Reinhold Environmental Ltd.

2008 NOx-Combustion Round Table & Expo Presentation

February 4-5, 2008 in Richmond, VA

Reinhold Environmental
NO_x Round table & Expo
WPCA SCR Training
Richmond, VA
February 5, 2008

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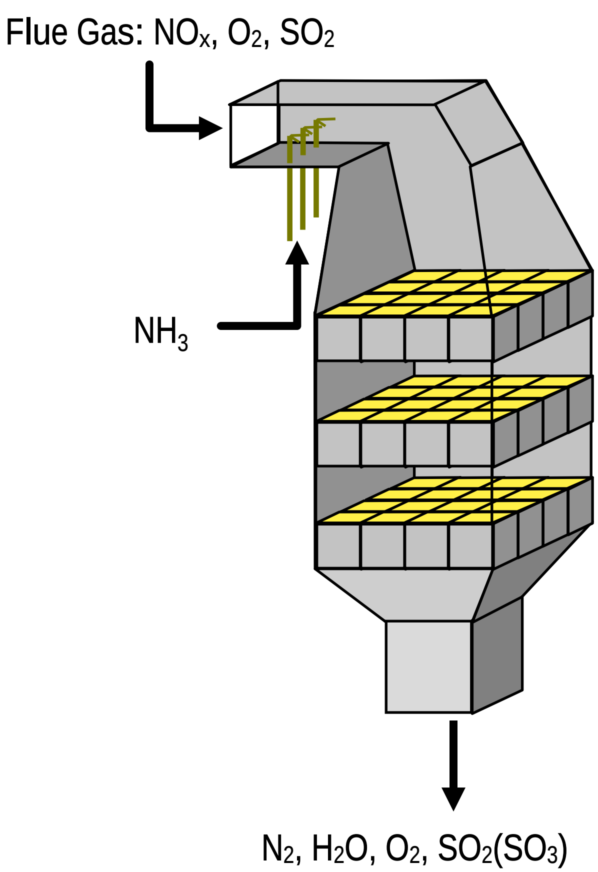
SCR Catalyst Selection & Design

Ken Jeffers

Quick Review of SCR Basics



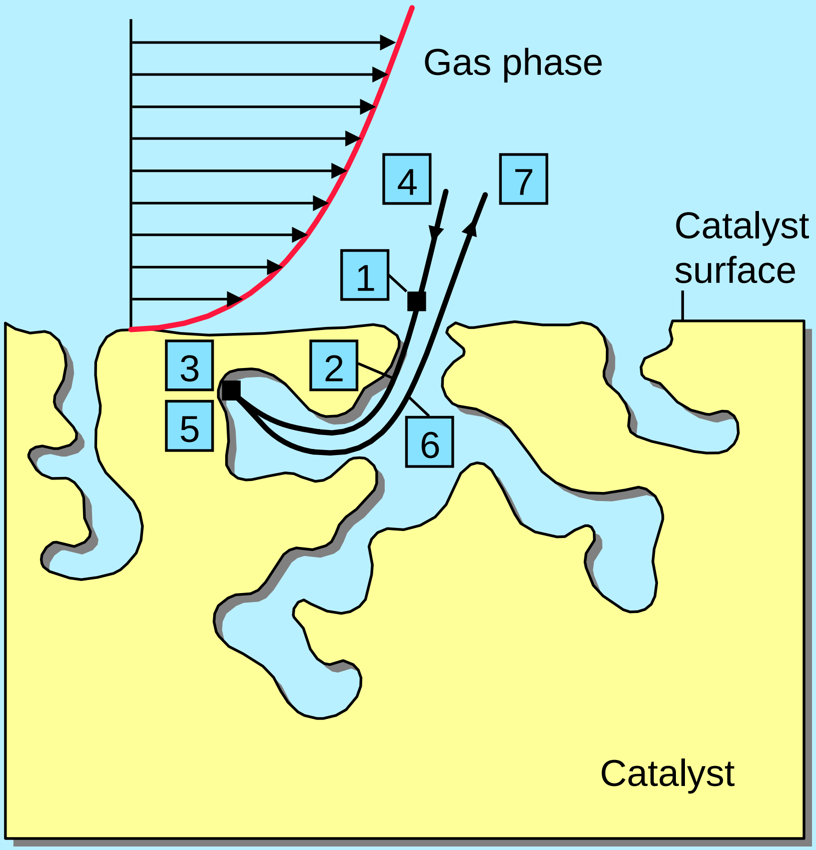
- SCR = <u>S</u>elective <u>C</u>atalytic <u>R</u>eduction
- Purpose is to reduce NO_x (NO & NO_2) from combustion exhaust
- Ammonia (NH_3) is injected into flue gas as reducing agent. Flue gas passes through catalyst layers installed in a reactor
- NH_3 reacts with NO_x on the catalyst surface to form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

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

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

How SCR Works

Catalyst has porous structure = lots of surface area



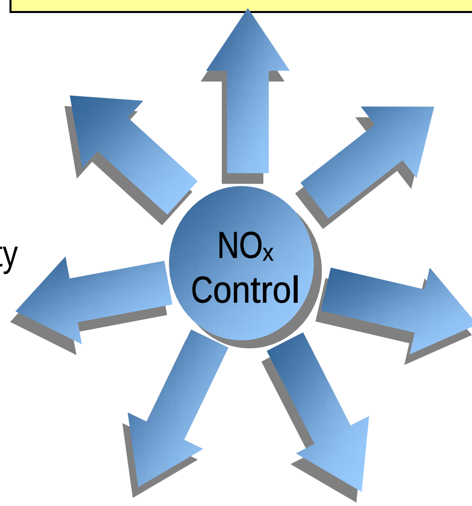
1. External diffusion of NH_3 to catalyst surface
2. Internal diffusion of NH_3 into the catalyst pore
3. NH_3 adsorption on the active centers
4. NO diffusion from gas phase to adsorbed NH_3
5. Reaction of NO and NH_3 to N_2 and H_2O
6. Desorption from N_2 and H_2O to catalyst surface
7. Diffusion of N_2 and H_2O into gas phase

