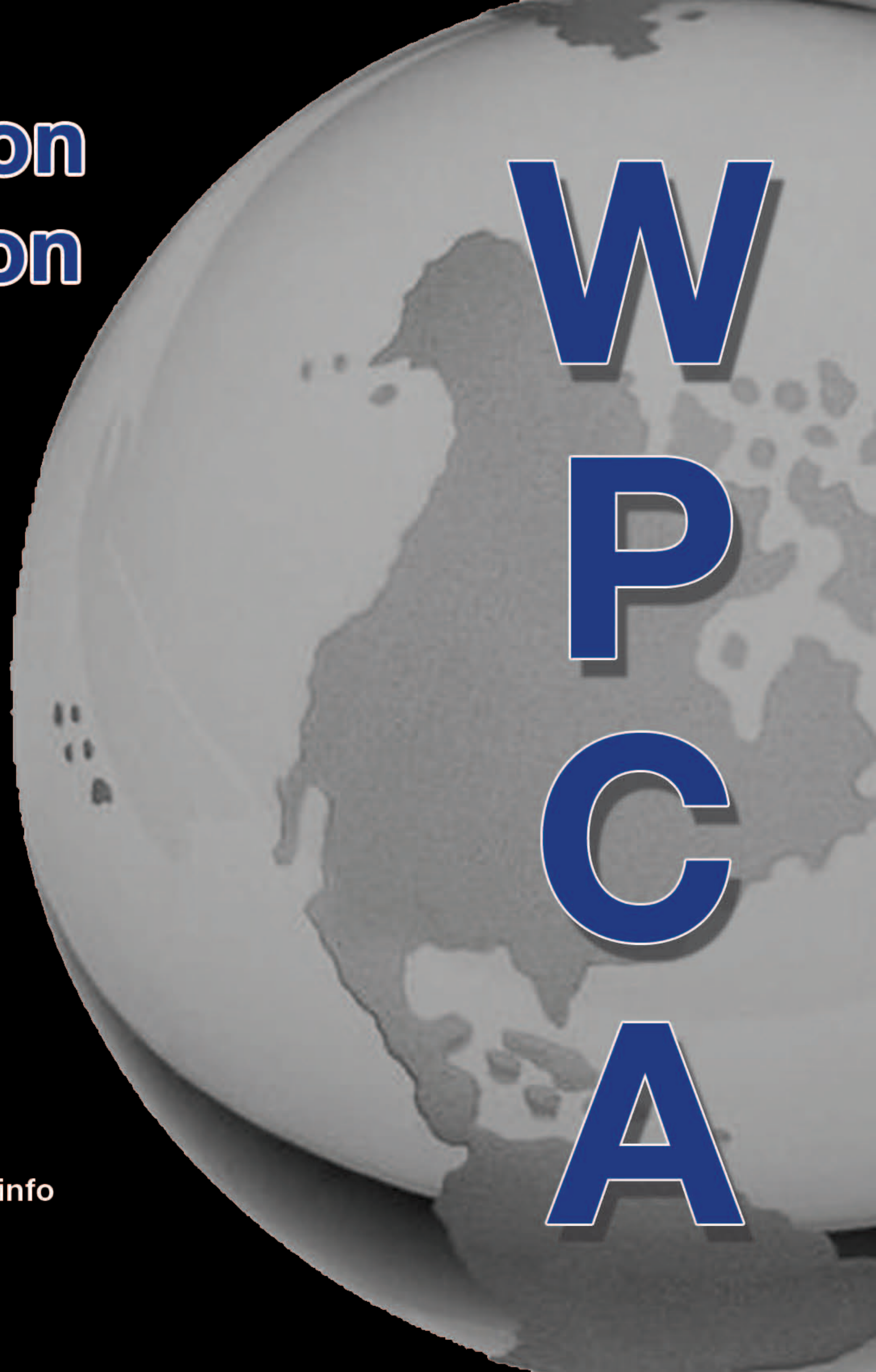
Worldwide Pollution Control Association

Ameren Seminar

August 19–20, 2008

Effingham, IL



WPCA

Vist our website at www.wpca.info

2008 WPCA/Ameren
ESP and SCR Seminar
Effingham, IL
August 20, 2008

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SCR Catalyst Management

Ken Jeffers

Agenda

- SCR Catalyst Basics
  - Background on SCR catalyst and design considerations
  - Provides basis for relevance of Catalyst Management
- Catalyst Management

