REINHOLD ENVIRONMENTAL Ltd.

2015 NOx-Combustion Round Table
& Expo Presentations

February 23 & 24, 2015, in Richmond, VA / Hosted by Dominion

Training Class 4: SCR Catalyst 101

Part 1: Joseph Spahn, *Johnson Matthey*

REINHOLD ENVIRONMENTAL LTD.
2015 NOx-Combustion Round Table
Richmond, Virginia
February 23, 2015

Johnson Matthey

Agenda

SCR Catalyst 101

Part 1

Theoretical

How it works

Catalyst Types

Chemistry

Catalyst Design

Deactivation

Catalyst Planning

Reload Considerations

Part 2

O & M Issues

Catalyst

Ammonia Injection

Turning Vanes

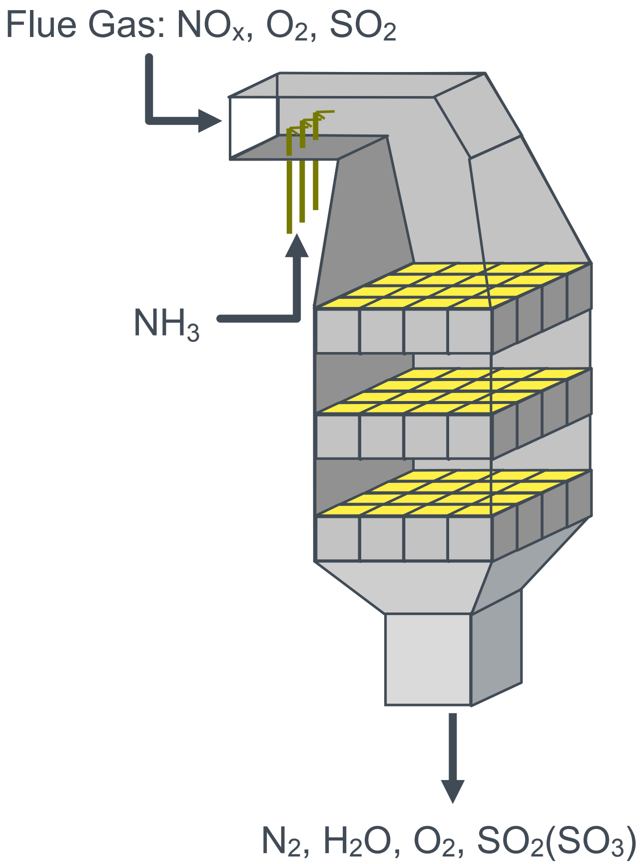
Soot Blowers

Sonic Horns

LPA Screens

Economizer Leaks

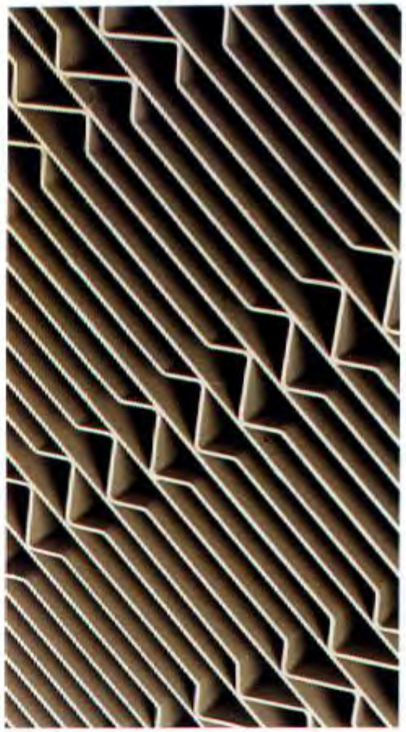
How it Works



- SCR = Selective Catalytic Reduction
- 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

SCR Catalyst Types

Plate



Honeycomb

Corrugated

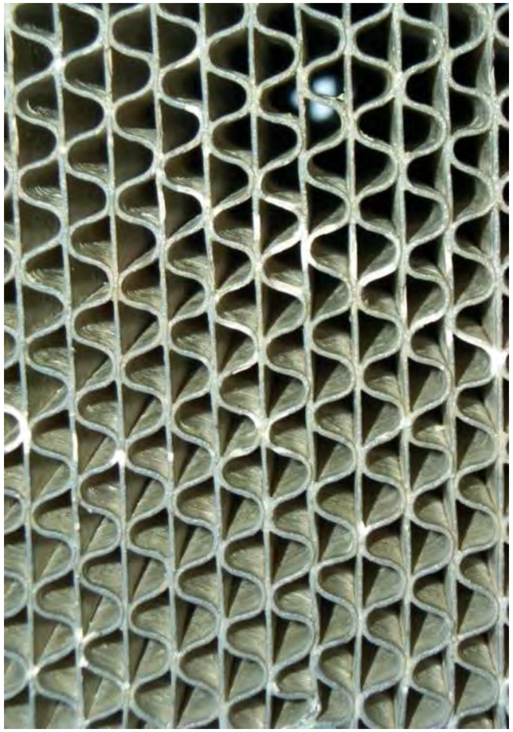
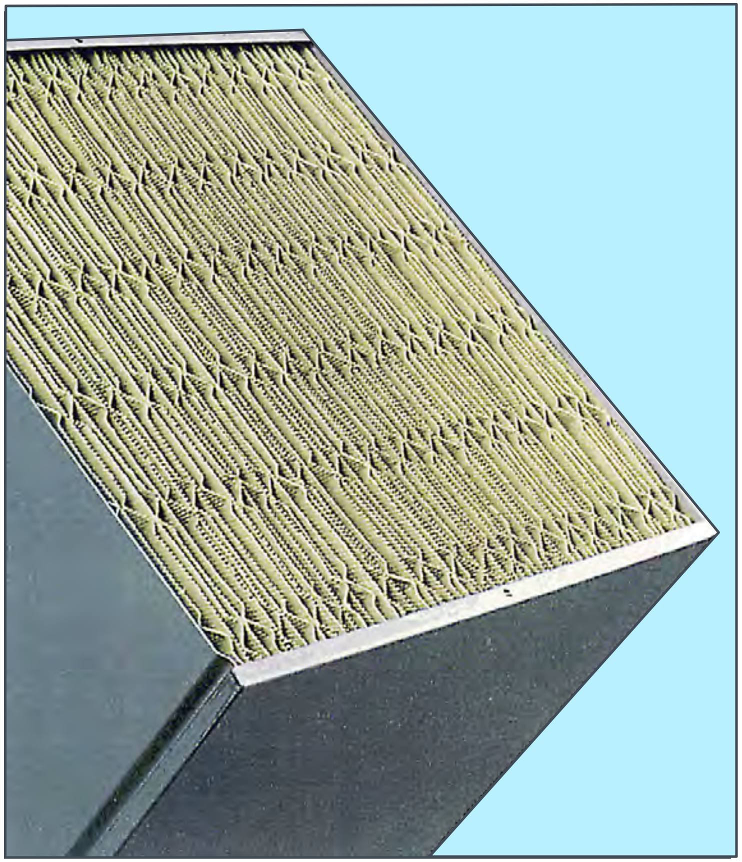