SCR Applications

Power Plants

Waste Incineration Plants

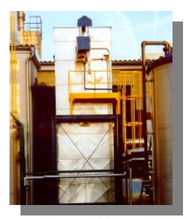
Gas Turbines



Heavy Duty Vehicles

Marine Engines

Greenhouses



Wood-Fired Boilers

Stationary Engines GEN SETS

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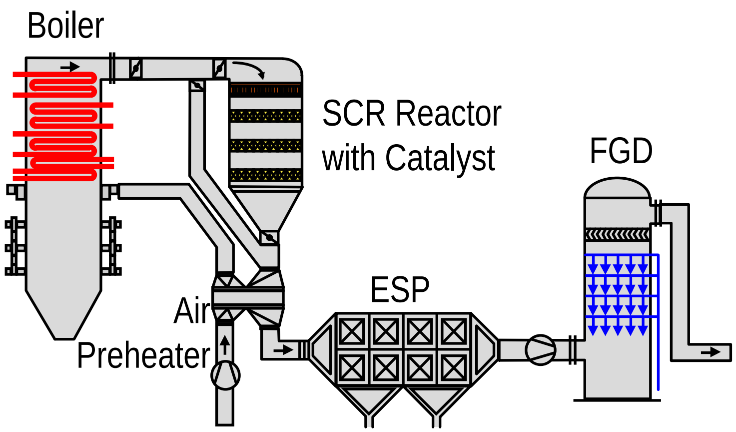
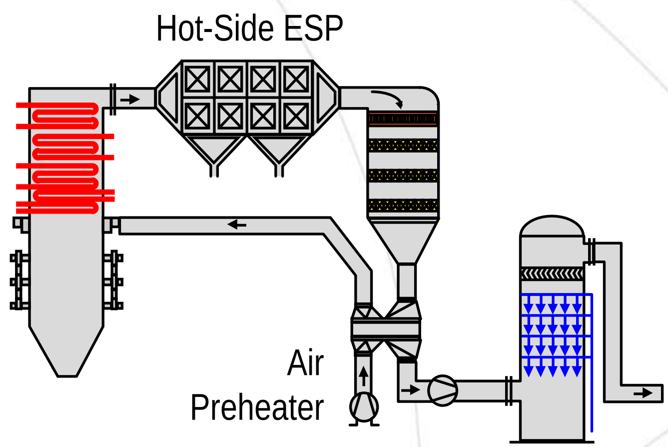
SCR Configuration in Power Plants



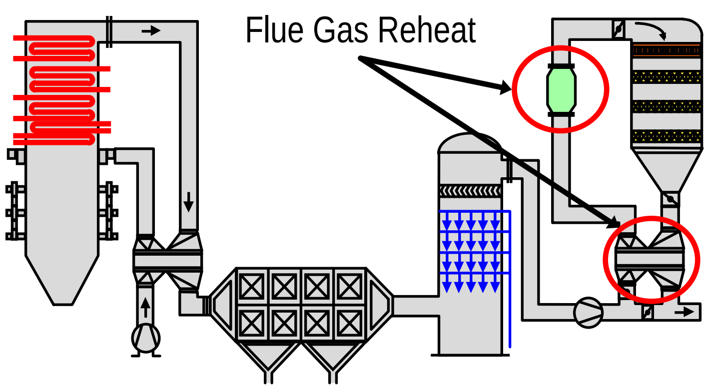
High Dust

- SCR upstream of air preheater and ESP
- Catalyst with higher pitch required



Low Dust

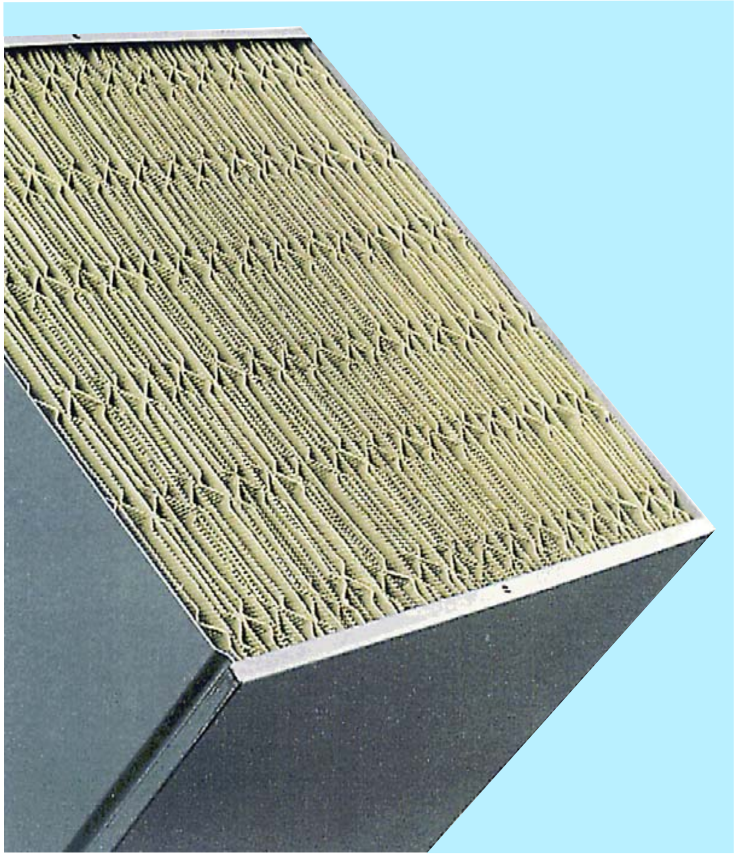
- SCR between ESP and air preheater
- Catalyst with lower pitch can be suitable



Tail End

- Mostly in Europe, none in US(?)
- SCR at the end after air preheater
- Flue gas reheating required

Geometry Selection: Plate-Type Catalyst



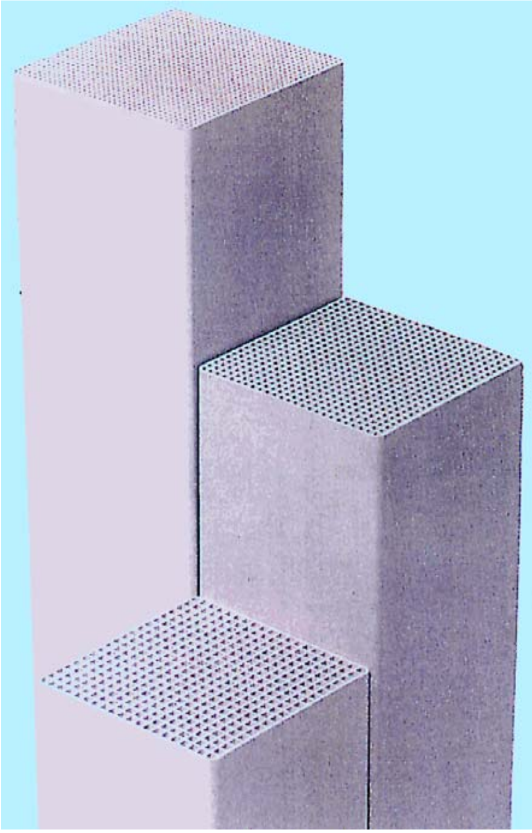
Composition

- Stainless steel carrier, ceramic material rolled on
- TiO_2, V-oxide/W-oxide/ Mo-oxide as the active catalytic material
- Variable plate-spacing: 60 to 100 plates per element box
- Variable plate height: 450 to 700 mm

