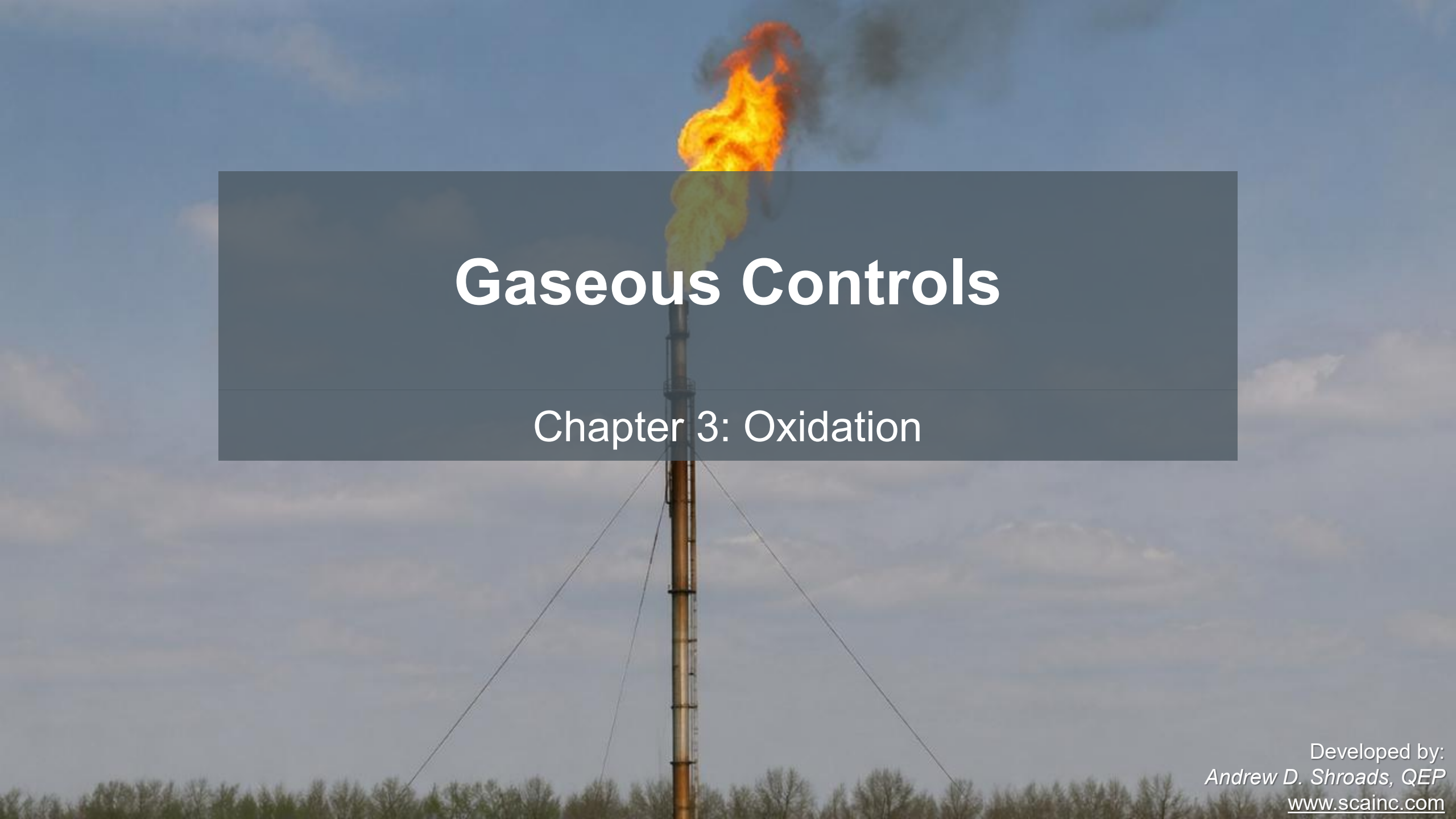


Gaseous Controls

Chapter 3: Oxidation

Developed by:
Andrew D. Shroads, QEP
www.scainc.com

Chapter 3: Oxidation
Objective

To improve understanding of oxidation control technologies

- What are the types of oxidation controls?
- How do oxidation controls operate?
- How are oxidation controls designed?
- What is the expected control efficiency for oxidation?
- What are common problems with oxidation control?
- How are oxidation controls monitored?

Oxidation

- Pollutants (CO & VOC) in process gas are heated near or above their auto-ignition temperature for destruction
  - Heat can be provided by pollutants in gas
  - Supplemental fuel (usually natural gas) may be used
- Rapid chemical reaction where combustible air pollutants are oxidized to form CO_2, water, and heat
  - Includes plume burners, flares, thermal oxidizers, and boilers



Heating Value

- Amount of heat generated from combusting a fuel
  - British Thermal Unit (Btu): Amount of heat required to increase one pound of water by 1ºF
  - Calorie: Amount of heat required to increase one gram of water by 1ºC
  - Joule: Amount of heat required to increase 0.239 grams of water by 1ºC

Wood	Bituminous Coal	#2 Fuel Oil	Natural Gas	Landfill Gas
17.48 mmBtu/ton	24.93 mmBtu/ton	0.138 mmBtu/gal	1,026 Btu/cubic ft	485 Btu/cubic ft
				

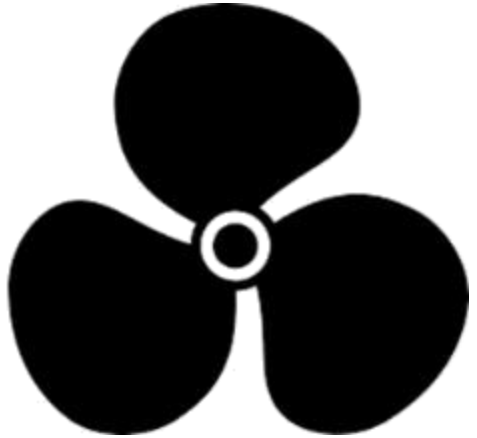
1 mmBtu = 1,000,000 (10^6) Btu

Good (3Ts) combustion requirements:

- **Time**: Sufficient time for complete oxidation reaction to occur
  - 0.3-2 seconds (depending on design and temperature)
- **Temperature**: Pollutant must reach autoignition temperature
  - 800-2,200ºF (operate 200-300ºF higher than autoignition temperature)
- **Turbulence**: Enough fuel and oxygen mixing for full oxidation







Air Pollutant Combustion

- Increase 3T's = more CO_2 and NO_X, less CO and VOC
- Decrease 3T's = more CO and VOC, less CO_2 and NO_X
- CO is oxidized to form CO_2
- VOC is oxidized to form CO_2 and water
- Combustion of chlorinated materials will form dioxins & furans
- Combustion of halogens will form acid gases (HCl & HF)
- Combustion of sulfur will form SO_2



Stoichiometry

Mathematical determination for amount of substance used and made in a chemical reaction

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

Unbalanced: 1C, 4H, & 2O on left | 1C, 3O, & 2H on right

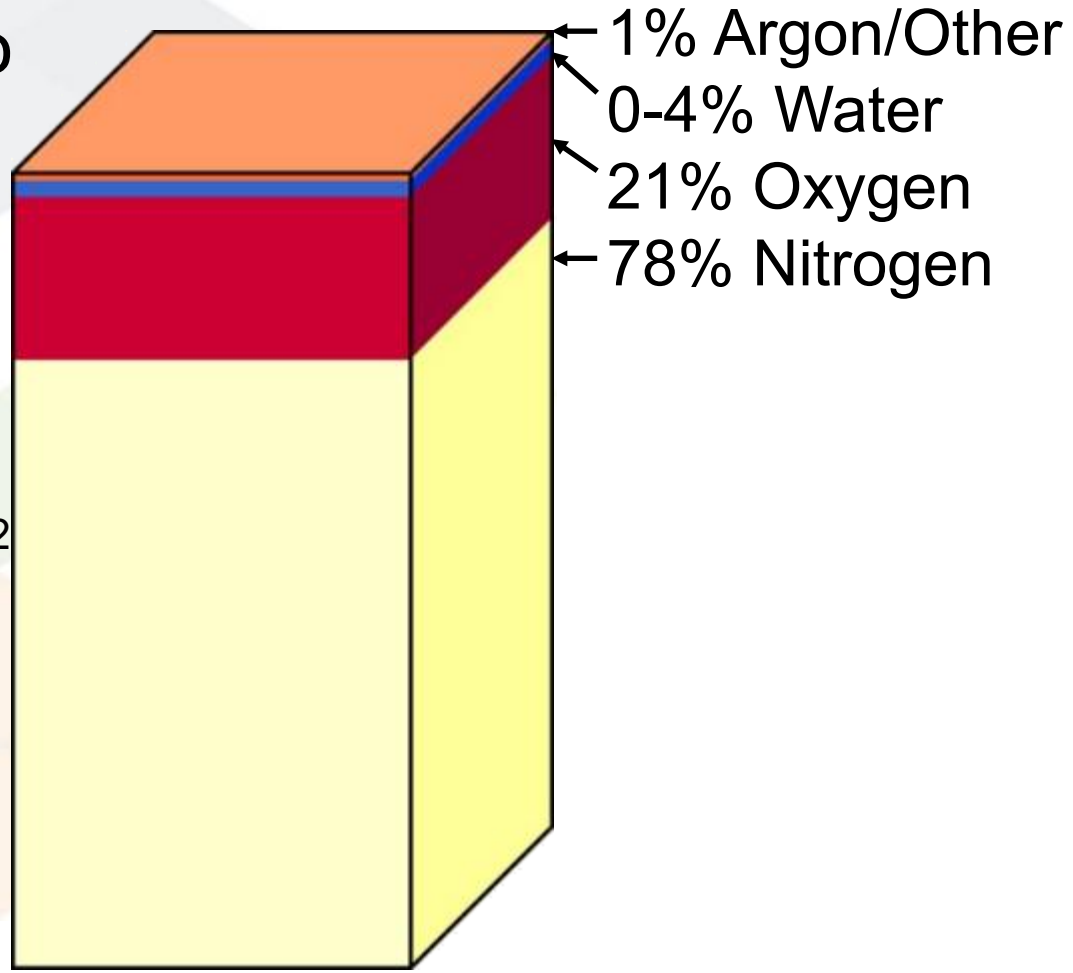
$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Balanced: 1C, 4H, and 4O on both sides

Air-to-Fuel Ratio (AFR)

- Stoichiometric combustion ratio mass air (O_2) per mass fuel
  - Mass of air and fuel to mix for combustion reaction
- Air does not just contain O_2
  - Use more air to provide enough O_2
  - Nitrogen oxidized at combustion temperatures to form NO_X

"Normal" Air

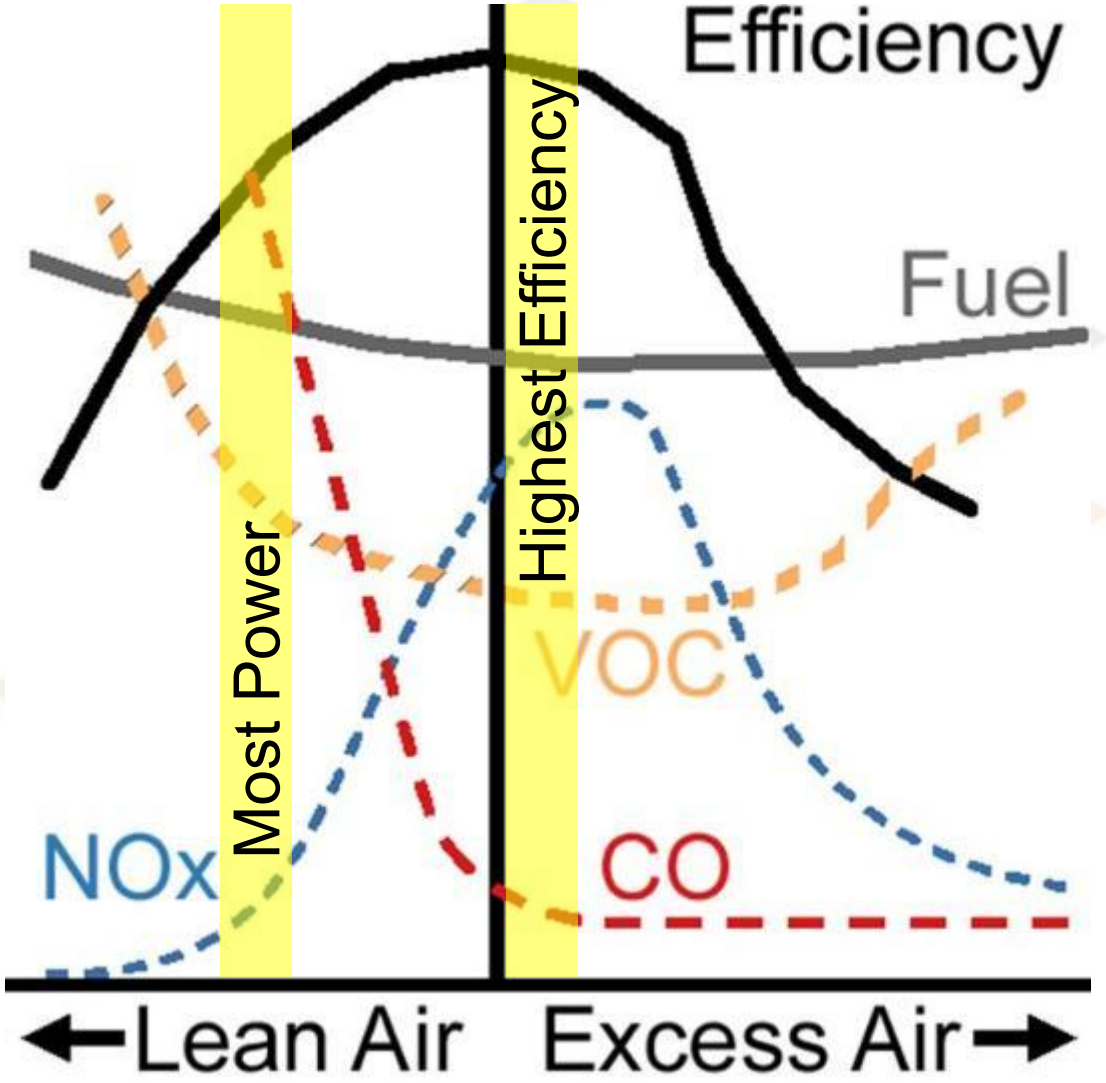


Air-to-Fuel Ratio (AFR)

- Equivalence to stoichiometric air supply (1:1 O_2 (as air) to fuel ratio)

- **Rich Burn/Lean Air**: Excess fuel; AFR ≤1.0 substoichiometric
  - AFR ≤1.0 – lower concentration of O_2
  - Operates at a higher temperature
  - More CO/VOC and less CO_2/NO_X in exhaust
- **Lean Burn/Excess Air**: Starved fuel; AFR >1.0 superstoichiometric
  - AFR near 1.5 – higher concentration of O_2 (usually 10-30% Excess Air)
  - Operates at a lower temperature
  - Less CO/VOC and more CO_2/NO_X in exhaust

More
Unburned Fuel



Decreased
Temperature

Chapter 3: Oxidation
Video

VOC 1.0 - Combustion Intro

Plume Burner

- No supplemental fuel (natural gas); combustion from waste gas ***only***



Flare

- Supplemental fuel (natural gas) ***may*** establish combustion



Thermal Oxidizer

- Supplemental fuel (natural gas) establishes combustion



Chapter 3: Oxidation Controls

Plume Burner

- Control large sources of CO
- Used primarily in iron, steel, and chemical manufacturing and oil & gas refining