Plate Catalyst



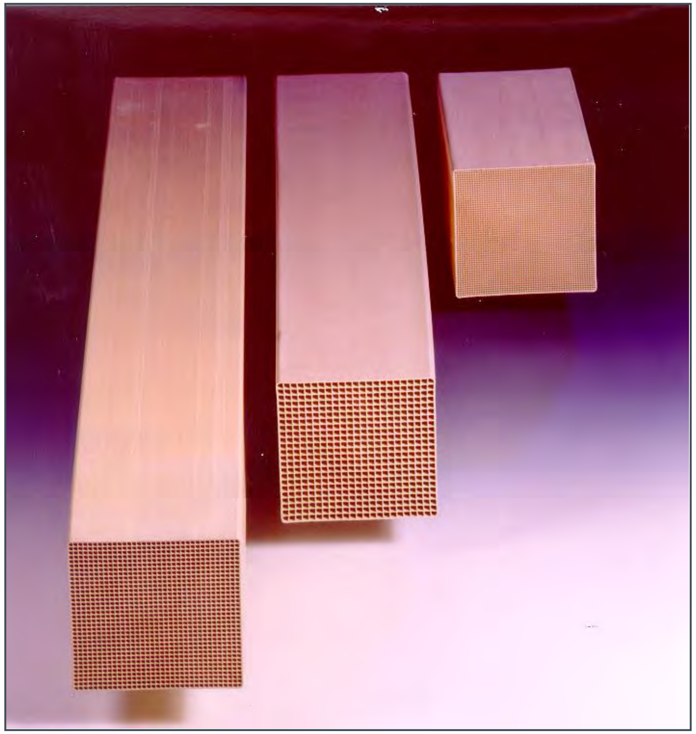
Composition

- 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

Honeycomb- Catalyst



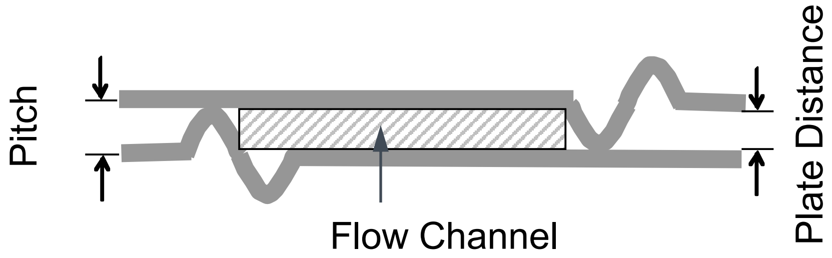
Composition

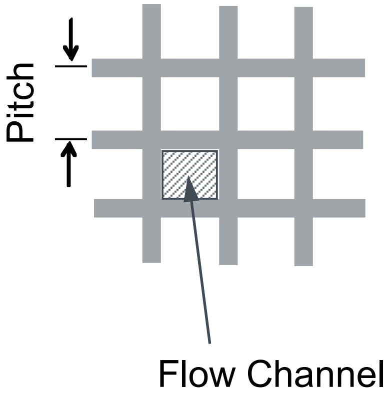
- Homogeneously extruded ceramic with square-opening cell structure
- TiO_2, V-oxide/W-oxide

Advantages

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

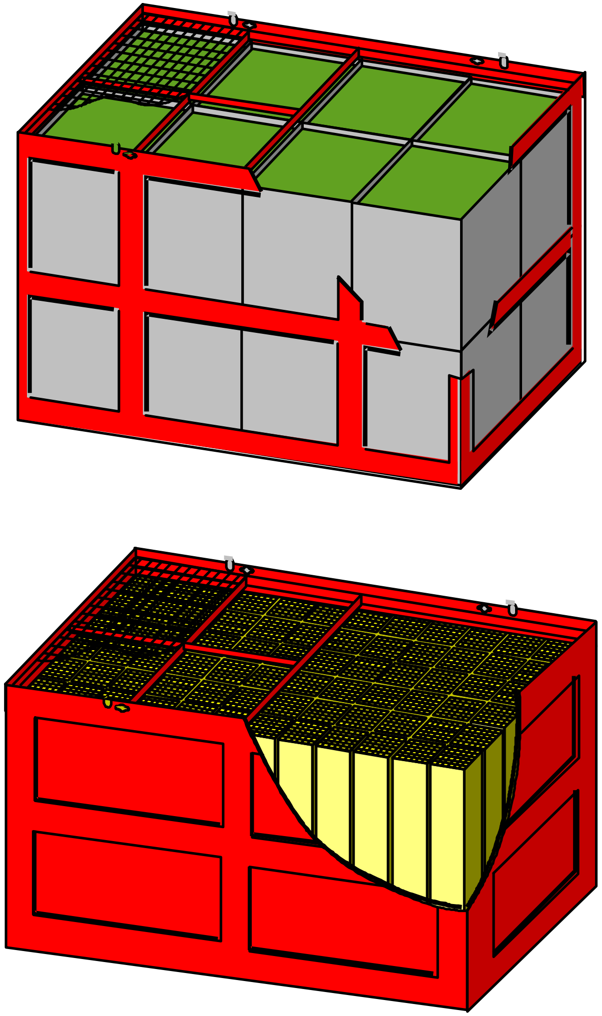
Catalyst Type Geometry





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 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