Advantages

- Most suitable for high dust configurations
- Thermal and mechanical resistance
- Low pressure loss
- Low SO_2/SO_3 conversion rate

Geometry Selection: Honeycomb Catalyst



Composition

- Homogeneously extruded ceramic
- TiO_2, V-oxide and W-oxide as the active catalytic material
- Variable monolith height: 250 mm – 1000 mm
- 10 to 100 cells per square inch (cpsi)

Advantages

- Most suitable for low/no dust applications
- Operating temperature range: 340°F - 800°F
- High active surface area per unit volume

Geometry: Structure & Pitch

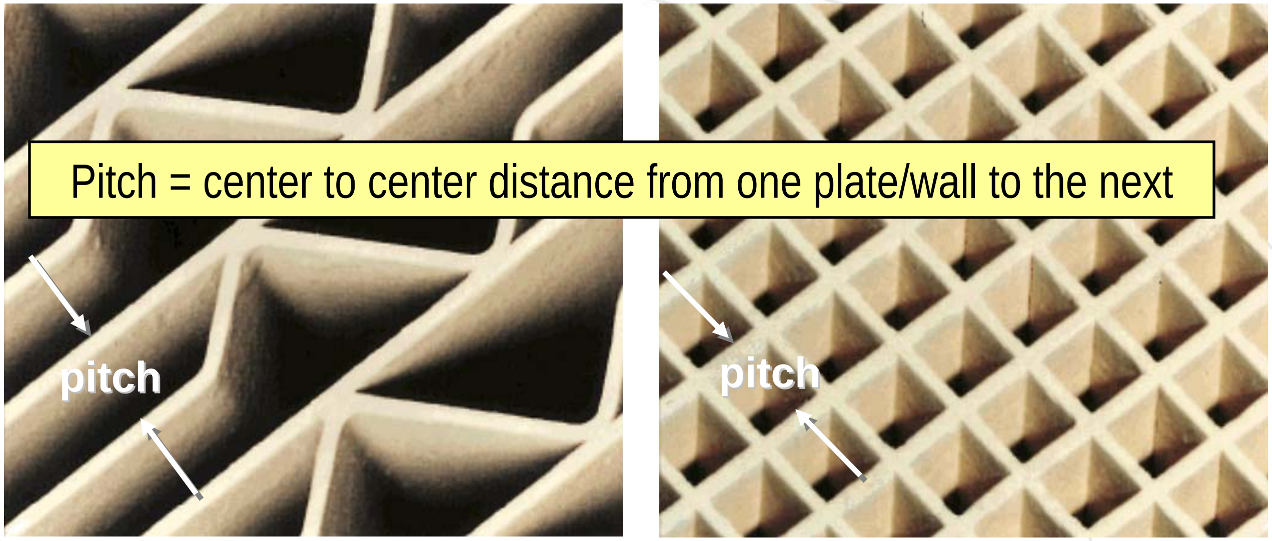


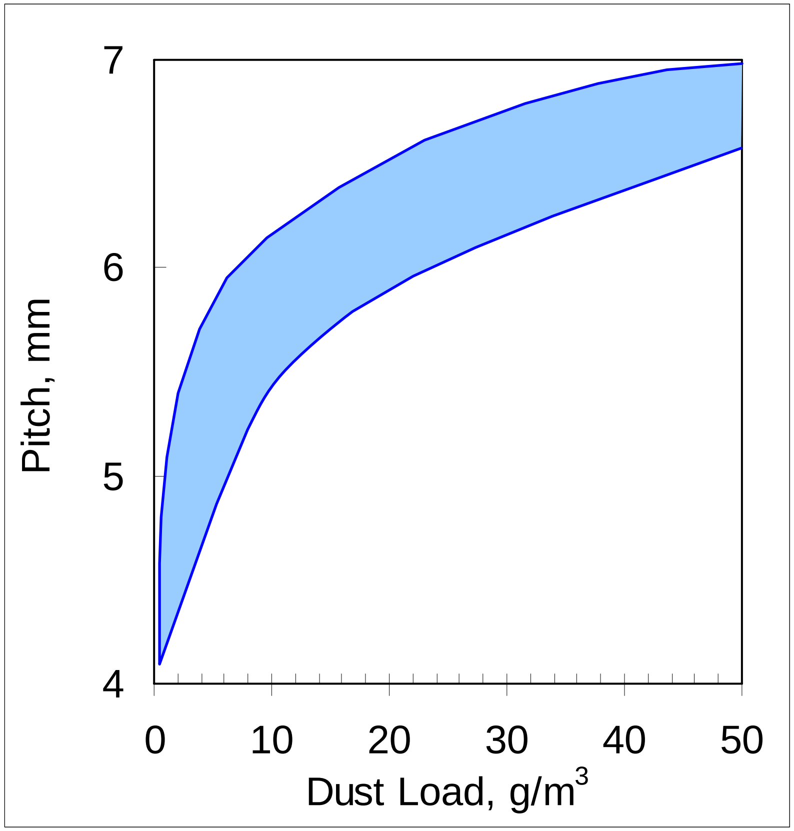
Plate-Type Structure

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

Honeycomb Structure

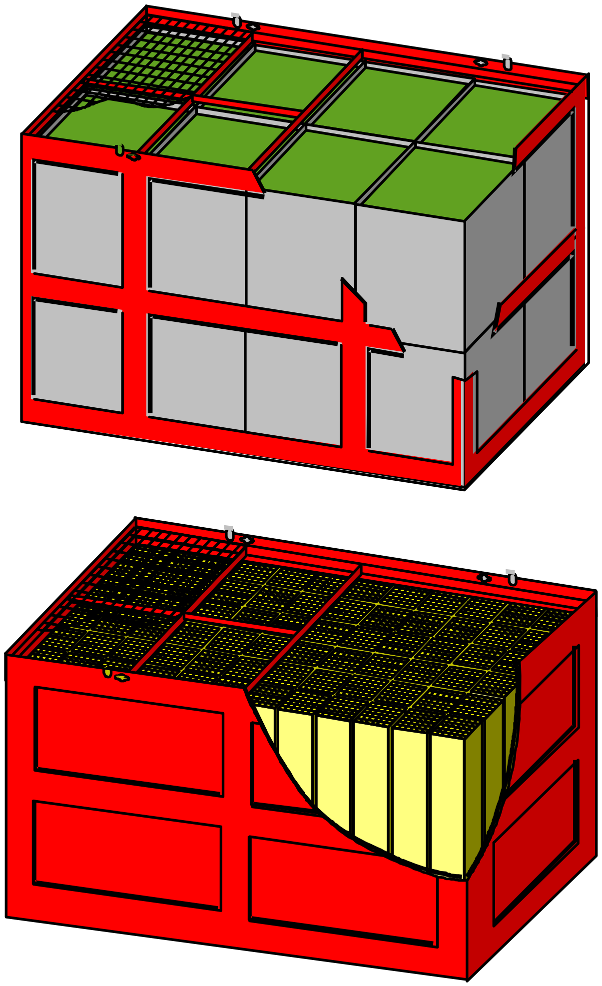
- Rigid structure
- Square openings
- Pitch: 3 mm to 8 mm

Pitch Selection vs Dust Load



Catalyst Type	High Dust	Low Dust
Plate	5 mm – 7 mm	<5 mm
Honeycomb	8 mm	4 mm – 5 mm

Geometry Selection: Module Structure



- Catalyst elements arranged in steel-frame modules
- Standardized cross-section
- Module height can vary as required
- Possible to interchange catalyst types within reactor