Flare

- Control variable sources of VOC & CO
- Used in landfills, oil & gas refining, coke ovens, and chemical manufacturing

Thermal Oxidizer

- Control continuous sources of VOC & CO
- Use in a wide variety of industries

Chapter 3: Oxidation Controls

Plume Burner



Flare

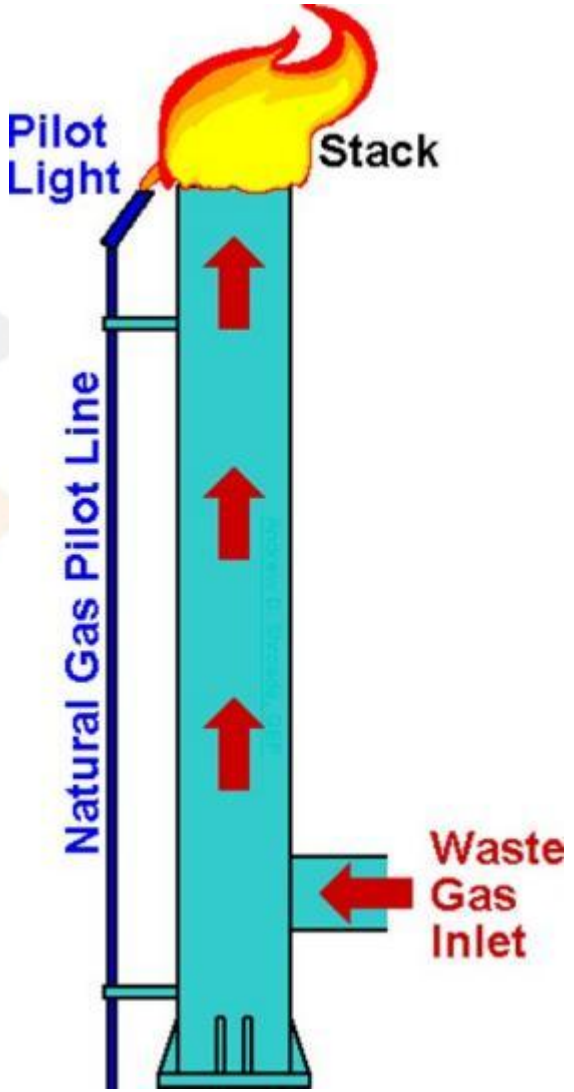


Thermal Oxidizer

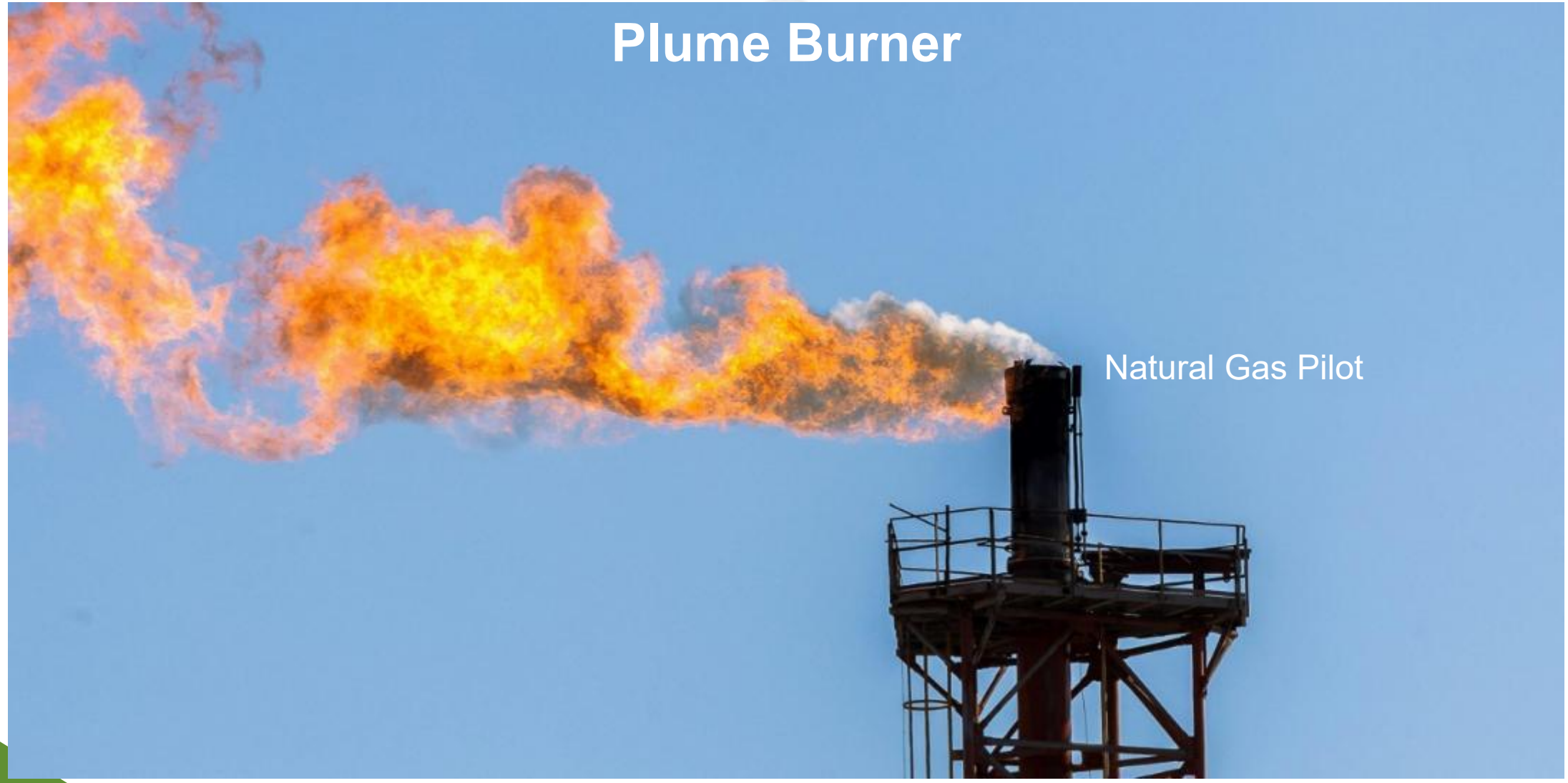


Plume Burner

- CO in exhaust gas is directly combusted in self-generated flame
  - Waste gas must be ≥300 British thermal units/cubic foot
  - No supplemental fuel is used as exhaust gas has sufficient heating value for combustion
  - Natural gas-fired pilot lights used to ensure combustion at stack tip



Plume Burner

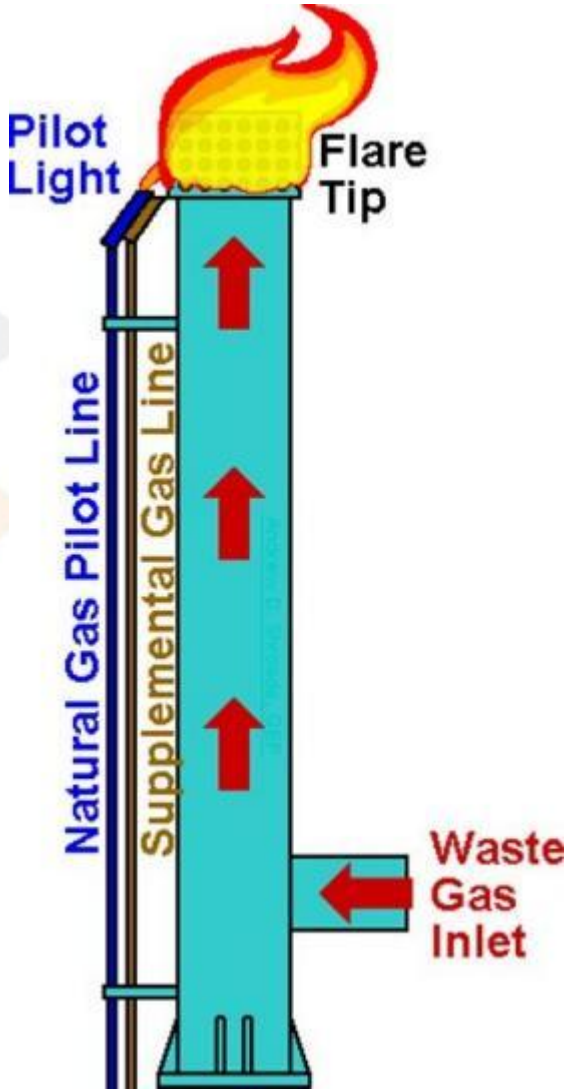


Chapter 3: Oxidation
Video

3.8 - Plume Burner

Flare

- VOC / CO in exhaust gas are directly combusted in flame
  - Supplemental fuel (natural gas) can be added to the exhaust gas to increase temperature
  - Natural gas-fired pilot lights used to ensure combustion at flare tip
- Steam or air usually added at flare tip to increase turbulence (mixing) and reduce smoke formation



Chapter 3: Oxidation Controls



Chapter 3: Oxidation
Video

VOC 1.1 - Combustion Flares

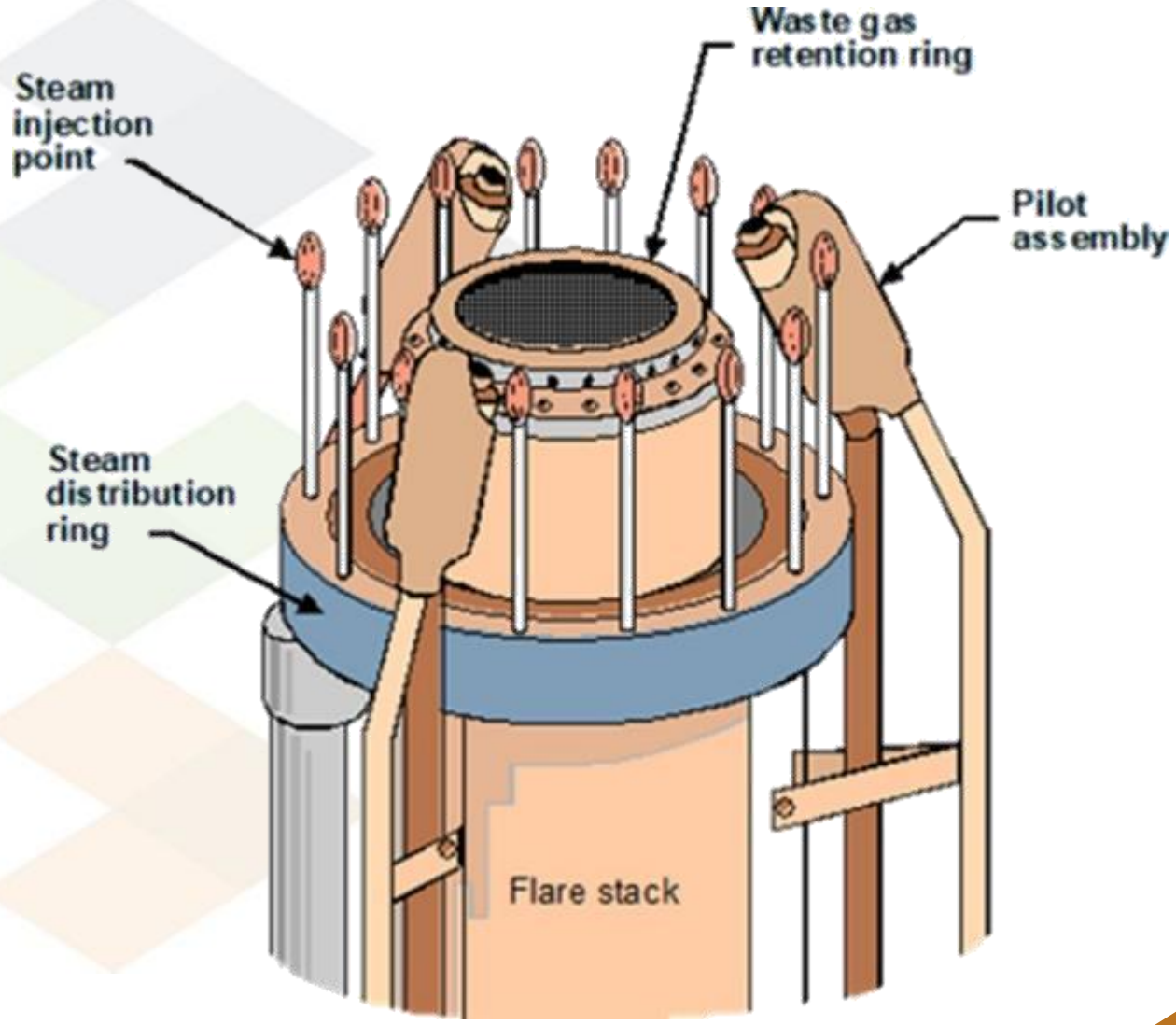
3.1 – Flare

3.2 - Ground Flare

3.3 – Flare

Flare Tip

- Exhaust gases are vented through holes in waste gas retention ring
  - Supplemental natural gas may also be used
- Steam is injected with waste gas, creating turbulence
- Natural gas pilots ignite exhaust gas

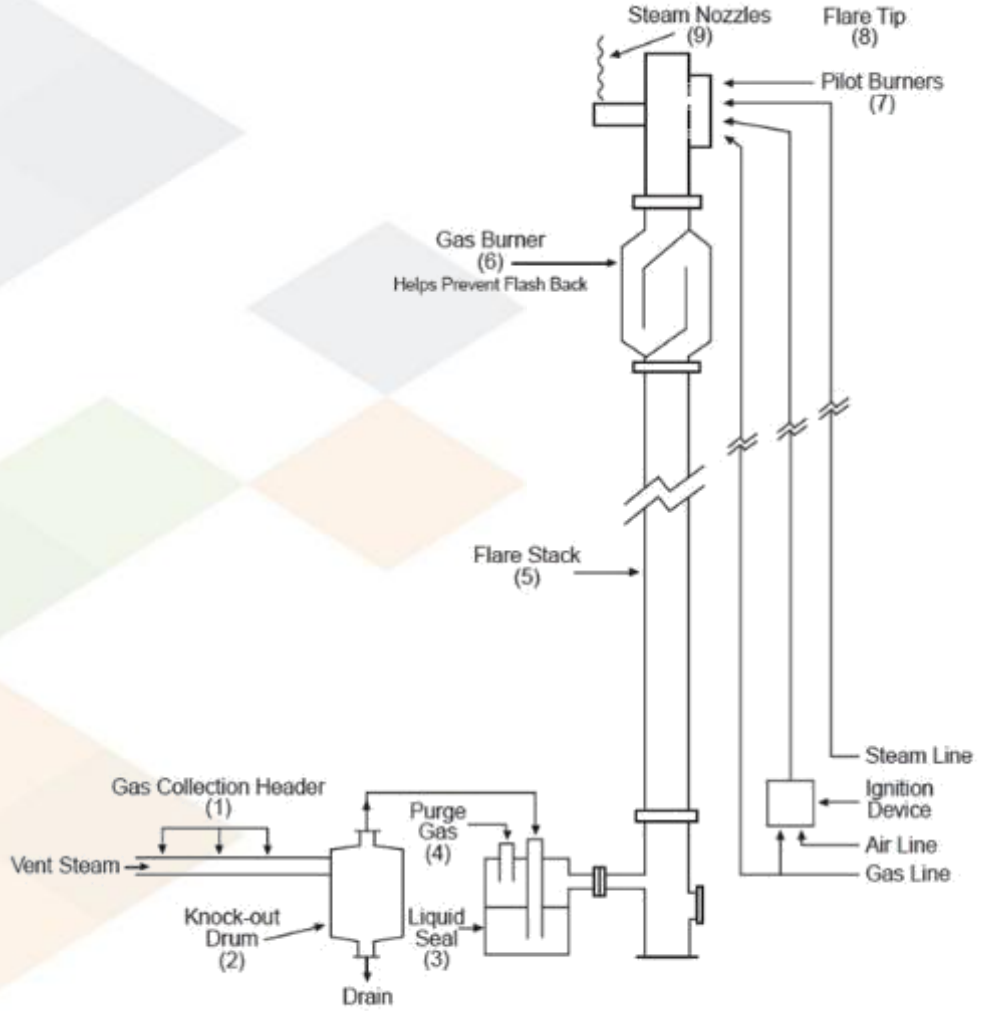


Flare Tip



Flare

- Flare height / location
  - Noise
  - Flame
  - Temperature
  - Exhaust gases
  - Airfields / heliports
  - Distance to property line
- Vent-Gas Flow
  - Maximum: flare tip size
  - Minimum: supplemental gas



