REINHOLD ENVIRONMENTAL Ltd.

2011 NOx-Combustion Round Table & Expo Presentation

February 7-8, 2011, in Birmingham, AL / Hosted by Southern Company

Reinhold Environmental
NOx Roundtable

SCR Catalyst Management
Training Class
Cormetech, Inc.

February 7, 2011

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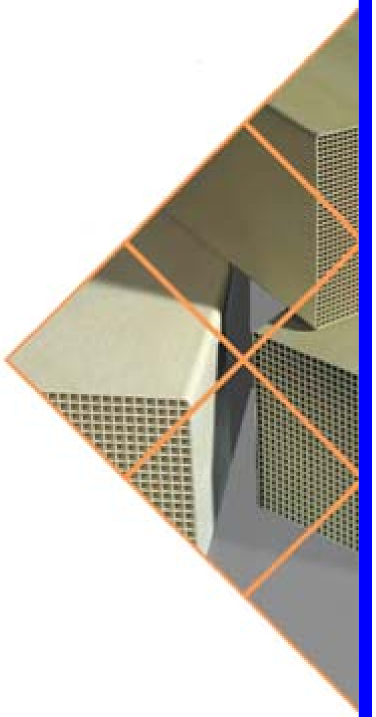
Reinhold Environmental NOx Roundtable

SCR Catalyst Management Training Class

Cormetech Presentation by
Jeremy Freeman
Manager, Engineering Services

How do we best use the SCR to meet the plant's objectives?



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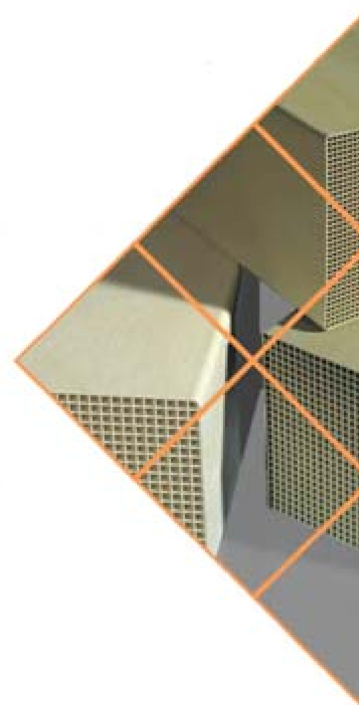
How do we best use the SCR to meet the plant's objectives?

- SCR Performance
- Fuels and Deactivation
- SCR Maintenance
- AIG Maintenance
- Low Load Operation



SCR Catalyst Management

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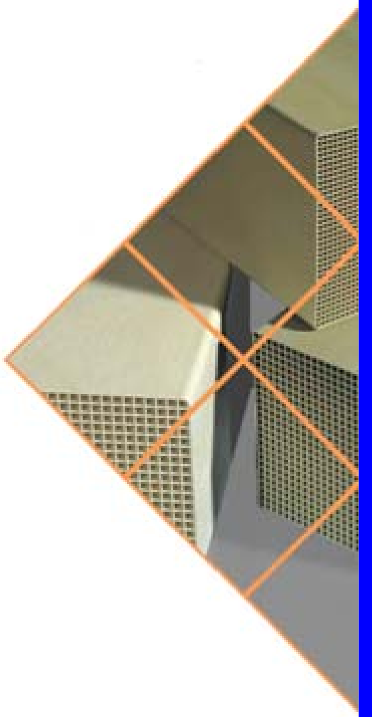
SCR Performance

- What does the SCR do?
- Overview of SCR Design
- How can we expand the range of operation?
  - – Use excess early in life
  - – Enhanced low load operation



How do we best use the SCR to meet the plant's objectives?

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SCR Reactions

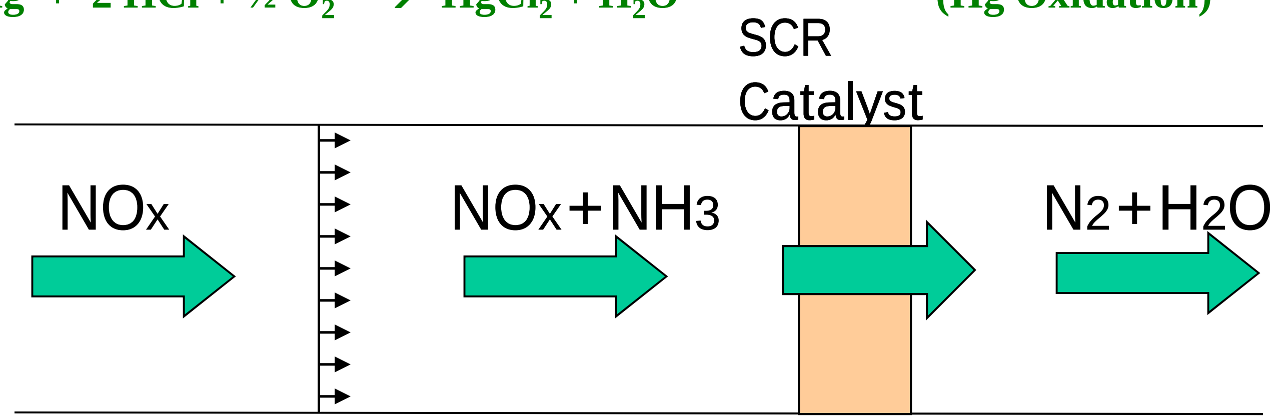
Desired Reactions:

$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$ (NO_x Reduction)

$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$ (NO_x Reduction)

$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$ (NO_x Reduction)

$Hg + 2\,HCl + \frac{1}{2}\,O_2 \rightarrow HgCl_2 + H_2O$ (Hg Oxidation)



Undesired Reactions:

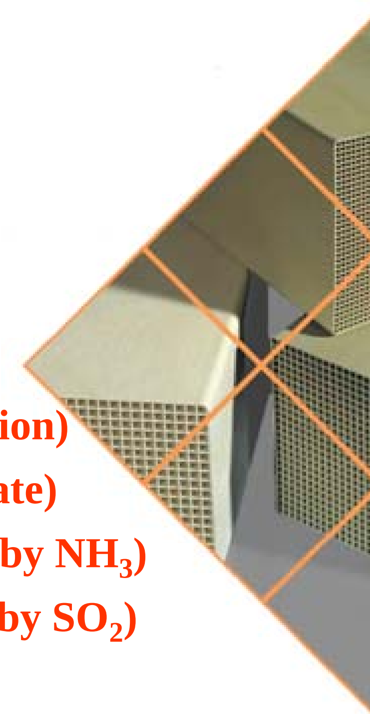
$SO_2 + \frac{1}{2}\,O_2 \rightarrow SO_3$ (SO_2 Oxidation)

$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$ (Ammonia Oxidation)

$NH_3 + SO_3 + H_2O \rightarrow NH_4SO_4$ (Ammonia BiSulfate)

$HgCl_2 + NH_3 + \frac{1}{4}\,O_2 \rightarrow Hg + 2\,HCl + \frac{1}{2}\,N_2 + \frac{1}{2}\,H_2O$ ($HgCl_2$ Reduction by NH_3)

$HgCl_2 + SO_2 + H_2O \rightarrow Hg + 2\,HCl + SO_3$ ($HgCl_2$ Reduction by SO_2)



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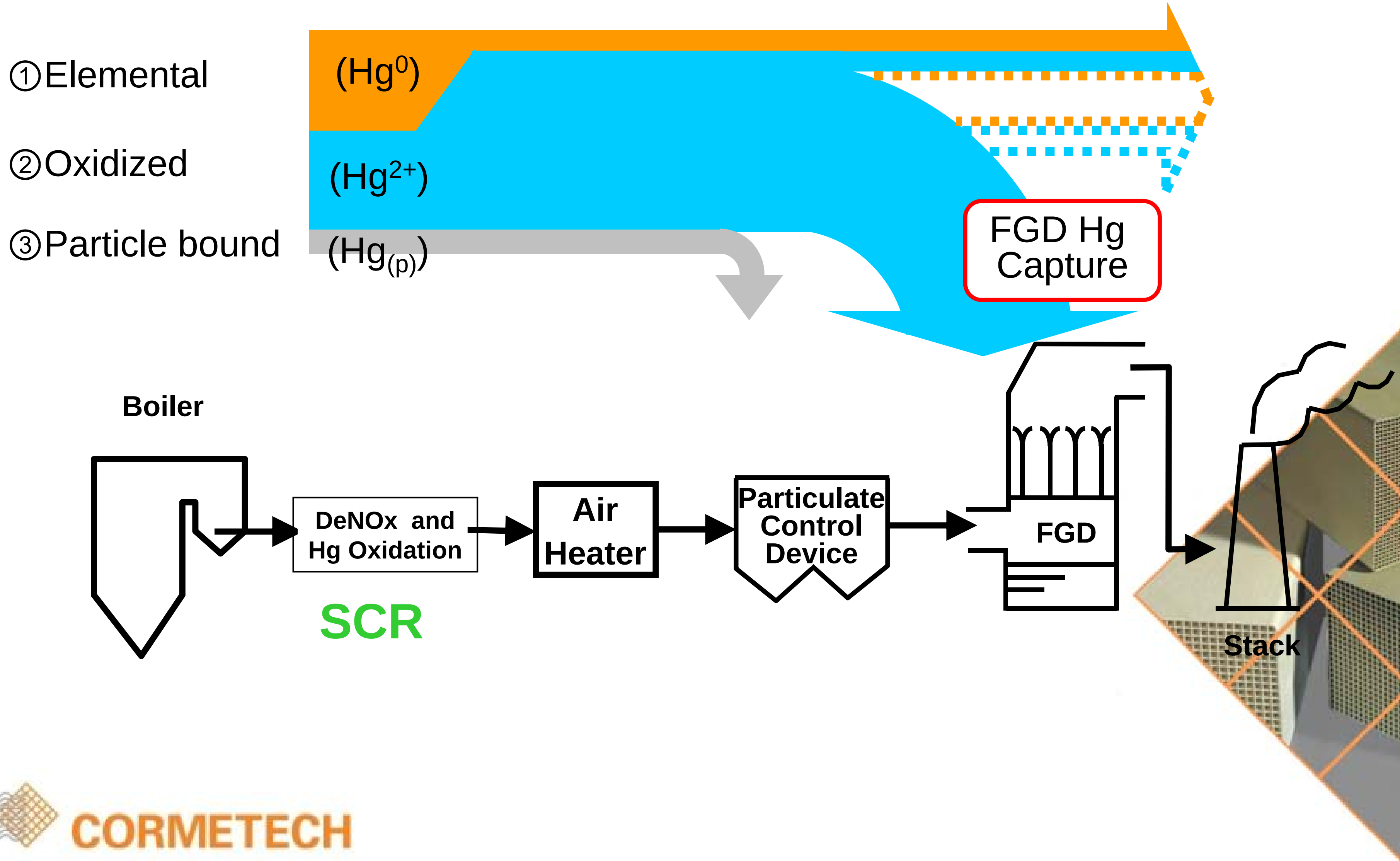
SCR Co-Benefit for Mercury Capture

$Hg + 2\,HCl + \frac{1}{2}\,O_2 \rightarrow HgCl_2 + H_2O$ **(Hg Oxidation)**



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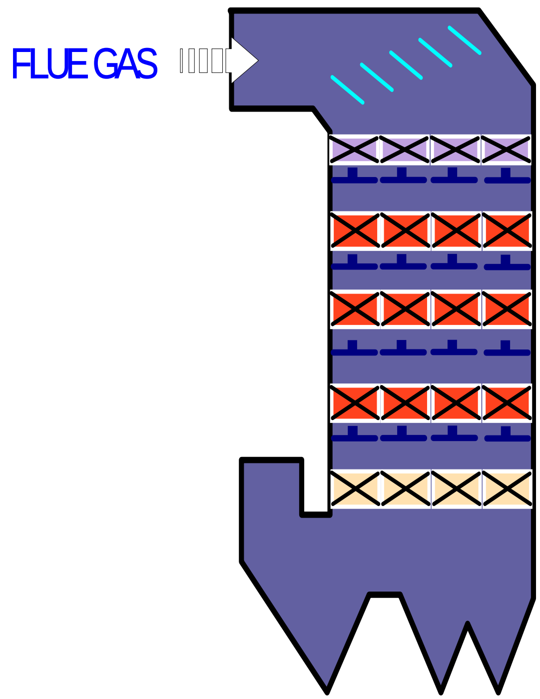
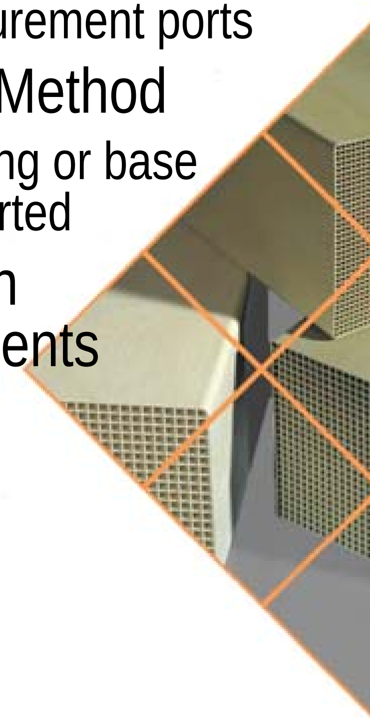
SCR Reactor Layout

- Max & min velocity requirements
  - Function of load swing
  - Dust loading
  - Orientation
- Reactor flow modeling
  - Flue design
  - Transitions
  - Bypass
    - SCR
    - Economizer
    - Damper selection



- Accessibility
  - Number of catalyst layers
  - Catalyst loading method
  - Sootblower /Sonic Horn arrangement
  - Measurement ports
- Support Method
  - Hanging or base supported
- Insulation requirements