- Modules can be customized to customer requirements

Catalyst Design Approach

- Starting Point
  - New SCR reactor vs existing SCR reactor
  - Initial catalyst charge or reload
  - SCR reactor layout - # of layers, # of modules per layer
  - SCR configuration – high dust / low dust
- Desired operating period, 16000/24000 hrs
- Understand performance requirements
  - DeNOx, amount of NO_X to reduce, 70 - 90%
  - SO_2 oxidation allowed, <0.5% per catalyst layer
  - NH_3 slip allowed, 2 ppm standard (5 ppm for low S fuel)
  - Pressure drop limitations, 0.5 - 1.0" WC
- Determine catalyst activity required at end of operating period (EOL)
- Specify appropriate catalyst to do the job: Volume, element height, pitch

Details of the Design Process

How to get k

- $\eta_{NO_x} = f\{k_{NO_x}(EOL)$, area velocity (AV), NH_3/NO_x ratio $(\alpha)\}$
- Calculate maximum AV (gas flow per total active surface area)
- Select pitch ➔ sets the catalyst specific area, A_{spec} = area/volume
- Determine required volume
- Adjust volume as necessary to fit the application
- Determine SO_2 oxidation rate, pressure drop

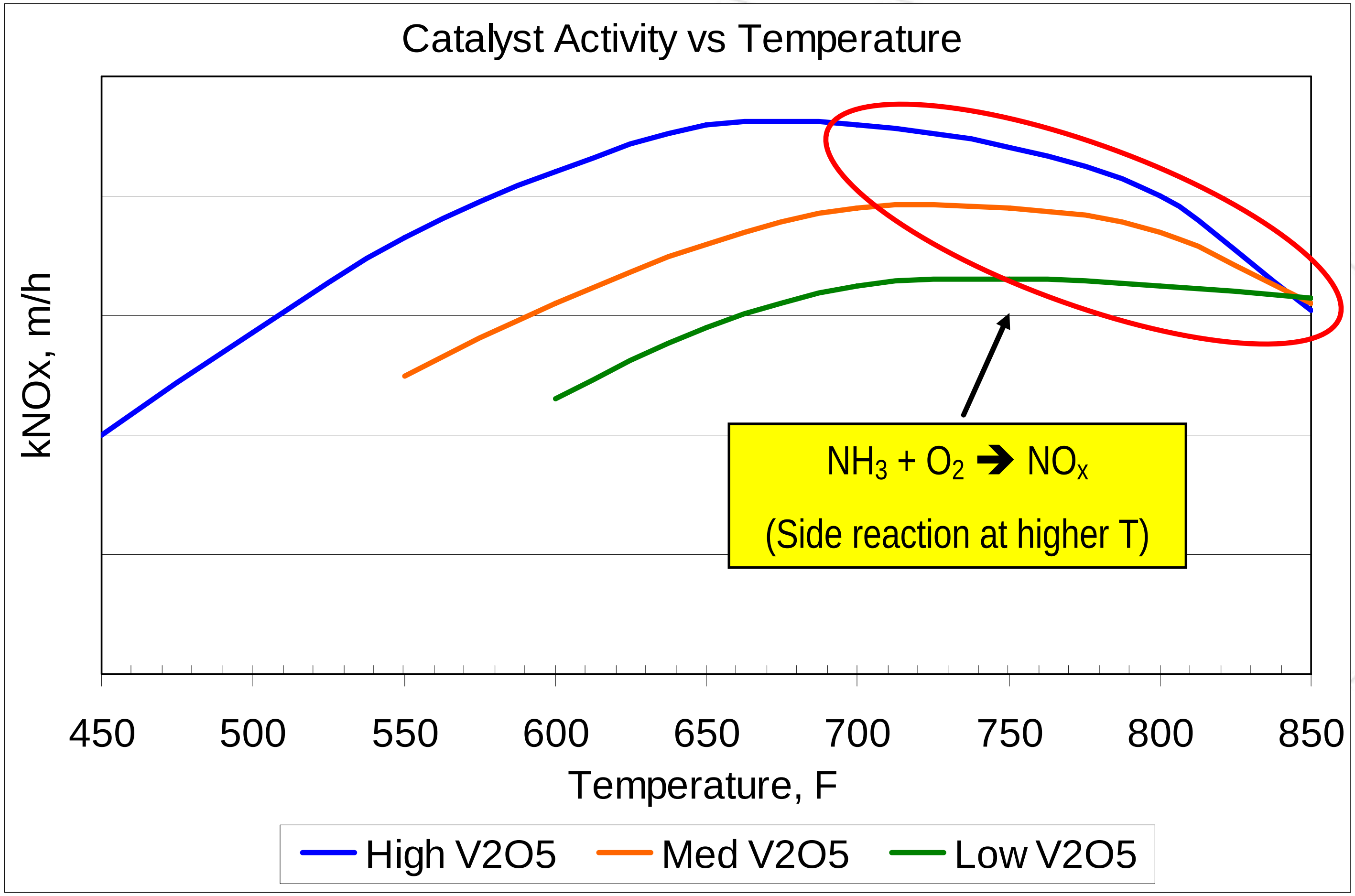
$$Vol_{cat} = \frac{V_{FG}}{AV*A_{spec}}$$

