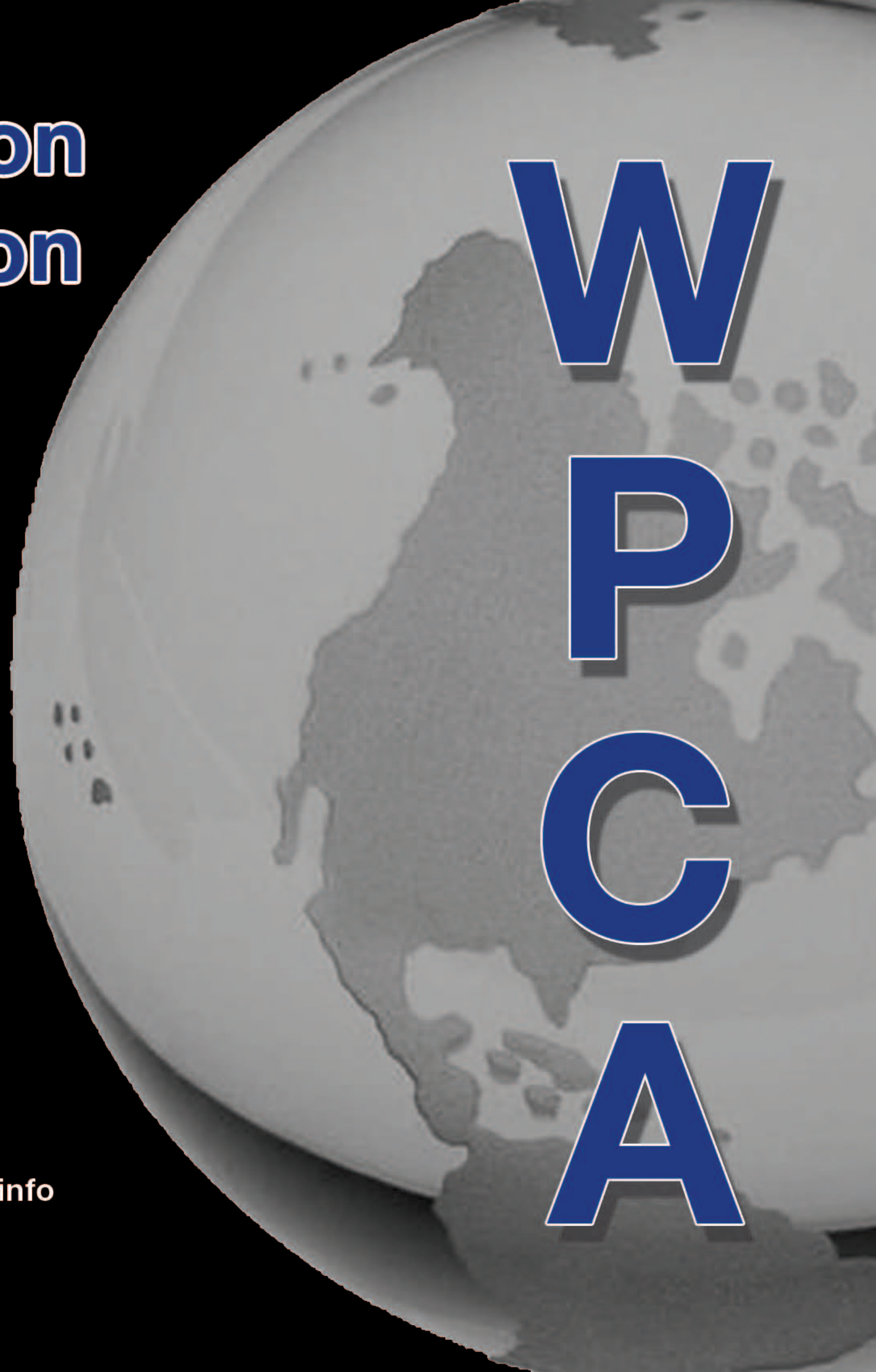
Worldwide Pollution Control Association

Duke Energy Seminar
September 3 – 5, 2008
Concord, NC



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Haldor Topsoe

2008 WPCA – Duke Pollution Control Seminar

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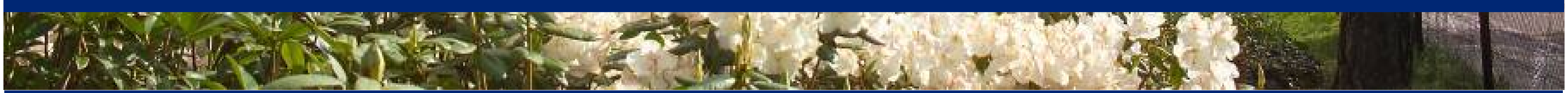
RESEARCH | TECHNOLOGY | CATALYSTS



SCR Catalyst Management

Nathan White

HALDOR TOPSØE

Agenda

- Catalyst 101
  - Catalyst Basics
  - Catalyst Types
  - Catalyst Modules
  - Design Considerations
- Catalyst Management
  - Catalyst Activity Monitoring
  - Wash, Regenerate, or New
  - SCR Housekeeping
  - Plant Operation Considerations
    - Operation below the catalyst T_{min}

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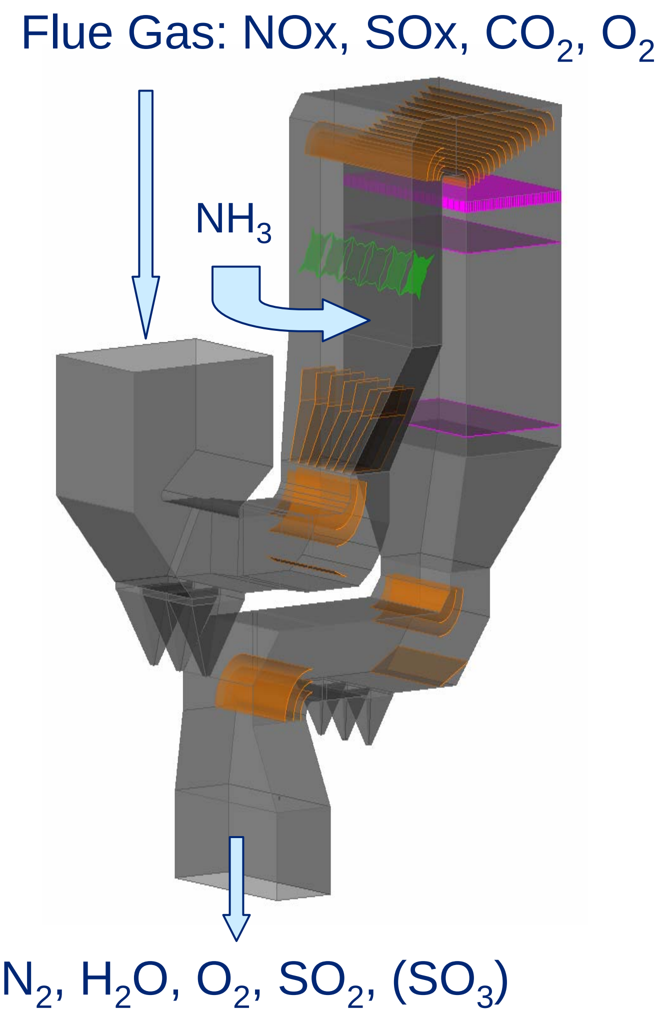
SCR Basics

- SCR = Selective Catalytic Reduction
- Propose is to reduce NOx from flue gas.
- A reducing agent, most commonly ammonia (NH_3), is injected into the flue gas as a reducing agent.
  - The NH_3 is mixed into the gas stream, sometimes using mixing plates.
  - The mixed gas then passes through the catalyst layers where the NH_3 reacts with NOx on the catalyst surface and in the pores to form N_2 and H_20 vapor.