Four Types of Flares

1. Steam-Assisted Flare
2. Air-Assisted Flare
3. Non-Assisted Flare
4. Pressure-Assisted Flare



Non-Assisted Flare

- Only flare tip, no additional material for mixing
- Typically used for gases with sufficient heating value and stable flow rates to sustain ignition



Steam-Assisted Flare

- Steam injected for turbulence and inducing air
- Most common type of flare with widespread use in refineries and chemical plants



Air-Assisted Flare

- Air injected for turbulence and combustion
- Air introduced by “spider” with many small orifices at burner tip
- Generally not used when exhaust gas volume is large



Multipoint Flare

- Pressure-Assisted flare with multiple flare tips
- Additional tips become active in response to more pressure

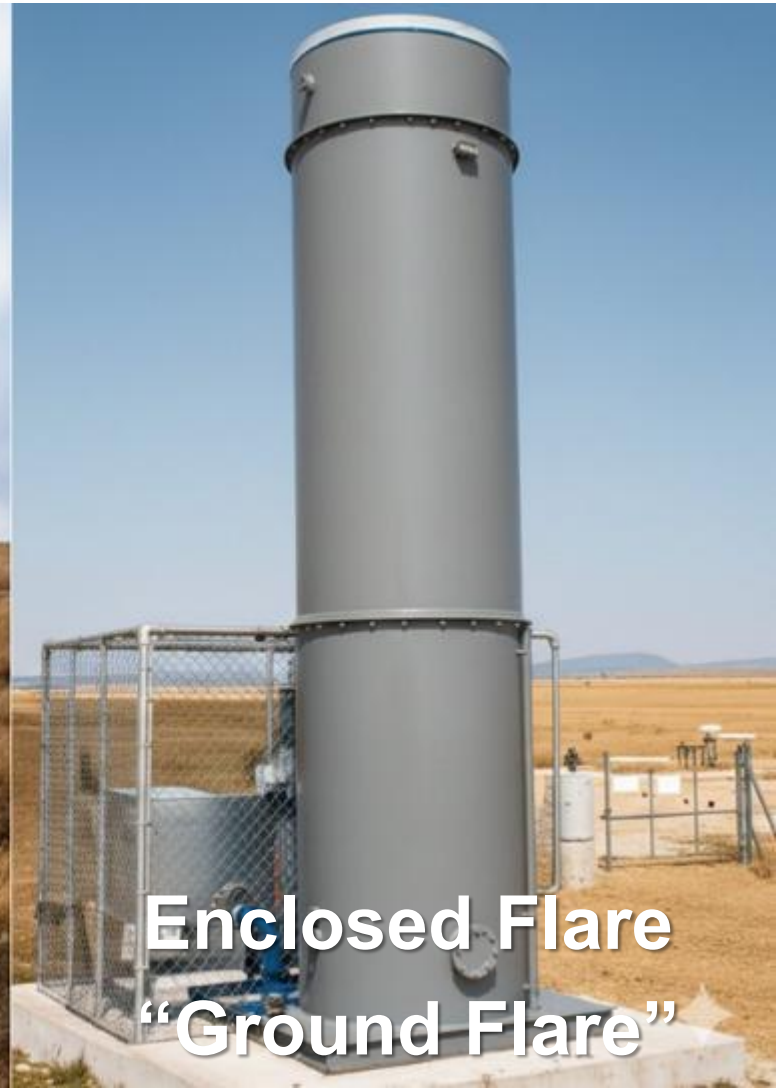


From ENCORE THERMOENGINEERING S.r.l., Milano

Chapter 3: Oxidation Controls



Elevated Flare
"Candlestick"



Enclosed Flare
"Ground Flare"

Enclosed (Ground) Flare

- Flare is located on the ground within the enclosure
- Enclosure protects nearby area from intense noise, heat, and flame
- Enclosure can have multiple flare tips (pressurized flare) for variable combustion
- Enclosure (duct) narrow enough for stack test



Enclosed (Ground) Flare

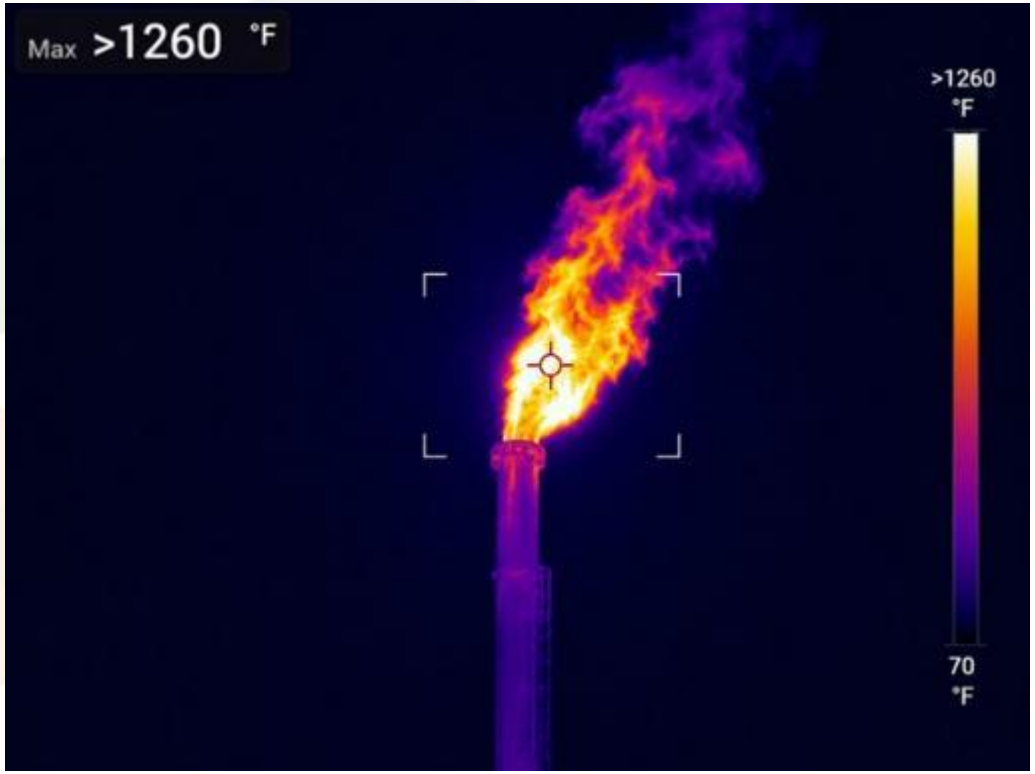
- Flare is located on the ground within the enclosure
- Enclosure protects nearby area from intense noise, heat, and flame
- Enclosure can have multiple flare tips (pressurized flare) for variable combustion
- Enclosure (shield) too wide for stack test



Flare Flame / Pilot Monitoring

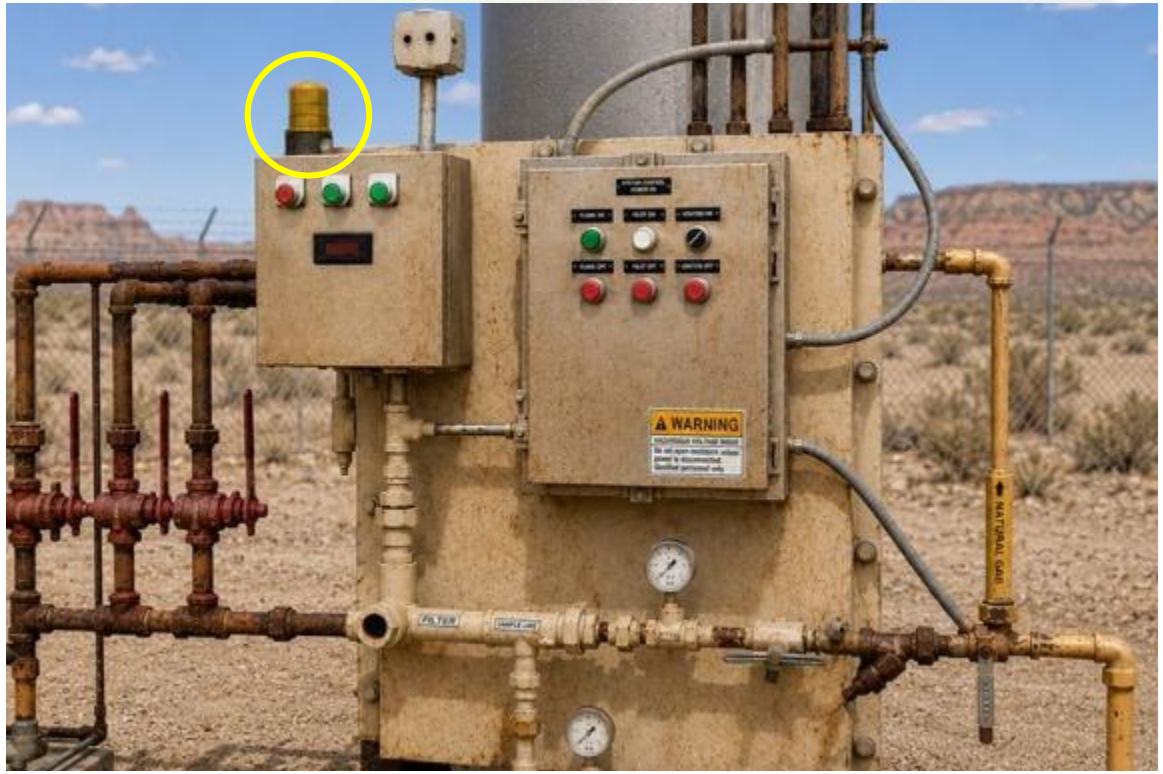
- Uses infrared to ensure that the flare / pilots are operating





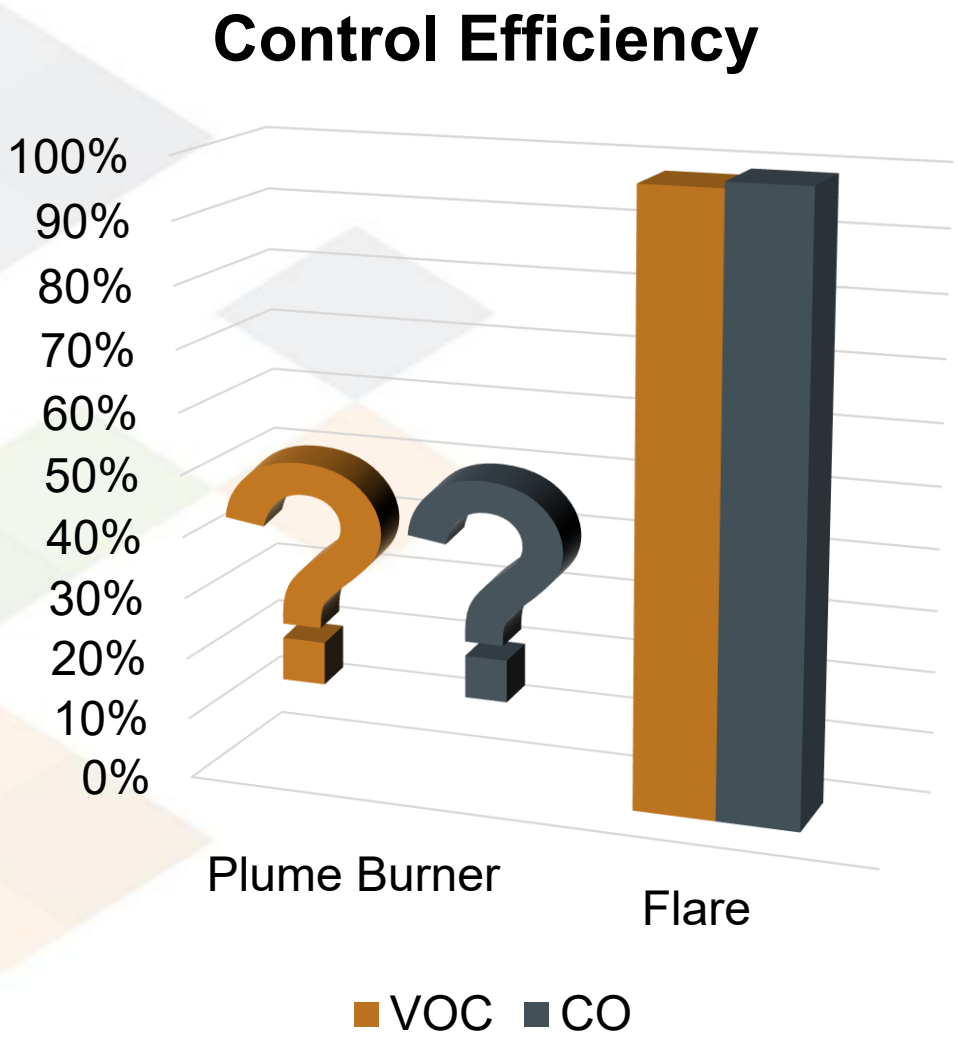
Flare Flame / Pilot Monitoring

- Flashing light indicates that flare pilot is active



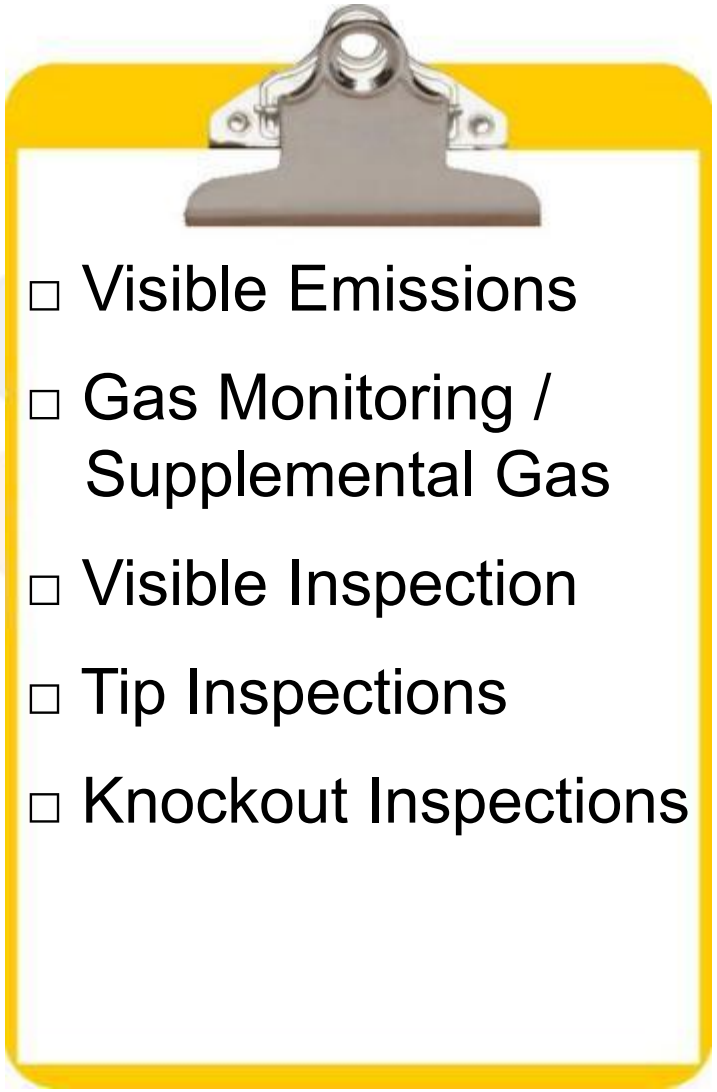
Control Efficiency

- Unknown control efficiency for plume burners
- >98% for flares when operated in accordance with regulatory requirements
  - Exhaust gas with 300 Btu/scf
  - Complies with requirements in 40 CFR §60.18(b)-(f)
  - Data based on heating value input to flare



