APTI Course 427

Combustion Source Evaluation

Chapter 5:

Air Pollution Formation

Chapter Overview (outline)

- Introduction
- Acid Gases
- Particulate Matter
- Metals
- Nitrogen Oxides
- Smoke, Carbon Monoxide & Organic Compounds
- Opacity

Introduction (ouline)

- Types of Pollutants
- Actual Emission Rates
- Potential Emission Rates
- Clean Fuels

Types of Pollutants

- Products of Incomplete Combustion (PIC)
- Pollutants resulting from inorganic contaminants in the fuel
- No_x
- Ozone, $PM_{2.5}$

Actual Emission Rates

- Measurements
- Mass balances
  - Gives an upper limit
- AP-42
  - Generic, not specific

Potential Emission Rates

Table 5-1. Emissions Originating in the Fuel					
Fuel Constituent	*Fuel Concentration*		*Pollutant Concentration*		*Primary Method of Control*
	No. 6 Oil	*Coal*	*Species*	*Conversion*	
Sulfur[1]	0.5 – 2%	1 – 4%	SO_2	99%	Low sulfur fuel
			H_2SO_4	1%	Very low excess air
Ash	<0.05%	10%	Particulate	20 – 98%	Dust collector
			PM-10, 2.5	20 – 80%	Dust collector
Nitrogen[2]	<0.5%	1%	NO_x	10 – 50%	Combustion mod
Chloride	(low)	(low)	HCl	100%	Fuel specs
C_nH_m	98%	85%	C, CO, HC	0 – small	Combustion tuning

Notes: [1] SO_4 in the fuel does not convert to SO_2 or sulfuric acid.
[2] Only organic nitrogen contributes to NOx formation.

Potential Emission Rates (cont.)

If 100% of contaminant converts to pollutant – eqn 5-1

$$\frac{\text{lb}}{\text{mmBTU}} = \frac{\%\ \text{contaminant}/100}{\text{HHV}\left(\frac{\text{BTU}}{\text{lb}}\right)/10^6} \times \frac{\text{lb pollutant}}{\text{lb contaminant}}$$

Example 5-1. Potential emissions

- Determine the potential SO_2 emission rate for 3% sulfur coal with HHV = 12,000 BTU/lb.

$$\frac{0.03\left(\frac{\text{lb S}}{\text{lb coal}}\right)}{0.012\left(\frac{\text{mmBTU}}{\text{lb coal}}\right)} \times \frac{64}{32} = 5\left(\text{lb of } SO_2 / \text{mmBTU}\right)$$

Clean Fuels

- Natural gas
  - Clean burning
  - Benefits catalysts
  - Significant pollutants
- Distillate oil
  - Some sulfur content
  - No premixed combustion

Acid Gases (outline)

- Sulfur Oxides
- Hydrochloric Acid

Sulfur Oxides

- SO_2
  - Emissions control by fuel S limits
  - Oxidizes slowly in the atmosphere

- SO_3 and Sulfuric Acid

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Fuel Sulfur Conversion

Sulfur Oxidation

Fuel S

↓ -- Combustion Zone

$O_2 \rightarrow SO_2$ (gas) ⟶ 98% to the stack

↓ -- 2% of fuel sulfur

$O_2 \rightarrow SO_3$ (gas)

↓ -- Cooling below -600^{o}F

$H_2O \rightarrow H_2SO_4$ (gas)

↓ -- Cooling below -260^{o}F

$H_2O \rightarrow H_2SO_4 \cdot nH_20$ (liquid)

↓ -- Cooling to ambient temperature

$H_2O \rightarrow$ dilute H_2SO_4

Example 5-2.

If 2% of the sulfur in oil with 1.5% S is converted to SO_3, what is the flue gas concentration?

Solution: (a) Determine emission rate (lb/mmBTU)

$$\frac{0.015\left(\frac{\text{lb S}}{\text{lb oil}}\right)}{0.0185\left(\frac{\text{mmBTU}}{\text{lb oil}}\right)} \times \frac{80}{32}\left(\frac{\text{lb } SO_3}{\text{lb S}}\right) \times 2\% = 0.0405\left(\frac{\text{lb } SO_3}{\text{mmBTU}}\right)$$

Example 5-2. (cont'd)

Convert this to ppm by volume

$$\frac{0.0405\left(\dfrac{\text{lb } SO_3}{\text{mmBTU}}\right)}{10{,}500\left(\dfrac{\text{ft}^3 \text{ fluegas}}{\text{mmBTU}}\right)} \times \frac{385}{80}\left(\frac{\text{ft}^3\ SO_3}{\text{lb } SO_3}\right) = 18.6\left(10^{-6}\right) = 18.6 \text{ ppm } SO_3$$

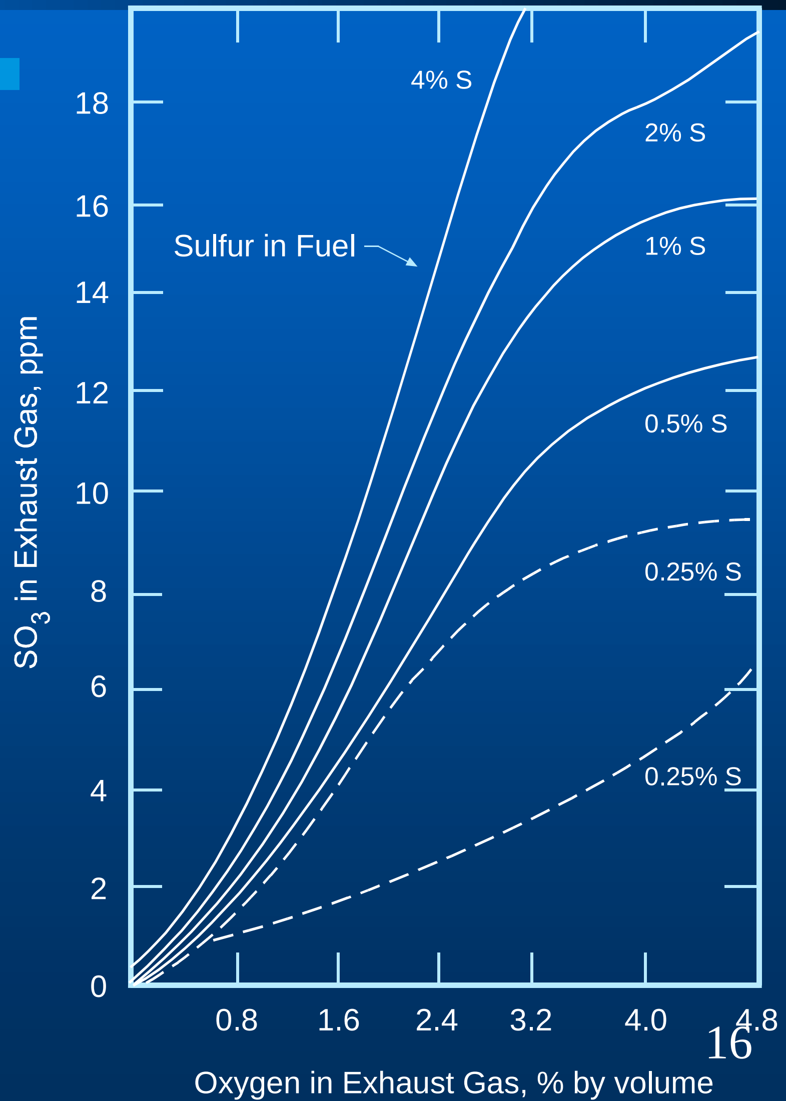
Correct this to a standard dilution level (3% O_2)

$$18.6 \text{ ppm} \times \frac{20.9\% - 3\%}{20.9\%} = 15.8 \text{ ppm } SO_3 \text{ @ } 3\%\ O_2$$

Conversion of Fuel Sulfur to SO_3

- Small but uncertain
- Vanadium influence
- Ash quantity and pH

Conversion of Fuel Sulfur to SO_3 (cont.)