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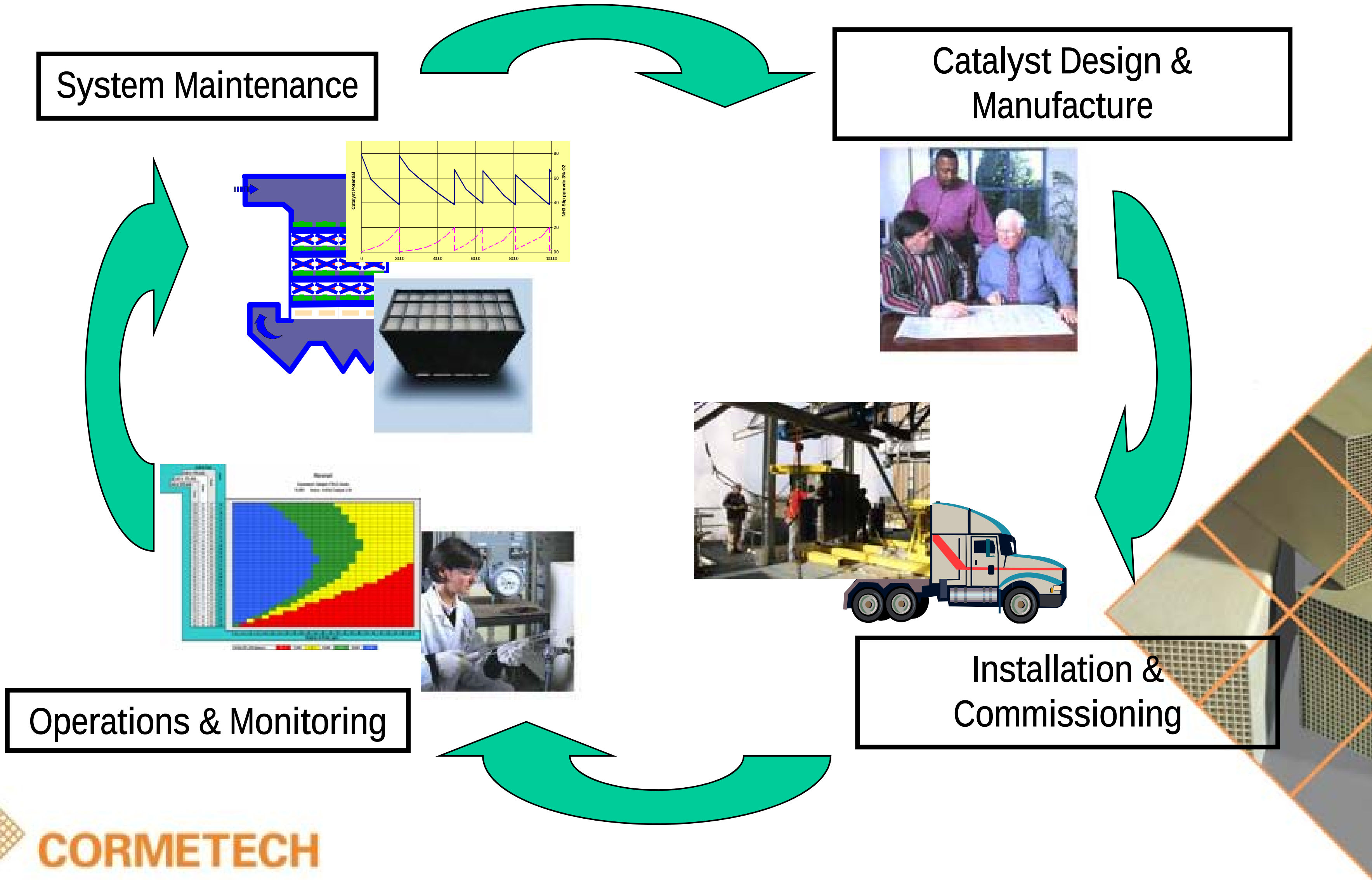
Catalyst Life-Cycle Management



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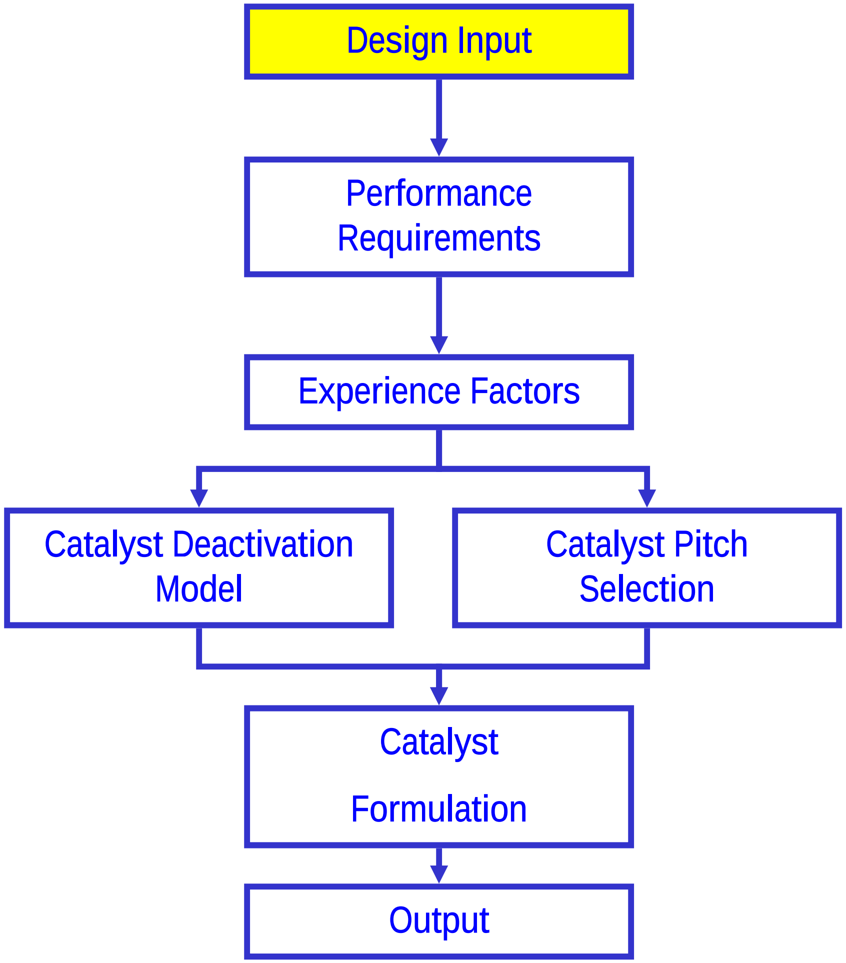
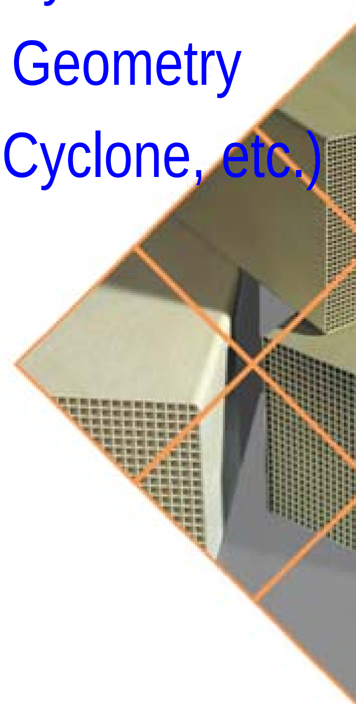
Catalyst Design Process



Design Inputs

- Flue Gas Flow Rate
- NOx Inlet
- Flue Gas Constituents
- Fuel Type & Analyses
- Reactor Size & Geometry
- Unit Type (PC, Cyclone, etc.)



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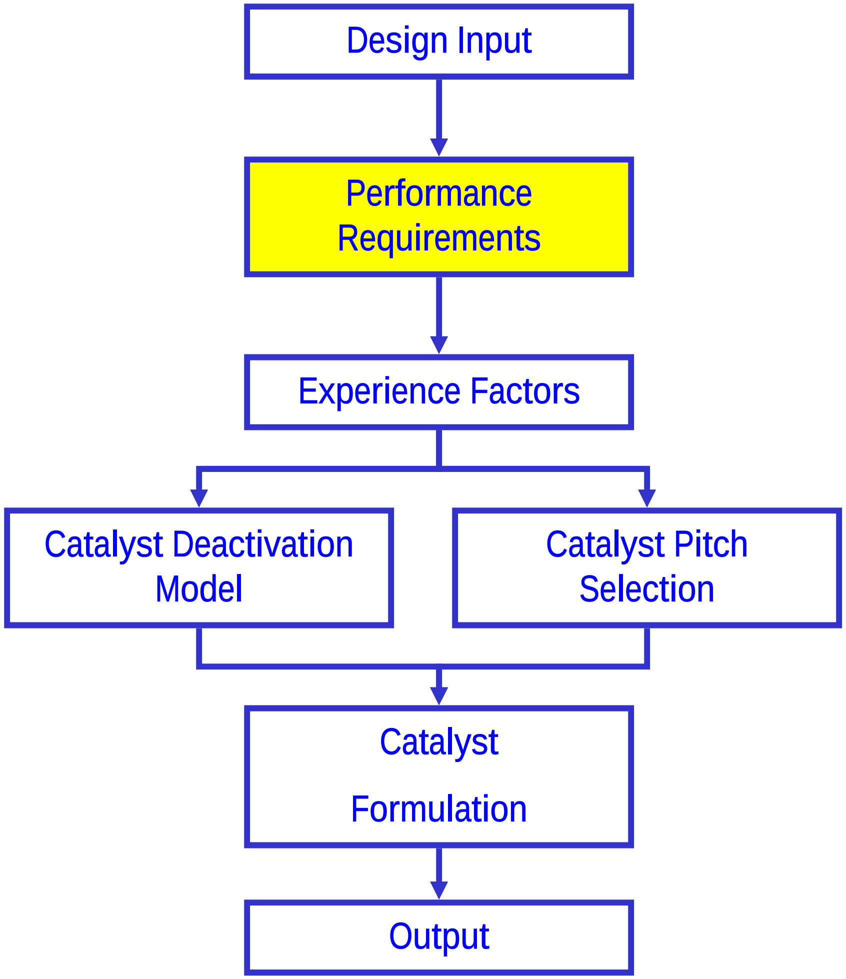
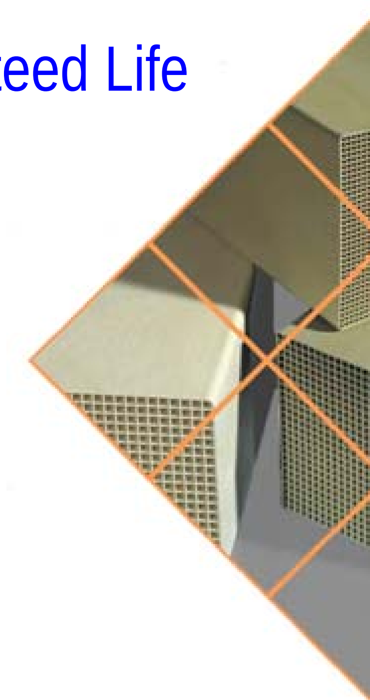


Performance Requirements

- NOx Removal Efficiency
- Ammonia Slip
- Pressure Drop
- SO_2 Oxidation Limit
- Initial Guaranteed Life



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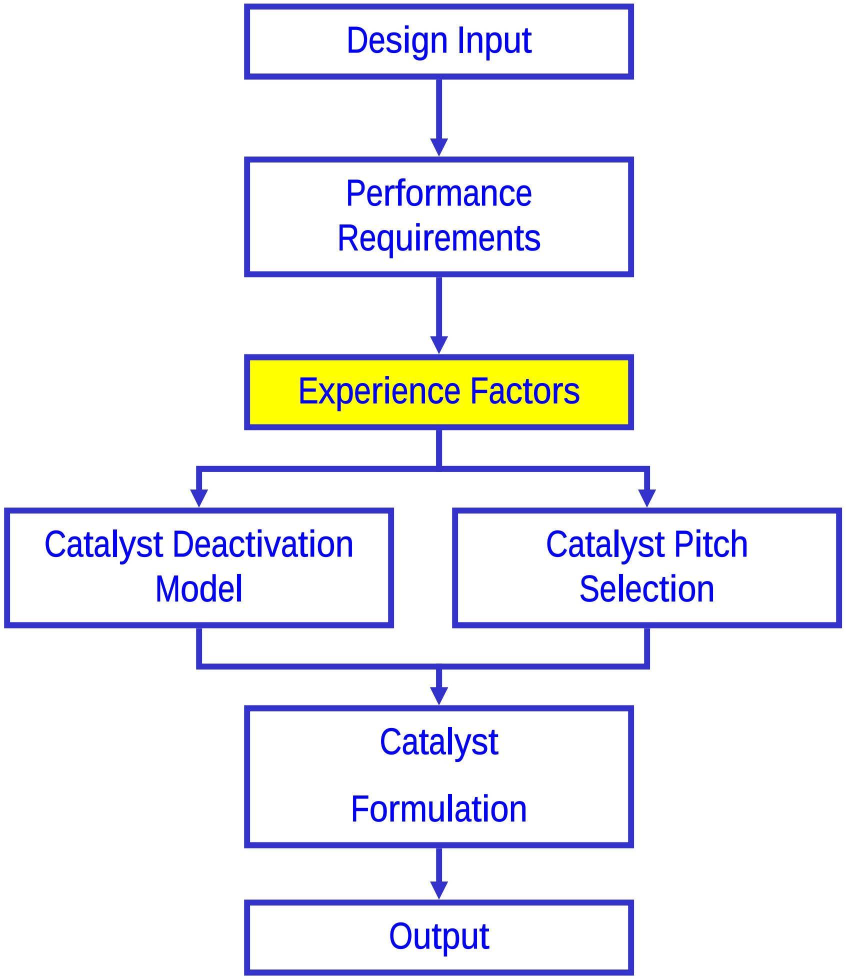
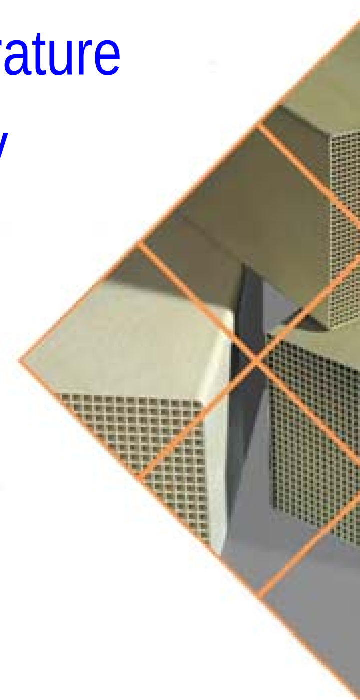


Experience Factors

- Catalyst Blockage
- Fouling / Plugging
- Maldistribution
  - NH_3 : NOx Molar Ratio
  - Temperature
  - Velocity



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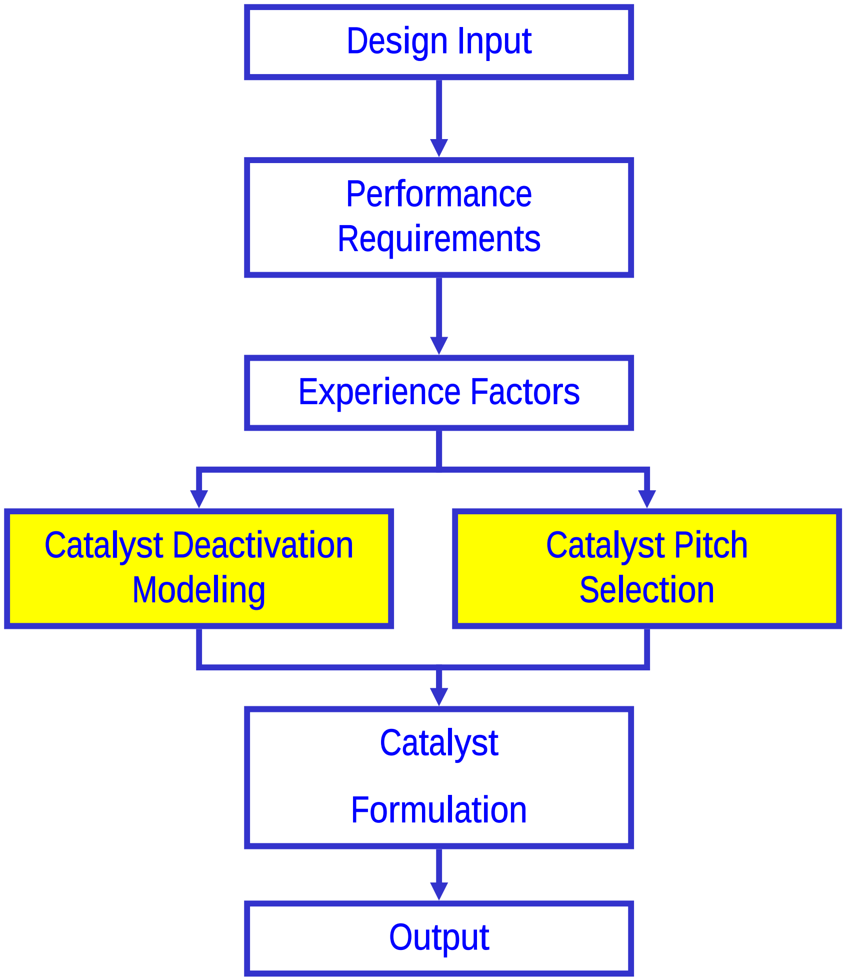
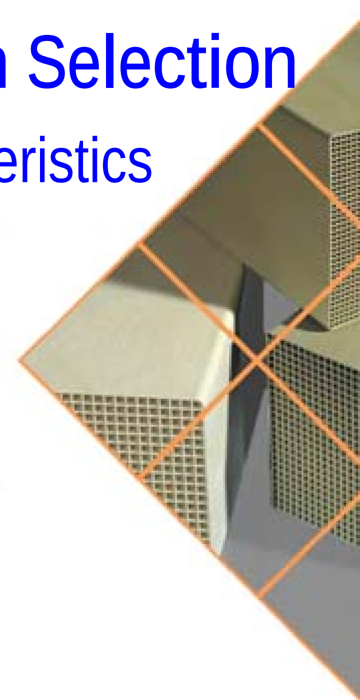