Inspection Parameters

- Visible emissions (Method 22)
- Gas monitoring (Btu value)
  - Addition of supplemental gas
- Confirm pilot(s) lit
- Flare tip inspection reports
- Flare knockout inspection reports



Chapter 3: Oxidation
Operating Problems

- Cannot stack test plume burners or elevated flares
  - May not be able to stack test enclosed flares
- Pilots can be extinguished during high winds
- Produce undesirable noise, light, and heat
- No heat recovery
- Plume burner flameout
  - CO concentration falls below minimum for combustion
- Flare tip subject to cracking due to heat
- Liquid slugs ejected from flare as flaming fireballs
  - Flare knockout drum removes liquid droplets from exhaust gas

Thermal Oxidizer (Incinerator)

- CO & VOC in process gas are combusted by increasing gas temperature above CO & VOC autoignition temperature
  - CO & VOC are not fuel generating combustion (but do contribute heat)
  - Auto-ignition temperatures range from 350-1,800ºF
  - Oxidizers operate 200-300ºF higher than auto-ignition temperature to ensure combustion
- Auxiliary fuel (natural gas / propane) is fired through a burner to increase process gas temperature
  - Large amounts of auxiliary fuel required

Chapter 3: Oxidation Controls

Thermal Oxidizers

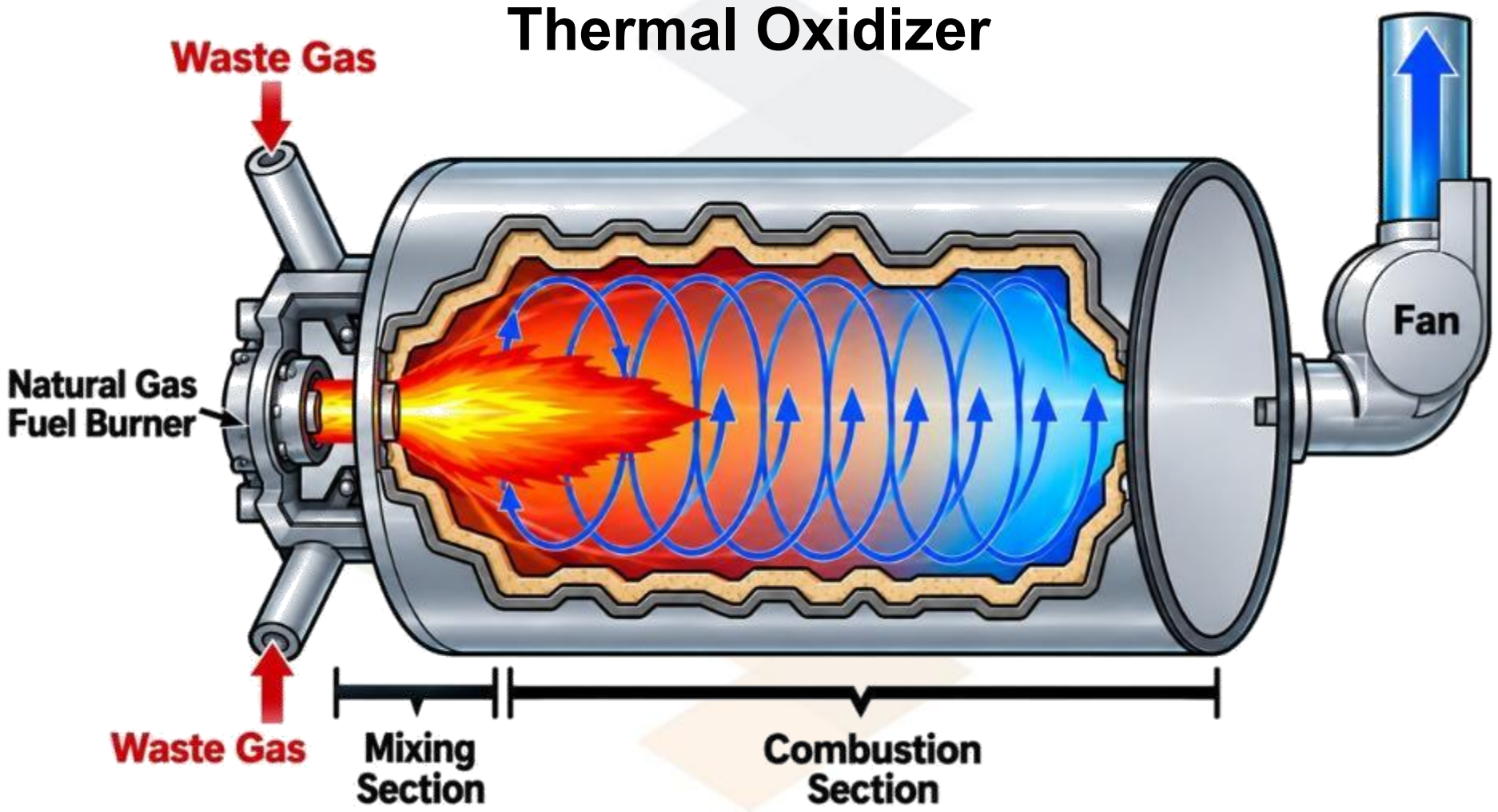




Chapter 3: Oxidation
Video

VOC 1.2 - Combustion TO.mp4

3.4 – DFTO.wmv


Thermal Oxidizer
Waste Gas
Natural Gas
Fuel Burner
Fan
Waste Gas
Mixing
Section
Combustion
Section

Primary Types of Thermal Oxidizers

1. Thermal Oxidizer (TOX) – Wastes natural gas
2. Recuperative Thermal Oxidizer (TRO)
3. Regenerative Thermal Oxidizer (RTO)
4. Catalytic Thermal Oxidizer (CTO)







TOX

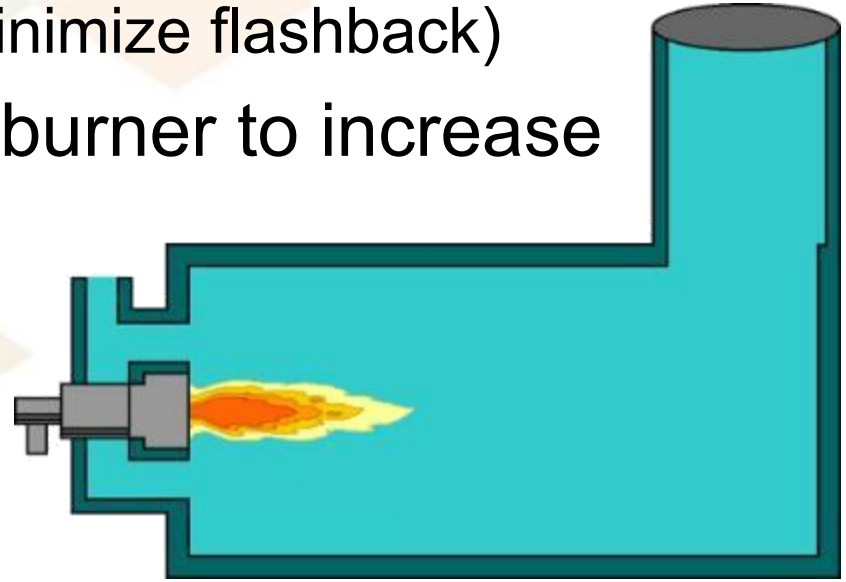
- Auxiliary (natural gas) use
- Combustion temperature
  - >Autoignition temperature
- Residence time
- Location (weight & size)
- Catalyst availability
- VOC & CO concentration
- Pollutants in exhaust stream

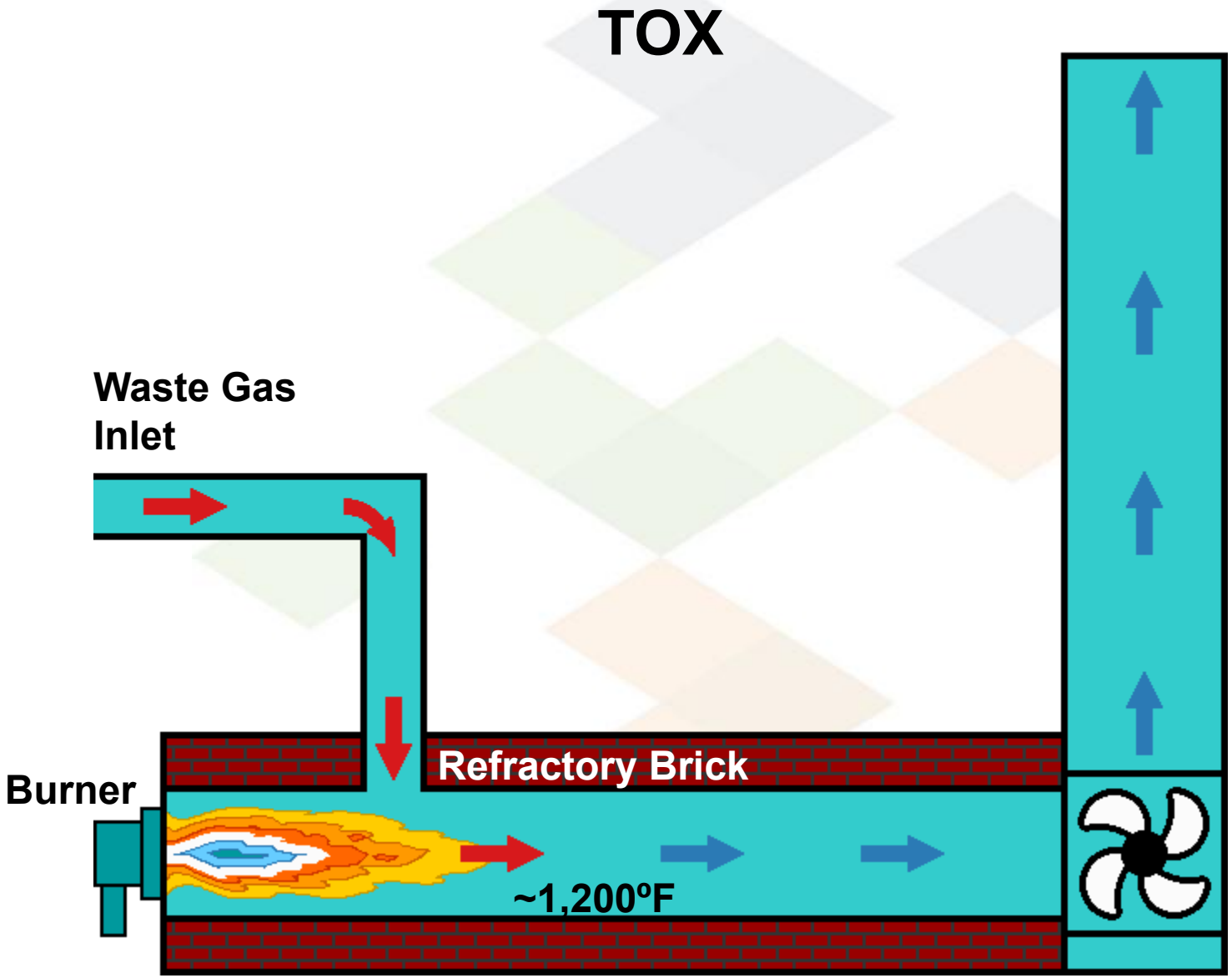
Compound	Autoignition Temperature (ºF)[1]
Acetone	870
Acetonitrile	428
Benzene	928
Carbon Monoxide	1,128
Isopropyl Alcohol	750
Methyl Alcohol	867
Methyl Ethyl Ketone	961
Toluene	986
Xylene	982

[1] From The Engineering Toolbox

TOX

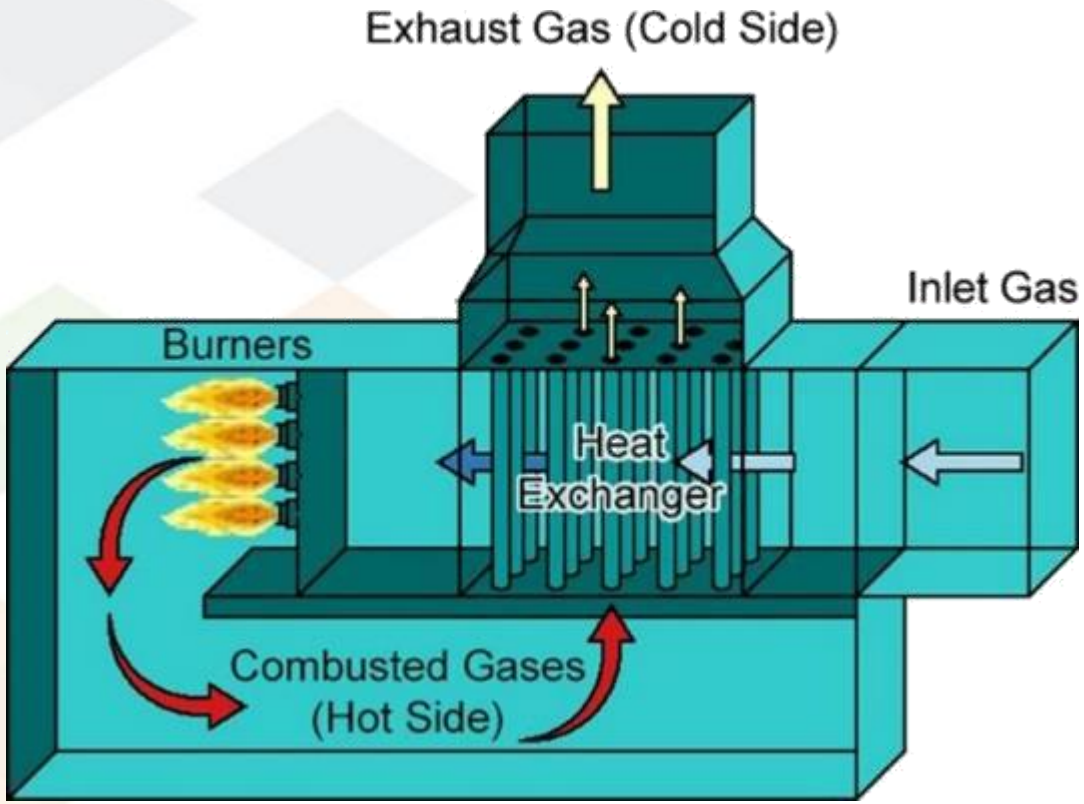
- VOC & CO in process gas are combusted by increasing process gas temperature above auto-ignition
  - Typical operating temperature 800-1,600ºF
  - Typical residence time 0.5-2 seconds
  - Typical inlet concentration <25% LEL (to minimize flashback)
- Auxiliary fuel (natural gas) is fired in a burner to increase process gas temperature
  - Large amounts of auxiliary fuel required