SCR Chemistry – The Basics

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

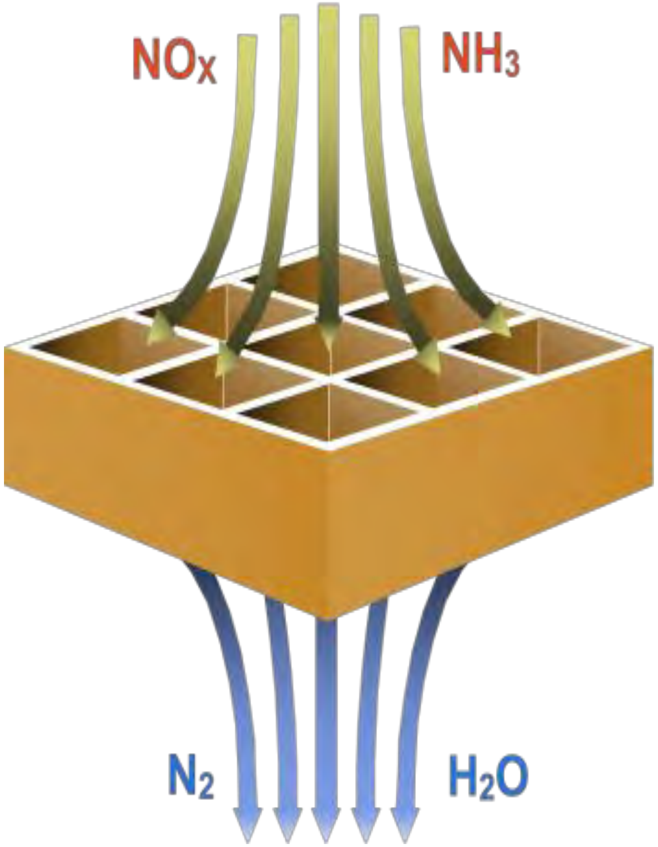
- $4\ NO + 4\ NH_3 + O_2 \rightarrow 4\ N_2 + 6\ H_2O$
- $NO_2 + 4\ NH_3 + O_2 \rightarrow 3\ N_2 + 6\ H_2O$
- $NO + NO_2 + 2\ NH_3 \rightarrow 2\ N_2 + 3\ H_2O$

NOx is reduced by urea as follows:

- $4\ NO + 2(NH_2)_2CO + O_2 \rightarrow 4\ N_2 + 4\ H_2O + 2\ CO_2$

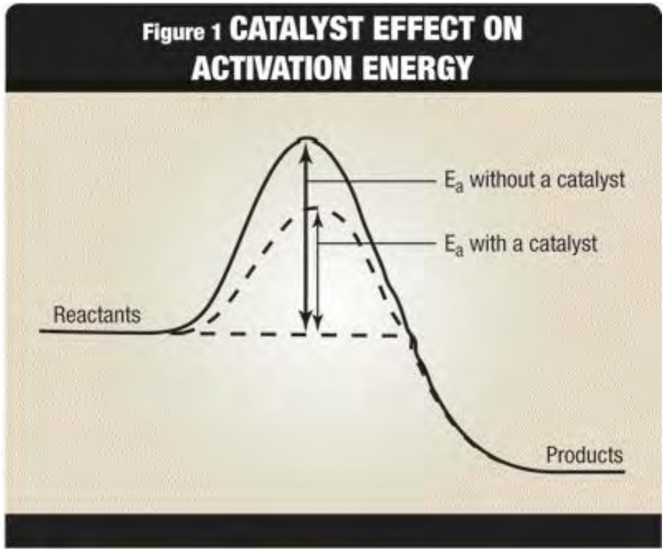
Undesirable side reactions:

- $4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$
- $2\ SO_2 + O_2 \rightarrow 2\ SO_3$
- $2\ NH_3 + SO_3 + H_2O \rightarrow (NH_4)_2SO_4$
- $NH_3 + SO_3 + H_2O \rightarrow NH_4HSO_4$

