

REINHOLD ENVIRONMENTAL Ltd.



2016 NO_x-Combustion-CCR Round Table Presentation

February 1 & 2, 2016, in Orlando, FL / Hosted by OUC

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Training Class 1: Catalyst Basics

David Repp, *Johnson Matthey*

2016 NO_x-Combustion Round Table



Johnson Matthey

SCR Catalyst Basics

How it works

Catalyst Types

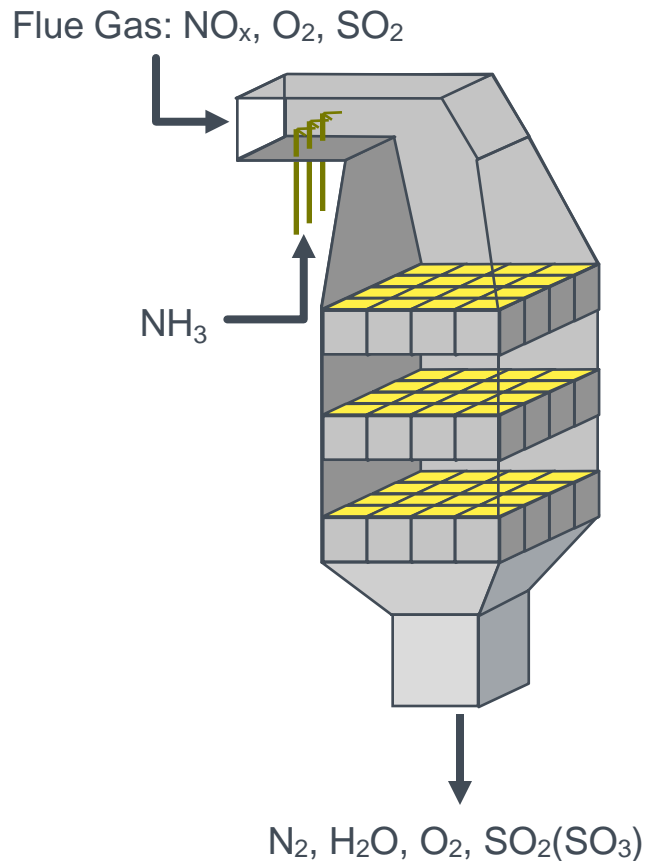
Chemistry

Catalyst Design

Deactivation

Catalyst Planning

Reload Considerations

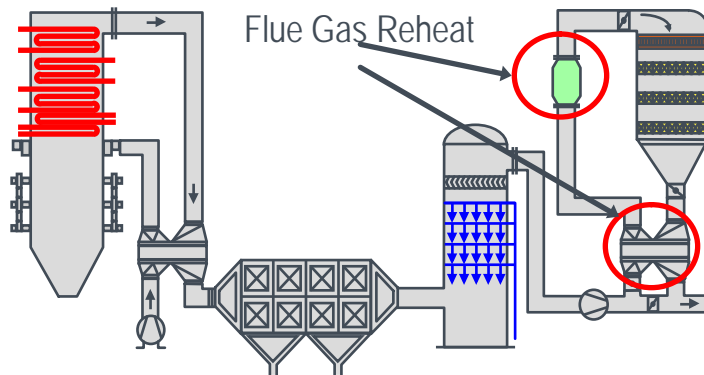
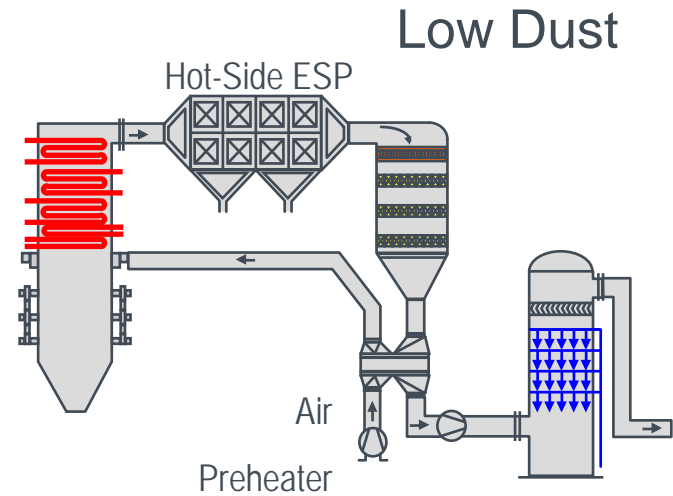
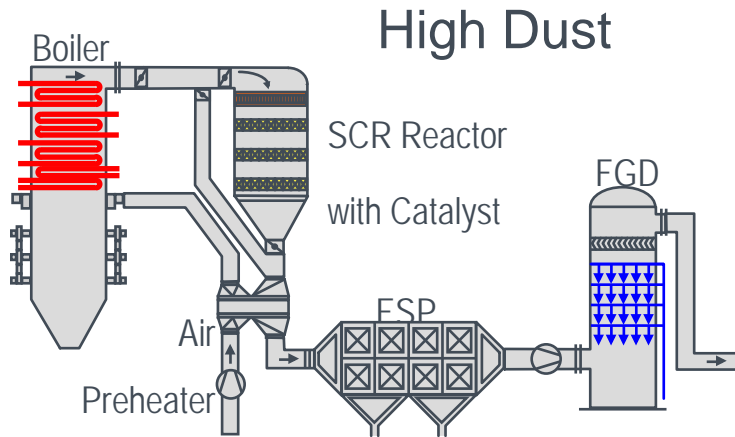


- SCR = Selective Catalytic Reduction
- Purpose is to reduce NO_x (NO & NO₂) from combustion exhaust
- Ammonia (NH₃) is injected into flue gas as reducing agent.
- Flue gas passes through catalyst layers installed in a reactor
- NH₃ reacts with NO_x on the catalyst surface to form nitrogen and water vapor

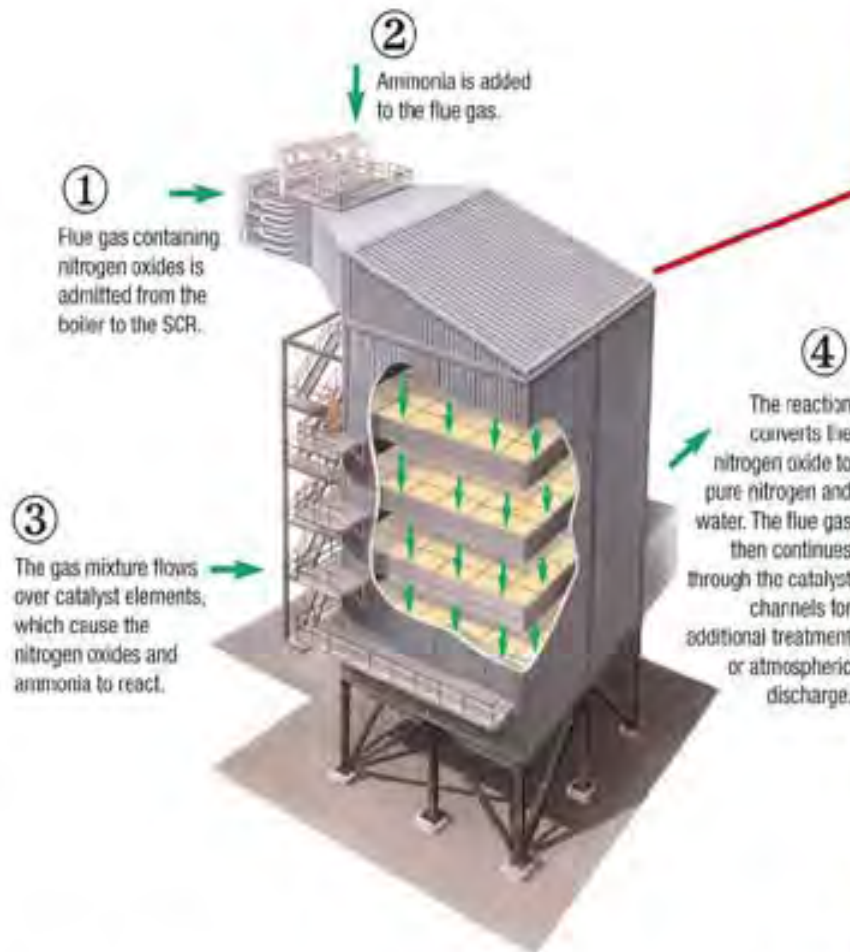
SCR Configuration in Power Plants



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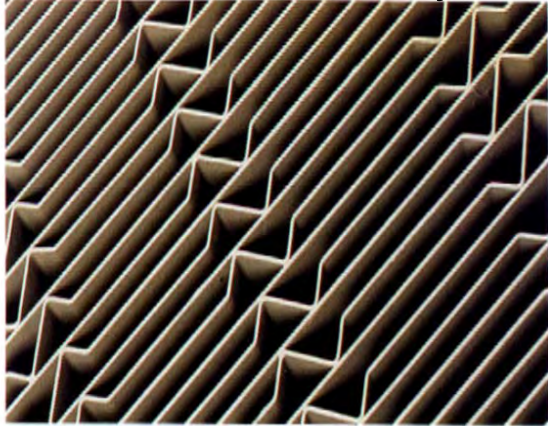


