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 2012

Updated by William Franek & Louis DeRose
February, 2024

Course 415

Control of Gaseous Emissions

February 5 - 9, 2024

AGENDA

LOCATION	**MODERATORS**
Virtual Training for CenSARA	Louis DeRose / William Franek

DAY & TIME	SUBJECT	SPEAKER
***Day One* (Central Time)**		
9:00	Introduction	W. Franek
9:15	Basic 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
1:15	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
1:15	ADJOURN	
Day Three		
9:00	Absorption Systems (continued)	W. Franek
10:45	BREAK	
11:00	Oxidation Systems Chapter 6	L. DeRose
1:15	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
1:15	ADJOURN	
Day Five		
9:00	Pre-Test Review	
9:30	Control of SO2 Chapter 9	W. Franek
10:45	BREAK	
11:00	Control of NOx Chapter 8	
12:30	Mercury and Multipollutant Controls Chapter 11	W. Franek
1:15	ADJOURN	

Course Instructors:

William J. Franek, Ph.D., P.E., DEE
William J. Franek, LLC
6807 West 64th Place,
Chicago, IL. 60638
E-mail: billfranek@gmail.com

Louis DeRose, J.D., M.S., P.E.
Attorney at Law
221 Orchard Lane,
Glen Ellyn, IL 60137
E-mail: louderose@yahoo.com

Presented Virtually
February 2024

CONTROL OF GASEOUS EMISSIONS

APTI COURSE 415
Air Pollution Training Institute | APTI

CHAPTER 1

INTRODUCTION TO CONTROL OF GASEOUS EMISSIONS

Air Pollution Training Institute | APTI

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.

Air Pollution Training Institute | APTI

Two Types of Gaseous Contaminants

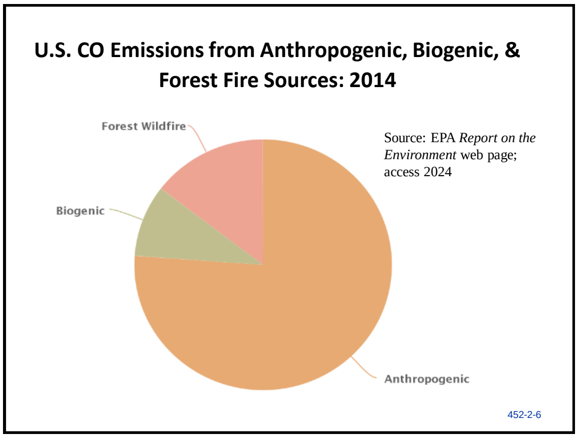
- **Primary contaminants**: emitted directly from the stack and/or process equipment:
  - Sulfur dioxide, nitric oxide and nitrogen dioxide, carbon monoxide, VOCs, hydrogen chloride and hydrogen fluoride, hydrogen sulfide, and ammonia
- **Secondary contaminants**: formed due to reactions between primary pollutants in the atmosphere and/or other compounds:
  - NO_2, (NO combines with oxygen in the air), ozone (from NO_2, VOC & sunlight), & sulfuric acid & nitric acid (when SO_2 and NO_2 mix with water in clouds)

Air Pollution Training Institute | APTI

Carbon Monoxide (CO) & Partially Oxidized Organic Compounds (POCs)

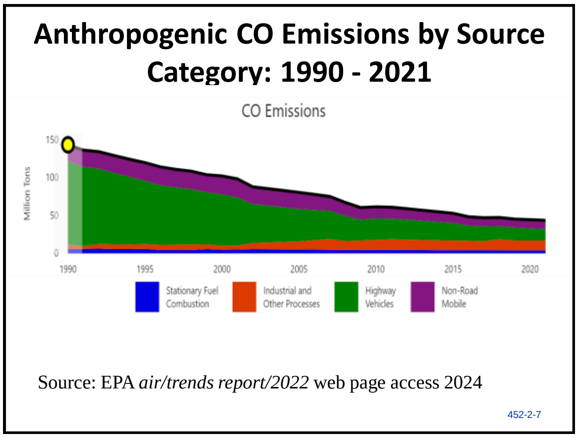
- ***Carbon Monoxide (CO)***
  - Results from the incomplete combustion of fuel and other organic compounds
  - Difficult to oxidize: Requires temperatures of >1800°F (1000°C)
  - Chemical asphyxiant: CO reduces the oxygen in blood because the affinity of hemoglobin for CO is over 200 times that for oxygen
  - Colorless, odorless and insoluble in water
- ***POCs*** refer to a broad range of species formed during incomplete combustion process

Air Pollution Training Institute | APTI



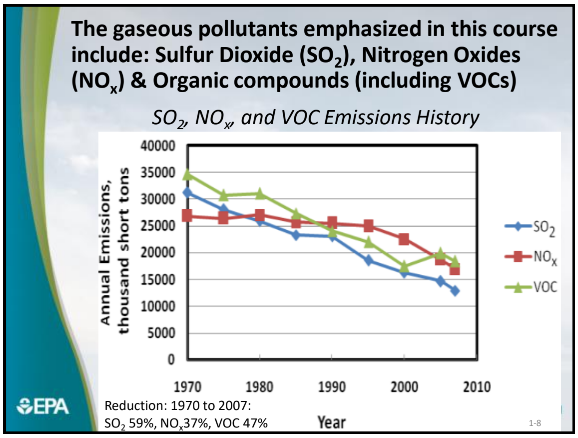
U.S. CO Emissions from Anthropogenic, Biogenic, & Forest Fire Sources: 2014

Source: EPA *Report on the Environment* web page; access 2024



Anthropogenic CO Emissions by Source Category: 1990 - 2021

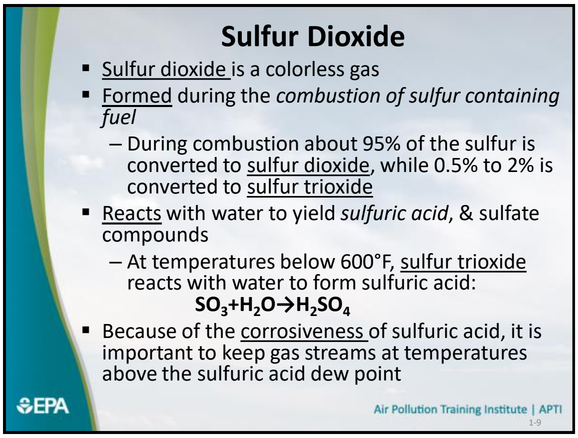
Source: EPA *air/trends report/2022* web page access 2024



The gaseous pollutants emphasized in this course include: Sulfur Dioxide (SO_2), Nitrogen Oxides (NO_x) & Organic compounds (including VOCs)

SO_2, NO_x, and VOC Emissions History

Reduction: 1970 to 2007:
SO_2 59%, NO_x37%, VOC 47%



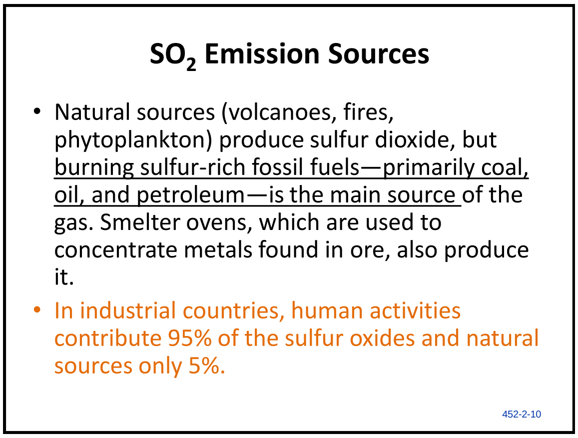
Sulfur Dioxide

- Sulfur dioxide is a colorless gas
- Formed during the *combustion of sulfur containing fuel*
  - During combustion about 95% of the sulfur is converted to sulfur dioxide, while 0.5% to 2% is converted to sulfur trioxide
- Reacts with water to yield *sulfuric acid*, & sulfate compounds
  - At temperatures below 600°F, sulfur trioxide reacts with water to form sulfuric acid:

$$SO_3 + H_2O \rightarrow H_2SO_4$$

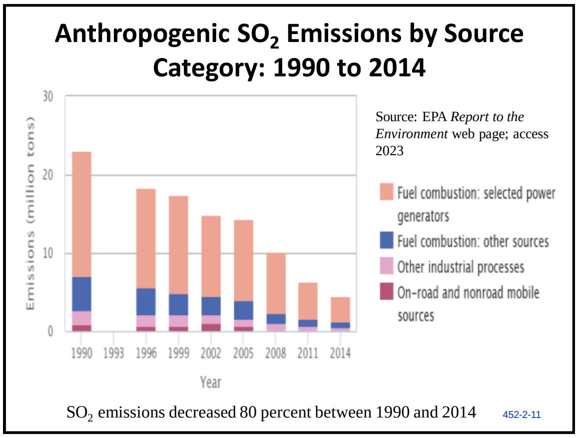
- Because of the corrosiveness of sulfuric acid, it is important to keep gas streams at temperatures above the sulfuric acid dew point

Air Pollution Training Institute | APTI



SO_2 Emission Sources

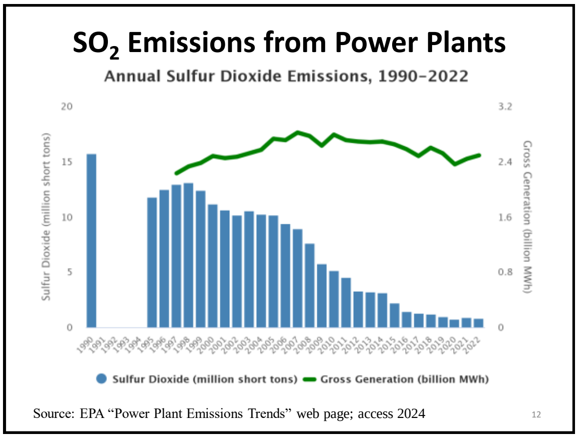
- Natural sources (volcanoes, fires, phytoplankton) produce sulfur dioxide, but burning sulfur-rich fossil fuels—primarily coal, oil, and petroleum—is the main source of the gas. Smelter ovens, which are used to concentrate metals found in ore, also produce it.
- In industrial countries, human activities contribute 95% of the sulfur oxides and natural sources only 5%.



Anthropogenic SO_2 Emissions by Source Category: 1990 to 2014

Source: EPA *Report to the Environment* web page; access 2023

SO_2 emissions decreased 80 percent between 1990 and 2014



SO_2 Emissions from Power Plants

Source: EPA “Power Plant Emissions Trends” web page; access 2024

Nitric Oxide and Nitrogen Dioxide

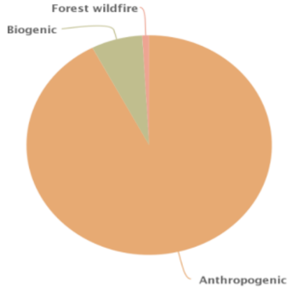
- Collectively referred to as NO_x
- 3 types of NO_x formation:
  - Thermal NO_x: *thermal* fixation of atmospheric N_2 [N_2 from air at high temperatures]
  - Fuel NO_x: *oxidation* of organic nitrogen compounds in the fuel (reacts with O_2 from excess air)
  - Prompt NO_x: *reaction* with partially oxidized compounds within the flame (least produced)
- Nitric Oxide (NO) –odorless gas & insoluble in water
- Nitrogen Dioxide (NO_2) –moderately soluble in water, has a distinct reddish-brown color
  - Nitric acid pickling operations

Air Pollution Training Institute | APTI

1-13

NOx Emissions in the U.S. (2014)

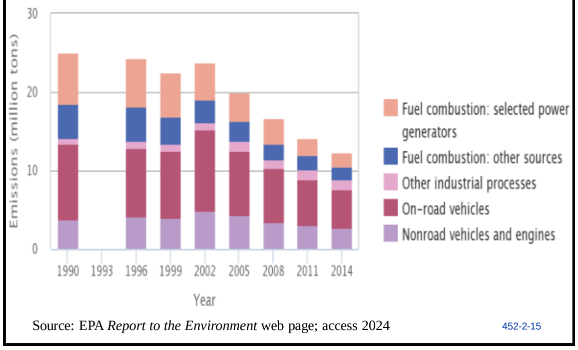
Emissions from Biogenic, Anthropogenic, & Wildfire Sources



Source: EPA *Report on the Environment* web page; access 2023

452-2-14

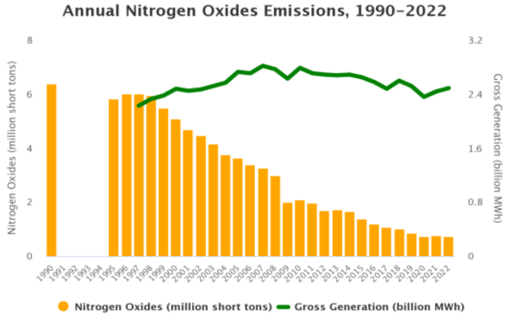
Anthropogenic NO_X Emissions by Source Category: 1990 - 2014



Source: EPA *Report to the Environment* web page; access 2024

452-2-15

NO_X Emissions from Power Plants



Source: EPA "Power Plant Emissions Trends " web page; access 2024

16

Volatile Organic Compounds (VOCs)

- VOCs are organic compounds that can volatilize and participate in photochemical reactions upon release to the atmosphere.
- (40 CFR 51.100) EPA defines *any organic compound* to be a VOC *unless* it is specifically determined to have negligible photochemical reactivity (list on next slide).
  - Most organic compounds are classified as VOCs.
- Dominant source is the vaporization of organic compounds used as solvents in industrial processes.

Air Pollution Training Institute | APTI

1-17

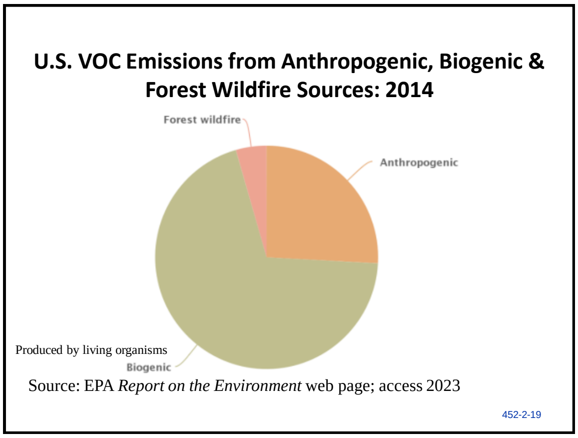
Organic Compounds NOT Classified as VOCS

(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

Air Pollution Training Institute | APTI

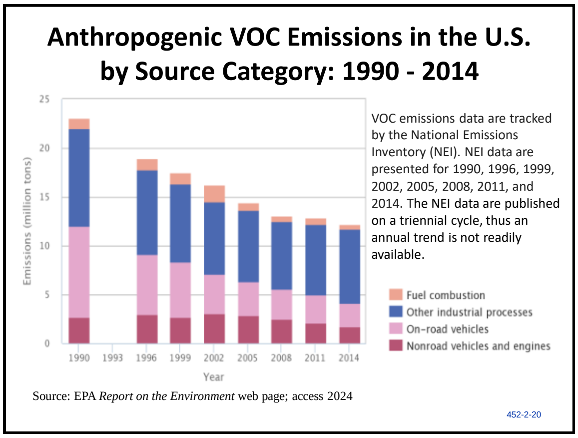
1-18



U.S. VOC Emissions from Anthropogenic, Biogenic & Forest Wildfire Sources: 2014

Produced by living organisms

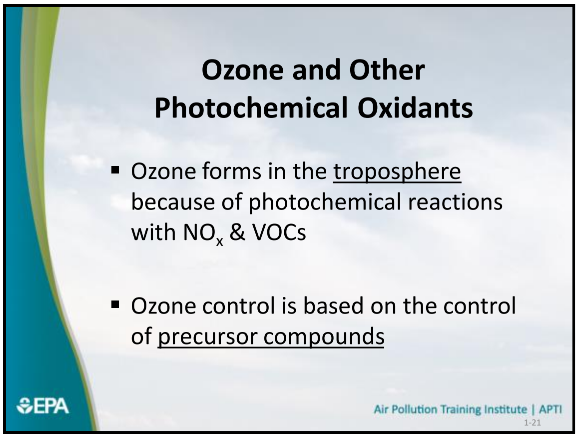
Source: EPA *Report on the Environment* web page; access 2023



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

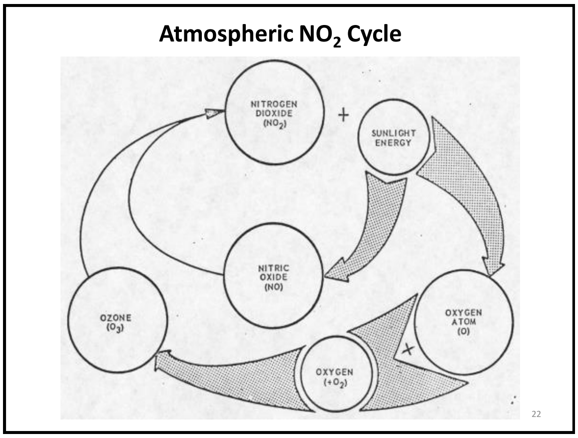
VOC emissions data are tracked by the National Emissions Inventory (NEI). NEI data are presented for 1990, 1996, 1999, 2002, 2005, 2008, 2011, and 2014. The NEI data are published on a triennial cycle, thus an annual trend is not readily available.

Source: EPA *Report on the Environment* web page; access 2024

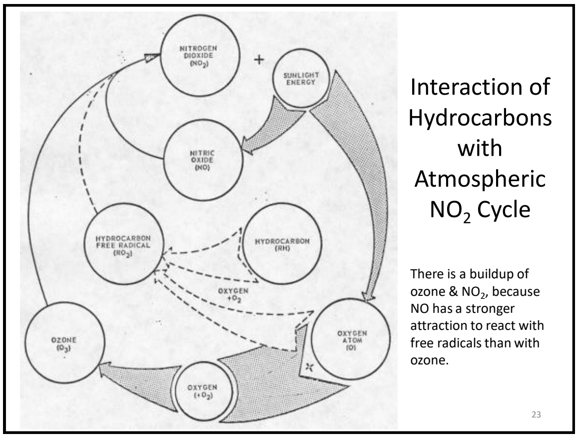


Ozone and Other Photochemical Oxidants

- Ozone forms in the troposphere because of photochemical reactions with NO_x & VOCs
- Ozone control is based on the control of precursor compounds

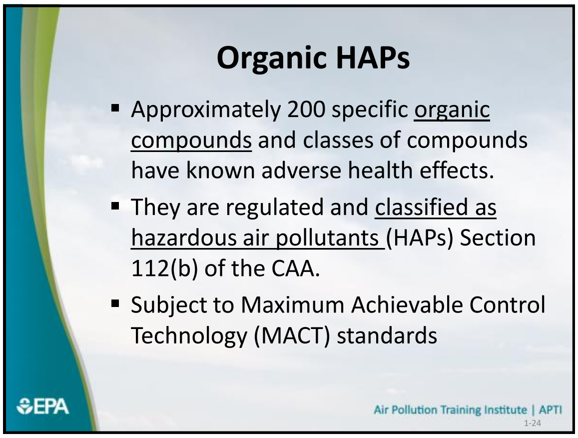


Atmospheric NO_2 Cycle



Interaction of Hydrocarbons with Atmospheric NO_2 Cycle

There is a buildup of ozone & NO_2, because NO has a stronger attraction to react with free radicals than with ozone.



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

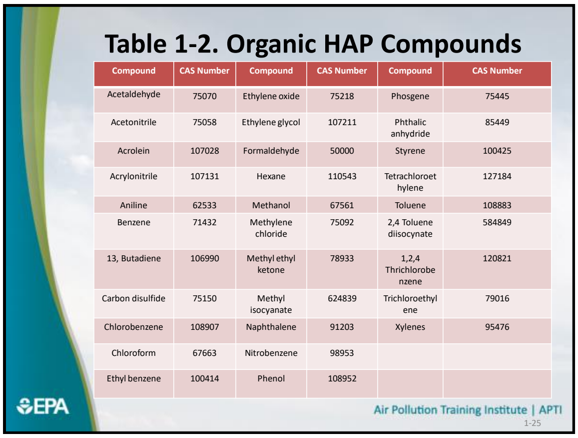
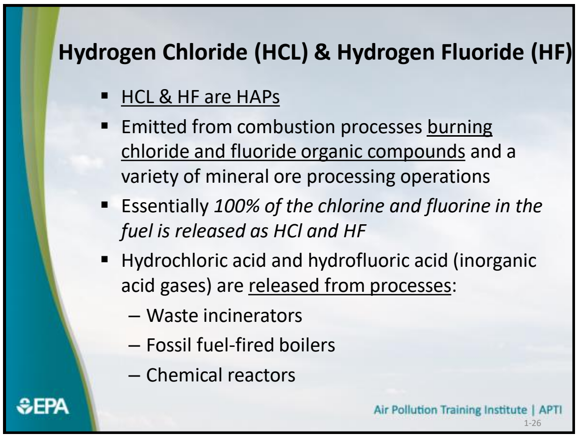


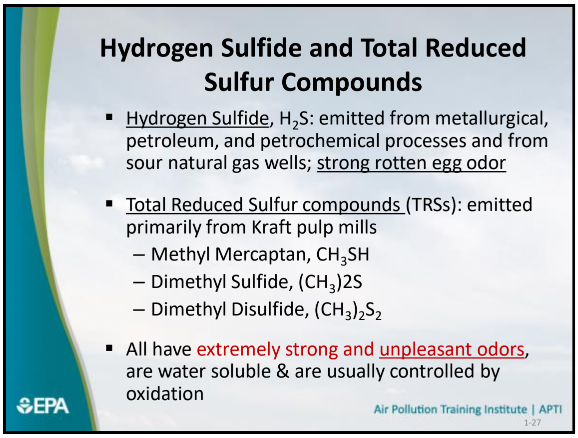
Table 1-2. Organic HAP Compounds

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	62533	Methanol	67561	Toluene	108883
Benzene	71432	Methylene chloride	75092	2,4 Toluene diisocynate	584849
13, Butadiene	106990	Methyl ethyl ketone	78933	1,2,4 Thrichlorobenzene	120821
Carbon disulfide	75150	Methyl isocyanate	624839	Trichloroethylene	79016
Chlorobenzene	108907	Naphthalene	91203	Xylenes	95476
Chloroform	67663	Nitrobenzene	98953		
Ethyl benzene	100414	Phenol	108952		



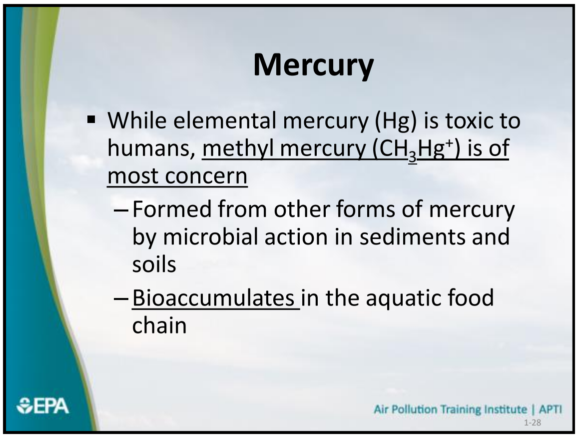
Hydrogen Chloride (HCL) & Hydrogen Fluoride (HF)

- HCL & HF are HAPs
- 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*
- Hydrochloric acid and hydrofluoric acid (inorganic acid gases) are released from processes:
  - Waste incinerators
  - Fossil fuel-fired boilers
  - Chemical reactors



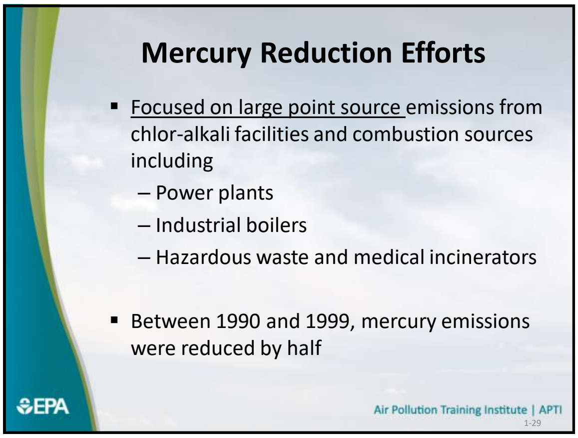
Hydrogen Sulfide and Total Reduced Sulfur Compounds

- Hydrogen Sulfide, H_2S: emitted from metallurgical, petroleum, and petrochemical processes and from sour natural gas wells; strong rotten egg odor
- Total Reduced Sulfur compounds (TRSs): emitted primarily from Kraft pulp mills
  - Methyl Mercaptan, CH_3SH
  - Dimethyl Sulfide, $(CH_3)2S$
  - Dimethyl Disulfide, $(CH_3)_2S_2$
- All have extremely strong and unpleasant odors, are water soluble & are usually controlled by oxidation



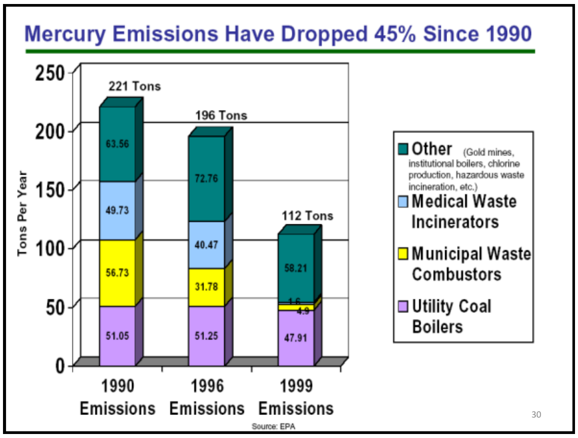
Mercury

- While elemental mercury (Hg) is toxic to humans, methyl mercury (CH_3Hg^+) is of most concern
  - Formed from other forms of mercury by microbial action in sediments and soils
  - Bioaccumulates in the aquatic food chain



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



Mercury Emissions Have Dropped 45% Since 1990

Source: EPA

Solid Waste Combustion: CAA δ129

- δ129 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)
- δ129 limits emissions of particulate matter, carbon monoxide, dioxins/furans, sulfur dioxide, nitrogen oxides, hydrogen chloride, lead, **mercury**, and cadmium
- δ129 does not regulate incineration of hazardous waste.

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.)

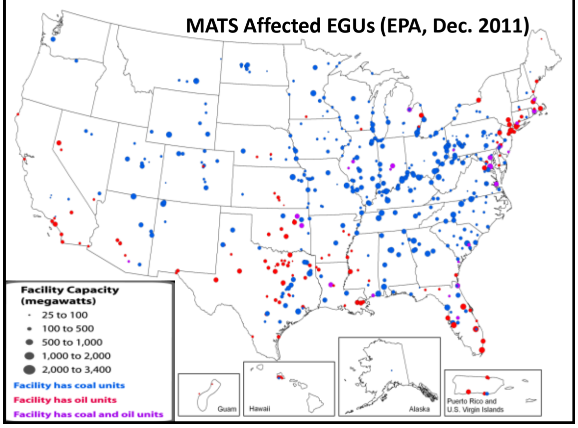
Mercury Emissions from Power Plants

- **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).

Mercury Emissions from Power Plants

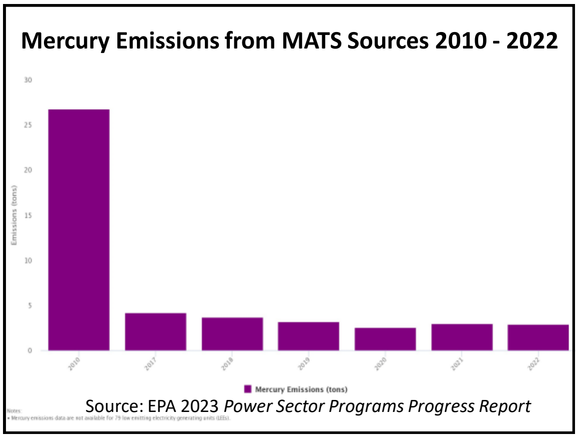
- **On Feb 6, 2012**, EPA passed a coal &/or oil fired power plant mercury MACT (called MATS –Mercury Air Toxic Standard)
  - Applies to EGUs larger than 25 megawatts (MW) that burn coal or oil for the purpose of generating electricity (600 power plants).
  - Will reduce emissions of mercury & other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

MATS Affected EGUs (EPA, Dec. 2011)



Mercury Emissions from Power Plants

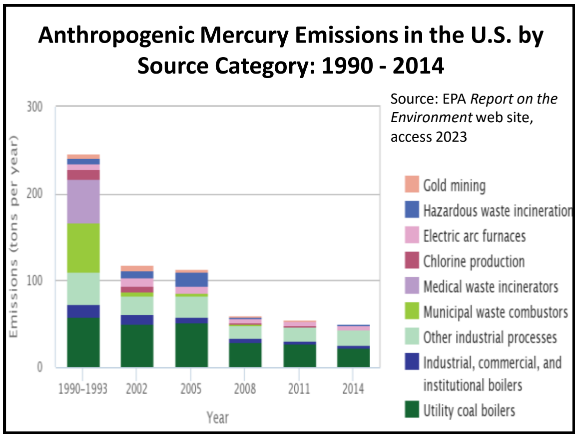
- **In 2016**, EPA finds that the cost of compliance with MATS is reasonable to satisfy the *2015 SCOTUS requirement*.
  - Costs = $10 billion/yr.
  - Benefits = $6 billion/yr. from mercury reductions only;
  - Co-benefits = $60 billion/yr. from reductions of non-HAPs
- **May 22, 2020**: EPA rejects the value of co-benefits, therefore the *costs* of such regulation grossly outweigh the HAP benefits.
- **Feb 15, 2023**: EPA final rule: This action revokes the above 2020 rule. (EPA's will use the previous, 2016, cost analysis.)
- **April 3, 2023**: EPA proposed rule:
  - that lignite-fired EGUs meet the same mercury emission standard as EGUs firing other types of coal (i.e., bituminous and subbituminous), &
  - to further limit the emission of non-mercury HAP metals from existing coal-fired power plants.



Mercury Emissions from MATS Sources 2010 - 2022

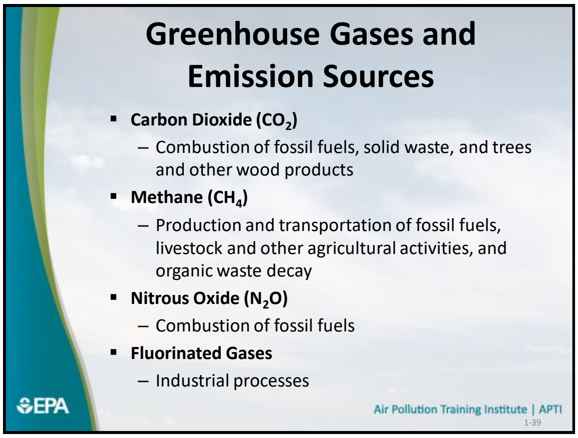
Source: EPA 2023 *Power Sector Programs Progress Report*

Notes:
• Mercury emissions data are not available for 79 low emitting electricity generating units (LEEs).



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

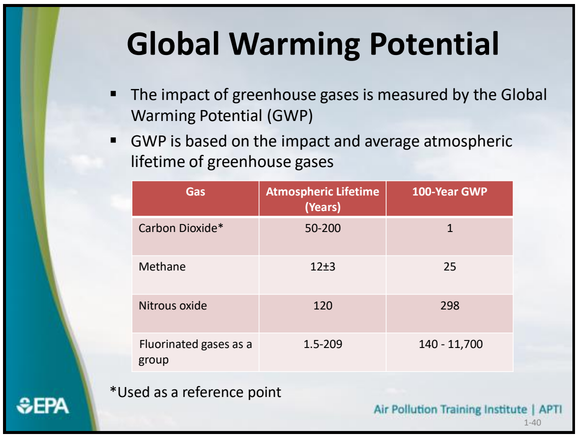
Source: EPA *Report on the Environment* web site, access 2023



Greenhouse Gases and Emission Sources

- **Carbon Dioxide (CO_2)**
  - Combustion of fossil fuels, solid waste, and trees and other wood products
- **Methane (CH_4)**
  - Production and transportation of fossil fuels, livestock and other agricultural activities, and organic waste decay
- **Nitrous Oxide (N_2O)**
  - Combustion of fossil fuels
- **Fluorinated Gases**
  - Industrial processes

Air Pollution Training Institute | APTI



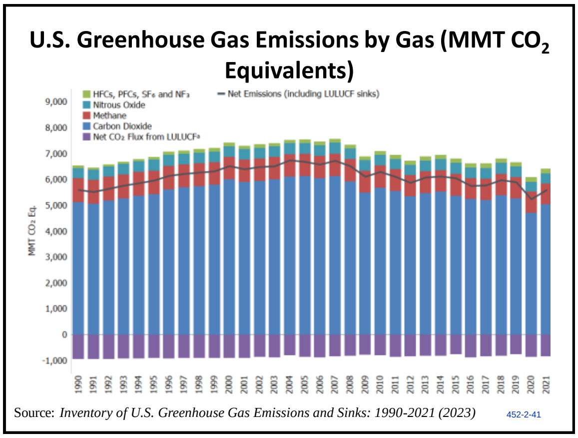
Global Warming Potential

- 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

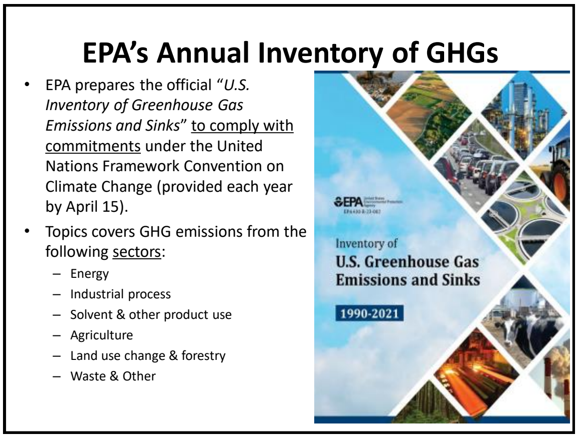
*Used as a reference point

Air Pollution Training Institute | APTI



U.S. Greenhouse Gas Emissions by Gas (MMT CO_2 Equivalents)

Source: *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2021 (2023)* 452-2-41



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

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

EPA Air Pollution Training Institute | APTI

State & Local Control Initiatives

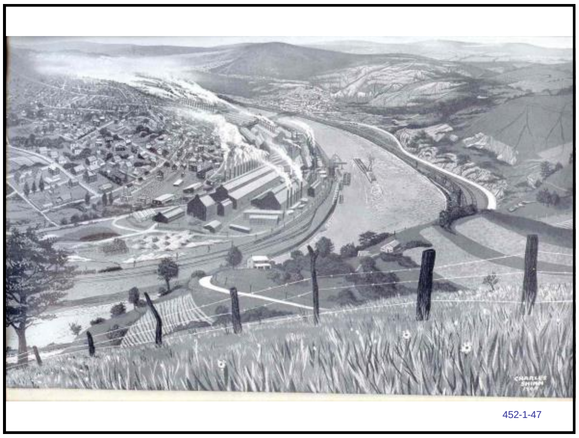
- After 1850, the U.S. industrial revolution took hold; centering on steel, iron with abundant coal usage.
  - "*Smoke is the incense burning on the altars of industry. It is beautiful to me*." by a Chicago businessman in 1892.
  - Public Policy favored business: economic growth over human health & property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

State & Local Control Initiatives

- After 1850, the U.S. industrial revolution started; 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: from 1860 to 1930, SCOTUS ruled for economic growth over human health & property protection until FDR & his New Deal programs.
- In 1881, Chicago & Cincinnati passed municipal regulations of smoke emissions, and by 1912, most major U.S. cities followed.

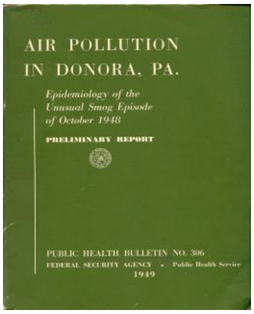
Donora Episode: Oct. 26, 1948

- 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.



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."



AIR POLLUTION IN DONORA, PA.

Epidemiology of the Unusual Smog Episode of October 1948

PRELIMINARY REPORT

PUBLIC HEALTH BULLETIN NO. 306
FEDERAL SECURITY AGENCY • Public Health Service
1949

Contaminant Regulations

- Prior to1950 some *states and local agencies enacted particulate pollutant control regulations (opacity)* & were not aware of gaseous contaminants effects such as SO_2, 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.

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

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

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

National Ambient Air Quality Standards (NAAQS)

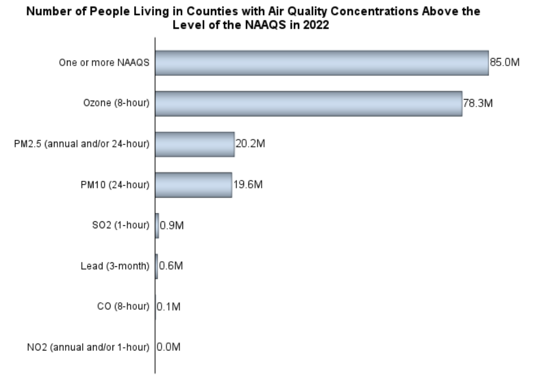
- Apply to sulfur dioxide, nitrogen oxides, photochemical oxidants, and carbon monoxide
- Primary standards are more restrictive and are designed to protect human health with an "*adequate margin of safety*"
- Secondary standards are intended to reduce adverse material effects, such as crop damage and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

EPA

Air Pollution Training Institute | APTI

National Ambient Air Quality Standards

Pollutant		*Averaging Time*	*Primary*	*Secondary*
PM-2.5	*(2012)*	Annual	12 µg/m³	None
PM-2.5	*(2006)*	Annual	None	15 µg/m³
PM-2.5	*(2006)*	24-hour	35 µg/m³	Same
PM-10	*(1987)*	24-hour	150 µg/m³	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/m³	Same



Source: EPA's Air Trends Website; access 2024

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.

.

NSPS for Fossil Fuel-fired Electric Power Generating Facilities

Table 1-7. New source performance standards for fossil fuel-fired electric power generating facilities

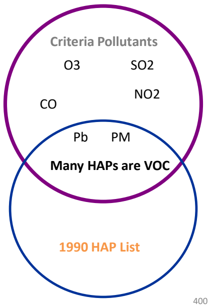
Category	Fuel Type	Emission Limit	Reduction Requirement
Particulate Matter	Solid	0.015 $lb_m/10^6$ Btu[A]	99.9%
SO_2	Liquid	1.4 lb_m/MWh	95%
SO_2	Coal Refuse	1.4 lb_m/MWh	94%
		<0.6 $lb_m/10^6$ Btu	70%
NO_X	Solid	0.5 $lb_m/10^6$ Btu	65%
NO_X	Liquid	0.3 $lb_m/10^6$ Btu	30%
NO_X	Gas	0.2 $lb_m/10^6$ Btu	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.

Overlap Between HAPs and Criteria Pollutants

- PMs is comprised of many chemicals, some which may be HAPs
- Lead Compounds: (HAP) Lead: Criteria Pollutant
- Many HAPs are VOC
  - Ozone formation

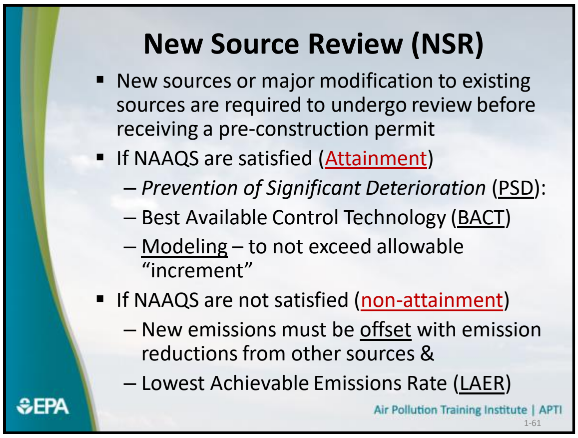


Hazardous Air Pollutants: Pre-1990 Program

- 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)

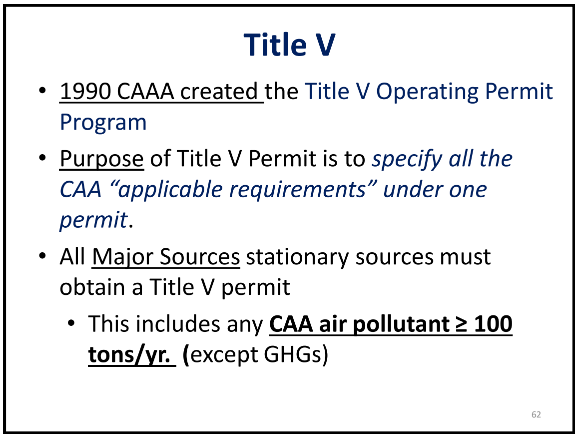
Post-1990 HAP Program

- 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)



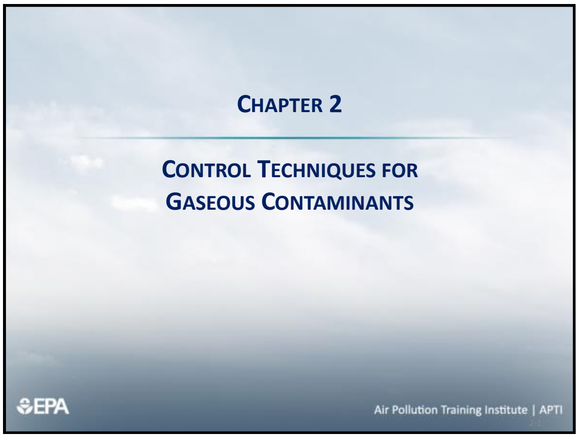
New Source Review (NSR)

- 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)



Title V

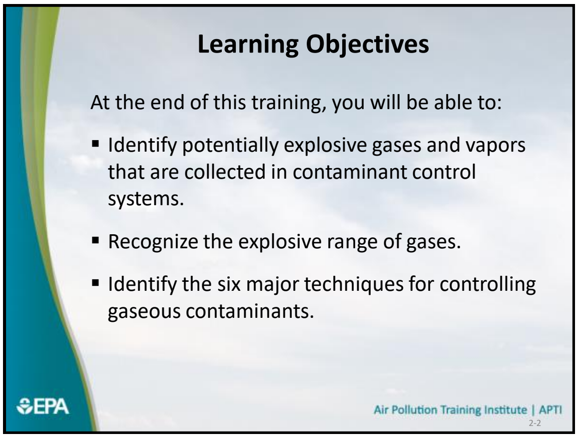
- 1990 CAAA created the Title V Operating Permit Program
- Purpose of Title V Permit is to *specify all the CAA "applicable requirements" under one permit*.
- All Major Sources stationary sources must obtain a Title V permit
  - This includes any **CAA air pollutant ≥ 100 tons/yr.** (except GHGs)



CHAPTER 2

CONTROL TECHNIQUES FOR GASEOUS CONTAMINANTS

EPA Air Pollution Training Institute | APTI

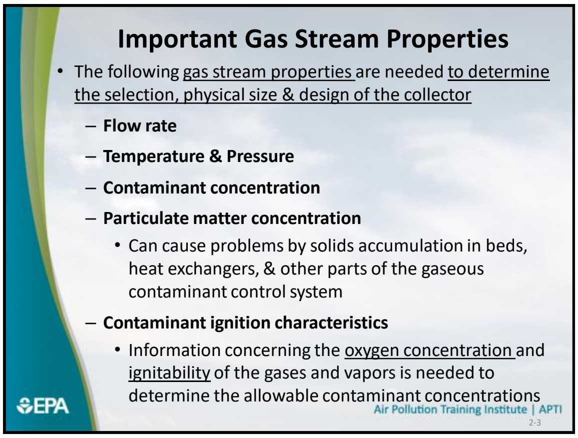


Learning Objectives

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.

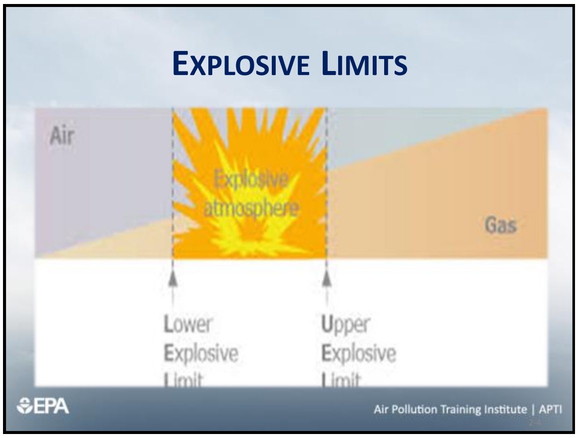
EPA Air Pollution Training Institute | APTI



Important Gas Stream Properties

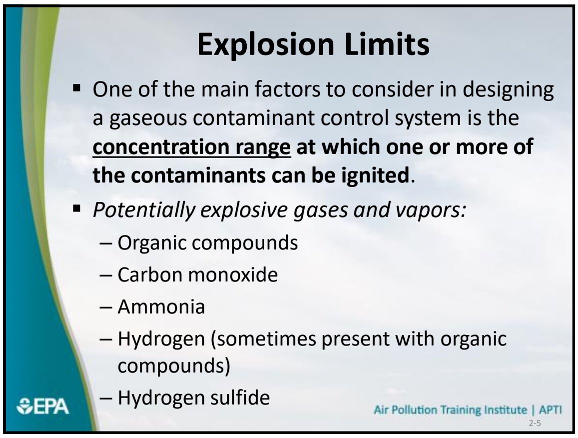
- The following gas stream properties are needed to determine the selection, physical size & design of the collector
  - **Flow rate**
  - **Temperature & Pressure**
  - **Contaminant concentration**
  - **Particulate matter concentration**
    - Can cause problems by solids accumulation in beds, heat exchangers, & other parts of the gaseous contaminant control system
  - **Contaminant ignition characteristics**
    - Information concerning the oxygen concentration and ignitability of the gases and vapors is needed to determine the allowable contaminant concentrations

EPA Air Pollution Training Institute | APTI



EXPLOSIVE LIMITS

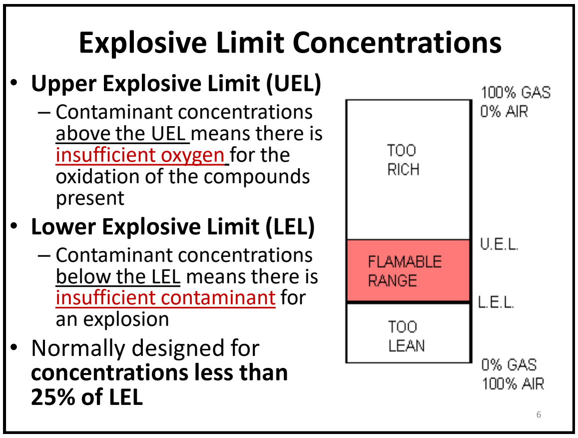
EPA Air Pollution Training Institute | APTI



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

EPA Air Pollution Training Institute | APTI



Explosive Limit Concentrations

- **Upper Explosive Limit (UEL)**
  - Contaminant concentrations above the UEL means there is insufficient oxygen for the oxidation of the compounds present
- **Lower Explosive Limit (LEL)**
  - Contaminant concentrations below the LEL means there is insufficient contaminant for an explosion
- Normally designed for **concentrations less than 25% of LEL**

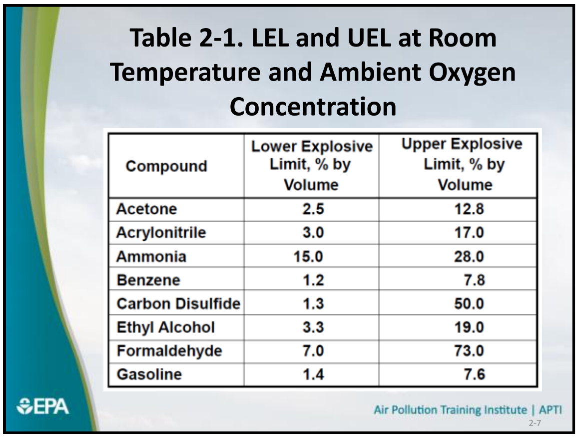


Table 2-1. LEL and UEL at Room Temperature and Ambient Oxygen Concentration

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

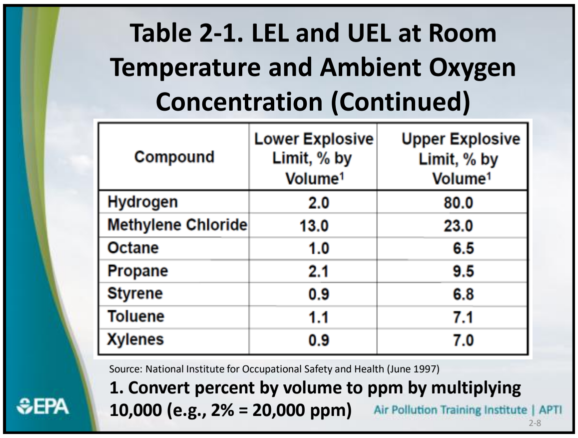
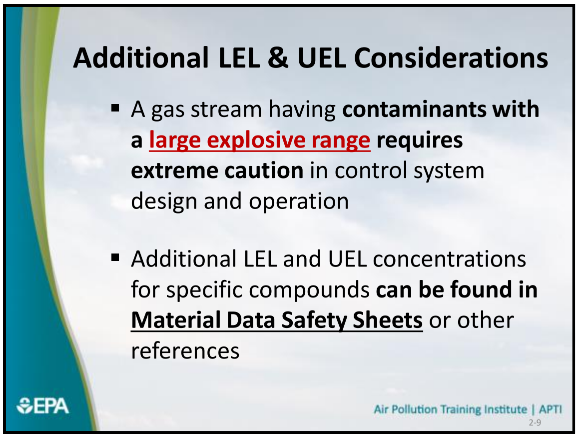


Table 2-1. LEL and UEL at Room Temperature and Ambient Oxygen Concentration (Continued)

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

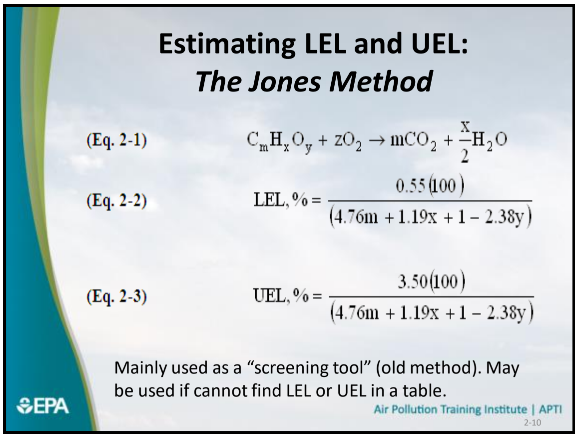
Source: National Institute for Occupational Safety and Health (June 1997)

1. Convert percent by volume to ppm by multiplying 10,000 (e.g., 2% = 20,000 ppm)



Additional LEL & UEL Considerations

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



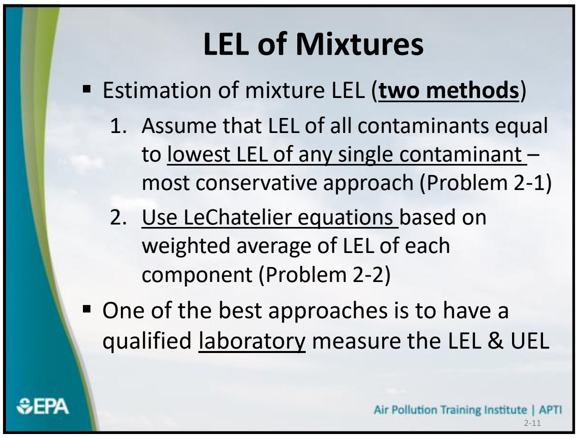
Estimating LEL and UEL:
The Jones Method

(Eq. 2-1) $$C_mH_xO_y + zO_2 \rightarrow mCO_2 + \frac{x}{2}H_2O$$

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

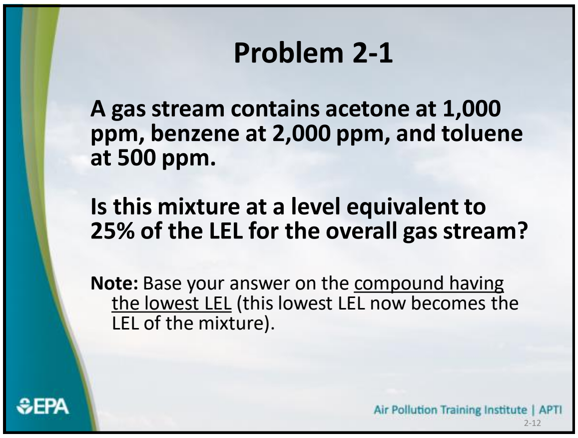
(Eq. 2-3) $$UEL, \% = \frac{3.50(100)}{(4.76m + 1.19x + 1 - 2.38y)}$$

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



LEL of Mixtures

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



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 (this lowest LEL now becomes the LEL of the mixture).

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**
  (*my "total contaminant concentration" must be less than 25% of the LEL limit*)
- Total contaminant concentration =
  1,000 ppm + 2,000 ppm + 500 ppm = **3,500 ppm**
- **Answer: No.** Total concentration exceeds 25% LEL value (because 3,500 ppm > 2,750 ppm).

LeChatelier Equations

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

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

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

Problem 2-2

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

LeChatelier Equation 2-4

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

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.

Problem 2-2: Solution

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

$$LEL_{mixture} = \frac{1}{\sum (y_i / LEL_i)}$$

Unit-less

% of concentration

$$LEL_{mixture} = \frac{1}{\left[\frac{\left(\frac{1000}{3500}\right)}{\left(\frac{25000}{1000000}\right)}\right] + \left[\frac{\left(\frac{2000}{3500}\right)}{\left(\frac{12000}{1000000}\right)}\right] + \left[\frac{\left(\frac{500}{3500}\right)}{\left(\frac{11000}{1000000}\right)}\right]}$$

Vi = Acetone (ppm)

Vt = total volume of combustible chemicals

LEL of Acetone in PPM

conversion of LEL from PPM to % of concentration

$$LEL_{mixture} = \frac{1}{11.43 + 47.62 + 12.99} = 0.014 = 14000\text{ppm}$$

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

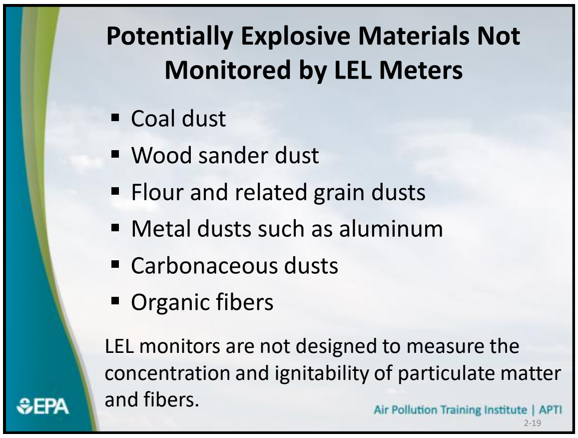
Sources of Ignition

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

Monitoring LEL Concentrations

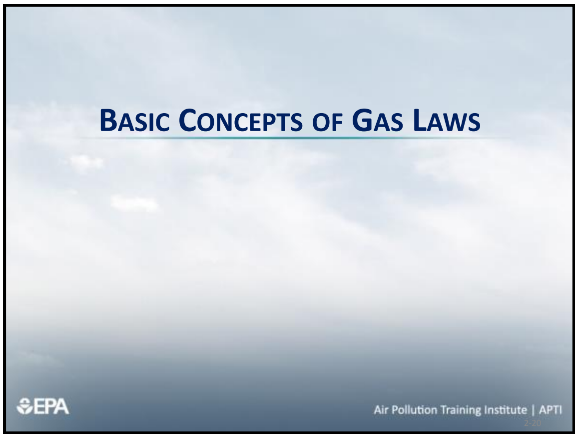
- **LEL monitor purpose**: If the concentration of contaminants exceeds the 25% LEL level, the system can be shut down and the problem corrected.
- Monitor **error readings** can be caused by:
  - – Oxygen levels are lower or higher than the 21% level that the monitor was calibrated at.
  - – Acid gases 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.



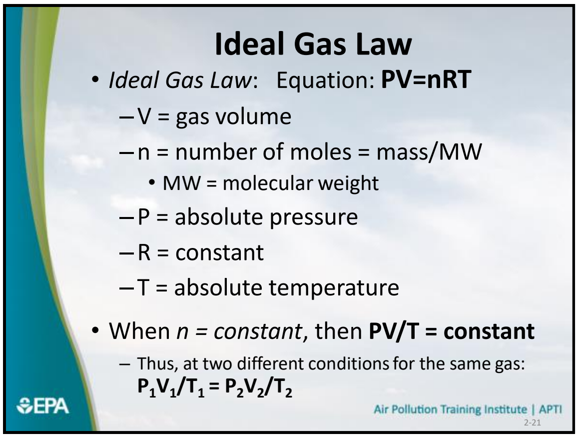
Potentially Explosive Materials Not Monitored by LEL Meters

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

LEL monitors are not designed to measure the concentration and ignitability of particulate matter and fibers.

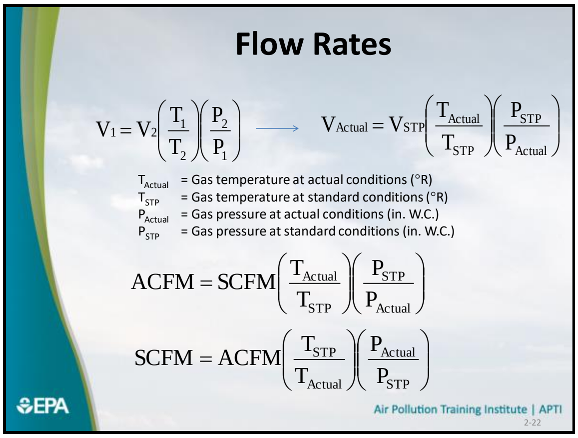


BASIC CONCEPTS OF GAS LAWS



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 = constant*, then **PV/T = constant**
  - Thus, at two different conditions for the same gas: **$P_1V_1/T_1 = P_2V_2/T_2$**



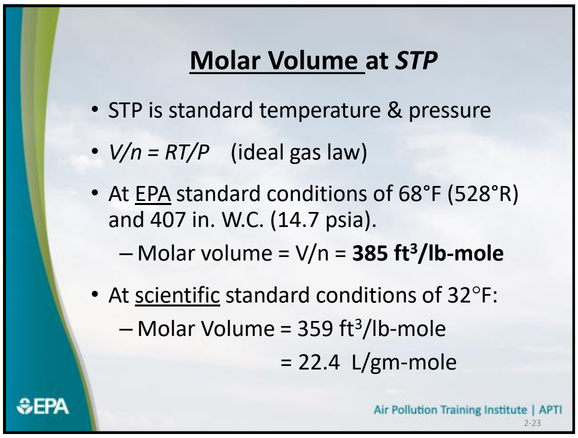
Flow Rates

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

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.)

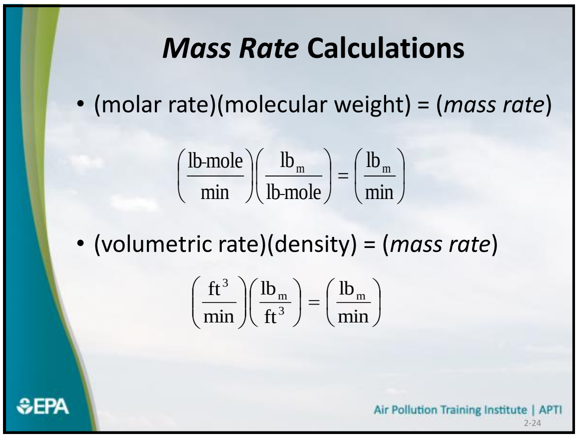
$$ACFM = SCFM\left(\frac{T_{Actual}}{T_{STP}}\right)\left(\frac{P_{STP}}{P_{Actual}}\right)$$

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



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 ft^3/lb-mole**
- At scientific standard conditions of 32°F:
  - Molar Volume = 359 ft^3/lb-mole
    = 22.4 L/gm-mole



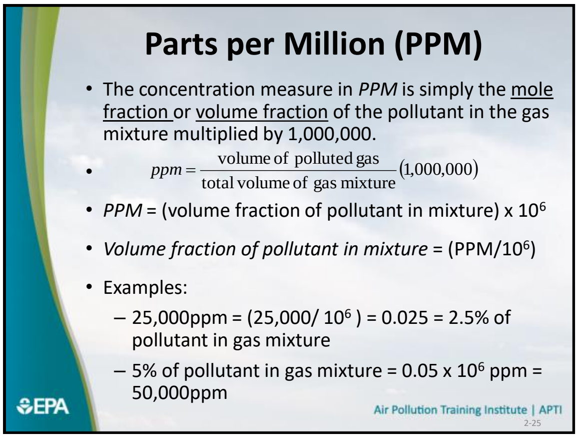
Mass Rate Calculations

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

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

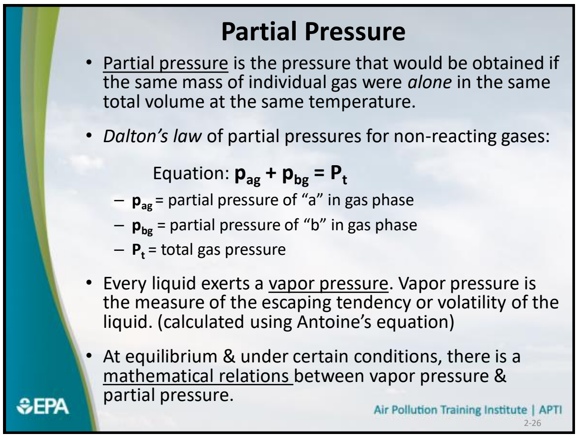
- (volumetric rate)(density) = (*mass rate*)

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



Parts per Million (PPM)

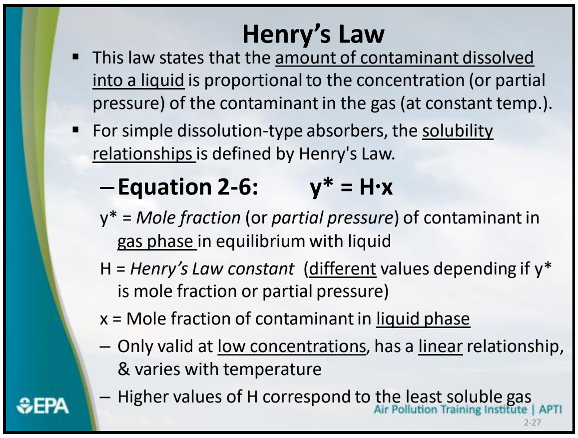
- The concentration measure in *PPM* is simply the mole fraction or volume fraction of the pollutant in the gas mixture multiplied by 1,000,000.
- $ppm = \frac{\text{volume of polluted gas}}{\text{total volume of gas mixture}}(1{,}000{,}000)$
- *PPM* = (volume fraction of pollutant in mixture) x 10^6
- *Volume fraction of pollutant in mixture* = (PPM/10^6)
- Examples:
  - 25,000ppm = (25,000/ 10^6) = 0.025 = 2.5% of pollutant in gas mixture
  - 5% of pollutant in gas mixture = 0.05 x 10^6 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:

  Equation: $\mathbf{p_{ag} + p_{bg} = P_t}$
  - $\mathbf{p_{ag}}$ = partial pressure of "a" in gas phase
  - $\mathbf{p_{bg}}$ = partial pressure of "b" in gas phase
  - $\mathbf{P_t}$ = 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.



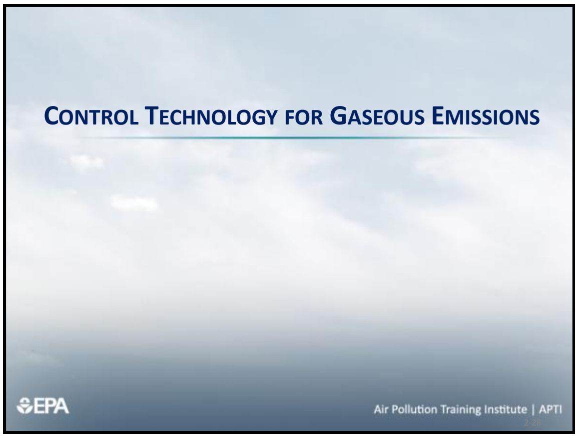
Henry's Law

- This law states that the amount of contaminant dissolved into a liquid is proportional to the concentration (or partial pressure) of the contaminant in the gas (at constant temp.).
- For simple dissolution-type absorbers, the solubility relationships is defined by Henry's Law.
  - **Equation 2-6:** $\mathbf{y^* = H \cdot x}$

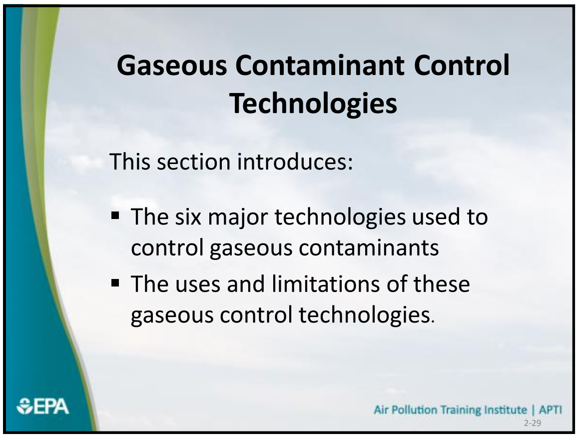
  y* = *Mole fraction* (or *partial pressure*) of contaminant in gas phase in equilibrium with liquid

  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



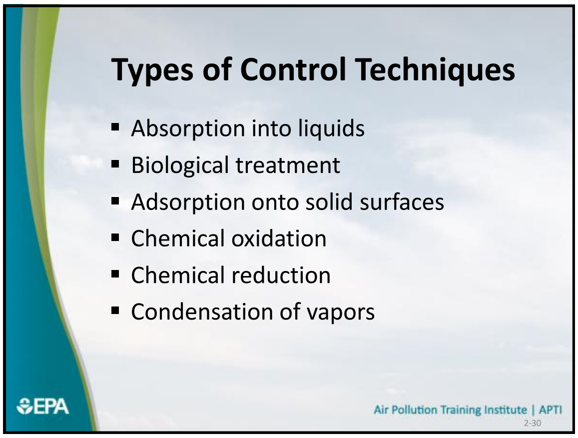
CONTROL TECHNOLOGY FOR GASEOUS EMISSIONS



Gaseous Contaminant Control Technologies

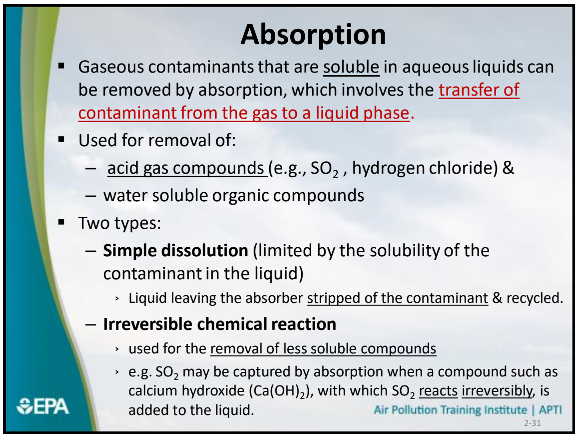
This section introduces:

- 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

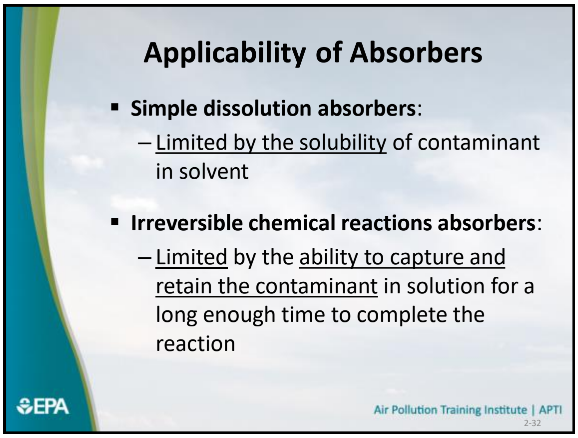


Absorption

- 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., SO_2 , hydrogen chloride) &
  - water soluble organic compounds
- Two types:
  - **Simple dissolution** (limited by the solubility of the contaminant in the liquid)
    - Liquid leaving the absorber stripped of the contaminant & recycled.
  - **Irreversible chemical reaction**
    - used for the removal of less soluble compounds
    - e.g. SO_2 may be captured by absorption when a compound such as calcium hydroxide ($Ca(OH)_2$), with which SO_2 reacts irreversibly, is added to the liquid.

Air Pollution Training Institute | APTI

2-31

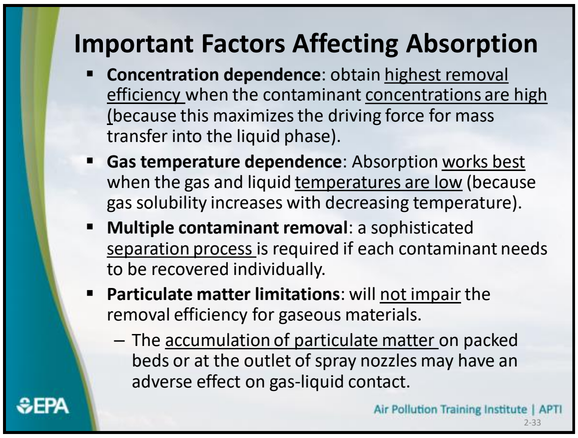


Applicability of Absorbers

- **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

Air Pollution Training Institute | APTI

2-32

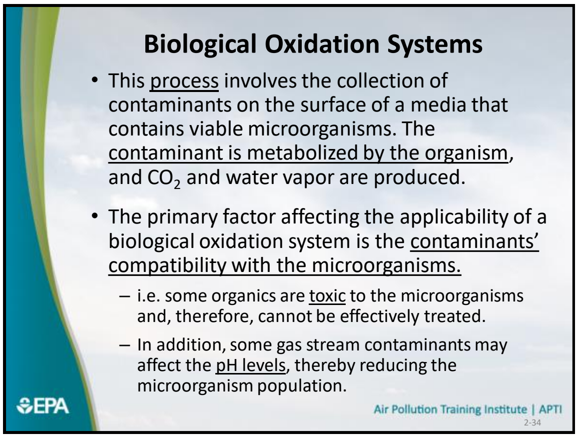


Important Factors Affecting Absorption

- **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.

Air Pollution Training Institute | APTI

2-33

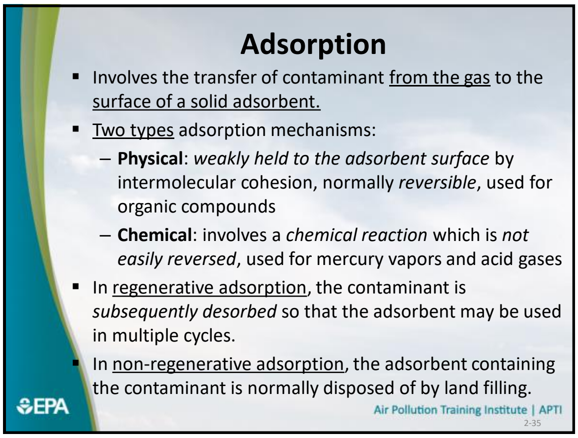


Biological Oxidation Systems

- 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 CO_2 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.

Air Pollution Training Institute | APTI

2-34

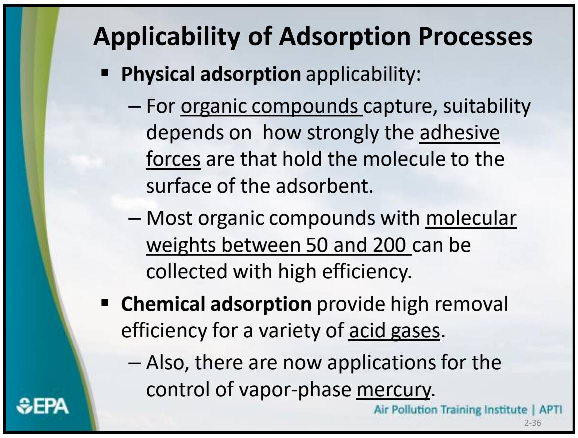


Adsorption

- 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.

Air Pollution Training Institute | APTI

2-35

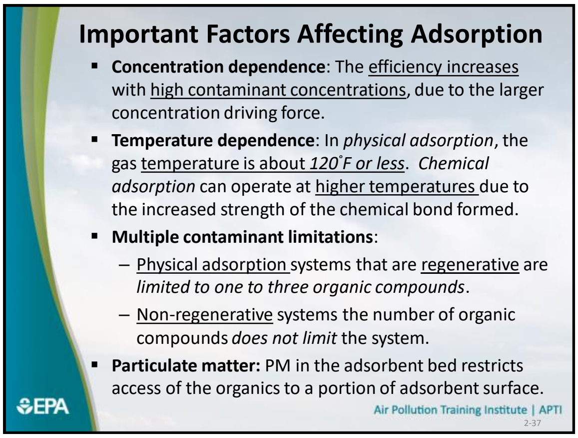


Applicability of Adsorption Processes

- **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.

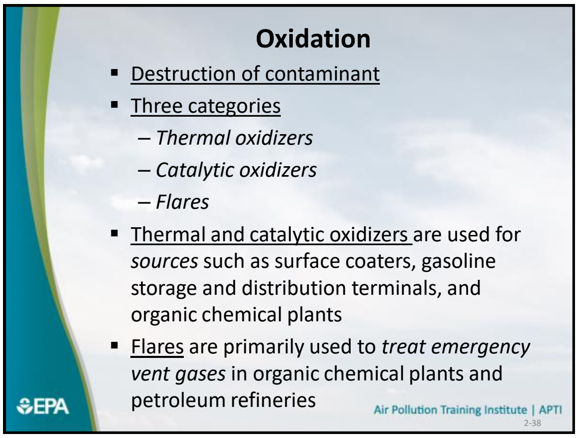
Air Pollution Training Institute | APTI

2-36



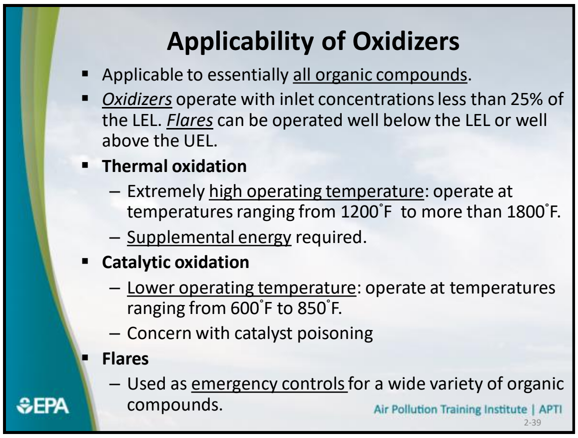
Important Factors Affecting Adsorption

- **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.



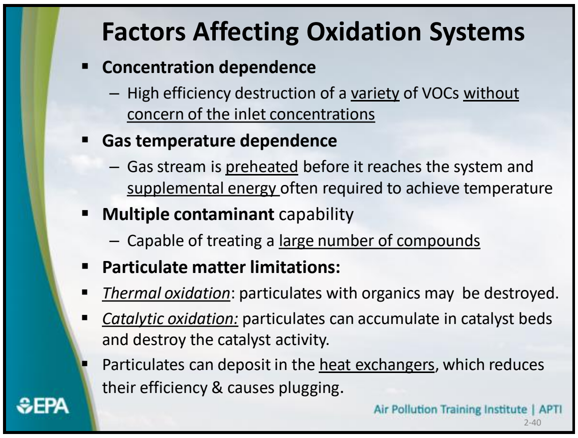
Oxidation

- 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



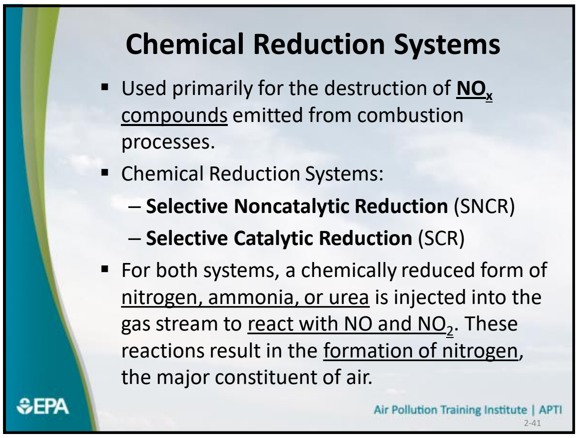
Applicability of Oxidizers

- 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.



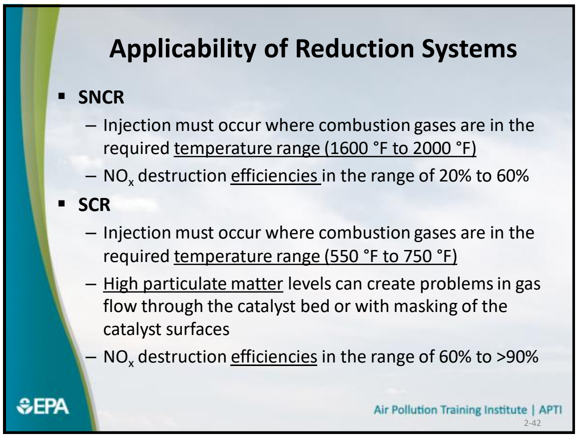
Factors Affecting Oxidation Systems

- **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.



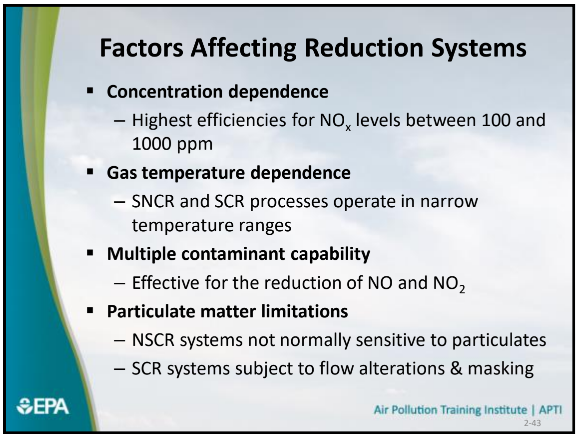
Chemical Reduction Systems

- 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 NO_2. These reactions result in the formation of nitrogen, the major constituent of air.



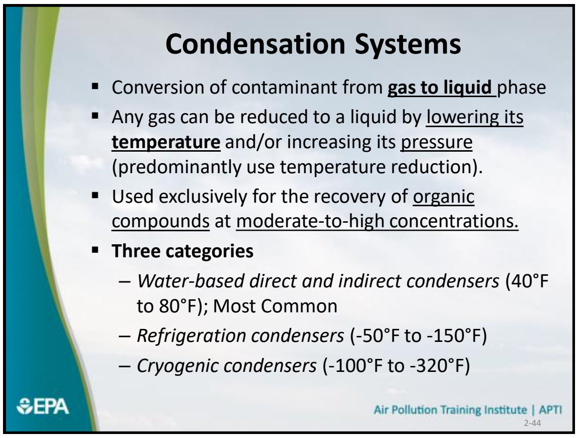
Applicability of Reduction Systems

- **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%



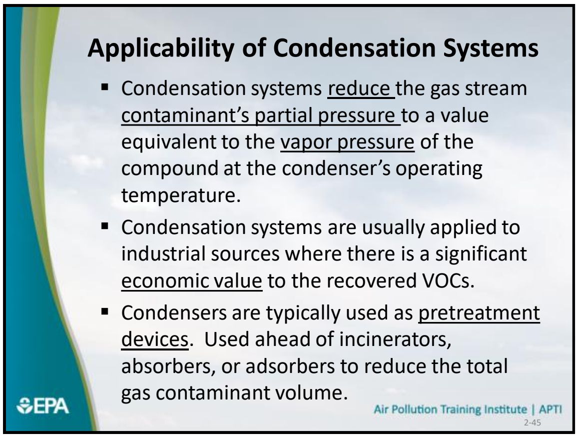
Factors Affecting Reduction Systems

- **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 NO_2
- **Particulate matter limitations**
  - NSCR systems not normally sensitive to particulates
  - SCR systems subject to flow alterations & masking



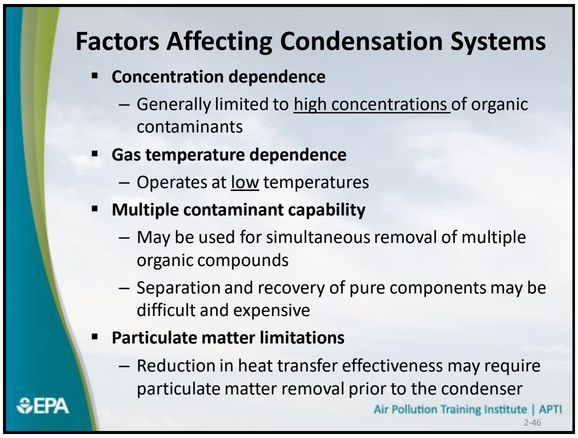
Condensation Systems

- 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)



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.



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

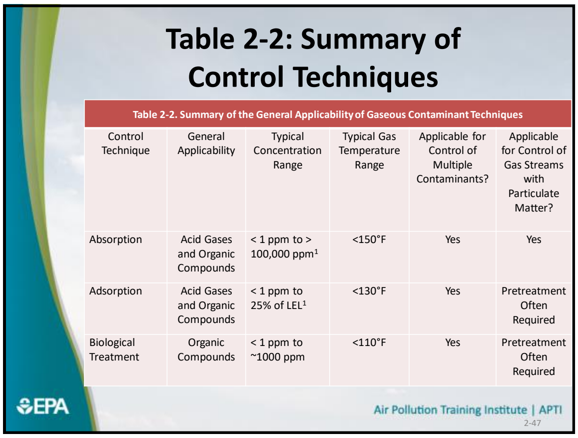


Table 2-2: Summary of Control Techniques

Table 2-2. Summary of the General Applicability of Gaseous Contaminant Techniques

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

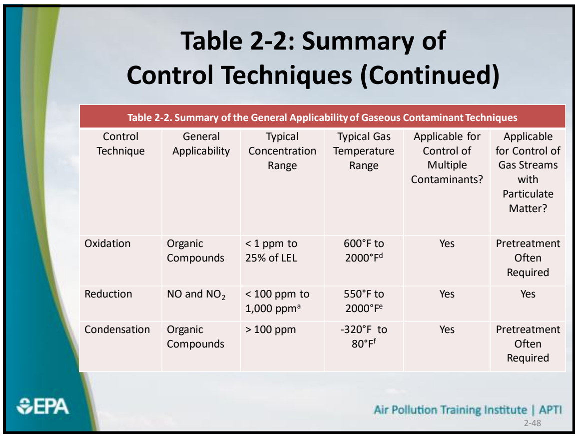


Table 2-2: Summary of Control Techniques (Continued)

Table 2-2. Summary of the General Applicability of Gaseous Contaminant Techniques

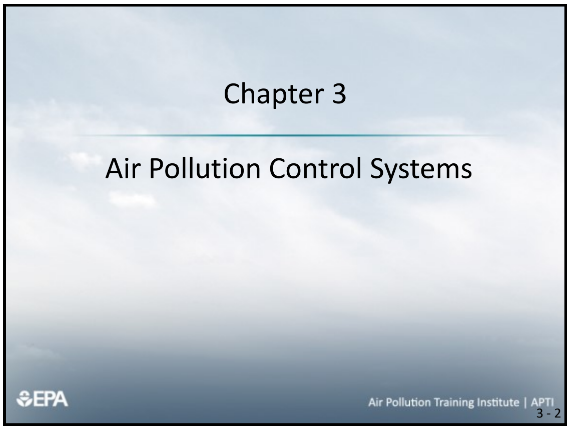
Control Technique	General Applicability	Typical Concentration Range	Typical Gas Temperature Range	Applicable for Control of Multiple Contaminants?	Applicable for Control of Gas Streams with Particulate Matter?
Oxidation	Organic Compounds	< 1 ppm to 25% of LEL	600°F to 2000°F[d]	Yes	Pretreatment Often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

Presented For
NESCAUM 2023

CHAPTER 3
AIR POLLUTION
CONTROL SYSTEMS

APTI COURSE 415
Air Pollution Training Institute | APTI

EPA

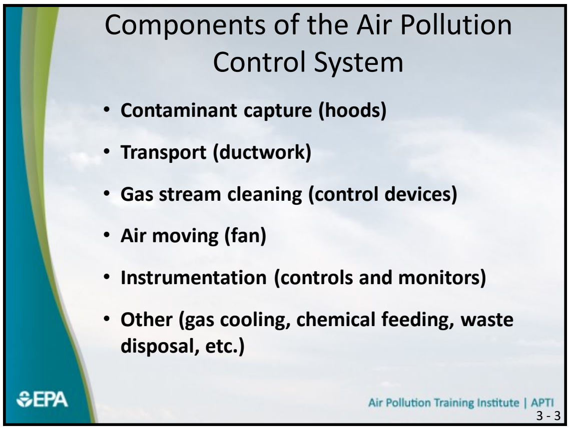


Chapter 3

Air Pollution Control Systems

EPA

Air Pollution Training Institute | APTI

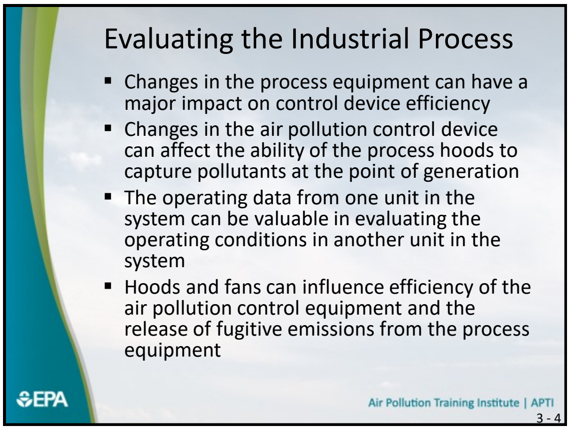


Components of the Air Pollution Control System

- **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.)**

EPA

Air Pollution Training Institute | APTI

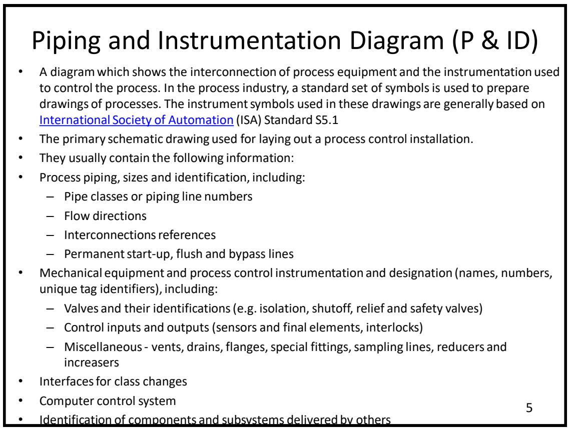


Evaluating the Industrial Process

- 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

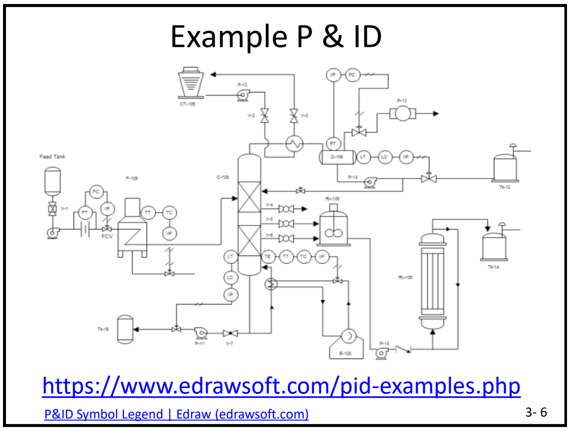
EPA

Air Pollution Training Institute | APTI



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 S5.1
- 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



Example P & ID

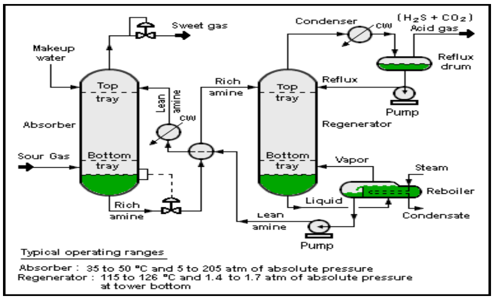
https://www.edrawsoft.com/pid-examples.php

P&ID Symbol Legend | Edraw (edrawsoft.com)

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

Process Flow diagram of a typical amine treating process



Typical operating ranges

Absorber : 35 to 50 °C and 5 to 205 atm of absolute pressure
Regenerator : 115 to 126 °C and 1.4 to 1.7 atm of absolute pressure at tower bottom

https://en.wikipedia.org/wiki/Process_flow_diagram

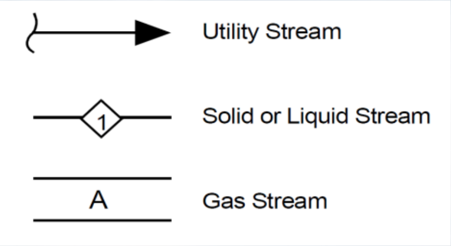
Flowcharts

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

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

Figure 3-1. Material Stream Symbols



P&ID and PFD Drawing Symbols and Legend list (PFS & PEFS) (hardhatengineer.com

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**

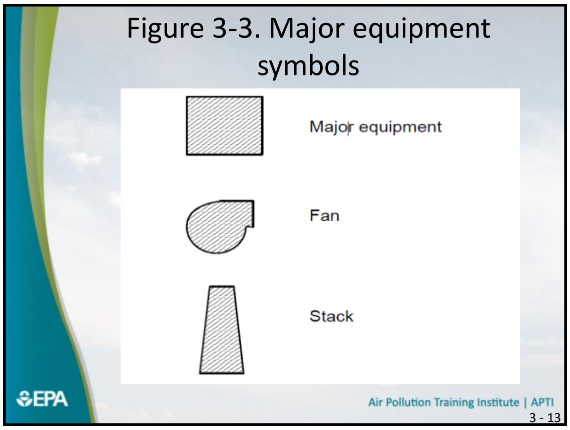


Figure 3-3. Major equipment symbols

Air Pollution Training Institute | APTI

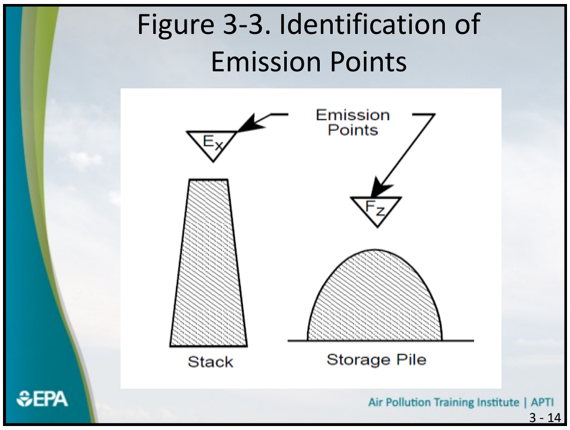


Figure 3-3. Identification of Emission Points

Air Pollution Training Institute | APTI

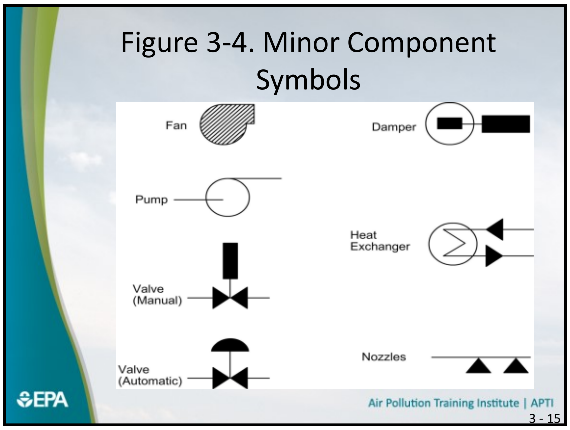


Figure 3-4. Minor Component Symbols

Air Pollution Training Institute | APTI

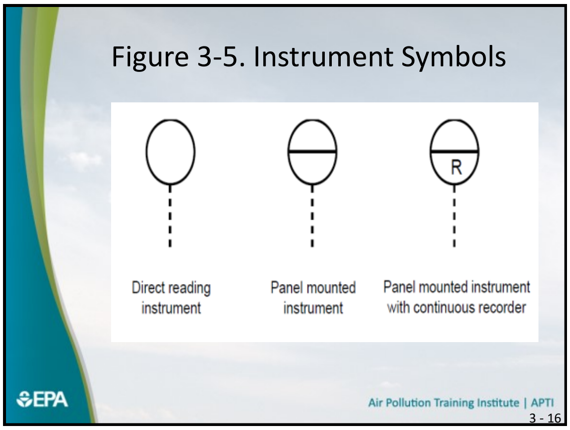


Figure 3-5. Instrument Symbols

Air Pollution Training Institute | APTI

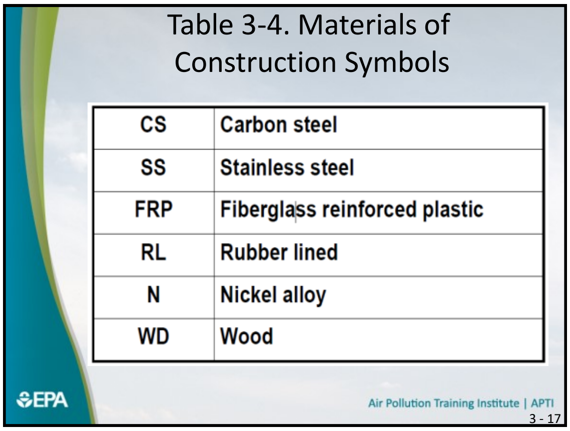
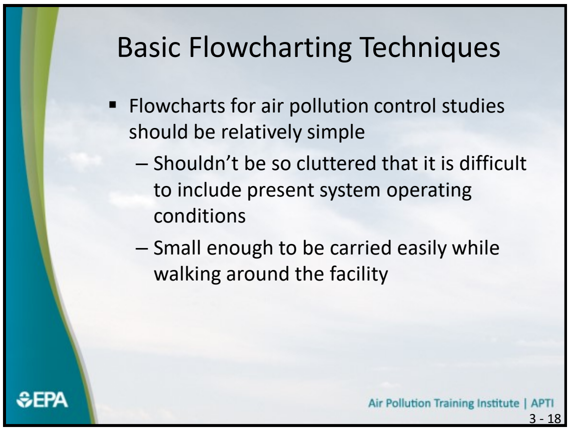


Table 3-4. Materials of Construction Symbols

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

Air Pollution Training Institute | APTI



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

Air Pollution Training Institute | APTI

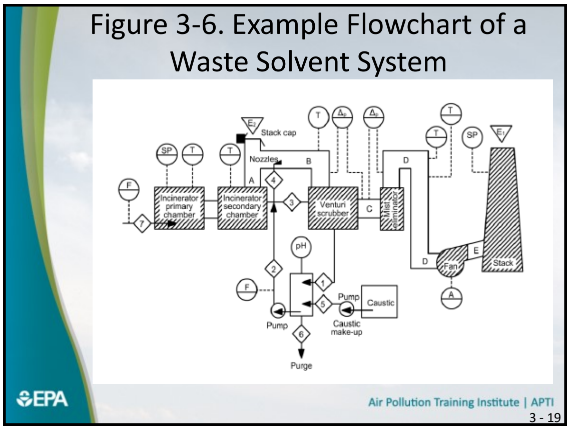


Figure 3-6. Example Flowchart of a Waste Solvent System

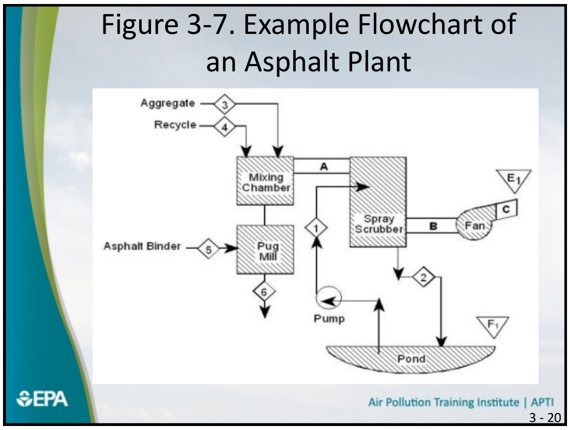
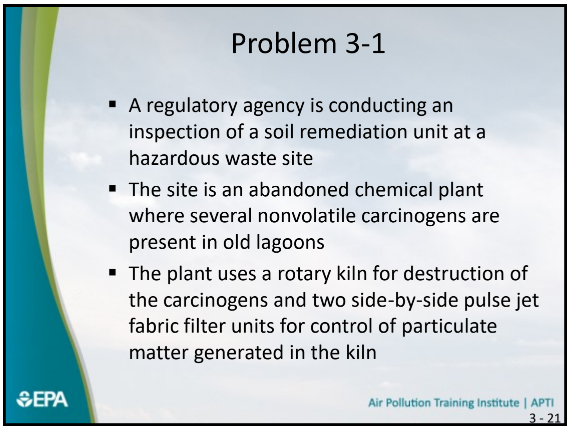
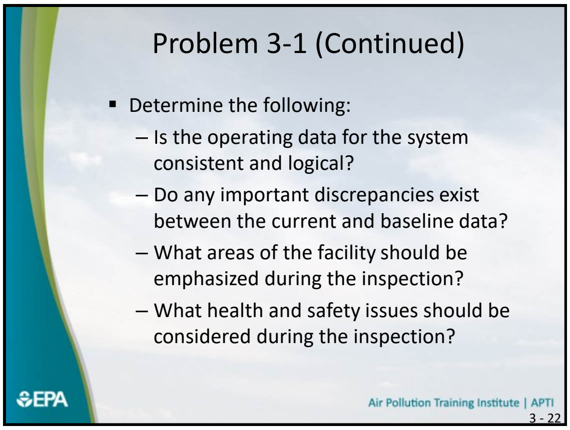


Figure 3-7. Example Flowchart of an Asphalt Plant



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?