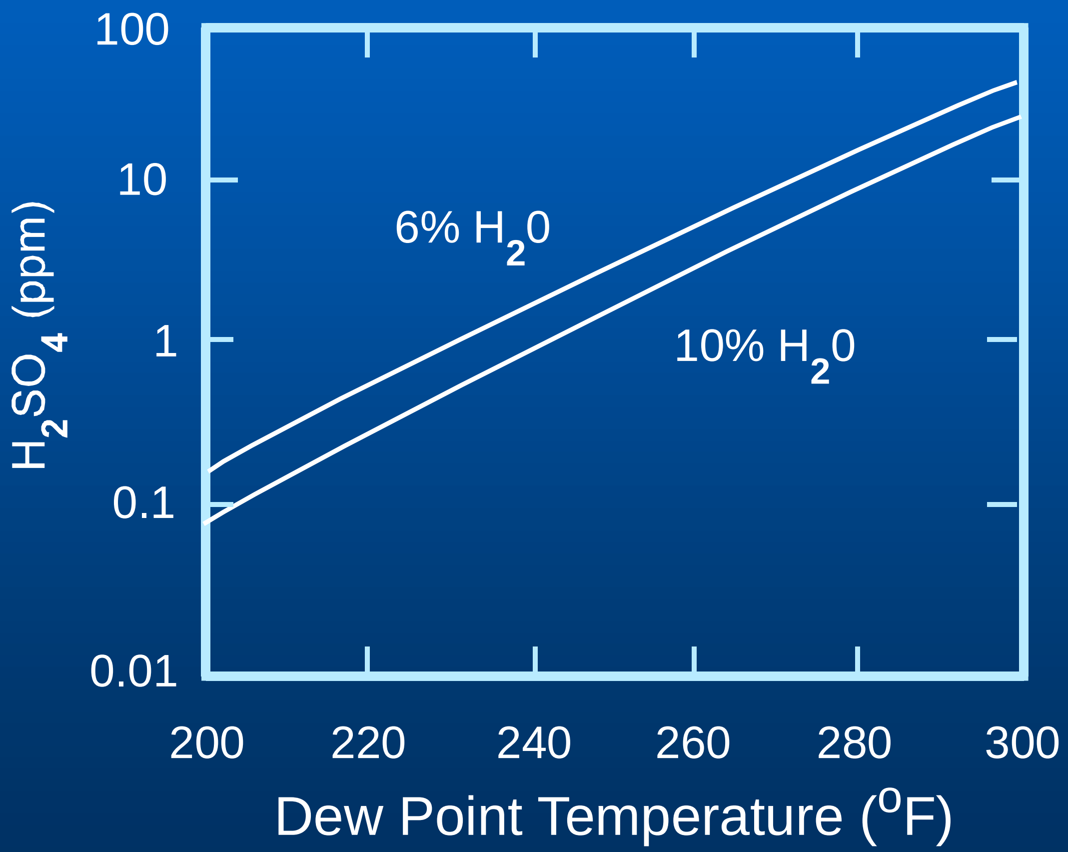


Sulfuric Acid Effects

- Plume impacts
  - Regional visibility
  - Plume behavior
  - Downwash

- Corrosion
  - Damage
  - Fallout

Sulfuric Acid Dew Point



Ash Interaction with Sulfur Oxides

- Coal ash
  - Acid interaction
  - Amount of scrubber solids
- #6 Oil ash
- Additives

Hydrochloric Acid

- Organic vs Inorganic conversion Cl → HCl
- Cl_2 versus HCl
- Cl contribution to dioxins

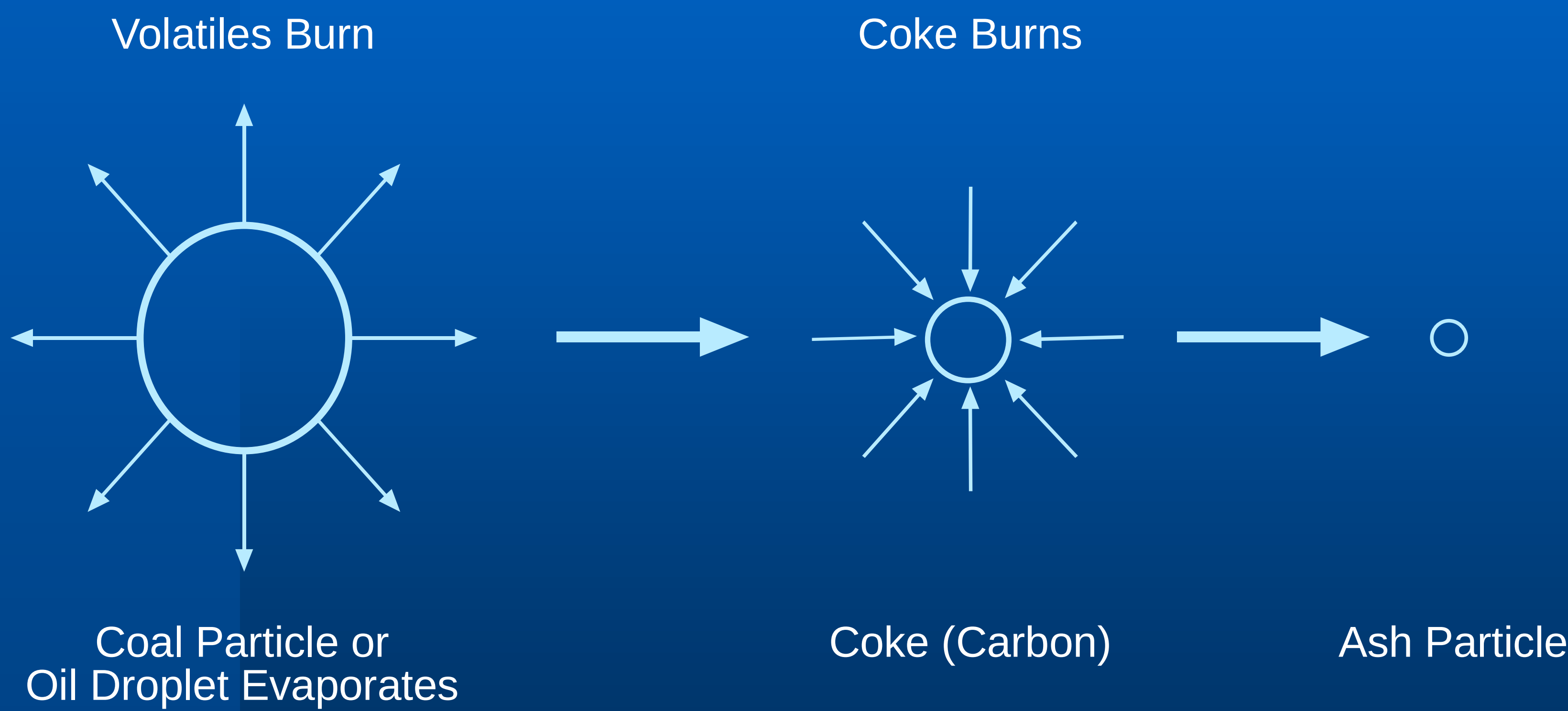
Particulate Matter (outline)