Tail-end

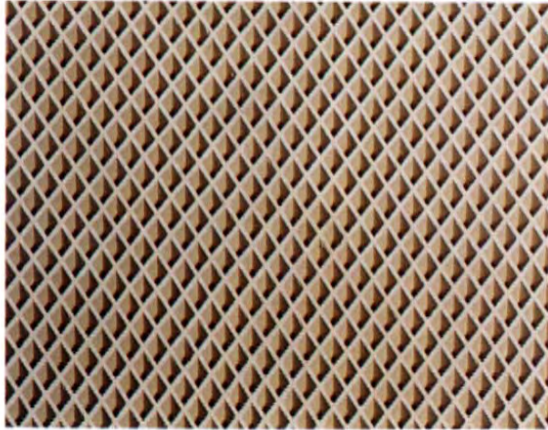


Selective catalytic reduction (SCR) systems are a means of reducing the nitrogen oxide emissions of power generators. Figure shows the typical design features and location of an SCR catalyst reactor installed in a coal-fired power plant.

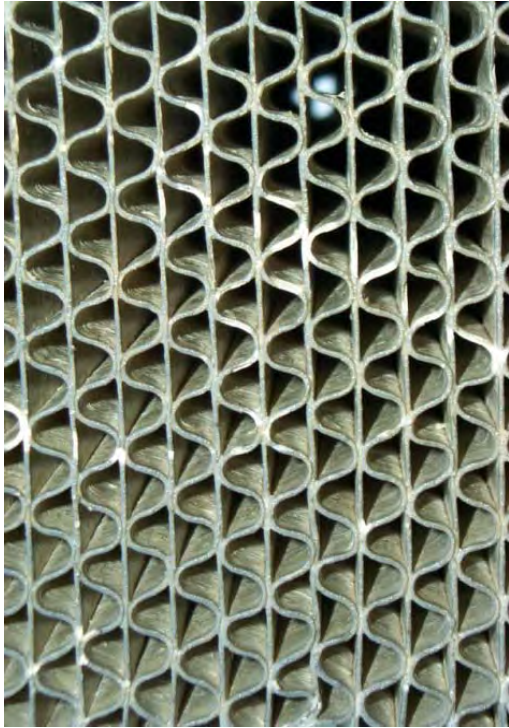
Plate

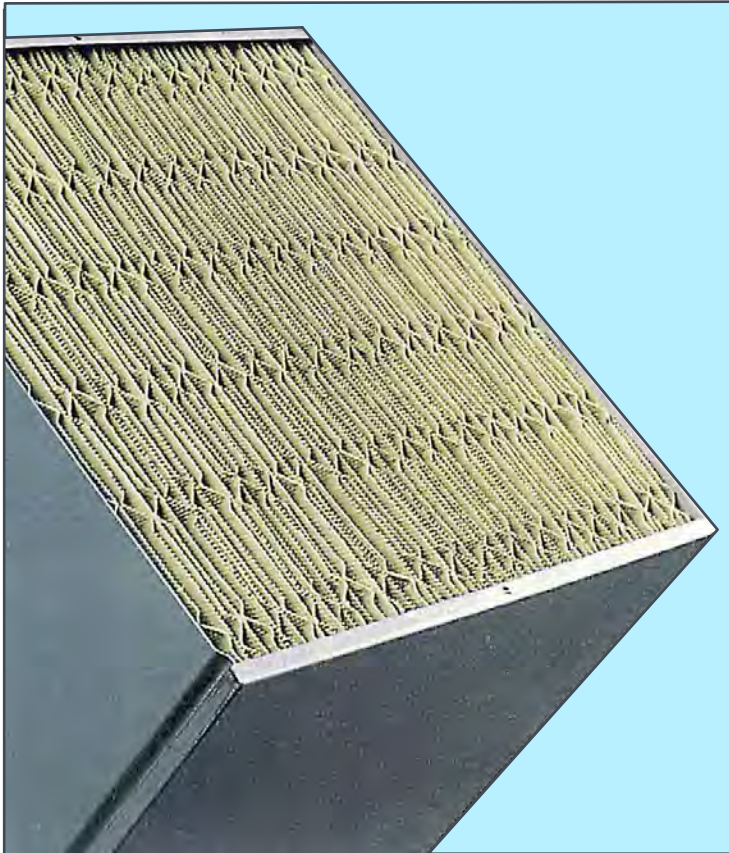


Honeycomb



Corrugated



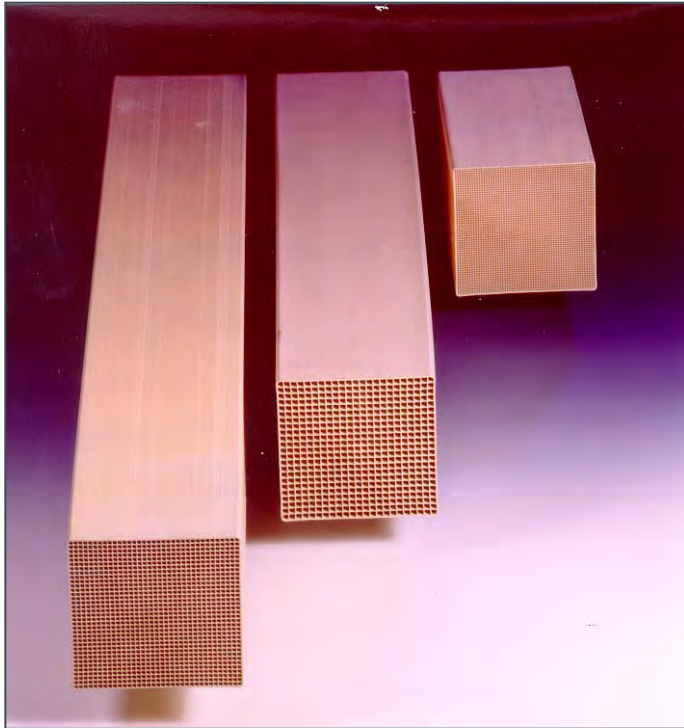


Composition

- Stainless steel carrier, ceramic material rolled on
- 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

Advantages

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

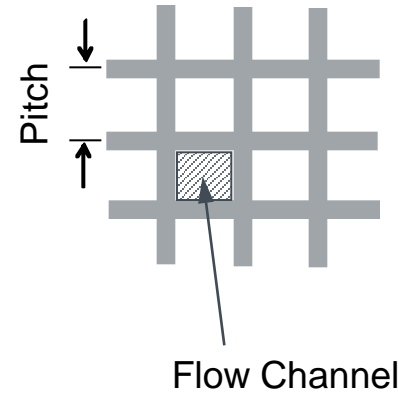
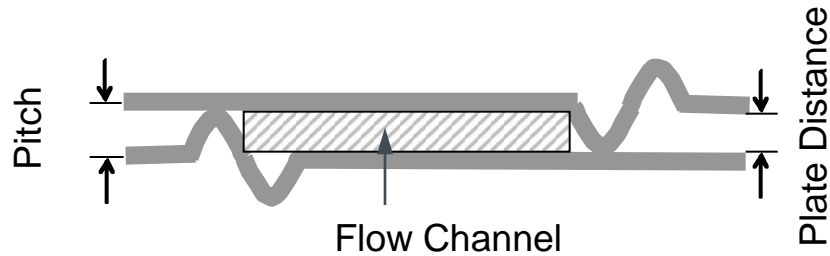


Composition

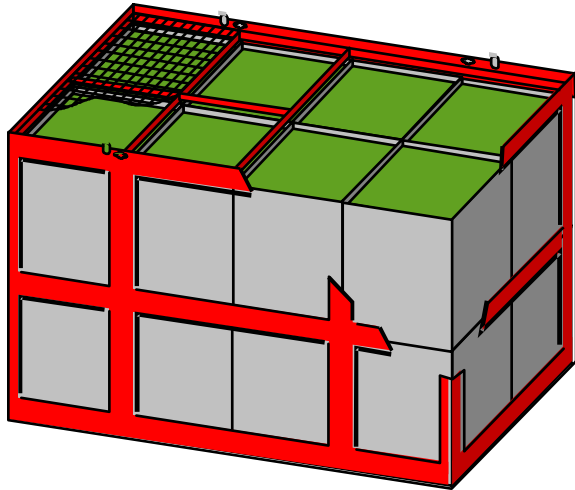
- Homogeneously extruded ceramic with square-opening cell structure
- TiO_2 , V-oxide/W-oxide