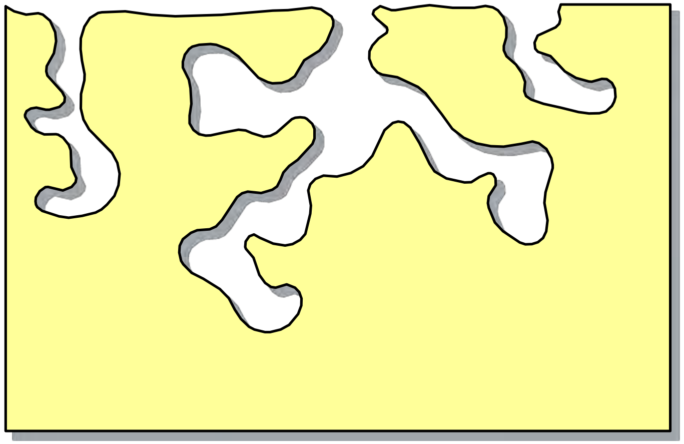


SCR Chemistry - Role of the Catalyst

Less Energy Needed = High Reaction Rates



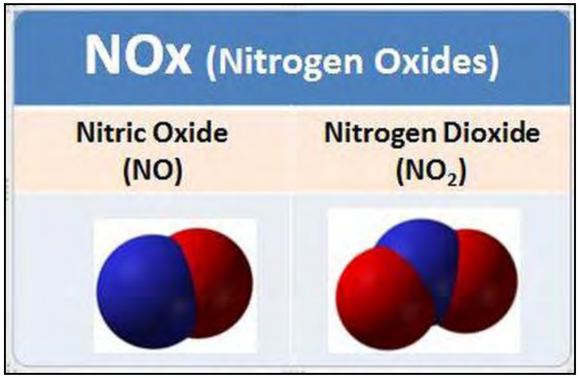
Porous structure = High surface area

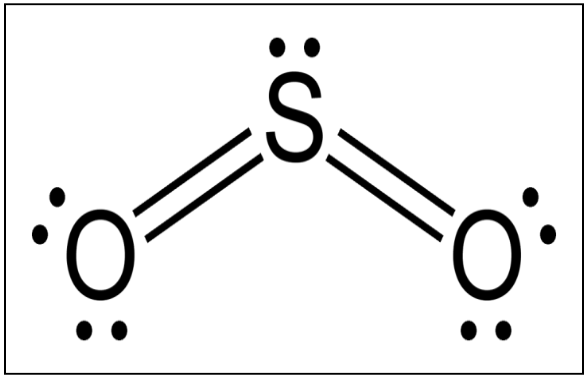


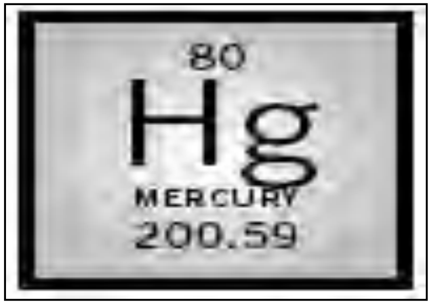
External & Internal diffusion of NH_3 into the pores and adsorption to the active sites, NO diffusion from gas phase to adsorbed NH_3, Reaction, Desorption of N_2 & H_2O, Diffusion of N_2 and H_2O

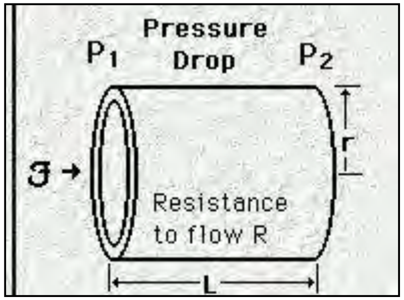
Catalyst Design – A Balancing Act

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









Equations Important to Catalyst Sizing

Area Velocity

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

Potential

$$P = \frac{kNOx}{AV}$$

Activity

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

Deactivation Rate

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

NH_3 to NO_x ratio

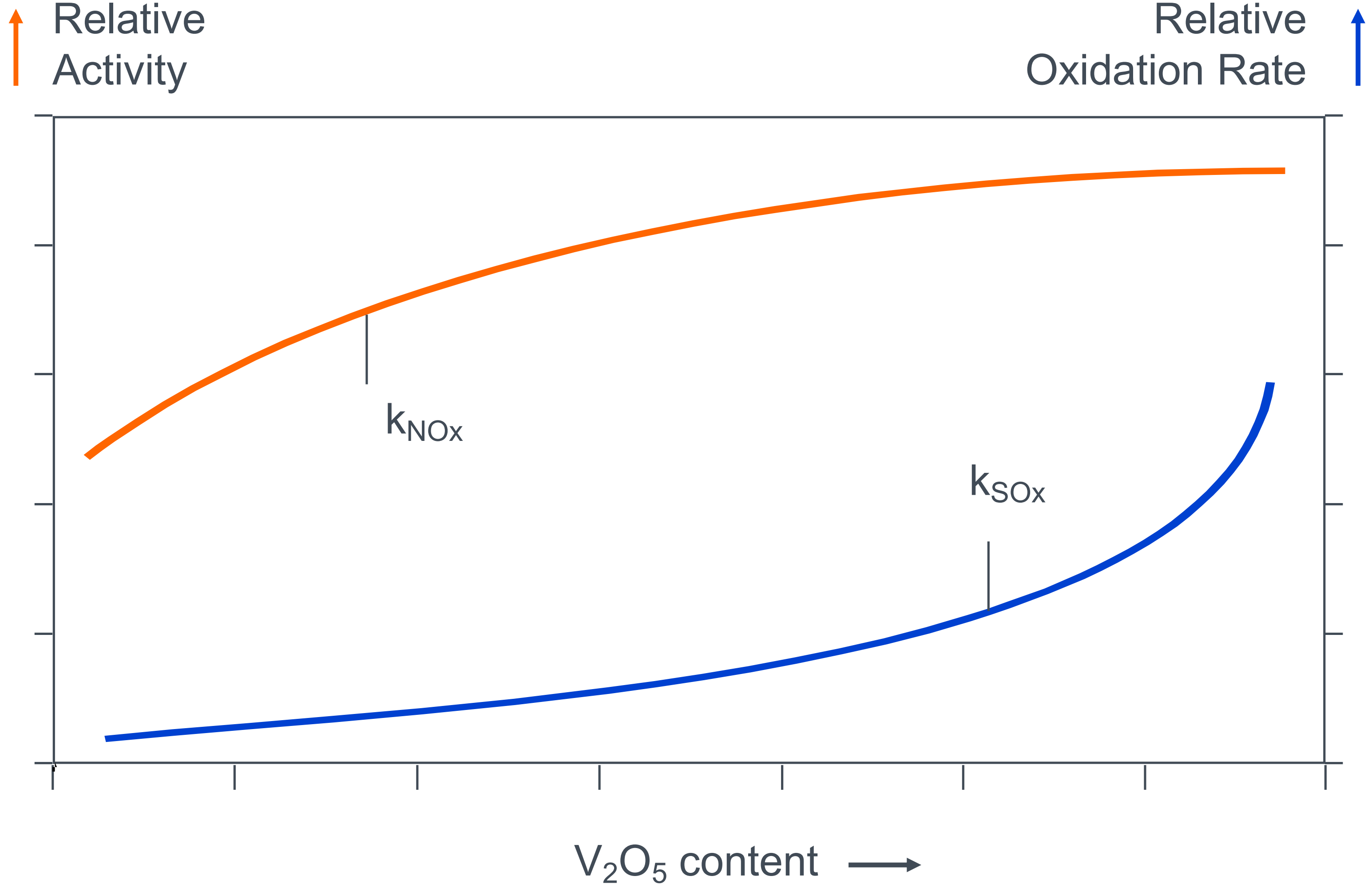
$$\alpha = \frac{NOx_{IN} - NOx_{OUT} + NH_{3\ OUT}}{NOx_{IN}}$$