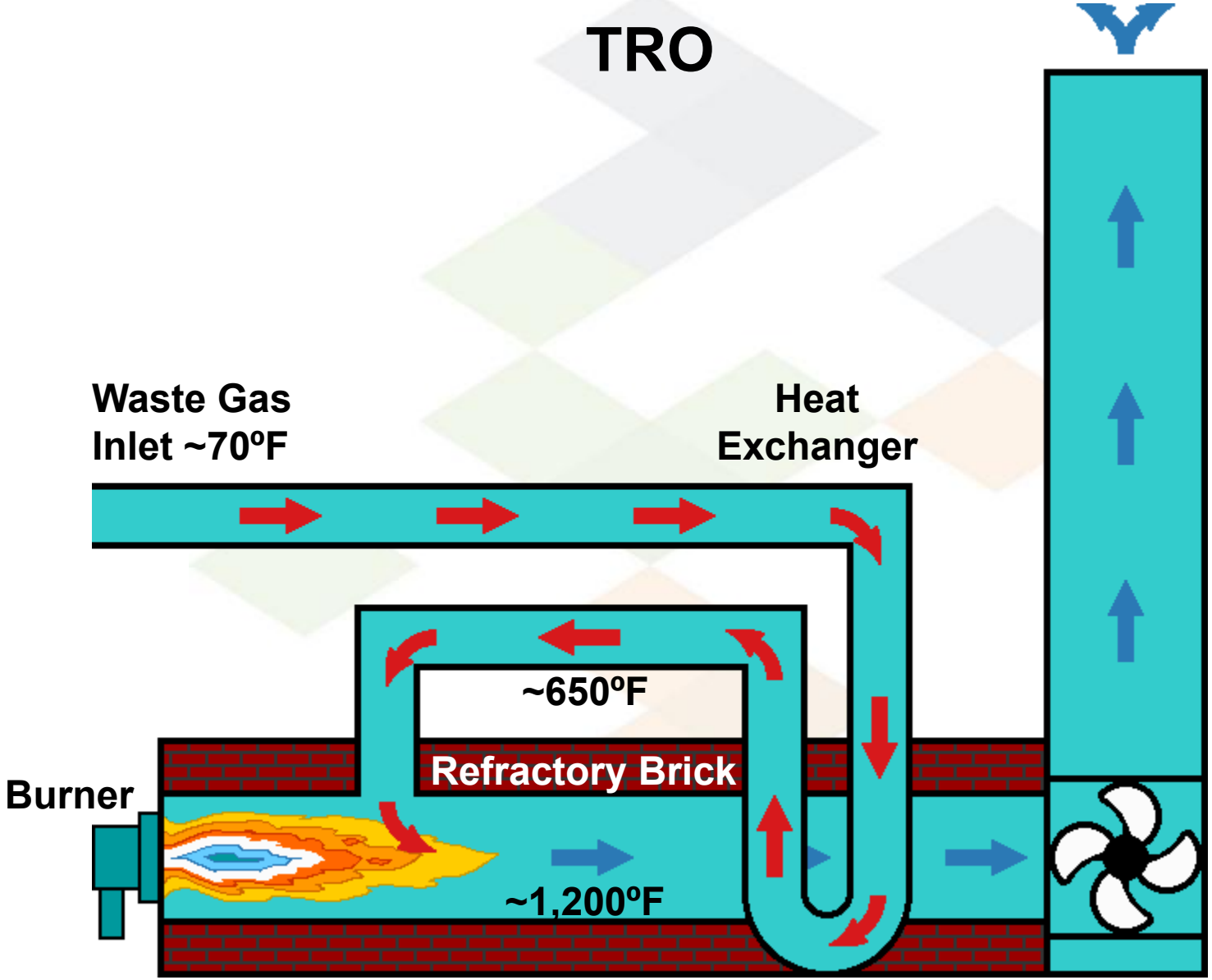

TOX
Waste Gas Inlet
Refractory Brick
Burner
~1,200ºF

TRO

- Pre-heat: heat exchanger transfers heat from hot exhaust gas stream to incoming process gas stream
- Combustion occurs at burners
  - Burners can be sized smaller, as incoming process air is pre-heated



Chapter 3: Oxidation Controls

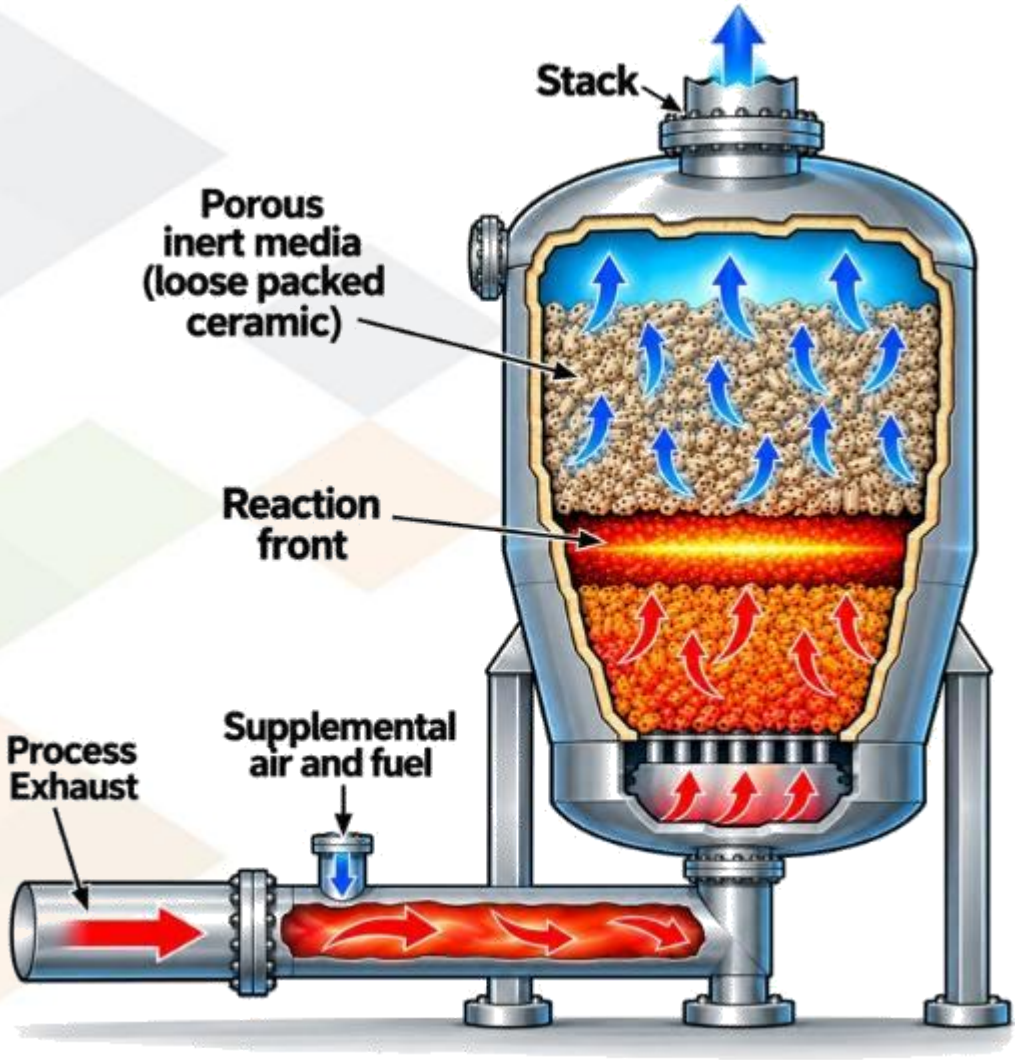


TRO

- Thermal efficiency range of 30% to 70% with corresponding reduction in fuel usage
- Shell & tube or plate-type heat exchanger
- Usually constructed of alloy steel
- Welded systems have very low leak rates
  - Susceptible to leakage as heat exchanger ages
  - Not used if acid gases (including SO_2) present; increases corrosion
- Susceptible to thermal shock on startup and shutdown

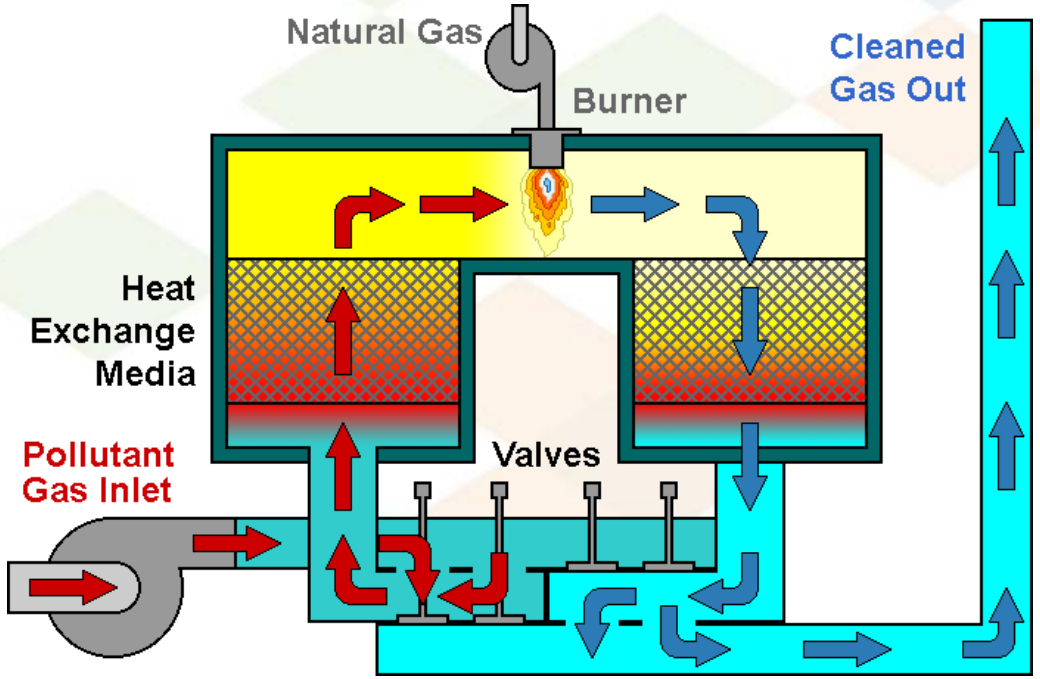
Flameless Thermal Oxidizer

- Ceramic packed bed above auto-ignition temperature
  - Ceramic bed is pre-heated
  - Exhaust gas, makeup air, and auxiliary fuel enter together
  - No open flame means more uniform oxidation in reaction zone and lower NO_X emissions
  - Ceramic beds absorb heat from oxidation, requiring less fuel