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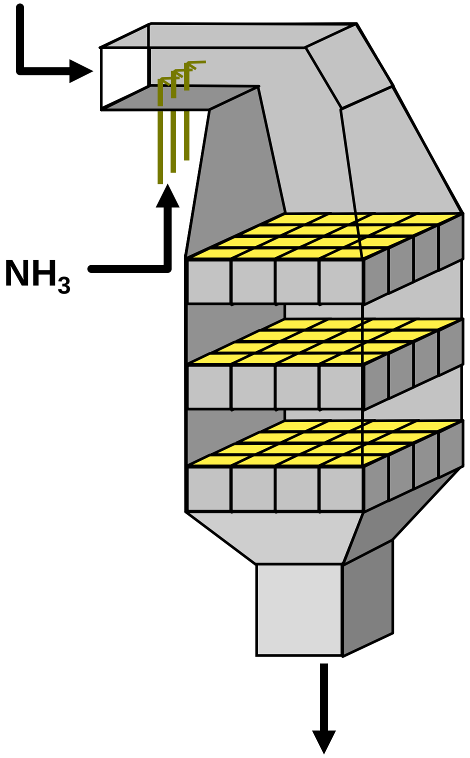
SCR Catalyst Basics

Quick Review of SCR Basics



- SCR = <u>S</u>elective <u>C</u>atalytic <u>R</u>eduction
- Purpose is to reduce NO_x (NO & NO_2) from combustion exhaust
- Ammonia (NH_3) is injected into flue gas as reducing agent. Flue gas passes through catalyst layers installed in a reactor
- NH_3 reacts with NO_x on the catalyst surface to form nitrogen and water vapor

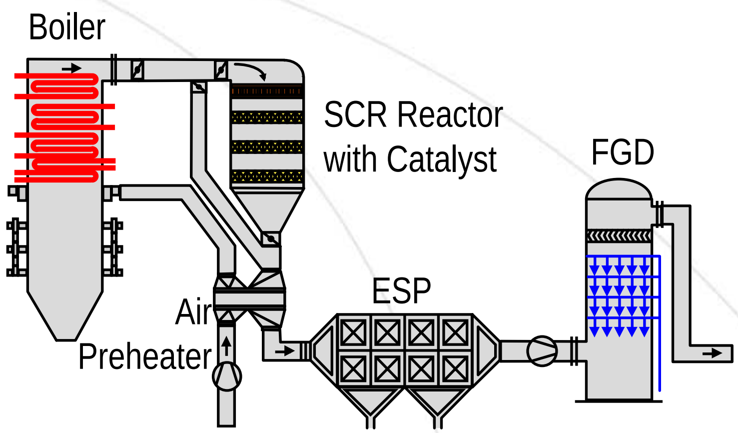
$$4NO + 4NH_3 + O_2 \xrightarrow{\text{Catalyst}} 4N_2 + 6H_2O$$

$$2NO_2 + 4NH_3 + O_2 \xrightarrow{\text{Catalyst}} 3N_2 + 6H_2O$$

SCR Configuration in Power Plants

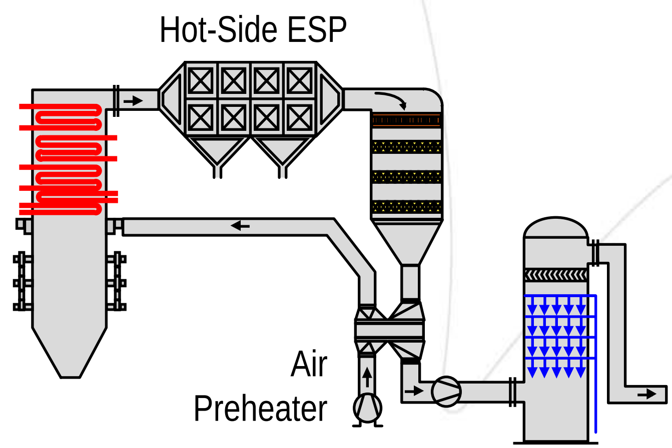
High Dust

- SCR upstream of air preheater and ESP
- High concentration of fly ash in exhaust
- Catalyst with higher pitch required



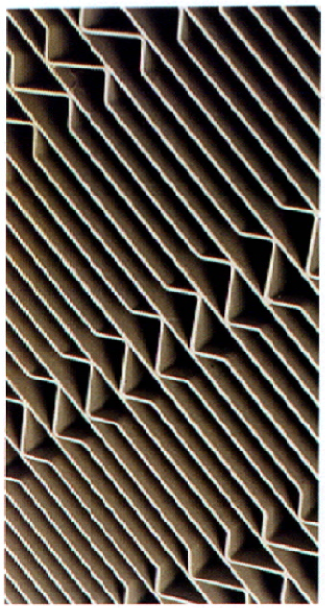
Low Dust

- SCR between ESP and air preheater
- Low concentration of fly ash
- Catalyst with smaller pitch can be suitable