Advantages

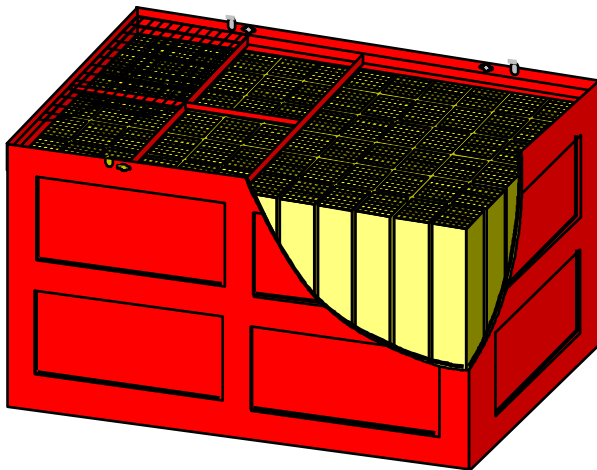
- Ideal for low/no-dust applications
- High active surface area per unit volume



Type	Pitch, mm	Hydraulic diameter, mm	Open Area
Plate	5.7	9.9	86%
HC, 16x16	9.3	8.3	78.4%
HC, 18x18	8.2	7.3	76.7%
HC, 20x20	7.4	6.6	77.4%
HC, 22x22	6.9	6.3	80.8%



- 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 Module Installation – Lifting



Monorail and Cart System



Lowering the catalyst module from the temporary hoist on the hydraulic trolley.

Module on Cart being Rolled into Position



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NO_x is reduced by ammonia across the SCR catalyst according to the following reactions:

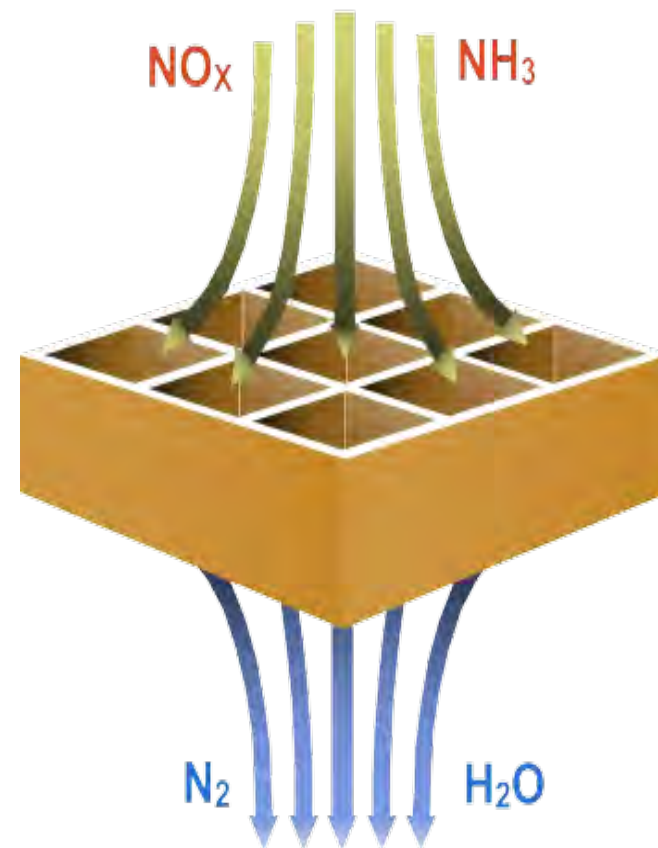
- $4 \text{NO} + 4 \text{NH}_3 + \text{O}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O}$
- $2 \text{NO}_2 + 4 \text{NH}_3 + \text{O}_2 \rightarrow 3 \text{N}_2 + 6 \text{H}_2\text{O}$
- $\text{NO} + \text{NO}_2 + 2 \text{NH}_3 \rightarrow 2 \text{N}_2 + 3 \text{H}_2\text{O}$

NO_x is reduced by urea as follows:

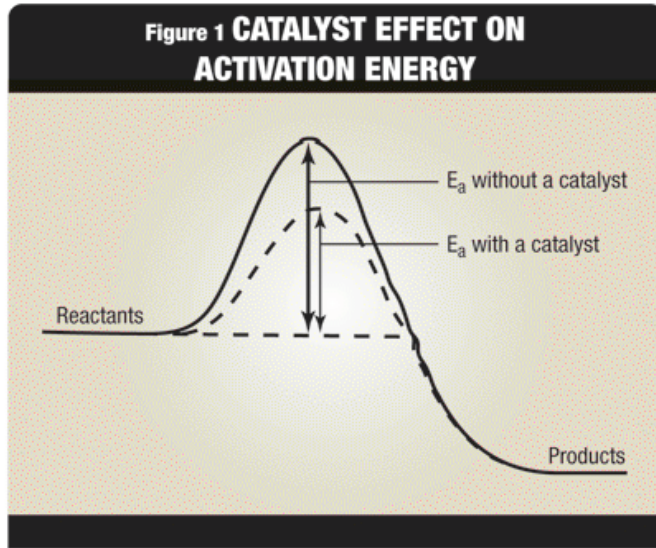
- $4 \text{NO} + 2(\text{NH}_2)_2\text{CO} + \text{O}_2 \rightarrow 4 \text{N}_2 + 4 \text{H}_2\text{O} + 2 \text{CO}_2$

Undesirable side reactions:

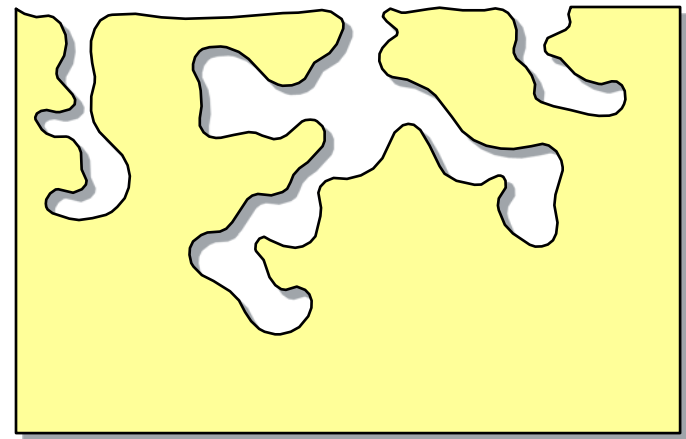
- $4 \text{NH}_3 + 5 \text{O}_2 \rightarrow 4 \text{NO} + 6 \text{H}_2\text{O}$
- $2 \text{SO}_2 + \text{O}_2 \rightarrow 2 \text{SO}_3$
- $2 \text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{SO}_4$
- $\text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{HSO}_4$



Less Energy Needed = High Reaction Rates

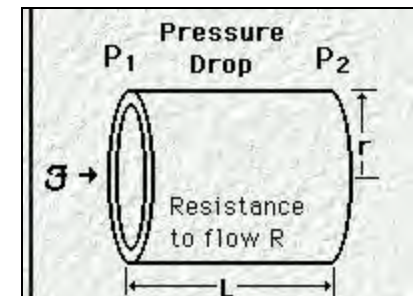
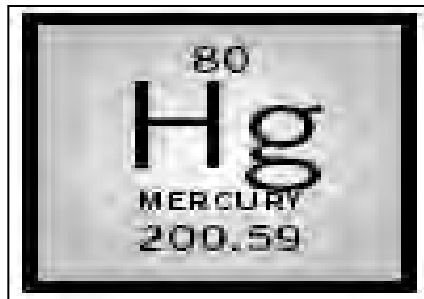
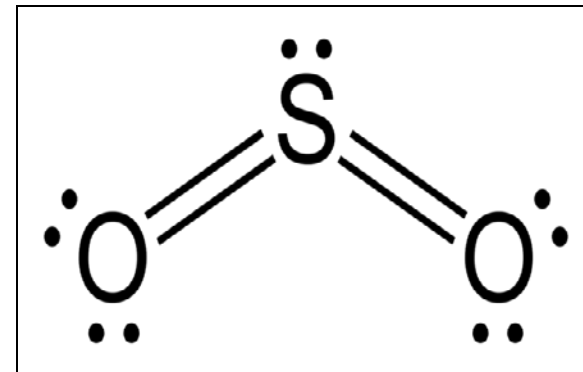
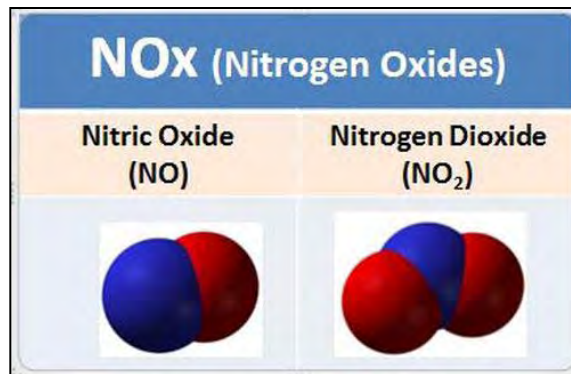


