND PAPER MANUFACTURING (INDIRECT EMISSIONS)

Table 10-2. Nationwide GHG Emissions from Pulp and Paper Manufacturing

Emission Source	Million metric tons of CO <sub>2</sub> e per year <sub>1</sub>	Million short tons of CO <sub>2</sub> e per year		
Indirect Emissions				
Electricity purchases by pulp and paper mills	25.4	28		
Electricity purchases by secondary manufacturing operations (i.e., converting primary products into final products)	8.9	9.8		
Steam purchases	Unavailable <sup>5</sup>	Unavailable <sup>5</sup>		



## TABLE 10-3. DIRECT GHG EMISSION SOURCESAT PULP, PAPER, & PAPERBOARD FACILITIES (CONTINUED)

Table 10-5. Direct GHG Emission Sources at Pulp, Paper, and Paperboard Facilities			
Emission Source	Types of pulp and paper mills where emissions sources typically are located	Type of GHG Emissions	
Fossil fuel- and/or biomass- fired boilers	All types of pulp and paper mills	Fossil CO <sub>2</sub> , CH <sub>4</sub> , N <sub>2</sub> O Biogenic CO <sub>2</sub> , CH <sub>4</sub> , N <sub>2</sub> O	
Thermal oxidizers and regenerative thermal oxidizers (RTOs)	Kraft pulp mills for NCG control and semi-chemical pulp mills (for combustion unit control)	Fossil CO <sub>2</sub> , CH <sub>4</sub> , N <sub>2</sub> O	
Direct-fired dryers	Gas-fired dryers at some pulp and paper mills	Fossil CO <sub>2</sub> , CH <sub>4</sub> , N <sub>2</sub> O	
Combustion turbines	All types of pulp and paper mills	Fossil CO <sub>2</sub> , CH <sub>4</sub> , N <sub>2</sub> O	
Chemical recovery furnaces – kraft & soda	Kraft and soda pulp mills	Fossil CO <sub>2</sub> , CH <sub>4</sub> , N <sub>2</sub> O Biogenic CO <sub>2</sub> , CH <sub>4</sub> , N <sub>2</sub> O	
Chemical recovery furnaces – sulfite	Sulfite pulp mills	Fossil CO <sub>2</sub> , CH <sub>4</sub> , N <sub>2</sub> O Biogenic CO <sub>2</sub> , CH <sub>4</sub> , N <sub>2</sub> O	

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## TABLE 10-3. DIRECT GHG EMISSION SOURCESAT PULP, PAPER, & PAPERBOARD FACILITIES

Table 10-3. Direct GHG Emission Sources a	at Pulp, Paper, and Paperboard Facilities
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Emission Source	Types of pulp and paper mills where emissions sources typically are located	Type of GHG Emissions
Chemical recovery combustion units – stand-alone semi- chemical	Stand-alone semi-chemical pulp mills	Fossil CO <sub>2</sub> , CH <sub>4</sub> , N <sub>2</sub> O Biogenic CO <sub>2</sub> , CH <sub>4</sub> , N <sub>2</sub> O
Kraft and soda lime kilns	Kraft and soda pulp mills	Fossil CO <sub>2</sub> , CH <sub>4</sub> , N <sub>2</sub> O Process biogenic CO <sub>2</sub>
Makeup chemicals (CaCO <sub>3</sub> , Na <sub>2</sub> CO <sub>3</sub> )	Kraft and soda pulp mills	Process CO <sub>2</sub>
Flue gas desulfurization systems	Mills that operate coal-fired boilers required to limit SO <sub>2</sub> emissions	Process CO <sub>2</sub>
Anaerobic wastewater treatment	Chemical pulp mills (kraft, mostly)	Biogenic CO <sub>2</sub> , CH <sub>4</sub>
On-site landfills	All types of pulp and paper mills	Biogenic $CO_2$ , $CH_4$

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## GHG EMISSIONS FROM CEMENT MANUFACTURING

- Second largest source of industrial CO<sub>2</sub> emissions in the U.S.
- Production process is two steps:
  - Clinker production (Source of 100% of CO<sub>2</sub> emissions)
  - Finish grinding (No direct emissions)

#### FIGURE 10-8. DIAGRAM FOR CEMENT MANUFACTURING PREHEATER PROCESS



### TOTAL COMBUSTION AND PROCESS-RELATED GHG EMISSIONS

- Emission Totals
  - Methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O) emissions from fossil fuel combustion -95.5 tons (86.8 million metric tons) of CO<sub>2</sub>e (MTonne CO<sub>2</sub>e)
  - Equivalent to 0.98 tons of  $CO_2e$  per ton of clinker, ( 0.46 tons are attributable to fuel combustion)
- Combustion emissions include:
  - CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> emissions resulting from the combustion of coal in the cement kiln

# TABLE 10-4. CO2 EMISSIONINTENSITY (LB/MMBTU)

Table 10-4. CO2 Emission Intensity (lb/MMBtu)					
Natural Gas	Heavy Fuel Oil	Western Sub- bituminous Coal <sup>1</sup>	Tires	Eastern Bituminous Coal <sup>2</sup>	Petroleum Coke
105.02	169.32	186.83	187.44	199.52	212.56

The direct  $CO_2$  emission intensity of fuels depends on the carbon content of the fuel which varies by type of fuel and further may vary within a given fuel type.

### GHG EMISSIONS FROM IRON AND STEEL INDUSTRY

- The GHG emissions are generated as:
- Process emissions in which raw materials and combustion may contribute to CO<sub>2</sub> emissions;
- (2) Emissions from combustion sources alone; and
- (3) Indirect emissions from consumption of electricity (Primarily in EAFs and in finishing operations such as rolling mills at both integrated and EAF plants).
#### **IRON AND STEEL PRODUCTION PROCESS**

- The production of steel at an integrated iron and steel plant is accomplished using several interrelated processes.
  - (1) Coke production
  - (2) Sinter production
  - (3) Iron production
  - (4) Raw steel production
  - (5) Ladle metallurgy
  - (6) Continuous casting
  - (7) Hot and cold rolling
  - (8) Finished product preparation

## FIGURE 10-9. GENERAL FLOW DIAGRAM OF THE IRON AND STEEL INDUSTRY

Steelmaking Routes: Integrated Route and Electric Arc Funace Route



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#### FACTORS IMPACTING GHG EMISSIONS IN IRON AND STEEL MANUFACTURING

#### Integrated Steelmaking - GHG emissions are primarily from:

- Blast furnace stoves —43 %
- Combustion sources (Natural Gas and Process Gases) 30 %
- Other process units —15 %
- Indirect emissions from electricity usage—12 %

#### EAF Steelmaking – GHG emissions are primarily from:

- indirect emissions from Electricity Use 50 %
- Combustion sources (Natural Gas) 40 %
- Steel production 10 %

## TABLE 10-5. ESTIMATES OF GHG EMISSIONS FROM IRON AND STEEL MANUFACTURING

Table 10-5. Estimates of GHG Emissions from Iron and Steel Manufacturing							
		<b>Emissions (million tonnes of CO<sub>2</sub>/yr)</b>					
Type of	Number	Process	Miscellaneous	Indirect	Facility	Average	
Facility	of Facilities	Units	<b>Combustion Units</b>	Emissions (Electricity)	Total	per Plant	
	Coke and EAF						
By-product coke (standalone)	9	2.8	2.7		5.5	0.6	
Nonrecovery coke	3	3.0			3.0	1.0	
EAF facilities	92	4.8	18.6	22.8	46.2	0.5	

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## TABLE 10-5. ESTIMATES OF GHG EMISSIONS FROM IRON AND STEEL MANUFACTURING (CONTINUED)

<b>Table 10-5.</b>	<b>Estimates of</b>	<b>GHG Emissions from</b>	n Iron and Steel Manufacturing

		<b>Emissions (million tonnes of CO<sub>2</sub>/yr)</b>				
<b>Type of Facility</b>	Number	Process	Miscellaneous	Indirect	Facility	Average
	of Facilities	Units	Combustion Units	Emissions (Electricity)	Total	per Plant
		Integ	rated Iron and S	teel Plants:		
By-product coke (co-located)	6	1.2			1.2	0.2
Blast furnace	17	23.9			23.9	1.4
BOF	18	4.4			4.4	0.2
Sinter plant	5	2.7			2.7	0.5
			Totals			
All Integrated Iron and Steel	18	32.2	16.8	6.5	55.5	3.1
All Facilities	130	42.8	38.0	29.3	110.1	0.8

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## GHG EMISSIONS FROM PETROLEUM REFINING

- There are three basic types of refineries:
  - Topping refineries
  - Hydroskimming refineries
  - Upgrading refineries ("conversion" or "complex refineries")

## GHG EMISSIONS FROM PETROLEUM REFINING

- The nation's second-highest industrial consumer of energy.
- Nearly all of the energy consumed is fossil fuel for combustion
- Other Process CO<sub>2</sub> Emissions
  - Process heaters and boilers)
  - Fluid catalytic cracking units (FCCU)
  - Hydrogen production units
  - Sulfur recovery plants

## FIGURE 10-10. NATIONWIDE CO<sub>2</sub> EQUIVALENT GHG EMISSIONS FROM PETROLEUM REFINERIES.



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#### FIGURE 10-11. GHG EMISSIONS FROM PETROLEUM REFINERIES.