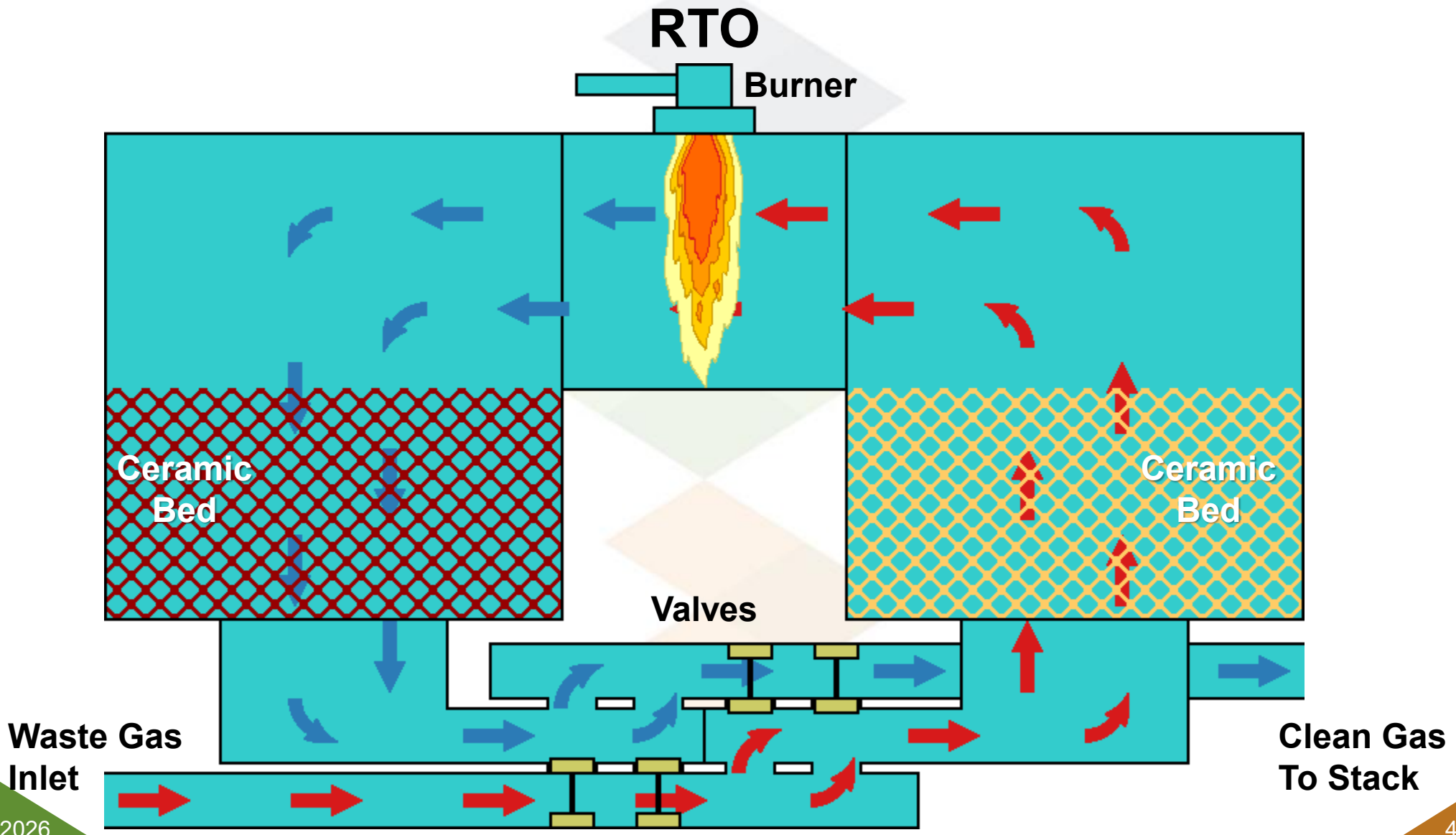


RTO

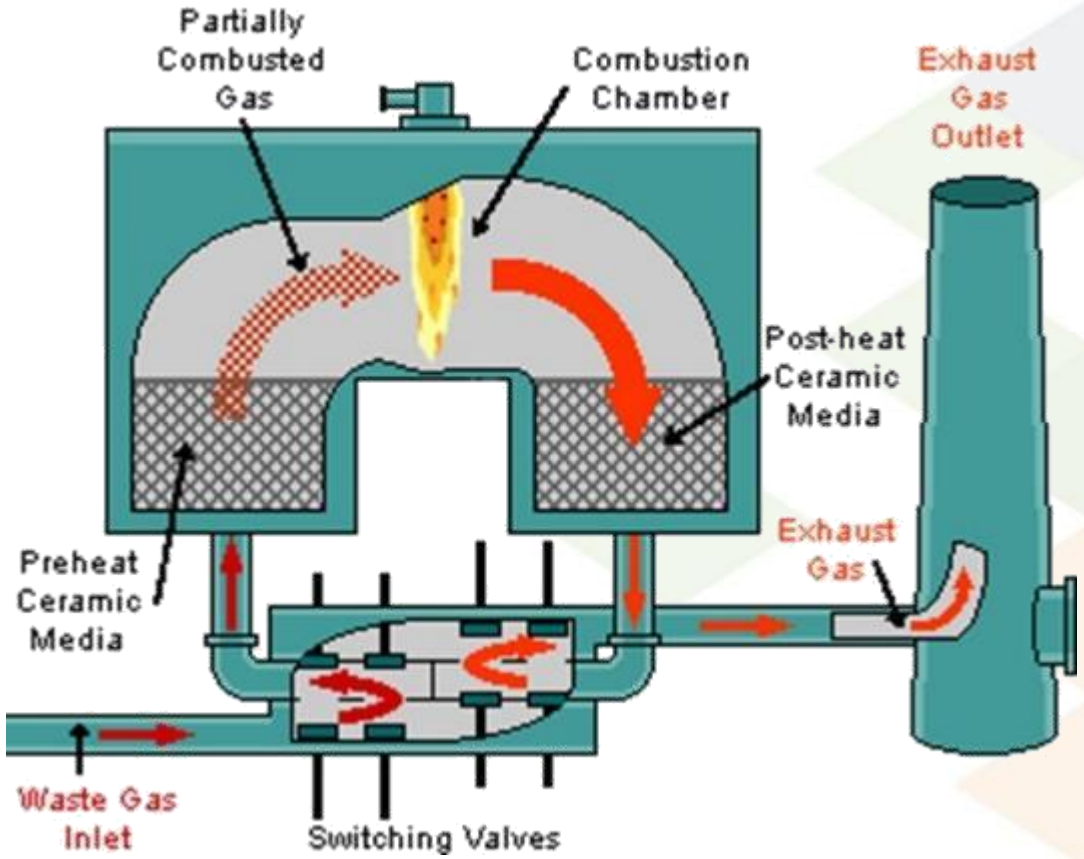
- Ceramic packed beds pre-heat incoming gas stream
  - Need ≥2 ceramic packed beds (1 pre-burner and 1 post-burner)
- Combustion still occurs at burner(s)



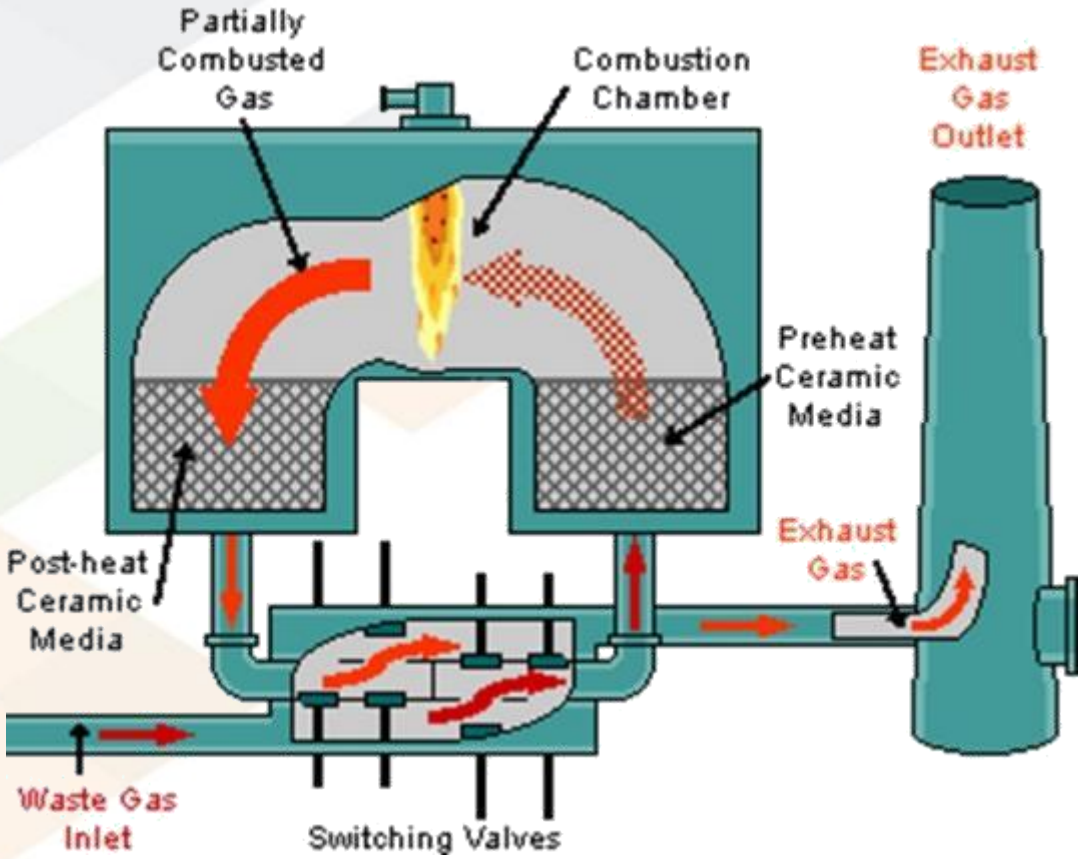
Chapter 3: Oxidation Controls



Left Preheat / Right Recover



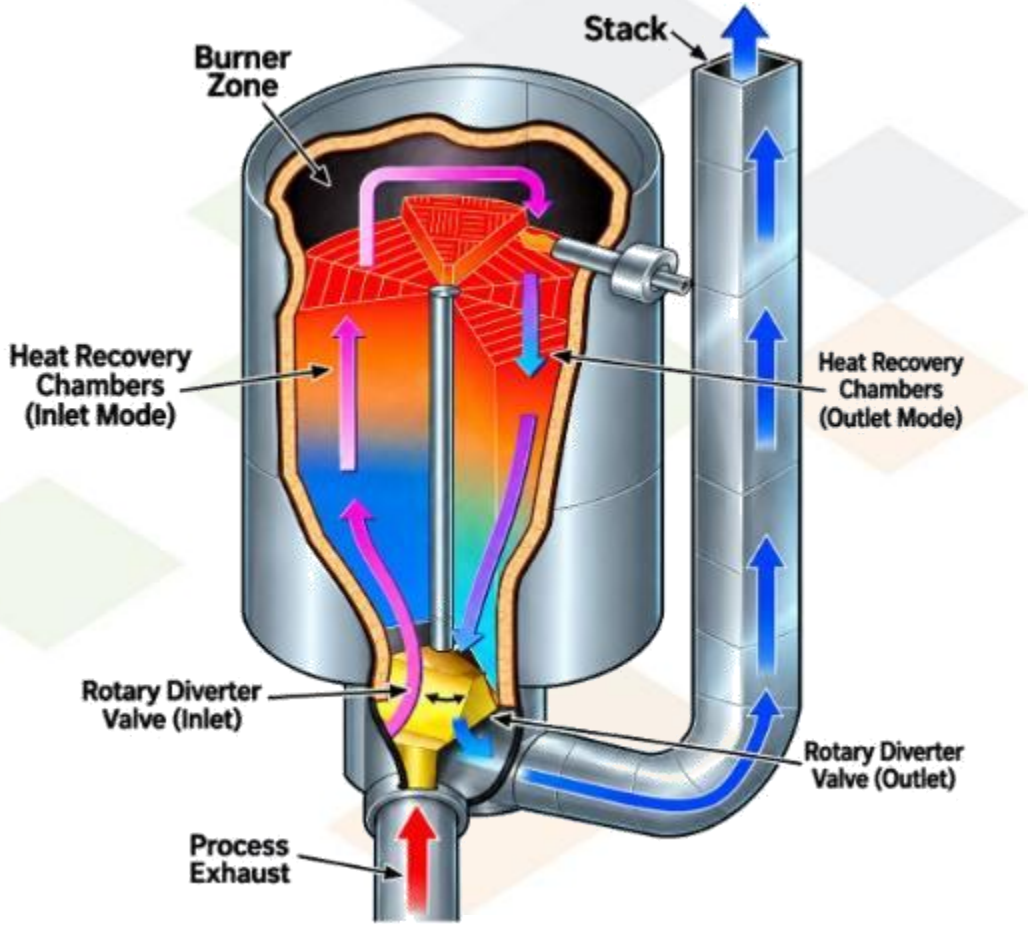
Left Recover / Right Preheat



RTO

- Heat recovery efficiency 80-95% with corresponding reduction in fuel usage
- Ceramic beds resist corrosion of acid gases
  - Susceptible to plugging by PM (increases pressure drop)
  - May need to incinerate PM buildup with very high temperatures
  - Ducts, stacks, monitors, and valves still susceptible to corrosion
- Highly resistant to thermal shock
  - Packing can be random or structured
  - Extremely tolerant of very high temperatures
- Plenums switching air flow can introduce leaks