Porous structure = High surface area



External & Internal diffusion of NH_3 into the pores and adsorption to the active sites, NO diffusion from gas phase to adsorbed NH_3 , Reaction, Desorption of N_2 & H_2O , Diffusion of N_2 and H_2O

Catalyst design is a balancing act driven by the NO_x Conversion, SO_2 Oxidation, Hg Oxidation, Pressure Drop, and Lifetime Guarantee requirements



Area Velocity

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

Activity

$$k_{NOx} = -AV * \ln \left(1 - \frac{\eta (NOx)}{100\%} \right)$$

NH₃ to NO_x ratio

$$\alpha = \frac{NOx_{IN} - NOx_{OUT} + NH_3_{OUT}}{NOx_{IN}}$$

Potential

$$P = \frac{k_{NOx}}{AV}$$

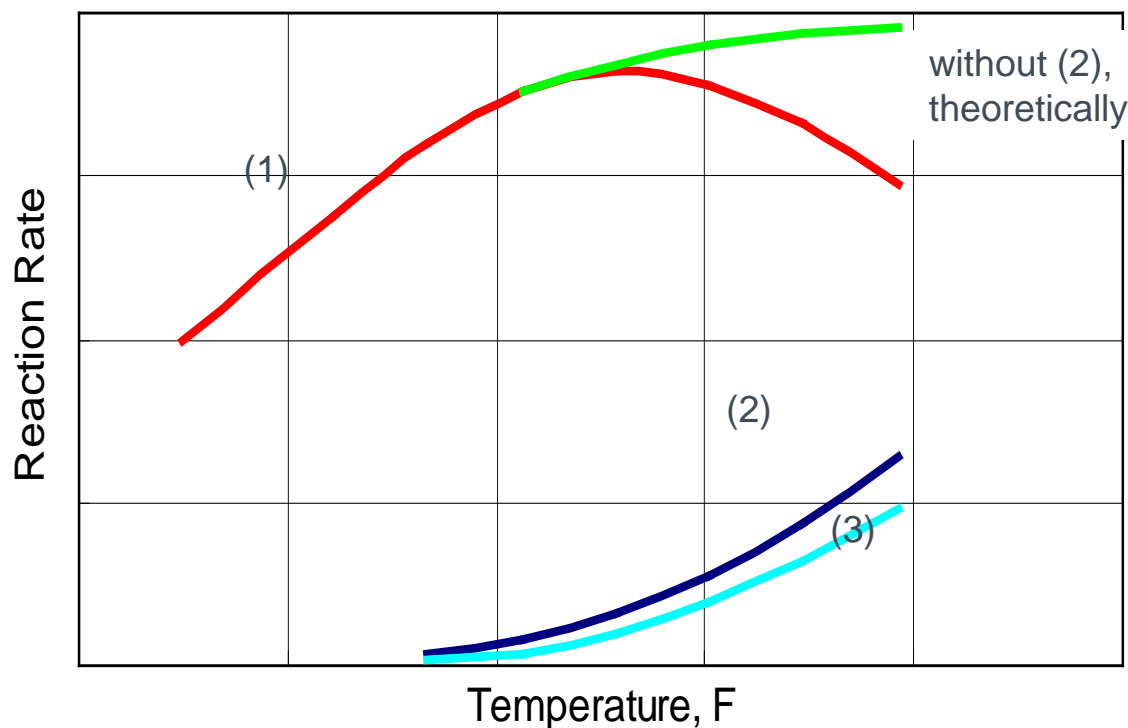
Deactivation Rate

λ = Rate Constant that predicts how the catalyst will deactivate over time

End of Life Activity / Potential

$$k_{EOL} = k_0 * e^{-t\lambda}$$

$$P_{EOL} = k_{EOL} / AV$$