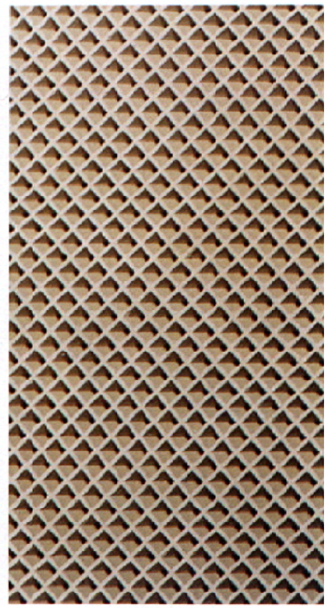


Catalyst Types

Plate



Honeycomb



Corrugated

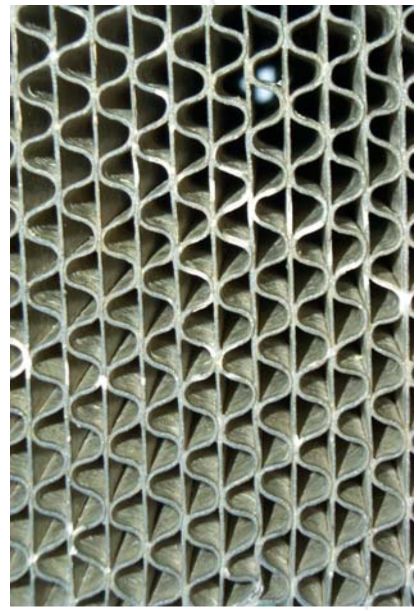
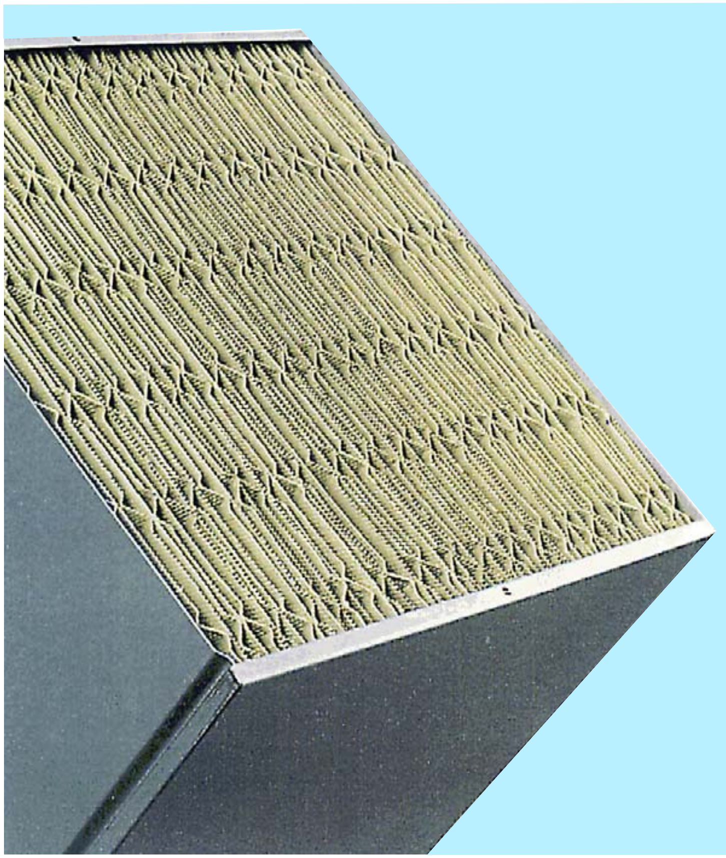


Plate-type Catalyst



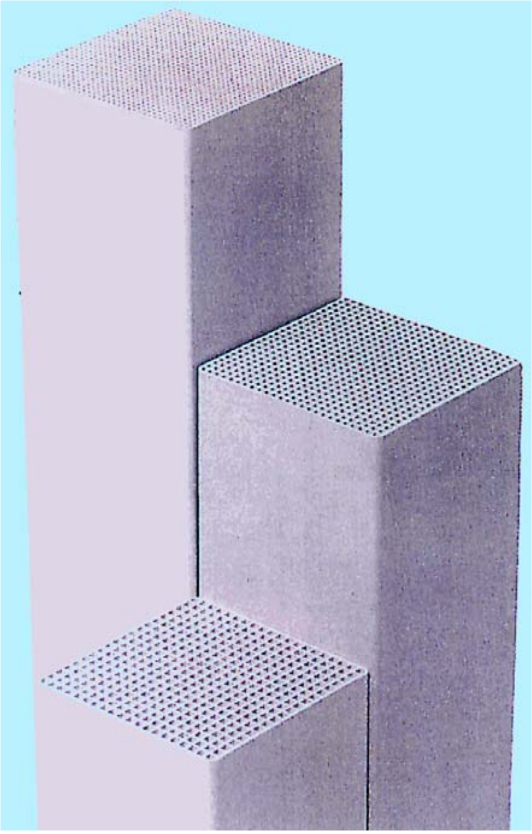
Composition

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

Advantages

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

Honeycomb Catalyst



Composition

- Homogeneously extruded ceramic with square-opening cell structure
- TiO_2, V-oxide and W-oxide as the active catalytic material
- Variable block height: 1200+ mm
- 8 to 14 cpsi for coal-fired applications