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#### DIRECT $CO_2$ EMISSIONS FROM FUEL CONSUMPTION AND INDIRECT $CO_2$ EMISSIONS FROM ELECTRICITY



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#### **GHG EMISSIONS FROM NITRIC ACID PLANTS**

- Two Production Methods
  - Weak Nitric Acid
    - Utilizes oxidation, condensation, and absorption to produce nitric acid.
    - Concentration: 30% and 70% nitric acid.
    - High-Strength Acid
    - Produced from dehydrating, bleaching, condensing.
    - Concentration: 90 % or greater nitric acid.

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## N<sub>2</sub>O EMISSIONS AND NITRIC ACID PRODUCTION PROCESS

**Industrial Process Emissions** 

- N<sub>2</sub>O emissions from nitric acid are a byproduct of the process stream.
- Ammonia oxidation is the source of N<sub>2</sub>O emissions.
- The amount of N<sub>2</sub>O formed depends on combustion conditions in the oxidizing unit, catalyst compositions, catalyst age, and burner design.

#### **REACTIONS 10-1, 10-2, AND 10-3**

**Reaction 10-1** 

**Reaction 10-2** 

**Reaction 10-3** 

 $2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O$  $2NH_3 + 8NO \rightarrow 5N_2O + 3H_2O$  $4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O$ 



# TABLE 10-6. DEFAULT N2OEMISSION FACTORS

Table 10	-6. Default	t N <sub>2</sub> O Em	ission Fact	ors
		- 2 -		

<b>Production Process</b>	Approximate	N <sub>2</sub> O Emissions				
	Pressure	(kg N <sub>2</sub> O/metric ton Nitric Acid)				
	(atm)	Low	Average	High		
Plants with NSCR		1.9	2.0	2.1		
Plants with process- integrated or tailgas $N_2O$ destruction		2.25	2.5	2.75		
Atmospheric pressure (low pressure)	1	4.5	5.0	5.5		
Medium pressure plants	4-8	5.6	7	8.4		
High Pressure plants	8-14	5.4	9	12.6		

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# TABLE 10-7. UNCONTROLLED N2OEMISSIONS – CDM PROJECTS

Table 10-7. Uncontrolled N2O Emissions – CDM Projects						
Type of Control	Number of Test Reports	Range (kg N <sub>2</sub> O /metric ton HNO <sub>3</sub> ; lb N <sub>2</sub> O /T)	Average (kg N <sub>2</sub> O /metric ton HNO <sub>3;</sub> lb N <sub>2</sub> O /T)			
Secondary	38	4.0 - 19;8.1 - 38	8.5; 17.1			
Tertiary	11	6.2 – 15.7; 12.4 –31.4;	10; 20.0			
Primary	49	4.0 – 19; 8.1 - 38	8.9; 17.8			



#### EFFICIENCY IMPROVEMENTS ACROSS INDUSTRIAL SECTORS

This section introduces the following topics:

- Alternative and Renewable Energy Sources
- EPA's Energy Star Program Incentives
- Energy Management Systems (EnMSs)
- Benchmarking/ Energy Performance Indicators (EPI)
- Carbon Capture and Storage (CCS)

The controls for many of these sectors place emphasis on:

- 1. Improving energy efficiency, thus reducing the amount of fuel used.
- 2. Separating the CO<sub>2</sub> for long-term storage using carbon capture technology.

#### **ALTERNATIVE AND RENEWABLE SOURCES**

- Alternative and Renewable Energy can:
  - Improve efficiency
  - Reduce GHG emissions
- Solar, wind, geothermal, nuclear, and biomass technologies reduce GHG emissions from traditional combustion processes

#### **EPA ENERGY STAR PROGRAM**

- U.S. EPA's ENERGY STAR Program
  - Used by hundreds of U.S. manufacturers
  - Assists with stronger energy management
  - Emphasizes continuous improvement of energy performance.
- Energy Management Systems (EnMSs)
  - Framework to manage energy
  - Facilitates improvement



#### **BENCHMARKING / EPI**

- Benchmarking
  - Measures improvements in energy efficiency
  - Set and track progress toward goals based on individual performance, or the industry
- Plant Energy Performance Indicators (EPI)
  - Part of the U.S. EPA ENERGY STAR Program
    - Benchmarking tools establish 'best in class' for specific industrial sectors.

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#### **CARBON CAPTURE AND STORAGE (CSS)**

Separation and capture of CO<sub>2</sub> from flue gas, or other process exhaust stream, involves:

- Pressurization of captured CO<sub>2</sub>
- Transportation via pipeline, if necessary
- Injection and long-term geologic storage.

Several different technologies:

- Slip-stream or pilot-scale
- Bench-top or laboratory stage

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#### **CSS PROCESSES**

U.S. DOE is developing a commercially viable processes for capturing CO<sub>2</sub> from EGUs:

- Amine-based solvent systems
- Solid sorbents
- Membrane-based capture
- Oxy-combustion

#### Storage Options/ Beneficial reuse

- Geologic formations
- Unmineable coal seams
- Underground saline formations
- Basalt formations /organic rich

#### **RESULTS OF CARBON CAPTURE TECHNOLOGIES**

- Task Force on Carbon Capture and Storage
  - Developing a comprehensive and coordinated federal strategy to speed the commercial development and deployment of CCS technologies to:
    - Overcome the barriers to affordable, and accessible CCS deployment.
    - Bring 5 to 10 commercial demonstration projects online by 2016.

Additional information :

http://www.epa.gov/climatechange/policy/ccs\_task\_force.html

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## GHG EMISSION CONTROLS FOR INDUSTRIAL SECTORS

This section provides an overview of the emission controls techniques, and strategies to control industrial GHG emissions in these sectors:

- Coal Fired Electric Generating Units (EGUs)
- Large Industrial/Commercial/Institutional Boilers
- Pulp and Paper
- Cement
- Iron and Steel Industry
- Refineries
- Nitric Acid Plants

#### **EMISSION CONTROLS FOR COAL-FIRED EGUS**

Possible energy efficiency and process modifications for coal-fired EGUs:

EGU thermodynamic Cycle	Using supercritical, or ultra-critical steam cycles
EGU Coal Rank and Quality-	Burning higher quality coals (tends to be more efficient).
EGU Plant Size	Varying equipment size; to reduce electricity requirements.
EGU Cooling System	<i>Temperature of water entering condenser can have impacts on steam turbine performance.</i>
EGU Geographic Location	Re-locating processes to improve efficiency. At higher elevations, air pressure is lower and less oxygen is available for combustion per unit volume of ambient air than at lower elevations.
EGU Load Generation Flexibility Requirements	Operating an EGU as a base load unit is more efficient than operating an EGU as a load cycling unit to respond to fluctuations in customer electricity demand.
EGU Equipment Manufacturers	The efficiency specifications of major EGU components such as boilers, turbines, and electrical generators provided by equipment manufacturers can affect EGU efficiency.
EGU Plant Components	Optimum number of feed water heaters, high- efficiency electric motors, variable speed drives, better materials for heat exchangers

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## RESULTS OF IMPLEMENTING EGU EFFICIENCY TECHNOLOGIES

Increased thermal efficiency of power production

- NETL study
  - Absolute Change in overall efficiency
    - 40% to 42% represents a 2% absolute increase.
  - Relative change in efficiency
    - 40% to 42% is a relative change in efficiency and fuel use of 5%.
    - Relative change is the most consistent.
- A summary of the findings from the NETL study is presented in Table 10-8.

# TABLE 10-8. EXISTING COAL-FIRED EGUEFFICIENCY IMPROVEMENTS PROJECTS.

Table 10-8. Existing coal-fired EGU efficiency improvements reported for actualefficiency improvement projects.

Efficiency Improvement Technology	EGU Efficiency	Reported Efficiency Increase
Combustion Control Optimization	Combustion controls adjust coal and air flow to optimize steam production for the steam turbine/generator set. However, combustion control for a coal-fired EGU is complex and impacts a number of important operating parameters including combustion efficiency, steam temperature, furnace slagging and fouling, and $NO_x$ formation. The technologies include instruments that measure carbon levels in ash, coal flow rates, air flow rates, CO levels, oxygen levels, slag deposits, and burner metrics as well as advanced coal nozzles and plasma assisted coal combustion.	0.15 to 0.84%
Cooling System Heat Loss Recovery	Recover a portion of the heat loss from the warm cooling water exiting the steam condenser prior to its circulation thorough a cooling tower or discharge to a water body. The identified technologies include replacing the cooling tower fill (heat transfer surface) and tuning the cooling tower and condenser.	0.2 to 1%
Flue Gas Heat Recovery	Flue gas exit temperature from the air preheater can range from 250 to 350°F depending on the acid dew point temperature of the flue gas, which is dependent on the concentration of vapor phase sulfuric acid and moisture. For power plants equipped with wet FGD systems, the flue gas is further cooled to approximately 125°F as it is sprayed with the FGD reagent slurry. However, it may be possible to recover some of this lost energy in the flue gas to preheat boiler feedwater via use of a condensing heat exchanger.	0.3 to 1.5%
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# TABLE 10-8. EXISTING COAL-FIRED EGU EFFICIENCYIMPROVEMENTS REPORTED (CONTINUED)

