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

January, 2023



Course 415 Control of Gaseous Emissions January 23 - 27, 2023

AGENDA

LOCATION

MODERATORS

Virtual Training for CenSARA Louis DeRose / William Franek				
DAY & TIME	SUE	JECT	SPEAKER	
Day One (Central	Time)	-1		
9:00	Intro Regio Con Cor	duction Seente Chapter 1	VV. Franek	
9.10 10·30	Basic Gas Coi BR		L. DERUSE	
10:45	LEL & Control	Types Chapter 2	L DeRose	
11:45	Air Pollution Contro	ol Systems Chapter 3	W. Franek	
	Includes Capture F	loods & Fan Designs		
1:15	ADJ	OURN		
Day Two				
9:00	Adsorption Sys	stems Chapter 4	W. Franek	
10:30	BR	EAK		
10:45	Adsorption Sys	tems (continued)	W. Franek	
12.10			W. Franek	
1.10	AB3			
Day Three				
9:00	Absorption Sys	tems (continued)	W. Franek	
10:45	BR	EAK		
11:00	Oxidation Sys	Stems Chapter 6	L. DeRose	
1.10	ADJ	OURN		
Day Four				
9:00	Condensation (Control Chapter 7	W. Franek	
10:45	BR	EAK		
11:00	Controls and Regulation	ons for GHGs Chapter 10	L. DeRose	
1:15	ADJ	UURN		
Dav Five				
9:00	Pre-Tes	st Review	L. DeRose	
9:30	Control of S	O2 Chapter 9	W. Franek	
10:45	BR	EAK		
11:00	Control of N	lOx Chapter 8		
12:30			vv. Franek	
	ADJ			
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	Sulfur Dioxide
- 1	Sulfur dioxide is a colorless gas
	<u>Formed</u> during the <i>combustion of sulfur containing fuel</i>
	 During combustion about 95% of the sulfur is converted to <u>sulfur dioxide</u>, while 0.5% to 2% is converted to <u>sulfur trioxide</u>
	<u>Reacts</u> with water to yield <i>sulfuric acid</i> , & sulfate compounds
	 At temperatures below 600°F, <u>sulfur trioxide</u> reacts with water to form sulfuric acid: SO₃+H₂O→H₂SO₄
	Because of the <u>corrosiveness</u> of sulfuric acid, it is important to keep gas streams at temperatures above the sulfuric acid dew point
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- Natural sources (volcanoes, fires, phytoplankton) produce sulfur dioxide, but <u>burning sulfur-rich fossil fuels—primarily coal,</u> <u>oil, and petroleum—is the main source</u> 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%.

452-2-10





























	Table	1-2. (Drgani	c HAP	Comp	ounds
	Compound	CAS Number	Compound	CAS Number	Compound	CAS Number
	Acetaldehyde	75070	Ethylene oxide	75218	Phosgene	75445
	Acetonitrile	75058	Ethylene glycol	107211	Phthalic anhydride	85449
	Acrolein	107028	Formaldehyde	50000	Styrene	100425
	Acrylonitrile	107131	Hexane	110543	Tetrachloroet hylene	127184
	Aniline	62533	Methanol	67561	Toluene	108883
	Benzene	71432	Methylene chloride	75092	2,4 Toluene diisocynate	584849
	13, Butadiene	106990	Methyl ethyl ketone	78933	1,2,4 Thrichlorobe nzene	120821
	Carbon disulfide	75150	Methyl isocyanate	624839	Trichloroethyl ene	79016
	Chlorobenzene	108907	Naphthalene	91203	Xylenes	95476
	Chloroform	67663	Nitrobenzene	98953		
	Ethyl benzene	100414	Phenol	108952		
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Solid Waste Combustion: CAA $\delta 129$

- δ 129 was added (1990 CAAA) & required EPA to pass NSPS for new & existing solid waste combustion units.
 - Municipal waste combustion units (MWC)
 - Hospital/medical/infectious waste incinerators
 - Commercial & industrial solid waste incinerators
 Other solid waste incinerators (small, residential, agricultural & construction waste, wood waste,
- crematories, & contaminated soil treatment waste)
 δ129 limits emissions of particulate matter, carbon monoxide, dioxins/furans, sulfur dioxide, nitrogen oxides, hydrogen chloride, lead, mercury, and cadmium
- δ129 <u>does not regulate</u> incineration of <u>hazardous</u> <u>waste</u>.

Recent Mercury Regulations

- <u>August 2010</u>: EPA issued NESHAP requiring reductions of mercury emission from *cement plants* (third-largest source of mercury air emissions in the U.S.)
- <u>Feb 17, 2011</u>: 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 <u>coal-fired power plants</u> to reduce <u>mercury</u> 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 <u>EPA must</u> establish a §112 mercury MACT for power plants (can't substitute a NSPS for it).

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Mercury Emissions from Power Plants

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

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State & Local Control Initiatives

- After 1850, the U.S. industrial revolution took hold; centering on steel, iron with abundant coal usage.
 - "Smoke is the incense burning on the altars of industry. It is beautiful to me." by a Chicago businessman in 1892.
 - <u>Public Policy favored business</u>: 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 <u>by 1912, most</u> <u>major U.S. cities followed</u>.

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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."



Contaminant Regulations

- Prior to1950 some states and local agencies enacted particulate pollutant control regulations (opacity) & were not aware of gaseous contaminants effects such as SO₂, VOCs, and HF.
- The <u>environmental awareness</u> 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
- <u>1963 CAA</u>: (compromise) Funding for state air programs
- <u>1965 CAAA</u>: Auto emission stds. (CO & HxCx)
- Debates: national stds. vs. regional stds. ambient air stds. vs. emission stds.
- <u>1967 Air Quality Act</u>: 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
- <u>1970 CAAA</u>: (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



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



New Source Performance Stds (NSPS)

- <u>EPA sets "NSPS"</u> for <u>new</u> sources that "contribute significantly" to air pollution.
 - 85 industrial categories identified (40 CFR Part 60)
 - Applies in <u>attainment and non-attainment areas</u>
- NSPS are <u>emission</u> or <u>performance standards</u> – new sources must meet standard once promulgated
- NSPS sets emission limits by application of the "best system of emission reduction" (BSER).

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- "costs" are considered
- NSPS to be <u>reviewed every 8 years</u>.

NSPS for Fossil Fuel-fired Electric **Power Generating Facilities** ce standards for fossil fuel-fired el Category Fuel Type Emission Limit Reduction Requirement Particulate Solid 0.015 lb.../106 BtuA 99.9% Matter 1.4 lb_m/MWh 95% SO₂ Liquid Coal Refus SO₂ 1.4 lb_m/MWh 0/1% <0.6 lb_/106 Btu 70% NO_v Solid 0.5 lb_/106 Btu 65% NOx 0.3 lb_m/10⁶ Btu 30% Liquid 0.2 lb_m/10⁶ Btu NO_x Gas 20% 1.0 lb_/MWh NO_v Liquid Backup Fuel[®] NOX 1.5 lb_/MWh : The owner/operator of a facility with a PM Continuous Emission Monitoring System (CEMS) may elect to comply with an alternate 0.14 lb_/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 €EPA based on design, equipment, work practice, or operational standard.