Can or Rotary RTO



Chapter 3: Oxidation
Video

VOC 1.3 - Combustion TRO-RTO.mp4

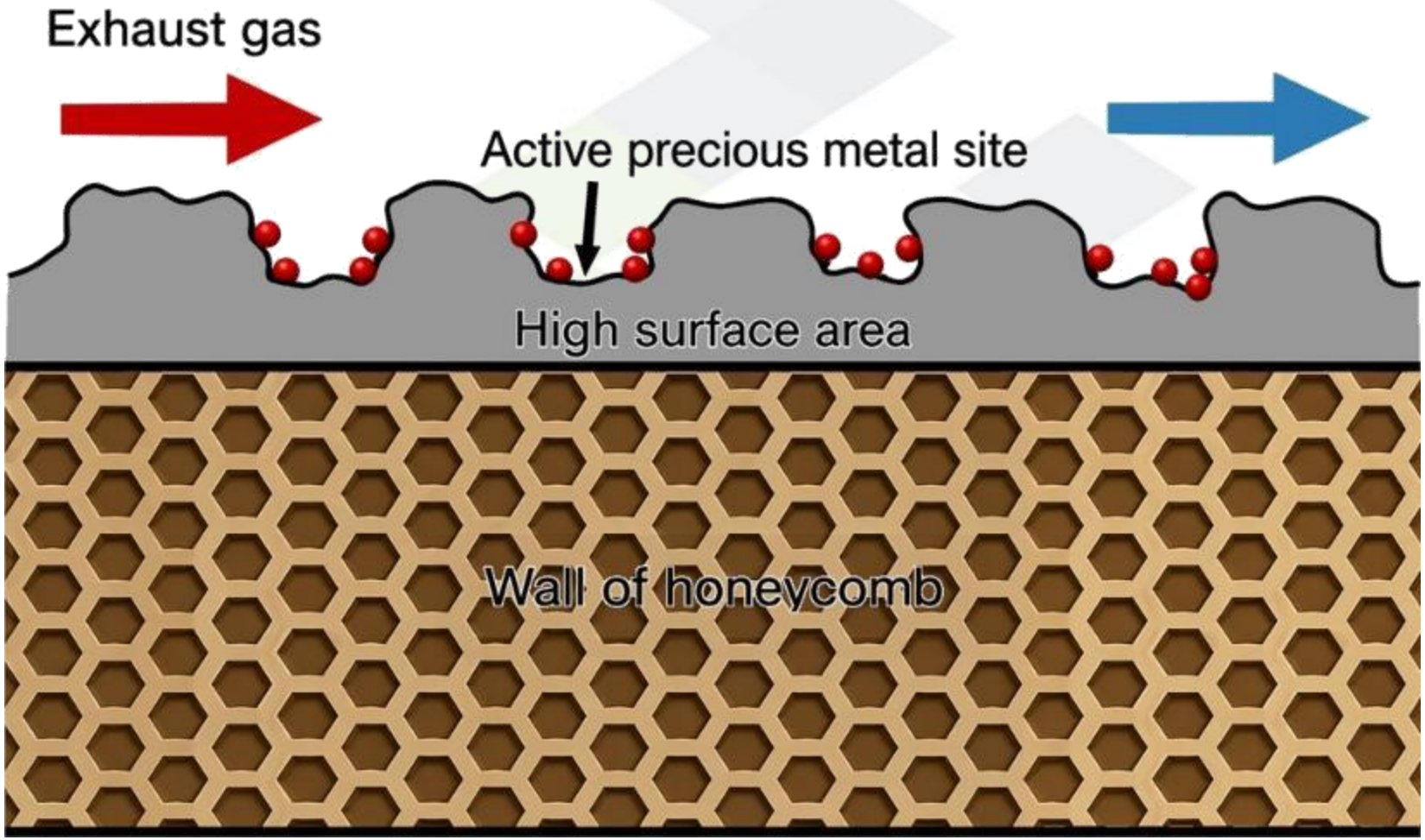
3.5 - TRO.wmv

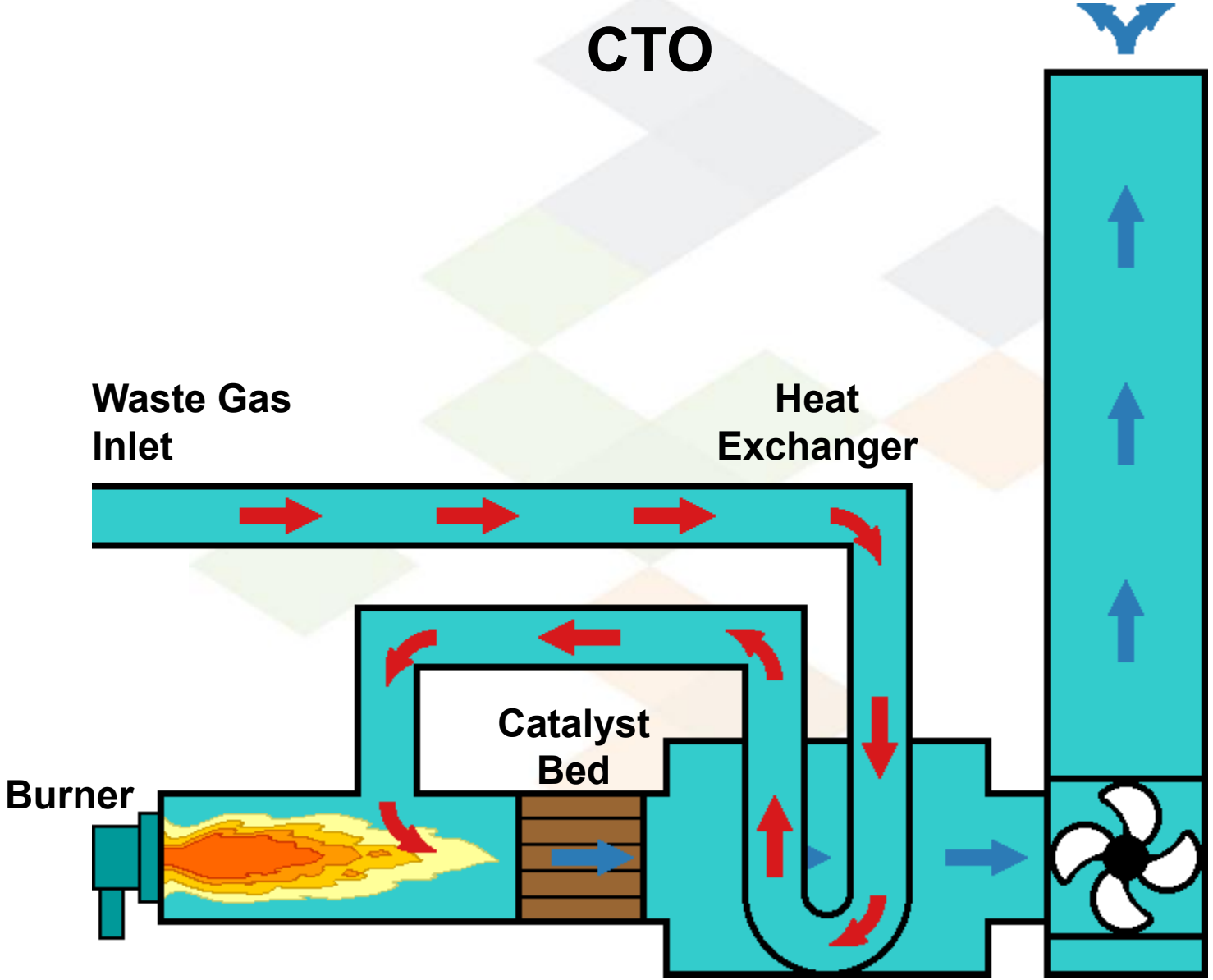
3.6 - RTO.wmv

CTO

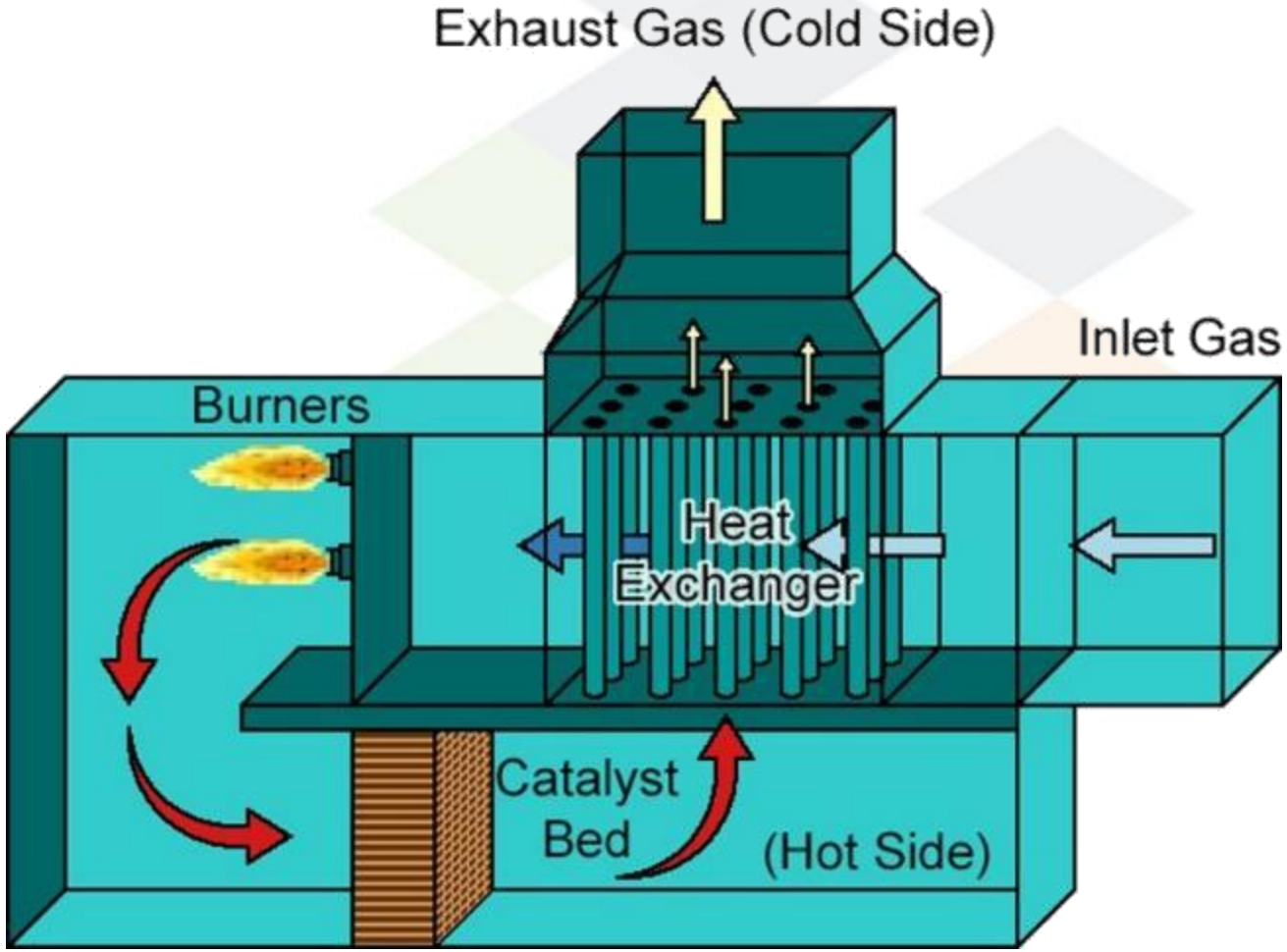
- Catalyst causes oxidation to occur faster and at a lower temperature by reducing energy required for autoignition
  - Reduces autoignition temperature to 600-800ºF
  - Lower temperature eliminates need for refractory lining
- Combustion starts in combustion chamber (burners) and ends at the catalyst
- Different catalysts work on different VOCs
  - Metal oxides are effective on a wide range of VOCs
  - Noble metals work best for CO and some VOCs

Catalyst Cross Section

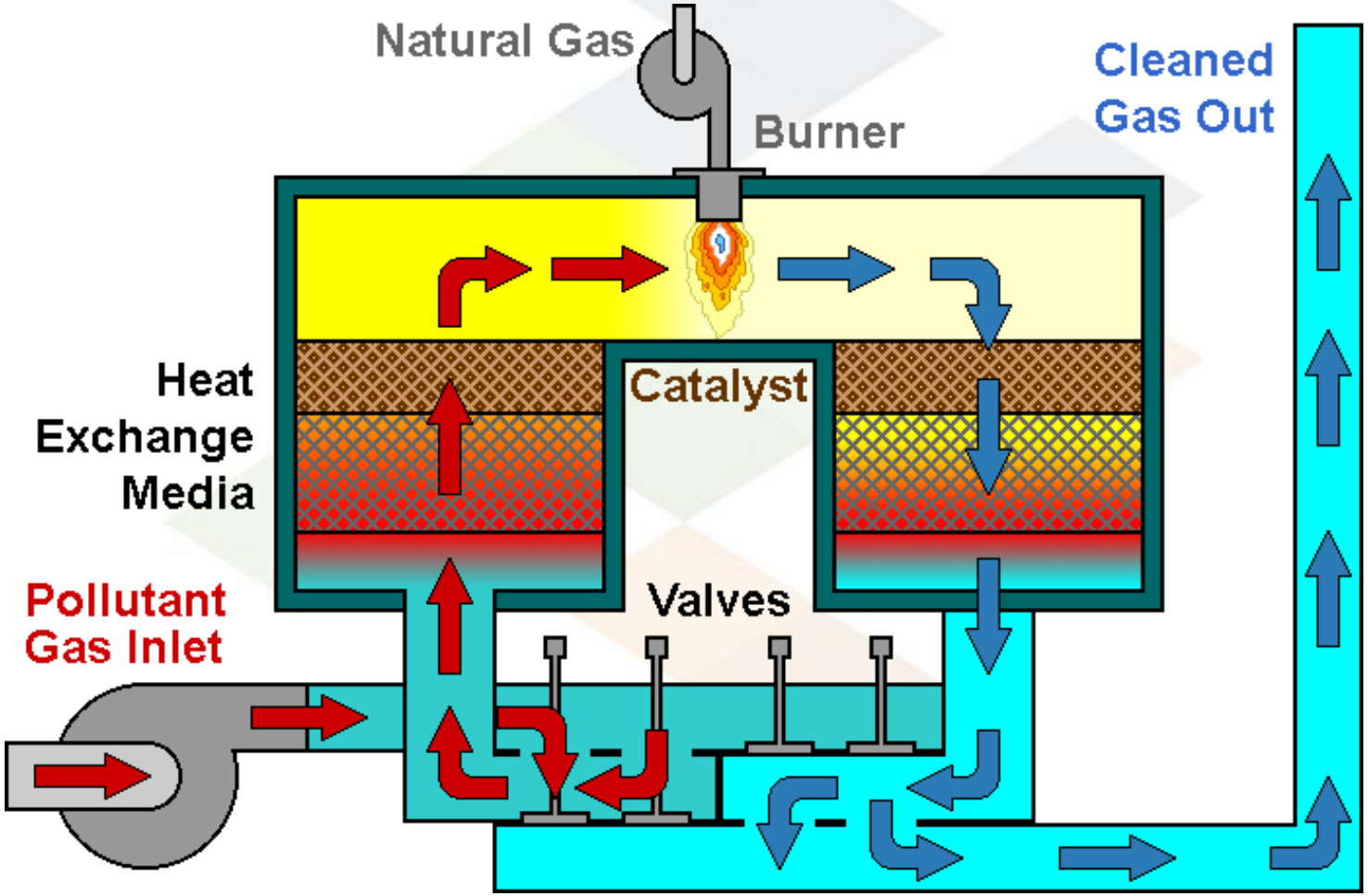



CTO
Waste Gas Inlet
Heat Exchanger
Catalyst Bed
Burner

Recuperative CTO (w/ Heat Exchanger)



Regenerative CTO (RCO)



Common Catalysts

- Noble Metals
  - Platinum
  - Palladium
  - Rhodium
- Metal Oxides
  - Chromium oxide
  - Magnesium oxide
  - Cobalt oxide







Chapter 3: Oxidation
Video

VOC 1.4 - Combustion CTO.mp4

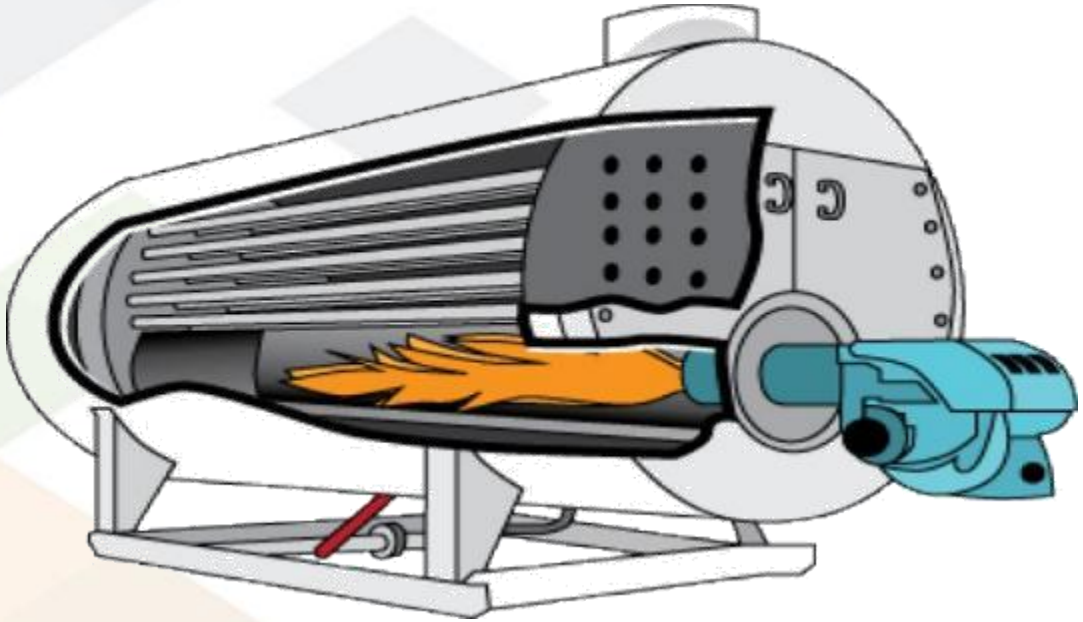
Boilers

- Boilers can combust CO & VOC in process gas if consistently generating a high concentration
- Same emissions profile as TO / TRO



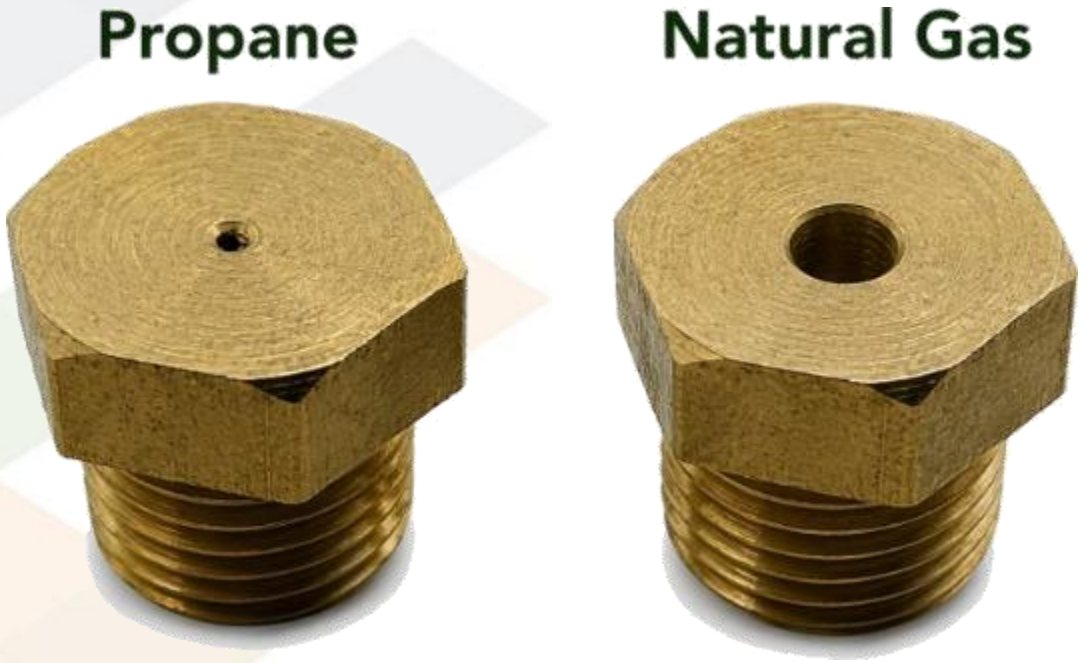
Boilers

- Waste gases (CO & VOC) are combusted instead of fossil fuels (oil or natural gas) to generate heat or steam
- Boilers are sized to specific heating value and pressure
  - Not easy to change to different fuels with different heating value and supply pressure



