

REINHOLD ENVIRONMENTAL Ltd.



## **2014 NO<sub>x</sub>-Combustion Round Table & Expo Presentations**

February 10 & 11, 2014, in Charlotte, NC / Hosted by Duke Energy

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# CO Catalyst

2014 Reinhold NOx Conference

February 10<sup>th</sup>, 2014

Charlotte, NC



Johnson Matthey

## Introduction

- Overview of CO Oxidation catalyst – what is it?
- Introduction to CO Catalyst Design
- Product Maintenance and Upkeep
- Emission Definitions and Impact on Catalyst Sizing

Objective: Explain CO catalyst fundamentals to a crowd of SCR experts

# CO / VOC Oxidation Catalyst

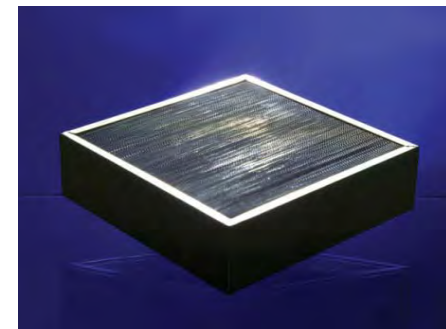
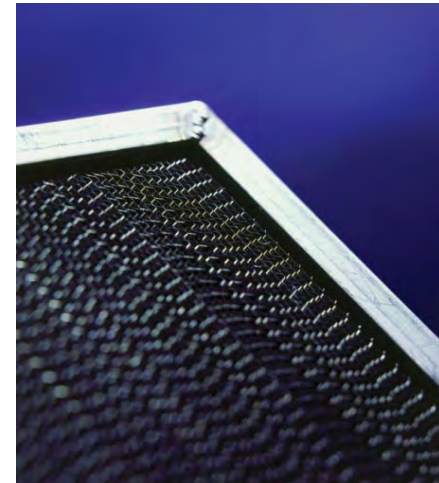


Coated Metal Honeycomb Catalyst

Typically 200 cells / in<sup>2</sup>

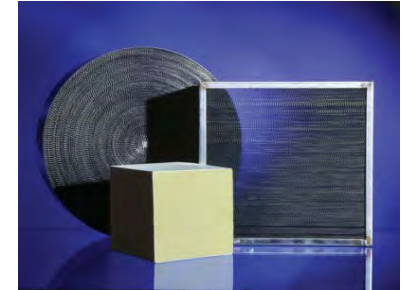
Custom Block Sizes

Invented by JM in 1970s

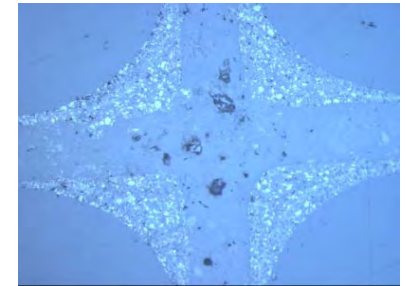


# CO Catalyst Components

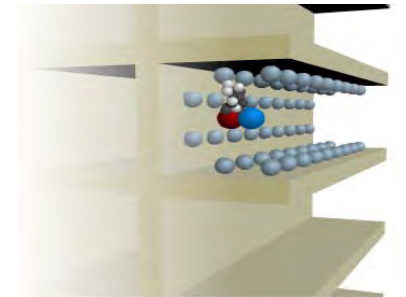
Substrate: The catalyst support media is metallic (*steel foil in SS frame*) monolithic honeycomb of high geometric surface area.



Washcoat: A high surface area material is applied to the substrate, providing strong adhesion and a highly porous surface, essential for high dispersion of small catalyst particles, and hence catalytic activity.



Platinum Group Metals (PGM): These are the highly active catalytic materials embedded in the washcoat which promote the required chemical reactions.

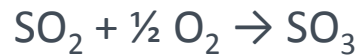


## Oxidation Catalyst Reactions

- Hydrocarbon, CO, and H<sub>2</sub> Oxidation



- NO and SO<sub>2</sub> Oxidation



- Typical Hydrocarbons are fuel related

Methane – CH<sub>4</sub>

Ethane – C<sub>2</sub>H<sub>6</sub>

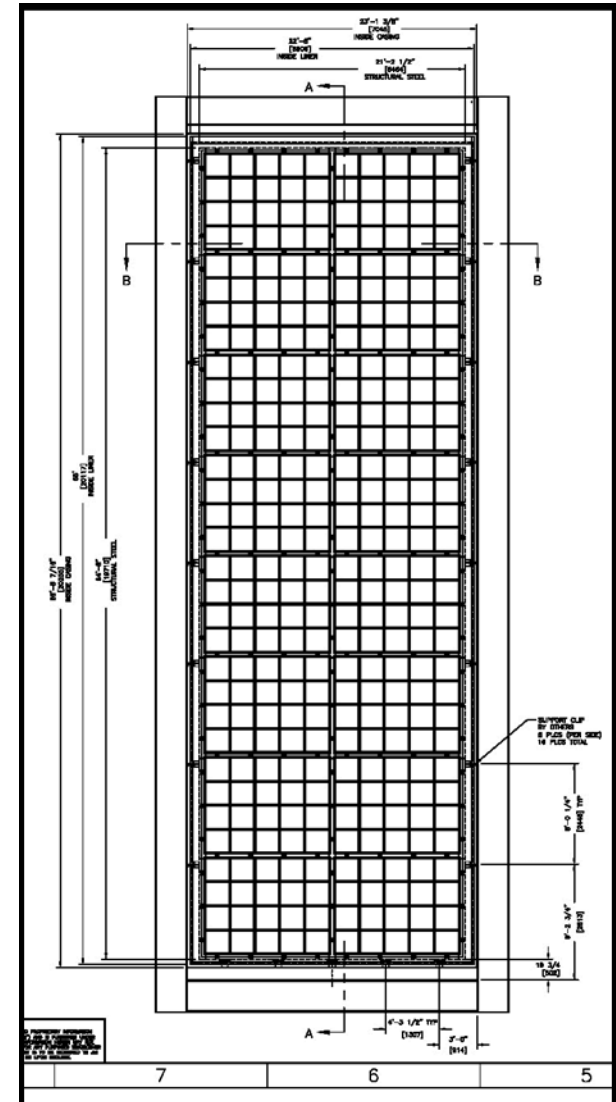
Formaldehyde – HCHO

Aromatics – Benzene (C<sub>6</sub>H<sub>6</sub>), Toluene (C<sub>7</sub>H<sub>8</sub>), Xylenes (C<sub>8</sub>H<sub>10</sub>)