Table 10-8. Existing coal-fired EGU efficiency improvements reported for actual efficiencyimprovement projects					
Efficiency Improvement Technology	EGU Efficiency	Reported Efficiency Increase			
Low-Rank Coal Drying	Subbituminous and lignite coals contain relatively large amounts of moisture (15 to 40%) compared to bituminous coal (less than 10%). A significant amount of the heat released during combustion of low-rank coals is used to evaporate this moisture, rather than generate steam for the turbine. As a result, boiler efficiency is typically lower for plants burning low-rank coal. The technologies include using waste heat from the flue gas and/or cooling water systems to dry low-rank coal prior to combustion.	0.1 to 1.7%			
Scotblower Optimization	Sootblowers intermittently inject high velocity jets of steam or air to clean coal ash deposits from boiler tube surfaces in order to maintain adequate heat transfer. Proper control of the timing and intensity of individual sootblowers is important to maintain steam temperature and boiler efficiency. The identified technologies include intelligent or neural-network sootblowing (i.e., sootblowing in response to real-time conditions in the boiler) and detonation sootblowing.	0.1 to 0.65%			
Steam Turbine Design	There are recoverable energy losses that result from the mechanical design or physical condition of the steam turbine. For example, steam turbine manufacturers have improved the design of turbine blades and steam seals that can increase both efficiency and output (i.e., steam turbine dense pack technology).	0.84 to 2.6			

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## SUMMARY OF CONTROLS FOR COAL-FIRED EGUS

- There is no one best available coal-fired EGU technology universally applicable to all
- Evaluate on a site-specific basis.
- An evaluation for a new facility would include:
  - Carbon capture and storage (CCS)
  - Efficient technologies
    - Ultra-supercritical steam conditions, IGCC, pressurized fluidized bed), double steam reheat, coal drying, FGD technology, and CHP

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## EMISSION CONTROLS FOR INDUSTRIAL, COMMERCIAL, AND INSTITUTIONAL BOILERS

- Energy and efficiency improvements
  - Physical controls
- A Summary of GHG reduction measures
  - GHG Measures
  - Applicability
  - Efficiency Improvement Percentage
  - CO<sub>2</sub> Reduction Percentage
  - Capital Costs
- Other measures to reduce GHG emissions from boilers
  - Alternative fuels Biomass
  - Co-firing
  - Fuel Switching (Fuel and Oil-fired Systems)

## EMISSION CONTROLS FOR INDUSTRIAL, COMMERCIAL, AND INSTITUTIONAL BOILERS

The physical controls presented in this chapter include:

- Operating and Maintenance (O&M) Practices
- Air Preheat and Economizers
- Turbulators for Firetube Boilers
- Boiler Insulation
- Minimization of Air filtration
- Boiler Blowdown Heat Exchanger
- Condensate Return System
- Refractory Material Selection
- Minimization of Gas-side Heat Transfer Surface Deposits
- Steam Line Maintenance

## TABLE 10-9. ICI BOILERS – SUMMARY OF GREENHOUSEGAS EMISSION REDUCTION MEASURES

Table 10-9. ICI Boilers – Summary of Greenhouse Gas Emission Reduction Measures								
GHG Measure	Applicability	Efficiency Improvement (percentage pt)	CO <sub>2</sub> Reduction (%)	Capital Costs	Notes/Issues			
	Energy Efficiency Improvements							
Replace/ Upgrade Burners	All, except for Stoker-type boilers and fluidized bed boilers	Up to 4-5%.	Up to ~ 6%.	\$2,500 – 5,100 per MMBtu/hr	Site specific considerations (retrofit ability) and economic factors may affect the installation of burners			
Tuning	All	CO from 1000-2000 to < 200 ppm Unburned carbon (UBC) from 20- 30% to 10-15%	Up to ~3%	Up to \$3000	Manual tuning with parametric testing			
Optimization	All	0.5% - 3.0%	Up to ~ 4%	\$100,000	Neural network- based			
Instrumentation & Controls	All, especially at large plants	0.5% – 3.0% (in addition to optimization)	Up to ~ 4%	>\$1million	System integration, calibration, and maintenance			
Economizer	Units with capacity over 25,000 pounds of steam per hour;	40°F decrease in flue gas temp. equals 1% improvement	Relates to efficiency Gain in boiler	\$2.3 million (For 650 MMBtu/hr)	Larger units; must consider pressure Loss, steam conditions			
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#### TABLE 10-9. ICI BOILERS – SUMMARY OF GREENHOUSE GAS **EMISSION REDUCTION MEASURES (CONTINUED)**

Table 10-9. ICI Boilers – Summary of Greenhouse Gas Emission Reduction Measures								
GHG Measure	Applicability	Efficiency Improvement (percentage pt)	CO <sub>2</sub> Reduction (%)	Capital Costs	Notes/Issues			
<b>Energy Efficiency Improvements</b>								
Air Preheater	Units with capacity over 25,000 pounds of steam per hour	A 300°F decrease in gas temperature represents about 6% improvement	~ 1% per 40°F temperature decrease	\$200,000 – 250,000 (for 10MMBtu/hr)	Used in large boiler applications, not widely used in ICIs due to increase in NO <sub>X</sub>			
Create turbulent flow within firetubes	Single or two pass firetube boilers	1% efficiency gain for 40°F reduction in flue gas temperature 100°F -150°F temperature decrease potential	~ 1% per 40°F temperature decrease up to ~ 4%	\$10 – 15 per tube	Widely accepted with older boilers			
Insulation	All, most suitable for surface temperatures above 120°F	Dependent on surface temperature	Up to 7%		Radiation losses increase with decreasing load			
Reduce air leakages	All	1.5 – 3% potential (Effect similar to reducing excess air)	Up to ~ 4%	Site-specific (None to cost of maintenance Program)	Requires routine maintenance procedures			
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## TABLE 10-9. ICI BOILERS – SUMMARY OF GREENHOUSE GASEMISSION REDUCTION MEASURES (CONTINUED)

 Table 10-9. ICI Boilers – Summary of Greenhouse Gas Emission
 Reduction Measures

GHG Measure	Applicability	Efficiency Improvement (percentage pt)	CO <sub>2</sub> Reduction (%)	Capital Costs	Notes/Issues
Capture energy from boiler blowdown	Most suitable for units w/ continuous boiler blowdown exceeding 5% of steam rate	Site specific depending on steam conditions Up to ~ 7%	Up to ~ 8% See efficiency comment	NA	Water quality is important
Condensate return system	All; However, larger units more economical to retrofit	Site specific - depends on condensate temperature and % recovery	Same as efficiency improvement, ratio of Btu/hr saved from condensate to Btu/hr input	\$75,000	Energy savings is the energy contained in the return condensate, condensate quality affects use
Reduce slagging and fouling of heat transfer surfaces	Watertube boilers	1% to 3% Site specific; fuel quality/operating condition have large impact	Up to ~ 4%	\$50,000 to \$125,000	Downtime/econom ic factors, regain lost capacity
Insulating jackets	Surfaces over 120°F		Same as efficiency improvement	Depends on length/type of insulation required for implementation	No deployment barriers
Reduce steam trap leaks	All			None to cost of maintenance program	No deployment barriers

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## TABLE 10-9. ICI BOILERS – SUMMARY OF GHG REDUCTION MEASURES (CONTINUED)

Table 10-9. ICI Boilers – Summary of Greenhouse Gas Emission Reduction Measures					
GHG Measure	Applicability	Efficiency Improvement (percentage pt)	CO <sub>2</sub> Reduction (%)	Capital Costs	Notes/Issues
Post-Combustion					
Carbon capture and storage					Demonstrated at the slip-stream or pilot-scale
Alternative fuels –biomass	All fossil fuels				Less caloric content than fossil fuel
Other Measures					
Co-firing	Coal-fired and oil- fired boilers	Reduction up to 2% for biomass co- firing	20-30% reduction with gas co-firing		Negative impact of boiler efficiency
Fuel switching	Coal-fired and oil- fired boilers		20-35% reduction switching from coal to oil; 20-35% reduction switching from coal to natural gas		Change in hardware to accommodate 100% fuel switch
Combined heat and power	All	Overall efficiency improves from 30- 50% to 70-80%		\$1,000- 2,500/kW	High capital investment

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## OTHER MEASURES TO REDUCE GHG EMISSIONS FROM BOILERS

- Alternative Fuels Biomass
- Co-firing
- Fuel Switching
  - Coal fired Systems
  - Oil-fired Systems

## OTHER MEASURES TO REDUCE GHG EMISSIONS FROM BOILERS

- Alternative Fuels Biomass
  - Replaces fossil fuel with biomass fuel based on: specific emissions for the fuel and its caloric value
    - Pure biomass fuels: animal meal, waste wood products and sawdust, and sewage sludge.
    - Other biomass fuels: wood, grasses, green algae (quickgrowing species)
  - <u>Potential issues:</u> caloric value, trace compounds, waste regulations, social acceptance, agricultural proximity
## OTHER MEASURES TO REDUCE GHG EMISSIONS FROM BOILERS

- Co-firing
  - Burning more than one fuel in one boiler
    - Gas co-firing in an oil or coal boiler
    - Solid biomass co-firing in a coal boiler
    - Liquid or gas biofuel co-firing in any boiler
  - Requires Efficient Boiler Design or Modification
    - <u>Potential Impacts</u>: Low biomass density, high moisture content, volatility, alkali sulfate formation, degradation, chloride concentrations.
    - <u>Other Considerations</u>: Availability and proximity of fuels, price and production, logistics of collection and transport.

