Worldwide Pollution Control Association

Michigan Coal to Gas Seminar

June 5-6, 2012

WPCA

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SCR/CO Catalyst Considerations

Johnson Matthey Catalysts

WPCA/Gulf Power
Coal to Gas Conversion Seminar
Detroit, FL
June 5-6, 2012

Ken Jeffers

ENVIRONMENTAL CATALYSTS AND TECHNOLOGIES

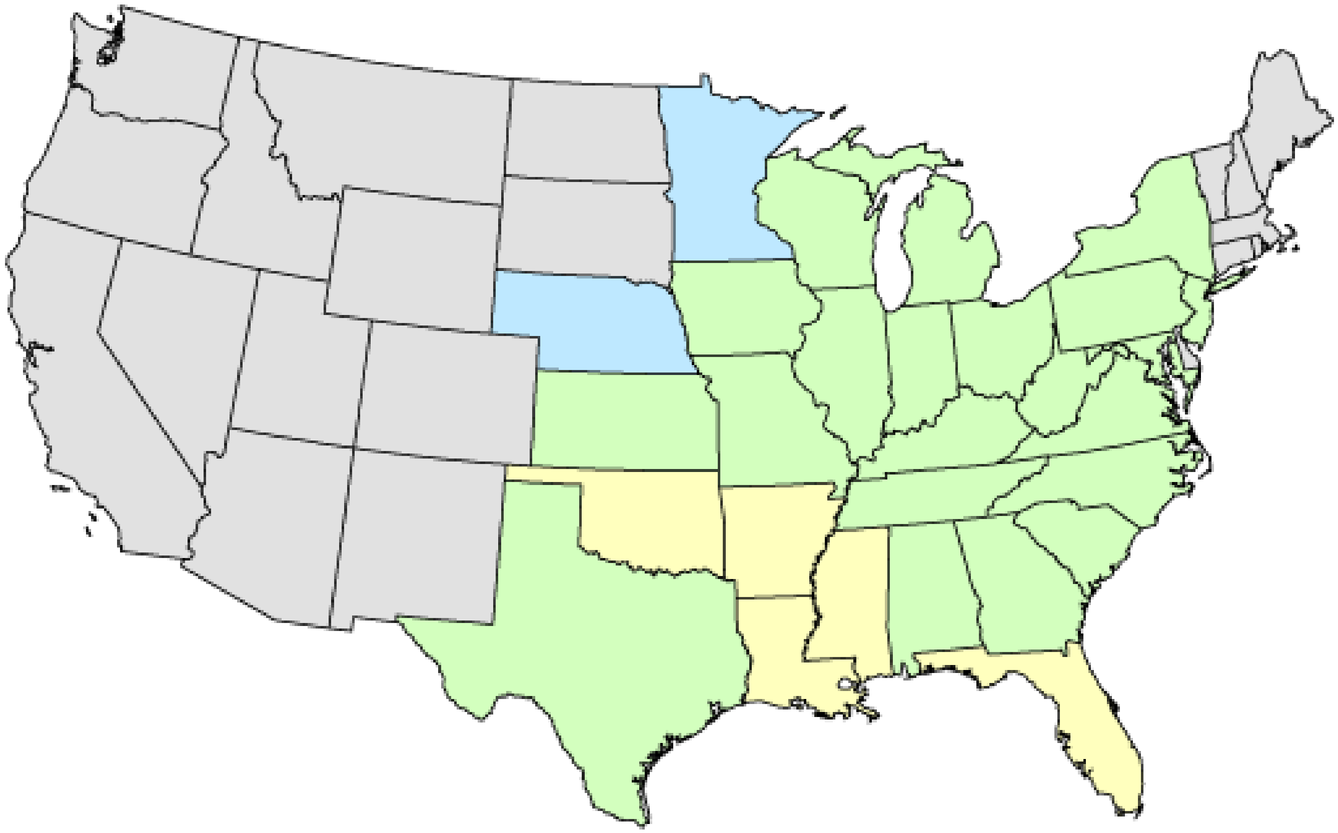
Topics

- Regulatory Drivers for Controlling Emissions – NO_x, CO
- SCR Catalyst for NO_x control
- CO oxidation catalyst

Regulatory Drivers - NO_x Control

- NO_2 is 1 of 6 criteria pollutants
- Respiratory irritant, contributes to low-level ozone formation
- Regulated per EPA NAAQS
- MATS, Amendments to NSPS: NO_x emission limit – 0.7 lb/MWh
- Further controls necessary per CSAPR which requires:
- 23 states to reduce SO_2 and NO_x to help downwind states attain 2006 24-hour and/or 1997 annual $PM_{2.5}$ NAAQS
- 20 states to reduce Ozone Season NO_x to help downwind areas attain 1997 8-hour Ozone NAAQS

CSAPR States



- States controlled for both fine particles (annual SO_2 and NOx) and ozone (ozone season NOx) (21 States)
- States controlled for fine particles only (annual SO_2 and NOx) (2 States)
- States controlled for ozone only (ozone season NOx) (5 States)
- States not covered by the Cross-State Air Pollution Rule