Decane – C<sub>10</sub>H<sub>22</sub>

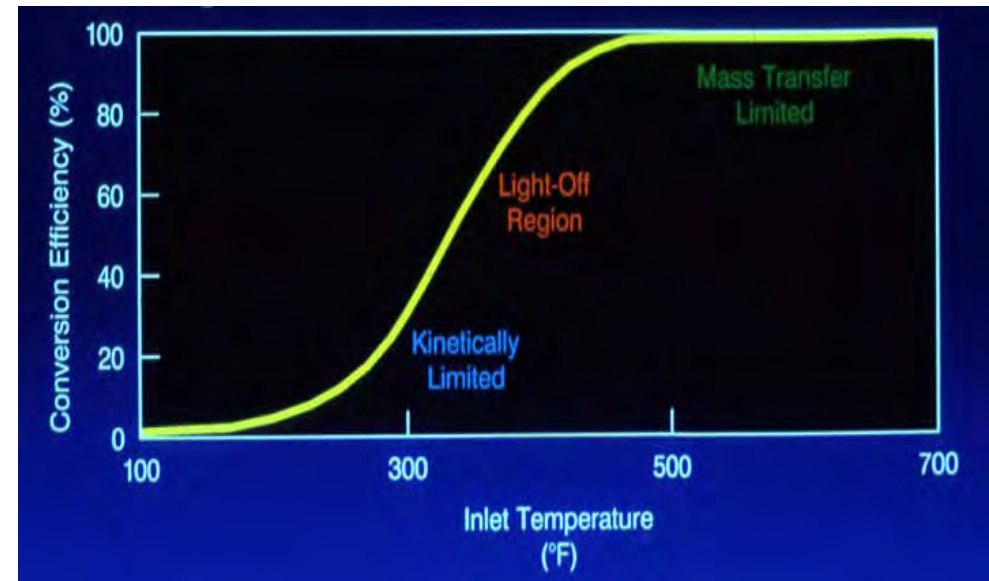
# CO Oxidation Catalyst Performance

- Fuels – Suitable for NG or ULSD
- CO Reduction
  - ✓ 50 - 95+% Range
  - ✓ 80 - 90% Typical
- VOC Reduction
  - ✓ 0 – 70% Range
  - ✓ 0 – 50% Typical
- Pressure Drop
  - ✓  $\leq 1.0$  iwg Typical
- Performance Guarantee Period
  - ✓ 3 years or 5 years Typical

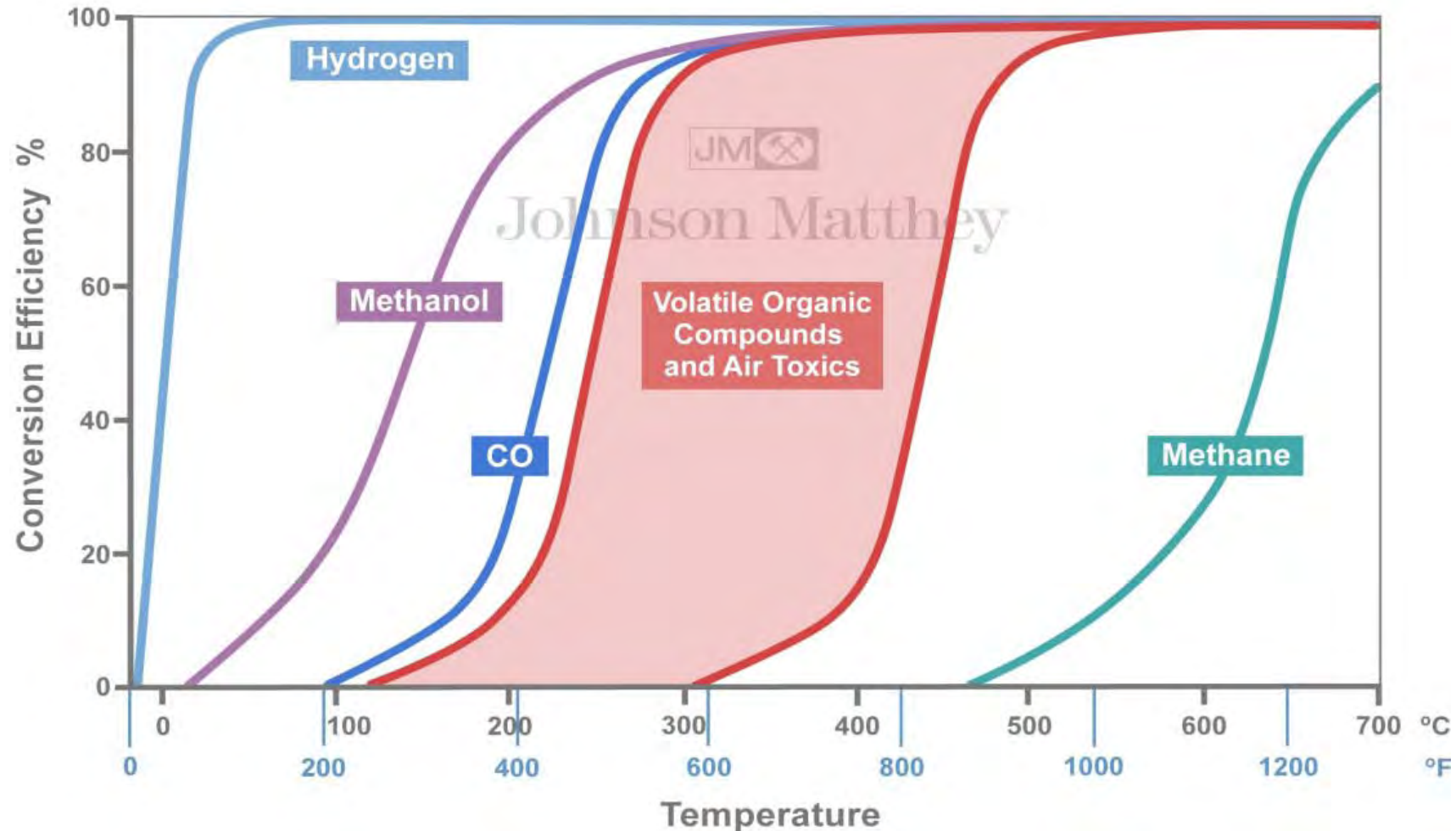


## Reaction Rates

- The catalytic reactions can only occur at the active sites on the catalyst surface
- Reactants and products must travel quickly to and from the active catalytic site, a process known as “mass transfer”
- The rate of reaction is a function of temperature, reactant concentration, number of active sites and the mass transfer rate
- The slowest “rate determining” step sets the overall reaction rate