## OTHER MEASURES TO REDUCE GHG EMISSIONS FROM BOILERS

- Fuel Switching in Other Systems
  - Feasible and relevant :
    - Pulverized Coal plants to any of the fuels mentioned
      - Coal to Oil (1960s)
      - Coal to Gas (1980s and 1990s)
    - FBC to biomass
    - Stoker boilers, burn oil, gas, coal-derived, or biofuels
    - Water tube and Fire tube boilers (NG) to clean liquid or gas fuels
  - Not Feasible:
    - FBC to oil, gas, coal-derived gas, or biofuels
    - Gas-fired boilers to coal-derived fuel, or biofuels
      - Unless price justifies investments to modify design.

## EMISSION CONTROLS FOR PULP AND PAPER MANUFACTURING

- Power Boilers
- Chemical Recovery Furnaces, Combustion Units, Turbines
- Combined Heat and Power (CHP) Systems
- Steam Systems

An extensive list of Control measures and efficiency options is listed in Table 10-10.

# TABLE 10-10. LIST OF CONTROL MEASURESAND ENERGY EFFICIENCY OPTIONS

 Table 10-10. List of Control Measures and Energy Efficiency Options

Boi	lers
Burner Replacement	Boiler Maintenance
Boiler Process Control	Condensate return
Reduction of Flue Gas Quantities	Minimizing boiler blow down
Reduction of excess air	Blow down steam recovery
Improved boiler insulation	Flue gas heat recovery
Chemical Reco	overy Furnaces
Boiler control measures and energy efficiency options (See above)	Recovery furnace deposition monitoring
Black liquor solids concentration	Quaternary air injection
Improved composite tubes for recovery furnaces	
Turk	pines
Boiler/steam turbine CHP	Replacement of pressure reducing valves
Simple cycle gas turbine CHP	Steam injected gas turbines
Combined cycle CHP	Regular performance monitoring and maintenance

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# TABLE 10-10. LIST OF CONTROL MEASURES ANDENERGY EFFICIENCY OPTIONS (CONTINUED)

 Table 10-10. List of Control Measures and Energy Efficiency Options

Natural-Gas Fired Drye	rs and Thermal Oxidizers					
Energy efficiency turbine CHP	Use of thermal oxidizers employing heat recovery (e.g., regenerative or recuperative thermal oxidizers)					
Use of existing combustion processes (e.g., power boilers or lime kilns) over a separate thermal oxidizer						
Kraft and So	oda Lime Kilns					
Piping of stack gas to adjacent PCC plant	Lime kiln modifications (e.g., high-efficiency filters, higher efficiency refractory insulation brick)					
Lime kiln oxygen enrichment	Lime kiln ESP					
Makeup	Chemicals					
Practices to ensure good chemical recovery rates in the pulping and chemical recovery processes	Addition of Na and Ca in forms that do not contain carbon (e.g., Na <sub>2</sub> SO <sub>4</sub> , NaOH, CaO)					
Flue Gas Desulfurization (FGD) Systems						
Use of sorbents other than carbonates	Use of lower-emitting FGD systems					

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# TABLE 10-10. LIST OF CONTROL MEASURES ANDENERGY EFFICIENCY OPTIONS (CONTINUED)

### Table 10-10. List of Control Measures and Energy Efficiency Options

Wastewate	r Treatment
Use of mechanical clarifiers or aerobic biological treatment systems (instead of anaerobic treatment systems)	Minimization of potential for formation of anaerobic zones in wastewater treatment systems (e.g., through placement of aerators where practical)
On-site 1	Landfills
Dewatering and burning of wastewater treatment plant residuals in on-site boiler	Capture and control of landfill gas by burning it in onsite combustion device (e.g., boilers) for energy recovery and solid waste management



## EMISSION CONTROLS FOR CEMENT MANUFACTURING

- Raw Materials Preparation
- Clinker Production
- Finish Grinding
- Facility Operations
- Raw Materials Substitution
- Carbon Capture
- Other Control Methods
- <u>Methods focus on:</u> energy efficiency, efficient processes, replacing high-carbon fuels with low-carbon fuels, and applying lower clinker to cement ratio.

## SUMMARY OF CONTROL MEASURES OF CEMENT PRODUCTION

Table 10-11. Portland Cement Manufacturing Sector- Summary of Greenhouse Gas Controls <sup>a,b.</sup>

Control Technology	Emission Reduction	Energy Savings	Capital Costs	Operating Costs	Applicability	In Practice ?	Other factors	
Energy Efficiency Improvements in Raw Material Preparation								
Switch from pneumatic to mechanical raw material transport	Calculated from energy savings	2.9 kWh/ton cement	\$4.1/annu al ton cement capacity	NA	New and Existing Facilities with LD, PH, PH/PC kilns	Yes		
Use of belt conveyors and bucket elevators instead of pneumatics	Calculated from energy savings	2.5 kWh/ton cement	\$3.43/ton cement capacity	Reduction of \$0.17/ton cement	New and Existing Facilities	Yes		
Convert raw meal blending silo to gravity-type homogenizing	Calculated from energy savings	1.4-3.5 kWh/ton cement	\$5.0/ton cement capacity (silo retrofit)	NA	New and Existing Facilities	Yes		
Improvements in raw material blending	Calculated from energy savings	1.0 kWh/ton cement	\$2.5/ton cement capacity	Increase of \$0.02/ton cement	New and Existing Facilities with LD, PH, PH/PC kilns	Yes	May increase production by up to 5%	



Continued...

Table 10-11. Portland Cement Manufacturing Sector- Summary of Greenhouse Gas Controls <sup>a,b.</sup>

Control Technology	Emission Reduction	Energy Savings	Capital Costs	Operating Costs	Applicabilit y	In Practice ?	Other factors
	Energy Effic	ciency Improve	ments in Cl	inker Produc	ction		
Process control and management systems	7-33 lb $CO_2$ /ton cement and 1.3 lb $CO_2$ /ton cement from electricity usage reduction	2.5-5% or 42- 167 MJ/ton cement and electricity savings of 1 kWh/ton cement	\$0.3/annua l ton cement capacity	NA	New and Existing Facilities. All kilns.	Yes	
Replacement of kiln seals	Calculated from energy savings	0.4% or 0.01 MMBtu/ ton cement	NA	New and Existing Facilities. All kilns.			
Kiln combustion System improvements	Calculated from energy savings	2-10% reduction in fuel usage	\$0.8/annua l ton cement capacity	NA	New and Existing Facilities. All kilns	Yes	May result in up to 10% increase in kiln output



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Continued...

Table 10-11. Portland Cement Manufacturing Sector- Summary of Greenhouse Gas Controls <sup>a,b.</sup>

Control Technology	Emission Reduction	Energy Savings	Capital Costs	Operating Costs	Applicability	In Practice ?		
Energy Efficiency Improvements in Clinker Production								
Fluxes and mineralizers to reduce energy demand	9-30 lb CO <sub>2</sub> /ton cement and 0-2 lb/ton cement from electricity usage reduction	42-150 MJ/ton cement	NA	Fuel savings may be offset by cost of fluxes and mineralizers	New and Existing Facilities. All kilns.	Yes		
Kiln/preheater insulation (internal)	Calculated from energy savings	0.1-0.31 MMBtu/ton cement	\$0.21/annual ton cement capacity	NA	New and Existing PH and PH/PC kilns	Yes		
Kiln/preheater insulation (external)	Calculated from energy savings	17 Btu/ton cement	\$0.25/ton cement capacity	NA	New and Existing PH and PH/PC kilns	Yes		
Refractory material selection	Calculated from energy savings	49,800 Btu/ton cement	\$0.50/ton cement capacity	NA	All kilns	Yes		
Replacement of planetary and travelling grate cooler with reciprocating grate cooler	Reduction of17- 52 lbCO <sub>2</sub> /ton cement, but increase of 2-6 lb/ton cement from increased electricity use	Reduce energy consumption by 8% or 84- 251 MJ/ton cement; increase electricity use by 1-5 kWh/ton cement	NA	NA	New and Existing kilns with capacity > 500 tonnes/day	Yes		

Table 10-11. Portland Cement Manufacturing Sector- Summary of Greenhouse Gas Controls <sup>a,b.</sup>

Control Technology	Emission Reduction	Energy Savings	Capital Costs	Operating Costs	Applicability	In Practice?
	Energy E	Efficiency Imp	provements in	n Clinker Pro	duction	
Heat recovery for power – cogeneration	Calculated from energy savings	Produce 7- 20 kWh/ton cement	\$2-4/annual ton cement capacity	\$0.2-0.3/ annual ton cement capacity	LD kilns	Yes
Suspension preheater low pressure drop cyclones	Up to 2 lb CO <sub>2</sub> /ton cement	0.5-0.6 kWh/ton cement per 50 mm water column pressure reduction	\$2.5- 2.9/annual ton cement capacity	NA	New and retrofitting PH and PH/PC kilns	
Multistage preheater	Calculated from energy savings	0.4 MMBtu/ Ton cement	\$12.8- 34/annual ton cement capacity	NA	New and retrofitting PH and PH/PC kilns	Yes
Conversion from long dry kiln to preheater/ precalciner kiln	50-460 lb CO <sub>2</sub> /ton cement	1.1MMBtu/t on cement	\$7.9-96/ annual ton cement capacity	Decrease by \$0.08/ton cement	LD kilns	Yes
Kiln drive efficiency improvements	Calculated from energy savings	0.5 kWh/ton cement	Increased by about 6%	Reduced power cost for kiln drive by 2- 8%	New and Existing Facilities.	Yes