EPA conducted risk assessment) Air Pollution Training Institute | APTI

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Title V

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

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Table 2-1. Temperatur C	LEL and UE e and Ambi oncentratio	L at Room ent Oxygen n
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

Concent	ration (Con	tinued)
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

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 Speets or other

Material Data Safety Sheets or other references

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- Higher values of H correspond to the least soluble gas



Gaseous Contaminant Control Technologies

This section introduces:

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

Types of Control TechniquesAbsorption into liquids
Biological treatment
Adsorption onto solid surfaces
Chemical oxidation
Chemical reduction
Condensation of vapors

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Chapter Two Control Techniques for Gaseous Emissions





Important Factors Affecting Absorption

- Concentration dependence: obtain highest removal <u>efficiency</u> when the contaminant <u>concentrations are high</u> <u>(because this maximizes the driving force for mass</u> 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 <u>not impair</u> the removal efficiency for gaseous materials.
 - The <u>accumulation of particulate matter</u> on packed beds or at the outlet of spray nozzles may have an adverse effect on gas-liquid contact.

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- Adsorption
- Involves the transfer of contaminant <u>from the gas</u> to the <u>surface of a solid adsorbent</u>.
- <u>Two types</u> 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 <u>regenerative adsorption</u>, the contaminant is subsequently desorbed so that the adsorbent may be used in multiple cycles.

In <u>non-regenerative adsorption</u>, the adsorbent containing the contaminant is normally disposed of by land filling. Air Polluton Training Institute | APT



<section-header><section-header><list-item><list-item><list-item><list-item> Applicability of Adsorption Processes • Physical adsorption applicability: • Or organic compounds capture, suitability depends on how strongly the <u>adhesive forces</u> are that hold the molecule to the surface of the adsorbent. • Most organic compounds with <u>molecular weights between 50 and 200</u> can be collected with high efficiency. • Chemical adsorption provide high removal efficiency for a variety of <u>acid gases</u>. • Also, there are now applications for the control of vapor-phase <u>mercury</u>.













Chapter Two Control Techniques for Gaseous Emissions





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	Table 2	Table Cont	2-2: Su trol Tec	mmar chniqu	y of es	niques
	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
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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	
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- 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

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- Process flow diagrams generally <u>do not include</u>: 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



















	Ta Co	ble 3-4. Materials of onstruction Symbols
	CS	Carbon steel
	SS	Stainless steel
	FRP	Fiberglass reinforced plastic
	RL	Rubber lined
	N	Nickel alloy
	WD	Wood
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Hazardous	Waste Inc	inerator
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







data to the exten	t possible	specific baseline
Table 3-6. Gas Temperatur	e profile for the hazardo	ous waste incinerator (°
	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: L the evaporative coo	arge differences pler inlet and acro	in temperatures oss the baghouse B and/or in the





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Chapter 3 Air Pollution Control Systems



weakened by corrosion. Air Pollution Training Institute | APT

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
- 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

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Table 3-8. Static pressures and static pressure drops (in. W.C.) Static Pressure Present Baseline Incinerator primary -0.1 -0.12 chamber Duct B -1.0 -1.10 Mist eliminator -35.0 -38.0 Fan inlet (Duct D) -39.0 -40.0 -0.1 Stack -0.1 Static Pressure Drops Present Baseline Venturi scrubber 23.0 36.0 Mist eliminator 2.1 1.6 €PA Air Pollution Training Institute | APT

	Table 3-9. Gas temperatures (°F)					
		Present	Baseline			
	Incinerator secondary chamber	1860	1835			
	Duct B	200	197			
	Fan inlet	143	142			
	Stack	148	147			
\$epa	All temperatures are in close agreement. Air Pollution Training Institute APTI 3 - 35					



Chapter 3 Air Pollution Control Systems





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 addon 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 €PA €PA § 63.14);



















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F	Table 3-10. Commonly Recommended Transport Velocities									
	Type of Pollutant	Transport Velocity								
	Gases	≈ 1000 – 2000 ft/min								
	Light particulate loading	≈ 3000 – 3500 ft/min								
	Normal particulate loading	≈ 3500 – 4500 ft/min								
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Chapter 3 Air Pollution Control Systems

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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.























	Types of A	dsorbents
	Polar	Non-polar
	Silica gel	Activated Carbon
	Activated oxides	Polymeric adsorbents
	Molecular sieves	Zeolites (siliceous)
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	Table 4	-1. Phy Type	ysical P es of A	Propert dsorbe	ties of I Ints	Major			
	Table 4-1. Physical properties of major types of adsorbents.								
	Adsorbent ²	Internal Porosity (%)	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Bulk Dry Density (g/cm ³)	Mean Pore Diameter (Å)			
	Activated Carbon	55-75	600-1600	0.80-1.20	0.35-0.50	1500-2000			
	Activated Alumina	30-40	200-300	0.29-0.37	0.90-1.00	1800-2000			
	Zeolites (Molecular Sieves)	40-55	600-700	0.27-0.38	0.80	300-900			
	Synthetic Polymers ²		1080-1100	0.94-1.16	0.34-0.40				
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	Comp	ound: A	s Suit Adsor	able ptio	e for C n	Carbon	
	Organic Compound	Boiling Point ^e F(^e 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 Estas	292 (144.4)	106.2	INO	res	1.00	
	Ester Bubl Acctoto	259 (126 1)	116.2	No	Voc	7.60	
	Ethyl Acetate	171 (77.2)	88.1	Yes	Yes	2.50	
	Luiyi Adelate	1/1 (//.2)	00.1	103	163	2.50	
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	Comp	Compounds Suitable for Carbon Adsorption									
	Organic Compound	Boiling Point ºF(ºC)	Molecular Weight	Solubility in Water	Flammable Liquid	Lower Explosive Limit, % Vol.					
	Halogenated Carbon Tetrachloride Ethylene Dichloride Methylene Chloride Perchloroethylene Trichloroethylene	170 (76.7) 210 (98.9) 104 (40.0) 250 (121.1) 189 (87.2)	153.8 85.0 84.9 165.8 131.4	No No Yes No No	No Yes No No	N.F. 6.20 N.F. N.F. N.F.					
	Ketones Acetone Diacetone Alcohol Methyl Ethyl Ketone Methyl Isobutyl Ketone	133 (56.1) 293 (145.0) 174 (78.9) 237 (113.9)	58.1 116.2 72.1	Yes Yes Yes Yes	Yes Yes Yes Yes	2.60 - 1.80 1.20					
	Alcohols Butyl Alcohol Ethanol Propyl Alcohol	241 (116.1) 165 (73.9) 205 (96.1)	74.1 46.1 60.1	Yes Yes Yes	Yes Yes Yes	1.40 4.30 2.10					
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	Compounds Not Su Adsor	uitable for Carbon ption
	Reactive Compounds	High Boiling Compounds
	Organic Acids	Plasticizers
	Aldehydes	Resins
	Monomers (some)	Long Chain HCs (+C ₁₄)
	Ketones (some)	Glycols, Phenols, Amines
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Table 4-2. Characteristics ofChemisorption and Physical Adsorption