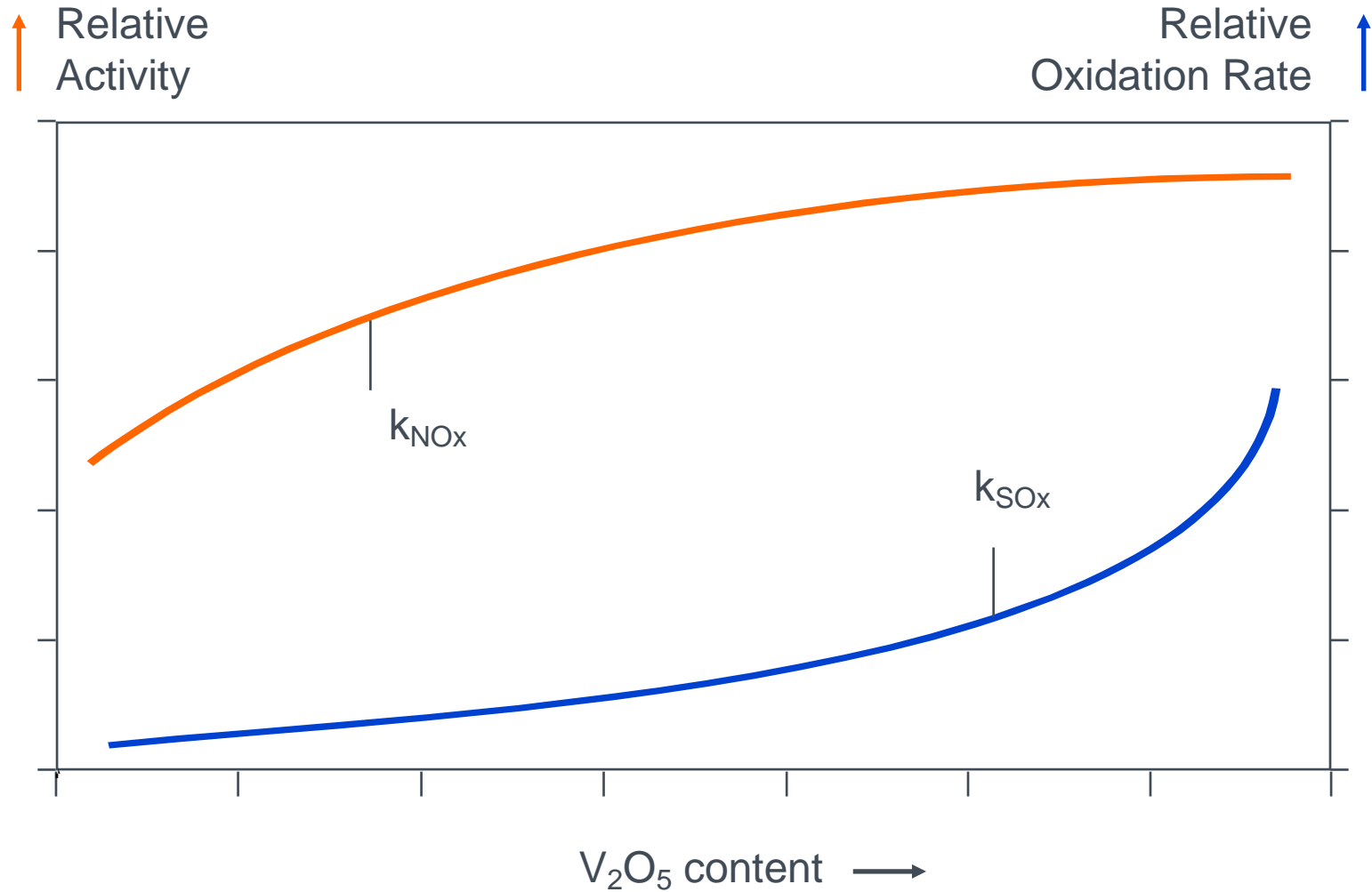


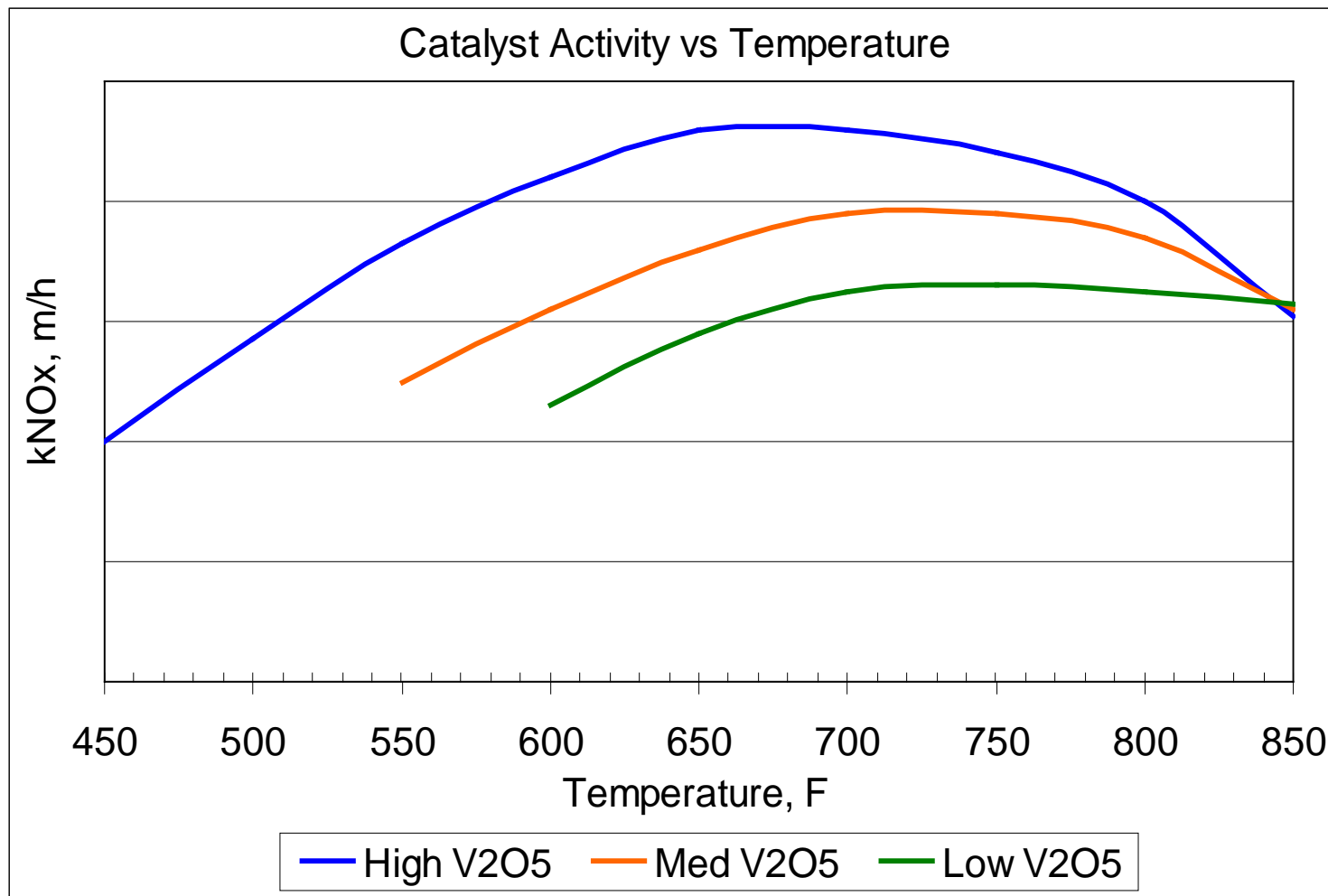
1. SCR-Reaction
 $\text{NO}_x + \text{NH}_3 = \text{N}_2 + \dots$

Side Reactions:
2. NH_3 Oxidation
 $\text{NH}_3 + \text{O}_2 = \text{NO}_x + \dots$

3. SO_2 Oxidation
 $\text{SO}_2 + \text{O}_2 = \text{SO}_3 + \dots$

All 3 reactions catalyzed
by V_2O_5





$T, V_2O_5, H_2O, O_2, \text{ flow rate} \rightarrow k_0$

$k_0 \rightarrow \text{Deactivation Model} \rightarrow k_{t=EOL}$

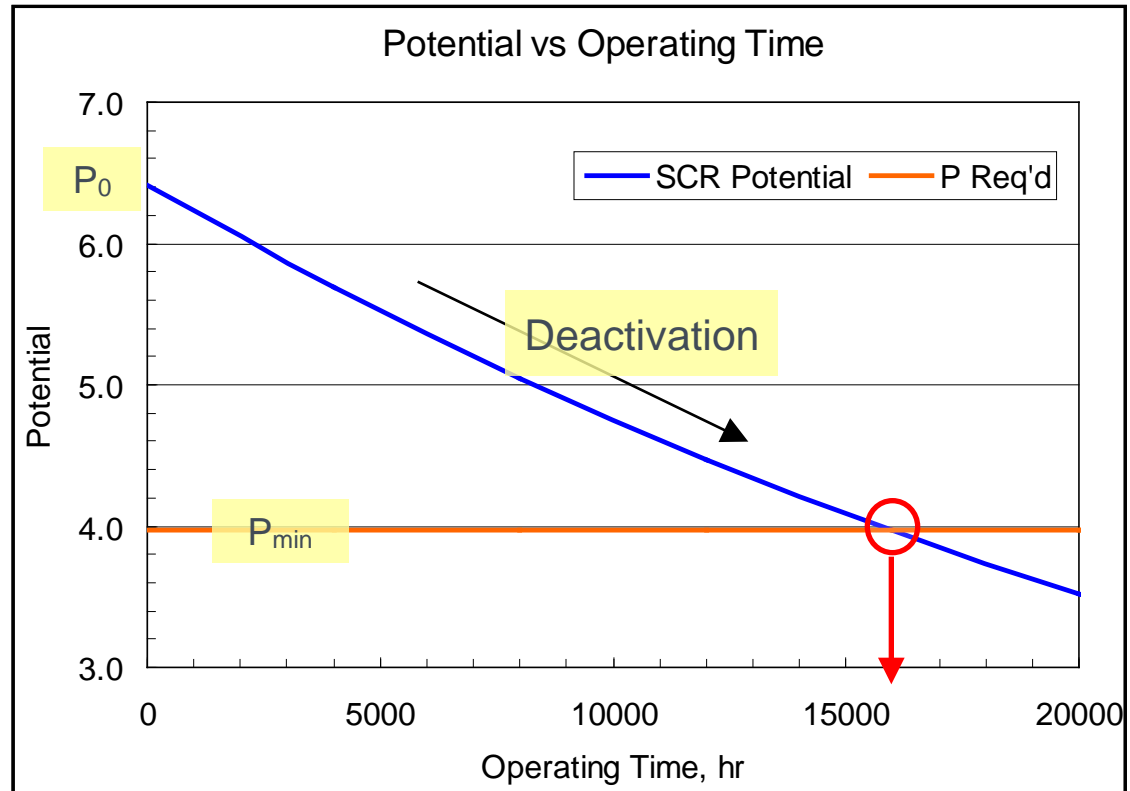
Required Catalytic Potential for Specified NO_x Reduction Performance

- Potential: measure of catalyst's ability to reduce NO_x
- $P_{\min} = f(\text{NO}_{x \text{ in}}, \text{NO}_{x \text{ out}}, \text{NH}_3 \text{ slip})$ – theoretical value
- Add margin for . . .
 - Mal-distributions of NH₃-NO_x mixing and flow
 - Unavailable catalyst surface due to channel plugging
 - Catalyst material lost to fly ash erosion

