

Air Pollution Training Institute

COURSE 415: CONTROL OF GASEOUS EMISSIONS



STUDENT WORKBOOK

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Office of Air and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, NC 27711

April, 2021

William Franek & Louis DeRose



Course 415
Control of Gaseous Emissions
 April 12 – 16, 2021

AGENDA

LOCATION

MODERATORS

Virtual Training

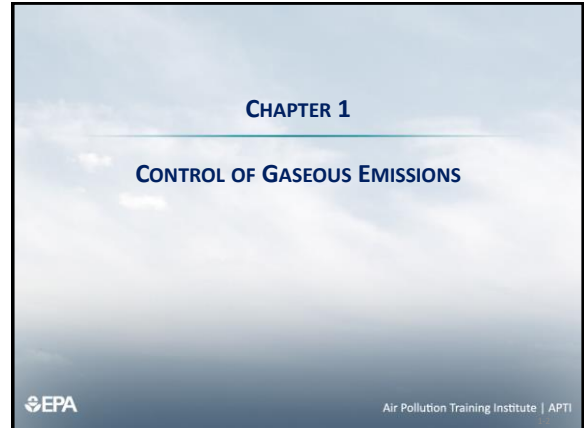
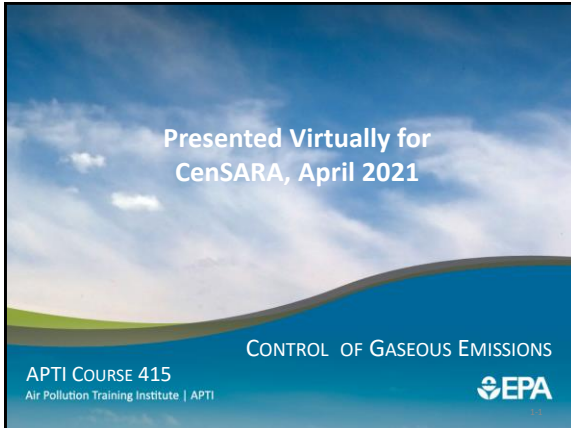
Louis DeRose / William Franek

DAY & TIME	SUBJECT	SPEAKER
Day One		
9:00	Introduction	W. Franek
9:15	Basic Gas Concepts Chapter 1	L. DeRose
10:30	BREAK	
10:45	LEL & Control Types Chapter 2	L. DeRose
11:45	Air Pollution Control Systems Chapter 3 Includes Capture Hoods & Fan Designs	W. Franek
1:00	ADJOURN	
Day Two		
9:00	Adsorption Systems Chapter 4	W. Franek
10:30	BREAK	
10:45	Adsorption Systems (continued)	W. Franek
12:15	Absorption Systems Chapter 5	W. Franek
1:00	ADJOURN	
Day Three		
9:00	Absorption Systems (continued)	W. Franek
10:45	BREAK	
11:00	Oxidation Systems Chapter 6	L. DeRose
1:00	ADJOURN	
Day Four		
9:00	Condensation Control Chapter 7	W. Franek
10:45	BREAK	
11:00	Controls and Regulations for GHGs Chapter 10	L. DeRose
1:00	ADJOURN	
Day Five		
9:00	Pre-Test Review	L. DeRose
9:30	Control of SO ₂ Chapter 9	W. Franek
10:45	BREAK	
11:00	Control of NO _x Chapter 8	
12:30	Mercury and Multipollutant Controls Chapter 11	W. Franek
1:00	ADJOURN	

Course Instructors:

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Learning Objectives

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

- Identify primary and secondary gaseous contaminants.
- Understand emission rates & sources of gaseous pollutants
- Recognize regulations that govern gaseous contaminants.

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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

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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

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Examples of Secondary Gaseous Contaminants

- Secondary Gaseous Contaminants
 - Nitrogen dioxide (NO₂)
 - Ozone (O₃) and other photochemical oxidants
 - Sulfuric acid (H₂SO₄)

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Sulfur Dioxide

- Sulfur dioxide is a colorless gas
 - Formed during the combustion of sulfur containing fuel such as:
 - > 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

- 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 $SO_3 + H_2O \rightarrow H_2SO_4$
- Because of the corrosiveness of sulfuric acid, it is important to keep gas streams at temperatures above the sulfuric acid dew point



Nitric Oxide and Nitrogen Dioxide

- Collectively referred to as NO_x
- 3 types of NO_x formation:
 - Thermal NO_x: *thermal* fixation of atmospheric N₂ [N₂ from air at high temperatures]
 - Fuel NO_x: *oxidation* of organic nitrogen compounds in the fuel
 - Prompt NO_x: *reaction* with partially oxidized compounds within the flame
- Nitric Oxide (NO) –odorless gas & insoluble in water
- Nitrogen Dioxide (NO₂) –moderately soluble in water, has a distinct reddish-brown color
 - Nitric acid pickling operations



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
 - CO reduces the oxygen in blood because the affinity of hemoglobin for CO is over 200 times that for oxygen
- 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.
 - VOCs are also released during surface coating operations, painting, gasoline distribution, and synthetic organic chemical manufacturing.
- Categorized as
 - Contained (captured in hoods)
 - Fugitive



Organic Compounds NOT Classified 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



Organic HAPs

- Approximately 200 specific organic compounds and classes of compounds have known adverse health effects.
- They are regulated and classified as hazardous air pollutants (HAPs) Section 112(b) of the CAA.
- 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	Tetrachloroethylene	127184
Aniline	62553	Methanol	67561	Toluene	108883
Benzene	71432	Methylene chloride	75092	2,4 Toluene diisocyanate	584849
1,3, Butadiene	106990	Methyl ethyl ketone	78933	1,2,4 Trichlorobenzene	120821
Carbon disulfide	75150	Methyl isocyanate	624839	Trichloroethylene	79016
Chlorobenzene	108907	Naphthalene	91203	Xylenes	95476
Chloroform	67663	Nitrobenzene	98953		
Ethyl benzene	100414	Phenol	108952		



Hydrogen Chloride and Hydrogen Fluoride

- HCl and HF are HAPs
- (hydrochloric acid and hydrofluoric acid) 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 compounds 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

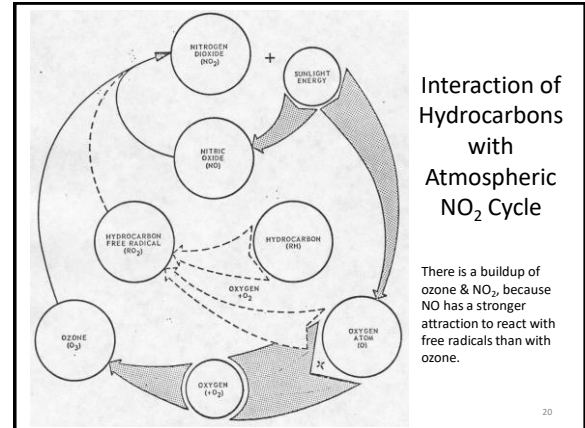
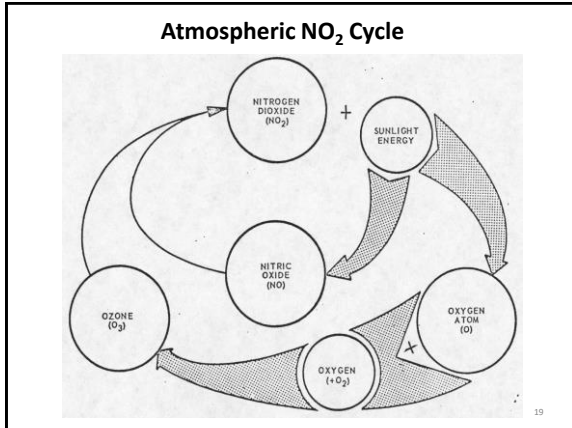
- Hydrogen Sulfide, H₂S: emitted from metallurgical, petroleum, and petrochemical processes and from sour natural gas wells; strong rotten egg odor
- Total Reduced Sulfur compounds (TRSs): emitted primarily from Kraft pulp mills
 - Methyl Mercaptan, CH₃SH
 - Dimethyl Sulfide, (CH₃)₂S
 - Dimethyl Disulfide, (CH₃)₂S₂
- All have extremely strong and unpleasant odors, are water soluble & are usually controlled by oxidation



Ozone and Other Photochemical Oxidants

- Ozone forms in the troposphere because of photochemical reactions with NO_x, VOCs, & 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





Mercury

- While elemental mercury (Hg) is toxic to humans, methyl mercury (CH₃Hg⁺) 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 primarily due to the combustion of coal and other fossil fuels that contain trace quantities of mercury

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Other Sources of Mercury Emissions

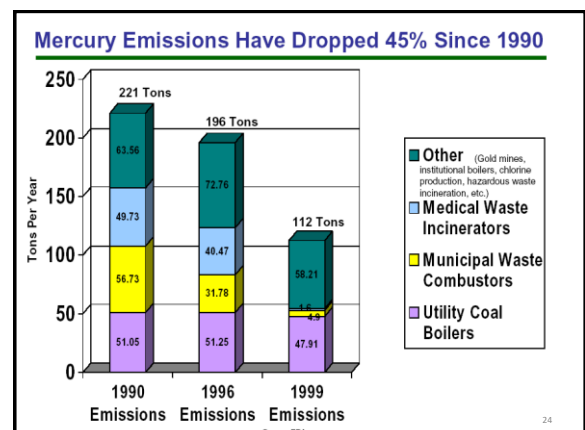
- Certain chlor-alkali chlorine manufacturing processes
- Mining operations
- Metal refining
- Products that contain elemental mercury
 - Batteries
 - Lamps
 - Thermometers

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Mercury Reduction Efforts

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

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Solid Waste Combustion: CAA §129

- §129 was added (1990 CAAA) & required EPA to pass NSPS for new & existing solid waste combustion units.
 - *Municipal waste combustion units (MWC)*
 - *Hospital/medical/infectious waste incinerators*
 - *Commercial & industrial solid waste incinerators*
 - *Other solid waste incinerators (small, residential, agricultural & construction waste, wood waste, crematories, & contaminated soil treatment waste)*
- §129 limits emissions of particulate matter, carbon monoxide, dioxins/furans, sulfur dioxide, nitrogen oxides, hydrogen chloride, lead, **mercury**, and cadmium
- §129 does not regulate incineration of hazardous waste.

400-2-25

Recent Mercury Regulations

- August 2010: EPA issued NESHAP requiring reductions of mercury emission from *cement plants* (third-largest source of mercury air emissions in the U.S.)
- Feb 17, 2011: EPA issued NESHAP for *gold ore processing & production facilities* (seventh-largest source of mercury air emission in the U.S.)

CAA-26

Mercury Emissions from Power Plants

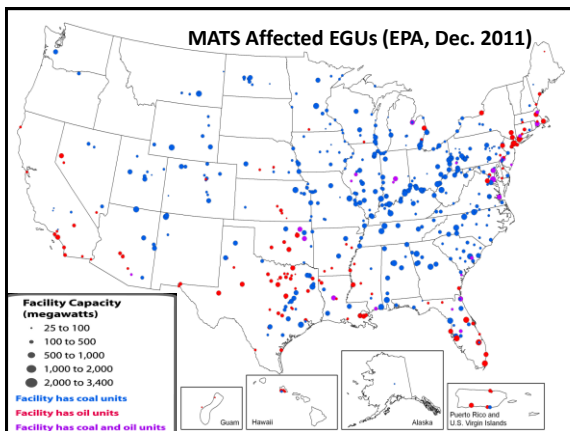
- 2005: Clean Air Mercury Rule (CAMR) required coal-fired power plants to reduce mercury emissions by 70% by establishing a “cap & trade” program (as a NSPS).
 - EPA said that MACT approach not necessary.
 - In 2008, Ct. **vacated** CAMR & said EPA must establish a §112 mercury MACT for power plants (can’t substitute a NSPS for it).

CAA-27

Mercury Emissions from Power Plants

- On Feb 6, 2012, EPA passed a coal &/or oil fired power plant mercury MACT (called MATS – Mercury Air Toxic Standard)
 - Applies to EGUs larger than 25 megawatts (MW) that burn coal or oil for the purpose of generating electricity (600 power plants).
 - Will reduce emissions of mercury & other HAPs i.e.
 - Heavy metals (mercury, arsenic, chromium, & nickel) & (HCl & HF).

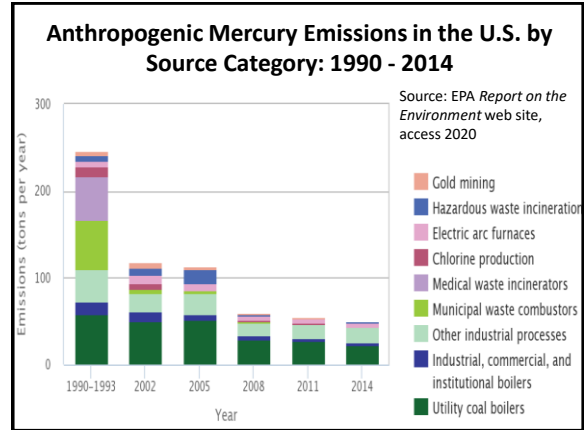
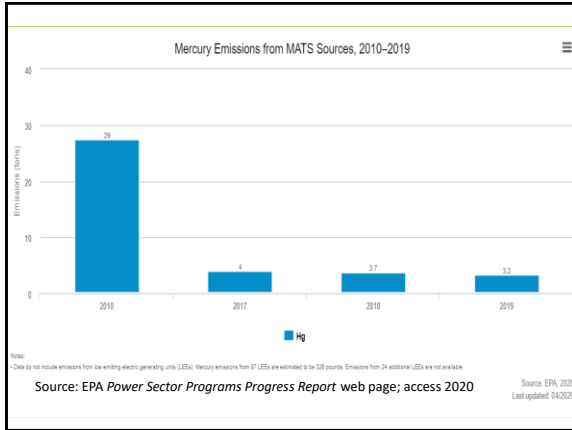
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Mercury Emissions from Power Plants

- June, 2015: US Supreme Ct. rejected the MATS rule because EPA *failed to consider the costs of compliance with the new regulations*.
- April 14, 2016, EPA finds that the cost of compliance with MATS is reasonable to satisfy the *2015 U.S. Supreme Ct. requirement* on this point.
- May 22, 2020: EPA Final Rule
 - EPA concluded that regulating mercury and other pollutants from power plants is not “appropriate and necessary” because the costs of such regulation grossly outweigh the HAP benefits (EPA rejects the value of co-benefits).
 - Its decision **does not revoke the MATS standard**, but rather withdraws the agency’s previous legal justification for the rule.

CAA-30



Boiler NESHAPs (Major and Area Sources)

- Applies to boilers and process heaters at these facilities: *industrial* (i.e. chemical plant), *commercial* (i.e. shopping malls) or *institutional* (i.e. universities).
- Reduce toxic air pollutants including mercury & other HAPs
- Major source MACT would not apply to:
 - A unit that combusts “*solid waste*” (units that burn solid waste are “incinerators” subject to CAA 129)
 - Power plants (because of “MATS”)

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Greenhouse Gases and Emission Sources

- **Carbon Dioxide (CO₂)**
 - Combustion of fossil fuels, solid waste, and trees and other wood products
- **Methane (CH₄)**
 - Production and transportation of fossil fuels, livestock and other agricultural activities, and organic waste decay
- **Nitrous Oxide (N₂O)**
 - Combustion of fossil fuels
- **Fluorinated Gases**
 - Industrial processes

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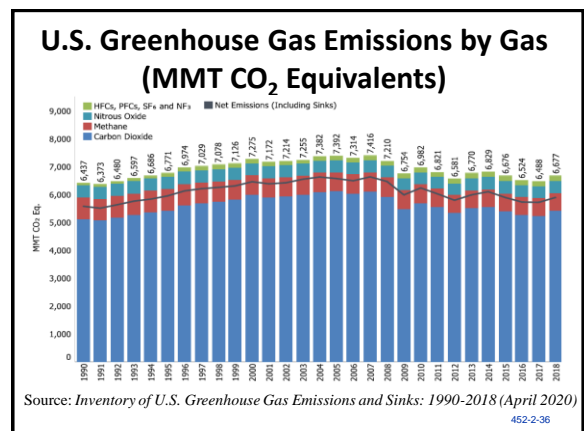
Global Warming Potential

- 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	25
Nitrous oxide	120	298
Fluorinated gases as a group	1.5-209	140 - 11,700

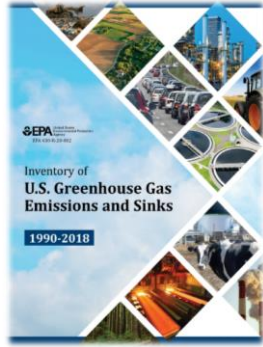
*Used as a reference point

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EPA's Annual Inventory of GHGs

- EPA prepares the official "U.S. Inventory of Greenhouse Gas Emissions and Sinks" to comply with commitments under the United Nations Framework Convention on Climate Change (provided each year by April 15).
- Topics covers GHG emissions from the following sectors:
 - Energy
 - Industrial process
 - Solvent & other product use
 - Agriculture
 - Land use change & forestry
 - Waste & Other



Emission Rates and Sources of Gaseous Contaminants

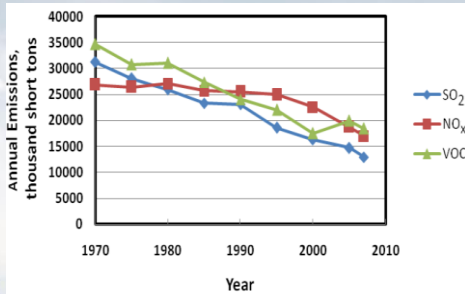
The gaseous pollutants emphasized in this course include:

- Sulfur Dioxide (SO₂)
- Nitrogen Oxides (NO_x)
- Organic compounds (including VOCs)



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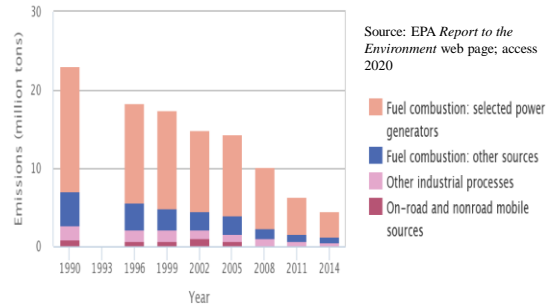
SO₂, NO_x, and VOC Emissions History



Reduction: 1970 to 2007
SO₂ 59%, NO_x 37%, VOC 47%

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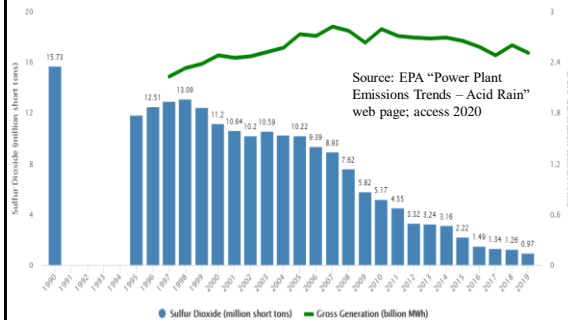
Anthropogenic SO₂ Emissions by Source Category: 1990 to 2014



SO₂ emissions decreased 80 percent between 1990 and 2014

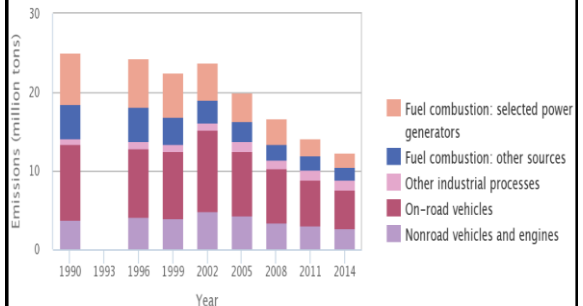
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Annual Sulfur Dioxide Emissions, 1990-2019



452-2-41

Anthropogenic NO_x Emissions by Source Category: 1990 - 2014



Source: EPA Report to the Environment web page; access 2020

452-2-42

Emission Source Categories: NO₂

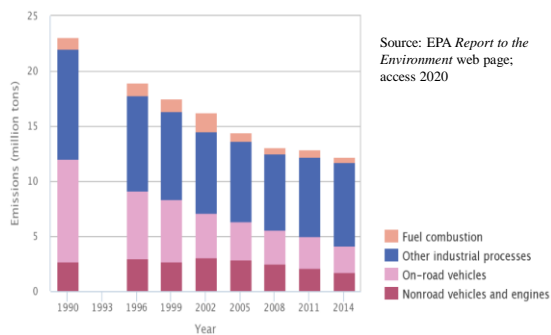
Table 1-5. NO_x emissions by source category, 1970 and 2008.

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



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Anthropogenic VOC Emissions in the U.S. by Source Category: 1990 - 2014



Emission Source Categories: VOC

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

Source Category	1970		2008	
	Thousands of Short Tons	Percent of Total	Thousands of Short Tons	Percent of Total
Fuel combustion, electric utilities	30	0	50	0
Fuel combustion, industrial	150	0	130	1
Fuel combustion, other	541	2	1269	8
Chemicals manufacture	1341	4	228	1



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Emission Source Categories: VOC (Continued)

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

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



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Pollution Control Regulations

- This section introduces pollution control regulations and standards:
 - National Ambient Air Quality Standards
 - New Source Performance Standards
 - National Emission Standards for Hazardous Air Pollutants
 - New Source Review
 - Title V Permit



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State & Local Control Initiatives

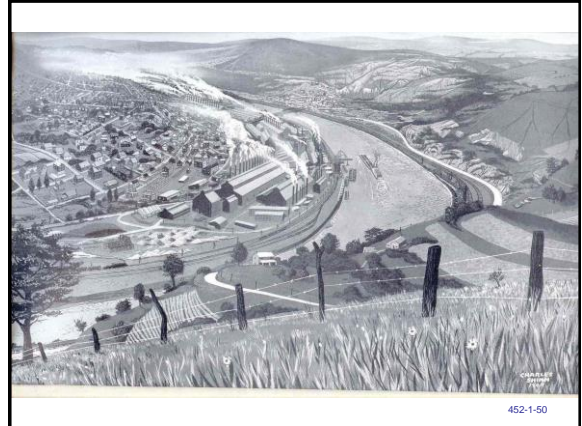
- After 1850, the U.S. industrial revolution took hold; centering on steel, iron with abundant coal usage.
 - “Smoke is the incense burning on the altars of industry. It is beautiful to me.” by a Chicago businessman in 1892.
 - **Public Policy favored business:** economic growth over human health & property protection until FDR & his New Deal programs. (From 1860 to 1930: pro-business SCOTUS justices policies – “laissez-faire” – leave corporations alone.)
 - Courts developed defenses (assumption of risk)
- In 1881, Chicago & Cincinnati passed municipal regulations of smoke emissions, and by 1912, most major U.S. cities followed.

452-1-48

Donora Episode: Oct. 26, 1948

- Start of a 5 day temperature inversion
- 50% of all residents sick (6,000 people)
 - Chest pains, cough & labored breathing
 - Irritation in eyes, nose and throat
- 20 people died
- Furnaces not shut down until the last day
 - Zinc furnaces like coke ovens were not allowed to stop, once cooled it cannot be restarted.
- Town doctor told everyone to leave town
 - Many went to a park high on a hill, as soon as they rose above smog, they started to feel better.

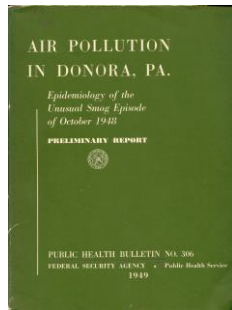
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452-1-50

Donora: Investigations resulted, but none could produce direct evidence of air pollution's harm.

Surgeon General, Scheele, wrote in the report's foreword: "This study is the opening move ...in improving the nations health. We have realized during our growing impatience with the annoyance of smoke, that pollution from gases, fumes & microscopic particles was also a factor to be reckoned with."



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Contaminant Regulations

- Prior to 1950 some *states and local agencies enacted particulate pollutant control regulations (opacity) & were not aware of gaseous contaminants effects* such as SO₂, 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.

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Federal Legislative Landmarks

- 1955 Air Poll. Control Act: Fed research funding
- *Debates*: Fed or state responsibility
- 1963 CAA: (compromise) Funding for state air programs
- 1965 CAAA: Auto emission stds. (CO & HxCx)
- *Debates*: national stds. vs. regional stds.
 - ambient air stds. vs. emission stds.
- 1967 Air Quality Act: States set regional air quality stds. based on federal air quality criteria
 - States failed to set stds., collect ambient air data & conduct emission inventories (21 SIPs submitted; none approved)
 - HEW (understaffed) failed to set air quality control regions
- 1970 CAAA: (sharply increased fed authority)
 - Uniform NAAQS, SIP, NSPS, NESHAP, & mobile sources

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Passage of the 1970 CAA

President Richard Nixon signs the CAA on Dec 31, 1970



Senator Edmund Muskie: Chairman of the Subcommittee on Water and Air Pollution



452-1-54

Federal Legislative Landmarks

- 1977 CAA Amendments
 - PSD
 - Non-attainment provisions
- 1990 CAA Amendments
 - Revised HAP program
 - Acid Rain & Ozone depletion
 - Title V Operating Permits
 - Strengthened enforcement provisions
 - New classifications for non-attainment areas

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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



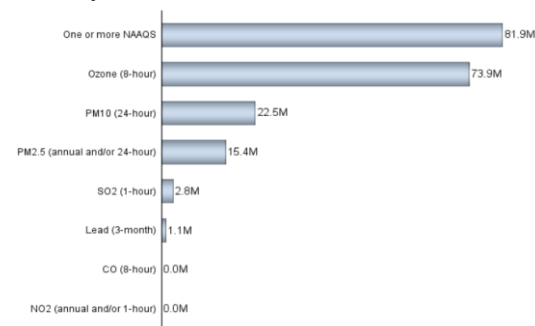
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National Ambient Air Quality Standards

Pollutant	Averaging Time	Primary	Secondary
PM-2.5 (2012)	Annual	12 µg/m ³	None
PM-2.5 (2006)	Annual	None	15 µg/m ³
PM-2.5 (2006)	24-hour	35 µg/m ³	Same
PM-10 (1987)	24-hour	150 µg/m ³	Same
SO ₂ (2010)	1-hour	75 ppb	None
(1971)	3-hour	None	500 ppb
CO (1971)	8-hour	9 ppm	None
(1971)	1-hour	35 ppm	None
Ozone (2015)	8-hour/day	0.070 ppm	Same
NO ₂ (2010)	1-hour/day	100 ppb	None
(1971)	Annual	53 ppb	Same
Lead (2008)	3mo. average	0.15 µg/m ³	Same

CAA-57

Number of People Living in Counties with Air Quality Concentrations above the NAAQS in 2019



New Source Performance Stds (NSPS)

- EPA sets “NSPS” for new sources that “**contribute significantly to air pollution.**”
 - 85 industrial categories identified (40 CFR Part 60)
 - Applies in attainment and non-attainment areas
- NSPS are emission or performance standards
 - **new sources must meet standard once promulgated**
- NSPS sets emission limits by application of the “**best system of emission reduction**” (BSER).
 - “**costs**” are considered
- NSPS to be reviewed every 8 years.

CAA-59

NSPS for Fossil Fuel-fired Electric Power Generating Facilities

Category	Fuel Type	Emission Limit	Reduction Requirement
Particulate Matter	Solid	0.015 lb _m /10 ⁶ Btu ^A	99.9%
SO ₂	Liquid	1.4 lb _m /MWh	95%
SO ₂	Coal Refuse	1.4 lb _m /MWh	94%
		<0.6 lb _m /10 ⁶ Btu	70%
NO _x	Solid	0.5 lb _m /10 ⁶ Btu	65%
NO _x	Liquid	0.3 lb _m /10 ⁶ Btu	30%
NO _x	Gas	0.2 lb _m /10 ⁶ Btu	20%
NO _x		1.0 lb _m /MWh	
NO _x	Liquid Backup Fuel ^B	1.5 lb _m /MWh	

A: The owner/operator of a facility with a PM Continuous Emission Monitoring System (CEMS) may elect to comply with an alternate 0.14 lb_m/MWh standard.

Note: NSPS under CAA 111(b) are emission limits only. But when emission limits are not “feasible” (i.e. fugitives) then under 111(h) the NSPS can be based on design, equipment, work practice, or operational standard.



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Hazardous Air Pollutants: Pre-1990 Program

- EPA designated substances as HAP
 - Arsenic, asbestos, beryllium, mercury, benzene, vinyl chloride, radionuclides and coke oven emissions
- EPA set emission limitations (NESHAP) for “ample margin of safety” protection:
 - Resulted in litigation (zero emissions)
 - Conduct risk analysis (Vinyl Chloride case)
 - Health based standard (no costs)

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Post-1990 HAP Program

- Congress lists 189 substances as HAP
 - EPA can add or delete
- EPA to establish a control technology -based emission standards (MACT) in 10 years
- All HAP major sources must meet MACT
- Major source: any stationary source that has the potential to emit *more* than:
 - 10 tpy of a listed HAP, or
 - 25 tpy of a combination of listed HAP
- Residual Risks program
 - 8 yrs. after MACT: EPA required to pass health-based emission standards if necessary (based on a EPA conducted risk assessment)

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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 (Attainment)
 - Prevention of Significant Deterioration (PSD):
 - Best Available Control Technology (BACT)
 - Modeling – to not exceed allowable “increment”
- If NAAQS are not satisfied (non-attainment)
 - New emissions must be offset with emission reductions from other sources &
 - Lowest Achievable Emissions Rate (LAER)

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Title V

- 1990 CAAA created the Title V Operating Permit Program
- Purpose of Title V Permit is to *specify all the CAA “applicable requirements” under one permit.*
- All Major Sources stationary sources must obtain a Title V permit
 - This includes any CAA air pollutant ≥ 100 tons/yr. (except GHGs)
- Title V required “periodic monitoring.” For example, for an uncontrolled glass furnace with a 20% opacity standard and a 0.04 gr/scf PM emission limit, *a state might determine that periodic monitoring is a weekly visible emission reading for the opacity standard and an annual stack test for the emission limit.*

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CHAPTER 2


**CONTROL TECHNIQUES FOR
GASEOUS CONTAMINANTS**

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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.


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Important Gas Stream Properties

- The selection and design of a gaseous contaminant control system relies on specific information about the gas stream
- The following gas stream properties are needed to determine the physical size of the collector
 - Flow rate
 - Temperature
 - Pressure
- Where the gas stream also contains particulate matter, it is important to know the concentration, particle size distribution, and composition of the particulate.
- Information concerning the oxygen concentration and ignitability of the gases and vapors is needed to determine the allowable contaminant concentrations


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EXPLOSIVE LIMITS

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Explosion Limits

- One of the main factors to consider in designing a gaseous contaminant control system is the concentration range at which one or more of the contaminants can be ignited.
- Potentially explosive gases and vapors:
 - Organic compounds
 - Carbon monoxide
 - Ammonia
 - Hydrogen (sometimes present with organic compounds)
 - Hydrogen sulfide

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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 designed for concentrations at no more than 25% of LEL


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

Compound	Lower Explosive Limit, % by Volume	Upper Explosive Limit, % by Volume
Acetone	2.5	12.8
Acrylonitrile	3.0	17.0
Ammonia	15.0	28.0
Benzene	1.2	7.8
Carbon Disulfide	1.3	50.0
Ethyl Alcohol	3.3	19.0
Formaldehyde	7.0	73.0
Gasoline	1.4	7.6



Table 2-1. LEL and UEL at Room Temperature and Ambient Oxygen Concentration (Continued)

Compound	Lower Explosive Limit, % by Volume ¹	Upper Explosive Limit, % by Volume ¹
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)

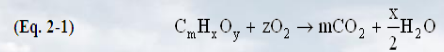


Additional LEL and UEL Considerations

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

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

Mainly used as a "screening tool" (old method). May be used if cannot find LEL or UEL in a table.



LEL of Mixtures

- One of the best approaches is to have a qualified laboratory measure the LEL and UEL for the exact range of conditions anticipated.
- Estimation of mixture LEL (two methods)
 - Assume that LEL of all contaminants equal to lowest LEL of any single contaminant – most conservative approach (Problem 2-1)
 - Use LeChatelier equations based on weighted average of LEL of each component (Problem 2-2)



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

▪ **The lowest LEL limit is 11,000 (toluene).**
25% of 11,000 ppm = **2,750 ppm**

▪ **Total contaminant concentration =**
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

$$LEL_{mixture}, \% = \frac{100}{\sum (y_i / LEL_i)} \quad \text{Eq. 2-4}$$

$$UEL_{mixture}, \% = \frac{100}{\sum (y_i / UEL_i)} \quad \text{Eq. 2-5}$$

y_i = 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

$$\text{Eq. 2-4} \quad LEL_{mixture}, \% = \frac{100}{\sum (y_i / LEL_i)}$$

Where: y_i = the concentration of component 'i' divided by the sum of the concentrations of all combustible components.
y_i = V_i/V_t

Where, V_i = volume of an individual chemical in mixture & V_t = total volume of all combustible chemicals in mixture.

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Problem 2-2: Solution

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

$$LEL_{mixture} = \frac{100}{\sum (y_i / LEL_i)}$$

Unit-less % of concentration

$\frac{1000}{3500}$	$\frac{2000}{3500}$	$\frac{500}{3500}$
$\left(\frac{25000}{1000000} \right)$	$\left(\frac{12000}{1000000} \right)$	$\left(\frac{11000}{1000000} \right)$

conversion of LEL from PPM to % of concentration

$$LEL_{mixture} = \frac{100}{11.43 + 47.62 + 12.99} = 0.014 = 14000\text{ppm}$$

25% of the LEL = 0.25 (14000) = 3500 ppm
Total gas mixture = 1,000ppm + 2,000ppm + 500ppm = 3,500 ppm
Therefore, the total gas mixture concentration = 25% of the LEL_{mixture}

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Sources of Ignition

If portions of the gas stream are above the LEL (even intermittently, there is a significant risk of serious fires or explosions, because it would only take an extremely small amount of energy to ignite the gas mixture. Examples of these energy sources that can cause ignition in the system are:

- 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

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Monitoring LEL Concentrations

- **LEL monitor purpose:** If the concentration of contaminants exceeds the 25% LEL level, the system can be shut down and the problem corrected.
- Monitor **error readings** can be caused by:
 - Oxygen levels are lower or higher than the 21% level that the monitor was calibrated at.
 - Acid gases are present in the gas stream and might have damaged the sensor.
 - The gas stream pressure is either much higher or lower than atmospheric pressure.

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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

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BASIC CONCEPTS OF GAS LAWS

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Ideal Gas Law

- *Ideal Gas Law*: Equation: $PV=nRT$
 - V = gas volume
 - n = number of moles = mass/MW
 - MW = molecular weight
 - P = absolute pressure
 - R = constant
 - T = absolute temperature
- When $n = \text{constant}$, then $PV/T = \text{constant}$
 - Thus, at two different conditions for the same gas: $P_1V_1/T_1 = P_2V_2/T_2$

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Flow Rates

$$V_1 = V_2 \left(\frac{T_1}{T_2} \right) \left(\frac{P_2}{P_1} \right) \longrightarrow V_{\text{Actual}} = V_{\text{STP}} \left(\frac{T_{\text{Actual}}}{T_{\text{STP}}} \right) \left(\frac{P_{\text{STP}}}{P_{\text{Actual}}} \right)$$

T_{Actual} = Gas temperature at actual conditions (°R)
 T_{STP} = Gas temperature at standard conditions (°R)
 P_{Actual} = Gas pressure at actual conditions (in. W.C.)
 P_{STP} = Gas pressure at standard conditions (in. W.C.)

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

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

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Molar Volume at STP

- STP is standard temperature & pressure
- $V/n = RT/P$ (ideal gas law)
- At EPA standard conditions of 68°F (528°R) and 407 in. W.C. (14.7 psia).
 - Molar volume = $V/n = 385 \text{ ft}^3/\text{lb-mole}$
- At scientific standard conditions of 32°F:
 - Molar Volume = $359 \text{ ft}^3/\text{lb-mole}$
= 22.4 L/gm-mole

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Mass Rate Calculations

- (molar rate)(molecular weight) = (mass rate)

$$\left(\frac{\text{lb-mole}}{\text{min}} \right) \left(\frac{\text{lb}_m}{\text{lb-mole}} \right) = \left(\frac{\text{lb}_m}{\text{min}} \right)$$

- (volumetric rate)(density) = (mass rate)

$$\left(\frac{\text{ft}^3}{\text{min}} \right) \left(\frac{\text{lb}_m}{\text{ft}^3} \right) = \left(\frac{\text{lb}_m}{\text{min}} \right)$$

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Parts per Million (PPM)

- The concentration measure in PPM is simply the mole fraction or volume fraction of the pollutant in the gas mixture multiplied by 1,000,000.

$$ppm = \frac{\text{volume of polluted gas}}{\text{total volume of gas mixture}} (1,000,000)$$

- PPM = (volume fraction of pollutant in mixture) x 10⁶
- Volume fraction of pollutant in mixture = (PPM/10⁶)
- Examples:
 - 25,000ppm = (25,000/ 10⁶) = 0.025 = 2.5% of pollutant in gas mixture
 - 5% of pollutant in gas mixture = 0.05 x 10⁶ ppm = 50,000ppm



Partial Pressure

- Partial pressure is the pressure that would be obtained if the same mass of individual gas were *alone* in the same total volume at the same temperature.

- Dalton's law of partial pressures for non-reacting gases:

$$\text{Equation: } p_{ag} + p_{bg} = P_t$$

- p_{ag} = partial pressure of "a" in gas phase
- p_{bg} = partial pressure of "b" in gas phase
- P_t = total gas pressure

- Every liquid exerts a vapor pressure. Vapor pressure is the measure of the escaping tendency or volatility of the liquid. (calculated using Antoine's equation)

- At equilibrium & under certain conditions, there is a mathematical relations between vapor pressure & partial pressure.



Henry's Law

- This law states that the amount of contaminant that can be dissolved into a liquid is proportional to the concentration (or partial pressure) of the contaminant in the gas.
- For simple dissolution-type absorbers, the solubility relationships is defined by Henry's Law.

– Equation 2-6: $y^* = H \cdot x$

y^* = Mole fraction (or partial pressure) of contaminant in gas phase in equilibrium with liquid

H = Henry's Law constant (different values depending if y^* is mole fraction or partial pressure)

x = Mole fraction of contaminant in liquid phase

- Only valid at low concentrations, has a linear relationship, & varies with temperature

- Higher values of H correspond to the least soluble gas



CONTROL TECHNOLOGY FOR GASEOUS EMISSIONS



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

- Gaseous contaminants that are soluble in aqueous liquids can be removed by absorption, which involves the transfer of contaminant from the gas to a liquid phase.
- Used for removal of:
 - acid gas compounds (e.g., SO₂, hydrogen chloride) &
 - water soluble organic compounds
- Two types
 - **Simple dissolution** (limited by the solubility of the contaminant in the liquid)
 - **Irreversible chemical reaction**
 - › used for the removal of less soluble compounds
 - › e.g., SO₂ may be captured by absorption when a compound such as calcium hydroxide (Ca(OH)₂), with which SO₂ reacts irreversibly, is added to the liquid.



Applicability of Absorbers

- **Simple dissolution absorbers:**
 - Limited by the solubility of contaminant in solvent
- **Irreversible chemical reactions absorbers:**
 - Limited by the ability to capture and retain the contaminant in solution for a long enough time to complete the reaction



Important Factors Affecting Absorption

- **Concentration dependence:** obtain highest removal efficiency when the contaminant concentrations are high (because this maximizes the driving force for mass transfer into the liquid phase).
- **Gas temperature dependence:** Absorption works best when the gas and liquid temperatures are low (because gas solubility increases with decreasing temperature).
- **Multiple contaminant removal:** a sophisticated separation process is required if each contaminant needs to be recovered individually.
- **Particulate matter limitations:** will not impair the removal efficiency for gaseous materials.
 - The accumulation of particulate matter on packed beds or at the outlet of spray nozzles may have an adverse effect on gas-liquid contact.



Biological Oxidation Systems

- This process involves the collection of contaminants on the surface of a media that contains viable microorganisms. The contaminant is metabolized by the organism, and CO₂ and water vapor are produced.
- The primary factor affecting the applicability of a biological oxidation system is the contaminants' compatibility with the microorganisms
 - i.e. some organics are toxic to the microorganisms and, therefore, cannot be effectively treated.
 - In addition, some gas stream contaminants may affect the pH levels, thereby reducing the microorganism population



Adsorption

- Involves the transfer of contaminant from the gas to the surface of a solid adsorbent
- Two types adsorption mechanisms:
 - **Physical:** *weakly held to the adsorbent surface* by intermolecular cohesion, normally *reversible*, used for organic compounds
 - **Chemical:** involves a *chemical reaction* which is *not easily reversed*, used for mercury vapors and acid gases
- In regenerative adsorption, the contaminant is subsequently desorbed so that the adsorbent may be used in multiple cycles.
- In non-regenerative adsorption, the adsorbent containing the contaminant is normally disposed of by land filling.



Applicability of Adsorption Processes

- **Physical adsorption** applicability:
 - For organic compounds capture, suitability depends on how strongly the adhesive forces are that hold the molecule to the surface of the adsorbent.
 - Most organic compounds with molecular weights between 50 and 200 can be collected with high efficiency.
- **Chemical adsorption** provide high removal efficiency for a variety of acid gases (Also, there are now applications for the control of vapor-phase mercury.)



Important Factors Affecting Adsorption

- **Concentration dependence:** The efficiency increases with high contaminant concentrations, due to the larger concentration driving force.
- **Temperature dependence:** In physical adsorption, the gas temperature is about 120°F or less. Chemical adsorption can operate at higher temperatures due to the increased strength of the chemical bond formed.
- **Multiple contaminant limitations:**
 - Physical adsorption systems that are regenerative are limited to one to three organic compounds.
 - Non-regenerative systems the number of organic compounds does not limit the system.
- **Particulate matter:** PM in the adsorbent bed restricts access of the organics to a portion of adsorbent surface.



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.
- Oxidizers operate with inlet concentrations less than 25% of the LEL. Flares can be operated well below the LEL or well above the UEL.
- **Thermal oxidation**
 - Extremely high operating temperature : operate at temperatures ranging from 1200°F to more than 1800°F.
 - Supplemental energy required
- **Catalytic oxidation**
 - Lower operating temperature :operate at temperatures ranging from 600°F to 850°F.)
 - Concern with catalyst poisoning
- **Flares**
 - Used as emergency controls for a wide variety of organic compounds



Factors Affecting Oxidation Systems

- **Concentration dependence**
 - High efficiency destruction of a variety of VOCs 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:**
 - Thermal oxidation: particulates with organics may be destroyed.
 - Catalytic oxidation: particulates can accumulate in catalyst beds and destroy the catalyst activity.
 - Particulates can deposit in the heat exchangers, which reduces their efficiency & causes plugging.



Chemical Reduction Systems

- Used primarily for the destruction of NO_x compounds emitted from combustion processes.
- Chemical Reduction Systems:
 - **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 to react with NO and NO₂. These reactions result in the formation of nitrogen, the major constituent of air.



Applicability of Reduction Systems

- **SNCR**
 - Injection must occur where combustion gases are in the required temperature range (1600 °F to 2000 °F)
 - NO_x destruction efficiencies in the range of 20% to 60%
- **SCR**
 - Injection must occur where combustion gases are in the required temperature range (550 °F to 750 °F)
 - 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_x 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 NO₂
- **Particulate matter limitations**
 - NSCR systems not normally sensitive to particulates
 - SCR systems subject to flow alterations & masking

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Condensation Systems

- Conversion of contaminant from gas to liquid phase
- Any gas can be reduced to a liquid by lowering its temperature and/or increasing its pressure (predominantly use temperature reduction).
- Used exclusively for the recovery of organic compounds 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)

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Applicability of Condensation Systems

- Condensation systems reduce the gas stream contaminant's partial pressure to a value equivalent to the vapor pressure of the compound at the condenser's operating temperature.
- Condensation systems are usually applied to industrial sources where there is a significant economic value to the recovered VOCs.
- Condensers are typically used as pretreatment devices. Used ahead of incinerators, absorbers, or adsorbers to reduce the total gas contaminant volume.

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Factors Affecting Condensation Systems

- **Concentration dependence**
 - Generally limited to high concentrations of 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

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Table 2-2: Summary of Control Techniques

Control Technique	General Applicability	Typical Concentration Range	Typical Gas Temperature Range	Applicable for Control of Multiple Contaminants?	Applicable for Control of Gas Streams with Particulate Matter?
Absorption	Acid Gases and Organic Compounds	< 1 ppm to > 100,000 ppm ¹	<150°F ²	Yes ⁴	Yes
Adsorption	Acid Gases and Organic Compounds	< 1 ppm to 25% of LEL ¹	<130°F ²	Yes ^{4,5}	Pretreatment Often Required
Biological Treatment	Organic Compounds	< 1 ppm to ~1000 ppm	<110°F ²	Yes	Pretreatment Often Required

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Table 2-2: Summary of Control Techniques (Continued)

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 ²	600°F to 2000°F ²	Yes	Pretreatment Often Required
Reduction	NO and NO ₂	< 100 ppm to 1,000 ppm ²	550°F to 2000°F ²	Yes ¹	Yes
Condensation	Organic Compounds	> 100 ppm ²	-320°F to 80°F ¹	Yes ^{4,5}	Pretreatment Often Required

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Chapter 3


Air Pollution Control Systems



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Components of the Air Pollution Control System


- Contaminant capture (hoods)
- Transport (ductwork)
- Gas stream cleaning (control devices)
- Air moving (fan)
- Instrumentation (controls and monitors)
- Other (gas cooling, chemical feeding, waste disposal, etc.)