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

Conclusions















	Design Parameters					Geoditions During Test							
est 0.	511.0	(SCFH)	Components [®] In inlet stream	Adapathat a Loading (1b/hr)	Temperature (F)	Stean Flow (1b/hr)	Plowrate (SCPN)	Components in Inist Stream	Adaozbate Leading T (1b/hc)	(F)	Stear uce Flow (1b/hc)	Red Age (years)	Efficient (1)
1	٨	11,200	MEX - 602 Tolumna - 40	375	95	2,375	11,400	MEX - 1001	284	94	2,410	0.4	84.9 ^b
2	•	12,700	THF - 501 Toluena - 501	140	90	900	9,800	78F - 501 Toluene = 501	195 ⁶	74	600	2	99.7
3	٠	12,700	THF - 501 Tolvens - 501	140	90	900	9,500	THF - 751 Toluene - 251	140	90	840	3.0	93.3 ⁴
٠	c	23,000	THP, Toluene, HEK, HIBK, Cycloberanone	600	85	2,400	19,800	THF, Toluene, MEK, MEBK, Cyclobezanone	1,260 ^e	81	2,900	0.4	94.8°
5	D	22,000	Hexane - 1001	1,300	95	4,130	17,700	Benace - 1001	355	89	3,200	э	99.1
7	к	11,100	Toluene - 1001	204	100	1,170	9,100	Toluene - 100X	2496	104	3,000	5	97.6
	E	11,100	Toluena - 1001	204	100	1,170	7,800	Toluene - 100X	101	132 ^f	2,800	6.5	94.6 ⁸ .h
9	,	80,000	Toluene - 601 IPAC - 601	810	120	1,180	33,400	Toluene - 601 1PAC - 401	929 ⁶	91	3,400	0.2	97.5
10	,	80,000	Toluene - 601 IPAC - 401	810	120	1,180	33,960	Toluene - 601 IPAC - 402	892 ⁰	67	3,300	3.6	97.8
11	G	MR ^L	**	yik	MR	-	8,400	MEX - 951 HIBK, Toluens - 51	3,550	NR	10.	8 8.	98.9
12		NR	-	SR.	MR.	NR	48,800	Toluene - 100X	980	94	11,000	50	983
13	ı	75,000		**	**	-	61,200	Toluene - 301 Xylene - 41 Lactol Spirits - 661	1,279	100		**	95.8
14	J	10,010 -	MEK - 20-50X	180 -	<200	12,000	60,000	THF - 5,410 (1b					
		83,700	Cyclohesanone - 20-502 THF - 5-253	2,800			70,000	per day) Toluene - 3,210 MEX - 4,480	MK	120	12,000	Variable	99.4
15	ĸ	24,000	Toluena - 5-258 MEK - 1901	1,209	NR.	1,750	24,000	NEX - 1001	402 ^b	83	1,750	2	99.6
	L	28,000	Toluene - 953 Hexane - 51	860 - 1,070	120	3,000	28,000		HR	120	3,000	N/A ¹	99.5











































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.


























































	Table Ammo	5-1. E nia o	Equilit ver Ac	orium queou	Partia s Solu	al Pres	sure , mm	of Hg
	Wt. NH ₂ per 100 wts. H ₂ O	0°C	10°C	20°C	30°C	40°C	50°C	60°C
	20.0	64	103.5	166	260	395	596	834
	15.0	42.7	70.1	114	179	273	405	583
	10.0	25.1	41.8	69.6	110	167	247	361
	7.5	17.7	29.9	50	79.7	120	179	261
	5.0	11.2	19.1	31.7	51	76.5	115	165
	4.0		16.1	24.9	40.1	60.8	91.1	129.2
	3.0		11.3	18.2	29.6	45	67.1	94.3
	2.5			15.0	24.4			77.0
	2.0			12.0	19.3			61.0
	1.6				15.3			48.7
	1.2				11.5			36.3
	1.0							30.2
	0.5							
\$epa					Ai	r Pollution T	raining Inst	itute APTI



























A	Fable 5 mmor	5-1. E nia ov	quilib ver Aq	rium l ueou:	Partia s Solu	l Pres tions,	sure o mm	of Hg
	Wt. NH ₄ per 100 wts. H.O	0°C	10°C	20*C	30°C	40°C	50°C	60°C
1000	20.0	64	103.5	166	260	395	596	834
	15.0	42.7	70.1	114	179	273	405	583
1000	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							
PA					Air	Pollution Tr	raining Insti	itute APT















SEPA



- - Height of bed or number of trays for removal
- Conducted preferably on the specific source to be controlled
- Costly and time consuming











































Packing	Size, (in.)	Weight, (lb _m /ft ³)	Surface Area, (ft²/ft3)	Void Fraction, (%)	Packing Factor, F _p (ft²/ft³)
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

Packing	Size, (in.)	Weight, (lb _m /ft ³)	Surface Area, (ft²/ft³)	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 purp	oses only.	Packing factor for	the specific appli	ication should





















































Tray	Metric ¹	English ²
Bubble Cap	0.0162	0.1386
Sieve	0.0140	0.1198
Valve	0.0125	0.1069
(expressed in in / i	i / and ig(expresse	
 English (expressed ACFM and ρ_g expressed 	in ft ^{0.25} min ^{0.5} /lb ^{0.2} ssed in lb/ft ³	¹⁵) for use with Q i
 English (expressed ACFM and ρ_g expre Directly applicable 	in ft ^{0.25} min ^{0.5} /lb ^{0.2} ssed in lb/ft ³ when tray spacing	¹⁵) for use with Q i g is 24 inches and

























	Table 5-4. G	as Veloci Mist Elim	ties Through iinators 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
≎EPA	1.Source, Reference 1 2.Termed chevron in 3.Source, Reference 1	2 remainder of manual 3	Air Pollution Training Institute APTI



Alkali Requirements

- Absorption systems may require an alkali addition system if the gas stream is acidic
- Sulfur dioxide (SO₂), hydrogen chloride (HCl), and hydrogen fluoride (HF) are the most common acid gases
- Calcium hydroxide is the most common alkali material used to neutralize acid gases

SEPA

Reaction 5-1 SO₂ + Ca(OH)₂ + 0.5 O₂ \rightarrow (CaSO₄) + H₂O Reaction 5-2 2HCl + Ca(OH)₂ \rightarrow Ca⁺² + 2Cl⁻ + 2H₂O Reaction 5-3 2HF + Ca(OH)₂ \rightarrow Ca⁺² + 2F⁻ + 2H₂O

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Conditions That Could Create Gas- Liquid Maldistribution

Ejectors

€EPA

 Inadequate distribution of liquid across the ejector inlet

- Erosion of the ejector nozzle

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Typical Biofilte	r Performance Da	ta (CEP April 20	01 Biofiltration	n – 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/ft3-h	90%	Media filter
Hydrogen Sulfide Emissions Control (Laboratory Scale) (6)	H ₂ S	1.9-8.6 mg/kg-min (25-2,651 ppmv)	93%-100%	Media filter
Styrene Removal (Bench Scale) (7)	Styrene	Up to 22 g/m ³ -h, 0.5 min retention time	>99%	Biotrickling filter
Styrene Removal (Bench Scale) (7)	Styrene	Up to 100 g/m3-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	500 ppm-cfm/ft ² , 500-1,500 ppm-cfm/ft ²	>95% 30%70%	Media filter

ι	JS 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
\$epa	Air Pollution Training Institute APTI 5 - 158





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 <u>ceramic packed beds</u> that alternately store and release heat.
 - Particulate matter can plug the packed bed.
 - Can resist corrosion from acid gases.