SCR Basics

High Dust

- SCR upstream of air preheater / ESP.
- High concentration of fly ash in exhaust, > 1,000 mg/Nm^3.
- Catalyst with a plate pitch > 5.0 mm.

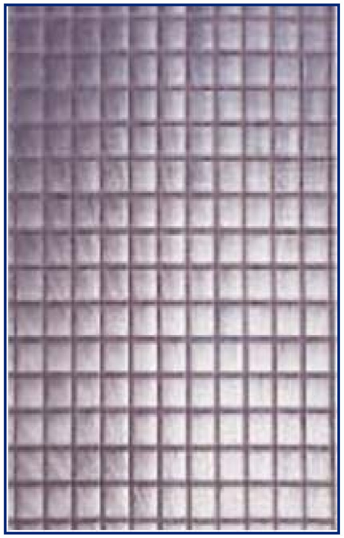
Low Dust

- SCR after ESP and before air preheater.
- Low concentration of fly ash in the exhaust < 500 mg/Nm^3.
- Catalyst with a plate pitch < 5.0 mm.

Types of SCR Catalyst

Plate

- Rolled
- Coated



Honeycomb

- Extruded
- Coated

Corrugated

- Composite
- Hybrid

➢ Composition; Titania catalyst support with Vanadium as principal active component, with other promoters, including Tungsten

Plate-type Catalyst

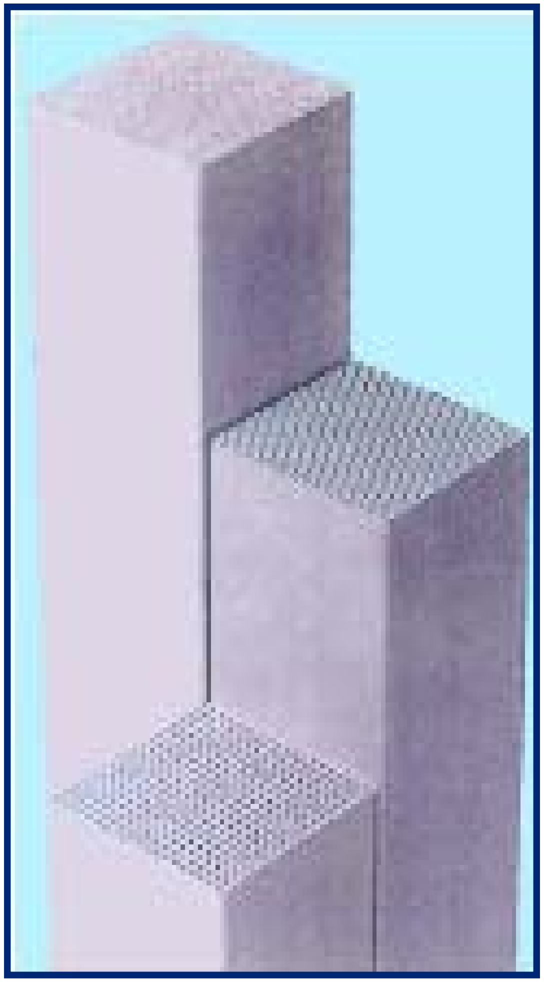
Manufacture

- Stainless steel carrier, ceramic material rolled on.
  - TiO_2, V-oxide/W-oxide as the active catalytic material. Active materials rolled on with ceramic material or coated on later.
  - Other promoters used, Mo-oxide.
- Notches (corrugations) formed into plates to provide separation.
- Inserted in element boxes with variable spacing to set pitch: 60 to 90 plates.
- Variable plate height: 450 to 625 mm

Application

- Both low dust and high dust configuration.

Honeycomb Catalyst



Manufacture

- Homogeneously extruded ceramic with square-opening cell structure.
  - TiO_2, V-oxide/W-oxide as the active catalytic material. Active materials extruded with ceramic material or coated on later.
- Variable block height: 1,200+ mm.

Application

- Both low dust and high dust configuration.

Corrugated Catalyst

Manufacture

- Plate carrier is corrugated to provided plate separation. It is fused with TiO_2 and fibers.
- A controlled pore volume is generated.
- V-oxide/W-oxide as the active catalytic material are impregnated generating a homogeneous ceramic.
- A full plate hardening promoter is added.
- Monolith inserted in element boxes.
- Variable plate height: 200 to 550 mm

Application

- Both low dust and high dust SCR.

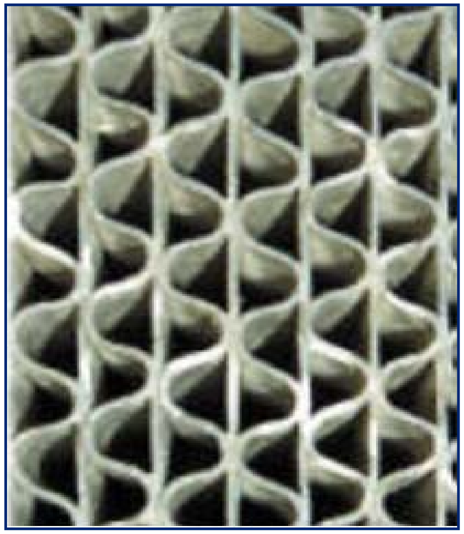
Catalyst Advantages

Plate

- Low pressure loss

Honeycomb

- High active surface area per unit volume



Corrugated

- High active surface area per unit volume
- Low SO_2-oxid. per unit activity

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Catalyst Pitch

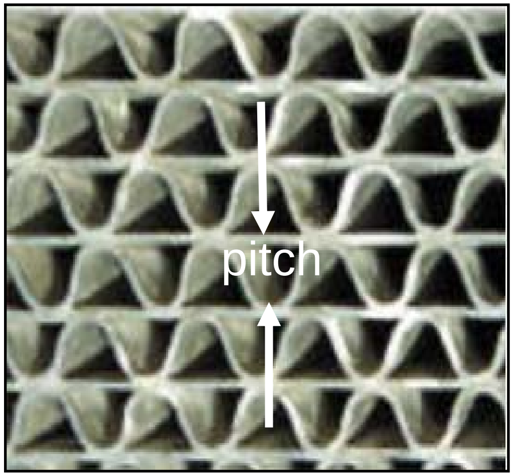
Plate Pitch = center to center line form one plate/wall to the next

Plate-type structure

- Flexible plates
- Rectangular opening
- Wall thickness: 0.6 to 0.8 mm
- Pitch: 5 to 7 mm

Honeycomb structure

- Rigid
- Square openings
- Wall thickness: 0.4 to 0.9 mm
- Pitch: 2 to 9.2 mm



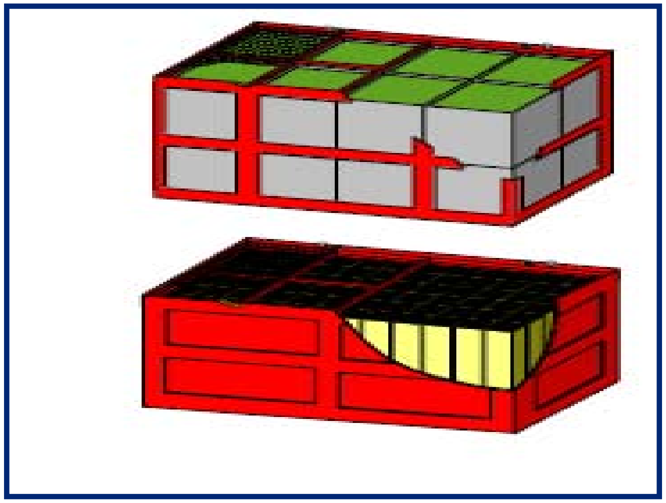
Hybrid plate-type structure

- Rigid
- Corrugated openings
- Wall thickness: 0.4 to 1.1 mm
- Pitch: 2 to 12 mm