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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



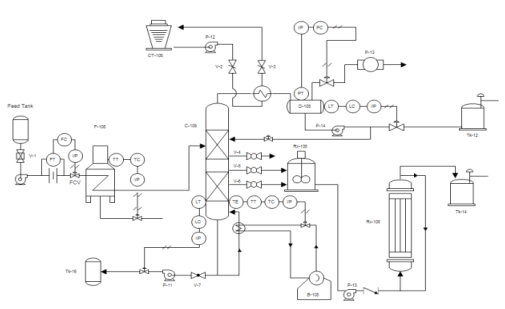
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Piping and Instrumentation Diagram (P & ID)

- A diagram which shows the interconnection of process equipment and the instrumentation used to control the process. In the process industry, a standard set of symbols is used to prepare drawings of processes. The instrument symbols used in these drawings are generally based on [International Society of Automation \(ISA\) Standard 55.1](http://www.isa.org)
- The primary schematic drawing used for laying out a process control installation.
- They usually contain the following information:
 - Process piping, sizes and identification, including:
 - Pipe classes or piping line numbers
 - Flow directions
 - Interconnections references
 - Permanent start-up, flush and bypass lines
 - Mechanical equipment and process control instrumentation and designation (names, numbers, unique tag identifiers), including:
 - Valves and their identifications (e.g. isolation, shutoff, relief and safety valves)
 - Control inputs and outputs (sensors and final elements, interlocks)
 - Miscellaneous - vents, drains, flanges, special fittings, sampling lines, reducers and increasers
- Interfaces for class changes
- Computer control system
- Identification of components and subsystems delivered by others

4

Example P & ID



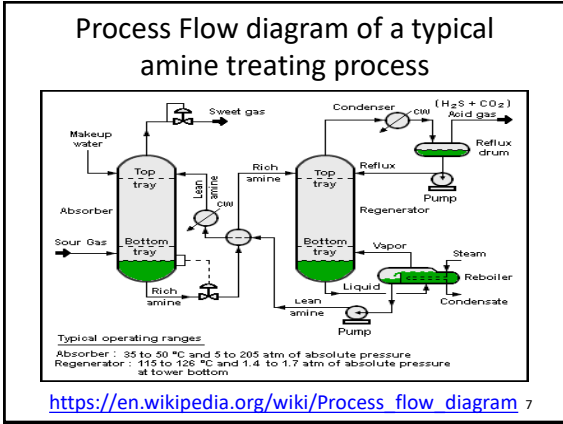
<https://www.edrawsoft.com/pid-examples.php>

5

Process Flow Diagrams (PFD)

- Typically, process flow diagrams of a single unit process will include the following:
 - Process piping
 - Major equipment items
 - Control Valves and other major valves
 - Connections with other systems
 - Major bypass and recirculation (recycle) streams
 - Operational data (temperature, pressure, mass flow rates, density, etc.), often by stream references to a mass balance.
- Process stream names
- Process flow diagrams generally **do not include**:
 - Pipe classes or piping line numbers
 - Process control instrumentation (sensors and final elements)
 - Minor bypass lines
 - Isolation and shutoff valves
 - Maintenance vents and drains
 - Relief and safety valves
 - Flanges

6



Flowcharts

- This section introduces:
 - The basics of a system flowchart
 - See handout
 - Video

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Uses of Flowcharts

- Evaluating process operating changes that are effecting control device performance
- Identifying instruments that are not functioning properly
- Identifying health and safety problems
- Communicating effectively with plant personnel during on-site work

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Figure 3-1. Material Stream Symbols

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Table 3-1 Codes for Utility Streams

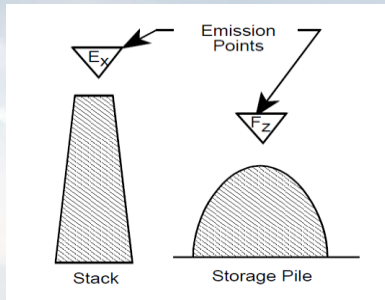
Cal	Compressed calibration gas
CA	Compressed air
CD	Condensate
IA	Instrument air
HS	High pressure steam
LS	Low pressure steam
CW	City (or plant) fresh water
Oil	No. 2 or No. 6 oil
Gas	Natural gas

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Figure 3-3. Major equipment symbols

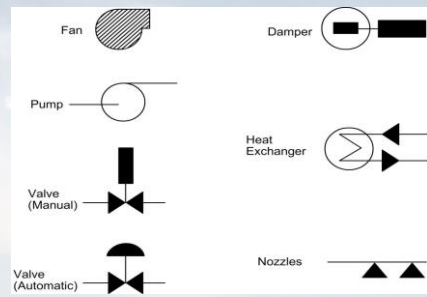
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Figure 3-3. Identification of Emission Points



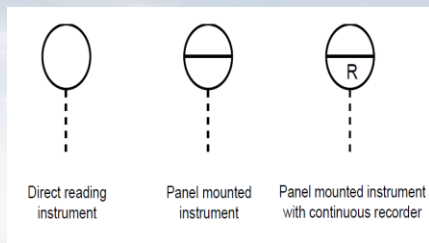
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Figure 3-4. Minor Component Symbols



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Figure 3-5. Instrument Symbols



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Table 3-4. Materials of Construction Symbols

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



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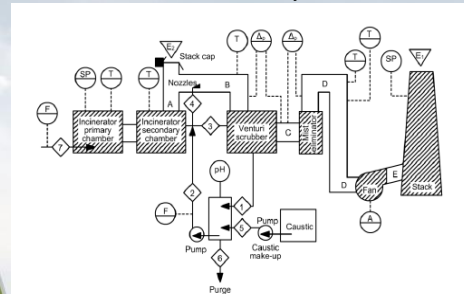
Basic Flowcharting Techniques

- 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



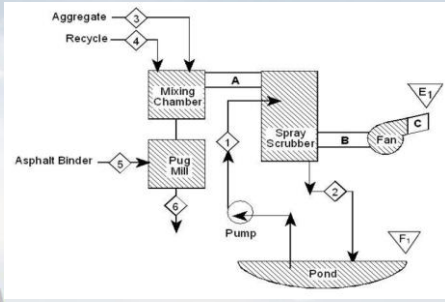
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Figure 3-6. Example Flowchart of a Waste Solvent System



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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?



Figure 3-8. Example Flowchart for Problem 3-1

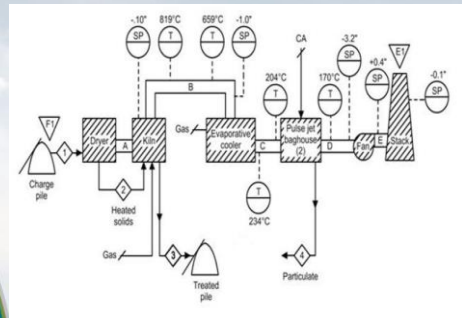


Table 3-5. Baseline Data for the Hazardous Waste Incinerator

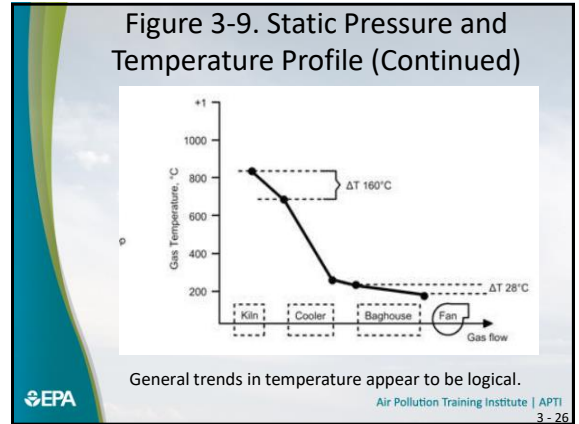
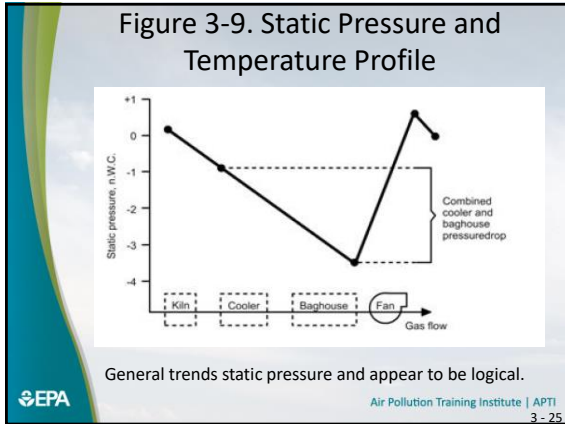
Location	Temperature (°C)	Static Pressure (in. W.C.)
Kiln hood	810	-0.1
Evaporative cooler inlet	785	-1.0
Evaporative cooler outlet	240	No Data
Baghouse inlet	195	No Data
Baghouse outlet	190	-5.1
Duct E	No Data	-1.5
Stack	No Data	-1.0



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.
 - Oxygen concentrations (combustion sources)
 - Other parameters along the direction of gas flow





Problem 3-1: Solution Part B

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

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

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

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Problem 3-1: Solution Part B

	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

Possible problem: ΔP between evaporative cooler inlet and baghouse outlet considerably lower now than baseline.
Possible cause: Air leakage due to torn or worn bags or holes in baghouse housing. But be aware that ΔP in a baghouse changes with time. Torn bags would decrease particulate collection efficiency.

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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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Problem 3-1: Solution Part D

- Determine what health and safety issues should be considered during the performance evaluation.
 - The pulse jet baghouses should be investigated and conducted carefully in order to minimize safety hazards.
 - The uninsulated metal housing at 176°C is a definite burn hazard.
 - The roof of the baghouse should be avoided both because of high temperature and the possibility that it has been weakened by corrosion.

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Problem 3-1: Solution Part D (cont.)

- Any fugitive emissions from the kiln, such as ductwork B, should be investigated, since the soil is contaminated with several suspected carcinogens.
- This should be noted on the flowchart to serve as a reminder to stay out of areas where inhalation problems or skin absorption hazards could exist



Figure 3-10. Example Flowchart for Problem 3-2

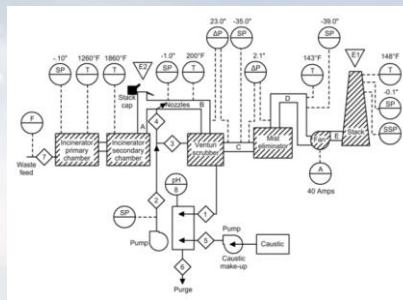


Table 3-8. Static pressures and static pressure drops (in. W.C.)

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



Table 3-9. Gas temperatures (°F)

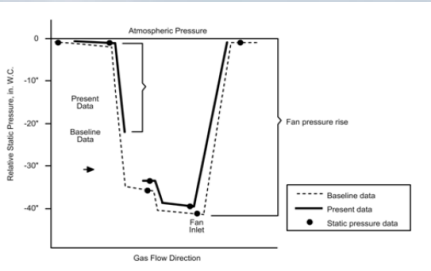
	Present	Baseline
Incinerator secondary chamber	1860	1835
Duct B	200	197
Fan inlet	143	142
Stack	148	147

All temperatures are in close agreement.



Problem 3-2: Solution

Part A



Since static pressures are close, it is reasonable to suspect a malfunctioning ΔP gauge.



Malfunctioning ΔP Magnehelic gauge



Problem 3-2: Solution (Continued)

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.



Importance of Capture/Collection Systems

- From Subpart RRR NESHAP for Secondary Aluminum Production § 63.1506
- Capture/collection systems. For each affected source or emission unit equipped with an add-on air pollution control device, the owner or operator
 - must:
 - (1) Design and install a system for the capture and collection of emissions to meet the engineering standards for minimum exhaust rates or facial inlet velocities as contained in the ACGIH Guidelines (incorporated by reference see § 63.14);



Importance of Capture/Collection Systems

- Subpart XXX—NESHAP for Ferrous Alloys Production: Ferromanganese and Silicomanganese § 63.1624 What are the operational and work practice standards for new, reconstructed, and existing facilities?
 - (a) Process fugitive emissions sources.
- (1) You must prepare, and at all times operate according to, a process fugitive emissions ventilation plan that: documents the equipment and operations designed to effectively capture process fugitive emissions. The plan will be deemed to achieve effective capture if it consists of the following elements: (i) Documentation of engineered hoods and secondary fugitive capture systems designed according to the most recent, at the time of construction, ventilation design principles recommended by the American Conference of Governmental Industrial Hygienists (ACGIH). The process fugitive emissions capture systems must be designed to achieve sufficient air changes to evacuate the collection area frequently enough to ensure process fugitive emissions are effectively collected by the ventilation system and ducted to the control device(s). The required ventilation systems should also use properly positioned hooding to take advantage of the inherent air flows of the source and capture systems that minimize air flows while also intercepting natural air flows or creating air flows to contain the fugitive emissions. Include a schematic for each building indicating duct sizes and locations, hood sizes and locations, control device types, size and locations and exhaust locations. The design plan must identify the key operating parameters and measurement locations to ensure proper operation of the system and establish monitoring parameter values that reflect effective capture.



Hoods

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

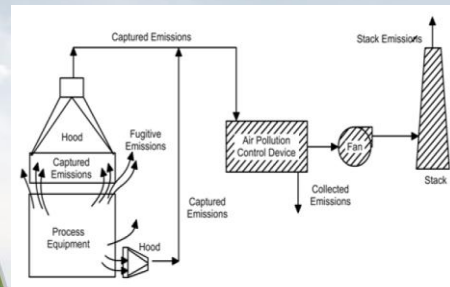


Hoods

- 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



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%.



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Equations 3-1 and 3-2: Fugitive and Stack Emissions

$$\text{Fugitive Emissions} = \text{Process Emissions} - \text{Emissions Captured by Hooding}$$

$$\text{Stack Emissions} = \text{Emissions Captured by Hooding} - \frac{100 - \eta}{100}$$

Where: η = Control Device Efficiency


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Problem 3-3: Solution

1. Calculate fugitive emissions:

$$\text{Fugitive Emissions} = \text{Process Emissions} - \text{Emissions Captured by Hooding}$$


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

2. Calculate stack emissions:

$$\text{Stack Emissions} = \text{Emissions Captured by Hooding} - \frac{1 - \eta (\text{Control Eff.})}{1}$$

$$= (95 \text{ lb}_m/\text{hr}) \frac{1.0 - 0.95}{1.0}$$

$$= 4.75 \text{ lb}_m/\text{hr}$$


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Problem 3-3: Solution

3. Calculate total emissions:

$$\text{Total emissions} = \text{Hood loss emissions} + \text{Stack emissions}$$


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

$$= 9.75 \text{ lb}_m/\text{hr}$$


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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%.


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Problem 3-4: Solution

1. Calculate fugitive emissions.

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


2. Calculate stack emissions.

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

$$= 4.5 \text{ lb}_m/\text{hr}$$

3. Calculate total emissions.

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


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Hood Operating Principles

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

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Figure 3-14. Hood Capture Velocities

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Equation 3-3: Volumetric Flow and Capture Velocity

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

Joseph Dalla Valle unflanged hoods equation:

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 (ft²)

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Equation 3-3: Volumetric Flow and Capture Velocity (cont.)

- Equation 3-3 applies to a free standing or unobstructed hood. For a square rectangular hood that is bounded on one side by a flat surface (floor or wall), equation 3-3 becomes:

$$Q = v_x \left(\frac{10x^2 + 2A}{2} \right)$$

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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.

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Problem 3-5: Solution - Part A

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

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

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

- $Q = 300 \text{ ft/min}$
- $[10 (1\text{ft})^2 + (201 \text{ in.}^2) * [1 \text{ ft}^2/144 \text{ in.}^2]]$
- = 3,420 ACFM

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Problem 3-5: Solution - Part B

- 1. 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.

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

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

$$= 12,585 \text{ ACFM}$$

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



Problem 3-5: Solution - Part B

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

$$Q = 300 \text{ ft/min} [10 (2\text{ft})^2 + (201 \text{ in.}^2) * [1 \text{ ft}^2/144 \text{ in.}^2]]$$

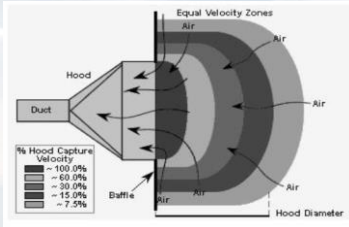
$$= 12,420 \text{ ACFM}$$

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



Hood Designs for Improved Performance

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



Velocity/Flow Equations Various for Hood Types*

HOOD TYPE	DESCRIPTION	ASPECT RATIO	AIR VOLUME
	SLOT	0.2 or less	Q=3.7 LVX
	FLANGED SLOT	0.2 or less	Q=2.8 LVX
	PLAIN OPENING	0.2 or greater and round	Q=V(10X + A)
	FLANGED OPENING	0.2 or greater and round	Q=0.75V(10X + A)
	BOOTH	To suit work	Q=VA-VWH
	CANOPY	To suit work	Q=1.4 PDV Perimeter of work D=height above work
	PLAIN MULTIPLE SLOT OPENING 2 or more slots	0.2 or greater	Q=V(10X ² + A)
	FLANGED MULTIPLE SLOT OPENING 2 or more slots	0.2 or greater	Q=0.75 V(10X ² + A)



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

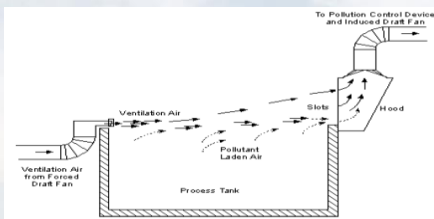
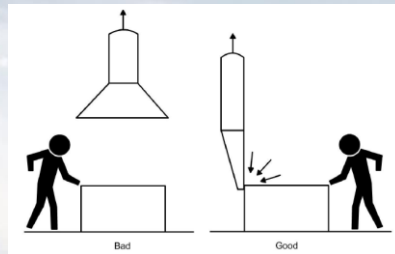


Figure 3-17. Hood Design for Protection of Plant Personnel



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

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Equation 3-4 and 3-5: Hood Static Pressure and Velocity Pressure

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

Where:

- SP_h = Hood static pressure (in. W.C.)
- VP_d = Duct velocity pressure (in. W.C.)
- h_e = Overall hood entry loss (in. W.C.)

$$h_e = (F_h)(VP_d)$$

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

Figure 3-18a: Plain End Duct, $F_h = 0.93$

Figure 3-18b: Flanged Duct, $F_h = 0.49$

Figure 3-18c: Bell-mouth Duct, $F_h = 0.04$

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Velocity Pressure from Bernoulli's Equation

- $V = \sqrt{\frac{2g\rho'(\Delta p)}{\rho}}$ ρ' = density of manometer fluid
 ρ = density of the fluid (air)

$$V^2 = 2g \Delta p / \rho \quad \Delta p = \text{manometer column height}$$

$$V^2 = 2g \Delta p / 0.075 \text{ lb}_m/\text{ft}^3 \quad g = 32.174 \text{ ft}/\text{sec}^2$$

$$V^2 = \Delta p \left[\frac{(2)(32.17)(3600)}{0.075} \right] \text{ ft}^4 \cdot \text{sec}^2 / \text{min}^2 \cdot \text{sec}^2 \cdot \text{lb}_f$$

1 inches $H_2O = (14.7 \text{ lb}_f/\text{in}^2) / (407 \text{ in. } H_2O) = (0.361 \text{ lb}_f/\text{in}^2) (12 \text{ in}/\text{ft})^2$

$$V^2 = \Delta p \left[\frac{(2)(32.17)(3600)(5.2)}{0.075} \right] \text{ ft}^4 / \text{min}^2 \cdot \text{in} \cdot H_2O$$

$$= 1.606 \times 10^6 \Delta p \text{ (ft}^2 / \text{min}^2 \cdot \text{in } H_2O)$$

$$V = 4005 \sqrt{\Delta p} \text{ feet}/\text{min}$$

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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:

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

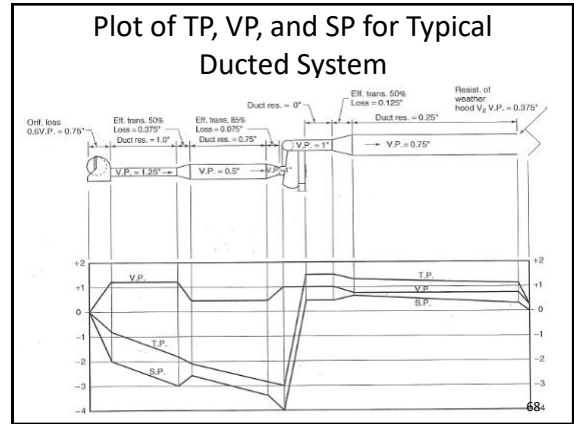
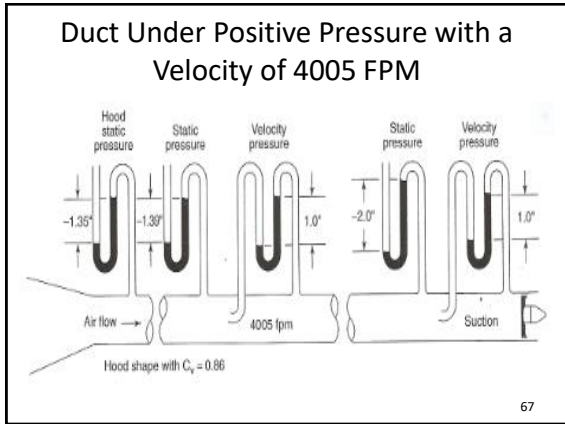
Note that this is a dimensional equation and the specified units of v must be used. Any consistent units for ρ may be used since the ratio is dimensionless.

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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 $F_h = 0.93$
 - Baseline air temperature = 68°F
 - Duct inside diameter = 2 ft
 - Baseline hood static pressure = -1.70 in. W.C.

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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_e , as follows. $h_e = (F_h)(VP_d) = (0.93)(VP_d)$

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

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

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

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

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Velocity Can Be Determined From Velocity Pressure

- $V = 1096.7 (VP/\rho)^{0.5}$
- V = velocity (ft/min)
- VP = velocity pressure (in. H₂O)
- ρ = density (lb/ft³)
- For standard air ($\rho = 0.075$ lb/ft³)
- $V = 4005 (VP)^{0.5}$

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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.

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

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

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

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Problem 3-6: Solution - Part A

Step 3. Calculate the gas flow rate:


Flow rate = Velocity × Area of duct

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

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

$$= 3.14 \text{ ft}^2$$

Flow rate = 3,024 ft/min × 3.14 ft² = 9,495 ACFM



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Problem 3-6: Solution - Part B

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


$$SP_h = -(VP_d) - h_c$$

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

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

Given $SP_h = -1.7 \text{ in. W.C.}$:

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

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



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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, $\rho_{Actual} = 0.075 \text{ lb}_m/\text{ft}^3$.

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

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

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


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Problem 3-6 Solution: Part B


Step 3. Calculate the gas flow rate:

Flow rate = Velocity x Area of duct

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

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


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



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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



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Table 3-10. Commonly Recommended Transport 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.

$$\begin{aligned} \text{Duct area} &= \frac{\text{Gas volumetric flow rate}}{\text{Minimum transport velocity}} \\ &= \frac{978 \text{ ft}^3/\text{min}}{2,800 \text{ ft}/\text{min}} \\ &= 0.349 \text{ ft}^2 \end{aligned}$$



Problem 3-7: Solution (Continued)

2. Calculate the duct diameter.

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

https://www.osha.gov/dts/osta/otm/otm_iii/otm_iii_3.html



Fans



Fans

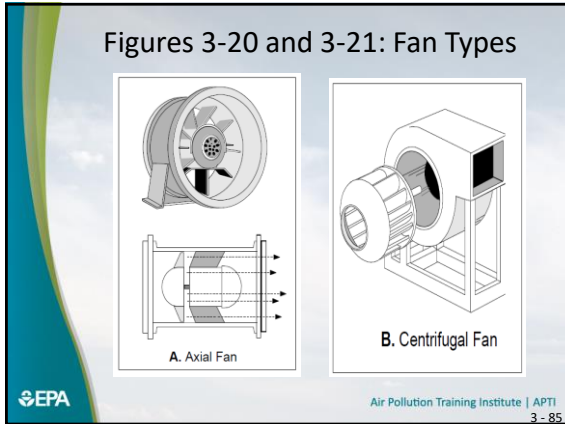
- This section introduces:
- The variables that contribute to fan performance



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)

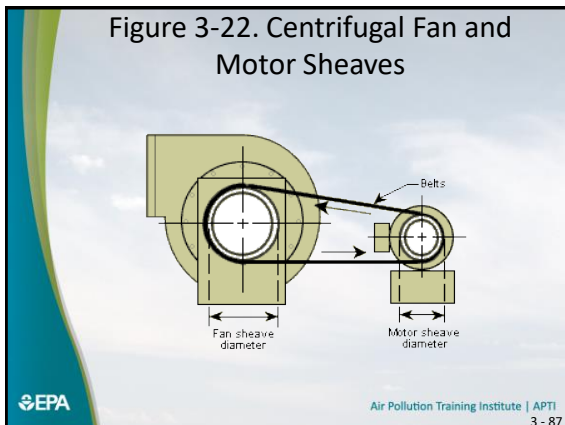




Categories of Fan Drives

- 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

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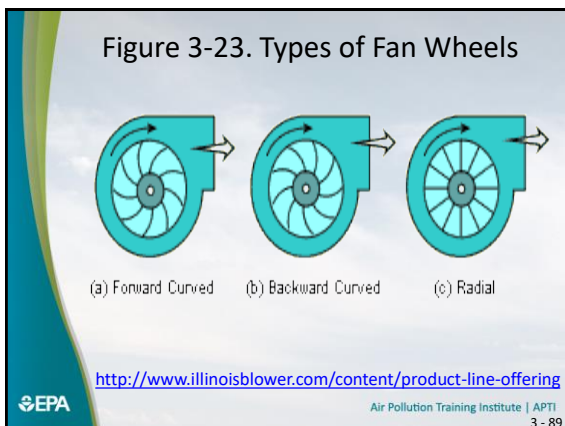
Equation 3-8: Fan Rotational Speed

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

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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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

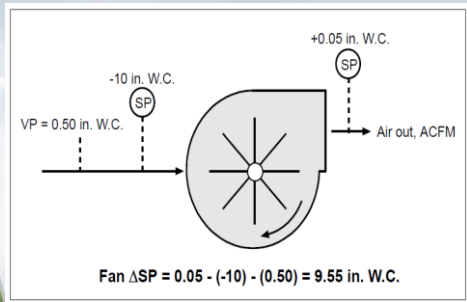
$$Q_2 = Q_1 \left(\frac{RPM_2}{RPM_1} \right)$$

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

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Figure 3-25. Fan Static Pressure Rise



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

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

Where:

ΔSP_1 = baseline fan static pressure rise (in. W.C.)

ΔSP_2 = present fan static pressure rise (in. W.C.)

RPM_1 = baseline fan wheel rotational speed

RPM_2 = present fan wheel rotational speed

Figure 3-26. Total System Static Pressure Drop

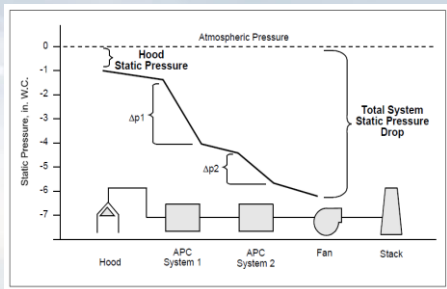


Figure 3-27. System Characteristic Curve

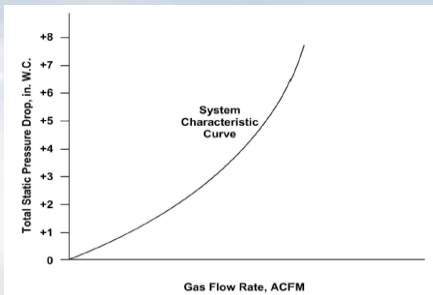


Figure 3-28. Fan Static Pressure Rise

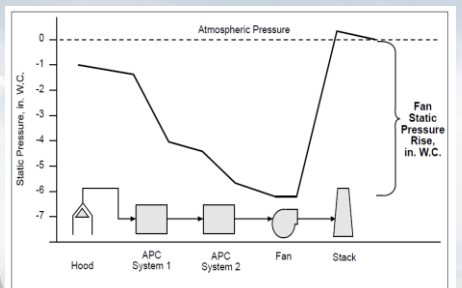


Figure 3-29. Portion of a Typical Multi-Rating Table

194 LS		Inlet diameter: 11" O.D.										Wheel diameter: 19 1/4"								
		Outlet area: 660 sq. ft. inside										Wheel circumference: 5.01 ft								
CFM	CV	2"SP		4"SP		6"SP		8"SP		10"SP		12"SP		14"SP		16"SP		R		
		RPM	BHP	RPM	BHP	RPM	BHP	RPM	BHP	RPM	BHP	RPM	BHP	RPM	BHP	RPM	BHP			
660	1000	1806	0.48	1302	1.01	1608	1.60	1950	2.27	2191	2.88	2399	3.74	2592	4.55	2769	5.38	2936	6.21	3
792	1200	2058	0.55	1398	1.11	1763	1.75	1965	2.45	2142	3.15	2296	3.99	2488	4.83	2749	5.71	2916	6.65	3
924	1400	2310	0.62	1494	1.21	1790	1.90	1965	2.64	2194	3.43	2321	4.27	2509	5.14	2706	6.05	2909	7.05	3
1056	1600	2562	0.71	1413	1.35	1716	2.27	1871	2.84	2107	3.67	2401	4.53	2593	5.46	2769	6.42	2955	7.41	3
1188	1800	2814	0.80	1431	1.45	1726	2.24	1808	3.06	2203	3.92	2407	4.83	2593	5.78	2771	6.79	2936	7.78	3
1320	2000	3066	0.90	1441	1.54	1739	2.41	1852	3.25	2296	4.16	2414	5.15	2593	6.11	2773	7.18	2943	8.78	3
1452	2200	3318	1.01	1465	1.66	1752	2.85	1868	3.57	2271	4.45	2427	5.47	2607	6.39	2778	7.35	2943	9.85	3
1584	2400	3570	1.13	1485	1.86	1759	2.87	1912	3.86	2229	4.70	2431	5.82	2612	6.87	2786	7.90	2943	10.91	3
1716	2600	3822	1.26	1505	2.06	1764	3.13	1925	4.08	2245	5.11	2441	6.11	2612	7.18	2791	8.46	2946	11.97	3
1848	2800	4074	1.39	1524	2.26	1824	3.42	1925	4.70	2272	5.62	2444	6.85	2614	8.14	2815	9.30	2943	12.97	3
1980	3000	4326	1.51	1566	2.46	1864	3.69	1988	5.08	2226	6.06	2451	7.63	2611	9.08	2828	10.4	2943	13.97	3
2112	3200	4578	1.64	1601	2.66	1919	4.04	2140	6.32	2245	7.44	2531	8.78	2743	10.1	2866	11.5	2943	14.97	3
2244	3400	4830	1.77	1636	2.86	1958	4.34	2189	6.95	2287	8.37	2569	9.80	2740	11.3	2900	12.0	2943	15.97	3
2376	3600	5082	1.90	1671	3.06	1998	4.64	2238	7.56	2326	9.36	2611	10.89	2740	11.5	2897	13.1	2943	16.97	3
2508	3800	5334	2.03	1706	3.26	2047	4.94	2287	8.17	2365	10.36	2611	11.88	2740	11.9	2894	14.1	2943	17.97	3
2640	4000	5586	2.16	1741	3.46	2096	5.24	2336	8.78	2404	11.36	2611	12.87	2740	12.8	2894	15.1	2943	18.97	3
2772	4200	5838	2.29	1776	3.66	2145	5.54	2385	9.39	2443	12.36	2611	13.86	2740	13.7	2894	16.1	2943	19.97	3
2904	4400	6090	2.42	1811	3.86	2194	5.84	2434	10.00	2482	13.36	2611	14.85	2740	14.6	2894	17.1	2943	20.97	3
3036	4600	6342	2.55	1846	4.06	2243	6.14	2483	10.61	2521	14.36	2611	15.84	2740	15.5	2894	18.1	2943	21.97	3
3168	4800	6594	2.68	1881	4.26	2292	6.44	2532	11.22	2560	15.36	2611	16.83	2740	16.4	2894	19.1	2943	22.97	3
3300	5000	6846	2.81	1916	4.46	2341	6.74	2581	11.83	2599	16.36	2611	17.82	2740	17.3	2894	20.1	2943	23.97	3
3432	5200	7098	2.94	1951	4.66	2390	7.04	2630	12.44	2638	17.36	2611	18.81	2740	18.2	2894	21.1	2943	24.97	3
3564	5400	7350	3.07	1986	4.86	2439	7.34	2679	13.05	2677	18.36	2611	19.80	2740	19.1	2894	22.1	2943	25.97	3
3696	5600	7602	3.20	2021	5.06	2488	7.64	2728	13.66	2716	19.36	2611	20.79	2740	20.0	2894	23.1	2943	26.97	3

Figure 3-31. Fan Characteristic Curve

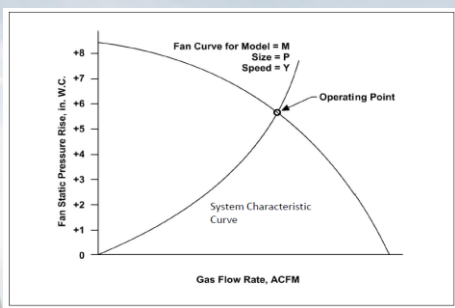
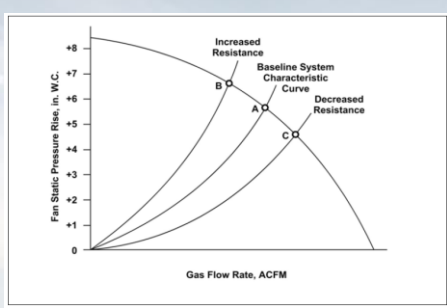


Figure 3-32. Changes in the System Resistance Curve



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

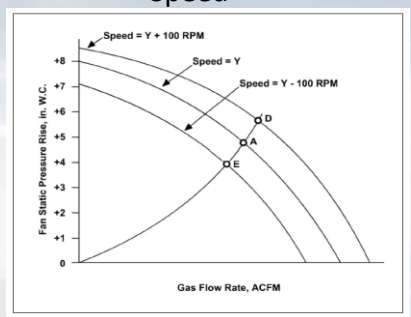
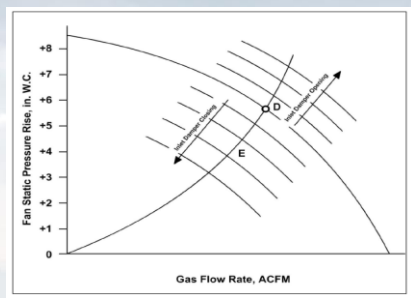
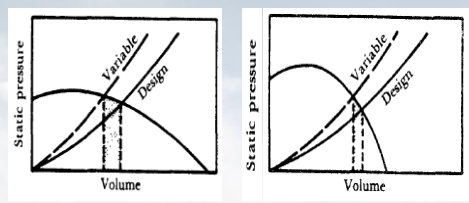


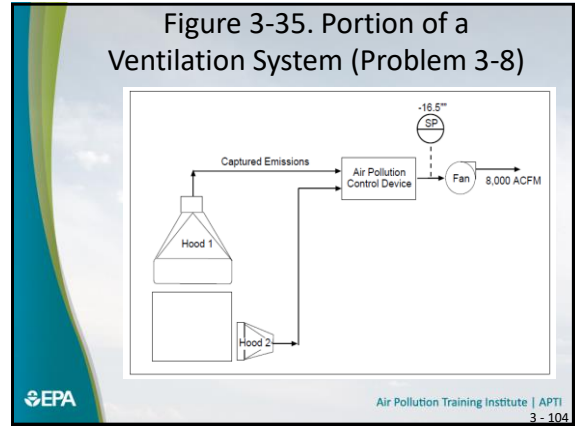
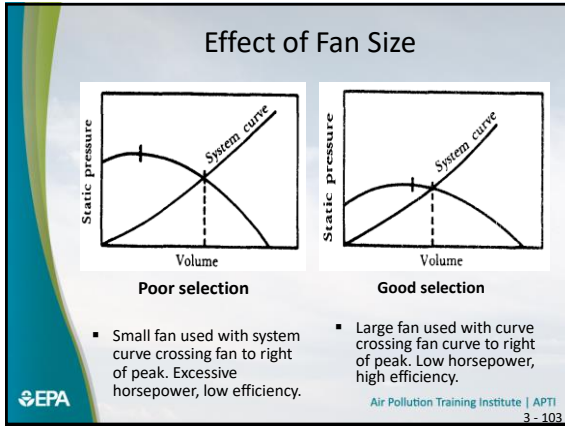
Figure 3-34. Changes in the Inlet Damper Position



Effect of Varying System Pressure



- Poor selection**
 - Fan with flat pressure curve gives wide volume variation with pressure change.
- Good selection**
 - Fan with steep pressure curve gives small volume variation with pressure.



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.

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Problem 3-8: Solution

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

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

$$= -16.5 \text{ in. W.C.} (2.25)$$

$$= -37.13 \text{ in. W.C.}$$

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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

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

BHP₁ = baseline brake horsepower
 BHP₂ = present brake horsepower
 RPM₁ = baseline fan wheel rotational speed
 RPM₂ = present fan wheel rotational speed

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Equation 3-11: Brake Horsepower

$$BHP = \frac{I \times E \times 1.73 \times \text{Eff} \times PF}{745}$$

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

1 hp = 745.69987158227022 W

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Brake Horsepower and Horsepower

- Brake Horsepower indicates the brake, the device for measuring the true power of the motor. Stating power in 'bhp' gives some indication this is a true reading, rather than a calculated or predicted one.
- The horsepower was first used by James Watt during a business venture where his steam engines substituted horses. It was defined that a horse can lift 33,000 pounds with a speed of 1 foot per minute: 33,000 ft/lbf/min⁻¹. This is roughly equivalent to lifting 147,000 Newtons (the weight of a 15,000 kg mass) at a speed of 0.005 metre per second.

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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

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

Where:

- I_{STP} = Fan motor current at standard conditions (Amperes)
- I_{Actual} = Fan motor current at actual conditions (Amperes)
- ρ_{STP} = Gas density at standard conditions (lb_m/ft³)
- ρ_{Actual} = Gas density at actual conditions (lb_m/ft³)

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Equations 3-13 and 3-14: Gas Density

Ideal Gas Law

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

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

Where:

- ρ = gas density, lb_m/ft³
- P = pressure, atm
- M = molecular weight of gas, lb_m/lb mole
- T = absolute temperature, R
- R = gas constant = 0.7302 ft³ atm/lb mole R

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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.

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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?

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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 (Continued)

Step 1. Calculate the gas density at actual conditions:

1a. Convert pressure from inches of water to psia.

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

$$= 14.34 \text{ psia}$$



Problem 3-9: Solution (Continued)

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

$$V = \frac{nRT}{P}$$

$$= \left(\frac{10.73 \text{ psia} \times \text{ft}^3}{^\circ\text{R} \times \text{lb mole}} \right) \left(\frac{460^\circ\text{F} + 300^\circ\text{F}}{14.34 \text{ psia}} \right)$$

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



Problem 3-9: Solution (Continued)

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

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

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



Problem 3-9: Solution (Continued)

Step 2. Calculate the gas density at standard conditions:

a. Calculate the gas volume at standard conditions using the Ideal Gas Law.

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

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



Problem 3-9: Solution (Continued)

Step 2b. Calculate gas density at standard conditions.

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

$$= \frac{29 \text{ lb}_m}{385.4 \text{ ft}^3}$$

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



Problem 3-9: Solution (Continued)

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

$$\begin{aligned}
 I_{STP} &= I_{Actual} \left(\frac{\rho_{STP}}{\rho_{Actual}} \right) \\
 &= 80 \text{ amps} \left(\frac{0.075 \text{ lb}_m/\text{ft}^3}{0.051 \text{ lb}_m/\text{ft}^3} \right) \\
 &= 80 \text{ amps} (1.47) \\
 &= 118 \text{ amps}
 \end{aligned}$$



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.

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

- Horsepower is related to the cube of the fan speed.

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



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.



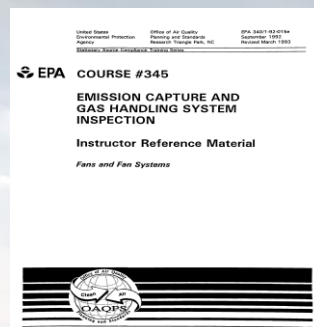
Summary (Continued)

- 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.



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.




<http://www2.epa.gov/nscep>



CHAPTER 4


ADSORPTION: TRANSFER OF POLLUTANTS FROM A GAS TO A SOLID



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Overview


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



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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




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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.



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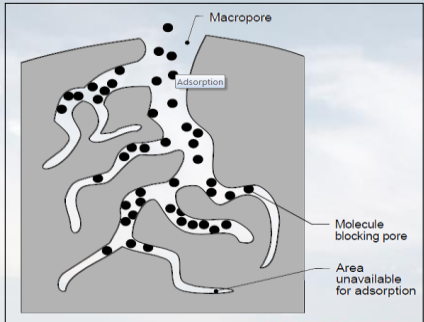
Adsorbents

- 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




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Figure 4-1. The Adsorption Process



The diagram illustrates the adsorption process within a porous material. It shows a network of interconnected pores. A gas stream, represented by small black dots, flows through these pores. Some of these dots are shown attached to the inner surface of the pore walls, indicating adsorption. A label 'Macropore' points to a large, open pore. Another label 'Adsorption' points to a molecule on the pore wall. A label 'Molecule blocking pore' points to a molecule that has adsorbed and is partially obstructing the pore's path. A label 'Area unavailable for adsorption' points to a region where the pore walls are so close together that molecules cannot reach them.



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Types of Adsorbents

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

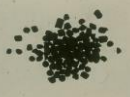
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Types of Adsorbents

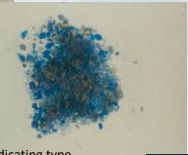
Polar	Non-polar
Silica gel	Activated Carbon
Activated oxides	Polymeric adsorbents
Molecular sieves	Zeolites (siliceous)

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Types of Adsorbents



Activated Carbon



Silica gel indicating type



Molecular sieves

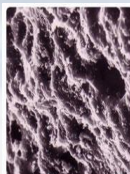
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Activated Carbon Derivatives


- Feedstocks
 - Wood
 - Coal
 - Coconut
 - Nutshells
 - Petroleum Products

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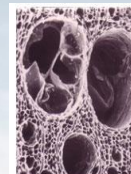
Stereo Scan Electron Micrograph Photos of Activated Carbons from Cameron Carbon web site



Coal



Coconut



Wood

http://cci.cglcarbon.com/activated_carbons.html

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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 CO₂ at high temperatures

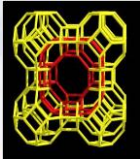
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Zeolites

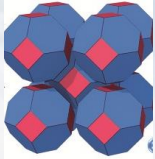
- Removes moisture from exhaust streams
- Separate hydrocarbons in refining processes
- Remove nitrogen oxides from air pollution sources

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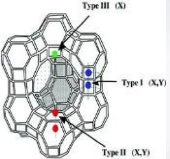
Figure 4-2. Structure of Zeolites



Zeolite structure type LTA



Sodalite



Faujasite (Type X,Y)

<http://www.epa.gov/ttn/catc/dir1/fzeolite.pdf>

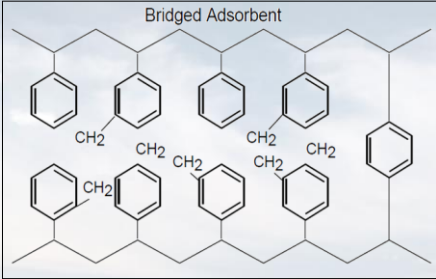
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Synthetic Polymers

- 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

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Figure 4-3. Synthetic Polymer Structure



Bridged Adsorbent

<http://www.epa.gov/ttn/catc/dir1/fadsorb.pdf>

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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

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Table 4-1. Physical Properties of Major Types of Adsorbents

Table 4-1. Physical properties of major types of adsorbents.

Adsorbent ²	Internal Porosity (%)	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Bulk Dry Density (g/cm ³)	Mean Pore Diameter (Å)
Activated Carbon	55-75	600-1600	0.80-1.20	0.35-0.50	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 ²		1080-1100	0.94-1.16	0.34-0.40	

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Compounds Suitable for Carbon Adsorption

Organic Compound	Boiling Point *(°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
Standard Solvent	379 (193)	-	No	Yes	1.10
Aromatic					
Benzene	176 (80.0)	78.1	No	Yes	1.40
Toluene	231 (110.6)	92.1	No	Yes	1.40
Xylene	292 (144.4)	106.2	No	Yes	1.00
Ester					
Butyl Acetate	259 (126.1)	116.2	No	Yes	7.60
Ethyl Acetate	171 (77.2)	88.1	Yes	Yes	2.90

continued ...