Advantages

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

Catalyst Pitch

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

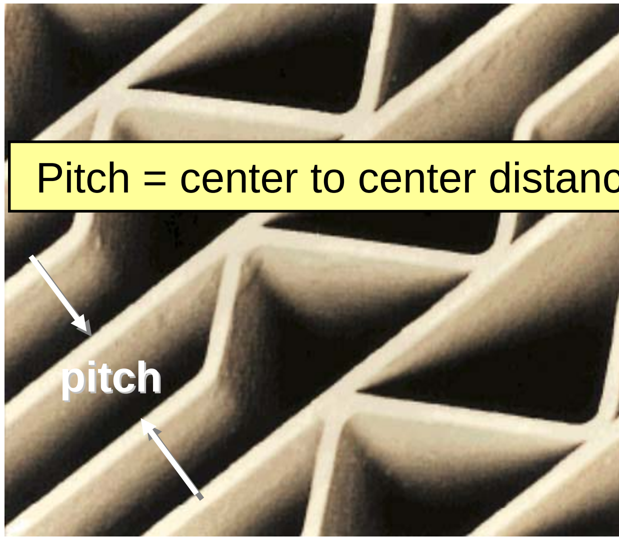
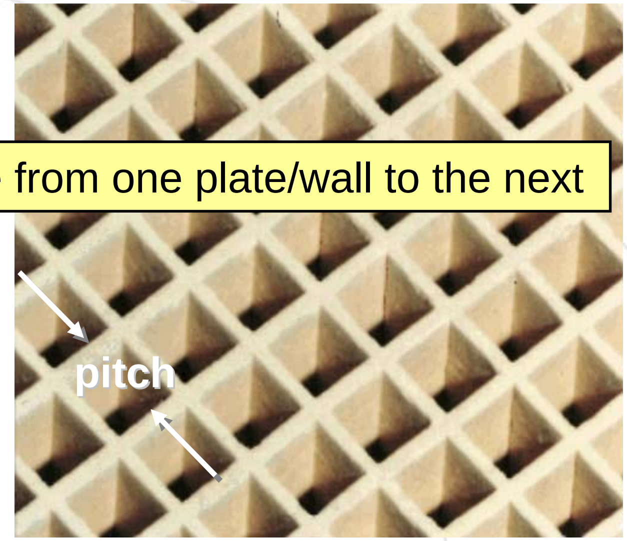


Plate-Type Structure

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



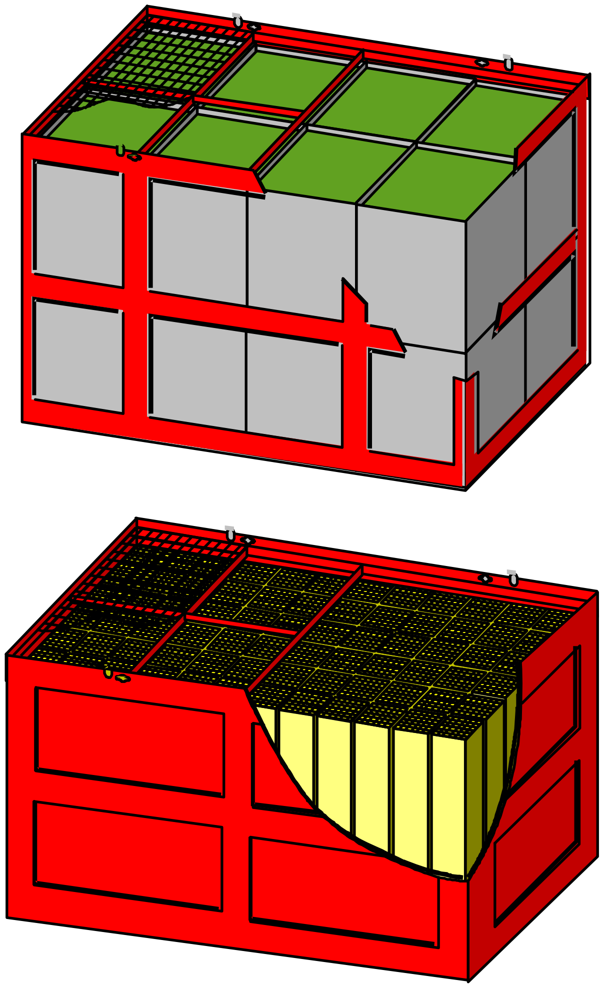
Honeycomb Structure

- Rigid structure
- Square openings
- Pitch: 6.7 mm to 9.2 mm

Pitch Selection vs Dust Load

Dust Load gr/dscf	Plate Pitch	Honeycomb Pitch
<2	5.0 mm	6.7 mm (22 Cell)
2 – 6	5.5 mm	7.4 mm (20 Cell)
6 – 10	6.0 mm	8.2 mm (18 Cell)
10 – 12	6.2 mm	9.2 mm (16 Cell)
>12	6.5 mm	NA

Catalyst Modules



- 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

Catalyst Design Considerations

- SCR Reactor
  - Initial catalyst charge or reload
  - Reactor size – layers, modules per layer
  - Plant configuration – high dust / low dust
- Flue Gas Operating Conditions
  - Operating Temperature
  - Fuel Characteristics
  - Fly ash concentration
- Performance Requirements
  - Amount of NO_x to reduce and operating life
  - NH_3 slip allowed, 2 ppm standard
  - SO_2 oxidation allowed
  - Pressure drop limit, < 1.0” wc per layer