Process Boilers Used for Thermal Oxidation

- Most plants equipped with one or more process boilers
- Combustion chamber <u>temperatures</u> in excess of 1800°F
- Flue gas <u>residence times</u> in excess of 1 to 2 seconds
- The <u>flow rate</u> 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 <u>long ductwork</u> (sometimes needed), VOC can condense

Flares

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



Flares Used for Thermal Oxidation

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

Smokeless Flares

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







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





Federal Flare Regulations: NSPS 40 CFR § 60.18

- <u>Pilot flame</u>: requires the presence of a continuous flame.
- <u>Max Tip Exit Velocity</u>: formula as function of the "heating value" of the fuel being combusted.
 - 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.
- <u>Min Net Heating Value</u> of the gas being combusted is 300 BTU/SCF for steam & air assisted. (200 BTU/SCF if the flare is non-assisted.)
- <u>No visible emissions</u> A five-minute exception period is allowed during any two consecutive hours.
- <u>Leak detection monitoring</u> 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 $u_{0f10}(v_{m27}) = \frac{H_f + 288}{317}$ $H_r(Btu/SCF) =$ The net heating value of the gas being combusted in the flare. $u_{0f10}(v_{m27}) = \frac{H_f + 288}{317}$ $H_r(Btu/SCF) =$ The net heating value of the gas being combusted in the flare. $u_{0f10}(v_{m27}) = \frac{H_f + 288}{317}$ $H_r(Btu/SCF) =$ The net heating value of the gas being combusted in the flare. $u_{0f10}(v_{m27}) = \frac{H_f + 288}{317}$ $H_r(Btu/SCF) =$ The net heating $u_{0f10}(v_{m27}) = \frac{H_f + 288}{317}$ $H_r(Btu/SCF) =$ The net heating $u_{0f10}(v_{m27}) = \frac{H_f + 288}{317}$ $H_r(Btu/SCF) =$ The net heating $u_{0f10}(v_{m27}) = \frac{H_f + 288}{317}$ $H_r(Btu/SCF) =$ The net heating $u_{0f10}(v_{m27}) = \frac{H_f + 288}{317}$ $H_r(Btu/SCF) =$ The net heating $u_{0f10}(v_{m27}) = \frac{H_f + 288}{317}$ $H_r(Btu/SCF) =$ The net heating $u_{0f10}(v_{m27}) = \frac{H_f + 288}{317}$ $H_r(Btu/SCF) =$ $H_r(Btu/SCF) =$ $H_r(Btu/SCF$



Safety and Operational Problems of Flares

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

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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.





The Inlet Temperature to the Catalyst Bed

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

	Ten	nperature, °F
Compound	CO3O4	Pt - Honeycomb
acrolein	382	294
n-butanol	413	440
n-propylamine	460	489
toluene	476	373
n-butyric acid	517	451
1, 1, 1-trichloroethane	661	>661
dimethyl sulfide	-	512

The inlet temperature to the catalyst bed must be above the catalytic ignition temperature required to give the desired destruction efficiency in the incinerator. It is impossible to predict the temperature needed for a *mixture of VOCs*. 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 metalmesh mat, ceramic honeycomb, or other ceramic matrix structure <u>designed to</u> <u>maximize catalyst</u> <u>surface area.</u>





Fouling & Masking: Reduction of Catalyst Activity

- Fouling: deposits on the surface of the catalyst and blocks the access of the organic compounds, may be reversible.
 - 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.

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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:
 - <u>Rate of mass transfer</u> (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 <u>controlling factor</u> is the <u>rate</u> <u>of mass transfer</u>.
- <u>Destruction Efficiency</u> is a function of *length of* the catalyst bed & mass transfer rates (see "Air Pollution Control" by Cooper & Alley 3rd Ed. page 344).







Space Velocity & Destruction Efficiency for Catalytic Incinerator System

				Space Velocity SV = Flow rate/	r- SV (hr⁻¹) 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 velo	cities (SV) rar	nge from 10,0	00 hr ^{_1} to 10	0,000 hr ⁻¹ .















Examples

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

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

Destruction Efficiency

- The means for estimating VOC <u>destruction</u> <u>efficiency</u> of thermal oxidation systems is a <u>function</u> of retention time, operating temperature, flame contact (turbulence), velocity.
- There is <u>no quantitative mathematical relationship</u> that relates efficiency to <u>these variables</u> because the <u>kinetics of combustion</u> 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 <u>best left to</u> <u>companies that have accumulated years of</u> <u>operating data</u> at a variety of conditions.

Auto-Ignition Temperature

- <u>VOC destruction rates</u> 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	o Ignition	Tempe	ratures	
Table 6-1. Auto-igniti	on temperatures.	Destruction Efficiency %	Degrees Above Auto-ignition	Residence Time (sec)
Compound	Auto-Ignition Temperature (°F)		Temp ^o F	
Acetone	870 970	95	300	0.5
Isopropyl Alcohol (IPA)	780	98	400	0.5
Methanol Methyl Ethyl Ketone	878 759	99	475	0.75
(MEK)	896	99.9	550	1.0
Xylene	850	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

- <u>Residence time</u>
- Amount of <u>fuel required</u> to reach the required temperature for complete combustion
- Proper <u>flow velocity</u> through the unit
 - Flow velocities of 20 to 40 ft./sec. (to promote turbulent mixing)
- VOCs should be less than <u>25% LEL</u>

Combustion Products and Gas Volumes

- In all high temperature combustion processes, a <u>complex</u> set chemical reactions occur simultaneously
- Objective is to $\underline{oxidize \ all \ carbon}$ to CO_2, hydrogen to H_2O, and sulfur to SO_2
- Represent the set of simultaneous reactions by the <u>single generalized reaction</u>

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

Minor Components in Waste Gas

- Sulfur
 - $\ge 98\%$ converted to SO₂
 - Small amount of SO₃ may be formed
- Chlorine –converted to HCl
- Fluorine –converted to HF
- Nitrogen (in waste gas) –may be converted to $\rm N_2,\, NO,\,$ or $\rm NO_2$
- Cl, F, N (in waste gas) <u>normally neglected</u> in material balance calculations

Composition of Air

- Oxygen is almost always supplied by air
- Air composition: 21% O₂ 79% N₂
- Neglect minor components in material balance calculations
- For Air: $x = \frac{0.79 \text{ moles of } N_2}{0.21 \text{ moles of } O_2}$ 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), <u>a</u> <u>sufficient supply of oxygen must be present</u> in the burner flame to convert all of the carbon to CO₂. This quantity of oxygen is referred to as the *stoichiometric* (or theoretical) *amount*.
- For example, 1 mole of methane (the major component of natural gas) requires 2 moles of oxygen for complete combustion

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

Lean and Rich

- Rich there is <u>insufficient O₂ available</u> for complete oxidation.
 - Partially oxidized products (e.g., CO) will be formed and flame temperature will be reduced
- Lean the amount of $\underline{O_2}$ exceeds the amount required for complete oxidation.
 - The excess air (un-reacted oxygen and nitrogen) will <u>carry away a portion of the heat</u> <u>released</u> by the combustion reactions, and therefore reduce the peak <u>flame temperature</u>.
- Normal operation -10% to 30% excess air

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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.
- <u>What is the residence time</u> in the combustion chamber? Assume that the fuel is 100% methane, and that the burner is operated at 125% of the stoichiometric requirement.