Compounds Suitable for Carbon Adsorption

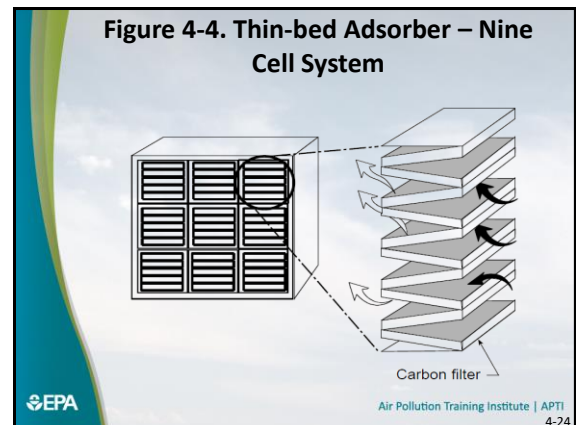
Organic Compound	Boiling Point *(°C)	Molecular Weight	Solubility in Water	Flammable Liquid	Lower Explosive Limit, % Vol.
Halogenated					
Carbon Tetrachloride	170 (76.7)	153.8	No	No	N.F.
Ethylene Dichloride	210 (98.9)	85.0	No	Yes	6.20
Methylene Chloride	104 (40.0)	84.9	Yes	No	N.F.
Perchloroethylene	250 (121.1)	165.8	No	No	N.F.
Trichloroethylene	189 (87.2)	131.4	No	No	N.F.
Tetrachloroethane	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

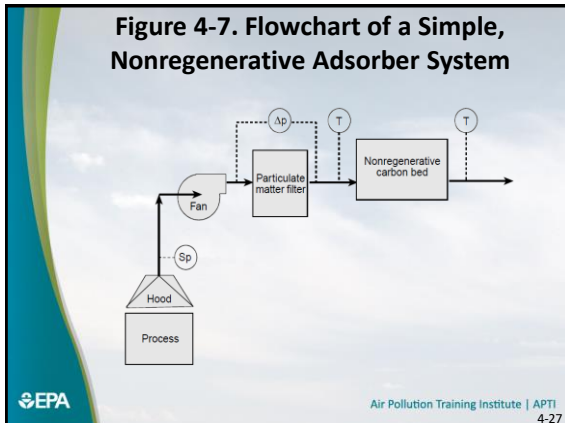
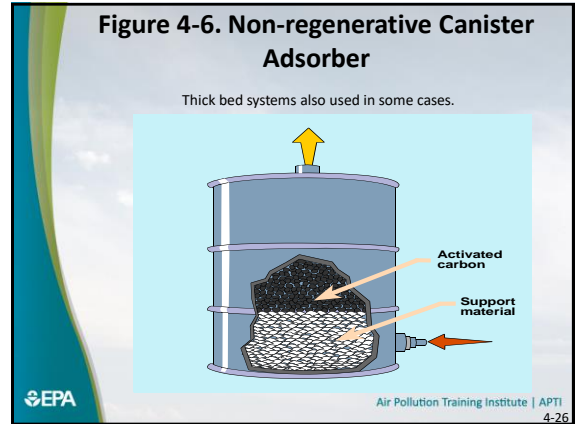
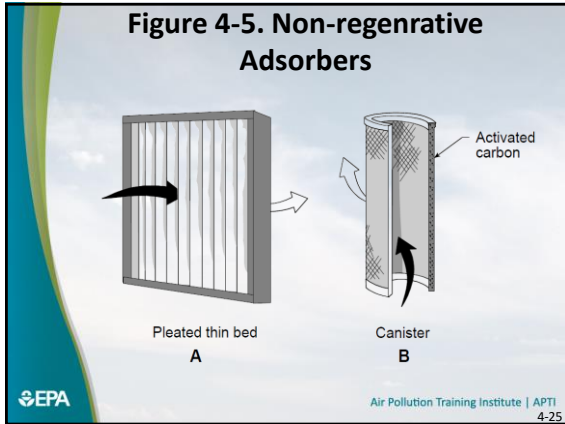
Compounds Not Suitable for Carbon Adsorption

Reactive Compounds	High Boiling Compounds
Organic Acids	Plasticizers
Aldehydes	Resins
Monomers (some)	Long Chain HCs (+C₁₄)
Ketones (some)	Glycols, Phenols, Amines

- ### Types of Adsorbers
- Five types of adsorption equipment are used in collecting gases:
- (1) fixed re-generable beds;
 - (2) disposable/rechargeable canisters;
 - (3) traveling bed adsorbers;
 - (4) fluid bed adsorbers; and
 - (5) chromatographic baghouses.
- Of these, the most commonly used in air pollution control are fixed-bed systems and canister types.

- ### 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





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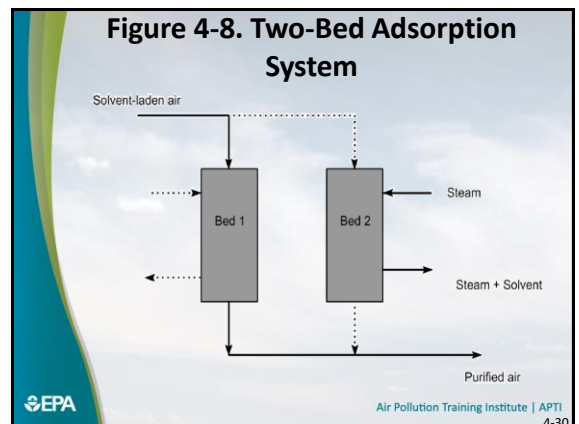
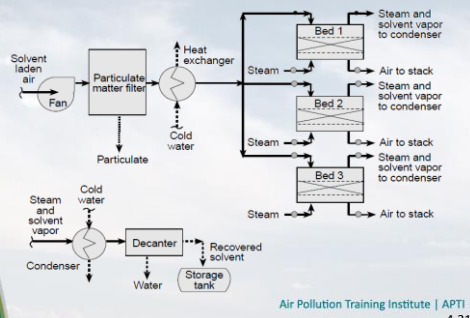
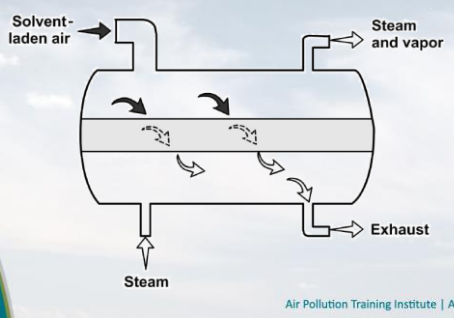


Figure 4-9. Multi-bed, Fixed-bed Adsorption System



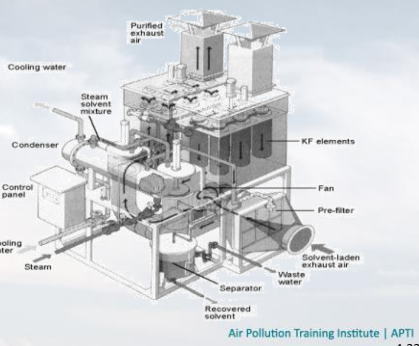
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Figure 4-10. Horizontal Adsorber Vessel



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Figure 4-11. Carbon Fiber System



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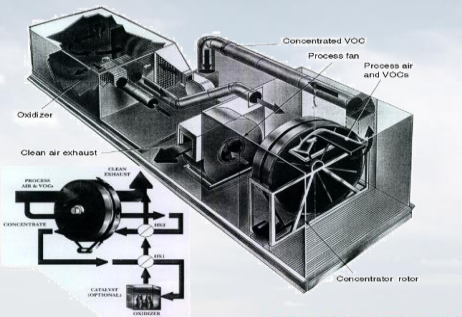
Moving Bed Designs

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



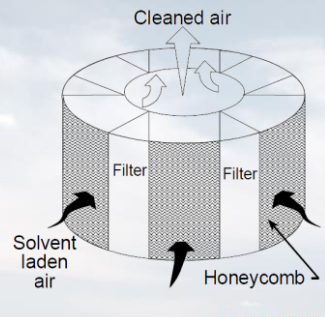
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Figure 4-12. Rotary Wheel Zeolite Adsorber



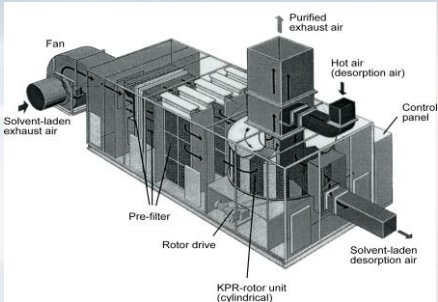
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Figure 4-13a. Rotor for Carbon Fiber System



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Figure 4-13b. Carbon Fiber Rotor System



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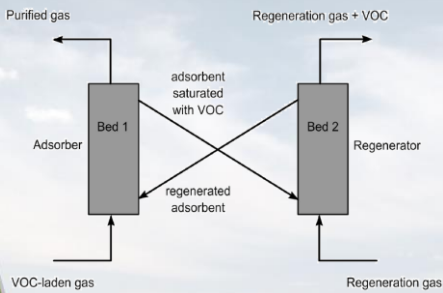
Fluidized Bed Adsorbers

- 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



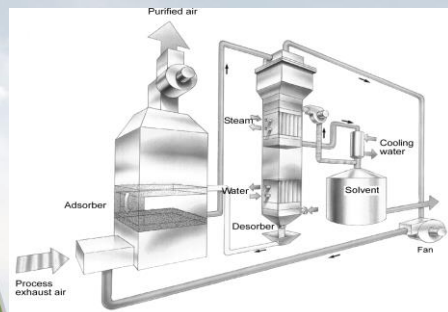
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Figure 4-14. Fluidized Bed Adsorber/Regenerator



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Figure 4-15. Fluidized Bed Adsorber



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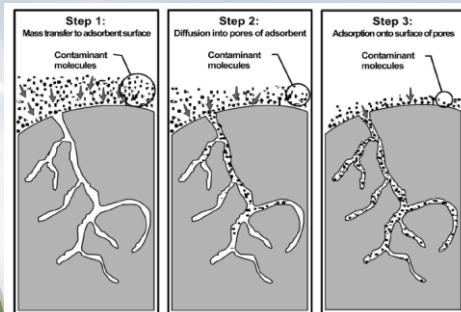
Operating Principles

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



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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

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Figure 4-17. Physical Forces

The diagram shows three panels illustrating physical forces between a gas molecule and a surface.
 1. **Orientation Effect (Polar-Polar):** A polar molecule with a positive end (+) and a negative end (-) is oriented towards a surface with alternating positive (+) and negative (-) charges. A wavy arrow points from the molecule towards the surface.
 2. **Dispersion Effect (Nonpolar-Nonpolar):** A nonpolar molecule is shown near a surface with alternating positive (+) and negative (-) charges. A wavy arrow points from the molecule towards the surface.
 3. **Induction Effect (Polar-Nonpolar):** A polar molecule is oriented towards a surface with alternating positive (+) and negative (-) charges. A wavy arrow points from the molecule towards the surface.

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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
 - Adsorbents used can be either pure substances or chemicals deposited on an inert carrier material

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Table 4-2. Characteristics of Chemisorption 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

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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.

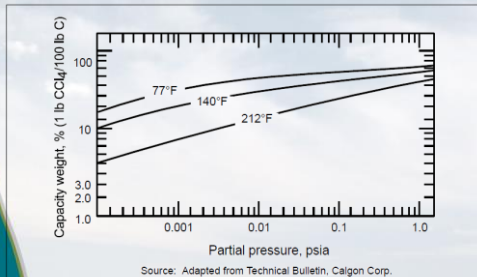
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Isotherm

- 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

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Figure 4-18. Adsorption Isotherm: Carbon Tetrachloride on a Specific Activated Carbon



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 140 °F 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.

$$y = 680 \text{ ppm} = 0.00068$$

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

$$P^* = yP = (0.00068)(14.7 \text{ psia}) = 0.01 \text{ psia}$$

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%.

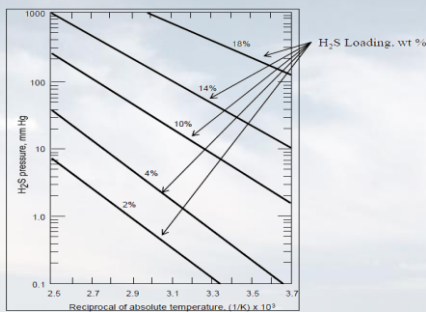


Isostere

- 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 Isotheres: H₂S on 13X Molecular Sieve

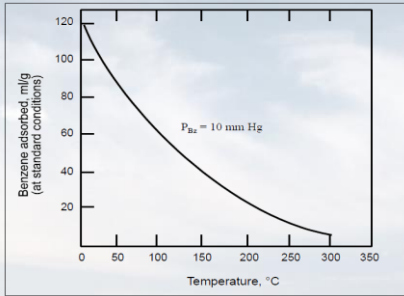


Isobar

- 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**



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Adsorption System Performance

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



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Applicability

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



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Applicability

- Regenerative
 - Organic compounds with molecular weights >50 and <200 or boiling points >20°C and <175°C
 - Limited concentrations of reactive compounds



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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



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Adsorption Capacity

Retention

- Lbs of VOC adsorbed per 100 lbs of carbon
- Weight percent



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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 4-hour cycle.
- **Note:** Saturation capacity of the activated carbon is 45% by weight. The molecular weight of CCl₄ is 154.
- Use a working capacity of 25% of the saturation capacity.



Problem 4-2: Solution

Step 1. Compute the flow rate of CCl₄.

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

Converting to pounds per hour:

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

For a 4-hour cycle, there are $4 \times 245 = 980 \text{ lb}_m \text{ CCl}_4$

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

$$980 \text{ lb}_m \text{ CCl}_4 \times \left(\frac{100 \text{ lb}_m \text{ carbon}}{45 \text{ lb}_m \text{ CCl}_4} \right) = 2,178 \text{ lb}_m \text{ activated carbon}$$

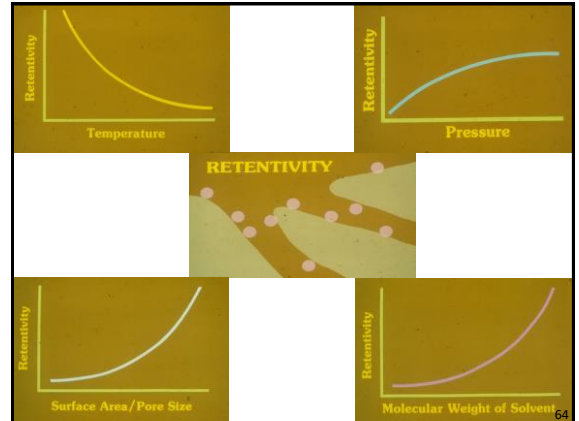
Estimate actual activated carbon requirement by multiplying the amount needed at saturation by four (working capacity of 25% of the saturation capacity).

$$4 \times 2,178 = 8,712 \text{ lb}_m \text{ carbon per four-hour cycle, per adsorber.}$$



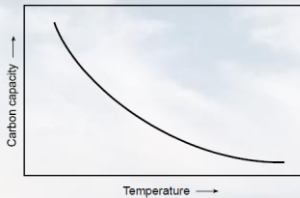
Factors Affecting Adsorption System Performance

- 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



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

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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 static 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?

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Problem 4-3: Solution

Step 1. Calculate the absolute pressure.

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

Step 2. Calculate the gas flow rate in ACFM.

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

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

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

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

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

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Figure 4-22. Mass Transfer Zone

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Operation 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

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MASS TRANSFER ZONE

- The Mass Transfer Zone (MTZ) (see following figure), exists in all adsorbents.
- The concentration of VOC in in the MTZ air goes from 100% of the inlet vapor concentration to the lowest available vapor pressure in equilibrium with the desorbed adsorbent.
- The depth of the bed is the dimension of the adsorbent in the direction of air flow, and the MTZ is usually much shorter than the depth of the bed.
- The MTZ moves through the bed as the bed reaches its capacity (the absorption isotherm becomes filled).

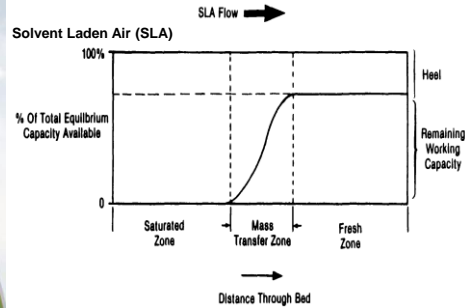
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MASS TRANSFER ZONE (cont.)

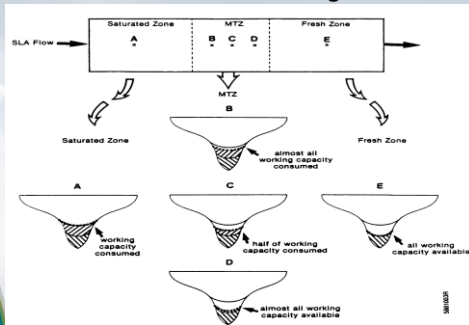
- Upstream of the MTZ, the bed has reached its capacity, while downstream the bed remains essentially desorbed.
- Breakthrough occurs when the MTZ reaches the downstream end of the adsorption bed.
- Breakthrough is observed as a rise in the VOC vapor concentration leaving the bed, which may occur at different times for different VOC.



Available Working Capacity as a Function of Distance Through an Operating Bed



Simplified Pore Representation of Capacity as a Function of Distance Through Bed



Equation 4-1. Estimating the length of the MTZ

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

Where:

- MIZ = Length of MTZ, meters
- X_s = Degree of saturation in the MTZ, % (usually assumed to be 50%)
- D = Bed depth, meters
- C_B = Breakthrough capacity, %
- C_s = Saturation capacity, %



Equation 4-2. Estimating Breakthrough Capacity

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

$$C_B = \frac{(X_s)(C_s)(MIZ) + C_s(D - MIZ)}{D}$$

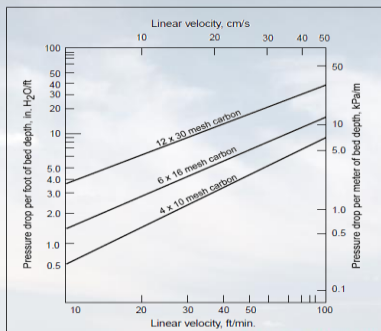


Bed Depth

- 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



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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



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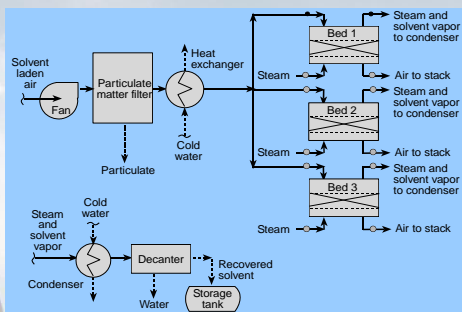
Steam Stripping Disadvantages

- 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)



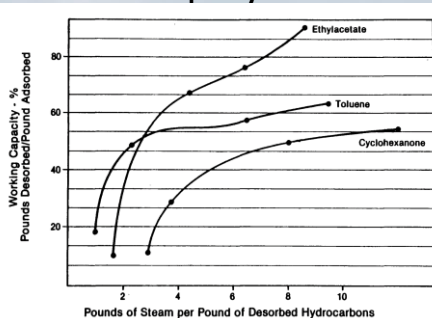
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Steam Regeneration

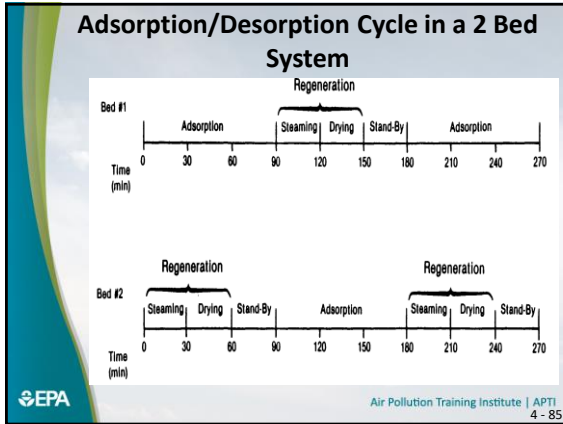


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Steam Consumption versus Working Capacity



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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

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Problem 4-4

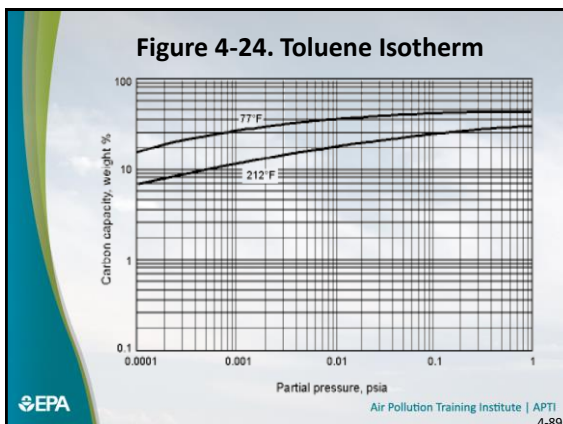
- A solvent degreaser is designed to recover toluene from an 8,000 ACFM air stream at 80°F (26.7°C) and atmospheric pressure. The company is planning to use a two-bed carbon adsorption system with a cycle time of 4 hours.
- The average concentration of toluene is 2,400 ppm.

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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_m/ft³)

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Problem 4-4: Solution

Step 1. Calculate the toluene flow rate.

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

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

$$= 0.0487 \text{ lb mol toluene / min}$$

The mass flow rate of toluene is:

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

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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 $T = 80^\circ\text{F}$.

Capacity ≈ 45 wt % or $45 \text{ lb}_m/100 \text{ lb}_m$ carbon



Problem 4-4: Solution (Continued)

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

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

= 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:

$$A = \frac{Q}{\text{Maximum Velocity}} = \frac{8,000 \text{ acf/min}}{100 \text{ ft/min}} = 80 \text{ ft}^2 \quad \text{[Answer 2]}$$



Problem 4-4: Solution (Continued)

Step 4: Estimate the bed depth.

At a carbon density of $30 \text{ lb}_m/\text{ft}^3$, the bed depth would be:

$$\text{Vol. carbon} = 9,680 \text{ lb}_m \text{ carbon} / (30 \text{ lb}_m/\text{ft}^3) = 320 \text{ ft}^3$$

$$\text{Bed Depth} = 320 \text{ ft}^3 / 80 \text{ ft}^2 = 4 \text{ ft}$$

[Answer 3]



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 .

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

The bed depth for this modified approach would be:

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

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

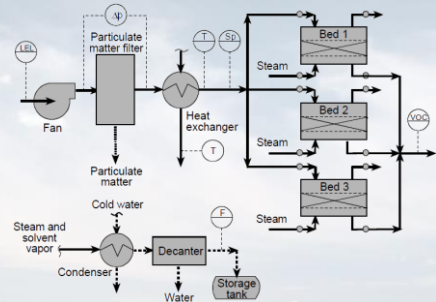


Factors that Contribute to Premature Organic Breakthrough and the Need for Instrumentation

- 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



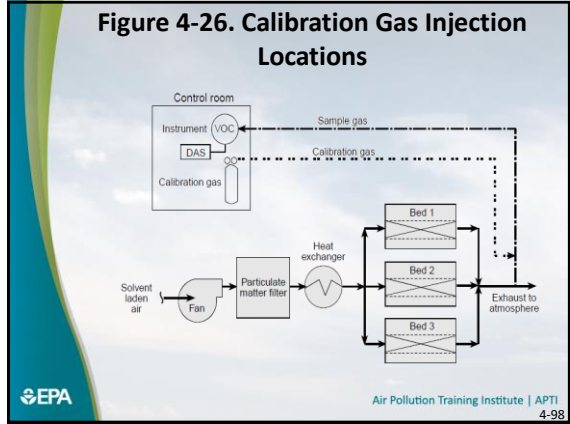
Figure 4-25. Flowchart of a Three-Bed Adsorber with Instrumentation



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

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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

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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

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Additional Monitoring Considerations

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

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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.

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Summary (Continued)

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 adsorbents.
- Factors that affect the performance of an adsorption system.
- Areas of an adsorption system that require monitoring.



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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. Adsorbents 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. Adsorbent removal efficiencies are usually in the range of 90% to 98%.



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Uses of Non-regenerable Adsorbents

- Control of odor
- Control of trace contaminants (Low VOC concentrations)



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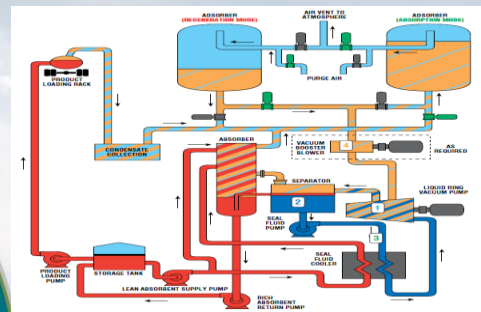
Non-Regenerable Carbon Adsorption Drums controlling mercaptan odors from re-refined crankcase oil product 4 - 106

Non-Regenerative Carbon Adsorption Drums



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4-107

John Zink Carbon Adsorption – Absorption Process with Liquid Ring Vacuum Pump



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<http://www.johnzink.com/wp-content/uploads/carbon-adsorption-vapor.pdf> 4-108

Carbon Adsorber – Fixed Bed Examples



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FIRE HAZARD FROM CARBON ADSORPTION DEODORIZING SYSTEMS

The Environmental Protection Agency (EPA) is issuing this Alert as part of its ongoing effort to protect human health and the environment by preventing chemical accidents. Under CERCLA, section 104(a) and under the Act itself, EPA has authority to conduct chemical accident investigations. Additionally, in January 1988, the Administration asked the Environmental Safety and Health Administration (ESHA) and EPA to jointly coordinate investigations to determine the root causes of chemical accidents and to issue public reports containing recommendations to prevent similar accidents. EPA has created a chemical accident investigation team to work jointly with ESHA in these efforts. Due to the nature of a full report, EPA wishes to provide Alert as promptly as possible to increase awareness of possible hazards. Alerts may also be issued under EPA's responsibility and a separate report. It is important that facilities, EPA's Regions, emergency responders and other interested organizations and state agencies take as necessary to minimize risk.

PROBLEM

Activated carbon systems used to adsorb organic vapors from industrial effluents may pose a fire hazard if certain types of substances, if proper procedures are not followed. In particular, volatile organic compounds, especially petroleum products in the pulp and paper industry, can pose a fire hazard if adsorption systems are not properly designed and properly maintained. The release of vapors from these systems may occur to avoid or mitigate these fire hazards.

HAZARD AWARENESS

Activated carbon is widely used to adsorb vapors to prevent their release to the air. For certain classes of chemicals, reactions or adsorption on the carbon surface is accompanied by the release of a large amount of heat and can cause the vapor in the carbon bed. Such chemicals include organic sulfur compounds (e.g., mercaptans), which may be found in wastewater or waste effluents together with other volatile organic compounds that may cause large thermal releases or reactions, including those of organic peroxides. Adsorption of high vapor concentrations can create a self-heating reaction. If flammable vapors are present, the heat released by adsorption can raise the surface of the carbon may reach a level sufficient to cause a fire. An increase in temperature of the vapor and oxygen is present to support a fire.

ACCIDENTS

In a 1995 accident at a chemical processing facility, fire and explosion occurred involving three tanks of activated carbon for deodorizing. The fire and explosion damaged other storage tanks, resulting in the release of toxic gases and a large-scale evacuation of non-residents.

Fire has occurred in the past in activated carbon systems used for deodorizing waste effluents. In general, such fires have not had effects as serious as those reported in the 1995 fire. Regions offices should alert the regulated carbon contractors and the use of tanks containing flammable or combustible substances.



Chemical Emergency Preparedness and Prevention Office

EPA 552/P-89-003

TABLE 3-2. PERFORMANCE TEST DATA FOR CARBON ADSORPTION SYSTEMS

Test No.	Fluorocarbon or other stream	Component ^a in inlet stream	Adsorbate		Conditions During Test		Flow Rate (lb/hr)	Temp. (°F)	Flow Rate (lb/hr)	Temp. (°F)	Flow Rate (lb/hr)	Bed Depth (ft)	Age (years)	Avg. Eff. (%)
			Flow Rate (lb/hr)	Temp. (°F)	Component in Inlet Stream ^b	Flow Rate (lb/hr)								
1	A	11,200	MEK - 40%	575	95	2,375	11,400	MEK - 100%	284	94	2,410	0.4	94.5 ^c	
2	B	12,700	TSP - 91%	140	90	900 ^d	TSP - 10%	195 ^e	74	400	2	99.7		
3	B	12,700	TSP - 30%	140	90	900	TSP - 73%	140	90	400	3.0	93.4 ^f		
4	C	23,000	TSP, Toluene, MEK, MEK, Cyclohexanone	400	85	2,400	19,800	TSP, Toluene, MEK, MEK, Cyclohexanone	1,200 ^g	85	2,500	0.4	94.0 ^h	
5	D	22,000	Hexane - 100%	1,300	93	4,130	17,700	Hexane - 100%	355	89	3,200	3	99.1	
6	E	11,100	Toluene - 100%	204	100	1,170	9,100	Toluene - 100%	245 ⁱ	104	3,000	3	97.4	
7	E	11,100	Toluene - 100%	204	100	1,170	7,800	Toluene - 100%	100	133 ^j	2,800	4.5	94.0 ^k	
8	F	80,000	Toluene - 40%	400	120	1,180	29,400	Toluene - 40%	920 ^l	93	3,400	0.2	91.5	
9	F	80,000	Toluene - 40%	400	120	1,180	29,400	Toluene - 40%	890 ^m	47	3,300	1.6	97.4	
10	G	80,000	Toluene - 40%	400	120	1,180	29,400	Toluene - 40%	890 ⁿ	47	3,300	1.6	97.4	
11	O	ME ¹	ME	80	80	80	4,400	MEK - 91%	3,550	88	80	80	90.9	
12	B	ME	ME	80	80	80	48,000	Toluene - 100%	700	94	11,000	80	90 ^o	
13	E	75,000	ME	80	80	80	41,200	Toluene - 10%	1,270	100	80	80	93.4	
14	J	10,000 - 83,700	MEK - 20-10%	100 - 2,800	100 - 1,200	10,000 - 80,000	TSP - 1,110 (10 per cent)	MEK - 100%	80	120	12,000	Variable	99.4	
15	K	24,000	Cyclohexanone - 20-10%	1,200	80	1,750	24,200	MEK - 100%	400 ^p	83	1,700	2	99.4	
16	L	28,000	Toluene - 93%	800 - 3,070	120	3,000	28,000	ME	80	120	3,000	80	99.5	

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Office of Air Quality Planning and Standards
Research Triangle Park NC 27711
EPA-450/3-88-012
June 1988

Carbon Adsorption for Control of VOC Emissions: Theory and Full Scale System Performance

Adsorption Publication Web sites

<http://www.epa.gov/ttn/catc/dir1/cs3-1ch1.pdf>

<http://www.epa.gov/ttn/catc/dir1/fadsorb.pdf>

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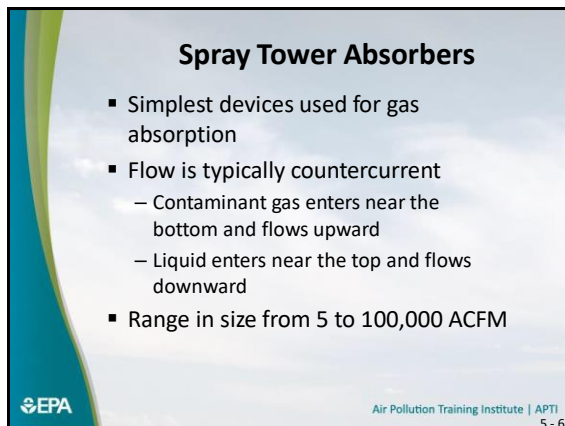
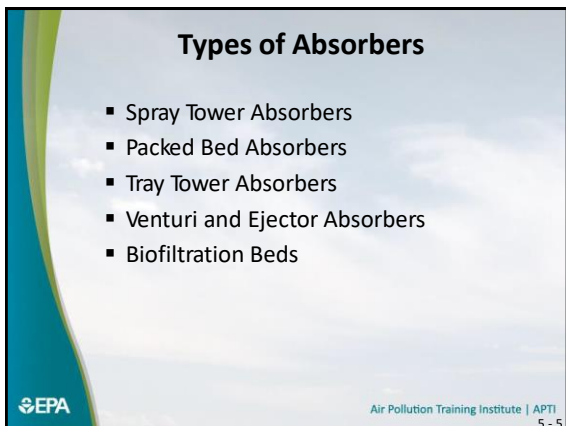
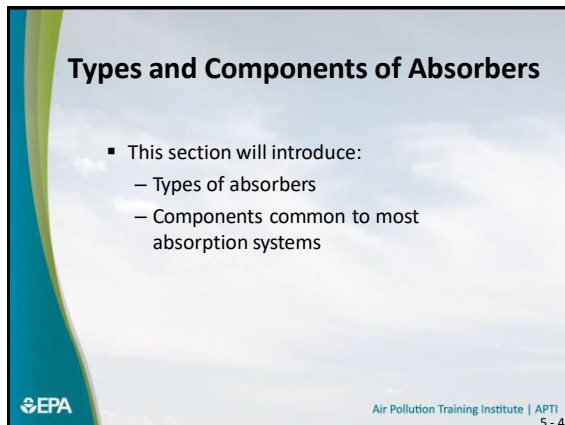
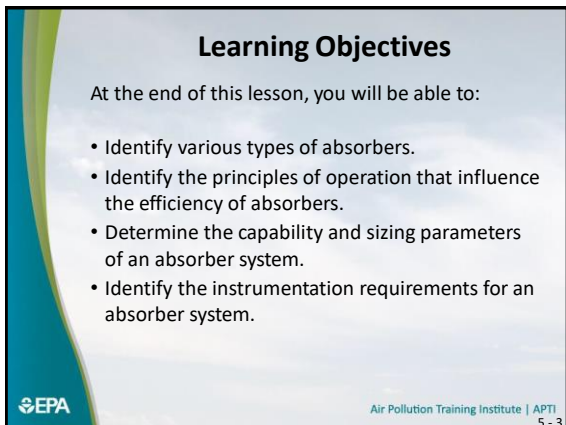
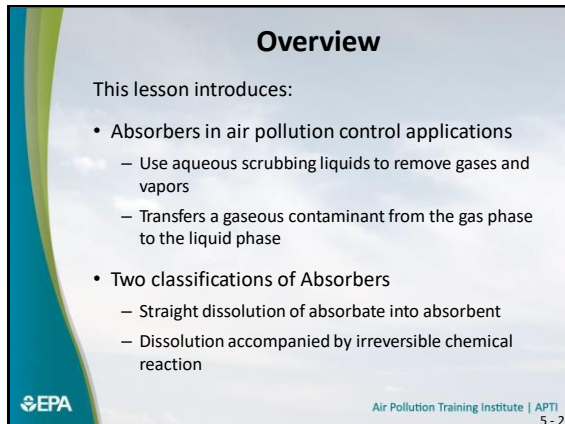
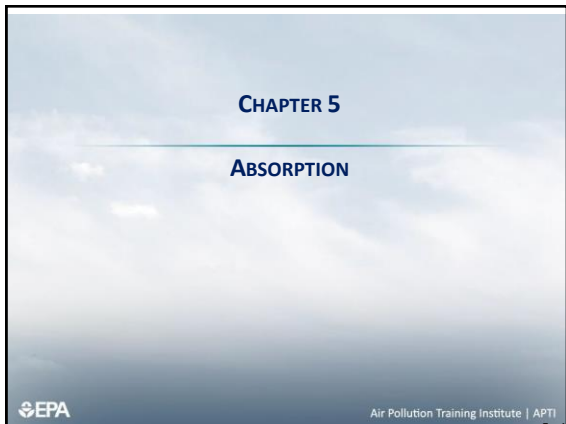
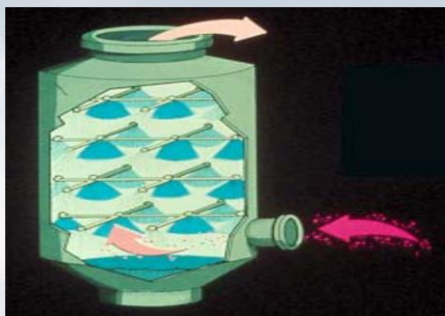


Figure 5-1. Spray Tower Scrubber



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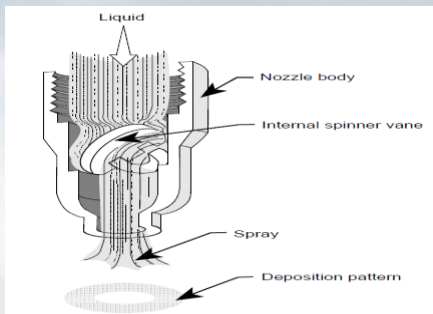
Flow Arrangements

- 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



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Figure 5-2. Full-Cone Spray Nozzle



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Various Nozzle Types



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Basic Nozzle and Spray Characteristics

Nozzle Type	Spray Pattern	Spray Characteristics	Spray Angle, deg	Typical Applications
Wide cone, wide-orifice type		Provides a good-to-medium distribution of wet air surface, large droplet coverage, best for large surface area	60-160	- All gas and water coating - Gas gas absorption (GAG) - Gas absorption, scrubbing and stripping
Wide cone, narrow-orifice type		Provides good spray area, but it is more concentrated and more of distributor surface	100-160	- Water washing - Gas absorption - Fine, uniform and low misting
Wide cone, roller type		Provides wide spray coverage, but it is more concentrated and more of distributor surface	60-160	- Water washing - Gas absorption
Full cone		Uniform coverage with medium to large droplets, good for large surface area and for large surface area	15-120	- Washing and rinsing - Chemical reaction - Gas absorption
Full cone, roller type		Uniform coverage with medium to large droplets, good for large surface area and for large surface area	30-170	- Gas absorption, scrubbing and rinsing - Good absorption
Edge, tapered edge		Provides the full cone spray, but it is more concentrated and more of distributor surface	15-100	- Chemical reaction - Product washing
Edge, flat edge		Provides the full cone spray, but it is more concentrated and more of distributor surface	20-60	- High pressure washing
Edge, flat edge type		Provides the full cone spray, but it is more concentrated and more of distributor surface	15-100	- Product washing
Roller stream		High impact water efficiency, reduced particle rebound	0	- Water washing
Advancing, turbulent, roller stream		Low-velocity flow, hollow cone spray, it can be compressed or expanded	30-160	- Deposition coating - Spray drying - Chemical reaction
All-advancing, roller stream		Produces medium, mass velocity, good dispersion, high turbulence	Wide variety	- Gas coating and distribution - Spray drying - Chemical reaction - Product washing
All-advancing, roller stream		High-velocity spray, high turbulence	Wide variety	- Product washing



APTI 5-11

Comparison

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



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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

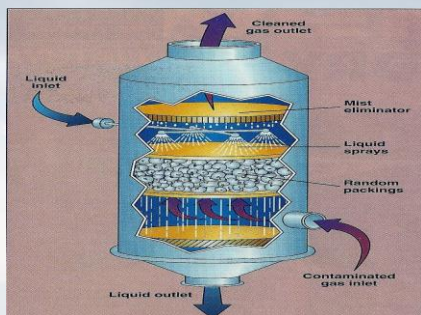


Types of Packed Bed Absorbers

- 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



Counter-current Packed Tower at a Plating Operation

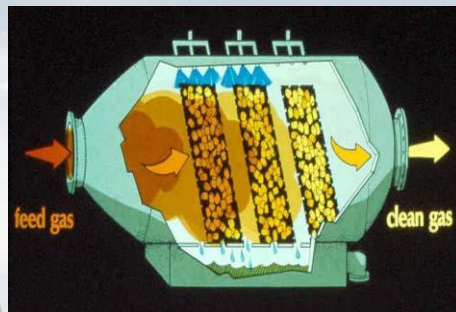


Types of Packed Bed Absorbers

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



Figure 5-4. Cross-flow Scrubber



Cross-Flow Scrubber Sections



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Record-size cross flow scrubber installed at B.C. kraft mill



Temperature of 93 deg C. (200° F) with a vacuum of -914 mm (-36 in.) of water gauge and a flow volume of 387,000 ACFM.

<http://www.fabricatedplastics.com/case/cross-flow-scrubber-2/>

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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

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Figure 5-5. Types of Packing



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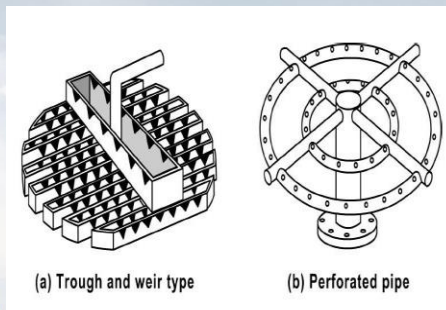
Liquid Distribution

- 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

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Figure 5-6. Types of Liquid Distributors



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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

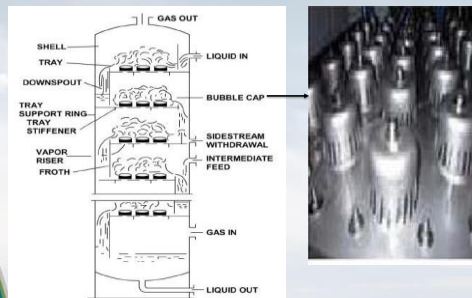
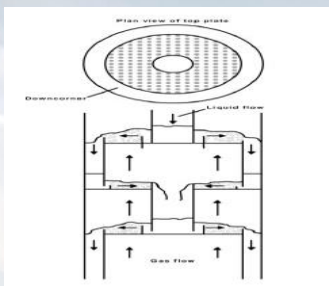


Figure 5-8. Gas-liquid Contact in a Disk-and-Donut Sieve Tray

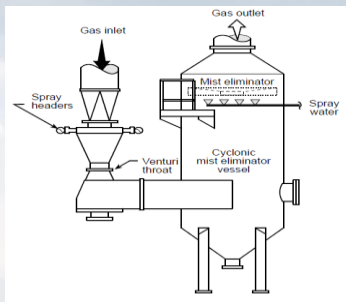


Venturi's

- 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

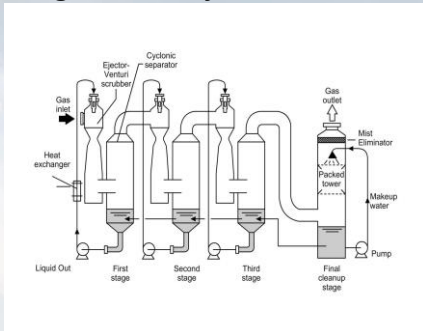


Ejector Absorbers

- 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



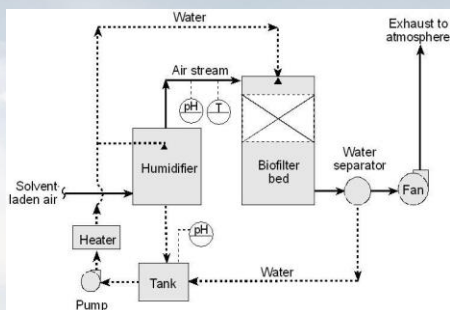
Figure 5-10. Ejector Absorbers



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)

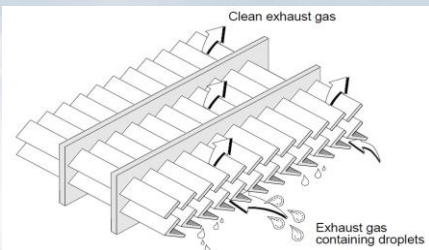
Figure 5-11. Biological Oxidation System



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



http://www.koch-glitsch.com/Document%20Library/ME_ProductCatalog.pdf

Figure 5-13. Radial Vane Mist Eliminator

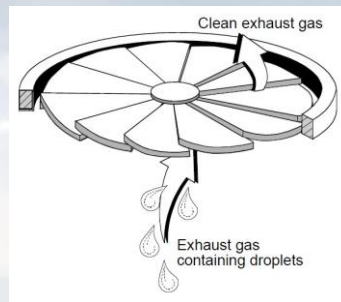
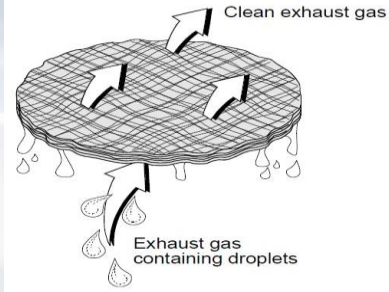


Figure 5-14. Mesh Pad Mist Eliminator



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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



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Instrumentation

- | | |
|----------------------|--|
| Gas Temperature | • Absorber inlet
• Absorber outlet |
| Liquid Flow Rate | • Recirculation liquid stream
• Purge liquid stream |
| Liquid Pressure | • Recirculation pump discharge
• Absorber liquid distribution headers |
| Liquid pH | • Recirculation liquid tank
• Recirculation liquid stream |
| Static Pressure Drop | • Absorber vessel
• Mist eliminator |



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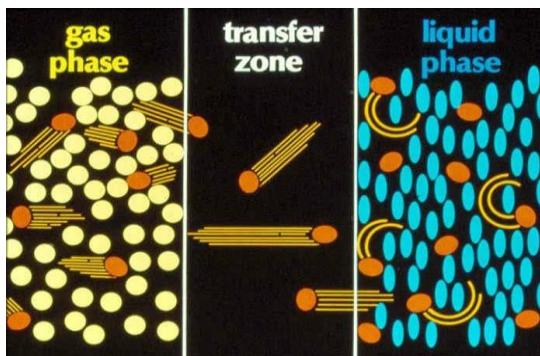
Basic Operating Principles

- Mechanisms of absorption
- Solubility
- Henry's Law



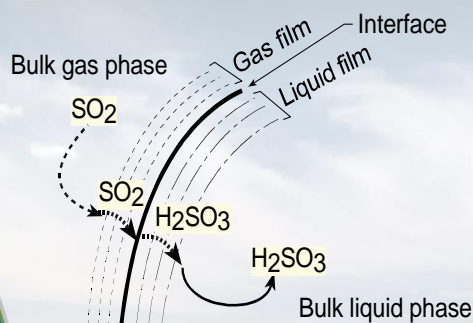
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Mechanisms of absorption



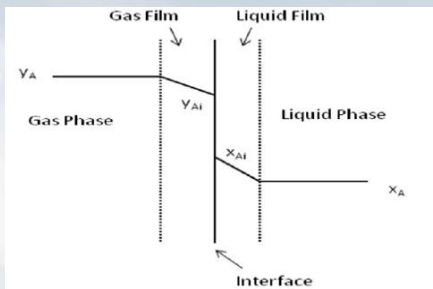
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Two-Film Theory of Absorption



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Figure 5-15. Two-Film Theory of Absorption



Gas Liquid Equilibrium Relationships

Basic principals of gas liquid equilibrium equations

Mole Fraction

$$\frac{\text{moles of solute}}{\text{moles of solute} + \text{moles of solvent}}$$