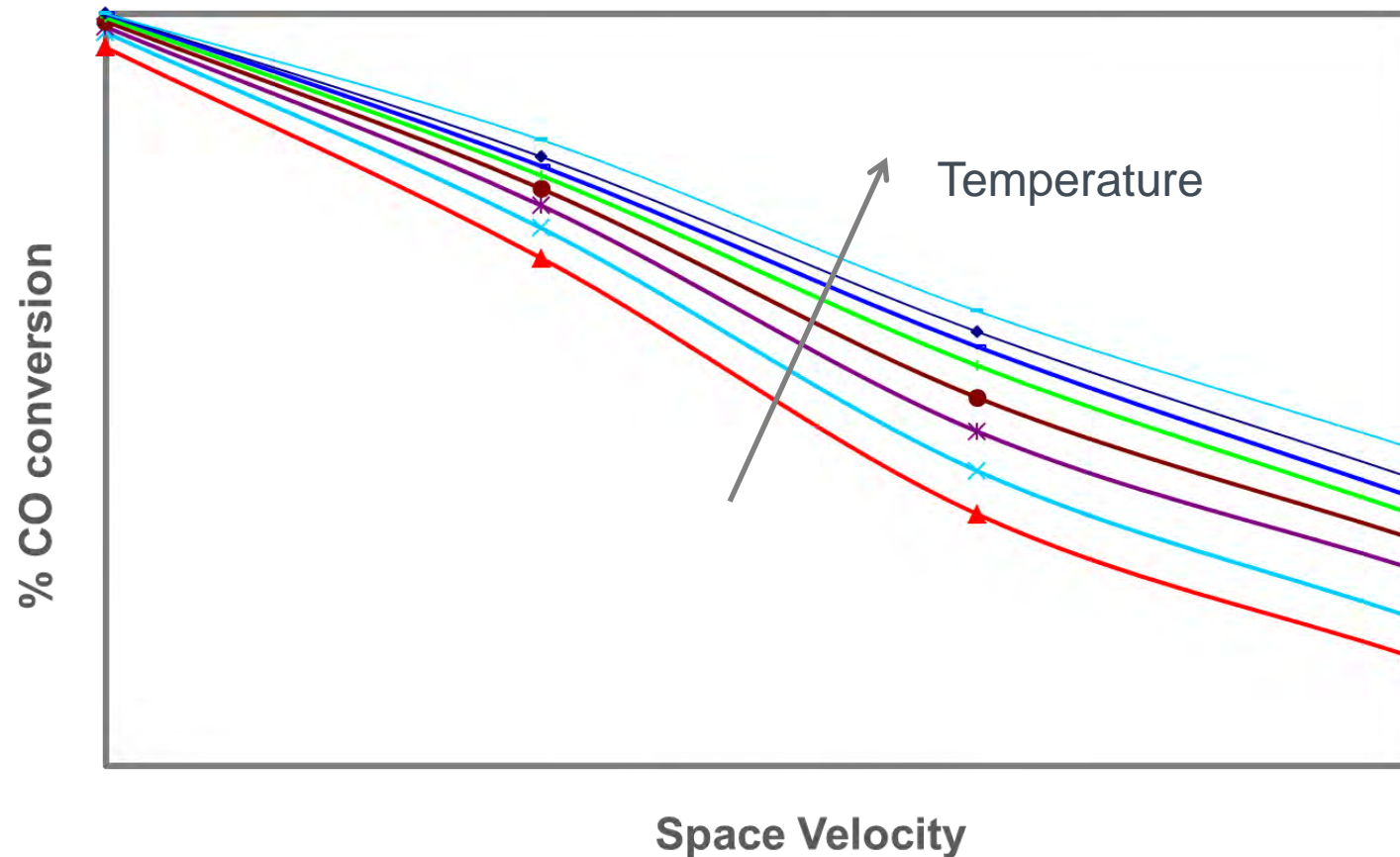


Catalyst “Light-Off” – Temperature range at which conversion increases rapidly

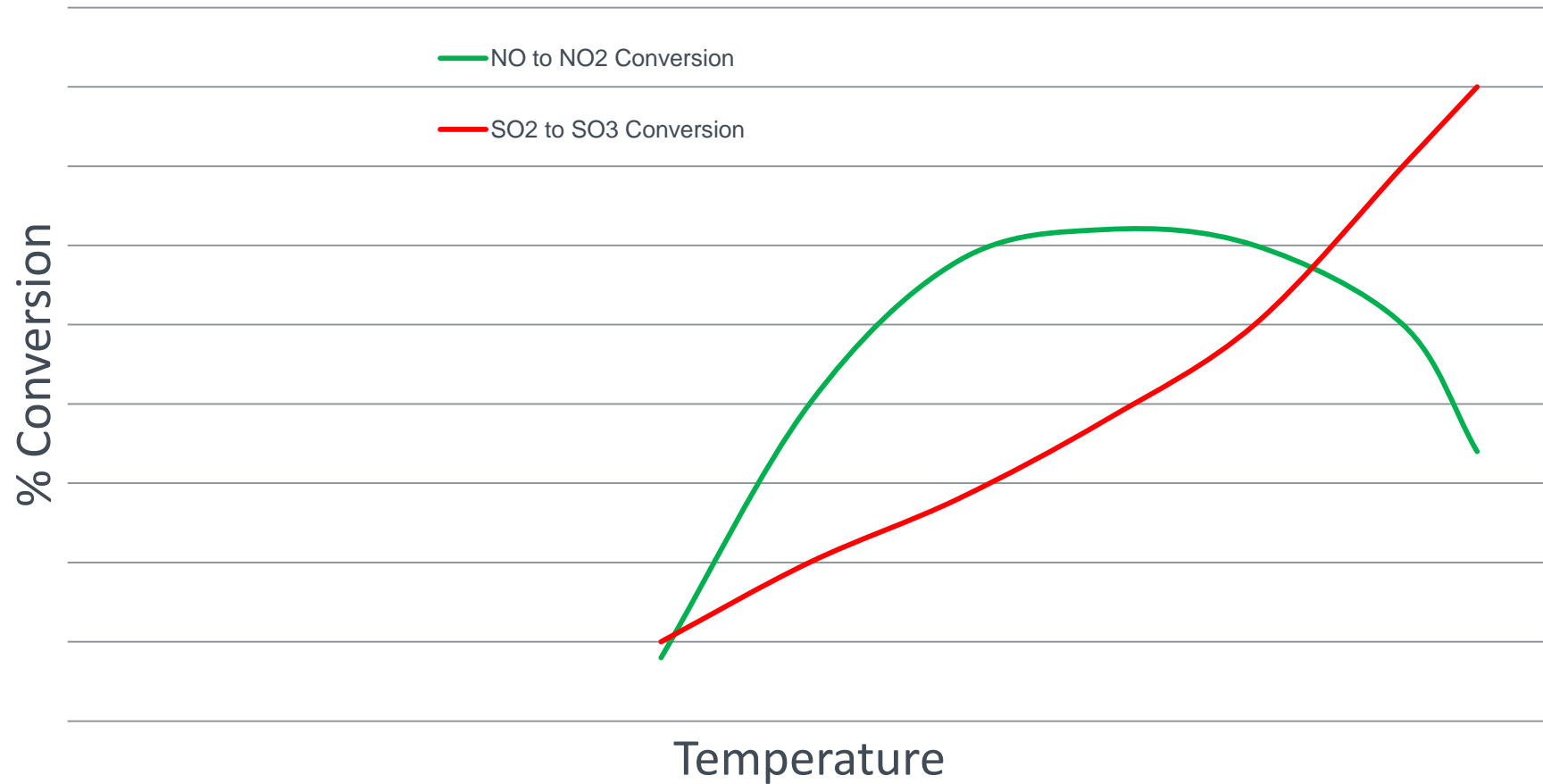


# Space Velocity vs. CO Conversion

## Example Operating Guidelines



## NO and SO<sub>2</sub> conversion



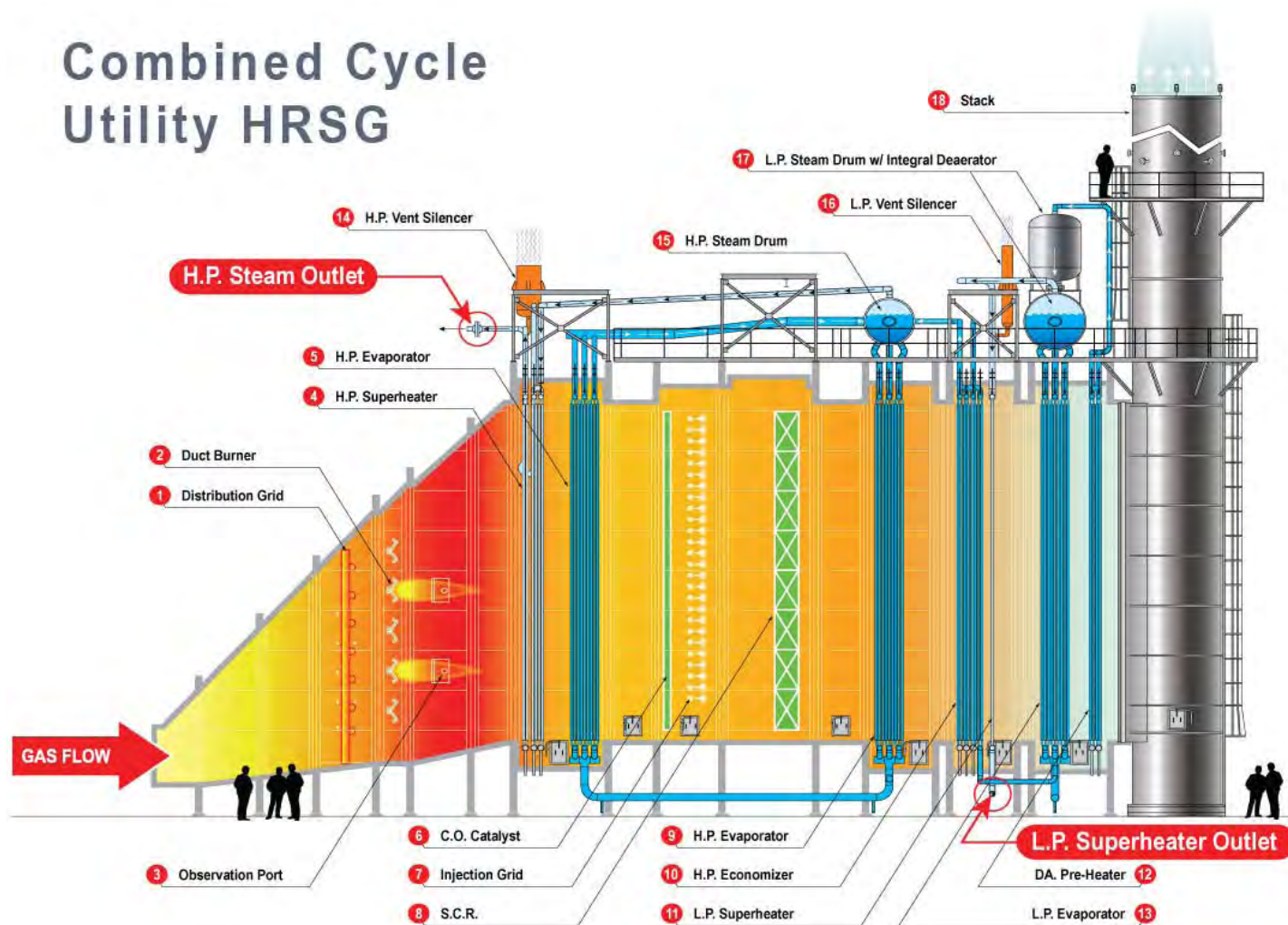
Decreasing Temperature May not decrease NO Conversion

## VOC Conversion Performance

- VOCs oxidized to CO<sub>2</sub> and H<sub>2</sub>O
- Non methane and ethane
- Specific VOCs present usually not known
- Rate of conversion strongly dependent on specific VOC
  - Conversion of saturated hydrocarbons difficult