3-54

























Heat Terms & Heat Balance

- Sensible Heat (S) the addition or removal of heat which results in a <u>change in temperature</u>.
- Latent Heat (L) heat associated with a change of phase (i.e. vapor to liquid) without a change in temperature.
- Heat in (S₁ + HHV) = Heat out (S₂ + L + Heat_{available})
 - Assume no heat loss from system
 - $-S_1$ = heat from combustion of <u>organics in waste stream</u>
 - $-S_2$ = heat required to raise the temp of <u>excess air</u>
 - LHV (lower heating value of fuel) = HHV (higher heating value of fuel) minus L (heat of vaporization of water)
- Heat_{available} = LHV + S₁ S₂
- Heat_{available} = LHV + S₁ (no excess air)

Available Heat and Enthalpy

- Available Heat –that portion of the *energy liberated by oxidation that is available to heat the waste gas* to the outlet temperature.
- Enthalpy a thermodynamic term that establishes the energy content of a compound or stream relative to reference conditions (for our purposes: H = 0 at T_{ref}= 60°F)

Enthalpy (H) = U + PV

 Available heat will be read from a <u>graph</u> while enthalpy will be obtained from tables or estimated from specific heat data.



-	Table 6-2	2a. En	thalpie	es of C	ombus	tion
		Gas	ses, Bt	u/SCF		
	Gas Temp (°F)	02	N ₂	CO ₂	H ₂ O	Air
	60	0.00	0.00	0.00	0.00	0.00
	100	0.74	0.74	0.39	0.36	0.74
	200	2.61	2.58	0.94	0.85	2.58
	300	4.50	4.42	3.39	2.98	4.42
	400	6.43	6.27	5.98	5.14	6.29
	500	8.40	8.14	8.69	7.33	8.17
	600	10.40	10.01	14.44	11.81	10.07
	700	12.43	11.93	17.45	14.11	12.00
	800	14.49	13.85	20.54	16.45	13.95
\$epa				Air Pol	lution Training	Institute APTI 6-70

	Table 6- Gas	2a. En ses, Bt	thalpi u/SCF	es of C (Cont	Combus inued)	stion
	Gas Temp (°F)	02	N ₂	CO ₂	H ₂ O	Air
	900	16.59	15.80	23.70	18.84	15.92
	1000	18.71	17.77	26.92	21.27	17.92
	1100	20.85	19.78	30.21	23.74	19.94
	1200	23.02	21.79	33.55	26.26	21.98
	1300	25.20	23.84	36.93	28.82	24.05
	1400	27.40	25.90	40.36	31.42	26.13
	1500	29.62	27.98	43.85	34.08	28.24
	2000	40.90	38.65	61.71	47.91	38.99
	2500	52.43	49.67	80.15	62.60	50.07
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	Ga	ases, B	tu/lb _m	1		
Gas Temp (°F)	02	N ₂	CO ₂	H ₂ O	Air	
60	0.0	0.0	0.0	0.0	0.0	
100	8.8	6.4	5.8	17.8	9.6	
200	30.9	34.8	29.3	62.7	33.6	
300	53.4	59.8	51.3	108.2	57.8	
400	76.2	84.9	74.9	154.3	82.1	
500	99.5	110.1	99.1	201.0	106.7	
600	123.2	135.6	124.5	248.7	131.6	
700	147.2	161.4	150.2	297.1	156.7	
800	171.7	187.4	176.8	346.4	182.2	
	Table 6- Ga	-2b. Er ises, B	nthalpi tu/lb _m	es of C (Conti	ombus nued)	tion
------	----------------	--------------------	-------------------------------	-------------------	------------------	--------------------------
	Gas Temp (°F)	02	N ₂	CO ₂	H ₂ O	Air
	900	196.5	213.8	204.1	396.7	211.4
	1000	221.6	240.5	231.9	447.7	234.1
	1100	247.0	267.5	260.2	499.7	260.5
	1200	272.7	294.9	289.0	552.9	287.2
	1300	298.5	326.1	318.0	606.8	314.2
	1400	324.6	350.5	347.6	661.3	341.5
	1500	350.8	378.7	377.6	717.6	369.0
	2000	484.5	523.0	531.4	1003.1	509.5
	2500	621.0	672.3	690.2	1318.1	654.3
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Enthalpy Estimations Using <u>Average Specific</u> <u>Heat</u> & Calculation of the <u>Total Heat Rate</u>

• To simplify this calculation, an <u>average specific heat</u> value, C_{p} between T_1 and T_2 , can be used. This reduces the prior equation to:

$$\Delta \mathbf{H} = \mathbf{C}_{\mathbf{p}}(\mathbf{T}_2 - \mathbf{T}_1)$$

• The total heat rate (q) required is given by: $\label{eq:q} q = m \varDelta H = m C_p (T_2 - T_1)$

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

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Thermodynamic Fundamentals

$$\begin{split} \Delta h_p &= \Delta u + P\Delta V \ (Enthalpy \ (h) \ at \ constant \ P(pressure)) \\ W &= P\Delta V \ (for \ a \ gas) \ (W = work) \ (V = Volume) \\ \Delta h_p &= \Delta u + W \\ \Delta u &= \Delta h_p - W \\ \Delta E &= \Delta u + \Delta KE + \Delta PE \ (Conservation \ of \ Energy) \\ \Delta E &= \Delta u \ (for \ a \ closed, \ stationary \ system) \\ \Delta E &= Q - W \ (first \ Law \ of \ Thermodynamics) \\ \Delta u &= Q - W \ (substitution) \\ \Delta u &= Q - W \ (substitution) \\ \Delta u &= Q - W \ (substitution) \\ \mathbf{Q} &= \mathbf{\Delta} \mathbf{h}_p = \mathbf{m} \ \mathbf{\Delta} \mathbf{H}_p \\ Q \ (Btu/hr); \ m \ (Ibm/hr); \ H_p \ (Btu/Ibm) \ or \\ Q \ (Btu/min); \ m \ (SCFM); \ H_p \ (Btu/SCF) \end{split}$$



























































