k_{NO_x} of Fresh Catalyst, k_0

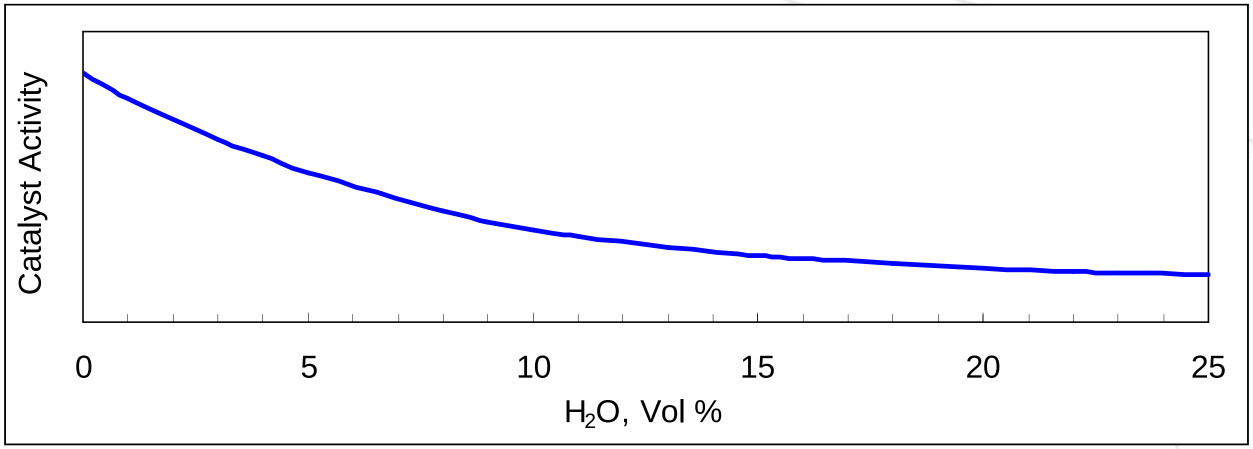
- k_0 depends on
  - Temperature
  - Composition of active, catalytic material ➔ V_2O_5
  - H_2O, O_2, flue gas flow rate

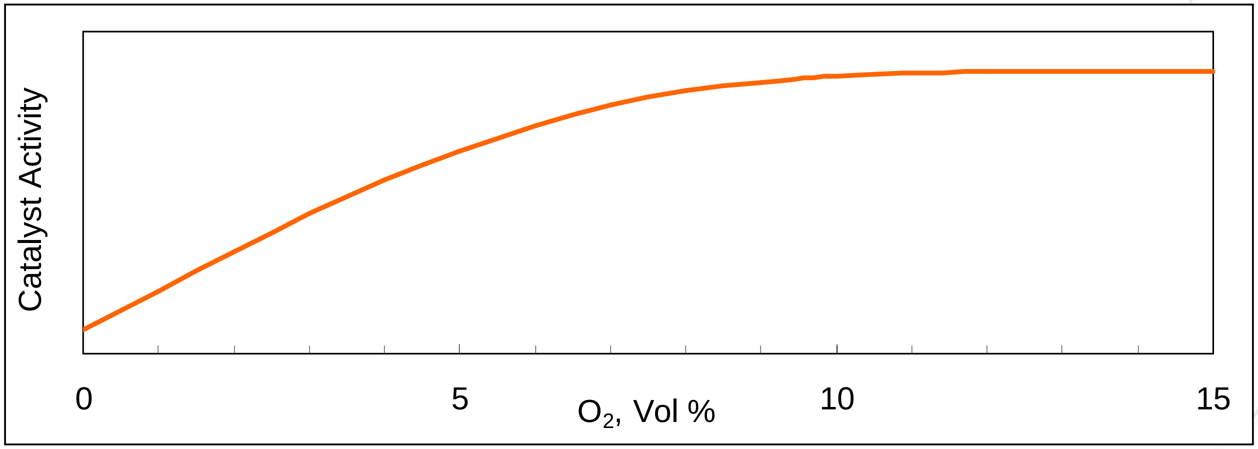
- k_0 data and correction factors are obtained from controlled experiments

k_{NO_x} – Influence of Temperature and V_2O_5



k_{NO_x} – Influence of Water and O_2





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T, V_2O_5, H_2O, O_2, flow rate → k_0

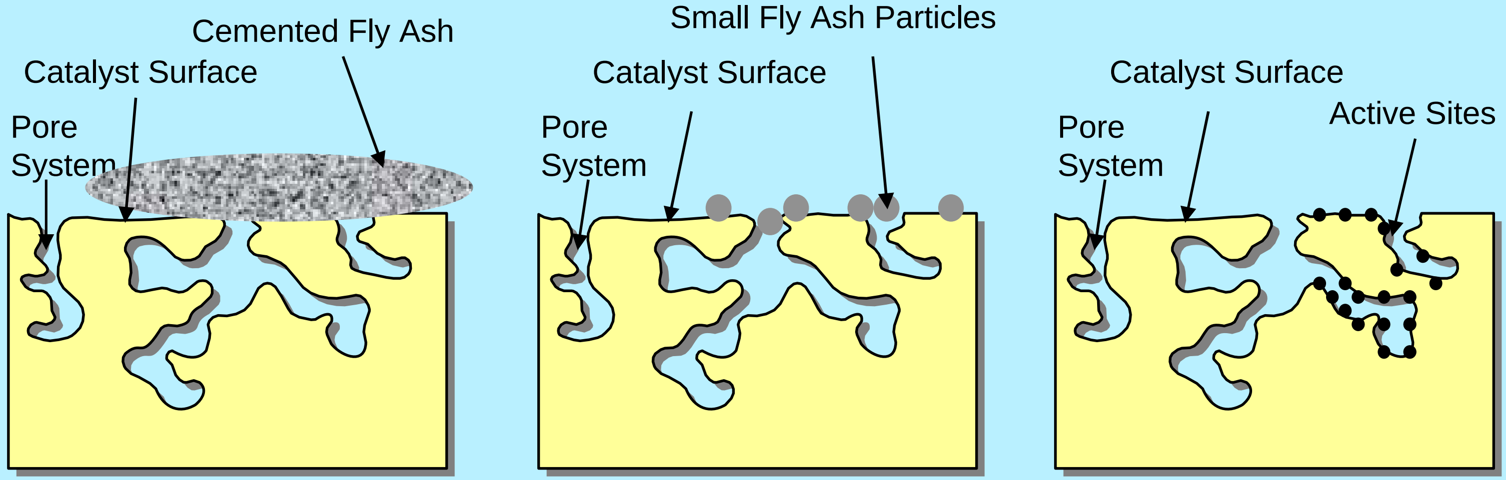
Catalyst deactivates over time → k_t?