Regulatory Drivers - CO Control

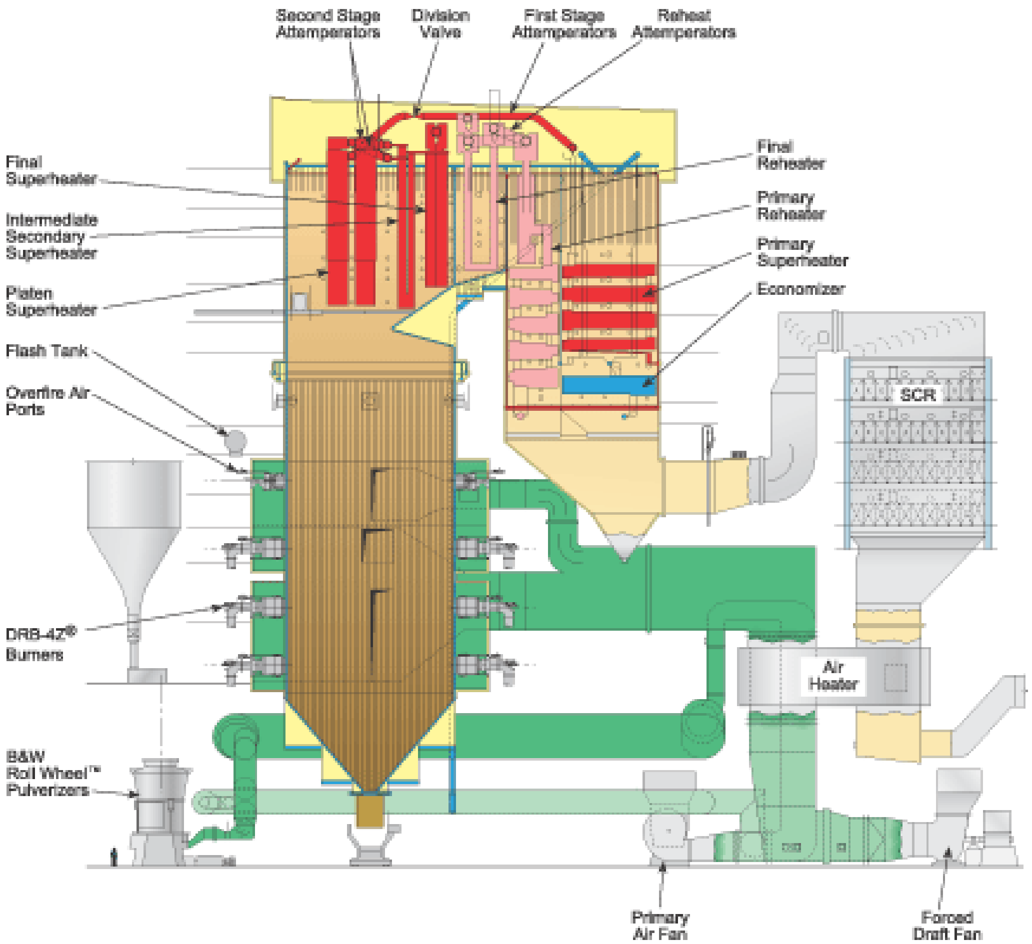
- CO is 1 of 6 criteria pollutants
- Majority of CO emissions come from mobile sources
- CO displaces oxygen to the heart and brain
- Contributes to low-level Ozone formation
  $CO + 2O_2 \rightarrow CO_2 + O_3$
- NAAQS for CO
  8-hour average: </= 9 ppmv
  1-hour average: </=35 ppmv

Fossil Fuel Air Emissions Comparison (lb/MMBTU of Energy Input)

Pollutant	**Natural Gas**	**Oil**	**Coal**
Carbon Dioxide	120	160	200
Carbon Monoxide	0.040 (?)	0.03	0.20
Nitrogen Oxides	0.35	0.40	0.40
Sulfur Dioxide	0.001	1.0	2.5
Particulates	0.007	0.08	2.7
Mercury	0.000	0.007×10^{-3}	0.016×10^{-3}

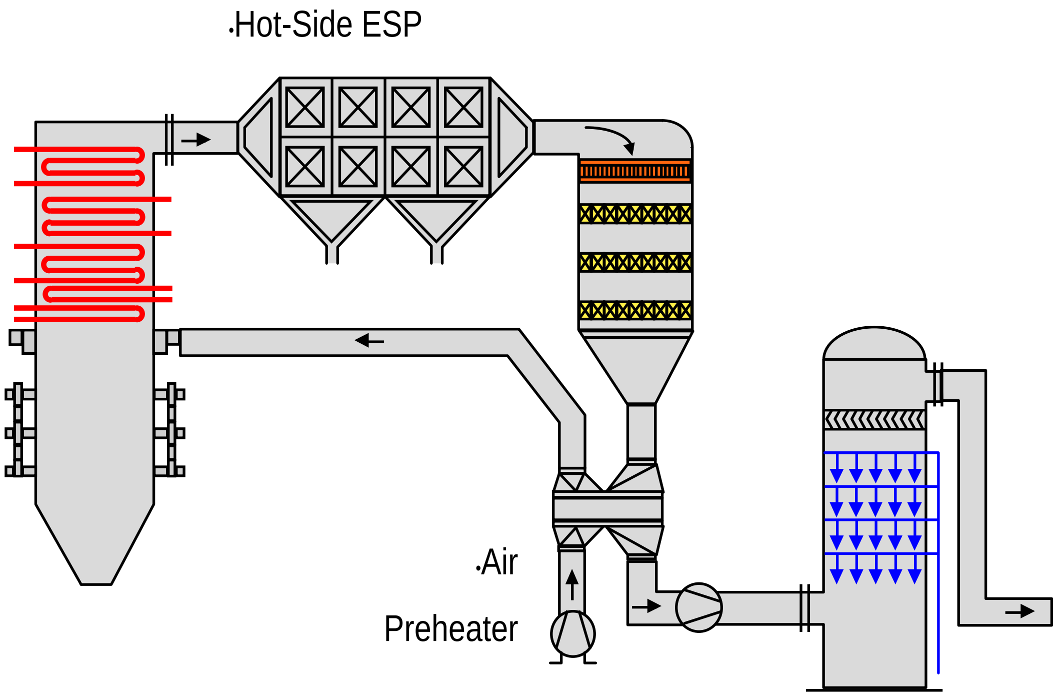
SCR Catalyst for NO_x Control

SCR Configuration with Coal-fired Boilers – "High Dust"



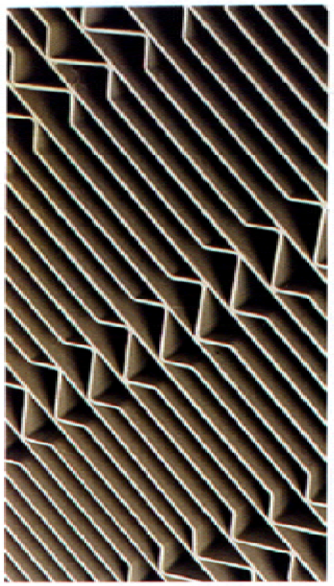
Source: The Babcock and Wilcox Company – www.babcock.com/products

SCR Configuration with Coal-fired Boilers – "Low Dust"