- Particle Formation – two groups
  - Large Particles (mass)
  - Fine Particles (visibility)

- Enrichment of Some Chemicals in Fine Particles

- Mass Emission Transients from Soot Blowing

Particle Formation - Large Particles



Formation of Coke and Ash Particulate

Particle Formation - Fine Particles

- Formation mechanism
- 0.5 micron “limit”
- Species & particle surface area

Pulverized Coal Particulate

- Size
- Process
- Combustion time vs residence time

Example 5-3.

- Determine potential emissions for a PC furnace with coal properties are 9% ash and 12,500 BTU/lb. Assume 10% ash retention and no control.

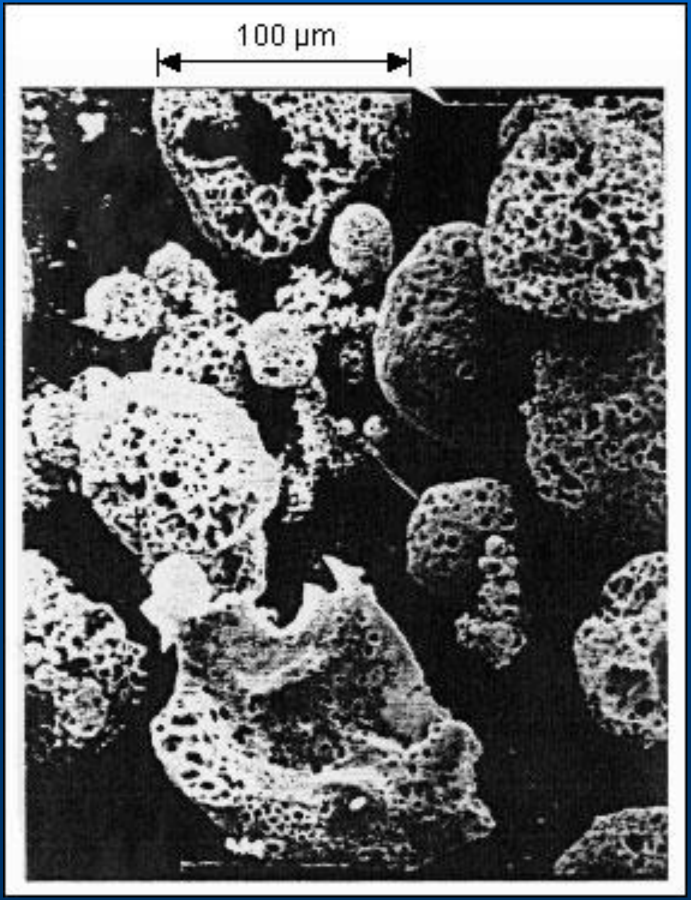
- Solution:

$$0.09\left(\frac{\text{lb ash}}{\text{lb coal}}\right) \div 0.0125\left(\frac{\text{mmBTU}}{\text{lb coal}}\right) \times 90\% = 6.48\left(\frac{\text{lb particulate}}{\text{mmBTU}}\right)$$

#6 Oil Emissions

- Particulate from
  - Ash
  - Sulfate
- Carbon
  - Coke
  - Soot (smoke)

Particulate from No. 6 Oil



Black Smoke

- Formation
- Combustion conditions required
  - Fuel rich area
  - Flame quenching
- Natural gas flames

Sulfuric Acid and Sulfate Particulate

- Acid or particulate or measurement method
- Coal-fired sulfate
- Oil-fired sulfate
- Formation factors
  - Fuel sulfur content
  - Vanadium
  - Excess air
  - Boiler ash deposits & temperatures

Example 5-4

A boiler fires #6 oil containing 1.4% sulfur and HHV = 18,500 BTU/lb. How much particulate is formed if 2% of the sulfur is oxidized to sulfate?

Solution:

$$0.014\left(\frac{\text{lb S}}{\text{lb oil}}\right) \div 0.0185\left(\frac{\text{mmBTU}}{\text{lb oil}}\right) \times \frac{96}{32}\left(\frac{\text{lb SO}_4}{\text{lb S}}\right) \times 2\% = 0.045\left(\frac{\text{lb particulate}}{\text{mmBTU}}\right)$$

Enrichment of Some Chemicals in Fine Particles

Table 5-2. Some Elements Enriched in Fine Coal Fly Ash		
Antimony	Gallium	Sodium
Arsenic	Lead	Thallium
Beryllium	Molybdenum	Uranium
Cadmium	Nickel	Vanadium
Chromium	Potassium	Zinc
Copper	Selenium	

Mass Emission Transients from Soot Blowing

- Most emissions are emitted directly
- Ash accumulation
- Soot blowers
  - Purpose
  - Typical operation
  - Air pollution impacts

Metals (outline)

- Volatility of Metals and Compounds
  - Determines fine or course particle size
  - Affects health risk
- Mercury

Volatility of Metals and Compounds

- Examples – Table 5-3
- Vapor species vs vapor pressure
- Chloride compounds

Mercury

- Combustion emissions – vapor phase
- Emission sources
  - Municipal waste
  - Coal fired utilities
- Chemical forms
- Environmental fate

Example 5-5. Mercury emissions

Determine daily mercury emissions for an 800-megawatt power plant. Plant heat rate is 9900 BTU/kw-hr with a 60% utilization factor. It burns coal with 0.13 ppm mercury and HHV = 11,900 BTU/lb.