Deactivation Example

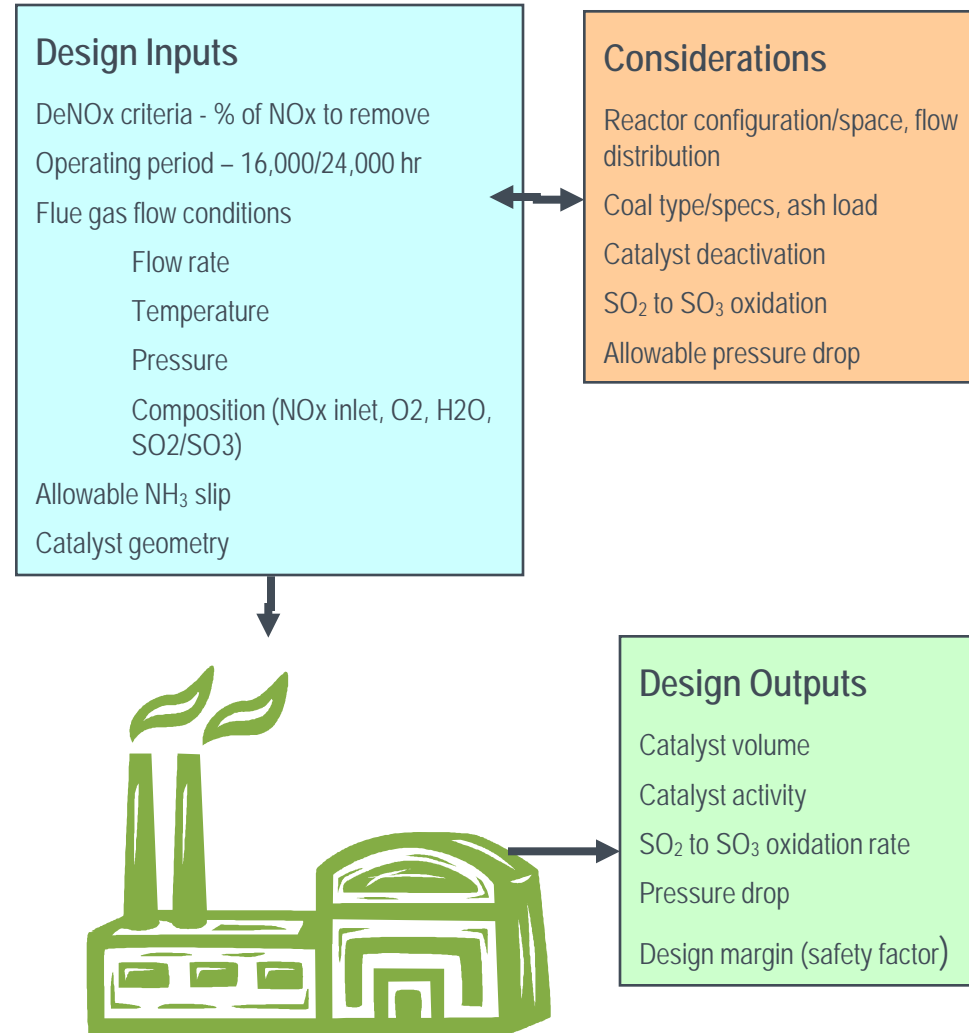


- Operating Life: 16,000 hr
- $P_{\min} = 4.0$
- Fuel: PRB Coal
- Relative potential at 16,000 hours: $P/P_0 = 0.62$
- Initial potential installed: $P_0 = 6.4$



- For the initial catalyst loading of a SCR, the catalyst supplier uses plant design information to obtain a suitable product
- Historic data for the fuel source must determine catalyst deactivation
 - No ability to utilize existing SCR performance

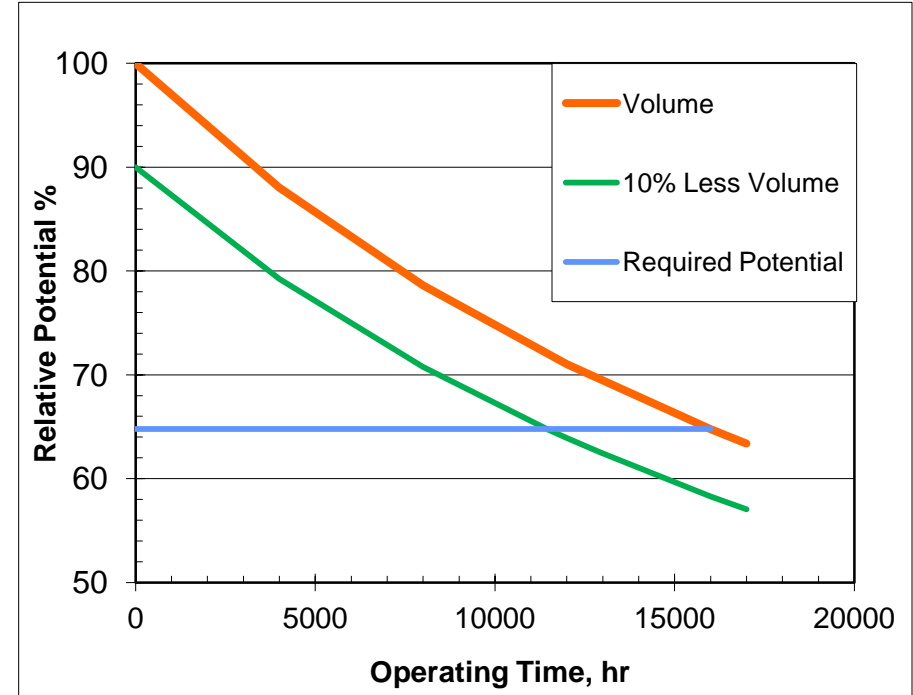
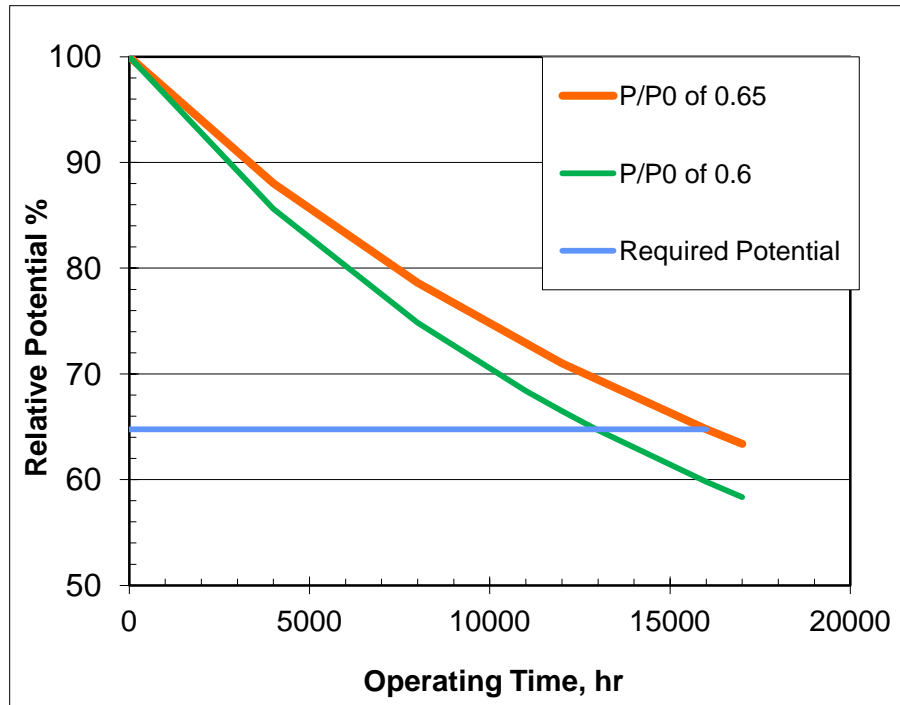
Application	Deactivation
Low dust configuration	Low
Bituminous firing	Medium
PRB firing	Medium-High
Lignite firing	High



Impact of Catalyst Sizing Decisions



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Assuming a slower deactivation rate than required will cause the SCR to not make required lifetime.

Causes: Excessive plugging, catalyst poisoning

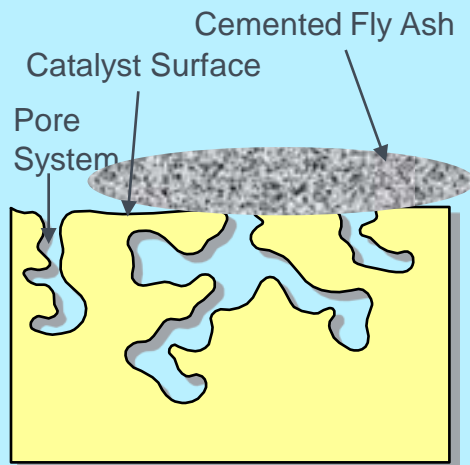
Not providing sufficient volume will cause the SCR to not make required lifetime.