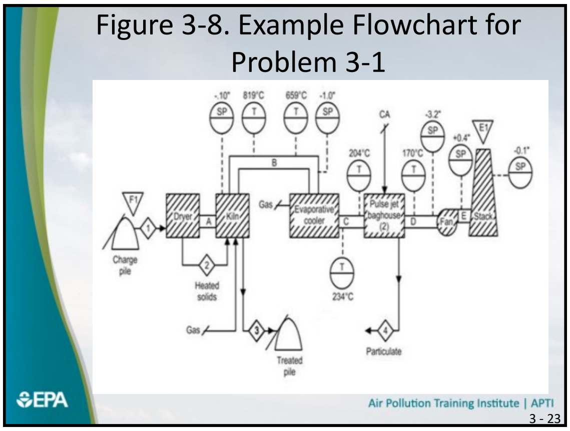


Figure 3-8. Example Flowchart for Problem 3-1

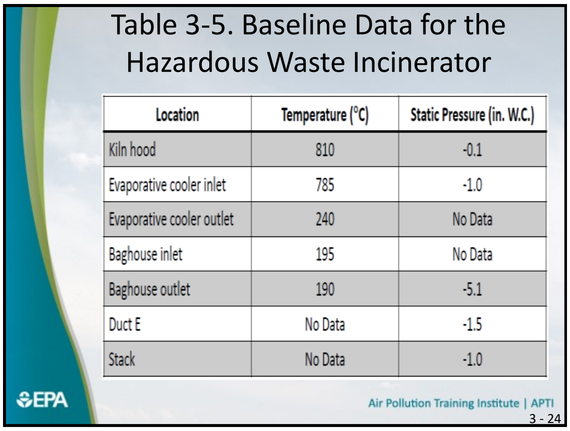
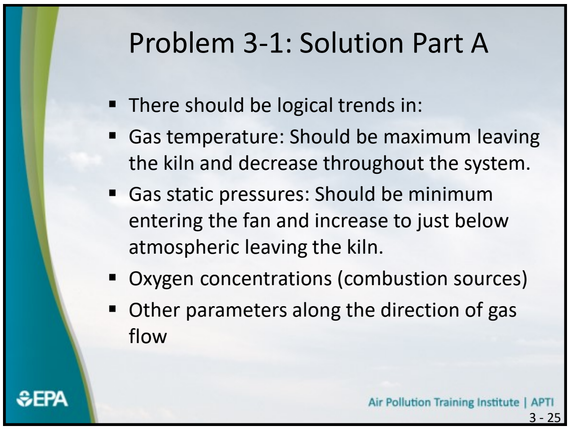


Table 3-5. Baseline Data for the Hazardous Waste Incinerator

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

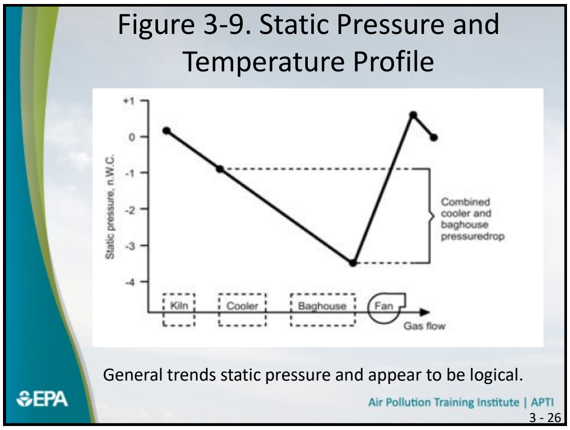


Figure 3-9. Static Pressure and Temperature Profile

General trends static pressure and appear to be logical.

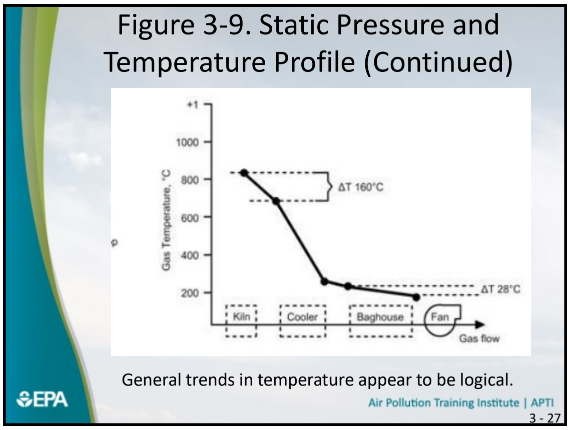
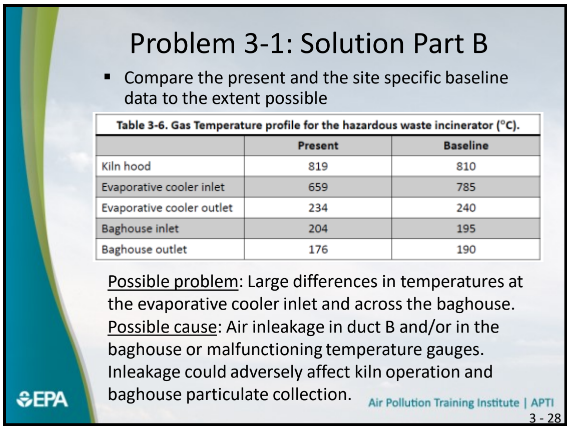


Figure 3-9. Static Pressure and Temperature Profile (Continued)

General trends in temperature appear to be logical.



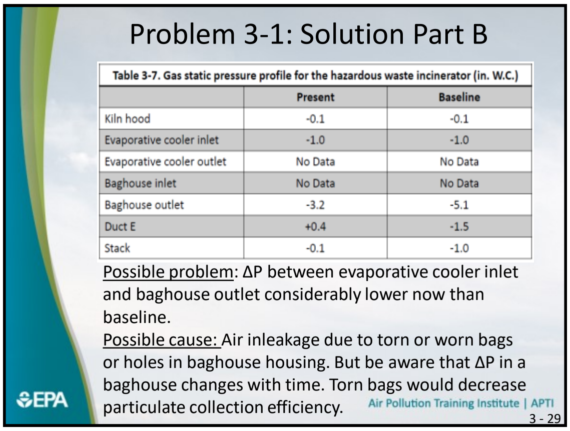
Problem 3-1: Solution Part B

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

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

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

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

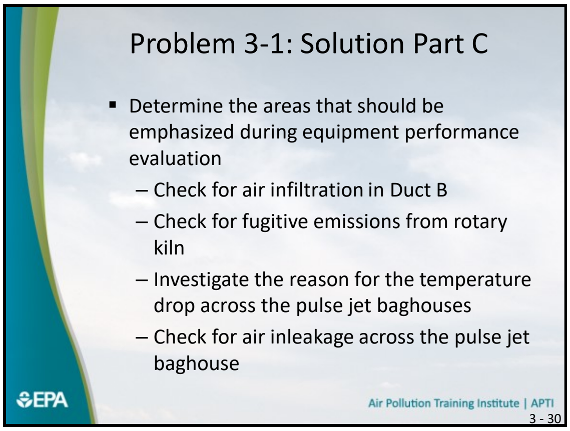


Problem 3-1: Solution Part B

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

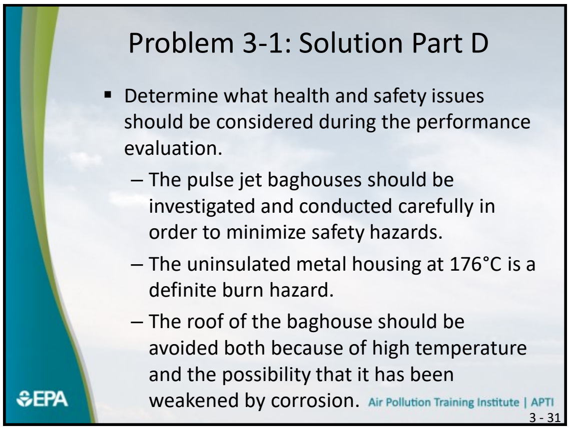
	Present	Baseline
Kiln hood	-0.1	-0.1
Evaporative cooler inlet	-1.0	-1.0
Evaporative cooler outlet	No Data	No Data
Baghouse inlet	No Data	No Data
Baghouse outlet	-3.2	-5.1
Duct E	+0.4	-1.5
Stack	-0.1	-1.0

Possible problem: ΔP between evaporative cooler inlet and baghouse outlet considerably lower now than baseline.
Possible cause: Air inleakage 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.



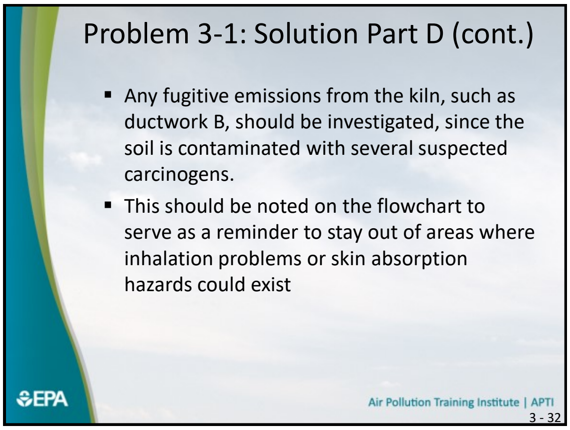
Problem 3-1: Solution Part C

- 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



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.



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

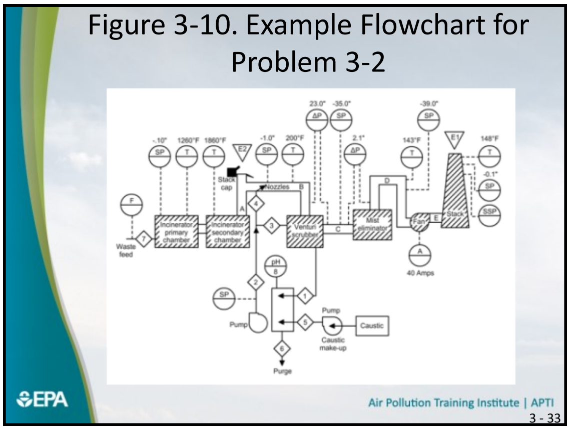


Figure 3-10. Example Flowchart for Problem 3-2

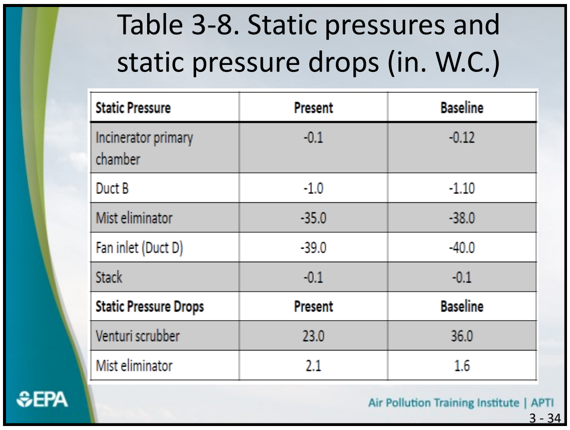


Table 3-8. Static pressures and static pressure drops (in. W.C.)

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

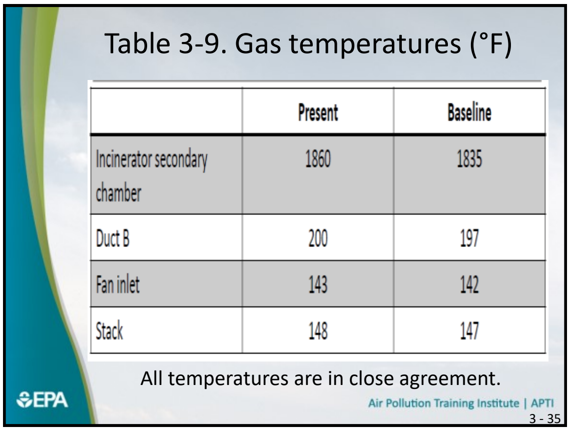
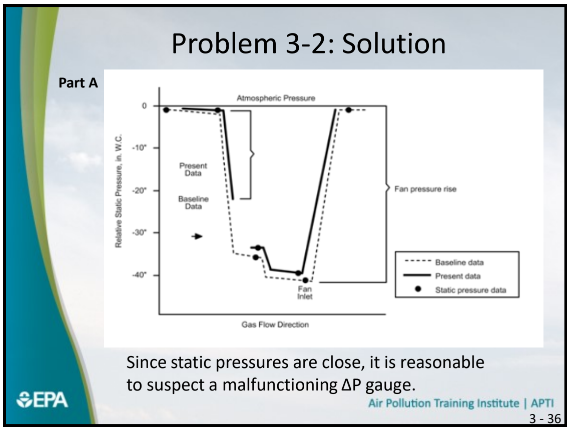


Table 3-9. Gas temperatures (°F)

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

All temperatures are in close agreement.

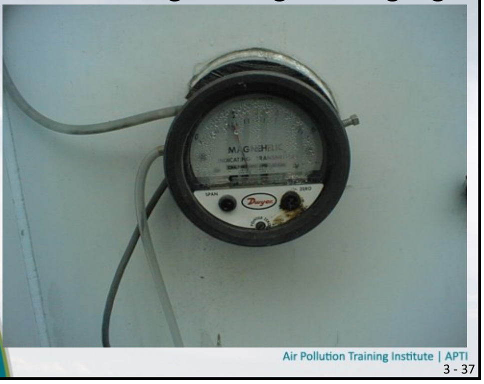


Problem 3-2: Solution

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 Ferroalloys 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

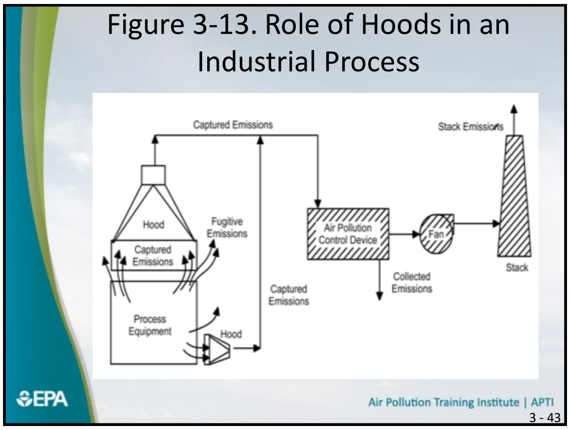
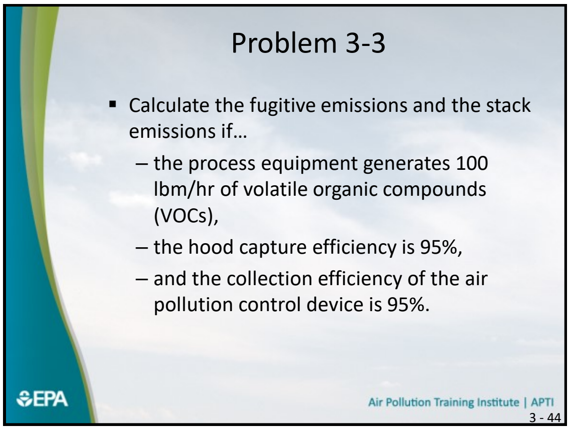
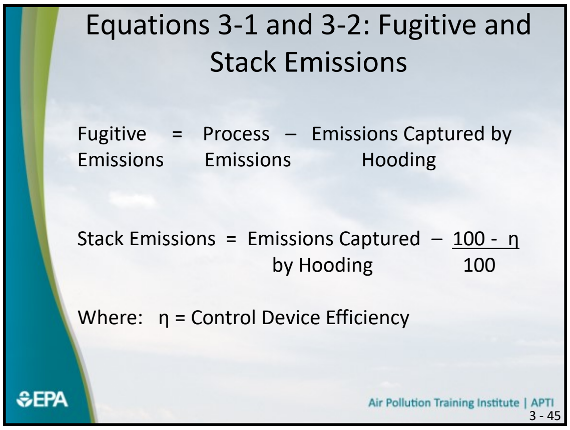


Figure 3-13. Role of Hoods in an Industrial Process



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%.

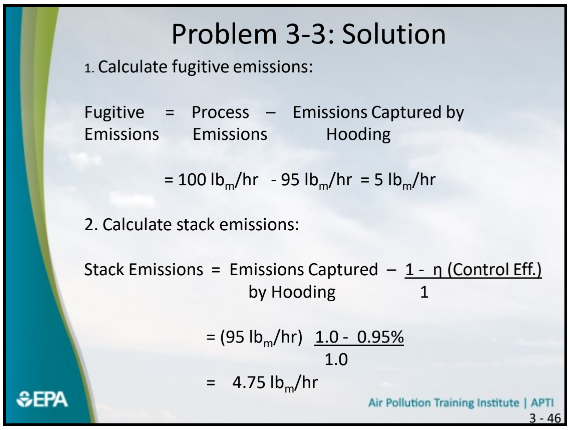


Equations 3-1 and 3-2: Fugitive and Stack Emissions

Fugitive Emissions = Process Emissions – Emissions Captured by Hooding

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

Where: η = Control Device Efficiency



Problem 3-3: Solution

1. Calculate fugitive emissions:

Fugitive Emissions = Process Emissions – Emissions Captured by Hooding

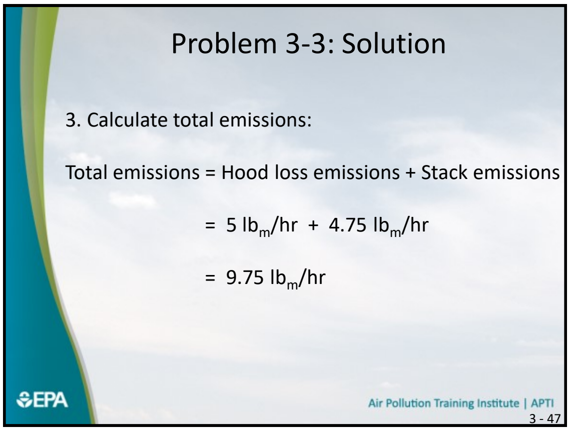
$= 100\ \text{lb}_m/\text{hr} - 95\ \text{lb}_m/\text{hr} = 5\ \text{lb}_m/\text{hr}$

2. Calculate stack emissions:

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

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

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



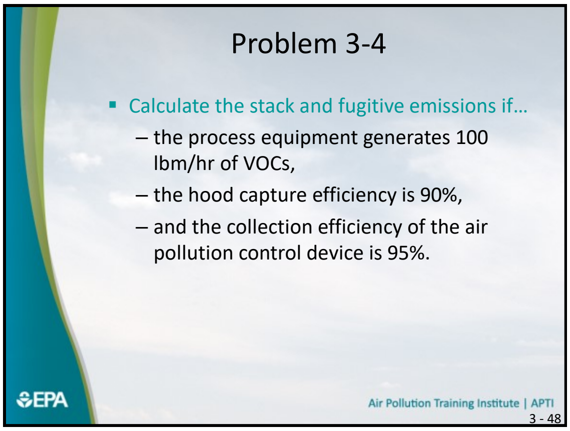
Problem 3-3: Solution

3. Calculate total emissions:

Total emissions = Hood loss emissions + Stack emissions

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

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



Problem 3-4

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

Problem 3-4: Solution

1. Calculate fugitive emissions.

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

2. Calculate stack emissions.

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

$$= 4.5\ lb_m/hr$$

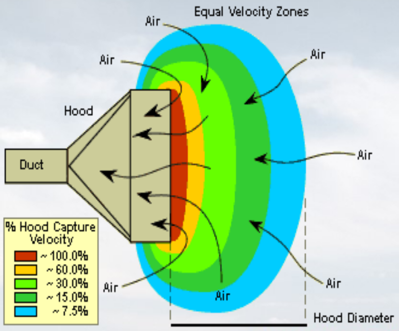
3. Calculate total emissions.

Total emissions = 10 lb_m/hr + 4.5 lb_m/hr = 14.5 lb_m/hr

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**

Figure 3-14. Hood Capture Velocities



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 (ft^2)

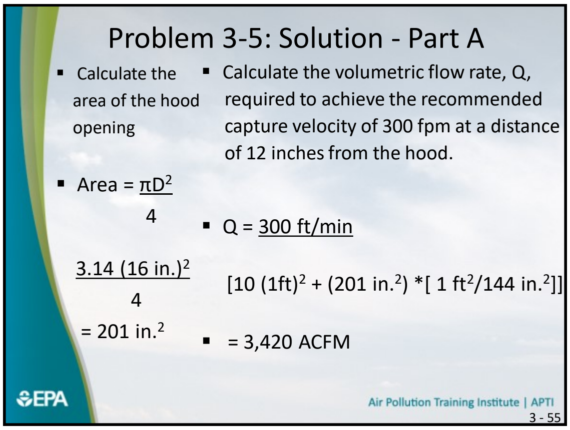
Equation 3-3: Volumetric Flow and Capture Velocity (cont.)

- 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:

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

Problem 3-5

- Calculate the required volumetric flow rate and capture velocity for the following distances from the hood face (X):
  - A. X= 12 in. (75% of hood diameter)
  - B. X= 24 in. (150% of hood diameter)
- Assume that the recommended capture velocity for the pollutant is 300 fpm entering a 16-inch diameter hood.
- Assume that X is the farthest distance from the hood face to the released contaminant.



Problem 3-5: Solution - Part A

- Calculate the area of the hood opening
- Area = $\frac{\pi D^2}{4}$

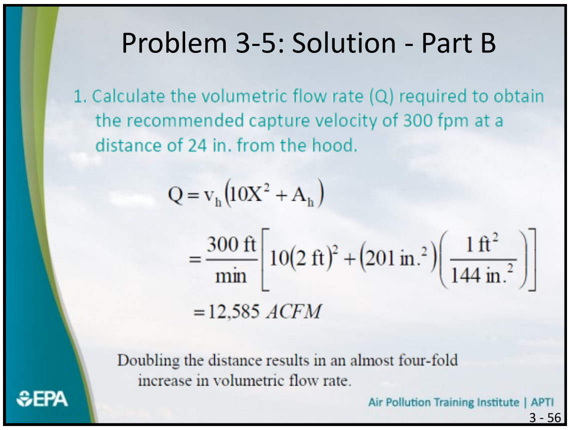
$\frac{3.14\ (16\text{ in.})^2}{4}$

= 201 in.^{2}

- Calculate the volumetric flow rate, Q, required to achieve the recommended capture velocity of 300 fpm at a distance of 12 inches from the hood.
- Q = $\underline{300\text{ ft/min}}$

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

- = 3,420 ACFM



Problem 3-5: Solution - Part B

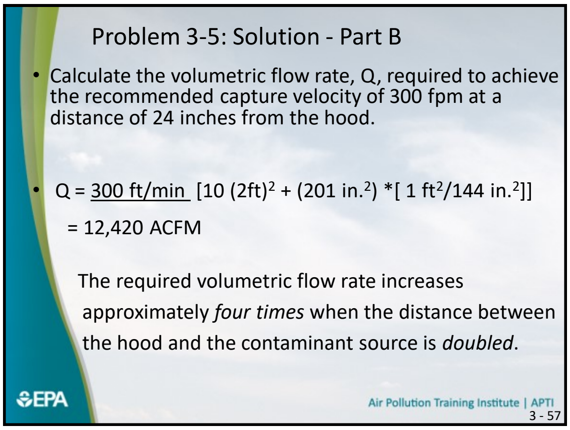
1. Calculate the volumetric flow rate (Q) required to obtain the recommended capture velocity of 300 fpm at a distance of 24 in. from the hood.

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

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

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

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

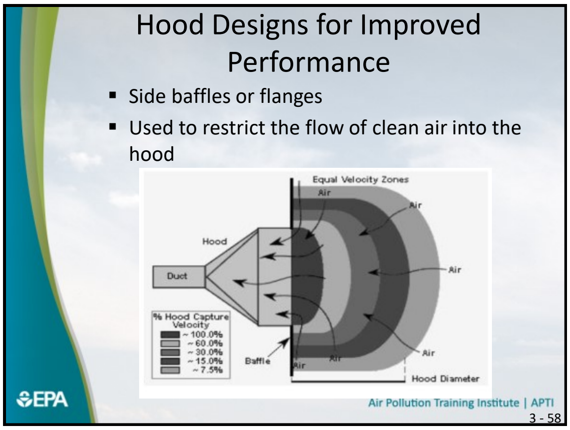


Problem 3-5: Solution - Part B

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

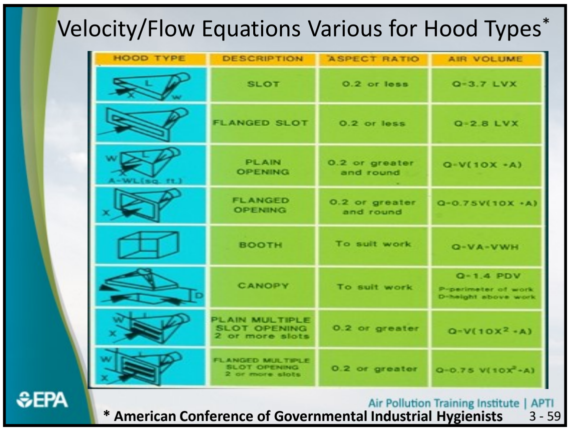
= 12,420 ACFM

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

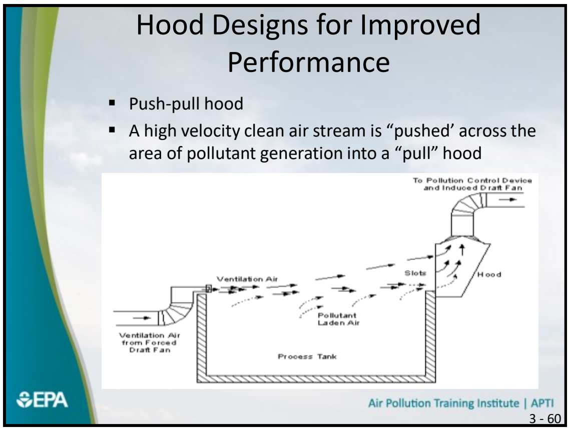
- Side baffles or flanges
- Used to restrict the flow of clean air into the hood



Velocity/Flow Equations Various for Hood Types*

HOOD TYPE	DESCRIPTION	ASPECT RATIO	AIR VOLUME
L, X, W	SLOT	0.2 or less	Q-3.7 LVX
	FLANGED SLOT	0.2 or less	Q-2.8 LVX
W, L, X, A-WL(sq. ft.)	PLAIN OPENING	0.2 or greater and round	Q-V(10X -A)
X	FLANGED OPENING	0.2 or greater and round	Q-0.75V(10X -A)
	BOOTH	To suit work	Q-VA-VWH
D	CANOPY	To suit work	Q-1.4 PDV P-perimeter of work D-height above work
W, L, X	PLAIN MULTIPLE SLOT OPENING 2 or more slots	0.2 or greater	Q-V(10X^2 -A)
W, L, X	FLANGED MULTIPLE SLOT OPENING 2 or more slots	0.2 or greater	Q-0.75 V(10X^2-A)

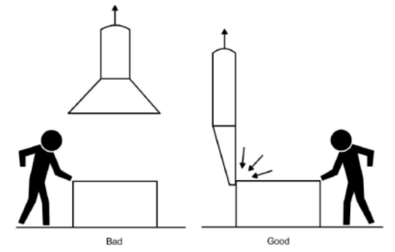
* American Conference of Governmental Industrial Hygienists



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

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

$$\mathbf{SP_h = -(VP_d) - h_e}$$

Where:

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

$$\mathbf{h_e = (F_h)(VP_d)}$$

Where:

F_h = Hood entry loss coefficient (dimensionless)

$$SP_h = -(VP_d) - (F_h)(VP_d) = -(VP_d)(1 + F_h)$$

Figures 3-18: Hood Entry Loss Coefficient

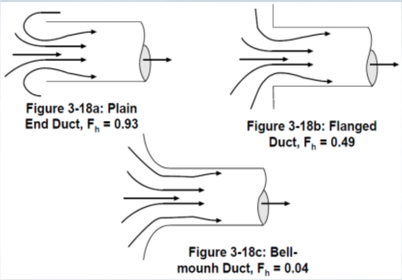


Figure 3-18a: Plain End Duct, F_h = 0.93

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

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

Velocity Pressure from Bernoullis Equation

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

ϱ = density of the fluid (air)

$V^2 = 2\ g\ \Delta p/\varrho$ Δp = manometer column height

$V^2 = 2\ g\ \Delta p/0.075\ lb_m/ft^3$ $g = 32.174\ ft/sec^2$

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

1 inches H_2O = (14.7 lb_f/in^2)/(407 in. H_2O) = (0.361lb_f/in^2)(12in/ft)^2

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

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

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

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.

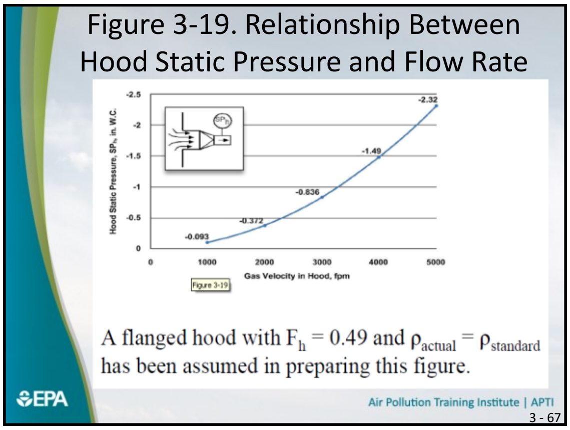
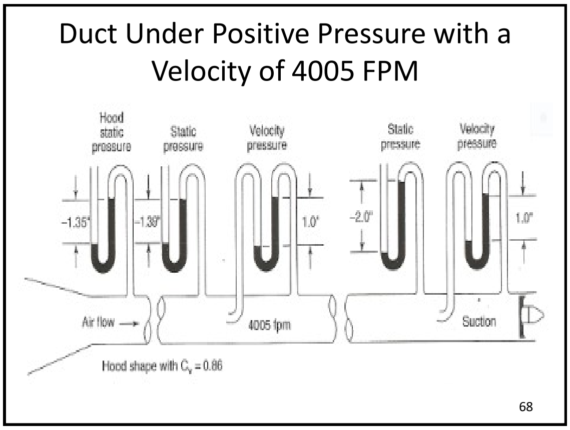
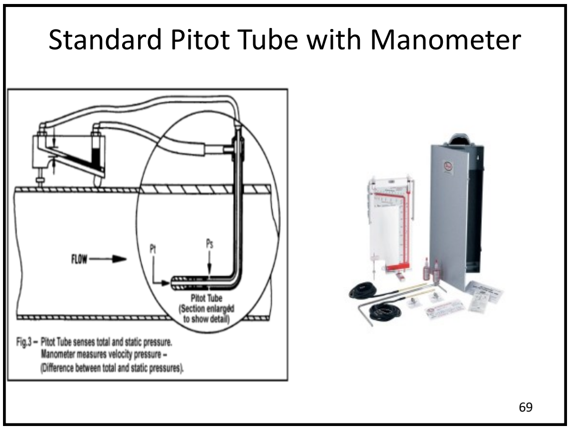


Figure 3-19. Relationship Between Hood Static Pressure and Flow Rate

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

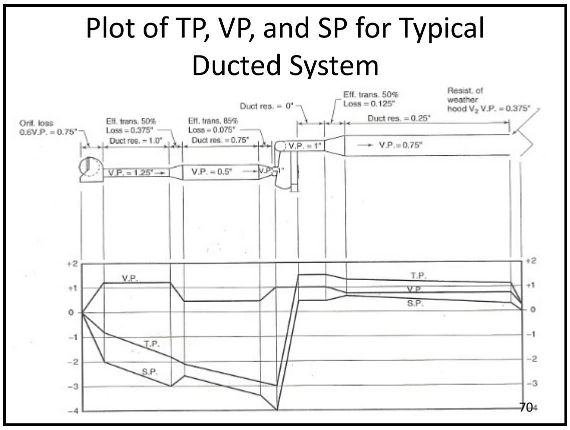


Duct Under Positive Pressure with a Velocity of 4005 FPM

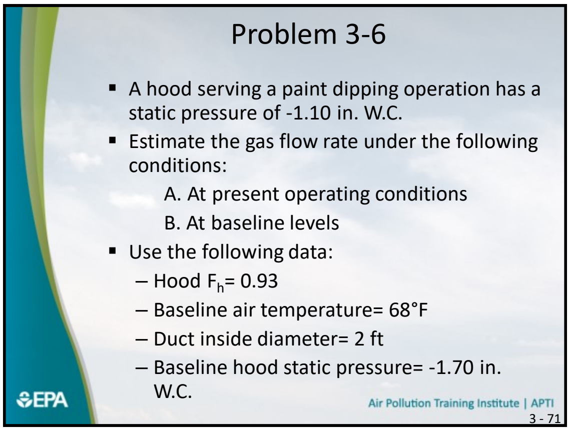


Standard Pitot Tube with Manometer

Fig.3 – Pitot Tube senses total and static pressure. Manometer measures velocity pressure – (Difference between total and static pressures).

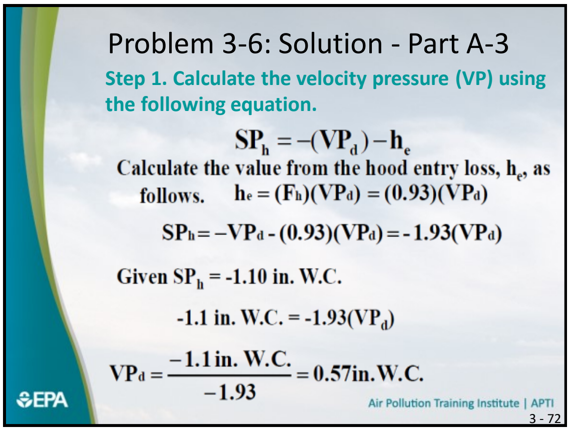


Plot of TP, VP, and SP for Typical Ducted System



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.



Problem 3-6: Solution - Part A-3

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

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

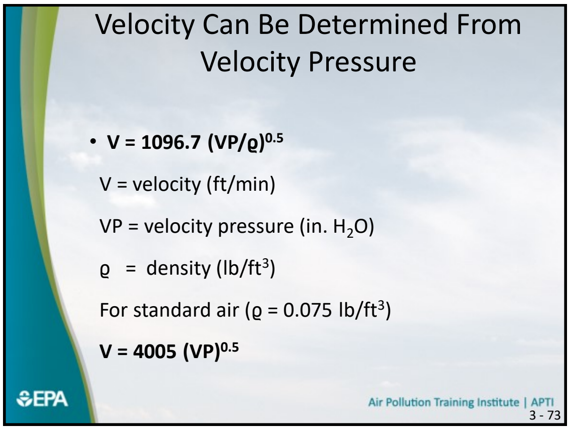
Calculate the value from the hood entry loss, h_e, as follows. $h_e = (F_h)(VP_d) = (0.93)(VP_d)$

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

Given SP_h = -1.10 in. W.C.

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

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



Velocity Can Be Determined From Velocity Pressure

- **$V = 1096.7 (VP/ϱ)^{0.5}$**

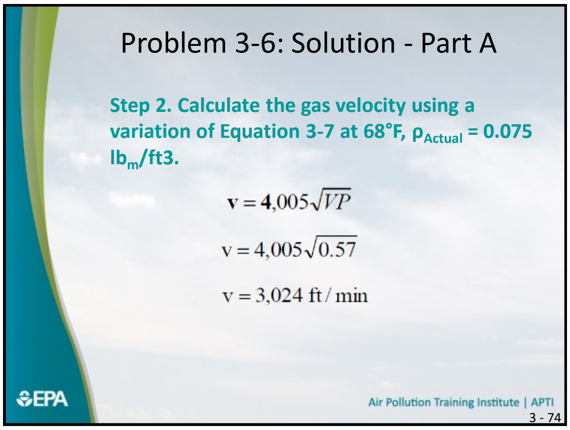
V = velocity (ft/min)

VP = velocity pressure (in. H_2O)

ϱ = density (lb/ft^3)

For standard air ($ϱ = 0.075\ lb/ft^3$)

$V = 4005 (VP)^{0.5}$



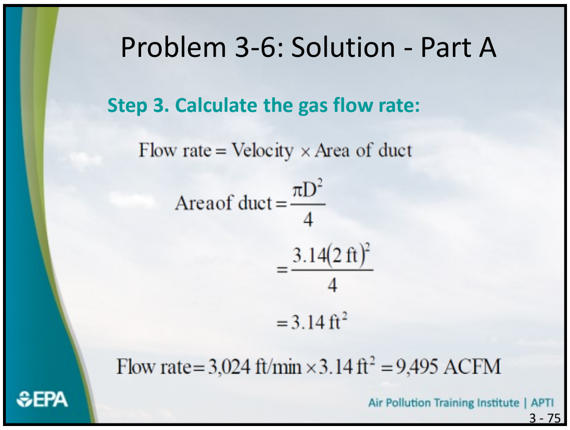
Problem 3-6: Solution - Part A

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

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

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

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



Problem 3-6: Solution - Part A

Step 3. Calculate the gas flow rate:

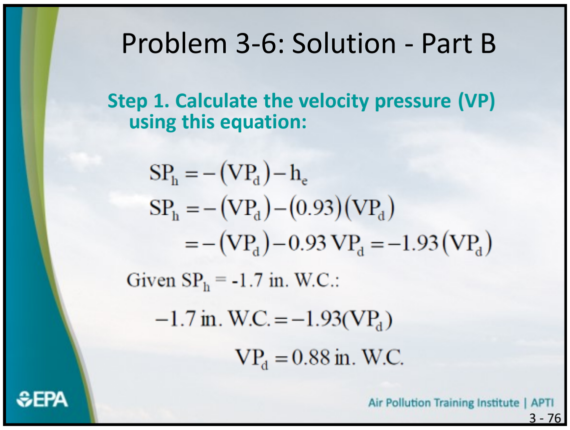
$$\text{Flow rate} = \text{Velocity} \times \text{Area of duct}$$

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

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

$$= 3.14\ ft^2$$

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



Problem 3-6: Solution - Part B

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

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

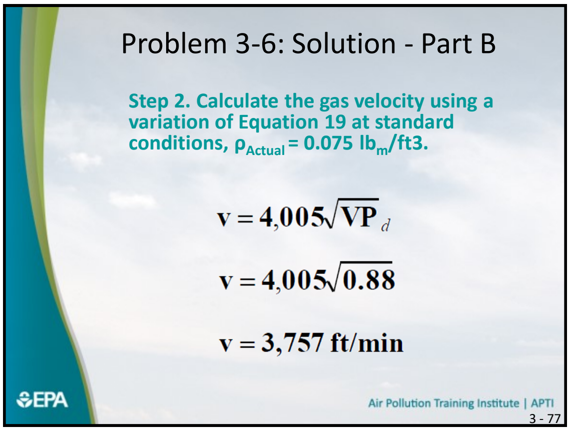
$$SP_h = -(VP_d) - (0.93)(VP_d)$$

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

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

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

$$VP_d = 0.88\ in.\ W.C.$$



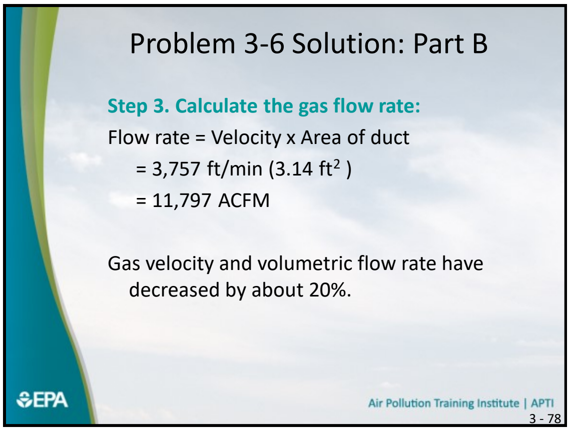
Problem 3-6: Solution - Part B

Step 2. Calculate the gas velocity using a variation of Equation 19 at standard conditions, $ρ_{Actual}$ = 0.075 lb_m/ft3.

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

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

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



Problem 3-6 Solution: Part B

Step 3. Calculate the gas flow rate:

Flow rate = Velocity x Area of duct
= 3,757 ft/min (3.14 ft^2)
= 11,797 ACFM

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

Transport Velocity

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

Table 3-10. Commonly 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

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.

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

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

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

Problem 3-7: Solution (Continued)

2. Calculate the duct diameter.

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

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

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

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

Fans

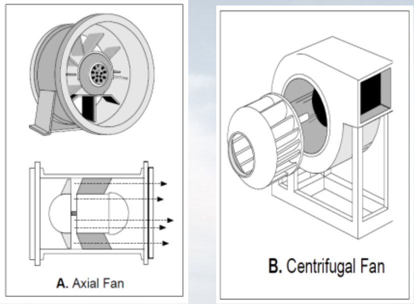
Fans

- 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)

Figures 3-20 and 3-21: Fan Types



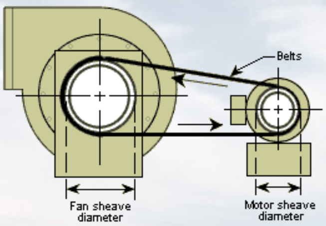
A. Axial Fan

B. Centrifugal Fan

Categories of Fan Drives

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

Figure 3-22. Centrifugal Fan and Motor Sheaves



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.)

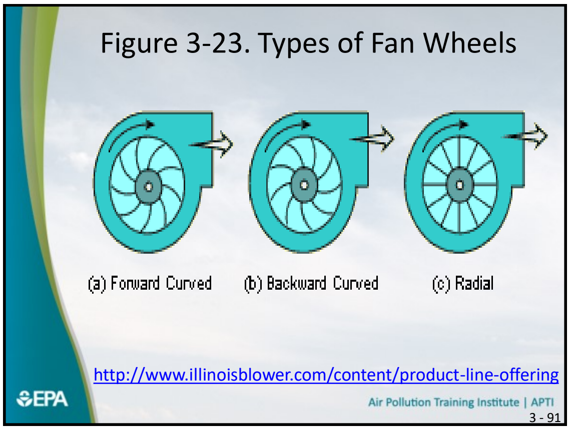
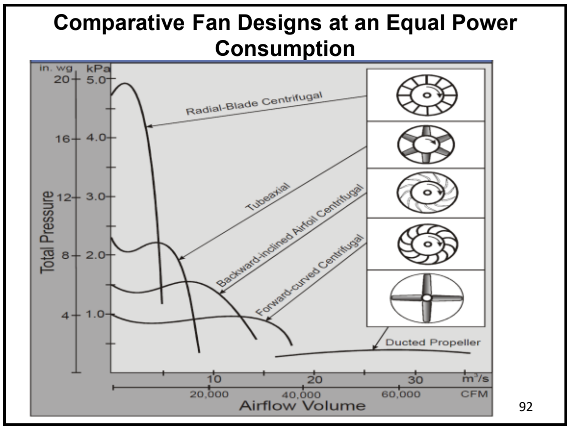
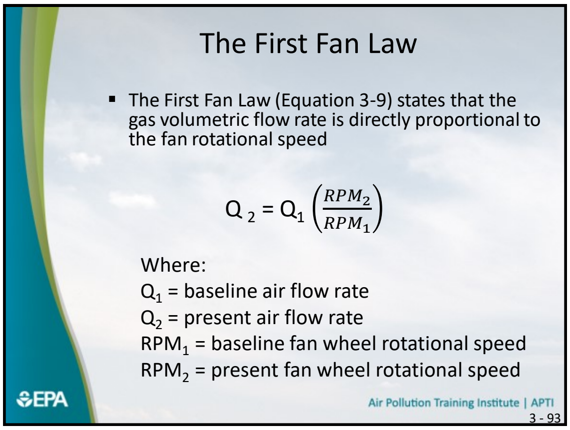


Figure 3-23. Types of Fan Wheels

http://www.illinoisblower.com/content/product-line-offering



Comparative Fan Designs at an Equal Power Consumption



The First Fan Law

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

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

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

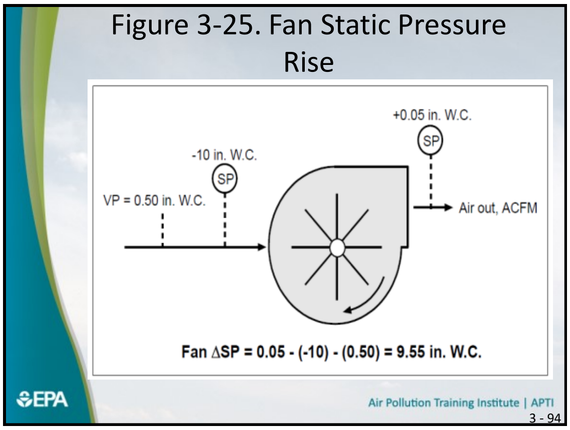
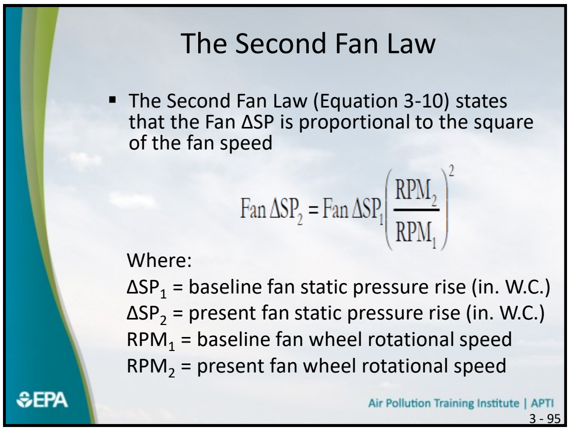


Figure 3-25. Fan Static Pressure Rise

Fan ΔSP = 0.05 - (-10) - (0.50) = 9.55 in. W.C.



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

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

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

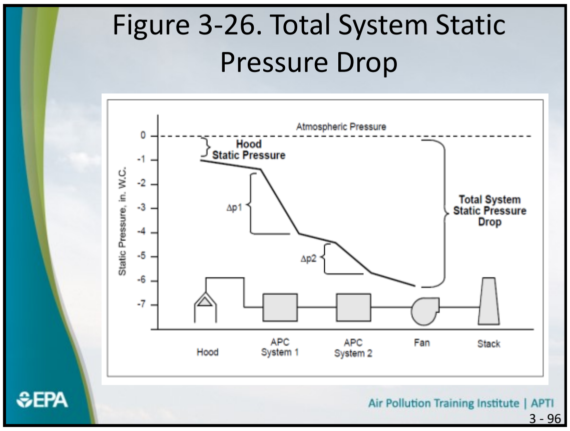


Figure 3-26. Total System Static Pressure Drop

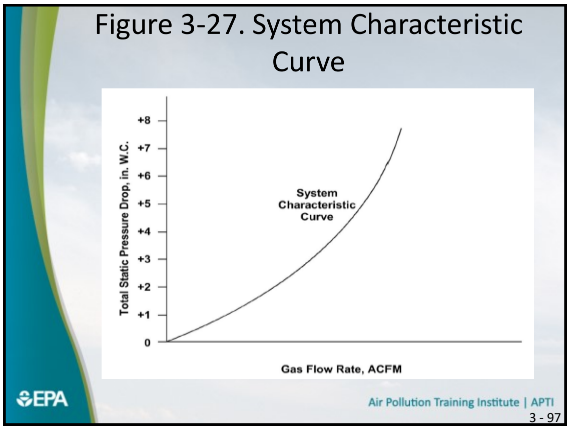


Figure 3-27. System Characteristic Curve

Air Pollution Training Institute | APTI

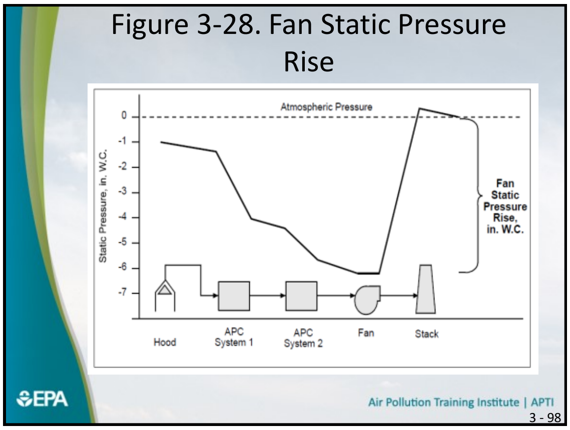


Figure 3-28. Fan Static Pressure Rise

Air Pollution Training Institute | APTI

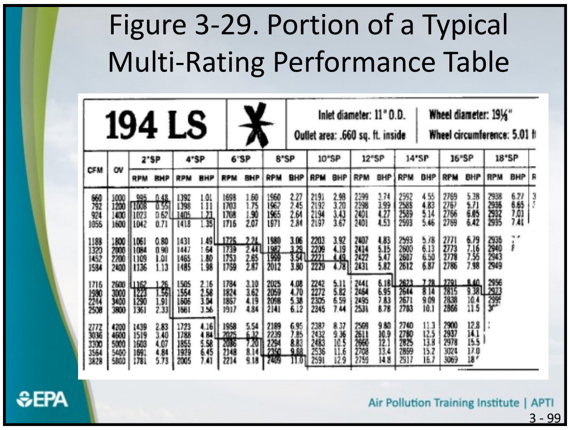


Figure 3-29. Portion of a Typical Multi-Rating Performance Table

194 LS

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

CFM	OV	2"SP		4"SP		6"SP		8"SP		10"SP		12"SP		14"SP		16"SP		18"SP	
		RPM	BHP	RPM	BHP	RPM	BHP	RPM	BHP	RPM	BHP	RPM	BHP	RPM	BHP	RPM	BHP	RPM	BHP
660	1000	995	0.48	1392	1.01	1698	1.60	1960	2.27	2191	2.98	2399	3.74	2592	4.55	2769	5.38	2938	6.27
792	1200	1008	0.55	1398	1.11	1703	1.75	1962	2.45	2192	3.20	2398	3.99	2588	4.83	2767	5.71	2936	6.65
924	1400	1023	0.62	1405	1.23	1708	1.90	1965	2.64	2194	3.43	2401	4.27	2589	5.14	2766	6.05	2932	7.01
1056	1600	1042	0.71	1418	1.35	1716	2.07	1971	2.84	2197	3.67	2401	4.53	2593	5.46	2769	6.42	2935	7.41
1188	1800	1061	0.80	1431	1.49	1726	2.24	1980	3.06	2203	3.92	2407	4.83	2593	5.78	2771	6.79	2936	
1320	2000	1084	0.90	1447	1.64	1739	2.44	1987	3.29	2209	4.19	2414	5.15	2600	6.13	2773	7.16	2940	
1452	2200	1109	1.01	1465	1.80	1753	2.65	1999	3.54	2221	4.49	2422	5.47	2607	6.50	2778	7.55	2943	
1584	2400	1136	1.13	1485	1.98	1769	2.87	2012	3.80	2229	4.78	2431	5.82	2612	6.87	2786	7.98	2949	
1716	2600	1162	1.26	1505	2.16	1784	3.10	2025	4.08	2242	5.11	2441	6.18	2623	7.28	2791	8.40	2956	
1980	3000	1223	1.56	1554	2.58	1824	3.62	2059	4.70	2272	5.82	2464	6.95	2644	8.14	2815	9.38	2973	
2244	3400	1290	1.91	1606	3.04	1867	4.19	2098	5.38	2305	6.59	2495	7.83	2671	9.09	2838	10.4		
2508	3800	1361	2.33	1661	3.56	1917	4.84	2141	6.12	2345	7.44	2531	8.78	2703	10.1	2866	11.5		
2772	4200	1439	2.83	1723	4.16	1958	5.54	2189	6.95	2387	8.37	2569	9.80	2740	11.3	2900	12.8		
3036	4600	1519	3.40	1788	4.84	2025	6.32	2239	7.85	2432	9.36	2611	10.9	2780	12.5	2937	14.1		
3300	5000	1603	4.07	1855	5.58	2086	7.20	2294	8.83	2483	10.5	2660	12.1	2825	13.8	2978	15.5		
3564	5400	1691	4.84	1929	6.45	2148	8.14	2350	9.88	2536	11.6	2708	13.4	2869	15.2	3024	17.0		
3828	5800	1781	5.73	2005	7.41	2214	9.18	2409	11.0	2591	12.9	2759	14.8	2917	16.7	3069	18		

Air Pollution Training Institute | APTI

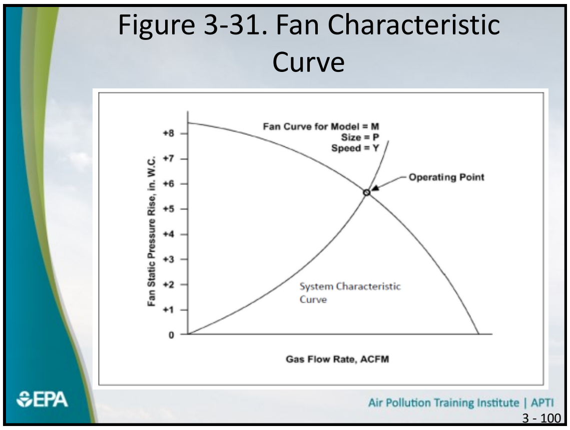
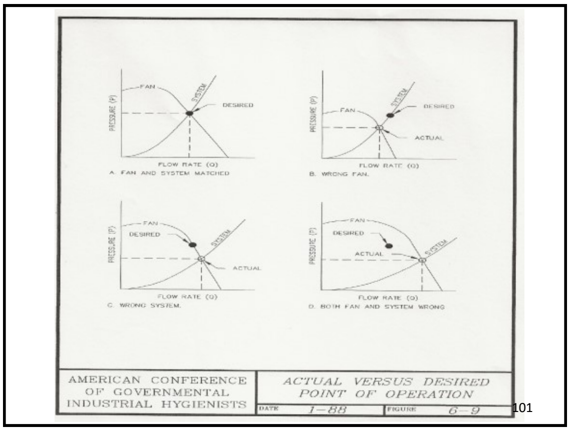


Figure 3-31. Fan Characteristic Curve

Air Pollution Training Institute | APTI



AMERICAN CONFERENCE OF GOVERNMENTAL INDUSTRIAL HYGIENISTS	*ACTUAL VERSUS DESIRED POINT OF OPERATION*			
	DATE	*1—88*	FIGURE	*6—9*

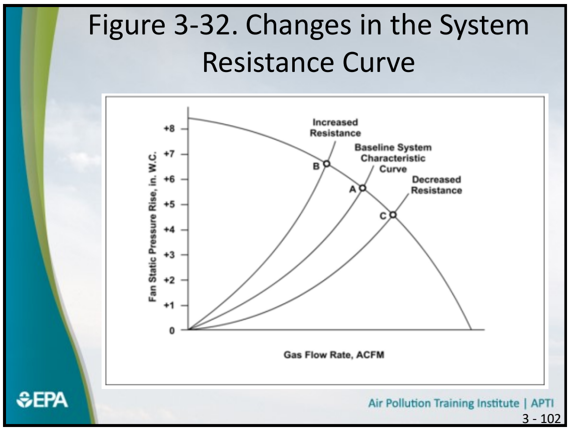


Figure 3-32. Changes in the System Resistance Curve

Air Pollution Training Institute | APTI

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

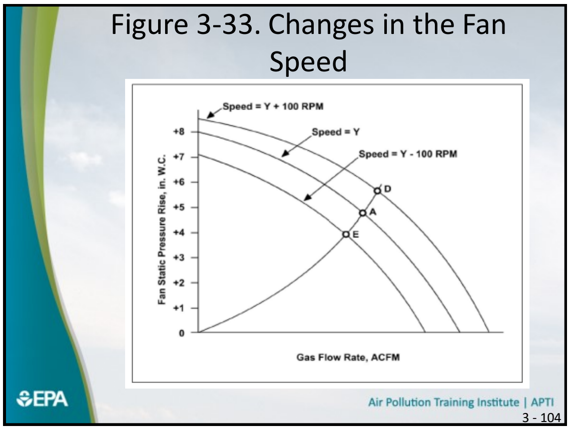
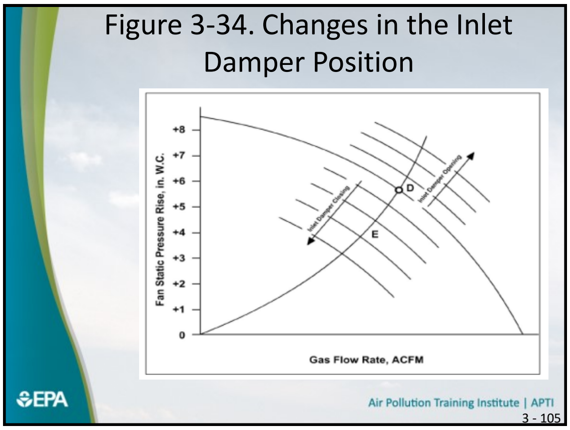
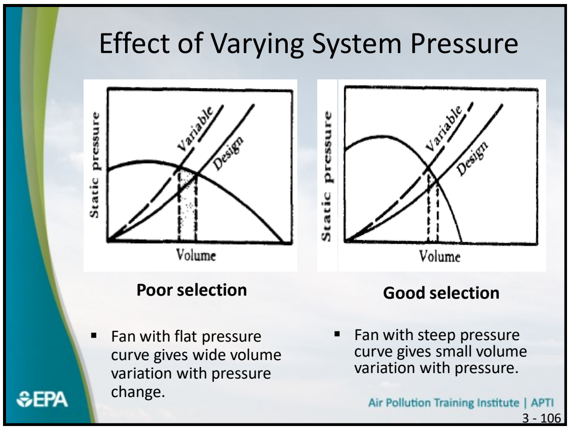


Figure 3-34. Changes in the Inlet Damper Position



Effect of Varying System Pressure



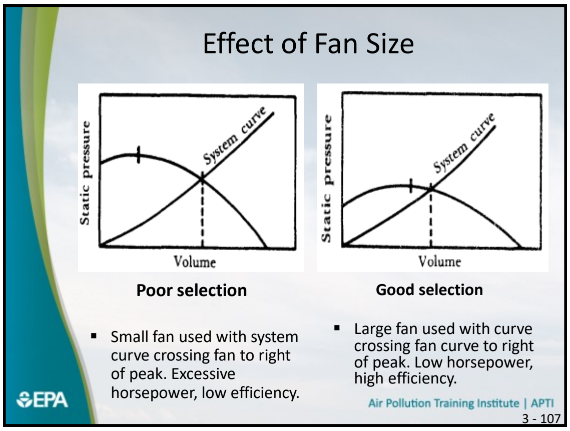
Poor selection

- 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.

Effect of Fan Size



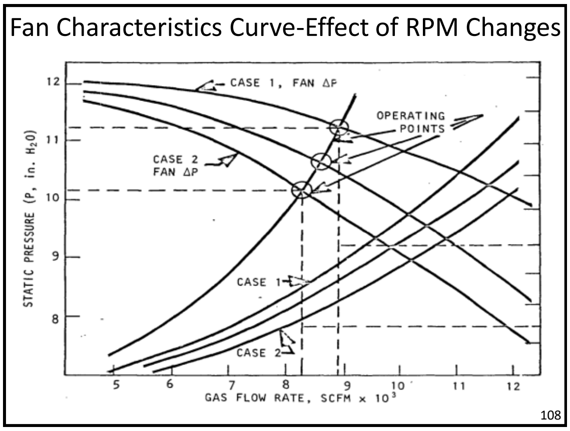
Poor selection

- Small fan used with system curve crossing fan to right of peak. Excessive horsepower, low efficiency.

Good selection

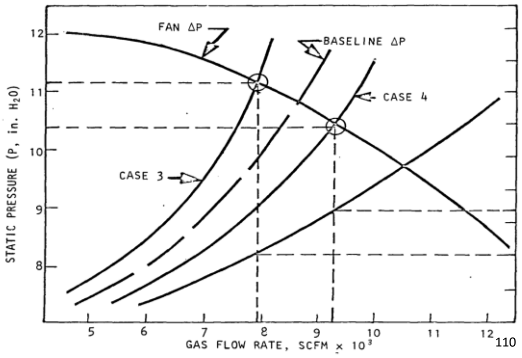
- Large fan used with curve crossing fan curve to right of peak. Low horsepower, high efficiency.

Fan Characteristics Curve-Effect of RPM Changes



- Case 1. An RPM increase causes an increase in the gas flow rate and a higher static pressure.
- Case 2. An RPM decrease decreases the gas flow rate greatly and can cause the control devices to not work properly.

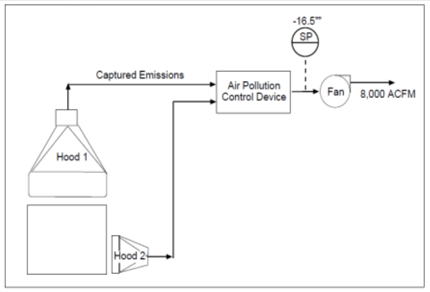
Fan Characteristics Curve – effect of System Pressure Drop Change



- Case 3. Decreasing fan motor current when the static pressure drop is increasing.

  Pressure drop increases can be caused by control device operational problems.
- Case 4. Decreasing pressure drop and increased motor amperage.

Figure 3-35. Portion of a Ventilation System (Problem 3-8)



Problem 3-8

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

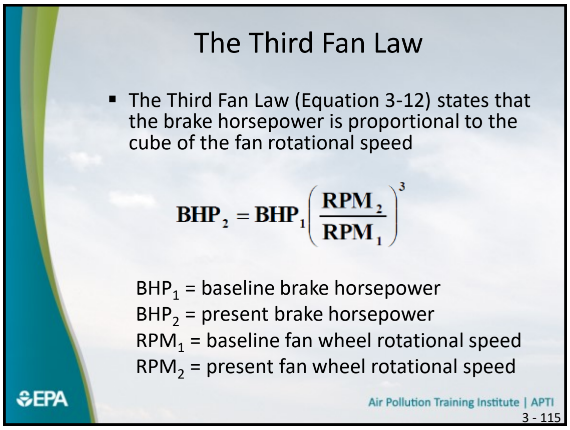
Problem 3-8: Solution

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

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

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

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

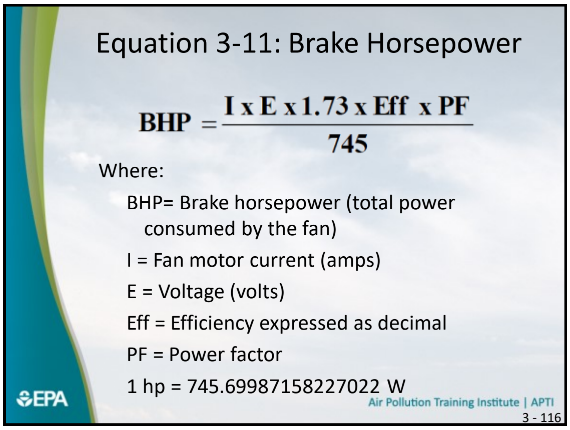


The Third Fan Law

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

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

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



Equation 3-11: Brake Horsepower

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

Where:

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

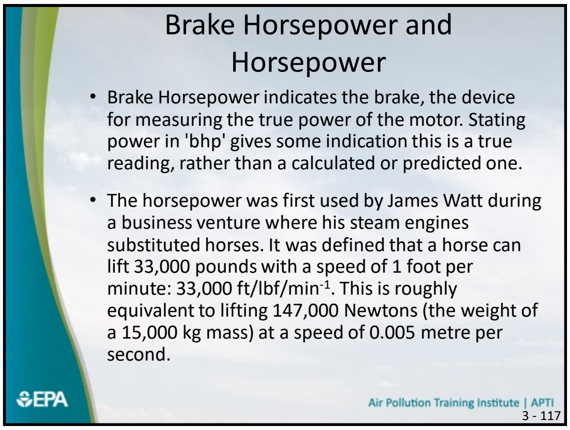
I = Fan motor current (amps)

E = Voltage (volts)

Eff = Efficiency expressed as decimal

PF = Power factor

1 hp = 745.69987158227022 W



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.

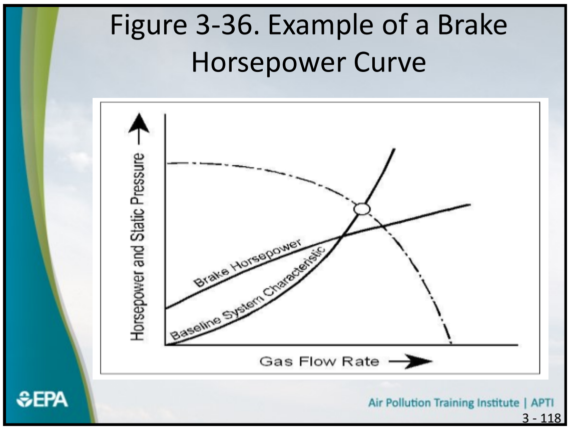
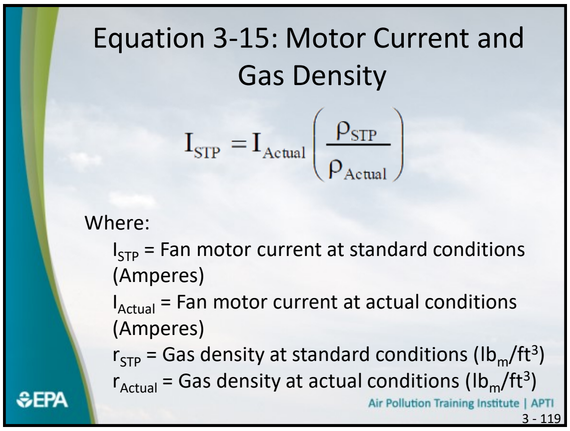


Figure 3-36. Example of a Brake Horsepower Curve



Equation 3-15: Motor Current and Gas Density

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

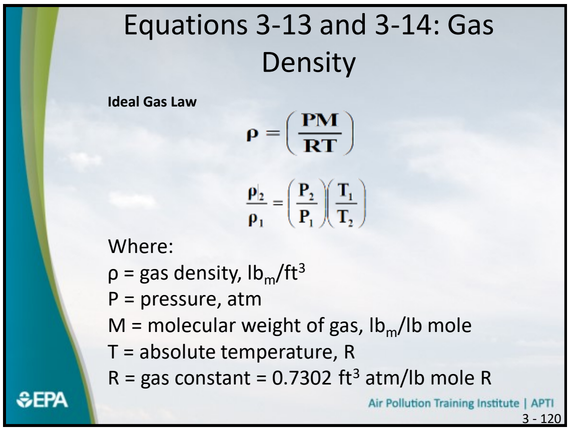
Where:

I_{STP} = Fan motor current at standard conditions (Amperes)

I_{Actual} = Fan motor current at actual conditions (Amperes)

r_{STP} = Gas density at standard conditions (lb_m/ft^3)

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



Equations 3-13 and 3-14: Gas Density

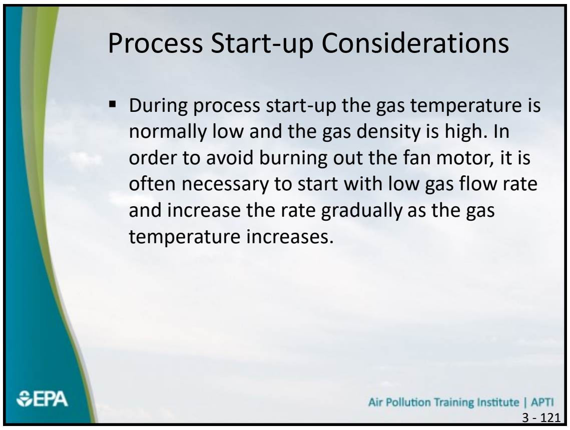
Ideal Gas Law

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

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

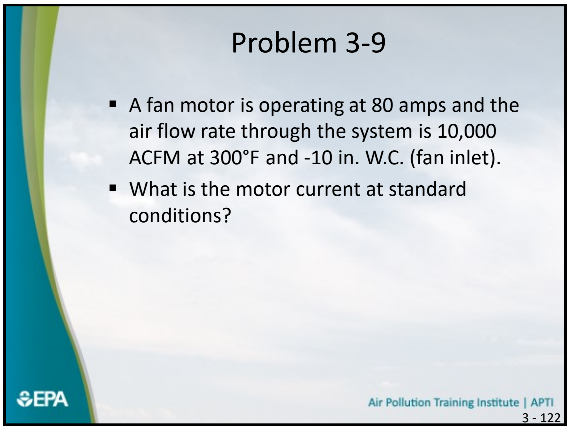
Where:

ρ = gas density, lb_m/ft^3
P = pressure, atm
M = molecular weight of gas, lb_m/lb mole
T = absolute temperature, R
R = gas constant = 0.7302 ft^3 atm/lb mole R



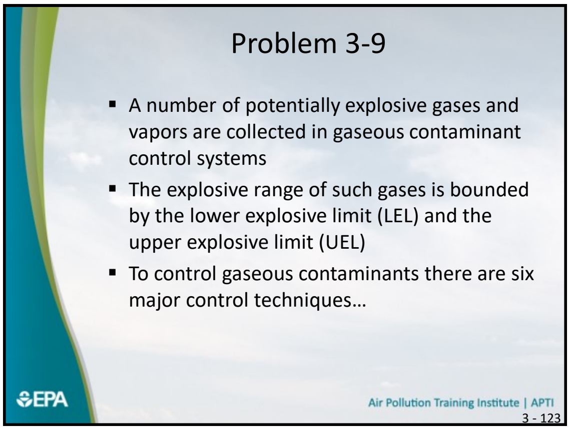
Process Start-up Considerations

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



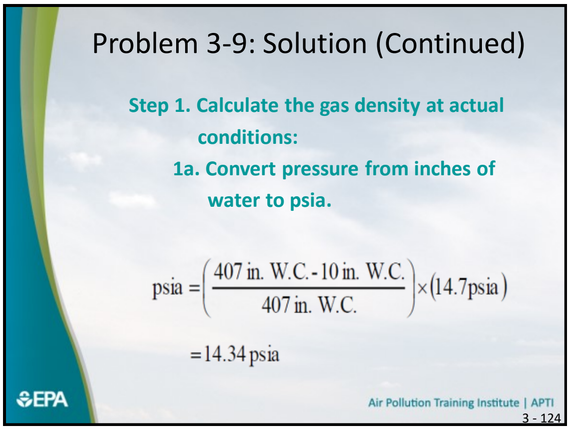
Problem 3-9

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



Problem 3-9

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



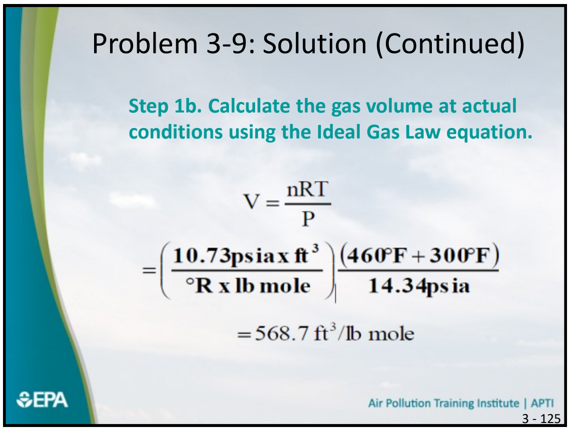
Problem 3-9: Solution (Continued)

Step 1. Calculate the gas density at actual conditions:

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

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

$$= 14.34\text{ psia}$$



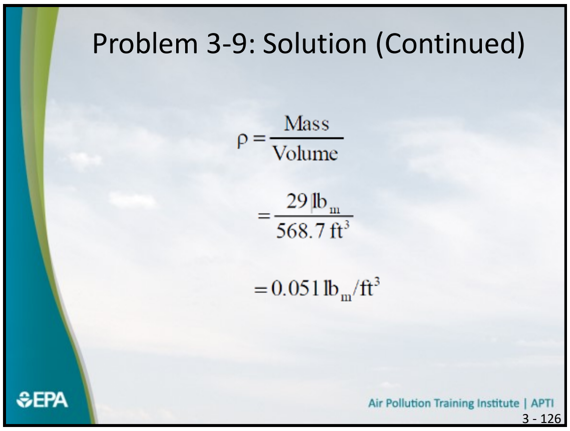
Problem 3-9: Solution (Continued)

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

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

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

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

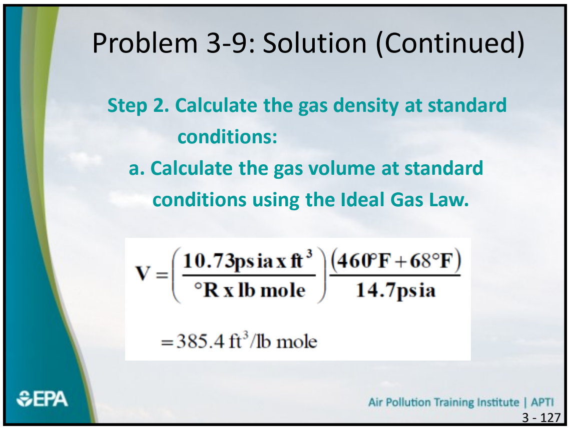


Problem 3-9: Solution (Continued)

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

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

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



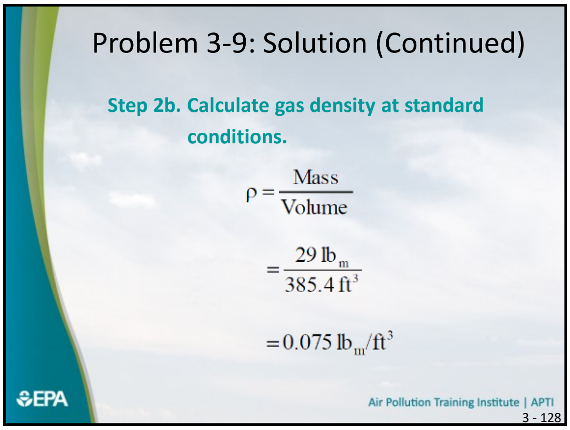
Problem 3-9: Solution (Continued)

Step 2. Calculate the gas density at standard conditions:

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

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

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



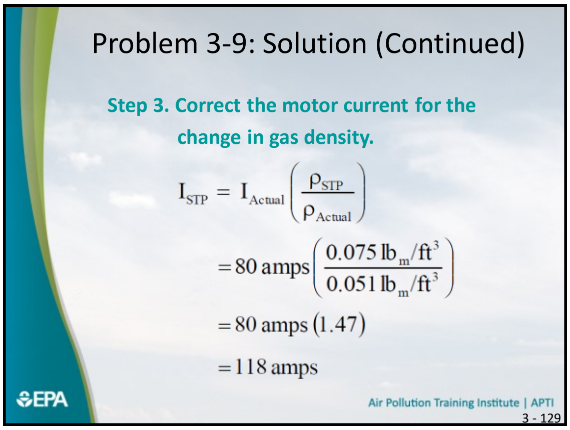
Problem 3-9: Solution (Continued)

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)

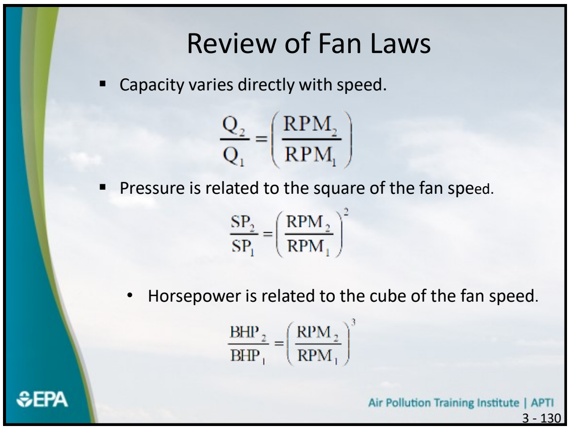
Step 3. Correct the motor current for the change in gas density.

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

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

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

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



Review of Fan Laws

- Capacity varies directly with speed.

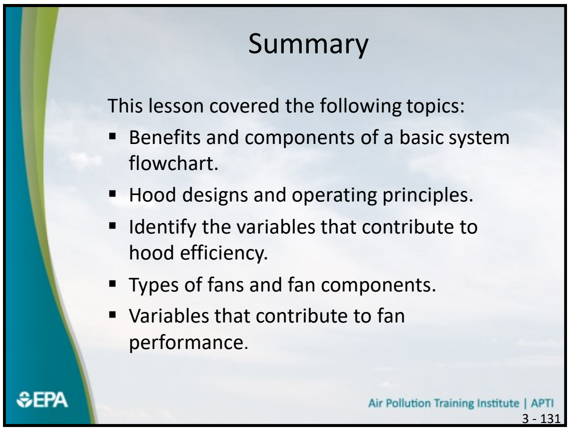
$$\frac{Q_2}{Q_1} = \left(\frac{\text{RPM}_2}{\text{RPM}_1}\right)$$

- Pressure is related to the square of the fan speed.

$$\frac{SP_2}{SP_1} = \left(\frac{\text{RPM}_2}{\text{RPM}_1}\right)^2$$

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

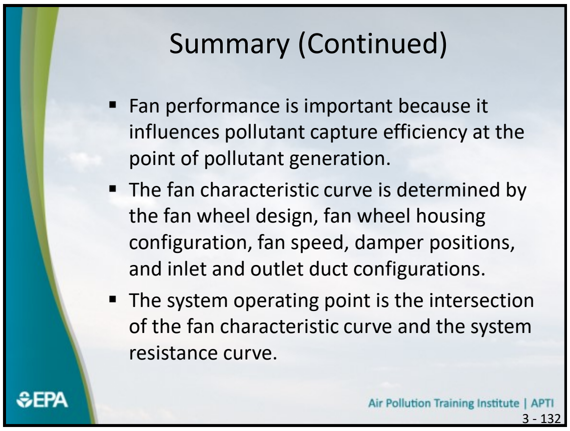
$$\frac{\text{BHP}_2}{\text{BHP}_1} = \left(\frac{\text{RPM}_2}{\text{RPM}_1}\right)^3$$



Summary

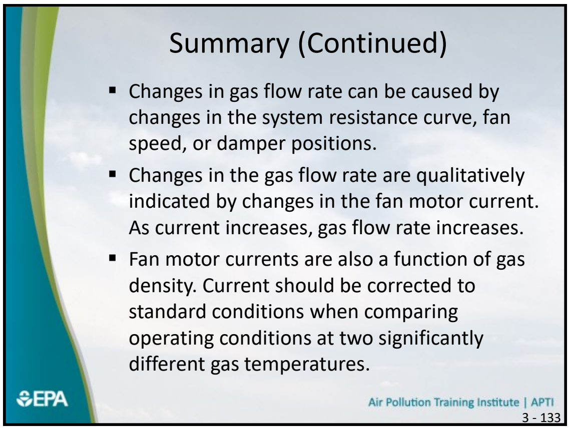
This lesson covered the following topics:

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



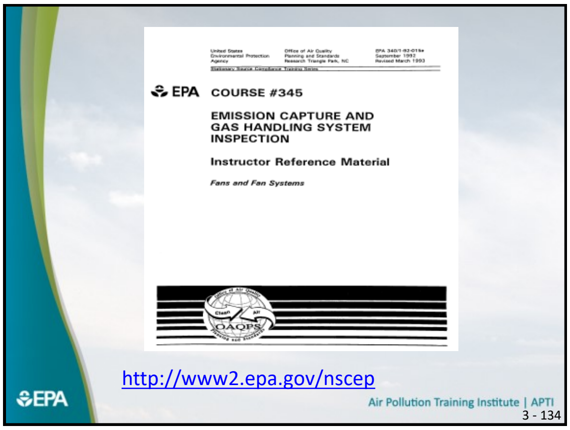
Summary (Continued)

- 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.



United States Environmental Protection Agency
Office of Air Quality Planning and Standards Research Triangle Park, NC
EPA 340/1-92-019a September 1992 Revised March 1993

Stationary Source Compliance Training Series

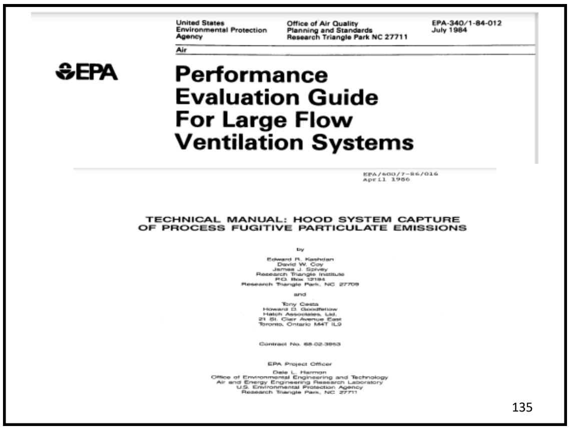
EPA COURSE #345

EMISSION CAPTURE AND GAS HANDLING SYSTEM INSPECTION

Instructor Reference Material

Fans and Fan Systems

http://www2.epa.gov/nscep



United States Environmental Protection Agency
Air
Office of Air Quality Planning and Standards Research Triangle Park NC 27711
EPA-340/1-84-012 July 1984

EPA

Performance Evaluation Guide For Large Flow Ventilation Systems

EPA/600/7-86/016
April 1986

TECHNICAL MANUAL: HOOD SYSTEM CAPTURE OF PROCESS FUGITIVE PARTICULATE EMISSIONS

by

Edward R. Kashdan
David W. Coy
James J. Spivey
Research Triangle Institute
P.O. Box 12194
Research Triangle Park, NC 27709

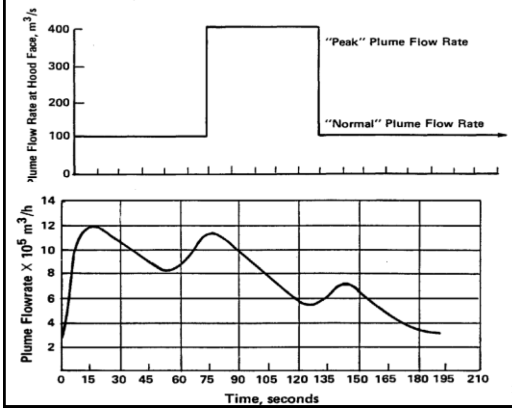
and

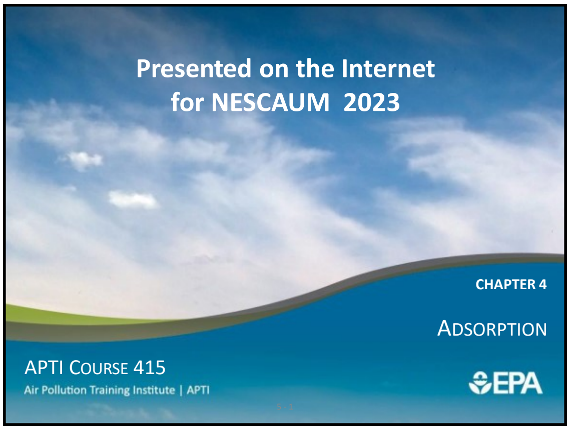
Tony Cesta
Howard D. Goodfellow
Hatch Associates, Ltd.
21 St. Clair Avenue East
Toronto, Ontario M4T IL9

Contract No. 68-02-3863

EPA Project Officer

Dale L. Harmon
Office of Environmental Engineering and Technology
Air and Energy Engineering Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711





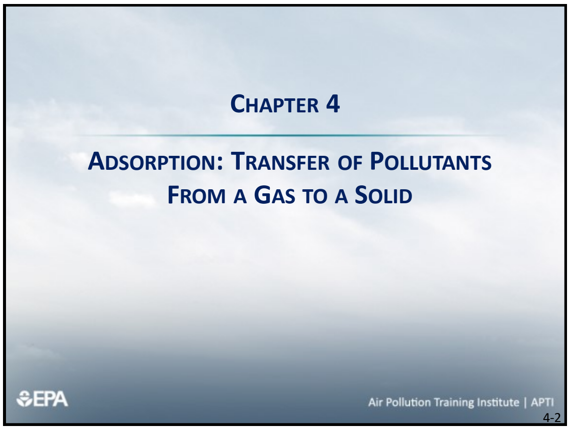
Presented on the Internet
for NESCAUM 2023

CHAPTER 4

ADSORPTION

APTI COURSE 415

Air Pollution Training Institute | APTI

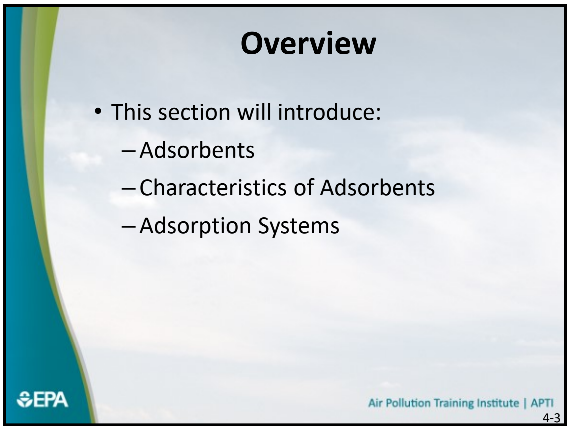


CHAPTER 4

ADSORPTION: TRANSFER OF POLLUTANTS FROM A GAS TO A SOLID

Air Pollution Training Institute | APTI

4-2

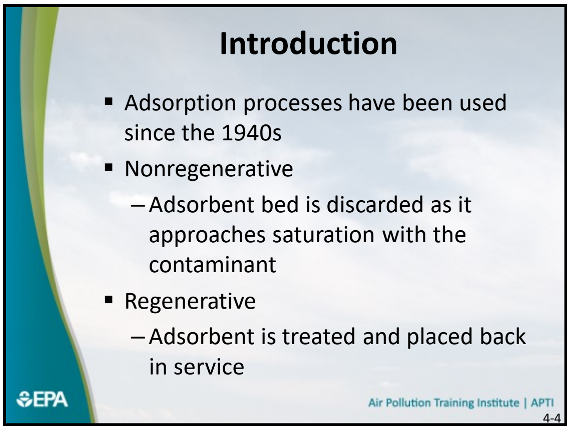


Overview

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

Air Pollution Training Institute | APTI

4-3

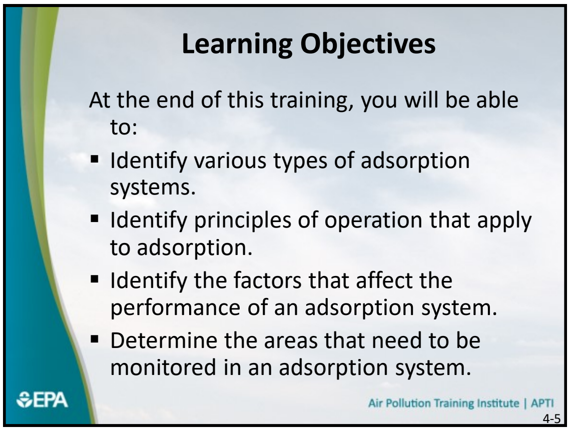


Introduction

- Adsorption processes have been used since the 1940s
- Nonregenerative
  - Adsorbent bed is discarded as it approaches saturation with the contaminant
- Regenerative
  - Adsorbent is treated and placed back in service

Air Pollution Training Institute | APTI

4-4



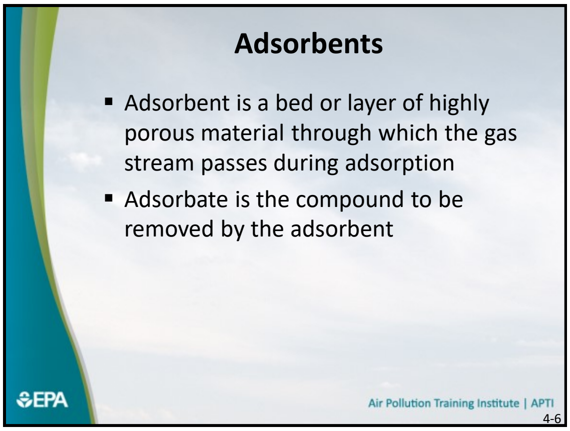
Learning Objectives

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.