Deactivation Modeling

- Fuels
- Unit Type
- Life Requirement

Catalyst Pitch Selection

- Ash Characteristics
- Unit Type



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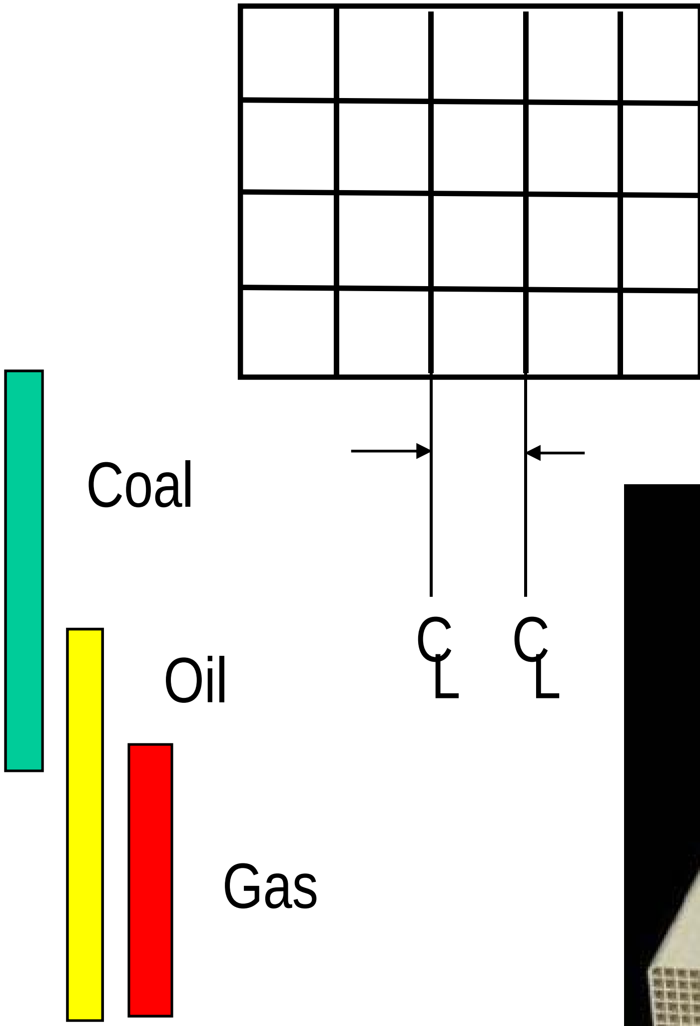
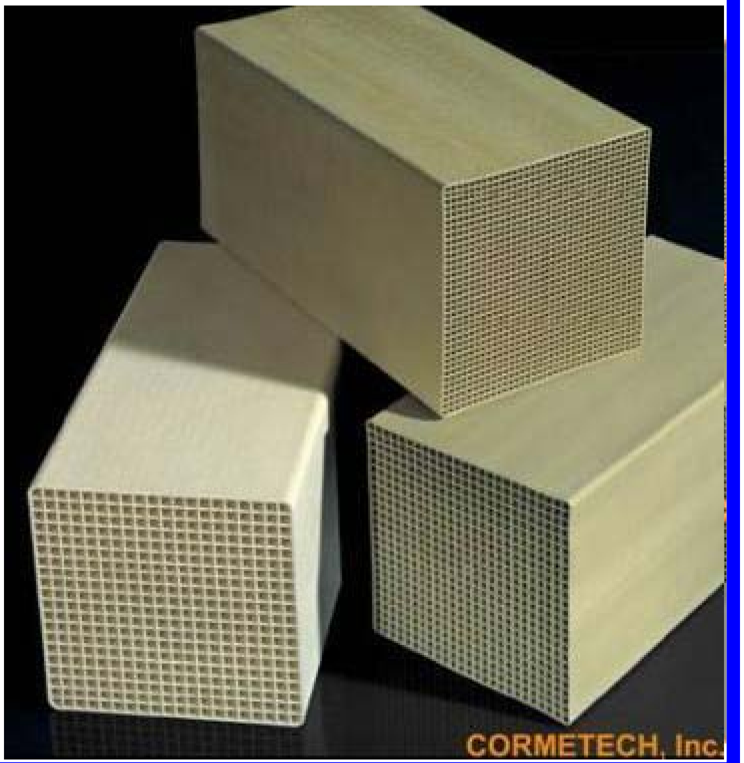
Catalyst Description: Geometry

Pitch

- 9.2 mm
- 8.2 mm
- 7.4 mm
- 7.1 mm
- 6.9 mm
- 5.9 mm
- 4.2 mm
- 3.7 mm
- 3.3 mm
- 2.7 mm
- 2.1 mm





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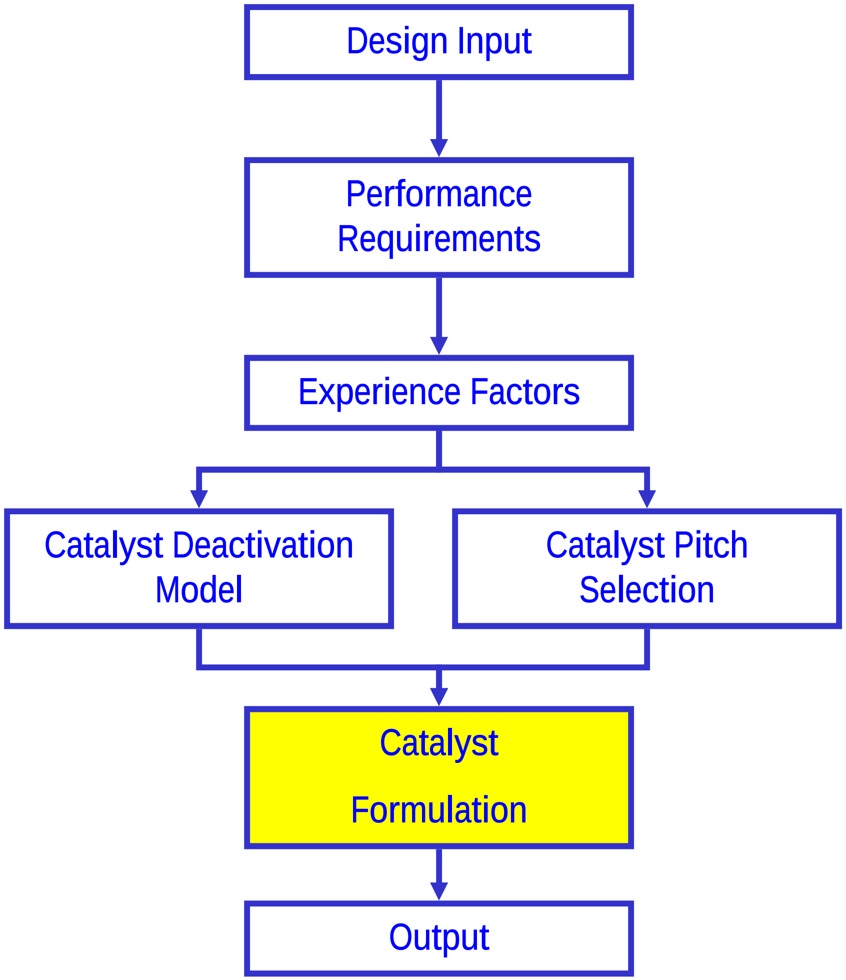
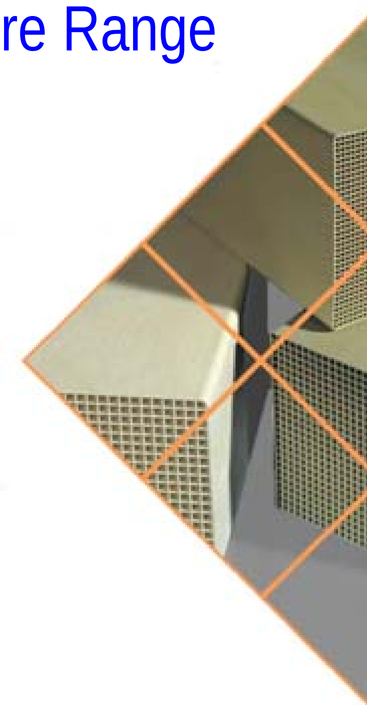


Catalyst Formulation

- Unit Type
- SO_2 Oxidation Limit
- Temperature Range



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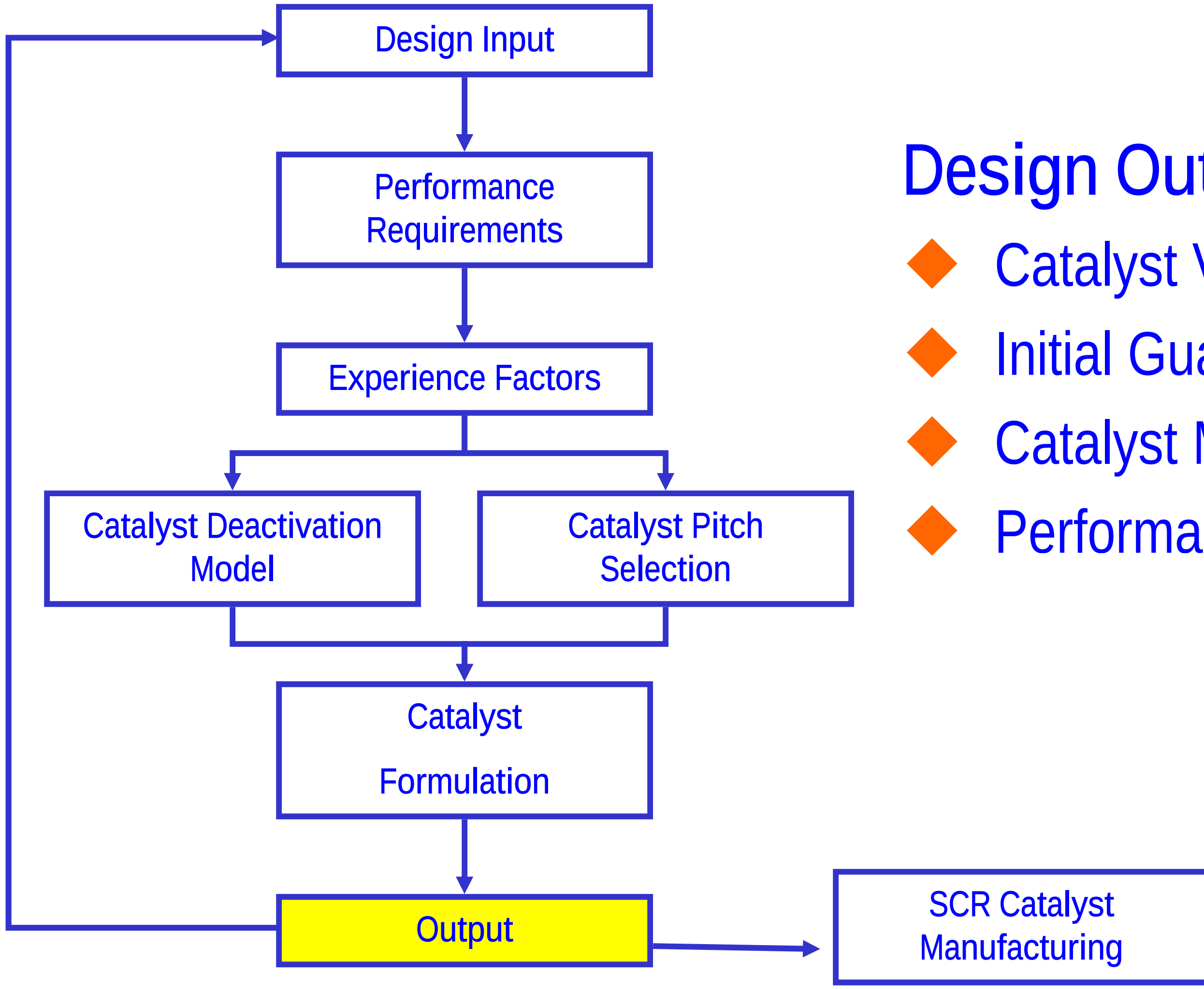
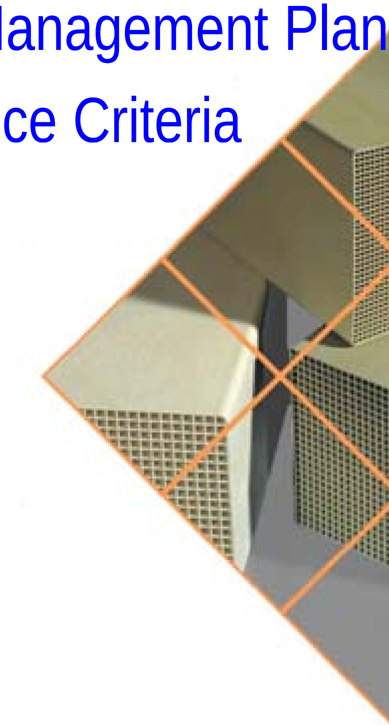


Design Output

- Catalyst Volume
- Initial Guaranteed Life
- Catalyst Management Plan
- Performance Criteria



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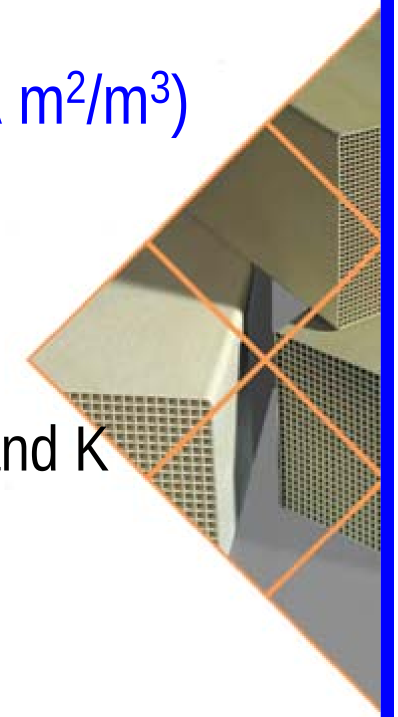
Catalyst Requirements

1. Determine minimum catalyst potential requirement K/AV = f(NOx in, efficiency, and NH_3 slip)
2. Determine initial catalyst activity K = f(Operating Conditions, Catalyst Formulation)
3. Know flue gas flow (Nm^3/hr)
4. Select catalyst pitch and determine Geometric Surface Area (GSA)
5. Area Velocity, AV = flow Nm^3/hr / (Volume m^3 * GSA m^2/m^3)
6. Determine design margin required for
   - Catalyst Deactivation (K/Ko) Fuels and Operating Conditions
   - Catalyst Blockage and Pluggage
   - Inlet Flue Gas Maldistribution (NH_3:NOx, temperature, flow)
7. Iterate solution based on margin impact on formulation and K