Causes: Design Flow << Actual Flow, Design NOx << Actual NOx, flow distribution

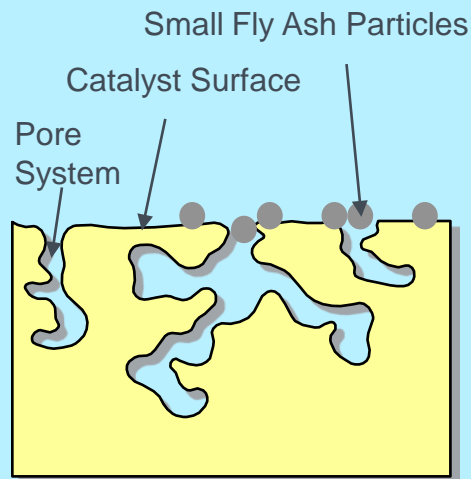
- Mercury emissions can exist in a variety of forms
 - Total – Hg^{T} includes Hg^0 , Hg^{2+} , Hg^{P}
 - Hg^{P} – Particulate bound mercury
 - Hg^0 – elemental mercury
 - Hg^{2+} – oxidized mercury
- SCR catalyst has the ability to oxidize elemental mercury
 - Reaction is complex, and dependent on many parameters
- Oxidized mercury
 - Water soluble - able to be captured in wet-FGD
 - Easier to capture by activated carbon than elemental mercury
- Creating oxidized mercury does not guarantee capture

- Flue Gas Temperature: 650 – 750 °F (preferred)
- Flue gas linear flow velocity: 5.0 – 5.5 m/s (preferred)
- Thorough NH₃-NO_x mixing: 5% RMS (required for >85% deNO_x)
- LPA screens upstream of catalyst (should be required)
- Soot-blowers or sonic horns (required)
- Even fly ash distribution, especially for low load operation

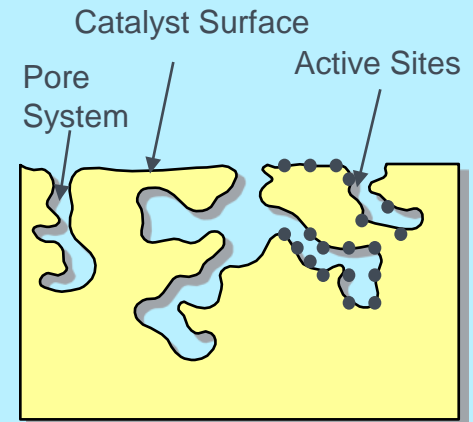
Masking:
Macroscopic blockage
of catalyst surface
by cemented fly ash



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



Poisoning:
Deactivation of active
sites by chemical attack



Poisoning is the result of active catalyst sites being blocked for NO_x reduction by chemically bound species. Some examples:

Alkali Metals

Water Soluble ...Condensation during “Cool Down”...Dew Point Considerations

Arsenic

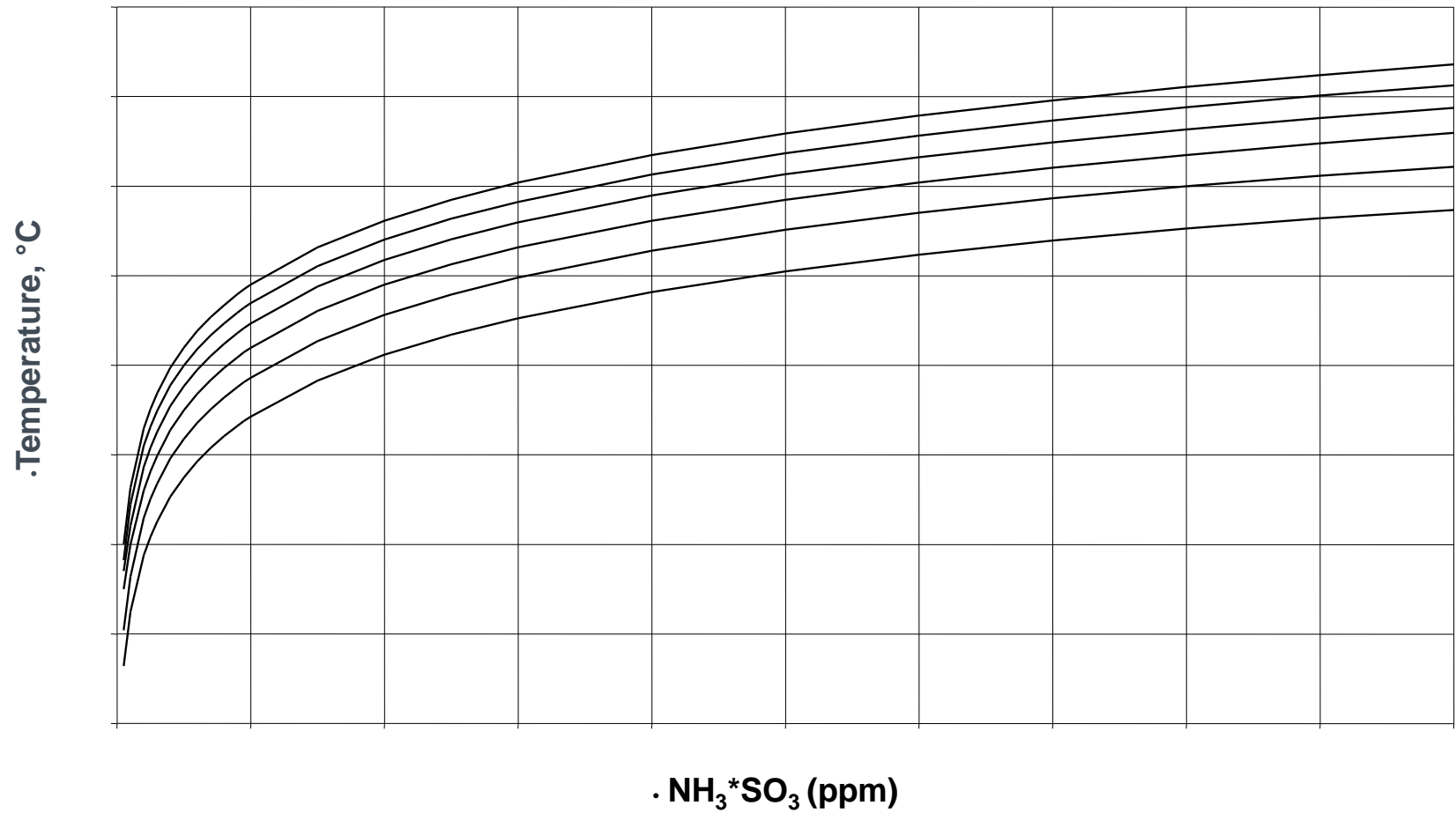
Some Eastern Bituminous Coals...Gaseous Arsenic during Combustion...Strong Catalyst Poison...Mitigating poisoning with Calcium... Calcium / Arsenic Ratio Considerations

Phosphorus

PRB Coals...Gas Phase Phosphorus...



.Minimum Operating Temperature f (NH₃, SO₃, H₂O, catalyst type)