Gas Phase Mole Fraction

$$Y_A = \frac{\text{moles of A}}{\text{moles of A} + \text{moles of air}}$$

Liquid Phase Mole Fraction

$$X_A = \frac{\text{moles of A}}{\text{moles of A} + \text{moles of water}}$$

Dolton's Law

For ideal gases there is a relationship between mole fraction and the partial pressure of the gas

$$Y_A = p_A / P_{\text{total}}$$

p_A = partial pressure of component A

P_{total} = Total pressure of system

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

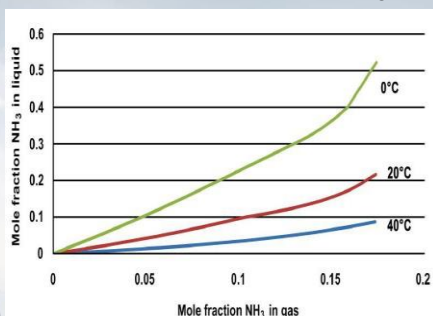


Table 5-1. Equilibrium Partial Pressure of Ammonia over Aqueous Solutions, mm Hg

Wt. NH ₃ per 100 wt. H ₂ 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 NH₃ in H₂O



Equation 5-1: Henry's Law

$$(Eq. 5.1) \quad p_A = H_p x_A$$

Where:

p_A = Partial pressure of contaminant in gas phase at equilibrium

H_p = Henry's Law constant when the gas concentration is expressed in partial pressure

x_A = Mole fraction of contaminant dissolved in the liquid phase at equilibrium



Equation 5-2: Alternate Form of Henry's Law

$$(Eq. 5.2) \quad y_A = H_y x_A$$

Where:

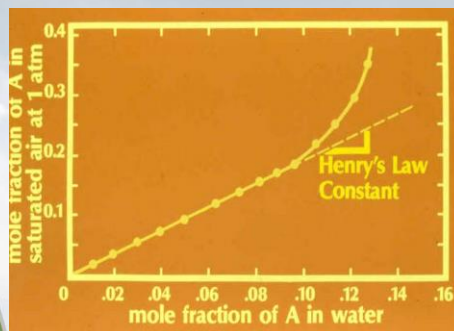
y_A = Mole fraction of the contaminant in the gas phase at equilibrium

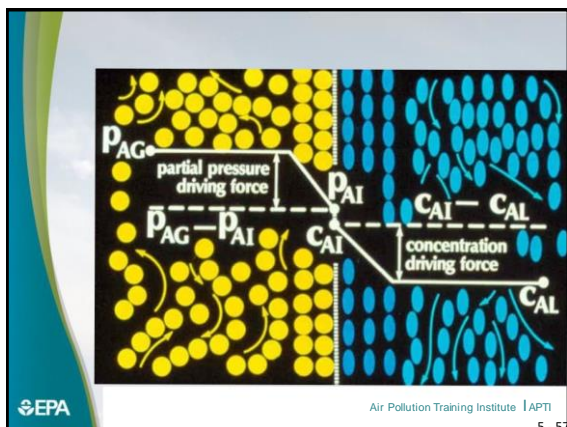
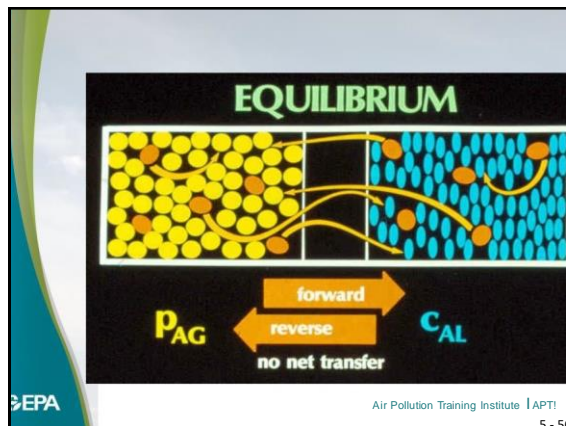
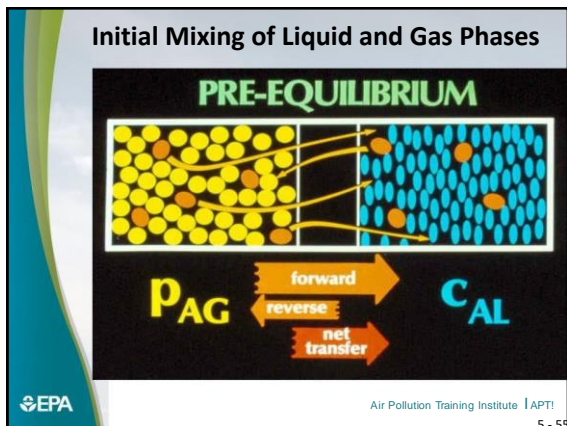
H_y = Henry's Law constant when the gas concentration is expressed in mole fraction

x_A = Mole fraction of contaminant dissolved in the liquid phase at equilibrium



Henry's Law Constant





Molar Flux

$$N_A = k_g(p_{AG} - p_{AI})$$

$$N_A = k_l(c_{AI} - c_{AL})$$

where:
 N_A = molar flux of A, lb mole/hr ft²
 k_g = gas local mass transfer coefficient, lb mole/hr ft² atm
 k_l = liquid local mass transfer coefficient, lb mole/hr ft² (lb mole/ft³)

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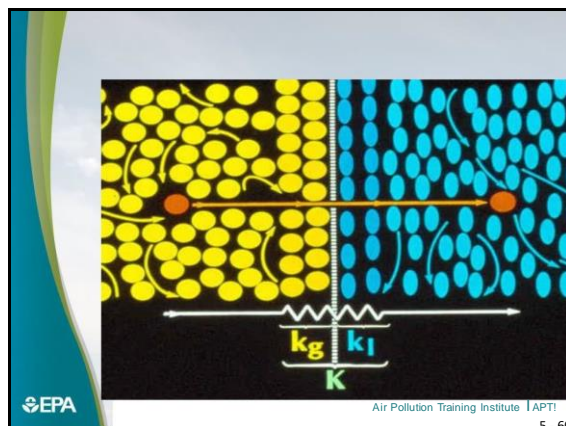
Molar Flux

$$N_A = K_{OG}(p_{AG} - p_A^*)$$

$$N_A = K_{OL}(c_A^* - c_{AL})$$

where:
 N_A = molar flux of A, lb mole/hr ft²
 K_{OG} = gas overall mass transfer coefficient, lb mole/hr ft² atm
 K_{OL} = liquid overall mass transfer coefficient, lb mole/hr ft² (lb mole/ft³)
 p_A^* = partial pressure of A in equilibrium with c_{AL} , atm
 c_A^* = concentration of A in equilibrium with p_{AG} , lb mole/ft³

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$$\frac{1}{K_{OG}} = \frac{1}{k_g} + \frac{H}{k_l}$$

$$\frac{1}{K_{OL}} = \frac{1}{k_l} + \frac{1}{Hk_g}$$

- | | |
|--|--|
| <p>Gas Phase Controlled</p> <ul style="list-style-type: none"> Contaminant is very soluble in liquid Diffusion through gas phase is rate controlling step | <p>Liquid Phase Controlled</p> <ul style="list-style-type: none"> Contaminant is relatively insoluble in liquid Diffusion through liquid phase is rate controlling step |
|--|--|

Problem 5-1

- Use the NH₃-H₂O data in Table 5-1 to show that Henry's Law is valid at low concentrations of NH₃ and calculate H_p and H_v at 20°C in this low concentration range.

Table 5-1. Equilibrium Partial Pressure of Ammonia over Aqueous Solutions, mm Hg

Wt. NH ₃ per 100 wts. H ₂ 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							

Problem 5-1: Solution

Step 1. From equation. 5-1, $H_p = P_A/x_A$. The mass concentration data from Figure 5-1 must be converted to x_A , the mole fraction of NH₃ in the liquid.

$$x_A = \frac{(\text{mol A})}{(\text{mol A} + \text{mol H}_2\text{O})}$$

$$= \frac{(m_A/M_A)}{[(m_A/M_A) + (m_{H_2O}/M_{H_2O})]}$$

Use the first data entry from Table 5-1 as an example: $m_A = 20$, $m_{H_2O} = 100$, $M_A = 17 \text{ lb/lb-mole}$, and $M_{H_2O} = 18 \text{ lb/lb-mole}$

$$x_A = \frac{(20/17)}{[(20/17) + (100/18)]} = 0.1755$$

Problem 5-1: Solution (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 .

x_A	P_A	H_p
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

Problem 5-1: Solution (Continued)

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:

$H_y = H_p / P$ P = total pressure (see pg. 5-21 in Student Guide)

$H_p = \frac{584 \text{ mm Hg/mole fraction NH}_3 \text{ in water}}{760 \text{ mm Hg/mole fraction NH}_3 \text{ in gas}}$

$H_y = 0.768 \frac{\text{mole fraction NH}_3 \text{ in gas}}{\text{mole fraction NH}_3 \text{ in water}}$



Problem 5-1: Solution (Continued)

The final values with units are:

$P = 760 \text{ mm Hg/mole fraction of NH}_3 \text{ in gas}$

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

$H_y = 0.768 \text{ mole fraction NH}_3 \text{ in gas/mole fraction NH}_3 \text{ in liquid}$



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



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

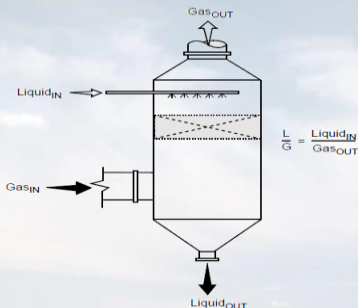


Absorber Sizing

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



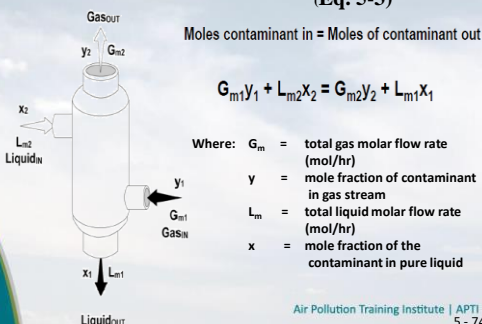
Figure 5-17. Definition of the Liquid-to-Gas Ratio



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Figure 5-18. Material Balance for Countercurrent Flow Absorber

(Eq. 5-3)



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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, $x \approx X$ and $y \approx Y$
- 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



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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
 $G_{m1}Y_1 + L_{m2}X_2 = G_{m2}Y_2 + L_{m1}X_1$

(Eq. 5-8) Dilute solutions
 $G_{m1} = G_{m2} = G_m$ and $L_{m1} = L_{m2} = L_m$

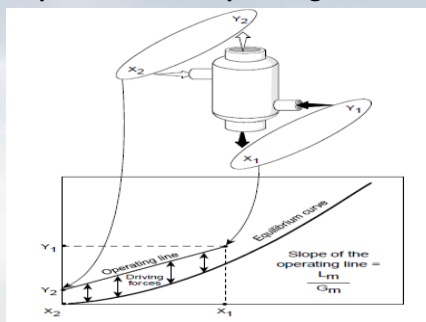
(Eq. 5-9) Rearranging
 $G_m(Y_1 - Y_2) = L_m(X_1 - X_2)$
 The equation of a straight line on a Y-X diagram,
 slope = L_m/G_m

(Eq. 5-10) $Y_1 - Y_2 = \frac{L_m}{G_m}(X_1 - X_2)$

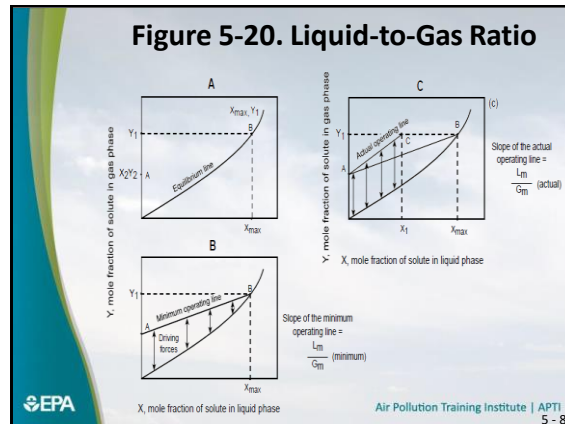
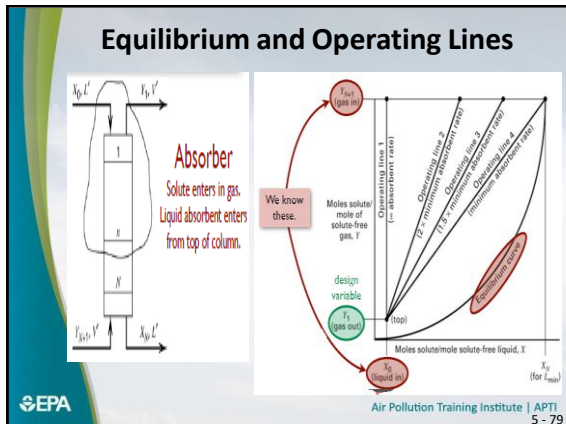


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Figure 5-19. Diagram Showing the Equilibrium and Operating Lines



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Problem 5-2

- Calculate $(L_m/G_m)_{min}$ for the removal of 90% of the NH_3 from a $85.0 \text{ m}^3/\text{min}$ (3000 ACFM) feed gas containing 3% NH_3 and 97% air.
- The inlet liquid is pure H_2O and the temperature and pressure are 293 °K and 1 atm, respectively.

Use the results from Problem 5-1.

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Problem 5-2: Solution

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

The sketch shows a vertical absorber column. Gas enters from the top with $Y_2 = 0.003$. Gas exits from the side with $Y_1 = 0.03$ and a flow rate of $G_{m1} = 85 \text{ m}^3/\text{min}$. Liquid enters from the bottom with $X_1 = ?$. Liquid exits from the side with $X_2 = 0$ and a flow rate of $L_{m2} = ?$.

Figure 5-21

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Problem 5-2: Solution (Continued)

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

$Y_1 = H_v X_1$ (Remember $y_1 = Y_1$ and $x_1 = X_1$ for dilute systems)

$H_v = 0.768 \frac{\text{mole fraction } NH_3 \text{ in air}}{\text{mole fraction } NH_3 \text{ in water}}$ (from Problem 5-1)

$0.03 = 0.68 X_1$

$X_1 = 0.0391 \text{ mole fraction}$

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Problem 5-2: Solution (Continued)

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

$$Y_1 - Y_2 = \frac{L_m}{G_m} (X_1 - X_2)$$

$$\left(\frac{L_m}{G_m}\right)_{min} = \frac{Y_1 - Y_2}{X_1 - X_2}$$

$$\left(\frac{L_m}{G_m}\right)_{min} = \frac{0.03 - 0.003}{0.0391 - 0}$$

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

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Problem 5-2: Solution (Continued)

Step 4. Convert m³ of air to gram moles, then compute the minimum required liquid flow rate. At 293 °K and 1 atm, the molar volume of an ideal gas (air) can be calculated as follows:

$$PV = nRT$$

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

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



Problem 5-2: Solution (Continued)

$$(L_{\min})_{\text{min}} = \left(0.6905 \frac{\text{gmol H}_2\text{O}}{\text{gmol air}}\right) * G_m$$

$$(L_{\min})_{\text{min}} = (0.6905) * (3542) = 2,446 \frac{\text{gmol H}_2\text{O}}{\text{min}}$$

$$L_{\min} = \left(2,446 \frac{\text{gmol H}_2\text{O}}{\text{min}}\right) * \left(18 \frac{\text{gH}_2\text{O}}{\text{gmol H}_2\text{O}}\right) = 44,024 \frac{\text{gH}_2\text{O}}{\text{min}}$$

$$L_{\min} = \left(44,024 \frac{\text{gH}_2\text{O}}{\text{min}}\right) * \left(\frac{1 \text{ lb}}{453.6 \text{ g}}\right) * \left(\frac{1 \text{ gal}}{8.34 \text{ lb H}_2\text{O}}\right)$$

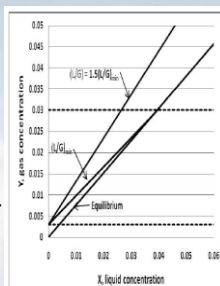
$$L_{\min} = 11.6 \frac{\text{gal H}_2\text{O}}{\text{min}}$$



Problem 5-2: Solution (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.

- $L = 1.5 L_{\min} = 1.5(2446 \text{ g mol/min}) = 3670 \text{ g mol/min}$, or
- $L = 1.5(44,024 \text{ g/min}) = 66,340 \text{ g/min}$, or
- $L = 1.5(11.6 \text{ gal/min}) = 17.4 \text{ gal/min}$



Equation 5-11: Absorption Factor

The relationship between the equilibrium line and the actual operating line used in the absorbers is termed the absorption factor. This is the ratio of the slopes of the operating line and the equilibrium line.

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

Where:

- AF = Absorption factor
- L₂ = Molar flow rate of liquid
- m = Slope of the equilibrium line on a mole fraction basis = H_v
- G₁ = Molar flow rate of gas

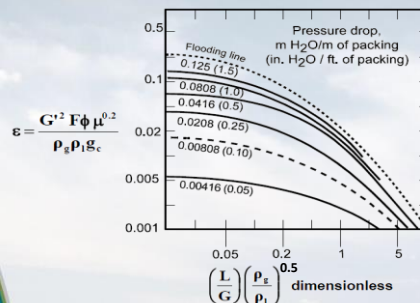


Packed Tower Absorber Diameter

- 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



Equation 5-12

$$\text{Abscissa} = \left(\frac{L}{G} \right) \left(\frac{\rho_g}{\rho_l} \right)^{0.5}$$

Where:

- L = Mass velocity of liquid stream, lb/sec·ft²
- G = Mass velocity of gas stream, lb/sec·ft²
- ρ_g = Gas density, lb/ft³
- ρ_l = Liquid density, lb/ft³



Equation 5-13

$$\text{Ordinate} = G^* = \left(\frac{\epsilon \rho_g \rho_l g_c}{F_p \phi \mu^{0.2}} \right)^{0.5}$$

Where:

- G* = gas mass velocity at flooding, lb_m/ft²·sec
- ε = Ordinate of Sherwood Correlation (Figure 5-23)
- ρ_g = Density of gas, lb_m/ft³
- ρ_l = Density of liquid, lb_m/ft³
- g_c = Gravitational acceleration (32.2 lb_m·ft/lb_f·sec²)
- F_p = Packing factor (Table 5-3), dimensionless
- φ = specific gravity of absorbent, dimensionless
- μ = Viscosity of liquid, cP



Equations: 5-14 through 5-17

Operate at some fraction of G*

$$\text{Where: } G_{op} = G^* f$$

- G_{op} = Actual gas flow rate per unit area (lb_m/ft²·sec)
- f = Coefficient, typically 0.75

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

$$\text{Tower Area} = \frac{\text{Total volumetric gas flow rate}}{\text{Gas flow rate per unit area}}$$

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

$$\text{Tower Diameter} = 1.13 (\text{Tower Area})^{0.5}$$



Table 5-2. Packing Data

Packing	Size, (in.)	Weight, (lb _m /ft ³)	Surface Area, (ft ² /ft ³)	Void Fraction, (%)	Packing Factor, F _p (ft ² /ft ³)
Raschig™ Rings (Ceramic, Porcelain)	1.0	44	58	70	155
	1.5	42	36	72	95
	2.0	38	28	75	65
Raschig™ Rings (Steel)	3.0	34	19	77	37
	1.0x1/32	40	63	92	115
Berl™ Saddles (Ceramic Porcelain)	2.0x1/16	38	31	92	57
	1.0	48	79	68	110
Intalox™ Saddles (Ceramic)	2.0	38	32	75	45
	1.0	44	78	77	98
Intalox™ Saddles (Ceramic)	2.0	42	36	79	40

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



Table 5-2. Packing Data (Continued)

Packing	Size, (in.)	Weight, (lb _m /ft ³)	Surface Area, (ft ² /ft ³)	Void Fraction, (%)	Packing Factor, F _p (ft ² /ft ³)
Intalox™ Saddles (Ceramic)	1.0	44	78	77	98
	2.0	42	36	79	40
Intalox™ Saddles (Plastic)	1.0	6.0	63	91	30
	2.0	3.8	33	93	20
	3.0	3.3	27	94	15
Pall™ Rings (Plastic)	1.0	5.5	63	90	52
	2.0	4.5	31	92	25
Pall™ Rings (Metal)	1.5 x 0.03	24	39	95	28
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.



Problem 5-3

- For the scrubber in Problem 5-2, determine the packed bed tower diameter if the operating liquid flow rate is 1.5 times the minimum.
- The gas velocity should be no greater than 75% of the flooding velocity and the packing material is two-inch ceramic Intalox™ saddles.



Problem 5-3: Solution

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

$$G_m = 3,540 \text{ g mole/min}$$


$$L = 3,670 \text{ g mole/min}$$

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).

$$G = (3,540 \text{ g moles/min})(29 \text{ g/g mole})$$

$$= 102,700 \text{ g/min (1 lb}_m/454 \text{ g)}$$

$$= 226 \text{ lb}_m/\text{min}$$


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Problem 5-3: Solution (Continued)

Step 1. (Continued) :

$$L = (3,670 \text{ g mole/min})(18 \text{ g/g mole})$$


$$= (66,060 \text{ g/min})(1 \text{ lb}_m/454 \text{ g})$$

$$= 146 \text{ lb}_m/\text{min}$$

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.

$$\text{Abscissa} = \left(\frac{L}{G} \right) \left(\frac{\rho_g}{\rho_1} \right)^{0.5}$$

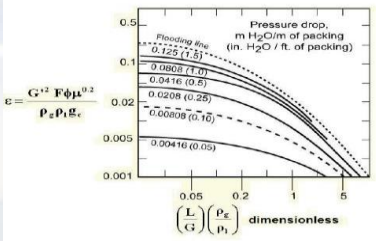
$$= \left(\frac{146}{226} \right) \left(\frac{0.074}{62.4} \right)^{0.5} = 0.0222$$



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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.



$$\epsilon = \frac{G^{1.2} F \phi \mu^{0.2}}{\rho_g \rho_1 g_c}$$


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Problem 5-3: Solution (Continued)


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

$$G^* = \left(\frac{\epsilon \rho_g \rho_1 g_c}{F_p \phi \mu^{0.2}} \right)^{0.5}$$

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

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

$$G^* = \left[\frac{(0.3) \left(0.074 \frac{\text{lb}_m}{\text{ft}^3} \right) \left(62.4 \frac{\text{lb}_m}{\text{ft}^3} \right) \left(32.2 \frac{\text{ft} \cdot \text{lb}_m}{\text{lb}_f \cdot \text{s}^2} \right)}{\left(40 \frac{\text{ft}^2}{\text{min}^2} \right) (1.0) (1 \text{ cP})^{0.2}} \right]^{0.5} = 1.056$$

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


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Problem 5-3: Solution (Continued)


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

$$G_{op} = 0.75 (1.056) = 0.792 \text{ lb}_m/\text{ft}^2 \text{ sec}$$

Step 5. Calculate the tower diameter.

Tower Area = gas flow rate/ G_{op}

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

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


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Problem 5-3: Solution (Continued)

Pressure Drop:
Use Figure 5-23 once again. The new value of the ordinate based on actual flow rate is:

$$\left(\frac{\epsilon_{new}}{\epsilon_{old}} \right) = \left(\frac{G_{actual}}{G_{flooding}} \right)^2 = \left(\frac{G_{op}}{G^*} \right)^2$$

$$\epsilon_{new} = \epsilon_{old} \cdot \left(\frac{G_{op}}{G^*} \right)^2 = (0.3) \cdot \left(\frac{0.792 \frac{\text{lb}_m}{\text{ft}^2}}{1.056 \frac{\text{lb}_m}{\text{ft}^2}} \right)^2 = 0.169$$

Use the original abscissa value of 0.0222 and the new ϵ value and estimate: from Figure 5-23, ΔP is approximately 1.5 in. W.C./ft of 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•ft²)
 Z = Height of packing, ft
 G = Molar flow rate of gas per unit cross-sectional area (lb mole/ft²•sec)
 a = Interfacial contact area per unit packing volume, ft²/ft³
 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

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

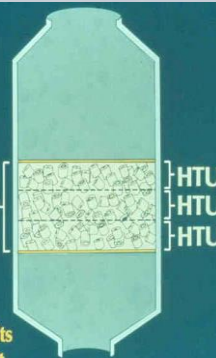
- Where:
 N_{OG} = Number of transfer units based on overall gas film coefficient
 H_{OG} = Height of a transfer unit based on overall gas film coefficient, ft
 N_{OL} = Number of transfer units based on overall liquid film coefficient
 H_{OL} = Height of a transfer unit based on overall liquid film coefficient, ft



PACKING HEIGHT (Z)

$$Z = NTU \times HTU$$

- Where:
 NTU = number of transfer units
 HTU = height per transfer unit

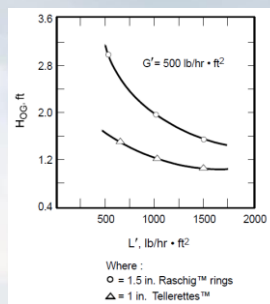


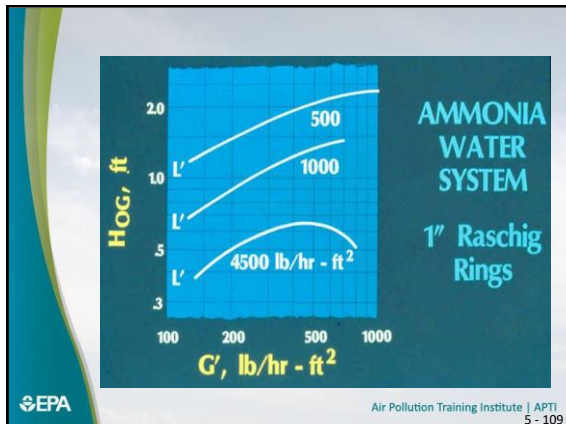
Factors Affecting HTU

- Gas flow rate
- Liquid flow rate
- Type of packing
- Chemistry of the system



Figure 5-24. Height of a Transfer Unit, Ammonia and Water System





Equation 5-21: Number of Transfer Units

$$N_{OG} = \frac{\ln \left[\frac{(Y_1 - mX_2) \left(1 - \frac{mG_m}{L_m} \right) + \left(\frac{mG_m}{L_m} \right)}{(Y_2 - mX_2) \left(1 - \frac{mG_m}{L_m} \right) + \left(\frac{mG_m}{L_m} \right)} \right]}{1 - \frac{mG_m}{L_m}}$$

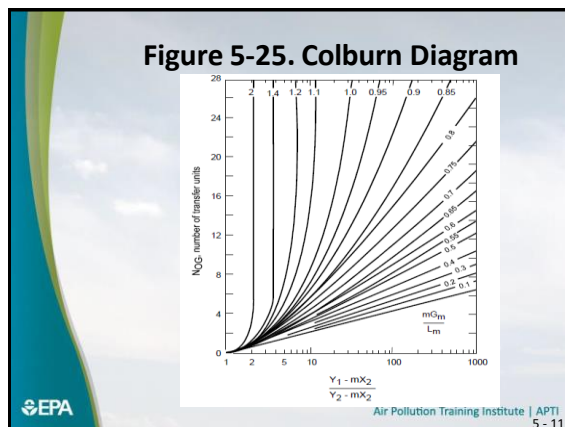
Where:

- Y_1 = Mole ratio of contaminant to contaminant-free gas entering the absorber
- m = Slope of the equilibrium line (= Henry's constant)
- X_2 = Mole ratio of contaminant to contaminant-free liquid entering the absorber in the liquid
- Y_2 = Mole ratio of contaminant to contaminant-free gas exiting the absorber
- G_m = Molar flow rate of gas, lb mole/hr
- L_m = 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

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



Problem 5-4

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

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

Problem 5-4 (continued)

Use data from previous problems:

- $m = 0.768$ mole ratio NH_3 in air/mole ratio NH_3 in water
- $G = 226 \text{ lb}_m/\text{min}$
- $L = 146 \text{ lb}_m/\text{min}$
- $X_2 = 0$ (no recirculated liquid)
- $Y_1 = 0.03$
- $Y_2 = 0.003$

Problem 5-4: Solution

Step 1. Compute the N_{OG} from Equation 5-21.

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

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

$$N_{OG} = \frac{\ln \left[\frac{(Y_1 - m X_2) \left(1 - \frac{m G_m}{L_m} \right) + \left(\frac{m G_m}{L_m} \right)}{(Y_2 - m X_1) \left(1 - \frac{m G_m}{L_m} \right) + \left(\frac{m G_m}{L_m} \right)} \right]}{1 - \frac{m G_m}{L_m}}$$

$$N_{OG} = \frac{\ln \left[\frac{(0.03) \left(1 - \frac{(0.772)(7.79)}{8.11} \right) + \left(\frac{(0.772)(7.79)}{8.11} \right)}{(0.003) \left(1 - \frac{(0.772)(7.79)}{8.11} \right) + \left(\frac{(0.772)(7.79)}{8.11} \right)} \right]}{1 - \frac{(0.772)(7.79)}{8.11}}$$

$N_{OG} = 4.65$

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Problem 5-4: Solution (Continued)

Step 3. Obtain H_{OG} from Figure 5-24.

$$L = \frac{\left(146 \frac{\text{lb}_m}{\text{min}} \right) \left(\frac{60 \text{ min}}{\text{hr}} \right)}{4.76 \text{ ft}^2} = 1840 \frac{\text{lb}_m}{\text{hr} * \text{ft}^2}$$

$H_{OG} = 1.5 \text{ ft}$

Step 4. Using Equation 5-20, the total packing height is:

$$Z = (H_{OG})(N_{OG}) = (1.5 \text{ ft})(4.62) = 6.93 \text{ ft}$$

Total Pressure Drop:

$$\Delta P_{tot} = \left(1.5 \frac{\text{in W.C.}}{\text{ft}} \right) * (6.9 \text{ ft}) = 10.4 \text{ in. W.C.}$$

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Tray Tower Absorber Diameter and Height

- Liquid and gas concentrations at the top of the tower are designated X_a and Y_a
- Liquid and gas concentrations at the bottom of the tower are designated X_b and Y_b
- 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

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Tray Tower Absorber Operation

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Types of Absorption Tower Trays Designs

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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

$$d = \psi(Q\sqrt{\rho_g})^{0.5}$$

Where:

ψ = Empirical correlation, $\text{ft}^{0.25}\cdot\text{min}^{0.5}/\text{lb}^{0.25}$

Q = Volumetric gas flow rate, ft^3/min

ρ_g = Gas density, lb_m/ft^3



Table 5-3. Tray Spacing Parameters, ψ

Tray	Metric ¹	English ²
Bubble Cap	0.0162	0.1386
Sieve	0.0140	0.1198
Valve	0.0125	0.1069

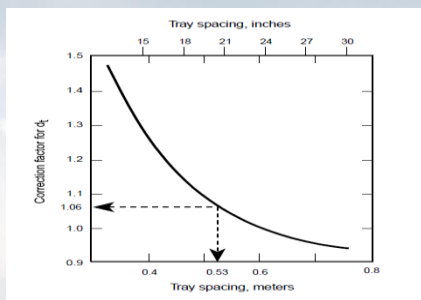
Note:

- Metric** (expressed in $\text{m}^{0.25} \cdot \text{hr}^{0.5}/\text{kg}^{0.25}$) for use with Q (expressed in m^3/hr) and ρ_g (expressed in kg/m^3).
- English** (expressed in $\text{ft}^{0.25}\text{min}^{0.5}/\text{lb}^{0.25}$) for use with Q in ACFM and ρ_g expressed in lb/ft^3

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



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 28 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^3



Problem 5-5: Solution

From Problem 5-2:

Gas flow rate = $Q = 85 \text{ m}^3/\text{min}$

$$\text{Density} = \rho_g = \left(\frac{\text{gm mole}}{0.024\text{m}^3}\right)\left(\frac{29 \text{ gm}}{\text{gm mole}}\right) = 1.21\text{kg}/\text{m}^3$$

From Table 5-2 for a bubble cap tray:

$$\psi = 0.0162 \text{ m}^{0.25}\cdot\text{hr}^{0.50}/\text{kg}^{0.25}$$

Before Equation 5-22 can be used, Q must be converted to m^3/hr :

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



Problem 5-5: Solution (Continued)

Step 1. Substitute these values into Equation 5-22 for a minimum diameter:

$$d = \psi(Q\sqrt{\rho_g})^{0.5}$$

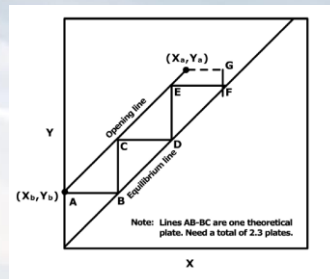
$$d = (0.0162)[5,100(1.21)^{0.5}]^{0.5} = 1.21 \text{ m}$$

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 $d = 1.21(1.06) = 1.28 \text{ m (4.20 ft)}$



Figure 5-28. Graphic Determination of the Number of Ideal Plates



Equation 5-24: Number of Ideal Plates

$$N_{OG} = \frac{\ln \left[\frac{(Y_1 - mX_2) \left(1 - \frac{mG_m}{L_m} \right) + \left(\frac{mG_m}{L_m} \right)}{(Y_2 - mX_2)} \right]}{\ln \left(\frac{L_m}{mG_m} \right)}$$

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



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 NH₃ 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.

- $Y_1 = 0.03$
- $Y_2 = 0.003$
- $X_2 = 0.0m$
- $L_m = 3669 \text{ g mole H}_2\text{O/min}$
- $G_m = 3540 \text{ g mole air/min}$
- $m = H_v = 0.768$



Problem 5-6 Solution (Continued)

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

$$N_{OG} = \frac{\ln \left[\frac{(Y_1 - mX_2) \left(1 - \frac{mG_m}{L_m} \right) + \left(\frac{mG_m}{L_m} \right)}{(Y_2 - mX_2) \left(1 - \frac{mG_m}{L_m} \right) + \left(\frac{mG_m}{L_m} \right)} \right]}{\ln \left(\frac{L_m}{mG_m} \right)}$$

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

$N_{OG} = 4.1$ theoretical plates

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Problem 5-6 Solution (Continued)

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

$$\text{Actual plates} = 4.1 / 0.40 \approx 10.3 \text{ trays}$$

Step 3. The height of the tower is given

$$\text{by: } Z = N_p \times \text{tray spacing} + \text{top height}$$

The top height is the distance over the top plate that allows the gas-vapor mixture to separate. This distance (sometimes termed the freeboard) is usually the same as the tray spacing.

$$Z = 10.3 \text{ trays} (0.53 \text{ m/tray}) + 0.53 \text{ m}$$

$$Z = 6.0 \text{ meters} = 17.2 \text{ ft}$$

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Table 5-4. Gas Velocities Through Mist Eliminators¹

Mist Eliminator Type	Orientation	Maximum Gas Velocity, ft/sec
Zigzag ²	Horizontal	15 – 20
Zigzag ²	Vertical	12 – 15
Mesh Pad	Horizontal	15 – 23
Mesh Pad	Vertical	10 – 15
Woven Pad ³	Vertical	7 – 15
Tube Bank	Horizontal	18 – 23
Tube Bank	Vertical	12 – 16

1. Source, Reference 12

2. Termed chevron in remainder of manual

3. Source, Reference 13

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Equation 5-25: Mist Eliminator Allowable Velocity

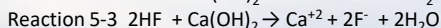
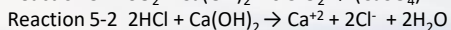
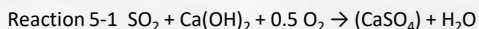
$$\text{Velocity} = \frac{\text{Gas flow rate, ft}^3/\text{min.}}{\text{Mist Eliminator area, ft}^2} \times \left(\frac{\text{min.}}{60 \text{ sec.}} \right)$$

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Alkali Requirements

- Absorption systems may require an alkali addition system if the gas stream is acidic
- Sulfur dioxide (SO₂), 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



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Problem 5-7

- Calculate the amount of calcium hydroxide (lime) needed to neutralize the HCl absorbed from a gas stream having 50 ppm HCl and a flow rate of 10,000 SCFM.
- Assume an HCl removal efficiency of 95%.

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Problem 5-7: Solution

$$\text{HCl} = 10,000 \text{ SCFM} \left(\frac{1 \text{ lb mole}}{385.4 \text{ SCF}} \right) \left(\frac{0.00005 \text{ lb mole HCl}}{\text{lb mole total}} \right) \left(\frac{95\% \text{ Efficiency}}{100\%} \right)$$

$$\text{HCl} = 0.00123 \text{ lb mole HCl/min}$$

$$\text{Ca(OH)}_2 \text{ req'd} = \left(\frac{1 \text{ lb mole Ca(OH)}_2}{2 \text{ lb mole HCl}} \right) \left(\frac{0.00123 \text{ lb mole HCl}}{\text{min}} \right)$$

$$= \frac{0.000615 \text{ lb mole Ca(OH)}_2}{\text{min}}$$

$$\text{Ca(OH)}_2 \text{ req'd} = 0.00062 \text{ lb mole/min (74 lb/lb mole)}$$

$$= 0.0455 \text{ lb/min}$$

$$= 2.73 \text{ lb/hr}$$



Instrumentation

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

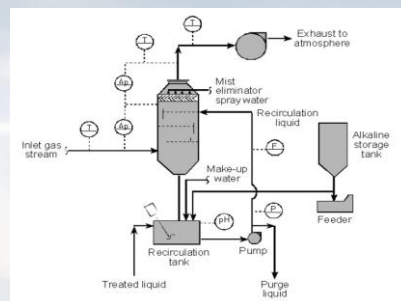


Most Common Problems Affecting Absorbers

- 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



Instrumentation

- 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)
- ΔP higher than baseline → Solids buildup
- ΔP lower than baseline → Mist eliminator damage



Instrumentation

- 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



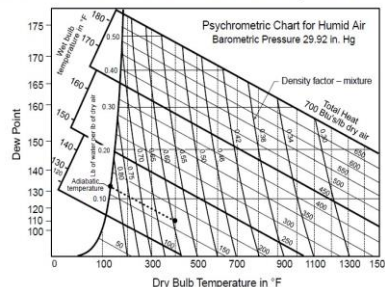
Instrumentation

- 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



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



Instrumentation

- 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



Instrumentation

- 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



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Biofiltration/Bioreactor Systems



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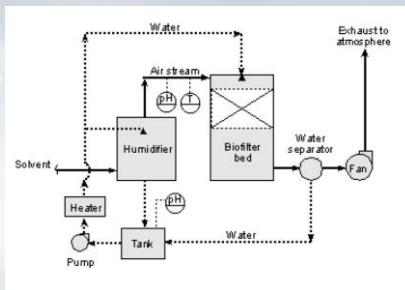
Biofiltration Systems

- 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



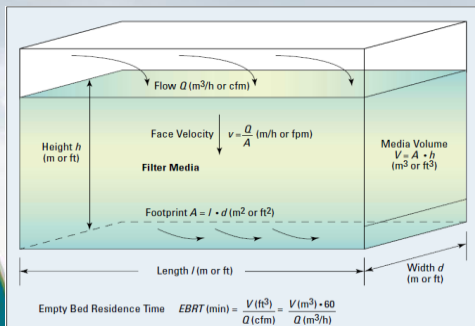
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Figure 5-31. Flowchart of a Typical Biofiltration Oxidation System



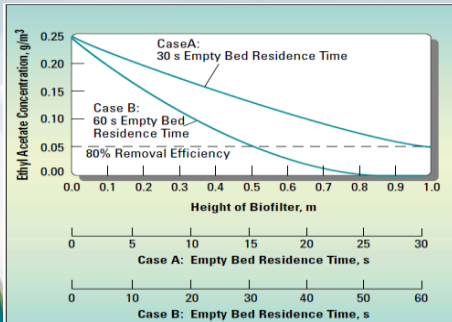
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Biofilter design parameters



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(CEP April 2001, Biofiltration – A Primer)

Removal Of Ethyl Acetate In A Biofilter as a Function Of Residence Time



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(CEP April 2001, Biofiltration – A Primer)


Typical Biofilter Performance Data (CEP April 2001 Biofiltration – A Primer)

Application (Reference)	Contaminant(s)	Loading	Removal	Biofilter Type
Yeast Production Facility (1)	Ethanol, Aldehydes	35,000 cfm/500 yd ³ media, 1 g/m ³	Overall VOC reduction of 85%	Media filter
Plastics Plant VOC Emissions Control (1)	Toluene, Phenol, Acetone	1,000 m ³ /h	80%–95%	Media filter
Pharmaceutical Production (2)	Organic carbon	1,000 m ³ /h, 2,000 mg/m ³ (5,000 mg/m ³ peak)	>98% first stage, >99.9% overall	Media filter (two-stage)
Artificial Glass Production (3)	Monomer methyl methacrylate (MMA), Dichloromethane (DCM)	125–150 m ³ /h, 50–250 mg/m ³	Biofilter: 100% MMA, 20% DCM, BTF: 95% DCM	Media filter plus biotrickling filter (BTF) in series
Hydrocarbon Emissions Control (1)	Hydrocarbon solvents	140,000 m ³ /h, 500 mg/m ³	95%	Media filter
Compost Plant for Garbage (4)	Odor	16,000 m ³ /h, 264 m ³ (1 m deep) 60 m ² /m ² h, 230 mg C/m ³	>95%	Media filter
Gasoline VOCs Emissions Control (Pilot Scale) (5)	Total VOCs	16 g/h ² h	90%	Media filter
Hydrogen Sulfide Emissions Control (Laboratory Scale) (6)	H ₂ S	1.9–8.6 mg/kg/min (25–2,651 ppmv)	93%–100%	Media filter
Styrene Removal (Bench Scale) (7)	Styrene	Up to 22 g/m ³ h, 0.5 min retention time	>99%	Biotrickling filter
Styrene Removal (Bench Scale) (7)	Styrene	Up to 100 g/m ³ h	>95%	Media filter (peat)
Rendering Plant (8)	Odor	1,100 m ³ h (650 cfm), 420 m ³ (4,500 ft ³)	99.9%	Media filter
Fuel-Derived VOC Emissions Control (9)	Nonmethane organic carbon (summed jet fuel)	500 ppm-cfm/h ² , 500–1,500 ppm-cfm/h ²	>95% 30%–70%	Media filter

US EPA Publication on Bioreactors

USING BIOREACTORS TO CONTROL AIR POLLUTION
 Prepared by The Clean Air Technology Center (CATC)
 U.S. Environmental Protection Agency (E143-03)
 Research Triangle Park, North Carolina 27711
 U.S. Environmental Protection Agency
 Office of Air Quality Planning and Standards
 Information Transfer and Program Integration Division
 Information Transfer Group (E143-03)
 Research Triangle

EPA-456/R-03-003
 September 2003




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Lesson 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.



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CHAPTER 6

OXIDATION SYSTEMS

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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.

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Types and Components of Oxidizers

High Temperature, Gas Phase Oxidation Processes

- Direct thermal oxidation (includes Flares)
- Recuperative (shell & tube) thermal oxidizers
- Regenerative (ceramic bed) thermal oxidizers
- Process boilers used for thermal oxidation

Catalytic Oxidation Processes

- Recuperative catalytic oxidizers
- Regenerative catalytic oxidizers

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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 ceramic packed beds that alternately store and release heat.

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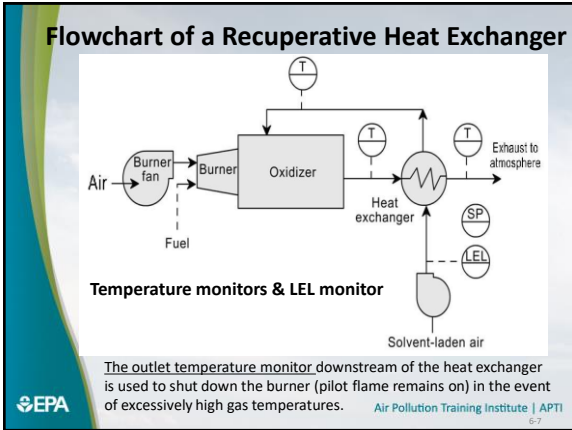
Recuperative Thermal Oxidizers

- The feed gas is preheated using the hot oxidizer product gas.
- Uses a tubular or plate-type heat exchanger.
- Heat recovery in range of **40% to 65%** of the total heat released in the combustion chamber.
- Particulate matter in the inlet gas stream must be minimized to prevent fouling the surface of the tubes.
- Not used for acid gases.

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Double Pass Recuperative Heat Exchanger

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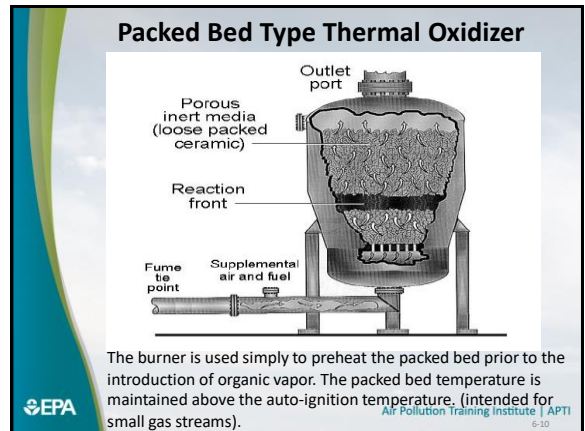
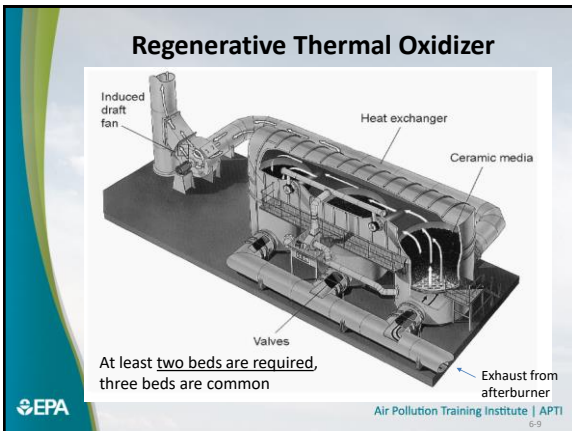


Regenerative Thermal Oxidizers

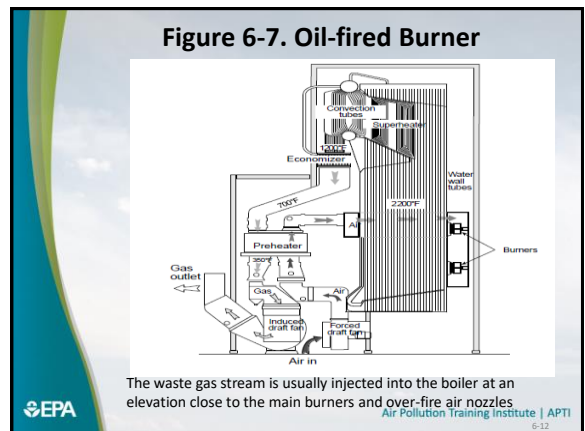
- Much higher heat recovery efficiencies than recuperative units, as high as **95%**.
- Because of the high inlet gas temperatures created by the heat recovery, burner fuel is required only if the organic vapor concentrations in the gas stream are very low.
- Particulate matter can plug the packed bed.
- Can resist corrosion from acid gases.