End of Life Activity / Potential

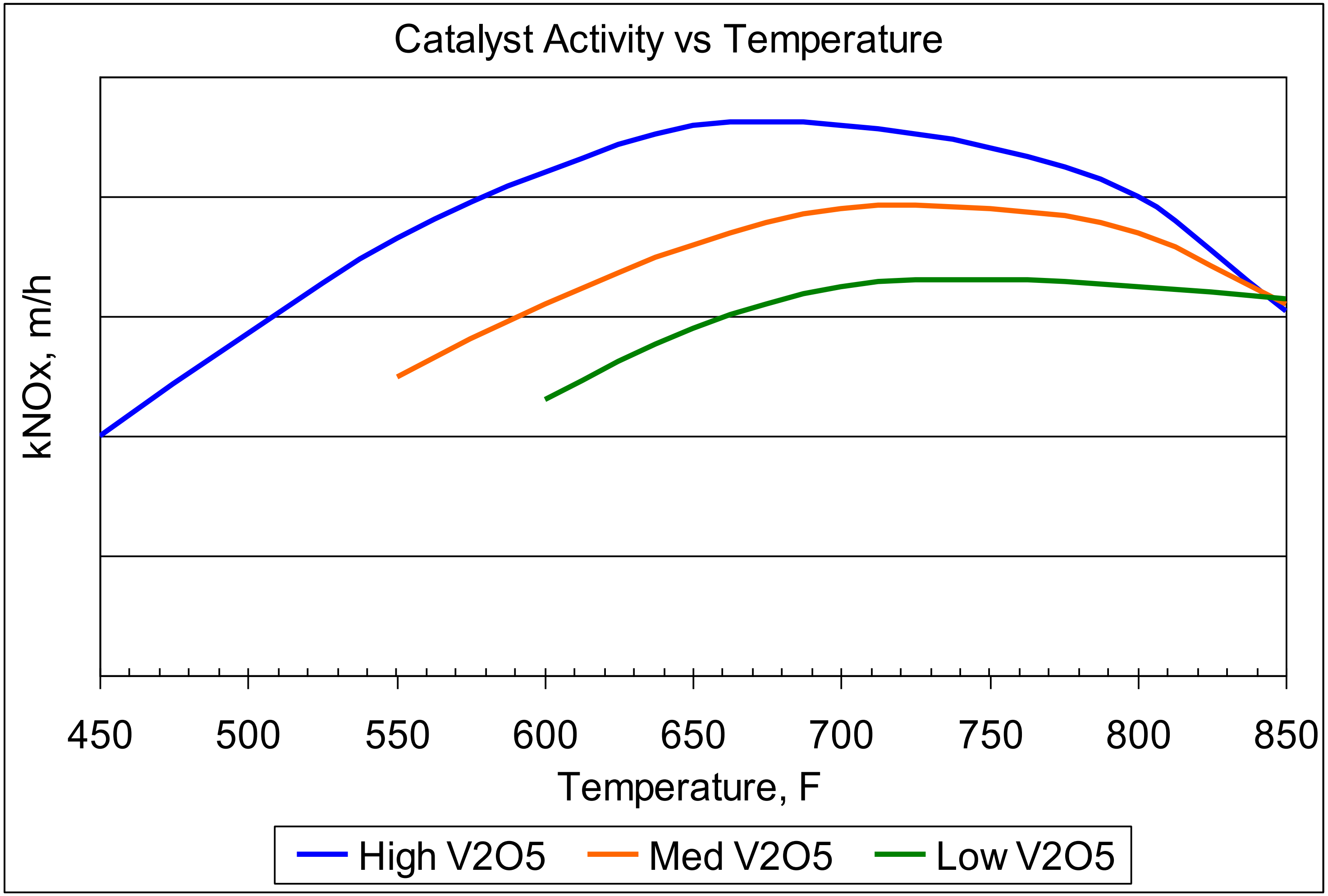
$$k_{EOL} = k_o * e^{-t\lambda}$$

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

Effects of V_2O_5



Effects of Temperature



K Summary

T, V_2O_5, H_2O, O_2, flow rate → k_0

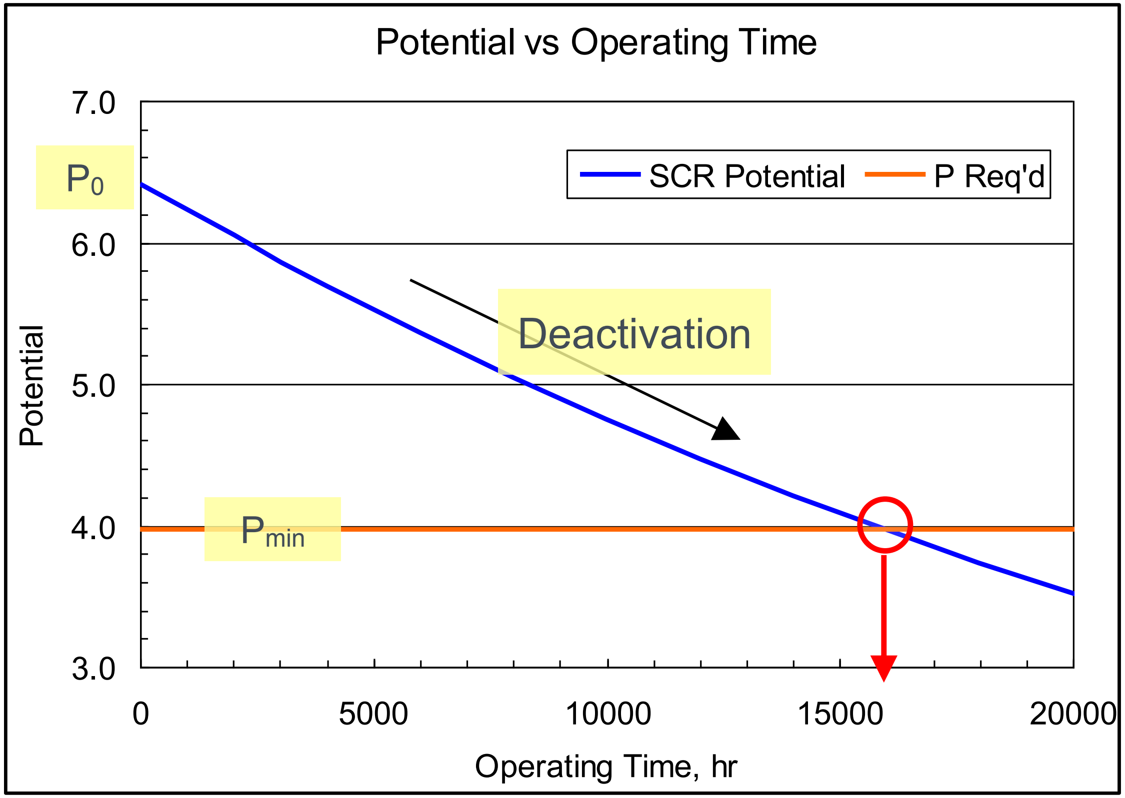
k_0 → Deactivation Model → $k_{t=EOL}$

Required Catalytic Potential for Specified NO_x Reduction Performance