Table 10-11. Portland Cement Manufacturing Sector- Summary of Greenhouse Gas Controls <sup>a,b.</sup>

Control Technology	Emission Reduction	Energy Savings	Capital Costs	Operating Costs	Applicability	In Practice ?	Other Factors	
Energy Efficiency Improvements in Clinker Production								
Adjustable speed drive for kiln fan	Calculated from energy savings	5 kWh/ton cement	NA	NA	New and Existing Facilities.	Yes		
Oxygen enrichment	18-37 lb CO <sub>2</sub> /ton cement; however, this may be completely offset by increased electricity consumption	NA	NA	NA	All Kilns	Yes	May increase production by 3- 7%. May increase NO <sub>x</sub> emissions.	
Mid kiln firing	Calculated from the emission factor of tires compared to fuel being replaced	NA	NA	NA	Existing Wet, LD kilns	Yes	Burning tires may result in lower NO <sub>x</sub> emissions	
Air mixing technology	Calculated from fuel reduction	Improves combustion efficiency reducing fuel use	\$520,00 0	Increases electricity usage by 0.23 kWh/ton cement	TBD	Yes	Likely reduces CO, $NO_x$ , and $SO_2$ emissions	
Preheater riser duct firing					Ph and PH/PC kilns			

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Table 10-11. Portland Cement Manufacturing Sector- Summary of Greenhouse Gas Controls <sup>a,b.</sup>

Control Technolog y	Emission Reduction	Energy Savings	Capital Costs	Operating Cos	sts Applic- ability	In Practice?	Other Factors
		Energy Effici	iency Improvem	ents in Finish	n Grinding		
Improved ball mill	Calculated from energy savings	6-25 kWh/ton cement	\$2.3-7.3/annual ton cement capacity; or \$35/ton cement capacity for a vertical roller mill	May reduce by 30-40%, but vertical roller mill may increase costs b \$0.17/ton Cement	Existing and New Facilities. All kilns.	Yes	
High efficiency classifiers	Calculated from energy savings	1.7-2.3 kWh/ton cement, but could be as high as 6 kWh/ton cement	\$2/annual ton cement	\$0.045/ton cement	Existing and New Facilities. All kilns.	Yes	May increase productio n by up to 25%
	E	Energy Efficie	ncy Improveme	nts in Facility	<b>Operations</b>		
High efficiency motors	Calculated from energy savings	5%, or about 5 kWh/ton clinker	\$0.67/ton cement	No change	Existing and New Facilities. All kilns.	Yes	
Variable speed drives	3-10 lb CO2/ton cement	3-8 kWh/ton cement	NA	NA ]	Existing and New Facilities. All kilns.	Yes	Capital and operating cost savings are highly site specific

Table 10-11. Portland Cement Manufacturing Sector- Summary of Greenhouse Gas Controls <sup>a,b.</sup>

Control Technology	Emission Reduction	Energy Savings	Capital Costs	Operating Costs	Appli- cability	In Practice ?	Other Factors			
	Energy Efficiency Improvements in Facility Operations									
High efficiency fans	Calculated from energy savings	0.9 kWh/ton cement	\$0.46/ton cement	NA	Existing and New Facilities. All kilns.	Yes				
Optimization of compressed air systems	Calculated from energy savings	Up to 20%	NA	NA	Existing and New Facilities. All kilns.	Yes				
Lighting system Efficiency improvements	Calculated from energy savings	12-50% depending on specific changes made	NA	NA	Existing and New Facilities. All kilns.	Yes				
		Raw M	aterial Substitutio	on						
Decarbonated feedstocks (steel slag or fly ash)	$0.02$ -0.51 ton $CO_2$ /ton material	1.12 MMBtu/ton cement; or 0.07-1.59 MMBtu/ton material	\$0.75/ton cement for steel slag fed into kiln without grinding	Increased by \$0.08/ton cement for steel slag fed into kiln without grinding	All Facilities	Yes	Energy savings may be offset by 0.08 MBtu/ton to dry feedstock			

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	<b>Table 10-11.</b>	Portland Cement M	Ianufacturing Sec	tor- Summary o	of Greenhouse Gas Con	trols <sup>a,b.</sup>	
Control Technology	Emission Reduction	Energy Savings	Capital Costs	Operating Costs	Applicability	In Practice ?	Other Factors
		l	Raw Material S	Substitution			
Calcereous oil shale	0.009 lb CO <sub>2</sub> /ton cement	0.07 MMBtu/ton cement	\$1/ton cement when replacing 8% of raw meal	Increase by \$0.08/ton cement when replacing 8% of raw meal	All Facilities	Yes	Energy savings may be offset by 0.08 MBtu/ton to dry feedstock
			Blended Co	ements			
Cementi- tious Materials	200-860 lb $CO_2$ /ton cement for cement with 30-70% blast furnace slag	380-1710MJ /ton cement for cement with 30- 70% blast furnace slag	NA	NA	All Facilities	Yes	
Pozzolanic materials	100-280 lb CO2/ton cement	200-500 MJ/ton cement	NA	NA	All Facilities	Yes	
			Carbon Ca	apture			
Calera process	90%, but varies with specific application	Parasitic load of 10-20 of the power plant	\$950/kW for coal-fired power plant	NA	TBD	Pilot testing	Pilot testing is on power pl

Table 10-11. Portland Cement Manufacturing Sector- Summary of Greenhouse Gas Controls <sup>a,b.</sup>									
Control Technology	Emission Reduction	Energy Savings	Capital Costs	Operating Costs	Applica- bility	In Practice?	Other Factors		
			Carbon Ca	apture					
Oxy- combustion	1000-1600 lb $CO_2$ /ton cement, but increased electricity usage could generate 110- 150 $CO_2$ /ton cement	Overall energy requirements decrease by 75- 84 MJ/ton cement, but electricity requirements increase by 92- 96 kWh/ton cement	NA	NA	TBD	No	No installations at cement plants; many technical issues to overcome		
Post- combustion solvent capture and stripping	Up to 95%	NA	NA	NA	TBD	Yes, but not at cement plants			
Post- combustion membranes	Up to 80%	NA	NA	NA	TBD	No, currently in research stage			
Superheated CaO	Up to 43%	NA	NA	NA	TBD	No, currently in research stage			

	Table 10-11. Portlan	nd Cement Manuf	acturing Sec	tor- Summary o	of Greenhouse (	Gas Controls <sup>a</sup>	,b.
Control Technology	Emission Reduction	Energy Savings	Capital Costs	Operating Costs	Applica- bility	In Practice?	Other Factors
		Othe	er Control	Measures			
Fuel switching	<ul><li>18% for</li><li>switching from</li><li>coal to heavy oil;</li><li>40% for</li><li>switching from</li><li>coal to natural</li><li>gas</li></ul>	NA	NA	NA	All Facilities	Yes	Does not affect emissions from calcinations reaction
Hybrid solar plants	Equivalent to emissions that would have been generated	NA	NA	NA	TBD	No, currently in research stage	Hybrid solar plants
Syngas coproduction	Up to 650 lb CO <sub>2</sub> /ton cement	NA	NA	NA	TBD	No, but has been applied to smaller streams	Syngas coproduction
Power plant/cement plant carbonate looping	830-1300 lb CO <sub>2</sub> /ton cement	NA	NA	NA	TBD	No, currently in research stage	Power plant/cement plant carbonate looping

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## **EMISSION CONTROLS FOR THE IRON AND STEEL INDUSTRY**

- Energy Efficiency Improvements
  - Energy Efficiencies for Integrated Iron and Steel Production
    - Preventative maintenance, facility modifications, coal moisture control and dry quenching, PC and NG injection, casting/hot rolling
  - Efficiencies for Electric Arc Furnace (EAF) Steelmaking
    - Process Controls
  - Long-Term Opportunities to Reduce CO<sub>2</sub> Emission
    - Top gas recycling blast furnace with CCS, HIsarna with CCS, advanced direct reduction with CSS, and electrolysis
  - Emerging Technologies
    - New transformational technologies and processes.

## EMISSION CONTROLS FOR THE IRON AND STEEL INDUSTRY (CONTINUED)

- Table 10-12 and 10-13 include the emission reduction potential, energy savings, costs, and feasibility of the measures when such information was available.
  - Studies for EPA and DOE Worrell et al. (1999) updated (2009)
  - Study for EPA's Climate Protection Partnerships Division as part of the ENERGY STAR Program.
- American Iron and Steel Institute (ASI) states:

Improvements in blast furnace efficiency are possible through optimized blast injection technologies, better sensors, and process controls.

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# TABLE 10-12. ENERGY EFFICIENCY TECHNOLOGIESAND MEASURES APPLIED TO INTEGRATED STEELPRODUCTION IN THE U.S.

Table 10-12. Energy Efficiency Technologies and Measures Applied to Integrated SteelProduction in the U.S.