- 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.

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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
 - The flow rate of the organic-contaminated stream must not overwhelm the gas-handling capability of the boiler
 - Operating schedules of boiler and oxidizer feed gas must match
 - In long ductwork (sometimes needed), VOC can condense
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Flares

- Flares are often used at chemical plants and petroleum refineries to control VOC vents
- Flares are used for:
 - Routine service
 - Low volumes of gas from routine operations
 - Short – usually < 100 ft
 - Operate continuously
 - Non-routine: emergency, maintenance, or upsets
 - Handle large volumes of gas
 - Tall – usually > 100 ft.
 - Operate intermittently



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Flares Used for Thermal Oxidation

- Have destruction efficiencies exceeding 98%
- Feed composition may exceed UEL
- Can be elevated or at ground level
- Flares can be used to control almost any VOC stream, and can handle fluctuations in
 - VOC concentration,
 - flow rate, &
 - heating value.



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Flare Types

- Flares are generally **categorized in two ways**:
 - (1) by the method of enhancing mixing at the flare tip (i.e., steam-assisted, air assisted, pressure-assisted, or non-assisted), &
 - (2) by the height of the flare tip (ground or elevated),
 - Elevating the flare can prevent potentially dangerous conditions at ground level where the open flame is located near a process unit. Further, the products of combustion can be dispersed above working areas to reduce the effects of noise, heat, smoke, and objectionable odors.

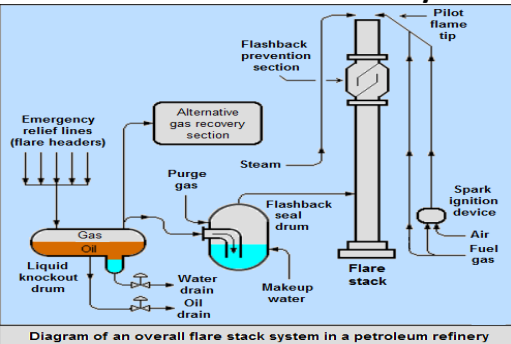
6-15

Smokeless Flares

- If a waste gas pressure (momentum) is inadequate & causes smoke, then steam or air are used to make it smokeless.
- **Steam assist is more effective** for smokeless burns than forced-air. This is because high-pressure steam provides more momentum which enhances ambient air entrainment and air-fuel mixing (turbulence).
- **Air-assisted flare** is good when steam is not available or freezing is an issue.

6-16

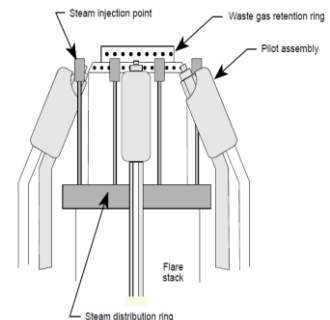
Steam-assisted Elevated Flare System



6-17

Steam-assisted Flare Tip

- Steam is injected into the combustion zone to promote turbulence for mixing and to induce air into the flame.
- They account for the majority of the flares installed and are the predominant flare type found in refineries and chemical plants.



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Air-assisted Flares

- Air-assisted smokeless combustion is achieved by supplying primary air with a low-pressure fan to provide turbulence to mix the flare gas and air.
- These flares are built with a spider-shaped burner located inside near the top of the flare.

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Enclosed Ground Flare

- Enclosed flares usually consist of multiple burners enclosed within a refractory shell. Can have efficient combustion without the use of steam injection.
- Enclosed flares generally have less capacity than open flares and are used to combust continuous, constant flow vent streams
- Mainly used at landfills

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Federal Flare Regulations: NSPS 40 CFR § 60.18

- Pilot flame:** requires the presence of a continuous flame.
- Max Tip Exit Velocity:** formula shown in next slides.
 - At too high an exit velocity, the flame can lift off the tip and flame out, while at too low a velocity, it can burn back into the tip or down the sides of the stack.
- Min Net Heating Value** of the gas being combusted is 300 BTU/SCF for steam & air assisted. (200 BTU/SCF if the flare is non-assisted.)
- No visible emissions** A five-minute exception period is allowed during any two consecutive hours.
- Leak detection monitoring** and record keeping requirements.
- Similar (& more extensive) requirements for **Petroleum Refineries** flares codified at NESHAP 40 CFR § 63.670.

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The Maximum Permitted Velocity, Vmax (ft/sec)

Steam and Non-assisted Flares

$$\log_{10}(V_{max}) = \frac{H_T + 28.8}{31.7}$$

H_T (Btu/SCF) = The net heating value of the gas being combusted in the flare.

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The Maximum Permitted Velocity, Vmax (ft/sec)

Air-assisted Flares

$$V_{max} = 8.706 + 0.7084(H_T)$$

H_T (Btu/SCF) = The net heating value of the gas being combusted in the flare.

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Safety and Operational Problems of Flares

- Thermal radiation:** heat given off to the surrounding area may be unacceptable
- Light:** may be a nuisance
- Noise:** jet-venturi used for mixing at the flare tip can cause excessive noise
- Smoke**
- Energy consumption:** waste energy because of the need to maintain a constant pilot flame

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Catalytic Oxidation

Catalytic Oxidizer Diagram

- A waste gas is passed through a catalyst bed, which causes the oxidation reactions to proceed at a *much lower temperature* than in a thermal oxidation.
- Operating temperature range of 600°F to 850°F

Catalytic Oxidation Systems

- An exothermic combustion reaction occurs as the VOC-laden *gas stream passes through the catalyst bed* resulting in an increased gas temperature by 50°F to 300°F.
- Good for treatment of very low VOCs concentration (odors).
- Pressure drop across catalyst bed: 1 to 2 in H₂O
- Control efficiency is over 90%

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
 - Catalyst beds generally last 2 to 5 years

Stationary Sources that Use Catalytic Incineration

- Surface coating and printing operations widely use catalytic incineration, the others are:
 - Varnish cookers;
 - Foundry core ovens;
 - Filter paper processing ovens;
 - Plywood veneer dryers;
 - Gasoline bulk loading stations;
 - Process vents in the synthetic organic chemical manufacturing industry (SOCMI);
 - Rubber products and polymer manufacturing; and
 - Polyethylene, polystyrene, and polyester resin manufacturing.

Cutaway of a Catalytic Oxidizer

There is no need for refractory lined combustion chambers due to the low combustion temperatures (this reduces the weight). If inlet gas temperature & concentration are too low to sustain catalytic reaction, then a pre-heat burner is utilized.

Catalytic Incinerator

- Auxiliary fuel, in combination with the preheat from the primary heat exchanger, is used to preheat the waste gas to the reactor inlet temperature.
- The inlet temperature to the catalyst bed itself must be above the catalytic ignition temperature required to give the desired destruction efficiency in the incinerator.

Catalyst Bed Honeycombs

- The catalyst bed (or matrix) is generally a metal-mesh mat, ceramic honeycomb, or other ceramic matrix structure designed to maximize catalyst surface area.
- The support material is arranged in a matrix shape to provide high surface area, low pressure drop (0.05 to 0.5 in H₂O/inch of bed depth), and uniform flow of the waste gas through the catalyst bed.
- The catalyst material is deposited on a carrier which, in turn, is supported on the rigid honeycomb.

Common Types of Catalyst Materials

- Noble Metals:** *Platinum, Palladium, & Rhodium*
 - Widely used for VOC incineration
 - This prevalence is due to their high activity, wide operating temperature range, thermal durability, and resistance to deactivation.
 - Platinum catalysts* are active for oxidation of *sulfur containing VOC*, although they are rapidly deactivated by the presence of *chlorine*.
- Metal Oxides:** *chromium oxide, magnesium oxide, & cobalt oxide* (also used for VOC oxidation)
 - Metal oxides used when *halogens* are present, because the *chlorine and fluorine* will deactivate the noble metal catalysts.
- The particular catalyst chosen:
 - Depends on the specific VOC or combination of VOCs that are to be treated
 - Must be selective to the desired oxidation reaction and resistant to deactivation by the VOC and by other materials present in the gas stream.

Fouling & Masking: Reduction of Catalyst Activity

- Fouling:** deposits on the surface of the catalyst and blocks the access of the organic compounds (can deactivate them over time), may be reversible.
 - Particulate matter
 - Oil droplets (unless they are vaporized in the preheat section)
- Masking:** materials that have a high adsorptive affinity for some catalytic surfaces, reducing the active sites available to the organic compounds (reversible).
 - Sulfur & halogens compounds

Catalyst Poisons

- Certain metals react irreversibly with catalyst, thereby making it inactive (called *catalyst poisoning*). Catalyst poisons can be divided into two categories:
 - (1) **fast acting poisons:** phosphorus, bismuth, arsenic, antimony and mercury, &
 - (2) **slow acting poisons:** iron, lead, tin, & silicon.
- Catalysts are more tolerant of the slow-acting poisons, particularly below 1,000°F.

High Temperature and Catalyst Life

- All catalysts deteriorate with normal use
- High temperatures can accelerate catalyst deactivation
 - The desired catalyst bed outlet temperature is typically 700 to 900°F
 - The maximum temperature to which the catalyst bed can be exposed continuously is limited to about 1200°F. (*EPA Cost Manual*)
- Lower operating temperatures generally result in a longer service life

Typical Ranges for Catalyst Service Life

Industry	Typical Compounds Treated	Number of Years Before Catalyst Replacement
Can Coating	MIBK, Mineral Spirits, Isophorone, DIBK, Buryl Cellosolve	7 to 14
Metal Coatings	MEK, MIBK, Toluene, i-Butanol	7 to 10
Automotive Paint Bake	MEK, Toluene, Xylene, Isopropyl alcohol	5 to 14
Glove Manufacturing	Formaldehyde, Phenolics	5
Phthalic Anhydride	PA, MA, S	16
Synthetic Fabrics	Scotchguard, Thermosol Dye	5

Catalytic Oxidation Systems

- The overall rate of catalytic oxidation depends on:
 - Rate of mass transfer (diffusion of the VOC to the surface of the catalyst) &
 - The rate of the chemical oxidation reactions on the catalyst (reaction kinetics)
- The temperature of the catalytic oxidizer is set at a level at which the controlling factor is the rate of mass transfer.

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Importance of Temperature in Catalytic Systems

Source: APTI 455 Chapter 3
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At low temperatures, the chemical rate process is a lot slower than the mass transfer and therefore the overall rate is determined by the chemical rate process. At high temperatures, the chemical rate has become a lot higher than the mass transfer rate and therefore the overall process is controlled by the mass transfer rate. This is where the temperature of the catalytic oxidizer is set.

Outlet Temperature from the Catalyst

- An outlet temperature from the catalyst, must be specified that will ensure the desired level of destruction of the VOC stream (this value varies from compound to compound and also varies from catalyst to catalyst).
- Final design of the incinerator should be done by firms with experience in incinerator design.

Destruction Efficiency Curves for Selected Organic Compounds

6-41

The Inlet Temperature to the Catalyst Bed

Catalyst Ignition Temperatures Required for Oxidizing 80% of Inlet VOC to CO₂, for 2 Catalysts

Compound	Temperature, °F	
	CO ₂ O ₂	Pt - Honeycomb
acrolein	382	294
n-butanol	413	440
n-propylamine	460	489
toluene	476	373
n-butyric acid	517	451
1, 1, 1-trichloroethane	661	>661
dimethyl sulfide	-	512

- The inlet temperature to the catalyst bed must be above the catalytic ignition temperature required to give the desired destruction efficiency in the incinerator.
- It is impossible to predict the temperature needed to obtain a given level of conversion of a VOC mixture. For example, the above table shows that the temperature required for this level of conversion of different VOCs on a given catalyst and of the same VOC on different catalysts can vary significantly.

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Space Velocity

- The amount of catalyst required in a catalytic oxidizer depends on the space velocity.
- **Space velocity** is defined as the volumetric flow rate (at standard conditions) of gas entering the catalyst bed chamber divided by the volume of the catalyst bed:
 - **Space velocity (hr⁻¹) = Flow rate/Bed Volume**
- The greater the reactivity of the catalyst, the higher the space velocity and the lower the volume of catalyst required for VOC destruction.

6-41

Space Velocity & Destruction Efficiency for Catalytic Incinerator System

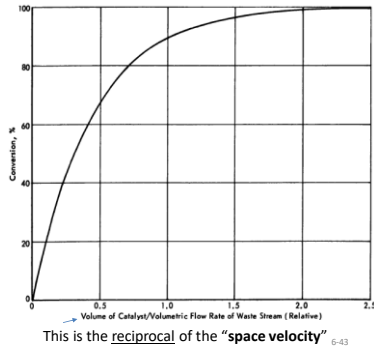
Required Destruction Efficiency (%)	Temperature at the Catalyst Bed Inlet °F	Temperature at the Catalyst Bed Outlet °F	Space Velocity- SV (hr ⁻¹) SV = Flow rate/Bed Volume	
			Base Metal	Precious Metal
95	600	1000 - 1200	10,000 – 15,000	30,000 – 40,000

Space velocities range from 10,000 hr⁻¹ to 100,000 hr⁻¹, with the lower values being necessary for the less reactive base metal catalysts.

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Calculate the Volume of Catalyst in the Catalyst Bed

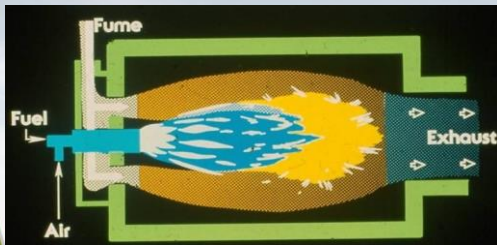
- If the volumetric flow rate of gas through the catalyst bed, and the nominal residence time (reciprocal space velocity) in the catalyst bed are known, then the **volume of catalyst can be estimated**.
- This Figure also shows that twice the amount of catalyst is required for 90% conversion than for 66%.



Design of Catalytic Units

- The overall rate of oxidation of catalytic oxidation is most often limited by mass transfer rather than chemical kinetics.
- Thus, their design reduces to the proper length of the bed to permit sufficient residence time (based on mass transfer rates) to achieve the desired degree of VOC destruction.
 - Destruction Efficiency is a function of *length of the catalyst bed & mass transfer rates* (see "Air Pollution Control" by Cooper & Alley 3rd Ed. pg 344).
 - Destruction Efficiency is dependent upon *VOC composition and concentration, operating temperature, oxygen concentration, catalyst characteristics, and space velocity* (See EPA-452/F-03-018). Air Pollution Training Institute | APTI

Thermal Oxidizer



- Due to these very high temperatures, thermal oxidizers are refractory-lined combustion chambers.
- Thermal oxidizers usually provide VOC destruction efficiencies that exceed 95% and often exceed 99%.

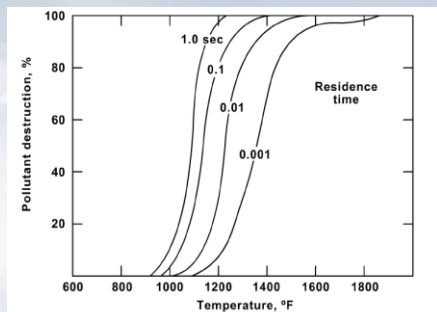
Design & Operating Principles of Thermal Oxidizers

- This section will introduce:
 - Principles of Operation**
 - Design Considerations** (sizing the device)
 - > Residence time
 - Oxidation chemistry
 - > Amount of fuel required to reach the *required temperature* for complete combustion

Principles of Operation

- Complete combustion is achieved by considering the **three —T's of combustion**
 - **Time** (at the desired temperature)
 - > 0.5 to 2.0 seconds
 - **Temperature**
 - > 1200 to 1800 °F
 - **Turbulence**
- Large residence times, high temperatures, and highly turbulent flow all contribute to the complete destruction (i.e., oxidation) of the organic pollutant.

The Effects of Time and Temperature



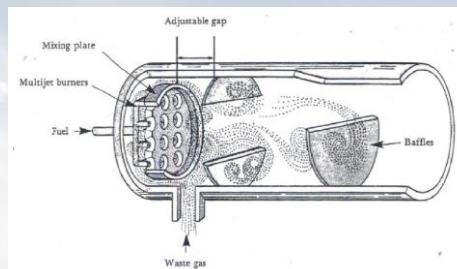
As residence time increase, you can operate at lower temperatures to get the same destruction efficiency.

Turbulence

- Mixing between the VOC molecules & oxygen molecules to ensure complete combustion.
- Flow velocities of 20 to 40 ft./sec through the unit (to promote turbulent mixing)



Thermal Oxidizer Using Multijet Burners and Baffles



Turbulent flow is needed to ensure that the oxidizer feed is well-mixed with the products from the supplemental fuel burners and that none of the pollutants are allowed to bypass the zone of maximum temperature.



Examples

- Hazardous waste incinerator
 - 99.99% destruction efficiency (required by 40 CFR Part 261, Subpart O)
 - About 2000 °F (depends on compounds burned)
 - Minimum of 2 seconds residence time
- Hospital waste incinerator
 - 1600 °F
 - 1.0 seconds



Table 2.1: Theoretical Reactor Temperatures Required for 99.99 Percent Destruction by Thermal Incineration for a 1-Second Residence Time [1]

Compound	Temperature, °F
acrylonitrile	1,344
allyl chloride	1,276
benzene	1,350
chlorobenzene	1,407
1,2-dichloroethane	1,368
methyl chloride	1,596
toluene	1,341
vinyl chloride	1,369

Source: EPA Cost Manual 2000

Destruction Efficiency

- The means for estimating the organic compound destruction efficiency of thermal oxidation systems is a function of retention time, operating temperature, flame contact (turbulence), velocity.
- There is no quantitative mathematical relationship that relates efficiency to these variables because the kinetics of combustion flow are complex & kinetic data is scarce & costly to obtain from pilot plant studies.
- But, methods for the prediction of kinetic data has been proposed by several authors. They have produced models to predict the temperature required to give various levels of destruction efficiency. (see Cooper & Alley 3rd Ed. page 328-334)



Destruction Efficiency

- **Desired control efficiency**—This efficiency should be based on requirements dictated by relevant state and federal regulations.
- **VOC destruction rates** are difficult to quantify from a purely theoretical standpoint. No parameter has a greater impact on VOC destruction than the **operating temperature of the thermal oxidizer**.
- Selection of thermal oxidizer operating parameters to achieve optimum VOC destruction is **best left to companies that have accumulated years of operating data** at a variety of conditions.
- Another generally accepted method of determining the temperature required for destruction of an organic compound is its **Auto-Ignition Temperature**.

Auto Ignition Temperatures

Table 6-1. Auto-ignition temperatures.

Compound	Auto-Ignition Temperature (°F)	Destruction Efficiency %	Degrees Above Auto-ignition Temp °F	Residence Time (sec)
Acetonitrile	970			
Isopropyl Alcohol (IPA)	780	98	400	0.5
Methanol	878			
Methyl Ethyl Ketone (MEK)	759	99	475	0.75
Toluene	896	99.9	550	1.0
Xylene	867	99.99	660	2.0

- The **auto ignition temperature** is the minimum temperature at which a gas will combust in the presence of oxygen in the absence of a spark or flame.
- Most oxidizers operate at temperatures 200°F to 300°F above the auto-ignition temperature of the most difficult to oxidize compound.

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Design Considerations

- Residence time
- Amount of fuel required to reach the *required temperature* for complete combustion
- Proper flow velocity through the unit
 - Flow velocities of 20 to 40 ft./sec
- VOCs should be less than 25% LEL

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Inlet Organic Vapor Concentration

- Thermal oxidizers and boilers usually operate at organic vapor concentrations below 25% of the LEL
- Since combustion does not occur readily in this range, the waste gas stream can be transported safely to the combustion device, and the risk of flashback from the oxidizer to the process equipment is minimized.

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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 CO₂, hydrogen to H₂O, and sulfur to SO₂
- Represent the set of simultaneous reactions by the single generalized reaction

Reaction 6-1

$$C_xH_yS_zO_w + \left(x + \frac{y}{4} + z - \frac{w}{2}\right)O_2 \longrightarrow xCO_2 + \left(\frac{y}{2}\right)H_2O + zSO_2$$

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Minor Components in Waste Gas

- Sulfur
 - ≥ 98% converted to SO₂
 - Small amount of SO₃ may be formed
- Chlorine –converted to HCl
- Fluorine –converted to HF
- Nitrogen (in waste gas) –may be converted to N₂, NO, or NO₂
- Cl, F, N (in waste gas) normally neglected in material balance calculations

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Composition of Air


- Oxygen is almost always supplied by air
- Air composition:
 - 21% O₂
 - 79% N₂
- Neglect minor components in material balance calculations

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Combustion Air Requirements

- To achieve complete combustion of the fuel (e.g., natural gas, propane, No. 2 oil), a sufficient supply of oxygen must be present in the burner flame to convert all of the carbon to CO₂. This quantity of oxygen is referred to as the **stoichiometric (or theoretical) amount**.
- For example, 1 mole of methane (the major component of natural gas) requires 2 moles of oxygen for complete combustion (Reaction 6-2).


Reaction 6-2

$$\text{CH}_4 + 2\text{O}_2 \longrightarrow \text{CO}_2 + 2\text{H}_2\text{O}$$


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Lean and Rich

- Rich** - there is insufficient O₂ available for complete oxidation.
 - Partially oxidized products (e.g., CO) will be formed and flame temperature will be reduced
- Lean** - the amount of O₂ exceeds the amount required for complete oxidation.
 - The excess air (un-reacted oxygen and nitrogen) will carry away a portion of the heat released by the combustion reactions, and therefore reduce the peak flame temperature.
- Normal operation -10% to 30% excess air



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Residence Time


Usually between 0.3 and 2 seconds

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

Where:

- t=Residence time, sec
- V=Chamber volume, ft³
- Q=Actual gas volumetric flow rate at combustion conditions, ft³/sec


Note: Adjustments to the flow rate must include any outside air added for combustion.



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Problem 6-1

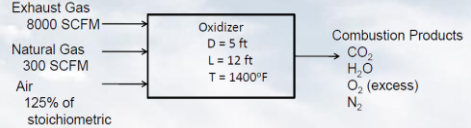
- Emissions from a paint baking oven are controlled by a thermal oxidizer. The cylindrical unit has a diameter of 5 feet and a length of 12 feet, with all combustion air supplied by an auxiliary source.
- The exhaust from the oven is 8,000 SCFM. The oxidizer uses 300 SCFM of natural gas and operates 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.



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Problem 6-1: Solution

- Draw a box diagram to represent the problem



t (retention time) sec = V (volume of chamber) ft³ / Q (total flue gas rate) Actual ft³/sec

Q (total flue gas rate) = Q (in) + Q (products of combustion) + Q (excess O₂) + Q (N₂)


Q (products of combustion) = volume of CO₂ & H₂O produced by combustion

Q (in) = exhaust gas from source (unreacted) = 8,000 SCFM

Q (excess O₂) = excess O₂ not combusted

Q (N₂) = unreacted in air

Note: we assume that any VOCs in exhaust gas is not oxidized (because VOC concentration is very low).




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Problem 6-1: Solution

Step 1. Write the combustion reaction.

$$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$$

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



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6-56

Problem 6-1: Solution (Continued)

Step 2. Calculate the total amount of O₂ at stoichiometric conditions.


$Pv = nRT \rightarrow \frac{V}{n} = \frac{RT}{P}$ Assume: standard temperature & pressure (stp)

$$\frac{V}{n} = \frac{\left(0.7302 \frac{\text{ft}^3 \text{ atm}}{\text{lb mole } ^\circ\text{R}}\right) (527.7 \text{ } ^\circ\text{R})}{1 \text{ atm}} = 385.4 \frac{\text{ft}^3}{\text{lb mole}}$$

$$300 \text{ SCFM} \left(\frac{\text{lb mole CH}_4}{385.4 \text{ ft}^3} \right) = 0.778 \frac{\text{lb mole CH}_4}{\text{min}}$$

Stoichiometric O₂ = 2 × (lb mole CH₄)

$$\frac{2 \text{ lb mole O}_2}{\text{lb mole CH}_4} \left(0.778 \frac{\text{lb mole CH}_4}{\text{min}} \right) = 1.56 \frac{\text{lb mole O}_2}{\text{min}}$$

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Problem 6-1 Solution

(Continued)

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

Total O₂ requirement = 1.25 × (stoichiometric requirement)

$$= 1.25 \left(1.56 \frac{\text{lb mole O}_2}{\text{min}} \right) = 1.95 \frac{\text{lb mole O}_2}{\text{min}}$$

$$\text{Total N}_2 = \frac{0.79 \text{ lb mole N}_2}{0.21 \text{ lb mole O}_2} \left(1.95 \frac{\text{lb mole O}_2}{\text{min}} \right)$$

$$= 7.34 \text{ lb mole N}_2/\text{min}$$

Continued... 6-68

Problem 6-1: Solution (Continued)

Step 4. Calculate the total flue gas flow rate.

Total flue gas flow rate =

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

a. Exhaust gas heated = 8,000 SCFM


b. Products of combustion = CO₂ + H₂O

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

$$\text{H}_2\text{O} = \frac{\text{lb mole H}_2\text{O}}{\text{lb mole CH}_4} \left(0.778 \frac{\text{lb mole CH}_4}{\text{min}} \right) = 1.56 \text{ lb mole H}_2\text{O}$$

CO₂ + H₂O = 2.34 lb mole/min

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

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Problem 6-1 Solution

(Continued)

c. Nitrogen and excess oxygen = total N₂ + O₂ remaining

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

Amount of nitrogen & excess oxygen = 7.34 lb mole N₂/min + 0.39 lb mole O₂/min
 = 7.73 lb mole/min

$$7.73 \frac{\text{lb mole}}{\text{min}} \left(\frac{385.4 \text{ SCF}}{\text{lb mole}} \right) = 2,979 \text{ SCFM}$$

Total flue gas = 8,000 SCFM + 902 SCFM + 2,979 SCFM = 11,881 SCFM

Continued... 6-70

Problem 6-1 Solution

(Continued)

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

Using the Ideal Gas Law, for the case of constant pressure and moles:

$$PV = nRT \rightarrow \frac{V_1}{T_1} = nR = \frac{V_2}{T_2} \rightarrow V_{\text{actual}} = \frac{V_{\text{STP}} T_{\text{actual}}}{T_{\text{STP}}}$$

$$\text{Total ACFM} = 11,881 \text{ SCFM} \left[\frac{1,400 + 460^\circ\text{R}}{527.7^\circ\text{R}} \right] = 41,877 \text{ ACFM}$$

Continued... 6-71

Problem 6-1 Solution

(Continued)

Step 6. Calculate the volume of the combustion chamber.

Combustion chamber volume = π(r)²L = 3.14(2.5ft)²12ft
 = 235.5ft²

Step 7. Calculate the residence time.

$$= \frac{\text{chamber volume}}{\text{volumetric flow rate}} = \frac{235.5 \text{ ft}^3}{41,877 \text{ ACFM}} = 0.00562 \text{ minutes}$$

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

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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).

Note: we are now using the O₂ in the waste gas stream to support the burner (which still uses 300 SCFM of natural gas) instead of outside fresh air.



Problem 6-2: Solution

Q (total flue gas rate) = Q (in) + Q (products of combustion)
 Q (in) = Q (waste gas) - Q (reacted O₂)
 Q (products of combustion) = same as Problem 6-1
 Note: no Q (excess air) & no Q (N₂) because we are not adding any air

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 O₂ is available

Because there is more than 1.56 lb mole/min of O₂ calculated in previous problem



Problem 6-2: Solution (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 SCFM $\left(\frac{\text{lb mole}}{385.4 \text{ SCF}} \right)$
 = 20.76 lb mole/min

Waste gas stream - reacted O₂
 = (20.76 - 1.56)
 = 19.20 lb mole/min

Products of combustion (see Problem 6-1)
 = (CO₂ + H₂O)
 = 2.34 lb mole/min

Flue gas
 = (19.20 lb mole/min + 2.34 lb mole/min)
 = 21.54 lb mole/min



Problem 6-2: Solution (Continued)

Step 3. Calculate total volumetric flow rate.

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

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 minutes
 = 0.00805 min $\left(\frac{60 \text{ sec}}{\text{min}} \right)$ = 0.483 sec



Fuel Requirements

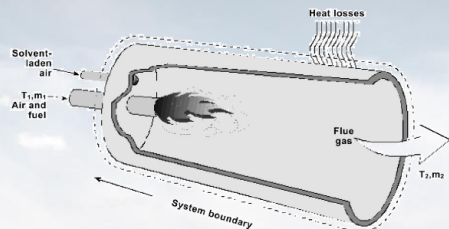
- The supplemental fuel requirement is one of the main parameters of concern in oxidation systems
- From the 1st Law of Thermodynamics & Conservation of Energy:

(Eq. 6-2)

Heat in = Heat out + Heat loss



Heat Balance Around an Oxidizer



Where: T₁ = waste gas inlet temperature
 T₂ = flue gas exit temperature
 m₁ = mass flow rate of waste gas plus air and fuel
 m₂ = mass flow rate of flue gas

The fuel requirement is estimated by determining the amount of heat in the outlet gas stream minus the amount of heat entering the inlet gas stream.



Heat Terms & Heat Balance

- **Sensible Heat (S)**– the addition or removal of heat which results in a change in temperature.
- **Latent Heat (L)** – heat associated with a change of phase (i.e. vapor to liquid) without a change in temperature.
- Heat in ($S_1 + HHV$) = Heat out ($S_2 + L + \text{Heat}_{\text{available}}$)
 - Assume no heat loss from system
 - S_1 = heat from combustion of organics in waste stream
 - S_2 = heat required to raise the temp of excess air
 - HHV (higher heating value of fuel) = LHV (lower heating value of fuel) minus L (heat of vaporization of water)
- $\text{Heat}_{\text{available}} = \text{LHV} + S_1 - S_2$
- $\text{Heat}_{\text{available}} = \text{LHV} + S_1$ (no excess air)



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 our purposes: $H = 0$ at $T_{\text{ref}} = 60^\circ\text{F}$)
 Enthalpy (H) = $U + PV$
- **Available heat** will be read from a graph while **enthalpy** will be obtained from tables or estimated from specific heat data.



Available Heat of Common Fuels

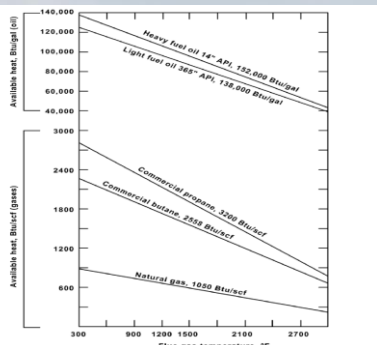


Table 6-2a. Enthalpies of Combustion Gases, Btu/SCF

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



Table 6-2a. Enthalpies of Combustion Gases, Btu/SCF (Continued)

Gas Temp (°F)	O ₂	N ₂	CO ₂	H ₂ 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



Table 6-2b. Enthalpies of Combustion Gases, Btu/lb_m

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



Table 6-2b. Enthalpies of Combustion Gases, Btu/lb_m (Continued)

Gas Temp (°F)	O ₂	N ₂	CO ₂	H ₂ 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)

$$H = C_p(T - T_0)$$

Where: H = enthalpy (Btu/lb_m)

C_p = mean specific heat between T and T₀ (Btu/lb_m °F)

T = temperature of the component (°F)

T₀ = 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 T₀ and T₂

C_{p1} = mean specific heat between T₀ and T₁



Equations 6-5 and 6-6

- To simplify this calculation, an average specific heat value, C_p between T₁ and T₂, 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)
$$q = m\Delta H = mC_p(T_2 - T_1)$$

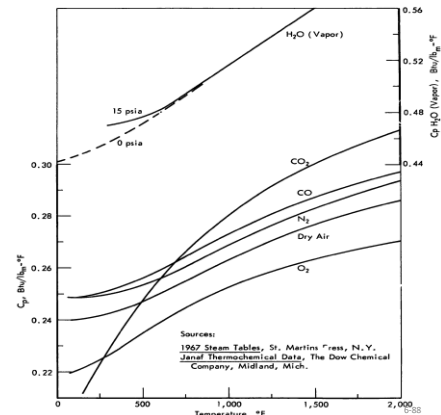
Where: q = total heat rate (Btu/hr)

m = mass flow rate of waste gases (lb_m/hr) or SCFM

H = enthalpy in Btu/lbm or Btu/SCF of combustion gases



Specific Heat of Gases



Source: Afterburner System Study

Sources: 1967 Steam Tables, St. Martins Press, N.Y. Janaf Thermochemical Data, The Dow Chemical Company, Midland, Mich.

Thermodynamic Fundamentals

$\Delta h_p = \Delta u + P\Delta V$ (Enthalpy (h) at constant P (pressure))

$W = P\Delta V$ (for a gas) (W = work) (V = Volume)

$\Delta h_p = \Delta u + W$

$\Delta u = \Delta h_p - W$

$\Delta E = \Delta u + \Delta KE + \Delta PE$ (Conservation of Energy)

$\Delta E = \Delta u$ (for a closed, stationary system)

$\Delta E = Q - W$ (First Law of Thermodynamics)

$\Delta u = Q - W$ (substitution)

$\Delta u = Q - W = \Delta h_p - W$ (substitution)

$Q = \Delta h_p = m \Delta H_p$

Q (Btu/hr); m (lbm/hr); H_p (Btu/lbm) or

Q (Btu/min); m (SCFM); H_p (Btu/SCF)

Amount of Fuel Required

Calculate the amount of fuel required to heat a waste gas stream from T₁ to T₂:

1. (Ignore any benefits for oxidation of the pollutants in waste gas stream).

2. Assume there are no Heat losses in the system.

$q = m\Delta H$

Where: q = total heat rate (Btu/hr)

m = mass flow rate of waste gases (lb_m/hr)

Heat Available = q = LHV + S₁

No heat from waste gas stream (S₁ = 0)

$q = LHV$ (Btu/min) = [LHV (Btu/ft³ of fuel)] x Ng

Where, Ng = amount of fuel needed in (ft³ of fuel/min)

$q = m\Delta H = LHV \times Ng$

$Ng = m\Delta H / LHV = [m(H_2 - H_1)] / LHV$



Problem 6-3

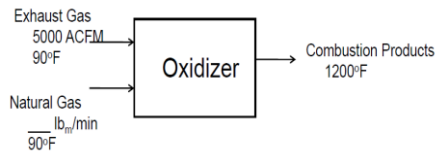
- The exhaust from a meat smoke house contains obnoxious odors and fumes. The company plans to oxidize the 5,000 ACFM exhaust stream.
- What quantity of natural gas is required to raise the waste gas stream from a temperature of 90°F to the required temperature of 1,200°F?
- The gross heating value of natural gas is 1,059 Btu/SCF. Assume no heat losses.



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Example 6-3

- Draw the picture



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

$$N_g = m\Delta H / LHV$$

$$m = 5,000 \text{ ACFM}$$

$$\Delta H = H @ 1200^\circ\text{F} - H @ 90^\circ\text{F}$$

$$LHV \text{ from graph @ } 1200^\circ\text{F}$$



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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.

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



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Problem 6-3: Solution (Continued)

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

Using the enthalpy values in Table 6-2b:

$$H \text{ for air at } 1,200^\circ\text{F} = 287.2 \text{ Btu/lb}_m$$

$$H \text{ for air at } 90^\circ\text{F} \text{ is obtained by interpolating} = 9.6 - [9.6 (10/40)] = 7.2 \text{ Btu/lb}_m$$

$$q = m \Delta H = m(H_{\text{air @ } 1,200} - H_{\text{air @ } 90})$$

$$= (21,700 \text{ lb}_m/\text{hr})(287.2 - 7.2 \text{ Btu/lb}_m)$$

$$= 6,070,000 \text{ Btu/hr}$$

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



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Problem 6-3: Solution (Continued)

- Using mean specific heat, Equation 6:
- For air $C_p = 0.26 \text{ Btu/lb}_m \text{ } ^\circ\text{F}$
 - $q = m C_p \Delta T$
 - $q = (21,700 \text{ lb}_m/\text{hr})(0.26 \text{ Btu/lb}_m \text{ } ^\circ\text{F})(1200 - 90)^\circ\text{F}$
 - $q = 6,260,000 \text{ Btu/hr}$
- The previous method is more accurate since C_p value used is only an approximation.



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Problem 6-3: Solution (Continued)

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

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

$$LHV \text{ from Table} \rightarrow H_A \approx 690 \text{ Btu/SCF}$$

$$N_g \text{ (Natural Gas)} \rightarrow Q_{\text{gas}} = q/H_A$$

$$q = m\Delta H \rightarrow \frac{6,070,000 \text{ Btu/hr}}{690 \text{ Btu/SCF}} = 8,780 \text{ SCF natural gas/hr}$$



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Instrumentation

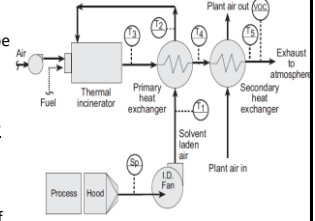
- Instrumentation considerations for high temperature, gas phase oxidation and catalytic oxidation systems.
- Problems Detected by Oxidizer Instrumentation:
 - Low gas temperatures
 - Burner combustion problems
 - Short-circuiting through the heat exchanger
 - Reduced pollutant capture due to restricted gas flow rate through the oxidizer
 - Fouling and/or plugging of the heat exchanger



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Flowchart of a Thermal Oxidizer System

- The most important operating parameter is the gas outlet temperature (T_3), which should be 200°F -300°F above the auto-ignition of the most difficult to oxidize compound.
- Temperature around the primary heat exchanger ($T_2 - T_1$) provide indication of fouling or other deterioration.
- Monitoring VOC concentration of outlet gas provides qualitative indication of composition.
- Static pressure to determine satisfactory performance of hood.
- LEL monitor (not shown) should be included on the gas inlet stream.

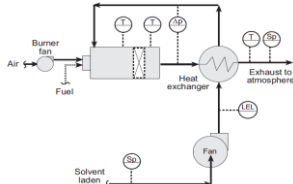


The outlet gas temperature (T_3) should be monitored carefully during *start-up* of the unit. The *combustion chamber should be preheated* before introducing the waste gas stream to ensure that the gas temperatures will be sufficiently high.

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Flowchart of a Catalytic Oxidizer System

- The inlet gas temperature should be above the minimum level necessary for high efficiency VOC destruction.
- The bed outlet temperature should be 50°F to 200°F higher than the inlet temperature. Low than normal temperature rises could indicate reduced catalyst activity or reduced quantities of organic vapor entering the oxidizer system.
- High outlet gas temperatures from the oxidizer (values higher than 1,000°F) can damage the recuperative heat exchanger.




- Outlet VOC concentration significantly above baseline (permit) values indicate problems affecting the catalyst bed or VOC emissions short-circuiting through the heat exchanger.
- Determine the static pressure drop across a catalytic oxidizer. An increase could mean partial pluggage of the catalyst bed.

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CHAPTER 7


CONDENSER SYSTEMS



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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.



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Types of Systems


- This section will introduce:
 - Conventional systems
 - Refrigeration systems
 - Cryogenic systems



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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



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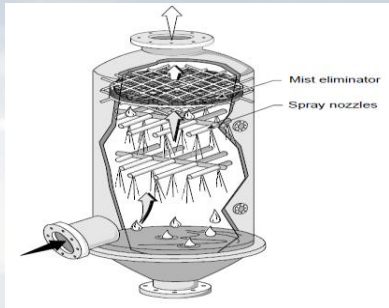
Direct Contact Condensers

- 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



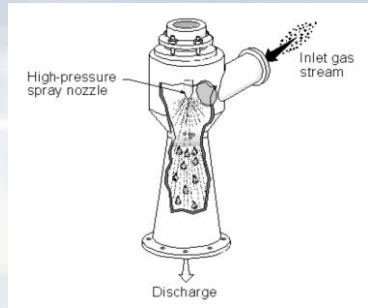
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Figure 7-1. Direct Contact Condenser



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Figure 7-2. Ejector Condenser



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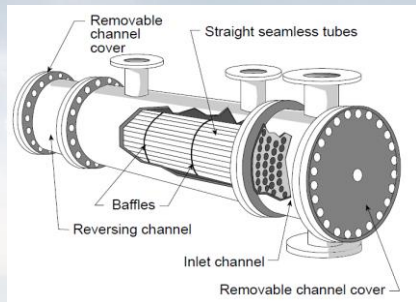
Surface Condensers

- 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



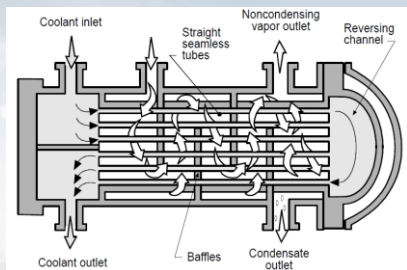
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Figure 7-3. Single Pass Condenser



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Figure 7-4. Multiple Pass Shell-and-Tube Condenser



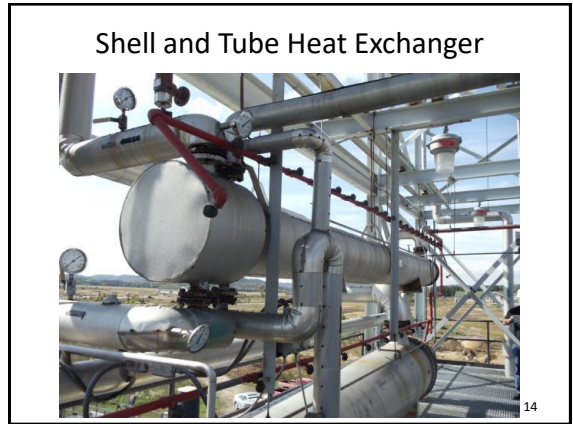
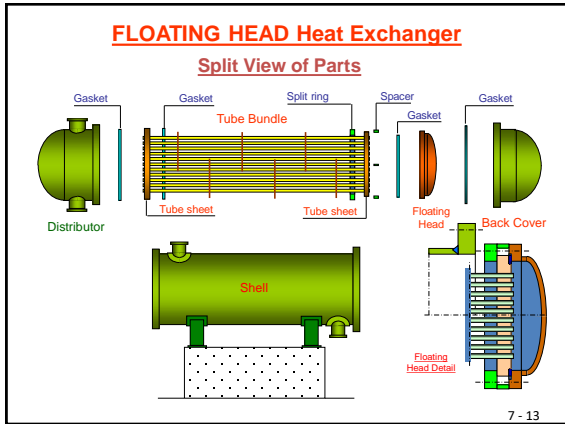
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Surface Condenser Concerns

- 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



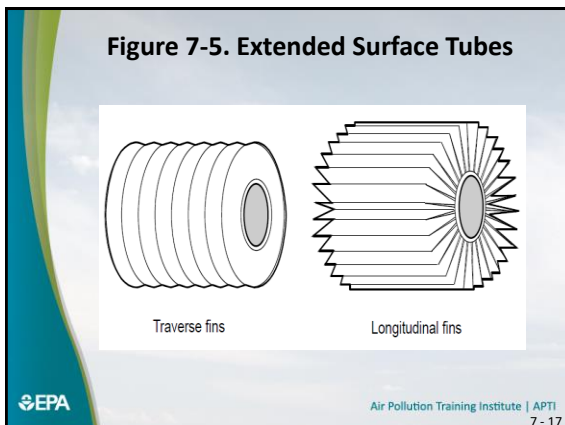
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Air Condensers

- 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

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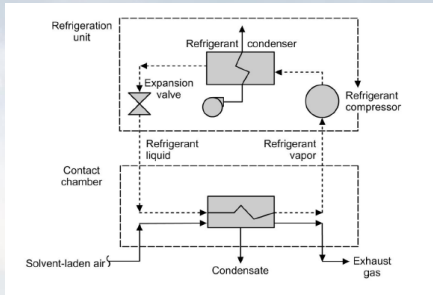


Refrigeration Systems

- Increased VOC condensation as a result of lower operating temperatures than a conventional system
- The most common refrigerants are chlorofluorocarbons (CFCs)

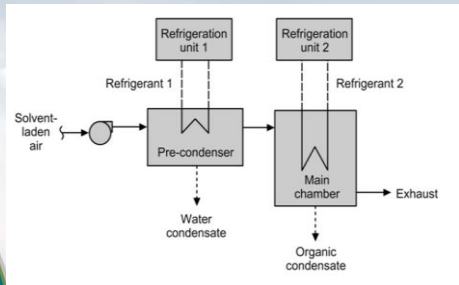
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Figure 7-6. Basic Refrigeration Cycle



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Figure 7-7. Two-Stage Refrigeration System for Organic Vapor Recovery



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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



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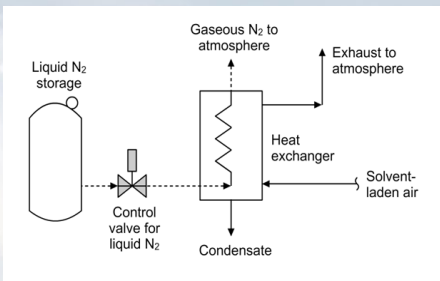
Indirect Contact – Single Heat Exchanger Systems

- 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



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Figure 7-8. Single Heat Exchanger, Indirect Contact Cryogenic System



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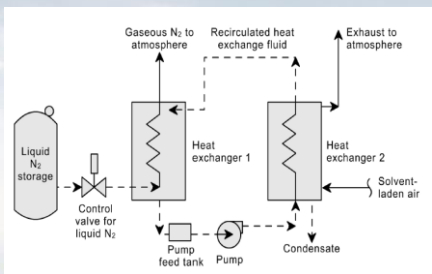
Indirect Contact – Dual Heat Exchanger Systems

- 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



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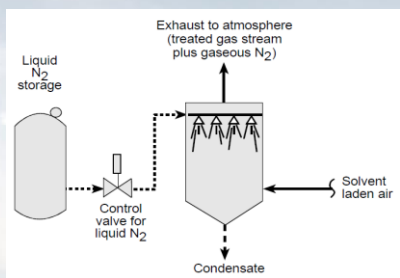
Figure 7-9. Dual Heat Exchange Cryogenic System



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



Operating Principles

- This section will introduce:
 - The principles of operating a condenser

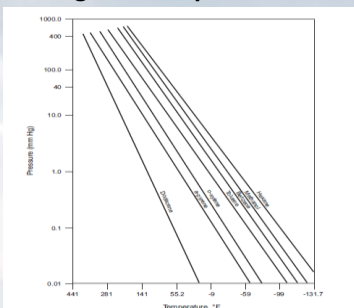
Condensation

- 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 as the temperature is lowered

Figure 7-11. Vapor Pressures and Organic Compounds



<http://184.168.171.185/BOOKS/Chemistry/MISC/Chemical%20Engineers%20Handbook%20Perry%20Vol%201.pdf>

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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.