Solution:

(a) Determine emissions rate

$$0.13\left(10^{-6}\right)\left(\frac{\text{lb Hg}}{\text{lb coal}}\right) \div 0.0119\left(\frac{\text{mmBTU}}{\text{lb coal}}\right) = 10.9\left(10^{-6}\right)\left(\frac{\text{lb Hg}}{\text{mmBTU}}\right)$$

Example 5-5 (cont'd)

(b) Determine daily energy use:

$$800{,}000(\text{kw}) \times 9900\left(\frac{\text{BTU}}{\text{kw - hr}}\right) \times 60\% \times 24\left(\frac{\text{hr}}{\text{day}}\right) = 114{,}048\left(\frac{\text{mmBTU}}{\text{day}}\right)$$

(c) Multiply energy use x emissions rate:

$10.9\ (10^{-6}) \times 114{,}048 = 1.24$ lb/day Hg emissions

Nitrogen Oxides (outline)

- Overview of NO_x
- Thermal NO_x Formation
- NO_x Formation from Fuel Nitrogen
- Premixed and Diffusion Combustion
- NO_x from Typical Combustion Systems
- Control covered in Chapter 6

Overview of NO_x

- $NO_x = NO_2 + NO$
- NO_2 used for weight
- Ambient concentrations
- Ozone formation
- Other oxides
- All combustion makes NOx: $N2 + O2 \leftrightarrow 2NO$

Control Approaches

- Two approaches
  - Combustion strategies
  - Back-end controls

Formation Mechanisms

- Thermal NOx
- Fuel NOx
- Prompt NOx

Typical Emission Rates

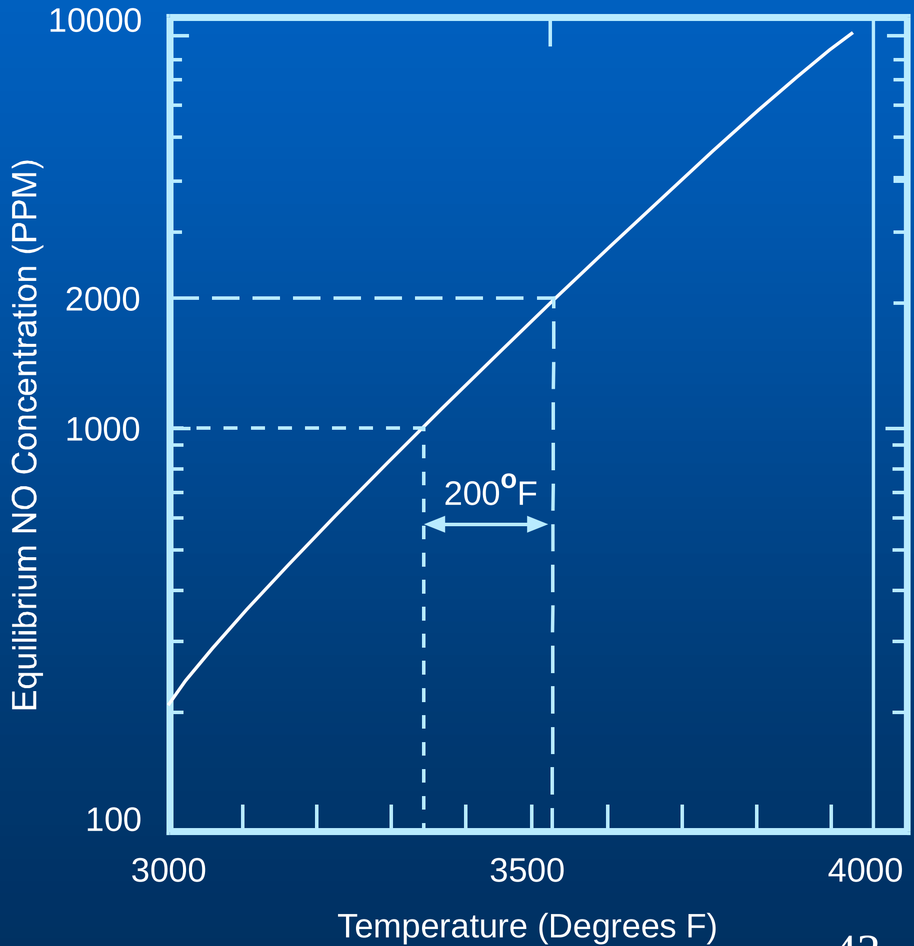
Table 5-4. AP-42 data for Uncontrolled NOx Emissions		
Combustion Source	*AP-42 Units*	*Heat Input Units*
Combustion Turbine	67.8 lb/1000 gal. fuel	0.5 lb/mmBTU
Diesel Engine	500 lb/1000 gal. fuel	3.7 lb/mmBTU
Utility Boiler Firing No. 6 Oil	67.8 lb/1000 gal. fuel	0.46 lb/mmBTU
Commercial Boiler Firing No. 2 Oil	20 lb/1000 gal fuel	0.15 lb/mmBTU
Pulverized Coal Boiler	21 lb/ton coal	0.81 lb/mmBTU
Wood Fireplace	1.8 lb/ton wood	0.15 lb/mmBTU

Thermal NO_x Formation

$N_2 + O_2 = NOx$

Modeling in real flames is complex

No significant decomposition



NO_x Formation

- Fuel impacts on NOx
  - Amount formed
  - Control techniques

- Analytical approaches to predicting NOx?

NO_x Formation from Fuel Nitrogen

- Fuel nitrogen can:
  - react with oxygen to form NO, or
  - react with another N atom to form N_2