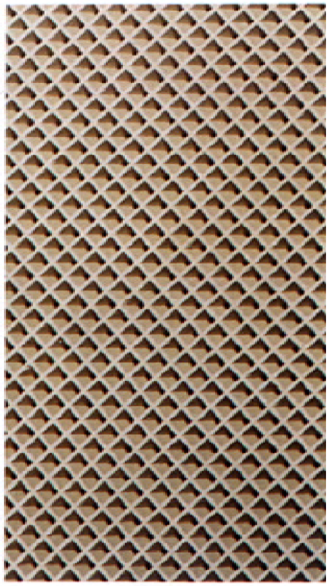


SCR Catalyst Types

Plate

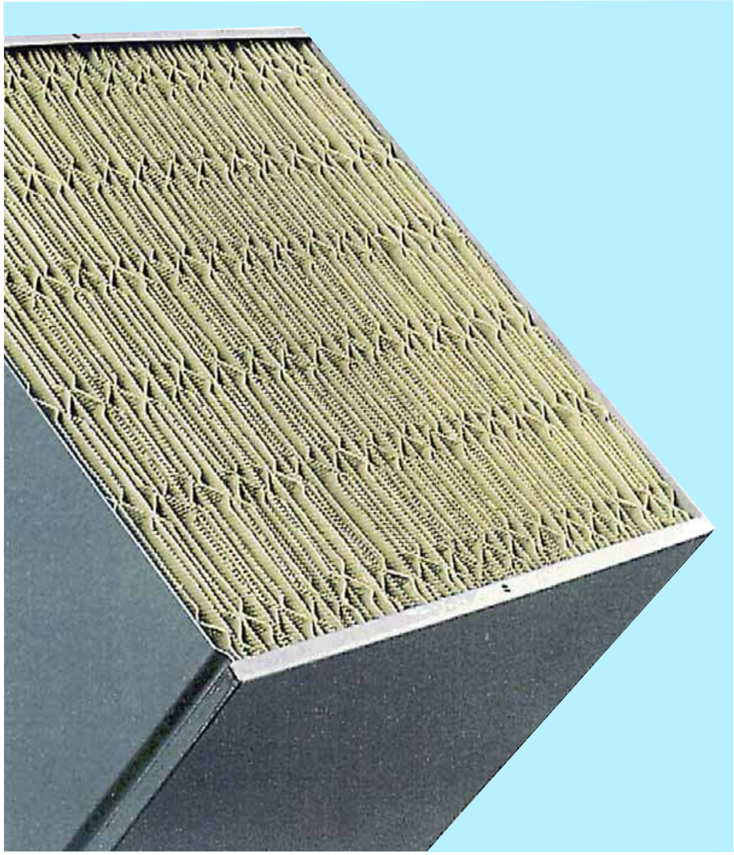


Honeycomb



Corrugated

Plate-type Catalyst



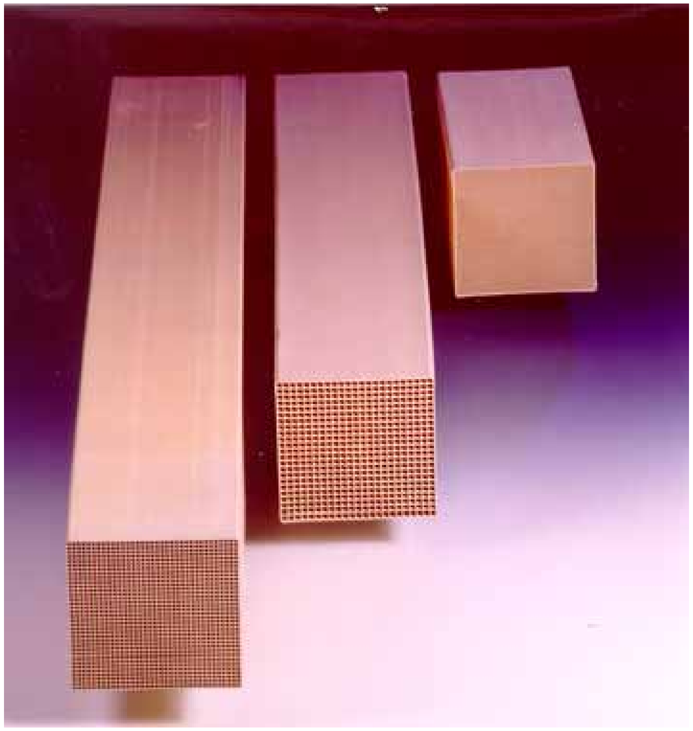
Composition

- Stainless steel expanded mesh substrate, coated with ceramic material
- TiO_2, V-oxide/W-oxide/Mo-oxide
- Notches formed into plates provide separation
- Inserted in element boxes with variable spacing: 60 to 90 plates
- Variable plate height up to 700 mm

Advantages

- Ideal for high dust configurations
- Plugging, erosion resistance
- Low pressure loss

Honeycomb Catalyst



Composition

- Homogeneously extruded ceramic with square-opening cell structure
- TiO_2, V-oxide/W-oxide
- Variable block height up to 1300 mm
- Pitch: 2.1 mm – 9.2 mm

Advantages

- Ideal for low/no-dust applications
- High active surface area per unit volume

Catalyst Pitch and Structure

Pitch = center to center distance from one plate/wall to the next

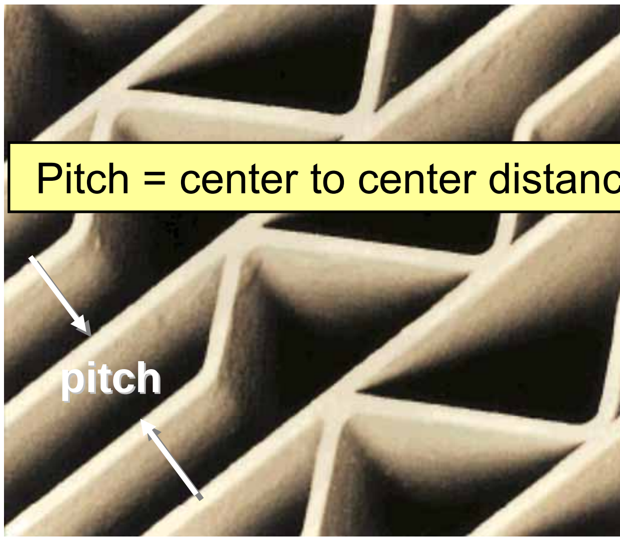
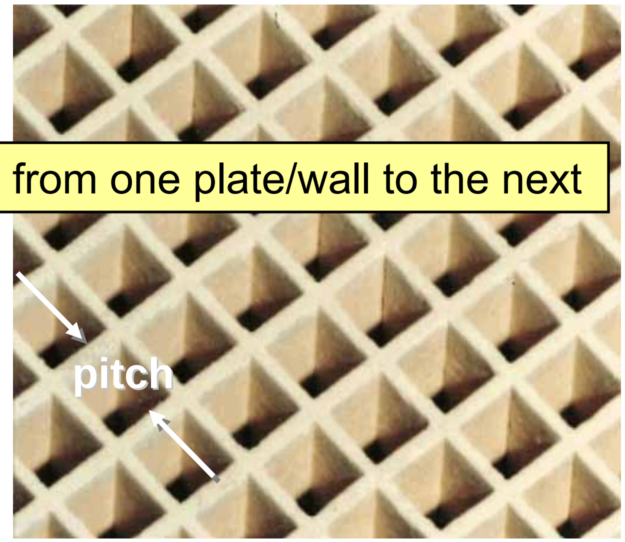