# Oxidation Catalyst Placement

## Combined Cycle Utility HRSG



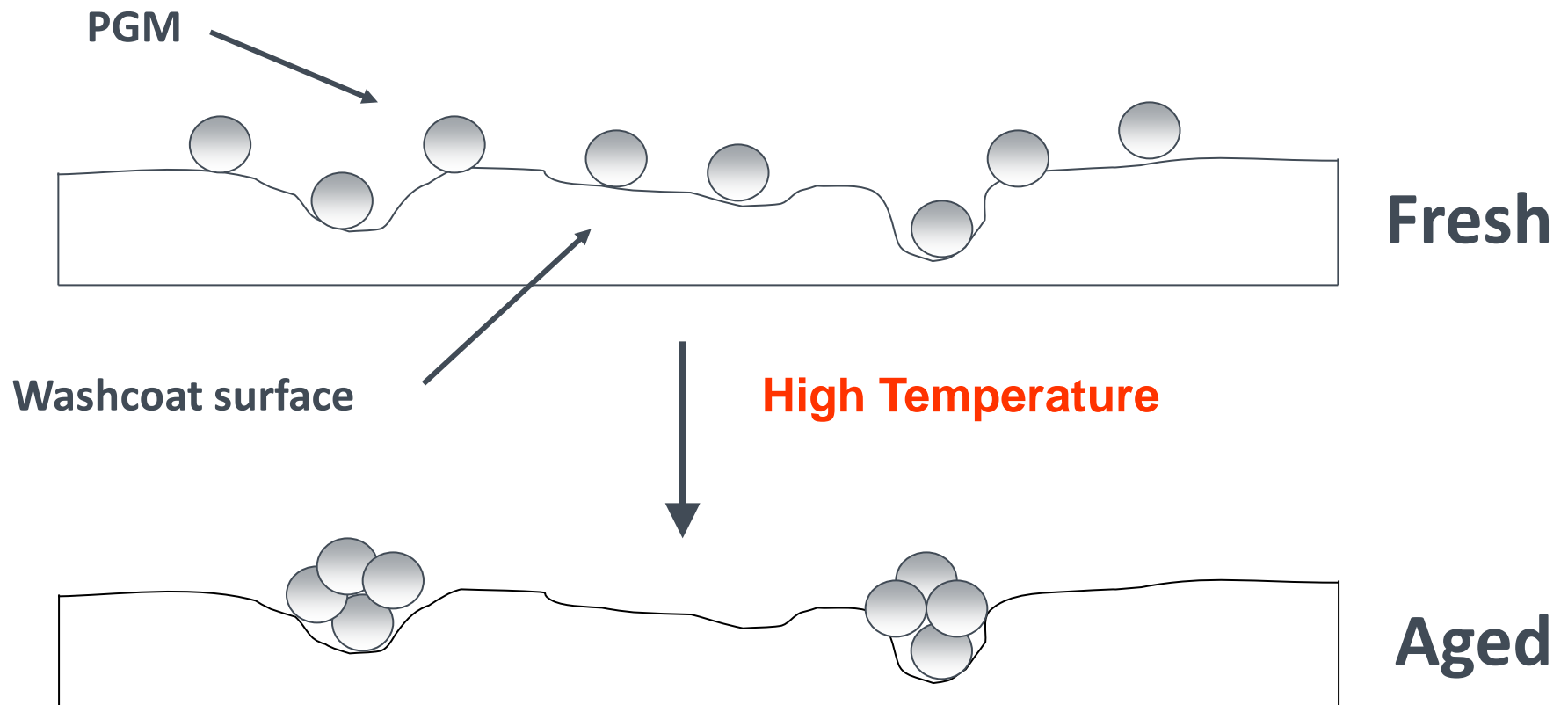
## Catalyst Lifetime

- Catalysts exhibit very high ‘fresh’ activity when first prepared/installed
- Over time, catalysts may be exposed to high temperatures and various chemical species that can reduce activity
- Catalyst activity will ‘age’ with operating time, eventually reaching a level at which the catalyst must either be regenerated or replaced

# Catalyst Deactivation Mechanisms

- Thermal deactivation: *(typically irreversible)* Occurs above 1200 °F
  - Failure of substrate material
  - Sintering of active catalytic species
  - Sintering of support
  - Reaction of catalyst materials
  - Catastrophic thermal event
- Poisoning: *(typically reversible)*
  - Chemical (selective) contamination of active sites
  - Physical (non-selective) contamination
    - *masking, fouling, plugging of cells/pores, washcoat attrition*

## Sintering of PGM Coating

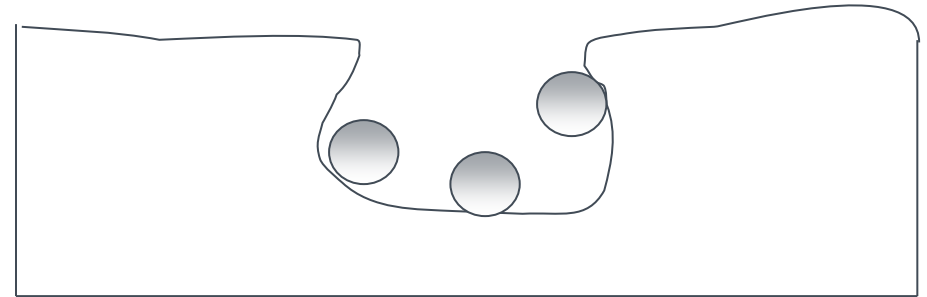


## Sintering of Washcoat Support

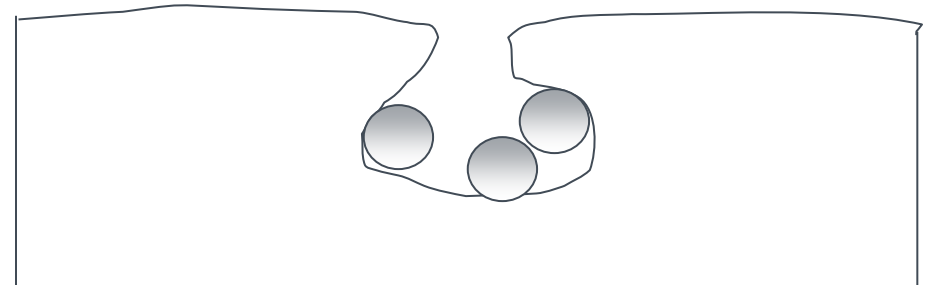
### Loss of accessible support surface area