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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.

$$\text{Outlet concentration} = \left(\frac{0.015 \text{ mm Hg}}{760 \text{ mm Hg}} \right) 10^6 \text{ ppm} = 19.7 \text{ ppm}$$

Step 3. Calculate the removal efficiency.

$$\eta = \frac{(\text{In} - \text{Out})}{\text{In}} (100\%) = \frac{10,000 - 19.7}{10,000} (100\%) = 99.8\%$$



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Capability and Sizing

- This section will introduce:
 - Condensation Efficiency
 - Sizing of Conventional Condensers



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Equation 7-1: The Antoine Equation for Calculating Vapor Pressure

Eq. 7-1 $\log_{10} (P^*) = A - \left[\frac{B}{C+t} \right]$

Where :

- P* = vapor pressure in mm Hg
- t = gas temperature in °C
- A, B, C = specific constants for each compound



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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.



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Table 7-1. Antoine Constants

Table 7-1. Antoine Constants				
Compound	Range (°C)	A	B	C
Acetaldehyde	-0.2 to 34.4	8.00552	1600.017	291.809
Acetic acid	29.8 to 126.5	7.38782	1533.313	222.309
Acetone	-12.9 to 55.3	7.11714	1210.595	229.664
Ammonia	-83 to 60	7.55466	1002.711	247.885
Benzene	14.5 to 80.9	6.89272	1203.531	219.888
n-Butane	-78.0 to -0.3	6.82485	943.453	239.711
i-Butane	-85.1 to -11.6	6.78866	899.617	241.942
1-Butene	-77.5 to -3.7	6.53101	810.261	228.066
Butyric acid	20.0 to 150.0	8.71019	2433.014	255.189
Carbon tetrachloride	14.1 to 76.0	6.87926	1212.021	226.409
Chlorobenzene	62.0 to 131.7	6.97808	1431.063	217.55
Chlorobenzene	0 to 42	7.106	1500.000	224.000



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Table 7-1. Antoine Constants (Continued)

Table 7-1. Antoine Constants				
Compound	Range (°C)	A	B	C
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 (Continued)

Table 7-1. Antoine Constants				
Compound	Range (°C)	A	B	C
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	6.86888	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



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Table 7-1. Antoine Constants (Continued)

Table 7-1. Antoine Constants				
Compound	Range (°C)	A	B	C
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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Table 7-1. Antoine Constants (Continued)

Table 7-1. Antoine Constants				
Compound	Range (°C)	A	B	C
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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Problem 7-2: Solution

Step 1. Convert the temperature to C.

$$^{\circ}\text{C} = (^{\circ}\text{F} - 32) / 1.8 = -45.6^{\circ}\text{C}$$

Step 2. Calculate the vapor pressure using the Antoine Equation.

For ortho-xylene, A = 7.00154, B = 1476.393, C = 213.872

$$\frac{B}{C + t} = \frac{1476.393}{213.872 - 45.6} = 8.774$$

$$\log_{10}(P) = 7.002 - 8.774 = -1.772$$

$$P = 0.0169 \text{ mm Hg}$$



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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)

$$q = m_G C_{pG} (T_{G\text{initial}} - T_{G\text{final}}) + m_C \Delta H_v = LC_{pL} (T_{L\text{initial}} - T_{L\text{final}})$$


Where:

- q = Heat transfer rate (Btu/hr)
- m_G = Mass flow rate of vapor (lb_m/hr)
- m_C = Mass flow rate of condensate (lb_m/hr)
- L = Mass flow rate of liquid coolant (lb_m/hr)
- C_p = Average specific heat of a gas or liquid (Btu/lb_m °F)
- T = Temperature of streams:
G for gas and L for liquid coolant (°F)
- ΔH_v = Heat of condensation or vaporization. (Btu/lb_m)


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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


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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 • ft² • hr)
- A = heat transfer surface area (ft²)
- ΔT_m = mean temperature difference (°F)


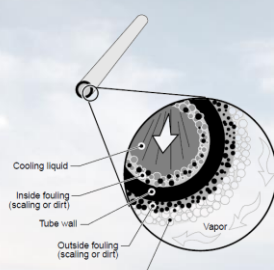

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Figure 7-12. Heat Transfer Resistances






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Table 7-1. Typical Overall Heat Transfer Coefficients in Tubular Heat Exchangers (use only for rough estimations)

Condensing Material (Shell Side)	Cooling Liquid	U, Btu/°F • ft ² • hr
Organic solvent vapor with high percent of noncondensable gases	Water	20 - 60
High boiling hydrocarbon vapor (vacuum)	Water	20 - 50
Low boiling hydrocarbon vapor	Water	80 - 200
Hydrocarbon vapor and steam	Water	80 - 100
Steam	Feedwater	400 - 1000
Water	Water	200 - 250

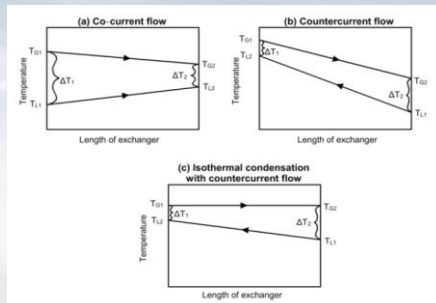

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Mean Temperature Difference

- 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



Figure 7-13. Temperature Profiles in a Heat Exchanger



Equation 7-4: Log Mean Temperature Difference

$$(Eq. 7-4) \quad \Delta T_{lm} = \frac{\Delta T_1 - \Delta T_2}{\ln(\Delta T_1 / \Delta T_2)}$$

Where: ΔT_{lm} = log mean temperature difference



Equation 7-5: Surface Area

$$(Eq. 7-5) \quad A = \frac{q}{U \Delta T_{lm}}$$

Where:

- A = Surface area of a shell-and-tube condenser (ft²)
- q = Heat transfer rate (Btu/hr)
- U = Overall heat transfer coefficient (Btu/°F•ft²•hr)
- ΔT_{lm} = Log mean temperature (°F)



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 sub-cooled liquid at 30°C.
- A single-pass countercurrent flow indirect contact condenser is used.



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: $C_p = 0.084$ kJ/mol K
- Heat capacity of liquid: $C_p = 0.13$ kJ/mol K
- Heat of condensation: $\Delta H_v = 25.1$ kJ/mol
- Molecular weight: $M = 58.1$ g/mol



Problem 7-3 (Continued)

The following data is available for water

- Heat capacity of liquid: $C_p = 0.0754$ kJ/mol °K = 4.19 kJ/kg °K
- Heat Transfer Coefficients:
 - Cooling Superheated Acetone Vapor: $U = 40$ Btu/hr ft² °F
 - Condensing Acetone: $U = 100$ Btu/hr ft² °F
 - Subcooling Acetone Liquid: $U = 50$ Btu/hr ft² °F
- Conversion Factor: 1 Btu/hr ft² °F = 0.34 kJ/min m² K



Problem 7-3: Solution

Step 1. Calculate the molar flow rate of acetone.

Molar flow rate

$$\begin{aligned} m &= (10\text{kg}/\text{min})/58.1\text{kg}/\text{kmol} \\ &= 0.172 \text{ kmol}/\text{min} \\ &= 172 \text{ mol}/\text{min} \end{aligned}$$



Problem 7-3: Solution (Continued)

Step 2. Calculate the total amount of heat that must be removed from the acetone.

$$\begin{aligned} q &= m[C_p v(120 - 56) + \Delta H_v + C_{pL}(56 - 30)] \\ &= 172[0.084(64) + 25.1 + 0.13(26)] \\ &= 172[5.4 + 25.1 + 3.4] \\ &= 5.83 \times 10^3 \text{ kJ}/\text{min} \end{aligned}$$



Problem 7-3: Solution (Continued)

Step 3. Calculate the flow rate of water needed to absorb the total amount of heat to be removed from Step 2.

$$\begin{aligned} q &= m C_{pL}(40^\circ\text{C} - 20^\circ\text{C}) \quad \Delta T(\text{K}) = \Delta T(^{\circ}\text{C}) \\ 5.83 \times 10^3 \text{ kJ}/\text{min} &= m(4.19 \text{ kJ}/\text{kg K})(20^\circ \text{K}) \\ m &= (5.83 \times 10^3 \text{ kJ}/\text{min})/(4.19 \text{ kJ}/\text{kg K})(20^\circ \text{K}) \\ &= 69.6 \text{ kg}/\text{min} \end{aligned}$$



Problem 7-3: Solution (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:

$$\begin{aligned} q &= m C_{pG}(120 - 56) \\ &= 172(0.084)(64) \\ &= 0.93 \times 10^3 \text{ kJ}/\text{min} \end{aligned}$$

Water temperature change over de-superheater

$$\begin{aligned} \Delta T_{\text{H}_2\text{O}} &= q/m C_p \\ &= (0.93 \times 10^3)/(69.6)(4.19) \\ &= 3.2^\circ \text{K} \end{aligned}$$



Problem 7-3: Solution (Continued)

Log mean temperature difference (Eq. 7-4)

$$\Delta T_{lm} = (\Delta T_2 - \Delta T_1) / \ln(\Delta T_2 / \Delta T_1)$$

$$= [(120 - 40) - (56 - 36.8)] / \ln[(120 - 40) / (56 - 36.8)]$$


$$= (80 - 19.2) / \ln(80 / 19.2) = 60.8 / 1.427$$

$$= 42.6 \text{ }^\circ\text{K}$$

Area

$$A = q / U \Delta T_{lm}$$

$$= (0.93 \times 10^3) / (40)(0.34)(42.6)$$

$$= 1.61 \text{ m}^2$$


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Problem 7-3: Solution (Continued)

Step 5: Calculate the area of the condenser.

Acetone condensation:


$$q = m \Delta H_v = 172(25.1)$$

$$= 4.32 \times 10^3 \text{ kJ/min}$$

Water temperature change over condenser

$$\Delta T_{H_2O} = q / m C_p$$

$$= 4.32 \times 10^3 / 69.6(4.19)$$

$$= 14.8 \text{ }^\circ\text{K}$$


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Problem 7-3: Solution (Continued)

Step 5.

Log mean temperature difference

$$\Delta T_{lm} = [(56 - 36.8) - (56 - 22)] / \ln[(56 - 36.8) / (56 - 22)]$$


$$= (19.2 - 34) / \ln(19.2 - 34)$$

$$= 26.2 \text{ }^\circ\text{K}$$

Area

$$A = q / U \Delta T_{lm}$$

$$= (4.32 \times 10^3) / (100)(0.34)(26.2)$$

$$= 4.84 \text{ m}^2$$


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Problem 7-3: Solution

Step 6: Calculate the area of the subcooler.

Subcooling liquid

$$q = m C_{pl} (56 - 30)$$


$$= 172(0.13)(26)$$

$$= 0.58 \times 10^3 \text{ kJ/min}$$

Water temp change over subcooler

$$\Delta T_{H_2O} = q / m C_p$$

$$= 0.58 \times 10^3 / (69.6)(4.19)$$

$$= 2 \text{ }^\circ\text{K}$$


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Problem 7-3: Solution (Continued)

Step 6

Log mean temperature difference


$$\Delta T_{lm} = [(56 - 22) - (30 - 20)] / \ln[(56 - 22) / (30 - 20)]$$

$$= 19.7 \text{ }^\circ\text{K}$$

Area

$$A = q / U \Delta T_{lm}$$

$$= (0.58 \times 10^3) / (50)(0.34)(19.7)$$

$$= 1.7 \text{ m}^2$$


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Problem 7-3: Solution (Continued)

Step 7: Check overall H₂O temperature change.

$$\Delta T = \Delta T_1 + \Delta T_2 + \Delta T_3$$


$$= 3.2 + 14.8 + 2$$

$$= 20 \text{ }^\circ\text{K}$$

Step 8. Calculate the total area.

$$A = A_1 + A_2 + A_3$$

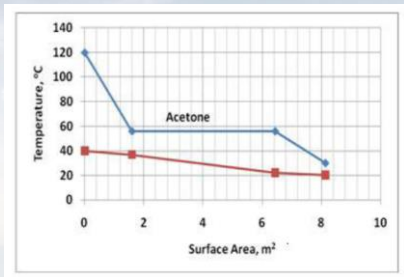
$$= 1.6 + 4.84 + 1.7$$

$$= 8.14 \text{ m}^2$$


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Graphical Solution

Temperature as a function of surface area



Problem 7-4

- In a rendering plant, tallow is obtained by removing the moisture from animal matter in cooker.
- Exhaust gases from the cooker contain mostly steam; however, the entrained vapors are highly odorous and must be controlled.
- Condensers are normally used to remove most of the moisture prior to incineration, scrubbing, or carbon adsorption



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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8 - 1

Introduction

This chapter provides an overview of:

- Mechanisms that Create Nitrogen Oxides
 - Thermal Fixation
 - Fuel Nitrogen (NO_x)
 - Prompt Nitrogen (NO_x)
- Sources of Nitrogen Oxides
- Methods for controlling Nitrogen Oxides




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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.




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Nitrogen Oxides Formation

Nitrogen oxides (NO_x) are formed during the combustion of fuel in the presence of air. NO_x is a generic term for mono-nitrogen oxides NO and NO₂ (nitric oxide and nitrogen dioxide)

At elevated temperatures, NO_x emissions are formed by:


- thermal fixation of molecular nitrogen in the combustion air,
- oxidation of nitrogen contained in the fuel, and
- formation of "prompt" nitrogen due to the presence of partially oxidized organic species present within the flame.



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Family of NO_x Compounds and Their Properties

Formula	Name	Nitrogen Valence	Properties
N ₂ O	Nitrous oxide	1	Colorless gas water soluble
NO	Nitric oxide	2	Colorless gas slightly water soluble
N ₂ O ₂	Dinitrogen dioxide	2	Colorless gas slightly water soluble
N ₂ O ₃	Dinitrogen trioxide	3	Black solid water soluble, decomposes in water
NO ₂	Nitrogen dioxide	4	Red-brown gas very water soluble decomposes in water
N ₂ O ₄	Dinitrogen tetroxide	4	Red-brown gas very water soluble decomposes in water
N ₂ O ₅	Dinitrogen pentoxide	5	White solid, very water soluble, decomposes in water




Reactions 8-1 and 8-2: Thermal Formation Mechanisms For Nitrogen Oxides

Factors affecting the quantity of NO_x 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 $N_2 + O_2 \leftrightarrow 2 NO$

Reaction 8-2 $NO + \frac{1}{2} O_2 \leftrightarrow NO_2$



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Fuel NO_x Formation Mechanisms

- Forms from organic nitrogen compounds in the fuel (i.e., nitrates, amines).
- A portion of organic nitrogen is oxidized to NO_x in peak temperature zones.
- A portion of organic nitrogen is reduced to N₂ in char.

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Prompt NO_x

- 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_x in most systems.

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Problem 8-1

- What are the total NO_x emissions in pounds per hour from an industrial boiler emitting 475 ppm NO and 25 ppm NO₂ in a flue gas stream of 100,000 SCFM?

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Figure 8-1. Distribution of Nitrogen Oxides Emissions

Nitrogen Oxide	Percentage
Nitrogen Oxide (NO)	95%
Nitrogen Dioxide (NO ₂)	5%

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Problem 8-1: Solution

Emission rate of NO_x

$$= \left(\frac{500 \text{ ppm}}{10^6 \text{ ppm total}} \right) \left(\frac{100,000 \text{ SCF}}{\text{min}} \right) \left(\frac{\text{lb mole}}{385.4 \text{ SCF}} \right) \left(\frac{46 \text{ lb NO}_2}{\text{lb mole NO}_2} \right)$$

$$= 5.97 \text{ lb}_m/\text{min NO}_x \text{ as NO}_2$$

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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

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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.

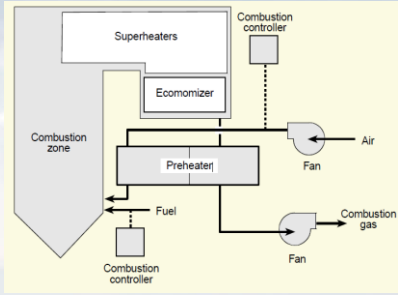

Designs based on the arrangement of the burners:

- Front-fired
- Opposed (front and back walls)
- Tangential (four corners)



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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_x 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



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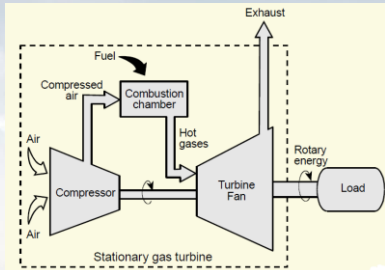

Gas Turbine Applications

- Peaking service
- Cogeneration systems
- Gas compressor stations
- Emergency service



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Figure 8-3. Simple Cycle Gas Turbine

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Figure 8-4. Simple Cycle Gas Turbine

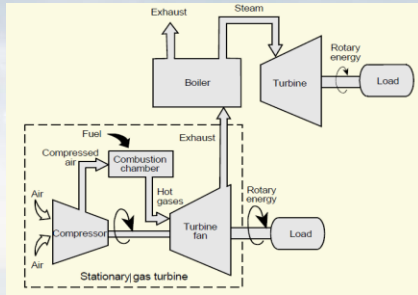


Figure 8-5. Typical Combustor

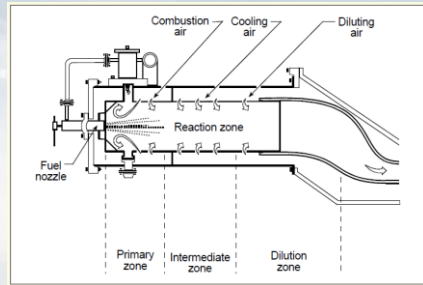


Figure 8-6. Municipal Waste Incinerator

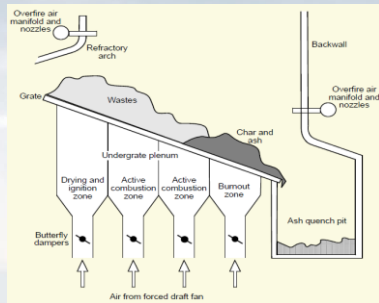
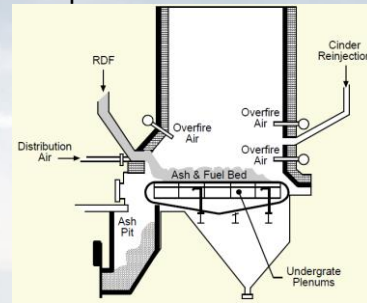


Figure 8-7. Coal or wood-Fired Spreader Stoker Boiler

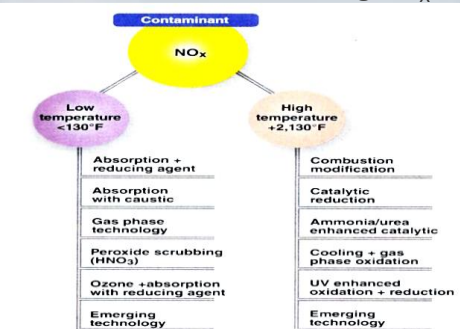


Types and Components of NO_x Control Techniques

This section introduces the following combustion modification topics :

- Low Excess Air Combustion
- Off-Stoichiometric Combustion
- Burners Out-of-Service
- Flue Gas Recirculation
- Low NO_x Burners
- Gas Reburning in Fossil Fuel-Fired Boilers
- Fuel Switching
- Selective Non-Catalytic Reduction
- Selective Catalytic Reduction (SCR)

Decision Tree for Controlling NO_x



NO_x Control Techniques

- Combustion modifications
- Add-on control systems
- Fuel switching

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Combustion Modifications

- Low excess air combustion
- Off-stoichiometric combustion
- Flue gas recirculation
- Low NO_x burners
- Gas reburning

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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 $S + O_2 \rightarrow SO_2$

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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 ₂ O	4.0%
<u>Ash</u>	<u>13.3%</u>
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.

Material	Composition	c Input Weight, lb/hr	d Input, lb mole/hr	e Consumed, lb mole/hr	f Formed, lb mole/hr	g Flue Gas, lb mole/hr, (columns d → f)
Fuel						
2,000,000						
C	65.0%	1,300,000	108,000	108,000	0	0
H	8.0%	160,000	160,000	160,000	0	0
O	7.5%	150,000	9,400	9,400	0	0
S	1.0%	20,000	625	625	0	0
N	1.2%	24,000	1,700	1,700	0	0
Water	4.0%	80,000	4,400	0	0	4,400
Ash	13.3%	266,000	N/A	N/A	0	N/A
Combustion Air						
O ₂	20.9%		146,000	146,000	0	0
N ₂	79.1%		552,000	0	0	552,000
Combustion Products						
CO ₂				0	108,000	108,000
H ₂ O				0	80,000	80,000
SO ₂				0	625	625
NO _x				0	1,700	1,700

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Problem 8-2: Solution (Continued)

Step 2. Calculate the input quantity of each fuel constituent by dividing the weight by the molecular weight.

C = (1,300,000 lb/hr)/(12 lb/lb mol) = 108,000 lb mol/hr
H = (160,000 lb/hr)/(1 lb/lb mol) = 160,000 lb mol/hr
O = (150,000 lb/hr)/(16 lb/lb mol) = 9,400 lb mol/hr
S = (20,000 lb/hr)/(32 lb/lb mol) = 625 lb mol/hr
N = (24,000 lb/hr)/(14 lb/lb mol) = 1,700 lb mol/hr
H₂O = (80,000 lb/hr)/(18 lb/lb mol) = 4,400 lb mol/hr

Some number are rounded off.
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Problem 8-2: Solution (Continued)

Step 3. Calculate the oxygen requirement using the lb mol/hr data and the stoichiometry 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% N₂ and 20.9% O₂.

$$N_2 = O_2 (0.79/0.209)$$

$$= 146,000 \text{ lb mole/hr} (0.79/0.209)$$

$$= 552,000 \text{ lb mole/hr}$$



Problem 8-2: Solution (Continued)

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.



Problem 8-2: Solution (Continued)

Step 6. Calculate the amount of combustion gases formed based on the stoichiometry of the reactions.

$$CO_2 = 1 \text{ (lb mol C/hr)} = 108,000 \text{ lb mol/hr}$$

$$H_2O = 1/2 \text{ (lb mol H/hr)} = 80,000 \text{ lb mol/hr}$$

$$SO_2 = 1 \text{ (lb mol S/hr)} = 625 \text{ lb mol/hr}$$

$$NO_2 = 1 \text{ (lb mol N/hr)} = 1,700 \text{ lb mol/hr}$$



Problem 8-2: Solution (Continued)

Step 7. Calculate the lb mole of material leaving the combustion process (combustion products, combustion air, and unburned constituents of fuel).

$$\text{Effluent gas stream} = \text{Fuel moisture} + \text{Combustion products} + \text{Remaining oxygen} + \text{Combustion air nitrogen}$$

$$\text{Effluent gas stream} = 4,400 + (108,000 + 80,000 + 625 + 1,700) + 0 + 552,000$$

$$\text{Effluent gas stream} = 747,000 \text{ lb mole/hr}$$



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	c	d	e	f	g
Material	Composition	Input Weight, lb/hr	Input, lb mole/hr	Consumed, lb mole/hr	Formed, lb mole/hr	Flue Gas, lb mole/hr (columns d - e + f)
Fuel						
		2,000,000				
C	85.0%	1,700,000	108,000	108,000	0	0
H	8.0%	160,000	180,000	180,000	0	0
O	7.5%	150,000	9,400	9,400	0	0
S	1.0%	20,000	625	625	0	0
N	1.2%	24,000	1,700	1,700	0	0
Water	4.0%	80,000	4,400	0	4,400	
Ash	13.3%	266,000	N/A	N/A	0	N/A
Combustion Air						
O ₂	20.9%		206,000	146,000	0	60,000
N ₂	79.0%		779,000	0	0	779,000
Combustion Products						
CO ₂				0	108,000	108,000
H ₂ O				0	80,000	80,000
SO ₂				0	625	625
NO ₂				0	1,700	1,700



Problem 8-3: Solution (Continued)

Step 2. Calculate the input quantity of each fuel constituent by dividing the weight by the molecular weight.

$C = (1,300,000 \text{ lb/hr}) / (12 \text{ lb/lb mol}) = 108,000 \text{ lb mol/hr}$
 $H = (160,000 \text{ lb/hr}) / (1 \text{ lb/lb mol}) = 160,000 \text{ lb mol/hr}$
 $O = (150,000 \text{ lb/hr}) / (16 \text{ lb/lb mol}) = 9,400 \text{ lb mol/hr}$
 $S = (20,000 \text{ lb/hr}) / (32 \text{ lb/lb mol}) = 625 \text{ lb mol/hr}$
 $N = (24,000 \text{ lb/hr}) / (14 \text{ lb/lb mol}) = 1,700 \text{ lb mol/hr}$
 $H_2O = (80,000 \text{ lb/hr}) / (18 \text{ lb/lb mol}) = 4,400 \text{ lb mol/hr}$

EPA Some numbers are rounded. Air Pollution Training Institute | APTI 37

Problem 8-3: Solution (Continued)

Step 3. Calculate the oxygen requirement using the lb mol/hr data and the stoichiometry of the combustion reactions.

$$O_2 = (140\% / 100\%) [CO_2 + 1/2 H_2O + SO_2 + NO_2] - O_2 (\text{Fuel})$$

$$= 1.40 [(108,000 + 1/2 H_2O + SO_2 + NO_2)] - \frac{9,400}{2}$$

$$= 206,000 \text{ lb mole/hr}$$

Step 4. Calculate the nitrogen present in the combustion air by using the ratio 79% N₂ and 20.9% O₂.

$$N_2 = O_2 (0.79 / 0.209)$$

$$= 206,000 \text{ lb mole/hr} (0.79 / 0.209)$$

$$= 779,000 \text{ lb mole/hr}$$

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Problem 8-3: Solution (Continued)

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.

$CO_2 = 1 \text{ (lb mol C/hr)}$	$= 108,000 \text{ lb mol/hr}$
$H_2O = 1/2 \text{ (lb mol H/hr)}$	$= 80,000 \text{ lb mol/hr}$
$SO_2 = 1 \text{ (lb mol S/hr)}$	$= 625 \text{ lb mol/hr}$
$NO_2 = 1 \text{ (lb mol N/hr)}$	$= 1,700 \text{ lb mol/hr}$

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Problem 8-3: Solution (Continued)

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

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Combustion Overfire Air (OFA)

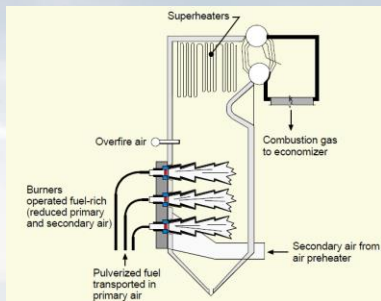
- Staged combustion can be accomplished by using overfire air (OFA) ports. These are separate air injection nozzles located above the burners as indicated in the following figure.
- Burners are operated fuel-rich, and the overfire air ports maintain the remainder of the combustion.
- Approximately 15% to 20% of the combustion air flow is diverted to the over-fire air ports.

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OFA in Tangentially Fired Units

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FIGURE 8-8. STAGED COMBUSTION USING OVERFIRE AIR PORTS



Overfire Air (OFA)

- As with LEA, OFA may increase CO or unburned hydrocarbon emissions.
- Applicable to process heaters by using air lances rather than changing the boiler configuration.
- OFA for small boilers and process heaters can be accomplished by inserting a lance through the upper furnace and injecting air through that lance.
- OFA provides modest NOX reductions in the range of 20%.
- Reduction must be balanced with the cost of additional air handling equipment and the increase in unburned carbon and CO emissions.

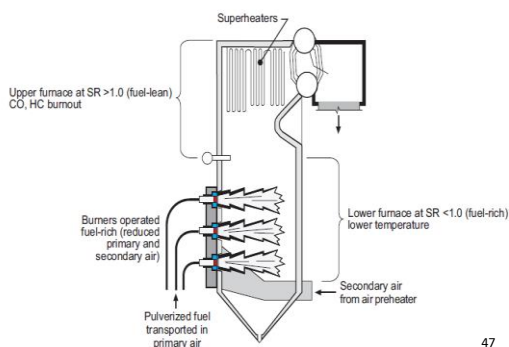
Overfire Air (OFA) cont.

- The following figure demonstrates the operating principles of the OFA method. A secondary air port or OFA injection port has been added above the primary air-fuel burner. Below this port is the fuel-rich zone (stoichiometric ratio less than 1) with peak temperatures lower than those associated with conventional combustion (stoichiometric ratio greater than 1).
- The injection of OFA allows the upper zone of the furnace to achieve a stoichiometric ratio greater than 1 (fuel-lean) and promotes the burnout of CO and hydrocarbons.
- If the secondary air ports are located too far from the burners, the residence time will be inadequate to allow for burnout of the CO and hydrocarbons.

Off Stoichiometric Combustion

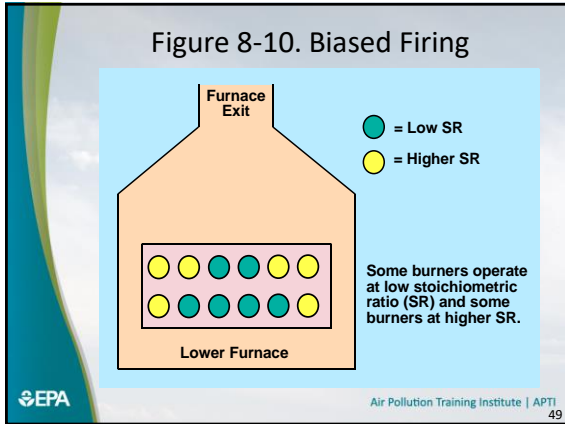
- The following figure demonstrates the operating principles of the OFA method.
- A secondary air port or OFA injection port has been added above the primary air-fuel burner.
- Below this port is the fuel-rich zone (stoichiometric ratio less than 1) with peak temperatures lower than those associated with conventional combustion (stoichiometric ratio greater than 1).
- The injection of OFA allows the upper zone of the furnace to achieve a stoichiometric ratio greater than 1 (fuel-lean) and promotes the burnout of CO and hydrocarbons.
- If the secondary air ports are located too far from the burners, the residence time will be inadequate to allow for burnout of the CO and hydrocarbons.

Off Stoichiometric Combustion



Biased Firing

- In some boilers, a number of burners are operated fuel-rich in a staggered configuration called biased firing as shown in the figure below.
- Rather than use some burners for air flow (as is done in BOOS), biased firing involves adjusting the stoichiometry in each burner by reducing combustion air in some burners and increasing combustion air flow to other burners.
- Fuel flow to all burners is maintained so that the stoichiometry ratio varies among burners, but an adequate overall stoichiometry is maintained.



Burners Out of Service

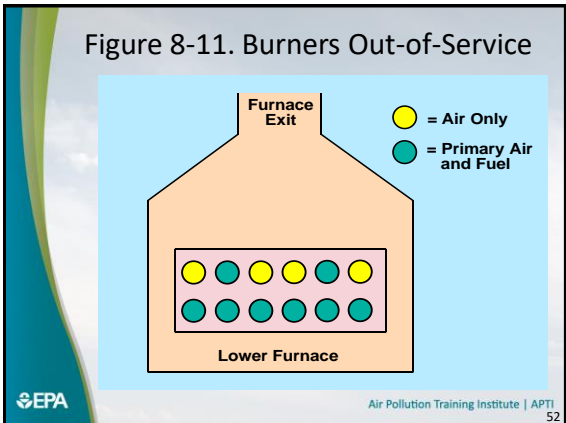
- When some burners are operated on air only, this modification is called burners-out-of-service (BOOS), as shown in the following figure.
- Burners out of service is typically performed with no more than 25% to 30% of the burners.

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Burners Out of Service (cont.)

- BOOS is similar to OFA, but does not require the installation of new OFA ports. The approach is to reduce air to several of the lower burners and to eliminate fuel in several upper level burners.
- This arrangement simulates an OFA air system because the reduced air in the lower burners creates a fuel-rich zone and the reduction of fuel in the upper ports creates a fuel-lean zone.
- Using BOOS on an existing boiler can result in a steam load reduction if the active fuel burners do not have the capacity to supply fuel for a full load.
- Therefore, BOOS is typically used on wall-fired units and other units that have the ability to operate at less than full load conditions.

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Flue Gas Recirculation (FGR)

- Flue gas recirculation (FGR) has been used to reduce thermal NOX emissions from large coal-, oil-, and gas-fired boilers.
- A portion (10% to 30%) of the flue gas exhaust is recycled back into the main combustion chamber by removing it from the effluent gas stream and mixing it with the secondary air entering the windbox that supplies the burners as shown in the following figure.
- The recirculated gas lowers the flame temperature and dilutes the oxygen content of the combustion air, thus lowering NOX emissions. of about 15% are typical with flue gas recirculation.

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Flue Gas Recirculation (cont.)

- NOX reduction of approximately 40% to 50% is possible with recirculation of 20% to 30% of the exhaust gas in gas- and oil-fired boilers.
- At high rates of recirculation (e.g., 30%), the flame can become unstable, increasing carbon monoxide and partially oxidized organic compound emissions.
- FGR requires greater capital expenditures than low excess air and staged combustion modifications.

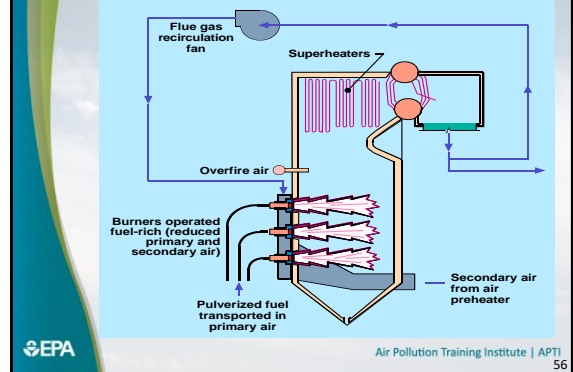
54

Flue Gas Recirculation (cont.)

- High temperature fans (forced or induced draft) ducts, and large spaces are required for recirculating the gas.
- FGR can be used with OFA techniques to achieve even greater reductions in NO_x emissions.
- FGR can also be conducted internally when used in conjunction with new, advanced burners.
- Internal FGR recirculates the flue gas by means of aerodynamic forces instead of the recirculating flue gas fan that is used with conventional FGR.

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Figure 8-12. Flue Gas Recirculation (FGR)



Staged Air Burners

- Staged air is an early LNB design that employs staged air within the burner.
- A general staged air burner design is shown in the following Figure 8-13.
- This is a wall-fired burner (also called a *dual register burner*) where, in the first stage, fuel and primary air enter through the center tube of the burner.
- There may also be swirl vanes in the primary fuel zone to control fuel flow.
- The fuel-air mixture is injected into the burner to create a fuel-rich axial flame core in the primary combustion zone of the burner.

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Figure 8-13. Example of a Controlled Flow Split Flame - Low NO_x burner

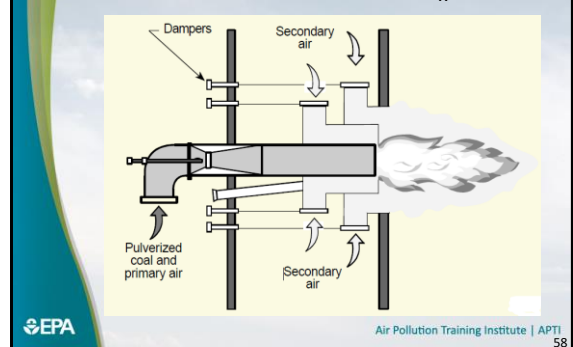
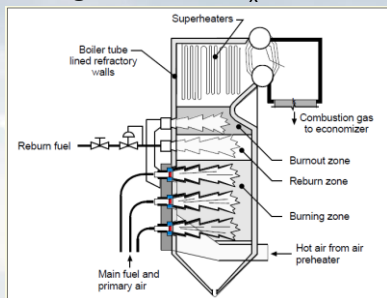


Figure 8-14. Example of a Dual Register Low NO_x Burner



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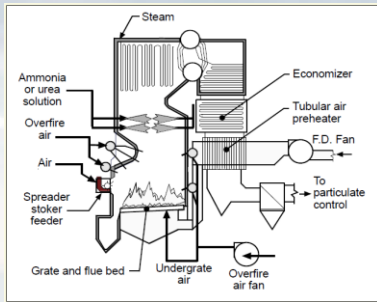
Gas Reburning in Fossil Fuel-Fired Boilers

- Gas or other low NO_x fuel replaces fossil fuel in boiler.
- Fossil fuels burned slightly fuel-rich.
- Overfire air used to complete combustion.

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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

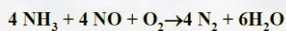


Reactions 8-6 and 8-7: Selective Non-Catalytic Reduction (SNCR)

In SNCR systems, ammonia (NH₃) or urea is injected into a very hot gas zone where thermal reactions leading to the chemical reduction of nitrogen oxides can occur.

The ammonia or urea reduces the NO to N₂

Reaction 8-6



Reaction 8-7

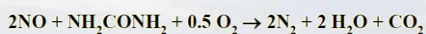


Figure 8-16. Temperature Sensitivity of SNCR Reactions

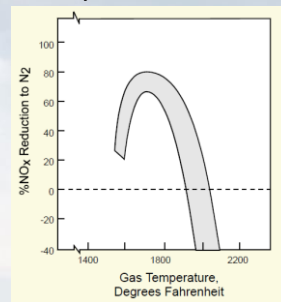


Figure 8-17. Ammonia Slip Emissions

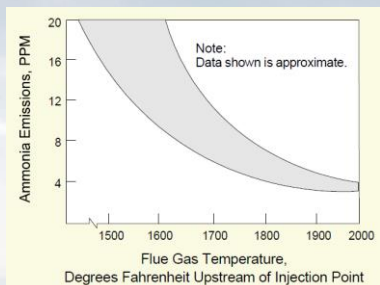


Figure 8-18. Boiler with SNCR Injection Nozzles

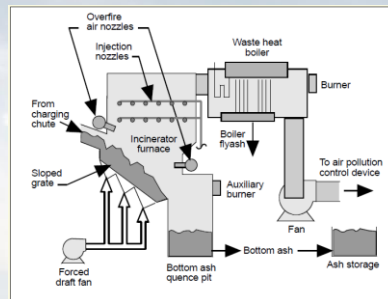
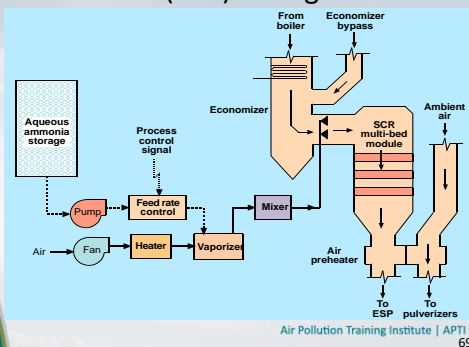


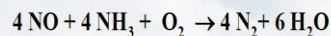
Figure 8-19. Selective Catalytic Reduction (SCR) Configuration



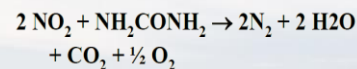
Reactions 8-10 and 8-11

The composite reactions involved in SCR nitrogen oxides reduction are shown in Reactions 8-10 and 8-11.

Reaction 8-10



Reaction 8-11



Capability and Sizing

This section introduces:

- Nitrogen Oxides Emissions Reduction Efficiencies
- Ammonia Or Urea Feed Requirements

Table 8-1. General Range of NO_x Suppression Efficiencies

Control Technique	Typical Applications	NO _x Reduction Efficiencies, %
Combustion Modifications		
Low Excess Air	Coal-Fired Boilers, Municipal Waste Incinerators	15-30%
Off-Stoichiometric Combustion	Coal-, Oil-, Gas-Fired Boilers	15-50%
Flue Gas Recirculation	Coal-, Oil-, Gas-Fired Boilers	15-50%
Low NO _x 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

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_x rate of an SNCR system.
- The boiler flue gas flow rate is 100,000 SCFM, and the present NO_x emissions rate is 200 ppm. The NO_x emissions limitation is equivalent to 100 ppm.



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_x at 200 ppm.

$$\left(\frac{0.0002 \text{ lb mole NO}_x}{\text{lb mole gas}} \right) \left(\frac{259.5 \text{ lb mole gas}}{\text{min}} \right) = 0.0519 \text{ lb mole NO}_x/\text{min}$$

Pound moles of NO_x reacted = 0.5 (0.0519 lb mol/ min)
= 0.026 lb mol/min

Pound moles of ammonia = $\frac{1 \text{ lb mol NH}_3}{1 \text{ lb mol NO}_x}$ (0.026 lb mol/min)

Pound moles of ammonia = 0.026 lb mol/min

Ammonia feed rate = 0.44 lb_m/min = 633.6 lbm/day



Evaluating Performance

This section covers the following topics:

- Continuous Emission Monitors
- NO₂ And NH₃ Visible Emissions
- Oxygen Concentrations
- Carbon Monoxide Concentrations
- SCR and SNCR Reagent Feed Rates and Injection Conditions
- Gas Turbine Steam or Water Steam Injection



Instrumentation

- NO₂ And NH₃ Visible Emissions
 - No plume if NO_x control systems work properly
- Oxygen Concentrations should be reviewed to :
 - Determine if air infiltration or burner operational problems increase NO_x

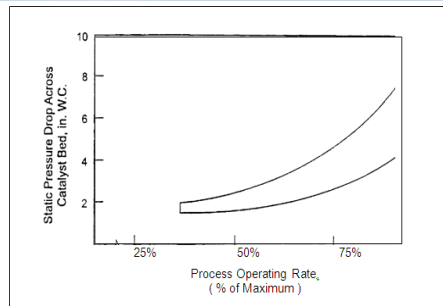


Carbon Monoxide Concentrations

- 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.

Summary (Continued)

- Add-on control techniques in common use include selective catalytic reduction and selective noncatalytic reduction systems. Both use a reagent that chemically reduces NO_x to N_2 .
- 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_x . SCR systems use a catalyst to complete the NO_x reduction reactions in the temperature range of 500°F to 750°F. In these systems, the condition of the catalyst is very important.

<http://nepis.epa.gov/Exe/ZyPDF.cgi?Dockkey=P10000S8.PDF>




System Categorization of Additional PM Control Technology Options

Description of System with SCR	Fine PM Control Technology Options
Low S Western coal with fabric filter or SD plus fabric filter	None required
Low S Western coal with ESP	Probably none required with high alkaline ash—otherwise reduce temperature ahead of ESP so H_2SO_4 condenses to be caught in ESP
Low to medium sulfur Eastern coal with ESP or fabric filter	Probably none if PCD operates <250 °F— otherwise reduce temperature ahead of ESP so H_2SO_4 condenses to be caught in PCD, sorbent injection. May require upgrade of ESP if it is an older unit with an SCA of -300 or less.
Eastern coal with hot-side ESP plus wet scrubber	Furnace sorbent injection, sorbent downstream from SCR, or wet ESP after scrubber
Eastern coal with cold-side ESP plus scrubber	Sorbent injection, otherwise reduce temperature ahead of ESP so H_2SO_4 condenses to be caught in ESP. May require upgrade of ESP if it is an older unit with an SCA of -300 or less. Alternatively, install wet ESP after scrubber
Any coal with spray dryer and cold-side ESP	Probably none but may require upgrade of ESP if it is an older unit with an SCA of -300 or less.

CHAPTER 9


SULFUR OXIDES CONTROL



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Introduction

- Sources of Sulfur Oxides
- Concerns about SO₂ emissions
 - Clean Air Act Amendments of 1990 (Title IV)
- Emissions and monitoring requirements




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Learning Objectives

At the end of this Chapter, you'll be able to:

- Recognize operating principles for sulfur dioxide 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.



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Reactions 9-1 Through 9-3: 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. Amounts can be determined from the Ultimate Analysis of the coal.

Reaction 9-1 $S + O_2 \rightarrow SO_2$

Reaction 9-2 $S + 1.5 O_2 \rightarrow SO_3$


Reaction 9-3 $SO_3 + H_2O \rightarrow H_2SO_4$



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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.



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Problem 9-1: Solution

Step 1. Calculate the amount of sulfur in the coal.