Required Reactor Potential

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- Minimum catalytic potential required to achieve desired $DeNO_x$ and NH_3 slip rates for given operating period

$$RP = \frac{k_t}{AV}$$

k_t = activity at time t (EOL)

AV = area velocity

$$AV = \frac{V_{fg}}{Vol_{cat} * A_{spec}}$$

- Catalyst deactivates with time, $k_0 \rightarrow k_t$ (time at end of life)
- Fresh catalyst activity, k_0,depends on
  - Catalyst formulation $\rightarrow V_2O_5$
  - Temperature
  - Flue gas composition – H_2O, O_2, SO_2
- Iterative process to determine required AV and k

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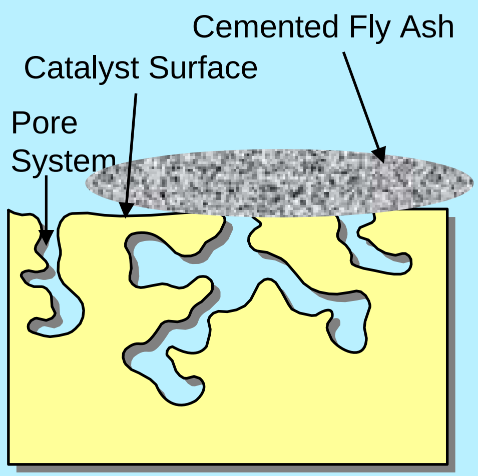
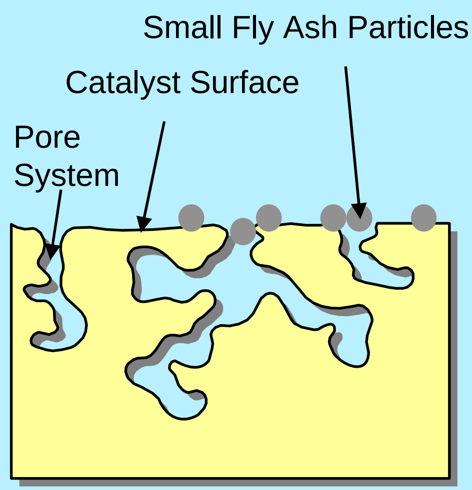
Catalyst Deactivation Mechanisms

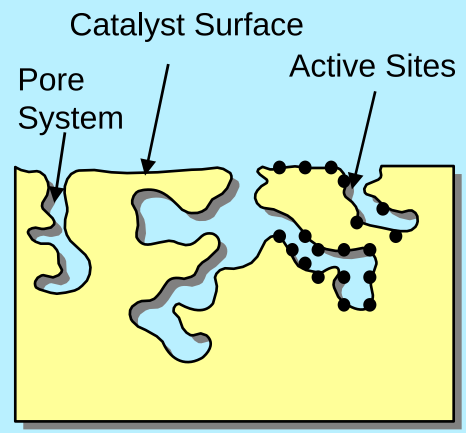
Masking:
Macroscopic blockage of catalyst surface by cemented fly ash



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



Poisoning:
Deactivation of active sites by chemical attack



Catalyst Poisons

- Arsenic – vapor phase As_2O_3
- Phosphorus – P_2O_5
- Alkali metals – Na, K

Relative Activity, k_t/k_0

- Initially (t=0), $k_t/k_0 = 1.0$
- k_t/k_0 decreases with time (exponentially decaying model)
- Characteristic of SCR configuration, fuel, deactivation mechanisms.
- Obtained from catalyst activity monitoring
- Have $k_t \rightarrow k_0$ or have $k_0 \rightarrow k_t$

Application	time, hr	k_t/k_0
Low dust config	16000	0.80 - 0.85
Bituminous firing	16000	0.70 - 0.75
PRB firing	16000	0.65 - 0.70
Lignite firing	16000	0.50 - 0.55

Effects of Sulfur in Fuel

- SO_2 oxidation, undesired side reaction in SCR catalyst

  $$2SO_2 + O_2 \longrightarrow 2SO_3$$

- Rate depends on T and catalyst formulation
- Occurs in the bulk mass of catalyst material

SO_3/H_2SO_4 aerosols cause the "Blue Plume"

- SO_3 reacts with NH_3 to form ammonium bisulfate (ABS) and ammonium sulfate (AS)