Two main mechanisms:

- Pore opening is reduced and pore diffusion resistance increases
- Carrier converts to new crystal structure. For example, gamma-alumina converts to alpha-alumina



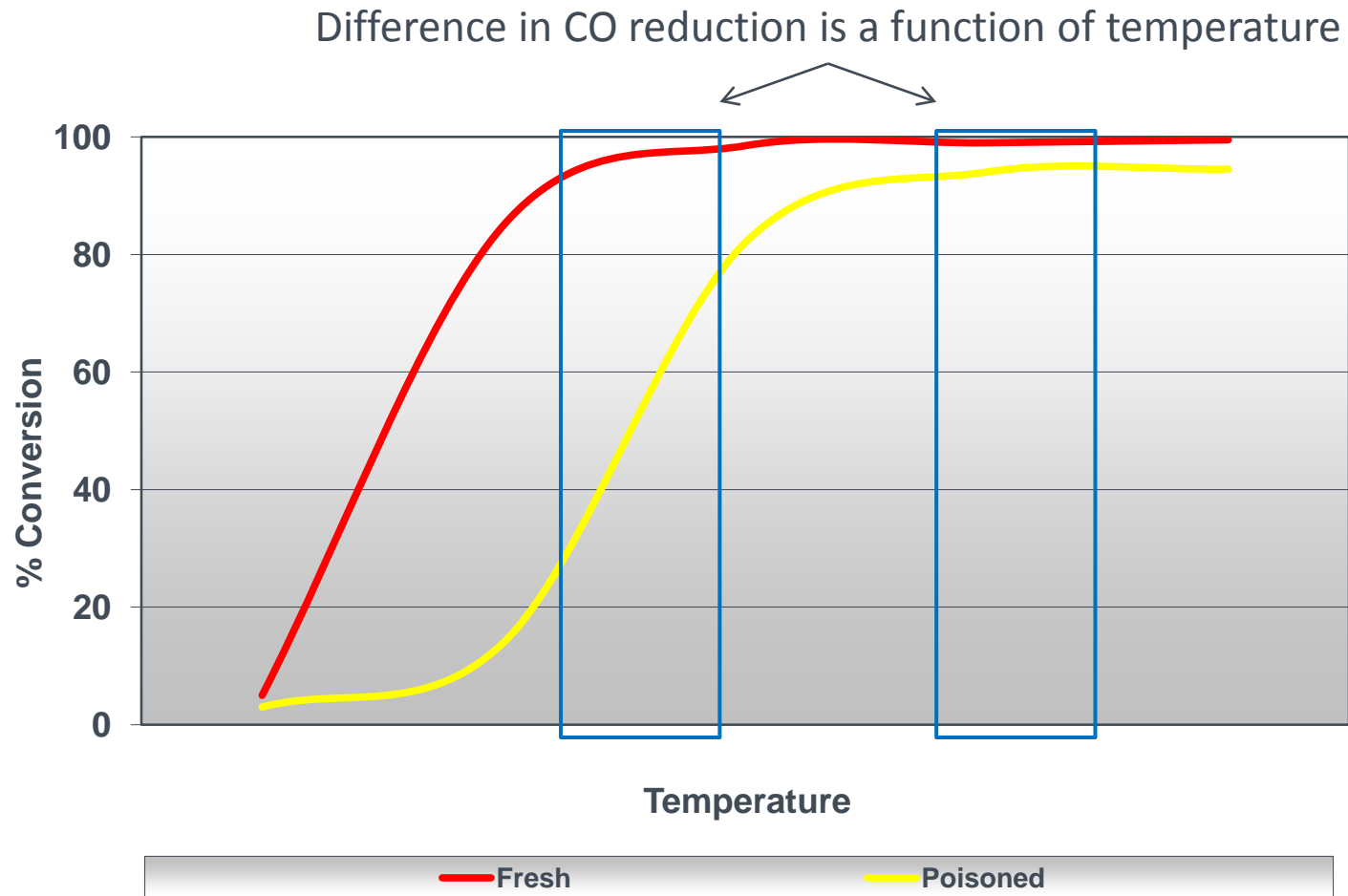
**High Temperature**



## Catalyst Poisons

- Heavy and Base Metals:
  - Lead (Pb)
  - Arsenic (As)
  - Zinc (Zn)
  - Copper (Cu)
  - Sulfur (S)
  - Mercury (Hg)
  - Tin (Sn)
  - Iron (Fe)
  - Chrome (Cr)
  - Phosphorous (P)
  - Silicon (Si)
  - Nickel (Ni)
  - Antimony (Sb)
- High Molecular Weight Organic Material
- Dust and Particulates
- CO Catalyst – NOT SUITABLE FOR COAL-FIRED APPLICATIONS
- Common Culprits – Fuel, Lube Oil, Water, Corrosion of upstream equipment