Plate-Type Structure

- Flexible plates
- Rectangular openings
- Pitch: 5 to 7 mm



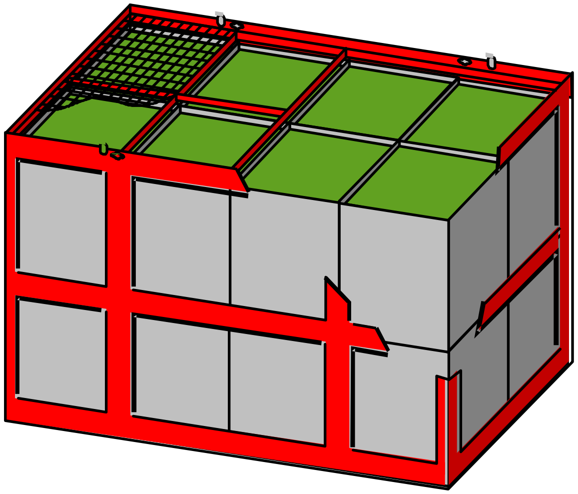
Honeycomb Structure

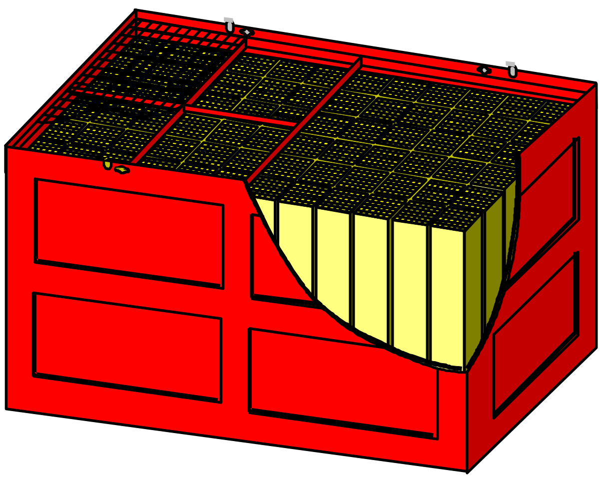
- Rigid structure
- Square openings
- Pitch: 2.1 to 9.2 mm

Pitch Selection by Application

Application	Plate Pitch	Honeycomb Pitch
Natural Gas, Diesel	-	2.1 mm (70 x 70 cell) – 3.7 mm (40 x 40 cell)
Tail-End, Low-dust	5.0 – 5.6 mm	3.7 mm (40 x 40 cell) – 6.7 mm (22 x 22 cell)
Fuel Oil	5.0 – 5.6 mm	4.9 mm (30 x 30 cell) – 6.4 mm (23 x 23 cell)
Bituminous Coal	5.6 – 6.0 mm	6.7 mm (22 x 22 cell) – 8.2 mm (18 x 18 cell)
PRB Coal	5.6 – 7.0 mm	8.2 mm (18 x 18 cell) – 9.2 mm (16 x 16 cell)
Lignite	6.0 – 7.0 mm	? (no US examples)

Catalyst Modules for Utility SCRs



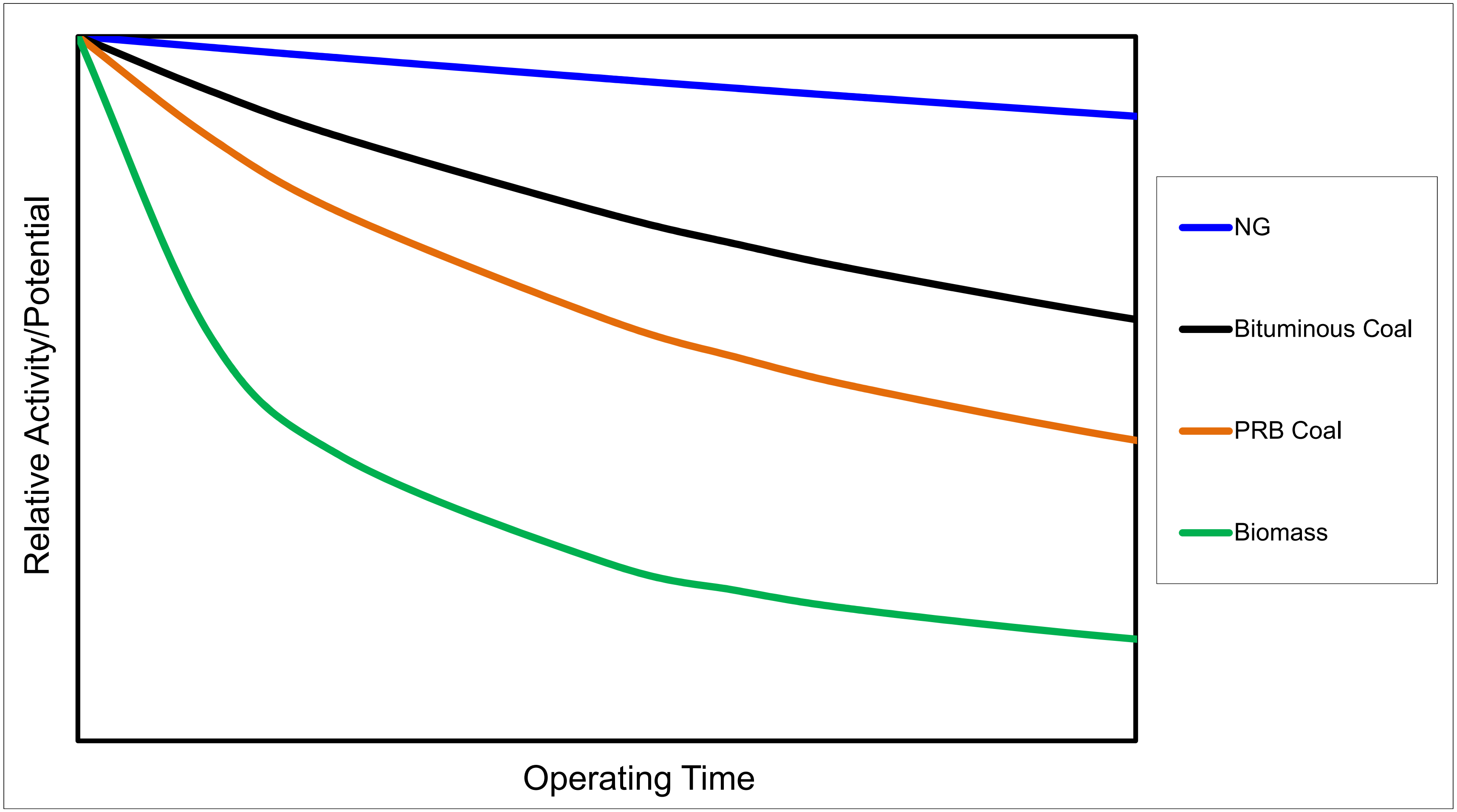


- Catalyst elements arranged in steel frames
  - Plate – 2 levels of 8 element boxes
  - Honeycomb – 72 monoliths
- Standardized cross-section
- Possible to interchange catalyst types within reactor
- Module height varies with catalyst height