Pitch Selection vs. Dust Load

Dust Load gr/dscf	Plate Pitch	Honeycomb Pitch	Corrugated Pitch
< 2	5.0 mm	6.7 mm (22 cell)	5.8 mm
2 to 6	5.5 mm	7.4 mm (20 cell)	7.2 mm
6 to 10	6.0 mm	8.2 mm (18 cell)	8.3 mm
10 to 12	6.2 mm	9.2 mm (16 cell)	9.3 mm
> 12	6.5 mm	NA	> 9.3 mm
12 to 16	6.5 mm	NA	10.3 mm
16 to 20	6.5 mm	NA	12 mm

Catalyst Modules



- Catalyst elements arranged in in and one steel frames.
  - Plate – 2 levels of 8 element boxes
  - Honeycomb – 72 monoliths
  - Corrugated – 2 to 3 levels of 8 element boxes.
- Standardized cross-section module
  - Possible to interchange corrugated and plate element boxes in most modules.
- Possible to interchange catalyst types within reactor
- Module height varies with catalyst monolith height

Catalyst Design Considerations

- Performance Requirements
  - NOx reduction (80 – 95%) and operating life (8,000 to 24,000 hours).
  - NH_3 slip allowed, 2 to 5 ppm.
  - SO_2 oxidation allowed, 0.1 to 1.0% per initial catalyst charge.
  - Pressure drop limit, usually 1 to 1.5” wc per layer.
- Flue Gas Operating Conditions
  - NOx concentration
  - Fuel characteristics
  - Fly ash concentration
- SCR Reactor
  - Initial catalyst charge
  - Reactor size – layers, catalyst depth, modules per layer
  - Plant configuration – high or low dust, AIG only, AIG/Mixers

Catalyst Management

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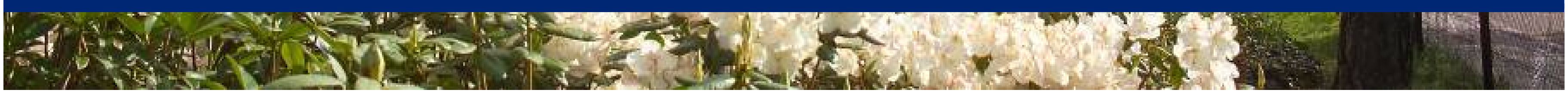

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Catalyst Management Goals

- Maintain target NOx reduction while maintaining NH_3 slip below required limits.
- Maintain catalyst active at the highest level for the longest period of time with the lowest economic impact.
- Replace lost catalyst activity by utilizing either washed, regenerated, or replaced catalyst potential.
- Conform catalyst activity potential replacement to plant outage schedule and budgetary constraints.
- Prevent excessive SO_2 conversion and pressure loss.

Catalyst Management Plan (CMP)

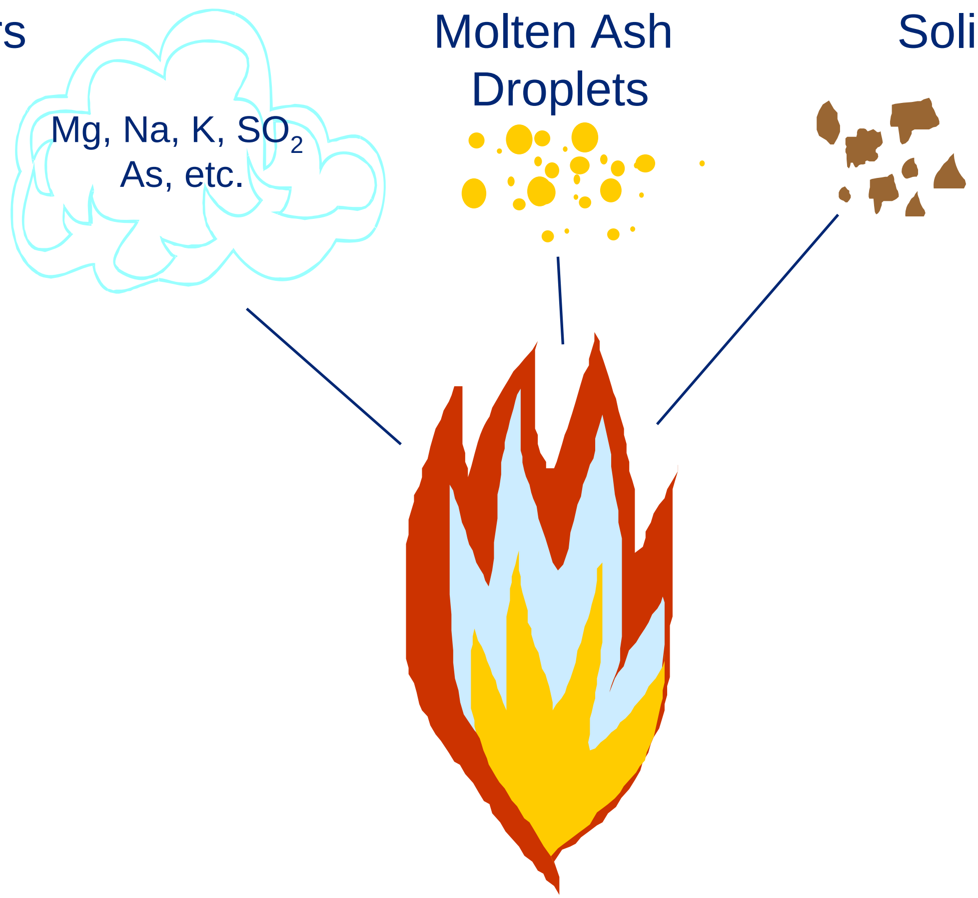
- Schedule for
  - SCR inspection and cleaning
  - AIG tuning
  - catalyst activity sampling
  - maintaining SCR catalyst potential
- Process for adding, replacing, and cleaning the catalyst
- With the above tailored to fit required NOx performance and outage schedule requirements for your unit and company.

Activity Monitoring

- When?
  - Once a year is typical
- Where?
  - Each layer
  - Area of highest dust loading
- How?
  - Bench or pilot scale
- Conditions?
  - Standard or unit specific, makes no differences as long as k_o is know at test conditions.
  - Activity testing at different temperatures can indicate deactivation mechanism.

What Reduces Catalyst Activity?

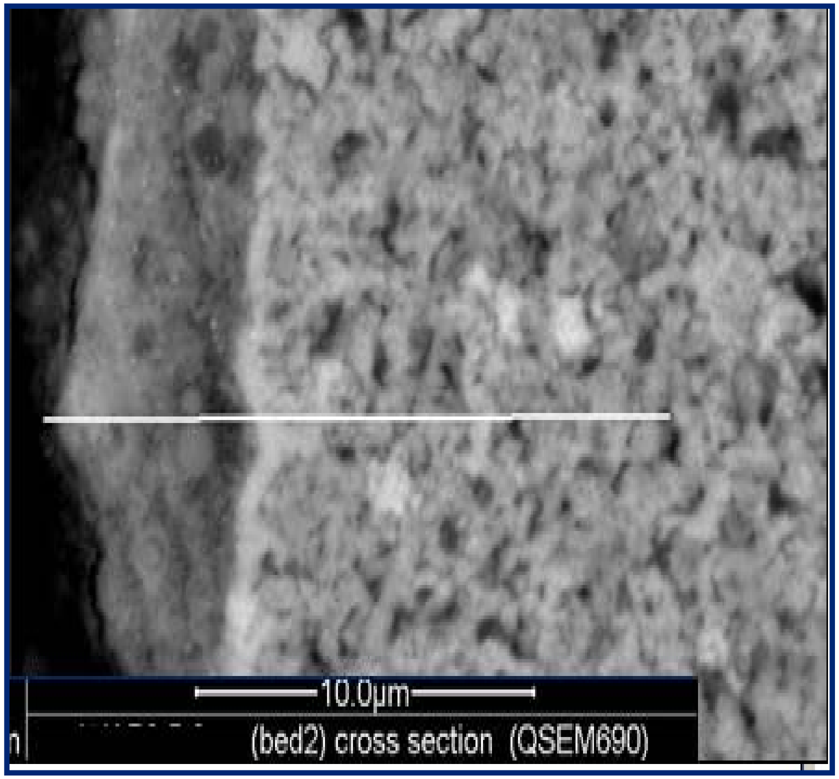
Constituents from Fossil Fuel Combustion