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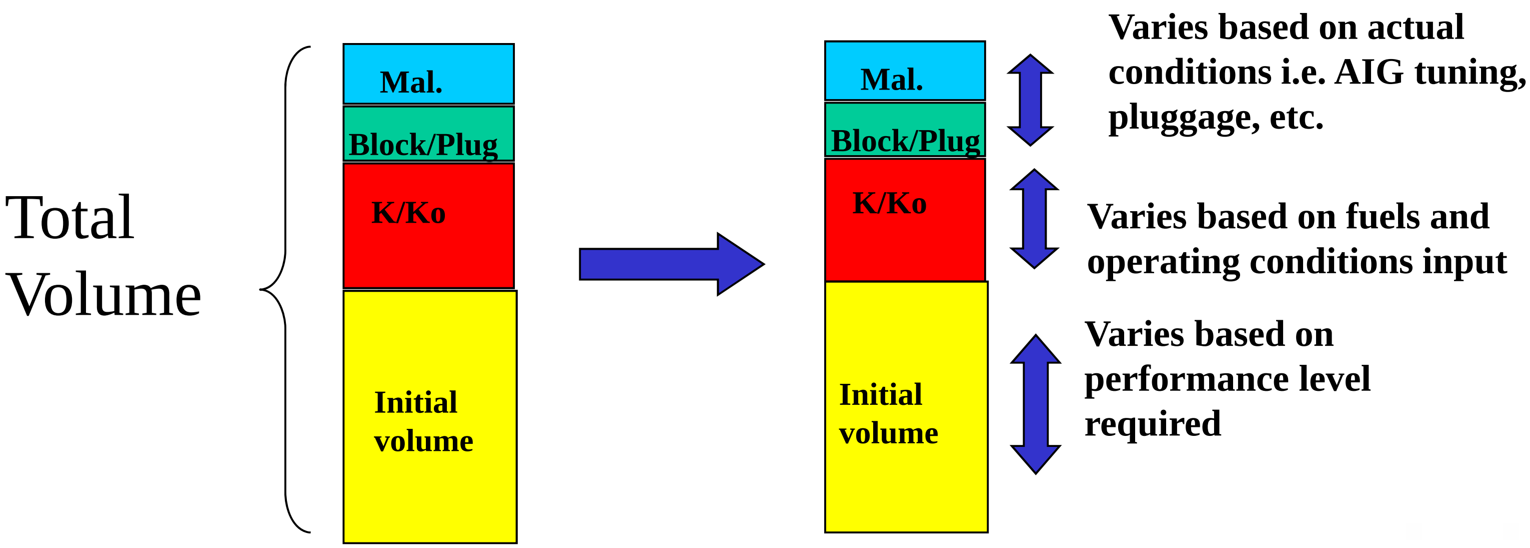
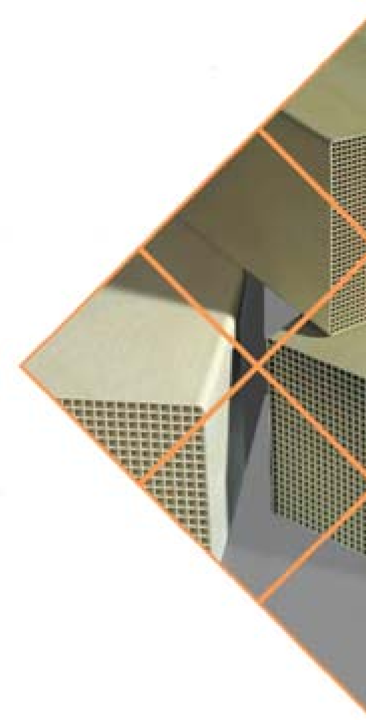
Catalyst Requirements





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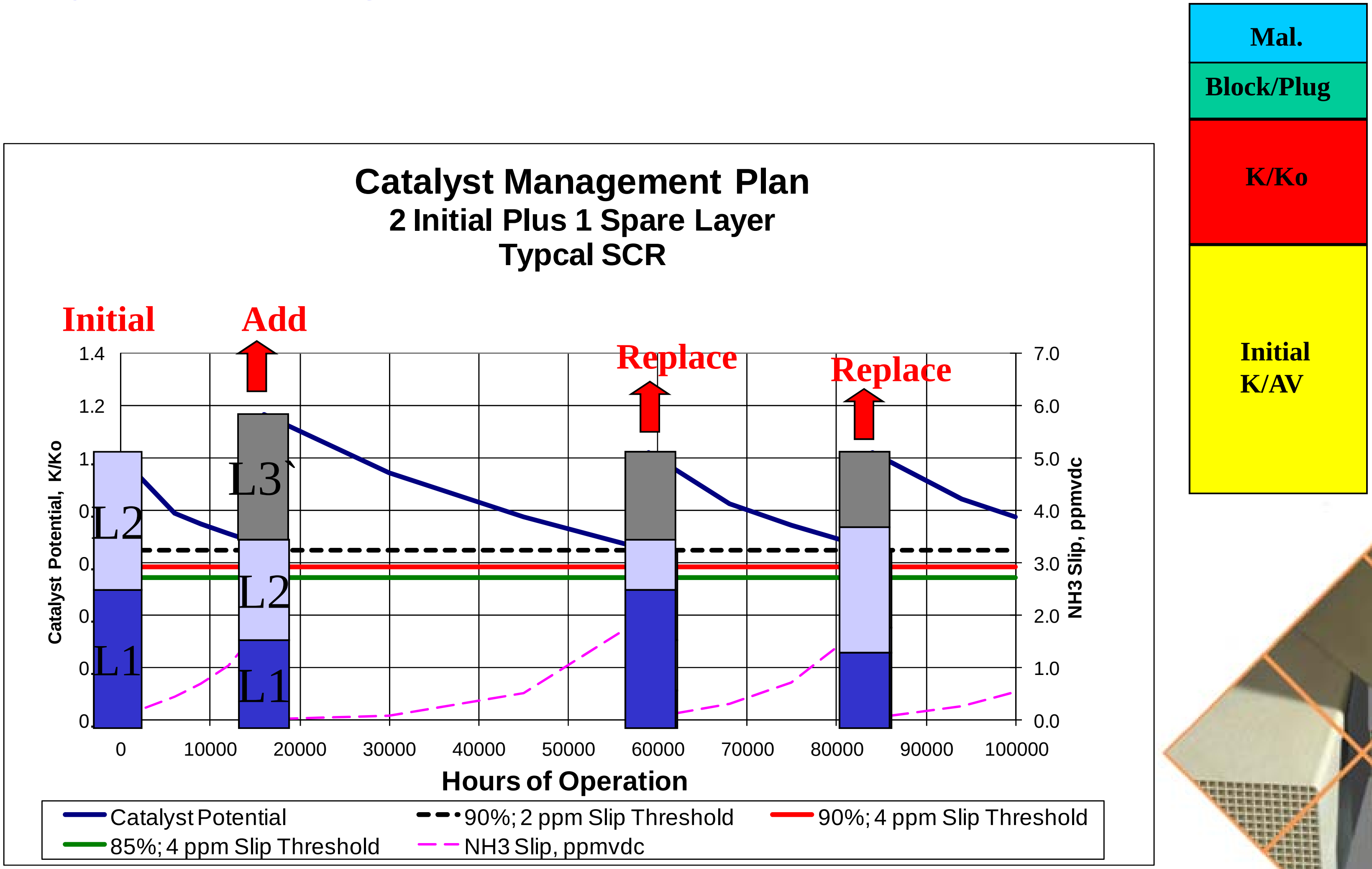
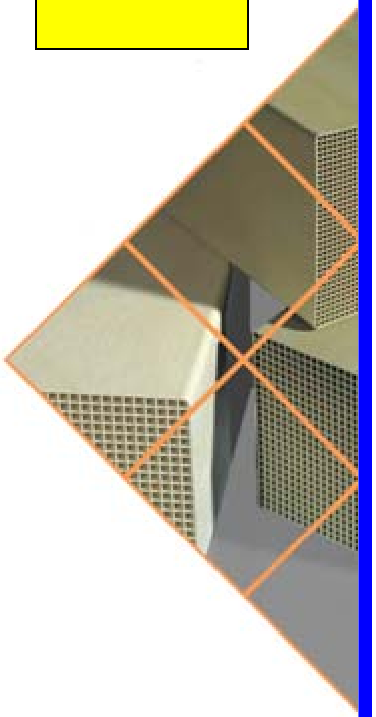
Catalyst Management Plan





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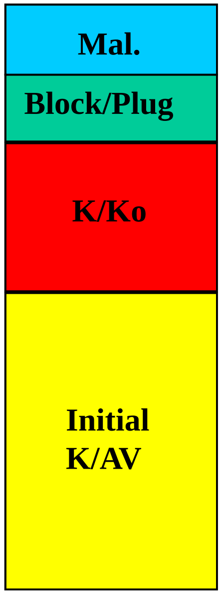
How do we best use the SCR to meet the plants objectives?

- Over inject NH_3 early in life to get extra NOx reduction?
- Operate in Enhanced Low Load operation mode to allow more turn down?
- Fuel flexibility
- Use the best monitoring and inspection practices to predict and extend life
- Flexibility Outage Planning and Optimization or maximize life of SCR
- AIG maintenance and tuning



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Fuels and Deactivation

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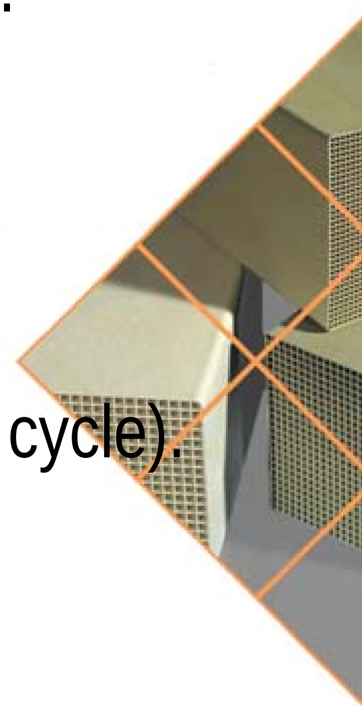
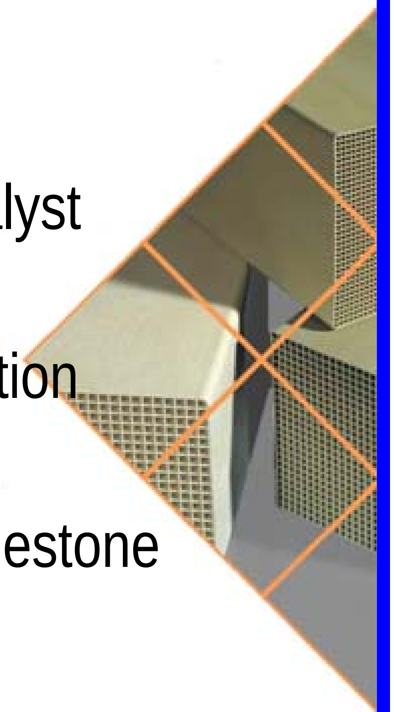
Catalyst Deactivation Mechanisms

- Fuel dependent.
  – Gas (Natural, Refinery).
  – Oil (Low Sulfur, High Sulfur, Particulate).
  – Coal (Low Sulfur, High Sulfur, CaO, As, Ash).
  – MSW (RDF, Mass Burn).
  – Biomass
- Application / Operation dependent.
  – Combustion turbine (Single cycle, Combined cycle).
  – Boiler (PC, Cyclone, CFB).



Catalyst Deactivation Mechanisms

- Plugging or Masking catalyst surface.
  - Ca, Mg as sulfates and ammonium sulfate compounds.
  - Low temperature.
  - Ash Particulates.
- Chemical Bonding
  - As, Na, K, P
- Sintering.
  - High temperature operation > 800°F
- Poisoning Potential.
  - CaO content.
  - As content.
  - Na, K, P content.
  - PSD
- Countermeasures.
  - Understand reaction.
  - Select appropriate catalyst formulation.
  - Account for in deactivation assumptions.
  - Fuel additives. (i.e. Limestone for As Mitigation)



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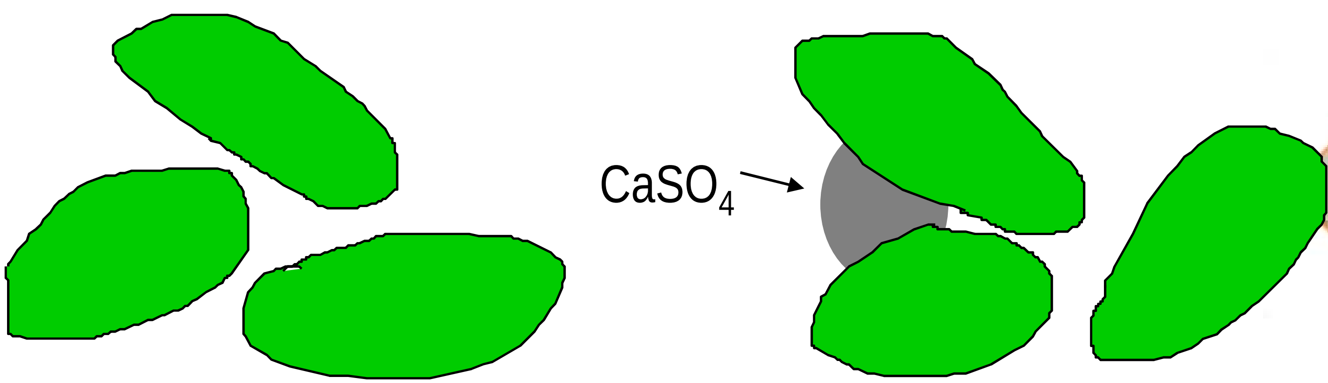
Catalyst Deactivation Mechanisms

Calcium Oxide (CaO)

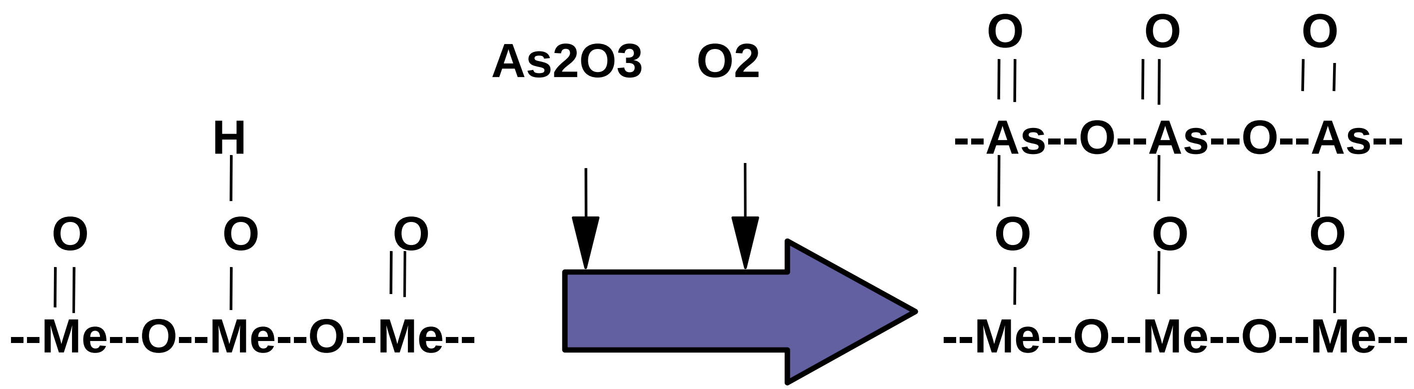
- Alkaline Earth Metal (Ca, Mg).
  - Primarily Ca. CaO in flyash reacts with SO_3 to form $CaSO_4$. $CaSO_4$ causes catalyst surface pore plugging (typically ~5 micron depth).