Suitable Operating Conditions

- Flue Gas Temperature: 600 – 800 °F
- Flue gas linear flow velocity: 5.0 – 6.0 m/s
- Thorough NH_3-NO_x mixing: 5% RMS (required for >85% deNOx with low NH_3 slip)
- For flue gas with particulate matter, need
  - Popcorn ash/LPA screens upstream of SCR reactor
  - Soot-blowers or sonic horns at catalyst layers
- Means to keep catalyst dry and frost-free during outage periods

SCR Catalyst Deactivation

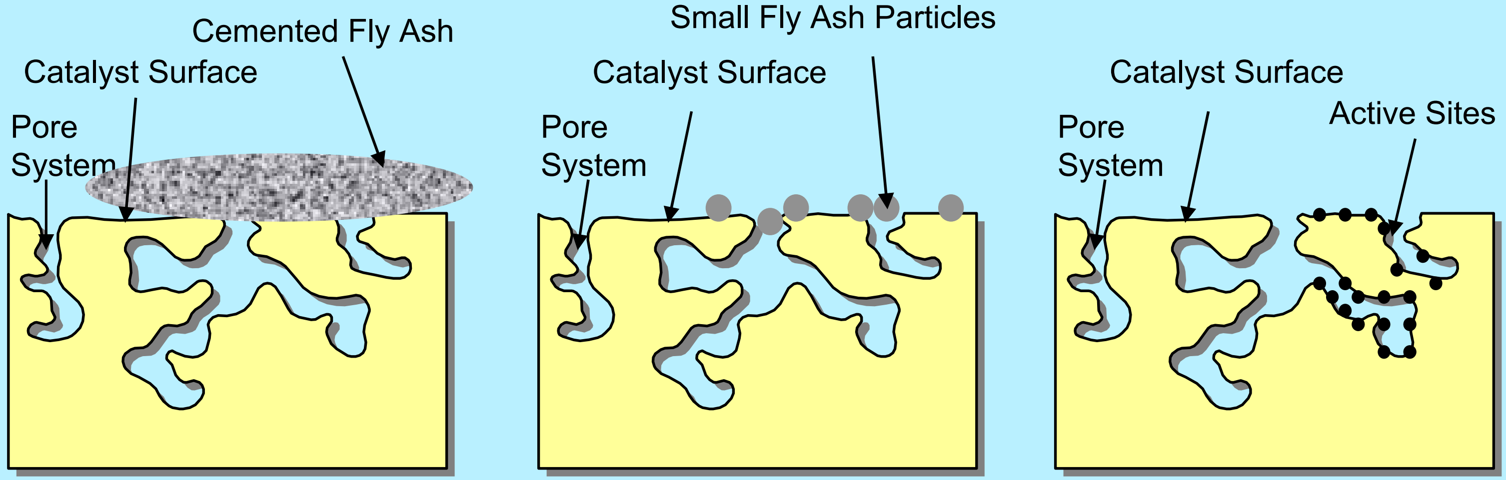


Catalyst Deactivation Mechanisms

Masking:
Macroscopic blockage of catalyst surface by cemented fly ash

Plugging:
Microsopic blockage of pore system by small fly ash particles

Poisoning:
Deactivation of active sites by chemical attack



Advantages with Gas-firing

- Catalyst Selection For Coal . . .
  - Large pitch to avoid ash plugging
  - Minimized SO_2-SO_3 oxidation
  - Frequent replacement – every 2 years
- For Natural Gas firing . . .
  - Much slower catalyst deactivation – longer catalyst life
  - Fewer catalyst replacements
  - No fly ash plugging
  - No Sulfur → no ABS, can tolerate higher NH_3 slip
  - Possible reduced NO_x reduction requirements
  - If 100% gas, can use higher cell density catalyst – reduced volume requirement

Sizing Examples

	Base Bit Coal Case	NG – equal NO_x load	NG – reduced NO_x load
NO_x in	300 ppmvd	300 ppmvd	240 ppmvd
NO_x out	40 ppmvd	40 ppmvd	40 ppmvd
NO_x Reduction	87%	87%	83%
NH_3 slip	2 ppmvd	2 ppmvd	5 ppmvd
Rel P0	1.00	0.83	0.77
Catalyst Pitch	5.6 mm plate	3.7 mm HC	3.7 mm HC
Relative Volume	1.00	0.26	0.21
Pressure drop	1.7 iwg	1.9 iwg	1.5 iwg

Catalyst Options for Coal to Gas Conversion

For Units already having SCR with coal-fired catalyst

•Conversion to 100% Gas firing is OK

- Remove portion of coal-fired catalyst for reuse in other coal units
- Replace all coal-fired catalyst with gas-fired catalyst