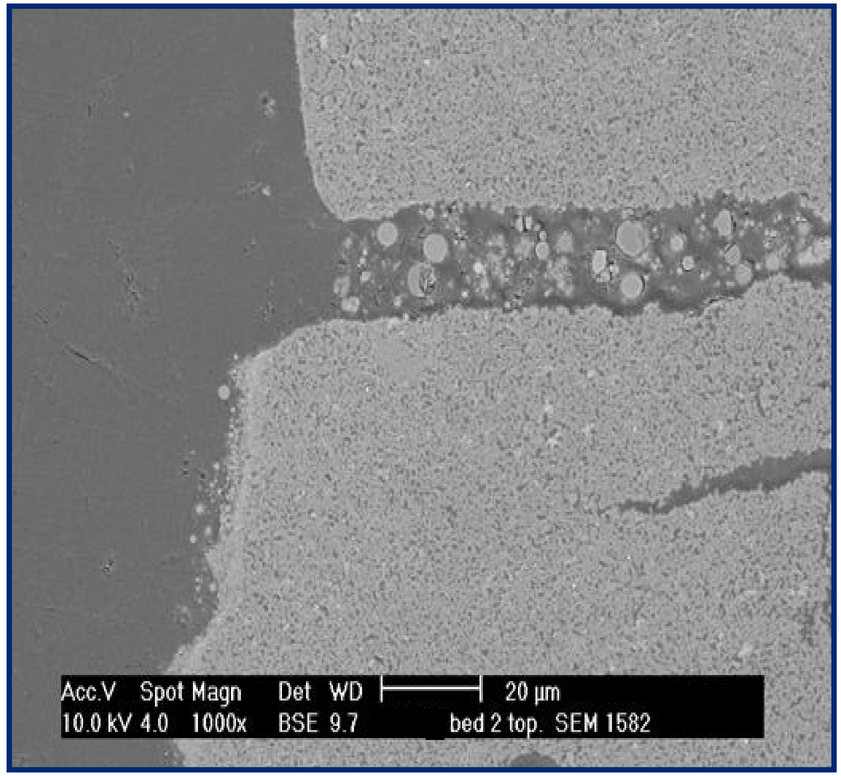
Catalyst Deactivation

Physical - ash and other solid particles

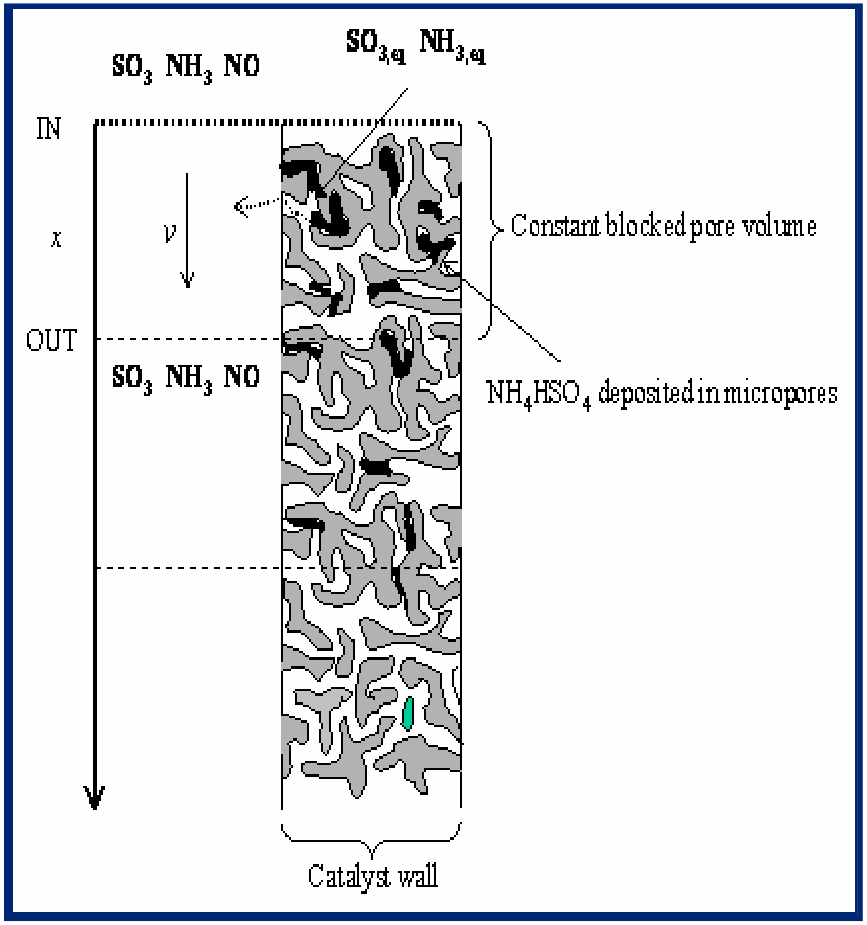
Masking: blocking catalyst surface



Fouling: physical pore blockage

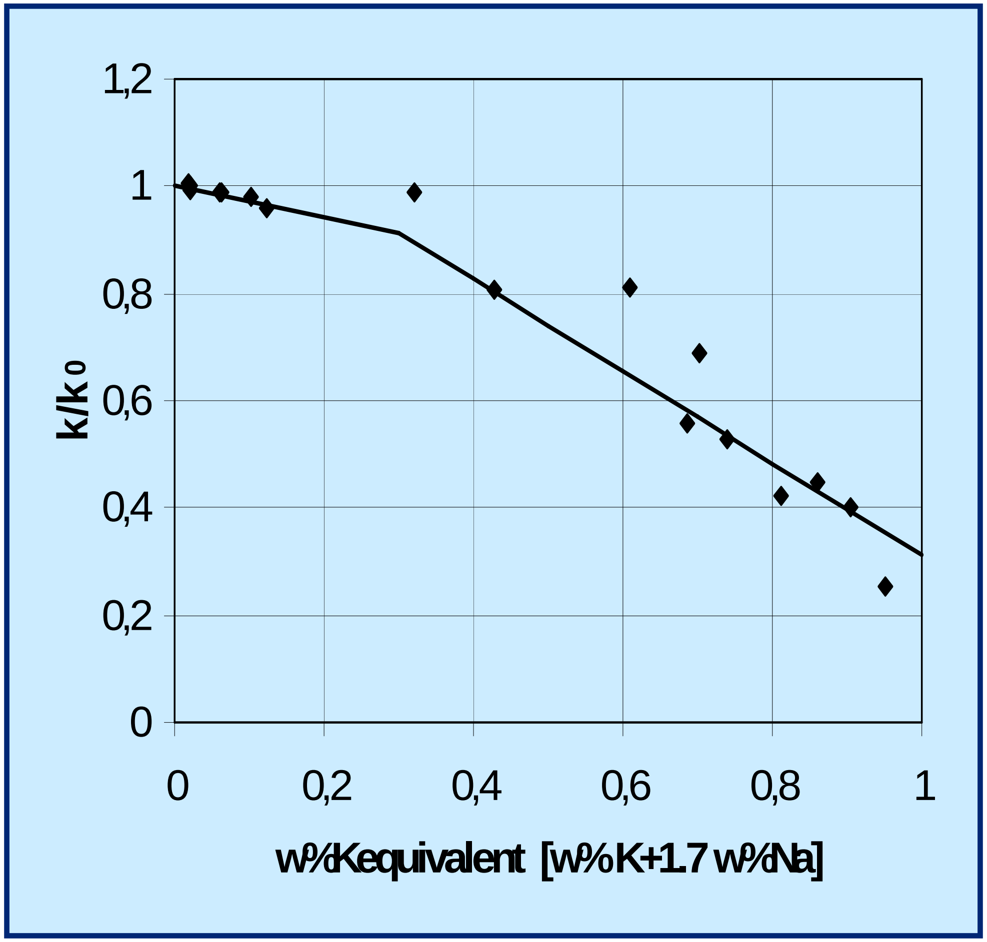


Catalyst Deactivation



- Chemical poisons that physically mask, foul and plug the catalyst surface and pores.
  - Arsenic – vapor phase condensation (As_2O_3).
  - Ammonium bisulfate (ABS) condensation.
  - Calcium - oxide (SO_4).
  - Vanadium sulfate.