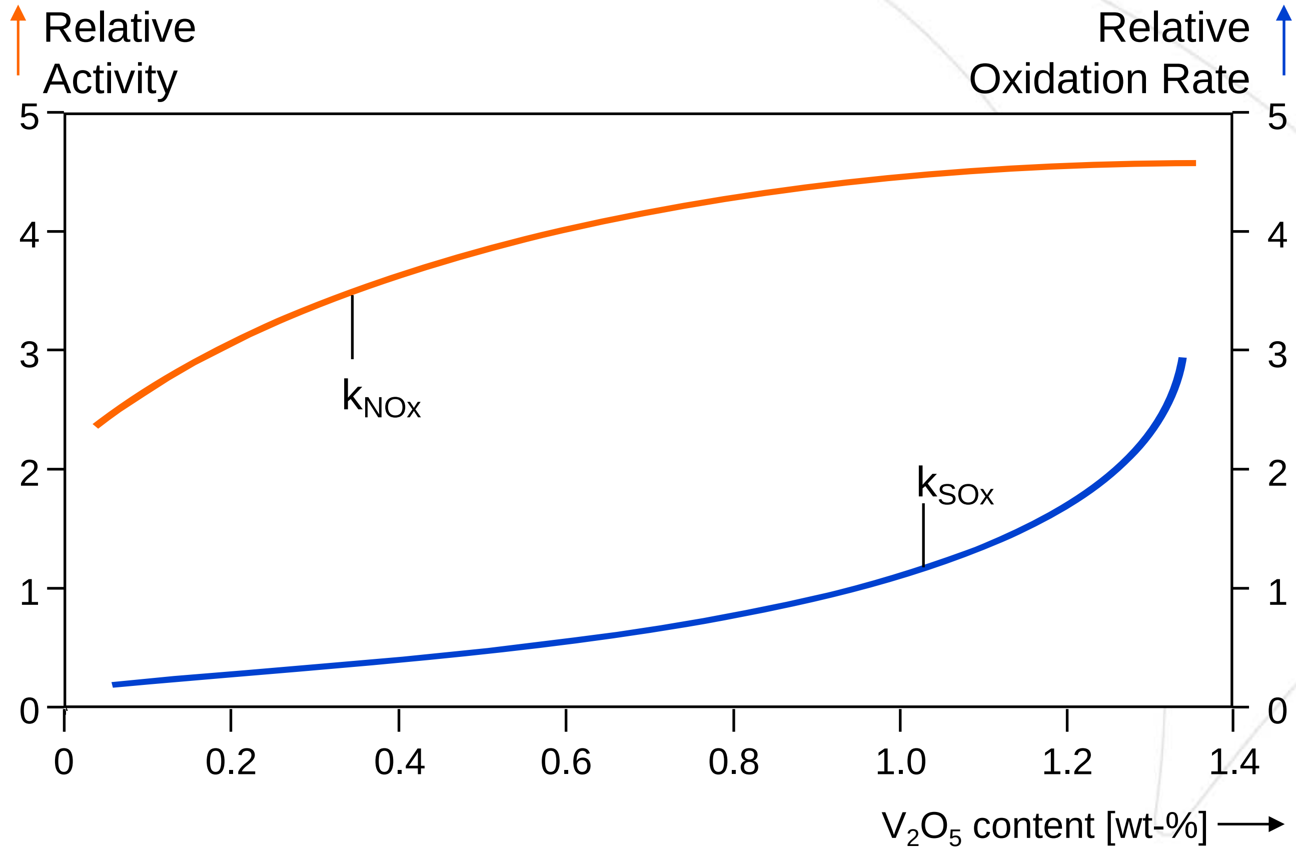
  $$NH_3 + SO_3 + H_2O \longrightarrow NH_4HSO_4 \text{ (ABS)}$$

  $$NH_4HSO_4 + NH_3 \longrightarrow (NH_4)_2SO_4 \text{ (AS)}$$

  $$2NH_3 + SO_3 + H_2O \longrightarrow (NH_4)_2SO_4 \text{ (AS)}$$

- AS is dry, powdery compound
- ABS is sticky, viscous compound that can plug catalyst and foul other equipment

SO_2 Oxidation – Influence of V_2O_5



Minimum Operating Temperature, (T_{min})