Option	Emission Reduction (kg of CO <sub>2</sub> /tonne of product)	Fuel Savings (GJ/tonne of product)	Electricity Savings (GJ/tonne of product)	Annual Operating Costs (\$/tonne of product)	Retrofit Capital Costs (\$/tonne of product)	Payback Time (years)
Iron Ore Preparation (Sintering)						
Sinter plant heat recovery	57.2	0.55	0.0	0.0	4.7	2.8
Emission optimized sintering						
Reduction of air leakage	2.0	0.0	0.0	0.0	0.14	1.3
Increasing bed depth	9.9	0.09	0.0	0.0	0.0	0.0
Improved process control	5.0	0.05	0.0	0.0	0.21	1.4
Use of waste fuels (e.g., lubricants) in sintering plant	19.5	0.18	0.0	0.0	0.29	0.5
Improve charging method						
Improve ignition oven efficiency						
Cokemaking						
Coal moisture control	6.7	0.30	0.0	0.0	76.6	> 50
Programmed heating	3.8	0.17	0.0	0.0	0.37	0.7
VSD COG compressor	0.12	0.0	0.0	0.0	0.47	21.2
Coke dry quenching	27.5	1.2	0.0	0.78	109.5	35.7
Additional use of COG						
Single chamber system						
Non-recovery coke ovens						

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## TABLE 10-12. ENERGY EFFICIENCY TECHNOLOGIES AND MEASURES APPLIEDTO INTEGRATED STEEL PRODUCTION IN THE U.S. (CONTINUED)

Table 10-12. Energy Enficiency recinologies and Measures Applied to Integrated Steel								
	Production in the U.S.							
Ironmaking - Blast Furnace								
Pulverized coal injection to 130 kg/ton iron	47.0	0.77	0.0	-3.1	11.0	2.0		
Pulverized coal injection to 225 kg/ton iron	34.7	0.57	0.0	-1.6	8.1	2.4		
Injection of natural gas to 140 kg/ton iron	54.9	0.90	0.0	-3.1	7.8	1.3		
Injection of oil								
Injection of COG and BOF gas						<1.0		
Charging carbon composite agglomerates								
Top pressure recovery turbines (wet type)	17.6	0.0	0.11	0.0	31.3	29.8		
Recovery of BFG	4.0	0.07	0.0	0.0	0.47	2.3		
Hot-blast stove automation	22.6	0.37	0.0	0.0	0.47	0.4		
Recuperator hot-blast stove	4.9	0.08	0.0	0.0	2.2	8.7		
Improvement of combustion in hot stove								
Improved blast furnace control systems	24.4	0.40	0.0	0.0	0.56	0.4		
Blast furnace gas recycling								
Slag heat recovery								
Steelmaking - Basic Oxygen Furnace (BOF	)							
BOF gas plus sensible heat	46.0	0.92	0.0	0.0	34.4	11.9		
VSD on ventilation fans	0.51	0.0	0.003	0.0	0.31	9.9		
Improvement of process monitoring and control								
Programmed and efficient ladle heating								

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## TABLE 10-12. ENERGY EFFICIENCY TECHNOLOGIES AND MEASURES APPLIEDTO INTEGRATED STEEL PRODUCTION IN THE U.S. (CONTINUED)

 Table 10-12. Energy Efficiency Technologies and Measures Applied to Integrated Steel

 Production in the U.S.

Carlina							
Casting							
Efficient caster ladle/tundish heating	1.1	0.02	0.0	0.0	0.09	1.3	
Near net shape casting - thin slab	728.8	3.5	0.64	-54.8	234.9	3.3	
Near net shape casting - strip				25% less			
General Measures for Rolling Mills	General Measures for Rolling Mills						
Energy efficient drives	1.6	0.0	0.01	0.0	0.30	3.2	
Gate communicated turn-off inverters							
Install lubrication system			0.016				
Hot Rolling							
Proper reheating temperature							
Avoiding overload of reheat furnaces							
Hot charging	30.2	0.60	0.0	-2.1	23.5	5.9	
Process control in hot strip mill	15.1	0.30	0.0	0.0	1.1	1.2	
Recuperative burners	35.2	0.70	0.0	0.0	3.9	1.8	
Flameless burners	60%	60%					
Insulation of furnaces	8.0	0.16	0.0	0.0	15.6	31.0	
Walking beam furnace			25%				
Controlling oxygen levels and VSDs on combustion air fans	16.6	0.33	0.0	0.0	0.79	0.8	
Heat recovery to the product		50%		32%			
Waste heat recovery (cooling water)	1.9	0.03	0.0	0.11	1.3	> 50	

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## TABLE 10-12. ENERGY EFFICIENCY TECHNOLOGIES AND MEASURES APPLIEDTO INTEGRATED STEEL PRODUCTION IN THE U.S. (CONTINUED)

 Table 10-12. Energy Efficiency Technologies and Measures Applied to Integrated Steel

 Production in the U.S.

Cold Rolling and Finishing						
Heat recovery on the annealing line	17.5	0.30	0.02	0.0	4.2	4.0
Reduced steam use (pickling line)	9.9	0.19	0.0	0.0	4.4	7.3
Automated monitoring and targeting system	35.3	0.0	0.21	0.0	1.7	0.8
Inter-electrode insulation in electrolytic pickling line						
Continuous annealing						
General						
Preventive maintenance	35.7	0.43	0.02	0.03	0.02	
Energy monitoring and management system	9.5	0.11	0.01	0.0	0.23	0.5
Combined heat and power/cogeneration	82.1	0.03	0.35	0.0	22.7	6.1
High-efficiency motors						
VSD—flue gas control, pumps, and fans	1.5	0.0	0.02	0.0	2.0	10.7

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## TABLE 10-13. ENERGY EFFICIENCY TECHNOLOGIES AND MEASURESAPPLIED TO INTEGRATED STEEL PRODUCTION IN THE U.S.

 Table 10-13. Energy Efficiency Technologies and Measures Applied to Integrated Steel

 Production in the U.S.

	Emissions Reduction for	Fuel Savings	Electricity Savings	Annual Operating	Retrofit Capital	
	CO <sub>2</sub> /tonne of	(GJ/tonne of	(GJ/tonne of	Costs (\$/tonne of	Costs (\$/tonne of	Payback Time
Option	product)	product)	product)	product)	product)	(years)
Steelmaking - Electric Arc Furnace						
Improved process control (neural network)	17.6	0.0	0.11	-1.6	1.5	0.5
Adjustable speed drives (ASDs)			0.05		2.0	2-3
Transformer efficiency—ultra-high power transformers	10.0	0.0	0.06	0.0	4.3	5.2
Bottom stirring/stirring gas injection	11.7	0.0	0.07	-3.1	0.94	0.2
Foamy slag practice	10.6	0.0	0.07	-2.8	15.6	4.2
Oxy-fuel burners	23.5	0.0	0.14	-6.2	7.5	0.9
Post-combustion of the flue gases						
DC arc furnace	52.9	0.0	0.32	-3.9	6.1	0.7
Scrap preheating—tunnel furnace (Consteel)	35.2	0.0	0.22	-3.0	7.8	1.3
Scrap preheating, post-combustion—shaft furnace (Fuchs)	35.3	-0.70	0.43	-6.2	9.4	1.0
Engineered refractories			0.036			
Airtight operation			0.36			
Contiarc furnace	Í		0.72			
Flue gas monitoring and control	8.8	0.0	0.05	0.0	3.1	4.3
Eccentric bottom tapping on existing furnace	8.8	0.0	0.05	0.0	5.0	6.8
Twin-shell DC with scrap preheating	11.1	0.0	0.07	-1.7	9.4	3.5

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### TABLE 10-13. ENERGY EFFICIENCY TECHNOLOGIES AND MEASURES APPLIED TO INTEGRATED STEEL PRODUCTION IN THE U.S. (CONTINUED)

Table 10-13. Energy Efficiency Technologies and Measures Applied to Integrated Steel									
	Product	ion in the	U.S.						
Option Steelmaking - Electric Arc Furnace	Emissions Reduction (kg CO <sub>2</sub> /tonne of product)	Fuel Savings (GJ/tonne of product)	Electricity Savings (GJ/tonne of product)	Annual Operating Costs (\$/tonne of product)	Retrofit Capital Costs (\$/tonne of product)	Payback Time (years)			
Casting									
Efficient caster ladle/tundish heating	1.1	0.02	0.0	0.0	0.09	1.3			
Near net shape casting - thin slab	265.3	3.2	0.64	-54.8	234.8	3.3			
Near net shape casting - strip				25% less					
Hot Rolling									
Proper reheating temperature									
Avoiding overload of reheat furnaces									
Energy efficient drives in the rolling mill	1.6	0.0	0.01	0.0	0.30	5.9			
Process control in hot strip mill	15.1	0.30	0.0	0.0	1.1	1.2			
Recuperative burners	35.2	0.70	0.0	0.0	3.9	1.8			
Flameless burners	60%	60%							
Insulation of furnaces	8.1	0.16	0.0	0.0	15.7	31.0			
Walking beam furnace			25%						
Controlling oxygen levels and VSDs on combustion air fans	16.6	0.33	0.0	0.0	0.79	0.8			
Heat recovery to the product		50%		32%					
General									
Preventive maintenance	15.0	0.09	0.05	0.03	0.02				
Energy monitoring and management systems	3.7	0.02	0.01	0.0	0.23	0.9			

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### SUMMARY OF CONTROL MEASURES IN THE IRON AND STEEL INDUSTRY

- Caveats = Estimated Costs, Savings, Potential Energy Reductions
- Site-Specific Planning
- Discuss options with Facility's engineering or energy manager