Air Pollution Training Institute | APTI

4-5



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

Air Pollution Training Institute | APTI

4-6

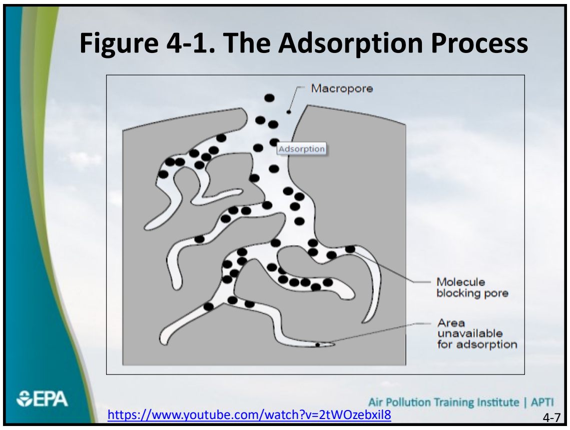


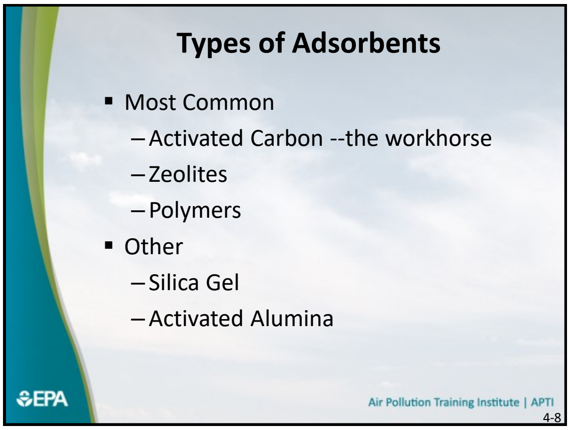
Figure 4-1. The Adsorption Process

EPA

Air Pollution Training Institute | APTI

https://www.youtube.com/watch?v=2tWOzebxil8

4-7



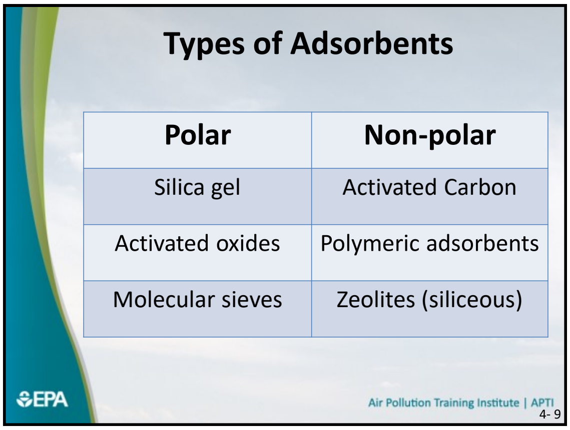
Types of Adsorbents

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

EPA

Air Pollution Training Institute | APTI

4-8



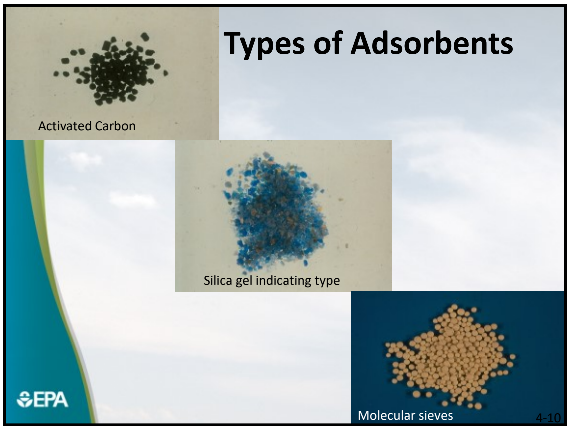
Types of Adsorbents

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

EPA

Air Pollution Training Institute | APTI

4- 9



Types of Adsorbents

Activated Carbon

Silica gel indicating type

Molecular sieves

EPA

4-10

Activated Carbon Derivatives

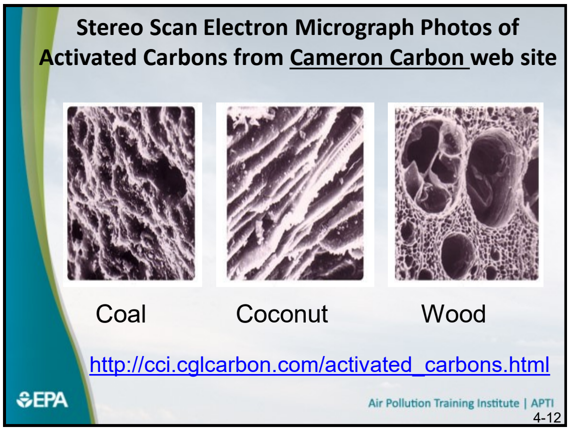
- Feedstocks
  - Wood
  - Coal
  - Coconut
  - Nutshells
  - Petroleum Products
  - Animal Bones

https://www.calgoncarbon.com/equipment/

EPA

Air Pollution Training Institute | APTI

4-11



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

Coal

Coconut

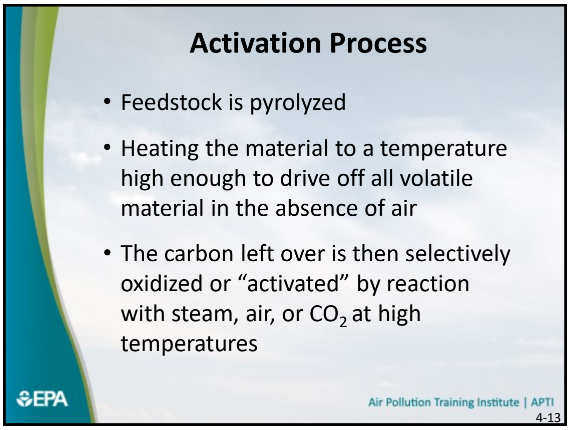
Wood

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

EPA

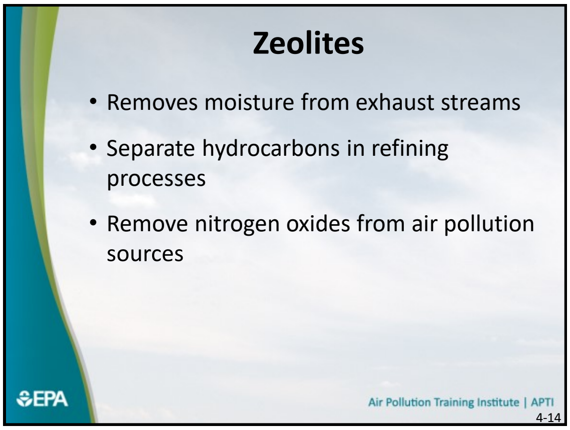
Air Pollution Training Institute | APTI

4-12



Activation Process

- Feedstock is pyrolyzed
- Heating the material to a temperature high enough to drive off all volatile material in the absence of air
- The carbon left over is then selectively oxidized or “activated” by reaction with steam, air, or CO_2 at high temperatures



Zeolites

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

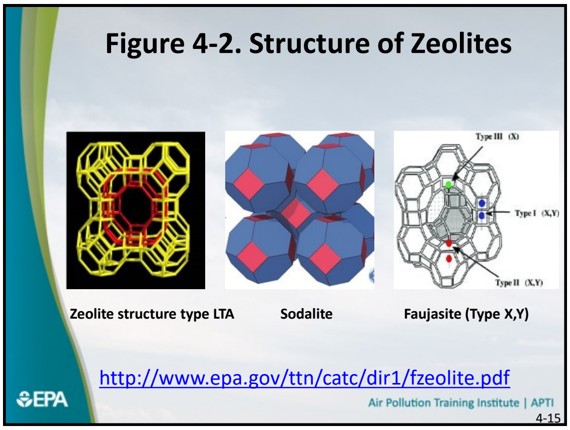
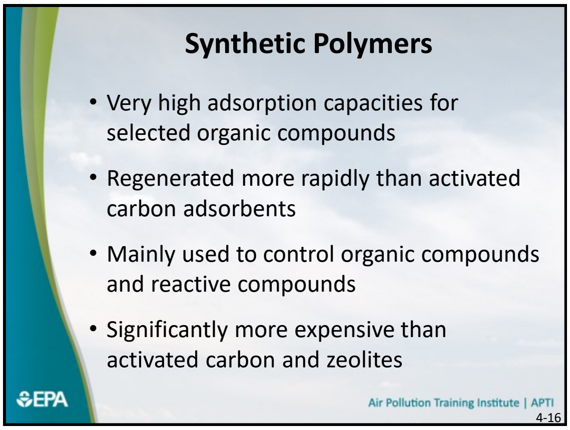


Figure 4-2. Structure of Zeolites

Zeolite structure type LTA **Sodalite** **Faujasite (Type X,Y)**

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



Synthetic Polymers

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

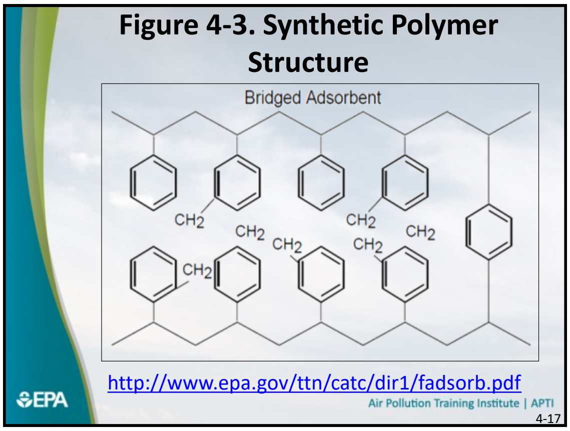
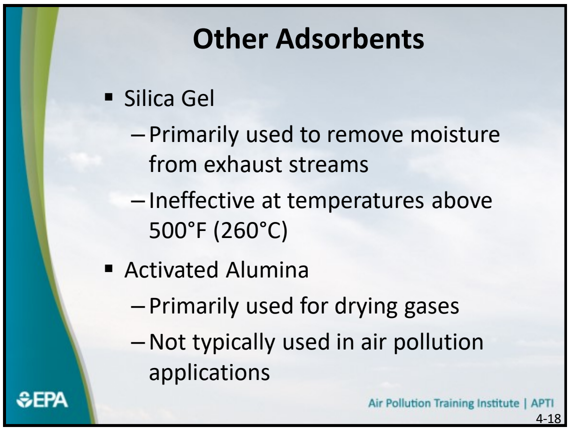


Figure 4-3. Synthetic Polymer Structure

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



Other Adsorbents

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

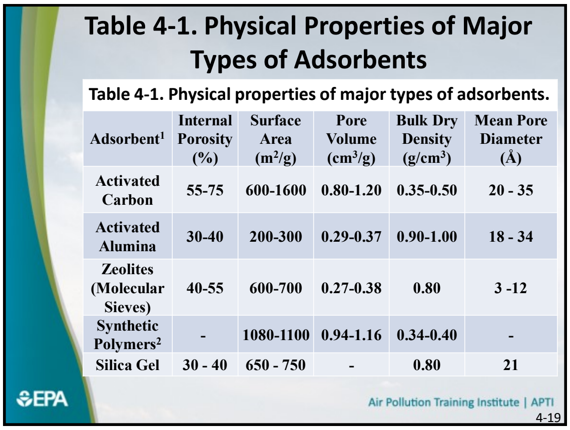


Table 4-1. Physical Properties of Major Types of Adsorbents

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

Adsorbent[1]	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	20 - 35
Activated Alumina	30-40	200-300	0.29-0.37	0.90-1.00	18 - 34
Zeolites (Molecular Sieves)	40-55	600-700	0.27-0.38	0.80	3 -12
Synthetic Polymers[2]	-	1080-1100	0.94-1.16	0.34-0.40	-
Silica Gel	30 - 40	650 - 750	-	0.80	21

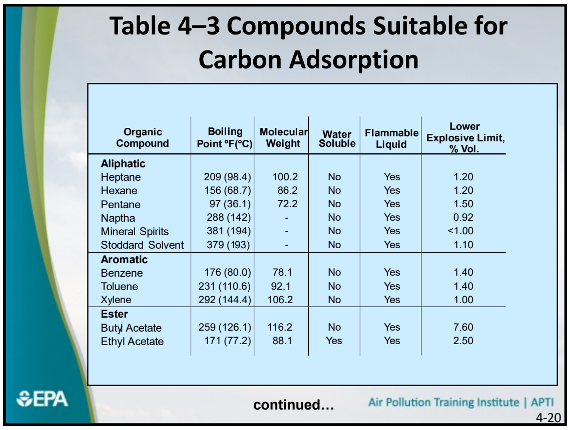


Table 4–3 Compounds Suitable for Carbon Adsorption

Organic Compound	Boiling Point °F(°C)	Molecular Weight	Water Soluble	Flammable Liquid	Lower Explosive Limit, % Vol.
Aliphatic					
Heptane	209 (98.4)	100.2	No	Yes	1.20
Hexane	156 (68.7)	86.2	No	Yes	1.20
Pentane	97 (36.1)	72.2	No	Yes	1.50
Naptha	288 (142)	-	No	Yes	0.92
Mineral Spirits	381 (194)	-	No	Yes	<1.00
Stoddard Solvent	379 (193)	-	No	Yes	1.10
Aromatic					
Benzene	176 (80.0)	78.1	No	Yes	1.40
Toluene	231 (110.6)	92.1	No	Yes	1.40
Xylene	292 (144.4)	106.2	No	Yes	1.00
Ester					
Butyl Acetate	259 (126.1)	116.2	No	Yes	7.60
Ethyl Acetate	171 (77.2)	88.1	Yes	Yes	2.50

continued...

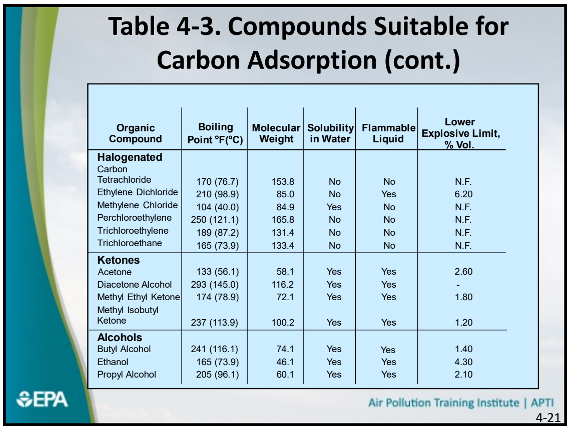


Table 4-3. Compounds Suitable for Carbon Adsorption (cont.)

Organic Compound	Boiling Point °F(°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.
Trichloroethane	165 (73.9)	133.4	No	No	N.F.
Ketones					
Acetone	133 (56.1)	58.1	Yes	Yes	2.60
Diacetone Alcohol	293 (145.0)	116.2	Yes	Yes	-
Methyl Ethyl Ketone	174 (78.9)	72.1	Yes	Yes	1.80
Methyl Isobutyl Ketone	237 (113.9)	100.2	Yes	Yes	1.20
Alcohols					
Butyl Alcohol	241 (116.1)	74.1	Yes	Yes	1.40
Ethanol	165 (73.9)	46.1	Yes	Yes	4.30
Propyl Alcohol	205 (96.1)	60.1	Yes	Yes	2.10

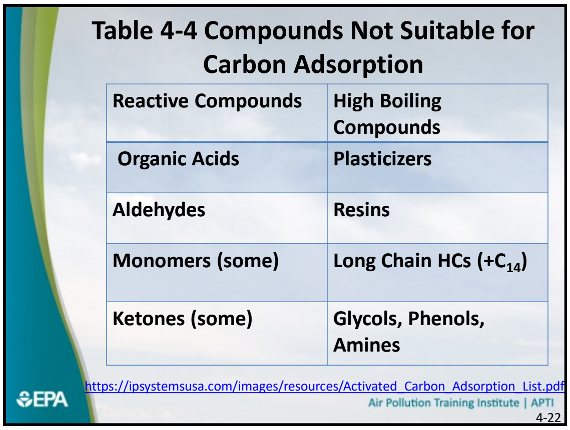
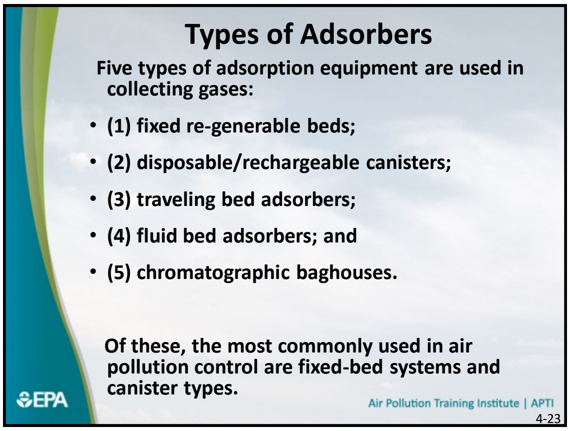


Table 4-4 Compounds Not Suitable for Carbon Adsorption

Reactive Compounds	**High Boiling Compounds**
Organic Acids	**Plasticizers**
Aldehydes	**Resins**
Monomers (some)	**Long Chain HCs (+C_{14})**
Ketones (some)	**Glycols, Phenols, Amines**

https://ipsystemsusa.com/images/resources/Activated_Carbon_Adsorption_List.pdf

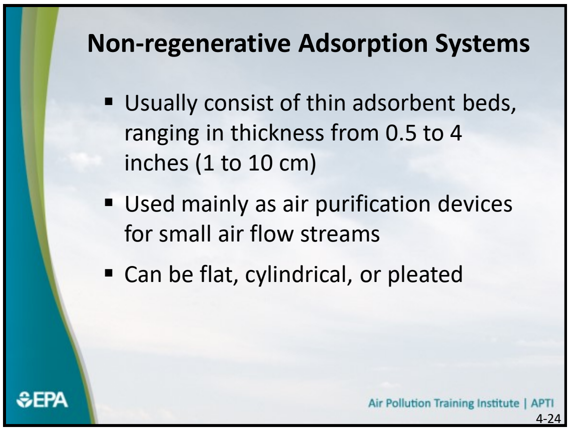


Types of Adsorbers

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.



Non-regenerative Adsorption Systems

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

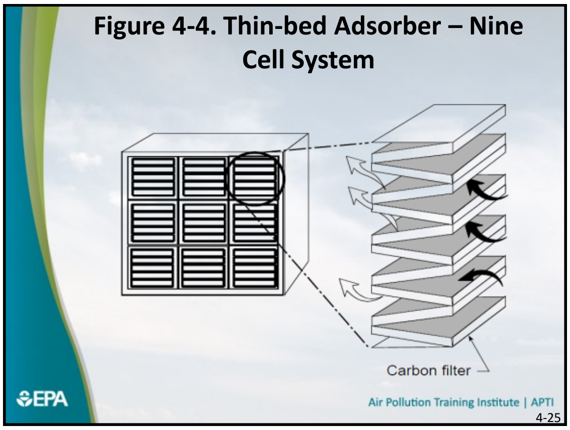


Figure 4-4. Thin-bed Adsorber – Nine Cell System

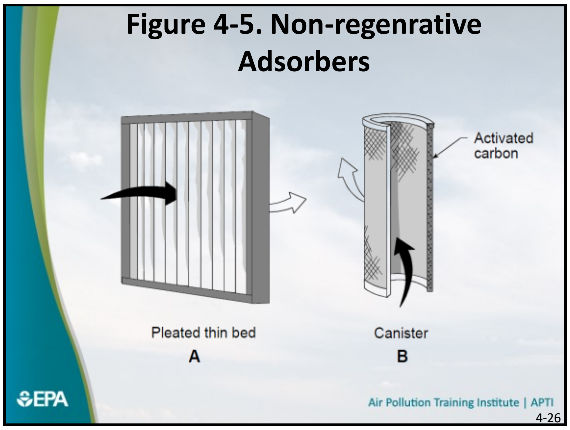


Figure 4-5. Non-regenrative Adsorbers

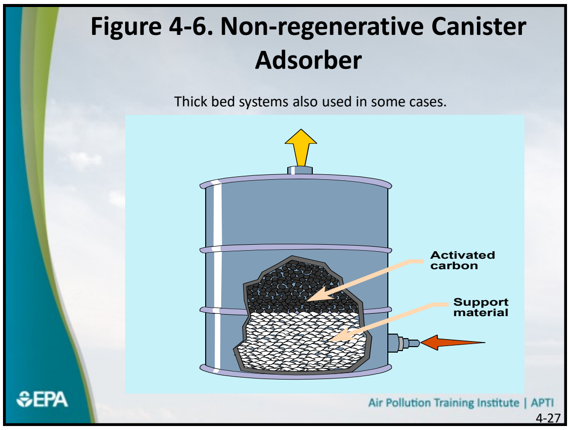


Figure 4-6. Non-regenerative Canister Adsorber

Thick bed systems also used in some cases.

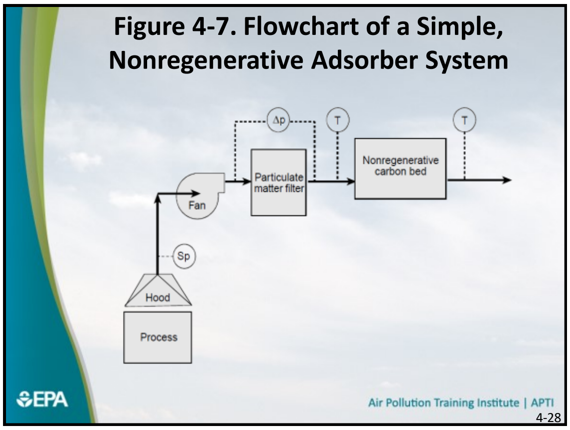
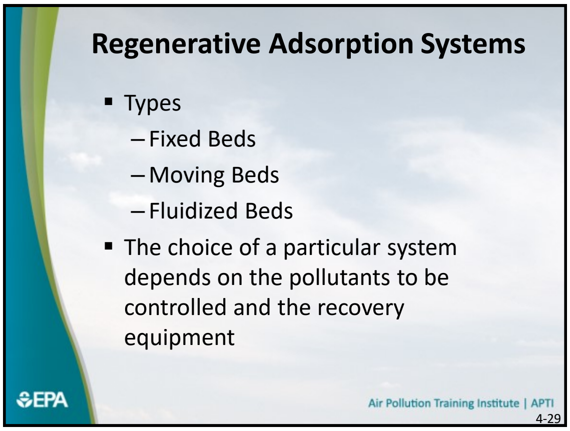
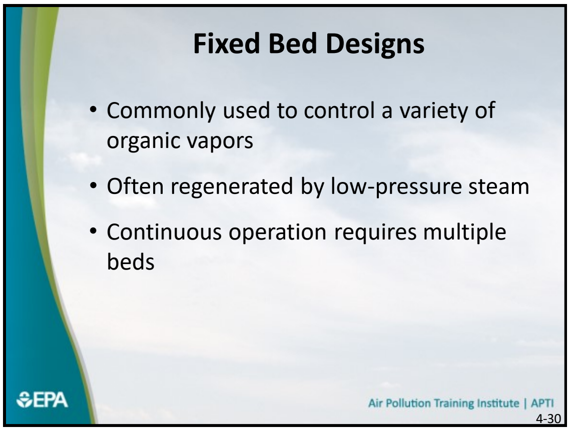


Figure 4-7. Flowchart of a Simple, Nonregenerative Adsorber System



Regenerative Adsorption Systems

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



Fixed Bed Designs

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

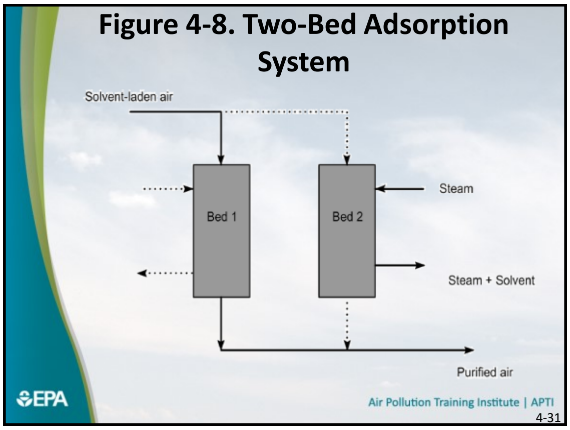


Figure 4-8. Two-Bed Adsorption System

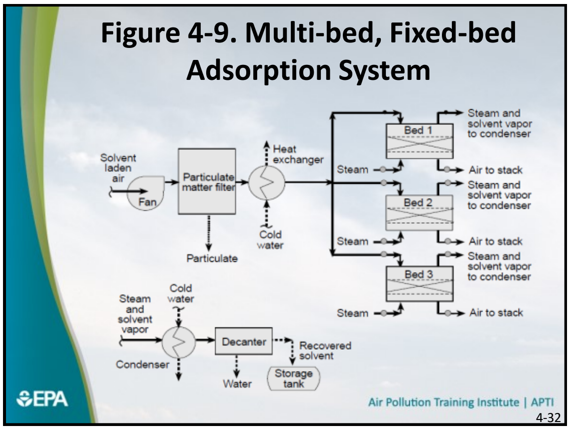


Figure 4-9. Multi-bed, Fixed-bed Adsorption System

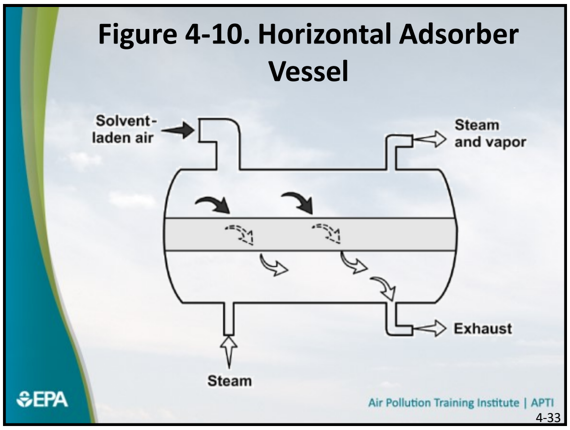


Figure 4-10. Horizontal Adsorber Vessel

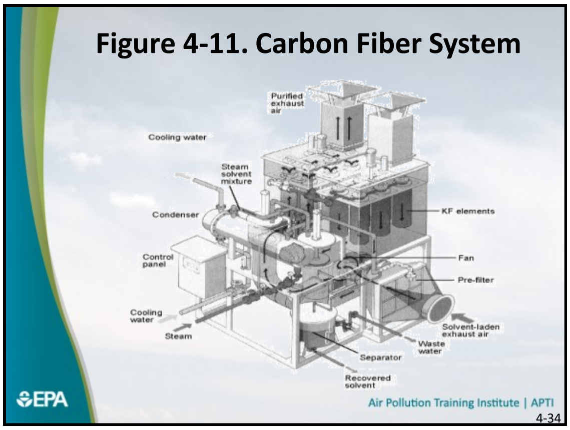
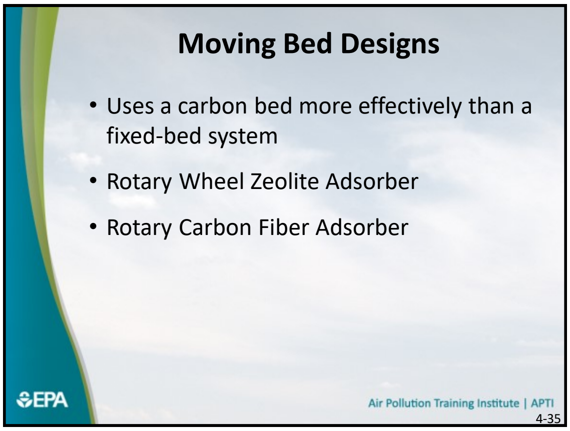


Figure 4-11. Carbon Fiber System



Moving Bed Designs

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

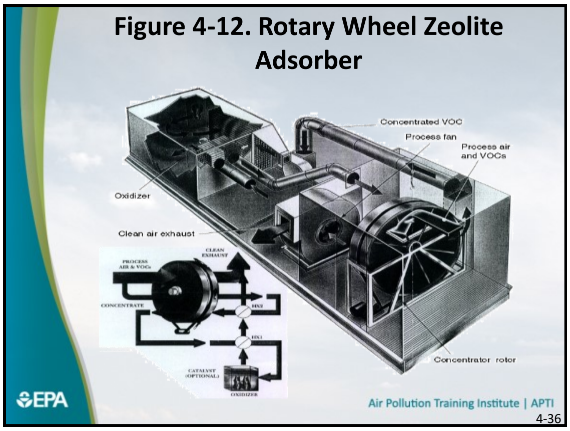


Figure 4-12. Rotary Wheel Zeolite Adsorber

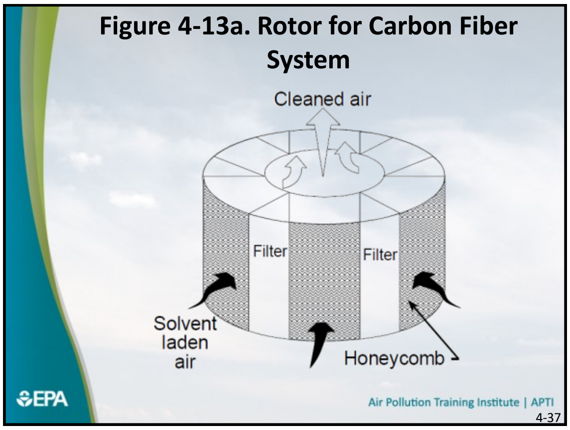


Figure 4-13a. Rotor for Carbon Fiber System

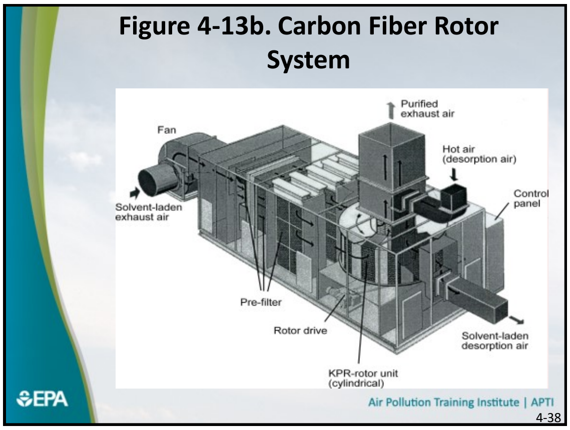
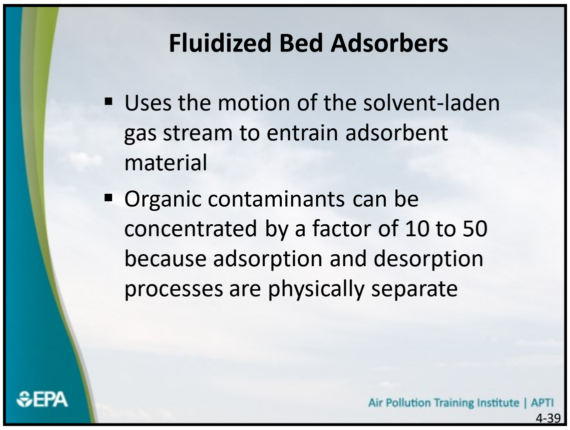


Figure 4-13b. Carbon Fiber Rotor System



Fluidized Bed Adsorbers

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

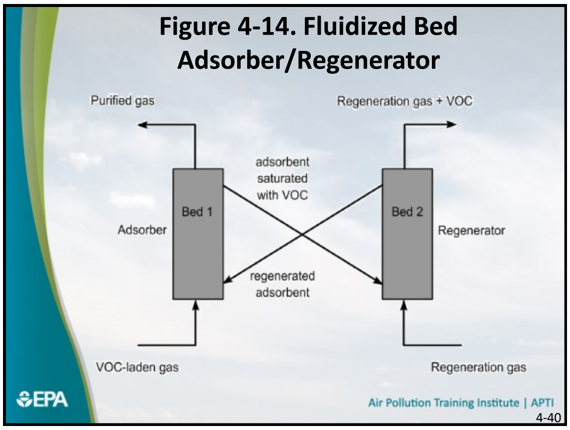


Figure 4-14. Fluidized Bed Adsorber/Regenerator

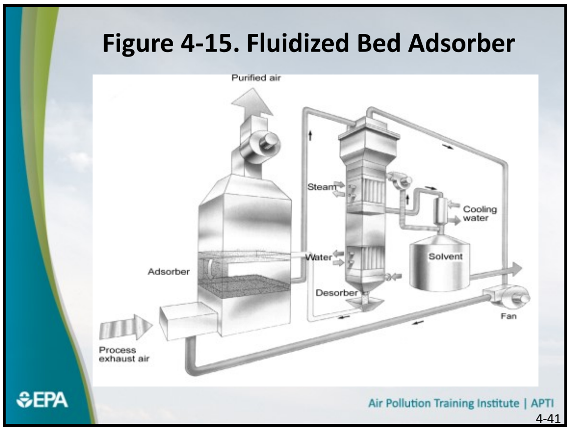
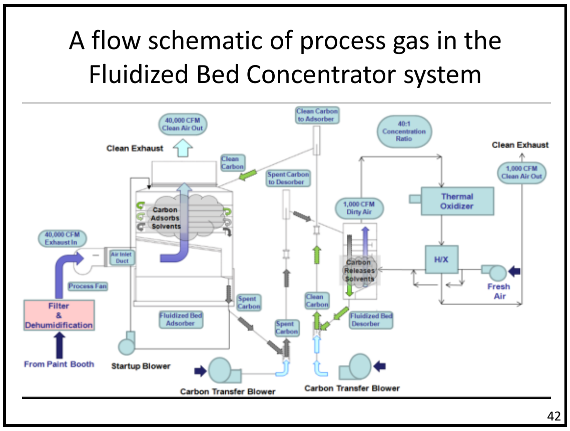


Figure 4-15. Fluidized Bed Adsorber



A flow schematic of process gas in the Fluidized Bed Concentrator system

Operating Principles

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

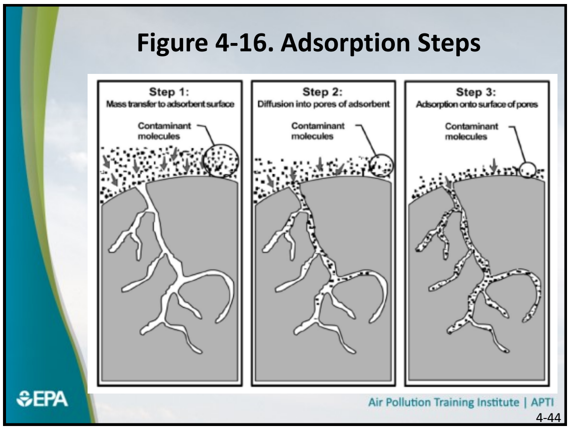


Figure 4-16. Adsorption Steps

Adsorption Forces

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

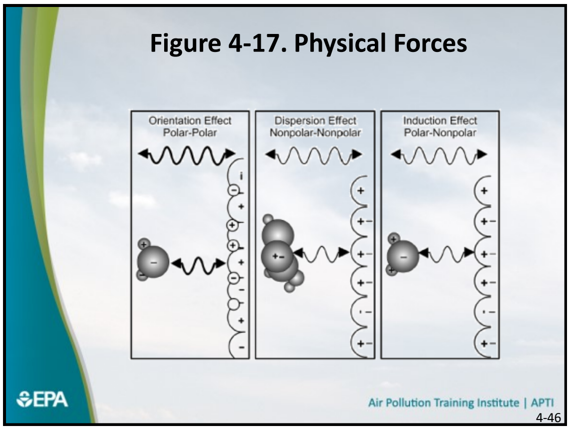


Figure 4-17. Physical Forces

Adsorption Forces

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

Table 4-2. Characteristics 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

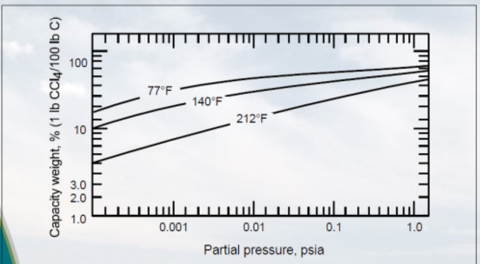
Adsorption Capacity

- 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.

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

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



Source: Adapted from Technical Bulletin, Calgon Corp.

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 10^6.

y = 680 ppm= 0.00068

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

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

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

Isostere

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

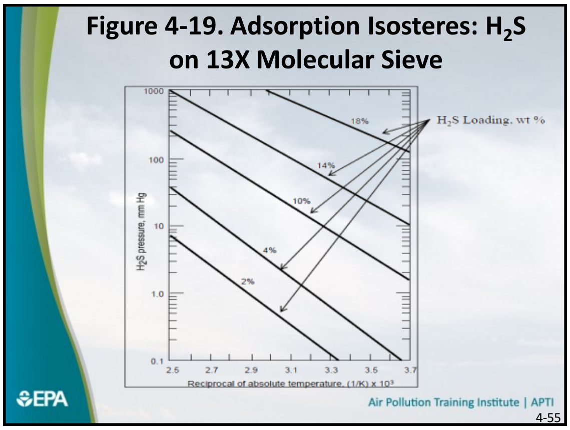
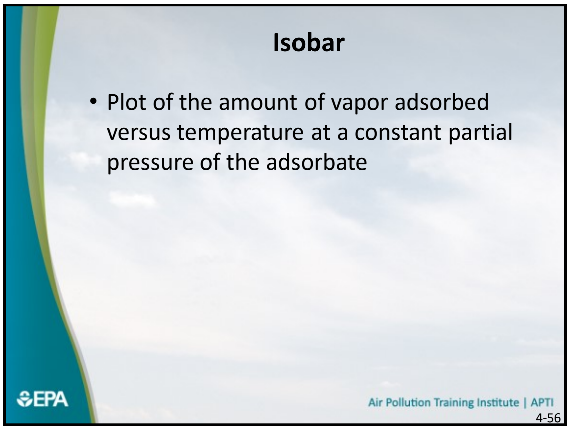


Figure 4-19. Adsorption Isosteres: H_2S on 13X Molecular Sieve



Isobar

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

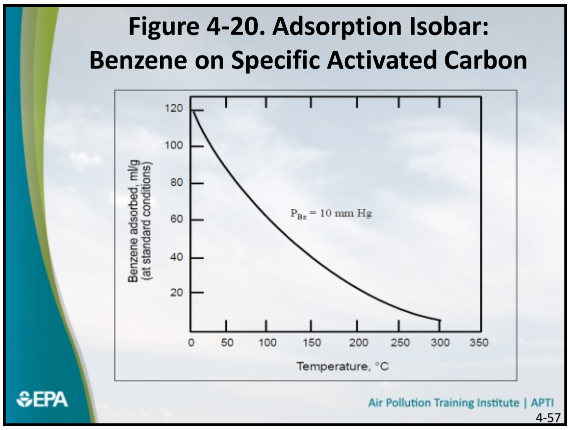
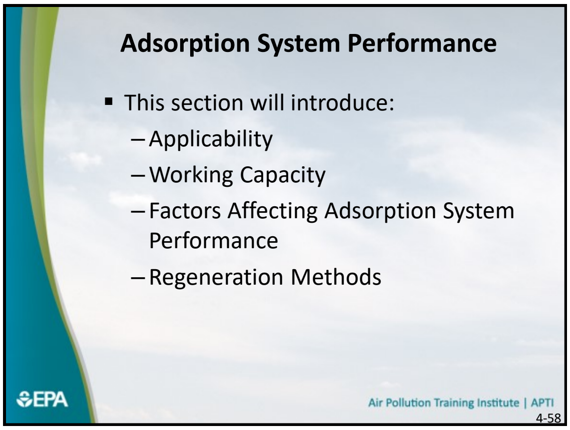
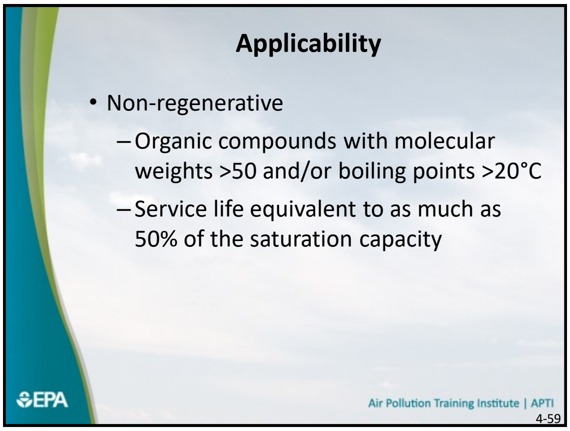


Figure 4-20. Adsorption Isobar: Benzene on Specific Activated Carbon



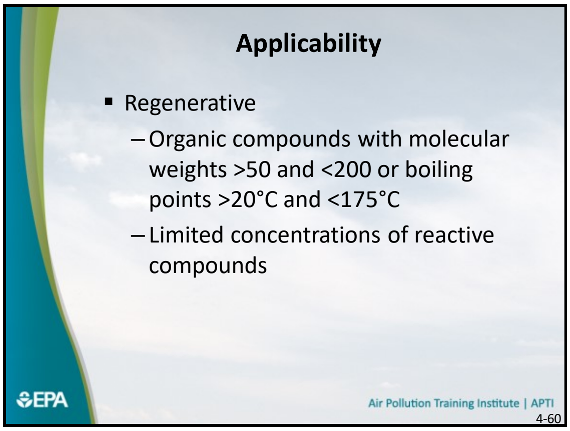
Adsorption System Performance

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



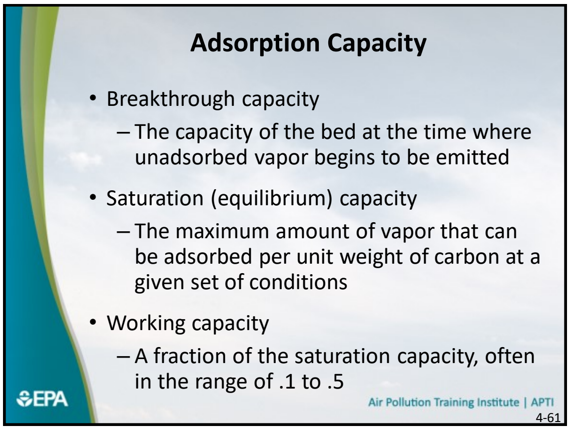
Applicability

- 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



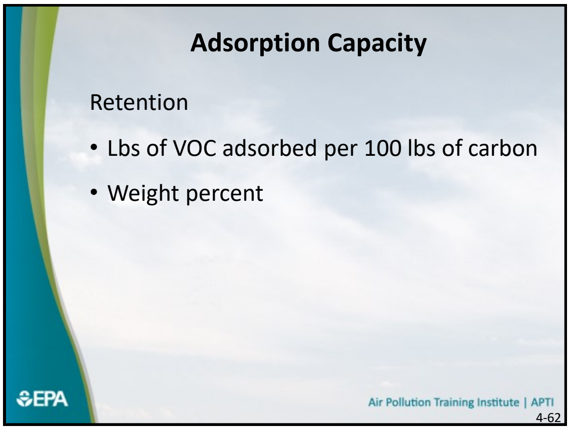
Applicability

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



Adsorption Capacity

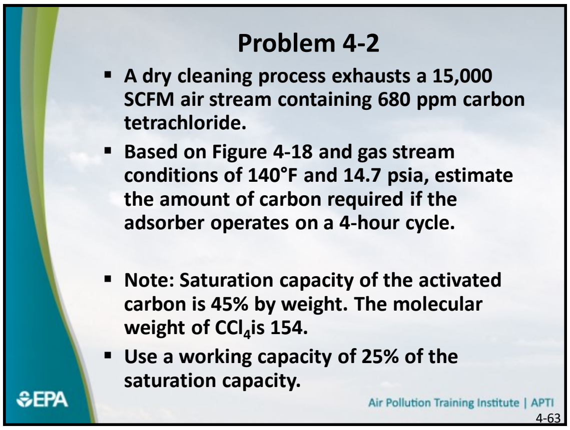
- Breakthrough capacity
  - The capacity of the bed at the time where unadsorbed vapor begins to be emitted
- Saturation (equilibrium) capacity
  - The maximum amount of vapor that can be adsorbed per unit weight of carbon at a given set of conditions
- Working capacity
  - A fraction of the saturation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



Adsorption Capacity

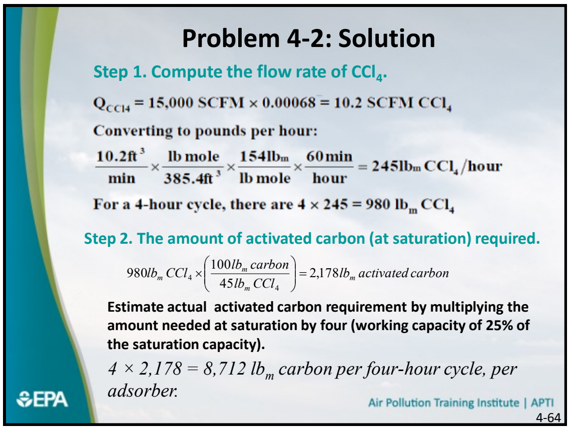
Retention

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



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 CCl_4 is 154.**
- **Use a working capacity of 25% of the saturation capacity.**



Problem 4-2: Solution

Step 1. Compute the flow rate of CCl_4.

$$Q_{CCl4} = 15{,}000 \text{ SCFM} \times 0.00068 = 10.2 \text{ SCFM } CCl_4$$

Converting to pounds per hour:

$$\frac{10.2\,\text{ft}^3}{\text{min}} \times \frac{\text{lb mole}}{385.4\,\text{ft}^3} \times \frac{154\,\text{lb}_m}{\text{lb mole}} \times \frac{60\,\text{min}}{\text{hour}} = 245\,\text{lb}_m\, CCl_4/\text{hour}$$

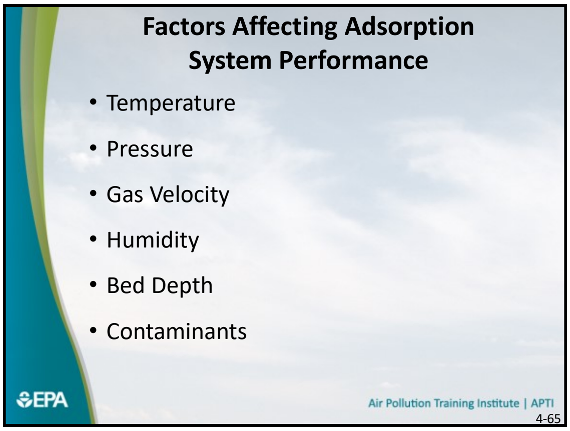
For a 4-hour cycle, there are $4 \times 245 = 980\ \text{lb}_m\ CCl_4$

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

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

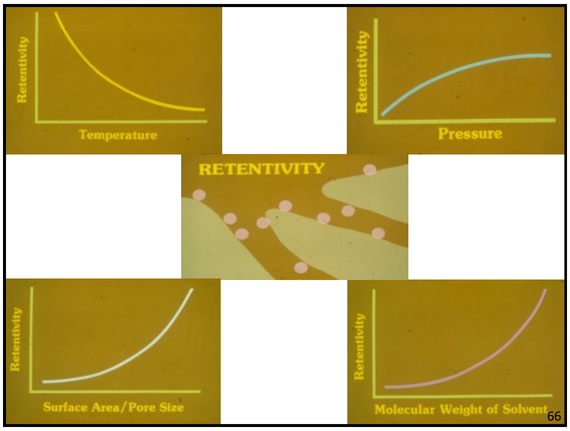
Estimate actual activated carbon requirement by multiplying the amount needed at saturation by four (working capacity of 25% of the saturation capacity).

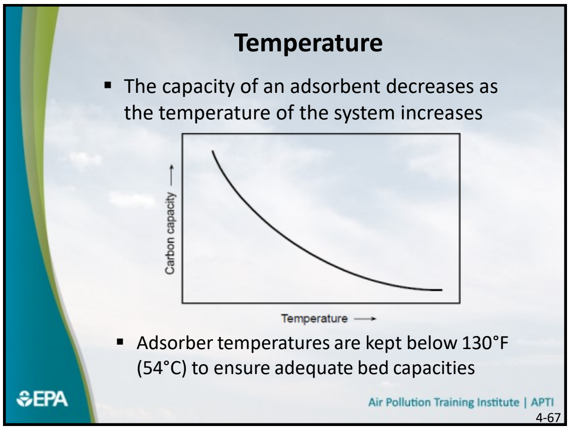
$4 \times 2{,}178 = 8{,}712\ lb_m$ *carbon per four-hour cycle, per adsorber.*



Factors Affecting Adsorption System Performance

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

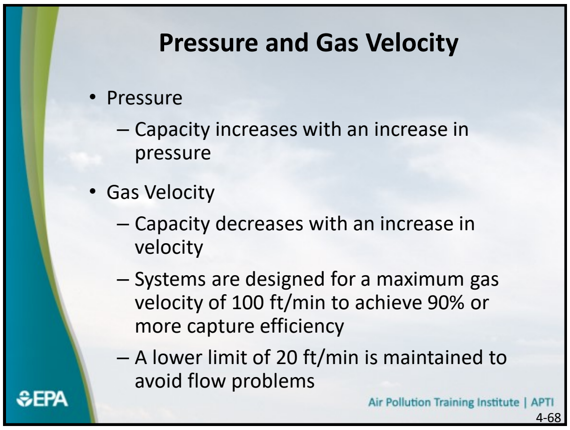




Temperature

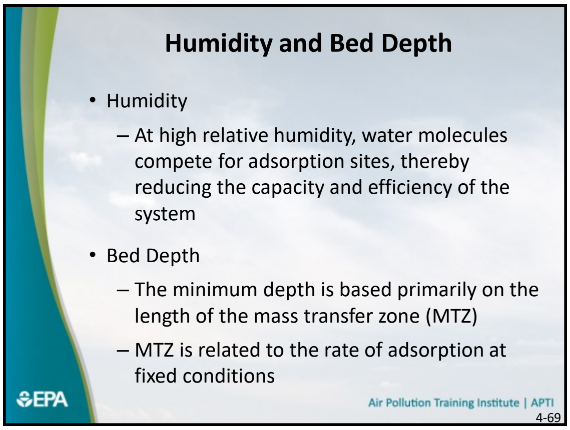
- The capacity of an adsorbent decreases as the temperature of the system increases

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



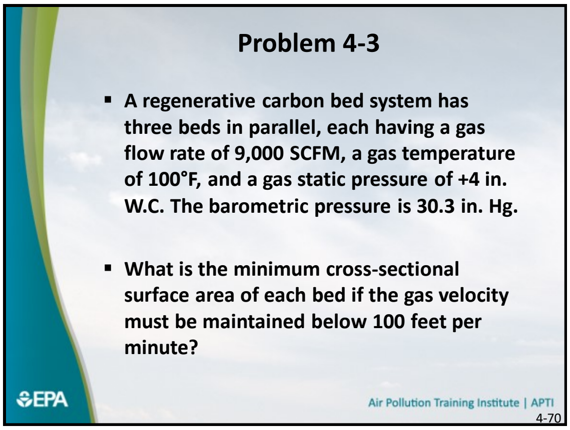
Pressure and Gas Velocity

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



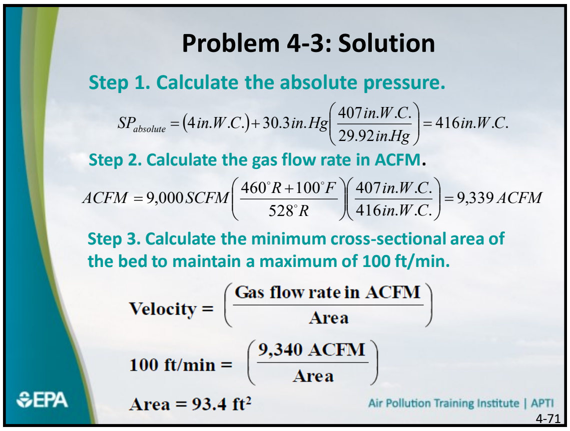
Humidity and Bed Depth

- 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



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?**



Problem 4-3: Solution

Step 1. Calculate the absolute pressure.

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

Step 2. Calculate the gas flow rate in ACFM.

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

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

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

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

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

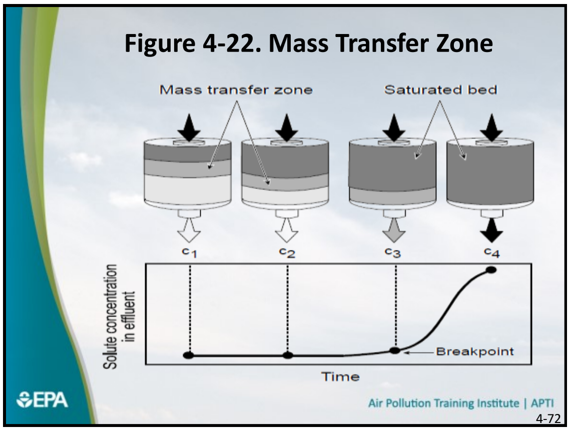
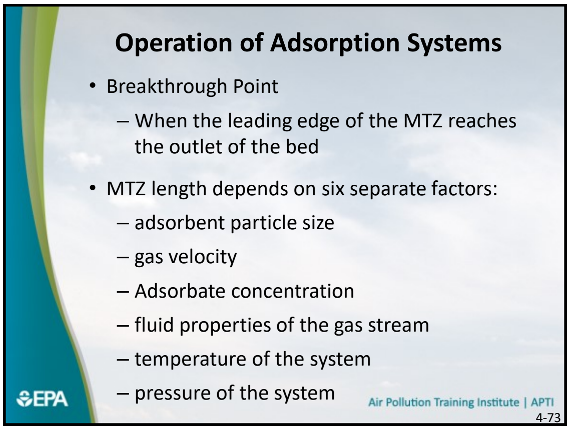
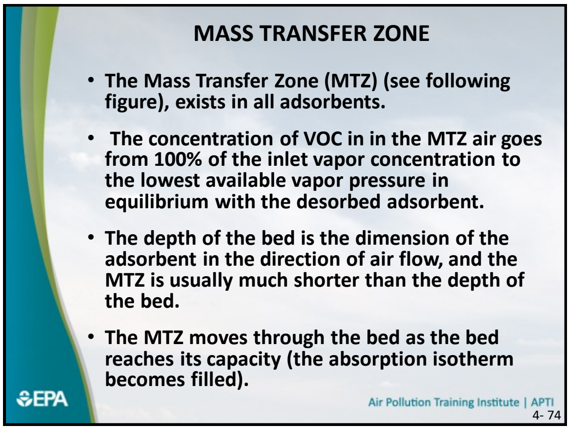


Figure 4-22. Mass Transfer Zone



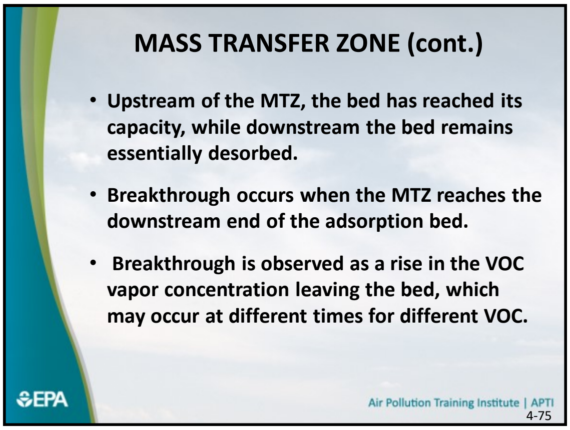
Operation of Adsorption Systems

- 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



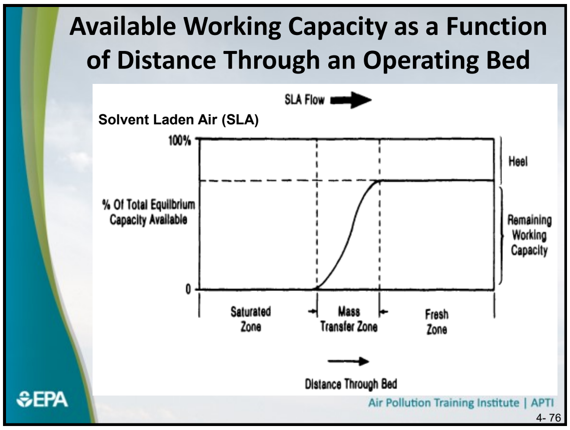
MASS TRANSFER ZONE

- **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).**

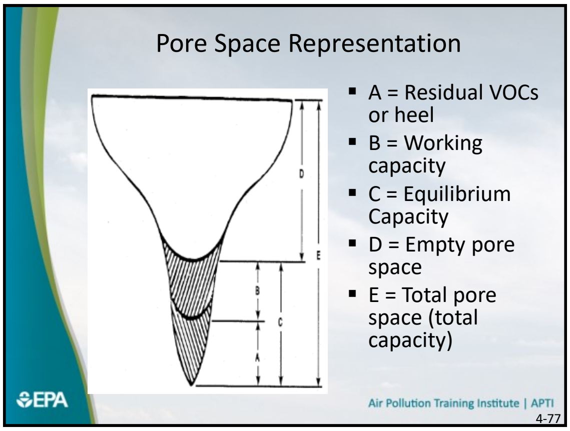


MASS TRANSFER ZONE (cont.)

- **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.**

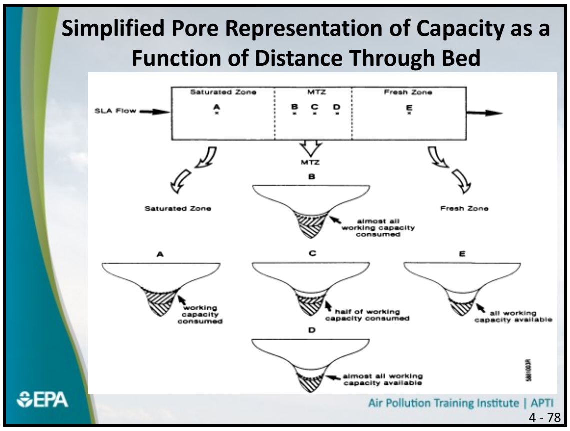


Available Working Capacity as a Function of Distance Through an Operating Bed

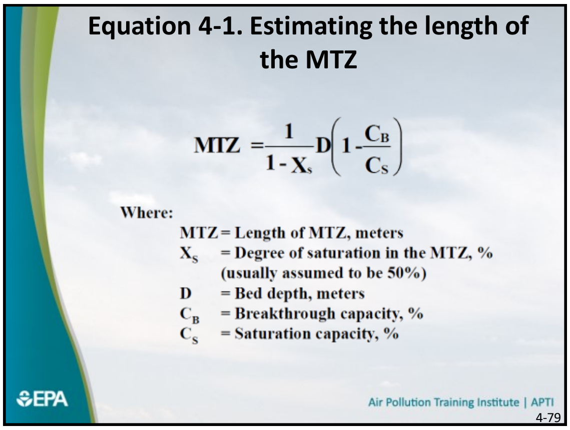


Pore Space Representation

- A = Residual VOCs or heel
- B = Working capacity
- C = Equilibrium Capacity
- D = Empty pore space
- E = Total pore space (total capacity)



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

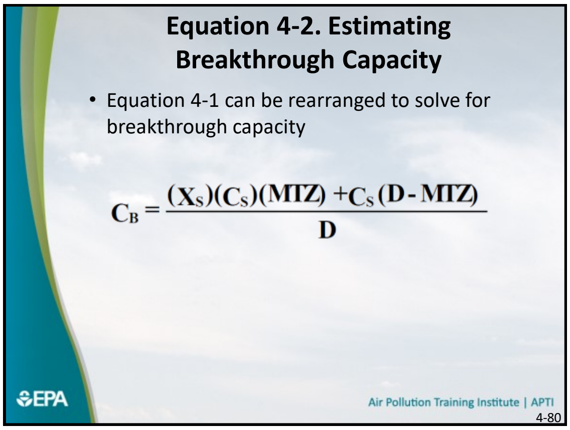


Equation 4-1. Estimating the length of the MTZ

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

Where:

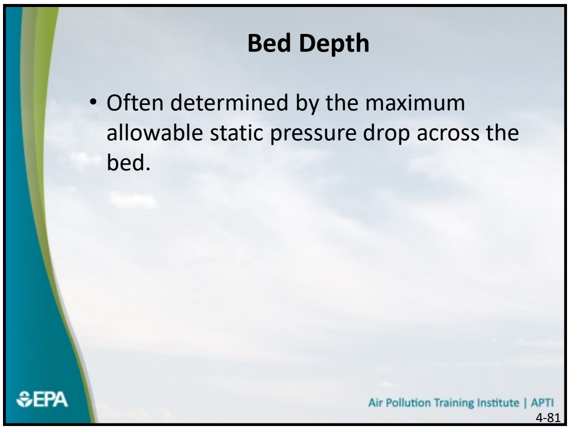
MTZ = Length of MTZ, meters
X_S = Degree of saturation in the MTZ, % (usually assumed to be 50%)
D = Bed depth, meters
C_B = Breakthrough capacity, %
C_S = Saturation capacity, %



Equation 4-2. Estimating Breakthrough Capacity

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

$$C_B = \frac{(X_S)(C_S)(MTZ) + C_S(D - MTZ)}{D}$$



Bed Depth

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

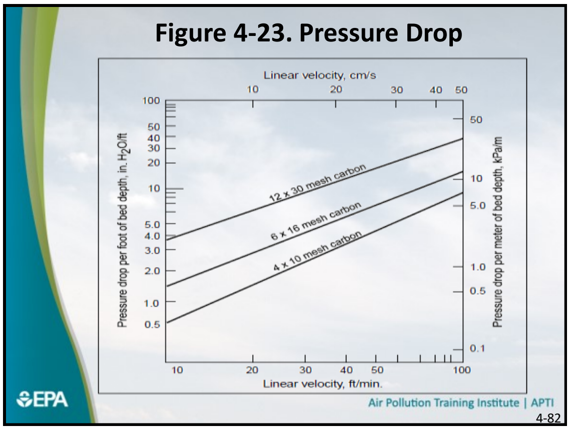
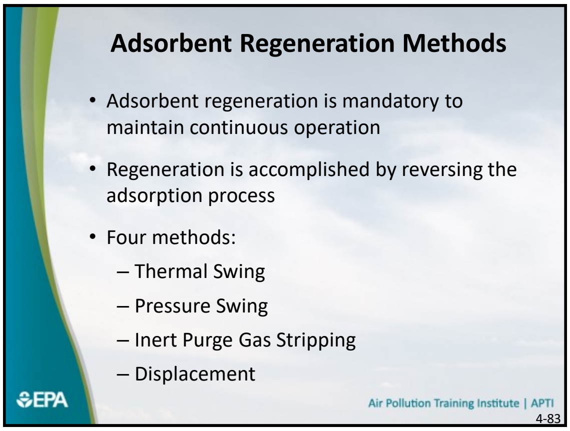
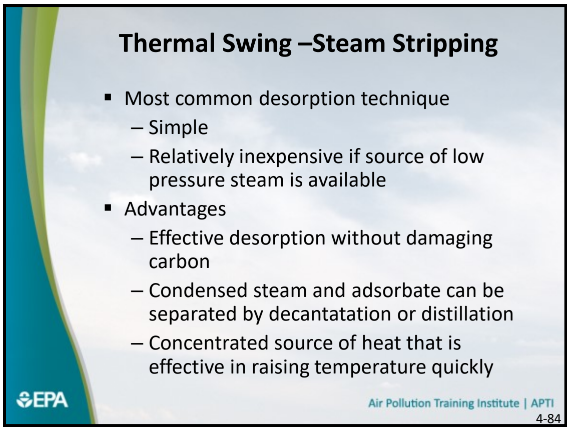


Figure 4-23. Pressure Drop



Adsorbent Regeneration Methods

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

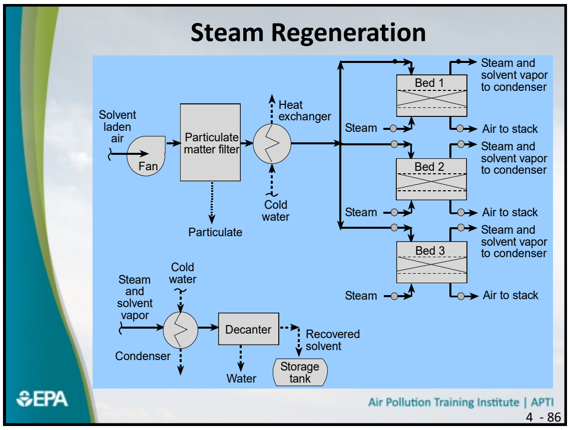


Thermal Swing –Steam Stripping

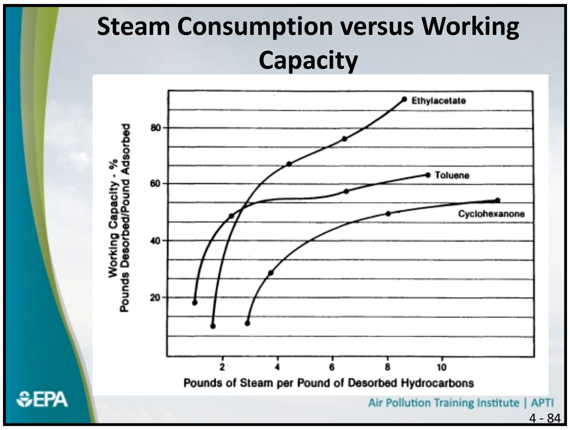
- Most common desorption technique
  - Simple
  - Relatively inexpensive if source of low pressure steam is available
- Advantages
  - Effective desorption without damaging carbon
  - Condensed steam and adsorbate can be separated by decantatation or distillation
  - Concentrated source of heat that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

Steam Stripping Disadvantages

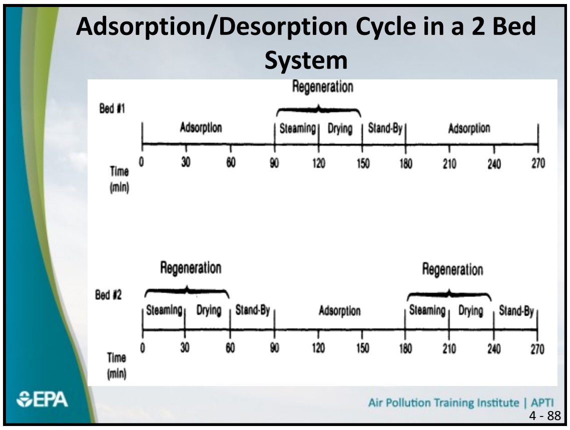
- Aqueous effluent can pose a water pollution problem
- Some organic compounds may hydrolyze or form corrosive solutions in the presence of water
- A hot, wet carbon bed will not effectively remove organic vapors (bed must be dried and cooled prior to next adsorption cycle)



Steam Regeneration



Steam Consumption versus Working Capacity



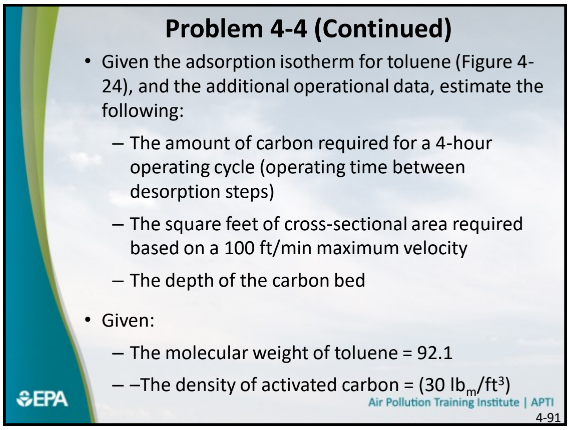
Adsorption/Desorption Cycle in a 2 Bed System

Pressure Swing – Vacuum Desorption

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

Problem 4-4

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



Problem 4-4 (Continued)

- Given the adsorption isotherm for toluene (Figure 4-24), and the additional operational data, estimate the following:
  - The amount of carbon required for a 4-hour operating cycle (operating time between desorption steps)
  - The square feet of cross-sectional area required based on a 100 ft/min maximum velocity
  - The depth of the carbon bed
- Given:
  - The molecular weight of toluene = 92.1
  - –The density of activated carbon = (30 lb_m/ft^3)

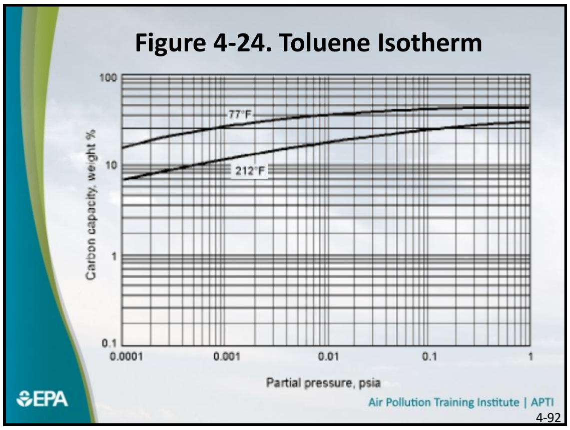
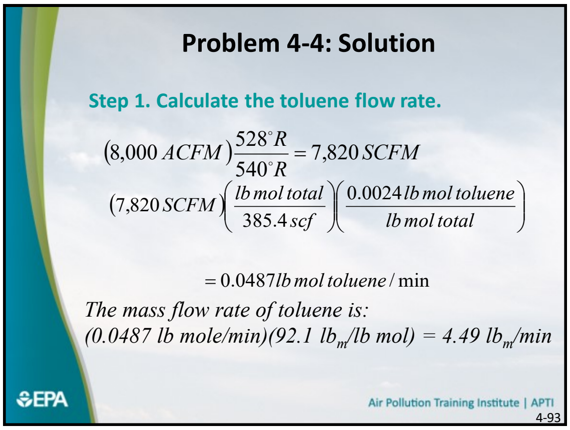


Figure 4-24. Toluene Isotherm



Problem 4-4: Solution

Step 1. Calculate the toluene flow rate.

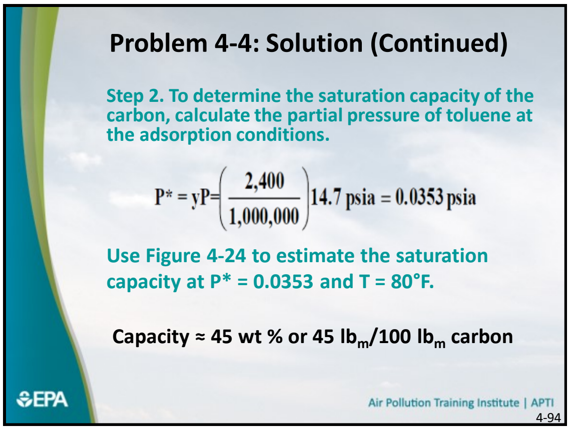
$$(8{,}000\,ACFM)\frac{528^\circ R}{540^\circ R} = 7{,}820\,SCFM$$

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

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

The mass flow rate of toluene is:

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



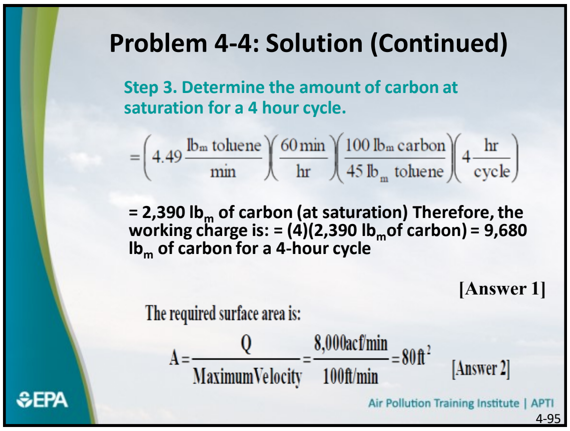
Problem 4-4: Solution (Continued)

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

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

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

Capacity ≈ 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.

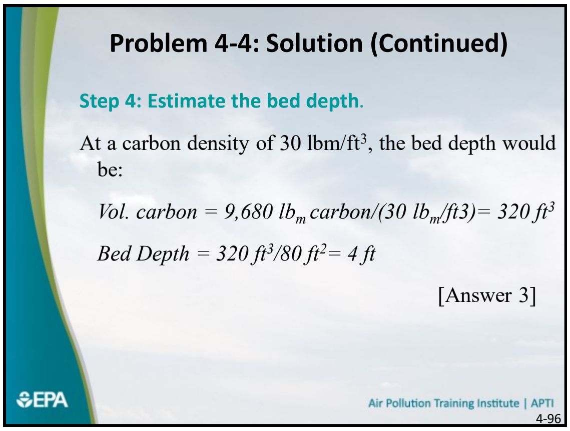
$$=\left(4.49\frac{\text{lb}_m\ \text{toluene}}{\text{min}}\right)\left(\frac{60\ \text{min}}{\text{hr}}\right)\left(\frac{100\ \text{lb}_m\ \text{carbon}}{45\ \text{lb}_m\ \text{toluene}}\right)\left(4\frac{\text{hr}}{\text{cycle}}\right)$$

= 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)

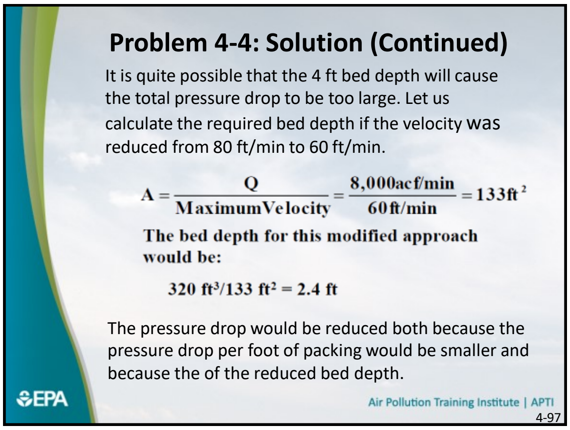
Step 4: Estimate the bed depth.

At a carbon density of 30 lbm/ft^3, the bed depth would be:

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

Bed Depth = 320 ft^3/80 ft^2= 4 ft

[Answer 3]



Problem 4-4: Solution (Continued)

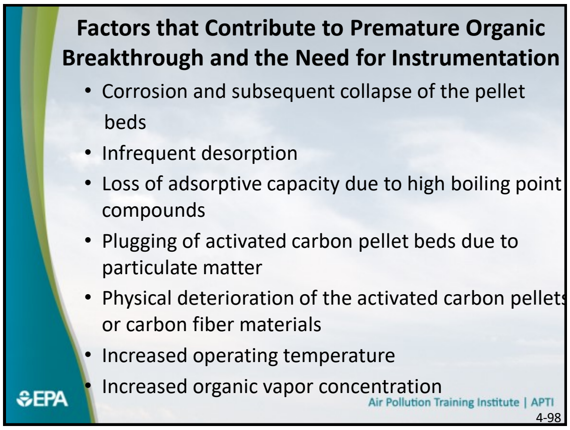
It is quite possible that the 4 ft bed depth will cause the total pressure drop to be too large. Let us calculate the required bed depth if the velocity was reduced from 80 ft/min to 60 ft/min.

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

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 the 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 pellet or carbon fiber materials
- Increased operating temperature
- Increased organic vapor concentration

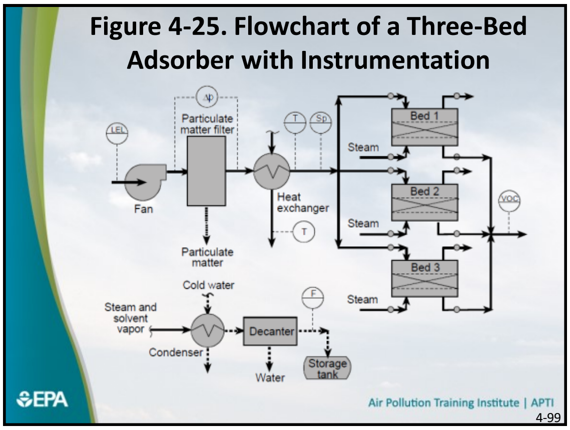
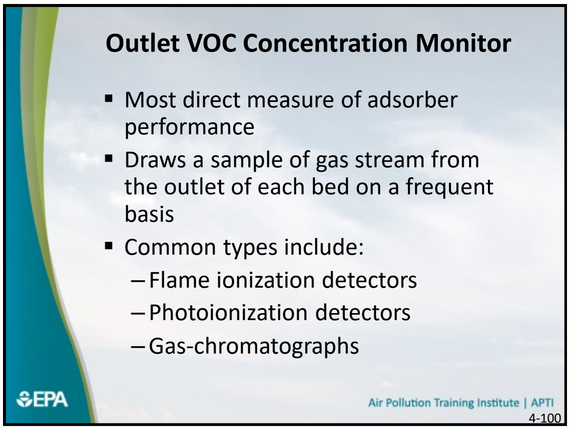


Figure 4-25. Flowchart of a Three-Bed Adsorber with Instrumentation



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

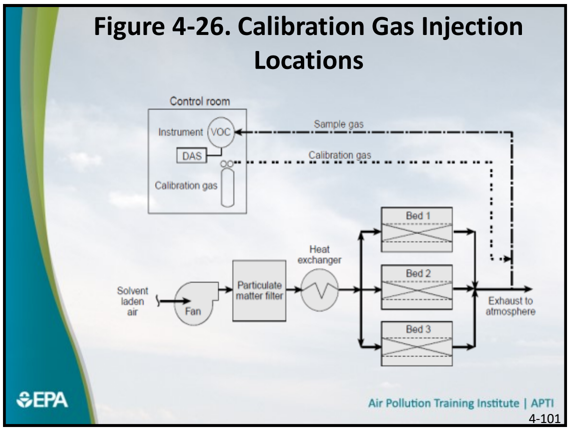
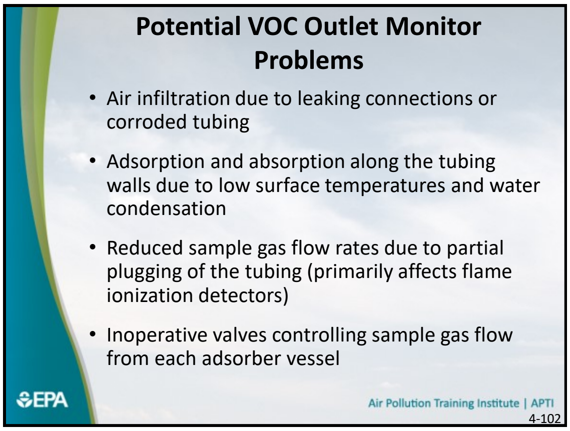


Figure 4-26. Calibration Gas Injection Locations



Potential VOC Outlet Monitor Problems

- Air infiltration due to leaking connections or corroded tubing
- Adsorption and absorption along the tubing walls due to low surface temperatures and water condensation
- Reduced sample gas flow rates due to partial plugging of the tubing (primarily affects flame ionization detectors)
- Inoperative valves controlling sample gas flow from each adsorber vessel

Portable VOC Detectors

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

Additional Monitoring Considerations

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

Summary

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

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

Summary (Continued)

Conclusions

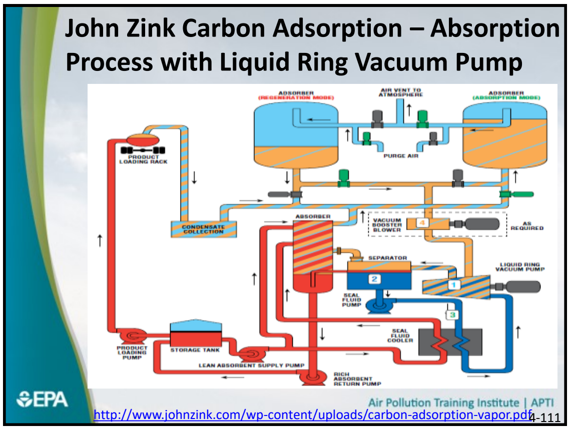
- Contaminants having molecular weights between about 50 and 200 are good candidates for adsorption. These compounds generally have boiling temperatures between about 70°F and 350°F.
- The size of an adsorption system depends, in part, on the temperature and inlet organic vapor concentration of the inlet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

Uses of Non-regenerable Adsorbers

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

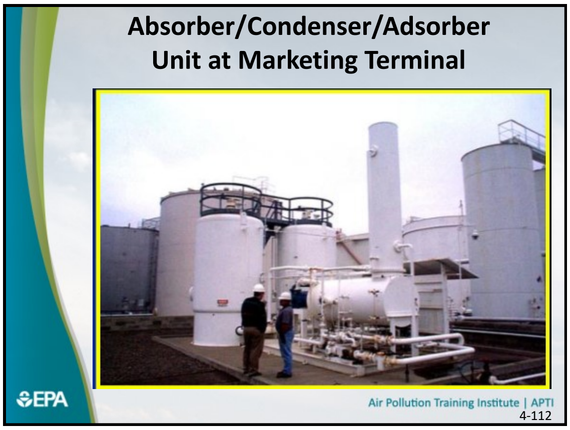
Non-Regenerative Carbon Adsorption Drums controlling mercaptan odors from re-refined crankcase oil product

Non-Regenerative Carbon Adsorption Drums



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

http://www.johnzink.com/wp-content/uploads/carbon-adsorption-vapor.pdf



Absorber/Condenser/Adsorber Unit at Marketing Terminal

Carbon Adsorber – Fixed Bed Examples

United States Environmental Protection Agency
Office of Solid Waste and Emergency Response (5104)
EPA 550-F-97-002e
May 1997

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(e) and Clean Air Act (CAA), EPA has authority to conduct chemical accident investigations. Additionally, in January 1995, the Administration asked the Occupational Safety and Health Administration (OSHA) and EPA to jointly undertake investigations to determine the root cause(s) 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 OSHA in these efforts. Prior to the release of a full report, EPA intends to publish *Alerts* as promptly as possible to increase awareness of possible hazards. *Alerts* may also be issued when EPA becomes aware of a significant hazard. It is important that facilities, SERCs, LEPCs, emergency responders and others review this information and take appropriate steps to minimize risk.

CHEMICAL SAFETY ALERT

PROBLEM

Activated carbon systems used to adsorb vapors for control of offensive odors may pose a fire hazard when used for certain types of substances, if proper procedures are not followed. In particular, crude sulfate turpentine, commonly produced in the pulp and paper industry, can pose a fire hazard if the adsorption system is not properly designed and proper procedures are not implemented. Facilities should take precautions to avoid or mitigate these fire hazards.

ACCIDENTS

In a 1995 accident at a chemical terminal facility, a fire and explosion occurred involving three tanks of crude sulfate turpentine. The tanks were connected to drums of activated carbon for deodorizing. The fire and explosion damaged other storage tanks, resulting in the release of toxic gases and forcing a large-scale evacuation of area residents.

Fires have occurred in the past in activated carbon systems used for deodorizing crude sulfate turpentine. In general, such fires have not had effects as serious as those reported in the 1995 fire. Serious effects would not be expected if fires are confined to the activated carbon containers and do not spread to tanks containing flammable or combustible substances.

HAZARD AWARENESS

Activated carbon is widely used to adsorb vapors to prevent their release to the air. For certain classes of chemicals, reaction or adsorption on the carbon surface is accompanied by release of a large amount of heat that may cause hot spots in the carbon bed. Such chemicals include organic sulfur compounds (e.g., mercaptans), which may be found as impurities in crude sulfate turpentine and other materials. Other classes of chemicals that may cause large thermal releases are ketones, aldehydes, and some organic acids. Adsorption of high vapor concentrations of organic compounds also can create hot spots. If flammable vapors are present, the heat released by adsorption or reaction on the carbon surface of the carbon may create a fire hazard (e.g., a fire may start if the temperature reaches the autoignition temperature of the vapor and oxygen is present to support ignition).

Chemical Emergency Preparedness and Prevention Office

Printed on recycled paper

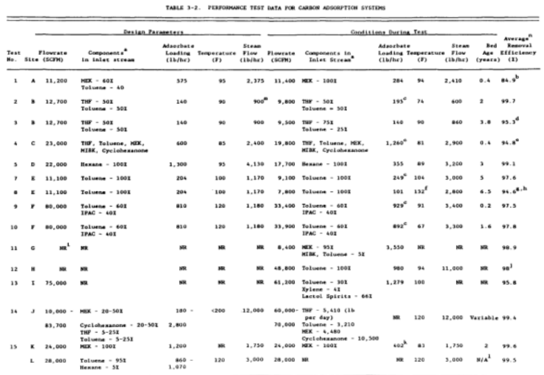
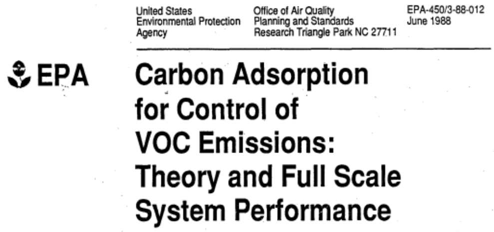


TABLE 3-2. PERFORMANCE TEST DATA FOR CARBON ADSORPTION SYSTEMS

		Design Parameters					Conditions During Test						
Test No.	Site	Flowrate (SCFM)	Components[a] in inlet stream	Adsorbate Loading (lb/hr)	Temperature (F)	Steam Flow (lb/hr)	Flowrate (SCFM)	Components in Inlet Stream[a]	Adsorbate Loading (lb/hr)	Temperature (F)	Steam Flow (lb/hr)	Bed Age (years)	Average[a] Removal Efficiency (%)
1	A	11,200	MEK - 60% Toluene - 40	575	95	2,375	11,400	MEK - 100%	284	94	2,410	0.4	84.9[b]
2	B	12,700	THF - 50% Toluene - 50%	140	90	900[m]	9,800	THF - 50% Toluene - 50%	195[c]	74	600	2	99.7
3	B	12,700	THF - 50% Toluene - 50%	140	90	900	9,500	THF - 75% Toluene - 25%	140	90	860	3.8	95.3[d]
4	C	23,000	THF, Toluene, MEK, MIBK, Cyclohexanone	600	85	2,400	19,800	THF, Toluene, MEK, MIBK, Cyclohexanone	1,260[e]	81	2,900	0.4	94.8[e]
5	D	22,000	Hexane - 100%	1,300	95	4,130	17,700	Hexane - 100%	355	89	3,200	3	99.1
7	E	11,100	Toluene - 100%	204	100	1,170	9,100	Toluene - 100%	249[c]	104	3,000	5	97.6
8	E	11,100	Toluene - 100%	204	100	1,170	7,800	Toluene - 100%	101	132[f]	2,800	6.5	94.6[g,h]
9	F	80,000	Toluene - 60% IPAC - 40%	810	120	1,180	33,400	Toluene - 60% IPAC - 40%	929[c]	91	3,400	0.2	97.5
10	F	80,000	Toluene - 60% IPAC - 40%	810	120	1,180	33,900	Toluene - 60% IPAC - 40%	892[c]	67	3,300	1.6	97.8
11	G	NR[i]	NR	NR	NR	NR	8,400	MEK - 95% MIBK, Toluene - 5%	3,550	NR	NR	NR	98.9
12	H	NR	NR	NR	NR	NR	48,800	Toluene - 100%	980	94	11,000	NR	98[j]
13	I	75,000	NR	NR	NR	NR	61,200	Toluene - 30% Xylene - 4% Lactol Spirits - 66%	1,279	100	NR	NR	95.8
14	J	10,000 - 83,700	MEK - 20-50% Cyclohexanone - 20-50% THF - 5-25% Toluene - 5-25%	180 - 2,800	<200	12,000	60,000- 70,000	THF - 5,410 (lb per day) Toluene - 3,210 MEK - 4,480 Cyclohexanone - 10,500	NR	120	12,000	Variable	99.4
15	K	24,000	MEK - 100%	1,200	NR	1,750	24,000	MEK - 100%	402[k]	83	1,750	2	99.6
	L	28,000	Toluene - 95% Hexane - 5%	860 - 1,070	120	3,000	28,000	NR	NR	120	3,000	N/A[l]	99.5



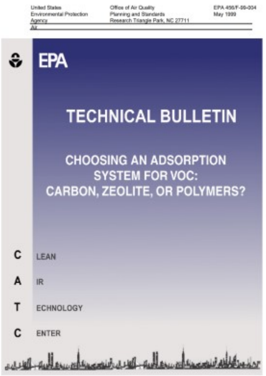
United States
Environmental Protection
Agency

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

EPA-450/3-88-012
June 1988

EPA

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



United States
Environmental Protection
Agency
Air

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

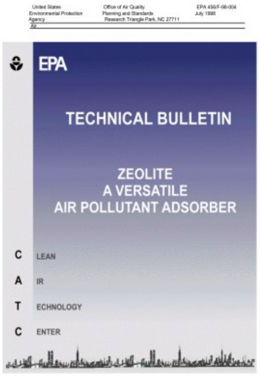
EPA 456/F-99-004
May 1999

EPA

TECHNICAL BULLETIN

CHOOSING AN ADSORPTION SYSTEM FOR VOC:
CARBON, ZEOLITE, OR POLYMERS?