		Table 7-1	. Antoine	Constants	
	Compound	Range (°C)	Α	В	с
	Acetaldehyde	-0.2 to 34.4	8.00552	1600.017	291.809
	Acetic acid	29.8 to 126.5	7.38782	1533.313	222.309
	Acetone	-12.9 to 55.3	7.11714	1210.595	229.664
	Ammonia	-83 to 60	7.55466	1002.711	247.885
	Benzene	14.5 to 80.9	6.89272	1203.531	219.888
	n-Butane	-78.0 to -0.3	6.82485	943.453	239.711
	i-Butane	-85.1 to -11.6	6.78866	899.617	241.942
	1-Butene	-77.5 to -3.7	6.53101	810.261	228.066
	Butyric acid	20.0 to 150.0	8.71019	2433.014	255.189
	Carbon	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 C	onstants	
	Compound	Range (°C)	А	в	с
	Chloroform	-10.4 to 60.3	6.95465	1170.966	226.232
	Cyclohexane	19.9 to 81.6	6.84941	1206.001	223.148
1000	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. A	Antoine (Constant	ts (Conti	nued)
		Table 7-1. /	Antoine Co	onstants	
	Compound	Range (°C)	А	В	с
	Formaldehyde	-109.4 to -22.3	7.19578	970.595	244.124
	Glycerol	183.3 to 260.4	6.16501	1036.056	28.097
	n-Heptane	25.9 to 99.3	6.90253	1267.828	216.823
	i-Heptane	18.5 to 90.9	6.87689	1238.122	219.783
	1-Heptene	21.6 to 94.5	6.91381	1265.12	220.051
	n-Hexane	13.0 to 68.5	6.88555	1175.817	224.867
	i-Hexane	12.8 to 61.1	6.86839	1151.401	228.477
	1-Hexene	15.9 to 64.3	6.8688	1154.646	226.046
	Hydrogen Cyanide	-16.4 to 46.2	7.52823	1329.49	260.418
	Methanol	14.9 to 83.7	8.08097	1582.271	239.726
	Methyl acetate	1.8 to 55.8	7.06524	1157.63	219.726
	Methyl chloride	-75.0 to 5.0	7.09349	948.582	249.336
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т	able 7.1	Antoing	Consta	nts (Con	tinued)	
	abie 7-1.	Table 7.1	- Consta		illinueu)	
		Table /-1	. Antome	Constants		
	Compound	Range (°C)	А	В	С	
	Nitrobenzene	134.1 to 210.6	7.11562	1746.586	201.783	
	Nitromethane	55.7 to 136.4	7.28166	1446.937	227.6	
1000	n-Nonane	70.3 to 151.8	6.93764	1430.459	201.808	
	1-Nonane	66.6 to 147.9	6.95777	1437.862	205.814	
	n-Octane	52.9 to 126.6	6.91874	1351.756	209.10	
	i-Octane	41.7 to 118.5	6.88814	1319.529	211.625	
	1-Octene	44.9 to 122.2	6.93637	1355.779	213.022	
	n-Pentane	13.3 to 36.8	6.84471	1060.793	231.541	
	i-Pentane	16.3 to 28.6	6.73457	992.019	229.564	
	1-Pentanol	74.7 to 156.0	7.18246	1287.625	161.33	
	1-Pentene	12.8 to 30.7	6.84268	1043.206	233.344	
	1-Propanol	60.2 to 104.6	7.74416	1437.686	198.463	
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	Table 7-1. Ar	ntoine Co	nstants	(Contin	ued)	
	Table 7-1. Antoine Constants					
	Compound	Range (°C)	A	в	с	
	Propionic acid	72.4 to 128.3	7.71423	1733.418	217.724	
	Propylene oxide	-24.2 to 34.8	7.01443	1086.369	228.594	
	Styrene	29.9 to 144.8	7.06623	1507.434	214.985	
	Toluene	35.3 to 111.5	6.95805	1346.773	219.693	
	1,1,1-Trichloroethane	-5.4 to 16.9	8.64344	2136.621	302.769	
	1,1,2-Trichloroethane	50 to 113.7	6.95185	1314.41	209.197	
	Trichloroethylene	17.8 to 86.5	6.51827	1018.603	192.731	
	Water	0 to 60	8.10765	1750.286	235.000	
	m-Xylene	59.2 to 140.0	7.00646	1460.183	214.827	
	o-Xylene	63.5 to 145.4	7.00154	1476.393	213.872	
	p-Xylene	58.3 to 139.3	6.9882	1451.792	215.111	
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APTI 415 Course Control of Gaseous Emissions











	Table 7-1. Typical Coefficients in Tul (use only for r	Overall Heat I bular Heat I ough estim	at Transfer Exchangers ations)
	Condensing Material (Shell Side)	Cooling Liquid	U, Btu/°F • ft²-hr
	Organic solvent vapor with high percent of noncondensable gases	Water	20 - 60
	High boiling hydrocarbon vapor (vacuum)	Water	20 - 50
	Low boiling hydrocarbon vapor	Water	80 - 200
	Hydrocarbon vapor and steam	Water	80 - 100
	Steam	Feedwater	400 - 1000
	Water	Water	200 - 250
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	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				
\$epa	N2O5	Dinitrogen pentoxide	5	White solid, very water soluble, decomposes in water				







































































Combustion Overfire Air (OFA)

- Staged combustion can be accomplished by using overfire air (OFA) ports. These are separate air injection nozzles located above the burners as indicated in the following figure.
- Burners are operated fuel-rich, and the overfire air ports maintain the remainder of the combustion.
- Approximately 15% to 20% of the combustion air flow is diverted to the over-fire air ports.

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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.

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Off Stoichiometric Combustion

- The following figure demonstrates the operating principles of the OFA method.
- A secondary air port or OFA injection port has been added above the primary air-fuel burner.
- Below this port is the fuel-rich zone (stoichiometric ratio less than 1) with peak temperatures lower than those associated with conventional combustion (stoichiometric ratio greater than 1).
- The injection of OFA allows the upper zone of the furnace to achieve a stoichiometric ratio greater than 1 (fuel-lean) and promotes the burnout of CO and hydrocarbons.
- If the secondary air ports are located too far from the burners, the residence time will be inadequate to allow for burnout of the CO and hydrocarbons.









Burners Out of Service (cont.)

- BOOS is similar to OFA, but does not require the installation of new OFA ports. The approach is to reduce air to several of the lower burners and to eliminate fuel in several upper level burners.
- This arrangement simulates an OFA air system because the reduced air in the lower burners creates a fuel-rich zone and the reduction of fuel in the upper ports creates a fuel-lean zone.
- Using BOOS on an existing boiler can result in a steam load reduction if the active fuel burners do not have the capacity to supply fuel for a full load.
- Therefore, BOOS is typically used on wall-fired units and other units that have the ability to operate at less than full load conditions.

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Flue Gas Recirculation (FGR)

- Flue gas recirculation (FGR) has been used to reduce thermal NOX emissions from large coal-, oil-, and gas-fired boilers.
- A portion (10% to 30%) of the flue gas exhaust is recycled back into the main combustion chamber by removing it from the effluent gas stream and mixing it with the secondary air entering the windbox that supplies the burners as shown in the following figure.
- The recirculated gas lowers the flame temperature and dilutes the oxygen content of the combustion air, thus lowering NOX emissions. of about 15% are typical with flue gas recirculation.

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.

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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.

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Staged Air Burners

- Staged air is an early LNB design that employs staged air within the burner.
- A general staged air burner design is shown in the following Figure 8- 13.
- This is a wall-fired burner (also called a *dual register burner*) where, in the first stage, fuel and primary air enter through the center tube of the burner.
- There may also be swirl vanes in the primary fuel zone to control fuel flow.
- The fuel-air mixture is injected into the burner to create a fuel-rich axial flame core in the primary combustion zone of the burner.

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Suppre	ssion Efficienci	ies
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

APTI Course 415 Control of Gaseous Emissions

CHAPTER 8 NITROGEN OXIDES CONTROL

















































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 Schnert Injection captures SO; at tradeate rates, downstream PM control dowice captures dry product. Rengenet - Trora, sodiam bicarbonate, hydratel mie Typora Fiur Typora - Most offen solid fuels (e., coals - lignite, sub-bituminous, bituminous) Co-benetitis - NOX and HC and HF reduction, Hg reduction, removal of chlorine, a procuro to dowinsframe.
Dry Scrubber with Fabric Filter	Method – Reagent - water react to capture acid gases and dry product captured in drowsteam fabric file Typical Fuel Types – Coal Capital Costs – High Capital Costs – High Costs – High Costs –
Wet Scrubber	Method – Reagent + water react to capture acid gases. Reagent – Limetschen, lime, causis soda Typical Fuel Types – Coat, petroleum coke, high sulfur fuel all Cablenetis – High Co-benetis – High est SO ₂ capture, high oxidized Hg and high HCI capture, PM capture
Wet Scrubber Upgrades	Method – Upgrade older sorubbers to provide performance approaching those of new scrubbers Reagant – Limistione Imme, etc. Typical Filed Types – Coal, patroleum coke, high sulfur fuel oil Capital Costs – Low to moderate Co-benefits – Same as wet scrubber