## EMISSION CONTROLS FOR PETROLEUM REFINING

- Energy Efficiency Improvements
  - Refinery emissions are influenced by:
    - Energy efficiency, fuel use, feed composition, products, size and number of operating processing units
  - Energy Management Systems (EnMSs)
  - Process Control Systems
- Table 10-14 summarizes the GHG reduction measures currently available for petroleum refining

 Table 10-14. Summary of GHG Reduction Measures for the Petroleum Refining Industry

GHG Control Measure	Description	Efficiency Improvement/ GHG emission reduction	Retrofit Capital Costs (\$/unit of CO <sub>2</sub> e)	Pay-back time (years)	In Practice ?	Other Factors
	Energy Efficiency Pr	rograms and Sy	stems			
Energy Efficiency Initiatives and Improvement s	<ul> <li>Benchmark GHG performance and implement energy management systems to improve energy efficiency, such as:</li> <li>improve process monitoring and control systems</li> <li>use high efficiency motors</li> <li>use variable speed drives</li> <li>optimize compressed air systems</li> <li>implement lighting system</li> <li>efficiency improvements</li> </ul>	4-17% of electricity consumpti on		1-2 years	Yes	
	Stationary Com	bustion Sour	ces			
	Steam Gener	ating Boilers				
Systems Approach to Steam Generation	<ul> <li>Analyze steam needs and energy recovery options, including:</li> <li>minimize steam generation at excess pressure or volume</li> <li>use turbo or steam expanders when excesses are unavoidable</li> <li>schedule boilers based on efficiency</li> </ul>				Yes	

Table 10-14. Summary of GHG Reduction Measures for the Petroleum Refining Industry

GHG Control Measure	Description	Efficiency Improvement/ GHG emission reduction	Pay-back time (years)	In Practice ?	Other Factors					
	Stationary Combust	ion Sources								
	Steam Generating Boilers									
Boiler Feed Water Preparation	Replace a hot lime water softener with a reverse osmosis membrane treatment system to remove hardness and reduce alkalinity of boiler feed.	70-90% reduction in blowdown steam loss; up to 10% reduction in GHG emissions	2-5 years	Yes						
Improved Process Control	Oxygen monitors and intake air flow monitors can be used to optimize the fuel/air mixture and limit excess air.	1-3% of boiler emissions	6 - 18 mos	Yes	Low excess air levels may increase CO emissions					
Improved Insulation	Insulation (or improved insulation) of boilers and distribution pipes.	3-13% of boiler emissions	6 - 18 mos	Yes						
Improved Maintenance	All boilers should be maintained according to a maintenance program. In particular, the burners and condensate return system should be properly adjusted and worn components replaced. Additionally, fouling on the fireside of the boiler and scaling on the waterside should be controlled.	1-10% of boiler emissions		Yes						
					Langer					

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 Table 10-14. Summary of GHG Reduction Measures for the Petroleum Refining Industry

GHG Control Measure	Description	Efficiency Improvement/ GHG emission reduction	Pay- back time (years)	In Practice ?	Other Factors				
Stationary Combustion Sources									
	Steam Generating Bo		2	N7					
from Process Flue Gas	sufficient heat content to make it economical to recover the heat. Typically, this is accomplished using an economizer to preheat the boiler feed water.	emissions	2 years	Yes					
Recover Steam from Blowdown	Install a steam recover system to recovery blowdown steam for low pressure steam needs (e.g., space heating and feed water preheating).	1 –3%	1 - 3 years	Yes					
Reduce Standby Losses	Reduce or eliminate steam production at standby by modifying the burner, combustion air supply, and boiler feedwater supply, and using automatic control systems to reduce the time needed to reach full boiler capacity.	Up to 85% reduction in standby losses (but likely a small fraction of facility total boiler emissions)	1.5 years	Yes					
Improve and Maintain Steam Traps	Implement a maintenance plan that includes regular inspection and maintenance of steam traps to prevent steam lost through malfunctioning steam traps.	1-10% of boiler emissions		Yes					
Install Steam Condensate Return Lines	Reuse of the steam condensate reduces the amount of feed water needed and reduces the amount of energy needed to produce steam since the condensate is preheated.	1- 10% of steam energy use	1-2 years	Yes					

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Table 10-14. Summary of GHG Reduction Measures for the Petroleum Refining Industry

GHG Control Measure	Description	Efficiency Improvement/ GHG emission reduction	Pay- back time (years)	In Practice?	Other Factors
	Process Heaters				
Combustion Air Controls- Limitations on Excess air	Oxygen monitors and intake air flow monitors can be used to optimize the fuel/air mixture and limit excess air.	1-3%	6-18 mos	Yes	Combustion Air Controls- Limitations on Excess air
Heat Recovery: Air Preheater	Air preheater package consists of a compact air-to-air heat exchanger installed at grade level through which the hot stack gases from the convective section exchange heat with the incoming combustion air. If the original heater is natural draft, a retrofit requires conversion to mechanical draft.	10-15% over units with no preheat.		Yes	May increase NO <sub>x</sub> emissions
	Combined Heat and Power				
Combined Heat and Power	Use internally generated fuels or natural gas for power (electricity) production using a gas turbine and generate steam from waste heat of combustion exhaust to achieve greater energy efficiencies		5 years	Yes	
	Carbon Capture				
Oxy-combustion	Use pure oxygen in large combustion sources to reduce flue gas volumes and increase $CO_2$ concentrations to improve capture efficiency and costs			No	
Post-combustion Solvent Capture	Use solvent scrubbing, typically using monoethanolamine (MEA) as the solvent, for separation of $CO_2$ in post-combustion exhaust streams			No	
Post-combustion membranes	Use membrane technology to separate or adsorb $CO_2$ in an exhaust stream		\$55-63	No	

Table 10-14. Summary of GHG Reduction Measures for the Petroleum Refining Industry

GHG Control Measure	Description	Efficiency Improvement/ GHG emission reduction	Pay-back time (years)	In Practice ?	Other Factors				
	Fuel Gas System and Fla	ıre							
	Fuel Gas System								
Compressor Selection	Use dry seal rather than wet seal compressors; use rod packing for reciprocating compressors			Yes					
Leak Detection and Repair	Use organic vapor analyzer or optical sensing technologies to identify leaks in natural gas lines, fuel gas lines, and other lines with high methane concentrations and repair the leaks as soon as possible.	80-90% of leak emissions; <0.1% refinery-wide		Yes					
Sulfur Scrubbing System	Evaluate different sulfur scrubbing technologies or solvents for energy efficiency			Yes					
	Flares								
Flare Gas Recover	Install flare gas recovery compressor system to recover flare gas to the fuel gas system		1 yr	Yes					
Proper Flare Operation	Maintain combustion efficiency of flare by controlling heating content of flare gas and steam- or air-assist rates			Yes					
Refrigerated Condensers	Refrigerated Condensers			Yes					
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	- -	Table 10-14. Summary of GHG Reduction Measures for	r the Petroleum	<b>Refining In</b>	dustry			
	GHG Control Measure	Description	Efficiency Improvement/ GHG emission reduction	Pay-back time (years)	In Practice ?	Other Factors		
	Cracking Units							
	Fluid Catalytic Cracking Units							
	Power/Was te Heat Recovery	Install or upgrade power recovery or waste heat boilers to recover latent heat from the FCCU regenerator exhaust			Yes			
	High- Efficiency Regenerato rs	Use specially designed FCCU regenerators for high efficiency, complete combustion of catalyst coke deposits			Yes			
	Hydrocracking Units							
	Power/Was te Heat Recovery	Install or upgrade power recovery.Power can be recovered from the pressure difference between the reactor and fractionation stages		2-5 years	Yes			
	Hydrogen Recovery	Use hydrogen recovery compressor and back- up compressor to ensure recovery of hydrogen in process off-gas			Yes			
Fluid Coking Units								
	Power/Was te Heat Recovery	Install or upgrade power recovery or waste heat boilers to recover latent heat from the fluid coking unit exhaust			Yes			

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Table 10-14. Summary of GHG Reduction Measures for the Petroleum Refining Industry

GHG Control	Description	Efficiency Improvement/ GHG	In					
Measure		emission reduction	Practice'					
Flexicoking Units								
Delayed Coking Units								
Steam Blowdown System	Use low back-pressure blowdown system and recycle hot blowdown system water for steam generation		Yes					
Catalytic Reforming Units								
	Sulfur Recovery Units							
Sulfur Recovery System Selection	Evaluate energy and CO2 intensity in selection of sulfur recovery unit and tail gas treatment system and a variety of different tail gas treatment units including Claus, SuperClaus® and EuroClaus®, SCOT, Beavon/amine,Beavon/Stretford, Cansolv®, LoCat®, and Wellman- Lord		Yes					
Hydrogen Production Optimization	Implement a comprehensive assessment of hydrogen needs and consider using additional catalytic reforming units to produce $H_2$		Yes					
Combustion Airand Feed/Steam Preheat	Use heat recovery systems to preheat the feed/steam and combustion air temperature	5% of total energy consumption for $H_2$ production	Yes					
Cogeneration	Use cogeneration of hydrogen and electricity: hot exhaust from a gas turbine is transferred to the reformer furnace; the reformer convection section is also used as a heat recovery steam generator (HRSG) in a cogeneration design; steam raised in the convection section can be put through either a topping or condensing turbine for additional power generation		Yes					
Hydrogen Purification	Evaluate hydrogen purification processes (i.e., pressure-swing adsorption, membrane separation, and cryogenic separation) for overall energy intensity and potential $CO_2$ recovery.		Yes					