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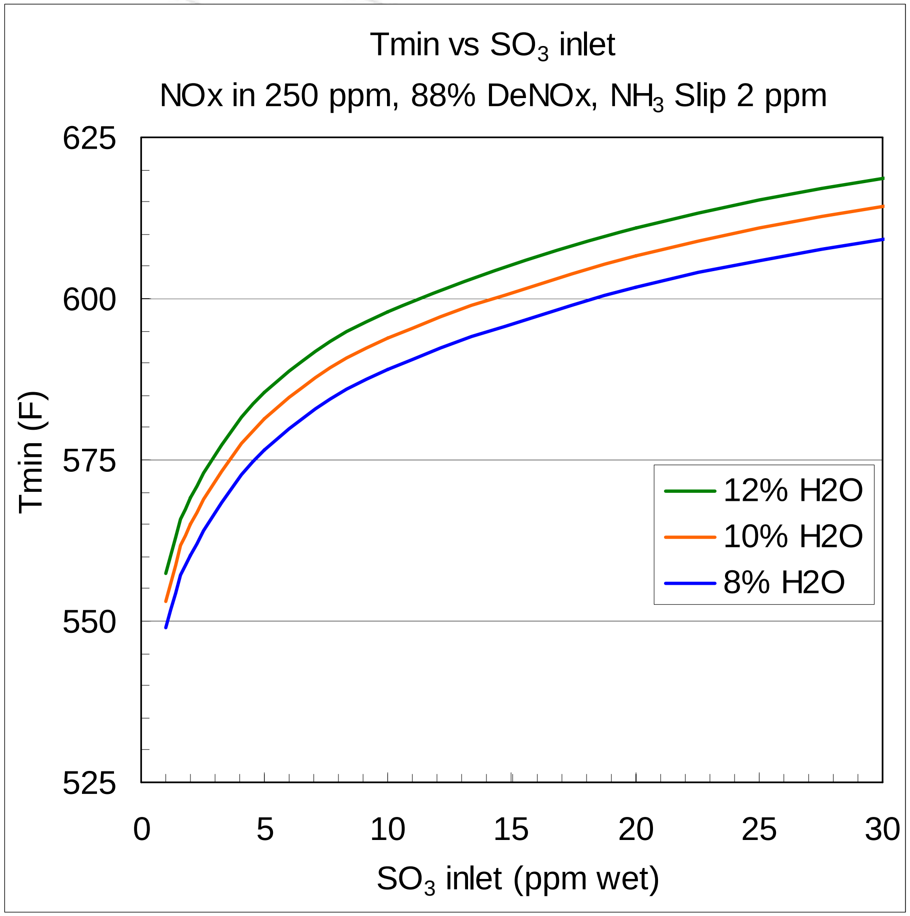
- Minimum temperature for NH_3 injection
- Of particular concern for low load operation and firing fuels containing sulfur
- Operating above T_{min} prevents AS/ABS formation
- Tmin depends on SO_3, NH_3, H_2O in flue gas
- Must stop NH_3 injection when operating below Tmin



Catalyst Management

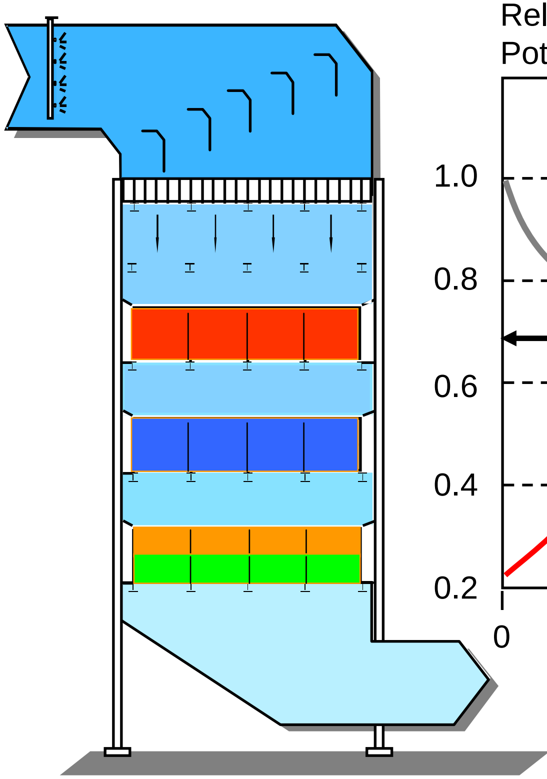
Catalyst Management Goals

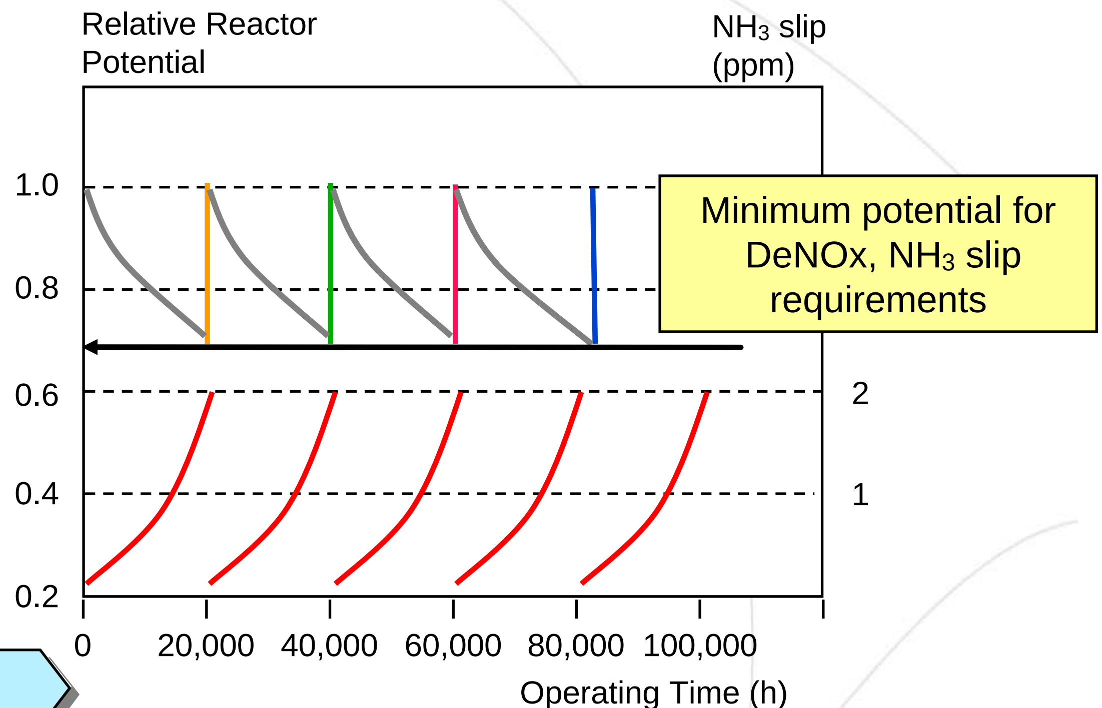
- Maintain target NO_x reduction of the SCR system
- Control NH_3 slip below required limit
- Replace activity potential lost to catalyst deactivation
- Optimize use of catalyst activity potential
- Conform catalyst replacements to plant outage schedule
- Conform to plant budgetary constraints
- Maximize operating life between catalyst replacements
- Prevent excessive pressure loss