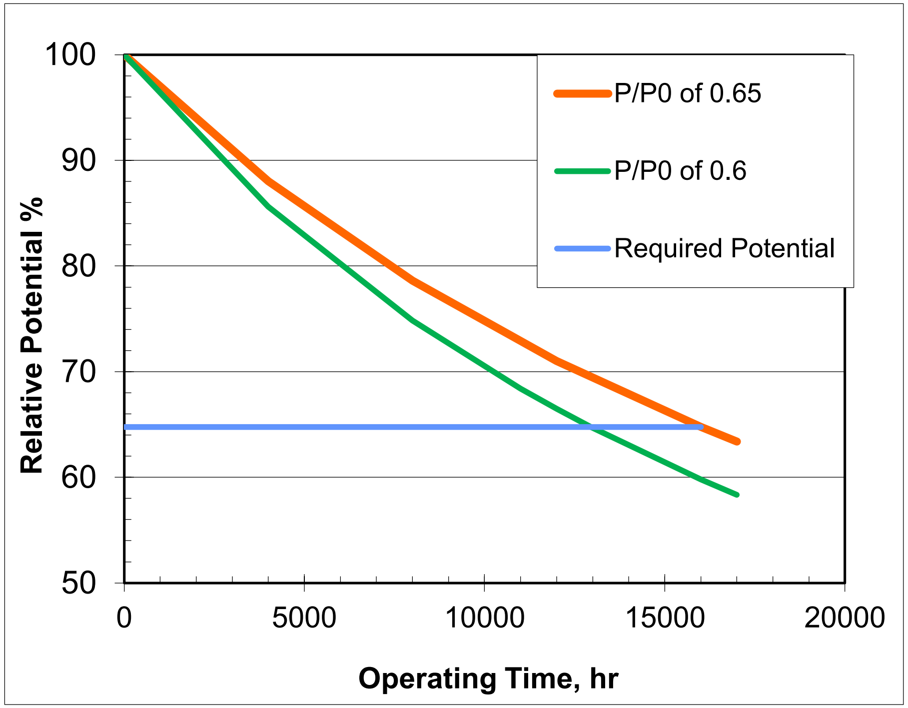
- Potential: measure of catalyst’s ability to reduce NO_x
- $P_{min} = ƒ(NO_{x\ in}, NO_{x\ out}, NH_3\ slip)$ – theoretical value
- Add margin for . . .
  - Mal-distributions of NH_3-NO_x mixing and flow
  - Unavailable catalyst surface due to channel plugging
  - Catalyst material lost to fly ash erosion