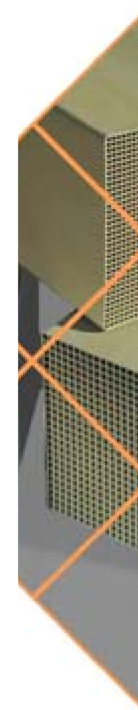


Fresh　　　　　　　Calcium Deterioration

Catalyst Deactivation Mechanisms
Arsenic (As)

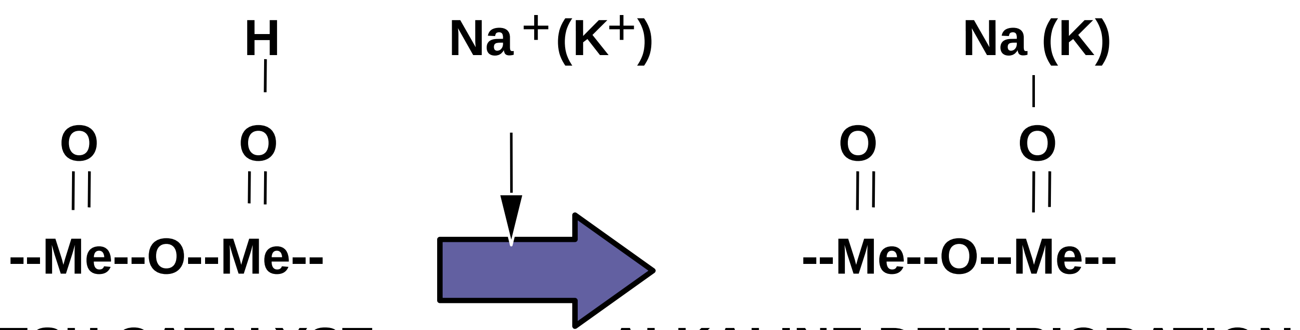
- Gaseous arsenic, As_2O_3, diffuses into the catalyst wall and covers active sites.



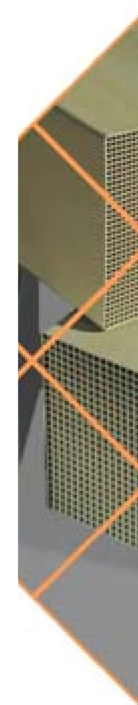


Catalyst Deactivation Mechanisms
Alkaline Metal (Na/K)

- Exist in the dust as sulfates, Na_2SO_4 and K_2SO_4, readily soluble in water. The alkaline ion moves freely through the catalyst wall and bonds with acid sites resulting in decreased capability to adsorb ammonia thus decreasing catalyst potential.

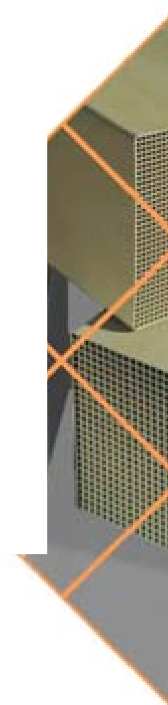


FRESH CATALYST   ALKALINE DETERIORATION



Catalyst Deactivation Mechanisms

- Vanadium (V).
  - Can have positive effect on catalyst DeNOx performance. However, causes higher SO_2 oxidation which degrade overall performance and may lead to downstream equipment fouling.
- Thermal Degradation.
  - Primary means of gas catalyst deterioration.
  - Sintering causes decrease in pore volume and surface area.



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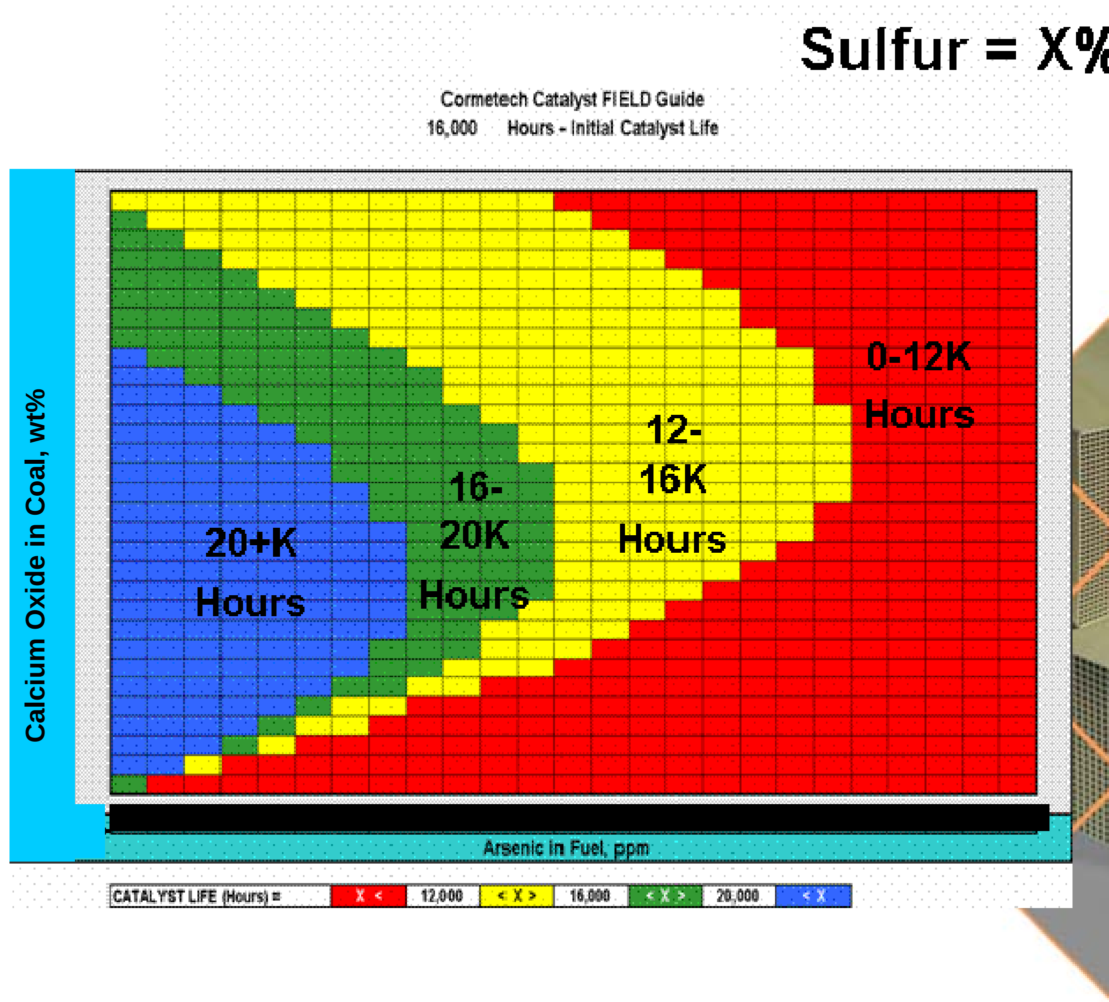
FIELD Guide™

For **F**uel **I**mpact **E**valuation & **L**ife **D**etermination™

Estimates catalyst life impacts for a defined coal-fired boiler SCR

- Uses arsenic (As) and calcium oxide (CaO) fuel content and their impact on deactivation only
- Assumes all other variables are constant.
- Customized modeling to plant specific needs
- Product of Cormetech, Inc.



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SCR Performance Monitoring and Sampling

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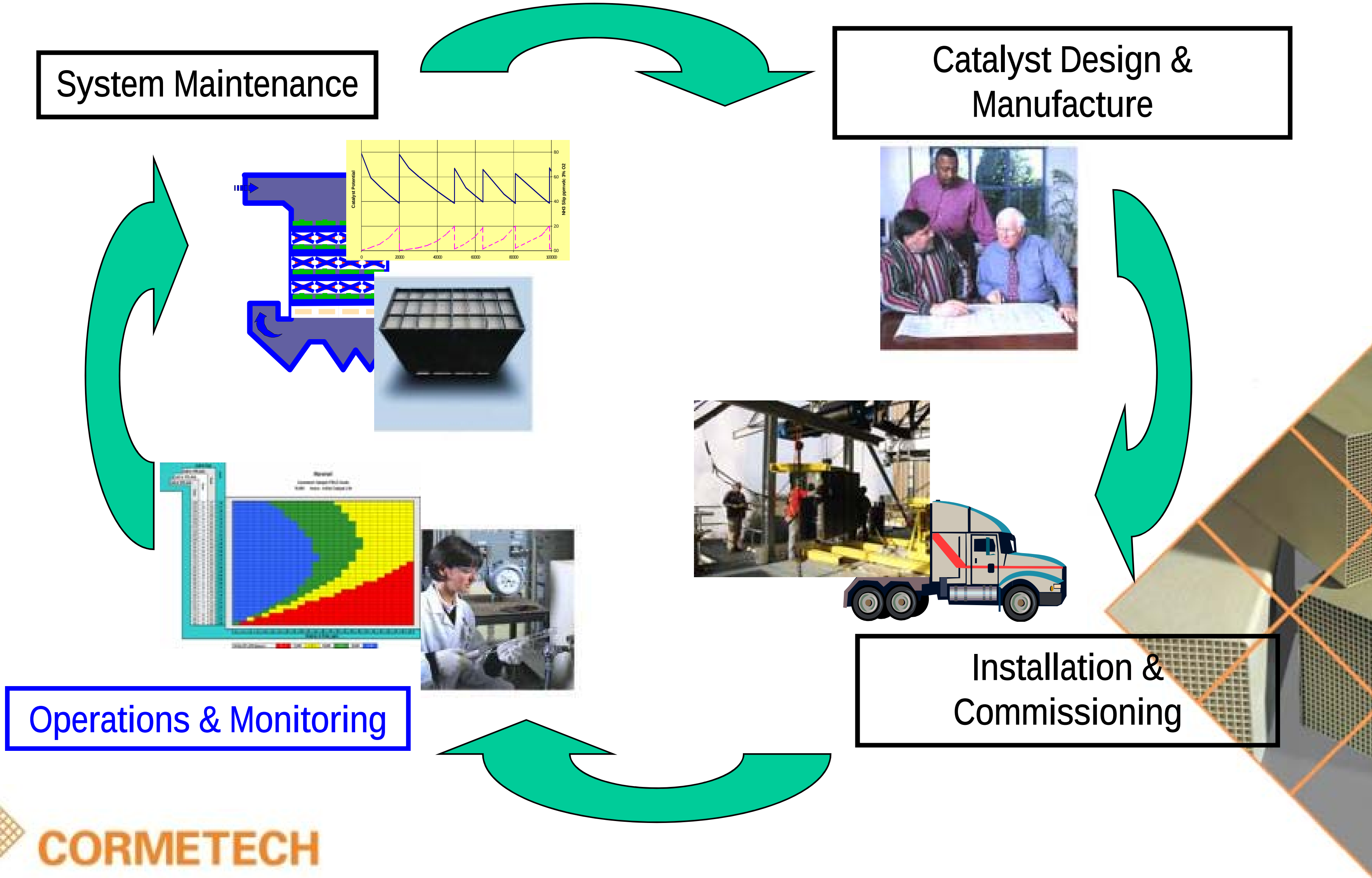
Catalyst Life-Cycle Management



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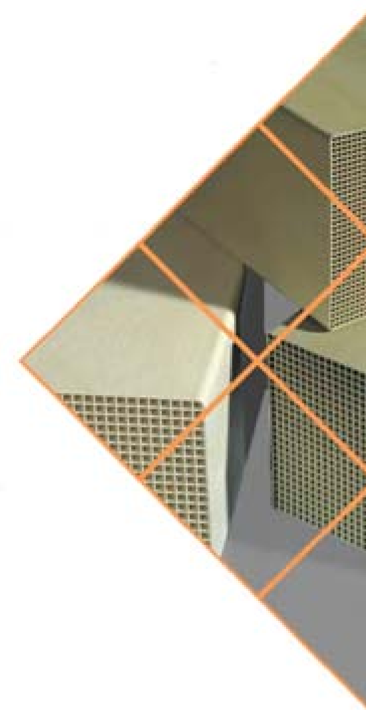
Operation & Monitoring

The objectives of SCR catalyst performance monitoring are:

1. to monitor the trends in important operating parameters and act upon abrupt changes in the trends,
2. to record data necessary to analyze remaining performance capability of the installed catalyst and project timing of when an addition/replacement of catalyst will be required.

- Fuels monitoring
- Performance monitoring
- NH_3 in ash
- SCR Inspections
- Catalyst testing
- AIG tuning/distribution measurement



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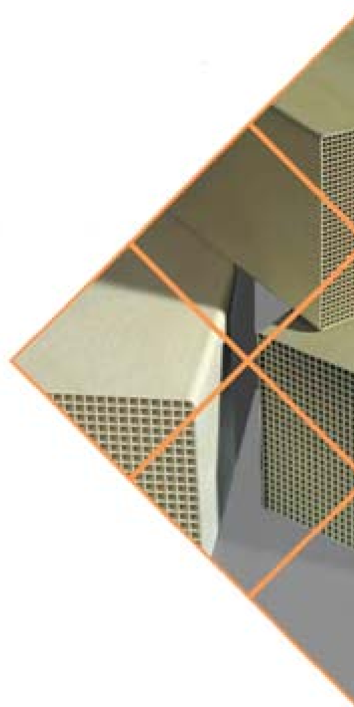
Monitor for abrupt changes

- Ammonia consumption rate
- Catalyst pressure loss
- NH3 concentration on the ash
- Air preheater pressure loss



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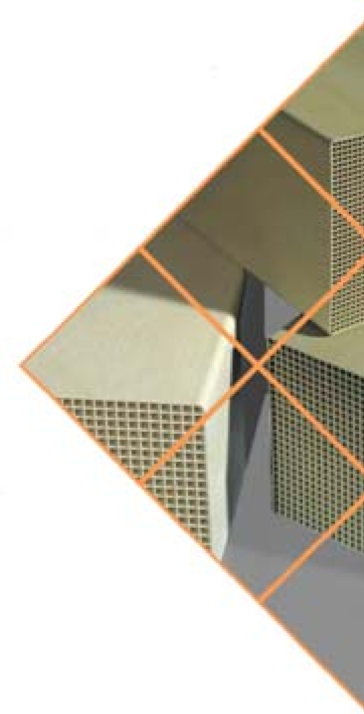
Operation & Monitoring
Fuels monitoring

- Create fuel sampling plan:
  - Used to monitor catalyst deactivation in between catalyst testing.
  - Fuel analysis on weekly/monthly basis depending upon expected variability / number of coals fired
  - Analysis of Fuel including:
    - Ultimate, Proximate Analysis, Ash Mineral Analysis, Trace Element Analysis
- Monitor impact of fuels with FIELD Guide™
  - Life estimation by FIELD Guide™
  - HHV, Sulfur, Ash, Arsenic, Calcium Oxide
  - More detail by Cormetech customized model