Catalyst Deactivation Mechanisms

Masking:
Macroscopic blockage of catalyst surface by cemented fly ash

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

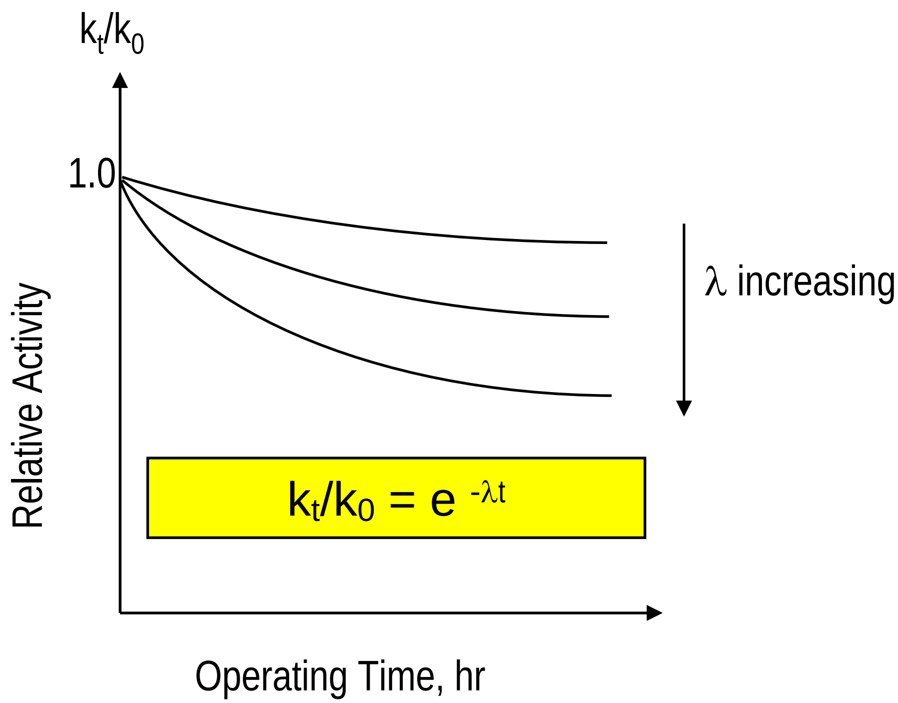
Poisoning:
Deactivation of active sites by chemical attack



Catalyst Poisons

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

k_{NO_x} Deactivation Model – Relative Activity, k_t/k_0



k_t/k_0 decreases exponentially with time

Proportionality constant, λ

- Characteristic of SCR configuration, fuel, deactivation mechanisms.
- Obtained from catalyst activity testing

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

T, V_2O_5, H_2O, O_2, flow rate ➔ k_0

k_0 ➔ Deactivation Model ➔ $k_{t=EOL}$

SO_2 to SO_3 Oxidation, k_{SO_X}

- Undesired side reaction in SCR catalyst

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

- Occurs in the bulk of catalyst material (in the walls)
- k_{SO_X} depends on V_2O_5 and Temperature
- "Blue Plume" is a result of SO_3/H_2SO_4
- SO_3 reacts with NH_3 to form ammonium bisulfate (ABS) and ammonium sulfate (AS)

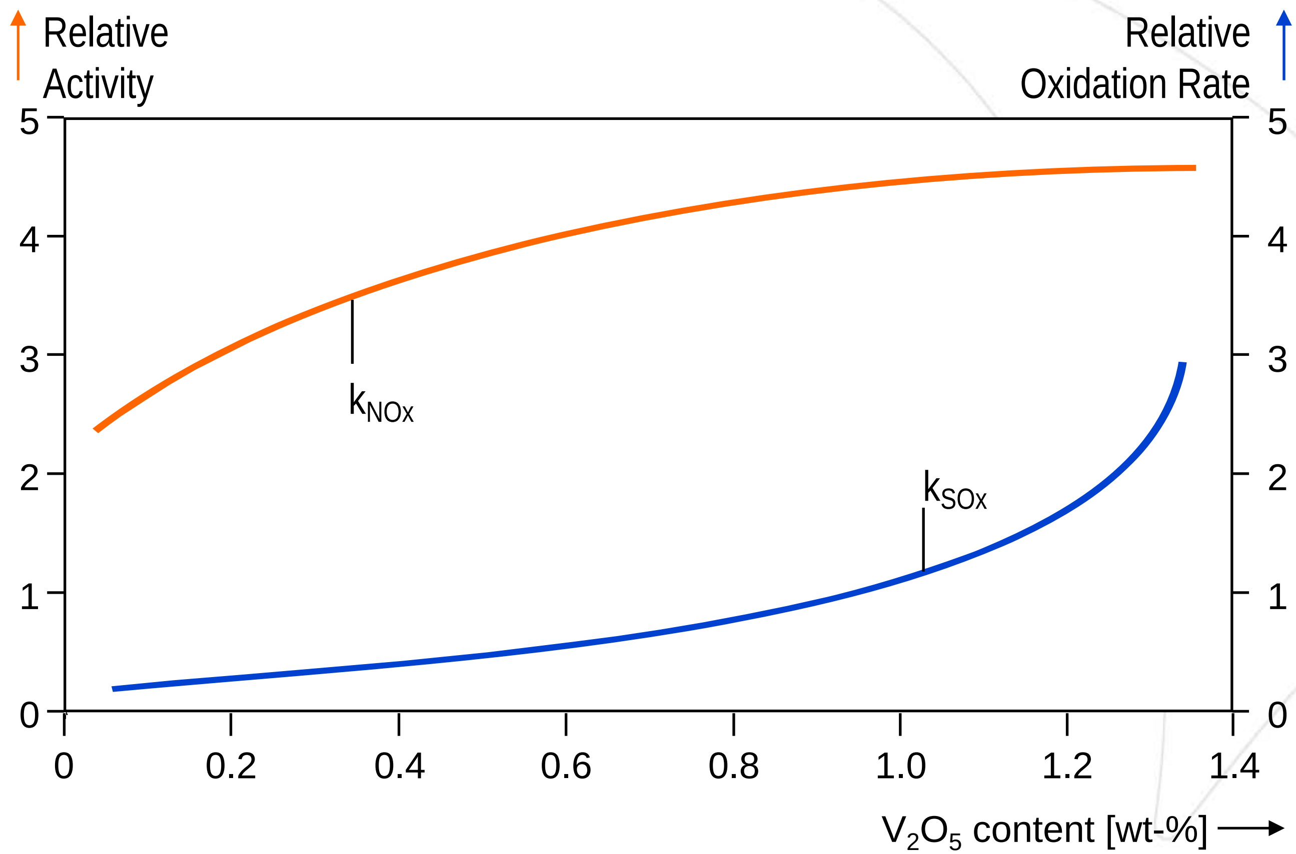
  $$NH_3 + SO_3 + H_2O \longrightarrow NH_4HSO_4 \text{ (ABS)}$$