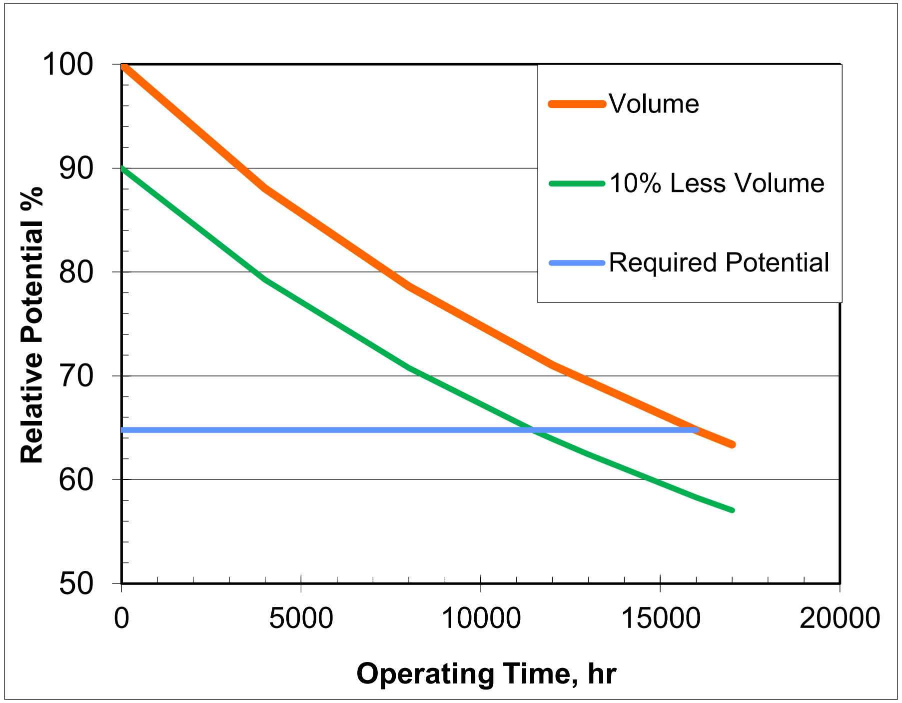
Deactivation Example

- 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: $P_0 = 6.4$



Impact of Catalyst Sizing Decisions





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

Catalyst Design and Mercury Oxidation

- Mercury emissions can exist in a variety of forms
  - Total – Hg^T includes Hg^0, Hg^{2+}, Hg^P
  - Hg^P – Particulate bound mercury
  - H^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

Ideal Operating Conditions

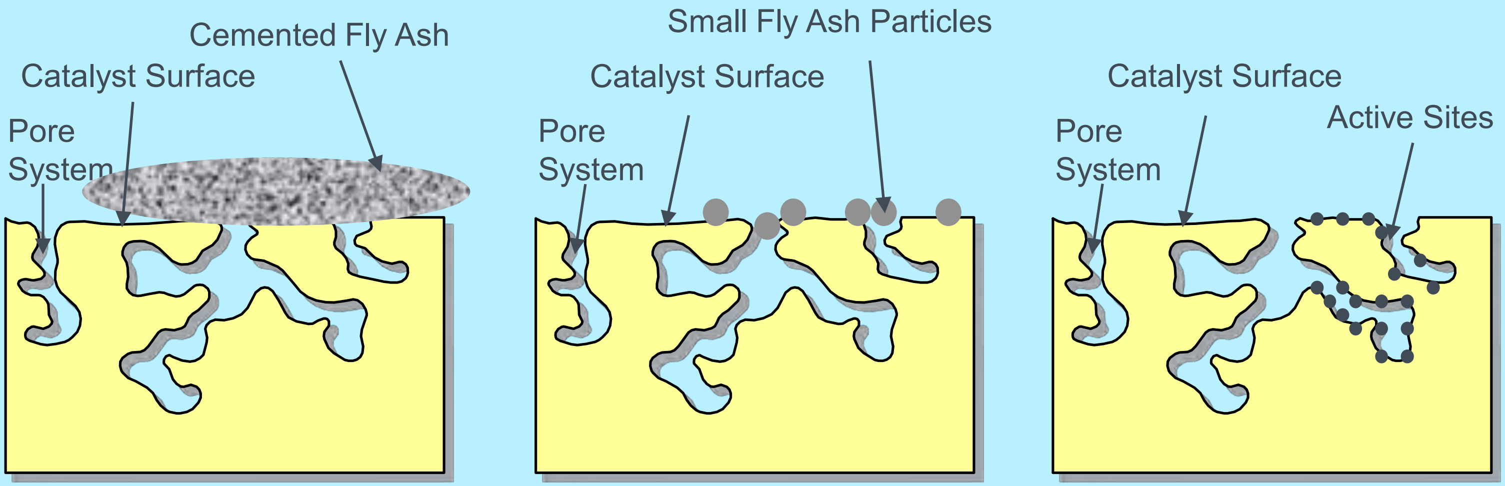
- Flue Gas Temperature: 650 – 750 °F (preferred)
- Flue gas linear flow velocity: 5.0 – 5.5 m/s (preferred)
- Thorough NH_3-NO_x mixing: 5% RMS (required for >85% deNOx)
- LPA screens upstream of catalyst (should be required)
- Soot-blowers or sonic horns (required)
- Even fly ash distribution, especially for low load operation

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



Poisons

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 Continuous Operating Temperature (MCOT)