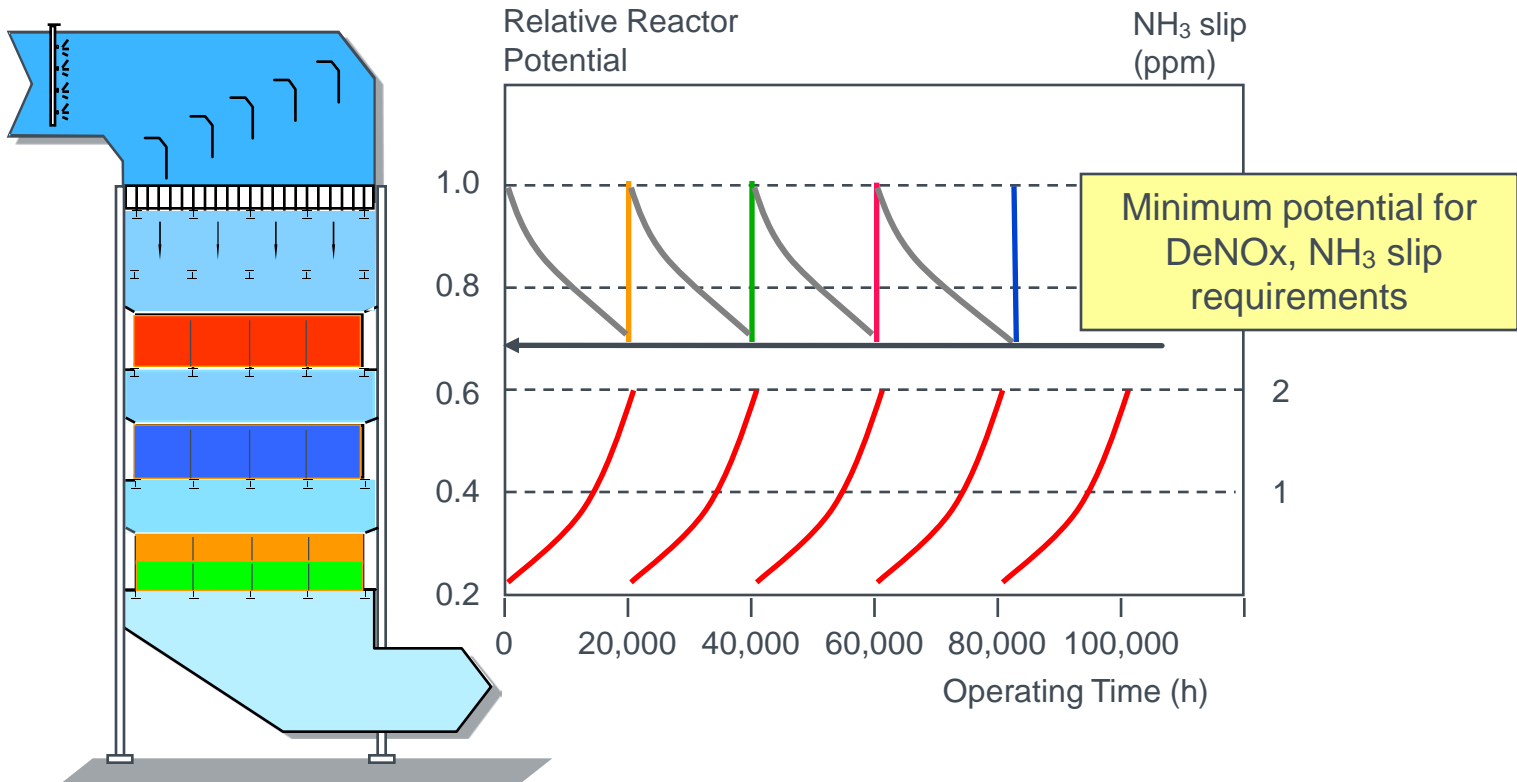
Formation of ammonium sulfate compounds

- Ammoniumbisulphate is a viscous compound, which may deposit on the surface of heat exchanger tubes downstream of the SCR and may cause corrosion problems. Ammoniumsulphate is a dry, powdery compound, which may also cause corrosion.
- The ammonium salts may lead to catalyst deactivation if condensation occurs in the catalyst pores.

CMP, 2 + 1 Example



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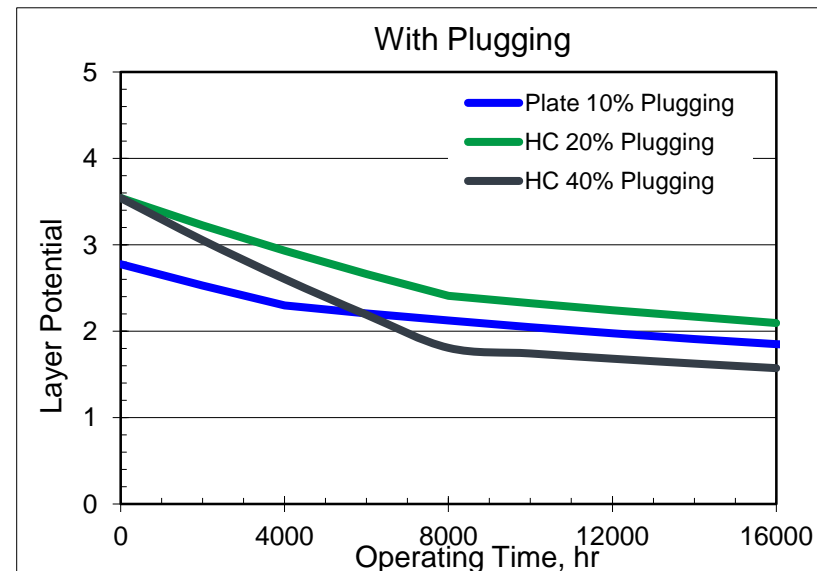
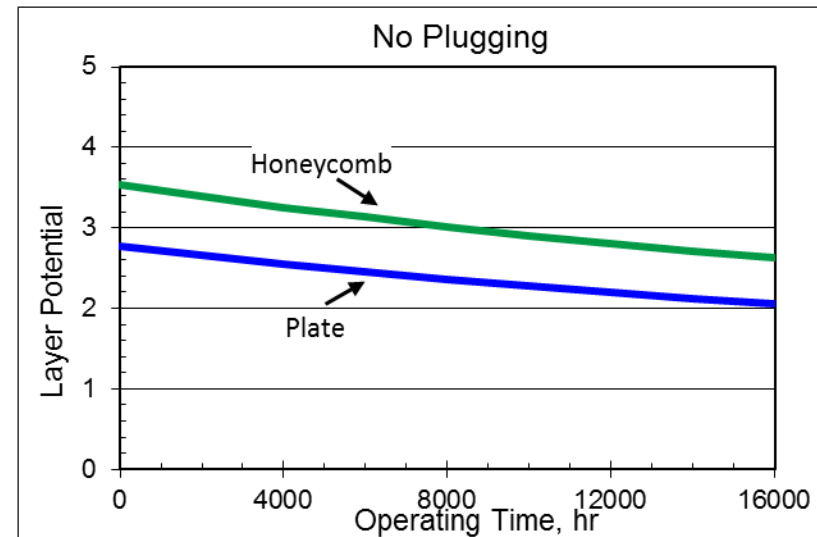
- Standardized module structure – catalyst mixing is possible and common
 - Multiple catalyst types in reactor
 - New and regen'd
 - Multiple suppliers
- Consider tooling requirements
 - Lifting, transport tooling for unloading/loading
 - Sealing systems
- Performance Guarantees from new supplier (other than initial)
 - Layer guarantees – geometry, durability, activity, SO₂ conversion, pressure drop – based on fuel and flue gas characteristics
 - System guarantees – DeNO_x, NH₃ slip, operating life – based on total reactor potential → requires info about existing catalyst

- 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

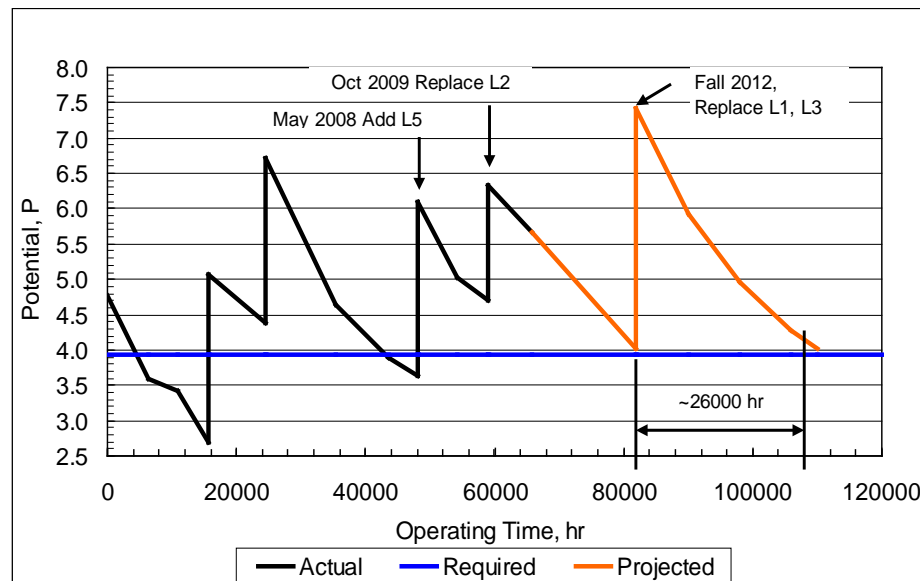
- Available sample sizes
 - Full Bench
 - 150 mm by 150 mm by Full element Length
 - Semi Bench
 - 65 mm by 65 mm by 500 mm
 - Micro Scale
 - 25 mm by 25 mm by 200-400 mm
- All sample sizes can perform SO₂ to SO₃ conversion and NO_x activity testing
- Performance Guarantee testing can be done by field testing or lab testing at design conditions
- Suppliers often will include catalyst activity testing during warranty period

- 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

- 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
- Plugging Percentage
- Above info used to ...
 - Calculate existing reactor potential
 - Determine rate of deactivation
 - Forecast catalyst lifetime



- Layer Replacement Bid Packages
 - Layer oriented
 - Request Initial Activity Guarantee
 - Request End of Life Activity Guarantee
 - Request layer SO_2 to SO_3 conversion guarantee, pressure drop
 - Normally tied to predetermined catalyst management plan (CMP)
- Catalyst Management Planning is only useful if calibrated to actual operating data
- Factors that change CMP
 - Change in fuel or DeNOx target
 - Desire to meet planned outage schedule
 - Faster than designed deactivation



Catalyst Supplier will always try and provide practical solutions that meet desired SCR performance

Questions?