C LEAN
A IR
T ECHNOLOGY
C ENTER



United States
Environmental Protection
Agency
Air

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

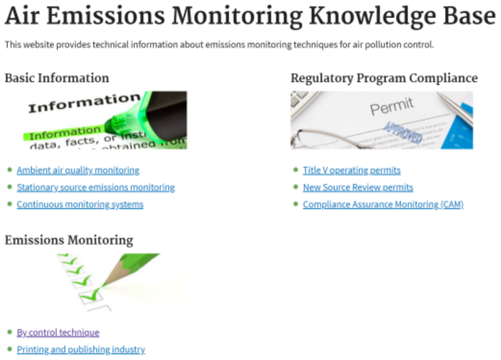
EPA 456/F-98-004
July 1998

EPA

TECHNICAL BULLETIN

ZEOLITE
A VERSATILE
AIR POLLUTANT ADSORBER

C LEAN
A IR
T ECHNOLOGY
C ENTER



Air Emissions Monitoring Knowledge Base

This website provides technical information about emissions monitoring techniques for air pollution control.

Basic Information

- Ambient air quality monitoring
- Stationary source emissions monitoring
- Continuous monitoring systems

Regulatory Program Compliance

- Title V operating permits
- New Source Review permits
- Compliance Assurance Monitoring (CAM)

Emissions Monitoring

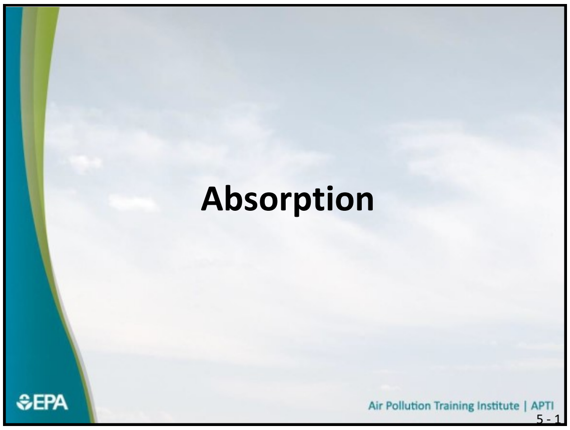
- By control technique
- Printing and publishing industry

Air Emissions Monitoring Knowledge Base | US EPA

Adsorption Publication Web sites

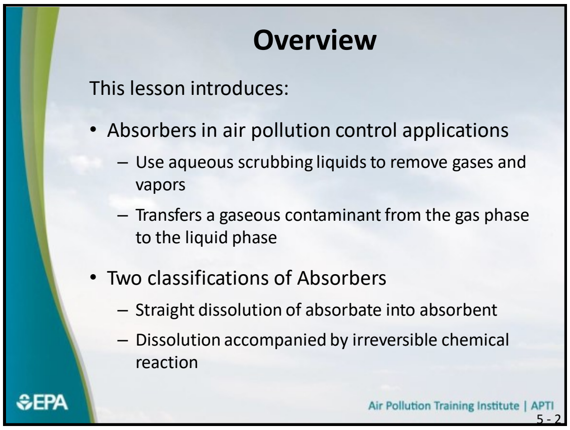
http://www.epa.gov/ttn/catc/dir1/cs3-1ch1.pdf

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



Absorption

Air Pollution Training Institute | APTI

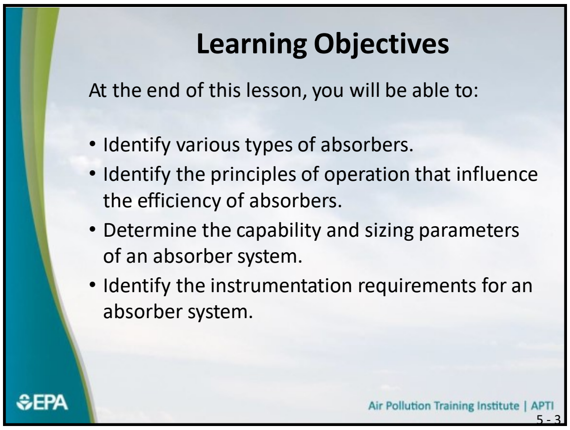


Overview

This lesson introduces:

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

Air Pollution Training Institute | APTI

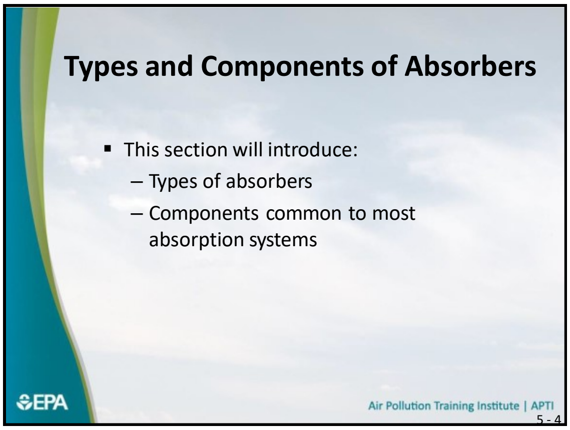


Learning Objectives

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

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

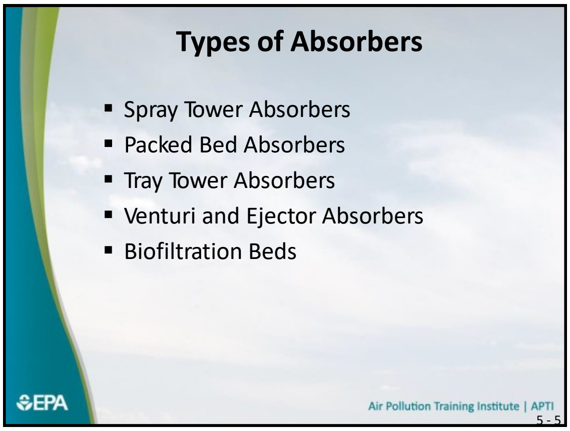
Air Pollution Training Institute | APTI



Types and Components of Absorbers

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

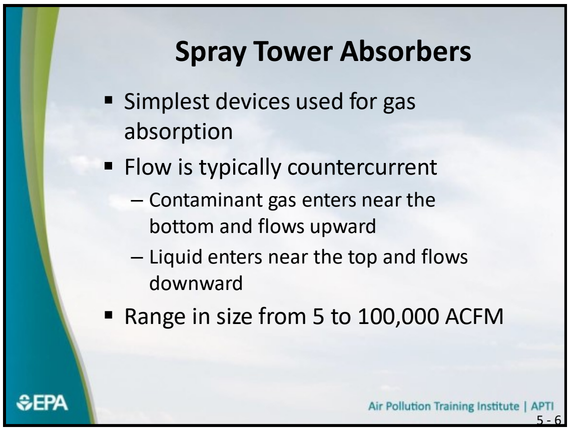
Air Pollution Training Institute | APTI



Types of Absorbers

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

Air Pollution Training Institute | APTI

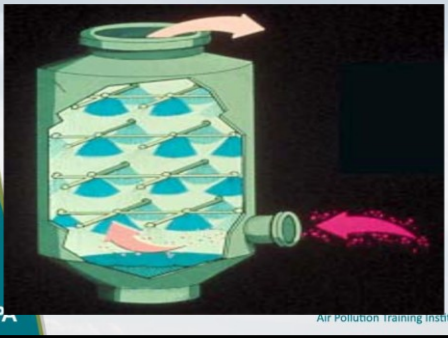


Spray Tower Absorbers

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

Air Pollution Training Institute | APTI

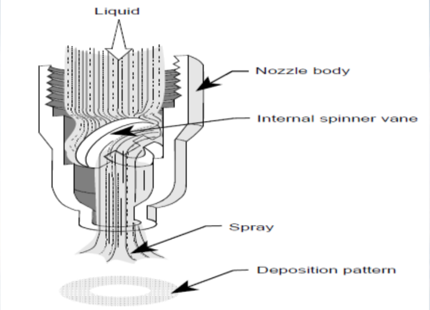
Figure 5-1. Spray Tower Scrubber



Flow Arrangements

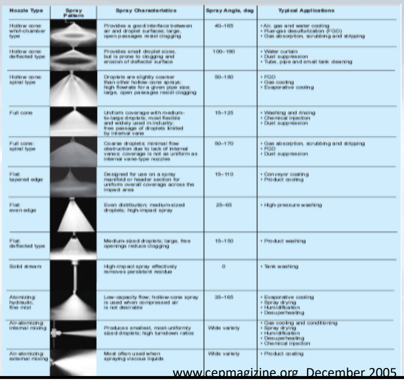
- Spray chambers can also operate
  - Cross-current: Gas flow is perpendicular to the liquid flow
  - Co-current: Gas and liquid flow in the same direction
- Both arrangements allow for higher gas stream velocities but are not as efficient as countercurrent units

Figure 5-2. Full-Cone Spray Nozzle



Various Nozzle Types

Basic Nozzle and Spray Characteristics



Nozzle Type	Spray Pattern	Spray Characteristics	Spray Angle, deg	Typical Applications
Hollow cone: whirl-chamber type		Provides a good interface between air and droplet surfaces; large, open passages resist clogging	40–165	• Air, gas and water cooling • Flue-gas desulfurization (FGD) • Gas absorption, scrubbing and stripping
Hollow cone: deflected type		Provides small droplet sizes, but is prone to clogging and erosion of deflector surface	100–180	• Water curtain • Dust suppression • Tube, pipe and small tank cleaning
Hollow cone: spiral type		Droplets are slightly coarser than other hollow-cone sprays; high flowrate for a given pipe size; large, open passages resist clogging	50–180	• FGD • Gas cooling • Evaporative cooling
Full cone		Uniform coverage with medium-to-large droplets; most flexible and widely used in industry; free passage of droplets limited by internal vane	15–125	• Washing and rinsing • Chemical injection • Dust suppression
Full cone: spiral type		Coarse droplets; minimal flow obstruction due to lack of internal vanes; coverage is not as uniform as internal vane-type nozzles	50–170	• Gas absorption, scrubbing and stripping • FGD • Dust suppression
Flat: tapered edge		Designed for use on a spray manifold or header section for uniform overall coverage across the impact area	15–110	• Conveyor coating • Product cooling
Flat: even edge		Even distribution; medium-sized droplets; high-impact spray	25–65	• High-pressure washing
Flat: deflected type		Medium-sized droplets; large, free openings reduce clogging	15–150	• Product washing
Solid stream		High-impact spray effectively removes persistent residue	0	• Tank washing
Atomizing: hydraulic, fine mist		Low-capacity flow; hollow-cone spray is used when compressed air is not desirable	35–165	• Evaporative cooling • Spray drying • Humidification • Desuperheating
Air-atomizing: internal mixing		Produces smallest, most-uniformly sized droplets; high turndown ratios	Wide variety	• Gas cooling and conditioning • Spray drying • Humidification • Desuperheating • Chemical injection
Air-atomizing: external mixing		Most often used when spraying viscous liquids	Wide variety	• Product coating

www.cepmagizine.org December 2005

Comparison

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

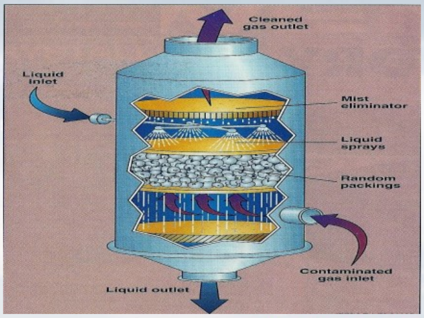
Packed Bed Absorbers

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

Types of Packed Bed Absorbers

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

Figure 5-3. Counter-current Packed Tower

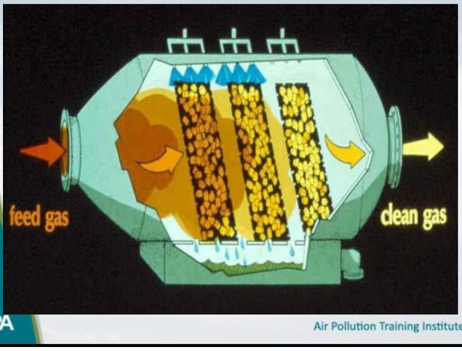


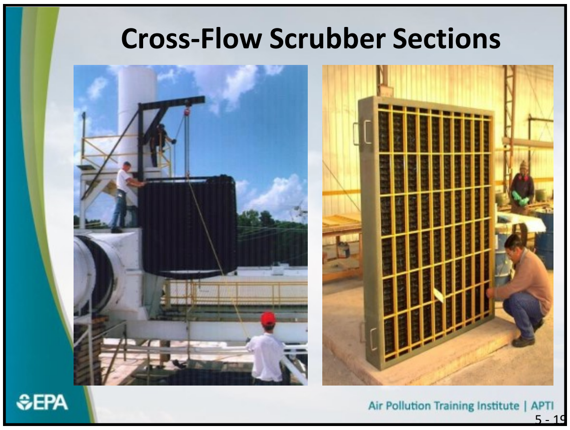
Counter-current Packed Tower at a Plating Operation

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

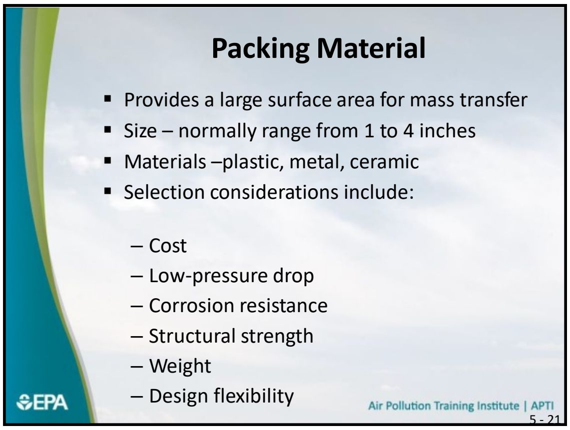




Cross-Flow Scrubber Sections

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/



Packing Material

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

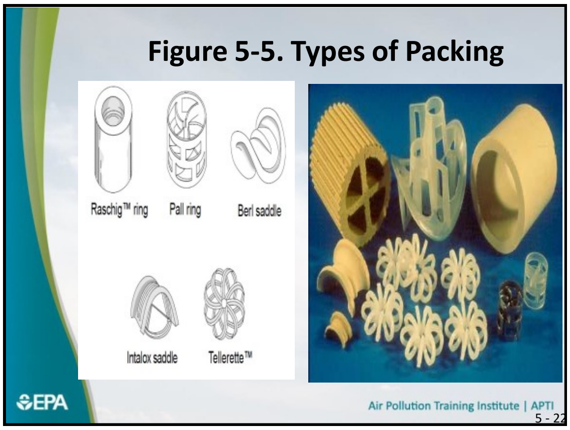
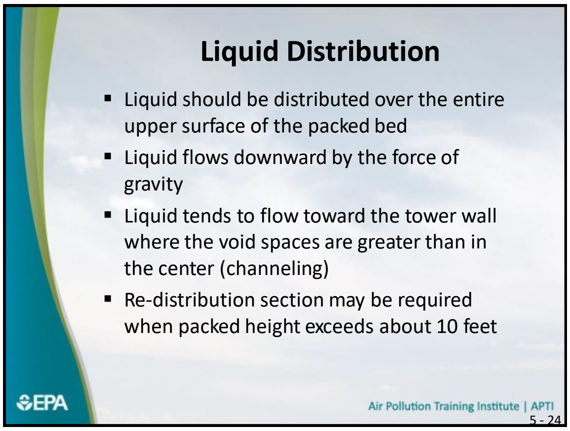


Figure 5-5. Types of Packing

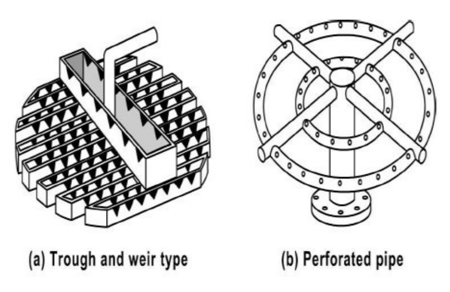
Typical Packing Material



Liquid Distribution

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

Figure 5-6. Types of Liquid Distributors


(a) Trough and weir type
(b) Perforated pipe

Tray Tower Absorbers

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

Figure 5-7. Bubble Cap Tray

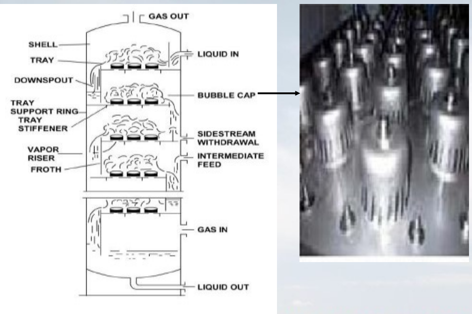
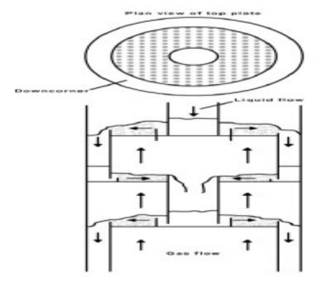


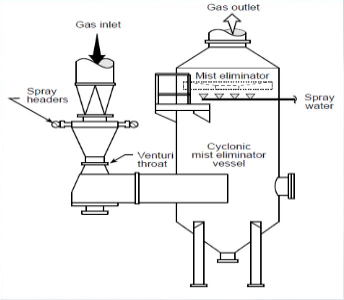
Figure 5-8. Gas-liquid Contact in a Disk-and-Donut Sieve Tray

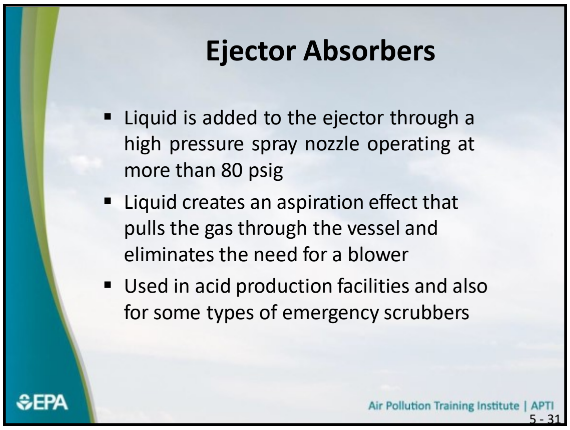


Venturi's

- 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

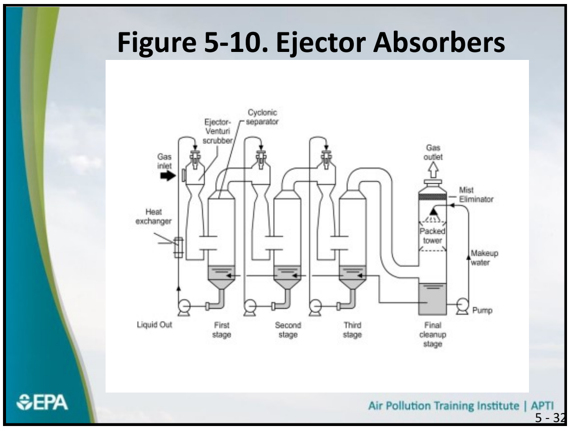
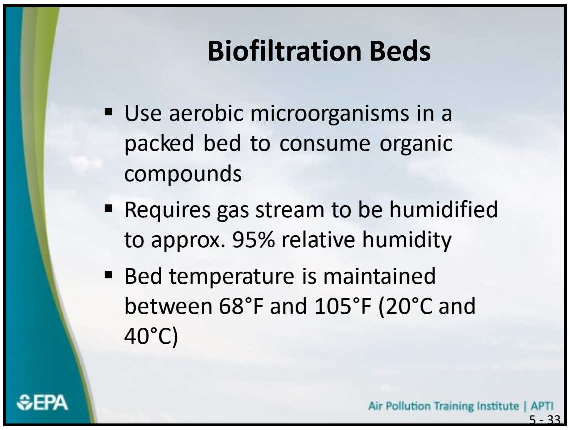


Figure 5-10. Ejector Absorbers



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)

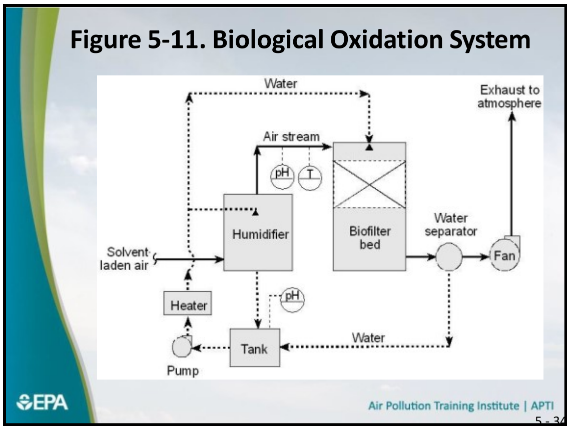
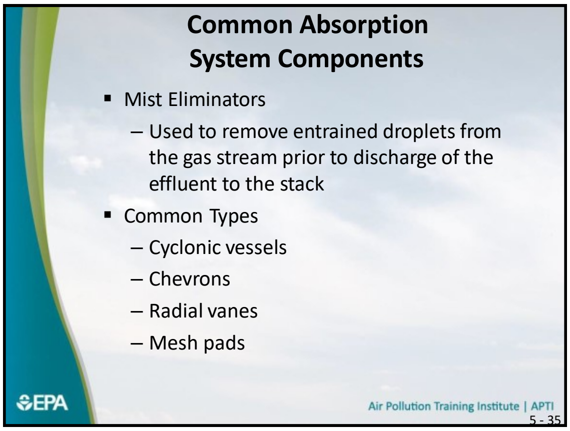


Figure 5-11. Biological Oxidation System



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

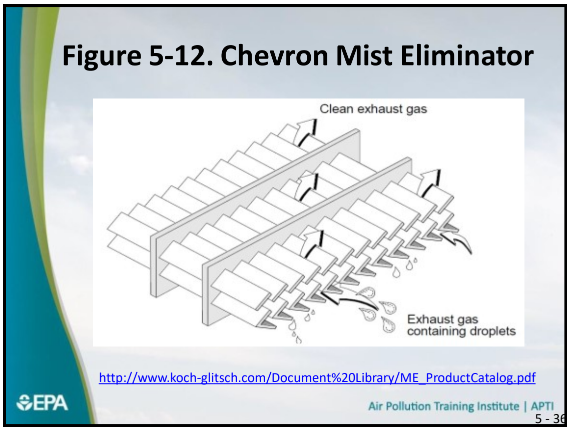


Figure 5-12. Chevron Mist Eliminator

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

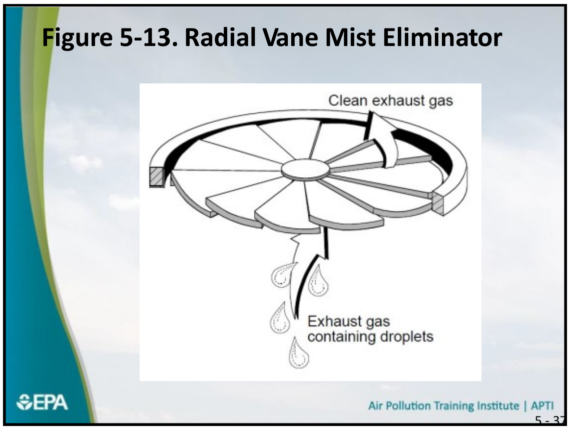


Figure 5-13. Radial Vane Mist Eliminator

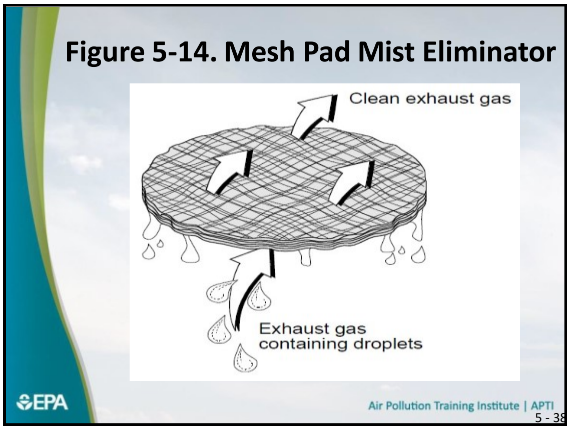


Figure 5-14. Mesh Pad Mist Eliminator

Absorption Systems Components

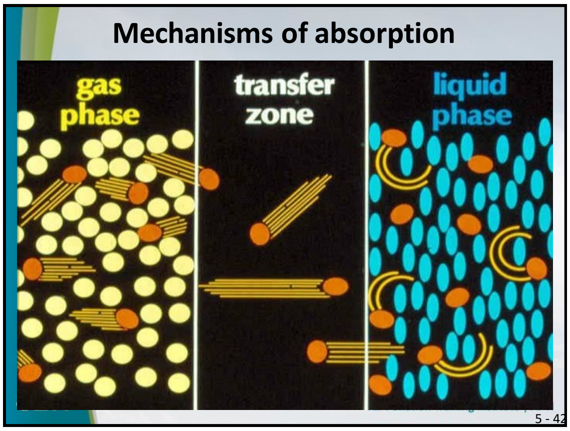
- Pumps and Piping Systems
  - Centrifugal pumps are commonly used
  - Piping system generally consists of a number of components
    - Suction pipe
    - Strainer
    - Suction side check valve
    - Discharge control valve

Instrumentation

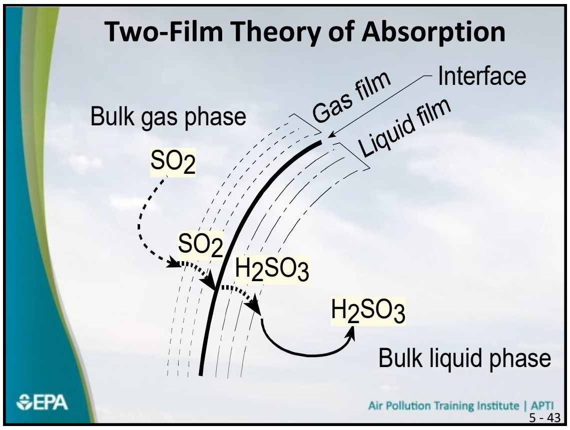
Gas Temperature	•Absorber inlet •Absorber outlet
Liquid Flow Rate	•Recirculation liquid stream •Purge liquid stream
Liquid Pressure	•Recirculation pump discharge •Absorber liquid distribution headers
Liquid pH	•Recirculation liquid tank •Recirculation liquid stream
Static Pressure Drop	•Absorber vessel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

Basic Operating Principles

- **Mechanisms of absorption**
- **Solubility**
- **Henry's Law**



Mechanisms of absorption



Two-Film Theory of Absorption

Bulk gas phase

Gas film

Interface

Liquid film

SO_2

SO_2

H_2SO_3

H_2SO_3

Bulk liquid phase

EPA

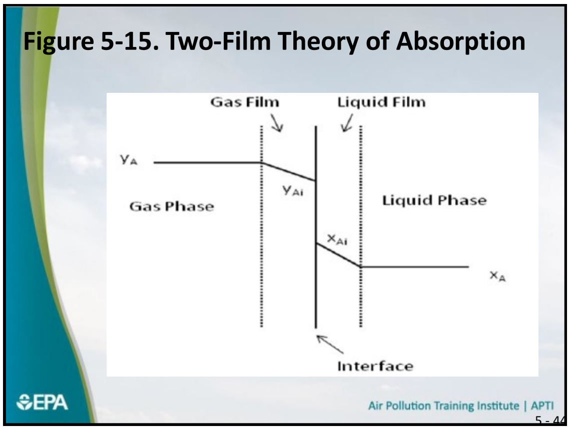


Figure 5-15. Two-Film Theory of Absorption

Gas Film

Liquid Film

y_A

y_{Ai}

Gas Phase

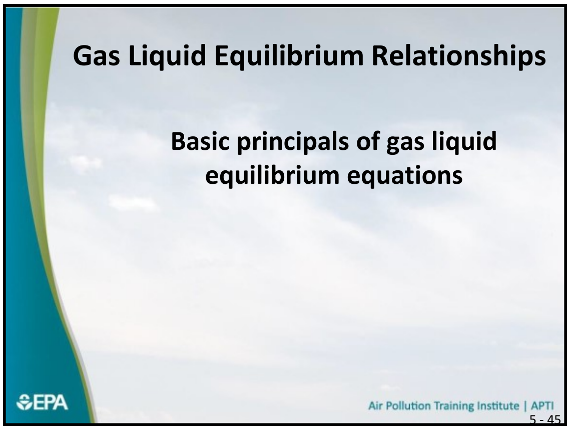
Liquid Phase

x_{Ai}

x_A

Interface

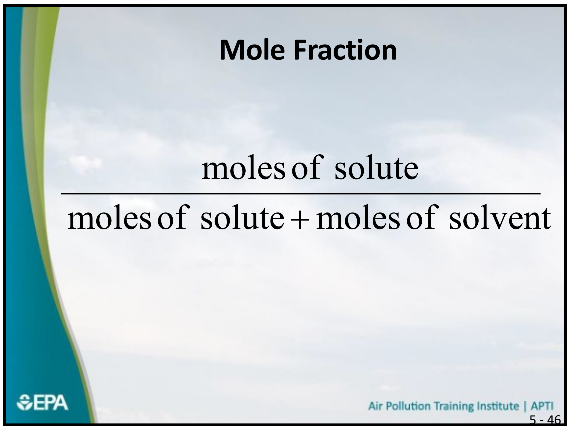
EPA



Gas Liquid Equilibrium Relationships

Basic principals of gas liquid equilibrium equations

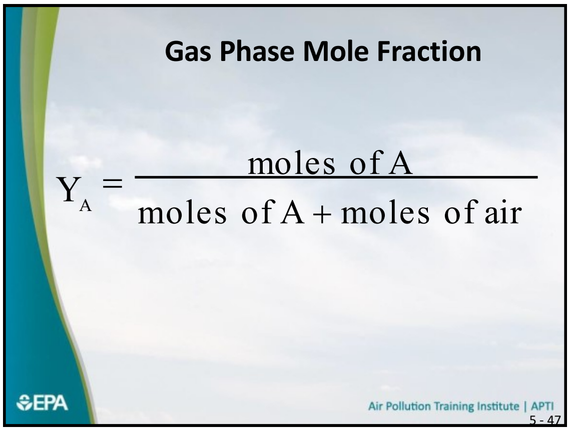
EPA



Mole Fraction

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

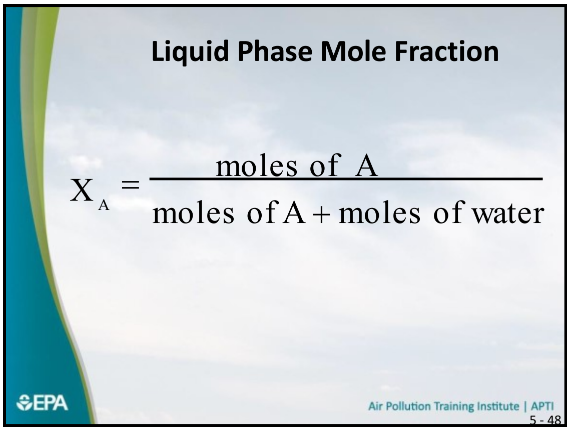
EPA



Gas Phase Mole Fraction

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

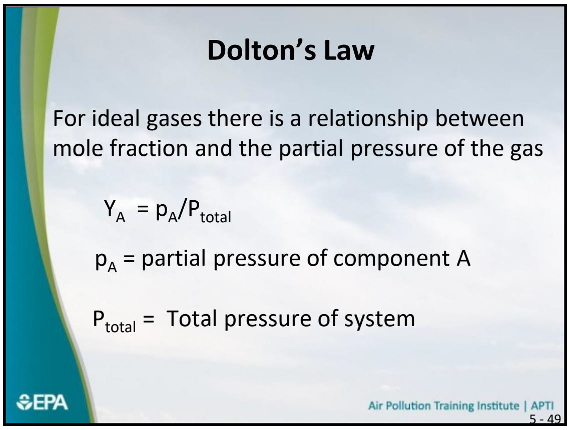
EPA



Liquid Phase Mole Fraction

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

EPA



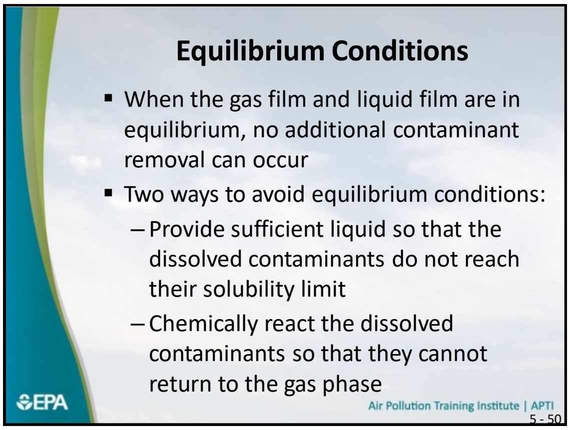
Dolton's Law

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

$Y_A = p_A/P_{total}$

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

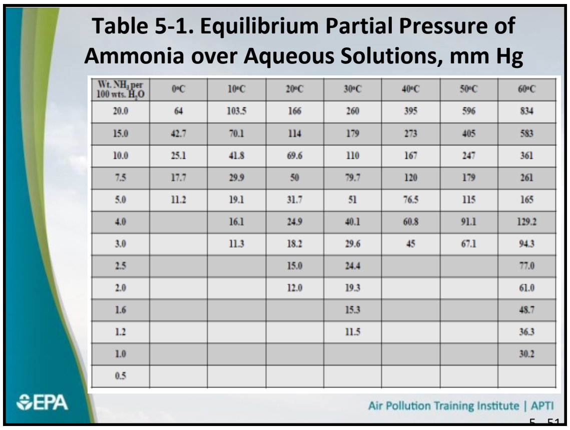
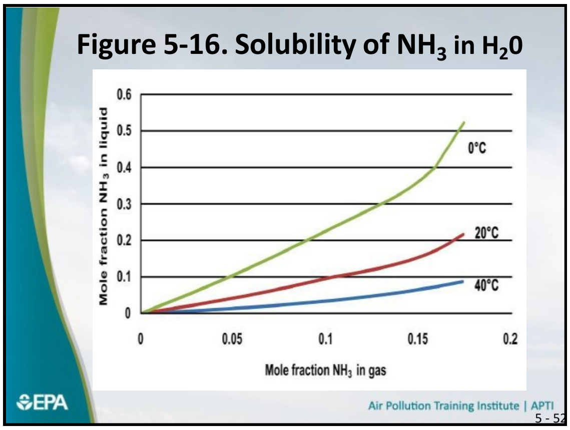
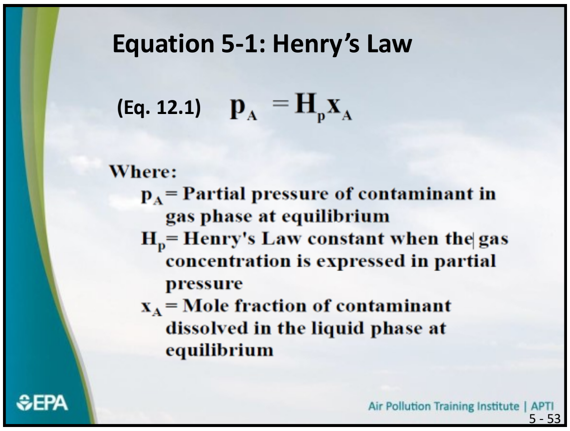


Table 5-1. Equilibrium Partial Pressure of Ammonia over Aqueous Solutions, mm Hg

Wt. NH_3 per 100 wts. H_2O	0°C	10°C	20°C	30°C	40°C	50°C	60°C
20.0	64	103.5	166	260	395	596	834
15.0	42.7	70.1	114	179	273	405	583
10.0	25.1	41.8	69.6	110	167	247	361
7.5	17.7	29.9	50	79.7	120	179	261
5.0	11.2	19.1	31.7	51	76.5	115	165
4.0		16.1	24.9	40.1	60.8	91.1	129.2
3.0		11.3	18.2	29.6	45	67.1	94.3
2.5			15.0	24.4			77.0
2.0			12.0	19.3			61.0
1.6				15.3			48.7
1.2				11.5			36.3
1.0							30.2
0.5							

Figure 5-16. Solubility of NH_3 in H_20





Equation 5-1: Henry's Law

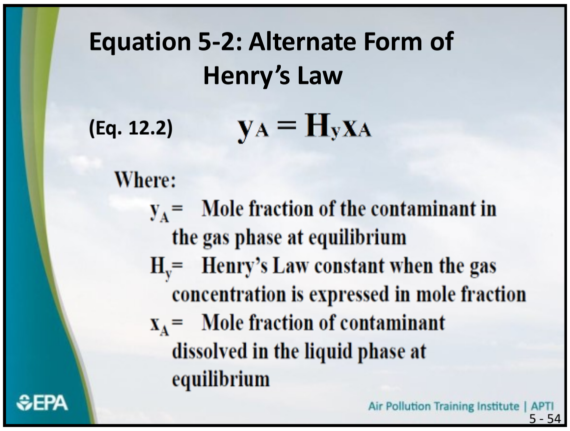
(Eq. 12.1) $p_A = H_p x_A$

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

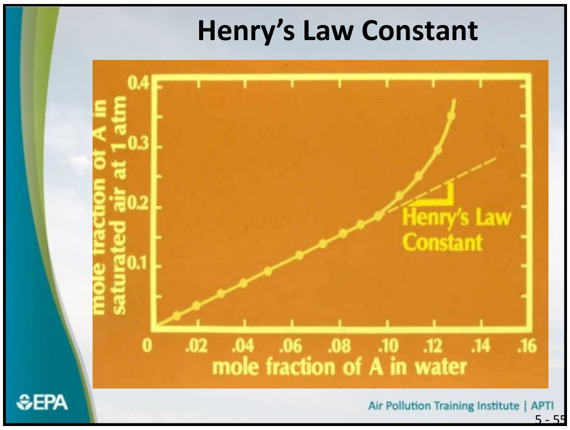
(Eq. 12.2) $y_A = H_y x_A$

Where:

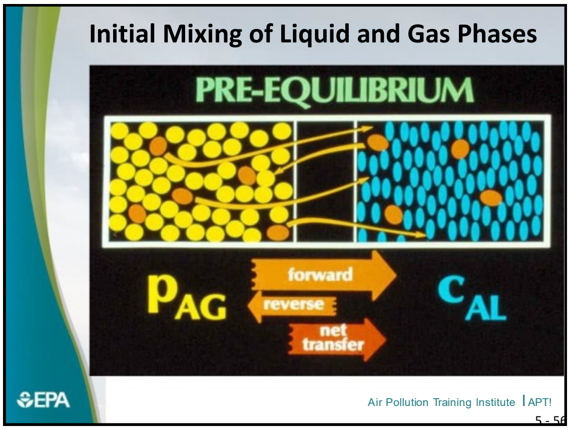
y_A = Mole fraction of the contaminant in the gas phase at equilibrium

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

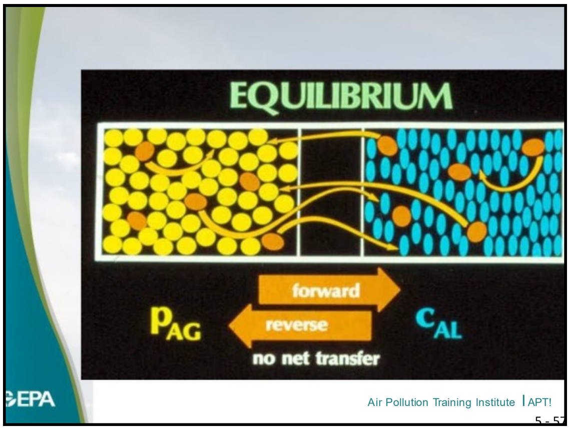
x_A = Mole fraction of contaminant dissolved in the liquid phase at equilibrium

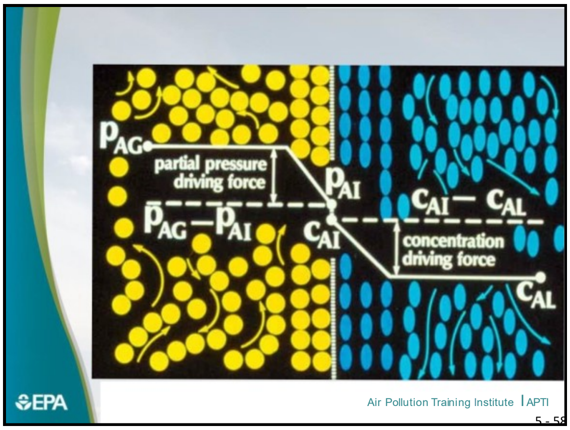


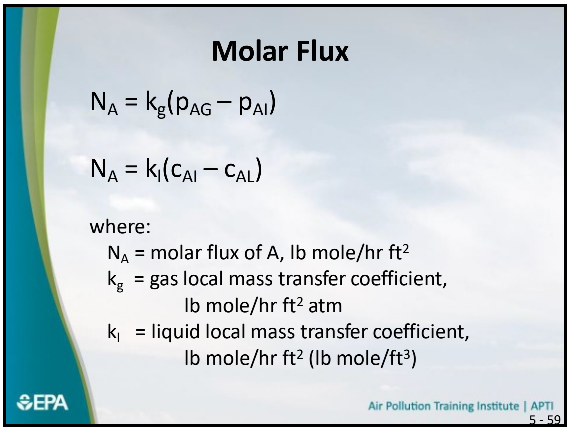
Henry's Law Constant



Initial Mixing of Liquid and Gas Phases







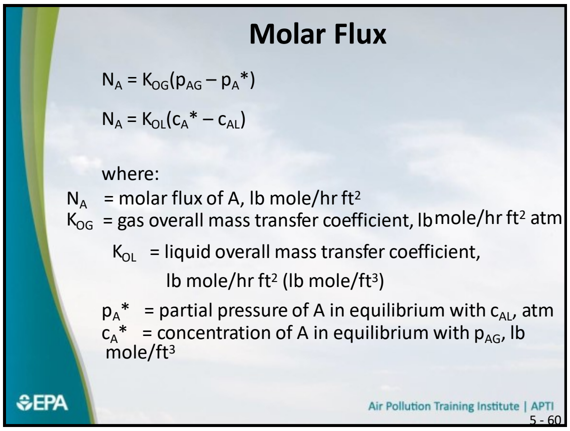
Molar Flux

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

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

where:

N_A = molar flux of A, lb mole/hr ft^2
k_g = gas local mass transfer coefficient, lb mole/hr ft^2 atm
k_l = liquid local mass transfer coefficient, lb mole/hr ft^2 (lb mole/ft^3)



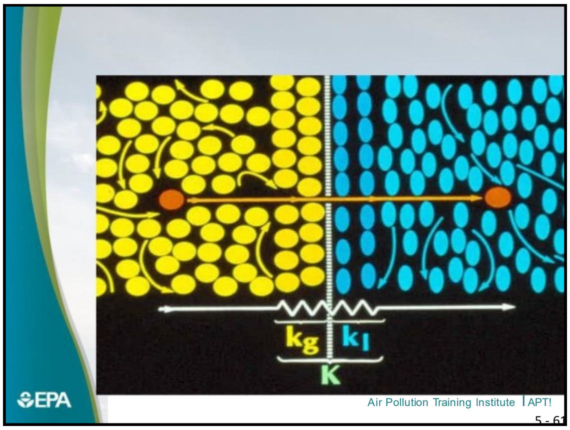
Molar Flux

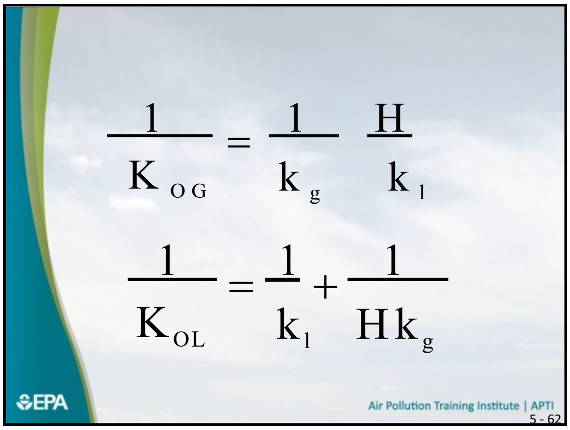
$N_A = K_{OG}(p_{AG} - p_A^*)$

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

where:

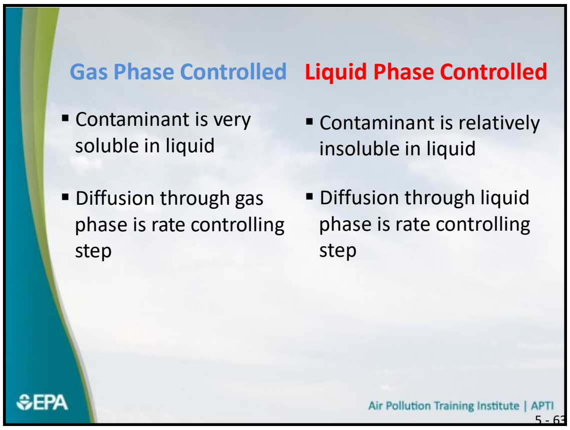
N_A = molar flux of A, lb mole/hr ft^2
K_{OG} = gas overall mass transfer coefficient, lb mole/hr ft^2 atm
K_{OL} = liquid overall mass transfer coefficient, lb mole/hr ft^2 (lb mole/ft^3)
p_A^* = partial pressure of A in equilibrium with c_{AL}, atm
c_A^* = concentration of A in equilibrium with p_{AG}, lb mole/ft^3





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

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

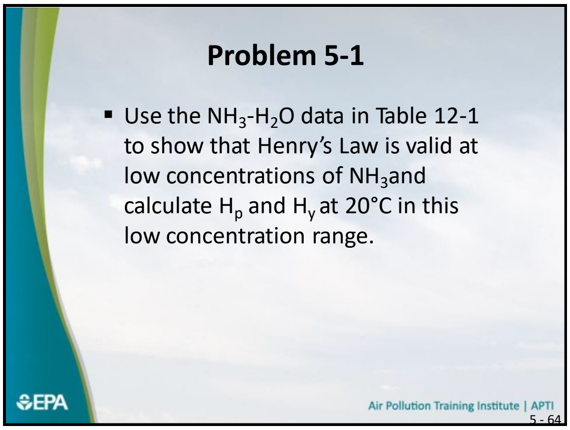


Gas Phase Controlled

- Contaminant is very soluble in liquid
- Diffusion through gas phase is rate controlling step

Liquid Phase Controlled

- Contaminant is relatively insoluble in liquid
- Diffusion through liquid phase is rate controlling step



Problem 5-1

- Use the NH_3-H_2O data in Table 12-1 to show that Henry's Law is valid at low concentrations of $NH_3$and calculate H_p and H_y at 20°C in this low concentration range.

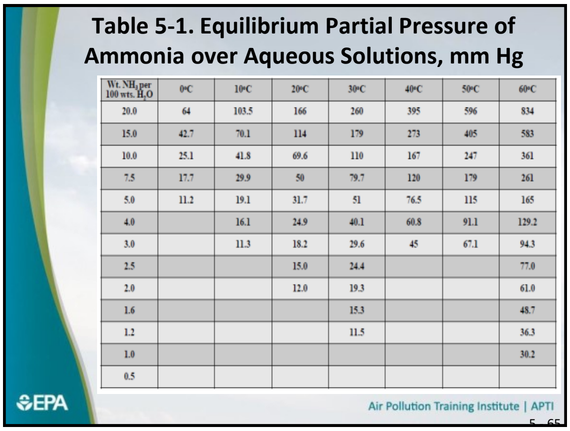
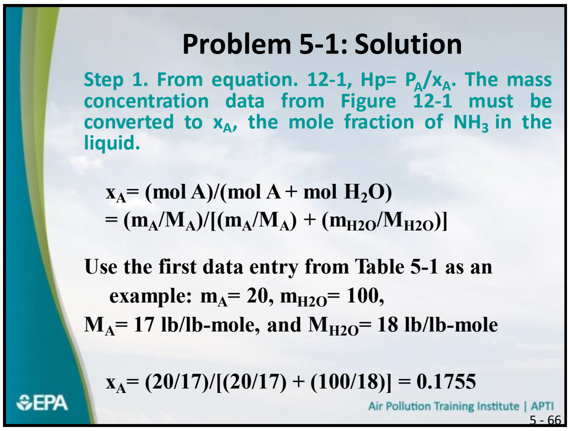


Table 5-1. Equilibrium Partial Pressure of Ammonia over Aqueous Solutions, mm Hg

Wt. NH_3 per 100 wts. H_2O	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							



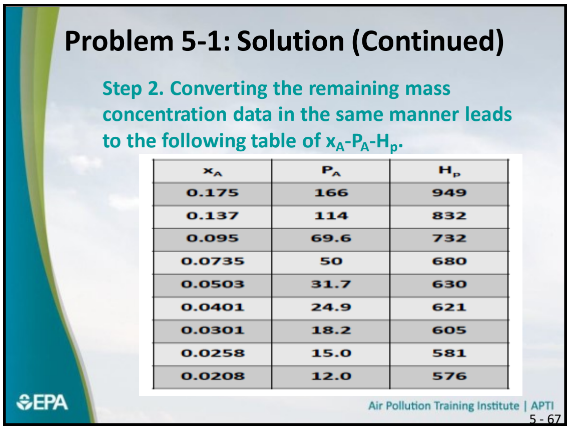
Problem 5-1: Solution

Step 1. From equation. 12-1, Hp= P_A/x_A. The mass concentration data from Figure 12-1 must be converted to x_A, the mole fraction of NH_3 in the liquid.

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

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

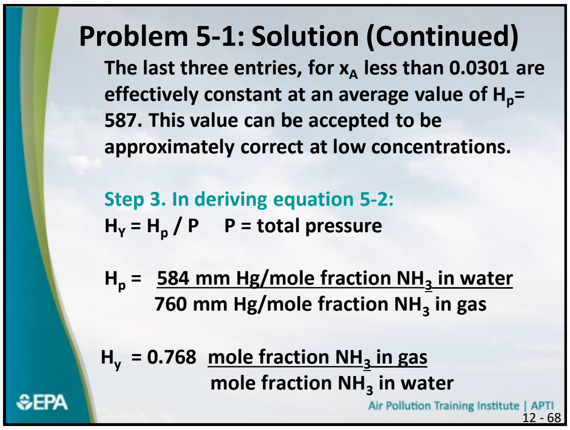
x_A= (20/17)/[(20/17) + (100/18)] = 0.1755



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)

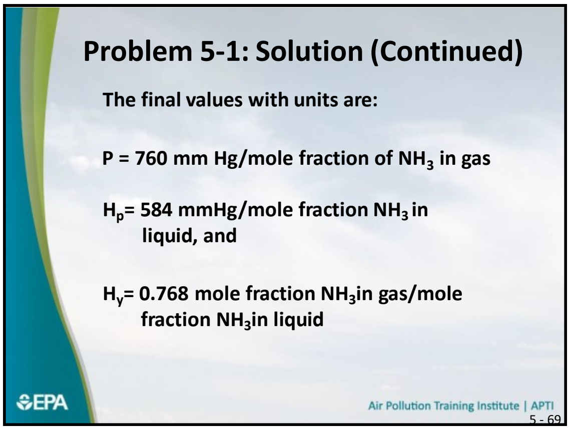
The last three entries, for x_A less than 0.0301 are effectively constant at an average value of H_p= 587. This value can be accepted to be approximately correct at low concentrations.

Step 3. In deriving equation 5-2:

$H_Y = H_p / P$ P = total pressure

$$H_p = \frac{\text{584 mm Hg/mole fraction } NH_3 \text{ in water}}{\text{760 mm Hg/mole fraction } NH_3 \text{ in gas}}$$

$$H_y = 0.768 \frac{\text{mole fraction } NH_3 \text{ in gas}}{\text{mole fraction } NH_3 \text{ in water}}$$



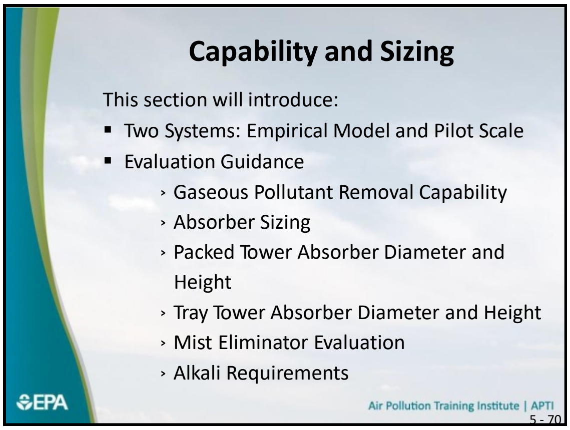
Problem 5-1: Solution (Continued)

The final values with units are:

P = 760 mm Hg/mole fraction of NH_3 in gas

H_p= 584 mmHg/mole fraction NH_3 in liquid, and

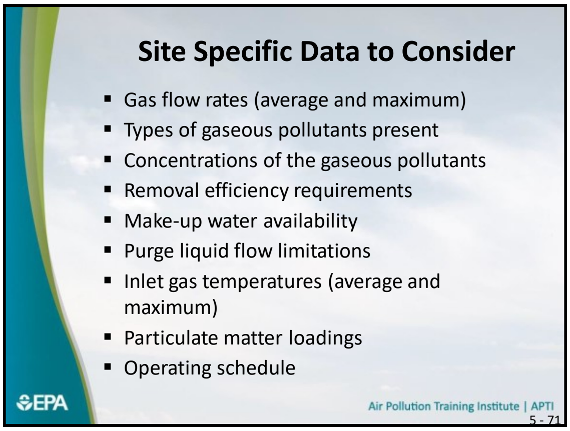
H_y= 0.768 mole fraction NH_3in gas/mole fraction NH_3in liquid



Capability and Sizing

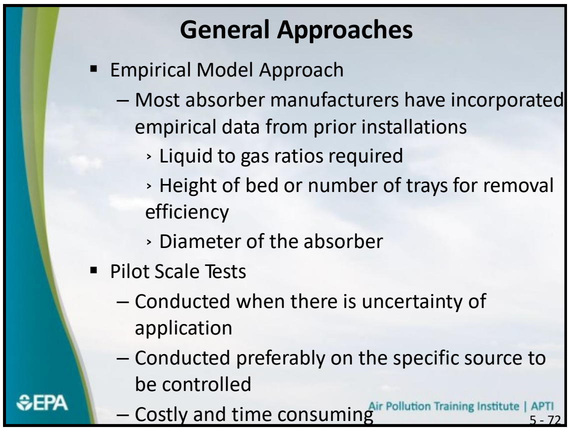
This section will introduce:

- 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



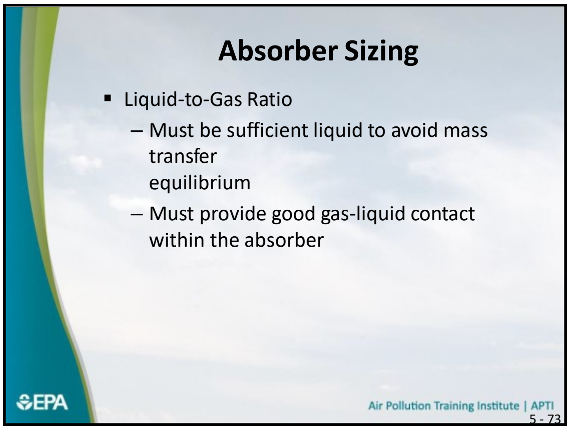
Site Specific Data to Consider

- 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

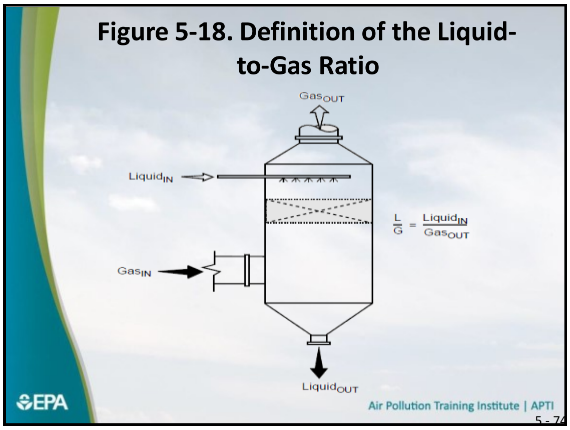


Figure 5-18. Definition of the Liquid-to-Gas Ratio

$$\frac{L}{G} = \frac{\text{Liquid}_{IN}}{\text{Gas}_{OUT}}$$

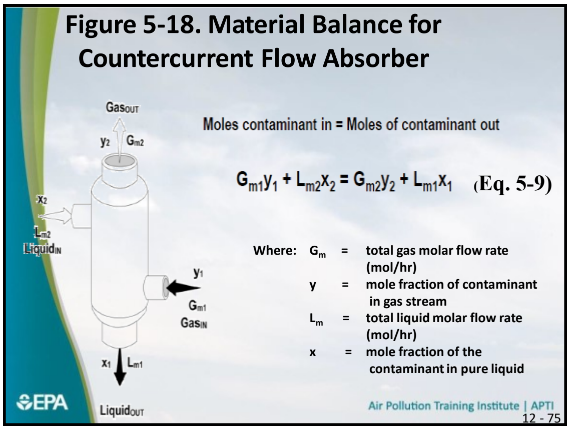
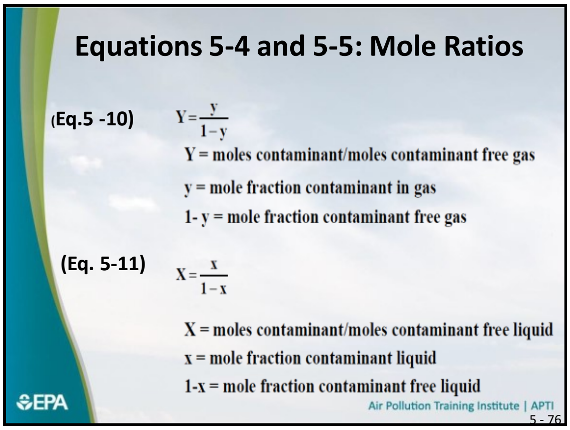


Figure 5-18. Material Balance for Countercurrent Flow Absorber

Moles contaminant in = Moles of contaminant out

$$G_{m1}y_1 + L_{m2}x_2 = G_{m2}y_2 + L_{m1}x_1 \quad \text{(Eq. 5-9)}$$

Where:
G_m = total gas molar flow rate (mol/hr)
y = mole fraction of contaminant in gas stream
L_m = total liquid molar flow rate (mol/hr)
x = mole fraction of the contaminant in pure liquid



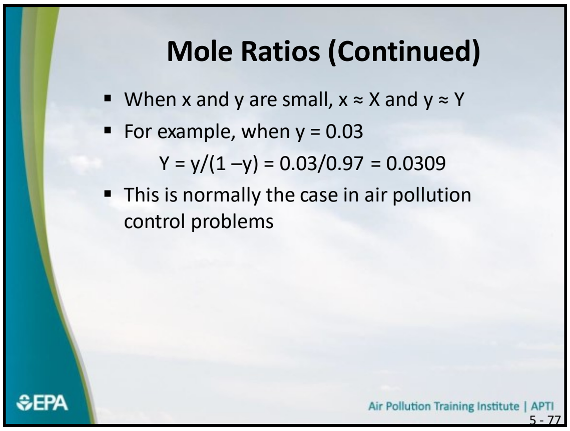
Equations 5-4 and 5-5: Mole Ratios

(Eq.5 -10)
$$Y = \frac{y}{1-y}$$

Y = moles contaminant/moles contaminant free gas
y = mole fraction contaminant in gas
1- y = mole fraction contaminant free gas

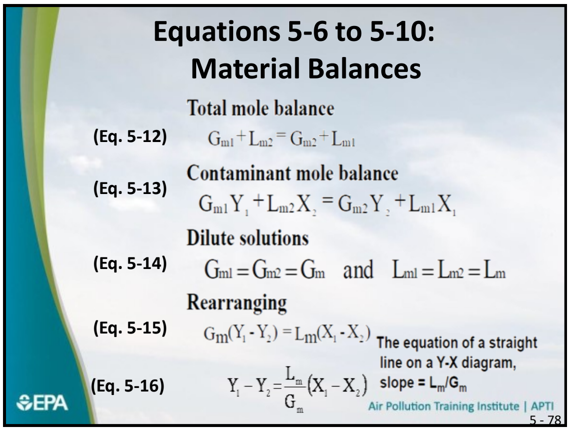
(Eq. 5-11)
$$X = \frac{x}{1-x}$$

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



Mole Ratios (Continued)

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



Equations 5-6 to 5-10: Material Balances

Total mole balance

(Eq. 5-12)
$$G_{m1} + L_{m2} = G_{m2} + L_{m1}$$

Contaminant mole balance

(Eq. 5-13)
$$G_{m1}Y_1 + L_{m2}X_2 = G_{m2}Y_2 + L_{m1}X_1$$

Dilute solutions

(Eq. 5-14)
$$G_{m1} = G_{m2} = G_m \quad \text{and} \quad L_{m1} = L_{m2} = L_m$$

Rearranging

(Eq. 5-15)
$$G_m(Y_1 - Y_2) = L_m(X_1 - X_2)$$

(Eq. 5-16)
$$Y_1 - Y_2 = \frac{L_m}{G_m}(X_1 - X_2)$$

The equation of a straight line on a Y-X diagram, slope = L_m/G_m

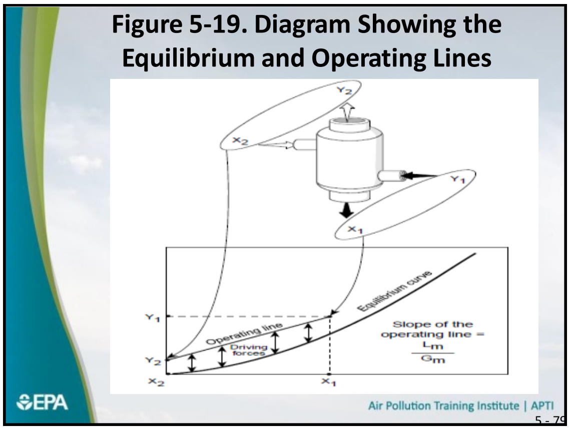
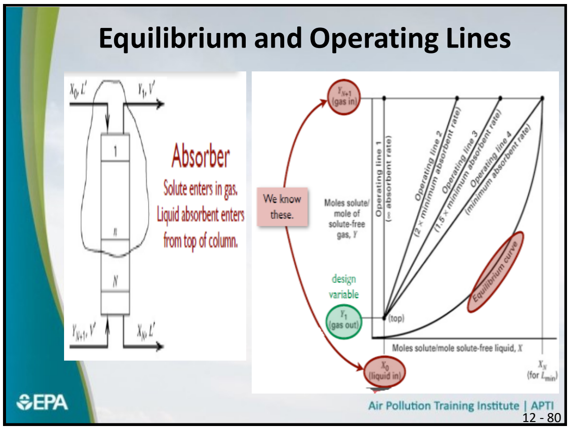


Figure 5-19. Diagram Showing the Equilibrium and Operating Lines



Equilibrium and Operating Lines

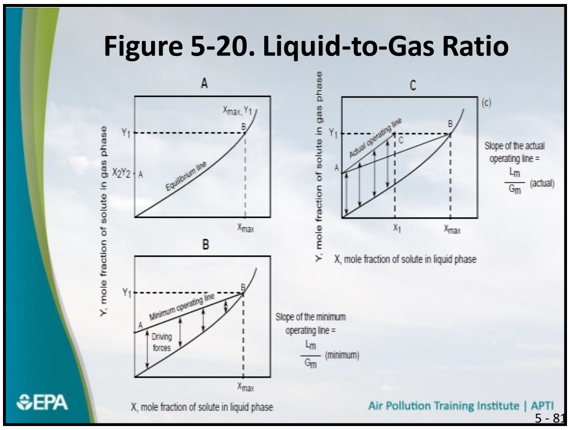
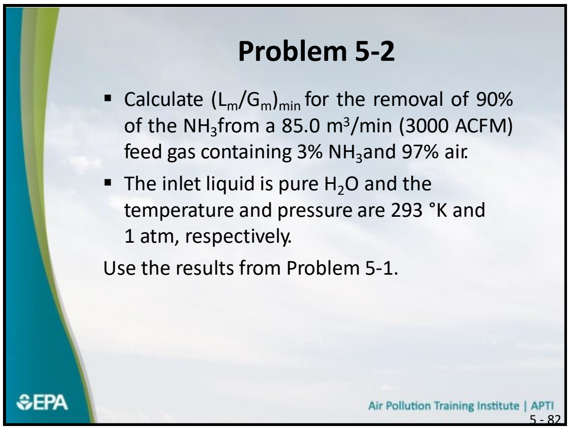


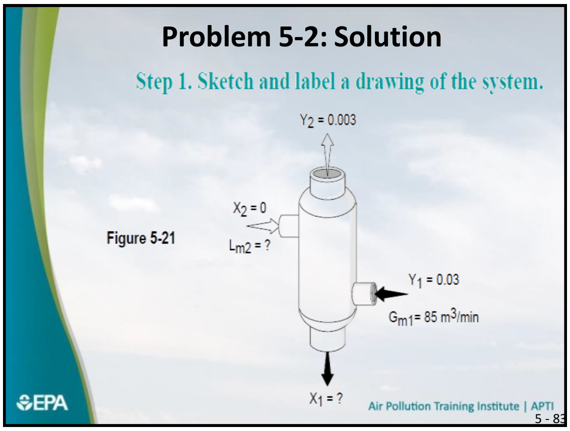
Figure 5-20. Liquid-to-Gas Ratio



Problem 5-2

- Calculate $(L_m/G_m)_{min}$ for the removal of 90% of the NH_3 from a 85.0 m^3/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.

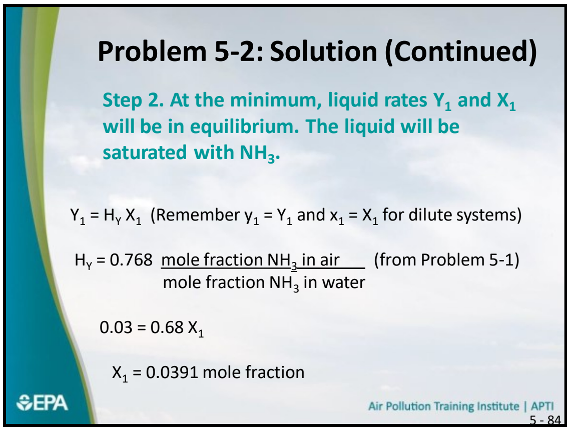
Use the results from Problem 5-1.



Problem 5-2: Solution

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

Figure 5-21



Problem 5-2: Solution (Continued)

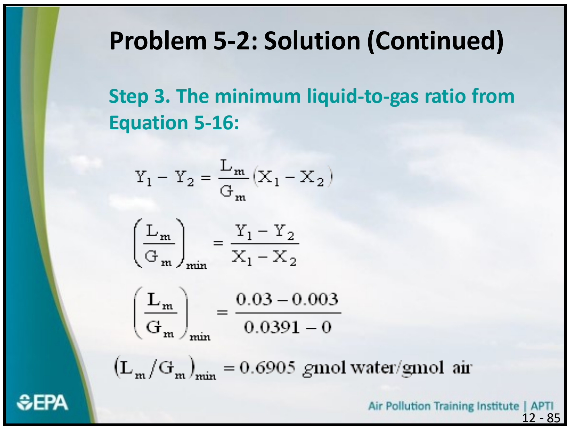
Step 2. At the minimum, liquid rates Y_1 and X_1 will be in equilibrium. The liquid will be saturated with NH_3.

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

$H_Y = 0.768 \frac{\text{mole fraction NH}_3\text{ in air}}{\text{mole fraction NH}_3\text{ in water}}$ (from Problem 5-1)

$0.03 = 0.68\ X_1$

X_1 = 0.0391 mole fraction



Problem 5-2: Solution (Continued)

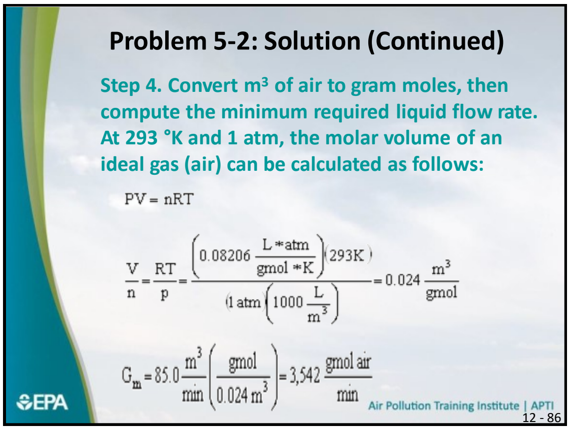
Step 3. The minimum liquid-to-gas ratio from Equation 5-16:

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

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

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

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



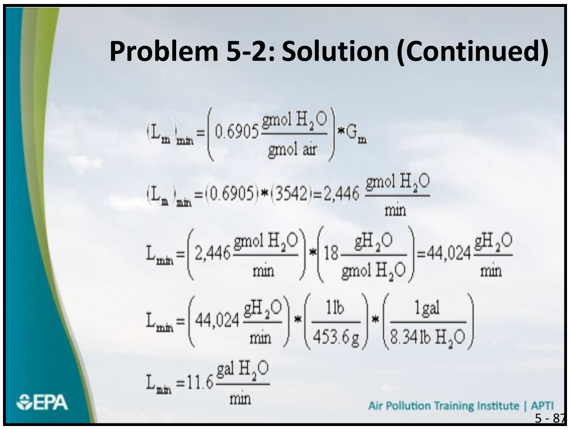
Problem 5-2: Solution (Continued)

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:

$$PV = nRT$$

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

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



Problem 5-2: Solution (Continued)

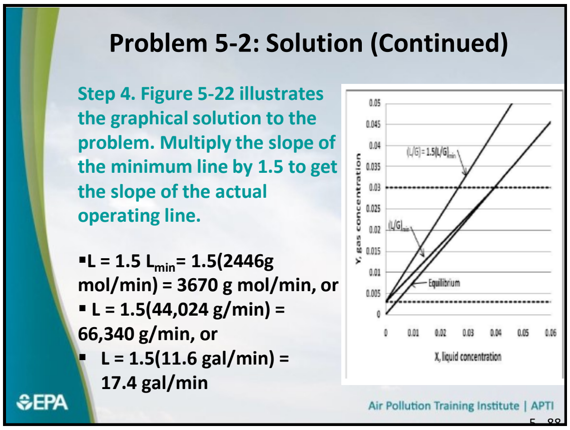
$$(L_m)_{min} = \left(0.6905 \frac{gmol\ H_2O}{gmol\ air}\right) * G_m$$

$$(L_m)_{min} = (0.6905) * (3542) = 2{,}446 \frac{gmol\ H_2O}{min}$$

$$L_{min} = \left(2{,}446 \frac{gmol\ H_2O}{min}\right) * \left(18 \frac{gH_2O}{gmol\ H_2O}\right) = 44{,}024 \frac{gH_2O}{min}$$

$$L_{min} = \left(44{,}024 \frac{gH_2O}{min}\right) * \left(\frac{1 lb}{453.6 g}\right) * \left(\frac{1 gal}{8.34 lb\ H_2O}\right)$$

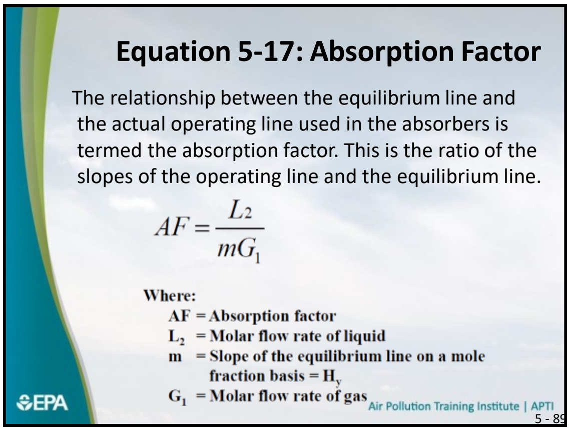
$$L_{min} = 11.6 \frac{gal\ H_2O}{min}$$



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(2446g mol/min) = 3670 g mol/min, or**
- **L = 1.5(44,024 g/min) = 66,340 g/min, or**
- **L = 1.5(11.6 gal/min) = 17.4 gal/min**



Equation 5-17: 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.

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

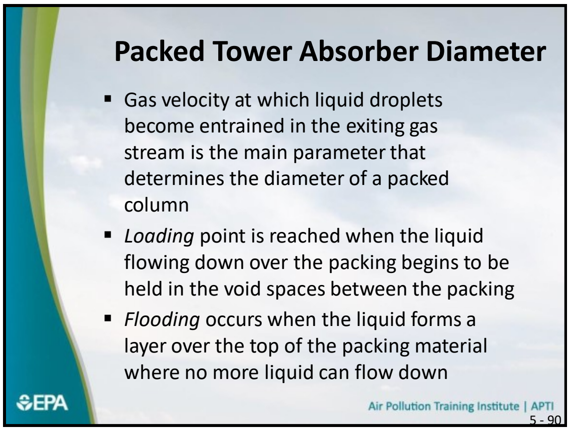
Where:

AF = Absorption factor

L_2 = Molar flow rate of liquid

m = Slope of the equilibrium line on a mole fraction basis = H_y

G_1 = Molar flow rate of gas



Packed Tower Absorber Diameter

- 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

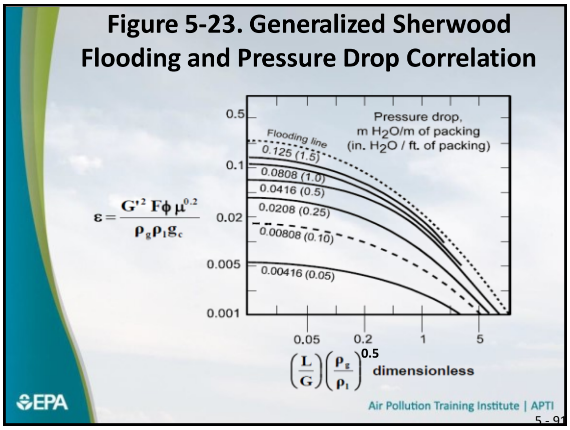
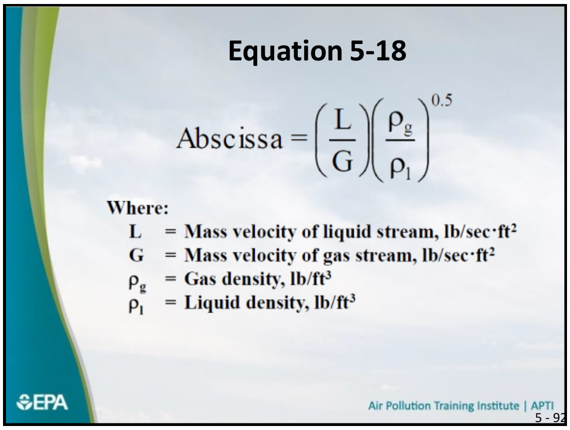


Figure 5-23. Generalized Sherwood Flooding and Pressure Drop Correlation

$$\varepsilon = \frac{G'^2 F \phi \mu^{0.2}}{\rho_g \rho_l g_c}$$

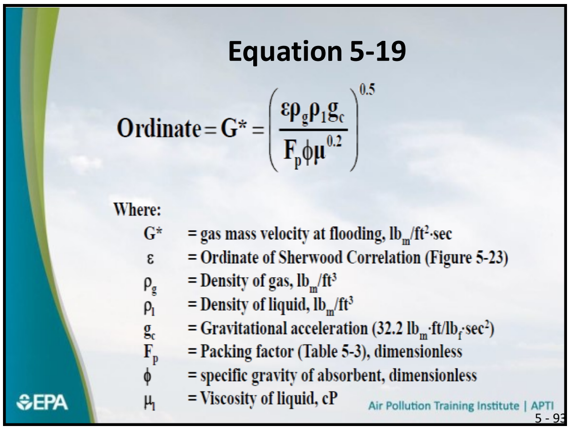


Equation 5-18

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

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

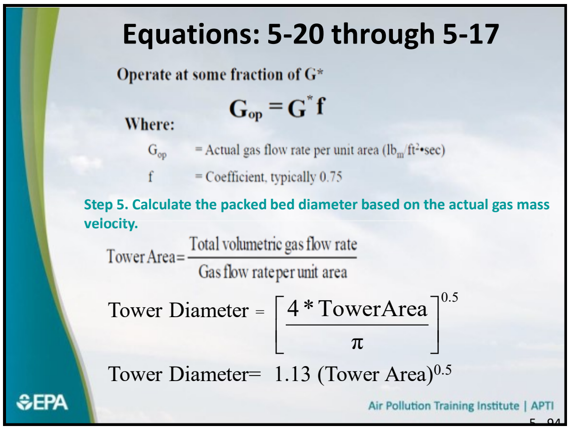


Equation 5-19

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

Where:

G^* = gas mass velocity at flooding, $lb_m/ft^2 \cdot sec$
ε = Ordinate of Sherwood Correlation (Figure 5-23)
ρ_g = Density of gas, lb_m/ft^3
ρ_l = Density of liquid, lb_m/ft^3
g_c = Gravitational acceleration (32.2 $lb_m \cdot ft/lb_f \cdot sec^2$)
F_p = Packing factor (Table 5-3), dimensionless
ϕ = specific gravity of absorbent, dimensionless
μ_l = Viscosity of liquid, cP



Equations: 5-20 through 5-17

Operate at some fraction of G*

$$G_{op} = G^* f$$

Where:

G_{op} = Actual gas flow rate per unit area ($lb_m/ft^2 \cdot sec$)
f = Coefficient, typically 0.75

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

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

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

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

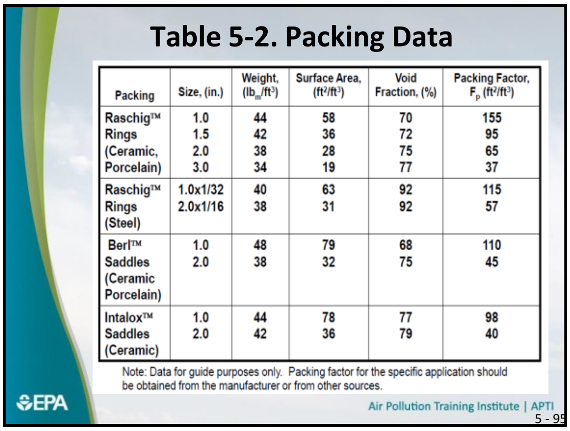


Table 5-2. Packing Data

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 1.5 2.0 3.0	44 42 38 34	58 36 28 19	70 72 75 77	155 95 65 37
Raschig™ Rings (Steel)	1.0x1/32 2.0x1/16	40 38	63 31	92 92	115 57
Berl™ Saddles (Ceramic Porcelain)	1.0 2.0	48 38	79 32	68 75	110 45
Intalox™ Saddles (Ceramic)	1.0 2.0	44 42	78 36	77 79	98 40

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

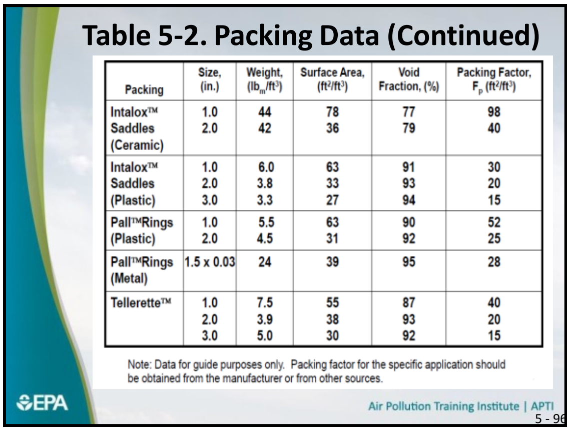
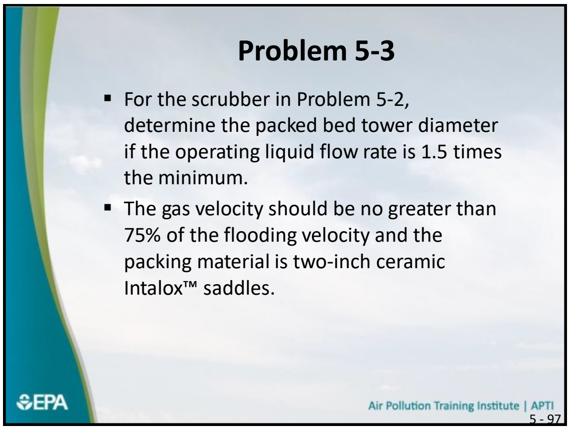


Table 5-2. Packing Data (Continued)

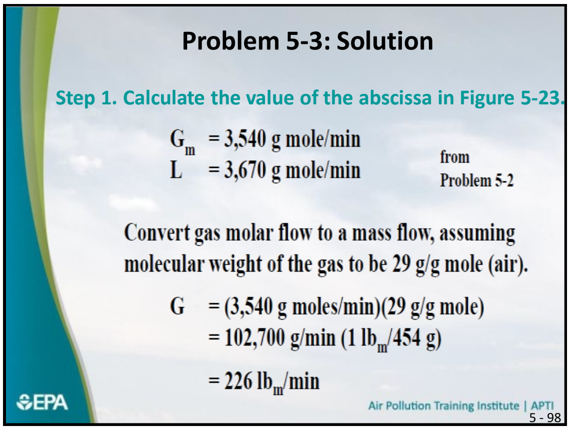
Packing	Size, (in.)	Weight, (lb_m/ft^3)	Surface Area, (ft^2/ft^3)	Void Fraction, (%)	Packing Factor, F_p (ft^2/ft^3)
Intalox™ Saddles (Ceramic)	1.0 2.0	44 42	78 36	77 79	98 40
Intalox™ Saddles (Plastic)	1.0 2.0 3.0	6.0 3.8 3.3	63 33 27	91 93 94	30 20 15
Pall™Rings (Plastic)	1.0 2.0	5.5 4.5	63 31	90 92	52 25
Pall™Rings (Metal)	1.5 x 0.03	24	39	95	28
Tellerette™	1.0 2.0 3.0	7.5 3.9 5.0	55 38 30	87 93 92	40 20 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

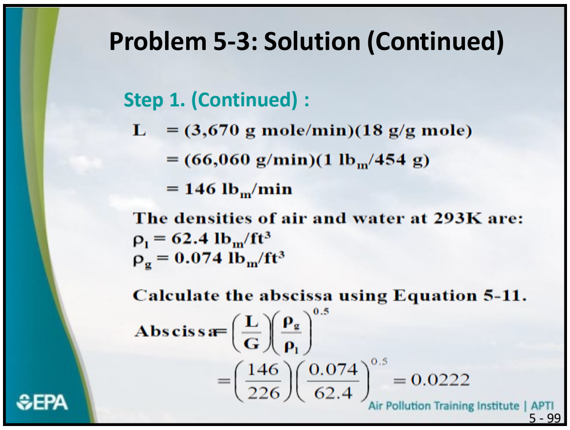
Step 1. Calculate the value of the abscissa in Figure 5-23.

G_m = 3,540 g mole/min
L = 3,670 g mole/min

from Problem 5-2

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

G = (3,540 g moles/min)(29 g/g mole)
= 102,700 g/min (1 lb_m/454 g)
= 226 lb_m/min



Problem 5-3: Solution (Continued)

Step 1. (Continued) :

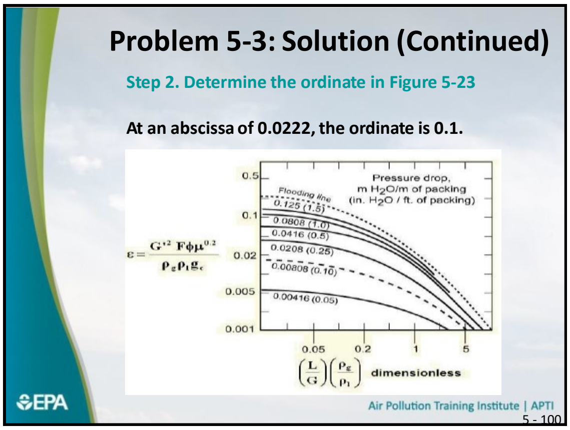
L = (3,670 g mole/min)(18 g/g mole)
= (66,060 g/min)(1 lb_m/454 g)
= 146 lb_m/min

The densities of air and water at 293K are:
$\rho_l = 62.4\ lb_m/ft^3$
$\rho_g = 0.074\ lb_m/ft^3$

Calculate the abscissa using Equation 5-11.

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

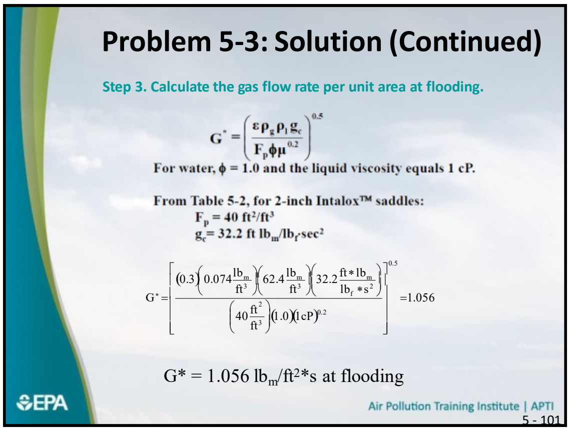
$$= \left(\frac{146}{226}\right)\left(\frac{0.074}{62.4}\right)^{0.5} = 0.0222$$



Problem 5-3: Solution (Continued)

Step 2. Determine the ordinate in Figure 5-23

At an abscissa of 0.0222, the ordinate is 0.1.



Problem 5-3: Solution (Continued)

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

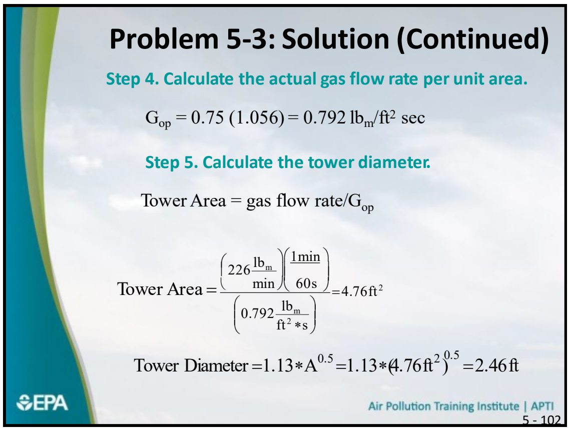
$$G^* = \left(\frac{\varepsilon \rho_g \rho_l g_c}{F_p \phi \mu^{0.2}}\right)^{0.5}$$

For water, ϕ = 1.0 and the liquid viscosity equals 1 cP.

From Table 5-2, for 2-inch Intalox™ saddles:
$F_p = 40\ ft^2/ft^3$
$g_c = 32.2\ ft\ lb_m/lb_f \cdot sec^2$

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

$G^* = 1.056\ lb_m/ft^2{*}s$ at flooding



Problem 5-3: Solution (Continued)

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

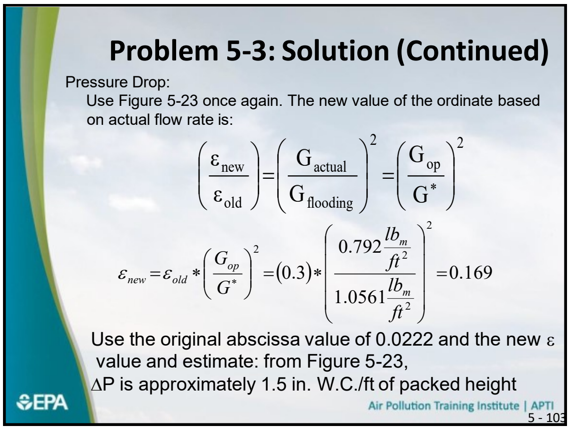
$G_{op} = 0.75\ (1.056) = 0.792\ lb_m/ft^2$ sec

Step 5. Calculate the tower diameter.