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

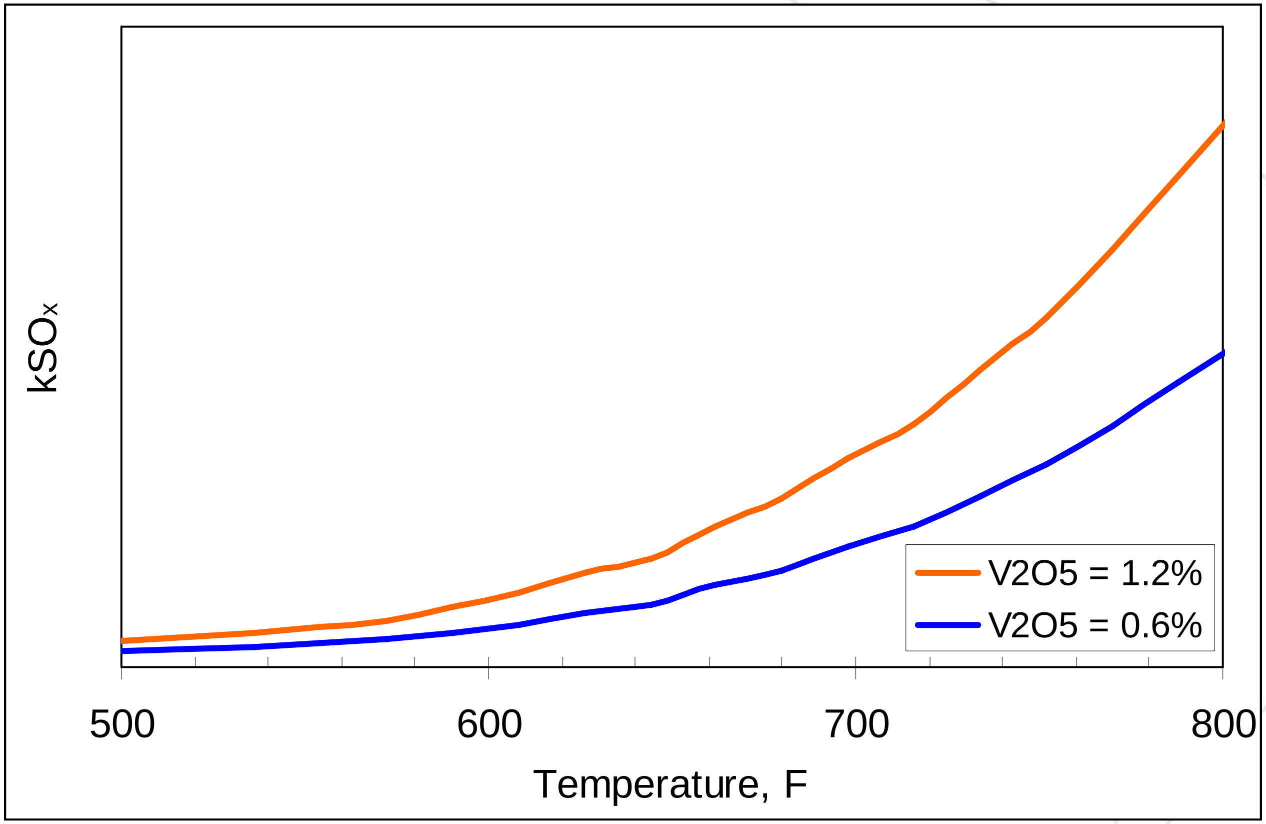
  $$2NH_3 + SO_3 + H_2O \longrightarrow (NH_4)_2SO_4 \text{ (AS)}$$

- AS is dry, powdery compound that can pass through SCR catalyst
- ABS is sticky, viscous compound that can plug catalyst and corrode downstream equipment – example: air preheater