Catalyst Management Plan (CMP)

- Schedule for maintaining SCR catalytic potential for NO_x reduction
- Process of adding, replacing, cleaning catalyst
- Tailored to fit unit performance based on activity monitoring

CMP, 2 + 1 Example





Activity Monitoring

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- Routine catalyst activity testing
- Once per year (typically)
- Pull samples from each installed catalyst layer
- Determine relative activity compared to fresh catalyst
- Determine rate of catalyst deactivation
- Predict when reactor potential reaches minimum level
- Verify or adjust CMP schedule

CMP Actions

- Install new catalyst
- Onsite (in situ) Cleaning – removing fly ash/LPA buildup
  - Vacuuming
  - Air blowing
  - Shaking/vibration
  - Water washing
- Rejuvenation – onsite or offsite washing/chemical treatment
  - Remove ash/particles from catalyst pores
  - Remove water soluble poisons
- Regeneration – offsite chemical treatment
  - Remove chemically bonded poisons – As, P
  - Replace active catalytic material

Pros/Cons for CMP Options

CMP Action	Pros	Cons
New Catalyst (Catalyst Supplier)	Longest operating life Performance guarantees	Highest Cost Option
Cleaning (by Owner)	Low(est) cost option Can be done in situ	Lowest activity restoration Limited extension of life
Rejuvenation (Service Supplier)	Lower cost than new catalyst Can be done onsite	Does not restore to “new” activity, limited life extension Performance guarantees?
Regeneration (Service Supplier)	Lower cost than new catalyst Can restore to “new” activity	Done offsite, may need spare catalyst May increase SO_2 conversion Performance guarantees?

Considerations for CMP Options

- CMPs are unit-specific
- Economic Trade-offs: New vs Regen
  - Lower cost for Regen, shorter operating life
  - Higher cost for New, longer operating life
  - Spare catalyst layer on-hand may be required to replace catalyst removed for regen
  - Catalyst supplier offers performance guarantees for new catalyst
  - Does regen supplier offer guarantees for Regen'd catalyst?
- Consider which options conform best to plant outage schedule
  - Cleaning/rejuvenation may not extend catalyst life to next outage
  - Consider operation with lower $DeNO_x$, higher NH_3 slip
  - Consider impact to plant emission standards

Catalyst Mixing

- Standardized module structure – catalyst mixing is possible and common
  - Multiple catalyst types in reactor
  - New and regen'd
  - Multiple suppliers
- Consider tooling requirements
  - Lifting, transport tooling for unloading/loading
  - Sealing systems
- Performance Guarantees from new supplier (other than initial)
  - Layer guarantees – geometry, durability, activity, SO_2 conversion, pressure drop – based on fuel and flue gas characteristics
  - System guarantees – DeNOx, NH_3 slip, operating life – based on total reactor potential → requires info about existing catalyst

Required Info for Existing Catalyst

- Geometry
  - Catalyst type
  - Volume
  - Specific area, m^2/m^3
- Activity Trends
  - Fresh catalyst, initial activity – k_0
  - Relative/absolute activity after exposure to flue gas
  - Age of catalyst at time of testing
- Above info used to . . .
  - Calculate existing reactor potential
  - Determine rate of deactivation
  - Develop CMP

Plant Operation Considerations

- Control Ash buildup
  - Sootblowers/Sonic horns
  - Cleaning/vacuuming during outages

- Uniform NH_3/NO_x distribution
  - AIG Tuning
  - Maintain NH_3 injection nozzles

- Limit injecting NH_3 below Tmin
  - Short time operation OK (< 8 hr, 100 hr/yr)
  - Period below Tmin must be followed by higher Temp operation (>350 °C for 8 hours)

- Effects of Operating changes on SCR performance
  - Fuel changes
  - Economizer modification

Thank You!

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