Catalyst Deactivation



- Poisons that chemically bond to the active site.
  - Arsenic – vapor phase condensation (As_2O_3)
  - Alkali Metals – Na, K
  - Phosphorous – P_2O_5
- Flue gas vapors that deplete active metals.
  - HCl / HF
  - H_2SO_4 , (acid dew point)

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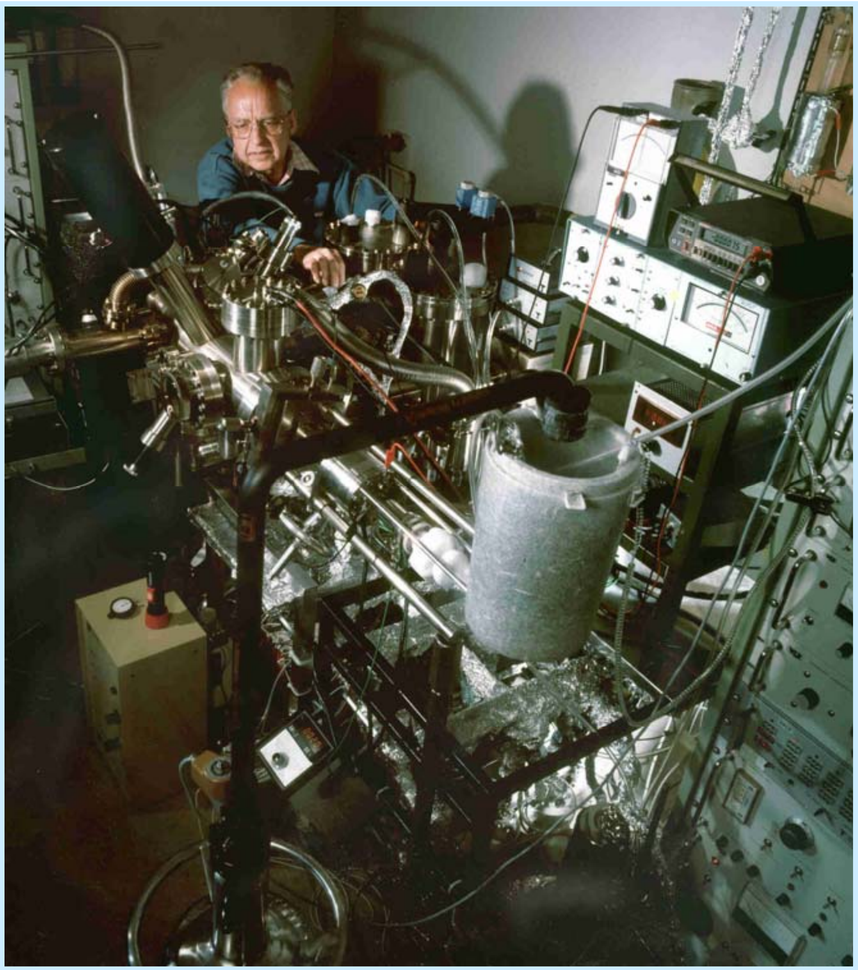
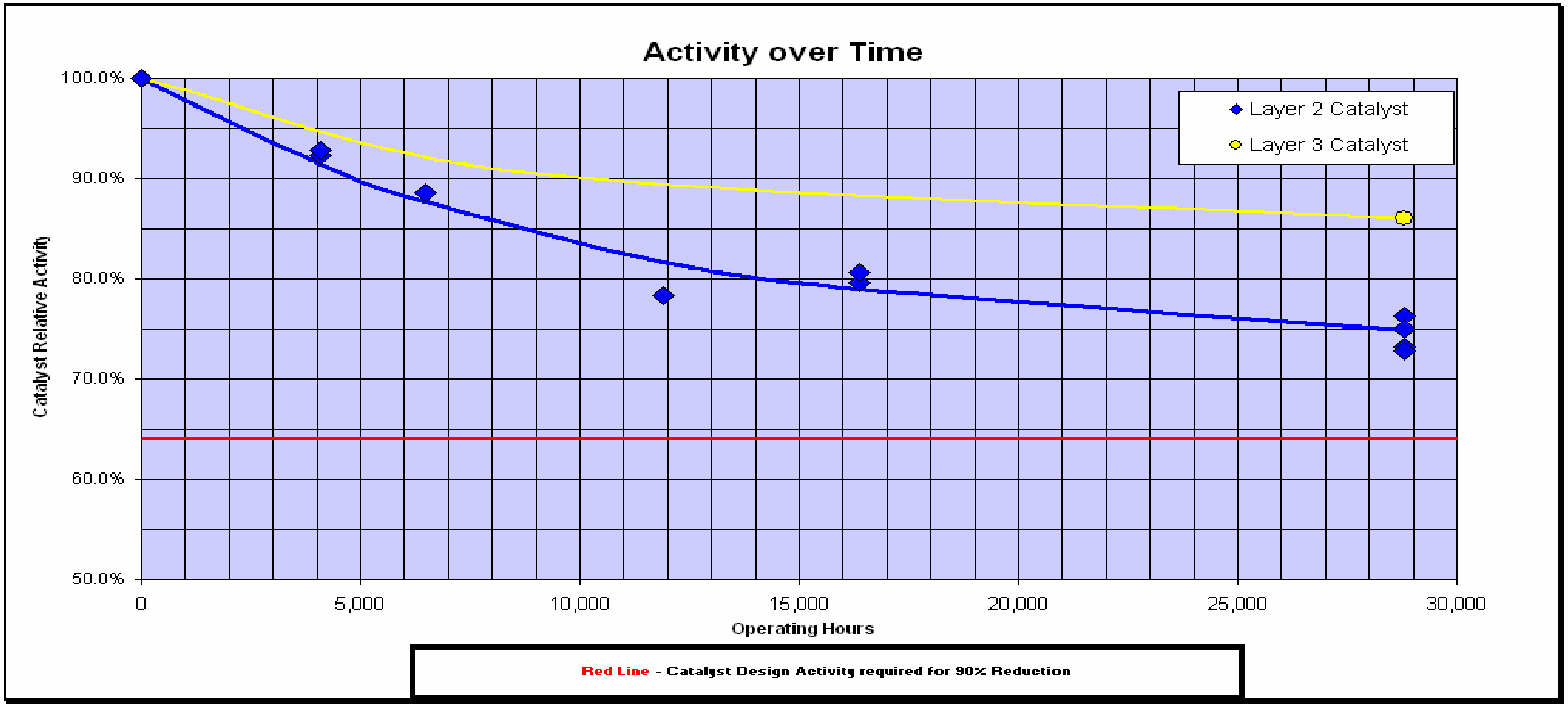
Relative Activity Loss



- Activity, k_t/k_o, decreases with time from 1.0 (exponentially decaying model).
- Decay depends on SCR configuration and design.
- Decay depends also on fuel, flue gas dust loading, flue gas composition along with ash composition.
- Deactivation usually takes place from the top down.
- Compare catalyst activity loss with chemical analysis.