- Affects boilers, not engines

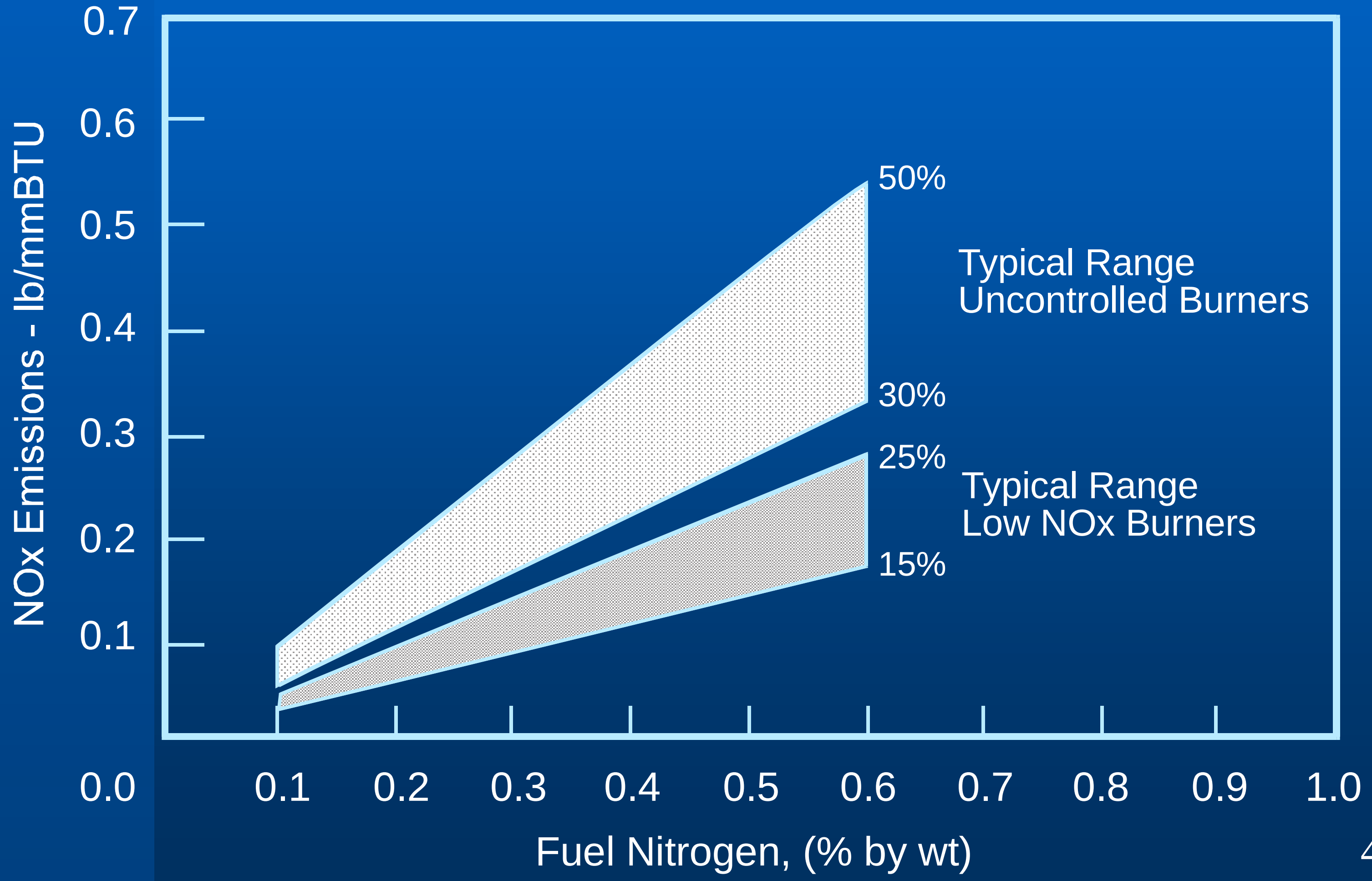
Example 5-6. Fuel NOx

A utility fires coal with 1.3% N and HHV = 13,200 BTU/lb. Find the potential NOx emissions from fuel N.

Solution:

$$0.013\left(\frac{\text{lb N}}{\text{lb coal}}\right) \div 0.0132\left(\frac{\text{mmBTU}}{\text{lb coal}}\right) \times \frac{46}{14}\left(\frac{NO_2}{N}\right) = 3.2\left(\frac{\text{lb NOx}}{\text{mmBTU}}\right)$$