•If coal will be backup fuel or co-fired, gas-specific catalyst is not suitable

- Fly ash plugging
- High SO_2 – SO_3 oxidation

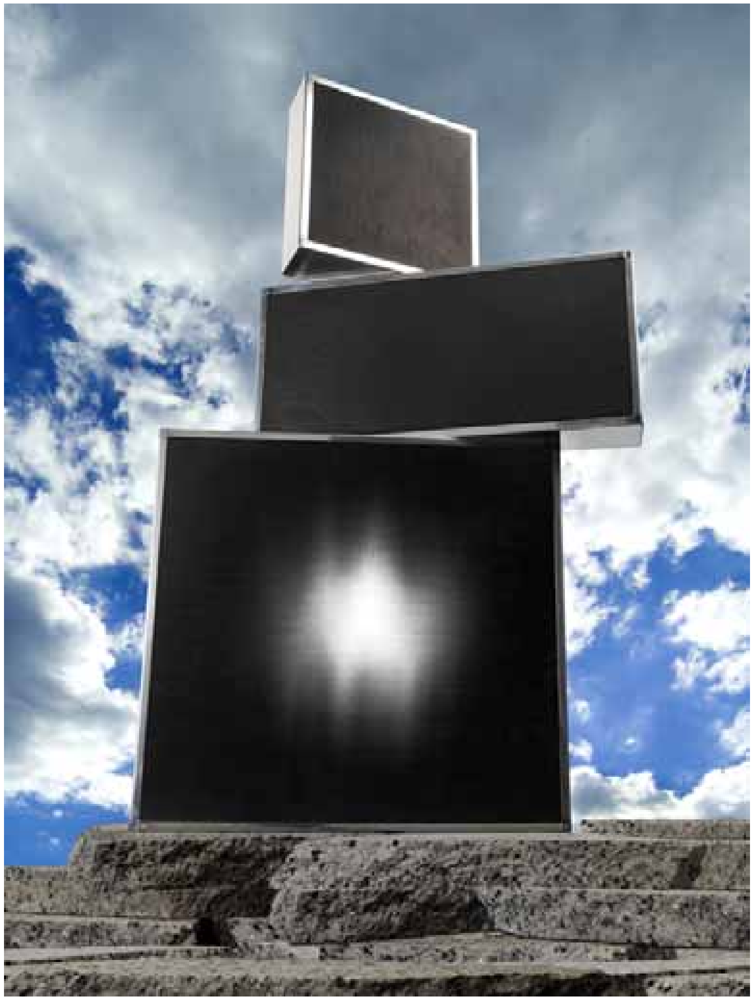
If SCR required on unit after conversion

•Conversion to 100% Gas firing – install gas-fired catalyst

•Conversion to Gas with Coal backup or co-firing gas and coal – need catalyst suitable for coal-firing.

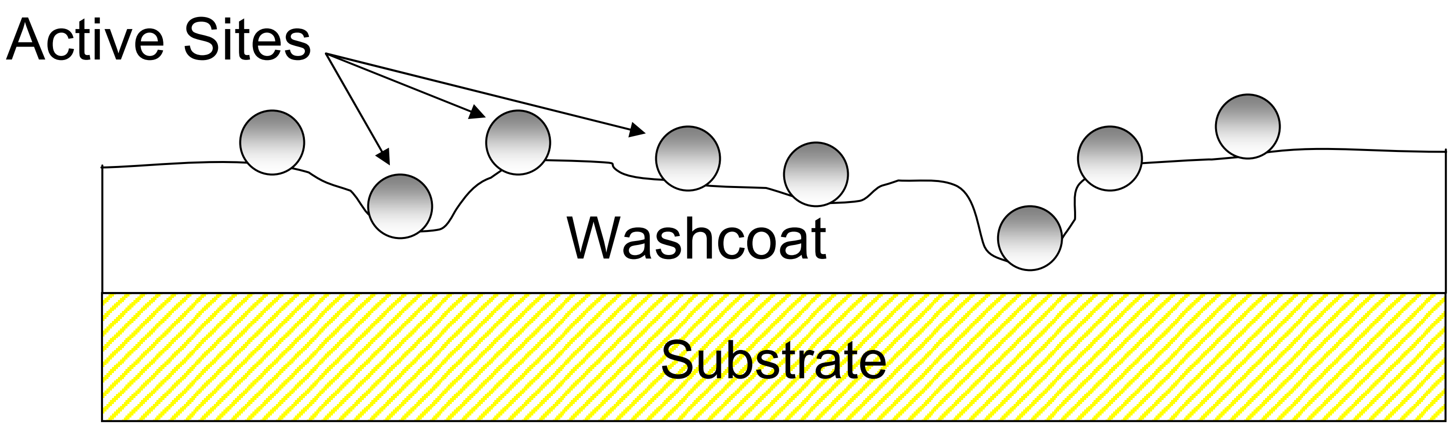
CO Oxidation Catalyst

- Oxidizes CO and VOCs to CO_2
- Stainless steel foil or ceramic honeycomb substrate, high surface area alumina washcoat, Platinum Group Metals (PGM) embedded in washcoat
- Blocks with 25 cpsi – 400 cpsi
- Standard block is 24" x 24", 200 cpsi metal foil for gas turbine applications
- Variable block cross-section possible
- Metal foil depths of 1.5 – 5 inches