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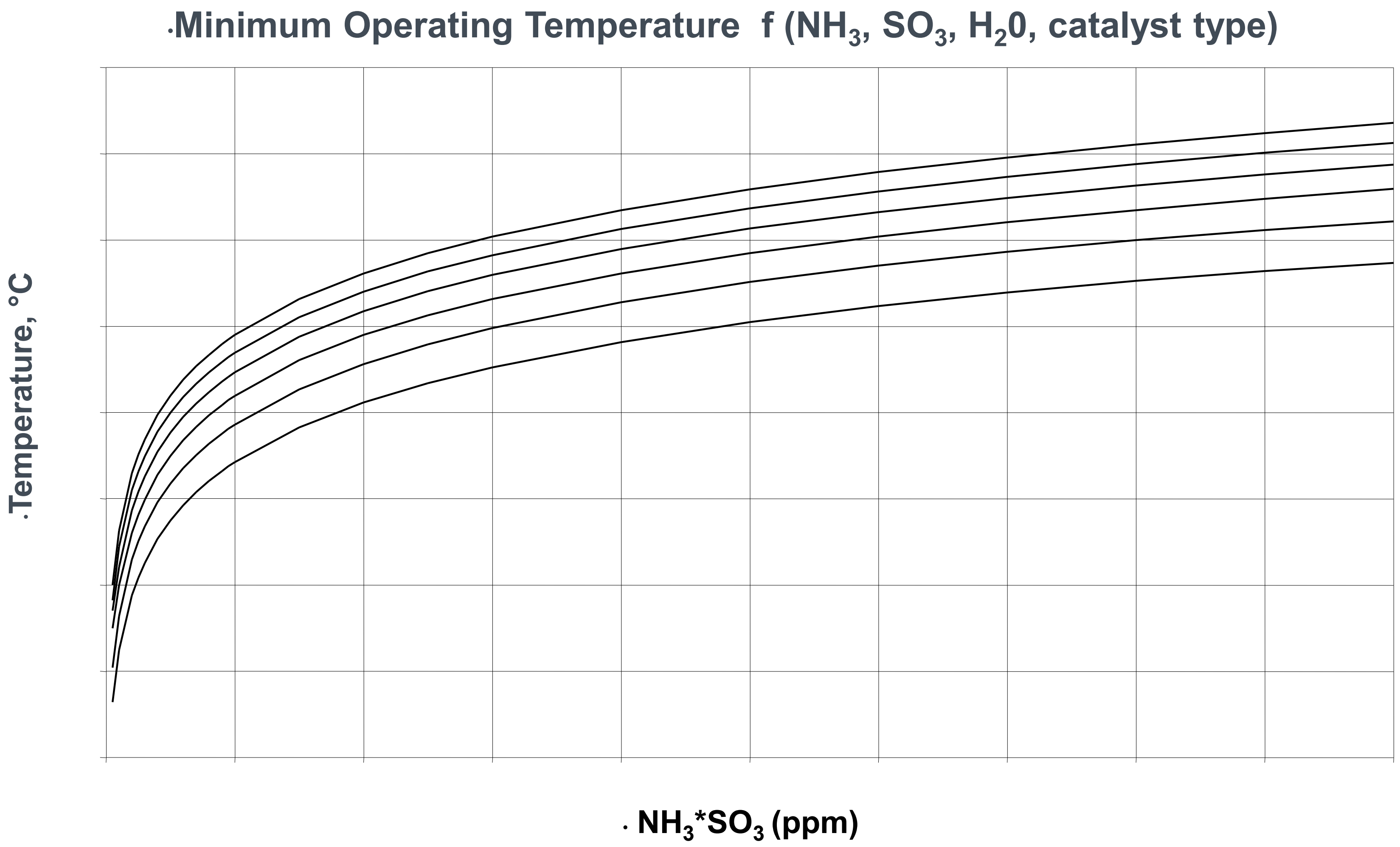


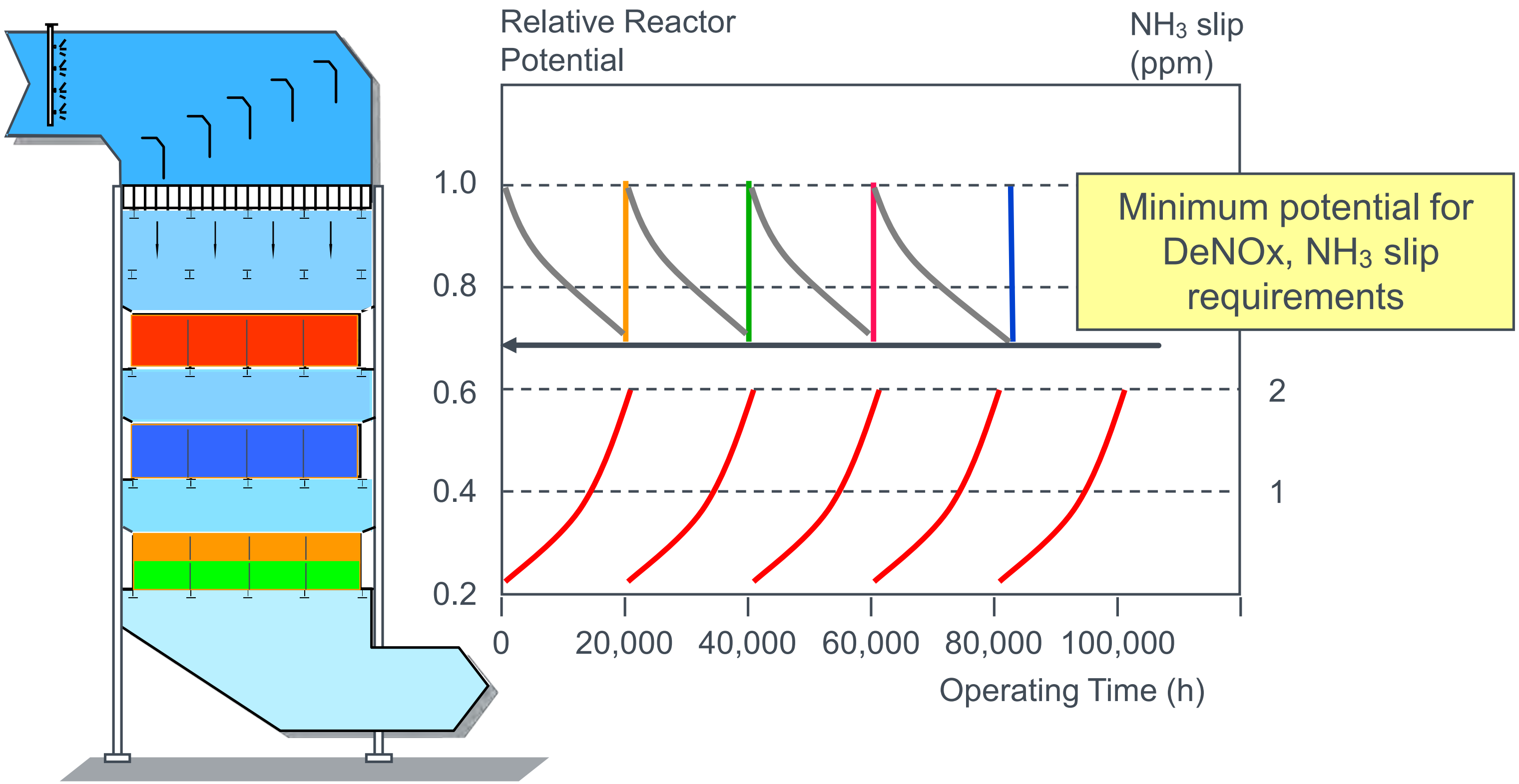
Ammonium Salts

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



Minimum potential for DeNOx, NH$_3$ slip requirements

Reload & 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