SO_2 Oxidation – Influence of V_2O_5

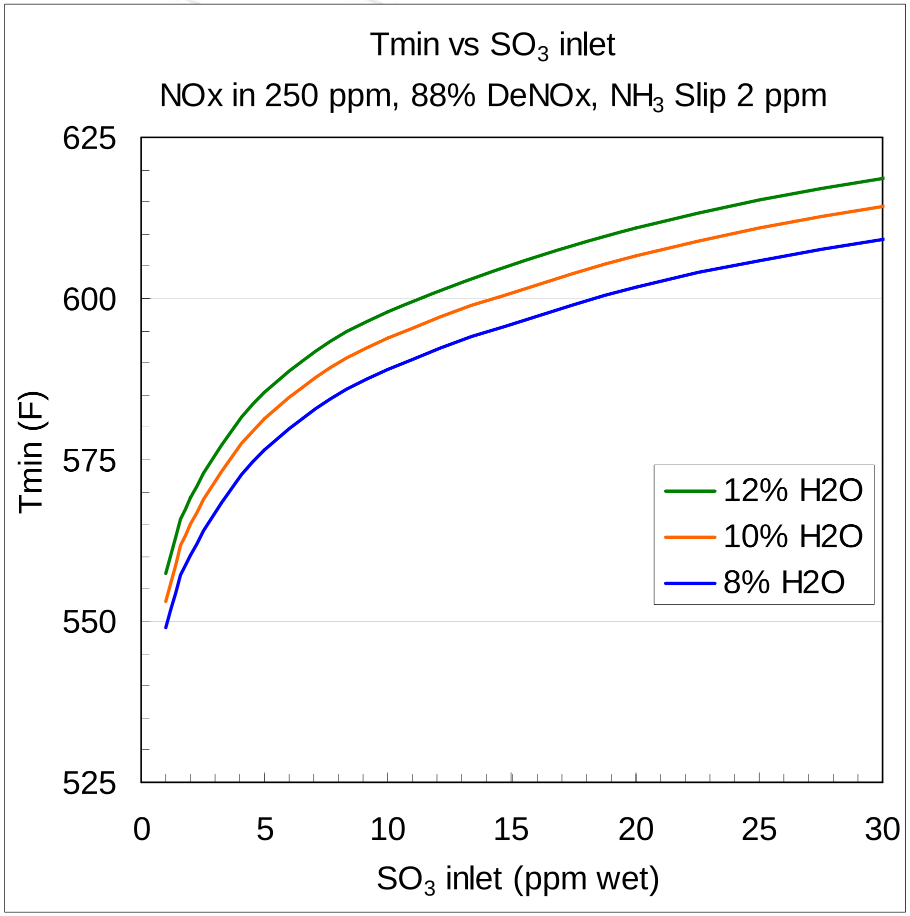


SO_2 Oxidation – Influence of Temperature



Minimum Operating Temperature, MOT (Tmin)

- Minimum temperature for continuous SCR operation
- Of particular concern for low load operation and firing fuels containing sulfur
- Operating above Tmin prevents AS/ABS formation
- Tmin depends on SO_2/SO_3, NH_3, H_2O in flue gas
- Must stop NH_3 when operating below Tmin



Catalyst Design is an Iterative Process

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Design Inputs

- DeNOx criteria - % of NOx to remove
- Operating period – 16,000/24,000 hr
- Flue gas flow conditions
  - Flow rate
  - Temperature
  - Pressure
  - Composition (NOx inlet, O2, H2O, SO2/SO3)
- Allowable NH_3 slip
- Catalyst geometry/composition

Considerations

- Reactor configuration/space, flow distribution
- Coal type/specs, ash load
- Catalyst deactivation
- SO_2 to SO_3 oxidation
- Allowable pressure drop

Design Outputs

- Catalyst volume
- Catalyst activity
- SO_2 to SO_3 oxidation rate
- Pressure drop
- Design margin (safety factor)

Catalyst Management Plan (CMP)

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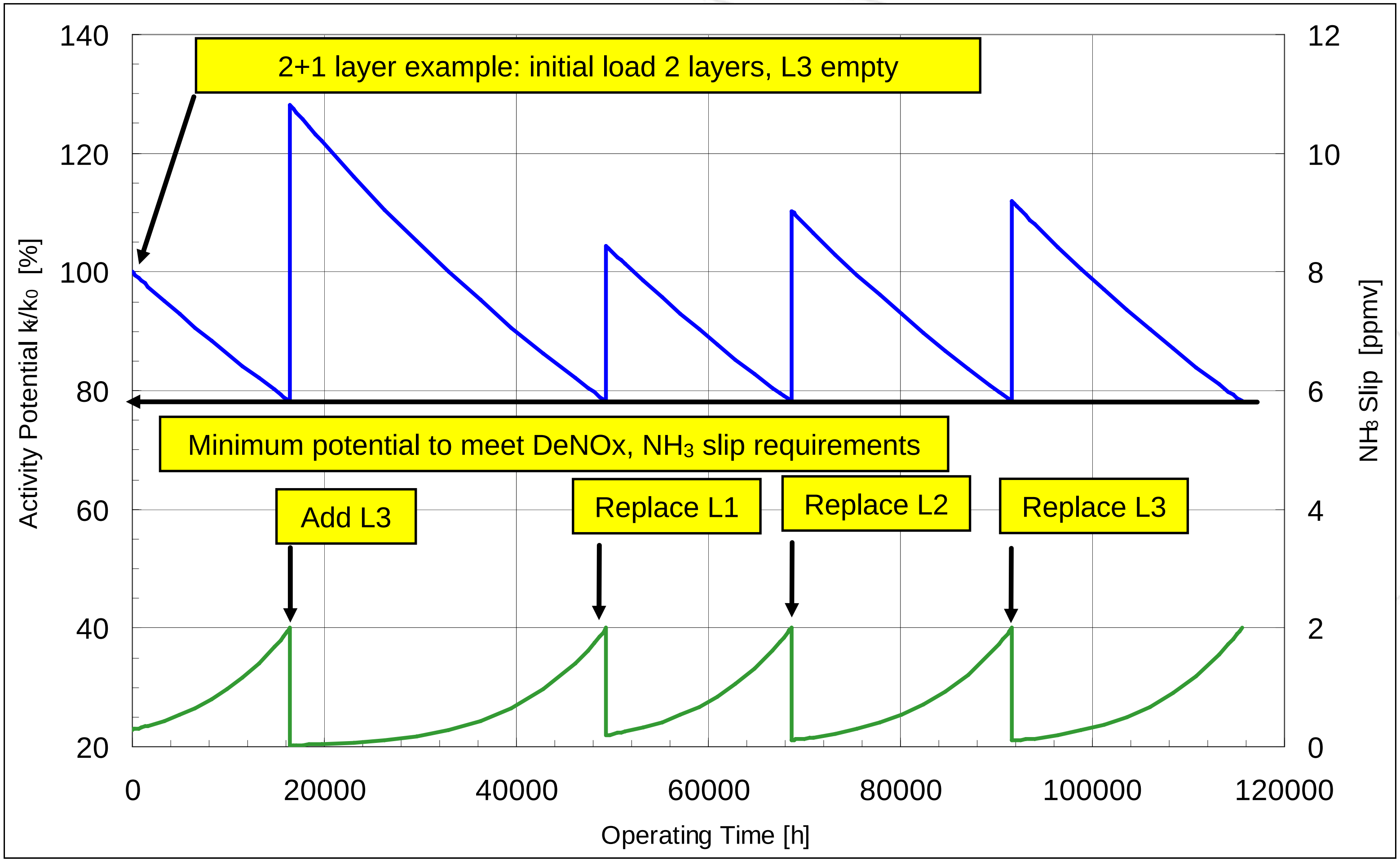

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Thank You

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