Tower Area = gas flow rate/G_{op}

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

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



Problem 5-3: Solution (Continued)

Pressure Drop:

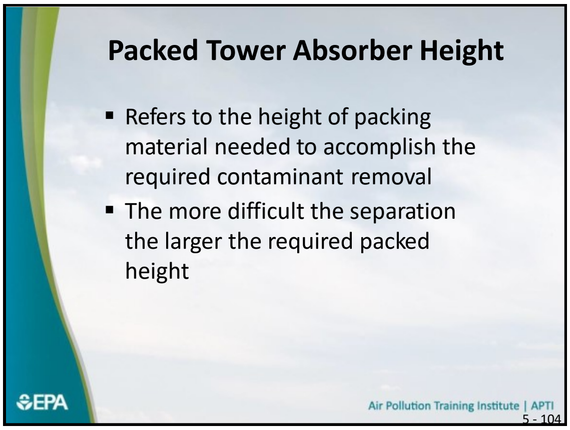
Use Figure 5-23 once again. The new value of the ordinate based on actual flow rate is:

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

$$\varepsilon_{new}=\varepsilon_{old}*\left(\frac{G_{op}}{G^*}\right)^2=(0.3)*\left(\frac{0.792\frac{lb_m}{ft^2}}{1.0561\frac{lb_m}{ft^2}}\right)^2=0.169$$

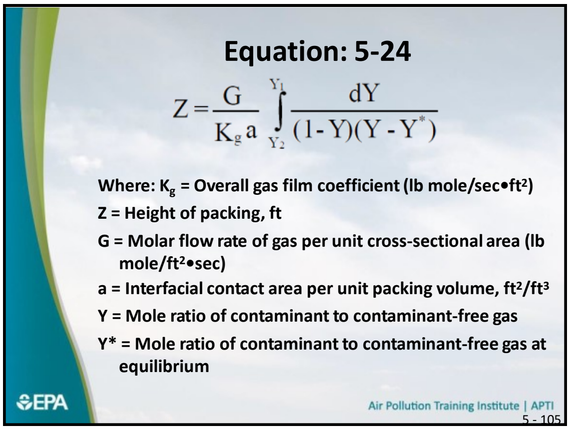
Use the original abscissa value of 0.0222 and the new ε value and estimate: from Figure 5-23,

ΔP is approximately 1.5 in. W.C./ft of packed height



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: 5-24

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

Where: K_g = Overall gas film coefficient (lb mole/sec•ft²)

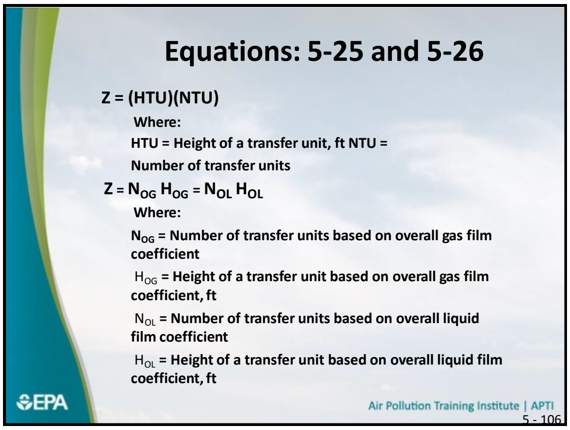
Z = Height of packing, ft

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: 5-25 and 5-26

Z = (HTU)(NTU)

Where:

HTU = Height of a transfer unit, ft NTU = Number of transfer units

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

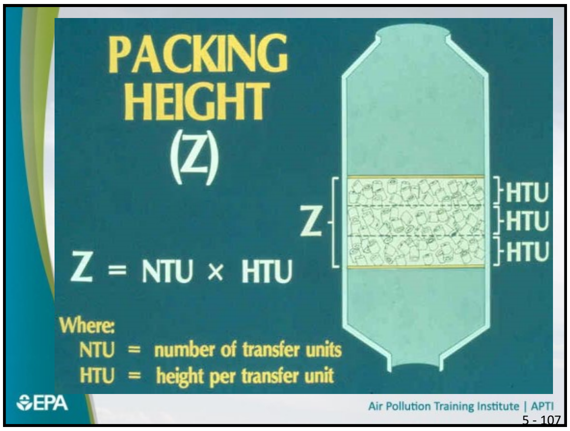
Where:

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 × HTU

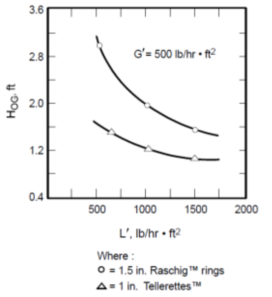
Where:
NTU = number of transfer units
HTU = height per transfer unit

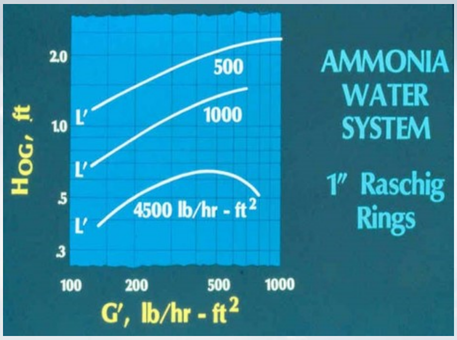
Counter-current Packed Tower at a Plating Operation

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 5-27: Number of Transfer Units

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

Where:

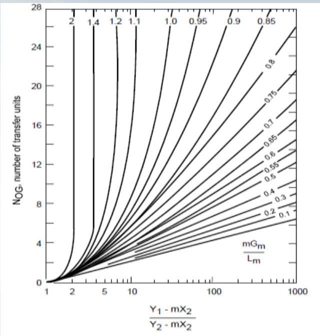
Y_1 = Mole ratio of contaminant to contaminant-free gas entering the absorber
m = Slope of the equilibrium line (= Henry's constant)
X_2 = Mole ratio of contaminant to contaminant-free liquid entering the absorber in the liquid
Y_2 = Mole ratio of contaminant to contaminant-free gas exiting the absorber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

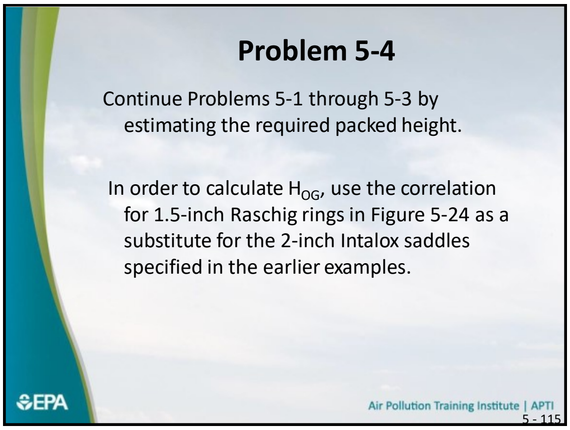
Equation 5-28: Number of Transfer Units

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

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

Figure Colburn Diagram

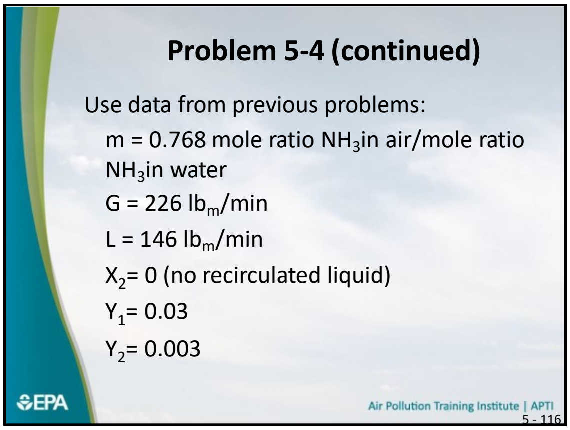




Problem 5-4

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_3in air/mole ratio NH_3in water

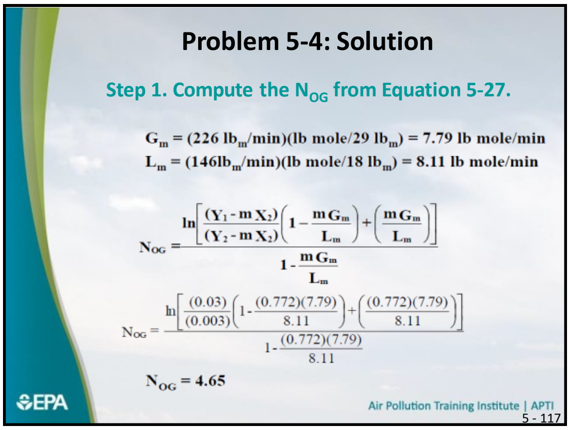
G = 226 lb_m/min

L = 146 lb_m/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 5-27.

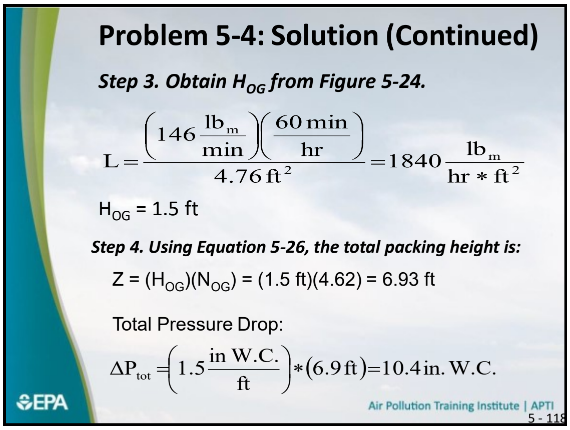
$$G_m = (226\ lb_m/min)(lb\ mole/29\ lb_m) = 7.79\ lb\ mole/min$$

$$L_m = (146 lb_m/min)(lb\ mole/18\ lb_m) = 8.11\ lb\ mole/min$$

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

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

$$N_{OG} = 4.65$$



Problem 5-4: Solution (Continued)

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

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

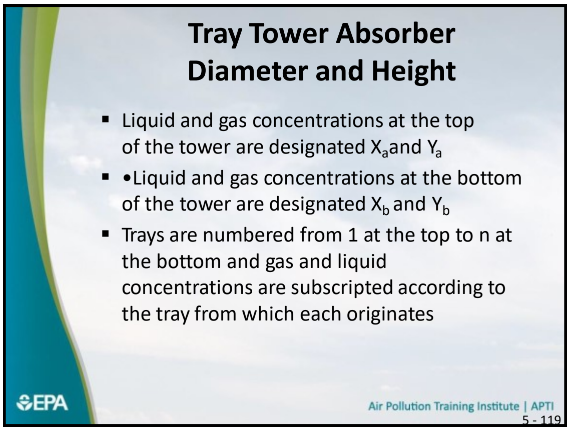
H_{OG} = 1.5 ft

Step 4. Using Equation 5-26, the total packing height is:

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

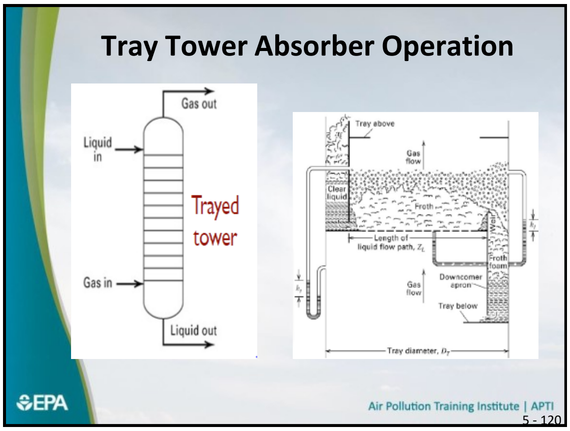
Total Pressure Drop:

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

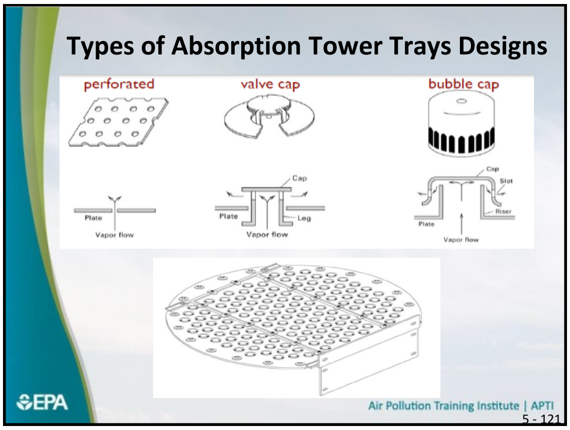


Tray Tower Absorber Diameter and Height

- 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



Tray Tower Absorber Operation



Types of Absorption Tower Trays Designs

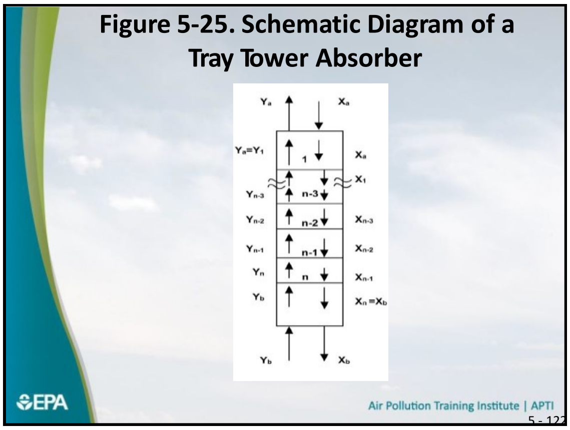


Figure 5-25. Schematic Diagram of a Tray Tower Absorber

Equation 5-29: 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, $ft^{0.25} \cdot min^{0.5}/lb^{0.25}$

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

ρ_g = Gas density, lb_m/ft^3

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:

1. **Metric (expressed in $m^{0.25} . hr^{0.5}/kg^{0.25}$) for use with Q (expressed in m^3/hr) and r_g(expressed in kg/m^3).**

2. **English (expressed in $ft^{0.25}min^{0.5}/lb^{0.25}$) for use with Q in ACFM and ρ_g expressed in lb/ft^3**

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

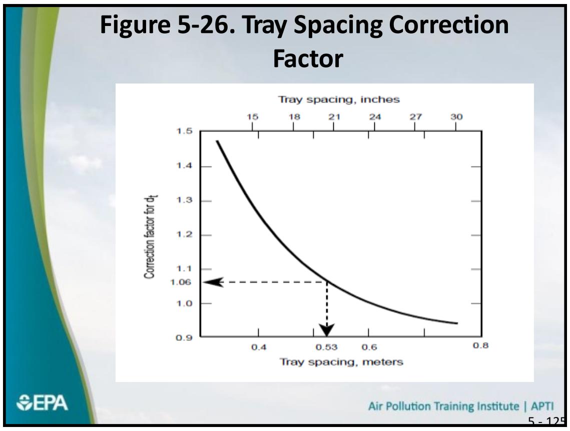


Figure 5-26. Tray Spacing Correction Factor

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 m^3/min

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

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:

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

Problem 5-5: Solution (Continued)

Step 1. Substitute these values into Equation 5-29 for a minimum diameter:

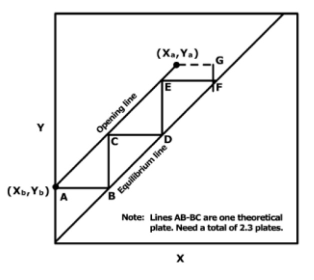
$$d = \psi(Q\sqrt{\rho_g})^{0.5}$$

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

Step 2. Correct the minimum diameter for a tray spacing of 0.53 m. From Figure 5-26, read a correction factor of 1.06.

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

Figure 5-27. Graphic Determination of the Number of Ideal Plates



Note: Lines AB-BC are one theoretical plate. Need a total of 2.3 plates.

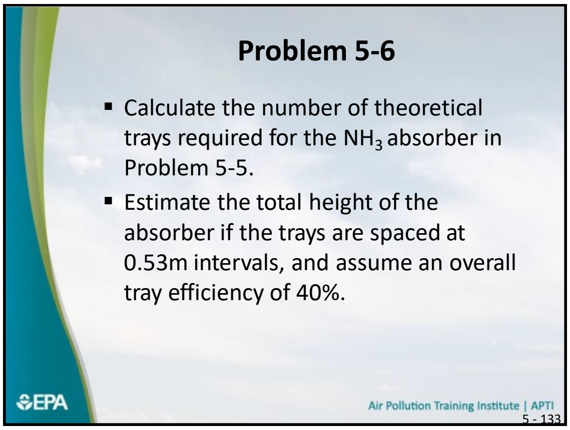
Equation 5-30: Number of Ideal Plates

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

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

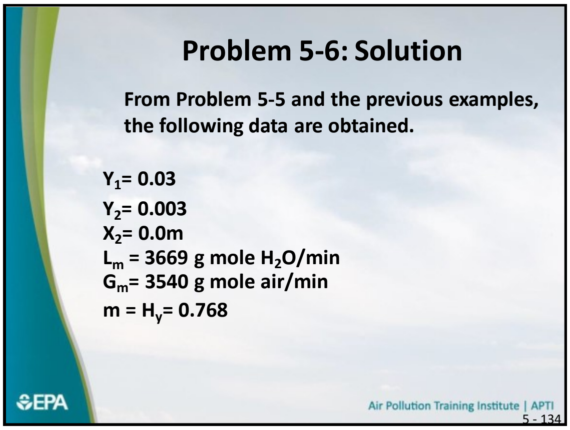
Three Types of Efficiencies

- 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

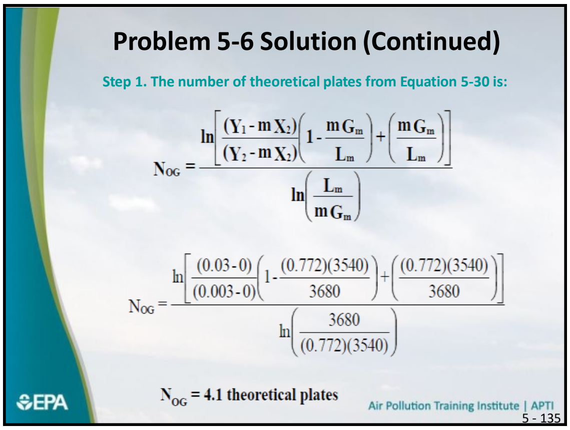
- Calculate the number of theoretical trays required for the NH_3 absorber in Problem 5-5.
- Estimate the total height of the absorber if the trays are spaced at 0.53m intervals, and assume an overall tray efficiency of 40%.



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 g mole H_2O/min
G_m= 3540 g mole air/min
m = H_y= 0.768



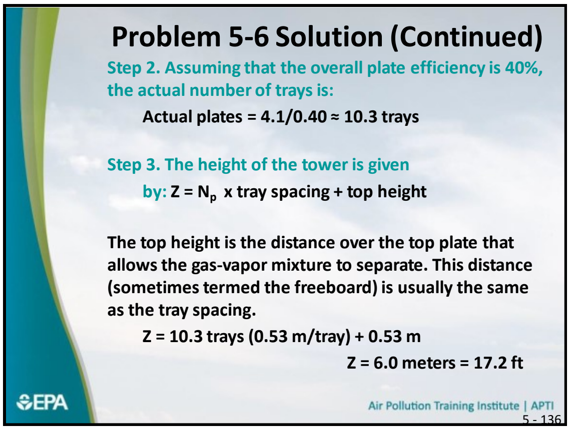
Problem 5-6 Solution (Continued)

Step 1. The number of theoretical plates from Equation 5-30 is:

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

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

N_{OG} = 4.1 theoretical plates



Problem 5-6 Solution (Continued)

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

Actual plates = 4.1/0.40 ≈ 10.3 trays

Step 3. The height of the tower is given by: Z = N_p x tray spacing + top height

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

Z = 10.3 trays (0.53 m/tray) + 0.53 m
Z = 6.0 meters = 17.2 ft

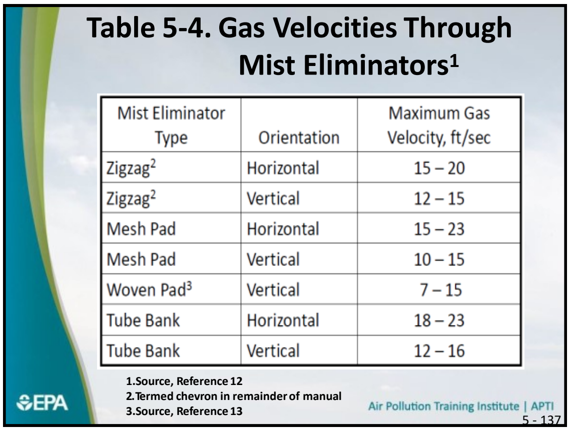
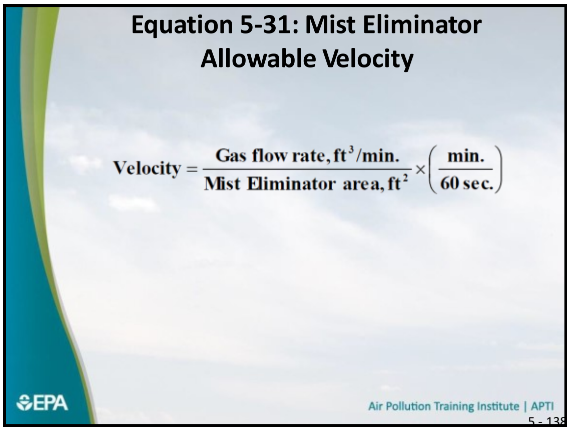


Table 5-4. Gas Velocities Through Mist Eliminators[1]

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

1.Source, Reference 12
2.Termed chevron in remainder of manual
3.Source, Reference 13



Equation 5-31: Mist Eliminator Allowable Velocity

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

Alkali Requirements

- Absorption systems may require an alkali addition system if the gas stream is acidic
- Sulfur dioxide (SO_2), hydrogen chloride (HCl), and hydrogen fluoride (HF) are the most common acid gases
- Calcium hydroxide is the most common alkali material used to neutralize acid gases

Reaction 5-1 $SO_2 + Ca(OH)_2 + 0.5\ O_2 \rightarrow (CaSO_4) + H_2O$

Reaction 5-2 $2HCl + Ca(OH)_2 \rightarrow Ca^{+2} + 2Cl^- + 2H_2O$

Reaction 5-3 $2HF + Ca(OH)_2 \rightarrow Ca^{+2} + 2F^- + 2H_2O$

Problem 5-7

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

Problem 5-7: Solution

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

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

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

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

$$\begin{aligned}\mathrm{Ca(OH)_2\ req'd} &= 0.00062\ \mathrm{lb\ mole/min}\ (74\ \mathrm{lb/lb\ mole})\\ &= 0.0455\ \mathrm{lb/min}\\ &= 2.73\ \mathrm{lb/hr}\end{aligned}$$

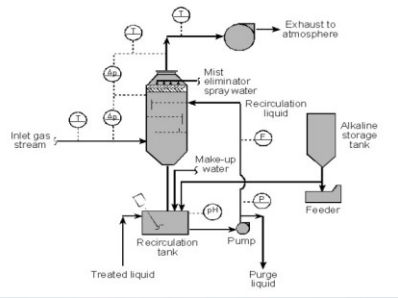
Instrumentation

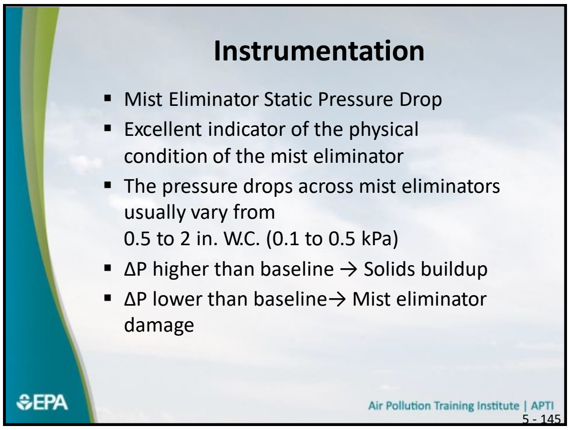
- This section will introduce:
- Standard Absorbers Instrumentation
- Biofiltration Systems Instrumentation

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

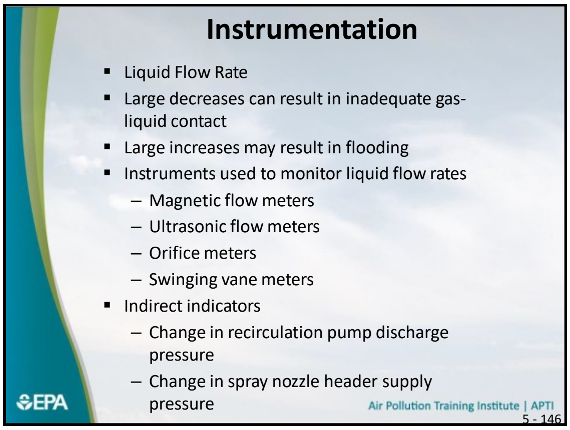
Figure 5-29. Performance Monitoring Instruments





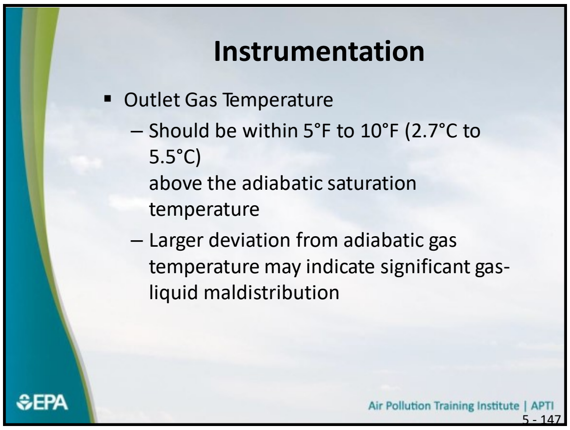
Instrumentation

- 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

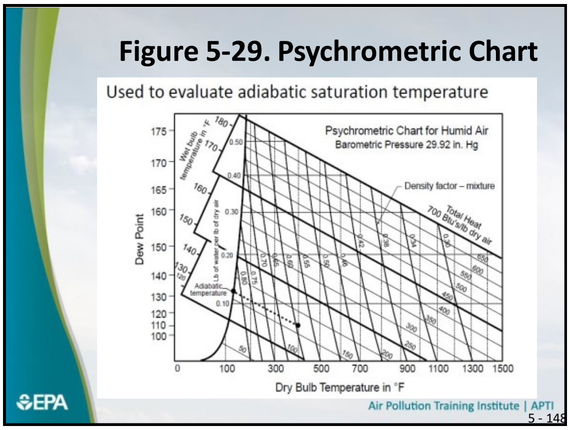
- Liquid Flow Rate
- Large decreases can result in inadequate gas-liquid contact
- Large increases may result in flooding
- Instruments used to monitor liquid flow rates
  - Magnetic flow meters
  - Ultrasonic flow meters
  - Orifice meters
  - Swinging vane meters
- Indirect indicators
  - Change in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



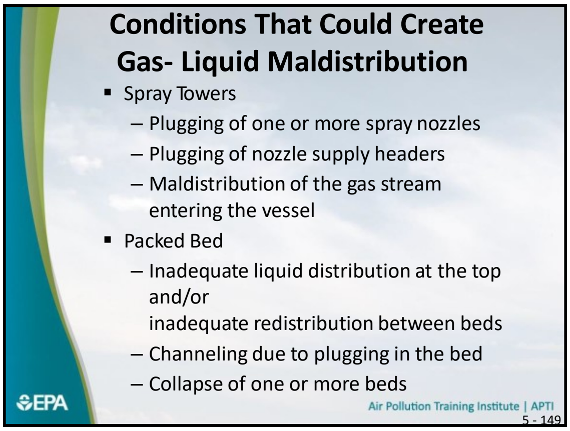
Instrumentation

- 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 5-29. Psychrometric Chart

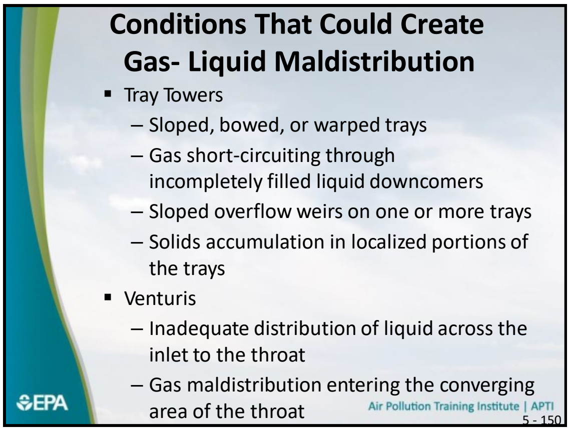


Used to evaluate adiabatic saturation temperature



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

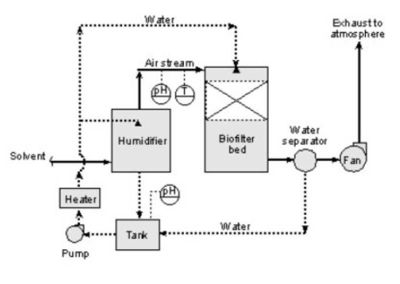
- Recirculation Liquid pH
- pH levels above 9 indicate the potential for precipitation of calcium and magnesium compounds
- pH levels below 5 indicate that insufficient alkali is being added to neutralize the acidic gases and increase the risk of corrosion

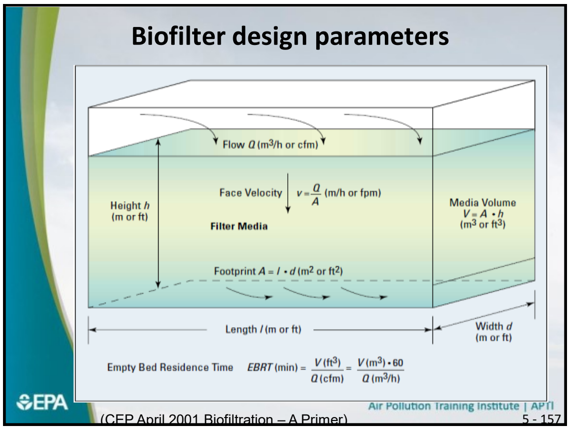
Biofiltration/Bioreactor Systems

Biofiltration Systems

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

Figure 5-30. Flowchart of a Typical Biofiltration Oxidation System

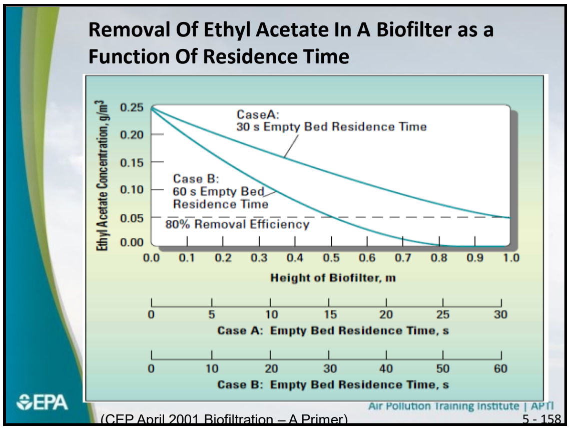




Biofilter design parameters

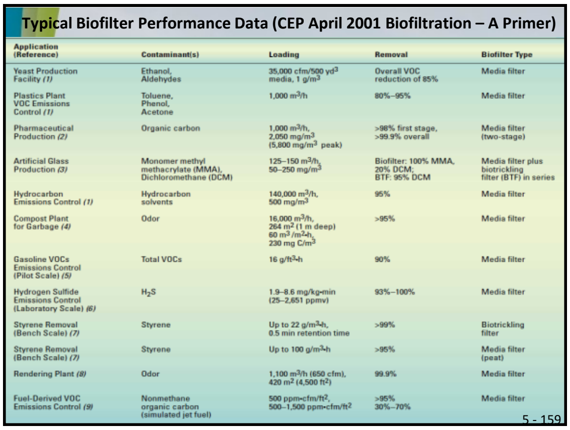
Empty Bed Residence Time $EBRT\text{ (min)} = \frac{V\text{ (ft}^3)}{Q\text{ (cfm)}} = \frac{V\text{ (m}^3) \cdot 60}{Q\text{ (m}^3\text{/h)}}$

(CEP April 2001 Biofiltration – A Primer)



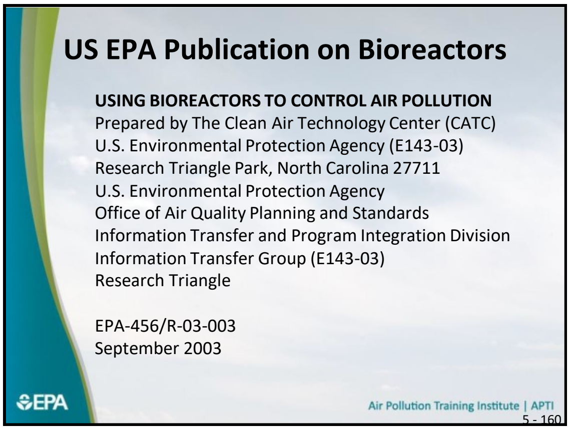
Removal Of Ethyl Acetate In A Biofilter as a Function Of Residence Time

(CEP April 2001 Biofiltration – A Primer)



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

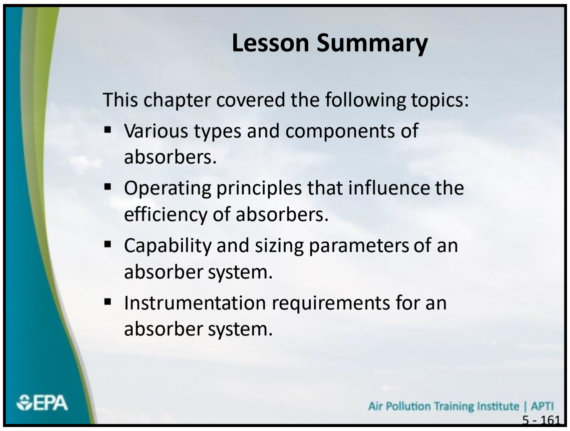
Application (Reference)	Contaminant(s)	Loading	Removal	Biofilter Type
Yeast Production Facility *(1)*	Ethanol, Aldehydes	35,000 cfm/500 yd^3 media, 1 g/m^3	Overall VOC reduction of 85%	Media filter
Plastics Plant VOC Emissions Control *(1)*	Toluene, Phenol, Acetone	1,000 m^3/h	80%–95%	Media filter
Pharmaceutical Production *(2)*	Organic carbon	1,000 m^3/h, 2,050 mg/m^3 (5,800 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^2 (1 m deep) 60 m^3/m^2•h, 230 mg C/m^3	>95%	Media filter
Gasoline VOCs Emissions Control (Pilot Scale) *(5)*	Total VOCs	16 g/ft^3•h	90%	Media filter
Hydrogen Sulfide Emissions Control (Laboratory Scale) *(6)*	H_2S	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^2 (4,500 ft^2)	99.9%	Media filter
Fuel-Derived VOC Emissions Control *(9)*	Nonmethane organic carbon (simulated jet fuel)	500 ppm•cfm/ft^2, 500–1,500 ppm•cfm/ft^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



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.

Chapter 6: Oxidation Systems

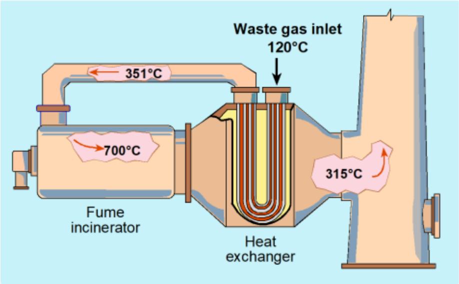
Types of Oxidizers

- **Thermal Oxidation**
  - Direct Flame
  - Flares
  - Process Boilers used for thermal oxidation
- **Catalytic Oxidation**

Types of Heat Exchangers for 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.
  - *Particulate matter* can plug the packed bed.
  - Can resist corrosion from *acid gases*.

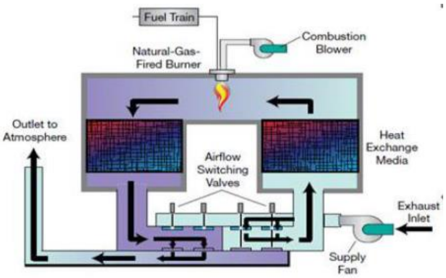
Recuperative Heat Exchanger



Heat recovery in range of 40% to 65% of the total heat released in the combustion chamber.

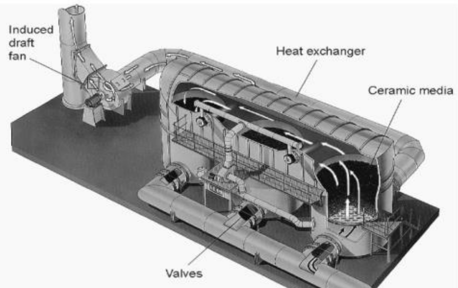
Regenerative Thermal Oxidizers

Heat recovery efficiencies as high as 95%.



- Inlet gas stream is passed through a large packed bed containing preheated ceramic packing.
- Product gas preheats a second bed containing ceramic packing.
- Flow directions are switched periodically.

Regenerative Thermal Oxidizer



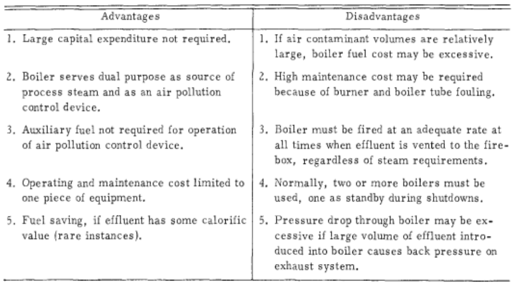
At least two beds are required, three beds are common

Exhaust from afterburner

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

Advantages and Disadvantages of Using a Boiler as an Afterburner



Advantages	Disadvantages
1. Large capital expenditure not required.	1. If air contaminant volumes are relatively large, boiler fuel cost may be excessive.
2. Boiler serves dual purpose as source of process steam and as an air pollution control device.	2. High maintenance cost may be required because of burner and boiler tube fouling.
3. Auxiliary fuel not required for operation of air pollution control device.	3. Boiler must be fired at an adequate rate at all times when effluent is vented to the firebox, regardless of steam requirements.
4. Operating and maintenance cost limited to one piece of equipment.	4. Normally, two or more boilers must be used, one as standby during shutdowns.
5. Fuel saving, if effluent has some calorific value (rare instances).	5. Pressure drop through boiler may be excessive if large volume of effluent introduced into boiler causes back pressure on exhaust system.

Source*: Air Pollution Engineering Manual* EPA 1973

Flares

Flares are often used at chemical plants and petroleum refineries to control VOC vents and get rid of excess gas.

Flares

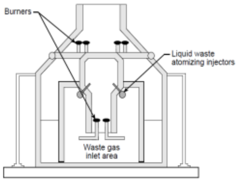
- Have destruction efficiencies exceeding 98%.
- Flares can be used to control almost any VOC stream, and can handle fluctuations in
  - VOC concentration,
  - flow rate, &
  - heating value.
- Feed composition may exceed UEL
- Can be elevated or at ground level

Flare Types

Elevated Flares

- Tall (usually > 100 ft.)
- Operate intermittently
- Handle large volumes of gas
- Used for emergency, maintenance, or upsets
- Combustion at the tip of the stack

Ground Level Flares



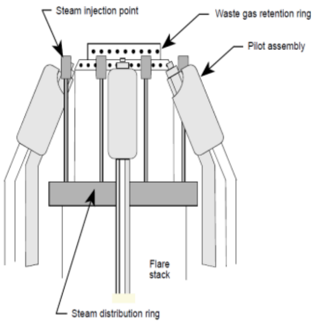
- Short (usually < 100 ft)
- Operate continuously
- Low volumes of gas from routine operations
- Mainly used at landfills
- Combustion zone in stack.

Smokeless Flares

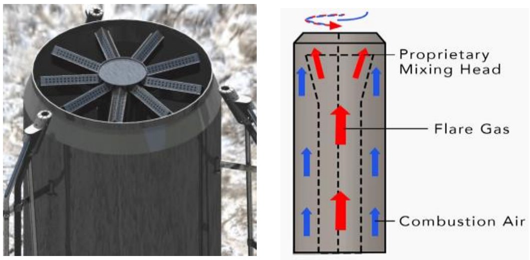
- If a waste gas pressure (momentum) is inadequate & causes smoke, then steam or air are used to make it smokeless.
- **Steam assist:** uses high-pressure steam to provide more momentum (than just "forced air") which will enhances air-fuel mixing (turbulence).
- **Air-assisted flare** is good when steam is not available or freezing is an issue.

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.



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.

Federal Flare Regulations: NSPS 40 CFR § 60.18

- Pilot flame: requires the presence of a continuous flame.
- Tip Exit Velocity: operated with an exit velocity > 60 ft/sec.
  - An exit velocity > 60 ft/sec but < 400 ft/sec may be used if the net heating value of the combustion gas is sufficiently high.
  - 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**.

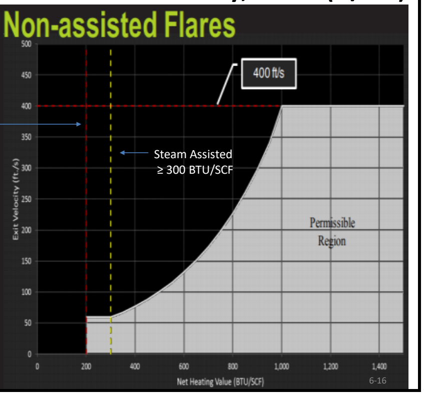
The Maximum Permitted Velocity, Vmax (ft/sec)

Steam and Non-assisted Flares

Non-Assisted
≥ 200 BTU/SCF

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

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

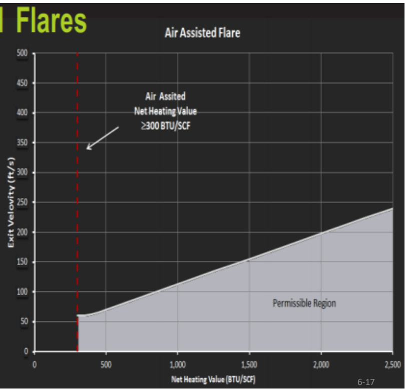


The Maximum Permitted Velocity, Vmax (ft/sec)

Air-assisted Flares

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

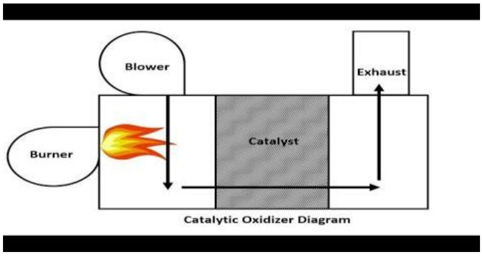
H_T (Btu/SCF) = The net heating value of the gas being combusted in the flare.



Safety and Operational Problems of Flares

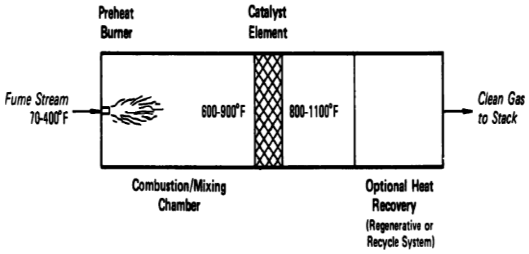
- Thermal radiation: heat given off to the surrounding area may be unacceptable
- Light: may be a nuisance
- Noise: jet-venturi used for mixing at the flare tip can cause excessive noise
- Smoke
- Energy consumption: waste energy because of the need to maintain a constant pilot flame

Catalytic Oxidation



- A waste gas is passed through a <u>catalyst bed</u>, which causes the oxidation reactions to proceed at a *much lower temperature* than in a thermal oxidation.
- A catalytic oxidizer operating at 600°F to 850°F can achieve the same efficiency as a thermal oxidizer operating between 1,000°F and 2,000°F.

Catalytic Oxidation Systems



- The <u>exothermic</u> oxidation reaction in *the catalyst bed* results in an <u>increased gas temperature by 50°F to 300°F.</u>
- Good for <u>treatment of very low VOCs concentration</u> (odors).
- Destruction efficiency is over 90%

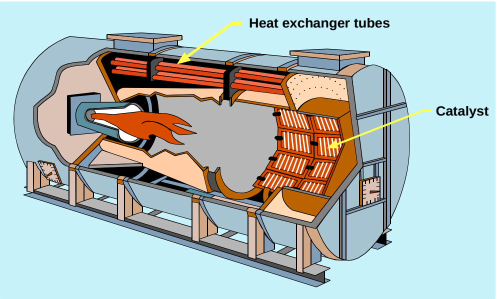
Advantages and Disadvantages

- <u>Advantages</u>
  - Lower temperatures
  - Reduced supplemental fuel requirements
  (in some cases may only be required during start-up)
- <u>Disadvantages</u>
  - 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

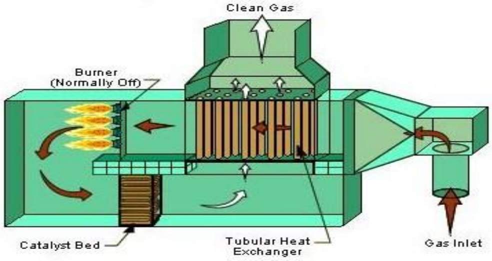
- Surface coating and printing operations widely use catalytic incineration, the others are:
- Varnish cookers;
- Foundry core ovens;
- Filter paper processing ovens;
- Plywood veneer dryers;
- Gasoline bulk loading stations;
- Process vents in the synthetic organic chemical manufacturing industry (SOCMI);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

Cutaway of a Catalytic Oxidizer



There is <u>no need for refractory lined combustion chambers</u> due to the low combustion temperatures (this reduces the weight).

Catalytic Incinerator



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

The Inlet Temperature to the Catalyst Bed

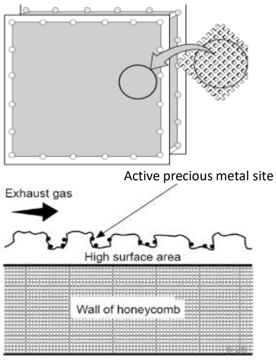
Catalyst <u>Ignition Temperatures</u> Required for Oxidizing 80% of Inlet VOC to CO2, for 2 Catalysts

	Temperature, °F	
Compound	**CO_3O_4**	**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.
- The catalyst's inlet <u>temperature must be chosen to be sufficiently high to **avoid adsorptive effects**</u> by the pollutants on the catalyst.
- <u>It is impossible to predict the temperature needed for a **mixture of VOCs**</u>. This is because the temperature required for different VOCs on a given catalyst can vary significantly.

Catalyst Bed Honeycombs

- The catalyst bed (or matrix) is generally a metal-mesh mat, ceramic honeycomb, or other ceramic matrix structure <u>designed to maximize catalyst surface area.</u>



Common Types of Catalyst Materials

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

Fouling & Masking:
Reduction of Catalyst Activity

- ***<u>Fouling</u>***: deposits on the surface of the catalyst and blocks the access of the organic compounds, <u>may be reversible.</u>
  - **Particulate matter**
  - **Oil droplets** (unless they are vaporized in the preheat section
- ***<u>Masking</u>*****:** occurs when materials are adsorbed to some catalytic surfaces, reducing the active sites available to the organic compounds (<u>reversible</u>).
  - **Sulfur & halogens compounds**

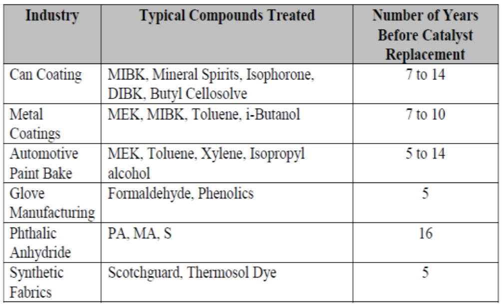
Catalyst Poisons

- Certain metals react <u>irreversibly</u> with catalyst, thereby <u>making it inactive</u> (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.

High Temperature and Catalyst Life

- All catalysts deteriorate with normal use.
- <u>High temperatures</u> can accelerate catalyst deactivation
  - The desired catalyst bed outlet temperature is typically 700 to 900°F
  - The <u>maximum temperature</u> 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

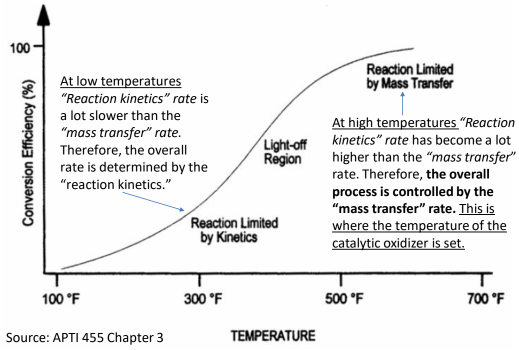


Industry	Typical Compounds Treated	Number of Years Before Catalyst Replacement
Can Coating	MIBK, Mineral Spirits, Isophorone, DIBK, Butyl Cellosolve	7 to 14
Metal Coatings	MEK, MIBK, Toluene, i-Butanol	7 to 10
Automotive Paint Bake	MEK, Toluene, Xylene, Isopropyl alcohol	5 to 14
Glove Manufacturing	Formaldehyde, 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.
- Destruction Efficiency is a function of *length of the catalyst bed* & *mass transfer rates* (see "*Air Pollution Control*" by Cooper & Alley 3rd Ed. page 344).

Importance of Temperature in Catalytic Systems



At low temperatures *"Reaction kinetics" rate* is a lot slower than the *"mass transfer" rate.* Therefore, the overall rate is determined by the "reaction kinetics."

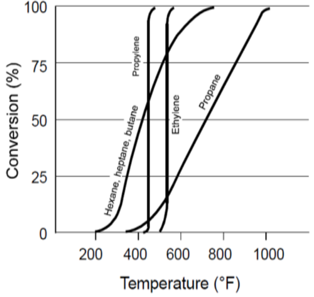
At high temperatures *"Reaction kinetics" rate* has become a lot higher than the *"mass transfer"* rate. Therefore, **the overall process is controlled by the "mass transfer" rate.** This is where the temperature of the catalytic oxidizer is set.

Source: APTI 455 Chapter 3

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**).

Destruction Efficiency Curves for Selected Organic Compounds



Space Velocity

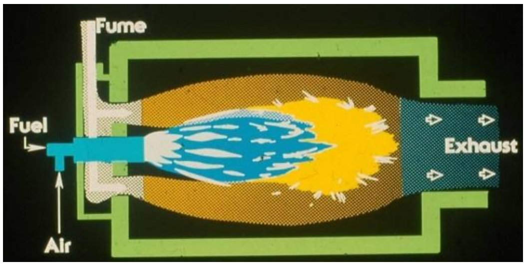
- The amount of catalyst required in a catalytic oxidizer depends on the *space velocity*.
- ***Space velocity*** is defined as the volumetric flow rate (at standard conditions) of gas entering the catalyst bed chamber divided by the volume of the catalyst bed:
  - **Space velocity (hr^{-1}) = Flow rate/Bed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

Space Velocity & Destruction Efficiency for Catalytic Incinerator System

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

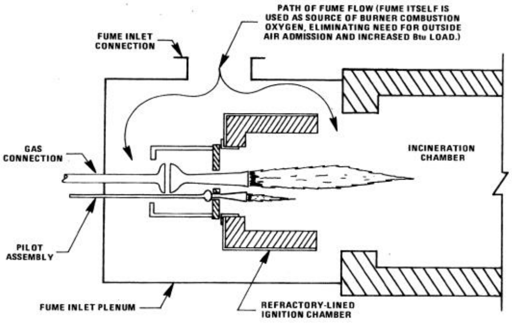
- Space velocities (SV) range from 10,000 hr^{-1} to 100,000 hr^{-1}.

Thermal Oxidizer (with outside air)



- 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%.

Thermal Oxidizer (without outside air)

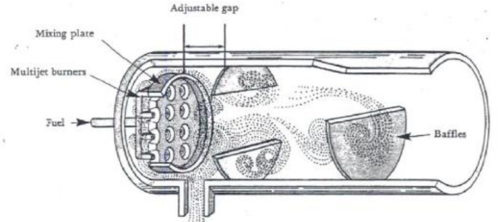


Principles of Operation

Complete combustion is achieved by considering the **three —T's of combustion**

- **Time** (at the desired temperature)
  - 0.5 to 2.0 seconds
  - Time must be allowed for the chemical kinetic reaction to occur.
- **Temperature**
  - 1200 to 1800 °F
- **Turbulence:** The organic-containing waste gases must be thoroughly mixed with the burner combustion gases to ensure complete combustion.

Turbulent Flow Created by Baffles in a Thermal Oxidizer



Flow velocities of 20 to 40 ft./sec. through the unit – to promote turbulent mixing.

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.

Residence Time

- Usually between 0.3 and 2 seconds

$$t = \frac{V}{Q}$$

Where:

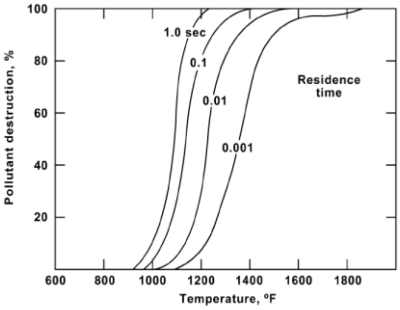
t=Residence time, sec

V=Chamber volume, ft^3

Q=Actual gas volumetric flow rate at combustion conditions, ft^3/sec

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

The Effects of Time and Temperature



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

The Effects of Operating Temperature

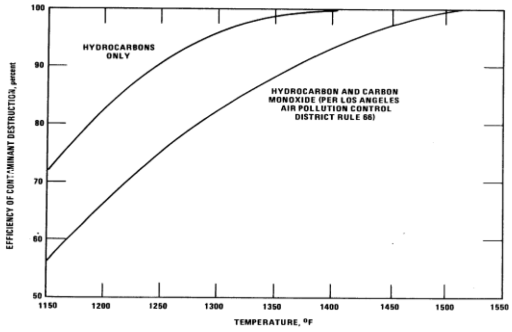


Figure 3-12. Typical effect of operating temperature on effectiveness of thermal afterburner for destruction of hydrocarbons and carbon monoxide.[1]

Examples

- Hazardous waste incinerator
  - **99.99%** destruction removal efficiency (DRE) for hazardous VOCs & **99.9999** DRE for waste that contain dioxin & furans (required by NESHAP 40 CFR Part 63 Subpart EEE)
  - Would need about 2000 °F (depends on compounds burned) & minimum of 2 seconds residence time (studies).
- Medical waste incinerator
  - EPA does not regulate medical waste as a hazardous waste
  - Regulated by NSPS 40 CFR Part 60 Subpart Ce
  - Would need about 1600°F & 1.0 second residence time (studies).

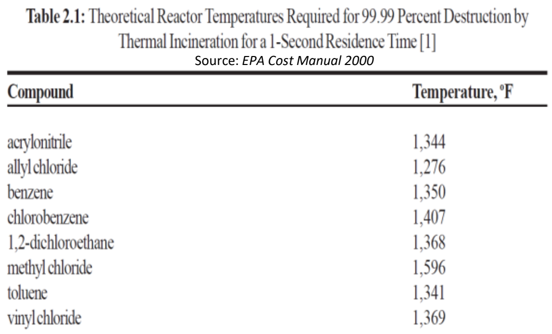


Table 2.1: Theoretical Reactor Temperatures Required for 99.99 Percent Destruction by Thermal Incineration for a 1-Second Residence Time [1]

Source: *EPA Cost Manual 2000*

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

The majority of hazardous waste incinerators are operated from 1,200 °F to 3,000 °F. Residence time usually ranges from 0.5 to 2.0. Turbulent mixing is important. (EPA *On Site Incineration – Superfund* 1998)

Destruction Efficiency

- The means for estimating VOC 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.
- 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.

Auto-Ignition Temperature

- 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**.
- A generally accepted method (old) of determining the temperature required for destruction of an organic compound is its **Auto-Ignition Temperature**.

Auto Ignition Temperatures

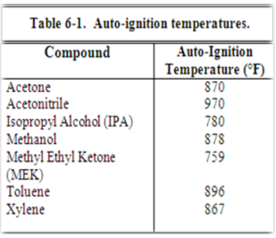


Table 6-1. Auto-ignition temperatures.

Compound	Auto-Ignition Temperature (°F)
Acetone	870
Acetonitrile	970
Isopropyl Alcohol (IPA)	780
Methanol	878
Methyl Ethyl Ketone (MEK)	759
Toluene	896
Xylene	867

Destruction Efficiency %	Degrees Above Auto-ignition Temp °F	Residence Time (sec)
95	300	0.5
98	400	0.5
99	475	0.75
99.9	550	1.0
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.

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. (to promote turbulent mixing)
- VOCs should be less than 25% LEL

Combustion Products and Gas Volumes

- In all high temperature combustion processes, a complex set chemical reactions occur simultaneously
- Objective is to oxidize all carbon to CO_2, hydrogen to H_2O, and sulfur to SO_2
- Represent the set of simultaneous reactions by the single generalized reaction

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

Minor Components in Waste Gas

- Sulfur
  - ≥ 98% converted to SO_2
  - Small amount of SO_3 may be formed
- Chlorine –converted to HCl
- Fluorine –converted to HF
- Nitrogen (in waste gas) –may be converted to N_2, NO, or NO_2
- Cl, F, N (in waste gas) normally neglected in material balance calculations

Composition of Air

- Oxygen is almost always supplied by air
- Air composition: 21% O_2
  79% N_2
- Neglect minor components in material balance calculations
- For Air: $x = \frac{0.79\ moles\ of\ N_2}{0.21\ moles\ of\ O_2}$

X = mole fraction of air = volume fraction of air

$N_1/N_2 = V_1/V_2$ (at constant T & P – from PV=NRT)

Combustion Air Requirements

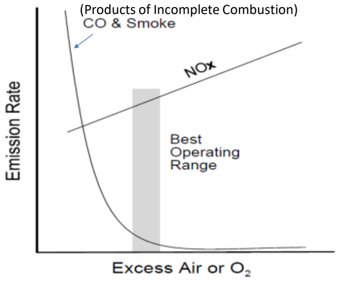
- To achieve complete combustion of the fuel (e.g., natural gas, propane, No. 2 oil), a sufficient supply of oxygen must be present in the burner flame to convert all of the carbon to CO_2. This quantity of oxygen is referred to as the ***stoichiometric*** **(or theoretical)** ***amount***.
- For example, 1 mole of methane (the major component of natural gas) requires 2 moles of oxygen for complete combustion

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

Lean and Rich

- *Rich* - there is insufficient O_2 available for complete oxidation.
  - This reduces the peak flame temperature and results in the formation of CO and other partially-oxidized compounds
- *Lean* - the amount of O_2 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

NOx and CO Emissions vs. Excess Air

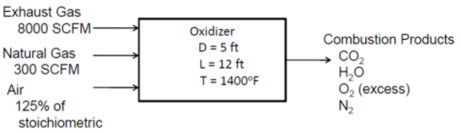


The **reason that NOx increases with excess air** is that as we increase excess air, large amount of nitrogen enters with the combustion air and more of the combustion is occurring in a region with extra oxygen.

Example 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.

Solution



t (retention time) sec = V (volume of chamber) ft^3 / Q (total flue gas rate) Actual ft^3/sec

Q (total flue gas rate) = Q (in) + Q (products of combustion) + Q (excess O_2) + Q (N_2)
Q (products of combustion) = volume of CO_2 & H_2O produced by combustion
Q (in) = exhaust gas from source (unreacted) = 8,000 SCFM
Q (excess O_2) = excess O_2 not combusted
Q (N_2)= unreacted in air
From excess air

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

Solution (continued)

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

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

  - Stoichiometric oxygen requirement is 2 moles of oxygen for every mole of methane
- **Step 2. Calculate the amount of O_2 required for stoichiometric conditions (no excess air)**

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

$$\text{Stoichiometric O}_2 = 2 \times (\text{lb mole CH}_4)$$

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

Solution (continued)

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

Total O_2 requirement = 1.25 × (stoichiometric requirement)

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

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

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

Continued…

Solution (continued)

- **Step 4. Calculate the total flue gas flow rate Q(out)**

Q(out)=Q(in)+Q(products of combustion)+Q(N_2)+Q(excessO_2)

Q(in) = 8,000 SCFM

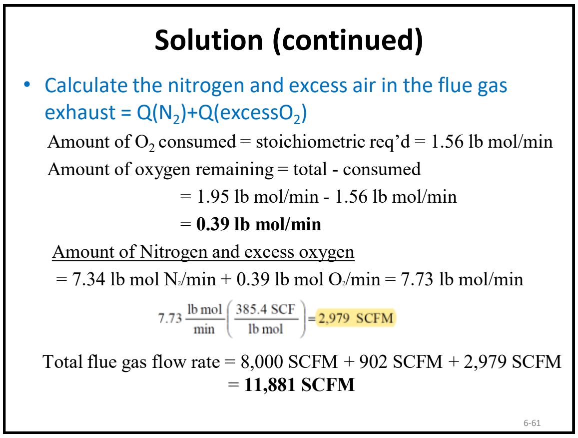
Q(products of combustion) = Q(CO_2) + Q(H_2O)

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

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

$$\text{CO}_2 + \text{H}_2\text{O} = 2.34\ \text{lb mol/min}$$

$$2.34\,\frac{\text{lb mol}}{\text{min}}\left(\frac{385.4\text{SCF}}{\text{lb mol}}\right) = \boxed{902\ \text{SCFM}\ \ \textbf{= Q(products of combustion)}}$$



Solution (continued)

- Calculate the nitrogen and excess air in the flue gas exhaust = $Q(N_2)$+$Q(\text{excess}O_2)$

Amount of O_2 consumed = stoichiometric req'd = 1.56 lb mol/min

Amount of oxygen remaining = total - consumed

= 1.95 lb mol/min - 1.56 lb mol/min

= **0.39 lb mol/min**

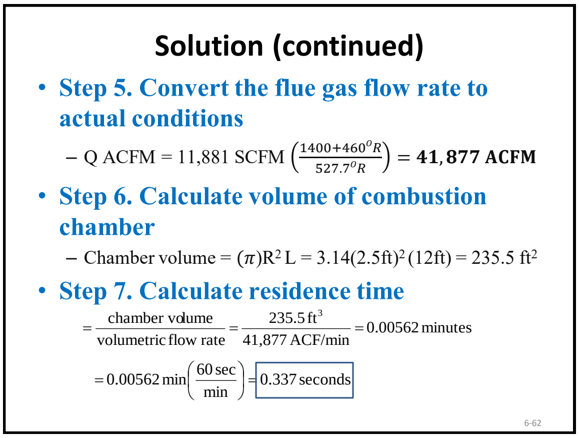
Amount of Nitrogen and excess oxygen

= 7.34 lb mol N_2/min + 0.39 lb mol O_2/min = 7.73 lb mol/min

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

Total flue gas flow rate = 8,000 SCFM + 902 SCFM + 2,979 SCFM

= **11,881 SCFM**

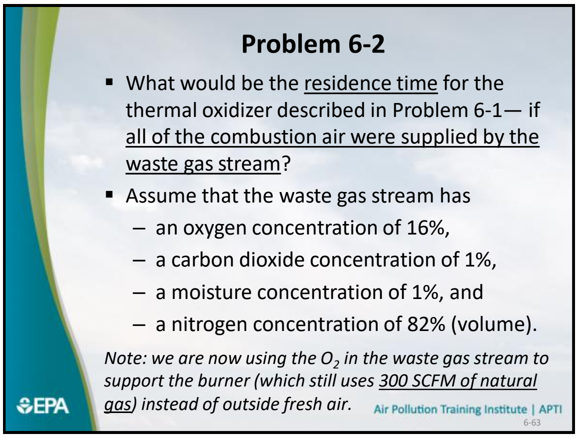


Solution (continued)

- **Step 5. Convert the flue gas flow rate to actual conditions**
  - Q ACFM = 11,881 SCFM $\left(\frac{1400+460^{o}R}{527.7^{o}R}\right)$ = **41,877 ACFM**
- **Step 6. Calculate volume of combustion chamber**
  - Chamber volume = $(\pi)R^2 L = 3.14(2.5\text{ft})^2(12\text{ft}) = 235.5\ \text{ft}^2$
- **Step 7. Calculate residence time**

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

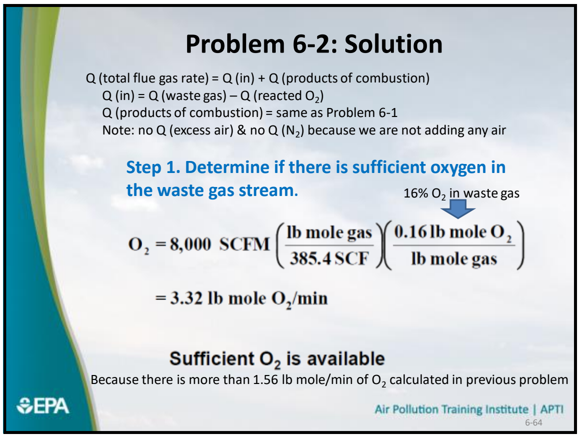
$$=0.00562\ \text{min}\left(\frac{60\ \text{sec}}{\text{min}}\right)=\boxed{0.337\ \text{seconds}}$$



Problem 6-2

- What would be the residence time for the thermal oxidizer described in Problem 6-1— if all of the combustion air 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 O_2 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 O_2)

Q (products of combustion) = same as Problem 6-1

Note: no Q (excess air) & no Q (N_2) because we are not adding any air

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

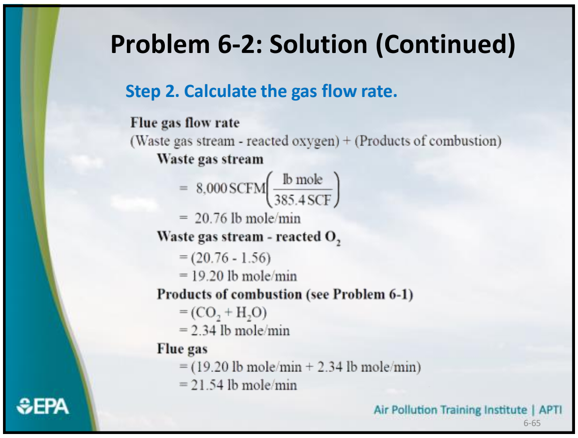
16% O_2 in waste gas

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

$$= 3.32\ \text{lb mole } O_2\text{/min}$$

Sufficient O_2 is available

Because there is more than 1.56 lb mole/min of O_2 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

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

= 20.76 lb mole/min

Waste gas stream - reacted O_2

= (20.76 - 1.56)

= 19.20 lb mole/min

Products of combustion (see Problem 6-1)

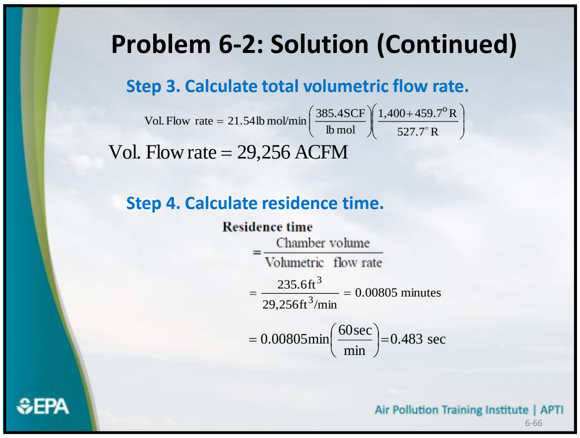
= (CO_2 + H_2O)

= 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.

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

Vol. Flow rate = 29,256 ACFM

Step 4. Calculate residence time.

Residence time

$$=\frac{\text{Chamber volume}}{\text{Volumetric flow rate}}$$

$$=\frac{235.6\text{ft}^3}{29{,}256\text{ft}^3/\text{min}} = 0.00805\ \text{minutes}$$

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

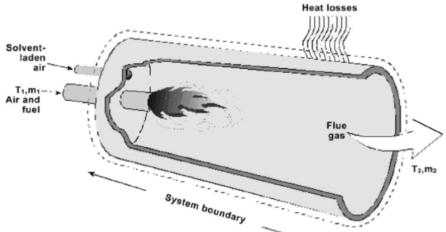
Fuel Requirements

- 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: T_1 = waste gas inlet temperature
T_2 = flue gas exit temperature
m_1 = mass flow rate of waste gas plus air and fuel
m_2 = 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.

Other Losses & Additions in a Heat Balance

- **Heat loses**
  - Ash: heating value of ash(BTU/lb) x mass of ash discharge = heat loss due to ash
  - Radiation: heat loss from radiation to the incinerator shell is usually expressed as a % of the “total heat of combustion”
  - Conduction: heat loss from conduction heat transfer to combustion chamber walls
  - Evaporation of water from combustion air: mass of water (lb/hr.) times the heat content of water (1000 BTU/lb)
  - Evaporation of water from material to be burned: (same)
- **Heat additions**:
  - Sensible energy released from combustion of different volatile portions in waste 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
  - **LHV** (lower heating value of fuel) = **HHV** (higher heating value of fuel) *minus* **L** (heat of vaporization of water)
- **$\text{Heat}_{\text{available}}$ = HHV – L + S_1 – S_2 = LHV + S_1 – S_2**
- **$\text{Heat}_{\text{available}}$ = LHV + S_1 (no excess air: S_2 =0)**

HHV & LHV for Different Fuels

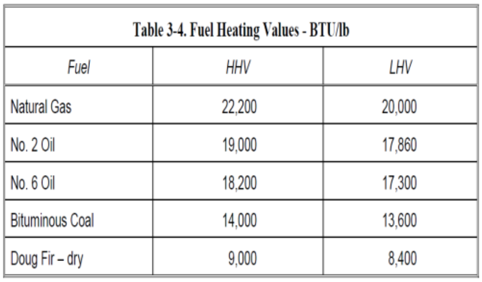
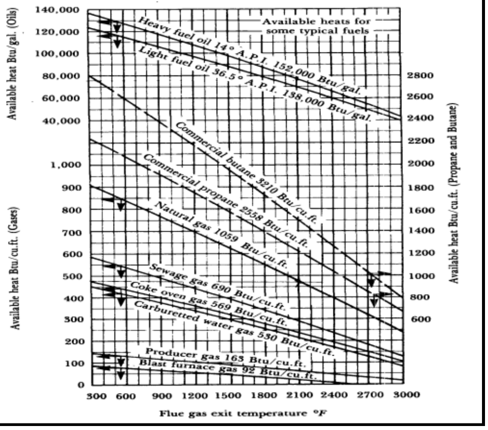
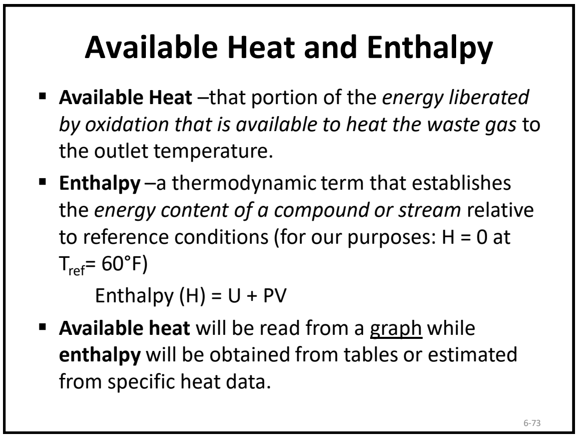


Table 3-4. Fuel Heating Values - BTU/lb

Fuel	HHV	LHV
Natural Gas	22,200	20,000
No. 2 Oil	19,000	17,860
No. 6 Oil	18,200	17,300
Bituminous Coal	14,000	13,600
Doug Fir – dry	9,000	8,400

Available Heat of Common Fuels





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_{ref}= 60°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.

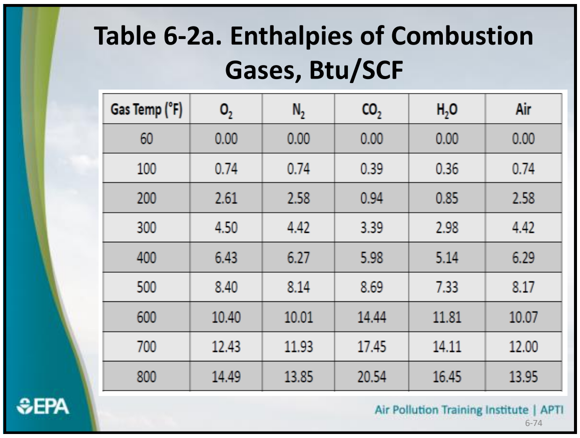


Table 6-2a. Enthalpies of Combustion Gases, Btu/SCF

Gas Temp (°F)	O_2	N_2	CO_2	H_2O	Air
60	0.00	0.00	0.00	0.00	0.00
100	0.74	0.74	0.39	0.36	0.74
200	2.61	2.58	0.94	0.85	2.58
300	4.50	4.42	3.39	2.98	4.42
400	6.43	6.27	5.98	5.14	6.29
500	8.40	8.14	8.69	7.33	8.17
600	10.40	10.01	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

Air Pollution Training Institute | APTI

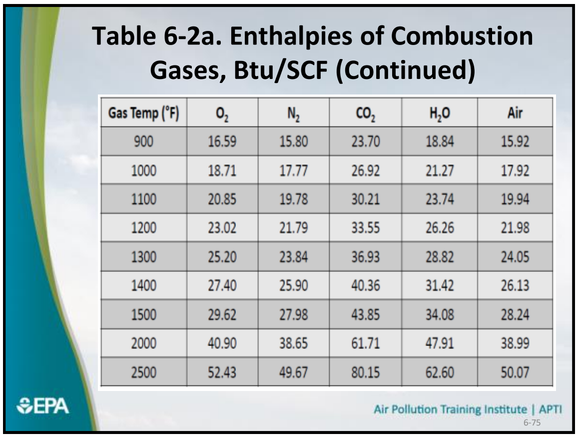


Table 6-2a. Enthalpies of Combustion Gases, Btu/SCF (Continued)

Gas Temp (°F)	O_2	N_2	CO_2	H_2O	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

Air Pollution Training Institute | APTI

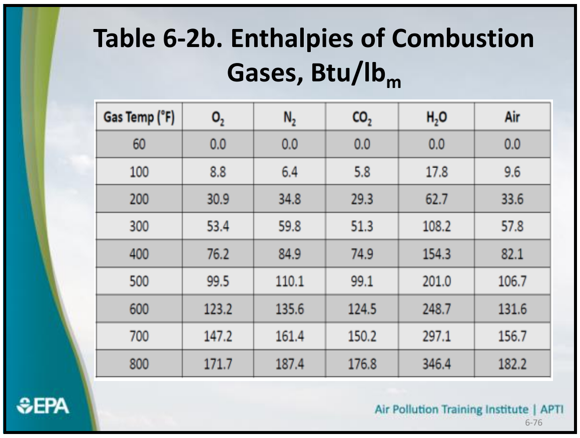


Table 6-2b. Enthalpies of Combustion Gases, Btu/lb_m

Gas Temp (°F)	O_2	N_2	CO_2	H_2O	Air
60	0.0	0.0	0.0	0.0	0.0
100	8.8	6.4	5.8	17.8	9.6
200	30.9	34.8	29.3	62.7	33.6
300	53.4	59.8	51.3	108.2	57.8
400	76.2	84.9	74.9	154.3	82.1
500	99.5	110.1	99.1	201.0	106.7
600	123.2	135.6	124.5	248.7	131.6
700	147.2	161.4	150.2	297.1	156.7
800	171.7	187.4	176.8	346.4	182.2

Air Pollution Training Institute | APTI

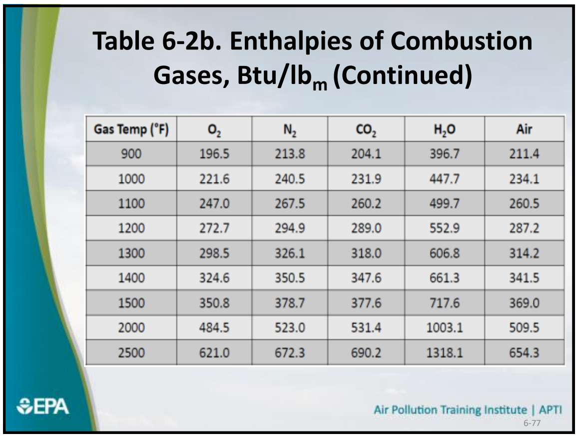
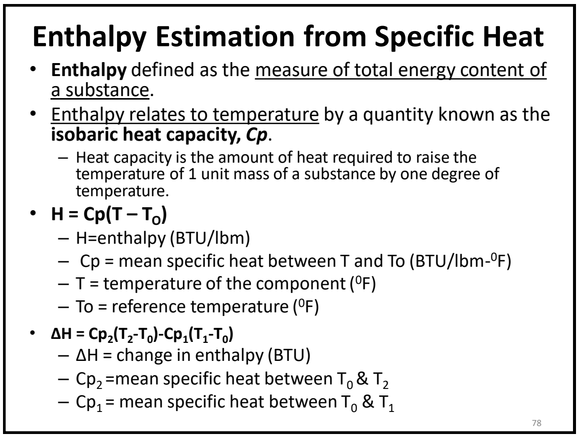


Table 6-2b. Enthalpies of Combustion Gases, Btu/lb_m (Continued)

Gas Temp (°F)	O_2	N_2	CO_2	H_2O	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

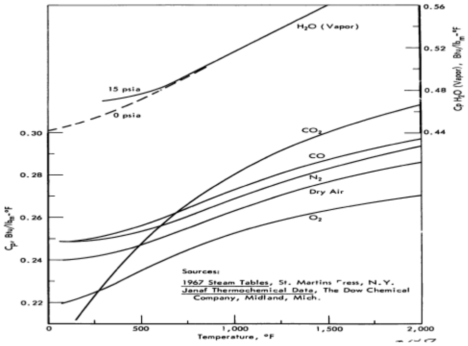
Air Pollution Training Institute | APTI



Enthalpy Estimation from Specific Heat

- **Enthalpy** defined as the measure of total energy content of a substance.
- Enthalpy relates to temperature by a quantity known as the **isobaric heat capacity, *Cp***.
  - Heat capacity is the amount of heat required to raise the temperature of 1 unit mass of a substance by one degree of temperature.
- **$H = Cp(T – T_O)$**
  - H=enthalpy (BTU/lbm)
  - Cp = mean specific heat between T and To (BTU/lbm-^{0}F)
  - T = temperature of the component (^{0}F)
  - To = reference temperature (^{0}F)
- **$\Delta H = Cp_2(T_2-T_0)-Cp_1(T_1-T_0)$**
  - ΔH = change in enthalpy (BTU)
  - Cp_2 =mean specific heat between T_0 & T_2
  - Cp_1 = mean specific heat between T_0 & T_1

Specific Heat of Gases at Constant Pressure



Source: *Afterburner System Study*

Enthalpy Estimations Using Average Specific Heat

- To simplify this calculation, an average specific heat value, C_p between T_1 and T_2, can be used. This reduces the prior equation to:

$$\Delta H = C_p(T_2 - T_1)$$

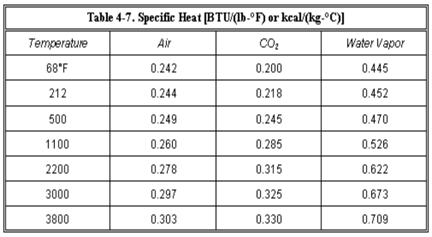


Table 4-7. Specific Heat [BTU/(lb-°F) or kcal/(kg-°C)]			
Temperature	Air	CO_2	Water Vapor
68°F	0.242	0.200	0.445
212	0.244	0.218	0.452
500	0.249	0.245	0.470
1100	0.260	0.285	0.526
2200	0.278	0.315	0.622
3000	0.297	0.325	0.673
3800	0.303	0.330	0.709

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)

Calculation of the Total Heat Rate

- Using the Conservation of Energy, First Law of Thermodynamics, and assuming enthalpy (H) at constant pressure.
- The total heat rate (Q) required is given by:

$$Q = m\Delta H = mC_p(T_2 - T_1)$$

- 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

Note: that these equations are for a simple heat balance. They do not take into account radiation energy loss from the combustion chamber or other energy losses.

Problem

- How much heat is necessary to increase the temperature of a 100 SCFM gas stream (assume air) from 100°F to 1,500°F? If necessary to solve the problem, assume that standard conditions are 32°F and 14.7 psia and assume that air has a molecular weight of 29.
- Solve the problem first by using the enthalpy tables, then solve it again by using the specific heat of air.

Solution Using Enthalpy Tables

$$Q = m\Delta H = mC_p(T_2 - T_1)$$

- $Q = m\,\Delta H = m\,(H_2 - H_1)$
- m = 100 SCFM
- H@1500 = 28.24 BTU/SCF
- H@100 = 0.74 BTU/SCF
- ΔH = 27.5 BTU/SCF
- Q = 100 SCFM (27.5 BTU/SCF)
- **Q = 2,750 BTU/Min.**

Solution Using Specific Heat

$$Q = m\Delta H = mC_p(T_2 - T_1)$$

- Average specific heat of air between 100 °F to 1500 °F is about 0.25 BTU/lb – °F (from earlier slide Table 4.7).
- Q =m Cp (T2 –T1)
- Calculate m:
  - m = 100 SCFM (1 lbmole air/385 SCF)(29 lbm/lbmole air)
  - m = 7.53 lbm/min
- Calculate Q:
  - Q = 7.53 lbm/min (0.25 BTU/lbm – °F) (1500 – 100) °F
  - **Q = 2636 BTU/min**

Amount of Fuel Required

Calculate the amount of fuel required to heat a waste gas stream from T_1 to T_2:

1. **Ignore any benefits for oxidation of the pollutants in waste gas stream.**
2. **Assume there are no Heat losses in the system.**
3. **No excess air added**

Heat Available = **$Q = LHV + Q_{S1} - Q_{S2}$**

No heat from waste gas stream (**$Q_{S1} = 0$**)

No excess air added (**Q_{S2}** = 0)

Q = LHV (Btu/ft³ of fuel) x Ng

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

$Q = m\Delta H$

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

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

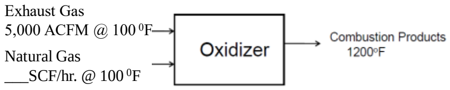
$Q = m\Delta H = LHV \times Ng$

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

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 100°F to the required temperature of 1,200°F?
- Assume no heat losses and no excess air.

Solution



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

$Ng = m\Delta H/LHV$

m = 5,000 ACFM

ΔH = H @ 1200 °F – H @ 100 °F

LHV from graph @ 1200 °F

Solution

- **First, the volume of waste gas must be corrected to standard conditions (68°F and 1 atm).**
- $G = 5000\,\frac{ACF}{MIN}\,[(460^0R + 68^0\mathrm{F})/(460^0R + 100^0\mathrm{F})](60\cancel{\mathrm{min}}/\mathrm{hr})$
- **G = 282,857 SCF/hr**

- **Next, determine the heat rate by using enthalpy tables**
  - H@ 1200 °F = 21.98 BTU/SCF
  - H@ 100 °F = 0.74 BTU/SCF
  - $\Delta H_{(1200-100)}$ = 21.24 BTU/SCF
  - **Q = m ΔH** = 282,857 SCF/hr (21.24) BTU/SCF = **6,007,883 BTU/hr.**
  - This is the energy needed to heat the exhaust gas stream from 100 to 1200

Solution

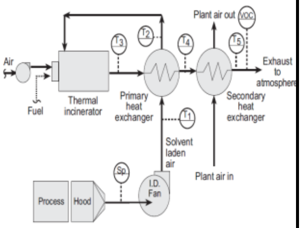
- **Finally, compute the amount of natural gas required from the heating rate, the available heat of the fuel (HA) must be computed.**
  - **$Ng = m\Delta H/LHV$**
  - From previous slide Figure, for natural gas at 1200°F
    - LHV ≈ 700 Btu/SCF
    - Ng = 6,007,883 BTU/hr. / 700 BTU/SCF
    - **Ng = 8,583 SCF of natural gas/hr.**

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

Flowchart of a Thermal Oxidizer System

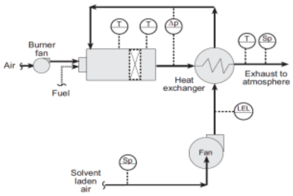
- The most important operating parameter is the gas outlet temperature (T_3), which should be 200°F -300°F above the auto-ignition of the most difficult to oxidize compound.
- Temperature around the primary heat exchanger ($T_2 – T_1$) provide indication of fouling or other deterioration.
- Monitoring 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.

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.



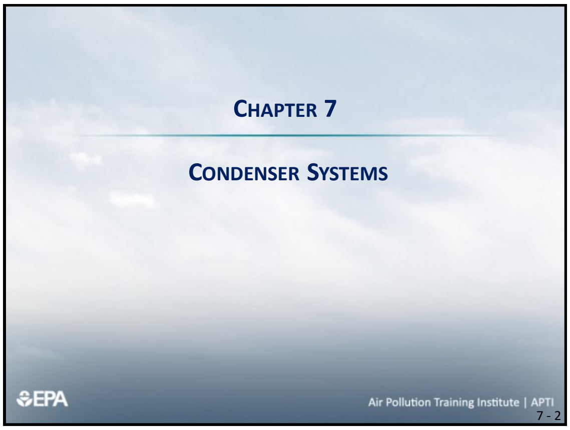
- Outlet VOC concentration significantly above baseline (permit) values indicate problems affecting the catalyst bed or VOC emissions short-circuiting through the heat exchanger.
- Determine the static pressure drop across a catalytic oxidizer. An increase could mean partial pluggage of the catalyst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

Presented For
NESCAUM 2023

CHAPTER 7

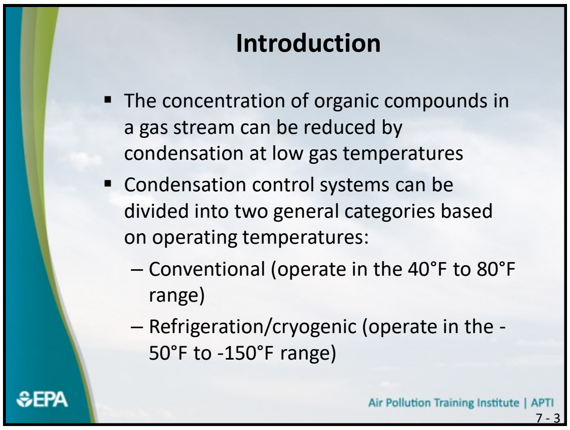
CONDENSER SYSTEMS

APTI COURSE 415
Air Pollution Training Institute | APTI



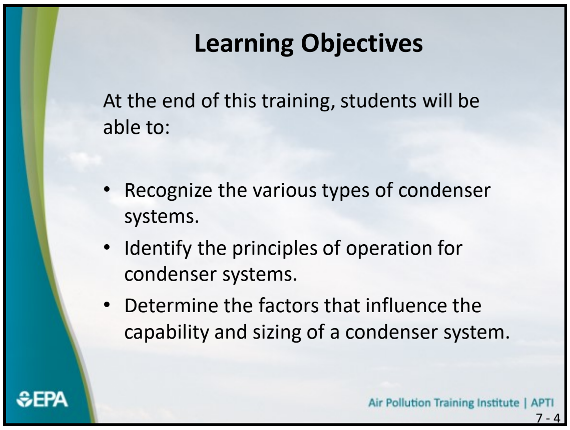
CHAPTER 7

CONDENSER SYSTEMS



Introduction

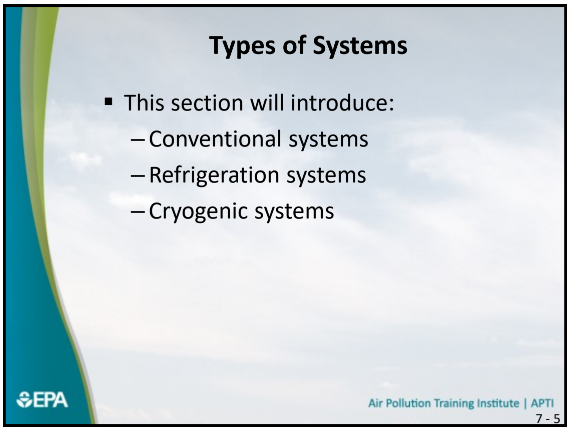
- The concentration of organic compounds in a gas stream can be reduced by condensation at low gas temperatures
- Condensation control systems can be divided into two general categories based on operating temperatures:
  - Conventional (operate in the 40°F to 80°F range)
  - Refrigeration/cryogenic (operate in the -50°F to -150°F range)



Learning Objectives

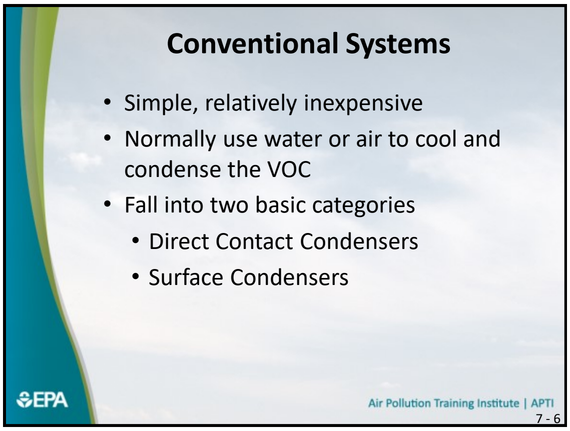
At the end of this training, students will be able to:

- Recognize the various types of condenser systems.
- Identify the principles of operation for condenser systems.
- Determine the factors that influence the capability and sizing of a condenser system.