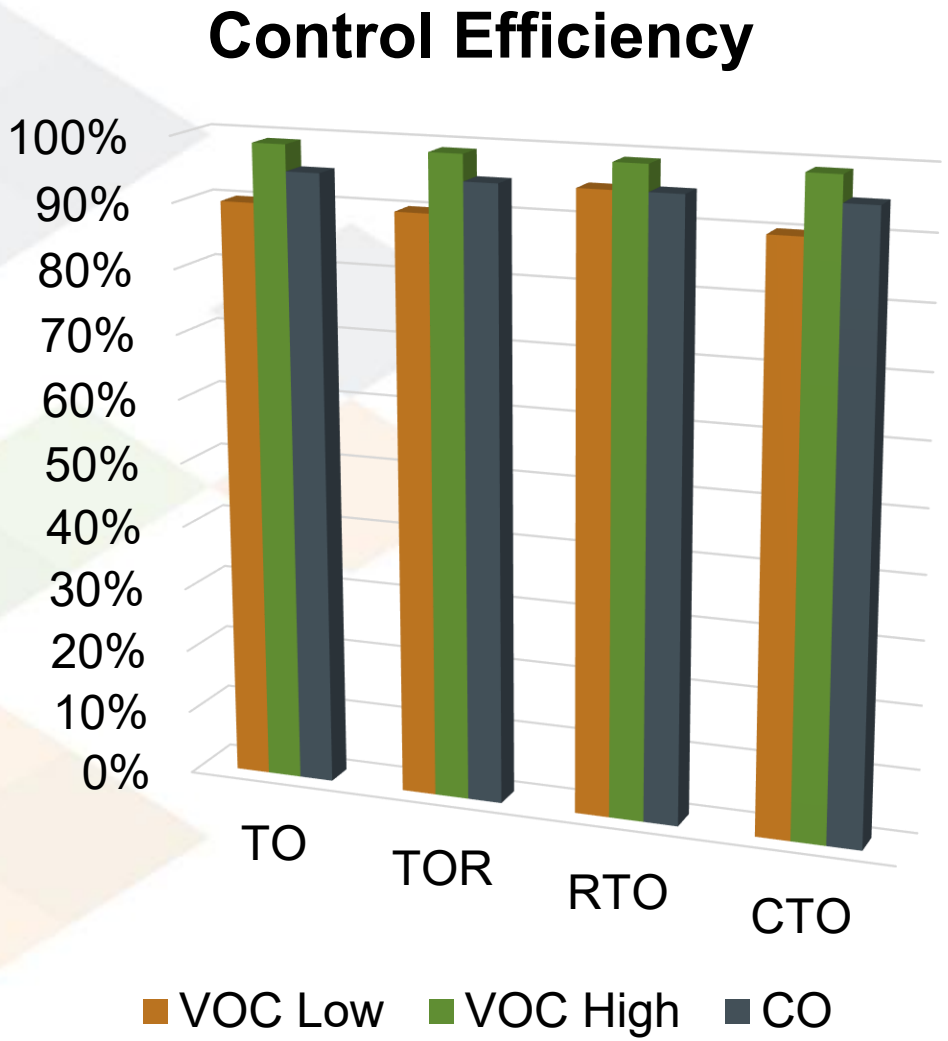
Boilers

- BTU content (heating value) of VOC process gas
  - Higher BTU requires smaller orifice in burner
  - May not be able to use variable BTU content from multiple VOC
- Boiler demand
  - Boiler must be operating while VOC process gas is generated
  - Is there sufficient boiler demand?



Control Efficiency

- TO: 90-99% VOC; 95% CO
- TOR: 90-99%; 95% CO
- RTO: 95-99%; 95% CO
- CTO: 90-99%; 95% CO
- Highly dependent on CO or VOC exhaust gas concentration



Parametric Monitoring

1. Combustion Temperature (Gas Outlet)
2. LEL Monitor
3. Pressure Differential
   - Heat Exchanger
   - Packed Beds
   - Catalyst Beds
4. Inlet Temperature (CTO)
5. Outlet Concentration (CTO)



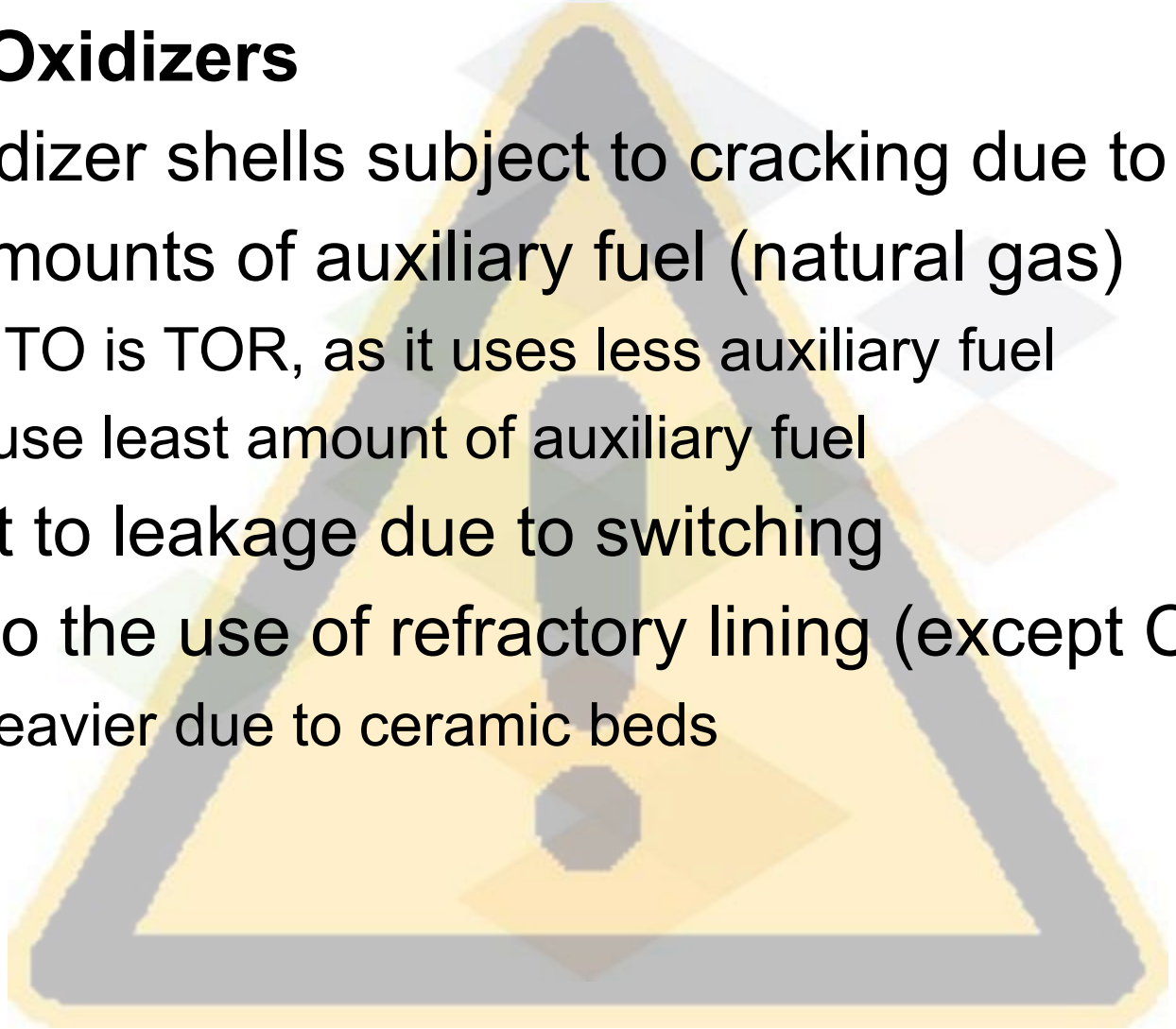






All Thermal Oxidizers

- Thermal oxidizer shells subject to cracking due to heat
- Use large amounts of auxiliary fuel (natural gas)
  - Base model TO is TOR, as it uses less auxiliary fuel
  - RTO / CTO use least amount of auxiliary fuel
- RTO subject to leakage due to switching
- Heavy due to the use of refractory lining (except CTO)
  - RTO even heavier due to ceramic beds

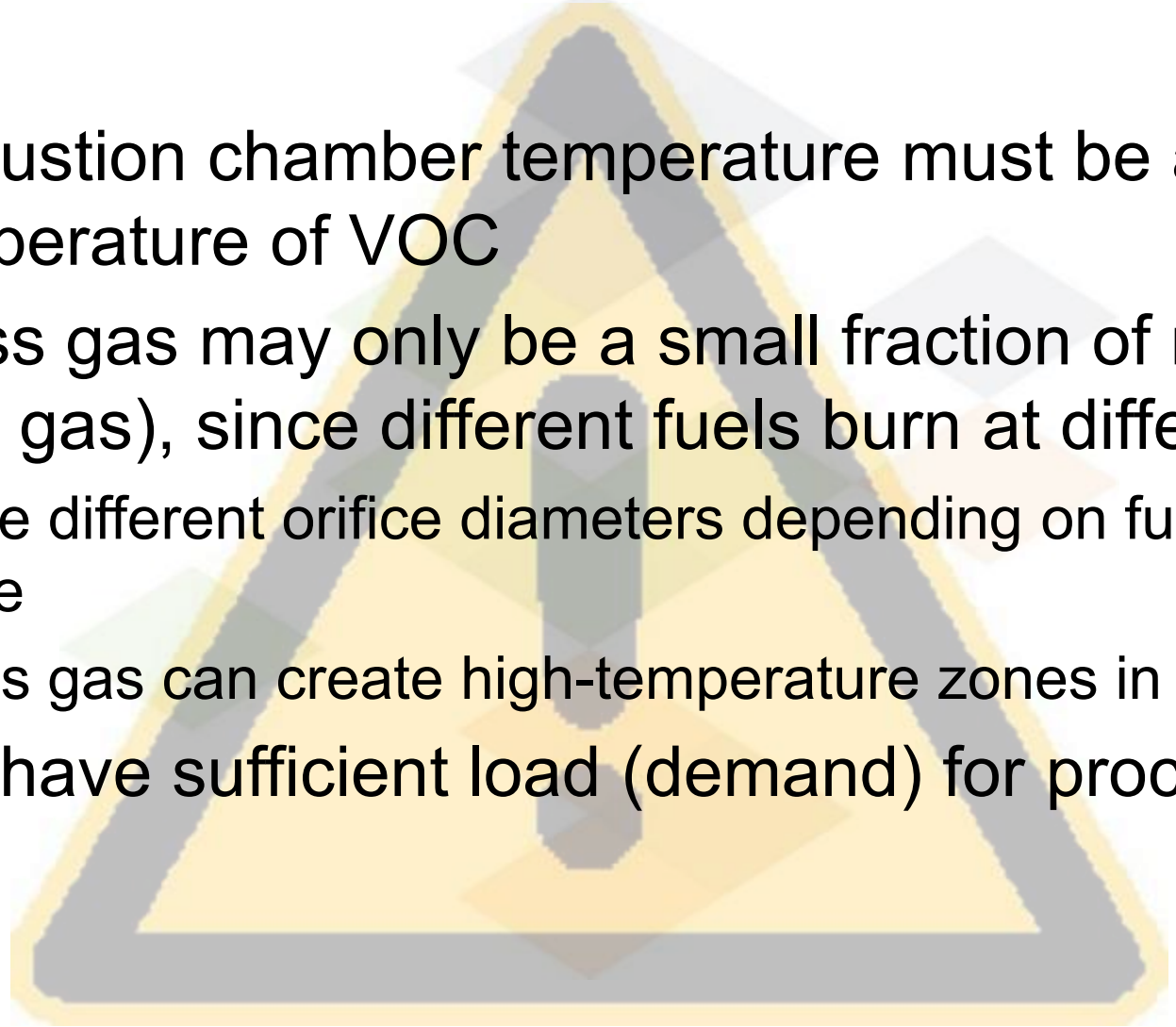


CTO

- Catalyst performance (control efficiency) reduction causes:
  - Fouling / Masking / Blinding: Material (PM, oil droplets, sulfur compounds) covers catalyst so that it is unable to function
  - Poisoning: Partial or total deactivation of catalyst by a chemical reaction (halides, sulfides, and nitriles); often irreversible
  - Thermal Aging: Elevated temperatures and relative humidity cause catalyst decomposition
    - Catalysts age during normal use, but lower operating temperatures can increase catalyst lifespan beyond 2-5 years
- Catalyst replacement and disposal is very expensive

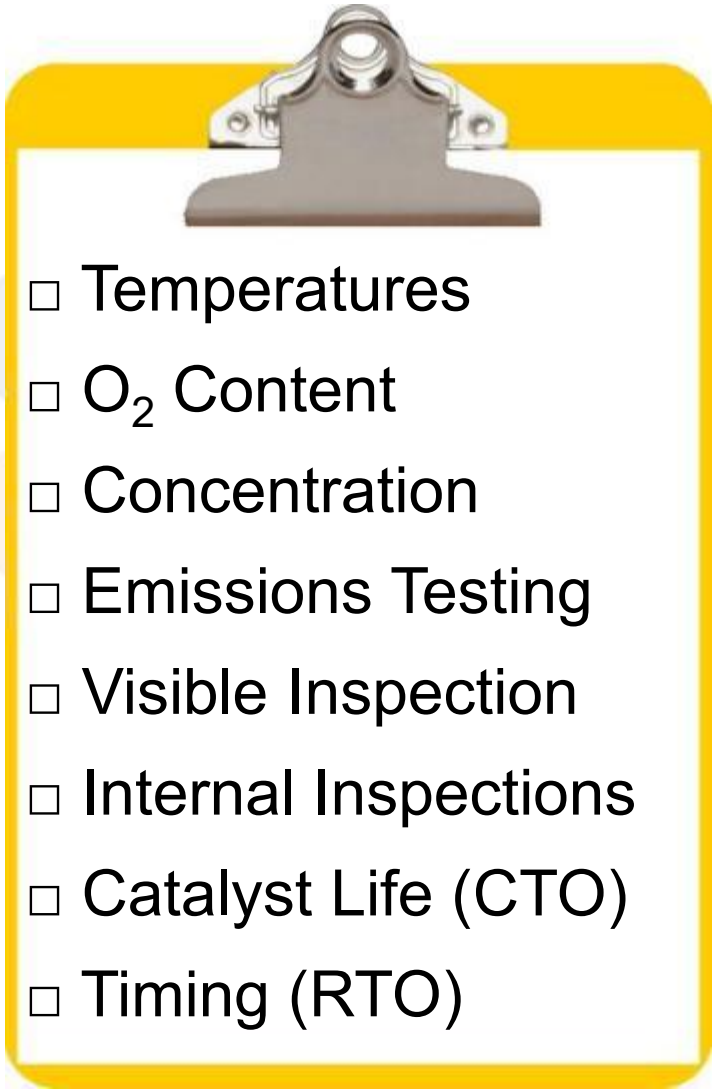
Boilers

- Boiler combustion chamber temperature must be above auto-ignition temperature of VOC
- VOC process gas may only be a small fraction of normal boiler fuel (natural gas), since different fuels burn at different rates
  - Burners have different orifice diameters depending on fuel BTU content and pressure
  - VOC process gas can create high-temperature zones in boiler
- Boiler must have sufficient load (demand) for process gas



Inspection Parameters

- Operating temperature (Inlet and Outlet)
- Oxygen content (Inlet and Outlet)
- Outlet CO or VOC concentration
  - Continuous Emissions Monitoring System (CEMS)
- Corrosion or rust
- Internal inspection report
- Catalyst life (CTO)
- Valve / rotation timing (RTO)



Chapter 3: Oxidation
Recap

In this chapter, we discussed:

- How oxidation control technologies operate
- Common types of oxidation control technologies
- Key design considerations for oxidation control technologies
- Typical achievable control efficiencies
- Monitoring methods for oxidation control technologies
- Common problems with oxidation control technologies
- Ensuring compliance