NOx Emissions vs. Fuel Nitrogen

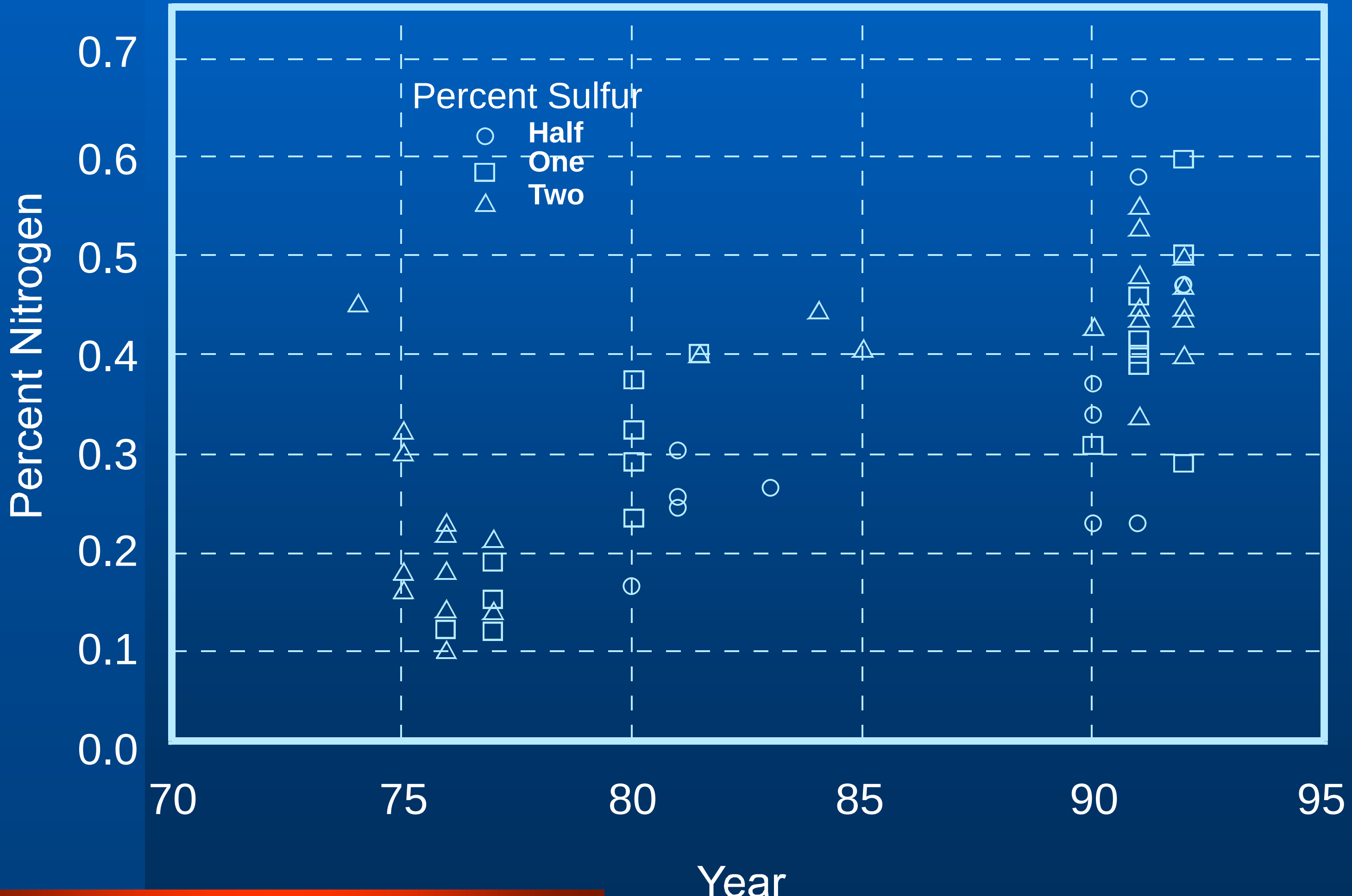


Typical Fuel N

Table 5-5. Typical Fuel Nitrogen Content

Fuel	*Nitrogen (% by wt.)*
Coal	0.5 - 2
Residual Oil	0.3 - 0.6
No. 2 Oil	< 0.1

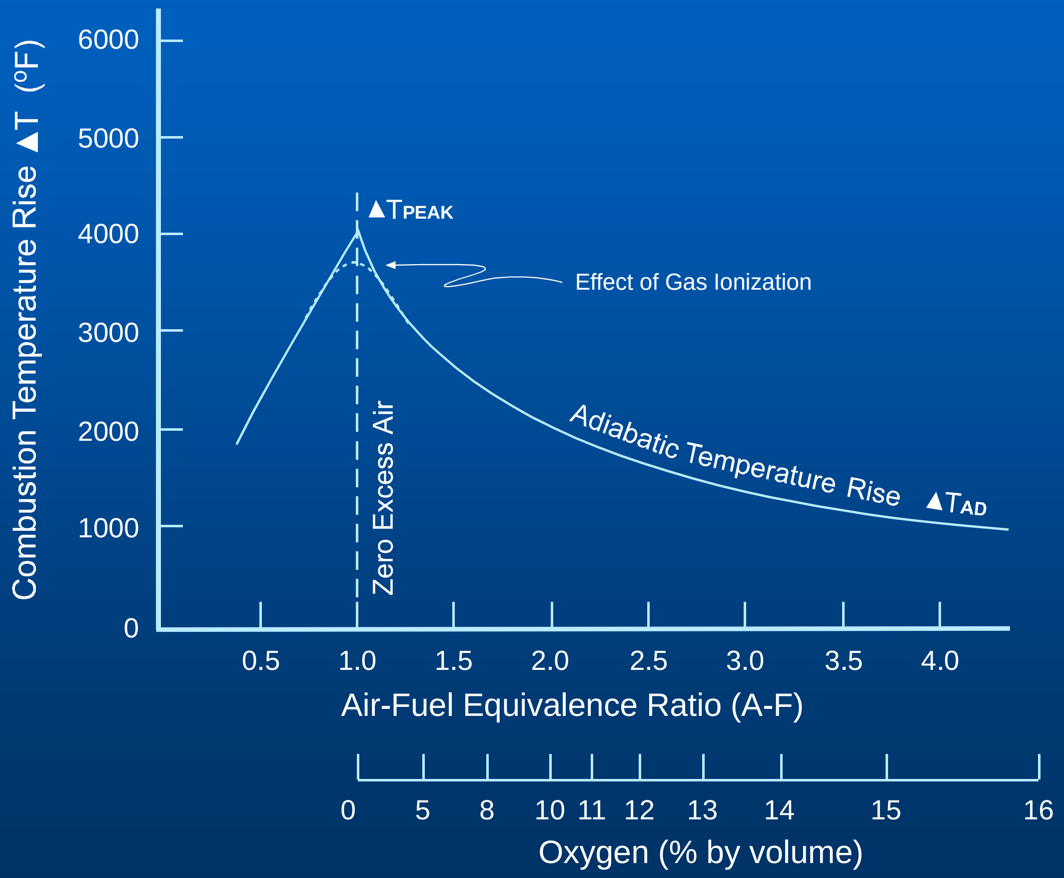
Residual Oil Nitrogen vs. Time



Premixed and Diffusion Combustion

- Diffusion
  - Typical of most combustors
- Premixed
  - Gas & gasoline reciprocating engines
  - Some low NOx combustors
- Temperatures of premixed & diffusion flames (Fig. 4-5)
- O2 concentrations

Premixed and Diffusion Combustion (cont.)



NO_x from Typical Combustion Systems (outline)

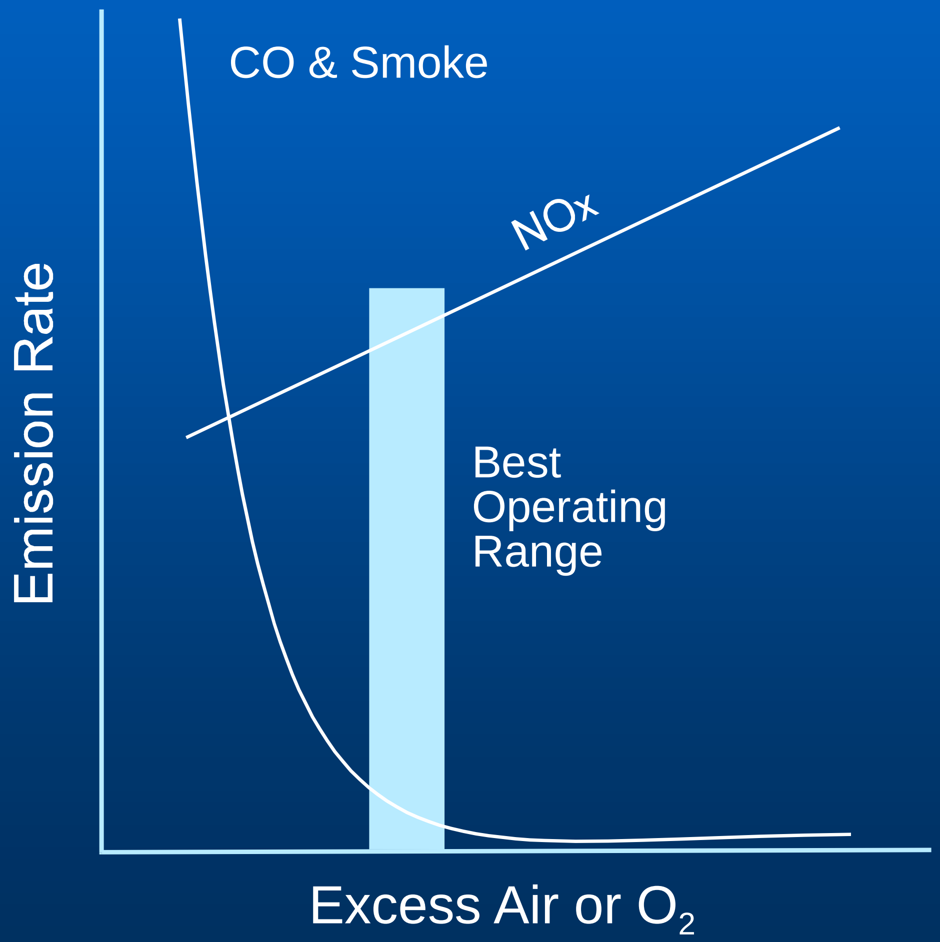
- History of NOx control
  - Combustion versus back end
- Combustor categories
  - Boilers and Furnaces
  - Reciprocating Engines
  - Combustion Turbines
- Load range impacts

NO_x from Boilers and Furnaces

- Wide range of sizes & fuels
- Temperatures
- Air & fuel flow control
  - Matching air to fuel
  - Trade off of PIC & NOx (Fig. 5-9)

NO_x from Boilers and Furnaces (cont.)

Typical NO_x and CO vs. Excess Air



Fuel Effects on Boiler Emissions

- Three fuel categories:
  - (1) Clean fuels
  - (2) Residual oil, pulverized coal sander dust
  - (3) Solid fuels

Fuel Effects on Boiler Emissions (cont.)