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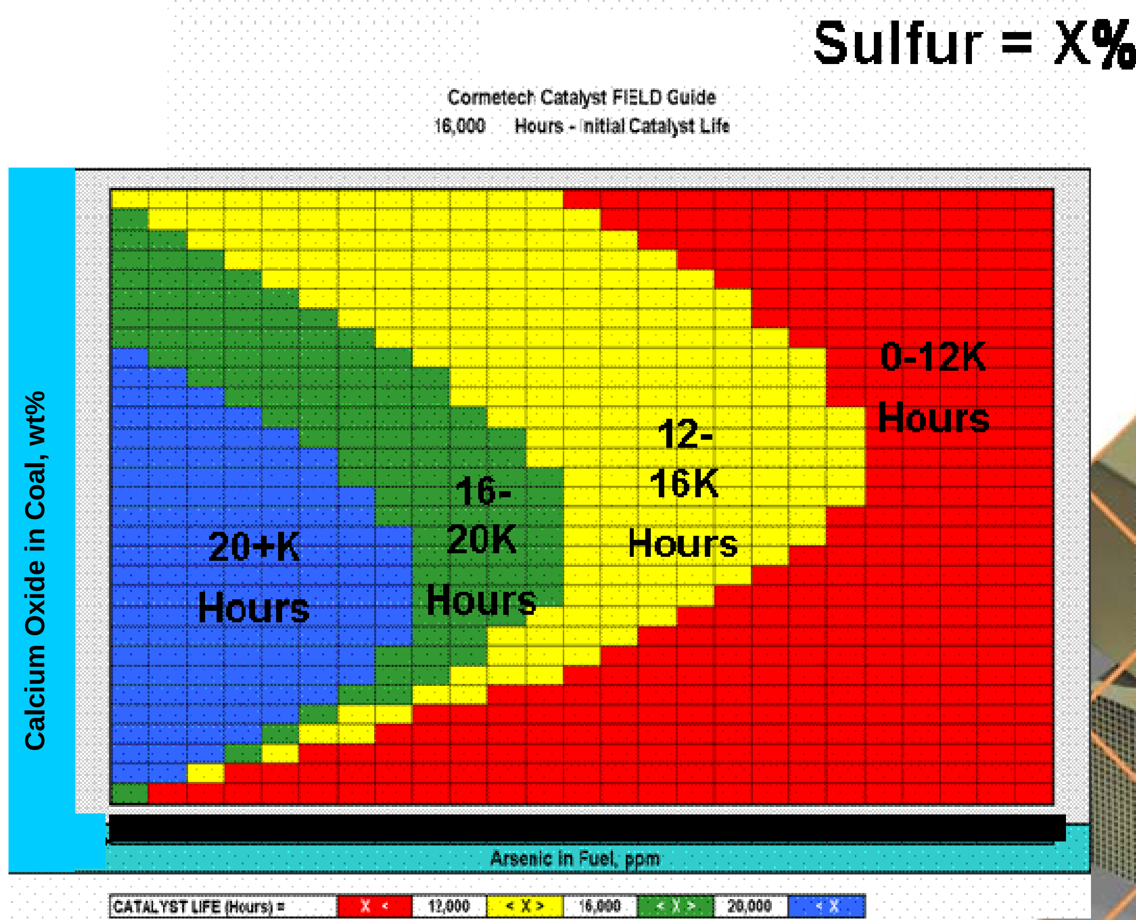

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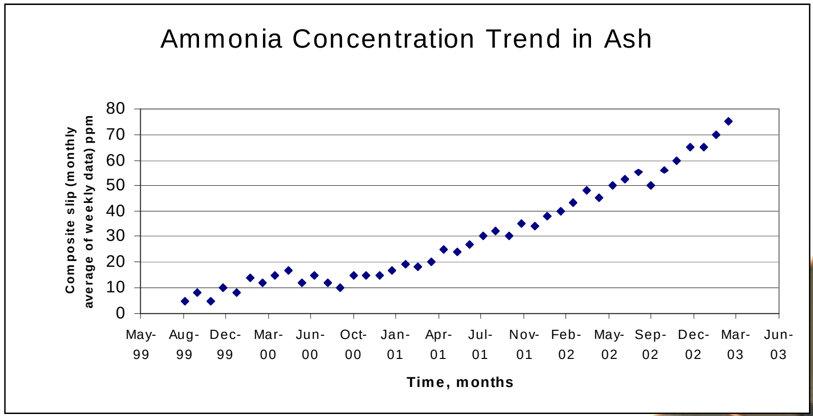
Operation & Monitoring

- Evaluation of NH_3 in ash results
  - Indicates when system needs attention
  - Surrogate of NH_3 slip
  - NH_3 testing in ash
    - Daily to weekly basis
    - Consistent sample location
    - Test methods
    - Sensitive to high fuel variability
    - Repeatable process
  - Plot and evaluate results



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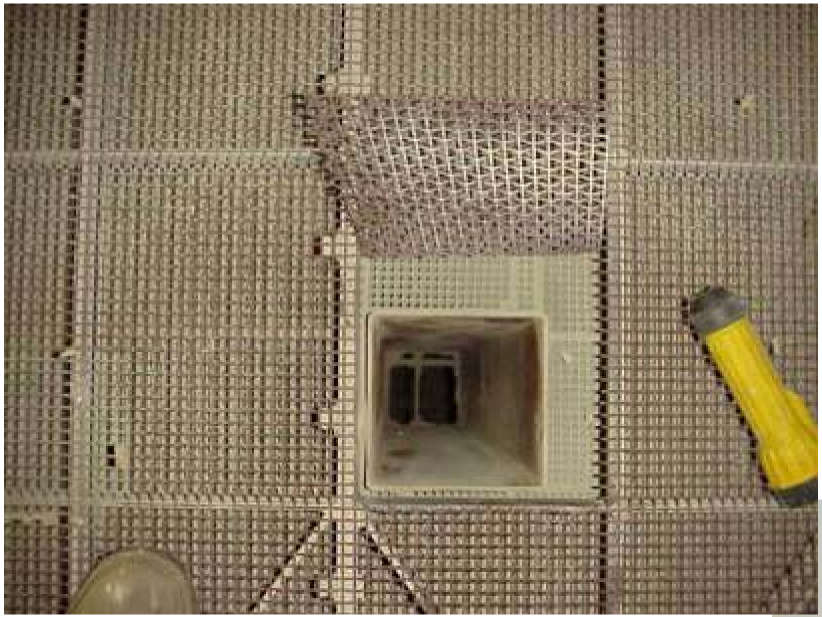
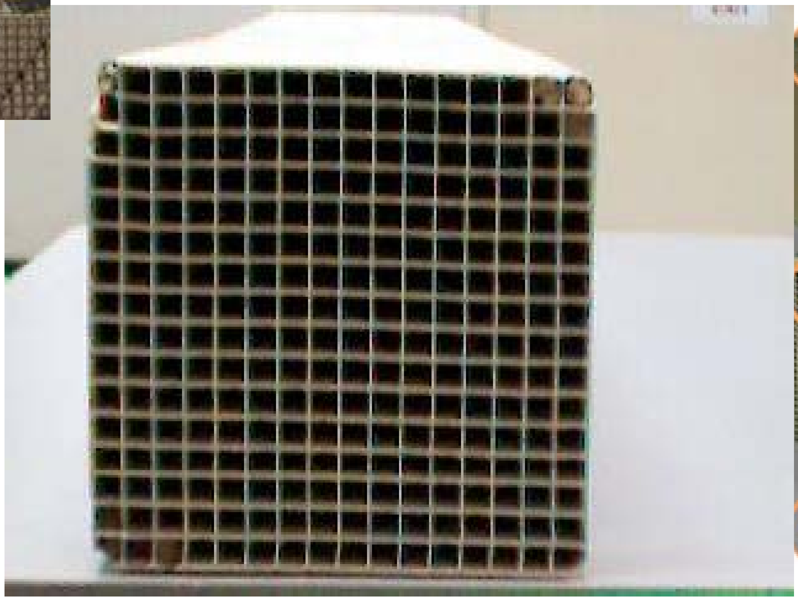
Performance Monitoring Protocol

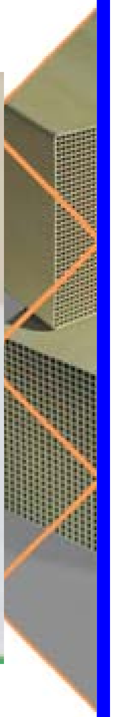
Test Description	Hourly	Daily	Weekly	Monthly	Annually
Operational Monitoring	record on DCS hourly averages of all parameters listed	Confirm Operation of Sootblowers / Sonic Horns			
Coal Sampling		coal sampling if burning Bituminous coal or changing fuels frequently	coal sampling if burning consistent or Western coal		
Coal Testing			testing of a composite sample of all coal burned in previous week (if sampled daily)	testing of a composite sample of all coal burned in previous month (if sampled weekly)	
Fly Ash Sampling		retrieve sample daily sample			
Fly Ash Testing		test NH3 on ash	composite mineral ash analysis (if burning Bituminous coal or changing fuels frequently)	composite mineral ash analysis (if burning consistent or Western fuel)	measure dust loading
NH3 Slip Measurements					direct measurements of NH3 slip
Catalyst Testing					Catalyst samples for audit (possibly 2x per year)
NH3:NOx Distribution at Catalyst Outlet					conduct audit of distribution and record AIG tuning valve positions

Catalyst Sampling



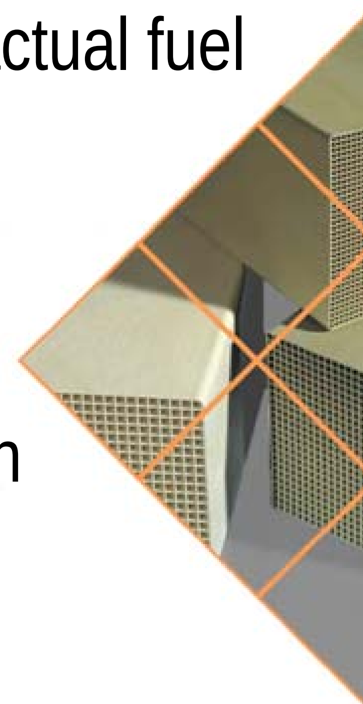


Full-size sample elements are removed and tested in a laboratory scale reactor



Catalyst Analytical Strategy

- Pilot tests to determine K_o (initial activity) for the catalyst design
- Pilot tests for field samples to determine K_t (activity at time t) for used catalysts materials
- Comparison of K_t/K_o with design expectations, actual fuel burned, and the required performance threshold
- Analytical techniques utilized for
  - Surface analysis
  - Bulk analysis from a percent to part per billion
  - Depth profiling of contaminants



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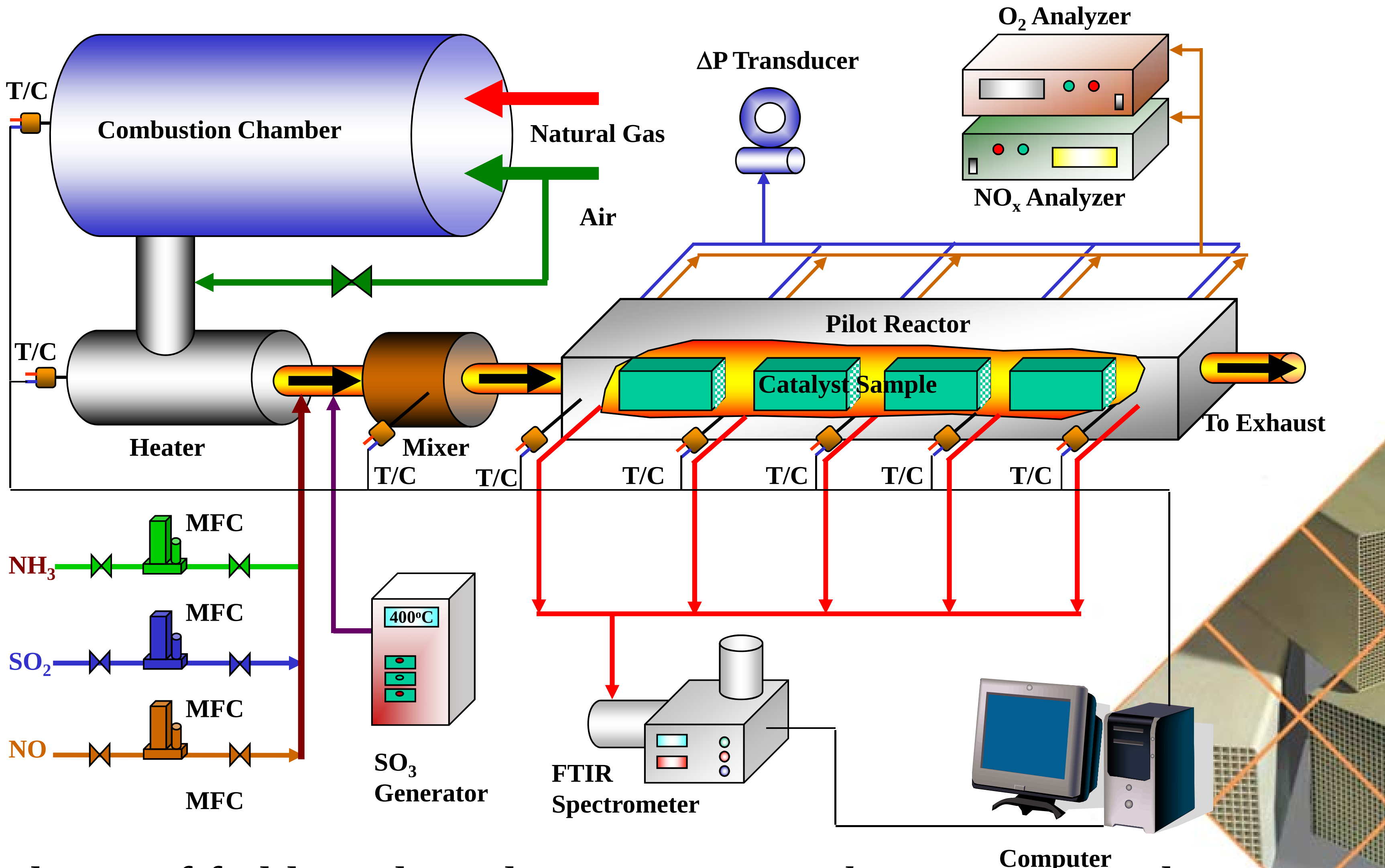
Pilot Test Plant



Auditing of field catalyst elements at *actual* operating conditions

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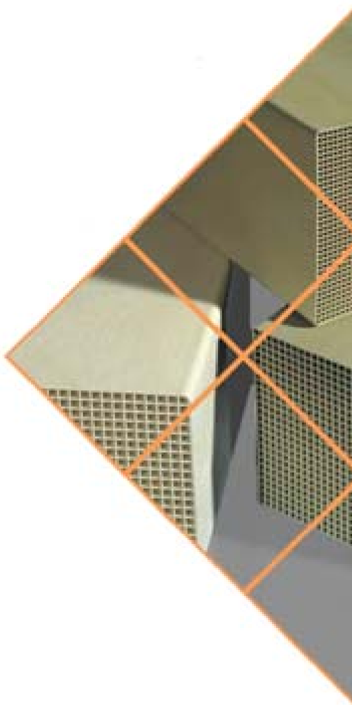
Catalyst Analytical Strategy

- Engineering analysis of fuels, process conditions
- Physical inspection of catalyst samples
- Bulk and surface analysis techniques
  - Inductively Coupled Plasma Mass Spectrometry (ICP)
  - X-Ray Fluorescence Spectroscopy (XRF)
  - Scanning Electron Microscopy with Energy Dispersive X-ray Analyzer (SEM/EDXS)
  - X-ray Photoelectron Spectroscopy (XPS/ESCA)
  - Secondary Ion Mass Spectrometry (SIMS)
  - Porosity and Surface area



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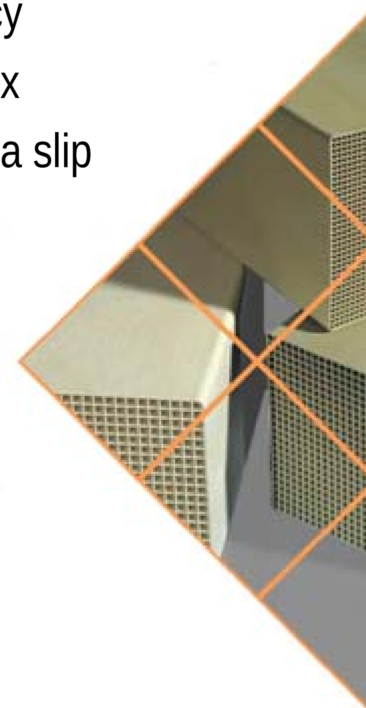
Basic Catalyst Sample Processing Steps

- Visual inspection
- Specification of appropriate test conditions/requirements
- Sample preparation
  - Chemical composition (catalyst, deposit)
  - Porosity, surface area, etc.
  - Pilot test
- Testing
- Results and analysis
- Comparison to expectations based on field data
- Report including recommendations

- Additional considerations
  - Engineering analysis to extend catalyst life or match boiler changes
    - Performance requirements
      - Efficiency
      - Inlet NOx
      - Ammonia slip
    - Fuel changes



How do we best use the SCR to meet the plant's objectives?