Pounds of fuel sulfur


$$= \frac{100 \text{ tons}}{\text{hour}} \frac{2,000 \text{ lb}_m}{\text{ton}} \frac{2 \text{ lb}_m \text{ S}}{100 \text{ lb}_m \text{ coal}}$$

$$= 4,000 \text{ lb}_m \text{ S/hour}$$

Step 2. Convert sulfur quantity to pound moles per hour.

Pound moles of sulfur/hour

$$= \frac{4,000 \text{ lb}_m}{\text{hr}} \frac{\text{lb mole S}}{32 \text{ lb}_m}$$

$$= 125 \text{ lb mole S/hr}$$


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Problem 9-1: Solution (Continued)

Step 3. Convert sulfur pound moles to SO₂ pound moles

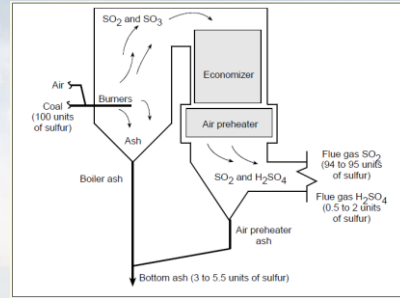
$$\begin{aligned} \text{Pound moles of sulfur converted to SO}_2 & \\ = \frac{125 \text{ lb mole S}}{\text{hr}} \times \frac{0.94 \text{ lb S converted}}{\text{lb S total}} \times \frac{1 \text{ lb mole SO}_2}{\text{lb mole S}} & \\ = 117.5 \text{ lb mole SO}_2/\text{hour} & \end{aligned}$$

Step 4. Convert SO₂ pound moles to pound mass.

$$\begin{aligned} \text{Pounds of SO}_2 \text{ emitted per hour} & \\ = \frac{117.5 \text{ lb mole SO}_2}{\text{hour}} \times \frac{64 \text{ lbm SO}_2}{\text{lb mole SO}_2} & \\ = 7,520 \text{ lb}_m \text{ SO}_2/\text{hour} & \end{aligned}$$



Figure 9-1. Conversion of Fuel Sulfur



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 SO₂, 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.

$$\begin{aligned} \text{SO}_2 \text{ (lb/hour)} = & \\ \left(\frac{2 \text{ lb}_m \text{ S}}{100 \text{ lb}_m \text{ coal}} \right) \left(\frac{0.94 \text{ lb}_m \text{ S Converted}}{\text{lb}_m \text{ S Total}} \right) \left(\frac{2 \text{ lb}_m \text{ SO}_2}{\text{lb}_m \text{ S}} \right) \left(\frac{\text{lb}_m \text{ coal}}{13,500 \text{ Btu}} \right) 100 \times 10^6 \text{ Btu/hr} & \end{aligned}$$

$$\text{SO}_2 \text{ (lb}_m \text{/hour)} = 279 \text{ lb SO}_2 \text{/hour}$$



Problem 9-2: Solution (Continued)

Step 2. Calculate the boiler sulfur dioxide emissions from the low sulfur fuel.

$$\begin{aligned} \text{SO}_2 \text{ (lb/hour)} = & \\ \left(\frac{1 \text{ lb}_m \text{ S}}{100 \text{ lb}_m \text{ coal}} \right) \left(\frac{0.94 \text{ lb}_m \text{ S Converted}}{\text{lb}_m \text{ S Total}} \right) \left(\frac{2 \text{ lb}_m \text{ SO}_2}{\text{lb}_m \text{ S}} \right) \left(\frac{\text{lb}_m \text{ coal}}{8,500 \text{ Btu}} \right) 100 \times 10^6 \text{ Btu/hr} & \\ = 221 \text{ lb}_m \text{ SO}_2 \text{/hour} & \end{aligned}$$

Step 3. Calculate the percent reduction.

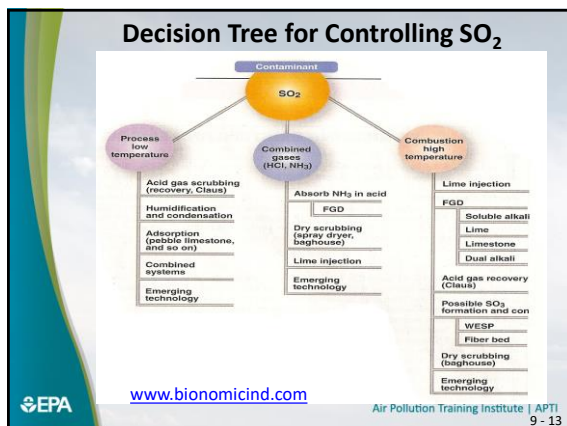
$$\text{Reduction} = \left(\frac{279 - 221}{279} \right) 100\% = 20.8\%$$



Sulfur Oxides Control Techniques

- Low sulfur fuel firing
- Flue gas desulfurization
- Dry scrubbing
- Fluidized bed combustion
- Fuel treatment

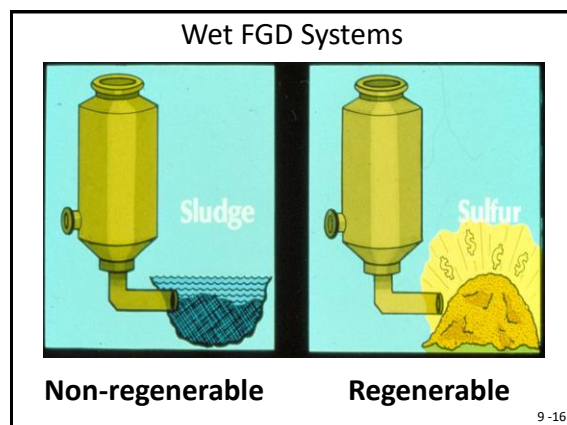
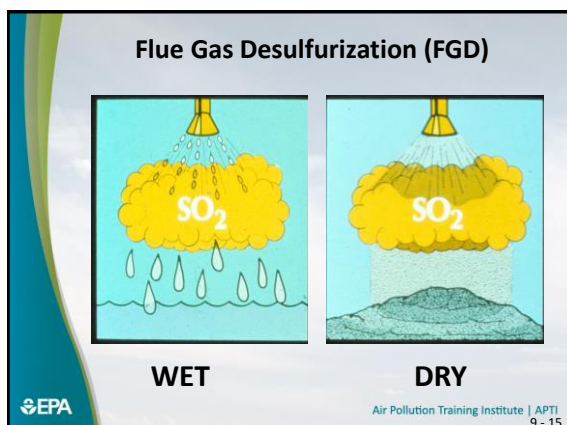




SO₂ Emissions Control Methods

Methods of Control	Method
Lower Sulfur Fuel	Method - Lower sulfur fuel reduces SO ₂ formation Reagent - None Typical fuel types - Powder River Basin coal and lower sulfur bituminous coal Capital Cost - Low Co-benefits - May reduce NO _x , HCl, and HF emissions
Dry Sorbent Injection	Method - Dry Sorbent Injection captures SO ₂ at moderate rates, downstream PM control devices captures dry product Reagent - Trona, sodium bicarbonate, hydrated lime Typical Fuel Types - Most often solid fuels (i.e. coals - lignite, sub-bituminous, bituminous) Capital Costs - Low to moderate Co-benefits - NO _x and HCl and HF reduction, Hg reduction, removal of chlorine, a precursor to dioxins/furans
Dry Scrubber with Fabric Filter	Method - Reagent + water react to capture acid gases and dry product captured in downstream fabric filter Reagent - Hydrated lime Typical Fuel Types - Coal Capital Costs - High Co-benefits - High SO ₂ and Hg capture (esp. bituminous coals), high PM and HCl capture
Wet Scrubber	Method - Reagent + water react to capture acid gases Reagent - Limestone, lime, caustic soda Typical Fuel Types - Coal, petroleum cokes, high sulfur fuel oil Capital Costs - High Co-benefits - Highest SO ₂ capture, high oxidized Hg and high HCl capture, PM capture
Wet Scrubber Upgrades	Method - Upgrade older scrubbers to provide performance approaching those of new scrubbers Reagent - Limestone, lime, etc. Typical Fuel Types - Coal, petroleum cokes, high sulfur fuel oil Capital Costs - Low to moderate Co-benefits - Same as wet scrubber

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- ### Classification of Flue Gas Desulfurization Systems.
- Classification of Flue Gas Desulfurization Systems can be based on what is done with the SO₂-absorbing or SO₂-reacting medium. This means processes are categorized as *throwaway* or *regenerative*.
 - In a throwaway process, the sulfur removed, together with the absorbing or reacting medium, is discarded.
 - In a regenerative process the sulfur is recovered in a usable form and the medium is reused.
 - Another way of classifying FGD processes is by the phase in which the main removal reactions occur. This means processes are categorized as *wet* or *dry*. Both wet and dry processes can be throwaway or regenerative, so there are, in effect, four categories of FGD processes.
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- ### Non-Regenerative Desulfurization Systems
- In the majority of the throwaway processes an alkaline agent reacts with the SO₂ leading to a product that is discarded.
 - Commonly used agents in this type of process are limestone (CaCO₃) and lime (CaO).
 - In another type of throwaway process the agent is injected directly into the furnace, and the sulfated product is subsequently scrubbed out of the flue gas with water. Part of the SO₂ is captured chemically within the furnace, the rest in the scrubbing step.
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Regenerative Desulfurization Systems

- In the regenerative alkaline processes, an alkaline agent strips SO₂ from the flue gas stream, combining chemically with the SO₂. In a separate regeneration step, the agent is reconstituted and sulfur is recovered, usually as liquid SO₂ or sulfuric acid.
- Some of the agents used include MgO, Na₂SO₃, and metal carbonates. Regenerative solid adsorption comprises several activated char processes, in which SO₂ is adsorbed on charcoal and desorbed to lead to the production of sulfuric acid.



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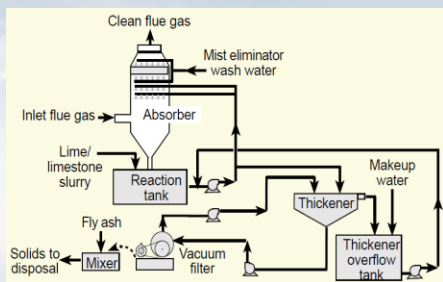
Table 9-1. Common Types of FGD Processes for Boilers (see handout)

Type of SO ₂ Control System	1989 (%)	2010 (%)
Wet Scrubbers, Non-regenerative (Throw-away)		
Lime	23.6	18.4
Limestone	50.6	45.5
Dual Alkali	3.4	2.3
Sodium Carbonate	4.0	3.3
Regenerative (Saleable Product)		
Magnesium Oxide	1.4	1.0
Wellman Lord	3.1	2.1
Lime/Limestone	4.0	4.7
Citrate/Undecided	0.0	0.3/7.8



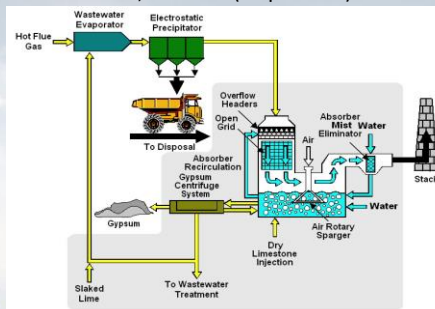
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Figure 9-2. Simplified Flowchart of a Lime Scrubbing System



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**Chesterton, Porter County, IN
(Northern Indiana Public Service Company's Bailly Generating Station, Units 7 and 8 (Completed 1996))**



http://www.netl.doe.gov/technologies/coalpower/ccct/cctdp/project_briefs/puair/adflugasdemo.html

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- The main problems with lime and limestone scrubbing are scaling and plugging inside the scrubber unit.
- The *dual alkali* system eliminates these problems. A solution of sodium sulfite (Na₂SO₃)/sodium hydroxide (NaOH) is sprayed in the tower.
- Sulfur dioxide is absorbed and neutralized in the solution, and since both Na₂SO₃ and Na₂SO₄ are soluble in water, no precipitation occurs in the scrubber.



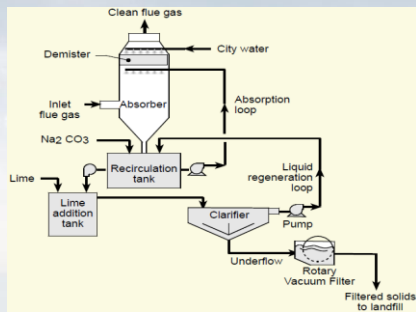
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Scaling and Plugging Inside the Scrubber Unit



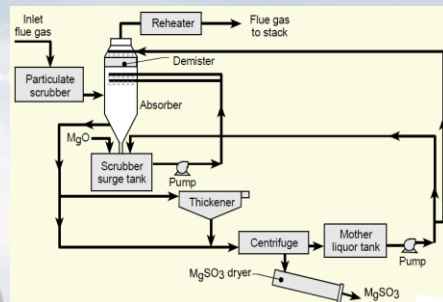
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Figure 9-3. Dual Alkali Scrubber System



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Figure 9-4. Simplified flowchart of the magnesium oxide process



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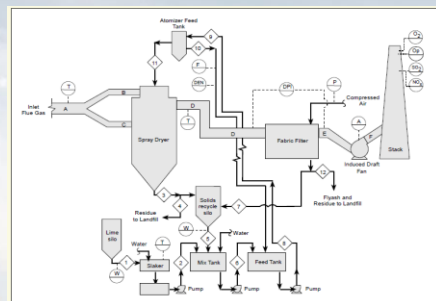
Dry Scrubber Processes

- 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



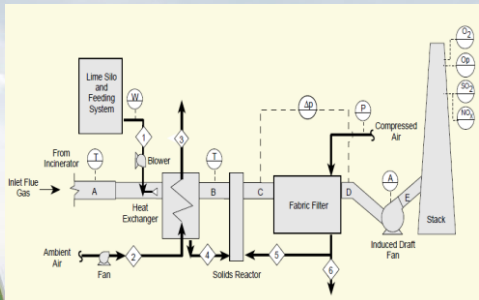
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Figure 9-5. Simplified flowchart of a spray dryer type dry scrubber



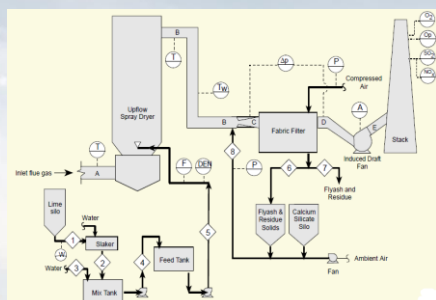
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Figure 9-6. Dry injection dry scrubber flowchart



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Figure 9-7. Combination Spray Dryer and Dry Injection Units



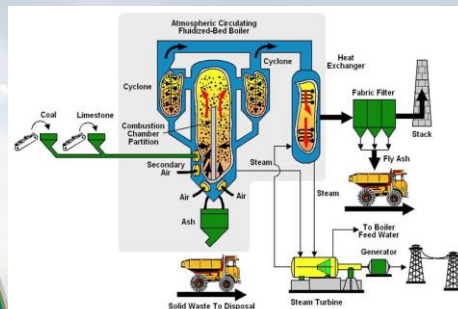
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Other Sulfur Oxide Control Techniques

- Fluidized Bed Combustion
- Fuel Treatment
 - Coal gasification
 - Coal liquefaction
 - Coal cleaning



Simplified schematic of an atmospheric circulating fluidized-bed (CFB) boiler power plant.



Operating Principles

Three basic steps in the removal of sulfur dioxide from combustion process flue gas:

- Absorption of SO₂ 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 SO₂ into water

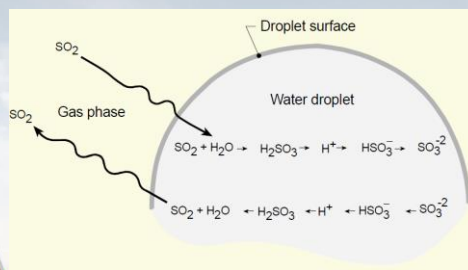
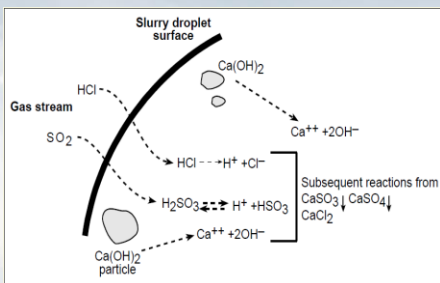
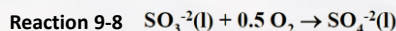
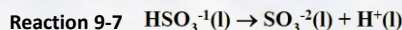
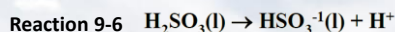
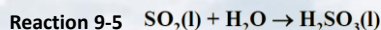
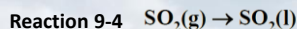


Figure 9-9. Absorption of SO₂ in alkaline slurry



Chemical Reactions in Solution and Precipitation of Reaction Products

Absorption Reactions




Note: (g) = gas phase
(l) = liquid phase
(s) = solid phase



Reactions 9-9 through 9-15

Limestone Reactions


9-9 $\text{CaCO}_3(\text{s}) \rightarrow \text{CaCO}_3(\text{l})$
 9-10 $\text{CaCO}_3(\text{l}) \rightarrow \text{Ca}^{+2} + \text{CO}_3^{-2}$
 9-11 $\text{CO}_3^{-2} + \text{H}^+ \rightarrow \text{HCO}_3^{-1}$
 9-12 $\text{SO}_3^{-2} + \text{H}^+ \rightarrow \text{HSO}_3^{-1}$
 9-13 $\text{SO}_3^{-2} + 0.5 \text{O}_2(\text{l}) \rightarrow \text{SO}_4^{-2}$
 9-14 $\text{Ca}^{+2} + \text{SO}_3^{-2} + 0.5 \text{H}_2\text{O} \rightarrow \text{CaSO}_3 \cdot \frac{1}{2} \text{H}_2\text{O}(\text{s})$
 9-15 $\text{Ca}^{+2} + \text{SO}_4^{-2} + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s})$

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Reactions 9-16 through 9-21

Lime Reactions


9-16 $\text{CaO}(\text{s}) + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2(\text{l})$
 9-17 $\text{Ca}(\text{OH})_2(\text{l}) \rightarrow \text{Ca}^{+2} + 2 \text{OH}^{-1}$
 9-18 $\text{OH}^{-1} + \text{H}^+ \rightarrow \text{H}_2\text{O}$
 9-19 $\text{SO}_3^{-2} + \text{H}^+ \rightarrow \text{HSO}_3^{-1}$
 9-20 $\text{Ca}^{+2} + \text{SO}_3^{-2} + 0.5 \text{H}_2\text{O} \rightarrow \text{CaSO}_3 \cdot \frac{1}{2} \text{H}_2\text{O}(\text{s})$
 9-21 $\text{Ca}^{+2} + \text{SO}_4^{-2} + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s})$

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Dual Alkali Scrubbing Reactions 9-22 through 9-27

Absorber Loop Reactions


9-22 $2\text{NaCO}_3 + \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SO}_3 + 2\text{NaHCO}_3$
 9-23 $\text{NaHCO}_3 + \text{SO}_2 \rightarrow \text{NaHSO}_3 + \text{CO}_2(\text{g})$
 9-24 $2\text{NaOH} + \text{SO}_2 \rightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O}$
 9-25 $\text{Na}_2\text{SO}_3 + \text{SO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{NaHSO}_3$
 9-26 $2\text{NaOH} + \text{SO}_3 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$
 9-27 $\text{Na}_2\text{SO}_3 + 0.5 \text{O}_2 \rightarrow \text{Na}_2\text{SO}_4$

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Reactions 9-28 and 9-29

Regeneration Loop Reactions


9-28 $2\text{NaHSO}_3(\text{l}) + \text{Ca}(\text{OH})_2 \rightarrow \text{Na}_2\text{SO}_3 + \text{CaSO}_3 \cdot 2\text{H}_2\text{O}(\text{s})$
 9-29 $\text{Na}_2\text{SO}_4 + \text{Ca}(\text{OH})_2 \rightarrow 2\text{NaOH} + \text{CaSO}_4$

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Reactions 9-30 through 9-33

Magnesium Oxide Scrubbing

9-30 $\text{Mg}(\text{OH})_2 + 5 \text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{MgSO}_3 \cdot 6\text{H}_2\text{O}$
 9-31 $\text{MgSO}_3 \cdot 6\text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{Mg}(\text{HSO}_3)_2 + 5\text{H}_2\text{O}$
 9-32 $\text{Mg}(\text{HSO}_3)_2 + \text{MgO} \rightarrow 2\text{MgSO}_3 + \text{H}_2\text{O}$
 9-33 $2\text{MgSO}_3 + \text{O}_2 + 7\text{H}_2\text{O} \rightarrow 2\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

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Reactions 9-34 through 9-38

Cake dryer

9-34 $\text{MgSO}_3 \cdot 6\text{H}_2\text{O} \rightarrow \text{MgSO}_3 + 6\text{H}_2\text{O}$
 9-35 $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} \rightarrow \text{MgSO}_4 + 7\text{H}_2\text{O}$

MgO Regeneration in Calciner

9-36 $\text{MgSO}_3 \rightarrow \text{MgO} + \text{SO}_2$
 9-37 $\text{C} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}$
 9-38 $\text{CO} + \text{MgSO}_4 \rightarrow \text{CO}_2 + \text{MgO} + \text{SO}_2$

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Wellman-Lord Reactions 9-39 through 9-42

Wellman-Lord Process

9-39 $\text{SO}_2 + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow 2\text{NaHSO}_3$

9-40 $\text{Na}_2\text{SO}_3 + \frac{1}{2}\text{O}_2 \rightarrow \text{Na}_2\text{SO}_4$

9-41 $\text{Na}_2\text{CO}_3 + 2\text{NaHSO}_3 \rightarrow 2\text{Na}_2\text{SO}_3 + \text{CO}_2 + \text{H}_2\text{O}$

9-42 $2\text{NaHSO}_3 \rightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} + \text{SO}_2$

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Reactions 9-43 and 9-44

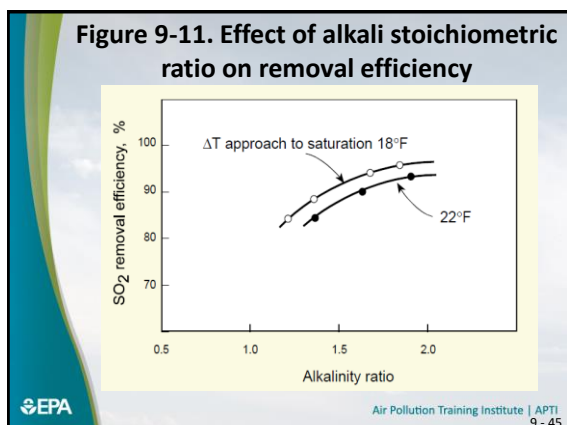
Dry Scrubbing

9-43 $\text{Ca}(\text{OH})_2 + 2 \text{HCl} \rightarrow \text{CaCl}_2 + 2 \text{H}_2\text{O}$

9-44 $\text{Ca}(\text{OH})_2 + \text{SO}_2 \rightarrow \text{CaSO}_3 + \text{H}_2\text{O}$

The stoichiometry involved in the reaction between calcium hydroxide and sulfur dioxide is one mole per mole. However, because of the problems in fully utilizing the alkali, dry injection systems often provide 3 to 3.5 moles of alkali per mole of sulfur dioxide. Slurry atomizing systems generally use 1.5 to 2.5 moles of alkali per mole of sulfur dioxide.

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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

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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

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Alkali Requirements Reactions 9-45 through 9-47

Alkali Requirements

9-45 $\text{SO}_2 + \text{Ca}(\text{OH})_2 + 0.5 \text{O}_2 \rightarrow (\text{CaSO}_4)_s + \text{H}_2\text{O}$


9-46 $2\text{HCl} + \text{Ca}(\text{OH})_2 \rightarrow 2\text{Ca}^{++} + 2 \text{Cl}^- + 2\text{H}_2\text{O}$

9-47 $2\text{HF} + \text{Ca}(\text{OH})_2 \rightarrow 2\text{Ca}^{++} + 2 \text{F}^- + 2\text{H}_2\text{O}$

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Problem 9-3

- Calculate the amount of calcium hydroxide Ca(OH)₂ (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.


$$HCl = 10,000 \text{ SCFM} \left(\frac{\text{lb mole}}{385.4 \text{ SCF}} \right) \left(\frac{0.00005 \text{ lb mole HCl}}{\text{lb mole total}} \right) \left(\frac{98 \% \text{ Efficiency}}{100 \%} \right)$$

HCl = 0.00127 HCl lb mol /min

Step 2. Calculate the amount of Ca(OH)₂ required.


$$= \left(\frac{1 \text{ lb mole Ca(OH)}_2}{2 \text{ lb mole HCl}} \right) \left(\frac{0.00127 \text{ lb mole HCl}}{\text{min}} \right) \left(\frac{74 \text{ lbm Ca(OH)}_2}{\text{lb mole Ca(OH)}_2} \right)$$

= 0.04699 lb_m Ca(OH)₂/min = 2.74 lb_m Ca(OH)₂

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Continuous Emission Monitors

- Performance Evaluation Analyzers
- Instrumentation
- Techniques
 - SO₂
 - O₂

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Reactions 9-48 and 9-49


Performance Evaluation

9-48 SO₂ + η hv → SO₂* → SO₂ + hv'

210 nm Excited
240-410 nm Molecule

9-49 SO₂ + 2H₂O → SO₄²⁻ + 4H⁺ + 2e⁻

E₀ = 0.17 V
298


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Equation 9-1

(Eq 9-1)
$$S = \frac{\delta^2}{4} \left[-cI \frac{d^2\alpha}{d\lambda^2} \right]$$


Where:

- S = oscillating signal monitored by the analyzer
- δ = scanning distance
- c = gas concentration
- l = light path length through the gas
- α = wavelength-dependent molecular absorption coefficient
- λ = wavelength
- I = intensity of the light leaving the probe

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Instrumentation


- Flue gas oxygen content
- Mist eliminator static pressure drop
- pH
- Alkali feed rate
- Inlet and outlet gas temperature
- Dry and Wet Scrubbing

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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.


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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.


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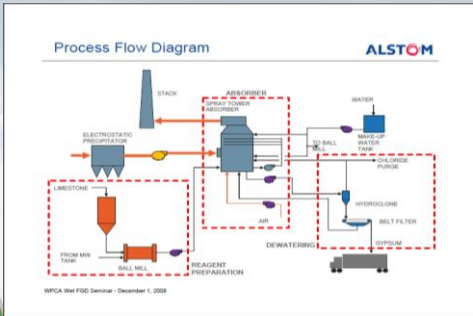
Summary (Continued)


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.


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Process Flow Diagram




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EPA/600/R-02/003
November 2000

CONTROLLING SO₂ EMISSIONS: A REVIEW OF TECHNOLOGIES


Prepared by:

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Prepared for:


U.S. Environmental Protection Agency
Office of Research and Development
Washington, D.C. 20460

<http://nepis.epa.gov/Adobe/PDF/P1007IQM.pdf>


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CHAPTER 10

CONTROL TECHNIQUES AND REGULATIONS FOR GREENHOUSE GAS EMISSIONS

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Effects: Snow and Ice

Snow and ice are melting at rates unseen for thousands of years. In Glacier National Park, for example, there were 150 glaciers in 1850. Today, there are 26.

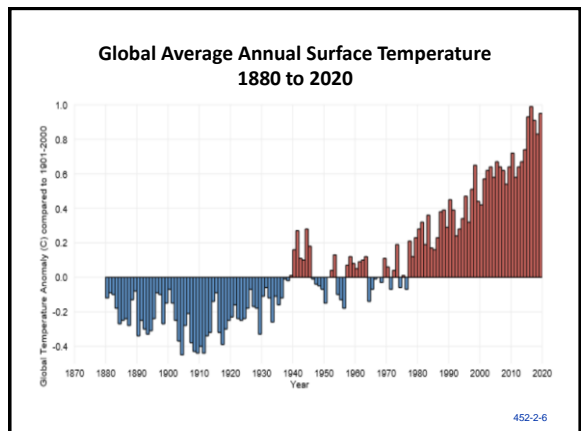
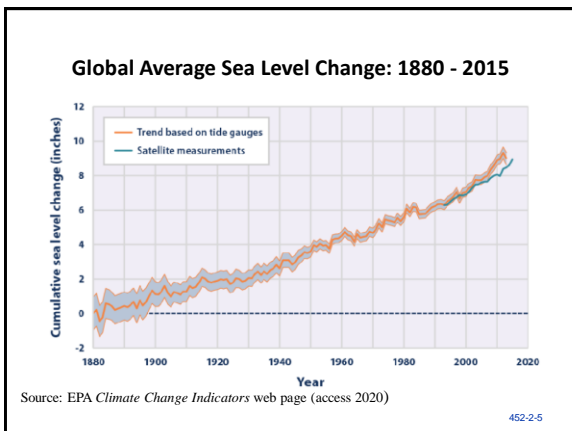
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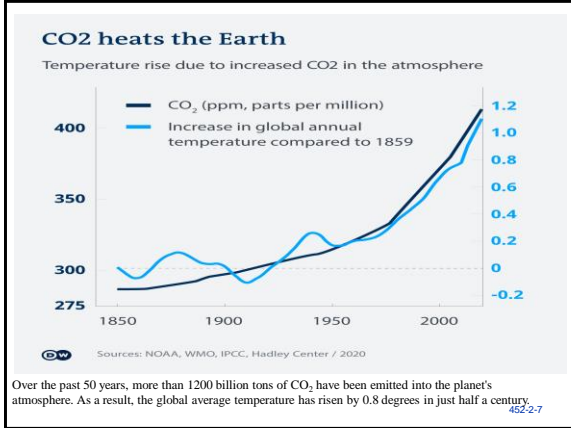
Muir Glacier in Alaska: Total Glacier Mass has Declined Around the Globe

August 13, 1941 **August 31, 2004**

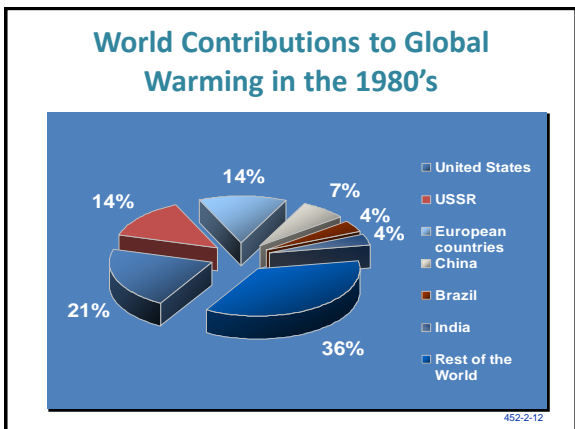
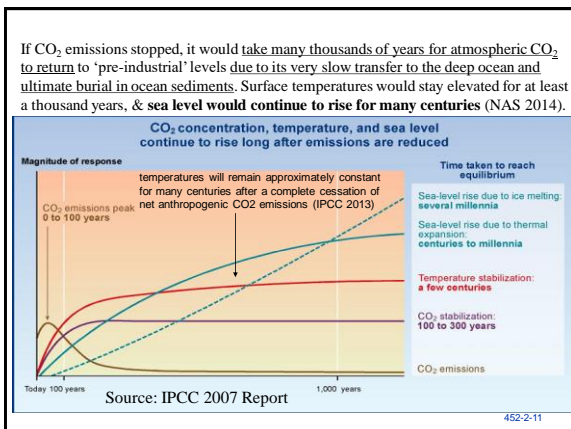
Source: EPA Climate Change Web Site

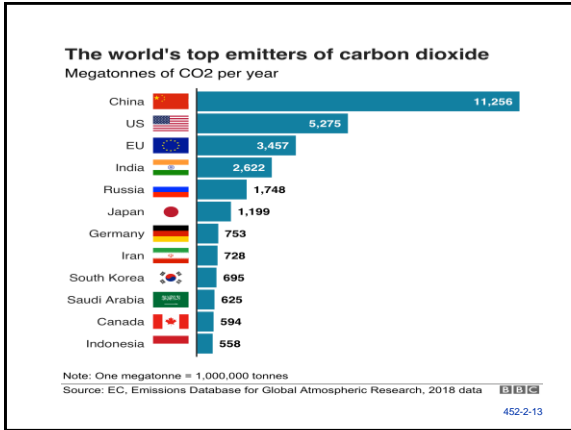
452-2-4





- ### Predicted Effects of Global Warming: IPCC (2007 Report)
- An **increase in global average annual precipitation** during the 21st century, although changes in precipitation will vary from region to region.
 - An **increase in the intensity of precipitation events**, particularly in tropical and high-latitude regions that experience overall increases in precipitation.
 - **Tropical storms and hurricanes** are likely to become more intense, produce stronger peak winds, and produce increased rainfall over some areas due to warming sea surface temperatures (which can energize these storms).





- ### Intergovernmental Action
- 1988: *Intergovernmental Panel on Climate Change (IPCC)* is formed to conduct scientific studies on climate change.
 - 1997: "*Kyoto Protocol*" 150 countries meet in Japan
 - 2007: A series of *reports* were completed by the *IPCC*: In Reports:
 - The IPCC concluded that: "*warming of the climate system is unequivocal*", and most of the observed increase is *very likely due to the increase in human-made GHG concentrations*.
 - Dec 2007: *Bali meeting*: all countries agree to a "*road map*":
 - All the UNFCCC annual conferences since have failed to produce a significant legally binding treaty on curbing GHGs.
 - The last conference (21st Session) was Dec 2015 in *Paris, France*. Under the agreement:
 - Countries set their own targets for reducing CO₂ & other GHGs
 - Targets are **not legally binding**

- ### Intergovernmental Panel on Climate Change (IPCC)
- IPCC produces the main reports on climate change, is a scientific intergovernmental body set up in 1988 by:
 - the World Meteorological Organization and
 - the United Nations Environment Program.
 - Their function is to:
 - assess the latest peer-reviewed literature,
 - compare different computer model results from various sources, and
 - to achieve consensus about where the weight of the evidence points and where uncertainties lie.
 - 2007: 4th Assessment Report (4 volumes).
 - 2014: 5th Assessment Report
 - 2022: 6th Assessment Report due
-



- ### Does the CAA Regulate GHG?
- April 2, 2007, U.S. Supreme Ct. held that EPA has authority to regulate CO₂ & other greenhouse gases (GHG) from new motor vehicles. (*Mass. v. EPA*)
 - The Ct. determined that CO₂ & GHGs fit the CAA §312 definition of "air pollution"

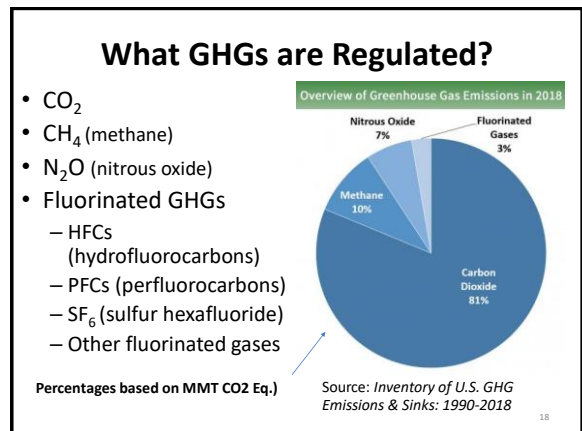


Table A-1 Subpart A List of GWP's

Name	CAS No.	Chemical formula	Global warming potential (100 yr.)
Carbon dioxide	124-38-9	CO ₂	1
Methane	74-82-8	CH ₄	21
Nitrous oxide	10024-97-2	N ₂ O	310
HFC-23	75-46-7	CHF ₃	11,700
HFC-32	75-10-5	CH ₂ F ₂	650
HFC-41	509-33-3	CHF ₂	150
HFC-125	359-33-6	C ₂ H ₅ F	2,800
HFC-134	359-35-3	C ₂ H ₂ F ₄	1,000
HFC-134a	811-97-2	CH ₂ FCF ₃	1,300
HFC-143	430-66-0	C ₂ H ₃ F ₅	300
HFC-143a	420-46-2	C ₂ H ₂ F ₆	3,800
HFC-152	624-72-6	CH ₂ FCF ₂	53
HFC-152a	75-37-6	CH ₂ CHF ₂	140
HFC-161	359-36-6	CH ₃ CHF ₂	12
HFC-227ea	431-63-0	C ₃ H ₂ F ₆	2,900
HFC-236cb	677-56-5	CH ₂ FCF ₂ CF ₃	1,840
HFC-236eb	401-65-0	CH ₂ FCF ₂ CF ₂ CF ₃	3,370
HFC-236fa	690-39-1	C ₃ H ₂ F ₈	6,300
HFC-245ca	678-86-7	C ₂ H ₃ ClF ₅	560
HFC-245fa	465-75-1	CH ₂ ClCF ₂	1,000
HFC-365mfc	406-58-6	CH ₂ ClCF ₂ CF ₃	794
HFC-43-10mee	138495-42-8	CF ₃ CH ₂ CF ₂ CF ₂ CF ₃	1,300
Sulfur hexafluoride	2551-62-4	SF ₆	23,900
Trifluoromethyl sulphur pentafluoride	373-80-8	CF ₃ CF ₂ CF ₂ CF ₂ CF ₃	17,700
Nitrogen trifluoride	7783-34-2	NF ₃	17,200
PFC-14 (Perfluoromethane)	75-35-0	CF ₄	6,500
PFC-116 (Perfluoroethane)	76-16-4	C ₂ F ₆	9,200
PFC-218 (Perfluoropropane)	75-19-7	C ₃ F ₈	7,000

10-19

Table A-1 Subpart A List of GWP's

Name	CAS No.	Chemical formula	Global warming potential (100 yr.)
Perfluorocyclopropane	931-81-9	C ₃ F ₆	17,340
PFC-3-1-10 (Perfluorobutane)	355-25-9	C ₄ F ₁₀	7,000
Perfluorocyclobutane	115-25-3	C ₄ F ₈	8,700
PFC-4-1-12 (Perfluoropentane)	678-26-2	C ₅ F ₁₂	7,500
PFC-5-1-14 (Perfluorohexane)	305-42-0	C ₆ F ₁₄	7,400
PFC-9-1-18 (Perfluorooctane)	305-84-8	C ₉ F ₂₀	7,300
HCFE-235b2 (sulfurane)	26275-46-7	CHF ₂ CHClCF ₂	350
HFE-43-10pcc (3H-1,3-dioxane 1043x)	11730183	CHF ₂ OCF ₂ OCF ₂ CHF ₂	14,800
HFE-125	3022-89-2	CHF ₂ OCF ₂	14,800
HFE-134	1991-17-4	CHF ₂ OCF ₂ CF ₃	6,300
HFE-143a	421-14-7	CH ₂ OCF ₂	750
HFE-227ea	2366-37-1	CF ₃ CH ₂ OCF ₂	1,540
HFE-236fa12 (HFC-10)	2366-37-1	CHF ₂ OCF ₂ OCF ₂ CF ₃	2,800
HFE-236fa2 (Desulfurane)	23041-67-5	CHF ₂ OCF ₂ OCF ₂ CF ₃	869
HFE-236fa	21189-47-3	CF ₃ CH ₂ OCF ₂ CF ₃	487
HFE-236fa	23410-44-2	CH ₂ OCF ₂ CF ₂	708
HFE-245fa	8011-15-4	CHF ₂ OCF ₂ CF ₂	659
HFE-245fa2	1885-43-0	CHF ₂ OCF ₂ CF ₂	659
HFE-259cb2	425-86-2	CH ₂ OCF ₂ CF ₂	559
HFE-259cb2	480-43-6	CF ₃ CH ₂ OCF ₂	11
HFE-259cb2	67490-36-2	CHF ₂ OCF ₂ OCF ₂	819
HFE-338mfc2	156058-88-2	CF ₃ OCF ₂ OCF ₂ CF ₃	502
HFE-341mfc2 (3H-0-1)	18826-36-2	CHF ₂ OCF ₂ OCF ₂ OCF ₂	1,500
HFE-341mfc2	21023-86-0	CH ₂ OCF ₂ OCF ₂	375
HFE-347mfc2	E1730136	CF ₃ OCF ₂ OCF ₂ OCF ₂	374
HFE-347mfc2	535-79-0	CH ₂ OCF ₂ OCF ₂	565
HFE-356mfc3	385-34-3	CH ₂ OCF ₂ OCF ₂ CF ₃	101
HFE-356mfc3	16920-00-0	CH ₂ OCF ₂ OCF ₂	105
HFE-356mfc3	E1730137	CHF ₂ OCF ₂ OCF ₂ CF ₃	265
HFE-356mfc3	36042-89-3	CH ₂ OCF ₂ OCF ₂	922
HFE-356mfc3	378-15-0	CF ₃ OCF ₂ OCF ₂	11
HFE-356mfc3	675-80-8	CH ₂ OCF ₂ OCF ₂	627
HFE-448a (HFE-7100)	161700-07-0	CF ₃ OCF ₂ OCF ₂	297
HFE-448a (HFE-7200)	161700-06-8	CF ₃ OCF ₂ OCF ₂	59
Chemical blend	161700-05-8	CF ₃ OCF ₂ OCF ₂	345
Chemical blend	161700-08-8	CF ₃ OCF ₂ OCF ₂	1,640
Chemical blend	13171-18-1	CF ₃ OCF ₂ OCF ₂	27
Chemical blend	26103-06-2	CHF ₂ OCF ₂ OCF ₂	960
HFE-338mfc1	NA	NA	73
(Octafluorostereamethylene)hydroxymethyl group	23052-3478-1	NA	343
Bis(trifluoromethyl)methane	803-66-1	CF ₃ OCF ₂ OCF ₂	195
2,2,3,3-tetrafluoropropane	422-33-2	CF ₃ OCF ₂ OCF ₂	6
PFMethyl	NA	CF ₃ OCF ₂ OCF ₂ OCF ₂	10,300

NA = not available.

10-20

Table 2 GHGs With Revised GWPs for Table A-1 (Nov 2013)

Name	CAS No.*	Global warming potential
Methane	74-82-8	25
Nitrous oxide	10024-97-2	298
HFC-23	75-46-7	14,800
HFC-32	75-10-5	675
HFC-41	590-53-3	92
HFC-125	354-33-6	3,500
HFC-134	359-35-3	1,100
HFC-134a	811-97-2	1,430
HFC-143	430-66-0	353
HFC-143a	420-46-2	4,470
HFC-152a	75-37-6	124
HFC-227ea	431-63-0	3,220
HFC-236fa	690-39-1	9,810
HFC-245ca	678-86-7	693
HFC-43-10mee	138495-42-8	1,640
Sulfur hexafluoride	2551-62-4	22,800
PFC-14 (Perfluoromethane)	75-73-0	7,590
PFC-116 (Perfluoroethane)	76-16-4	12,200
PFC-218 (Perfluoropropane)	76-19-7	8,630
PFC-3-1-10 (Perfluorobutane)	355-25-9	8,860
Perfluorocyclobutane	115-25-3	10,300
PFC-4-1-12 (Perfluoropentane)	678-26-2	9,160
PFC-5-1-14 (Perfluorohexane)	355-42-0	9,300

10-21

Global Warming Potentials (GWP) (for 100 year time horizon)

Gas	GWP
CO ₂	1
CH ₄ ^a	25
N ₂ O	298
HFC-23	14,800
HFC-32	675
HFC-125	3,500
HFC-134a	1,430
HFC-143a	4,470
HFC-152a	124
HFC-227ea	3,220
HFC-236fa	9,810
HFC-4310mee	1,640
CF ₄	7,390
C ₂ F ₆	12,200
C ₂ F ₁₀	8,860
C ₂ F ₁₄	9,300
SF ₆	22,800
NF ₃	17,200

TPY of a GHG x GWP = # TPY CO₂ equivalent

Source: IPCC (2007). The CH₄ GWP includes the direct effects and those indirect effects due to the production of F tropospheric ozone and stratospheric water vapor. The indirect effect due to production of CO₂ is not included.