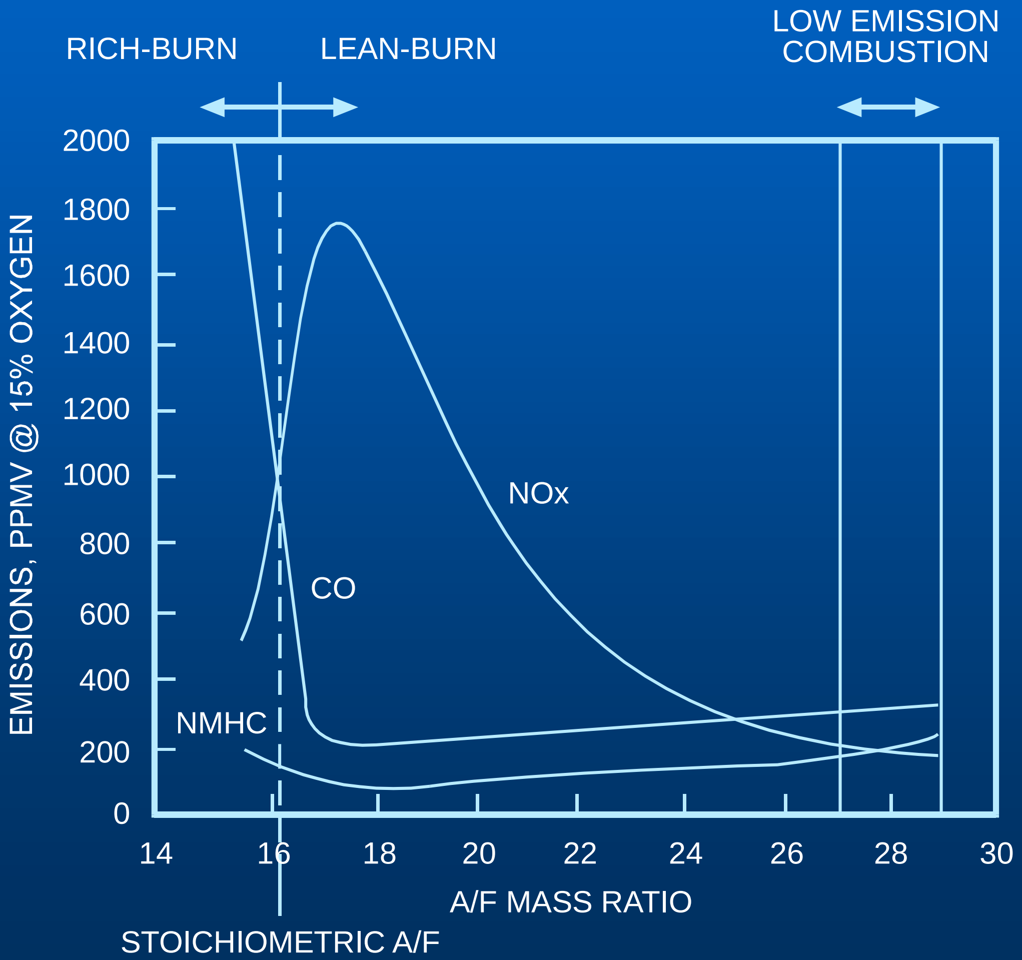
- Suspension versus grate burning
- Size implications
  - Small boilers =?? Clean fuel
  - Multiple burner implications

NO_x from Reciprocating Engines

- Fuels
- Operating temperature & pressure
- NOx emission levels (Fig 5-10)
- Diesel versus gas engines
  - Diffusion vs premix
  - Rich burn & lean burn
- Emission predictability

NO_x from Reciprocating Engines (cont.)

Emissions vs. Excess Air for Gas Fired Engines



Combustion Turbines

- Overview
  - Aircraft derivative
  - Steady state combustion
  - Traditional versus new “low NOx” combustors
- Fuel flexibility
- NOx emissions
  - Use of water injection
- Predictability
  - Integration of engine & emission controls
  - Ambient conditions

Smoke, Carbon Monoxide & Organic Compounds (outline)

- Complete Combustion and Fuel-Air Mixing
- Burner Geometry
- Excess Air
- Incinerator Temperatures
- Dioxin-Furan Formation

Complete Combustion and Fuel-Air Mixing

- PIC
  - Organics (VOC)
  - Smoke (carbon) & CO
  - Startup & transient operation
- CO
  - Surrogate for organics
  - Typical levels