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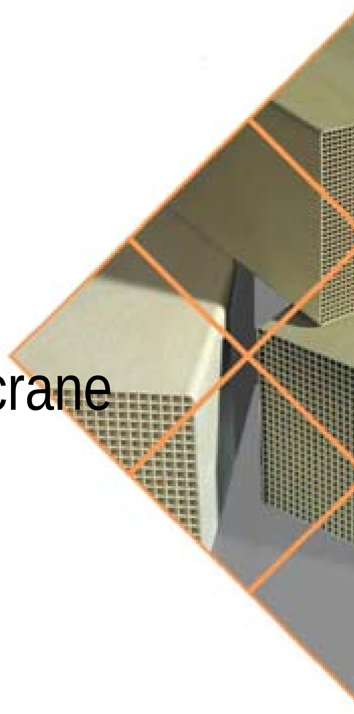
Outage Planning for SCR Add/Replacement

- Catalyst addition/replacement timing. Evaluation very utility/unit dependent
  - Seasonal vs. year round
  - Use of SCR bypass with boiler in operation
  - Cost of outage
  - Flexibility on NOx reduction and NH3 slip requirements
  - Preparedness for SCR work during forced outage
- Initial Cleaning
- Removal of old catalyst and seals
- Installation of replacement catalyst and seals
- Timing / manpower depends on loading access, hoist vs. crane



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SCR Inspection

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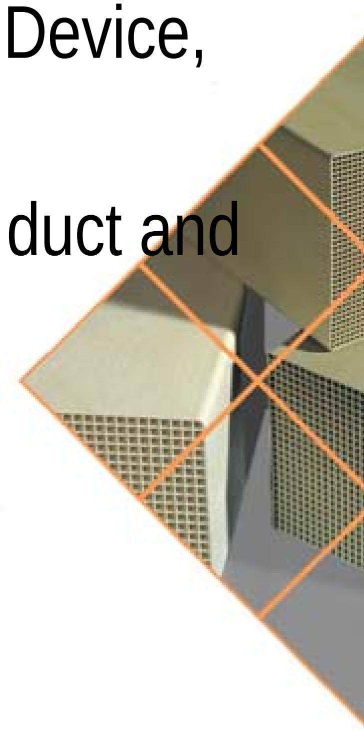
Catalyst System Inspection

- Each Catalyst Layer
- Sonic Horns / Soot Blowers
- Seals
- Plugging (Sonic Horn / Sootblower effectiveness)
- Erosion
- Condition of sampling grid
- SCR Inlet Ducting and Turning Vanes
- Ammonia Injection Grid, Flow Distribution Device, Static Mixer
- Condition of inlet duct and vanes

Sampling done in conjunction with inspection



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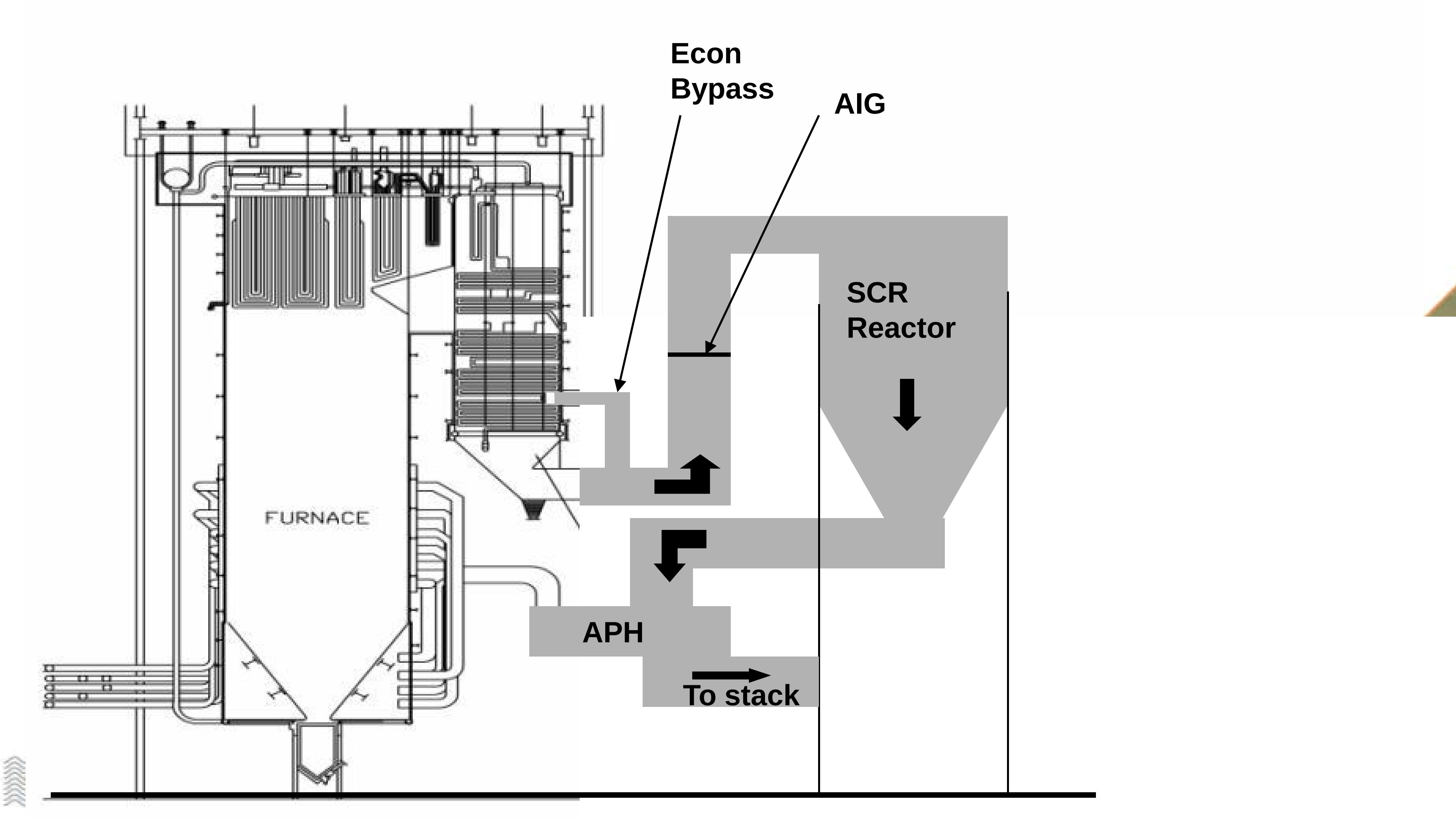
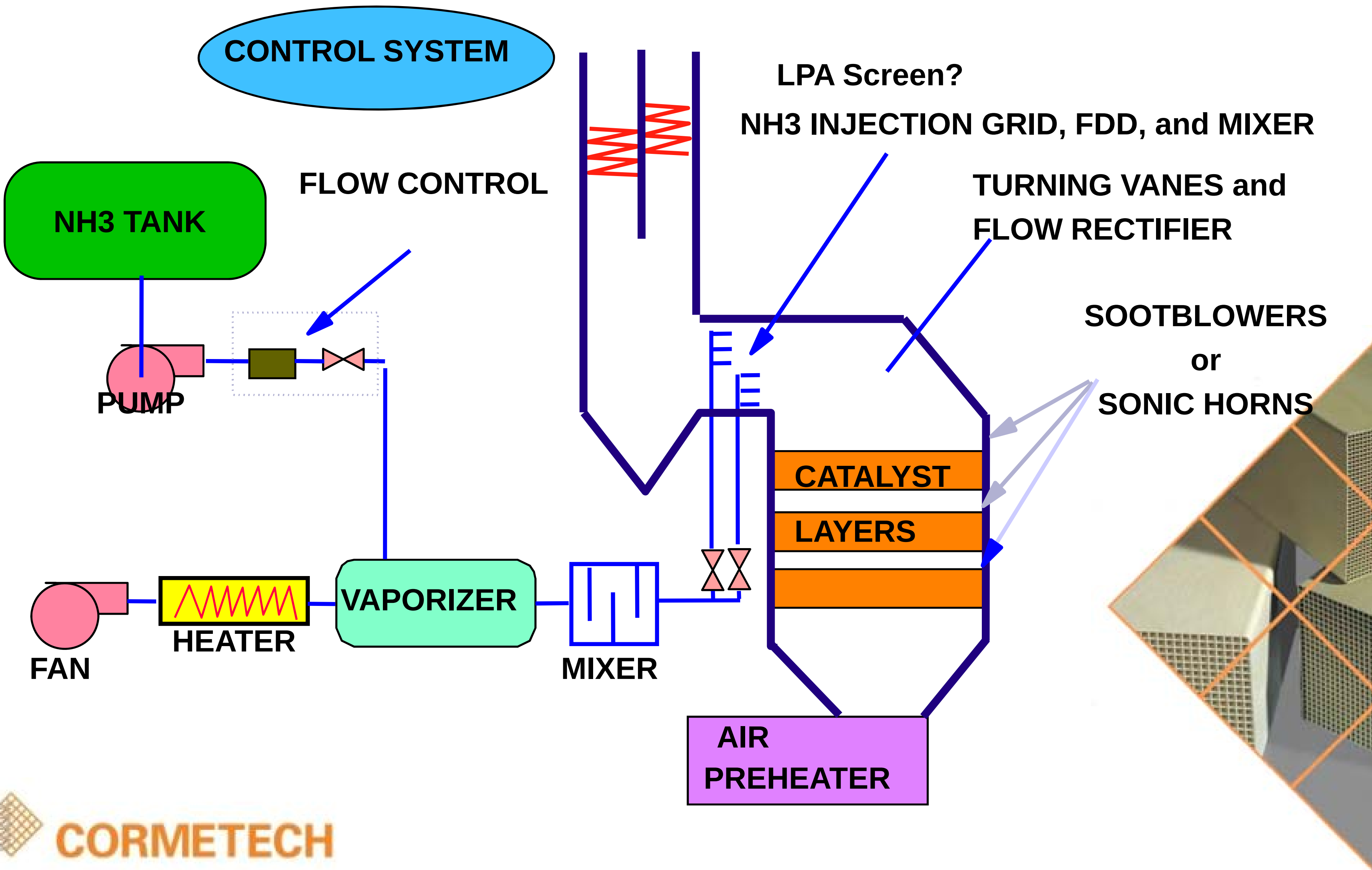
Typical Boiler Train – High Dust SCR



SCR Components



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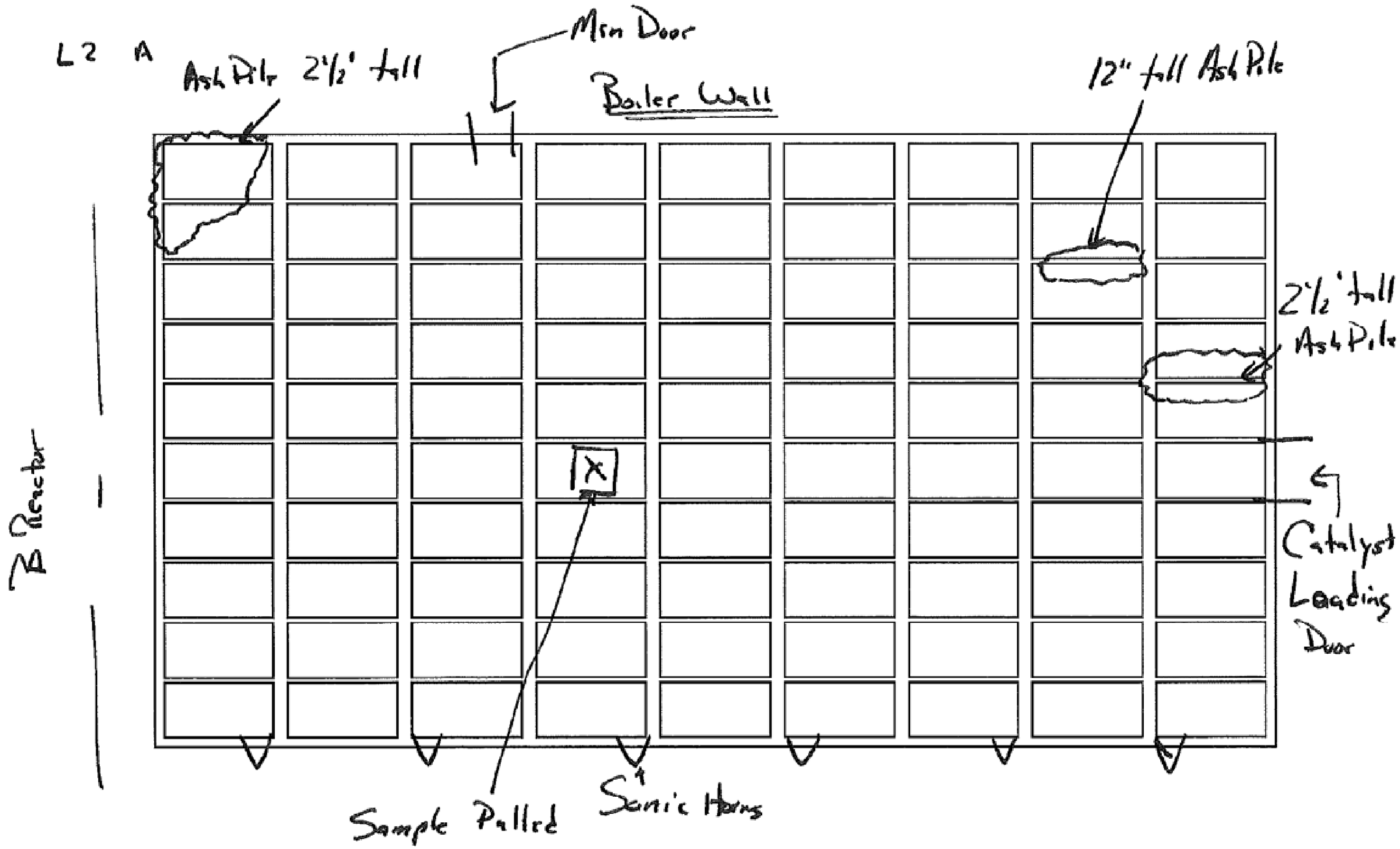
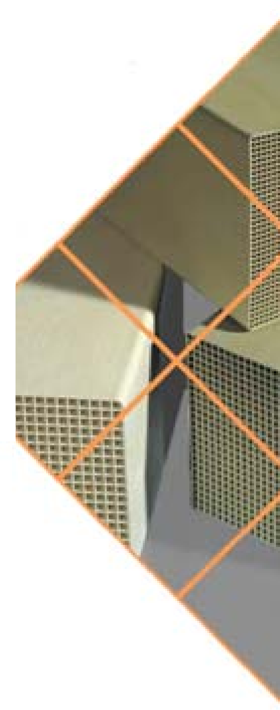
Map the findings





What have we just learned we need to do/monitor/plan, so we use the SCR to meet the plant's objectives?