Typical Relative Activity Loss

Application – High Dust	Time, hr	Relative Activity, k_t/k_o
Eastern Bituminous firing	24,000	0.70 – 0.75



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Typical Relative Activity Loss

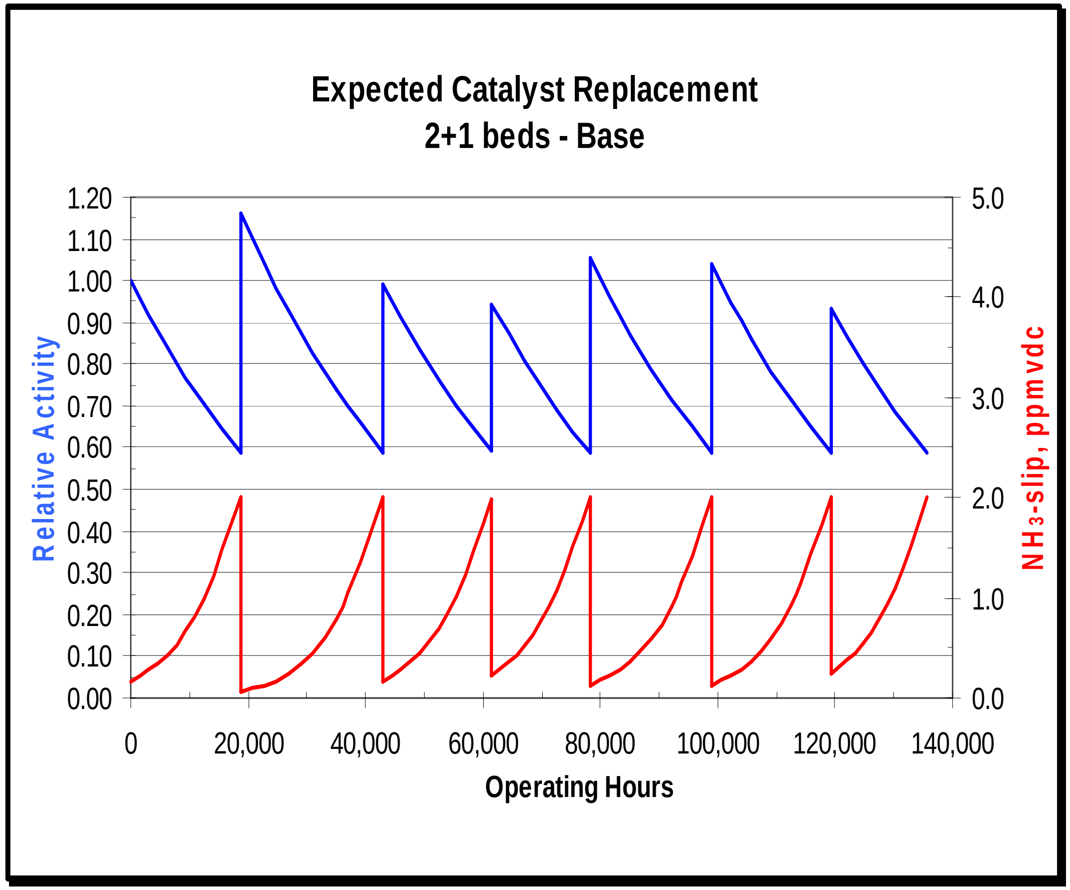
Application – High Dust	Time, hr	Relative Activity, k_t/k_o
PRB firing	16,000	0.65 – 0.70
Lignite firing	16,000	0.50 – 0.55
Bituminous with 10 – 20% bio-fuels co-firing	24,000	0.70 – 0.75
Bio-fuels firing	10,000	0.30 – 0.60

Application - Low Dust	24,000	0.85 – 0.95

Activity Monitoring

- Determine
  - relative activity compared to fresh catalyst
  - deactivation rate of catalyst
- Predict when reactor potential (Po) reaches minimum level
- Adjust CMP as required.

- **Relative Catalyst Activity Prediction**



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CMP Actions / Options

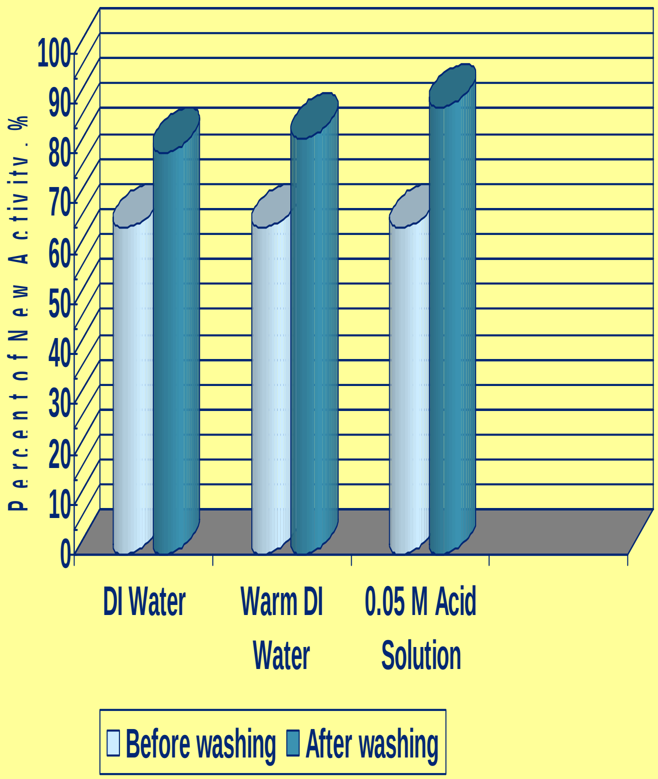
- Plant could water wash – removes ash particles from catalyst surface / pores and some poisons

CMP Actions /Options

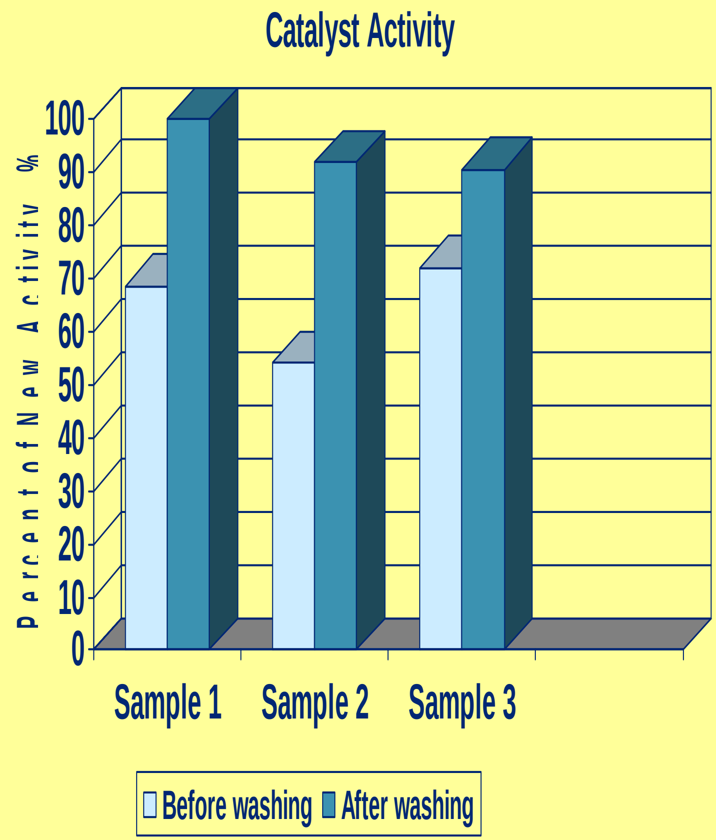
- Plant Water Washing (Pros)
  - Can be done in situ and many times
  - Many times, so far (9) times on the same catalyst charge
  - Restores catalyst activity
    - Amount depends on application and poisons
    - Relative activity experience after cleaning
      - » Bituminous – 0.80 to 0.90
      - » PRB – 0.90 to 1.0
      - » Bio-fuels - 0.90 to 1.0
- Plant Water Washing (Cons)
  - No guarantee on restored activity, performance or service life
  - Service life is limited (In situ cleaning results in less activity gain)
  - Could remove active metals over time if not careful