Elements of Complete Combustion

- Effective fuel air mixing
- Sufficient O_2
- No quenching

3 T's of Combustion

- Time
- Temperature
- Turbulence

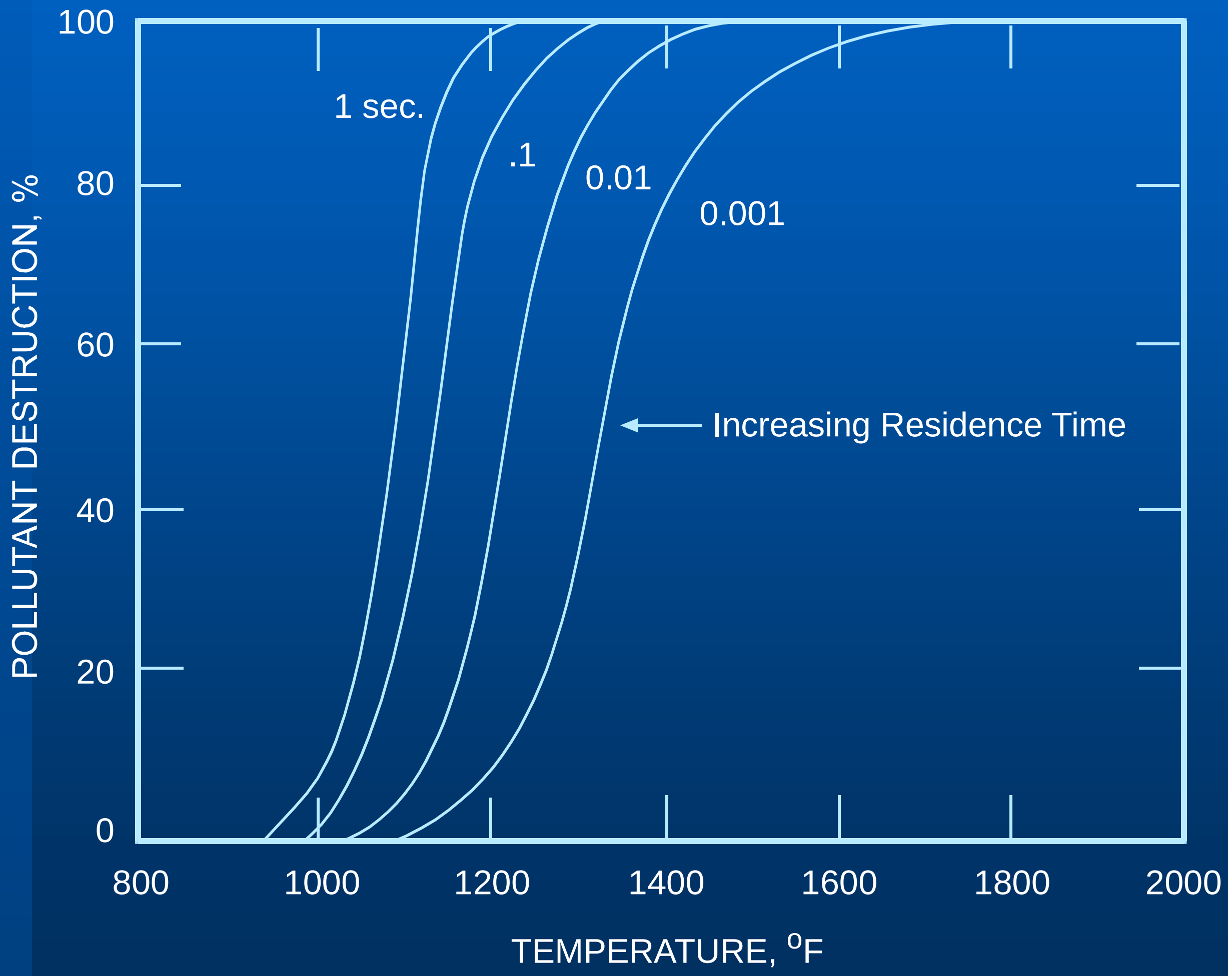
Burner Geometry

- Objective: complete, fast fuel-air mixing
- Geometry (design) governs mixing
  - Air flow pattern
  - Fuel injection pattern
- Good mixing → low PIC emissions
- Low NOx combustion is different

Excess Air (review)

- A basic requirement
- Burner performance characterized by LEA
- Minimum (& maximum) excess air levels
- Operating for no smoke versus low NOx

Incinerator Temperatures



Solid Waste Incinerators

- Basic design is important
  - Nonuniform combustion is a given
- High temperatures typically necessary
- Good excess air control

Dioxin-Furan Formation

- PCDD and PCDF
  - Stable & persistent
  - Combustion generated
- Toxicity
  - Very low levels are of concern
- PIC formation
  - Mostly from Cl aromatics, but . . .
  - Some organic fragments required
- Sources
  - Transformer fires, bad incinerators, forest fires
- Elimination

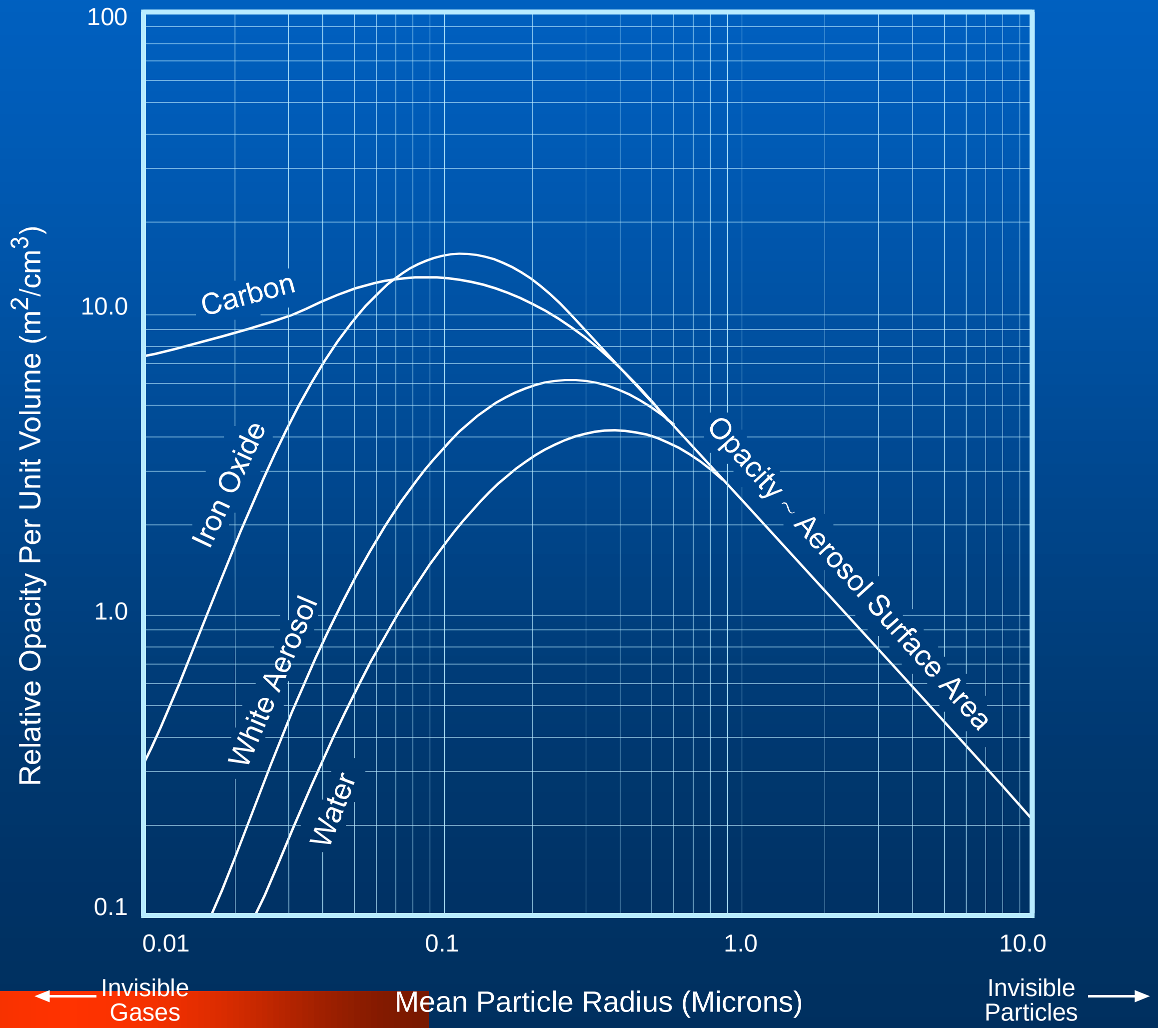
Dioxin-Furan Formation (cont.)

- Back end formation
  - 500°F
  - Cl_2 & organic PIC
- Avoidance

Opacity

- Regulatory background
- Method 9 versus Method 5
- Opacity vs. Particle Size

Dust Opacity vs. Particle Size



Opacity vs. Emission Rate

- Coal fired particulate emissions
- Residual oil-fired particulate
  - Mass emissions
  - Black plumes
  - White, brown, misc. plumes
- Sulfuric acid mist opacity

Conclusions

- Emission generating mechanisms
- Pollutant quantity – conservation of mass
- Combustion influence on PIC and NOx
- Particulate emissions
  - Large particles
  - Fine particles

Chapter Summary

- Introduction
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- Particulate Matter
- Metals
- Nitrogen Oxides
- Smoke, Carbon Monoxide & Organic Compounds
- Opacity