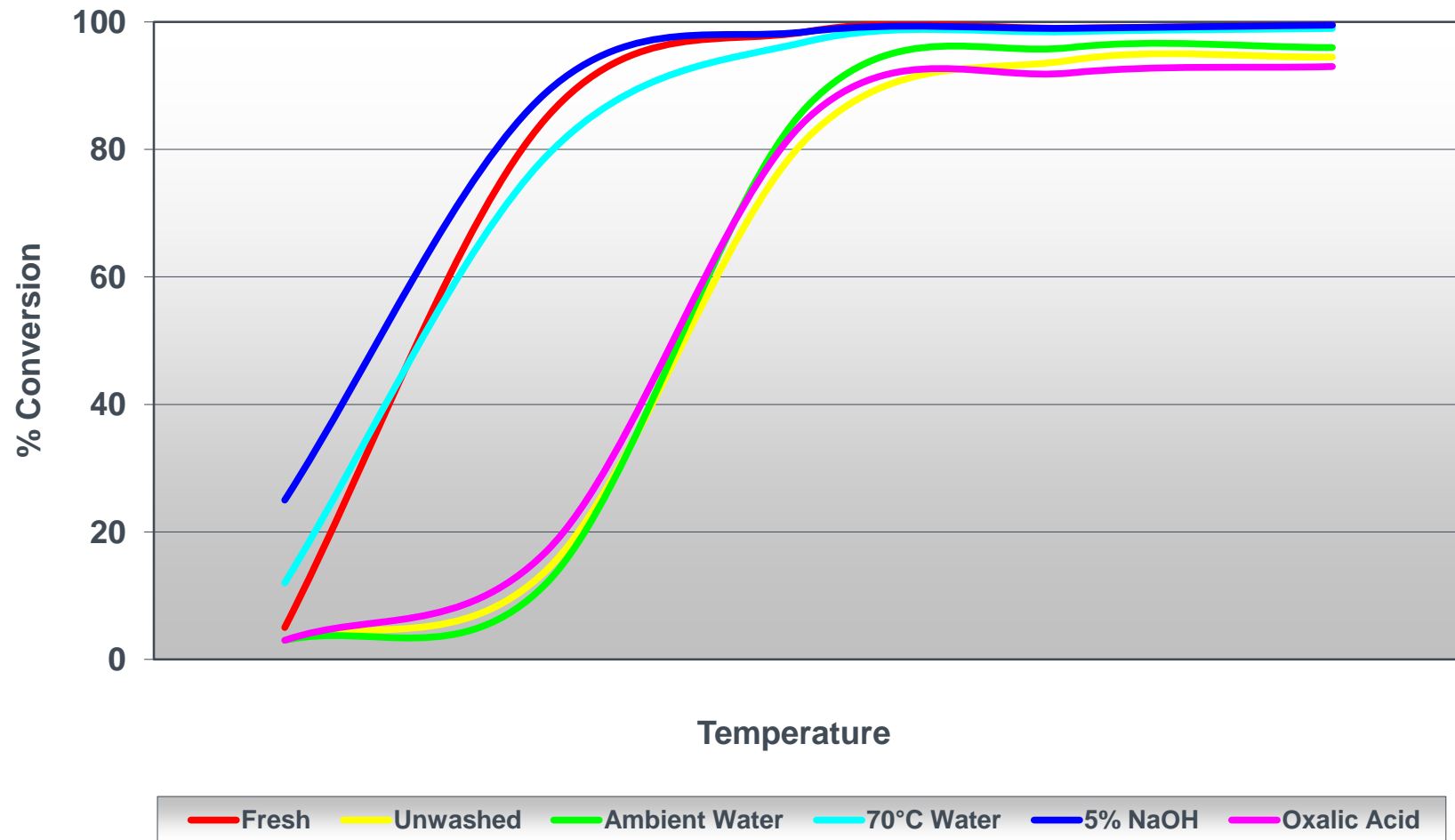
# Poisoning



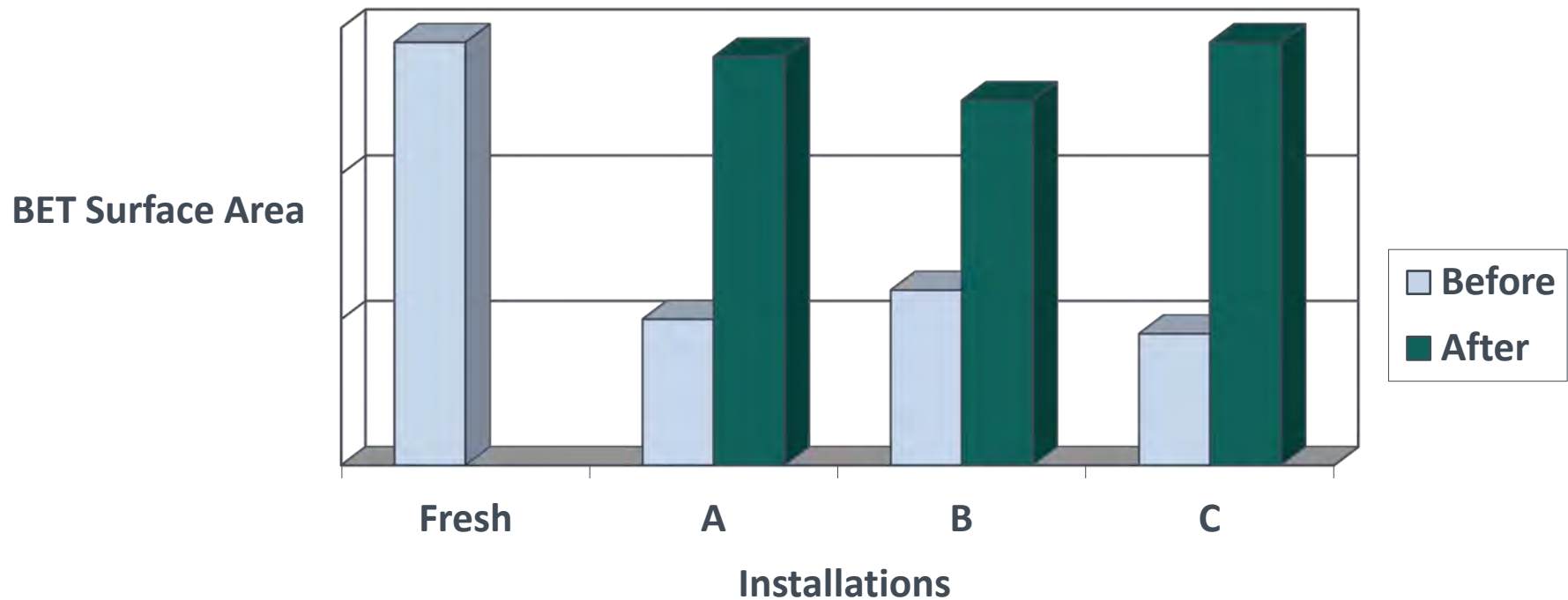
## Catalyst Regeneration or Cleaning Options

- Thermal
  - Elevating Temperature
    - *Oxidizes organic material*
- Physical
  - Vacuuming or Compressed Air Blowing
    - *Removes dust and debris*
- Chemical (including DI Water)
  - Washing
    - *Removes masking agents*
    - *Restores surface area*
    - *Reduces poison concentration*

# Washing Study



## Recovery of Surface Area by Chemical Washing



## Coal to Gas Conversion



## CO Catalyst Options if required after Coal to Gas Conversion

- Suitable for units converted to 100% Gas firing
- Not suitable for coal firing (or fuels containing particulate and Sulfur)
  - Back-up fuel or co-firing
- Suitable for low S fuel oil (ULSD) used as back-up fuel.
- Not suitable for heavy fuel oil
- Be mindful of operating temperature ranges required for oxidation