Plant Water Washing Results

Bituminous - High Dust



PRB – High Dust

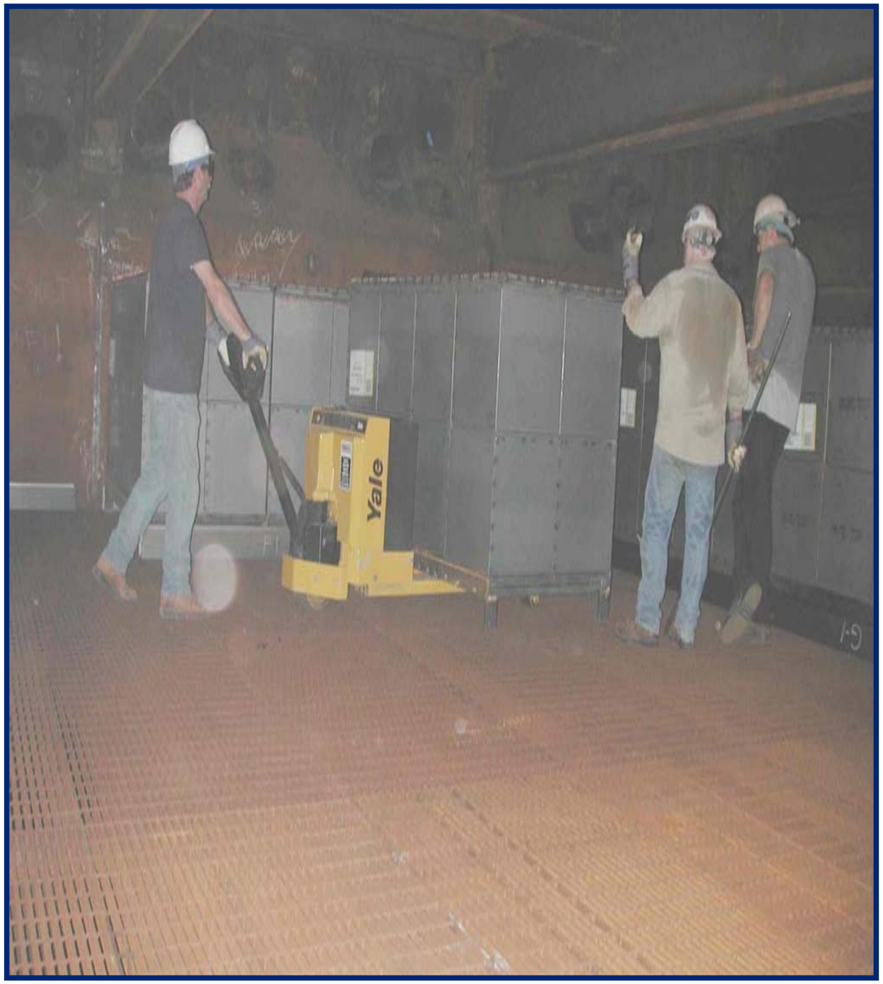


CMP Actions / Options

- Regeneration – offsite chemical treatment
  - Remove chemically bonded poisons – As and others
  - Replace active catalytic promoters
- Regeneration (Pros)
  - Can restore catalyst activity to near new levels
  - Lower cost than new catalyst??
- Regeneration (Cons)
  - Done offsite, may need spare catalyst
  - Reduces catalyst porosity (poison resistance could be lowered)
  - May increase SO_2 oxidation
  - Performance guarantees??

CMP Actions / Options

- Install New Catalyst
- Pros
  - Longest operating life
  - Highest poison resistance
  - Lowest SO_2 conversion per unit activity
  - Performance and service life guarantees provided
- Cons
  - Highest cost option??



CMP Actions / Options

- Economic Trade-offs:
  - Washed vs. New
    - No guarantees of performance or service life.
    - Both performance / service life based on experience.
    - Cost savings achieved could be wiped out by a shorter operating life, lower performance and unexpected unit outages.
  - Regenerated vs. New
    - How will regenerated catalyst respond with reduced porosity?
    - Are performance and service life guarantees provided?
    - Will SO_2 conversion increase?
    - Cost savings achieved can be wiped by a shorter operating life, lower performance and one unexpected unit outage.

CMP Actions / Options - Bottom Line

- CMP are unit specific

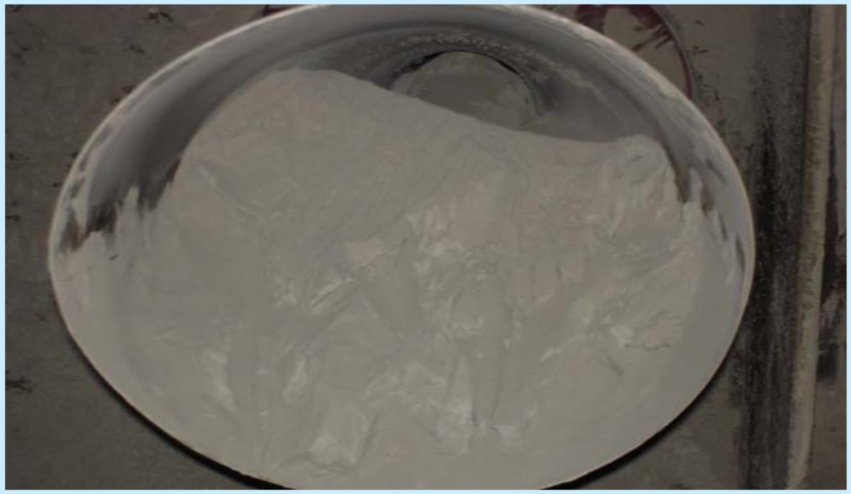
- What needs to be considered is which option conforms best to your company's / plant's
  - NOx performance / compliance strategy
  - and outage schedule requirements.

Catalyst Mixing

- Catalyst mixing is possible and common
  - Standard module structure (not identical)
  - Multiple catalyst types in reactor
    - New (multiple suppliers), washed, regenerated
- Considerations
  - Lifting tools
  - Module sealing system
- Performance guarantees
  - Layer guarantees – activity, potential, deactivation, SO_2 oxidation, pressure drop, mechanical service life
  - Reactor guarantees – NOx reduction, NH_3 slip, operating life, SO_2 oxidation, pressure drop – req. information on existing catalyst

SCR Housekeeping

- Control ash build up
  - Inspect Soot blowers, Sonic Horns regularly.
  - Clean, air blow, and vacuum reactor during outages.
  - Remove excessive LPA from catalyst protective screens.



SCR Housekeeping

- Maintain NH_3/NOx distribution
  - Inspect injection nozzles regularly.
  - Control ash build up in, on and around mixer elements.
  - Tune AIG as required or at least annually.
  - Inspect SCR seals for NH_3 bypass.

SCR Housekeeping

- Maintain SCR ducts
  - Inspect Inlet duct, mixers, turning vanes, rectifier and catalyst at least annually.
- Control ash build up in ducts, turning vanes, rectifiers, etc.