452-222

Example Calculation of CO₂equivalent

- A proposed emissions unit emits the following GHGs in the following amounts:
 - 50,000 TPY of CO₂
 - 60 TPY of methane
 - 1 TPY of nitrous oxide
 - 5 TPY of HFC-32
 - 3 TPY of PFC-14

GHG	GWP
Carbon Dioxide	1
Methane	25
Nitrous Oxide	298
HFC-32	675
PFC-14	7390

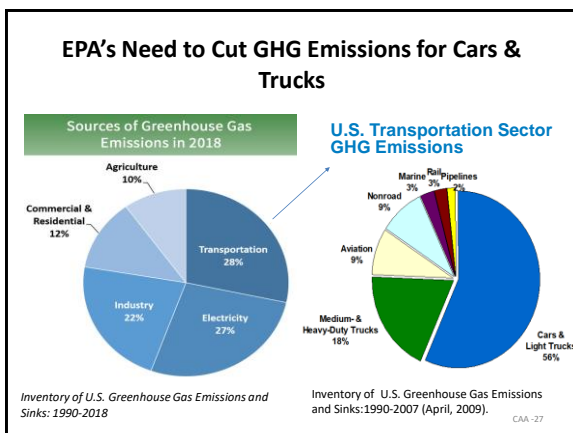
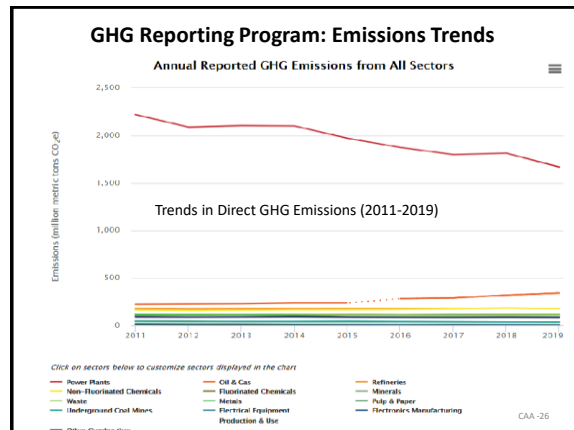
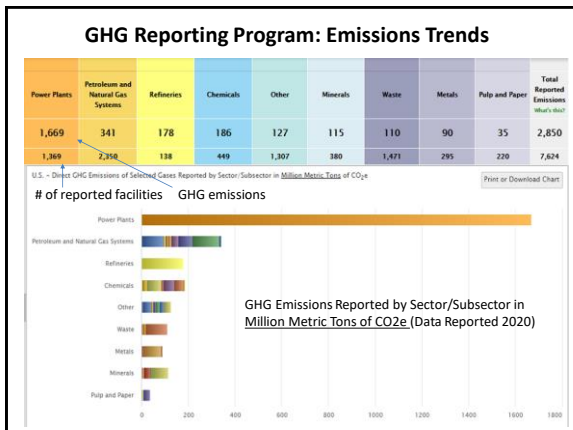
(50,000 TPY x 1) + (60 TPY x 25) + (1 TPY x 298) + (5 TPY x 675) + (3 TPY x 7390) = 50,000 + 1,500 + 298 + 3,375 + 22,170 = 77,343 CO_{2e}

23

GHG Reporting Program

- On Oct 30, 2009, EPA issued 40 CFR Part 98, which **requires reporting of GHG emissions** from large sources and suppliers in the United States.
- Purpose:** to develop policies and programs to address climate change.
- Under Part 98, **suppliers** of fossil fuels or industrial GHGs, **manufacturers of vehicles and engines, and facilities that emit ≥ 25,000 metric tons per year of GHG emissions** are required to **submit annual reports** to EPA. (first reports submitted in 2011)

CAA-24



EPA Regulations to Cut GHG Emissions for Cars & Trucks

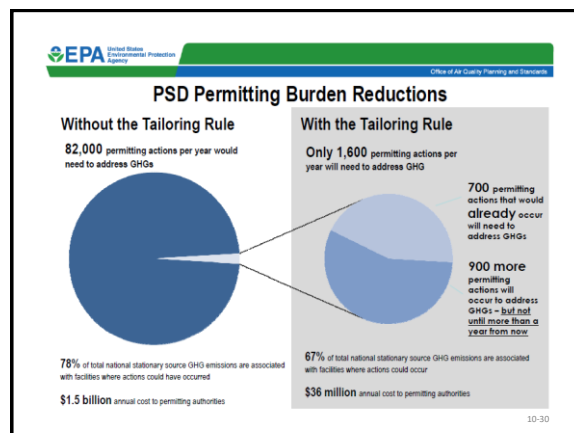
- In May 2010, EPA passed CO₂ emission standards for light duty vehicles (cars & trucks) for years 2012 to 2016.
- In Oct 2012, EPA passed CO₂ emissions standards for cars & trucks: model years 2017 - 2025.
- In April 2020, EPA amended the GHG emissions standards for passenger cars & light trucks & established new less stringent standards, covering model years 2021 - 2026.

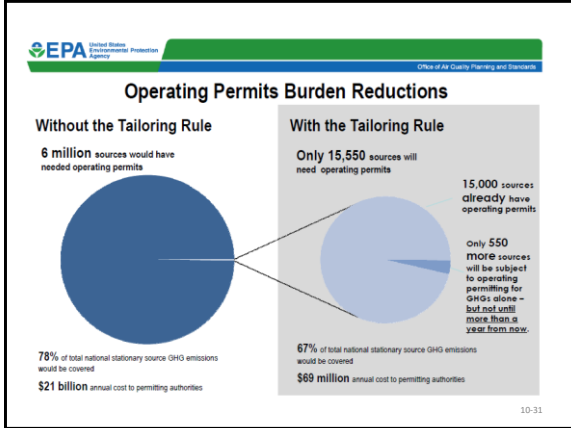
28

EPA's GHG Tailoring Rule

- June 3, 2010: EPA sets *thresholds for GHG emissions* that define when permits under PSD & Title V Operating Permit programs are required.
 - PSD:** 250 tpy or 100 tpy (specific industries) "*any pollutant regulated under the CAA*"
 - New: 100,000 tpy of CO₂e; Modified: 75,000 tpy of CO₂e
 - Title V:** major source is, among other things, any source with a PTE at least 100 tpy of *any CAA regulated pollutant*.
 - Existing or new sources with PTE \geq 100,000 tpy of CO₂e

10-29





U.S. Supreme Court Decision: Vacating the Tailoring Rule

- On June 23, 2014, the U.S. Supreme Court issued its decision in *Utility Air Regulatory Group v. EPA*.
- The Court said that EPA may **not** treat GHG as an air pollutant for purposes of determining **whether a source is a major source** required to obtain a PSD or Title V permit. Changing the CAA (by using the Tailoring Rule) is something only Congress can do.
- The Court also said that PSD permits that are otherwise required (based on emissions of other pollutants) may require limitations on GHG emissions based on the application of Best Available Control Technology (BACT).

PSD: Major for One, Major for All Policy

- Once a source is major for any regulated NSR pollutant, BACT is required for each regulated NSR pollutant that is emitted above its "significant quantity."
- Any source which is required to obtain a PSD permit will have to apply a GHG BACT if their GHG emissions exceed 75,000 tpy of CO₂e (significance quantity).
 - This significant quantity was recognized by EPA in July, 2014 memo. EPA passed a *proposed rule* establishing this level on August 26, 2016.

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Also in 2011 EPA released: "GUIDANCE FOR DETERMINING BEST AVAILABLE CONTROL TECHNOLOGY FOR REDUCING CARBON DIOXIDE EMISSIONS FROM BIOENERGY PRODUCTION."

BACT for GHGs

- BACT is a case-by-case determination
 - Provides considerable discretion to the permitting authority
 - EPA does not prescribe GHG BACT for any source type
- EPA did publish GHG BACT guidance for EGUs
 - Clean fuels need to be considered
 - Feasibility of CCS needs to be considered in BACT analysis (presently too expensive to be selected)
 - Focus on energy efficiency as means of reducing GHGs
- NSPS serves as a floor for BACT determinations

BACT Determinations Steps

- Step 1: Identify available pollution control options.
- Step 2: Eliminate technically infeasible options.
- Step 3: Rank controls by control effectiveness.
- Step 4: Evaluate controls by cost and energy & environmental impacts.
- Step 5: Make the BACT selection.

BACT Determination Example

- Control A: 60% efficient @ cost = \$50,000/yr.
- Control B: 90% efficient @ cost = \$60,000/yr.
- Control C: 94% efficient @ cost = \$90,000/yr.
- Control B would be BACT because it is the most *cost effective* for tons of pollutant removed.

10-37

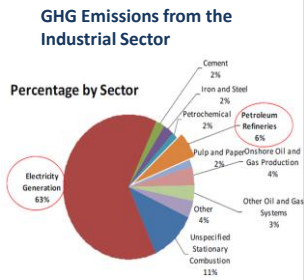
Carbon Capture and Storage (CCS)

- CCS is "available" and should be considered in Step 1.
- CCS may be eliminated in Step 2 if technically infeasible for the proposed source;
 - i.e., *no space available for CO₂ capture equipment at an existing facility; right-of-ways prevent building a pipeline or access to an existing CO₂ pipeline; no access to suitable geologic reservoirs for sequestration or other storage options.*
- Currently, CCS is an expensive technology and makes the price of electricity from a power plant uncompetitive, even when underground storage of the captured CO₂ exists near the power plant. Therefore, CCS will often be eliminated from consideration in Step 4.

10-38

EPA has "White Papers" for Industrial Sectors that Emit the Highest Amounts of GHGs

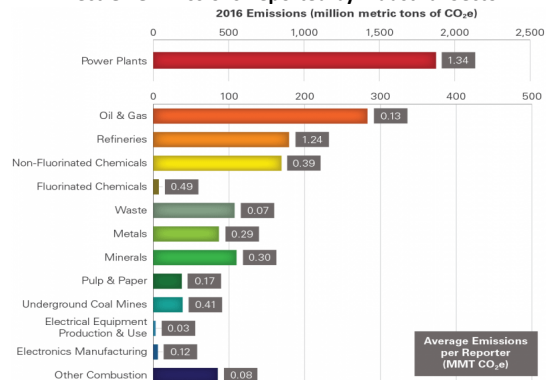
- Coal Fired Electric Generating Units (EGUs)
- Large Industrial/Commercial Boilers
- Pulp and Paper
- Cement
- Iron and Steel Industry
- Refineries
- Nitric Acid Plants
- These "white papers" provide information on GHG control options, etc. particularly in the assessment of (BACT)



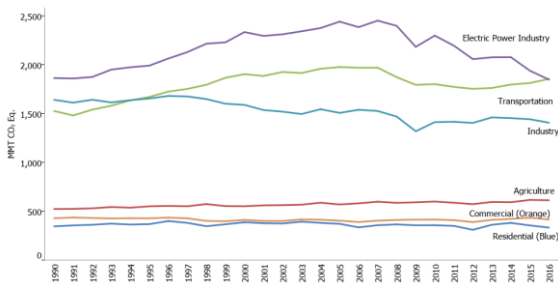
Papers are located at: <https://www.epa.gov/nsr/clean-air-act-permitting-greenhouse-gases>

CAA-39

Direct GHG Emissions Reported by Industrial Sector



U.S. Greenhouse Gas Emissions Allocated to Economic Sectors (MMT CO₂ Eq.)



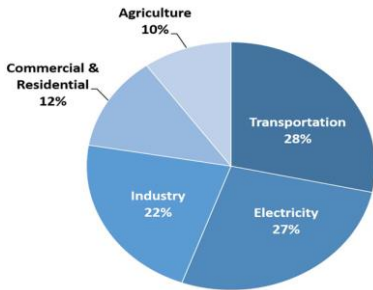
10-41

GHG from Power Plants (EGUs)



CAA-42

Total GHG Emissions Sources in U.S. (2018)



Source: Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2018 (April 2020). 452-2-43

NSPS: CAA Section 111

- CAA Section **111(b)**: Requires EPA to establish emission standards for any category of **new and modified** stationary sources that “causes, or **contributes significantly** to, air pollution which may reasonably be anticipated to endanger public health or welfare.”
- CAA Section **111(d)**: Required for **existing** sources upon promulgation of a **111(b)** standard for **new and modified sources** in specific circumstances (whose pollutants are not regulated under NAAQS or HAPs under the CAA).

CAA-44

Carbon Pollution Standards (NSPS) for New, Modified and Reconstructed EGU

- **August 3, 2015**: Because EGUs are the largest contributor of GHGs (33%), EPA says Section 111(b) “**significantly contribute**” requirement is satisfied. Therefore EPA passed a NSPS for GHG emissions for **new, modified & reconstructed EGUs**.
 - Does **not apply** to “**existing**” units that have **not** been modified or reconstructed.
 - **Only regulates CO₂** emissions (will not regulate nitrous oxide or methane (both are GHGs)).
 - Has different standards for different types of new EGUs.

CAA-45

Carbon Pollution Standards (NSPS) for New, Modified & Reconstructed EGUs

- **New and Reconstructed Natural gas-fired stationary turbines**
 - 1,000 lb CO₂/MWh gross for all base load units
 - Non-base load units uses clean fuel-based input standard
 - base-load is determined by design efficiency and sales
- **Modified gas-fired units**: EPA is not setting a standard at this time.

Carbon Pollution Standards (NSPS) for New, Modified & Reconstructed EGUs

- **New coal-fired Energy Generating Units**
 - 1,400 lb CO₂/MWh gross limit & **include partial carbon capture and storage (CCS)**
- **Modified coal-fired EGUs**:
 - applies only to **modifications** resulting in an increase of hourly CO₂ emission of **more than 10 percent**
 - will be required to **meet a standard** consistent with its best historical annual performance during the years from 2002 to the time of modification.
 - **no CCS required**
- **Reconstructed coal-fired EGUs**:
 - 1,800 lb CO₂/MWh-gross limit for sources with heat input greater than 2,000 MMBtu/hr.
 - 2,000 lb CO₂/MWh-gross limit for sources with a heat input of less than or equal to 2,000 MMBtu/hr.

New “Significant Contribution” Test for GHG δ111(b) NSPS

- On **January 7, 2021**, an **EPA final rule** provides that **source categories can contribute significantly** [δ111(b)] if their **GHG emissions exceeds 3 percent of total U.S. GHG emissions**.
 - Above this threshold, then **secondary criteria** can be used to further evaluate (i.e. vulnerability to international trade competition).
- EPA **also determined** that **EGU source category contributes significantly** because their GHG emissions are substantially above the 3% threshold. (The EGU source category represents over 25% of total U.S. GHG emissions.)

CAA-48

Carbon Pollution Standards For Existing EGUs

- **Aug 3, 2015:** **Clean Power Plan (CPP)** rule was passed under CAA §111(d) for “existing” sources.
 - EPA establishes **guidelines** for emission standards. **States then design programs to meet EPA guidelines.** (a state-based program)
 - Aimed to reduce EGU CO2 emissions by 32% by 2030.
- **Feb, 2016:** SCOTUS puts a “stay” on CPP-to allow lawsuits
- **June 19, 2019** – EPA passed **Affordable Clean Energy (ACE)** rule – replacing CPP.
 - Controls would be based on **efficiency improvements.**
 - Lower EGU CO2 emissions between 0.7% & 1.5% by 2030
- **Jan 19, 2021:** The app. Ct. **struck down** the 2019 ACE rule
 - Also, criticized the EPA that it only allowed to regulate emissions directly at the source (the power plants themselves) rather than across the power sector as a whole.
 - This opens the door for CO2 cap & trade or CO2 taxing

CAA-49

Many CO₂ Reduction Opportunities

- Heat rate improvements
- Fuel switching to a lower carbon content fuel
- Integration of renewable energy into EGU operations
- Combined heat and power
- Qualified biomass co-firing and repowering
- Renewable energy (new & capacity uprates)
- Wind, solar, hydro
- Nuclear generation (new & capacity uprates)
- Demand-side energy efficiency programs and policies
- Demand-side management measures
- Electricity transmission and distribution improvements
- Carbon capture and utilization for existing sources
- Carbon capture and sequestration for existing sources

10-50

Results of Implementing EGU Efficiency Technologies

Increased thermal efficiency of power production

- One specific example is the **NETL study** (2008), which conducted a literature review of published articles and technical papers **identifying potential efficiency improvement techniques** applicable to existing coal-fired EGUs
- A **summary of the findings** from the NETL study is presented in Table 10-8 of your Student Manual for Course APTI 415.



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10-51

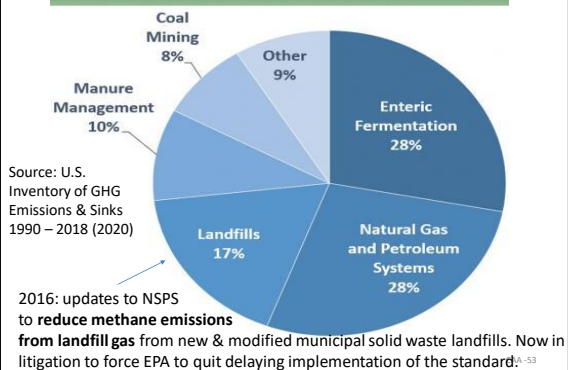
Summary of CO₂ Controls for Coal-Fired EGUs

- There is **no one best available coal-fired EGU technology** universally applicable to all EGUs, therefore **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, and FGD technology



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10-52

2018 U.S. Methane Emissions, By Source



Regulation of Methane Emissions from the Oil and Natural Gas Industry

- **May 16, 2016:** EPA passed **NSPS** rules that will **curb emissions of methane, VOCs, and toxic air pollutants** such as benzene from **new, reconstructed, and modified** oil and gas sources.



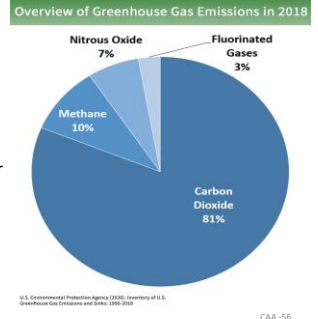
Regulation of Methane Emissions from the Oil and Natural Gas Industry

- Aug 13, 2020, EPA passed a **final Rule** that make changes to the NSPS for emissions from the oil and gas industry by **rescinding the methane NSPS for all segments of the oil and gas industry**.
 - The Rule finds that the **2016 NSPS regulation of methane was improper**, because the Obama EPA did not establish criteria to support its **“significant contribution”** finding. Therefore, the additional methane control requirements in the 2016 rule are thereby removed from NSPS regulation.

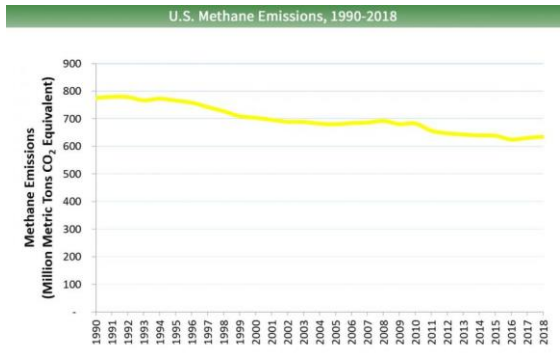
CAA-55

What Percentage of U.S. Total GHG Emissions are from the Oil & Gas Industry?

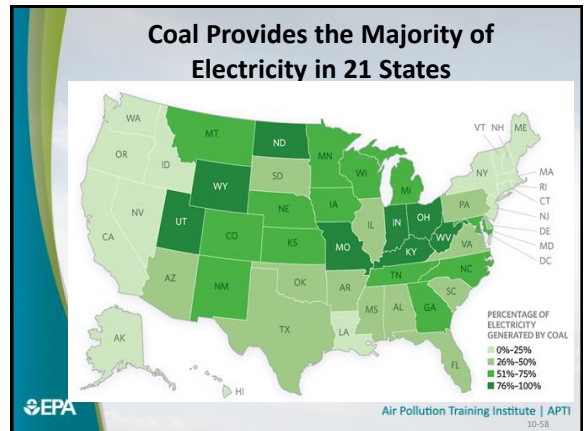
- All GHGs are in CO2 equivalent
- 10% of all US GHGs are Methane
- 28% of U.S. Methane emissions are from Oil & Gas Industry (from earlier slide)
- Therefore, **2.8% of total U.S. GHG emissions are from the Oil & Gas Industry**.



U.S. Methane emissions decreased by 18.1 percent between 1990 and 2018. During this time period, **emissions increased** from agricultural activities sources, while **emissions decreased** from landfills, coal mining, & natural gas and petroleum sources.



Coal Provides the Majority of Electricity in 21 States



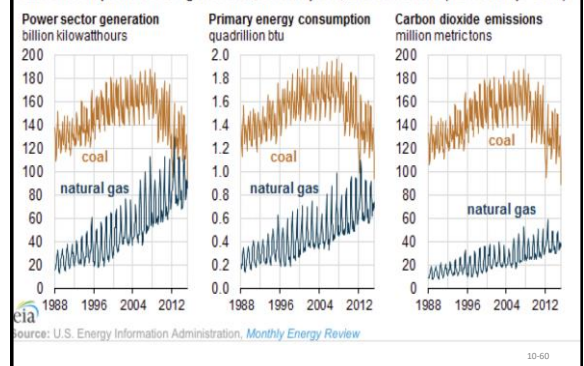
Electricity Net Generation in 2011

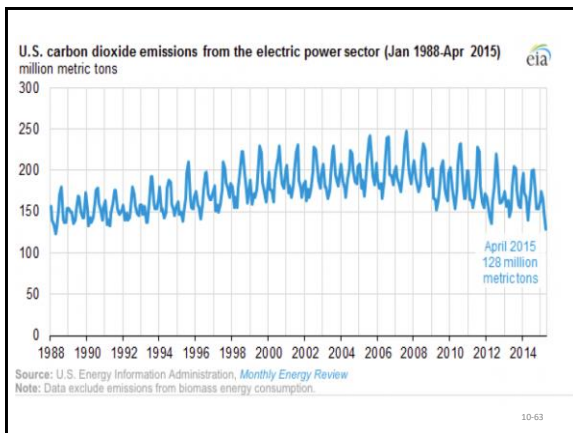
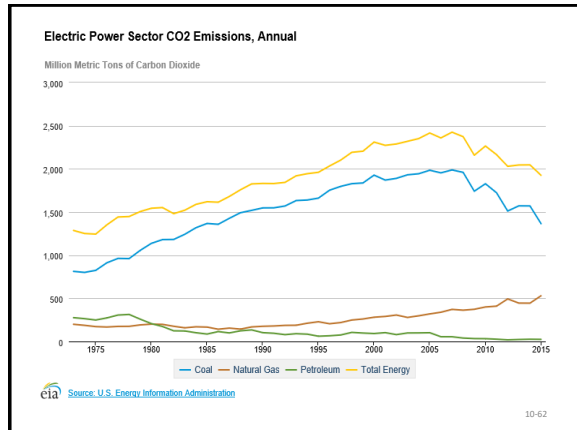
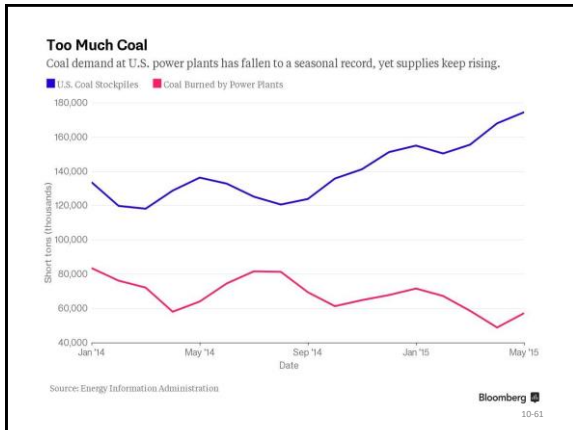
	Net Generation (Billion kWh)	Fuel Source Share
Coal	1,718	43.5%
Petroleum	28	0.7%
Natural Gas	926	23.5%
Other Gases	3	0.1%
Nuclear	790	20.0%
Hydroelectric	312	7.9%
Other	172	4.3%
Total	3,949	100%

Note: Excludes generation from commercial and industrial sectors.
Electric Generating Unit (EGU) – means a solid fuel-fired steam generating unit that produces electricity for sale

10-59

U.S. electric power sector generation, consumption, and emissions (Jan 1988-Apr 2015)





CO₂ Emission Factors for Coal

Coal Rank	CO ₂ Emissions per Unit of Heat Input (lbs CO ₂ /MMBtu)	
	U.S. Average	Range Across States with Coal Rank Deposits
Anthracite	227.4	227.4
Bituminous	205.3	201.3 to 211.6
Subbituminous	211.9	207.1 to 214.0
Lignite	216.3	211.7 to 220.6

Source: U.S. EIA (Honz, R. and E. Slatick, 1994).

Bituminous is also better because it has less moisture than Subbituminous and lignite coals.

EPA Air Pollution Training Institute | APTI 10-64

Selected characteristics for major coal ranks used in EGUs in the U.S.

Coal Rank ²	Higher Heating Value (HHV) Range Defined by ASTM D-388	Typical Coal Moisture Content ³	Coal Delivered for U.S. Electric Power Production in 2008 ⁴		
			Total Coal Quantity Delivered Nationwide (1,000 tons)	Average Ash Content	Average Sulfur Content
Bituminous	>10,500 Btu/lb	2 to 16%	463,943	10.6%	1.68%
Subbituminous	<10,500 Btu/lb and >8,300 Btu/lb	15 to 30%	522,228	5.8%	0.34%
Lignite	< 8,300 Btu/lb	25 to 40%	68,945	13.8%	0.86%

The largest sources of bituminous coals burned in EGUs are mines in regions along the Appalachian Mountains, in southern Illinois, and in Indiana.

The vast majority of subbituminous coals are supplied from mines in Wyoming and Montana, and many EGUs burn subbituminous coals in Wyoming.

10-65

- ### GHG Emissions from ICI Boilers
- Boilers are not EGUs because they are not used for generating electricity (they do not use the steam to run a turbine and generate electricity for the grid).
 - Types and Uses
 - Industrial (Manufacturing, Processing, Mining, etc.)
 - Commercial (Hotels, Motels, Restaurants, etc.)
 - Institutional (Hospitals, Gov. Buildings, Schools, etc.)
 - ICI boilers can use a number of different fuels
 - Coal, fuel oil, natural gas, biomass, & petroleum
 - Coal - highest CO₂ emission factor (93.98 kg CO₂/MMBtu)
 - Natural gas - lowest CO₂ emissions (53.06 kg CO₂/MMBtu)
- EPA Air Pollution Training Institute | APTI 10-66

Efficiency Opportunities for ICI Boilers

- As boilers deteriorate, this results in:
 - Higher heat rates,
 - Increased CO₂ emissions,
 - Reduced reliability and reduced output
- Efficiency can be improved by upgrading burners, adding boiler insulation and other measures outlined in Table 10-9 your Student Guide (APTI 415).
 - Efficiency Improvement Percentage
 - CO₂ Reduction Percentage
 - Capital Costs

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Other Measures to Reduce GHG Emissions from Boilers

- Alternative Fuels – Biomass
 - Biomass has less calorific content than traditional fossil fuels
 - Biomass examples: *waste wood products, grasses, and green algae*
- Co-firing: Burning more than one fuel
 - Biomass or gas fuels contain less sulfur or mercury, therefore less SO₂ and mercury emissions.
 - CO₂ emissions are lower from co-firing biomass with coal than those from burning coal alone (EPA).
- Fuel Switching
 - Coal fired Systems
 - Oil-fired Systems

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Key Characteristics of Biomass Co-firing Compared to Coal

- Biomass has lower density; hence it is bulkier and affects the fuel handling equipment (pulverizers, fuel transport and fuel feed systems).
- High moisture content, above 40 percent, increases the time required for complete combustion and affect boiler efficiency.
- Biomass is more volatile than coal; biomass contains up to 80 percent volatile matter (on a dry-weight basis) compared to a maximum of 45 percent for coal; hence it is easier to self-ignite.
- High alkali biomass may contribute to formation of alkali sulfates, which make it easier to clean the boiler heating surface through sootblowing.
- Biomass degrades over time, which means that it cannot be stored for long periods of time.
- Biomass may contain high concentration of chloride, causing corrosion, especially if sulfur is also present in the fuel (either in the biomass or the coal).

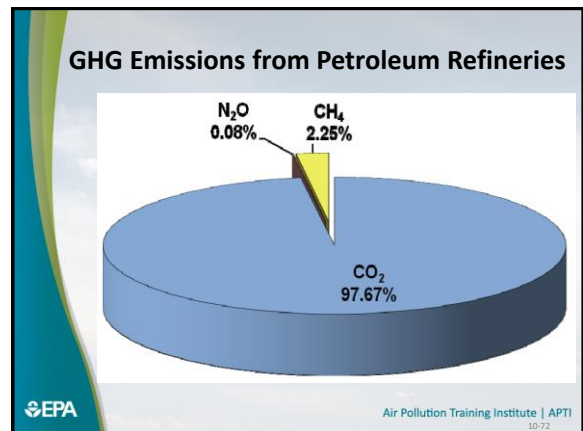
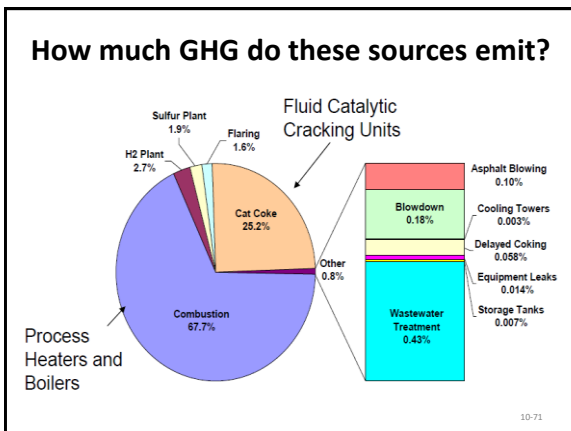
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The Petroleum Refinery Sector

- ▶ 150 refineries in US
- ▶ About 20% of world crude production
- ▶ The nation's second largest industrial source of GHGs & the second-highest industrial consumer of energy (mostly fossil fuel for combustion)




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GHG Emission Reduction Measures 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
 - Process Control Systems
- Table 10-14 (in Student Guide –APTI 415) summarizes the GHG reduction measures currently available for petroleum refining



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10-73

CARBON DIOXIDE REDUCTION TECHNOLOGIES



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Adaption & Mitigation

- Adaptation and mitigation are two strategies for responding to climate change.
- **Adaptation** is the process of adjustment to climate change & its effects in order to either lessen harm or exploit beneficial opportunities.
 - i.e. farmer planting more drought-resistant crops to a city ensuring that new coastal infrastructure can accommodate future sea level rise.
- **Mitigation** is the process of reducing emissions or enhancing sinks of GHGs, so as to limit future climate change.

452-2-75

Possible Mitigating Solutions

- Carbon cap & trade system and carbon tax
- Reducing the carbon intensity of the energy sector
 - Energy efficiency
 - Eliminate coal-fired power plants
 - In 2015, 50% of nations electricity was from coal-fired plants. In 2020, it was reduced to 20% because of increase efficiency & reduced cost of alternative forms of energy (including low cost of natural gas). Source: U.S. Energy Information Agency
 - Carbon capture & sequestration
 - Alternate forms of energy production: wind, solar, nuclear power, & biomass technologies
 - Clean energy vehicles & green buildings
- Conservation of forests, wetlands, agriculture, land use

452-2-76

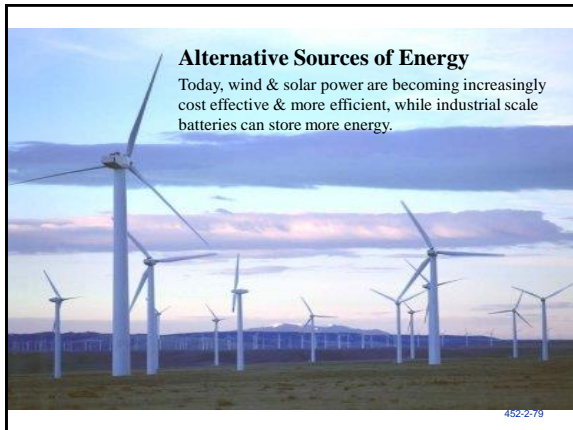
IPCC 2007 Report: Key Mitigation Technologies & Practices by Sector

Sector	Key mitigation technologies and practices currently commercially available	Key mitigation technologies and practices projected to be commercialized before 2030
Energy supply [4.3, 4.4]	Improved supply and distribution efficiency; fuel switching from coal to gas; nuclear power; renewable heat and power (hydropower, solar, wind, geothermal, and bioenergy); combined heat and power; early applications of Carbon Capture and Storage (CCS, e.g. storage of removed CO ₂ from natural gas).	CCS for gas, biomass and coal-fired electricity generating facilities; advanced nuclear power; advanced renewable energy, including tidal and waves energy, concentrating solar, and solar PV.
Transport [5.4]	More fuel efficient vehicles; hybrid vehicles; cleaner diesel vehicles; biofuels; modal shifts from road transport to rail and public transport systems; non-motorised transport (cycling, walking); land-use and transport planning.	Second generation biofuels; higher efficiency aircraft; advanced electric and hybrid vehicles with more powerful and reliable batteries.
Buildings [6.5]	Efficient lighting and daylighting; more efficient electrical appliances and heating and cooling devices; improved cook stoves, improved insulation; passive and active solar design for heating and cooling; alternative refrigeration fluids, recovery and recycle of fluorinated gases.	Integrated design of commercial buildings including technologies, such as intelligent meters that provide feedback and control; solar PV integrated in buildings.

452-2-77

Sector	Key mitigation technologies and practices currently commercially available	Key mitigation technologies and practices projected to be commercialized before 2030
Industry [7.5]	More efficient end-use electrical equipment; heat and power recovery; material recycling and substitution; control of non-CO ₂ gas emissions; and a wide array of process-specific technologies.	Advanced energy efficiency; CCS for cement, ammonia, and iron manufacture; inert electrodes for aluminium manufacture.
Agriculture [8.4]	Improved crop and grazing land management to increase soil carbon storage; restoration of cultivated peaty soils and degraded lands; improved rice cultivation techniques and livestock and manure management to reduce CH ₄ emissions; improved nitrogen fertilizer application techniques to reduce N ₂ O emissions; dedicated energy crops to replace fossil fuel use; improved energy efficiency.	Improvements of crops yields.
Forestry/forests [9.4]	Afforestation; reforestation; forest management; reduced deforestation; harvested wood product management; use of forestry products for bioenergy to replace fossil fuel use.	Tree species improvement to increase biomass productivity and carbon sequestration. Improved remote sensing technologies for analysis of vegetation/ soil carbon sequestration potential and mapping land use change.
Waste management [10.4]	Landfill methane recovery; waste incineration with energy recovery; composting of organic waste; controlled waste water treatment; recycling and waste minimization.	Biocovers and biotifiers to optimize CH ₄ oxidation.

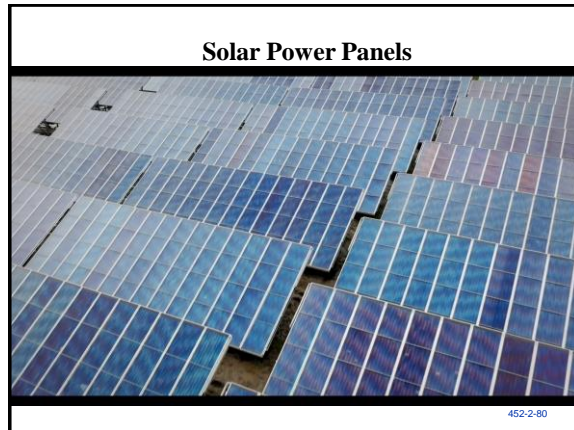
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Alternative Sources of Energy

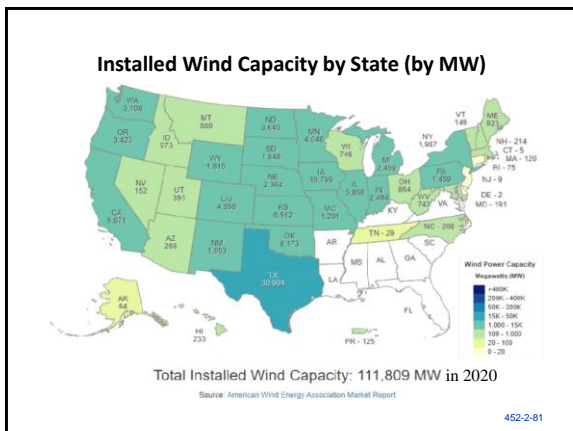
Today, wind & solar power are becoming increasingly cost effective & more efficient, while industrial scale batteries can store more energy.

452-2-79



Solar Power Panels

452-2-80



452-2-81

Carbon Capture and Storage (CCS): A Three Step Process

- Capture of CO₂ from power plants or industrial processes
- Transport of the captured & compressed CO₂ (usually in pipelines)
- Underground injection and geologic sequestration (also referred to as storage) of the CO₂ into deep underground rock formations. These formations are often a mile or more beneath the surface and consist of porous rock that holds the CO₂. Overlying these formations are impermeable, non-porous layers of rock that trap the CO₂ and prevent it from migrating upward.
- EPA's CCS Web site: <http://www.epa.gov/climatechange/ccs/index.html#Federal>

452-2-82

CCS Processes: Capturing CO₂

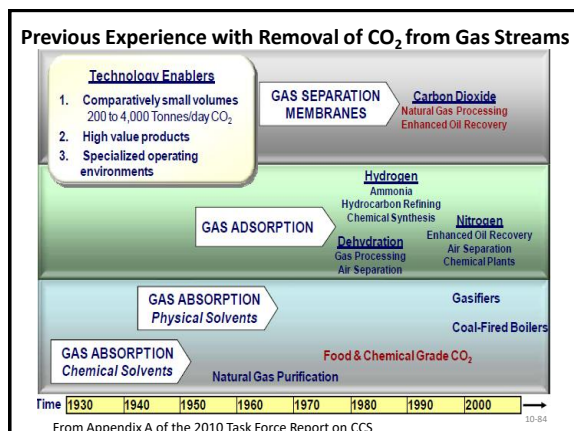
U.S. DOE is developing a commercially viable processes for capturing CO₂ from EGUs:

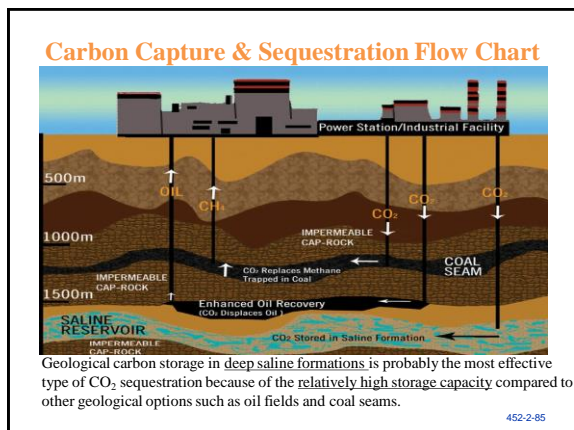
- Amine-based solvent systems (absorption)
- Solid sorbents (adsorption)
- Membrane-based capture
- Oxy-combustion

CO₂ is stripped from the flue gas by the absorption process. Upon saturation, the absorbent is regenerated by desorbing the CO₂ back to gaseous form. The removed CO₂ is then compressed, sent to storage and sequestered.

Since the 1930s, the CO₂ absorption processes has been used to produce food & chemical grade CO₂ from gas streams containing 3 to 25 percent CO₂.

EPA





Problems with CCS (at Fossil Fuel Combustion Units)

- The challenge from a separation perspective is the low driving force for CO₂ separation because of:
 - low CO₂ partial pressure & low CO₂ concentrations &
 - large volume of gas to be treated.
- As a result, CCS requires intensive energy use and a high cost.
 - Carbon capture (using absorption process) at a pulverized coal-fired power plant will impose an increase in the cost of electricity of approximately 80%. The majority is attributable to parasitic power loss (60%).

10-86

March 2015 AWMA Article

- The challenge from a separation perspective is:
 - that the flue gas from conventional fossil fuel combustion exhibits relatively low CO₂ concentrations (i.e., 10–15 vol% from coal-fired boilers and 4–7 vol% from natural gas combined cycles and boilers) and
 - low pressures (i.e., near atmospheric pressure).
- This results in a low driving force for CO₂ separation (i.e., low CO₂ partial pressure) and a large volume of gas to be treated. As a result, PCC requires intensive energy use and tends to incur a large equipment footprint and a high cost.
- Carbon capture (using absorption process) at a pulverized coal-fired power plant equipped will impose an increase in the cost of electricity (COE) of approximately 80%. Of this COE increase, the majority is attributable to parasitic power loss (60%).

10-87

U.S. Task Force on CCS: 2010 Report

- Concluded that cost-effective deployment of CCS will occur only if the technology is commercially available at economically competitive prices and supportive national policy frameworks are in place.
- Barriers:
 - First, rates of conversion must be comparable to rates of CO₂ capture.
 - Second, energy requirements for conversion must be low.
 - Third, potential volumes of reactants and/or products may limit the scale of reuse relative to total emissions.

452-2-88

Congressional Research Service Report (Jan. 2020)

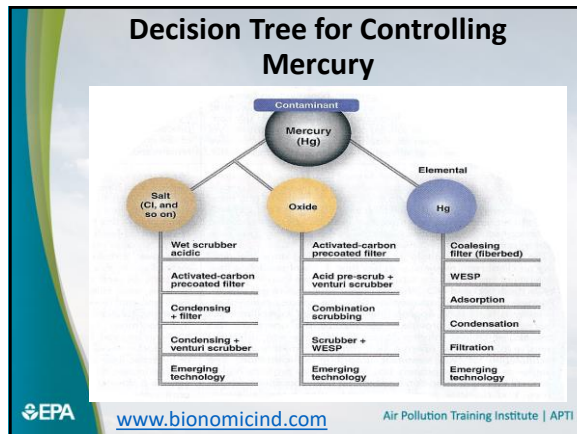
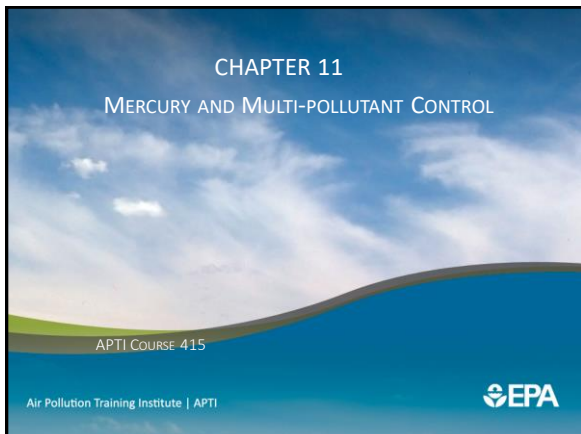
- Analysts expect that the costs of CCS (on new or existing facilities) are likely to total several billion dollars per project, which could act as a barrier to future CCS deployment without the continuation of subsidies.
- To date in the U.S., there are nine DOE-supported CCS projects (injected large volumes of CO₂ into underground formations).
- Earthquakes induced by CO₂ injection could fracture the rocks in the reservoir or, more importantly, the caprock above the reservoir.

452-2-89

CO₂ Mineralization

- This is a chemical reaction that occurs when certain minerals are exposed to the CO₂, resulting in the CO₂ being transformed into rock.
- CO₂ mineralization processes fall under three main categories:
 - Carbonation: CO₂ reacts with calcium (Ca) or magnesium (Mg) oxide to form a solid carbonated mineral. These carbonated products can be used in building materials, etc.
 - Concrete Curing: A similar process to carbonation, but with a focus on producing solid calcium carbonate (CaCO₃)-limestone. (It can also be added to concrete).
 - Novel Cements: CO₂ is used as an ingredient within the cement. The CO₂ is mineralized within the cement as a solid carbonate, creating a new carbon negative cement.
- CO₂ mineralization is one of the only options that results in permanent storage of CO₂ as a solid. Other technologies merely delay the time that the CO₂ takes to go back into the atmosphere.

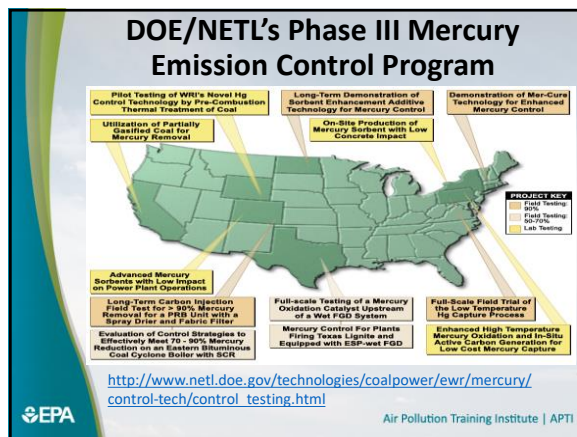
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- ### Control Technologies for Mercury Emissions
- Mercury's high vapor pressure at typical APCD operating temperatures causes collection by PM control devices is highly variable.
 - Factors that enhance mercury control are low temperature, high levels of carbon in the fly ash and the presence of hydrogen chloride (HCl).
 - Conversely, sulfur dioxide (SO₂) in flue gas can convert oxidized mercury to elemental mercury, making it more difficult to collect.
- Air Pollution Training Institute | APTI

- ### Common Controls to Reduce Mercury Emissions
- Some of the most common add-on controls to reduce mercury emissions include:
- Carbon filter beds
 - Wet scrubbing
 - Selenium filters
 - Activated carbon injection
- Air Pollution Training Institute | APTI

- ### Controlling Power Plant Mercury Emissions
- Currently, there are two main approaches being considered for controlling power plant mercury emissions:
- Reducing mercury emissions using technologies primarily designed to remove SO₂, NO_x, and particulate emissions (often called co-benefit reductions), and
 - Reducing mercury emissions using technologies specifically designed to reduce mercury in coal prior to burning.
- Air Pollution Training Institute | APTI



DOE/NETL's Phase II Mercury Control Program

DOE/NETL's Phase II Mercury Control Technology Field Testing Program
 UPDATED Economic Analysis of Activated Carbon Injection

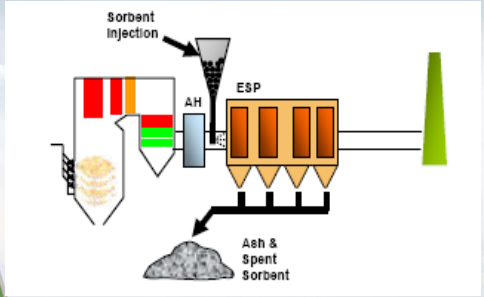
Prepared for:
 U.S. Department of Energy
 Office of Fossil Energy
 National Energy Technology Laboratory
 Innovations for Existing Plants Program

Prepared by:
 Andrew P. Jones¹, Jeffrey W. Hoffmann², Dennis N. Smith¹, Thomas J. Feeley, III¹,
 and James T. Schryber¹

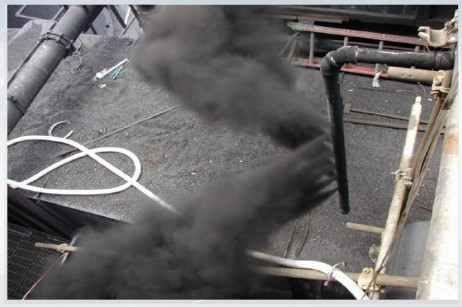
¹ Research and Development Solutions, LLC
² U.S. Department of Energy, National Energy Technology Laboratory
 U.S. Department of Energy, Office of Fossil Energy

May 2007

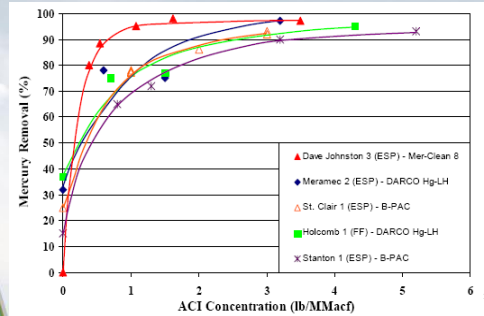
Activated Carbon Injection Technology Schematic



Powdered Activated Carbon Injection



ACI Performance Data for Phase II Units Firing PRB Coal



Integrated Multi-pollutant Control