## PPM Definitions

- $$ppmvd@actualO_2 = \frac{ppm,wet@actualO_2}{(100 - H_2O \text{ vol}\%)}$$
- $$ppmvd@15\%O_2 = ppmvd@actualO_2 \frac{(20.9\% - 15\%)}{(20.9\% - Actual O_2 \text{ vol}\%, dry \text{ basis})}$$
- $$Actual O_2 \text{ vol}\%, dry \text{ basis} = \frac{O_2 \text{ vol}\%, wet \text{ basis}}{(100 - H_2O \text{ vol}\%)}$$

## Inlet Calculations More Complicated Than SCR?

- For coal boiler, only source of NO<sub>x</sub> is from boiler
- For Gas Turbine there can be duct burners or tempering air after turbine outlet
  - Duct firing adds source of CO
  - Both alter flue gas composition
- Integration of supplier inputs (gas turbine, duct burners, tempering air flow) need to be carefully calculated to ensure correct design basis
- Guarantees are sometimes given in different concentrations units as inlet

## Impact on Sizing? – wrong O<sub>2</sub> basis

- Inlet CO emission given as ppmvd @ 15% O<sub>2</sub>, but emission guarantee is given as ppmvd
- Example Case
  - Inlet CO = 11.85 ppmvd @ 15% O<sub>2</sub>
  - Vol%H<sub>2</sub>O = 11.65%
  - Vol%O<sub>2</sub> = 10.55%, wet basis
  - Vol%O<sub>2</sub> = 11.94%, dry basis
- CO outlet @15% O<sub>2</sub> vs Actual O<sub>2</sub>

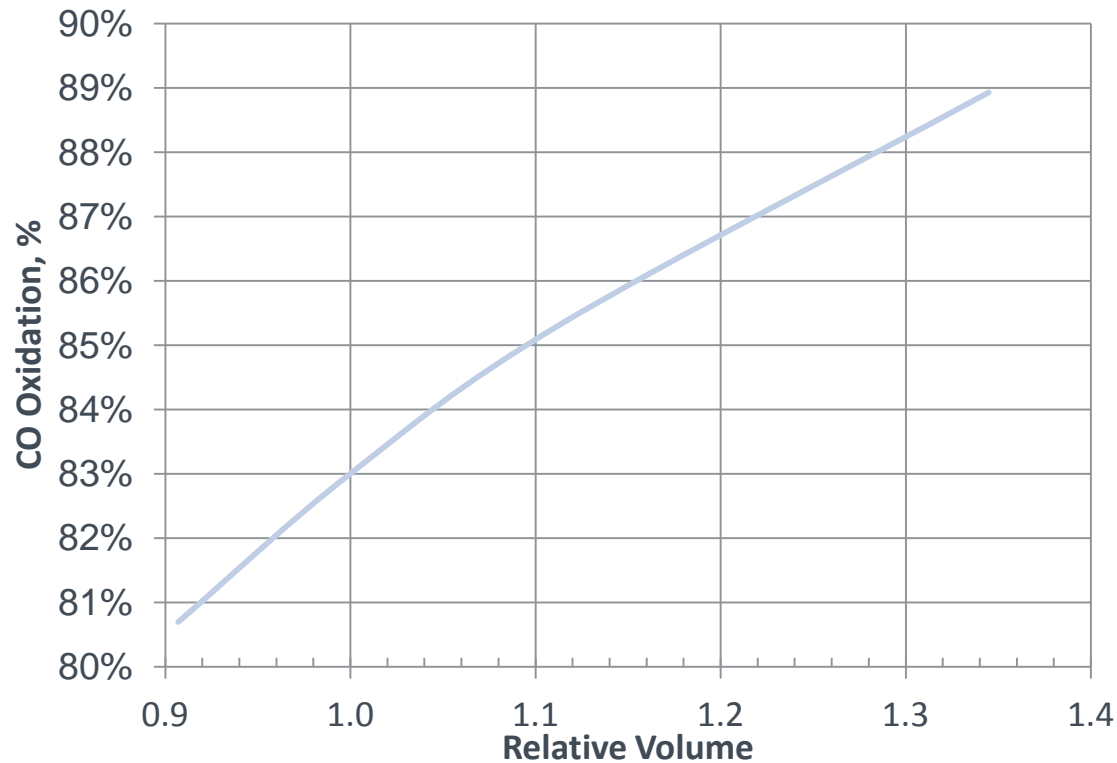
$$x \text{ ppmvd@15\%O}_2 = 2 \text{ ppmvd@actualO}_2 \frac{(20.9\% - 15\%)}{(20.9\% - \text{Actual O}_2 \text{ vol\%, dry basis})}$$

$$x \text{ ppmvd@15\%O}_2 = \mathbf{1.32}$$

- Difference in % reduction?
  - $(11.85 - 2)/11.85 = \mathbf{83.1\% \text{ reduction}}$

# Volume Impact?

Example Case - CO oxidation vs. Volume



Going from 83% to 89%  
results in ~35% more  
volume!

## Impact on Sizing – Different burner emission rates, same heat load

- Constant Gas Turbine Outlet of 9 ppmvd (15% O<sub>2</sub>) CO and 1.4 ppmvd (15% O<sub>2</sub>) VOC
- Burner 1 adds 0.08 lb CO/(MMBTU/hr) and 0.004 lb VOC/(MMBTU/hr)
- Burner 2 adds 0.12 lb CO/(MMBTU/hr) and 0.008 lb VOC/(MMBTU/hr)
- Plant needs to achieve 2 ppmvd (15% O<sub>2</sub>) CO and 1 ppmvd (15% O<sub>2</sub>) VOC in the stack
- GT + Burner 1: 82% CO Reduction, 33% VOC Reduction
- GT + Burner 2: 85% CO Reduction, 47% VOC Reduction

	GT + Burner 1	GT + Burner 2
Inlet CO (ppmvd, 15% O <sub>2</sub> )	11.1	13.6
Inlet VOC (ppmvd, 15% O <sub>2</sub> )	1.5	1.9

## Summary/Conclusions

- CO Catalyst for Natural Gas applications is a mature technology
- Temperature and Space Velocity are the two most important parameters affecting catalyst performance
- Performance of poisoned catalyst is a function of temperature
- Take care in performing CO concentration calculations
- Evaluate system economics holistically



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