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Plant Operation Considerations

- SO_2 oxidation (slow reaction)
  - $2\ SO_2 + O_2 \longrightarrow 2\ SO_3$ (Blue Plume)
  - Kinetically controlled, increases with vanadium content and flue gas temperature.
  - Low SO_2 conversion rates < 0.05 % with high catalyst activity and Po per layer, is possible.
  - Excessive Alkali metals and Fe deposits will increase SO_2 conversion.
- SO_3 reacts with NH_3 to form ammonium bisulfate (ABS) and ammonium sulfate (AS)
  - $NH_3 + SO_3 + H_2O \longrightarrow (NH_4)_2HSO_4$ (ABS)
  - $NH_3 + NH_4HSO_4 \longrightarrow (NH_4)_2SO_4$ (AS)
  - $2NH_3 + SO_3 + H_2O \longrightarrow (NH_4)_2SO_4$ (AS)
- AS is a dry powdery compound
- ABS is sticky, viscous compound

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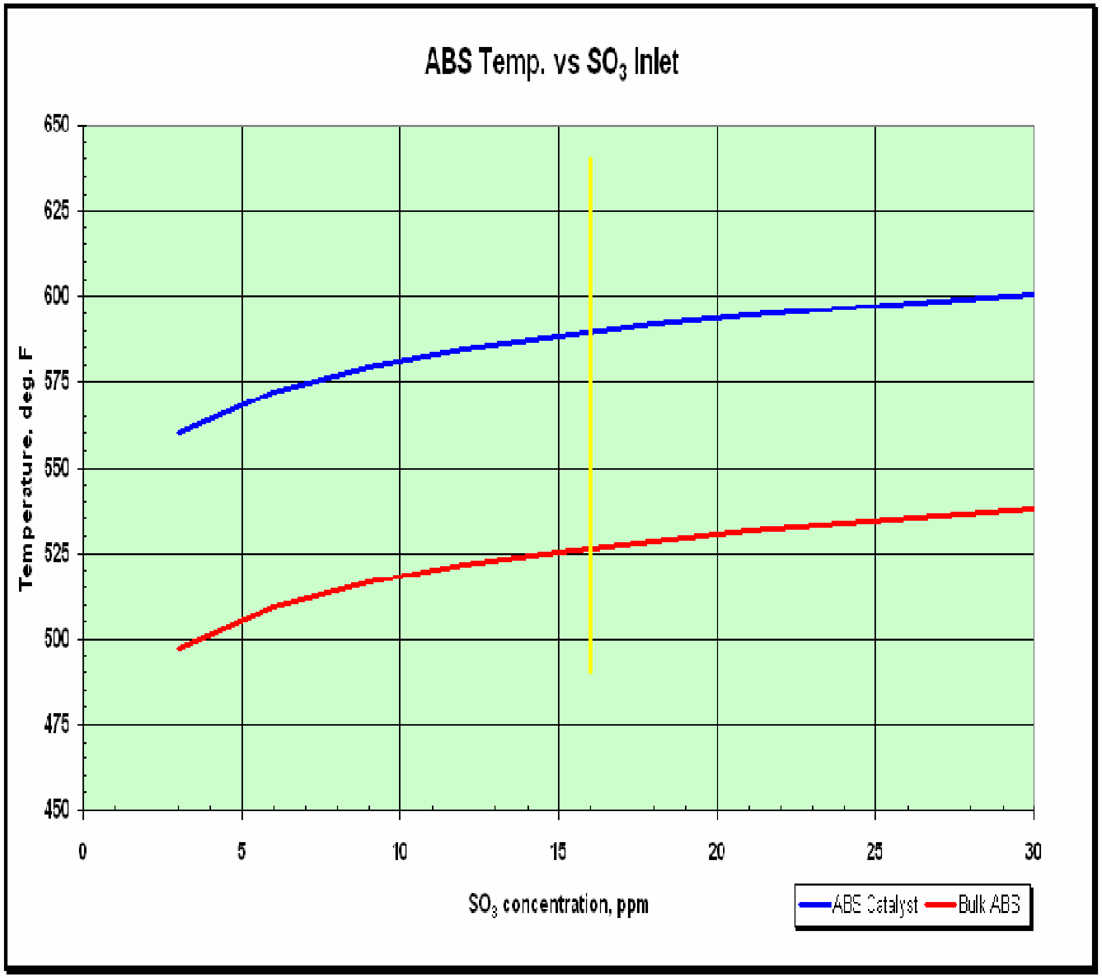
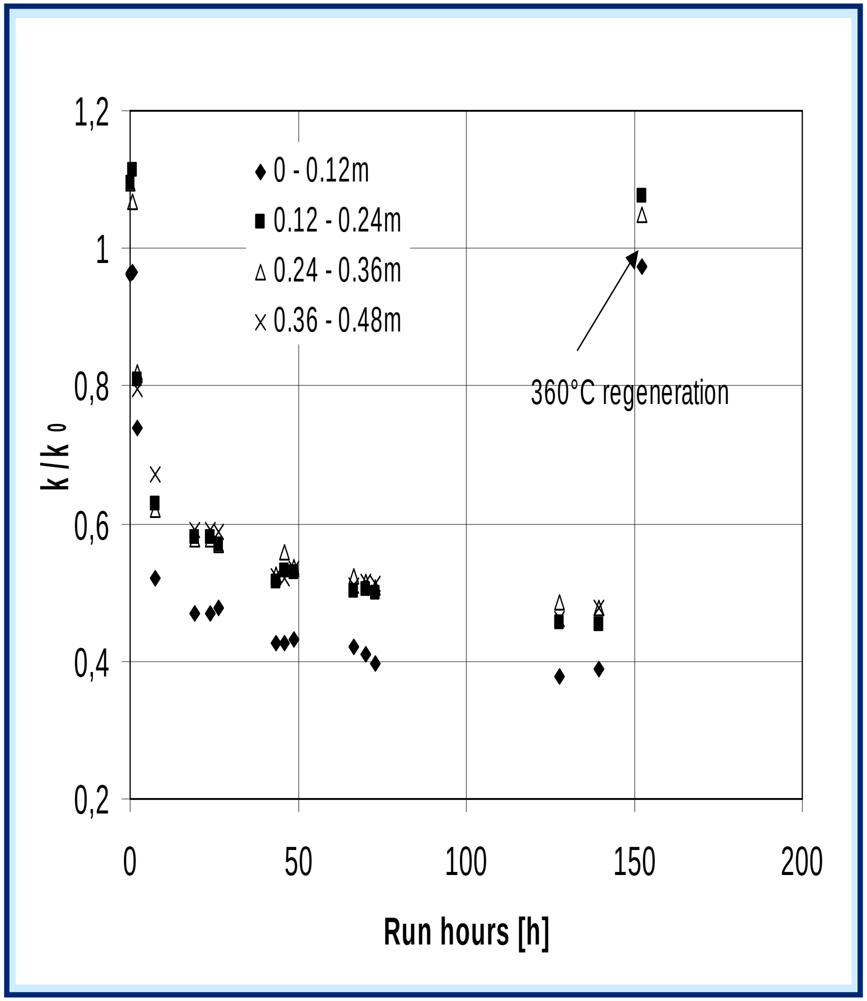
Plant Operation Considerations



- Minimum Operating Temperature (T_{min}) for NH_3 injection
  - Concern for low load operation firing fuels containing sulfur
  - Depends on SO_3, NH_3, H_20 in the flue gas
  - Operation above T_{min} prevents AS/ABS formation

Plant Operation Considerations



- NH_3 injection below the T_{min} is possible for a continuous and intermittent period.
- Duration depends on
  - Catalyst
  - fuel sulfur content
  - flue gas temperature, SO_3, NH_3, and H_20 composition
  - NOx performance upon return
- Typically, for 8 hours below T_{min}, 8 hours above T_{min}
- No NH_3 injection at or below the bulk ABS dew point, approx. 40 degrees below T_{min}

Thank You!

Any Questions?

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Reference – for Plate and Honeycomb catalyst information and pictures

1) Jeffers, Ken; "SCR Catalyst Management; WPCA/Ameren, ESP and SCR Seminar. Effingham, IL; August 20, 2008"