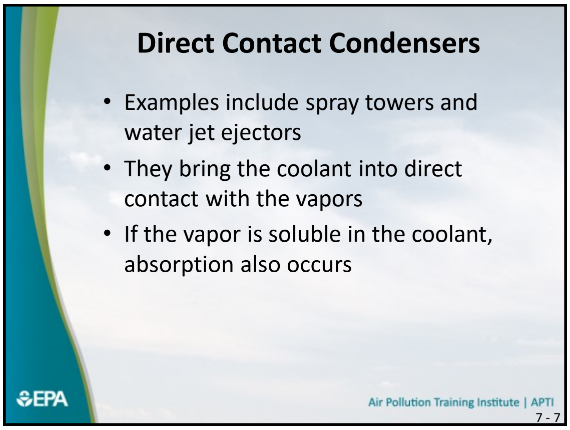
Types of Systems

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



Conventional Systems

- Simple, relatively inexpensive
- Normally use water or air to cool and condense the VOC
- Fall into two basic categories
  - Direct Contact Condensers
  - Surface Condensers



Direct Contact Condensers

- Examples include spray towers and water jet ejectors
- They bring the coolant into direct contact with the vapors
- If the vapor is soluble in the coolant, absorption also occurs

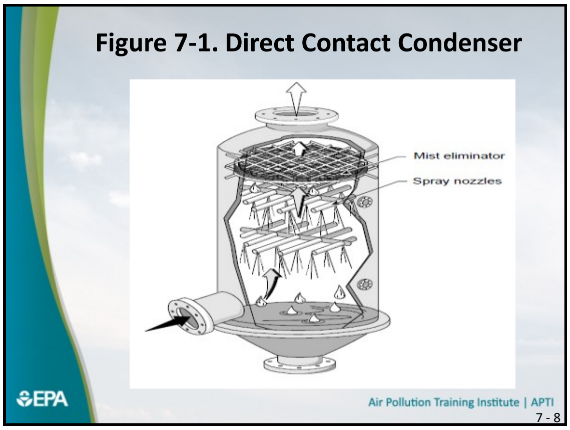


Figure 7-1. Direct Contact Condenser

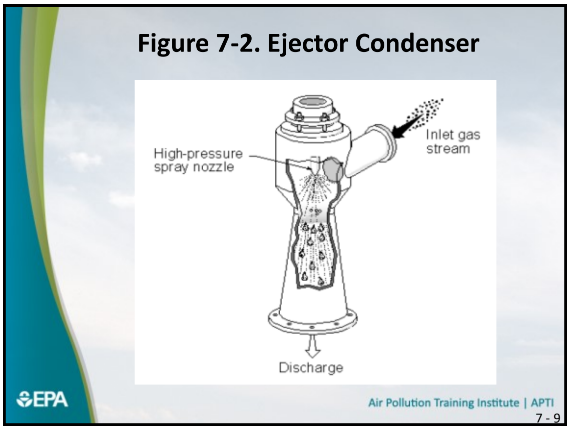
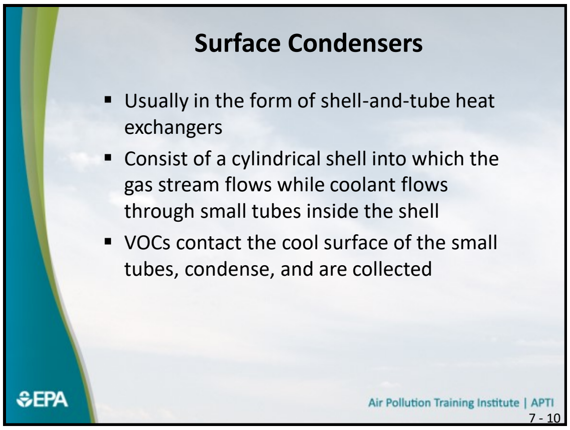
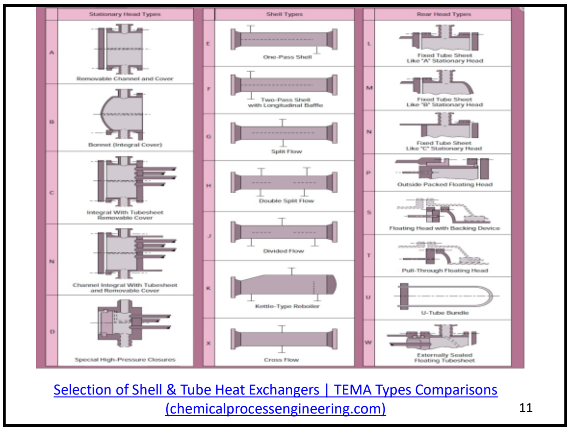


Figure 7-2. Ejector Condenser



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



Selection of Shell & Tube Heat Exchangers | TEMA Types Comparisons (chemicalprocessengineering.com)

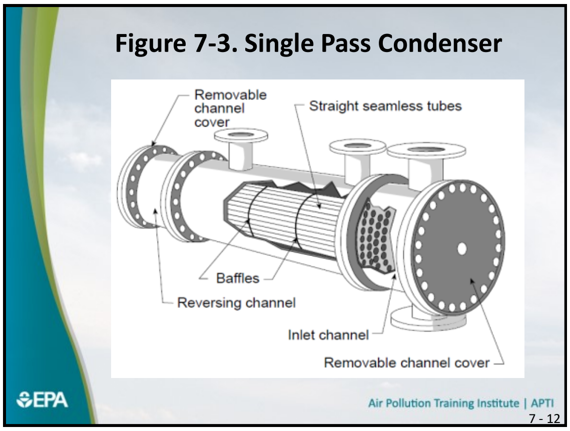


Figure 7-3. Single Pass Condenser

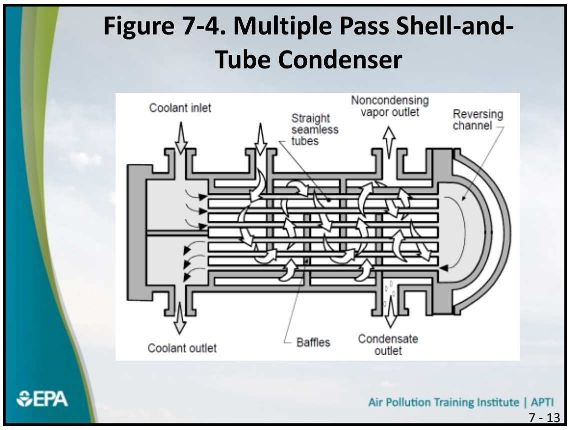
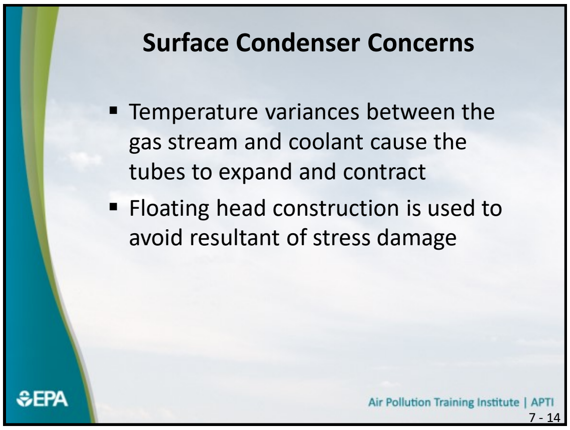


Figure 7-4. Multiple Pass Shell-and-Tube Condenser

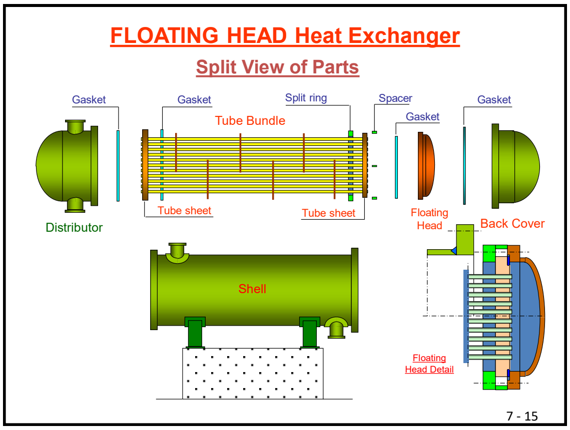
Air Pollution Training Institute | APTI



Surface Condenser Concerns

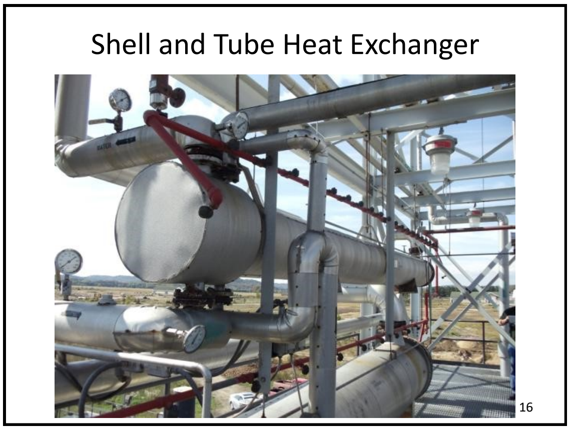
- Temperature variances between the gas stream and coolant cause the tubes to expand and contract
- Floating head construction is used to avoid resultant of stress damage

Air Pollution Training Institute | APTI

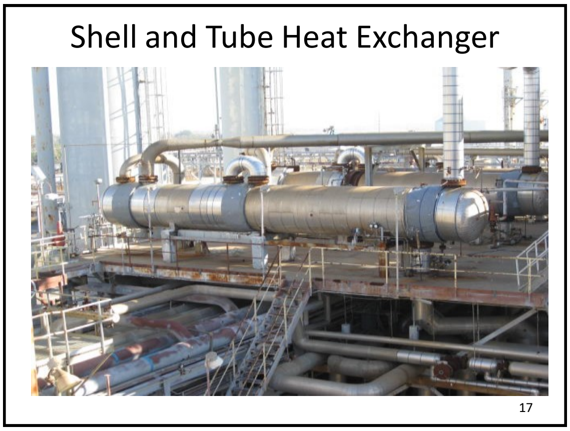


FLOATING HEAD Heat Exchanger

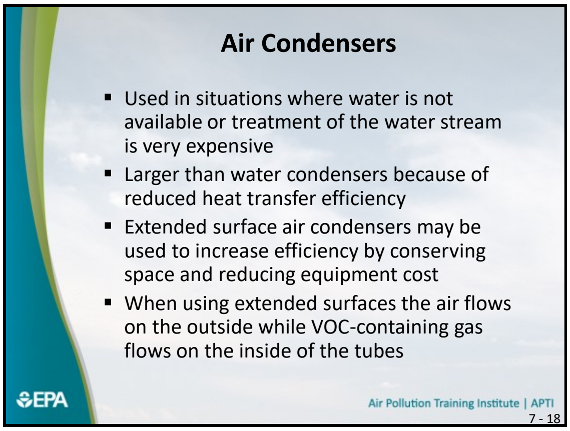
Split View of Parts



Shell and Tube Heat Exchanger



Shell and Tube Heat Exchanger



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

Air Pollution Training Institute | APTI

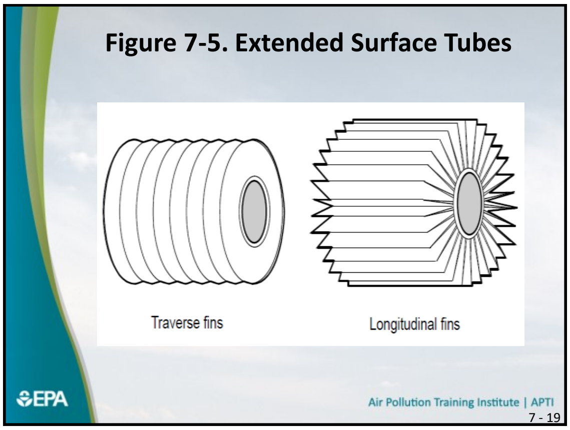
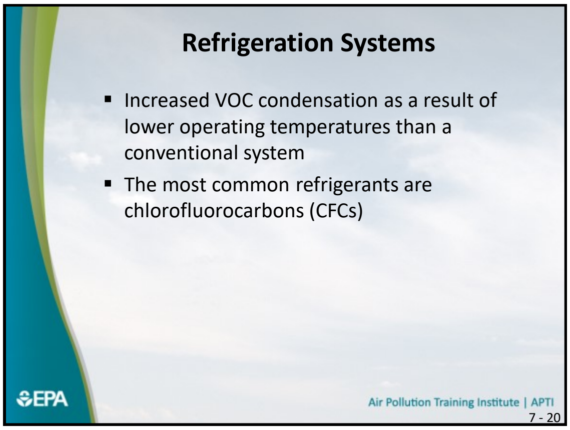


Figure 7-5. Extended Surface Tubes



Refrigeration Systems

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

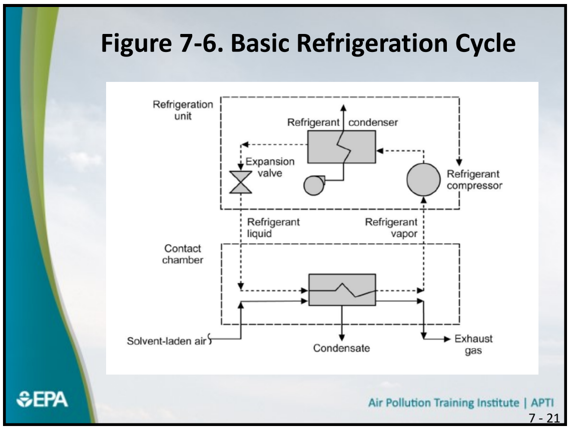


Figure 7-6. Basic Refrigeration Cycle

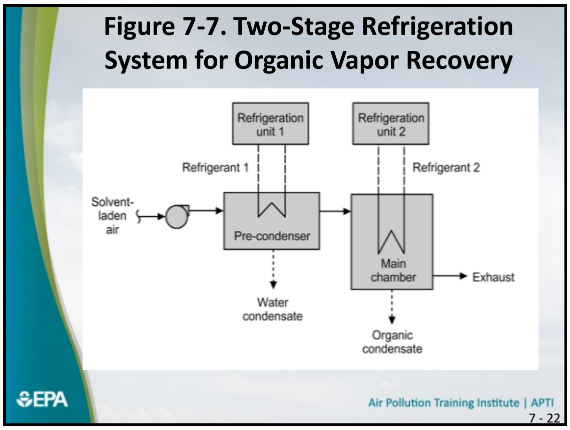
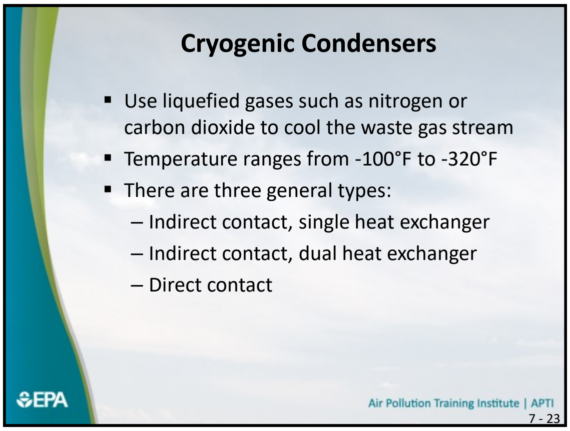
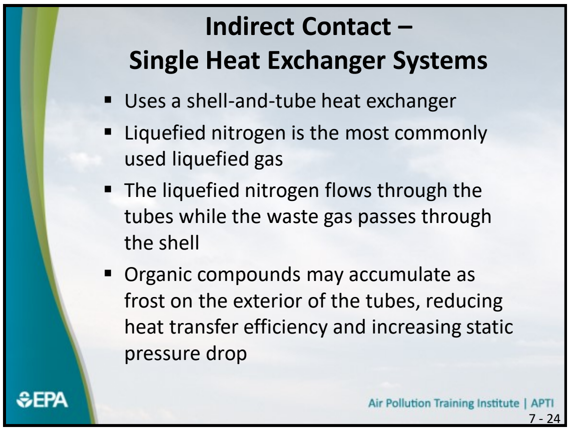


Figure 7-7. Two-Stage Refrigeration System for Organic Vapor Recovery



Cryogenic Condensers

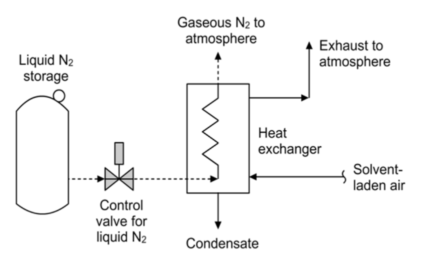
- Use liquefied gases such as nitrogen or carbon dioxide to cool the waste gas stream
- Temperature ranges from -100°F to -320°F
- There are three general types:
  - Indirect contact, single heat exchanger
  - Indirect contact, dual heat exchanger
  - Direct contact



Indirect Contact – Single Heat Exchanger Systems

- Uses a shell-and-tube heat exchanger
- Liquefied nitrogen is the most commonly used liquefied gas
- The liquefied nitrogen flows through the tubes while the waste gas passes through the shell
- Organic compounds may accumulate as frost on the exterior of the tubes, reducing heat transfer efficiency and increasing static pressure drop

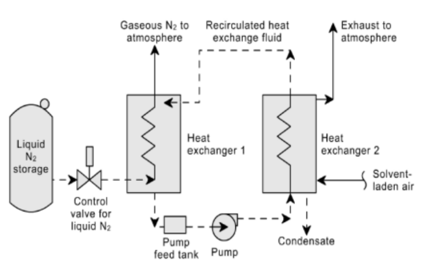
Figure 7-8. Single Heat Exchanger, Indirect Contact Cryogenic System



Indirect Contact – Dual Heat Exchanger Systems

- Does not have the same frost buildup problem that the single heat exchanger system has
- The capacity is limited by the size of the heat exchanger
- Applicable to gas streams less than 5,000 ACFM

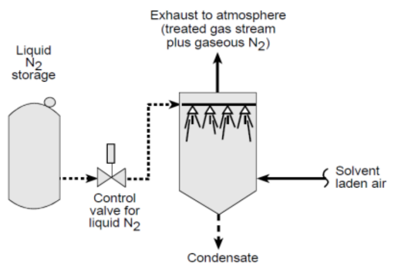
Figure 7-9. Dual Heat Exchange Cryogenic System



Direct Contact Systems

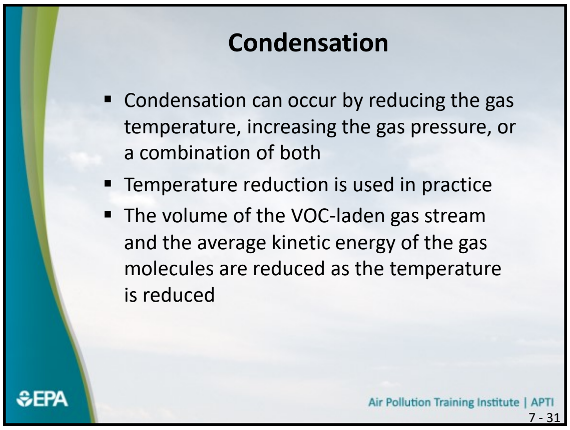
- Liquid nitrogen is dispersed using spray nozzles
- The outlet gas stream includes the uncondensed compounds from the inlet gas stream and the vaporized nitrogen
- Must operate at lower temperatures than an indirect contact condenser to achieve the same VOC removal efficiency since the vaporized nitrogen reduces the partial pressure of the VOC

Figure 7-10. Direct Contact Cryogenic System



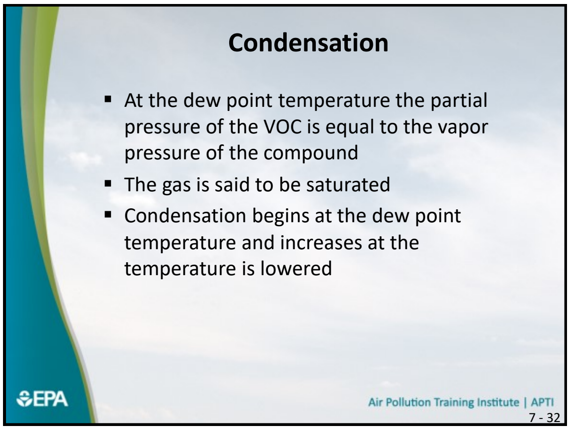
Operating Principles

- 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 at the temperature is lowered

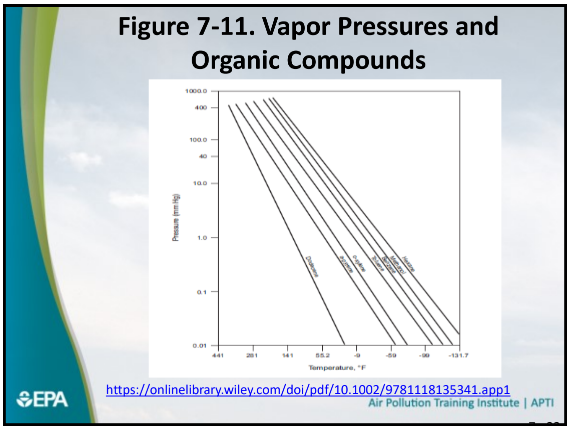
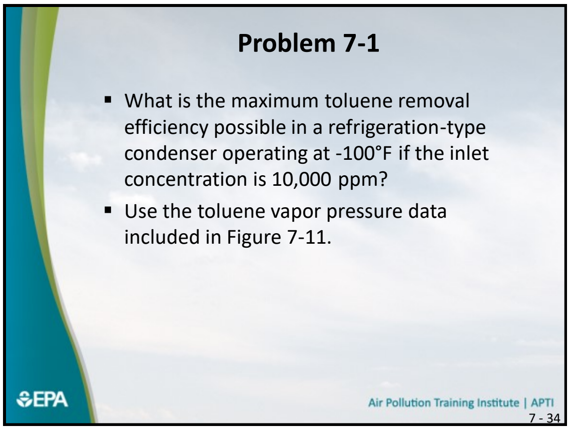


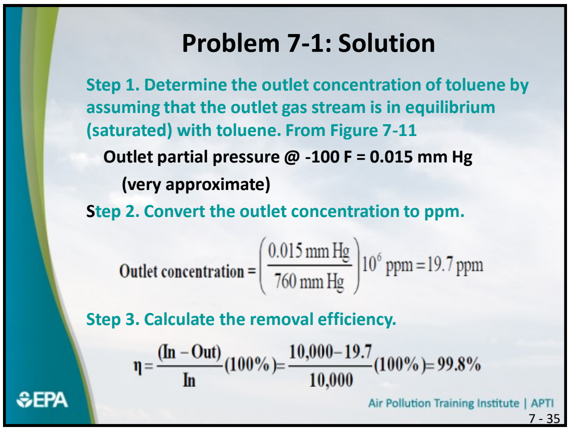
Figure 7-11. Vapor Pressures and Organic Compounds

https://onlinelibrary.wiley.com/doi/pdf/10.1002/9781118135341.app1



Problem 7-1

- What is the maximum toluene removal efficiency possible in a refrigeration-type condenser operating at -100°F if the inlet concentration is 10,000 ppm?
- Use the toluene vapor pressure data included in Figure 7-11.



Problem 7-1: Solution

Step 1. Determine the outlet concentration of toluene by assuming that the outlet gas stream is in equilibrium (saturated) with toluene. From Figure 7-11

Outlet partial pressure @ -100 F = 0.015 mm Hg

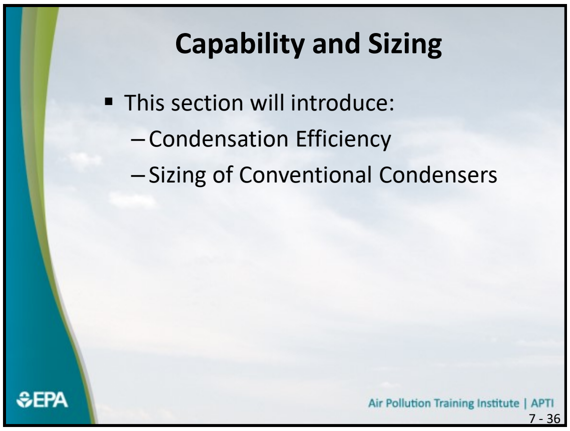
(very approximate)

Step 2. Convert the outlet concentration to ppm.

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

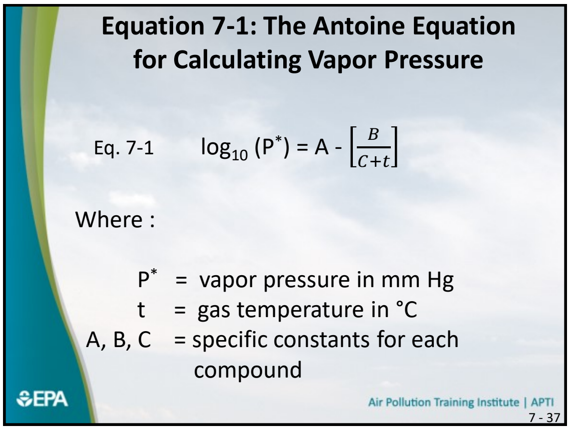
Step 3. Calculate the removal efficiency.

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



Capability and Sizing

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

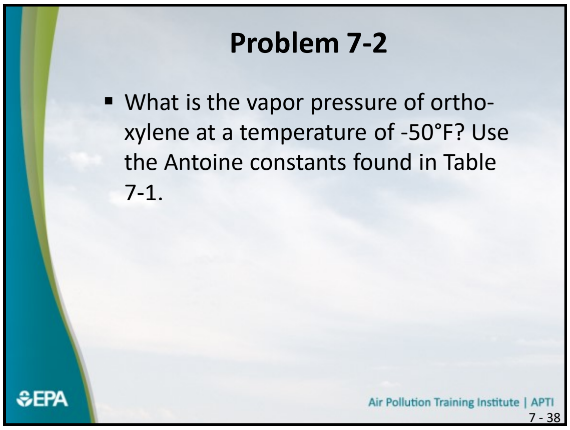


Equation 7-1: The Antoine Equation for Calculating Vapor Pressure

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



Problem 7-2

- What is the vapor pressure of ortho-xylene at a temperature of -50°F? Use the Antoine constants found in Table 7-1.

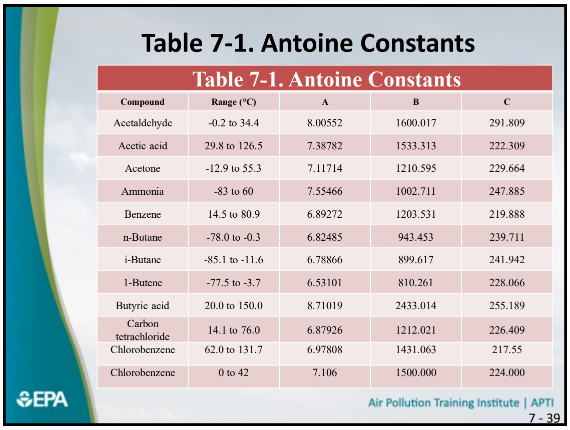


Table 7-1. Antoine Constants

Table 7-1. Antoine Constants

Compound	Range (°C)	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

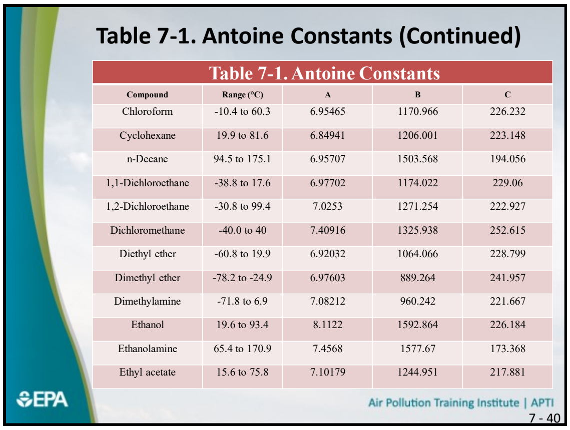


Table 7-1. Antoine Constants (Continued)

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

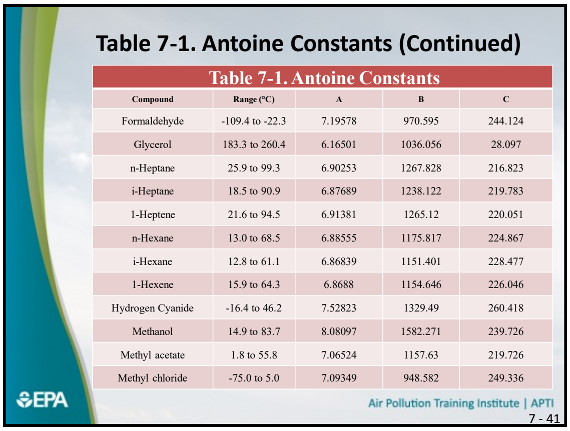


Table 7-1. Antoine Constants (Continued)

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	6.8688	1154.646	226.046
Hydrogen Cyanide	-16.4 to 46.2	7.52823	1329.49	260.418
Methanol	14.9 to 83.7	8.08097	1582.271	239.726
Methyl acetate	1.8 to 55.8	7.06524	1157.63	219.726
Methyl chloride	-75.0 to 5.0	7.09349	948.582	249.336

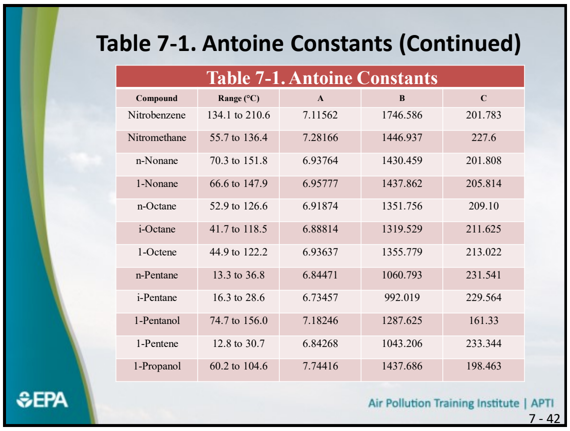


Table 7-1. Antoine Constants (Continued)

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

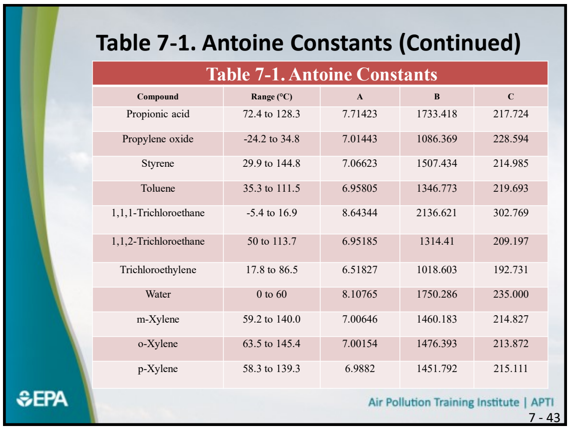
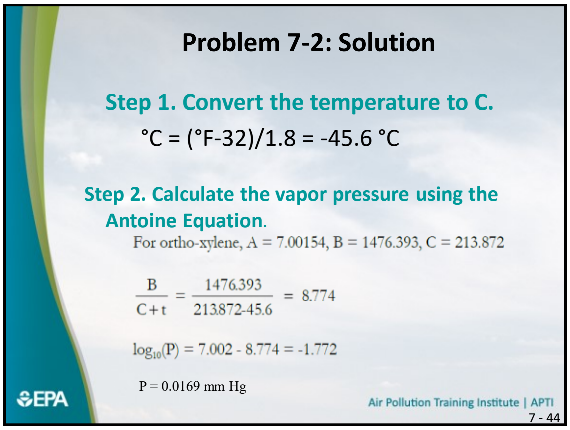


Table 7-1. Antoine Constants (Continued)

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

Air Pollution Training Institute | APTI



Problem 7-2: Solution

Step 1. Convert the temperature to C.

°C = (°F-32)/1.8 = -45.6 °C

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

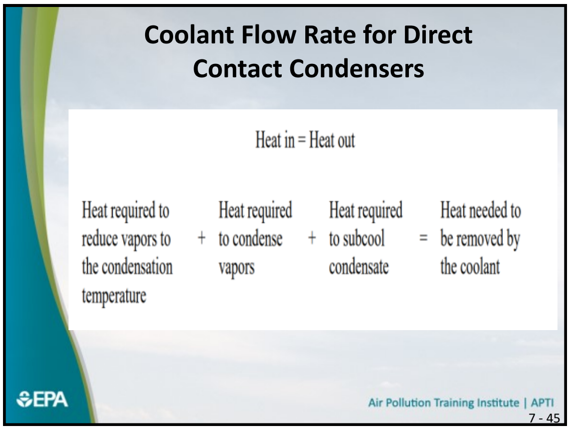
For ortho-xylene, A = 7.00154, B = 1476.393, C = 213.872

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

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

P = 0.0169 mm Hg

Air Pollution Training Institute | APTI

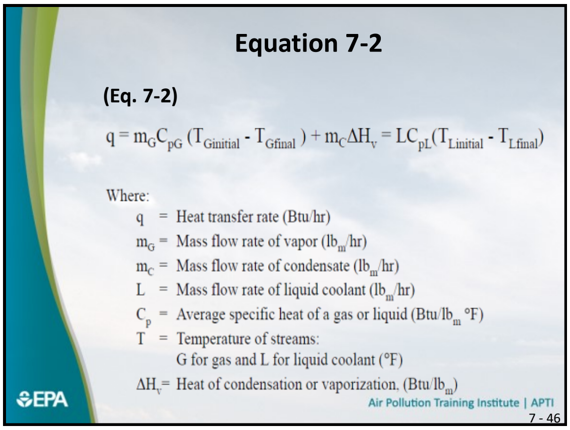


Coolant Flow Rate for Direct Contact Condensers

Heat in = Heat out

Heat required to reduce vapors to the condensation temperature + Heat required to condense vapors + Heat required to subcool condensate = Heat needed to be removed by the coolant

Air Pollution Training Institute | APTI



Equation 7-2

(Eq. 7-2)

$$q = m_G C_{pG} (T_{Ginitial} - T_{Gfinal}) + m_C \Delta H_v = L C_{pL} (T_{Linitial} - T_{Lfinal})$$

Where:

q = Heat transfer rate (Btu/hr)

m_G = Mass flow rate of vapor (lb_m/hr)

m_C = Mass flow rate of condensate (lb_m/hr)

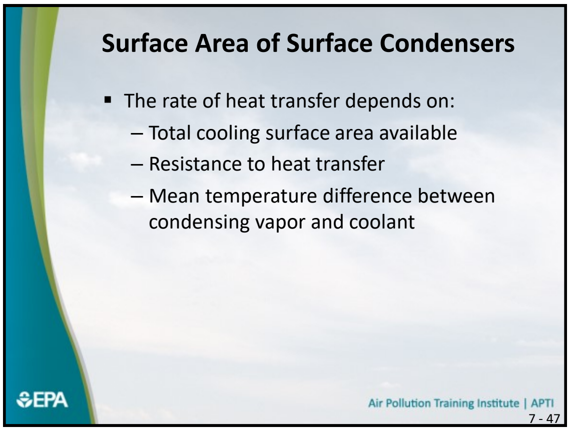
L = Mass flow rate of liquid coolant (lb_m/hr)

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)

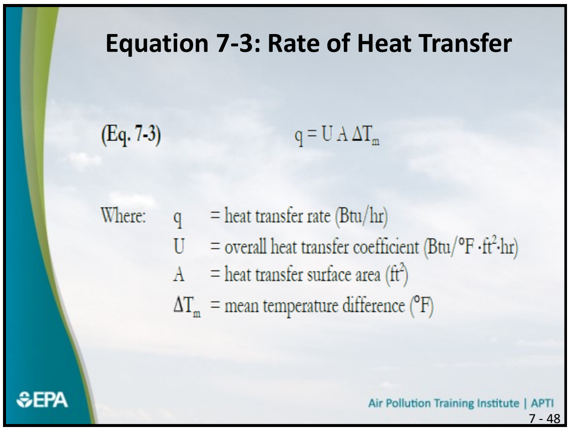
Air Pollution Training Institute | APTI



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

Air Pollution Training Institute | APTI



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)

Air Pollution Training Institute | APTI

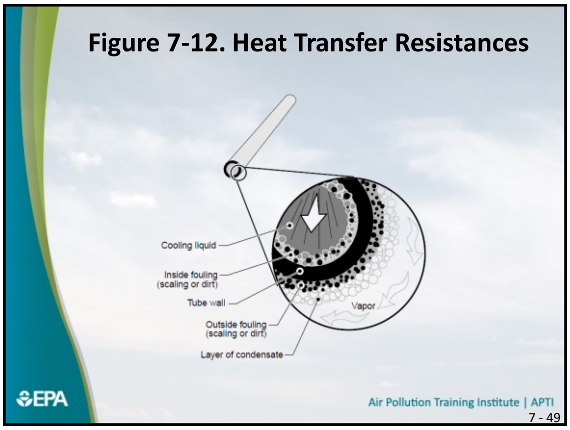


Figure 7-12. Heat Transfer Resistances

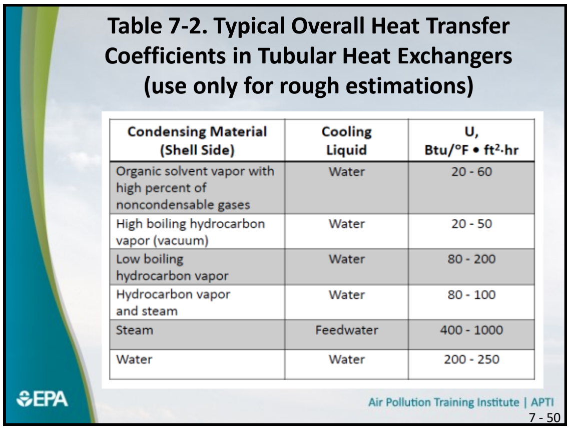
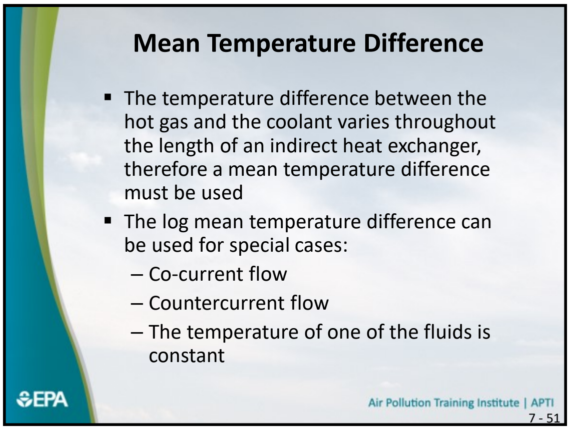


Table 7-2. Typical Overall Heat Transfer Coefficients in Tubular Heat Exchangers (use only for rough estimations)

Condensing Material (Shell Side)	Cooling Liquid	U, Btu/°F • ft²·hr
Organic solvent vapor with high percent of noncondensable gases	Water	20 - 60
High boiling hydrocarbon vapor (vacuum)	Water	20 - 50
Low boiling hydrocarbon vapor	Water	80 - 200
Hydrocarbon vapor and steam	Water	80 - 100
Steam	Feedwater	400 - 1000
Water	Water	200 - 250



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

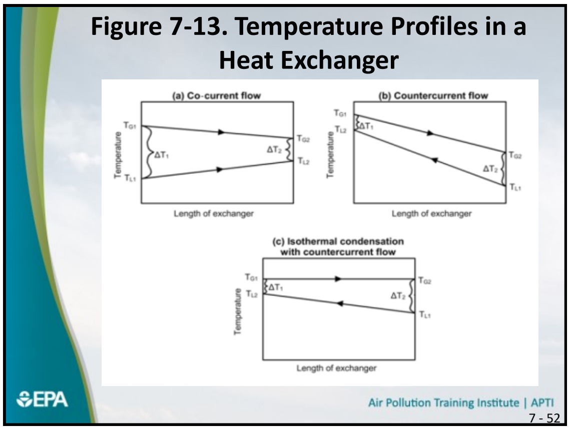
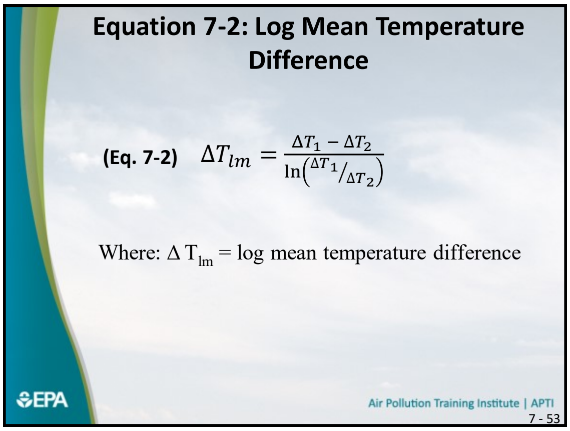


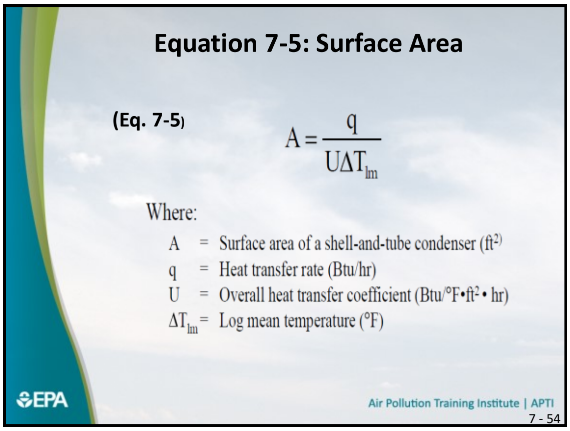
Figure 7-13. Temperature Profiles in a Heat Exchanger



Equation 7-2: Log Mean Temperature Difference

(Eq. 7-2) $$\Delta T_{lm} = \frac{\Delta T_1 - \Delta T_2}{\ln\left({}^{\Delta T_1}/_{\Delta T_2}\right)}$$

Where: ΔT_{lm} = log mean temperature difference

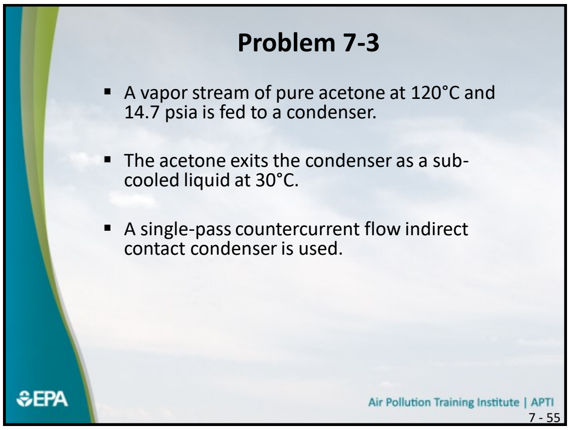


Equation 7-5: Surface Area

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

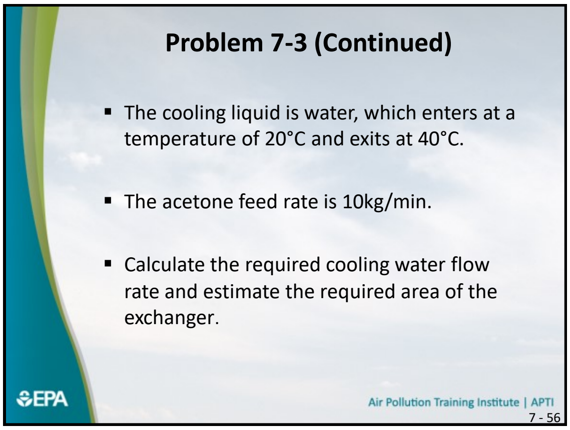
Where:

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



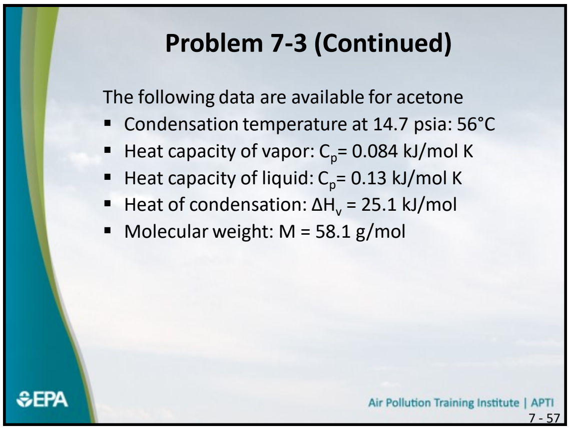
Problem 7-3

- 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)

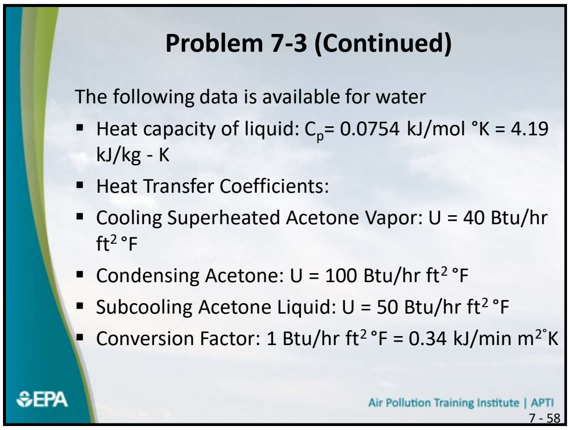
- The cooling liquid is water, which enters at a temperature of 20°C and exits at 40°C.
- The acetone feed rate is 10kg/min.
- Calculate the required cooling water flow rate and estimate the required area of the exchanger.



Problem 7-3 (Continued)

The following data are available for acetone

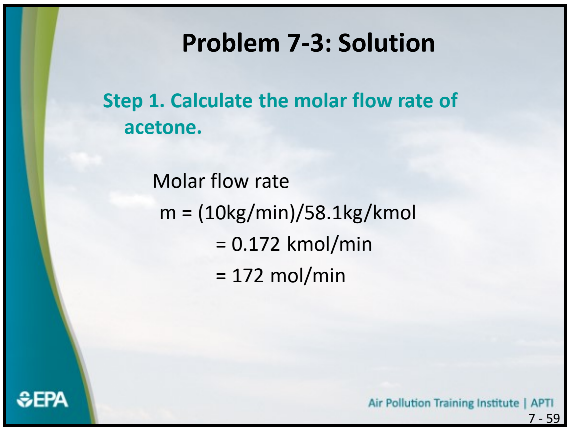
- Condensation temperature at 14.7 psia: 56°C
- Heat capacity of vapor: C_p= 0.084 kJ/mol K
- Heat capacity of liquid: C_p= 0.13 kJ/mol K
- Heat of condensation: ΔH_v = 25.1 kJ/mol
- Molecular weight: M = 58.1 g/mol



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 ft^2 °F
- Condensing Acetone: U = 100 Btu/hr ft^2 °F
- Subcooling Acetone Liquid: U = 50 Btu/hr ft^2 °F
- Conversion Factor: 1 Btu/hr ft^2 °F = 0.34 kJ/min $m^{2°}$K



Problem 7-3: Solution

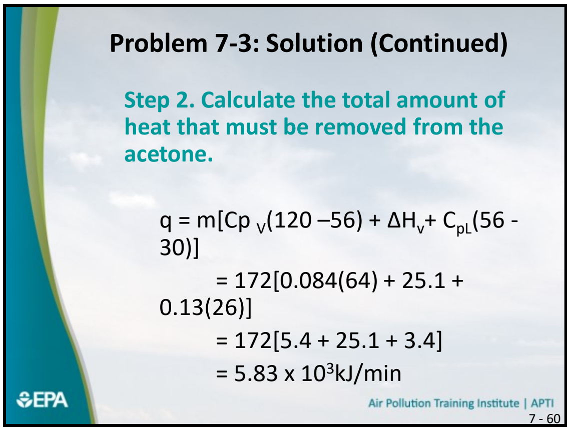
Step 1. Calculate the molar flow rate of acetone.

Molar flow rate

m = (10kg/min)/58.1kg/kmol

= 0.172 kmol/min

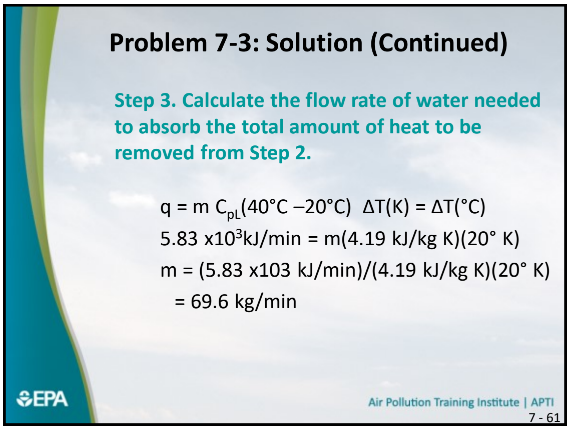
= 172 mol/min



Problem 7-3: Solution (Continued)

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

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



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.

$q = m\ C_{pL}(40°C – 20°C)$ $\Delta T(K) = \Delta T(°C)$

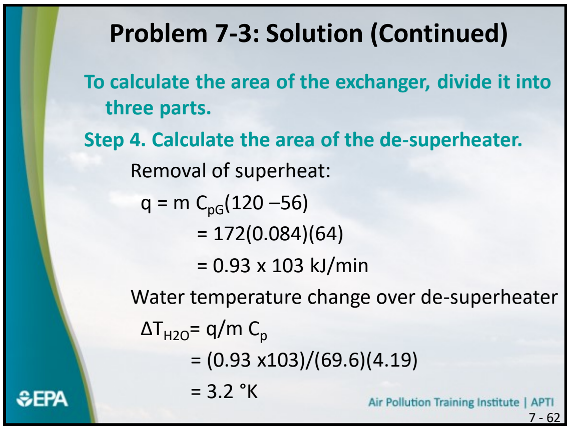
$5.83\ x10^3 kJ/min = m(4.19\ kJ/kg\ K)(20°\ K)$

$m = (5.83\ x103\ kJ/min)/(4.19\ kJ/kg\ K)(20°\ K)$

$= 69.6\ kg/min$

EPA Air Pollution Training Institute | APTI

7 - 61



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:

$q = m\ C_{pG}(120 – 56)$

$= 172(0.084)(64)$

$= 0.93\ x\ 103\ kJ/min$

Water temperature change over de-superheater

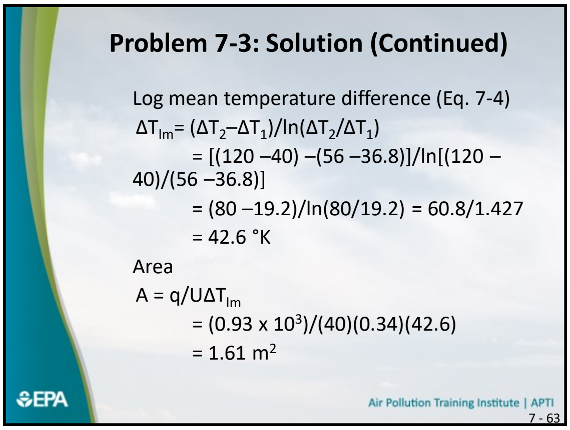
$\Delta T_{H2O} = q/m\ C_p$

$= (0.93\ x103)/(69.6)(4.19)$

$= 3.2\ °K$

EPA Air Pollution Training Institute | APTI

7 - 62



Problem 7-3: Solution (Continued)

Log mean temperature difference (Eq. 7-4)

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

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

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

$= 42.6\ °K$

Area

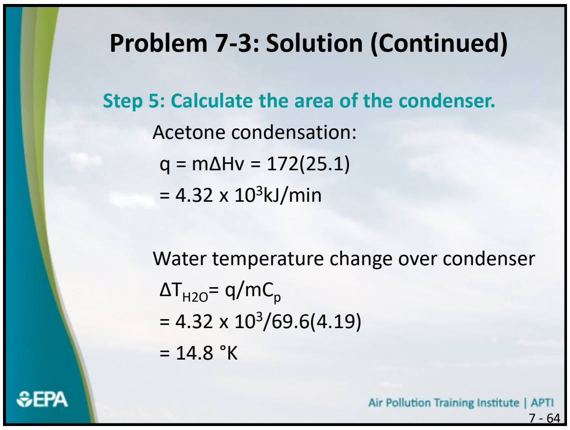
$A = q/U\Delta T_{lm}$

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

$= 1.61\ m^2$

EPA Air Pollution Training Institute | APTI

7 - 63



Problem 7-3: Solution (Continued)

Step 5: Calculate the area of the condenser.

Acetone condensation:

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

$= 4.32\ x\ 10^3 kJ/min$

Water temperature change over condenser

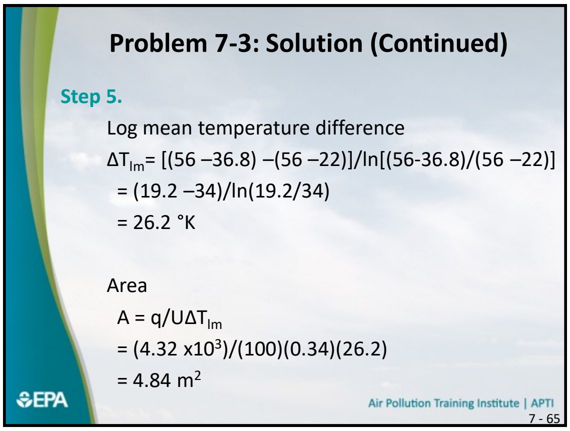
$\Delta T_{H2O} = q/mC_p$

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

$= 14.8\ °K$

EPA Air Pollution Training Institute | APTI

7 - 64



Problem 7-3: Solution (Continued)

Step 5.

Log mean temperature difference

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

$= (19.2 – 34)/\ln(19.2/34)$

$= 26.2\ °K$

Area

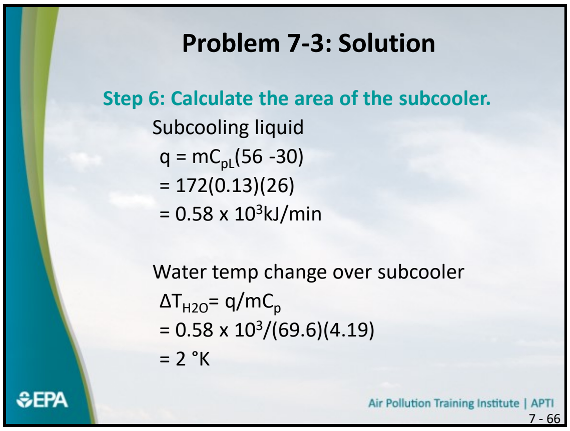
$A = q/U\Delta T_{lm}$

$= (4.32\ x10^3)/(100)(0.34)(26.2)$

$= 4.84\ m^2$

EPA Air Pollution Training Institute | APTI

7 - 65



Problem 7-3: Solution

Step 6: Calculate the area of the subcooler.

Subcooling liquid

$q = mC_{pL}(56 - 30)$

$= 172(0.13)(26)$

$= 0.58\ x\ 10^3 kJ/min$

Water temp change over subcooler

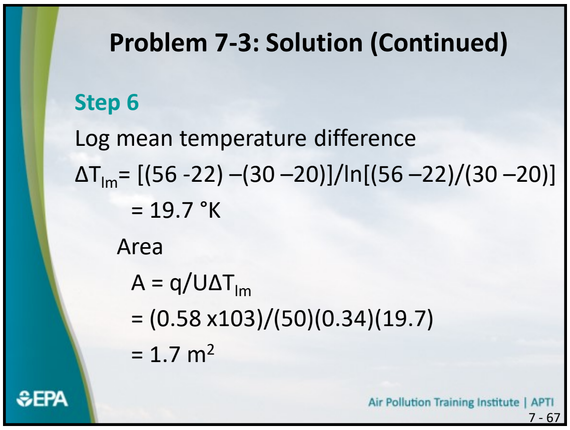
$\Delta T_{H2O} = q/mC_p$

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

$= 2\ °K$

EPA Air Pollution Training Institute | APTI

7 - 66



Problem 7-3: Solution (Continued)

Step 6

Log mean temperature difference

ΔT_{lm}= [(56 -22) –(30 –20)]/ln[(56 –22)/(30 –20)]

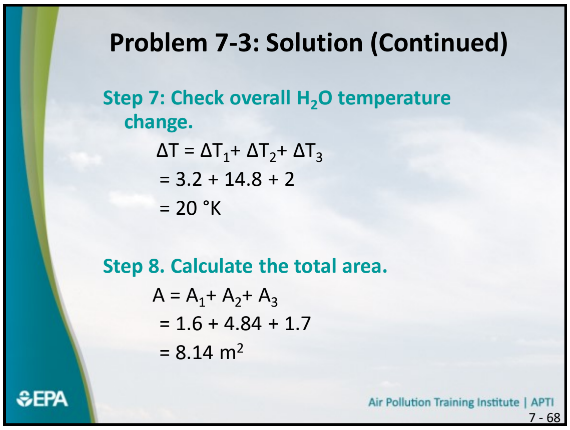
= 19.7 °K

Area

A = q/UΔT_{lm}

= (0.58 x103)/(50)(0.34)(19.7)

= 1.7 m^2



Problem 7-3: Solution (Continued)

Step 7: Check overall H_2O temperature change.

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

= 3.2 + 14.8 + 2

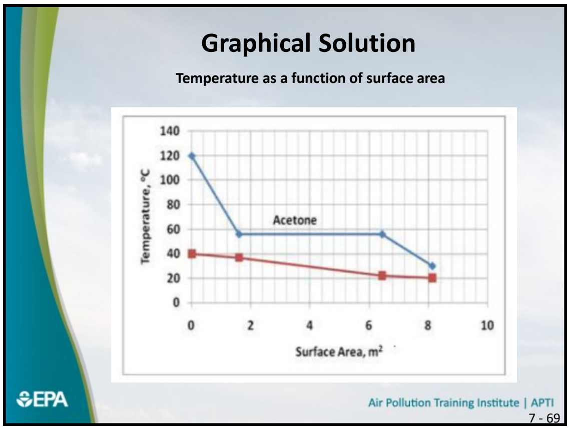
= 20 °K

Step 8. Calculate the total area.

$A = A_1 + A_2 + A_3$

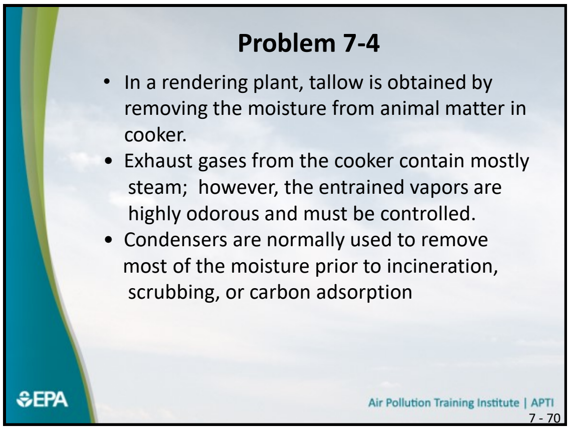
= 1.6 + 4.84 + 1.7

= 8.14 m^2



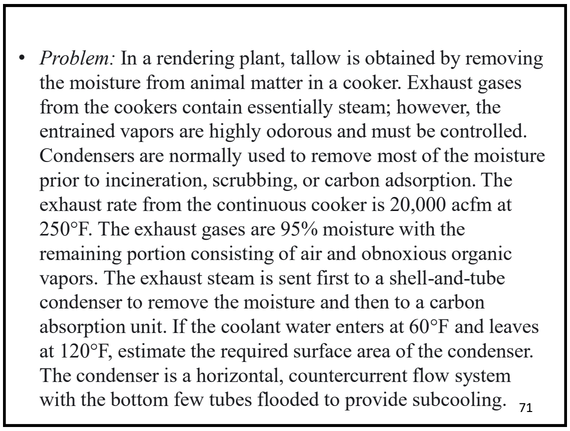
Graphical Solution

Temperature as a function of surface area

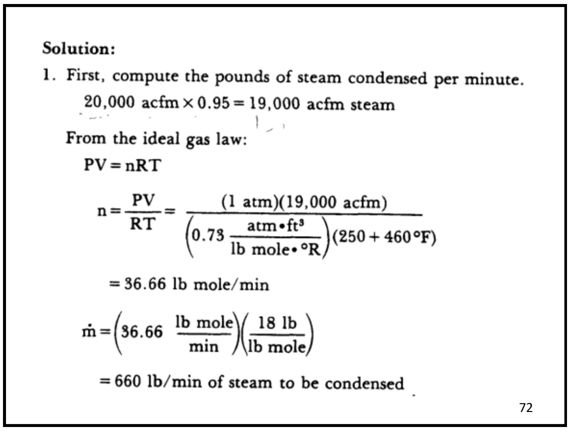


Problem 7-4

- 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



- *Problem:* In a rendering plant, tallow is obtained by removing the moisture from animal matter in a cooker. Exhaust gases from the cookers contain essentially steam; however, the entrained vapors are highly odorous and must be controlled. Condensers are normally used to remove most of the moisture prior to incineration, scrubbing, or carbon adsorption. The exhaust rate from the continuous cooker is 20,000 acfm at 250°F. The exhaust gases are 95% moisture with the remaining portion consisting of air and obnoxious organic vapors. The exhaust steam is sent first to a shell-and-tube condenser to remove the moisture and then to a carbon absorption unit. If the coolant water enters at 60°F and leaves at 120°F, estimate the required surface area of the condenser. The condenser is a horizontal, countercurrent flow system with the bottom few tubes flooded to provide subcooling.



Solution:

1. First, compute the pounds of steam condensed per minute.

$$20{,}000 \text{ acfm} \times 0.95 = 19{,}000 \text{ acfm steam}$$

From the ideal gas law:

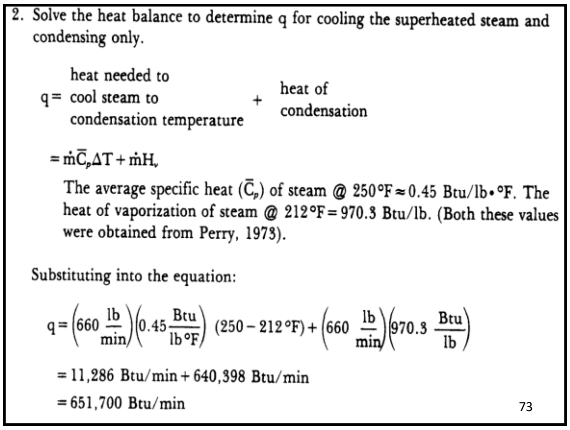
$$PV = nRT$$

$$n = \frac{PV}{RT} = \frac{(1 \text{ atm})(19{,}000 \text{ acfm})}{\left(0.73 \frac{\text{atm}\bullet\text{ft}^3}{\text{lb mole}\bullet{}^\circ\text{R}}\right)(250 + 460\,^\circ\text{F})}$$

$$= 36.66 \text{ lb mole/min}$$

$$\dot{m} = \left(36.66 \frac{\text{lb mole}}{\text{min}}\right)\left(\frac{18 \text{ lb}}{\text{lb mole}}\right)$$

$$= 660 \text{ lb/min of steam to be condensed}$$



2. Solve the heat balance to determine q for cooling the superheated steam and condensing only.

$$q = \begin{matrix}\text{heat needed to}\\ \text{cool steam to}\\ \text{condensation temperature}\end{matrix} + \begin{matrix}\text{heat of}\\ \text{condensation}\end{matrix}$$

$$= \dot{m}\bar{C}_p\Delta T + \dot{m}H_v$$

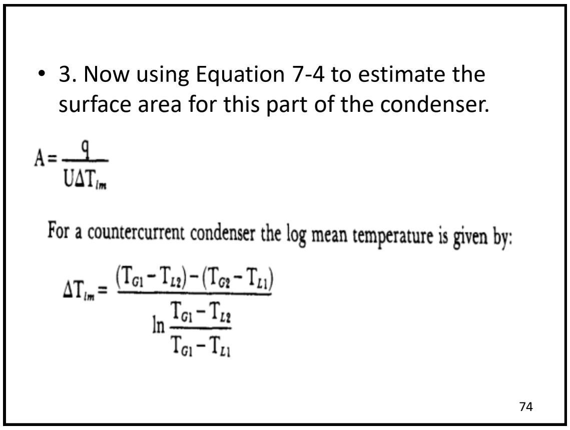
The average specific heat ($\bar{C}_p$) of steam @ 250°F ≈ 0.45 Btu/lb•°F. The heat of vaporization of steam @ 212°F = 970.3 Btu/lb. (Both these values were obtained from Perry, 1973).

Substituting into the equation:

$$q = \left(660\ \frac{\text{lb}}{\text{min}}\right)\left(0.45\frac{\text{Btu}}{\text{lb}\,°\text{F}}\right)(250 - 212\,°\text{F}) + \left(660\ \frac{\text{lb}}{\text{min}}\right)\left(970.3\ \frac{\text{Btu}}{\text{lb}}\right)$$

$$= 11{,}286\ \text{Btu/min} + 640{,}398\ \text{Btu/min}$$

$$= 651{,}700\ \text{Btu/min}$$

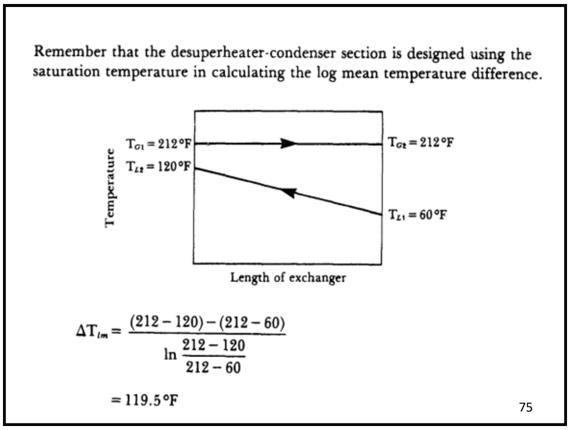


- 3. Now using Equation 7-4 to estimate the surface area for this part of the condenser.

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

For a countercurrent condenser the log mean temperature is given by:

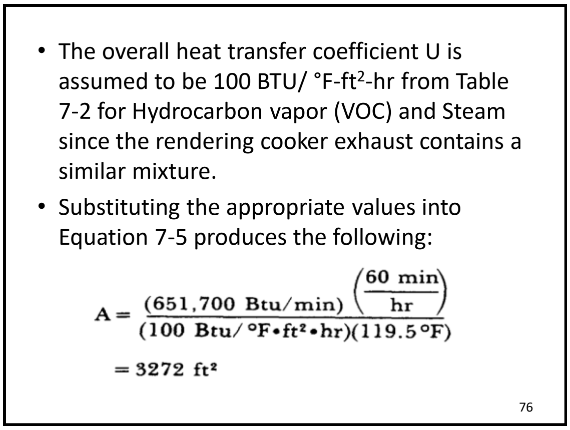
$$\Delta T_{lm} = \frac{(T_{G1} - T_{L2}) - (T_{G2} - T_{L1})}{\ln \dfrac{T_{G1} - T_{L2}}{T_{G1} - T_{L1}}}$$



Remember that the desuperheater-condenser section is designed using the saturation temperature in calculating the log mean temperature difference.

$$\Delta T_{lm} = \frac{(212 - 120) - (212 - 60)}{\ln \dfrac{212 - 120}{212 - 60}}$$

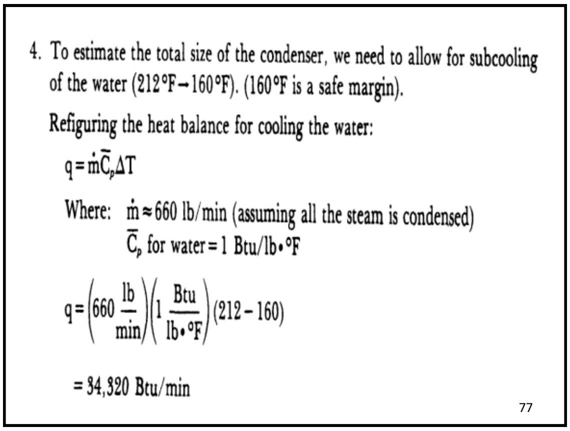
$$= 119.5\,°\text{F}$$



- The overall heat transfer coefficient U is assumed to be 100 BTU/ °F-ft^2-hr from Table 7-2 for Hydrocarbon vapor (VOC) and Steam since the rendering cooker exhaust contains a similar mixture.
- Substituting the appropriate values into Equation 7-5 produces the following:

$$A = \frac{(651{,}700\ \text{Btu/min})\left(\dfrac{60\ \text{min}}{\text{hr}}\right)}{(100\ \text{Btu/°F}\bullet\text{ft}^2\bullet\text{hr})(119.5\,°\text{F})}$$

$$= 3272\ \text{ft}^2$$



4. To estimate the total size of the condenser, we need to allow for subcooling of the water (212°F→160°F). (160°F is a safe margin).

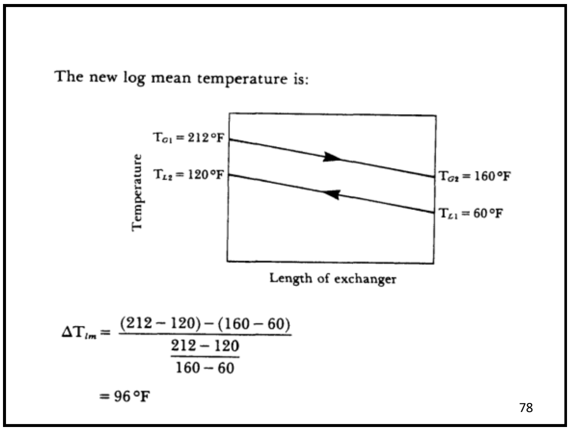
Refiguring the heat balance for cooling the water:

$$q = \dot{m}\bar{C}_p\Delta T$$

Where: $\dot{m} \approx 660$ lb/min (assuming all the steam is condensed)
$\bar{C}_p$ for water = 1 Btu/lb•°F

$$q = \left(660\ \frac{\text{lb}}{\text{min}}\right)\left(1\ \frac{\text{Btu}}{\text{lb}\bullet°\text{F}}\right)(212 - 160)$$

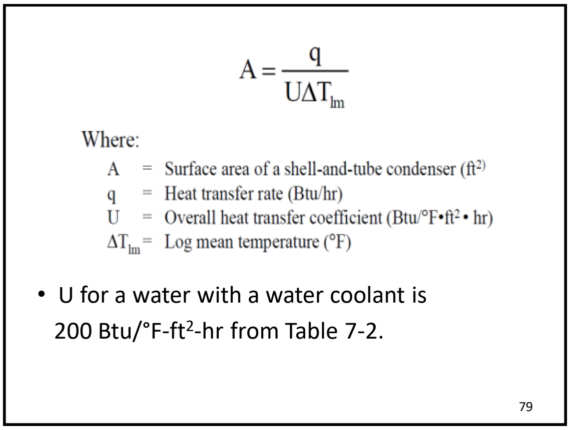
$$= 34{,}320\ \text{Btu/min}$$



The new log mean temperature is:

$$\Delta T_{lm} = \frac{(212 - 120) - (160 - 60)}{\dfrac{212 - 120}{160 - 60}}$$

$$= 96\,°\text{F}$$

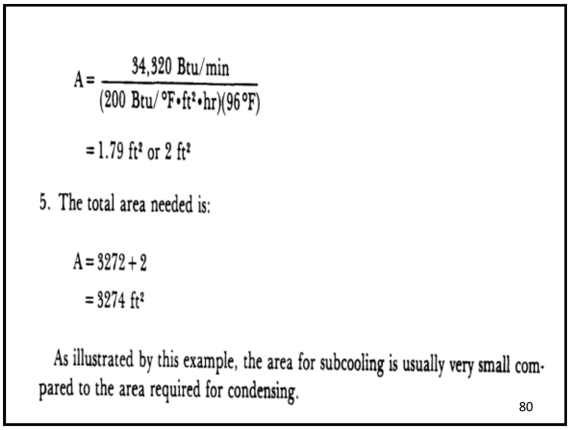


$$A = \frac{q}{U\Delta T_{lm}}$$

Where:

A = Surface area of a shell-and-tube condenser (ft^2)
q = Heat transfer rate (Btu/hr)
U = Overall heat transfer coefficient (Btu/°F•ft^2 • hr)
ΔT_{lm} = Log mean temperature (°F)

- U for a water with a water coolant is 200 Btu/°F-ft^2-hr from Table 7-2.



$$A = \frac{34{,}320\ \text{Btu/min}}{(200\ \text{Btu/°F}\bullet\text{ft}^2\bullet\text{hr})(96\text{°F})}$$

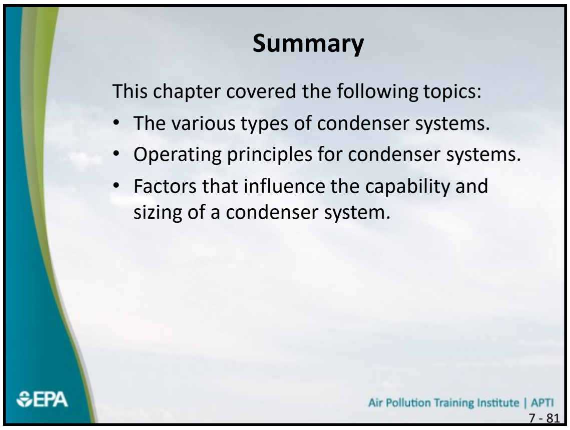
$$= 1.79\ \text{ft}^2 \text{ or } 2\ \text{ft}^2$$

5. The total area needed is:

$$A = 3272 + 2$$

$$= 3274\ \text{ft}^2$$

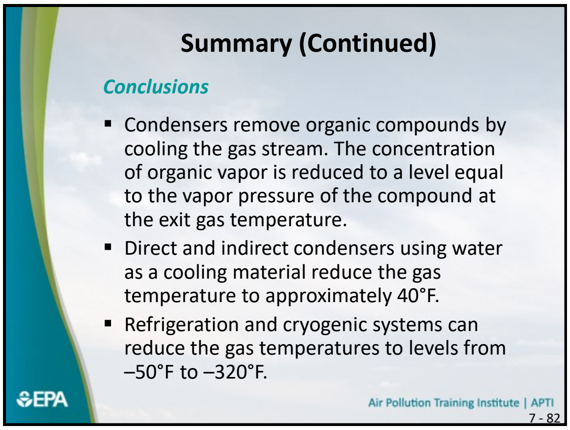
As illustrated by this example, the area for subcooling is usually very small compared to the area required for condensing.



Summary

This chapter covered the following topics:

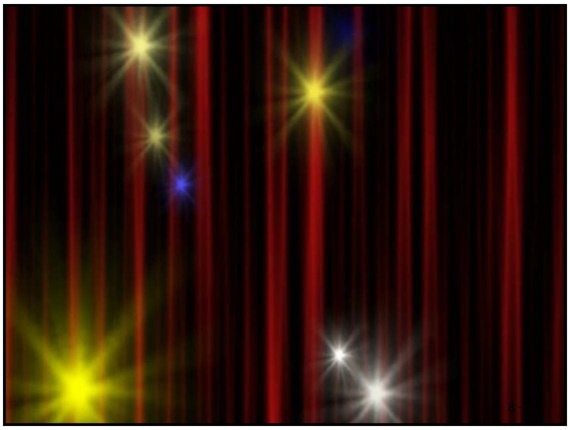
- The various types of condenser systems.
- Operating principles for condenser systems.
- Factors that influence the capability and sizing of a condenser system.

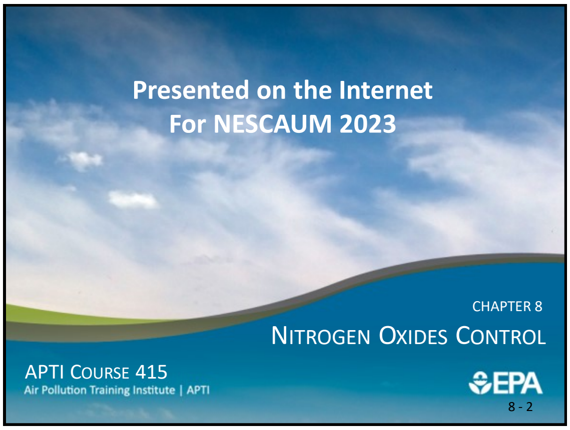


Summary (Continued)

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.



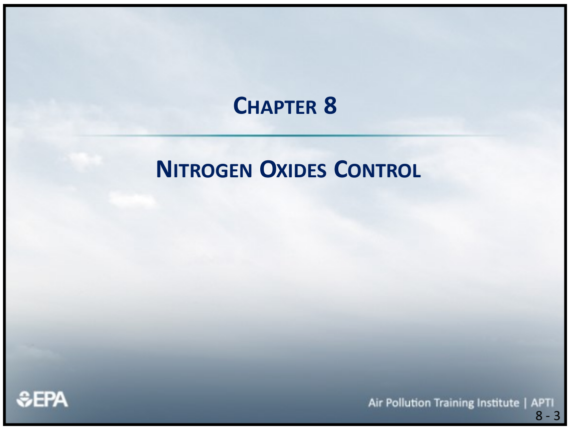


Presented on the Internet
For NESCAUM 2023

CHAPTER 8

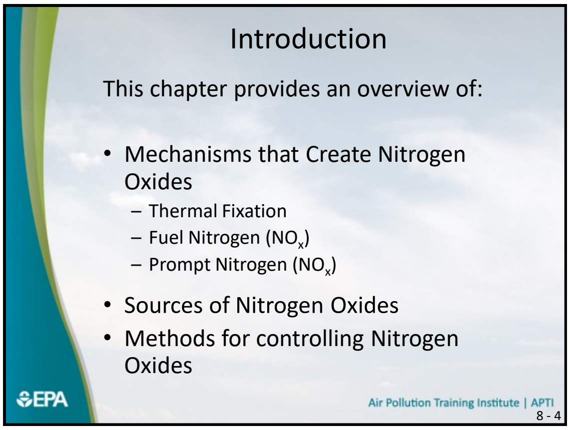
NITROGEN OXIDES CONTROL

APTI COURSE 415
Air Pollution Training Institute | APTI



CHAPTER 8

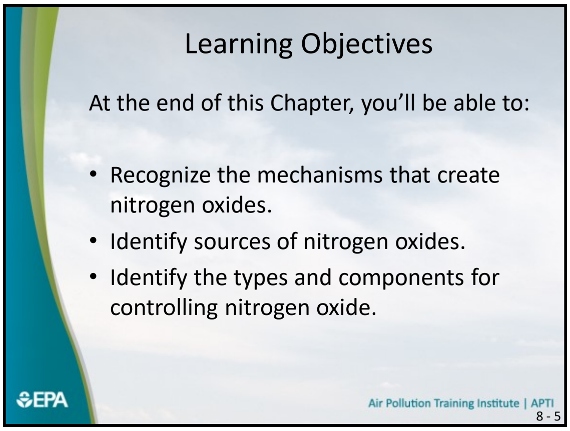
NITROGEN OXIDES CONTROL



Introduction

This chapter provides an overview of:

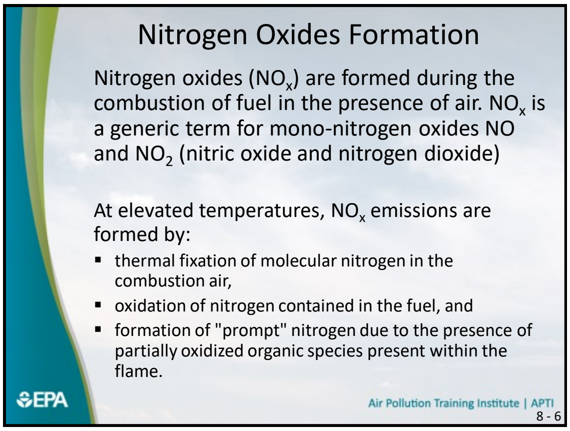
- Mechanisms that Create Nitrogen Oxides
  - Thermal Fixation
  - Fuel Nitrogen (NO_x)
  - Prompt Nitrogen (NO_x)
- Sources of Nitrogen Oxides
- Methods for controlling Nitrogen Oxides



Learning Objectives

At the end of this Chapter, you'll be able to:

- Recognize the mechanisms that create nitrogen oxides.
- Identify sources of nitrogen oxides.
- Identify the types and components for controlling nitrogen oxide.

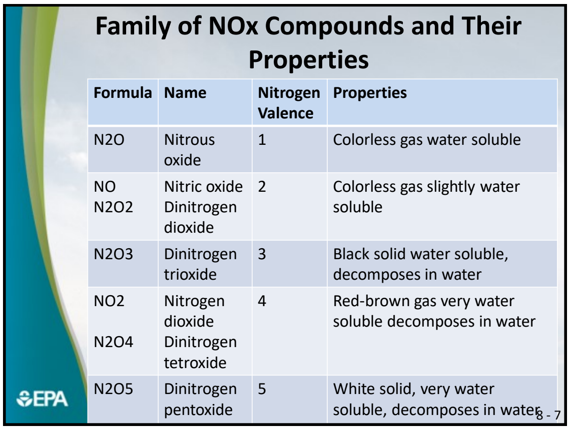


Nitrogen Oxides Formation

Nitrogen oxides (NO_x) are formed during the combustion of fuel in the presence of air. NO_x is a generic term for mono-nitrogen oxides NO and NO_2 (nitric oxide and nitrogen dioxide)

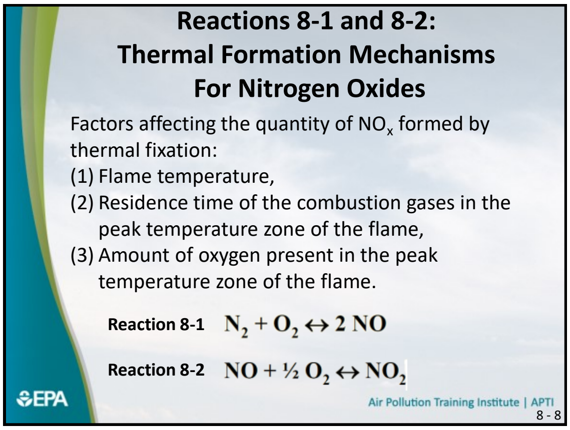
At elevated temperatures, NO_x emissions are formed by:

- 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.



Family of NOx Compounds and Their Properties

Formula	Name	Nitrogen Valence	Properties
N2O	Nitrous oxide	1	Colorless gas water soluble
NO N2O2	Nitric oxide Dinitrogen dioxide	2	Colorless gas slightly water soluble
N2O3	Dinitrogen trioxide	3	Black solid water soluble, decomposes in water
NO2 N2O4	Nitrogen dioxide Dinitrogen tetroxide	4	Red-brown gas very water soluble decomposes in water
N2O5	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:

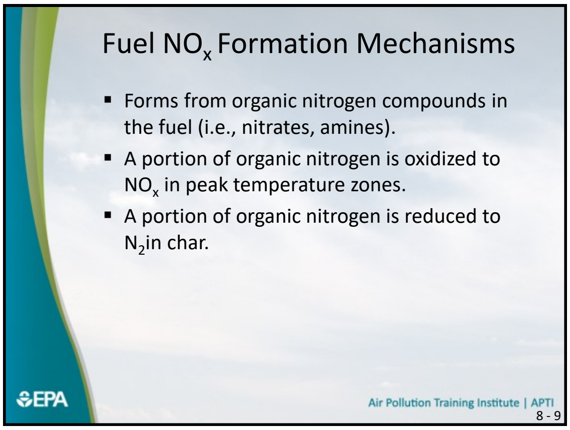
(1) Flame temperature,

(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.

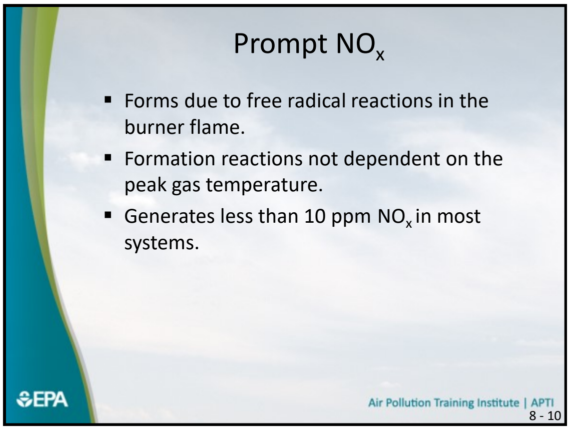
Reaction 8-1 $N_2 + O_2 \leftrightarrow 2\,NO$

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



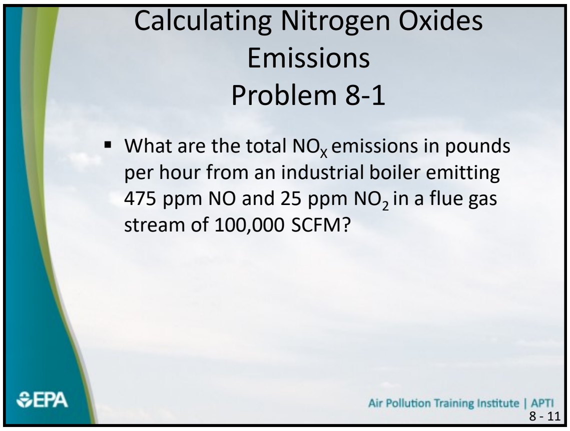
Fuel NO_x Formation Mechanisms

- 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 N_2in char.



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.



Calculating Nitrogen Oxides Emissions Problem 8-1

- What are the total NO_x emissions in pounds per hour from an industrial boiler emitting 475 ppm NO and 25 ppm NO_2 in a flue gas stream of 100,000 SCFM?

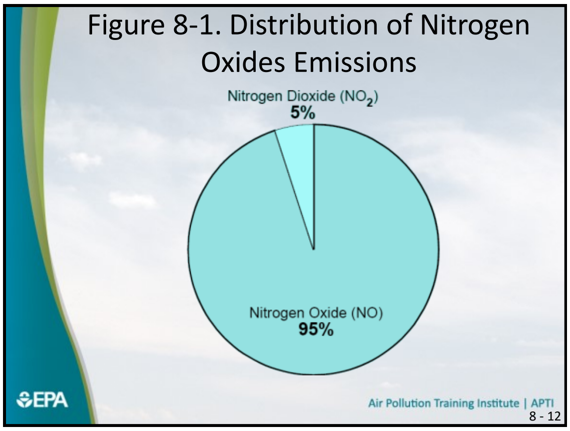
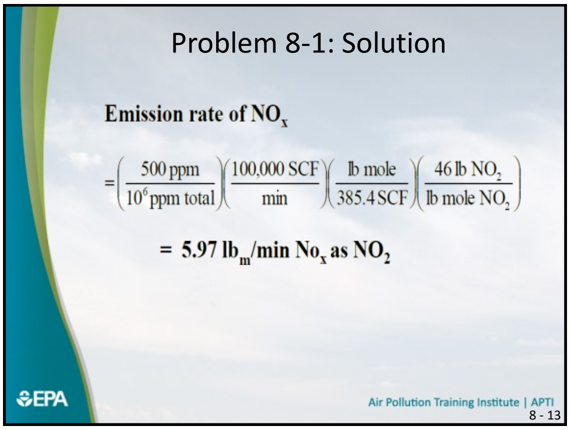


Figure 8-1. Distribution of Nitrogen Oxides Emissions

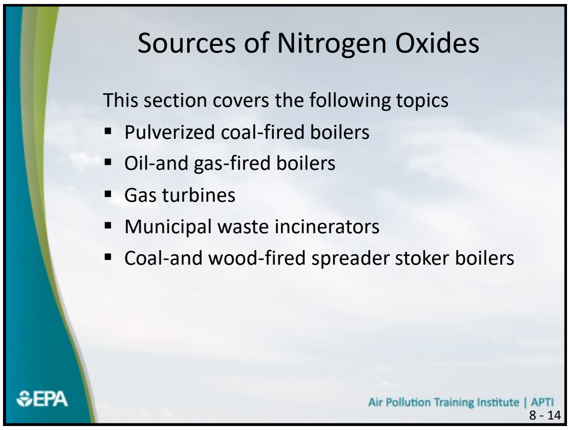


Problem 8-1: Solution

Emission rate of NO_x

$$= \left(\frac{500\ \text{ppm}}{10^6\ \text{ppm total}}\right)\left(\frac{100{,}000\ \text{SCF}}{\text{min}}\right)\left(\frac{\text{lb mole}}{385.4\ \text{SCF}}\right)\left(\frac{46\ \text{lb}\ NO_2}{\text{lb mole}\ NO_2}\right)$$

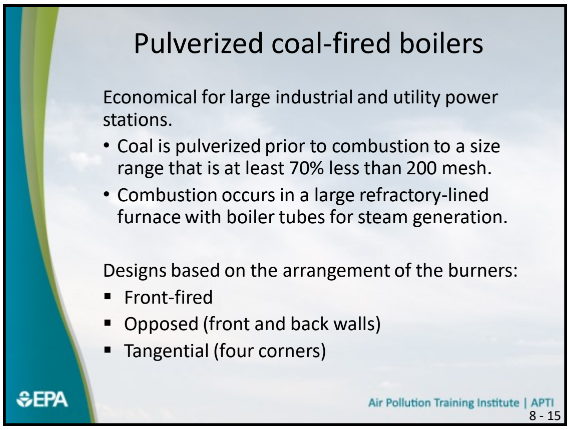
$$= 5.97\ \text{lb}_m/\text{min No}_x\ \text{as}\ NO_2$$



Sources of Nitrogen Oxides

This section covers the following topics

- Pulverized coal-fired boilers
- Oil-and gas-fired boilers
- Gas turbines
- Municipal waste incinerators
- Coal-and wood-fired spreader stoker boilers



Pulverized coal-fired boilers

Economical for large industrial and utility power stations.

- Coal is pulverized prior to combustion to a size range that is at least 70% less than 200 mesh.
- Combustion occurs in a large refractory-lined furnace with boiler tubes for steam generation.