Non-Regenerative Desulfurization Systems

- In the majority of the throwaway processes an alkaline agent reacts with the SO₂ leading to a product that is discarded.
- Commonly used agents in this type of process are limestone (CaCO₃) and lime (CaO).
- In another type of throwaway process the agent is injected directly into the furnace, and the sulfated product is subsequently scrubbed out of the flue gas with water. Part of the SO_2 is captured chemically within the furnace, the rest in the scrubbing step. Air Pollution Training Institut (APTT) 9 - 18

SEPA



	Table 9-1. Common Processes for Boilers	Types of (see han	FGD dout)		
	Type of SO2 Control System	1989 (%)	2010 (%)		
100	Wet Scrubbers, Non-regenerativ	e (Throw-aw	ay)		
1000	Lime	23.6	18.4		
	Limestone	50.6	45.5		
	Dual Alkali	3.4	2.3		
	Sodium Carbonate	4.0	3.3		
	Regenerative (Saleable Product)				
	Magnesium Oxide	1.4	1.0		
	Wellman Lord	3.1	2.1		
	Lime/Limestone	4.0	4.7		
	Citrate/Undecided	0.0	0.3/7.8		
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		Reactions 9-9 through 9-15
	Limest	one Reactions
	9-9	$CaCO_3(s) \rightarrow CaCO_3(l)$
	9-10	$CaCO_3(l) \rightarrow Ca^{+2} + CO_3^{-2}$
	9-11	$\mathrm{CO}_3^{-2} + \mathrm{H}^+ \rightarrow \mathrm{HCO}_3^{-1}$
	9-12	$\mathrm{SO}_3^{-2} + \mathrm{H}^+ \rightarrow \mathrm{HSO}_3^{-1}$
	9-13	$SO_3^{-2} + 0.5 O_2(l) \rightarrow SO_4^{-2}$
	9-14	$Ca^{+2} + SO_3^{-2} + 0.5 H_2O \rightarrow CaSO_3^{-1/2}H_2O(s)$
	9-15	$Ca^{+2} + SO_4^{-2} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O(s)$
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CHAPTER 9 SULFUR OXIDES CONTROL



Summary (Continued)

- The majority of the sulfur entering with fuel into combustion systems is converted to sulfur dioxide.
 There are no combustion modifications that
- There are no combustion modifications that minimize the rate of sulfur dioxide generation. However, the reduction of fuel sulfur levels has a direct and proportional impact on the sulfur dioxide emissions.

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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).















IPCC produces the main reports on climate	
change, is a scientific intergovernmental	ipcc
body <u>set up in 1988 by:</u>	INTERCEVERANENTAL PAREL ON CONTINTS COURSE
 the World Meteorological Organization and 	CLIMATE CHANGE 2014
 the United Nations Environment Program. 	Synthesis Report
Their <u>function</u> 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. 	warden Billi
2007: 4 th Assessment Report (4 volumes).	
2014: 5th Assessment Report	
2022: 6th Assessment Report due	











GHG Reporting Program On Oct 30, 2009, EPA issued 40 CFR Part 98, which requires reporting of GHG emissions from large sources and suppliers in the United States. Purpose: to develop policies and programs to address climate change. Under Part 98, suppliers of fossil fuels or industrial GHGs, manufacturers of vehicles and engines, and facilities that emit ≥ 25,000 metric tons per year of GHG emissions are required to submit annual reports to EPA. (first reports submitted in 2011)

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EPA Regulations to Cut GHG Emissions for Cars & Trucks

- May <u>2010</u>, EPA passed CO₂ emission standards for cars & trucks for model years (MY) 2012 to 2016.
- Oct <u>2012</u>, EPA passed CO₂ emissions standards for cars & trucks: <u>MY 2017 - 2025</u>.
- April <u>2020</u>, EPA amended these GHG emissions stds. with <u>less stringent standards</u>, for MY 2021 2026.
- Dec. <u>2021</u>, EPA revised current GHG cars & trucks standards for MY 2023 to MY 2026. These standards <u>are the strongest vehicle emissions standards</u> ever established for these vehicles.





GHG Tailoring Rule (Vacated 2014) PSD: 250tpy or 100tpy (specific industries) "any pollutant regulated under the CAA" <u>Title V</u>: 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 CO₂e ; Modified: 75,000 tpy of CO₂e Title V: Existing or new sources with PTE ≥ 100,000 tpy of CO₂e In 2014, SCOTUS overturned Tailoring Rule

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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</u> <u>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 CO₂e (significance quantity).
 - This significant quantity was recognized by EPA in July, 2014 memo. EPA passed a *proposed rule* establishing this level on August 26, 2016.



BACT for GHGs

- BACT is a case-by-case 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 guidance for EGUs
 - Clean fuels 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

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BACT Determinations Steps

- Step 1: <u>Identify</u> available pollution control options.
- Step 2: Eliminate technically infeasible options.
- Step 3: Rank controls by control effectiveness.
- Step 4: Evaluate controls by <u>cost</u> and energy & environmental impacts.
- Step 5: Make the BACT selection.

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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.

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Carbon Capture and Storage (CCS)

- CCS is "available" and should be considered in Step 1.
- CCS may be <u>eliminated in Step 2</u> if technically infeasible for the proposed source;
 - i.e., no space available for CO₂ capture equipment at an existing facility; right-of-ways prevent building a pipeline or access to an existing CO₂ pipeline; no access to suitable geologic reservoirs for sequestration or other storage options.
- Currently, <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 CO₂ exists near the power plant. Therefore, <u>CCS will often be eliminated from consideration in</u> <u>Step4.</u>









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."
- ٠ CAA Section 111(d): Required for existing sources upon promulgation of a 111(b) standard for new and modified sources in specific circumstances (whose pollutants are not regulated under NAAQS or HAPs under the CAA).

CAA -43

Carbon Pollution Standards (NSPS) for New, Modified and Reconstructed EGU

- August 3, 2015: Because EGUs are the largest contributor of GHGs (33%), EPA says Section 111(b) "significantly contribute" requirement is satisfied. Therefore EPA passed a NSPS for GHG emissions for new, modified & reconstructed EGUs.
 - Does not apply to "existing" units that have not been modified or reconstructed.
 - Only regulates CO₂ emissions (will not regulate nitrous oxide or methane (both are GHGs)).
 - Has different standards for different types of new EGUs.

Carbon Pollution Standards (NSPS) for New, **Modified & Reconstructed EGUs**

- · New and Reconstructed Natural gas-fired stationary turbines
 - 1,000 lb CO2/MWh gross for all base load units
 - Non-base load units uses clean fuel-based input standard
 - base-load is determined by design efficiency and sales
- · Modified gas-fired units: EPA is not setting a standard at this time.

Carbon Pollution Standards (NSPS) for New, Modified & Reconstructed EGUs

- New coal-fired Energy Generating Units
 - 1,400 lb CO2/MWh gross limit & include partial carbon capture and storage (CCS)
- Modified coal-fired EGUs:
 - applies only to modifications resulting in an increase of hourly CO2 emission of more than 10 percent
 - will be required to meet a standard consistent with its best historical annual performance during the years from 2002 to the time of modification.
 - no CCS required
- Reconstructed coal-fired EGUs:
 - 1,800 lb CO2/MWh-gross limit for sources with heat input greater than 2,000 MMBtu/hr.
 - 2,000 lb CO2/MWh-gross limit for sources with a heat input of less than or equal to 2,000 MMBtu/hr.