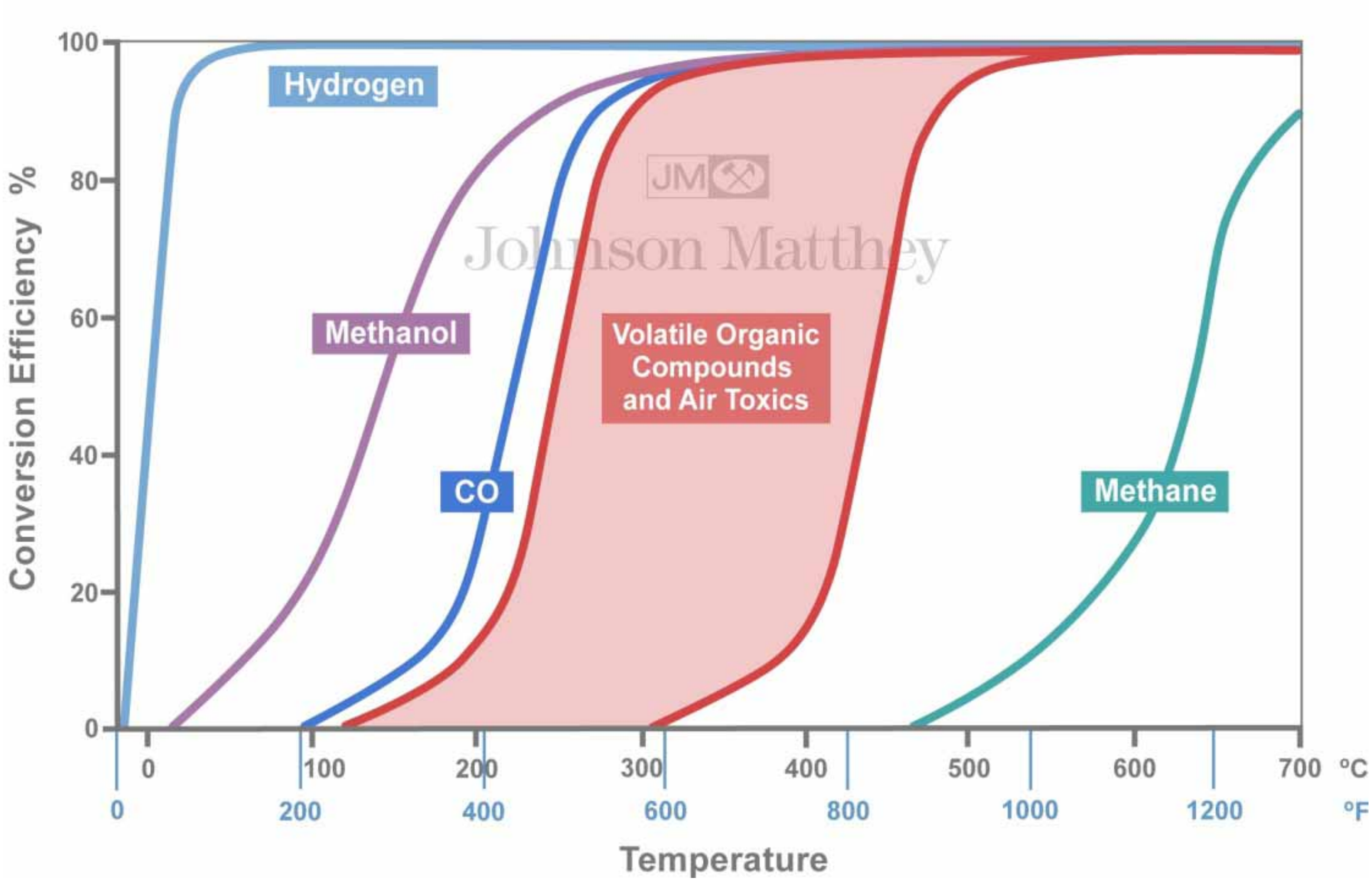
Catalyst Conversion Efficiency

- Catalyst conversion efficiency depends on catalyst durability, reactant residence time and the active surface area of the catalyst



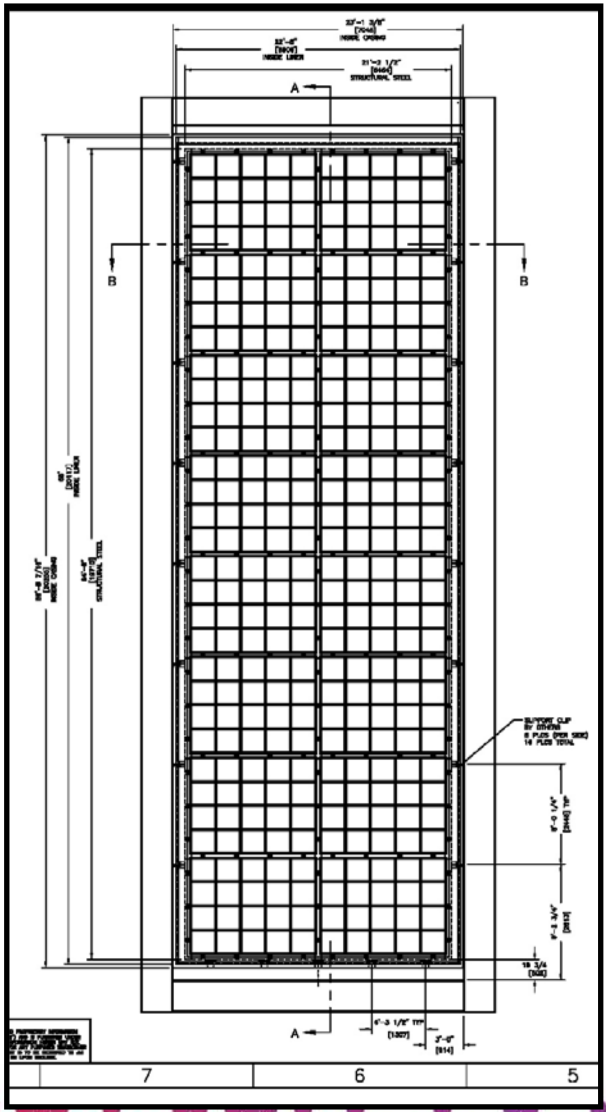
- Catalyst activity maximized by dispersing the active metals throughout the high surface-area washcoat on the substrate media