Designs based on the arrangement of the burners:

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

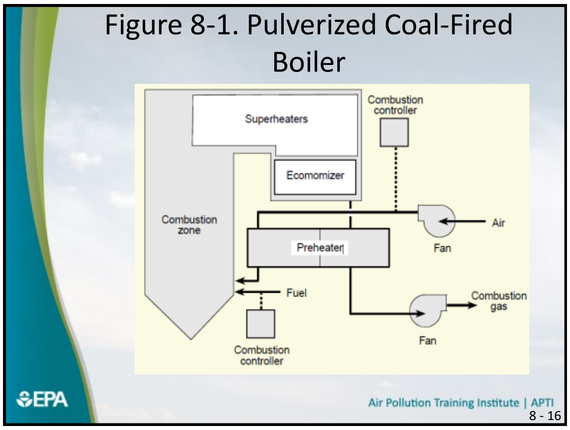
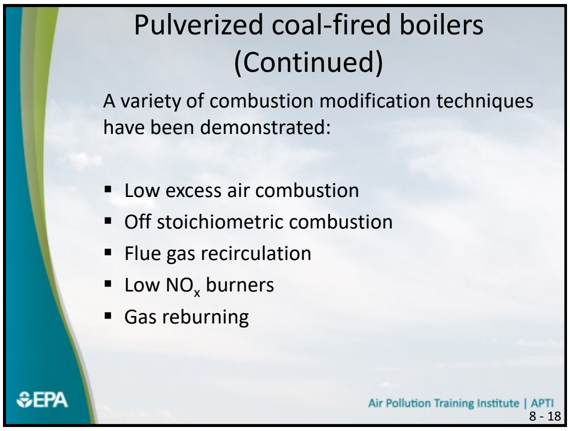


Figure 8-1. Pulverized Coal-Fired Boiler

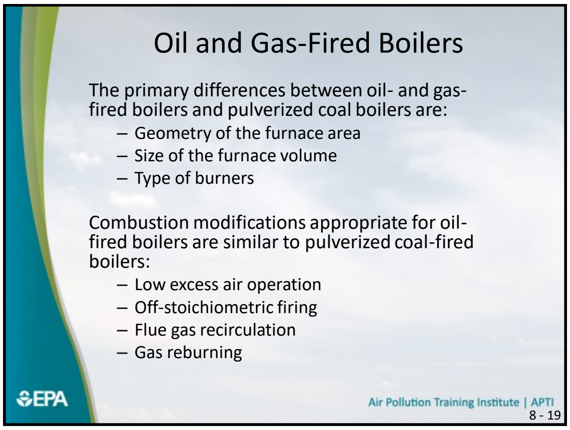
Coal Pulverizing Mills



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



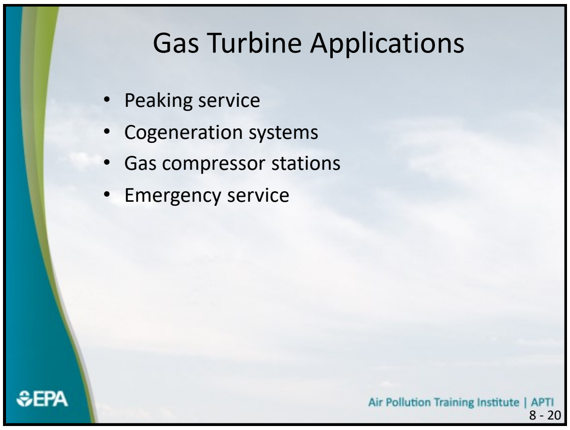
Oil and Gas-Fired Boilers

The primary differences between oil- and gas-fired boilers and pulverized coal boilers are:

- Geometry of the furnace area
- Size of the furnace volume
- Type of burners

Combustion modifications appropriate for oil-fired boilers are similar to pulverized coal-fired boilers:

- Low excess air operation
- Off-stoichiometric firing
- Flue gas recirculation
- Gas reburning



Gas Turbine Applications

- Peaking service
- Cogeneration systems
- Gas compressor stations
- Emergency service

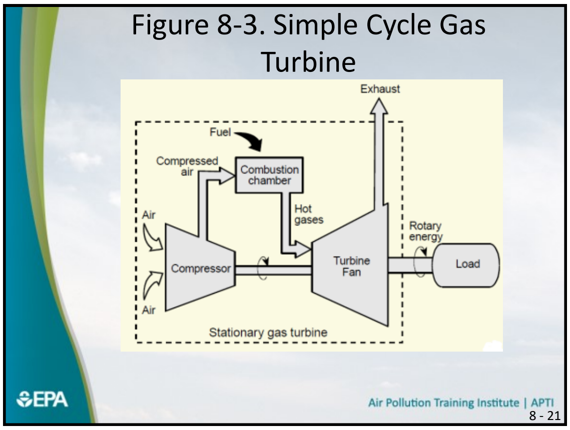


Figure 8-3. Simple Cycle Gas Turbine

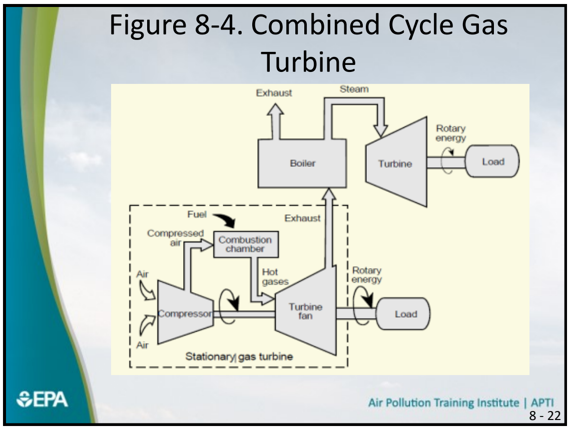


Figure 8-4. Combined Cycle Gas Turbine

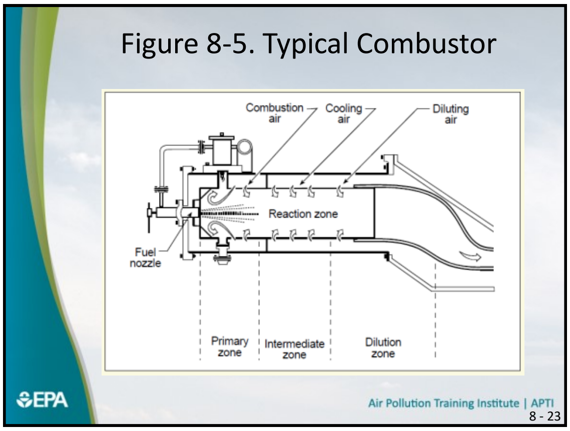


Figure 8-5. Typical Combustor

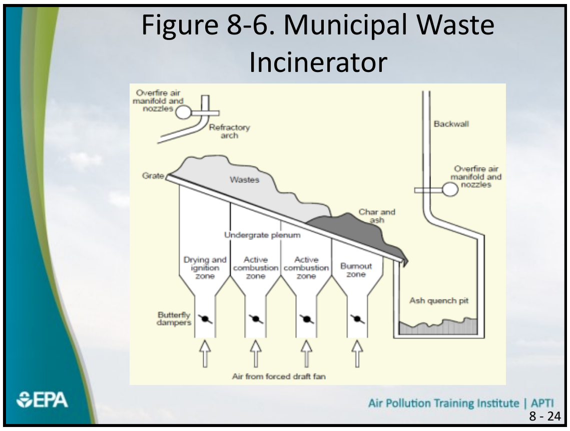
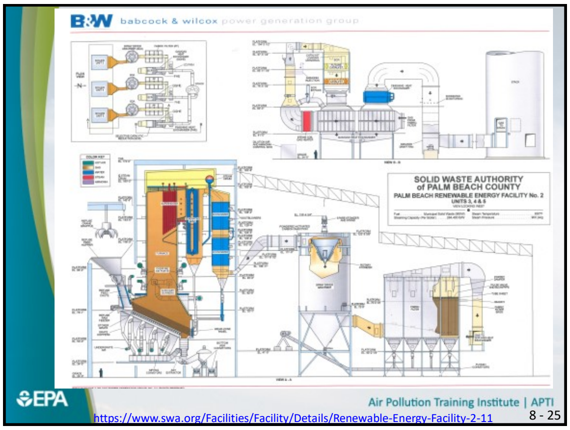


Figure 8-6. Municipal Waste Incinerator



https://www.swa.org/Facilities/Facility/Details/Renewable-Energy-Facility-2-11

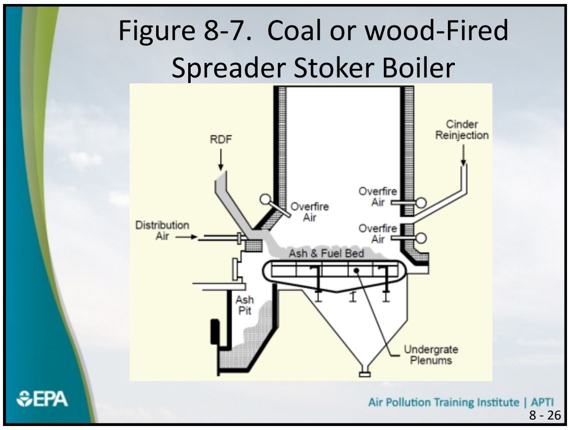
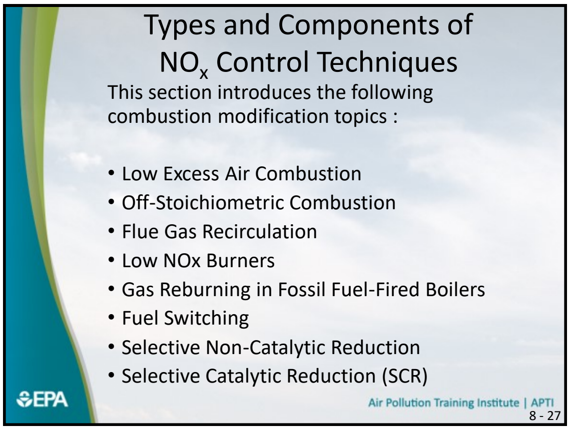


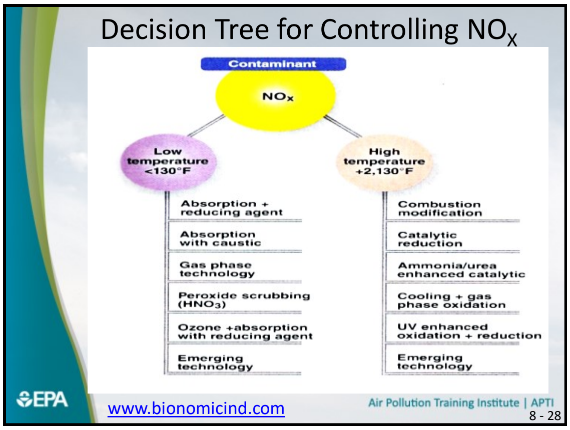
Figure 8-7. Coal or wood-Fired Spreader Stoker Boiler



Types and Components of NO_x Control Techniques

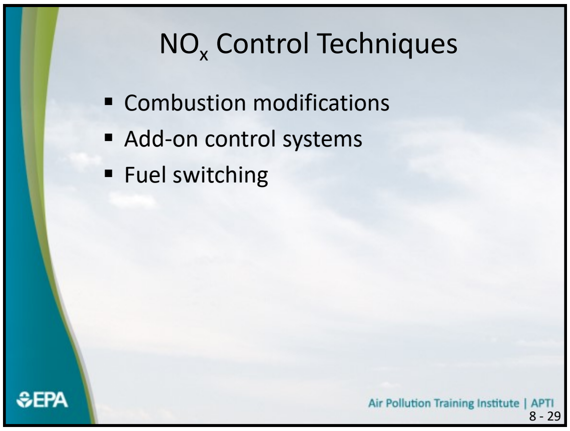
This section introduces the following combustion modification topics :

- Low Excess Air Combustion
- Off-Stoichiometric Combustion
- Flue Gas Recirculation
- Low NOx Burners
- Gas Reburning in Fossil Fuel-Fired Boilers
- Fuel Switching
- Selective Non-Catalytic Reduction
- Selective Catalytic Reduction (SCR)



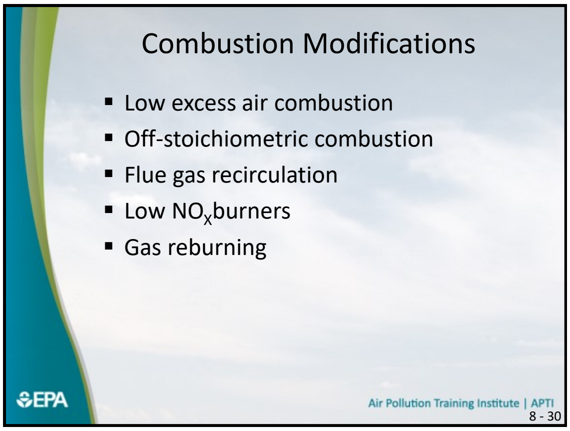
Decision Tree for Controlling NO_X

www.bionomicind.com



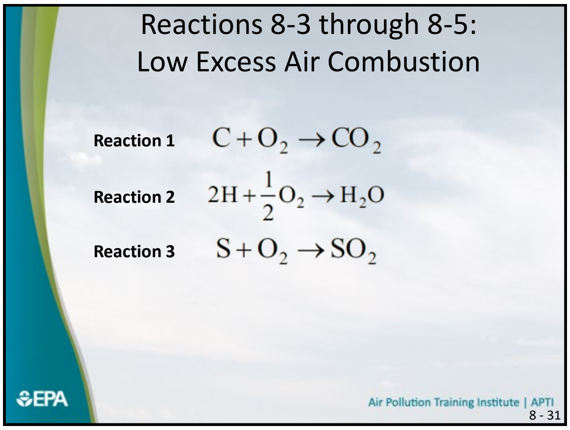
NO_x Control Techniques

- Combustion modifications
- Add-on control systems
- Fuel switching



Combustion Modifications

- Low excess air combustion
- Off-stoichiometric combustion
- Flue gas recirculation
- Low NO_x burners
- Gas reburning

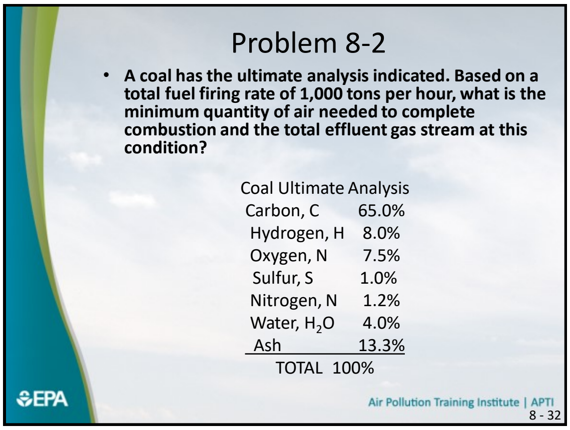


Reactions 8-3 through 8-5: Low Excess Air Combustion

Reaction 1 $C + O_2 \rightarrow CO_2$

Reaction 2 $2H + \frac{1}{2}O_2 \rightarrow H_2O$

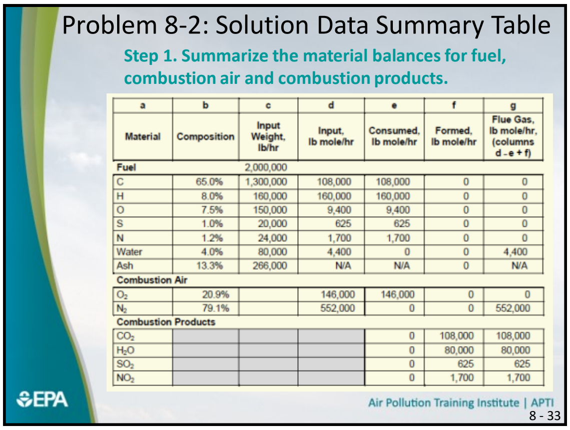
Reaction 3 $S + O_2 \rightarrow SO_2$



Problem 8-2

- **A coal has the ultimate analysis indicated. Based on a total fuel firing rate of 1,000 tons per hour, what is the minimum quantity of air needed to complete combustion and the total effluent gas stream at this condition?**

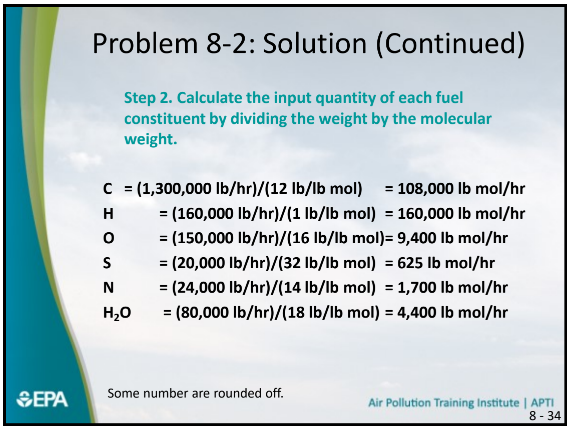
Coal Ultimate Analysis	
Carbon, C	65.0%
Hydrogen, H	8.0%
Oxygen, N	7.5%
Sulfur, S	1.0%
Nitrogen, N	1.2%
Water, H_2O	4.0%
Ash	13.3%
TOTAL	100%



Problem 8-2: Solution Data Summary Table

Step 1. Summarize the material balances for fuel, combustion air and combustion products.

a	b	c	d	e	f	g
Material	Composition	Input Weight, 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	65.0%	1,300,000	108,000	108,000	0	0
H	8.0%	160,000	160,000	160,000	0	0
O	7.5%	150,000	9,400	9,400	0	0
S	1.0%	20,000	625	625	0	0
N	1.2%	24,000	1,700	1,700	0	0
Water	4.0%	80,000	4,400	0	0	4,400
Ash	13.3%	266,000	N/A	N/A	0	N/A
Combustion Air						
O_2	20.9%		146,000	146,000	0	0
N_2	79.1%		552,000	0	0	552,000
Combustion Products						
CO_2				0	108,000	108,000
H_2O				0	80,000	80,000
SO_2				0	625	625
NO_2				0	1,700	1,700

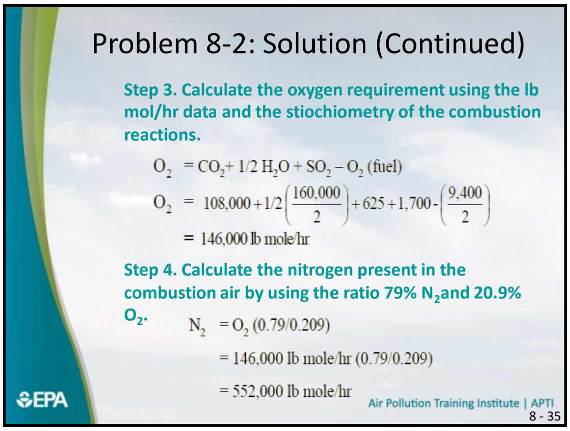


Problem 8-2: Solution (Continued)

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
H_2O = (80,000 lb/hr)/(18 lb/lb mol) = 4,400 lb mol/hr

Some number are rounded off.



Problem 8-2: Solution (Continued)

Step 3. Calculate the oxygen requirement using the lb mol/hr data and the stoichiometry of the combustion reactions.

$$O_2 = CO_2 + 1/2\, H_2O + SO_2 - O_2\ (\text{fuel})$$

$$O_2 = 108{,}000 + 1/2\left(\frac{160{,}000}{2}\right) + 625 + 1{,}700 - \left(\frac{9{,}400}{2}\right)$$

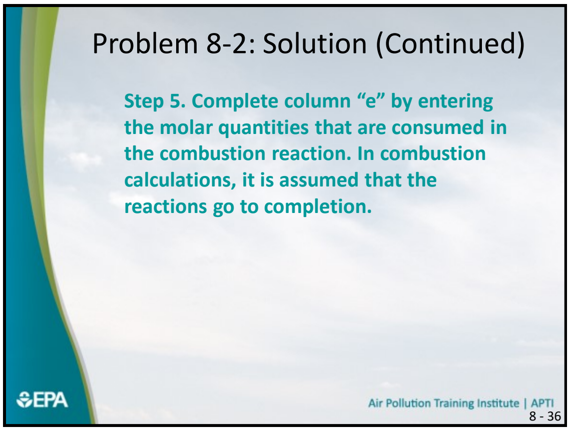
$$= 146{,}000 \text{ lb mole/hr}$$

Step 4. Calculate the nitrogen present in the combustion air by using the ratio 79% $N_2$and 20.9% O_2.

$$N_2 = O_2\,(0.79/0.209)$$

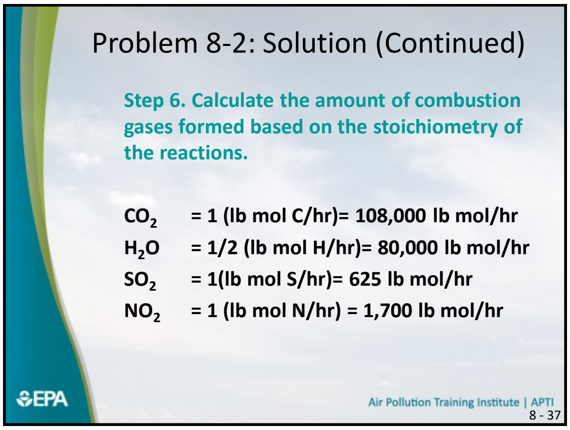
$$= 146{,}000 \text{ lb mole/hr } (0.79/0.209)$$

$$= 552{,}000 \text{ lb mole/hr}$$



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)

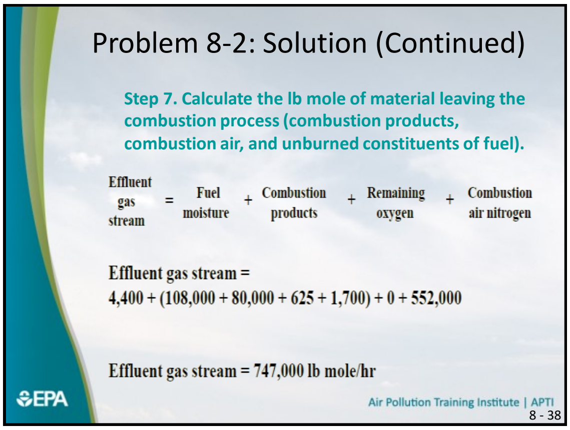
Step 6. Calculate the amount of combustion gases formed based on the stoichiometry of the reactions.

CO_2 = 1 (lb mol C/hr)= 108,000 lb mol/hr

H_2O = 1/2 (lb mol H/hr)= 80,000 lb mol/hr

SO_2 = 1(lb mol S/hr)= 625 lb mol/hr

NO_2 = 1 (lb mol N/hr) = 1,700 lb mol/hr



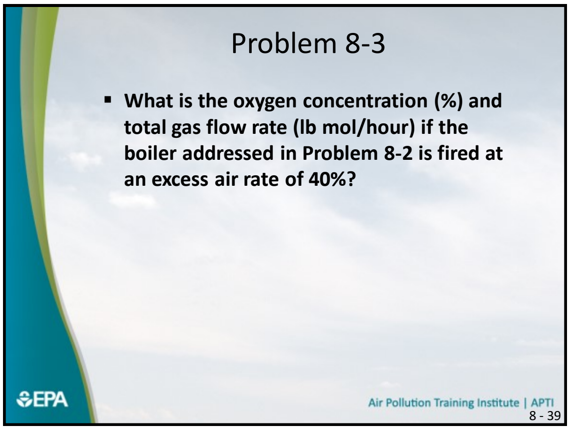
Problem 8-2: Solution (Continued)

Step 7. Calculate the lb mole of material leaving the combustion process (combustion products, combustion air, and unburned constituents of fuel).

$$\text{Effluent gas stream} = \text{Fuel moisture} + \text{Combustion products} + \text{Remaining oxygen} + \text{Combustion air nitrogen}$$

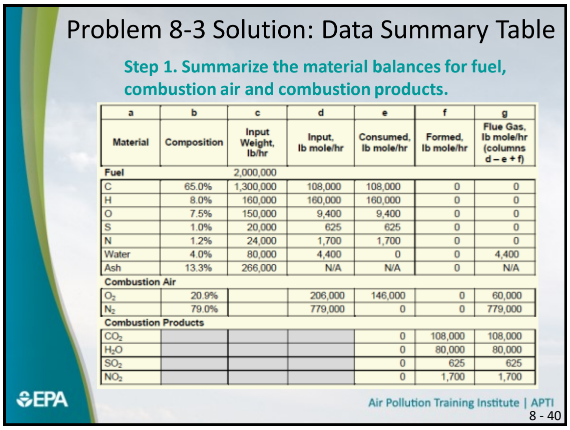
Effluent gas stream =
4,400 + (108,000 + 80,000 + 625 + 1,700) + 0 + 552,000

Effluent gas stream = 747,000 lb mole/hr



Problem 8-3

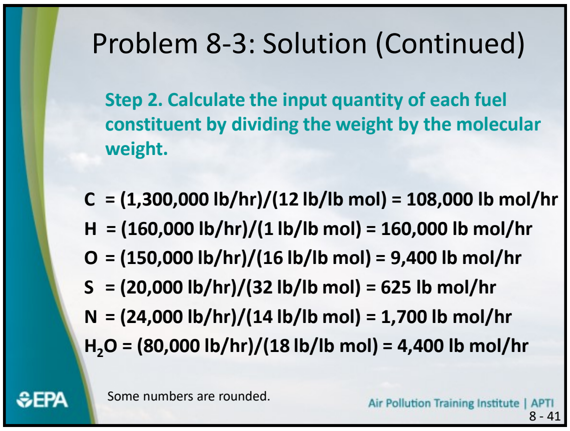
- **What is the oxygen concentration (%) and total gas flow rate (lb mol/hour) if the boiler addressed in Problem 8-2 is fired at an excess air rate of 40%?**



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	65.0%	1,300,000	108,000	108,000	0	0
H	8.0%	160,000	160,000	160,000	0	0
O	7.5%	150,000	9,400	9,400	0	0
S	1.0%	20,000	625	625	0	0
N	1.2%	24,000	1,700	1,700	0	0
Water	4.0%	80,000	4,400	0	0	4,400
Ash	13.3%	266,000	N/A	N/A	0	N/A
Combustion Air						
O_2	20.9%		206,000	146,000	0	60,000
N_2	79.0%		779,000	0	0	779,000
Combustion Products						
CO_2				0	108,000	108,000
H_2O				0	80,000	80,000
SO_2				0	625	625
NO_2				0	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 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

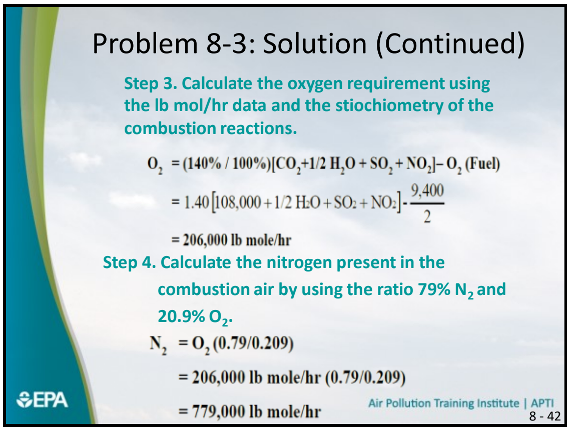
O = (150,000 lb/hr)/(16 lb/lb mol) = 9,400 lb mol/hr

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

H_2O = (80,000 lb/hr)/(18 lb/lb mol) = 4,400 lb mol/hr

Some numbers are rounded.



Problem 8-3: Solution (Continued)

Step 3. Calculate the oxygen requirement using the lb mol/hr data and the stiochiometry of the combustion reactions.

$$O_2 = (140\% / 100\%)[CO_2 + 1/2\ H_2O + SO_2 + NO_2] - O_2\ (\text{Fuel})$$

$$= 1.40\left[108{,}000 + 1/2\ H_2O + SO_2 + NO_2\right] - \frac{9{,}400}{2}$$

$$= 206{,}000 \text{ lb mole/hr}$$

Step 4. Calculate the nitrogen present in the combustion air by using the ratio 79% N_2 and 20.9% O_2.

$$N_2 = O_2\ (0.79/0.209)$$

$$= 206{,}000 \text{ lb mole/hr } (0.79/0.209)$$

$$= 779{,}000 \text{ lb mole/hr}$$

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 (lb mol C/hr) = 108,000 lb mol/hr
H_2O = 1/2 (lb mol H/hr) = 80,000 lb mol/hr
SO_2 = 1(lb mol S/hr) = 625 lb mol/hr
NO_2 =1(lb mol N/hr) = 1,700 lb mol/hr

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).

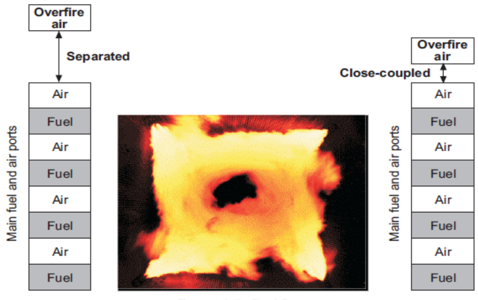
Total effluent = 4,400 + (108,000 + 80,000 + 625 + 1,700) + 60,000 + 779,000

Total effluent = 1,034, 000 lb mol/hr

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.

OFA in Tangentially Fired Units



Tangentially-fired flame
(Top view)

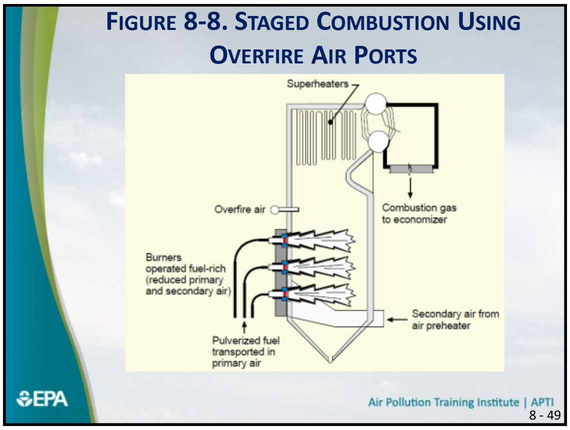
Overfire Air (OFA)

- 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.

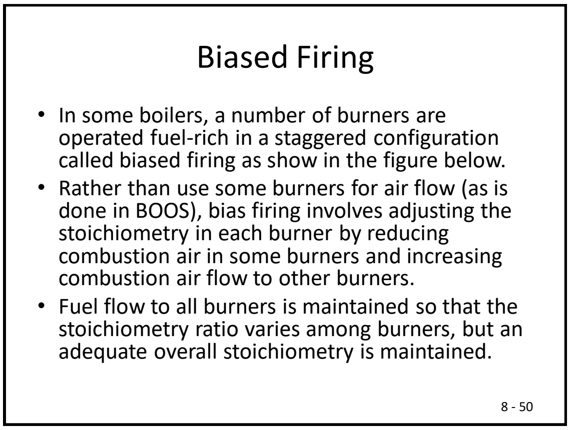
- The following figure demonstrates the operating principles of the OFA method. A secondary air port or OFA injection port has been added above the primary air-fuel burner. Below this port is the fuel-rich zone (stoichiometric ratio less than 1) with peak temperatures lower than those associated with 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.

FIGURE 8-8. STAGED COMBUSTION USING OVERFIRE AIR PORTS



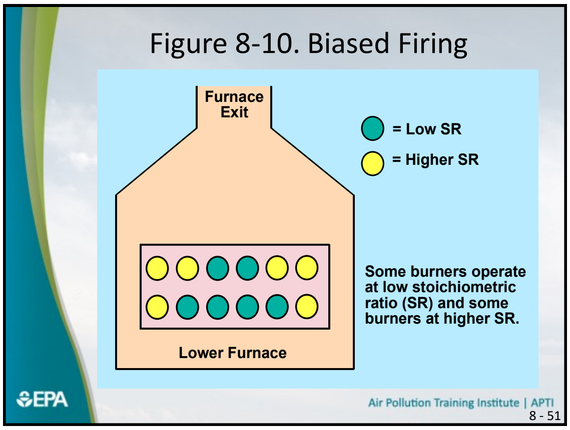
Air Pollution Training Institute | APTI

Biased Firing



- In some boilers, a number of burners are operated fuel-rich in a staggered configuration called biased firing as show in the figure below.
- Rather than use some burners for air flow (as is done in BOOS), bias 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.

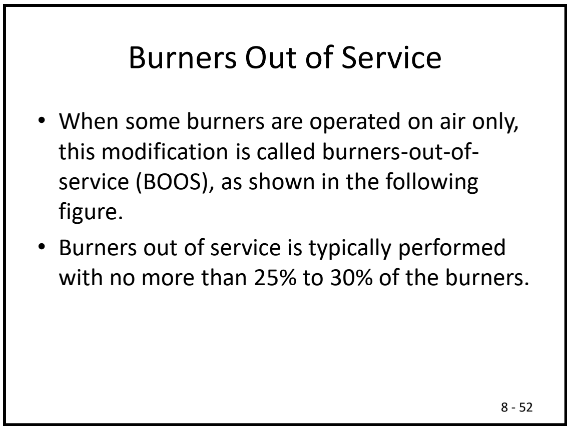
Figure 8-10. Biased Firing



Some burners operate at low stoichiometric ratio (SR) and some burners at higher SR.

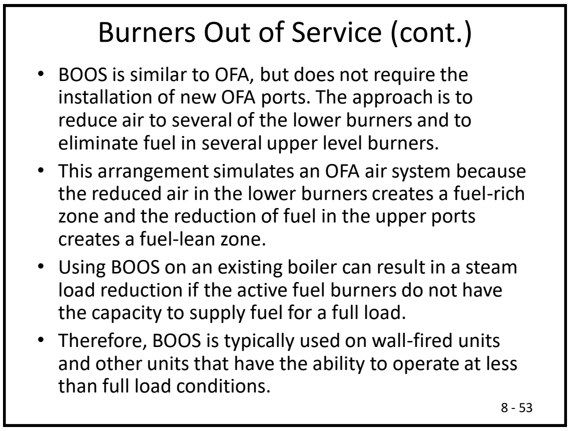
Air Pollution Training Institute | APTI

Burners Out of Service



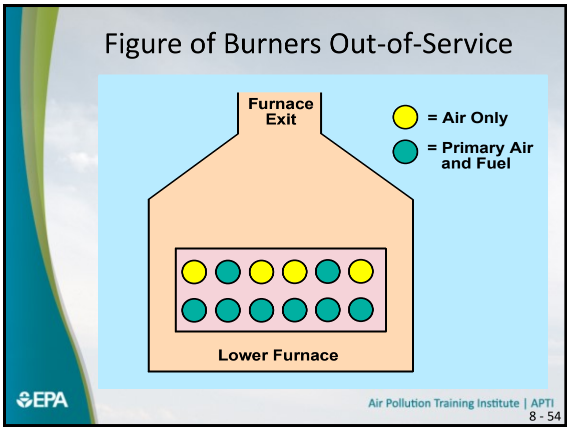
- When some burners are operated on air only, this modification is called burners-out-of-service (BOOS), as shown in the following figure.
- Burners out of service is typically performed with no more than 25% to 30% of the burners.

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.

Figure of Burners Out-of-Service



Air Pollution Training Institute | APTI

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.

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.

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 NOX 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.

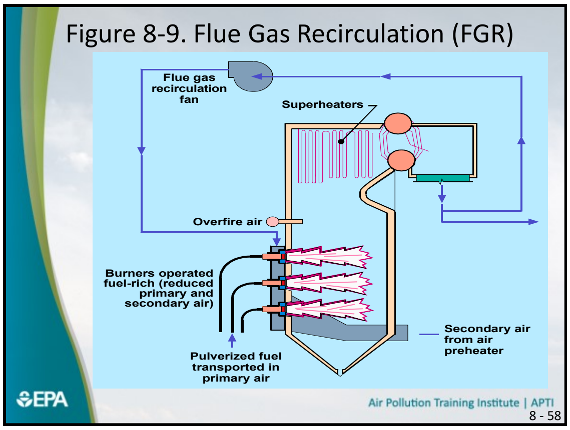
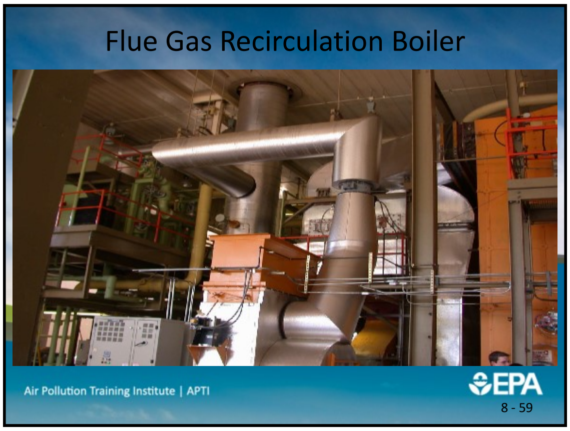


Figure 8-9. Flue Gas Recirculation (FGR)



Flue Gas Recirculation Boiler

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- 10.
- 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.

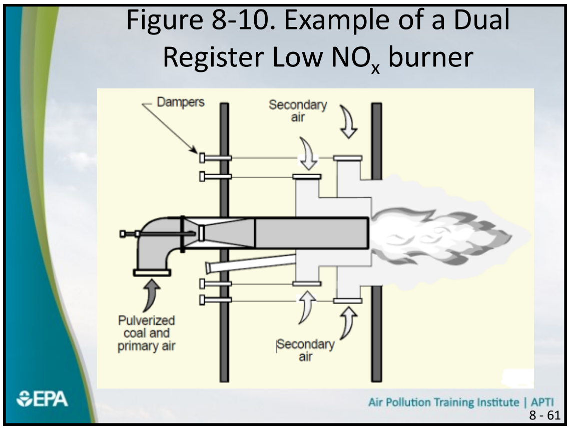


Figure 8-10. Example of a Dual Register Low NO_x burner

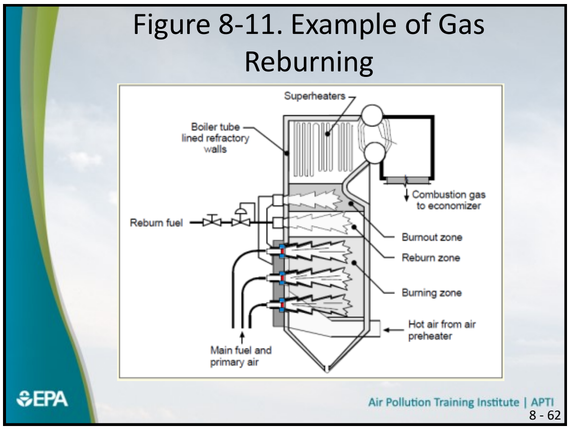
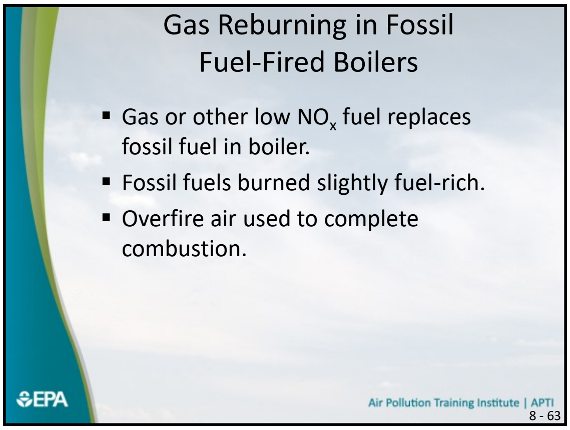
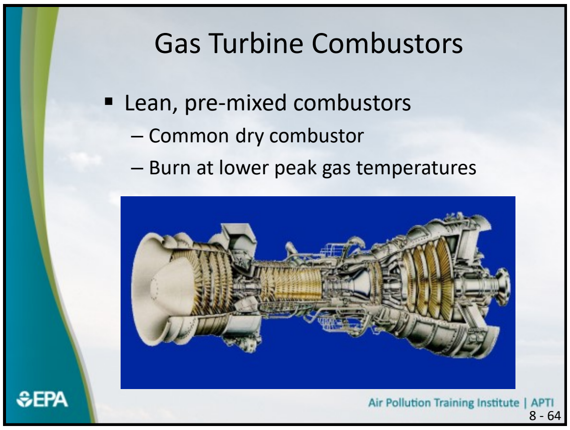


Figure 8-11. Example of Gas Reburning



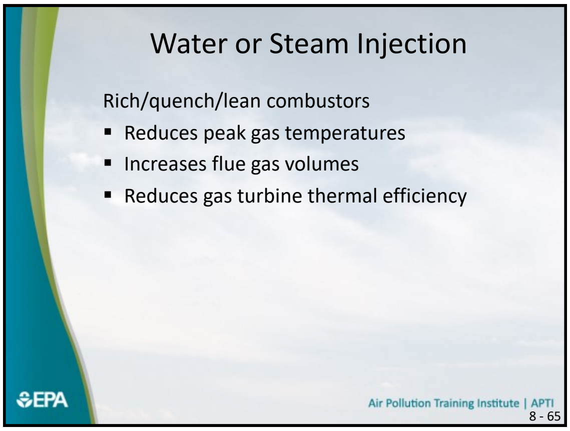
Gas Reburning in Fossil Fuel-Fired Boilers

- Gas or other low NO_x fuel replaces fossil fuel in boiler.
- Fossil fuels burned slightly fuel-rich.
- Overfire air used to complete combustion.



Gas Turbine Combustors

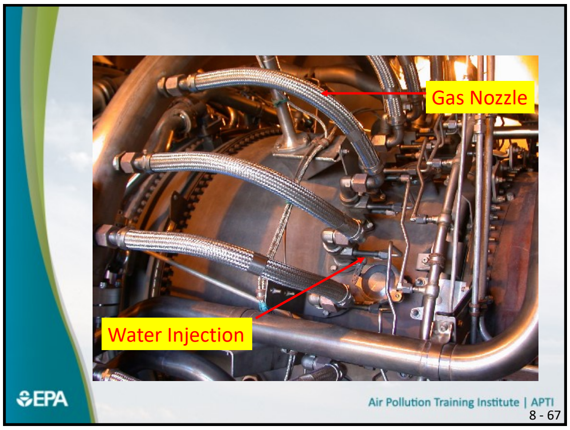
- Lean, pre-mixed combustors
  - Common dry combustor
  - Burn at lower peak gas temperatures

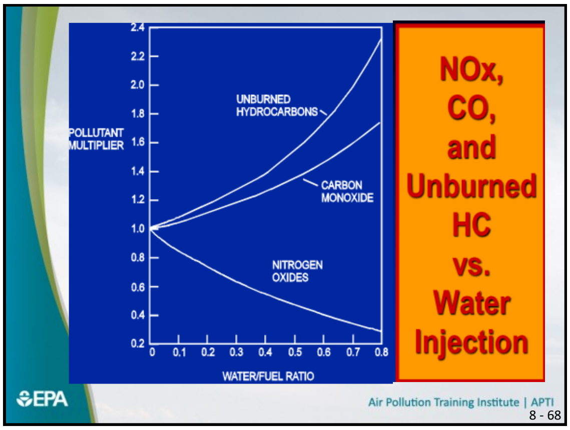


Water or Steam Injection

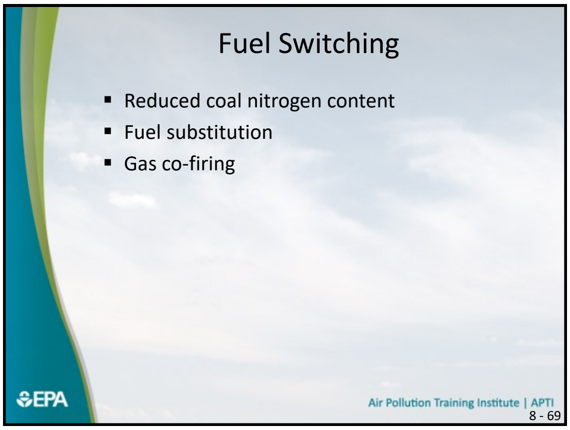
Rich/quench/lean combustors

- Reduces peak gas temperatures
- Increases flue gas volumes
- Reduces gas turbine thermal efficiency





NOx, CO, and Unburned HC vs. Water Injection



Fuel Switching

- Reduced coal nitrogen content
- Fuel substitution
- Gas co-firing

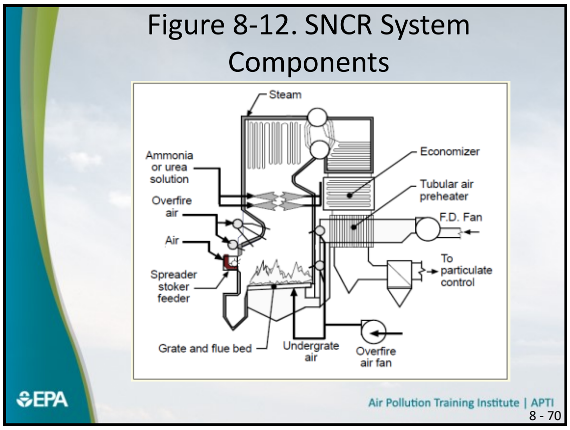
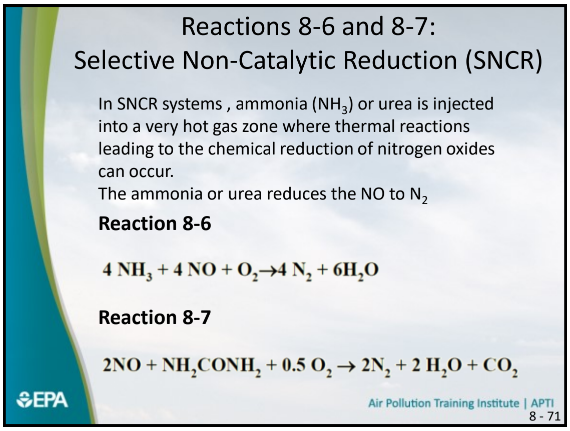


Figure 8-12. SNCR System Components



Reactions 8-6 and 8-7: Selective Non-Catalytic Reduction (SNCR)

In SNCR systems , ammonia (NH_3) or urea is injected into a very hot gas zone where thermal reactions leading to the chemical reduction of nitrogen oxides can occur.

The ammonia or urea reduces the NO to N_2

Reaction 8-6

$$4\ NH_3 + 4\ NO + O_2 \rightarrow 4\ N_2 + 6H_2O$$

Reaction 8-7

$$2NO + NH_2CONH_2 + 0.5\ O_2 \rightarrow 2N_2 + 2\ H_2O + CO_2$$

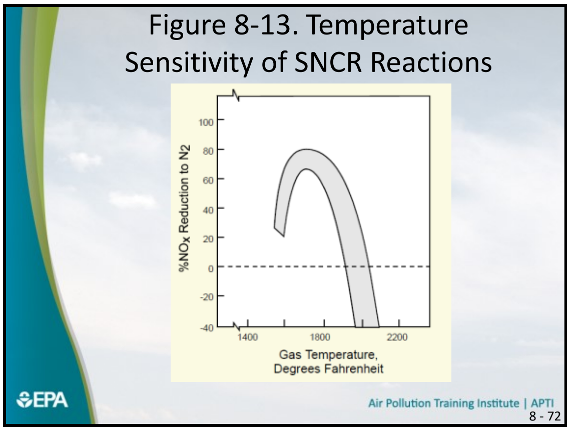


Figure 8-13. Temperature Sensitivity of SNCR Reactions

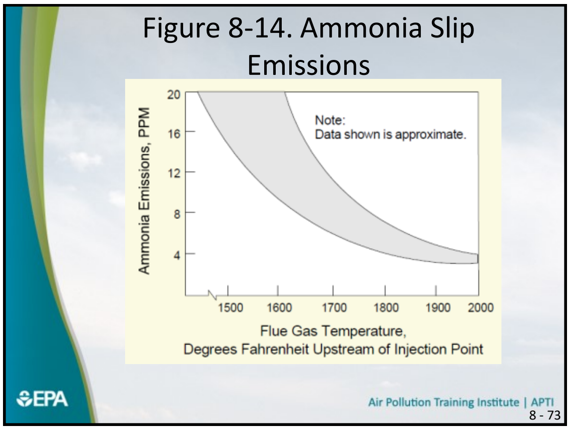


Figure 8-14. Ammonia Slip Emissions

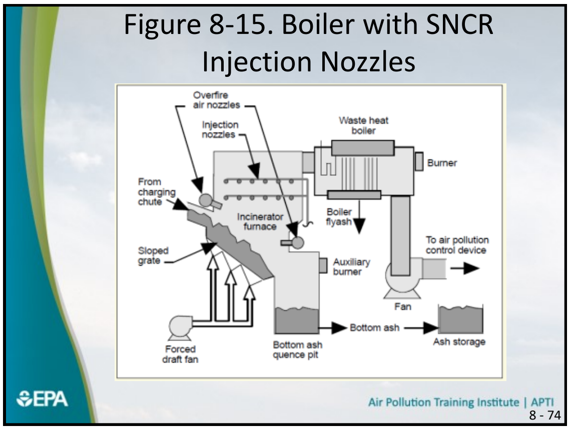


Figure 8-15. Boiler with SNCR Injection Nozzles

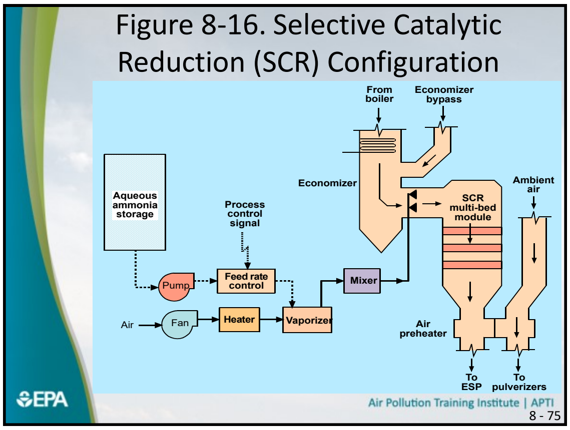
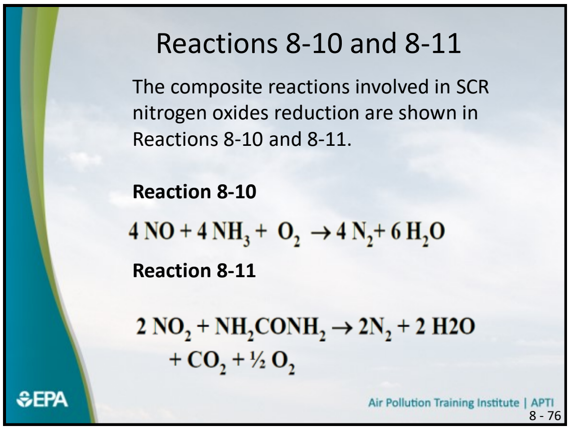


Figure 8-16. Selective Catalytic Reduction (SCR) Configuration



Reactions 8-10 and 8-11

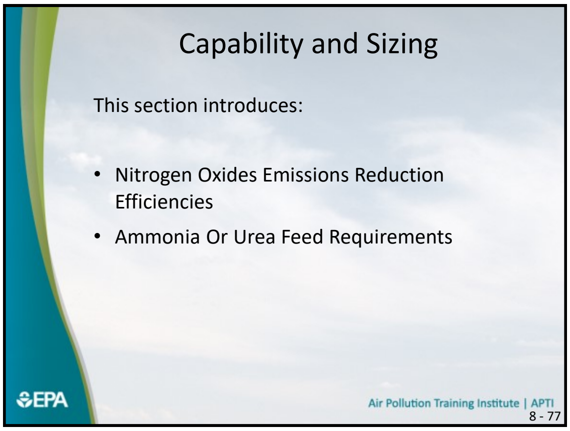
The composite reactions involved in SCR nitrogen oxides reduction are shown in Reactions 8-10 and 8-11.

Reaction 8-10

$$4\,NO + 4\,NH_3 + O_2 \rightarrow 4\,N_2 + 6\,H_2O$$

Reaction 8-11

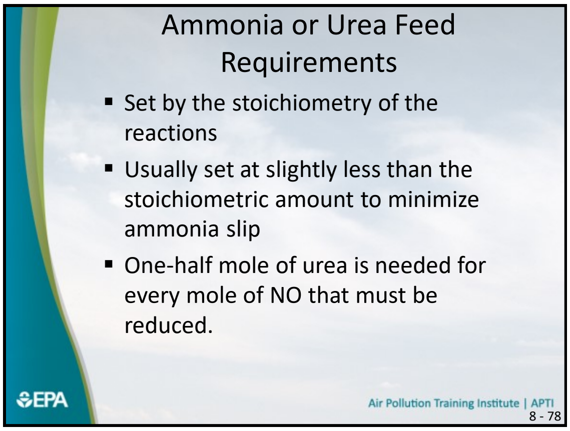
$$2\,NO_2 + NH_2CONH_2 \rightarrow 2N_2 + 2\,\mathrm{H2O} + CO_2 + \tfrac{1}{2}\,O_2$$



Capability and Sizing

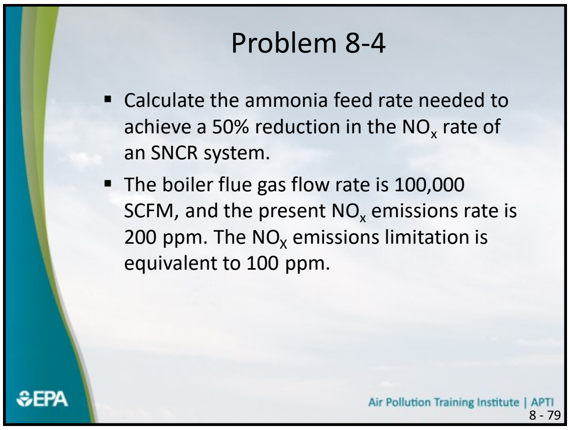
This section introduces:

- Nitrogen Oxides Emissions Reduction Efficiencies
- Ammonia Or Urea Feed Requirements



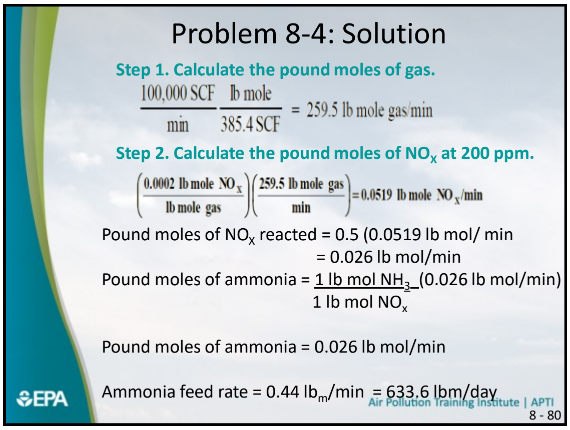
Ammonia or Urea Feed Requirements

- 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 50% 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

$$\text{Pound moles of ammonia} = \frac{1\ \text{lb mol}\ NH_3}{1\ \text{lb mol}\ NO_x}(0.026\ \text{lb mol/min})$$

Pound moles of ammonia = 0.026 lb mol/min

Ammonia feed rate = 0.44 lb_m/min = 633.6 lbm/day

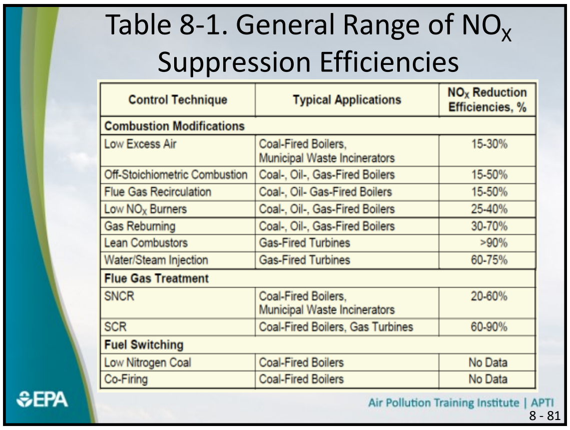
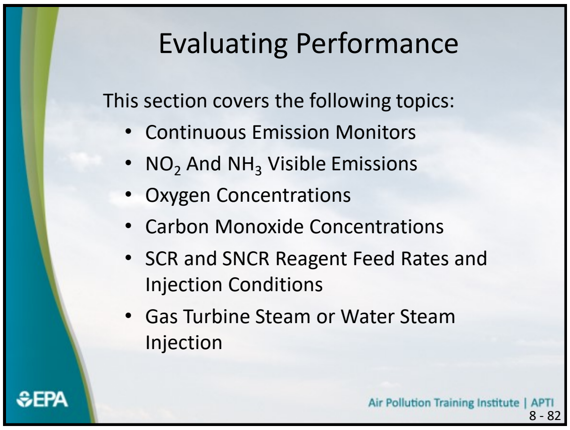


Table 8-1. General Range of NO_X Suppression Efficiencies

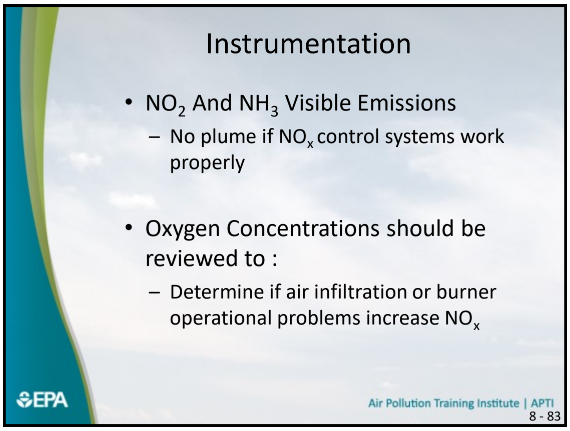
Control Technique	Typical Applications	NO_X Reduction Efficiencies, %
Combustion Modifications		
Low Excess Air	Coal-Fired Boilers, Municipal Waste Incinerators	15-30%
Off-Stoichiometric Combustion	Coal-, Oil-, Gas-Fired Boilers	15-50%
Flue Gas Recirculation	Coal-, Oil- Gas-Fired Boilers	15-50%
Low NO_X 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



Evaluating Performance

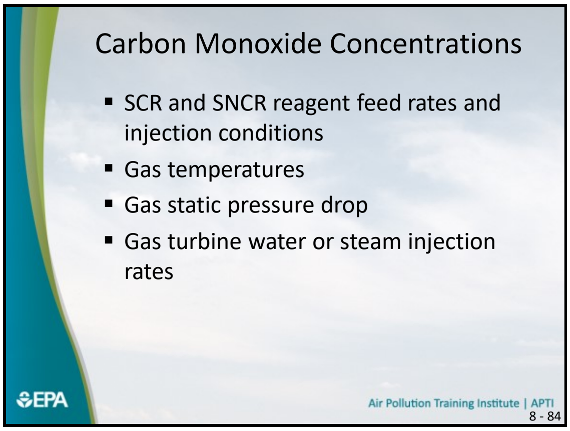
This section covers the following topics:

- Continuous Emission Monitors
- NO_2 And NH_3 Visible Emissions
- Oxygen Concentrations
- Carbon Monoxide Concentrations
- SCR and SNCR Reagent Feed Rates and Injection Conditions
- Gas Turbine Steam or Water Steam Injection



Instrumentation

- NO_2 And NH_3 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

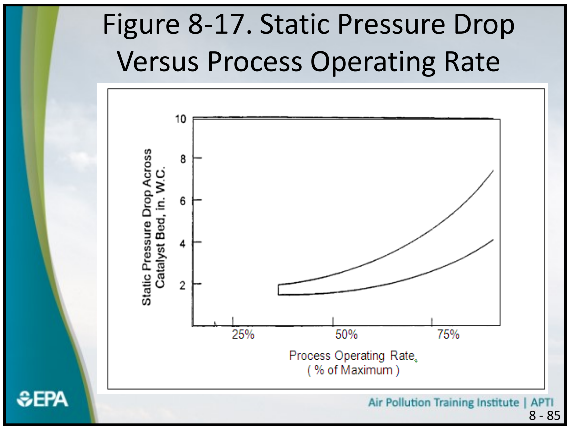
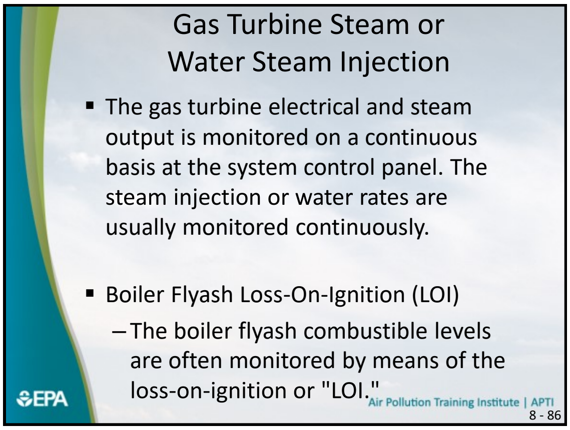
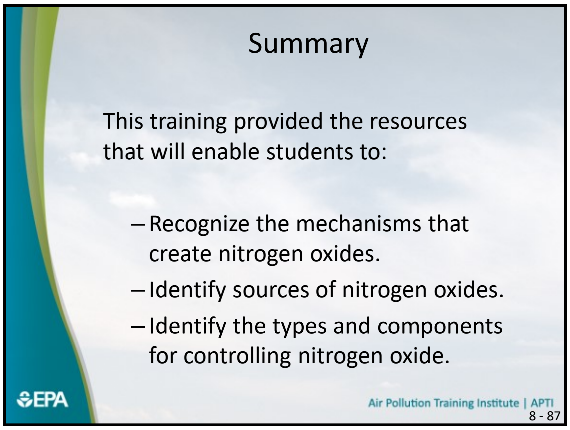


Figure 8-17. Static Pressure Drop Versus Process Operating Rate



Gas Turbine Steam or Water Steam Injection

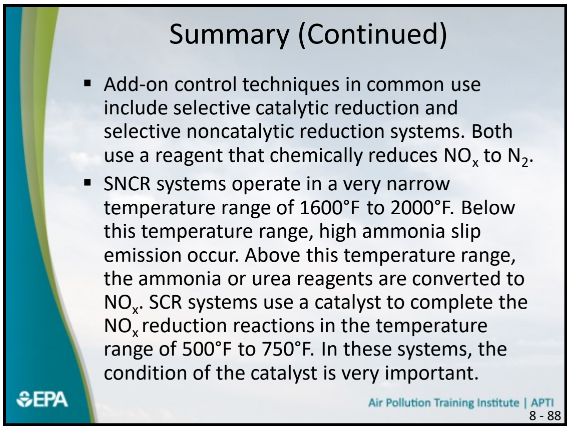
- The gas turbine electrical and steam output is monitored on a continuous basis at the system control panel. The steam injection or water rates are usually monitored continuously.
- Boiler Flyash Loss-On-Ignition (LOI)
  - The boiler flyash combustible levels are often monitored by means of the loss-on-ignition or "LOI."



Summary

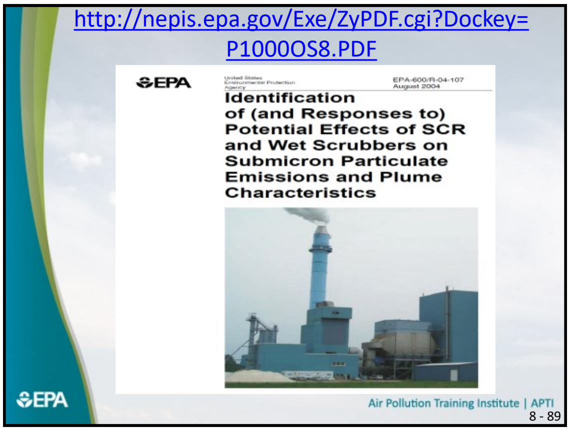
This training provided the resources that will enable students to:

- 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.

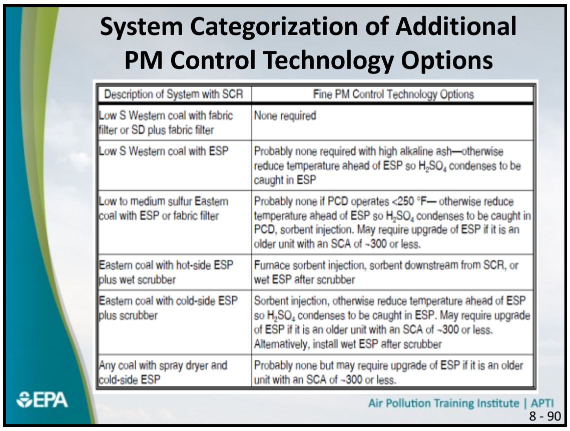


http://nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=P1000OS8.PDF

United States
Environmental Protection
Agency

EPA-600/R-04-107
August 2004

Identification of (and Responses to) Potential Effects of SCR and Wet Scrubbers on Submicron Particulate Emissions and Plume Characteristics



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.

Presented on the Internet
For NESCAUM 2023

CHAPTER 9

SULFUR OXIDES CONTROL

APTI COURSE 415
Air Pollution Training Institute | APTI

CHAPTER 9

SULFUR OXIDES CONTROL

Introduction

- Sources of Sulfur Oxides
- Concerns about SO_2 emissions
  - —Clean Air Act Amendments of 1990 (Title IV)
- Emissions and monitoring requirements

Learning Objectives

At the end of this Chapter, you'll be able to:

- Recognize operating principles for sulfur 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.

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 $SO_3 + H_2O \rightarrow H_2SO_4$

Problem 9-1

- What is the emission rate of sulfur dioxide if 100 tons of coal are being burned per hour and the fuel sulfur content is 2% by weight?
- Assume that 94% of the fuel sulfur reacts by means of Reaction 9-1.

Problem 9-1: Solution

Step 1. Calculate the amount of sulfur in the coal.

Pounds of fuel sulfur

$$= \frac{100 \text{ tons}}{\text{hour}} \frac{2{,}000 \text{ lb}_m}{\text{ton}} \frac{2 \text{ lb}_m \text{ S}}{100 \text{ lb}_m \text{ coal}}$$

$$= 4{,}000 \text{ lb}_m \text{ S/hour}$$

Step 2. Convert sulfur quantity to pound moles per hour.

Pound moles of sulfur/hour

$$= \frac{4{,}000 \text{ lb}_m}{\text{hr}} \frac{\text{lb mole S}}{32 \text{ lb}_m}$$

$$= 125 \text{ lb mole S/hr}$$

Problem 9-1: Solution (Continued)

Step 3. Convert sulfur pound moles to SO_2 pound moles.

Pound moles of sulfur converted to SO_2

$$= \frac{125 \text{ lb mole S}}{\text{hr}} \text{ x } \frac{0.94 \text{ lb S converted}}{\text{lb S total}} \text{ x } \frac{1 \text{ lb mole SO}_2}{\text{lb mole S}}$$

$$= 117.5 \text{ lb mole SO}_2\text{/hour}$$

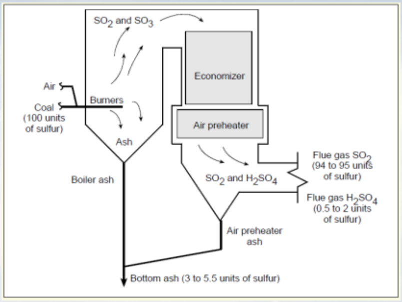
Step 4. Convert SO_2 pound moles to pound mass.

Pounds of SO_2 emitted per hour

$$= \frac{117.5 \text{ lb mole SO}_2}{\text{hour}} \frac{64 \text{ lb}_m \text{ SO}_2}{\text{lb mole SO}_2}$$

$$= 7{,}520 \text{ lb}_m \text{ SO}_2\text{/hour}$$

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 SO_2, what is the percent reduction in sulfur dioxide emissions due to this fuel conversion?

Problem 9-2: Solution

Step 1. Calculate the boiler sulfur dioxide emissions for the high sulfur fuel.

As indicated in Problem 9-1, 2 pounds of sulfur dioxide form for every pound of sulfur escaping the combustion chamber. Choose a boiler firing rate of 100 MMBtu.

SO_2 (lb/hour) =

$$\left(\frac{2 \text{ lb}_m \text{ S}}{100 \text{ lb}_m \text{ coal}}\right)\left(\frac{0.94 \text{ lb}_m \text{ S Converted}}{\text{lb}_m \text{ S Total}}\right)\left(\frac{2 \text{ lb}_m \text{ SO}_2}{\text{lb}_m \text{ S}}\right)\left(\frac{\text{lb}_m \text{ coal}}{13{,}500 \text{ Btu}}\right) 100 \text{ x } 10^6 \text{ Btu/hr}$$

$$SO_2 (\text{lb}_m\text{/hour}) = 279 \text{ lb SO}_2\text{/hour}$$

Problem 9-2: Solution (Continued)

Step 2. Calculate the boiler sulfur dioxide emissions from the low sulfur fuel.

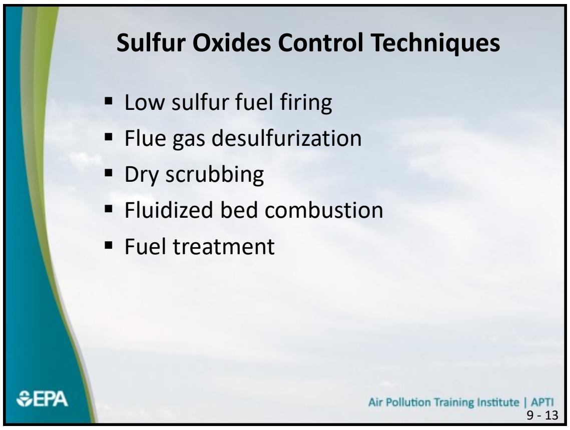
SO_2 (lb/hour) =

$$\left(\frac{1 \text{ lb}_m \text{ S}}{100 \text{ lb}_m \text{ coal}}\right)\left(\frac{0.94 \text{ lb}_m \text{ S Converted}}{\text{lb}_m \text{ S Total}}\right)\left(\frac{2 \text{ lb}_m \text{ SO}_2}{\text{lb}_m \text{ S}}\right)\left(\frac{\text{lb}_m \text{ coal}}{8{,}500 \text{ Btu}}\right) 100 \text{ x } 10^6 \text{ Btu/hr}$$

$$= 221 \text{ lb}_m \text{ SO}_2\text{/hour}$$

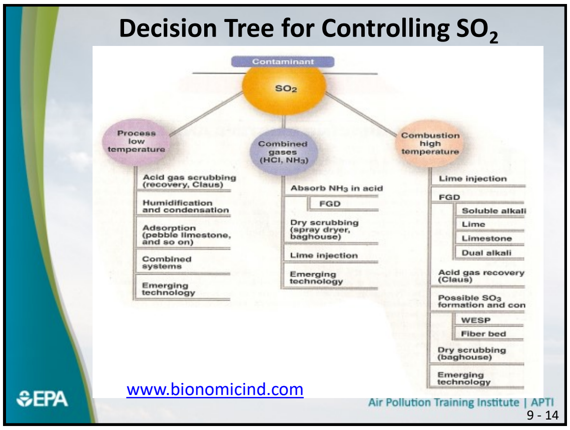
Step 3. Calculate the percent reduction.

$$\text{Reduction} = \left(\frac{279 - 221}{279}\right) 100\% = 20.8\%$$



Sulfur Oxides Control Techniques

- Low sulfur fuel firing
- Flue gas desulfurization
- Dry scrubbing
- Fluidized bed combustion
- Fuel treatment



Decision Tree for Controlling SO_2

Contaminant

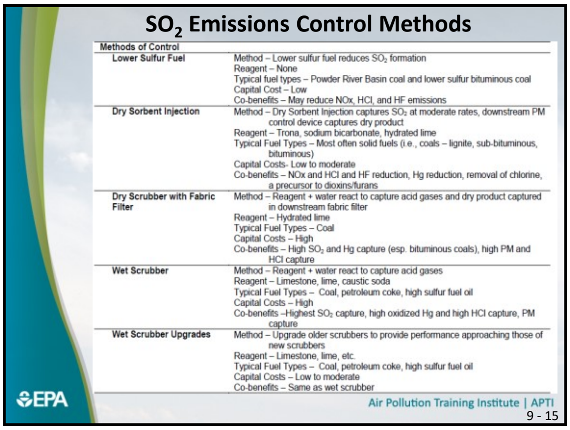
SO_2

Process low temperature
- Acid gas scrubbing (recovery, Claus)
- Humidification and condensation
- Adsorption (pebble limestone, and so on)
- Combined systems
- Emerging technology

Combined gases (HCl, NH_3)
- Absorb NH_3 in acid
  - FGD
- Dry scrubbing (spray dryer, baghouse)
- Lime injection
- Emerging technology

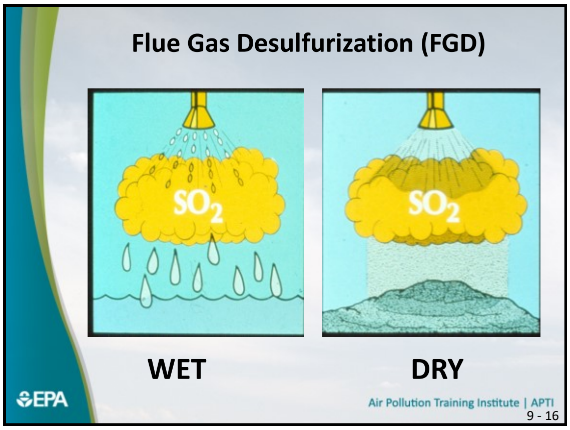
Combustion high temperature
- Lime injection
- FGD
  - Soluble alkali
  - Lime
  - Limestone
  - Dual alkali
- Acid gas recovery (Claus)
- Possible SO_3 formation and con
  - WESP
  - Fiber bed
- Dry scrubbing (baghouse)
- Emerging technology

www.bionomicind.com



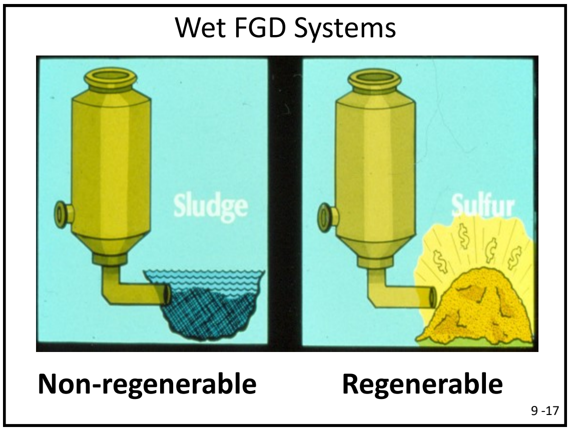
SO_2 Emissions Control Methods

Methods of Control	
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 NOx, HCl, and HF emissions
Dry Sorbent Injection	Method – Dry Sorbent Injection captures SO_2 at moderate rates, downstream PM control device 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 – NOx 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 coke, 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 coke, high sulfur fuel oil Capital Costs – Low to moderate Co-benefits – Same as wet scrubber



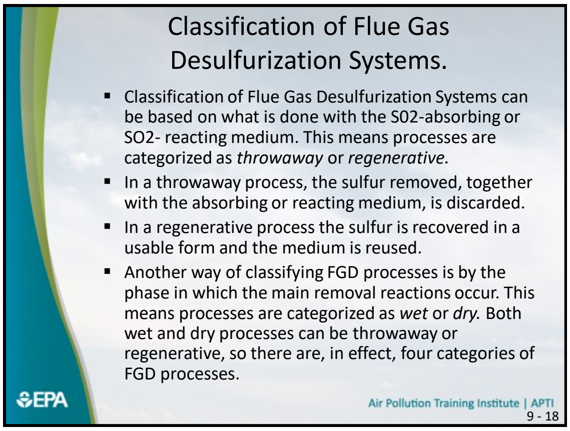
Flue Gas Desulfurization (FGD)

WET **DRY**



Wet FGD Systems

Non-regenerable **Regenerable**



Classification of Flue Gas Desulfurization Systems.

- Classification of Flue Gas Desulfurization Systems can be based on what is done with the S02-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.

Non-Regenerative Desulfurization Systems

- In the majority of the throwaway processes an alkaline agent reacts with the $S0_2$ leading to a product that is discarded.
- Commonly used agents in this type of process are limestone ($CaC0_3$) 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 $S0_2$ is captured chemically within the furnace, the rest in the scrubbing step.

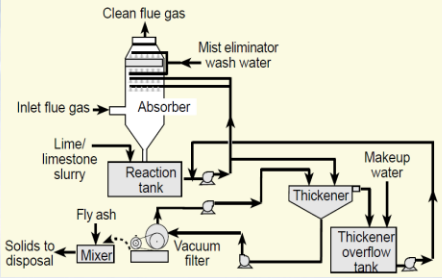
Regenerative Desulfurization Systems

- In the regenerative alkaline processes, an alkaline agent strips $S0_2$ from the flue gas stream, combining chemically with the $S0_2$. In a separate regeneration step, the agent is reconstituted and sulfur is recovered, usually as liquid $S0_2$ or sulfuric acid.
- Some of the agents used include MgO, Na_2S0_3, and metal carbonates. Regenerative solid adsorption comprises several activated char processes, in which $S0_2$ is adsorbed on charcoal and desorbed to lead to the production of sulfuric acid.

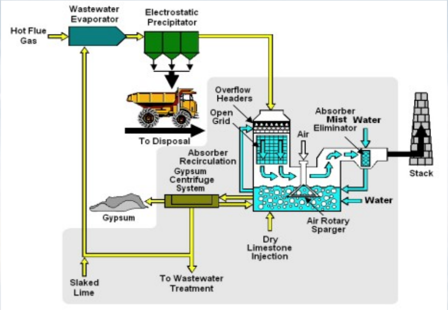
Table 9-1. Common Types of FGD Processes for Boilers (see handout)

Type of SO2 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

Figure 9-2. Simplified Flowchart of a Lime Scrubbing System

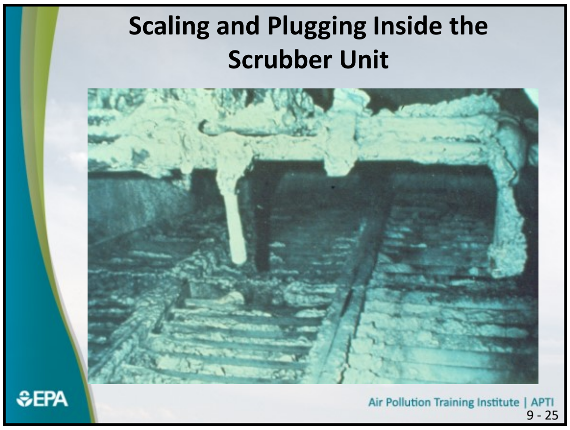


Chesterton, Porter County, IN (Northern Indiana Public Service Company's Bailly Generating Station, Units 7 and 8 (Completed 1996)



http://www.netl.doe.gov/technologies/coalpower/cctc/cctdp/project_briefs/puair/adflugasdemo.html

- 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 (Na_2S0_3)/sodium hydroxide ($NaOH$) is sprayed in the tower.
- Sulfur dioxide is absorbed and neutralized in the solution, and since both Na_2S0_3 and $Na_2\ S0_4$ are soluble in water, no precipitation occurs in the scrubber.



Scaling and Plugging Inside the Scrubber Unit

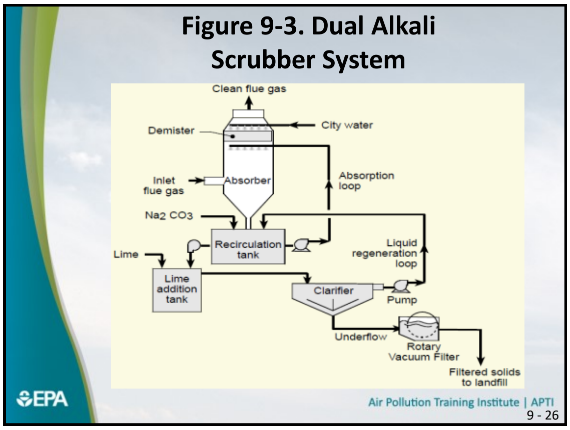


Figure 9-3. Dual Alkali Scrubber System

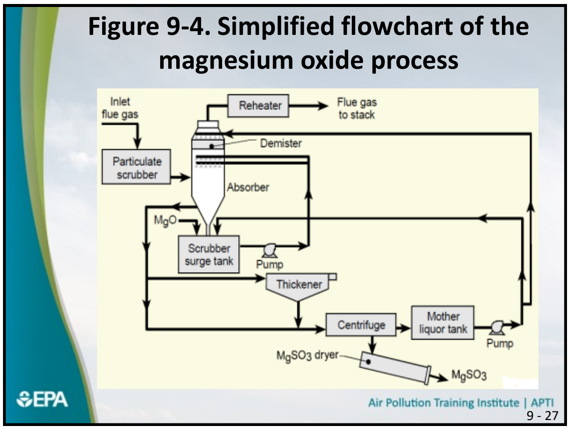
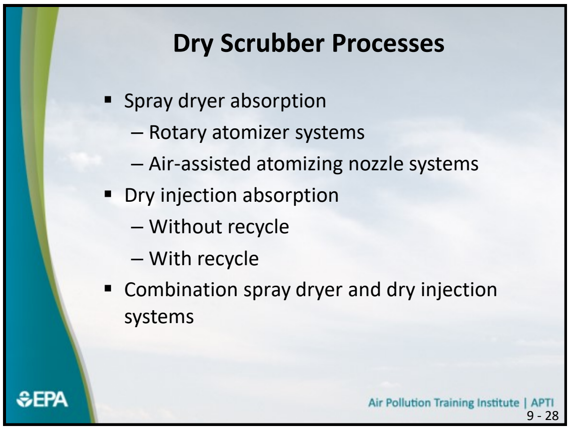


Figure 9-4. Simplified flowchart of the magnesium oxide process



Dry Scrubber Processes

- Spray dryer absorption
  - Rotary atomizer systems
  - Air-assisted atomizing nozzle systems
- Dry injection absorption
  - Without recycle
  - With recycle
- Combination spray dryer and dry injection systems

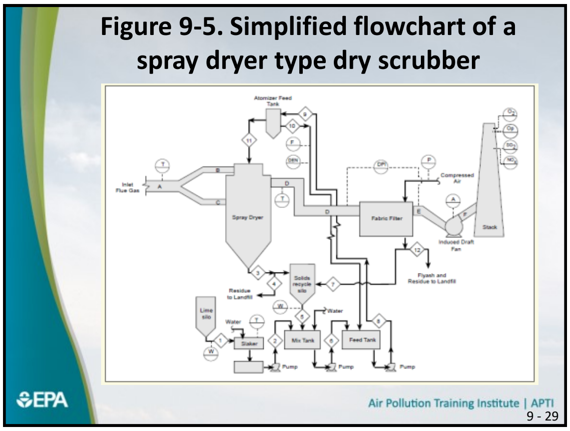


Figure 9-5. Simplified flowchart of a spray dryer type dry scrubber

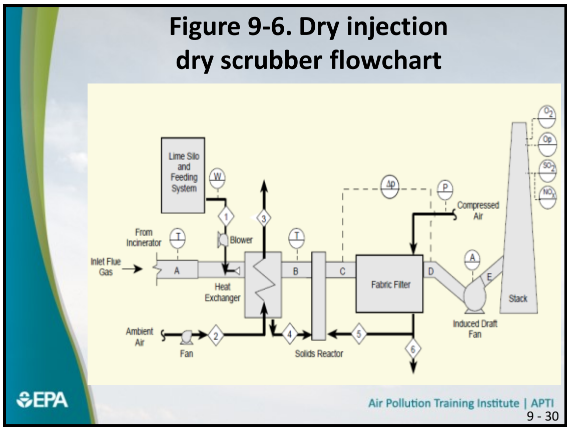


Figure 9-6. Dry injection dry scrubber flowchart

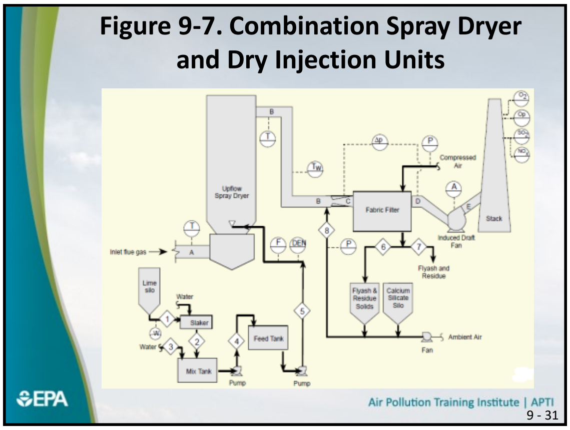
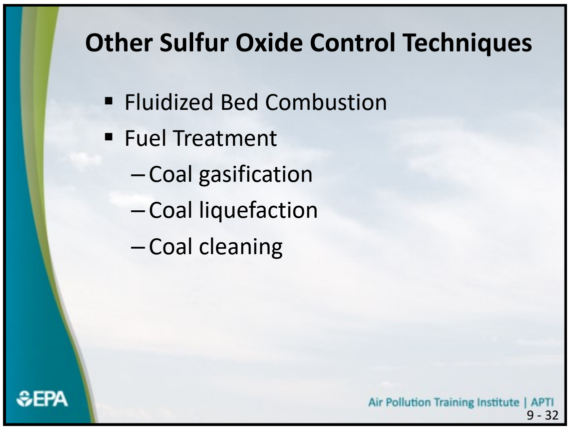
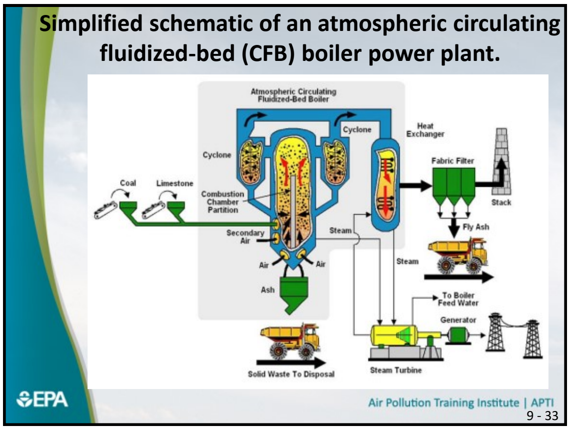


Figure 9-7. Combination Spray Dryer and Dry Injection Units

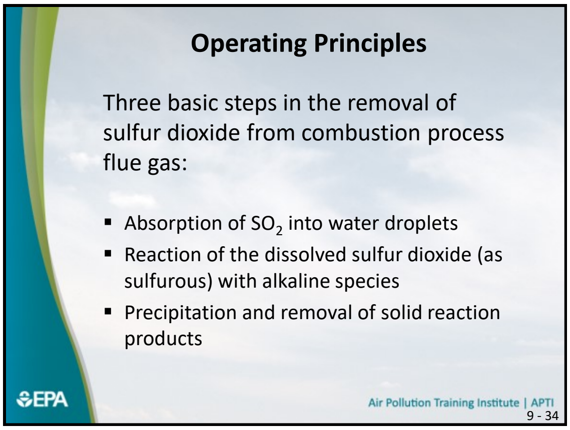


Other Sulfur Oxide Control Techniques

- 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 SO_2 into water droplets
- Reaction of the dissolved sulfur dioxide (as sulfurous) with alkaline species
- Precipitation and removal of solid reaction products

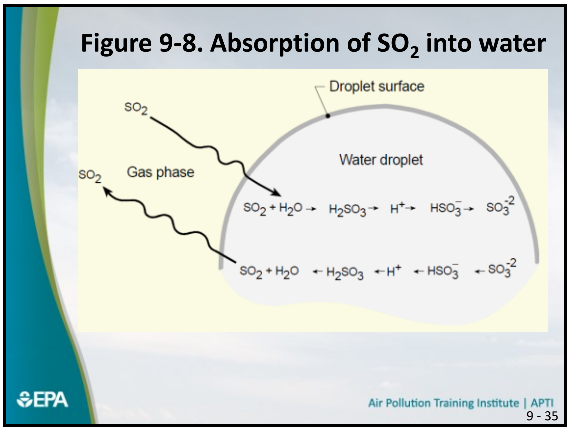


Figure 9-8. Absorption of SO_2 into water

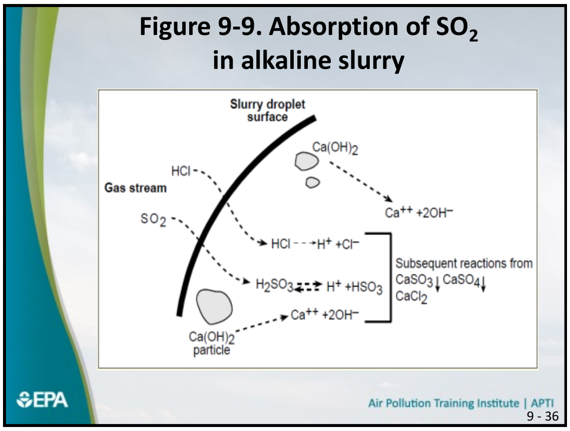
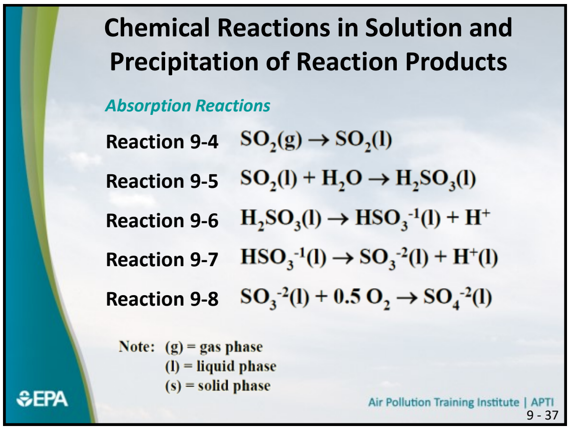


Figure 9-9. Absorption of SO_2 in alkaline slurry



Chemical Reactions in Solution and Precipitation of Reaction Products

Absorption Reactions

Reaction 9-4 $SO_2(g) \rightarrow SO_2(l)$

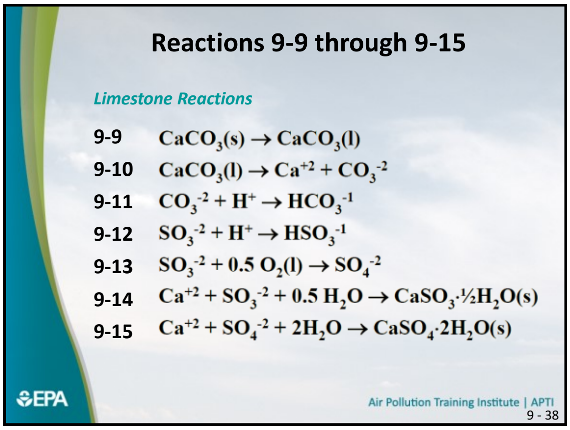
Reaction 9-5 $SO_2(l) + H_2O \rightarrow H_2SO_3(l)$

Reaction 9-6 $H_2SO_3(l) \rightarrow HSO_3^{-1}(l) + H^+$

Reaction 9-7 $HSO_3^{-1}(l) \rightarrow SO_3^{-2}(l) + H^+(l)$

Reaction 9-8 $SO_3^{-2}(l) + 0.5\ O_2 \rightarrow SO_4^{-2}(l)$

Note: (g) = gas phase
(l) = liquid phase
(s) = solid phase



Reactions 9-9 through 9-15

Limestone Reactions

9-9 $CaCO_3(s) \rightarrow CaCO_3(l)$

9-10 $CaCO_3(l) \rightarrow Ca^{+2} + CO_3^{-2}$

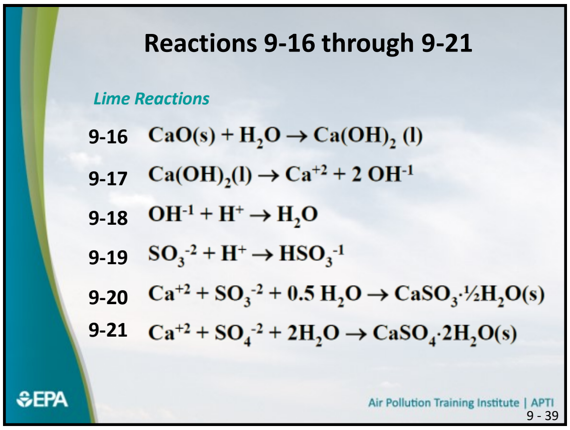
9-11 $CO_3^{-2} + H^+ \rightarrow HCO_3^{-1}$

9-12 $SO_3^{-2} + H^+ \rightarrow HSO_3^{-1}$

9-13 $SO_3^{-2} + 0.5\ O_2(l) \rightarrow SO_4^{-2}$

9-14 $Ca^{+2} + SO_3^{-2} + 0.5\ H_2O \rightarrow CaSO_3 \cdot ½H_2O(s)$

9-15 $Ca^{+2} + SO_4^{-2} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O(s)$



Reactions 9-16 through 9-21

Lime Reactions

9-16 $CaO(s) + H_2O \rightarrow Ca(OH)_2\ (l)$

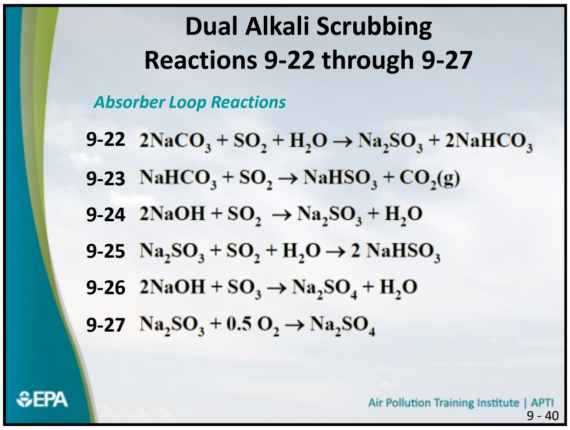
9-17 $Ca(OH)_2(l) \rightarrow Ca^{+2} + 2\ OH^{-1}$

9-18 $OH^{-1} + H^+ \rightarrow H_2O$

9-19 $SO_3^{-2} + H^+ \rightarrow HSO_3^{-1}$

9-20 $Ca^{+2} + SO_3^{-2} + 0.5\ H_2O \rightarrow CaSO_3 \cdot ½H_2O(s)$

9-21 $Ca^{+2} + SO_4^{-2} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O(s)$



Dual Alkali Scrubbing
Reactions 9-22 through 9-27

Absorber Loop Reactions

9-22 $2NaCO_3 + SO_2 + H_2O \rightarrow Na_2SO_3 + 2NaHCO_3$

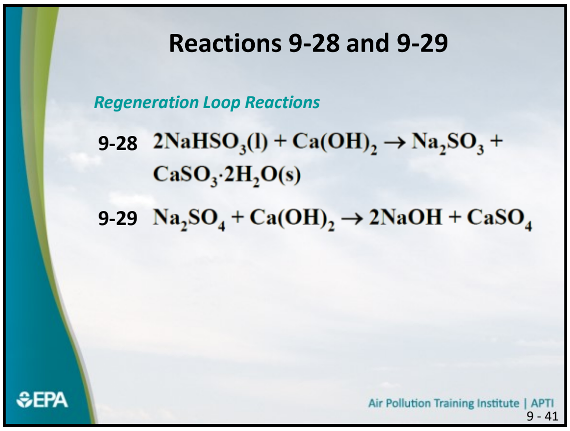
9-23 $NaHCO_3 + SO_2 \rightarrow NaHSO_3 + CO_2(g)$

9-24 $2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$

9-25 $Na_2SO_3 + SO_2 + H_2O \rightarrow 2\ NaHSO_3$

9-26 $2NaOH + SO_3 \rightarrow Na_2SO_4 + H_2O$

9-27 $Na_2SO_3 + 0.5\ O_2 \rightarrow Na_2SO_4$

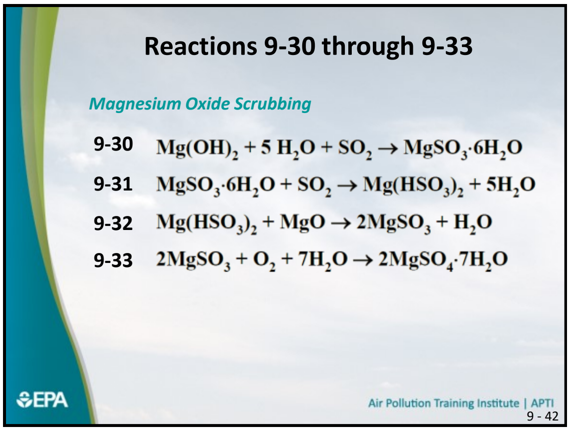


Reactions 9-28 and 9-29

Regeneration Loop Reactions

9-28 $2NaHSO_3(l) + Ca(OH)_2 \rightarrow Na_2SO_3 + CaSO_3 \cdot 2H_2O(s)$

9-29 $Na_2SO_4 + Ca(OH)_2 \rightarrow 2NaOH + CaSO_4$



Reactions 9-30 through 9-33

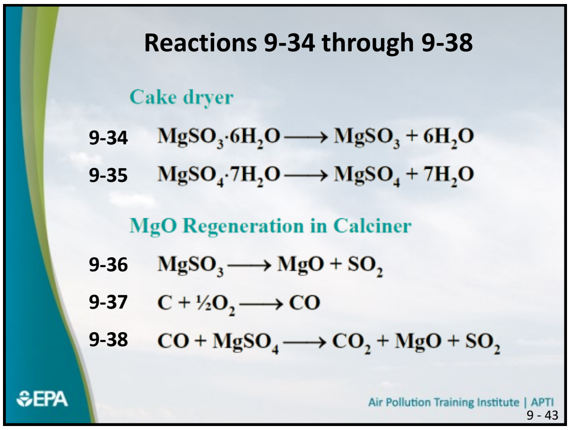
Magnesium Oxide Scrubbing

9-30 $Mg(OH)_2 + 5\ H_2O + SO_2 \rightarrow MgSO_3 \cdot 6H_2O$

9-31 $MgSO_3 \cdot 6H_2O + SO_2 \rightarrow Mg(HSO_3)_2 + 5H_2O$

9-32 $Mg(HSO_3)_2 + MgO \rightarrow 2MgSO_3 + H_2O$

9-33 $2MgSO_3 + O_2 + 7H_2O \rightarrow 2MgSO_4 \cdot 7H_2O$



Reactions 9-34 through 9-38

Cake dryer

9-34 $MgSO_3 \cdot 6H_2O \longrightarrow MgSO_3 + 6H_2O$

9-35 $MgSO_4 \cdot 7H_2O \longrightarrow MgSO_4 + 7H_2O$

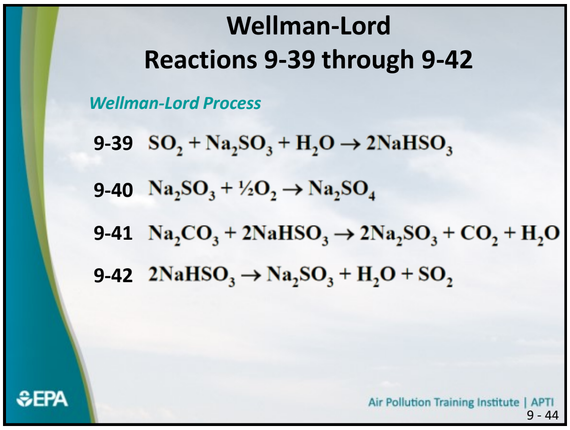
MgO Regeneration in Calciner

9-36 $MgSO_3 \longrightarrow MgO + SO_2$

9-37 $C + \frac{1}{2}O_2 \longrightarrow CO$

9-38 $CO + MgSO_4 \longrightarrow CO_2 + MgO + SO_2$

Air Pollution Training Institute | APTI



Wellman-Lord
Reactions 9-39 through 9-42

Wellman-Lord Process

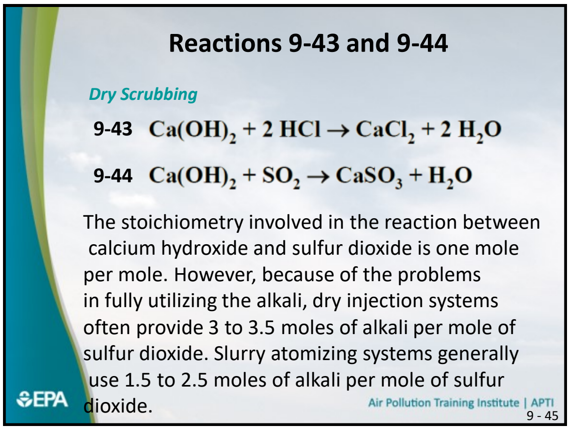
9-39 $SO_2 + Na_2SO_3 + H_2O \rightarrow 2NaHSO_3$

9-40 $Na_2SO_3 + \frac{1}{2}O_2 \rightarrow Na_2SO_4$

9-41 $Na_2CO_3 + 2NaHSO_3 \rightarrow 2Na_2SO_3 + CO_2 + H_2O$

9-42 $2NaHSO_3 \rightarrow Na_2SO_3 + H_2O + SO_2$

Air Pollution Training Institute | APTI



Reactions 9-43 and 9-44

Dry Scrubbing

9-43 $Ca(OH)_2 + 2\ HCl \rightarrow CaCl_2 + 2\ H_2O$

9-44 $Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O$

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.