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Table 10-14. Summary of GHG Reduction Measures for the Petroleum Refining Industry

GHG Control Measure	Description	Efficiency Improvement/ GHG emission reduction	Pay- back time (years)	In Practic e?						
Hydrotreating Units										
Hydrotreater Design	Use energy efficient hydrotreated designs and new catalyst to increase sulfur removal.			Yes						
Crude Desalting and Distillation Units										
Desalter Design	Alternative designs for the desalter, such as multi-stage units and combinations of AC and DC fields, may increase efficiency and reduce energy consumption.			Yes						
Progressive Distillation Design	Progressive distillation process uses as series of distillation towers working at different temperatures to avoid superheating lighter fractions of the crude oil.	30% reduction in crude heater emissions; 5% or more refinery-wide		Yes						
	Storage Tanks									
Vapor Recovery or Control for Unstabilized Crude Oil Tanks	Consider use of a vapor recovery or control system for crude oil storage tanks that receive crude oil that has been stored under pressure ("unstabilized" crude oil).	90-95% reduction in $CH_4$ from these tanks		Yes						
Heated Storage Tank Insulation	Insulate heated storage tanks			Yes						

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## EMISSION CONTROLS FOR NITRIC ACID PLANTS

- Primary Controls Suppression of N<sub>2</sub>O Formation
- Secondary Controls Catalytic N<sub>2</sub>O Decomposition in the Oxidation Reactor
- Tertiary Controls
  - Catalytic Reduction
  - Catalytic Decomposition
  - Nonselective Catalytic Reduction (NSCR)
## TABLE 10-15. SUMMARY OF CONTROLMEASURES FOR NITRIC ACID PRODUCTION

 Table 10-15.
 Summary of GHG Control Measures in the Nitric Acid Production Industry

Pollutant	Control Technology	Emission Reduction (%)	Energy Savings	Capital Costs (\$/ton CO <sub>2</sub> e)	Operating Costs (\$/ton CO <sub>2</sub> e)	Demonstrated in Practice
N <sub>2</sub> O	Primary	30 - 85	None	NA	Na	Yes
N <sub>2</sub> O	Secondary	70 -90	None	NA	0.12 – 0.97	Yes
N <sub>2</sub> O	NSCR	> 80	None	6.27	0.14 - 0.22	Yes
N <sub>2</sub> O	Other Tertiary Controls	>80	None	2.18 – 3.55	0.14 – 1.91	Yes

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## PRIMARY CONTROLS- SUPPRESSION OF N<sub>2</sub>O FORMATION

- Extension of the NH<sub>3</sub> oxidation reactor
  - "Empty" reaction chamber
  - Allows an additional residence time of 1 to 3 seconds.
  - Reductions are estimated to be 70% to 85% (4 to 6 lb N<sub>2</sub>O/ton 100% acid or about 400 ppm)
  - Applicable to new plants with low additional investments.
- Modify ammonia oxidation gauzes
  - Catalysts can be improved platinum catalysts.
  - Potential 30 -40 % N<sub>2</sub>O reduction.
  - Alternative oxidation catalysts (not platinum based) achieve 80 – 90% reduction --lower NO produced
  - Data showed a range of 3.6 –9.7 kg N<sub>2</sub>O/tonne (7.2 19.4 lb N<sub>2</sub>O/ton). The average was 6.2 kg N<sub>2</sub>O/tonne (12.4 lb N<sub>2</sub>O/ton).

## SECONDARY CONTROL - CATALYTIC N<sub>2</sub>O DECOMPOSITION IN THE OXIDATION REACTOR

- Catalyst is located immediately downstream of the NH<sub>3</sub> oxidation step.
  - N<sub>2</sub>O is decomposed to N<sub>2</sub> and O<sub>2</sub> almost instantly
  - The "Selective" catalyst in the ammonia burner promotes decomposition of  $N_2O$  to  $N_2$  and  $O_2$

#### **Reaction 10-7** $2N_2O \rightarrow 2N_2 + O_2$

- No modification of the ammonia oxidation reactor is required
- Catalyst has shown no effect on ammonia conversion.
- Placement of the catalyst in the ammonia burner allows for reduction of  $N_2O$  emissions
- Average lifetime of pellet catalyst —4 years

## FIGURE 10-13. YARA SECONDARY N<sub>2</sub>O CONTROL FROM NITRIC ACID PRODUCTION



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## TABLE 10-16. N2O EMISSION TEST RESULTSSECONDARY CONTROLS

 Table 10-16.
 N<sub>2</sub>O Emission Test Results – Secondary Controls

Source	Units tested	Range (lb N <sub>2</sub> O/ton)	Average (lb N <sub>2</sub> O/ton)	% Reduction Range	% Reduction Average
EC	8	1.8 - 5.0	3.2	Unknown	Unknown
EC*	4*	3.0-3.8*	3.4*	Unknown	Unknown
CDM Projects	30 (37 test periods)	0.15 – 11.6	4.1	9 – 98	76

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### FIGURE 10-14. N<sub>2</sub>O EMISSIONS FROM SECONDARY CONTROLS – CDM PROJECTS



**Company and Location** 

## TERTIARY CONTROLS – NONSELECTIVE CATALYTIC REDUCTION

- Nonselective Catalytic Reduction (NSCR)
  - Process to reduce NO<sub>x</sub> emissions where:
    - Fuels; natural gas, propane, butane, or ammonia plant purge gas (mainly H<sub>2</sub>) to reduce NO<sub>x</sub>
    - N<sub>2</sub>O over a catalyst to produce N<sub>2</sub> and water
  - Catalysts for NSCR:
    - Platinum, vanadium pentoxide, iron oxide or titanium
    - NSCR is typically used at plants that preheat tailgas to 200 -450° C and requires a greater reagent input than SCR

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#### FIGURE 10-15. UHDE COMBINATION N<sub>2</sub>O AND NO<sub>X</sub> CONTROL FOR NITRIC ACID PRODUCTION PLANTS



- Catalytic N<sub>2</sub>O decomposition
- DeN<sub>2</sub>O<sup>®</sup> rates of up to 99+%
- NOx removal to <10 ppm</li>
- Low NH<sub>3</sub> consumption
- Best at temperatures ~ 430°C up (806°F)



- Catalytic Reduction of N<sub>2</sub>O & NOx
- Very high DeN<sub>2</sub>O<sup>®</sup> rate of up to 99+%
- NOx removal down to 0 ppm
- Moderate HC & NH<sub>3</sub> consumption
- Wide temperature range ~330°C up (626°F)

## FIGURE 10-16. UHDE ENVINO<sub>X</sub><sup>®</sup> REACTOR IN LINZ, AUSTRIA



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## TERTIARY CONTROLS – CATALYTIC DECOMPOSITION

- Decompose N<sub>2</sub>O to form nitrogen and oxygen
- EnviNO<sub>X</sub>®
  - Variant 1- catalytic decomposition.
- Shell N<sub>2</sub>O Abatement Technology (C-NAT).
  - A pellet catalyst
- BASF NO<sub>X</sub> CAT  $^{\text{TM}}$  ZN<sub>2</sub>0 Catalyst.
  - Ammonia is injected into a catalyst bed that consists of an SCR catalyst (e.g,. Vandium/Titanium) and the NOxCAT<sup>™</sup> Z N<sub>2</sub>O reduction catalyst

# TABLE 10-17. N2O EMISSION TEST RESULTS - TERTIARY CONTROLS

Table 10-17. N2O Emission Test Results – Tertiary Controls							
Source	Units tested	Range (lb N <sub>2</sub> O/ton)	Average (lb N <sub>2</sub> O/ton)	% Reduction Range	% Reduction Average		
EC	7	0.02 - 0.48	0.18	Unknown	Unknown		
CDM Projects	11	0.41 – 2.2	1.2	88 - 98	94		



### FIGURE 10-17. N<sub>2</sub>O EMISSIONS FROM TERTIARY CONTROLS



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## **ENERGY EFFICIENCY IMPROVEMENTS TO REDUCE OTHER GHG EMISSIONS**

- Energy Recovery
  - Minimize external fuel sources through recovery
  - Exothermic reactions: oxidation and absorption
  - Single and Dual pressure plants
  - Steam and Heat recovery
- Energy Efficiency
  - Building lighting and HVAC
  - Motors, compressed air and pumps



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## ADDITIONAL RESOURCES FOR GHG EMISSION CONTROL

• EPA's Greenhouse Gas Permitting website

http://www.epa.gov/nsr/ghgpermitting.html

- Resources for Estimating GHG Emissions
   <u>http://www.epa.gov/nsr/ghgresources.html</u>
- Clean Air Act Permitting for Greenhouse Gases
   <u>http://www.epa.gov/nsr/ghgpermitting.html</u>
- BACT/RACT/LAER Clearinghouse (RBLC)

http://cfpub.epa.gov/RBLC/

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### **SUMMARY**

The chapter covered the following topics:

- Definition of GHG and the primary sources of GHG emissions
- Main GHG control techniques and strategies for these industries:
  - Electric Generating Units (EGUs),
  - Large Industrial/Commercial/Institutional Boilers,
  - Pulp and Paper Manufacturing, Cement Manufacturing,
  - Iron and Steel Industry,
  - Petroleum Refineries, and
  - Nitric Acid Plants
- Additional GHG emission control and reduction resources