Catalyst "Light-Off" – Temperature range at which conversion occurs

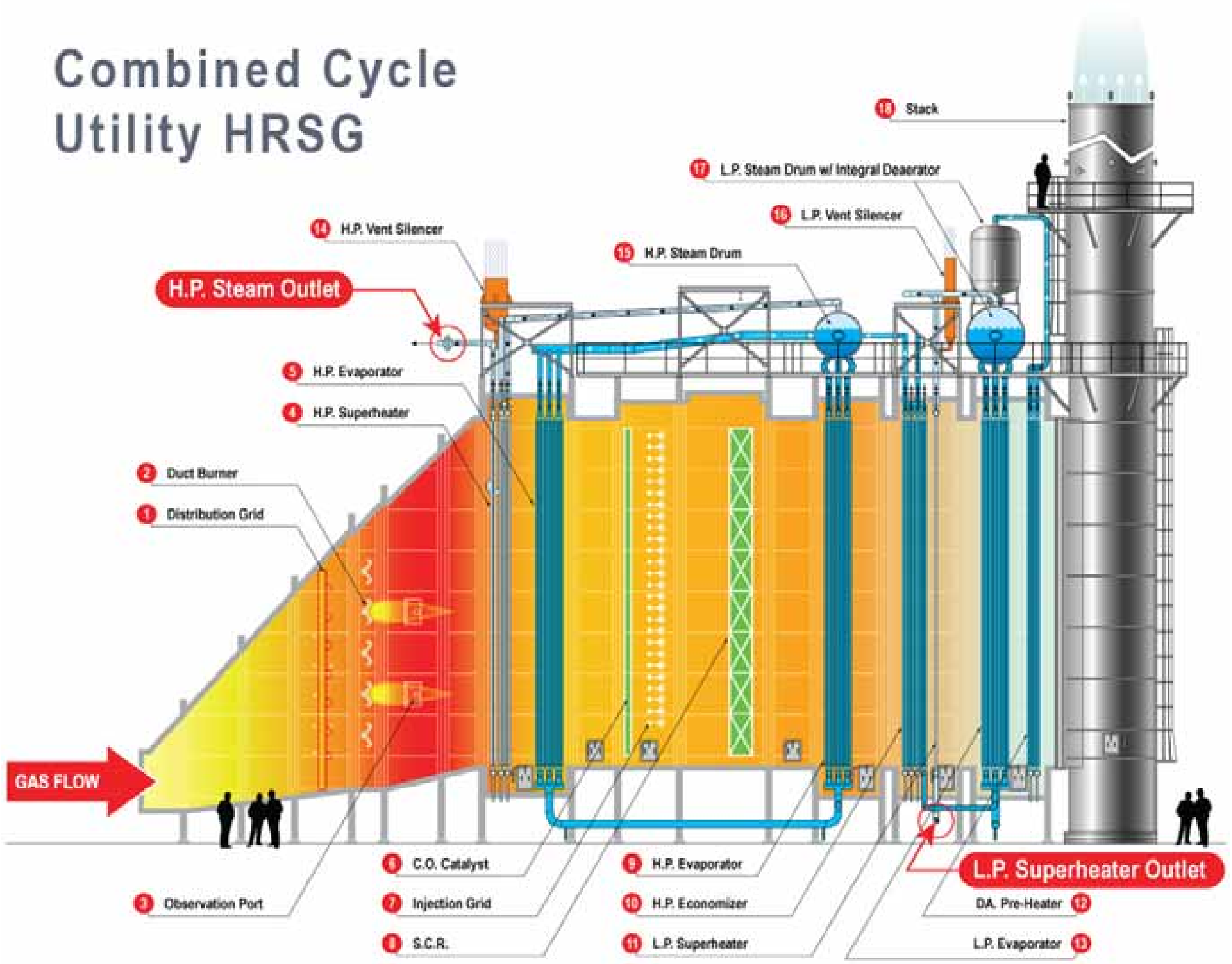


CO Oxidation Catalyst Performance

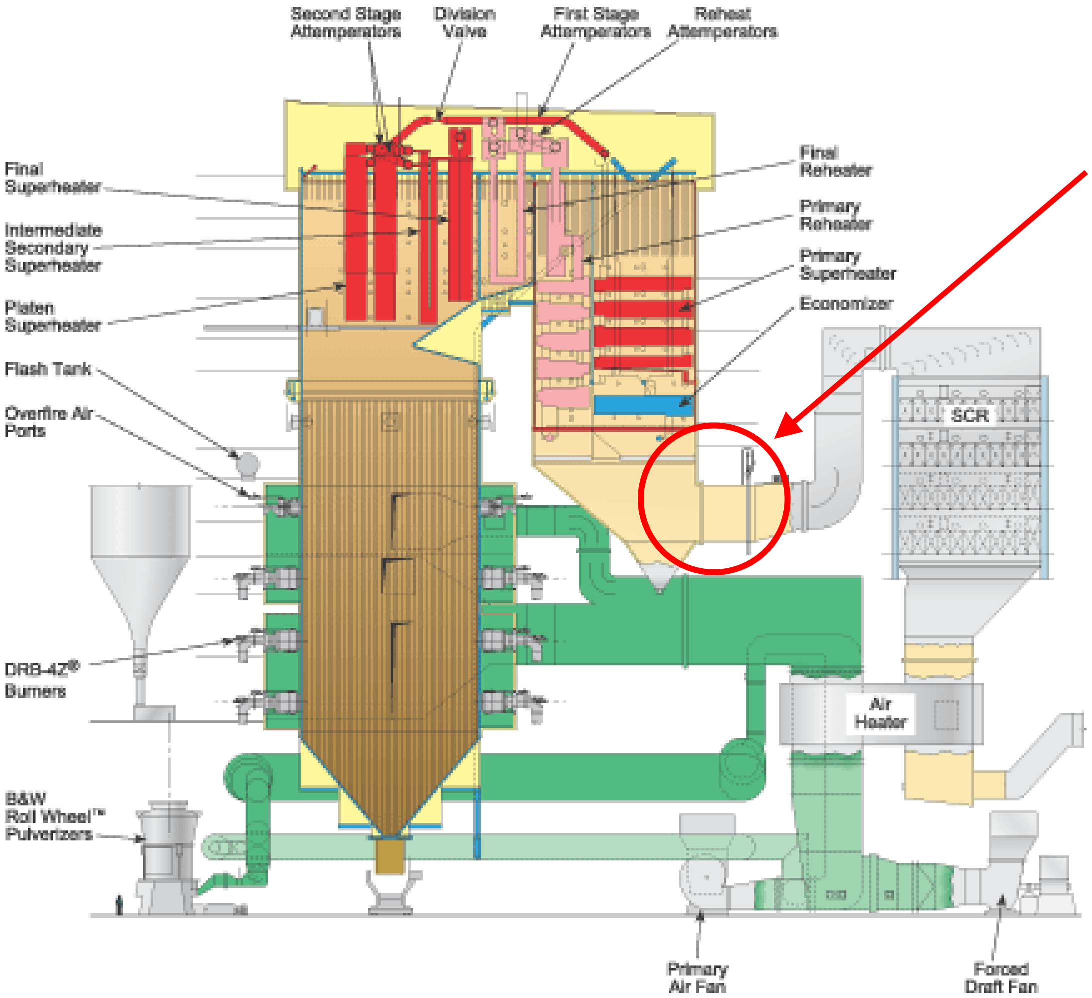
- Fuels – Suitable for NG or ULSD
- CO Reduction
  - ✓ 50 - 95+% Range
  - ✓ 80 - 90% Typical
- VOC Reduction
  - ✓ 0 – 70% Range
  - ✓ 0 – 50% Typical
- Pressure Drop
  - ✓ ≤1.0 iwg Typical
- Performance Guarantee Period
  - ✓ 3 years or 5 years Typical



Oxidation Catalyst Placement – CCGT HRSG Example



Oxidation Catalyst Placement in a Boiler



Possible CO catalyst location – upstream from NH_3 injection for SCR

Source: The Babcock and Wilcox Company – www.babcock.com/products

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*

Catalyst Deactivators (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

Selective (Chemical) Poisoning

- Example – Sulfur can react directly with active site and degrade performance.

$$Pt + S \longrightarrow PtS \text{ alloy}$$

Alloy has low activity

(For certain poisons it is possible to reactivate the catalyst by thermal treatment)

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*

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 / Light oil (?) used as back-up fuel.
  - Firing should be limited – Typically < 500 hours per year
- Not suitable for HFO

Summary Points

- Gas-firing has many advantages for SCR
  - Slower deactivation – longer lifetime
  - Low/No Sulfur → No ABS, higher NH_3 slip tolerable
  - No fly ash/particulate plugging
  - May result in Lower NO_x load, lower deNOx requirement
  - Low pitch, high cell density catalyst elements – lower volume requirement as compared to coal applications
- Catalyst sized for natural gas not suitable for coal-firing
- CO Oxidation catalyst suitable for gas-firing and low/no sulfur fuels
- High rates of CO oxidation are possible
- CO Oxidation catalyst is not suitable for coal-firing or fuels with ash/particulate

Thank You!

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