Air Pollution Training Institute | APTI

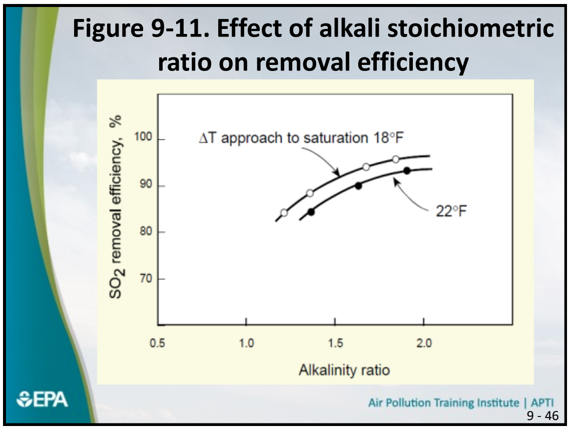
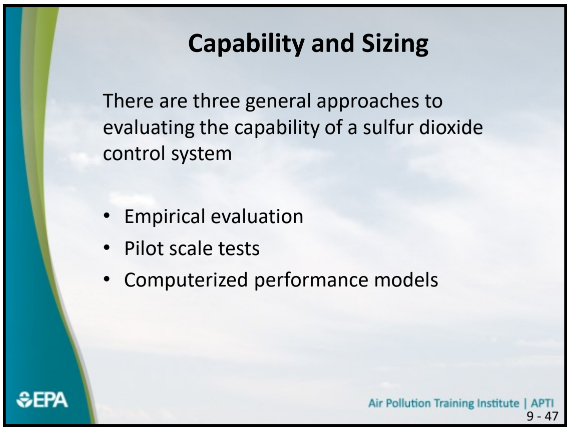


Figure 9-11. Effect of alkali stoichiometric ratio on removal efficiency

Air Pollution Training Institute | APTI

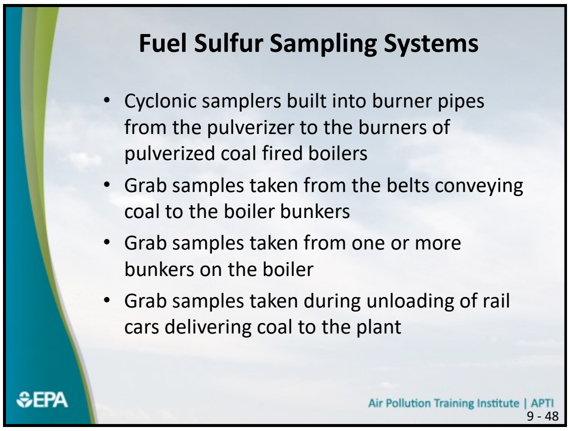


Capability and Sizing

There are three general approaches to evaluating the capability of a sulfur dioxide control system

- Empirical evaluation
- Pilot scale tests
- Computerized performance models

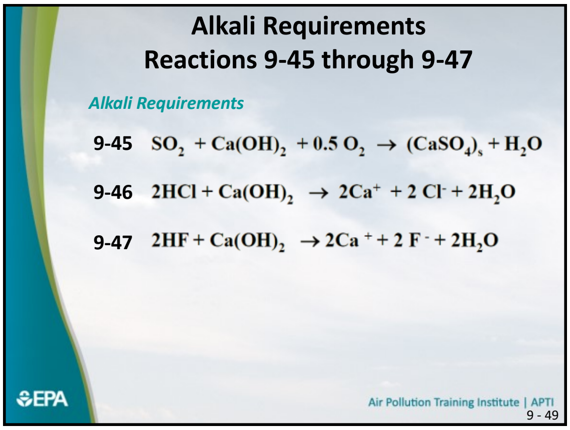
Air Pollution Training Institute | APTI



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

Air Pollution Training Institute | APTI



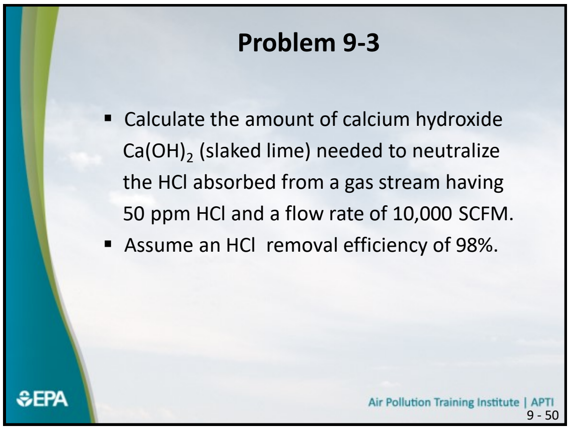
Alkali Requirements Reactions 9-45 through 9-47

Alkali Requirements

9-45 $SO_2 + Ca(OH)_2 + 0.5\,O_2 \rightarrow (CaSO_4)_s + H_2O$

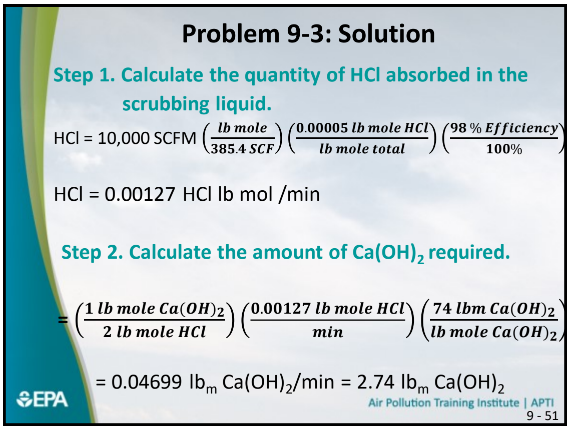
9-46 $2HCl + Ca(OH)_2 \rightarrow 2Ca^+ + 2\,Cl^- + 2H_2O$

9-47 $2HF + Ca(OH)_2 \rightarrow 2Ca^+ + 2\,F^- + 2H_2O$



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%.



Problem 9-3: Solution

Step 1. Calculate the quantity of HCl absorbed in the scrubbing liquid.

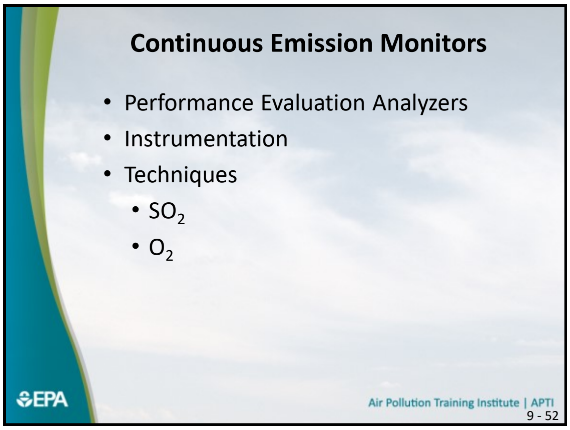
HCl = 10,000 SCFM $\left(\frac{lb\ mole}{385.4\ SCF}\right)\left(\frac{0.00005\ lb\ mole\ HCl}{lb\ mole\ total}\right)\left(\frac{98\,\%\ Efficiency}{100\%}\right)$

HCl = 0.00127 HCl lb mol /min

Step 2. Calculate the amount of $Ca(OH)_2$ required.

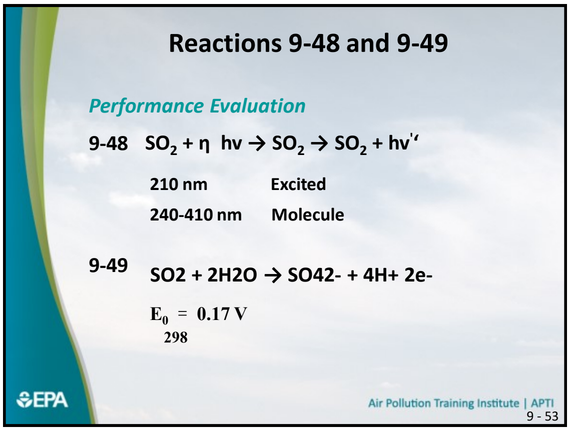
$= \left(\frac{1\ lb\ mole\ Ca(OH)_2}{2\ lb\ mole\ HCl}\right)\left(\frac{0.00127\ lb\ mole\ HCl}{min}\right)\left(\frac{74\ lbm\ Ca(OH)_2}{lb\ mole\ Ca(OH)_2}\right)$

= 0.04699 lb_m $Ca(OH)_2$/min = 2.74 lb_m $Ca(OH)_2$



Continuous Emission Monitors

- Performance Evaluation Analyzers
- Instrumentation
- Techniques
  - SO_2
  - O_2



Reactions 9-48 and 9-49

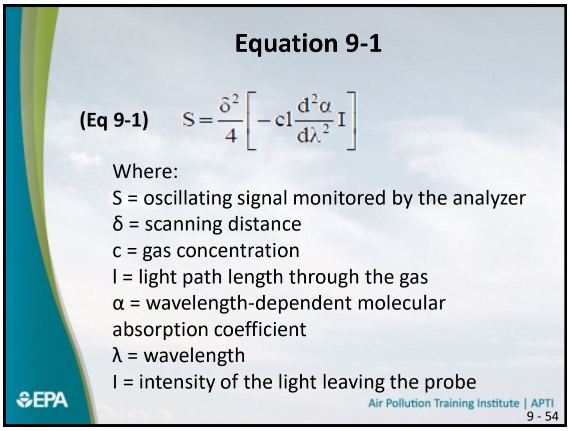
Performance Evaluation

9-48 $SO_2 + \eta\ hv \rightarrow SO_2 \rightarrow SO_2 + hv'$

210 nm	Excited
240-410 nm	Molecule

9-49 SO2 + 2H2O → SO42- + 4H+ 2e-

$E_{0\,298} = 0.17\ V$



Equation 9-1

(Eq 9-1) $$S = \frac{\delta^2}{4}\left[-cl\frac{d^2\alpha}{d\lambda^2}I\right]$$

Where:
S = oscillating signal monitored by the analyzer
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

Instrumentation

- Flue gas oxygen content
- Mist eliminator static pressure drop
- pH
- Alkali feed rate
- Inlet and outlet gas temperature
- Dry and Wet Scrubbing

Summary

This chapter covered the following topics:

- Recognize operating principles for sulfur dioxides control.
- Identify appropriate evaluation and test methods for controlling sulfur dioxide.
- Identify appropriate evaluation and test methods when using fuel sulfur sampling systems.
- Recognize appropriate methods and evaluation for dry and wet scrubbing systems.

Summary (Continued)

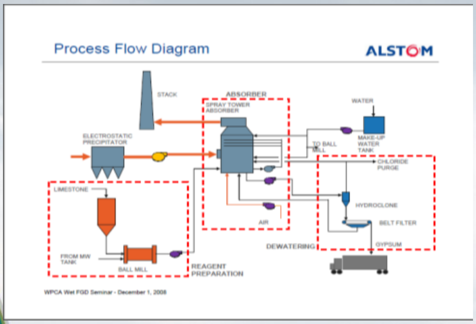
Conclusions

- 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.

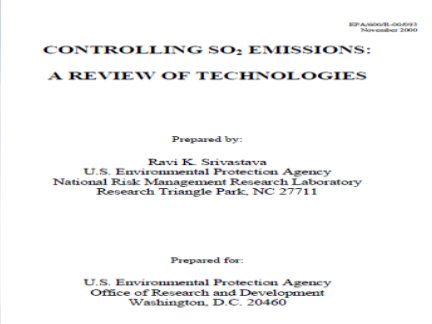
Summary (Continued)

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.



http://wpca.info/pdf/presentations/Orlando_Dec2008/5-Wet%20FGD%20maintenance.pdf



EPA/600/R-00/093
November 2000

CONTROLLING SO_2 EMISSIONS:

A REVIEW OF TECHNOLOGIES

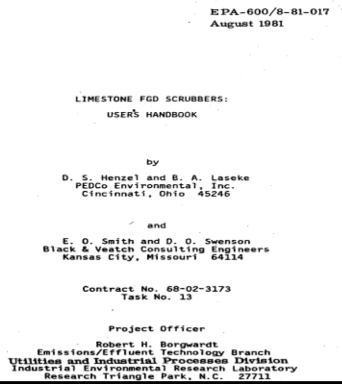
Prepared by:

Ravi K. Srivastava
U.S. Environmental Protection Agency
National Risk Management Research Laboratory
Research Triangle Park, NC 27711

Prepared for:

U.S. Environmental Protection Agency
Office of Research and Development
Washington, D.C. 20460

http://nepis.epa.gov/Adobe/PDF/P1007IQM.pdf



EPA-600/8-81-017
August 1981

LIMESTONE FGD SCRUBBERS:
USER'S HANDBOOK

by

D. S. Henzel and B. A. Laseke
PEDCo Environmental, Inc.
Cincinnati, Ohio 45246

and

E. O. Smith and D. O. Swenson
Black & Veatch Consulting Engineers
Kansas City, Missouri 64114

Contract No. 68-02-3173
Task No. 13

Project Officer

Robert H. Borgwardt
Emissions/Effluent Technology Branch
Utilities and Industrial Processes Division
Industrial Environmental Research Laboratory
Research Triangle Park, N.C. 27711

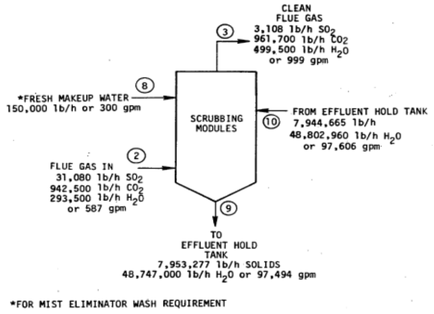
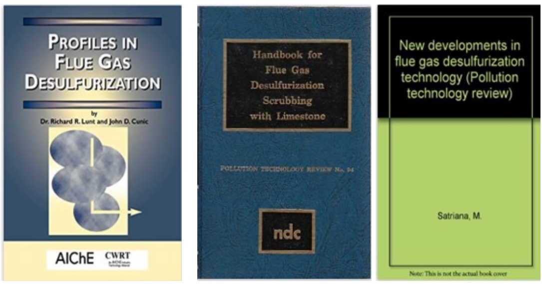
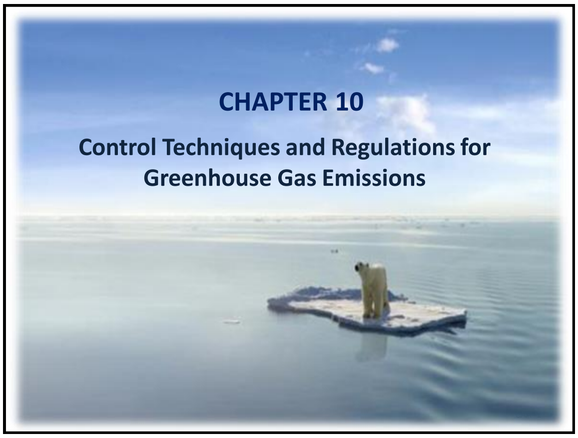


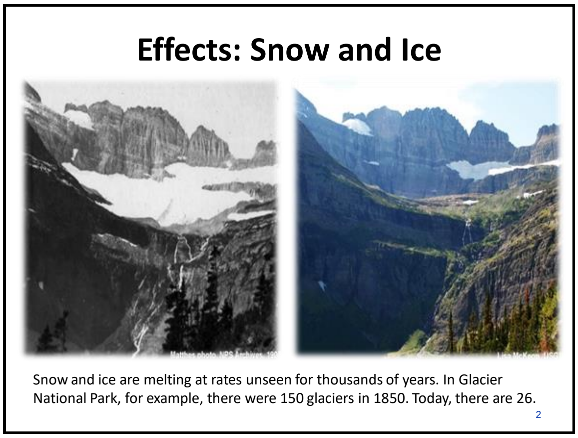
Figure E-5. Material balance around scrubbers.





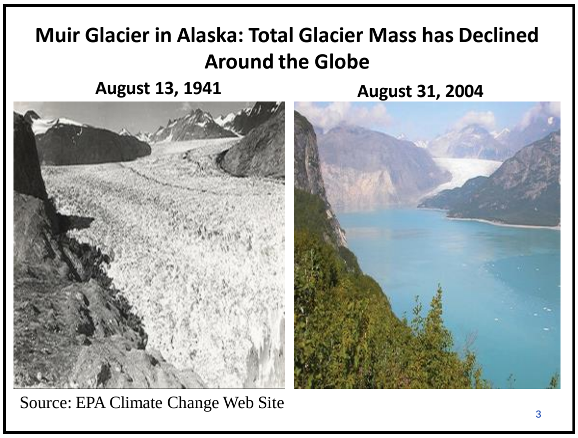
CHAPTER 10

Control Techniques and Regulations for Greenhouse Gas Emissions



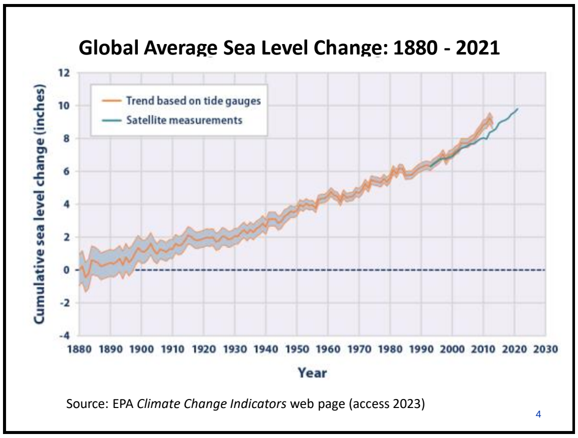
Effects: Snow and Ice

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.



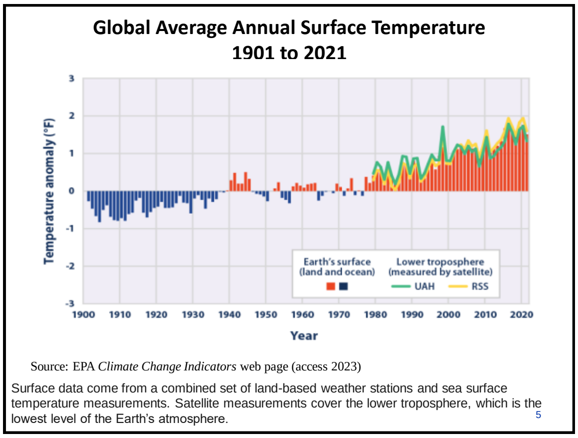
Muir Glacier in Alaska: Total Glacier Mass has Declined Around the Globe

Source: EPA Climate Change Web Site



Global Average Sea Level Change: 1880 - 2021

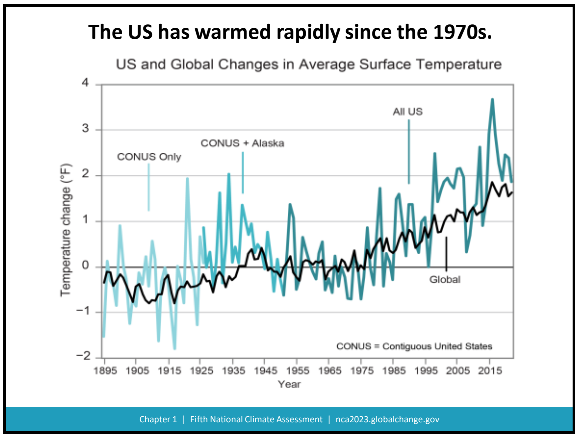
Source: EPA *Climate Change Indicators* web page (access 2023)



Global Average Annual Surface Temperature 1901 to 2021

Source: EPA *Climate Change Indicators* web page (access 2023)

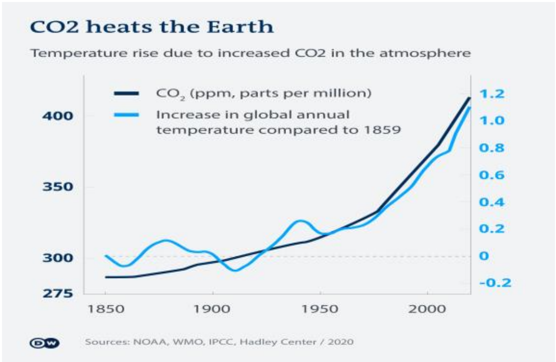
Surface data come from a combined set of land-based weather stations and sea surface temperature measurements. Satellite measurements cover the lower troposphere, which is the lowest level of the Earth's atmosphere.



The US has warmed rapidly since the 1970s.

US and Global Changes in Average Surface Temperature

Chapter 1 | Fifth National Climate Assessment | nca2023.globalchange.gov



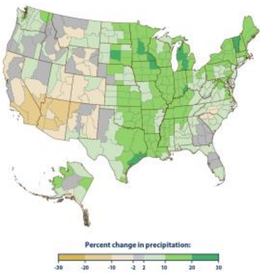
Over the past 50 years, more than 1200 billion tons of CO_2 have been emitted into the planet's atmosphere. As a result, the global average temperature has risen by 0.8 degrees in just half a century.

Predicted Effects of Global Warming: IPCC (2007 Report)

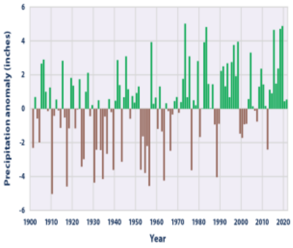
- An **increase in global average annual precipitation** during the 21st century, although changes in precipitation will vary from region to region.
- An **increase in the intensity of precipitation events**, particularly in tropical and high-latitude regions that experience overall increases in precipitation.
- **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).

Precipitation in the U.S., 1901–2021

Change in Precipitation in the United States, 1901–2021

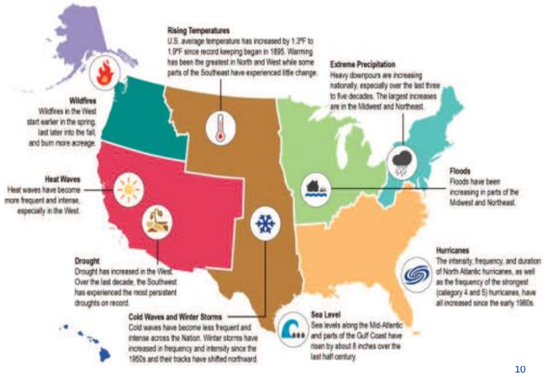


Precipitation in the Contiguous 48 States, 1901–2021



Source: EPA *Climate Change Indicators* web page (access 2023)

Climate Change Effects Across The U.S.



Rising Temperatures
U.S. average temperature has increased by 1.3°F to 1.9°F since record keeping began in 1895. Warming has been the greatest in North and West while some parts of the Southeast have experienced little change.

Extreme Precipitation
Heavy downpours are increasing nationally, especially over the last three to five decades. The largest increases are in the Midwest and Northeast.

Wildfires
Wildfires in the West start earlier in the spring, last later into the fall, and burn more acreage.

Heat Waves
Heat waves have become more frequent and intense, especially in the West.

Floods
Floods have been increasing in parts of the Midwest and Northeast.

Hurricanes
The intensity, frequency, and duration of North Atlantic hurricanes, as well as the frequency of the strongest (category 4 and 5) hurricanes, have all increased since the early 1980s.

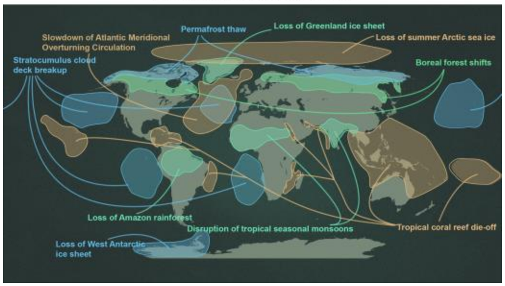
Drought
Drought has increased in the West. Over the last decade, the Southwest has experienced the most persistent droughts on record.

Cold Waves and Winter Storms
Cold waves have become less frequent and intense across the Nation. Winter storms have increased in frequency and intensity since the 1950s and their tracks have shifted northward.

Sea Level
Sea levels along the Mid-Atlantic and parts of the Gulf Coast have risen by about 8 inches over the last half century.

Continued warming could push some aspects of the Earth system past tipping points.

Possible Regional Tipping Elements

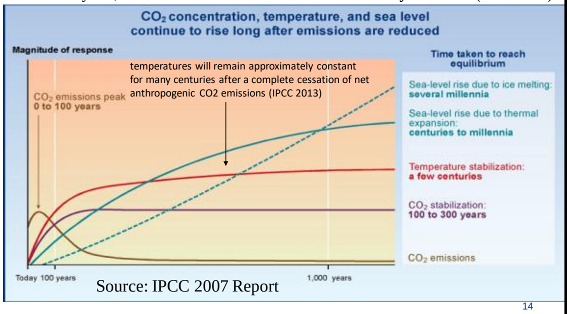


Scientists cannot rule out the possibility of still more dramatic shifts if certain tipping elements trigger rapid and irreversible changes.

Chapter 1 | Fifth National Climate Assessment | nca2023.globalchange.gov

---

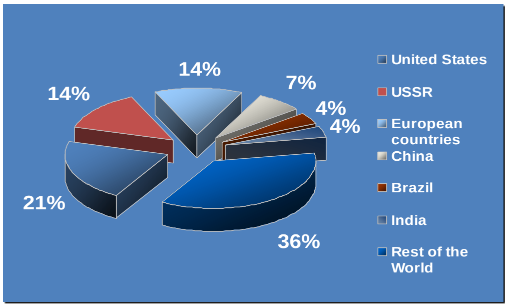
If CO_2 emissions stopped, it would take many thousands of years for atmospheric CO_2 to return to 'pre-industrial' levels due to its very slow transfer to the deep ocean and ultimate burial in ocean sediments. Surface temperatures would stay elevated for at least a thousand years, & **sea level would continue to rise for many centuries** (NAS 2014).



temperatures will remain approximately constant for many centuries after a complete cessation of net anthropogenic CO2 emissions (IPCC 2013)

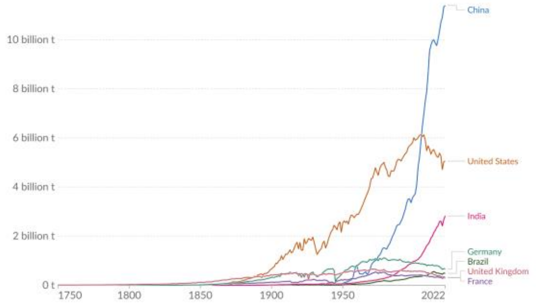
Source: IPCC 2007 Report

World Contributions to Global Warming in the 1980's



Annual CO_2 emissions

Carbon dioxide (CO_2) emissions from fossil fuels and industry[1]. Land-use change is not included.



Data source: Global Carbon Budget (2023)

OurWorldInData.org/co2-and-greenhouse-gas-emissions | CC BY

SOURCE ourworldindata.org

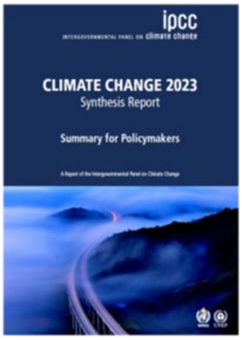
1. Fossil emissions: Fossil emissions measure the quantity of carbon dioxide (CO_2) emitted from the burning of fossil fuels, and directly from industrial processes such as cement and steel production. Fossil CO_2 includes emissions from coal, oil, gas, flaring, cement, steel, and other industrial processes. Fossil emissions do not include land use change, deforestation, soils, or vegetation.

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*:
  - 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*.
- All the UNFCCC annual conferences have failed to produce a significant legally binding treaty on curbing GHGs.
- The Dec 2015 conference (21st Session) in *Paris, France* Under the agreement:
  - Countries set their own targets for reducing CO_2 & other GHGs (targets are not legally binding)
  - Goal: limit warming to 2.7°F (1.5°C) by 2030 from pre-industrial times. (already warmed 2°F (1.1°C))

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
  - 2023 IPCC Synthesis Report available on-line



In 2006, global warming is making headlines in the U.S.

Does the CAA Regulate GHG?

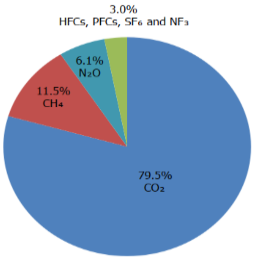
- April 2, 2007, <u>U.S. Supreme Ct.</u> held that EPA has authority to regulate CO_2 & other greenhouse gases (GHG) <u>from new motor vehicles</u>. (*Mass. v. EPA*)
- The Ct. determined that CO_2 & GHGs fit the CAA δ312 **definition of "air pollution"**

What GHGs are Regulated?

- CO_2
- CH_4 (methane)
- N_2O (nitrous oxide)
- Fluorinated GHGs
  - HFCs (hydrofluorocarbons)
  - PFCs (perfluorocarbons)
  - SF_6 (sulfur hexafluoride)
  - Other fluorinated gases

Percentages based on MMT CO2 Eq.

2021 U.S. GHGs Emissions



Source: Draft *Inventory of U.S. GHG Emissions & Sinks: 1990-2021 (2023)*

Global Warming Potentials (GWP)

(for 100 year time horizon)

Gas	GWP
CO_2	1
CH_4[a]	25
N_2O	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_2F_6	12,200
C_4F_{10}	8,860
C_6F_{14}	9,300
SF_6	22,800
NF_3	17,200

Source: IPCC (2007)

[a] The CH_4 GWP includes the direct effects and those indirect effects due to the production of tropospheric ozone and stratospheric water vapor. The indirect effect due to production of CO_2 is not included.

TPY of a GHG x GWP = # TPY CO_2 equivalent

Example Calculation of CO_2eqivalent

- 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

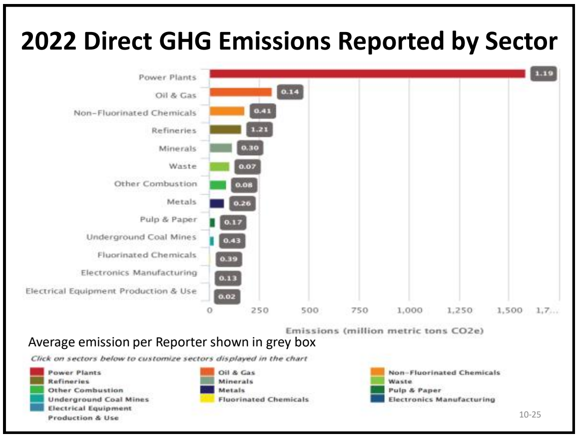
(50,000 TPY x 1) + (60 TPY x 25) + (1 TPY x 298) + (5 TPY x 675) + (3 TPY x 7390)

= 50,000 + 1,500 + 298 + 3,375 + 22,170 = 77,343 CO_{2e}

GHG Reporting Program

- On Oct 30, 2009, EPA issued 40 CFR Part 98, which *<u>requires reporting of GHG emissions</u>* from large sources and suppliers in the United States.
- **<u>Purpose</u>**: to develop policies and programs to address climate change.
- Under Part 98, *<u>suppliers</u>* of fossil fuels or industrial GHGs, *<u>manufacturers of vehicles</u> and engines*, <u>and</u> *<u>facilities that emit ≥ 25,000 metric tons per year</u> of GHG emissions* are required to <u>submit annual reports</u> <u>to EPA</u>. (first reports submitted in 2011)

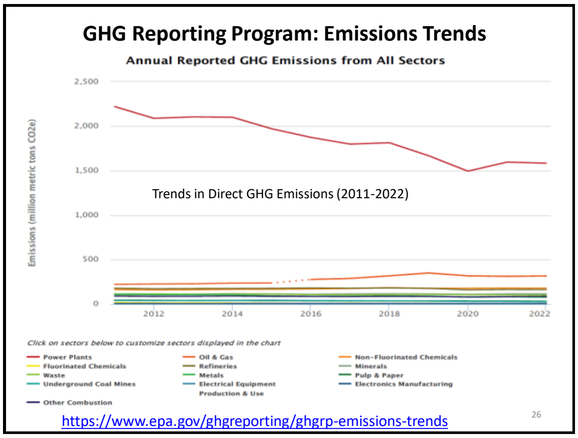
<u>https://www.epa.gov/ghgreporting</u>



2022 Direct GHG Emissions Reported by Sector

Average emission per Reporter shown in grey box

Click on sectors below to customize sectors displayed in the chart



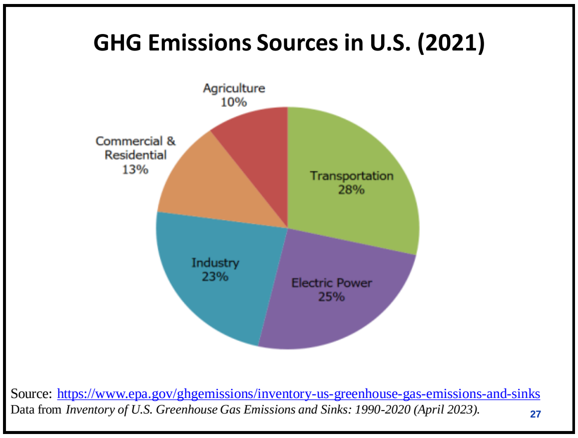
GHG Reporting Program: Emissions Trends

Annual Reported GHG Emissions from All Sectors

Trends in Direct GHG Emissions (2011-2022)

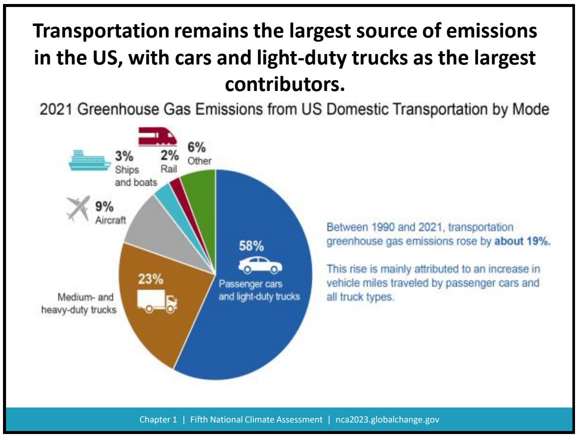
Click on sectors below to customize sectors displayed in the chart

https://www.epa.gov/ghgreporting/ghgrp-emissions-trends



GHG Emissions Sources in U.S. (2021)

Source: https://www.epa.gov/ghgemissions/inventory-us-greenhouse-gas-emissions-and-sinks
Data from *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2020 (April 2023).*



Transportation remains the largest source of emissions in the US, with cars and light-duty trucks as the largest contributors.

2021 Greenhouse Gas Emissions from US Domestic Transportation by Mode

Between 1990 and 2021, transportation greenhouse gas emissions rose by **about 19%.**

This rise is mainly attributed to an increase in vehicle miles traveled by passenger cars and all truck types.

Chapter 1 | Fifth National Climate Assessment | nca2023.globalchange.gov

EPA Regulations to Cut GHG Emissions for Cars & Trucks

- May 2010, EPA passed CO_2 emission standards for cars & trucks for model years (MY) 2012 to 2016.
- Oct 2012, EPA passed CO_2 emissions standards for cars & trucks: MY 2017 - 2025.
- April 2020, EPA amended these GHG emissions stds. with less stringent standards, for MY 2021 - 2026.
- Dec. 2021, EPA revised current GHG cars & trucks standards for MY 2023 to MY 2026. These standards are the strongest vehicle emissions standards ever established for these vehicles.

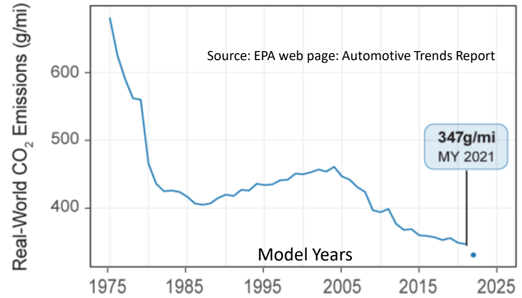
The
2022
EPA Automotive
Trends Report

Greenhouse Gas Emissions,
Fuel Economy, and
Technology since 1975

EPA United States Environmental Protection Agency
EPA-420-R-22-029 December 2022

EPA Web Page: https://www.epa.gov/automotive-trends

Average Estimated Real World CO_2 Emission Rate for All New Vehicles

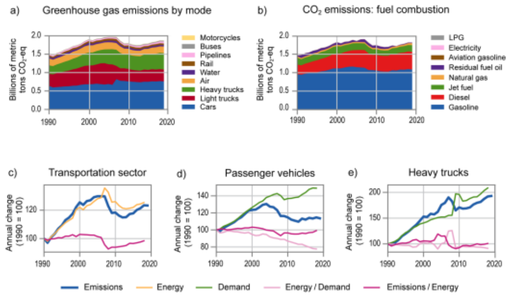


Source: EPA web page: Automotive Trends Report

EPA's first defines standards for each manufacturer's car and truck **fleets** based on the type of vehicles produced. Then the **manufacturers are required to calculate unique CO_2 standards** for these **fleets** for that model year. (*Credits* & *deficits* are used if the fleet average emissions performance is above or below the standards.)

Transportations emissions fell from 2007–2012 but have climbed since then.

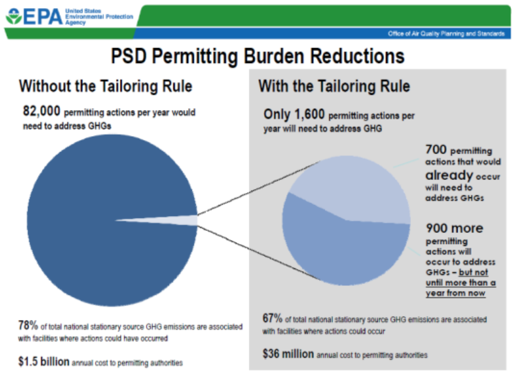
Trends in Transportation Emissions and Underlying Drivers



Chapter 32 | Fifth National Climate Assessment | nca2023.globalchange.gov

GHG Tailoring Rule (Vacated 2014)

- PSD: 250tpy or 100tpy (specific industries) "*any pollutant regulated under the CAA*"
- Title V: major source - with a PTE at least 100tpy *of any CAA regulated pollutant*
- Because these programs would require an extreme amount of new permits, in 2010 EPA passed the Tailoring Rule that *sets thresholds for GHG emissions* for when PSD & Title V permits will be required.
  - **PSD**: New:100,000 tpy of CO_2e ; Modified: 75,000 tpy of CO_2e
  - **Title V**: Existing or new sources with PTE ≥ 100,000 tpy of CO_2e
- In 2014, SCOTUS overturned Tailoring Rule



PSD Permitting Burden Reductions

Without the Tailoring Rule

82,000 permitting actions per year would need to address GHGs

78% of total national stationary source GHG emissions are associated with facilities where actions could have occurred

$1.5 billion annual cost to permitting authorities

With the Tailoring Rule

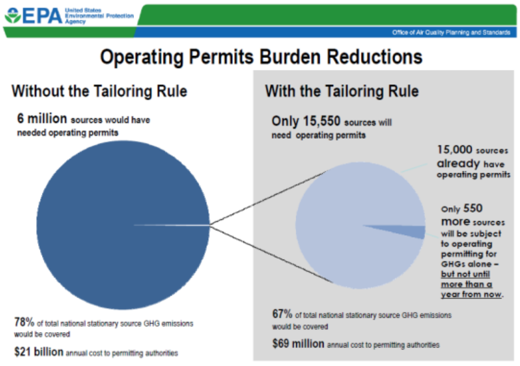
Only 1,600 permitting actions per year will need to address GHG

700 permitting actions that would **already** occur will need to address GHGs

900 more permitting actions will occur to address GHGs – but not until more than a year from now

67% of total national stationary source GHG emissions are associated with facilities where actions could occur

$36 million annual cost to permitting authorities



Operating Permits Burden Reductions

Without the Tailoring Rule

6 million sources would have needed operating permits

78% of total national stationary source GHG emissions would be covered

$21 billion annual cost to permitting authorities

With the Tailoring Rule

Only 15,550 sources will need operating permits

15,000 sources **already** have operating permits

Only **550 more** sources will be subject to operating permitting for GHGs alone – but not until more than a year from now.

67% of total national stationary source GHG emissions would be covered

$69 million annual cost to permitting authorities

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 <u>major</u> for any regulated NSR pollutant, BACT is required for <u>each regulated NSR pollutant</u> 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 CO_2e (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.

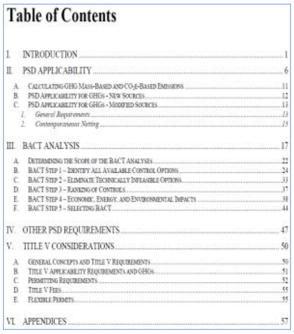
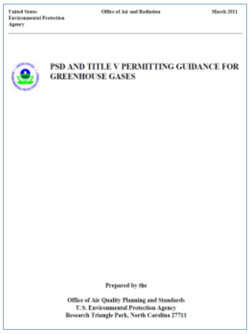


Table of Contents

I. INTRODUCTION 1
II. PSD APPLICABILITY 6
  A. Calculating GHG Mass-Based and CO_2e-Based Emissions 11
  B. PSD Applicability for GHGs - New Sources 12
  C. PSD Applicability for GHGs - Modified Sources 13
    1. *General Requirements* *13*
    2. *Contemporaneous Netting* *15*
III. BACT ANALYSIS 17
  A. Determining the Scope of the BACT Analyses 22
  B. BACT Step 1 – Identify All Available Control Options 24
  C. BACT Step 2 – Eliminate Technically Infeasible Options 33
  D. BACT Step 3 – Ranking of Controls 37
  E. BACT Step 4 – Economic, Energy, and Environmental Impacts 38
  F. BACT Step 5 – Selecting BACT 44
IV. OTHER PSD REQUIREMENTS 47
V. TITLE V CONSIDERATIONS 50
  A. General Concepts and Title V Requirements 50
  B. Title V Applicability Requirements and GHGs 51
  C. Permitting Requirements 52
  D. Title V Fees 55
  E. Flexible Permits 55
VI. APPENDICES 57



United States
Environmental Protection
Agency

Office of Air and Radiation

March 2011

PSD AND TITLE V PERMITTING GUIDANCE FOR GREENHOUSE GASES

Prepared by the

Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

https://www.epa.gov/nsr/clean-air-act-permitting-greenhouse-gases

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 <u>case-by-case</u> determination
  - Provides considerable discretion to the permitting authority
  - EPA does <u>not</u> prescribe GHG BACT for any source type
- EPA did publish GHG BACT <u>guidance</u> for EGUs
  - <u>Clean fuels</u> need to be considered
  - Feasibility of <u>CCS</u> needs to be considered in BACT analysis (presently too expensive to be selected)
  - Focus on <u>energy efficiency</u> as means of reducing GHGs
- NSPS serves as a floor for BACT determinations

BACT Determinations Steps

Step 1: <u>Identify</u> available pollution control options.

Step 2: Eliminate technically <u>infeasible</u> options.

Step 3: Rank controls by <u>control effectiveness</u>.

Step 4: Evaluate controls by <u>cost</u> 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.

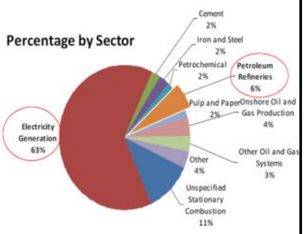
Carbon Capture and Storage (CCS)

- CCS is "available" and <u>should be considered in Step 1.</u>
- CCS may be <u>eliminated in Step 2</u> if technically infeasible for the proposed source;
  - i.e., *no space available for CO_2 capture equipment at an existing facility; right-of-ways prevent building a pipeline or access to an existing CO_2 pipeline; no access to suitable geologic reservoirs for sequestration or other storage options.*
- Currently, <u>CCS is an expensive technology</u> and makes the price of electricity from a power plant uncompetitive, even when underground storage of the captured CO_2 exists near the power plant. Therefore, <u>CCS will often be eliminated from consideration in Step4.</u>

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 <u>GHG control options,</u> particularly <u>in the assessment of (BACT)</u>**

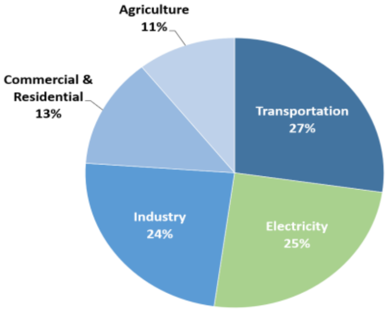
GHG Emissions from the Industrial Sector



Papers are located at: https://www.epa.gov/nsr/clean-air-act-permitting-greenhouse-gases

GHG from Power Plants (EGUs)

GHG Emissions Sources in U.S. (2021)



Source: https://www.epa.gov/ghgemissions/inventory-us-greenhouse-gas-emissions-and-sinks
Data from *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2021 (April 2023).*

NSPS: CAA Section 111

- CAA **Section <u>111(b)</u>:** 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 <u>111(d):</u>** Required for **existing** sources <u>upon promulgation of a 111(b) standard for new and modified sources</u> in specific circumstances (whose pollutants are not regulated under NAAQS or HAPs under the CAA).

Carbon Pollution Standards (NSPS) for <u>New, Modified and Reconstructed EGU</u>

- <u>August 3, 2015</u>: 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 <u>not apply to “*existing*”</u> units that have <u>not</u> been modified or reconstructed.
  - <u>Only regulates CO_2</u> emissions (will not regulate nitrous oxide or methane (both are GHGs)).
  - Has different standards for different types of new EGUs.

Carbon Pollution Standards (NSPS) for <u>New, Modified & Reconstructed</u> EGUs

- ***New and Reconstructed*** **Natural <u>gas-fired</u> 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*** **<u>gas-fired</u> 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.

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.
- 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 & reinstated the CPP rule
- June 30, 2022: **SCOTUS** held that the "Clean Power Plan rule" (2015) exceeded the agency's authority to regulate carbon emissions at existing EGUs. This is a "**major question**" that should be resolved by legislature not the EPA. They also reinstated the "Affordable Clean Energy" (ACE) rule.

Proposed Carbon Pollution Standards For EGUs

- May 11, 2023, EPA issued **proposed** CO_2 emission limits and guidelines for new & existing fossil fuel-fired power plants (EGUs) based on cost-effective and available control technologies.
  - **Repeal ACE rule**
    - EPA explains that since ACE was promulgated, CCS technology has improved and costs have fallen, and natural gas co-firing costs are lower due to a decrease in the cost differential between gas and coal.
  - Would set limits for **new** *gas-fired* *combustion turbines EGUs*
    - Three subcategories: base load, intermediate load, low load
    - Base load units have two pathways: 90% CCS in 2035 or 96% low-GHG hydrogen in 2038
    - These standards would replace the current 2015 standards
  - Set guidelines for **existing** coal, oil and gas-fired steam generating units, and certain existing gas-fired combustion turbines.

Proposed Carbon Pollution Emission Guidelines For Existing EGUs

- **Long-term Coal-fired Steam Generating Units** (elects to continue operation)
  - BSER: Carbon capture and storage with 90% CO2 capture by 2030
  - Emission limitation: 88.4% reduction in emission rate
- **Medium-term Coal-fired Steam Generating Units** (elect to cease operation by to 2040
  - BSER: co-firing 40% (by heat input) natural gas by 2030
  - Emission limitation: 16% reduction in emission rate
- **Imminent-term** (cease operation by 2032) **and Near-term Coal-fired Steam Generating Units** (cease operation by 2035 & operate at capacity < 20%)
  - BSER: Routine methods of operation and maintenance
  - Emission limitation: no increase in emission rate (presumptive standard of a unit-specific baseline)
- **Natural gas- and oil-fired steam generating units**
  - BSER: Routine methods of operation and maintenance
  - Emission limitation: no increase in emission rate (in general, fixed presumptive standards for intermediate load and base load units)

CO_2 Controls for New & Existing Coal-Fired EGUs

New Coal-fired EGUs

- Carbon capture and storage (CCS)
- Efficient technologies (some examples)
  - Ultra-supercritical steam conditions, pressurized fluidized bed, double steam reheat, coal drying, and FGD technology

Existing Coal-fired EGUs

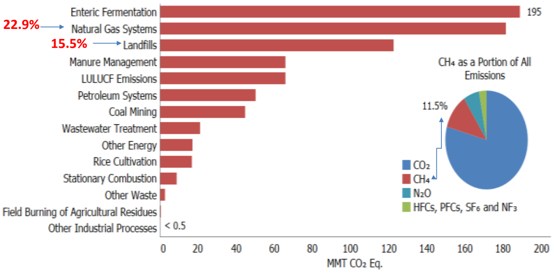
Increased thermal efficiency of power production

- 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.

Many CO_2 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

2021 Sources of Methane (CH_4)Emissions



Source: https://www.epa.gov/ghgemissions/overview-greenhouse-gases
Data: *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2021 (April 2023)*

Regulation of Methane Emissions from Landfills

- 2016: updates to NSPS to **reduce methane emissions from landfill gas** from **new** & modified municipal solid waste (MSW) landfills.
- 2019: EPA passed "*Trump Delay Rule*."(it delayed implementation of 2016 rule)
- April 2021: US App. Ct. **vacated** *"Trump Delay Rule."*
  - This reactivates 2016 methane rule for ***new*** & modified MSW landfills.
- May 17, 2021: EPA issued a final rule (under ∫111(d)) to reduce methane emissions from **existing** MSW landfills (rule contains emission guidelines).
  - Landfills will be required to install and operate a gas collection and control system.
  - EPA estimates about 1,600 existing landfills.

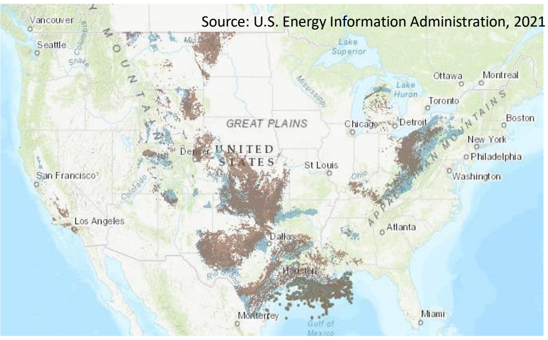
Regulation of Methane Emissions from the Oil and Natural Gas Industry

- 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

- In 2020, the Trump EPA rescinded the 2016 NSPS regulations, replacing them with a non-methane program. (because the 2016 rule did not meet the NSPS "*significant contribution*" requirement.)
- In 2021, Congress (under *Congressional Review Act)* reinstated the 2016 methane NSPS for new facilities.
- Dec. 2, 2023 - EPA final rule strengthens 2016 standards for methane and other air pollutants from **new, modified, & reconstructed sources**. It also, for the first time, includes Emissions Guidelines, which set procedures for states to develop plans to limit methane from **existing sources**.

Existing Oil & Gas Wells (lower 48 states)

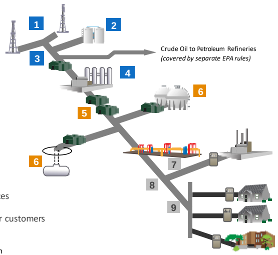


Source: U.S. Energy Information Administration, 2021

The final rule would extend regulatory coverage from new facilities & to over 300,000 existing facilities.

Crude Oil and Natural Gas Industry: Where EPA's Methane Rules Apply

The regulation would cover facilities in the onshore production, gathering, processing, and transmission and storage segments of the oil and gas sector.



🟦 **Production & Processing**

EPA's methane rule covers equipment & processes at:

1. Onshore well sites
2. Storage tank batteries
3. Gathering & boosting compressor stations
4. Natural gas processing plants

🟧 **Natural Gas Transmission & Storage**

EPA's methane rule covers equipment & processes at:

5. Compressor stations
6. Storage tank batteries

⬜ **Distribution**

(not covered by EPA rules)

7. Distribution mains/services
8. City gate
9. Regulators and meters for customers

Figure: Adapted from American Gas Association and EPA Natural Gas STAR Program

Required technology by the Rule*: Leak detection & repair, venting & flaring, storage tanks, & pneumatic controllers & pumps.*

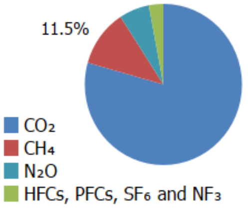
New “*Significant Contribution*” Test for GHG δ111(b) NSPS

- 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.**
- April 5, 2021 - The D.C. circuit **vacated this “significant contribution” final rule**.

What Percentage of U.S. Total GHG Emissions are from the Oil & Gas Industry?

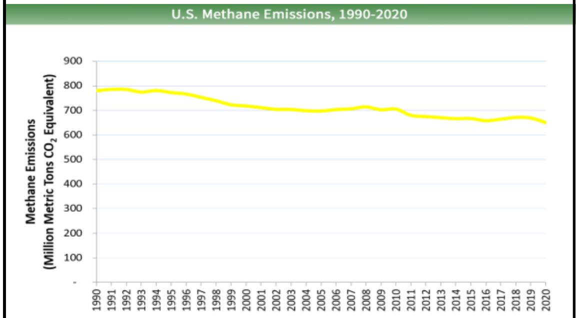
- All GHGs are in CO_2 equivalent
- 11.5% of all US GHGs are Methane
- 22.9% of U.S. Methane emissions are from Oil & Gas Industry (from earlier slide)
- Therefore, about **2.6% of total U.S. GHG emissions are from the Oil & Gas Industry.** (0.115 x 22.9% = 2.6%)

2021 CH_4 as a portion of U.S. GHGs Emissions



Source: EPA *Inventory of U.S. GHG Emissions 2021* (2023)

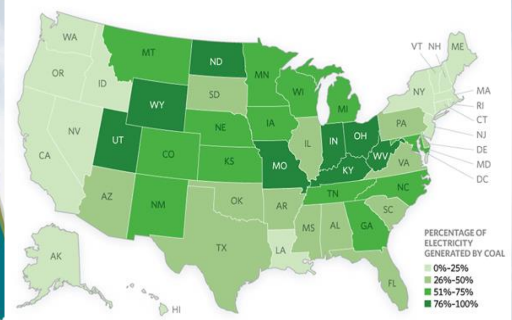
U.S. Methane emissions decreased by 17% between 1990 and 2020. During this time period, emissions increased from agricultural activities sources, while emissions decreased from landfills, coal mining, & natural gas and petroleum sources.



Source: https://www.epa.gov/ghgemissions/overview-greenhouse-gases

Data: *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2020* (*April 2022*)

Coal Provides the Majority of Electricity in 21 States



Air Pollution Training Institute | APTI

Electricity Net Generation in 2011

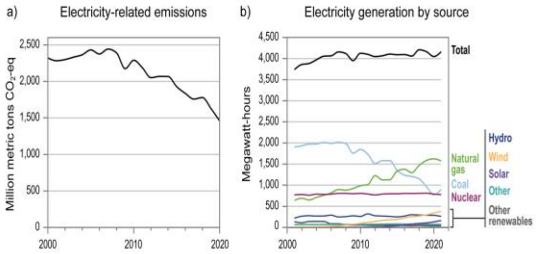
	Net Generation (Billion kWh)	Fuel Source Share
Coal	1,718	43.5%
Petroleum	28	0.7%
Natural Gas	926	23.5%
Other Gases	3	0.1%
Nuclear	790	20.0%
Hydroelectric	312	7.9%
Other	172	4.3%
Total	**3,949**	**100%**

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

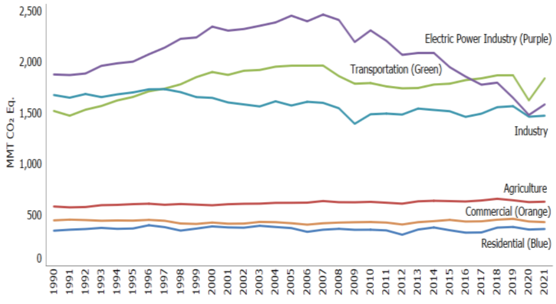
CO_2 emissions from electricity generation decreased by almost 40% between 2005 and 2020.

Trends in Electricity Generation by Source and Related CO_2 Emissions



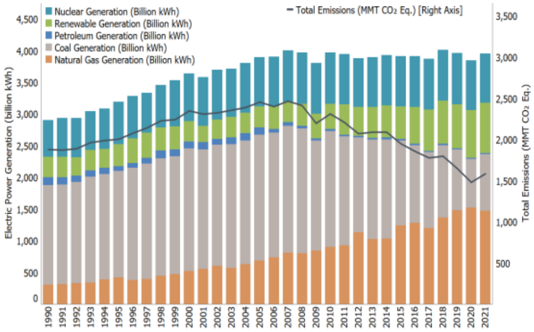
Chapter 32 | Fifth National Climate Assessment | nca2023.globalchange.gov

U.S. Greenhouse Gas Emissions Allocated to Economic Sectors (MMT CO2 Eq.)



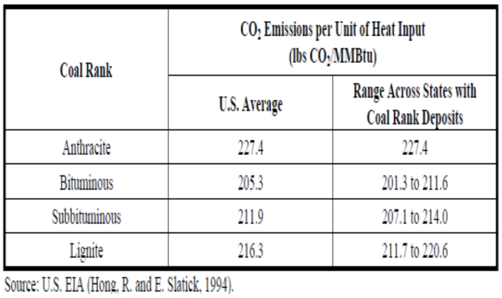
Source: Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990–2021 (2023)

Electric Power Generation and Emissions



Source: Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990–2021 (2023)

CO_2 Emission Factors for Coal

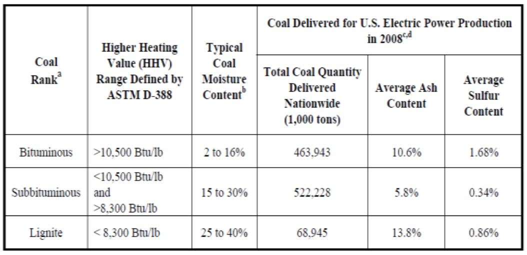


Coal Rank	CO_2 Emissions per Unit of Heat Input (lbs CO_2/MMBtu)	
	U.S. Average	Range Across States with Coal Rank Deposits
Anthracite	227.4	227.4
Bituminous	205.3	201.3 to 211.6
Subbituminous	211.9	207.1 to 214.0
Lignite	216.3	211.7 to 220.6

Source: U.S. EIA (Hong, R. and E. Slatick, 1994).

Bituminous is also better because it has less moisture than Subbituminous and lignite coals.

Selected characteristics for major coal ranks used in EGUs in the U.S.

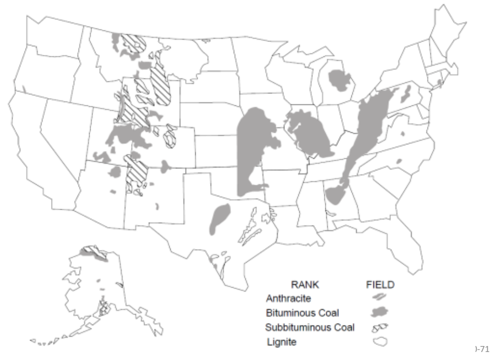


Coal Rank[a]	Higher Heating Value (HHV) Range Defined by ASTM D-388	Typical Coal Moisture Content[b]	Coal Delivered for U.S. Electric Power Production in 2008[c,d]		
			Total Coal Quantity Delivered Nationwide (1,000 tons)	Average Ash Content	Average Sulfur Content
Bituminous	>10,500 Btu/lb	2 to 16%	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.

Geographic Distribution of Coal Reserves



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* CO_2 emission factor (93.98 kg CO_2/MMBtu)
- Natural gas -*lowest* CO_2 emissions (53.06 kg CO_2/MMBtu)

Measures to Reduce GHG Emissions from Boilers

- <u>Alternative Fuels</u> – Biomass
  - Biomass has <u>less caloric content</u> than traditional fossil fuels
  - Biomass examples: *waste wood products, grasses, and green algae*
- <u>Co-firing</u>: Burning more than one fuel
  - <u>Biomass</u> or <u>gas</u> fuels contain less sulfur or mercury, therefore less SO_2 and mercury emissions.
  - <u>CO_2 emissions</u> are lower from co-firing biomass with coal than those from burning coal alone (EPA).
- <u>Fuel Switching</u>
  - Coal fired Systems
  - Oil-fired Systems

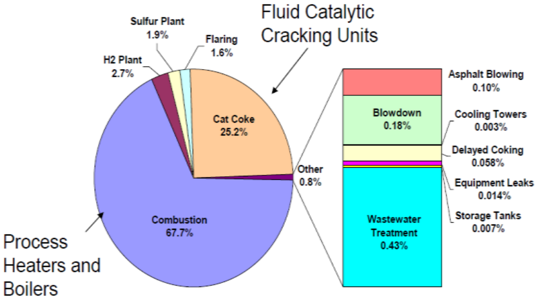
Key Characteristics of <u>Biomass Co-firing</u> Compared to Coal

- Biomass has <u>lower density</u>; hence it is bulkier and affects the fuel handling equipment (pulverizers, fuel transport and fuel feed systems).
- <u>High moisture content</u>, above 40 percent, increases the time required for complete combustion and affect boiler efficiency.
- Biomass is <u>more volatile</u> 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.
- <u>High alkali</u> biomass may contribute to formation of alkali sulfates, which make it easier to clean the boiler heating surface through soot-blowing.
- <u>Biomass degrades</u> over time, which means that it cannot be stored for long periods of time.
- Biomass may contain high concentration of chloride, causing <u>corrosion</u>, especially if sulfur is also present in the fuel (either in the biomass or the coal).

The Petroleum Refinery Sector

- 150 refineries in US
- About 20% of world crude production
- The nation's <u>third largest</u> industrial source of *GHGs* & the <u>second-highest</u> *industrial consumer of energy* (mostly fossil fuel for combustion)

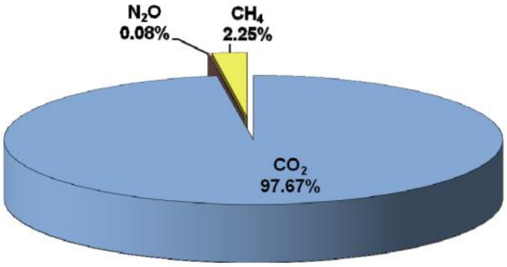
How much GHG do these sources emit?



Fluid Catalytic Cracking Units

Process Heaters and Boilers

GHG Emissions from Petroleum Refineries



GHG Emission Reduction Measures For Petroleum Refining

- <u>Energy Efficiency Improvements</u>
  - 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) <u>summarizes</u> the GHG reduction measures currently available for petroleum refining

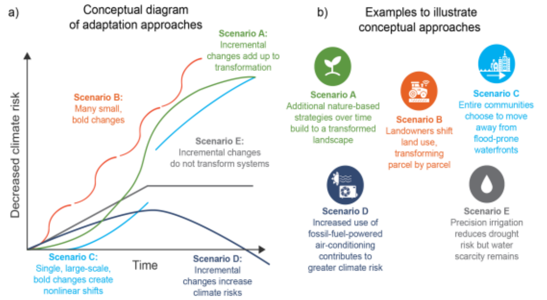
Carbon Dioxide Reduction Technologies

Adaption & Mitigation

- Adaptation and mitigation are <u>two strategies for responding to climate change</u>.
- **Adaptation** is the process of <u>adjustment to climate change</u> & its effects in order to either lessen harm or exploit beneficial opportunities.
  - 2021: EPA Passes "*Climate Adaptive Action Plan*"
    - https://www.epa.gov/climate-adaptation
- **Mitigation** is the process of <u>reducing emissions</u> or enhancing sinks of GHGs, so as to limit future climate change.

<u>Adaptation</u> may take many forms, but incremental adaptation involves small changes while transformative adaptation involves profound shifts.

Incremental and Transformative Adaptation Approaches

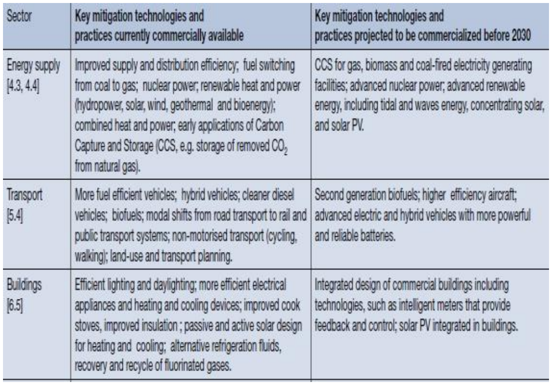


Chapter 1 | Fifth National Climate Assessment | nca2023.globalchange.gov

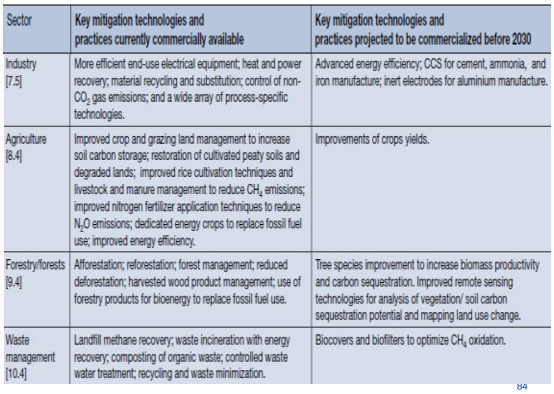
Possible Mitigating Solutions

- <u>Carbon cap & trade</u> system and <u>carbon tax</u>
- <u>Reducing the carbon intensity of the energy sector</u>
  - *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*
- <u>Conservation</u> of forests, wetlands, agriculture, land use

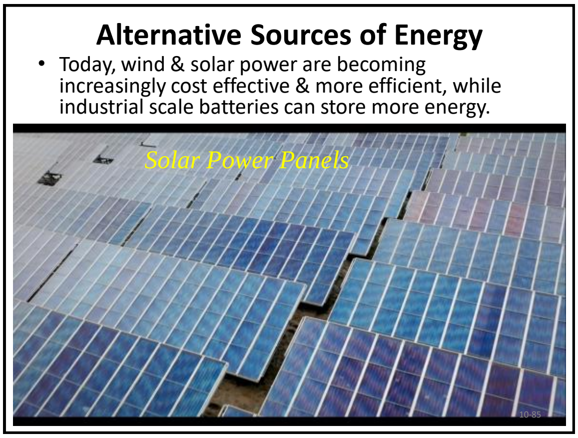
IPCC 2007 Report: Key Mitigation Technologies & Practices by Sector



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.



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_2O 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 biofilters to optimize CH_4 oxidation.



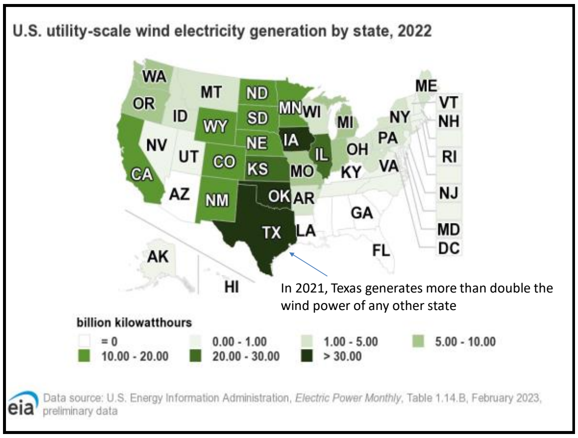
Alternative Sources of Energy

- Today, wind & solar power are becoming increasingly cost effective & more efficient, while industrial scale batteries can store more energy.

Solar Power Panels

Wind Power

Wind power makes up 8.4% of America's electricity generation & is the country's largest renewable source of electricity in 2021.



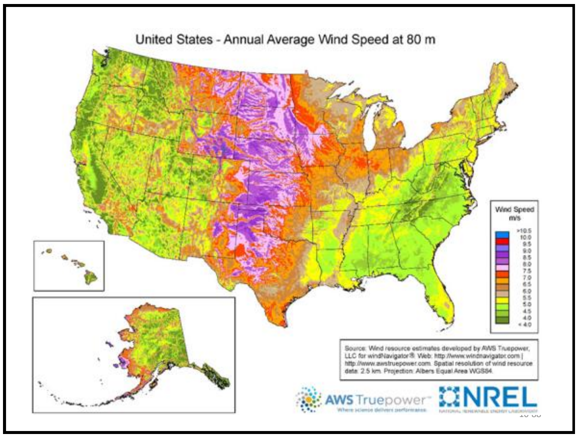
U.S. utility-scale wind electricity generation by state, 2022

In 2021, Texas generates more than double the wind power of any other state

billion kilowatthours

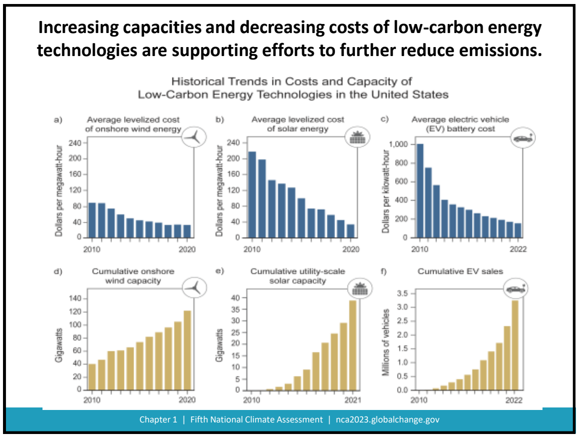
☐ = 0	☐ 0.00 - 1.00	☐ 1.00 - 5.00	☐ 5.00 - 10.00
☐ 10.00 - 20.00	☐ 20.00 - 30.00	■ > 30.00	

Data source: U.S. Energy Information Administration, *Electric Power Monthly*, Table 1.14.B, February 2023, preliminary data



United States - Annual Average Wind Speed at 80 m

Source: Wind resource estimates developed by AWS Truepower, LLC for windNavigator®. Web: http://www.windnavigator.com | http://www.awstruepower.com. Spatial resolution of wind resource data: 2.5 km. Projection: Albers Equal Area WGS84.



Increasing capacities and decreasing costs of low-carbon energy technologies are supporting efforts to further reduce emissions.

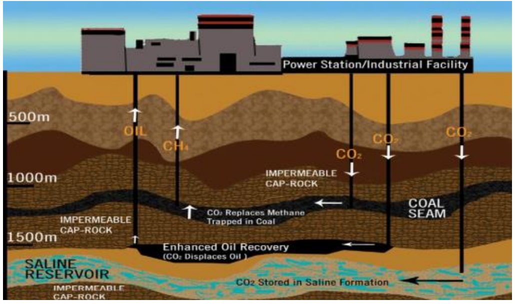
Historical Trends in Costs and Capacity of Low-Carbon Energy Technologies in the United States

Chapter 1 | Fifth National Climate Assessment | nca2023.globalchange.gov

Carbon Capture and Storage (CCS): A Three Step Process

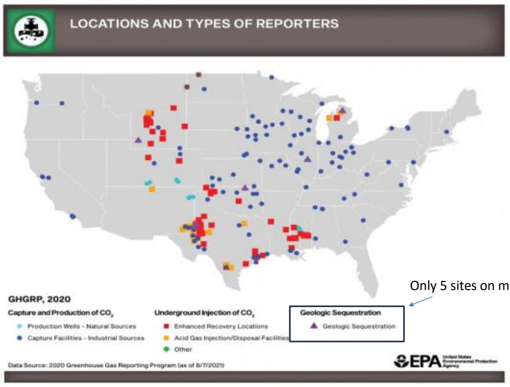
- Capture of CO_2 from power plants or industrial processes
- Transport of the captured & compressed CO_2 (usually in pipelines)
- Underground injection and geologic sequestration (also referred to as storage) of the CO_2 into deep underground rock formations.
  - These formations are often a mile or more beneath the surface and consist of porous rock that holds the CO_2. Overlying these formations are impermeable, non-porous layers of rock that trap the CO_2 and prevent it from migrating upward.

Carbon Capture & Sequestration Flow Chart



Geological carbon storage in <u>deep saline formations</u> is probably the most effective type of CO_2 sequestration because of the <u>relatively high storage capacity</u> compared to other geological options such as oil fields and coal seams.

CC&S U.S. Sites



Only 5 sites on map

CCS Processes: Capturing CO_2

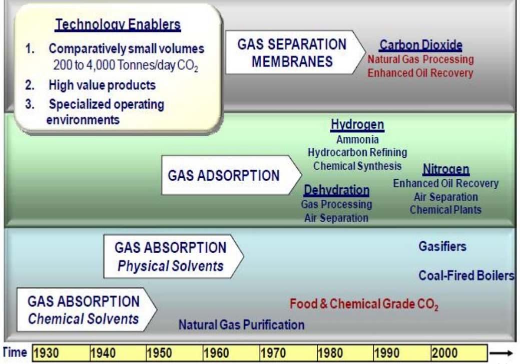
U.S. DOE is <u>developing</u> a commercially viable processes for <u>capturing CO_2 from EGUs</u>:

- Amine-based solvent systems (absorption)
- Solid sorbents (adsorption)
- Membrane-based capture
- Oxy-combustion

$C0_2$ is stripped from the flue gas by the <u>absorption process</u>. Upon saturation, the absorbent is regenerated by desorbing the CO_2 back to gaseous form. The removed CO_2 is then <u>compressed</u>, sent to storage and sequestered.

<u>Since the 1930s</u>, the CO_2 absorption processes has been used to produce food & chemical grade CO_2 from <u>gas streams containing 3 to 25 percent CO_2.</u>

Previous Experience with Removal of CO_2 from Gas Streams



From Appendix A of the 2010 Task Force Report on CCS

Problems with CCS (at Fossil Fuel Combustion Units)

- The <u>challenge from a separation perspective</u> is the *low driving force for CO_2 separation* because of:
  - low CO_2 partial pressure & low CO_2 concentrations &
  - large volume of gas to be treated.
- As a result, CCS <u>requires intensive energy use</u> and a high cost.
  - Carbon capture (using absorption process) at a pulverized coal-fired power plant will impose <u>an increase in the cost of electricity of approximately 80%.</u> (The majority is <u>attributable to parasitic power loss at 60%).</u>
- Source: March 2015 AWMA article (pg. 8)

Congressional Research Service Report January 2020

- Analysts expect that the <u>costs of CCS</u> (on new or existing facilities) are likely to total *several billion dollars per project*, <u>which could act as a barrier to future CCS</u> deployment without the continuation of subsidies.
- To date in the U.S., there are <u>nine DOE-supported CCS projects</u> (injected large volumes of CO_2 into underground formations).
- <u>Earthquakes induced by CO_2 injection could fracture the rocks in the reservoir</u> or, more importantly, the cap-rock above the reservoir.

2021 Report by the Government Accountability Office

- The US Department of Energy (DOE) has wasted hundreds of millions of dollars on failed carbon capture projects mostly because of "factors affecting their economic viability."

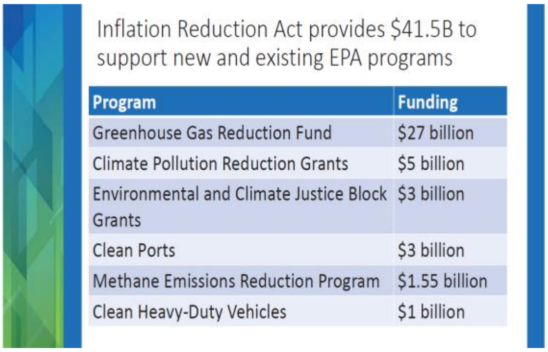
CO_2 Mineralization

- This is a chemical reaction that occurs when certain minerals are exposed to the CO_2, resulting in the CO_2 being transformed into rock.
- CO_2 mineralization processes fall under three main categories:
  - *Carbonation*: CO_2 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 ($CaCO_3$) -limestone,. (It can also be added to concrete).
  - *Novel Cements:* CO_2 is used as an ingredient within the cement. The CO_2 is mineralized within the cement as a solid carbonate, creating a new carbon negative cement.
- CO_2 mineralization is one of the only options that results in permanent storage of CO_2 as a solid. Other technologies merely delay the time that the CO_2 takes to go back into the atmosphere.

Pres. Biden's Inflation Reduction Act

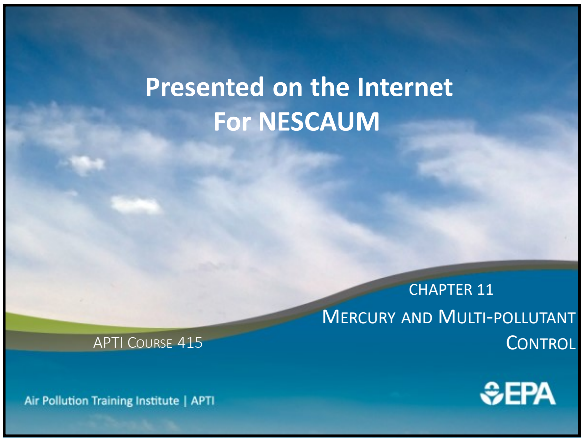
- Developing regulations to reduce methane from the oil and natural gas sector, leveraging proven best practices and technologies, as well as innovative and highly effective methane detection technologies.
- Creating new pollution standards for cars, trucks, and heavy-duty vehicles that, if finalized, would set the strongest pollution (GHGs) and other harmful air pollutants in EPA's history and contribute to meaningful worldwide progress toward clean transportation.
- Developing standards to significantly reduce GHG pollution from fossil fuel- fired power plants based on available and cost-effective technologies.
- Implementing a program to reduce the U.S. production and consumption of climate-disrupting "super-pollutants" known as hydrofluorocarbons (HFCs) by 85%, as required by bipartisan legislation enacted in 2020.

Source: *EM Article (AWMA), August 23, 2023*



Inflation Reduction Act provides $41.5B to support new and existing EPA programs

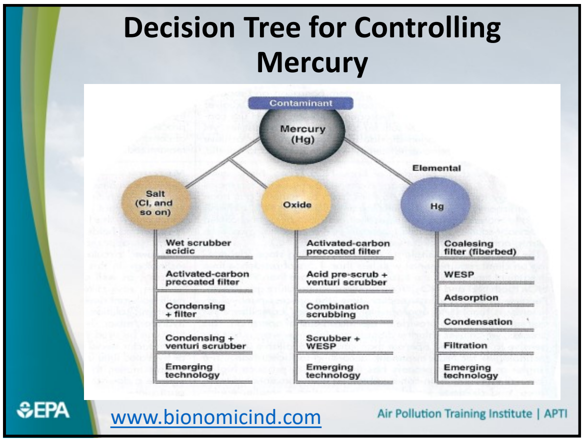
Program	Funding
Greenhouse Gas Reduction Fund	$27 billion
Climate Pollution Reduction Grants	$5 billion
Environmental and Climate Justice Block Grants	$3 billion
Clean Ports	$3 billion
Methane Emissions Reduction Program	$1.55 billion
Clean Heavy-Duty Vehicles	$1 billion



Presented on the Internet
For NESCAUM

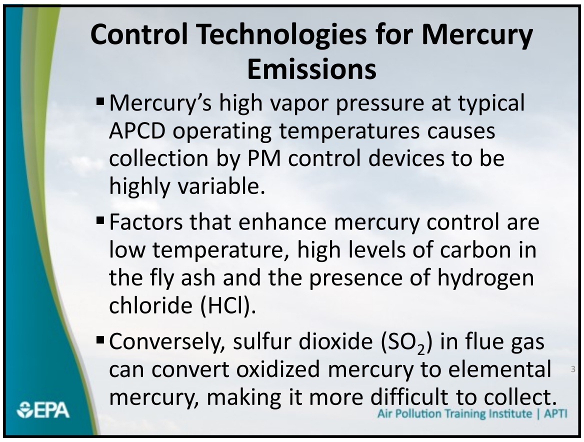
CHAPTER 11
MERCURY AND MULTI-POLLUTANT CONTROL

APTI COURSE 415



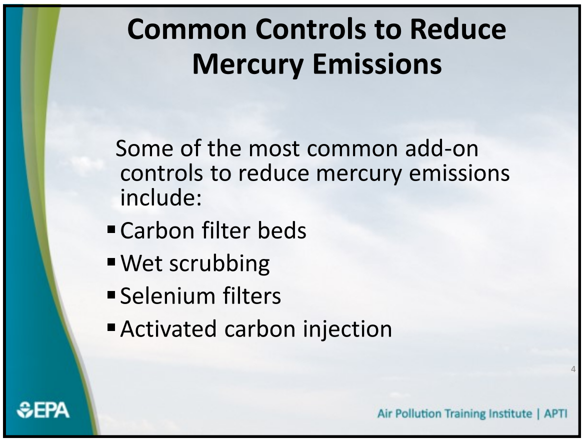
Decision Tree for Controlling Mercury

www.bionomicind.com



Control Technologies for Mercury Emissions

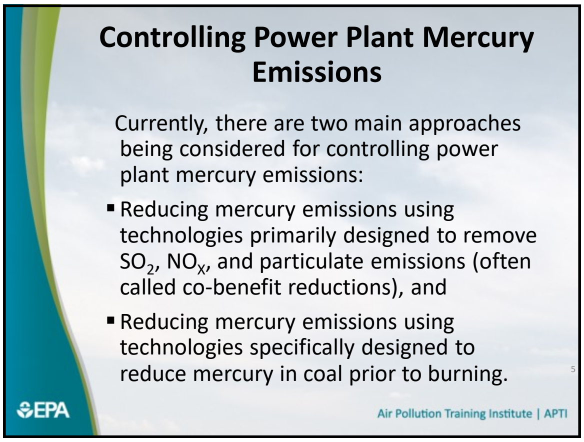
- Mercury's high vapor pressure at typical APCD operating temperatures causes collection by PM control devices to be highly variable.
- Factors that enhance mercury control are low temperature, high levels of carbon in the fly ash and the presence of hydrogen chloride (HCl).
- Conversely, sulfur dioxide (SO_2) in flue gas can convert oxidized mercury to elemental mercury, making it more difficult to collect.



Common Controls to Reduce Mercury Emissions

Some of the most common add-on controls to reduce mercury emissions include:

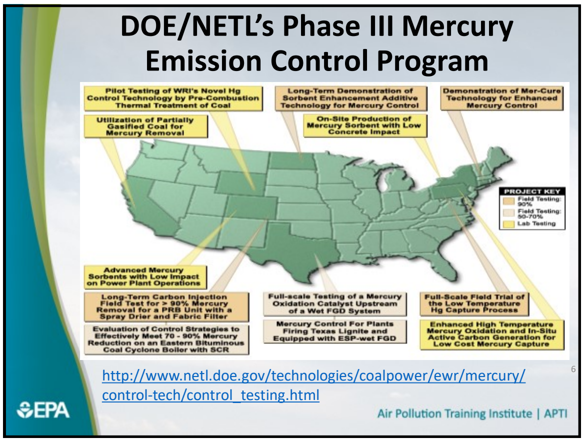
- Carbon filter beds
- Wet scrubbing
- Selenium filters
- Activated carbon injection



Controlling Power Plant Mercury Emissions

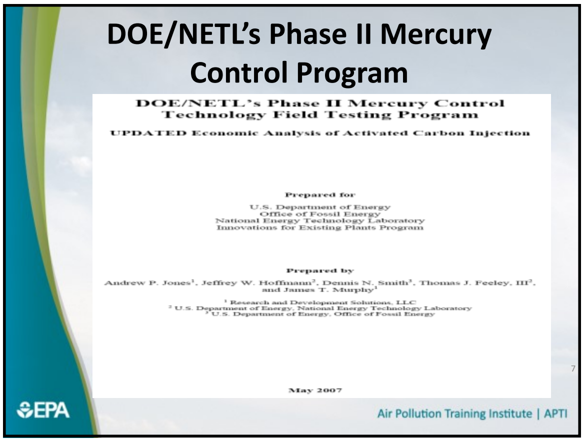
Currently, there are two main approaches being considered for controlling power plant mercury emissions:

- Reducing mercury emissions using technologies primarily designed to remove SO_2, 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.



DOE/NETL's Phase III Mercury Emission Control Program

http://www.netl.doe.gov/technologies/coalpower/ewr/mercury/control-tech/control_testing.html



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

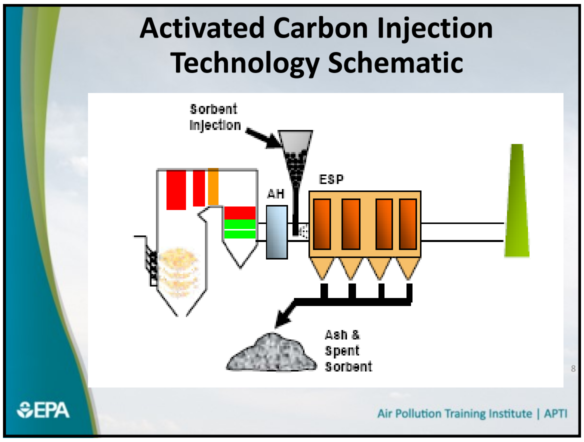
U.S. Department of Energy
Office of Fossil Energy
National Energy Technology Laboratory
Innovations for Existing Plants Program

Prepared by

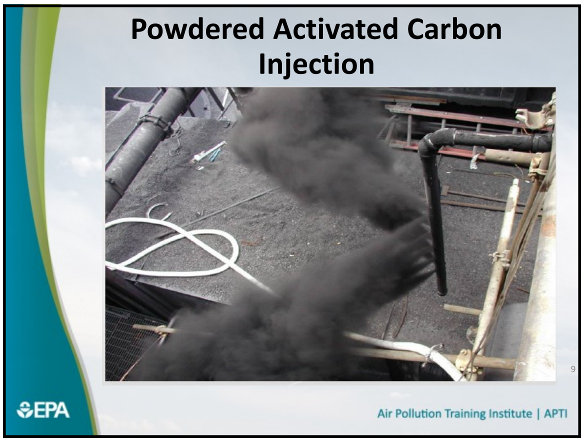
Andrew P. Jones[1], Jeffrey W. Hoffmann[2], Dennis N. Smith[3], Thomas J. Feeley, III[2], and James T. Murphy[1]

[1] Research and Development Solutions, LLC
[2] U.S. Department of Energy, National Energy Technology Laboratory
[3] U.S. Department of Energy, Office of Fossil Energy

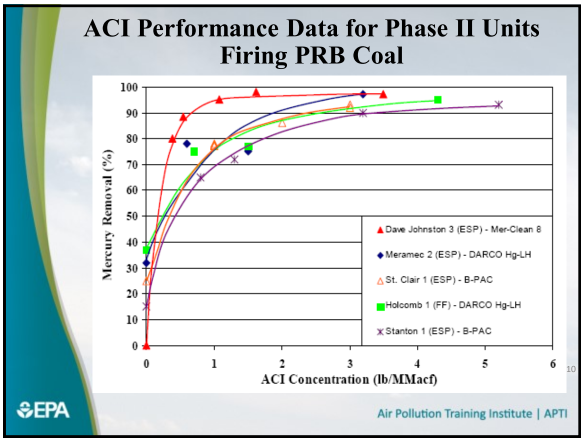
May 2007



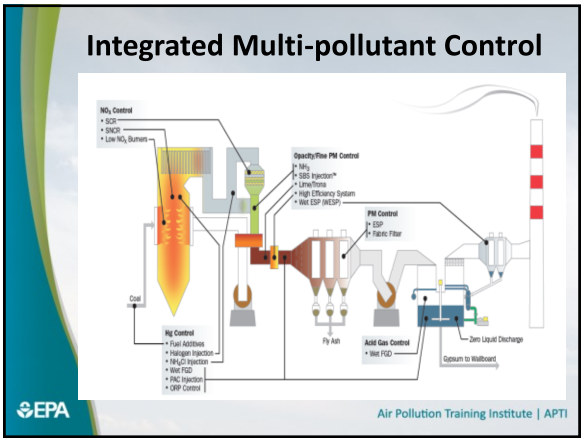
Activated Carbon Injection Technology Schematic



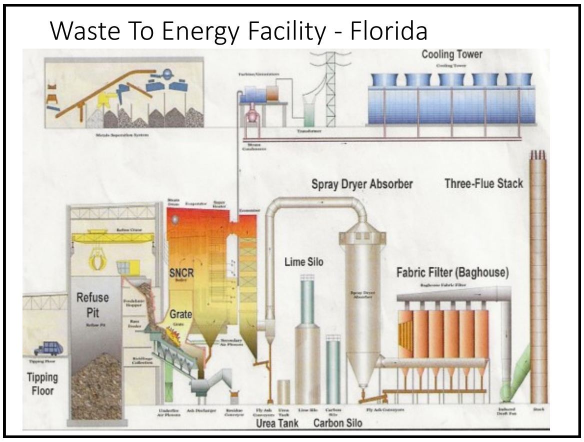
Powdered Activated Carbon Injection



ACI Performance Data for Phase II Units Firing PRB Coal



Integrated Multi-pollutant Control



Waste To Energy Facility - Florida

Waste To Energy Facility - Florida