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AIG tuning and maintenance

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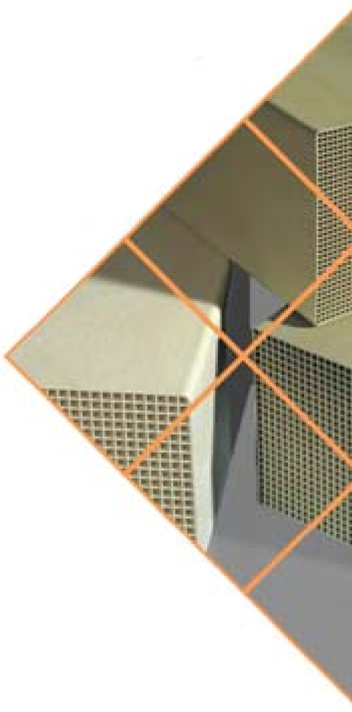
AIG Maintenance

- Plugging / erosion of lances?
- Bad gauges?
- Plugging of balancing valves?
- Ash plugging/piling upstream of AIG?
- Retune?



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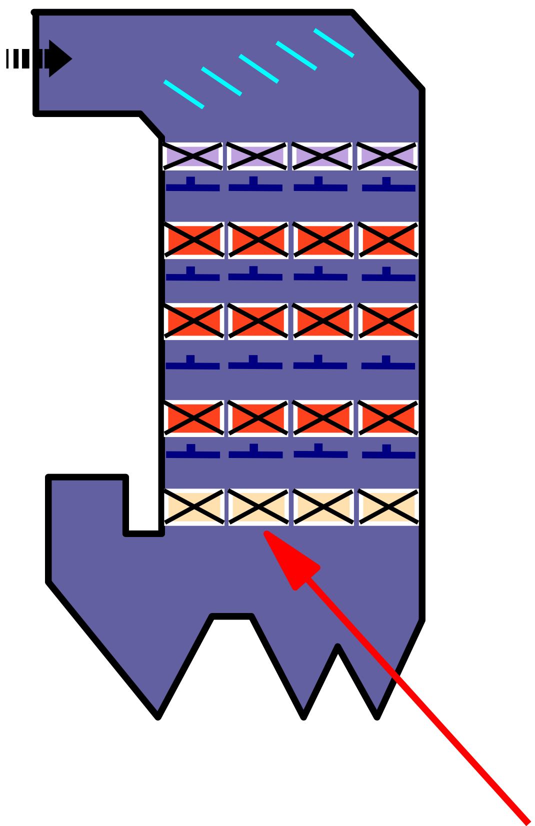
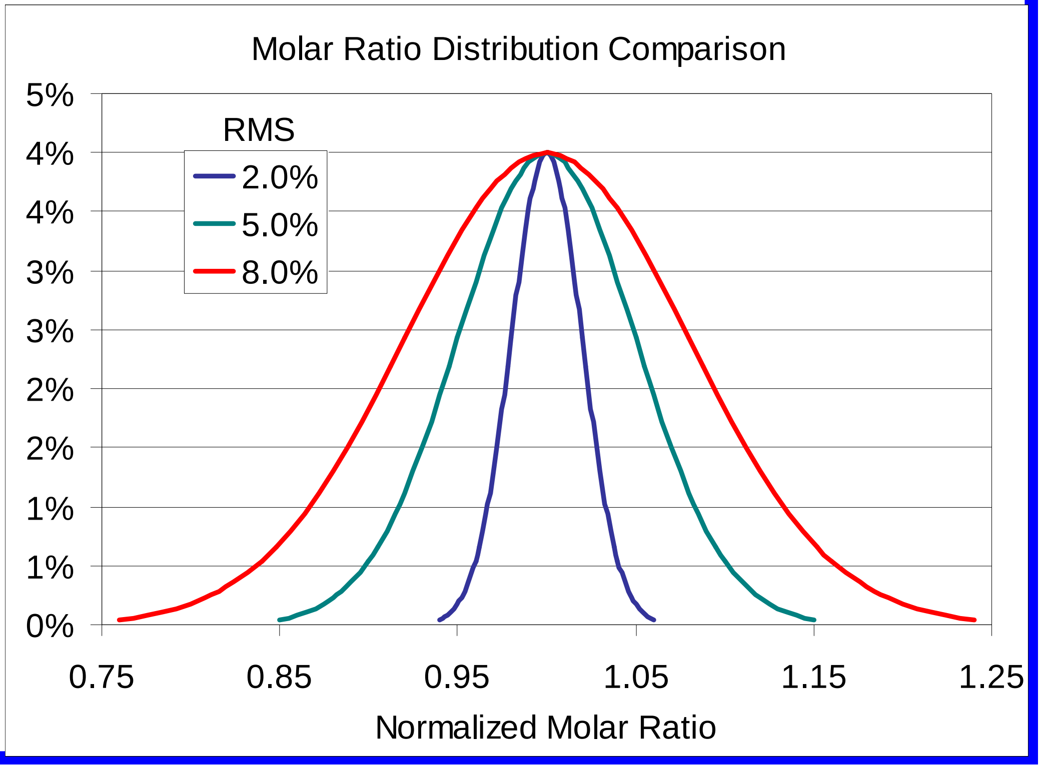
AIG Tuning



- Permanent measurement grid utilized below last layer of catalyst.
- Grid used to measure NOx distribution.
- NOx distribution used to adjust AIG to avoid high slip areas.
- Localized slip measurements taken at low NOx areas to assure max slip is below acceptable level.

Adjustment of AIG Valves

- Map NH_3:NOx molar ratio values (efficiency) back to associated AIG valve location
- Adjust valve position as needed to effect desired change in molar ratio
- Record and fix
- Check applicability over load range



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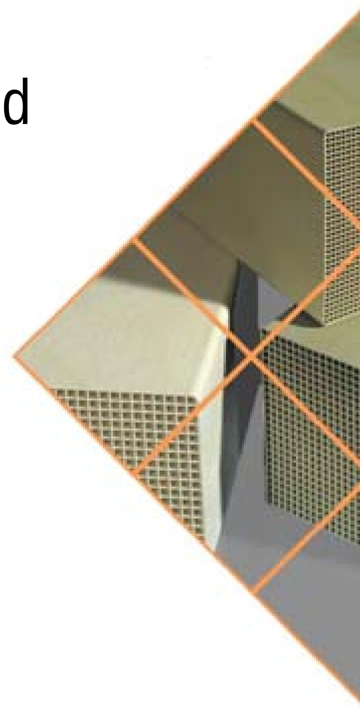
How often to tune?

Factors that affect the need to tune:

- Major boiler overhaul; new burners; etc.
- When catalyst is nearing performance threshold
- When higher performance than original design is desired
- For higher performance units [i.e. 85+ deNOx and above], tuning is more beneficial

How do we best use the SCR
to meet the plant's objectives?



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Low Load/Temperature SCR Operation

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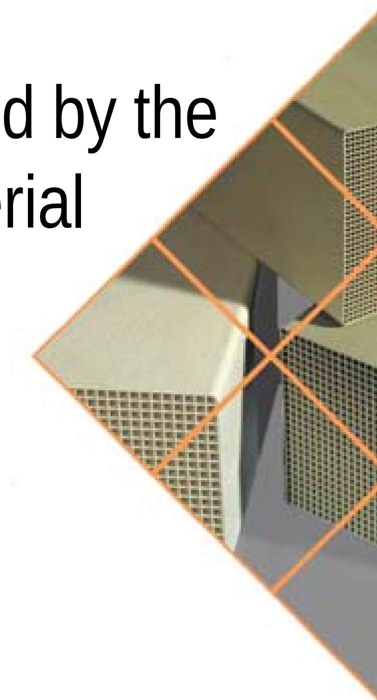
SCR Operating Temperature

- Operating temperatures
  - Minimum operating temperature for partial load conditions is determined by the formation temperature of ammonia sulfates
  - Maximum operating temperature is determined by the SO_2 oxidation requirements and module material limitations
  - Typically 600 – 800°F (320 – 425°C)



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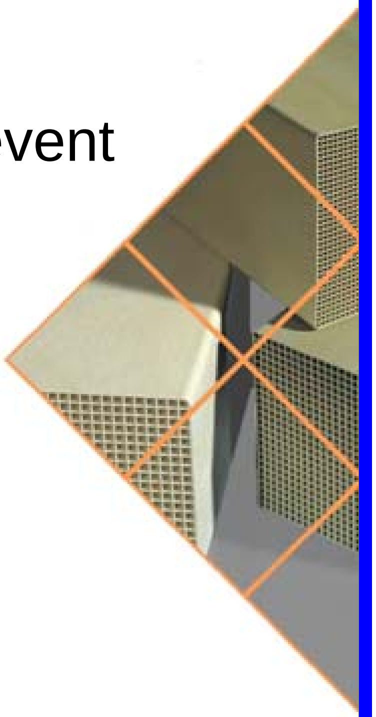
Ammonia Salt Formation

- Ammonium bisulfate (ABS) deposition:
  - $NH_{3(g)} + SO_{3(g)} + H_2O_{(g)} \leftrightarrow NH_4HSO_{4(l)}$
- Liquid ABS can form in SCR catalyst pores at temperatures above the bulk phase dew point
- Typically minimum operating temperature limits prevent ABS formation



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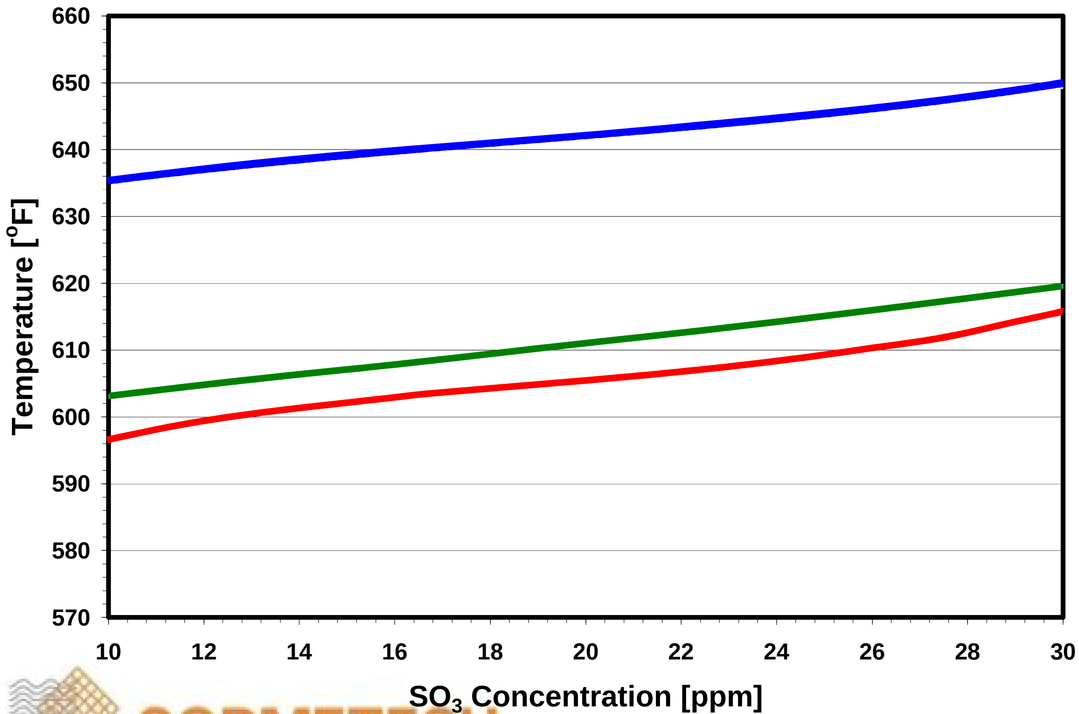
Cormetech Tmin Design Strategy

- **“Basic Approach”:**
  - Avoids risk of ABS deposition on the catalyst
  - ABS-induced deactivation consumes performance margin



RT = recovery temperature

MOT = minimum operating T

MIT = minimum injection T for NH_3

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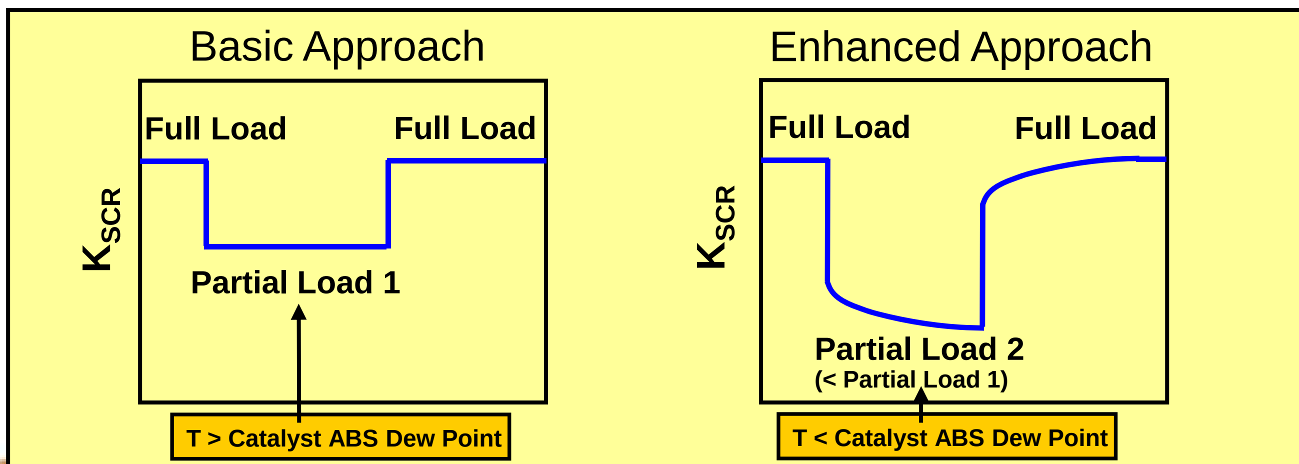
Low Temperature SCR Operation

- Enhanced Approach:
  - Allows operation down toward the bulk ABS dew point
    - Controlled amount of ABS deposition and deactivation
    - Recover catalyst potential by reheating above recovery temperature
  - Evaluate: catalyst K/AV vs. performance requirement
    - Catalyst type and properties influence capability
  - Successfully implemented in >14 boilers



End of Presentation….

Thank you for your attention…

Questions?

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