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 A 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
- Feb, 2021: EPA asked app. Ct. & was granted a "stay" on the CPP rule so that it could consider a new 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. CAA -4





Many CO₂ Reduction Opportunities

- Heat rate improvements
- Fuel switching to a lower carbon content fuel
- Integration of renewable energy into EGU operations
- Combined heat and power
- Qualified biomass co-firing and repowering
- Renewable energy (new & capacity uprates)
- Wind, solar, hydro
- Nuclear generation (new & capacity uprates)
- Demand-side energy efficiency programs and policies
- Demand-side management measures
- Electricity transmission and distribution improvements
- · Carbon capture and utilization for existing sources
- Carbon capture and sequestration for existing sources



Regulation of Methane Emissions from Landfills

- <u>2016</u>: updates to NSPS to reduce methane emissions from landfill gas from <u>new</u> & modified municipal solid waste (MSW) landfills.
- <u>2019</u>: EPA passed "Trump Delay Rule." (it delayed implementation of 2016 rule)
- <u>April 2021</u>: US App. Ct. vacated "Trump Delay Rule."
 This reactivates 2016 methane rule for new & modified MSW landfills.
- <u>May 17, 2021</u>: EPA issued a final rule (under [111(d)) to reduce methane emissions from <u>existing</u> 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.

CAA -52

Regulation of Methane Emissions from the Oil and Natural Gas Industry

 <u>May 16, 2016</u>: EPA passed <u>NSPS</u> rules that will <u>curb</u> <u>emissions of methane</u>, 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 <u>2020</u>, the Trump EPA <u>rescinded</u> the 2016 NSPS regulations, replacing them with a <u>non-methane program</u>. (Reason: EPA did not establish criteria to support its *"significant contribution"* finding.)
- June 30, 2021, Congress passed a Congressional Review Act resolution disapproving the Trump rescission, thereby reinstating the 2016 methane NSPS for new facilities.
- <u>November 2, 2021</u> EPA passed a <u>proposed rule</u> that would reduce methane & other pollutants from both new & existing sources in the oil and natural gas industry.
 - <u>November 8, 2022</u> EPA passed a <u>supplemental proposal</u> that will strengthen and expand its November 2021 proposal.





New "Significant Contribution" Test for GHG δ 111(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.
 - EPA <u>also determined that EGU source category</u> <u>contributes significantly</u> because their GHG emissions are substantially above the 3% threshold. (The EGU source category represents over 25% of total U.S. GHG emissions.)
- <u>April 5, 2021</u> The D.C. circuit vacated this "significant contribution" final rule.







	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%





Coal Pank	CO ₂ Emissions per Unit of Heat Input (Ibs CO ₂ /MMBtu)		
Coar Kairk	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	





















Adaption & Mitigation

- Adaptation and mitigation are <u>two strategies for</u> responding to climate change.
- Adaptation is the process of <u>adjustment to climate</u> <u>change</u> & its effects in order to either lessen harm or exploit beneficial opportunities.
 - i.e. farmer planting more drought-resistant crops to a city ensuring that new coastal infrastructure can accommodate future sea level rise.
- Mitigation is the process of <u>reducing emissions</u> or enhancing sinks of GHGs, so as to limit future climate change.

452-2-75

Possible Mitigating Solutions

- <u>Carbon cap & trade system and 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

452-2-76

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; rerewable heat and power (hydpopwer, 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-fred 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 biofuleis; 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 stows; improved insulation; passive and active solar design for heating and cooling; alternative enfigration 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 orop and grazing land management to increase sol carbon storage, restoration of cultivated peaky solis and degraded lands; improved rice cultivation techniques and investock and manue management to reduce CH4, emissions; improved nitrogen fattilizer application techniques to reduce N ₂ O emissions; dedicated energy crops to replace fossil fuel use; improved energy efficiency.	Improvements of crops yields.	
Forestry/forests [9.4]	Afforestation; reforestation; forest management; reduced deforestation; harvested wood product management; use of forestry products for bioenergy to replace fossil fuel use.	Tree species improvement to increase biomass productivity and carbon sequestration. Improved remote sensing technologies for analysis of vegetation/ soil carbon sequestration potential and mapping land use change.	
Waste management [10.4]	Landfill methane recovery; waste incineration with energy recovery; composting of organic waste; controlled waste water treatment; recycling and waste minimization.	Biocovers and biofilters to optimize CH_4 oxidation.	







Carbon Capture and Storage (CCS): A Three Step Process

- <u>Capture</u> of CO₂ from power plants or industrial processes
- <u>Transport</u> of the captured & compressed CO₂ (usually in pipelines)
- Underground injection and geologic sequestration (also referred to as storage) of the CO₂ into deep underground rock formations. These formations are often a mile or more beneath the surface and consist of porous rock that holds the CO₂. Overlying these formations are impermeable, non-porous layers of rock that trap the CO₂ and prevent it from migrating upward.
- EPA's CCS Web site: <u>http://www.epa.gov/climatechange/ccs/index.html#Federal</u>

452-2-82







Problems with CCS (at Fossil Fuel Combustion Units)

- The <u>challenge from a separation perspective</u> is the low driving force for CO₂ separation because of:
 - low CO₂ partial pressure & low CO₂ concentrations &
 - large volume of gas to be treated.
- As a result, CCS requires intensive energy use and a high cost.
 - Carbon capture (using absorption process) at a pulverized coal-fired power plant will impose <u>an</u> <u>increase in the cost of electricity of approximately 80%</u>. The majority is <u>attributable to parasitic power loss</u> (60%).

U.S. Task Force on CCS: 2010 Report

- Concluded that cost-effective deployment of CCS will occur only if the technology is <u>commercially</u> <u>available at economically competitive prices</u> and supportive national policy frameworks are in place.
- Barriers:
 - <u>First</u>, rates of conversion must be comparable to rates of CO₂ capture.
 - <u>Second</u>, energy requirements for conversion must be low.
 - <u>Third</u>, potential volumes of reactants and/or products may limit the scale of reuse relative to total emissions.

452-2-87

Congressional Research Service Report (Jan. 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</u> <u>future CCS</u> deployment without the continuation of subsidies.
- To date in the U.S., there are <u>nine DOE-supported</u> <u>CCS projects</u> (injected large volumes of CO₂ into underground formations).
- <u>Earthquakes induced by CO₂ injection could fracture</u> the rocks in the reservoir or, more importantly, the caprock above the reservoir.

452-2-88

10-86

CO₂ Mineralization

- This is a <u>chemical reaction</u> that occurs when certain minerals are exposed to the CO₂, resulting in the <u>CO₂ being transformed into</u> <u>rock</u>.
- CO₂ mineralization processes fall under three main categories:
 - Carbonation: CO₂ reacts with calcium (Ca) or magnesium (Mg) oxide to form a solid carbonated mineral. <u>These carbonated products can be used in building materials, etc.</u>
 - Concrete Curing: A similar process to carbonation, but with a focus on producing solid <u>calcium carbonate (CaCO₃)-limestone</u>,. (It can also be added to concrete).
- Novel Cements: CO₂ is used as an ingredient within the cement. The CO₂ is mineralized within the cement as a solid carbonate, creating a new carbon negative cement.
- CO₂ mineralization is one of the only options that <u>results in</u> permanent storage of CO₂ as a solid. Other technologies merely delay the time that the CO₂ takes to go back into the atmosphere.









Controlling Power Plant Mercury Emissions

Currently, there are two main approaches being considered for controlling power plant mercury emissions:

- Reducing mercury emissions using technologies primarily designed to remove SO₂, NO_x, and particulate emissions (often called co-benefit reductions), and
- Reducing mercury emissions using technologies specifically designed to reduce mercury in coal prior to burning.

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