REINHOLD ENVIRONMENTAL Ltd.

2016 NOx-Combustion-CCR Round Table Presentation

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SCR Catalyst Management for Optimal NOx and Hg Emissions Control

Scott Rutherford

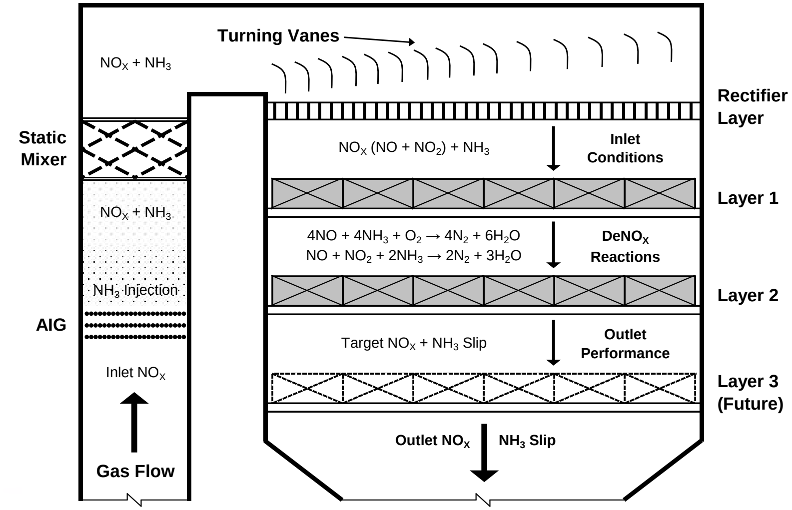
Chris Reeves

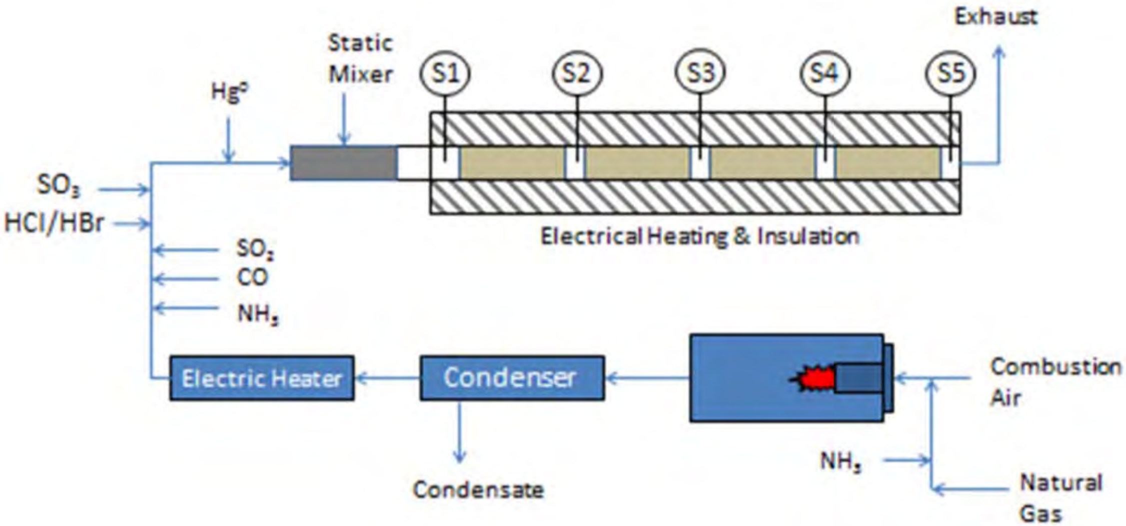
Cormetech, Inc.

Reinhold Conference, 2016

Presentation Outline

- **Catalyst Management**
  - Overview
  - Tools
  - Case Study





SCR Catalyst Functionality

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❑ Reduce NOx

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

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

❑ Minimize undesirable side reaction

$$2SO_2 + O_2 \rightarrow 2SO_3$$

❑ Oxidize elemental Hg

$$2Hg + 4HCl + O_2 \rightarrow 2HgCl_2 + 2H_2O$$

The SCR's Role in Hg Removal

Oxidize Hg for Downstream Capture!

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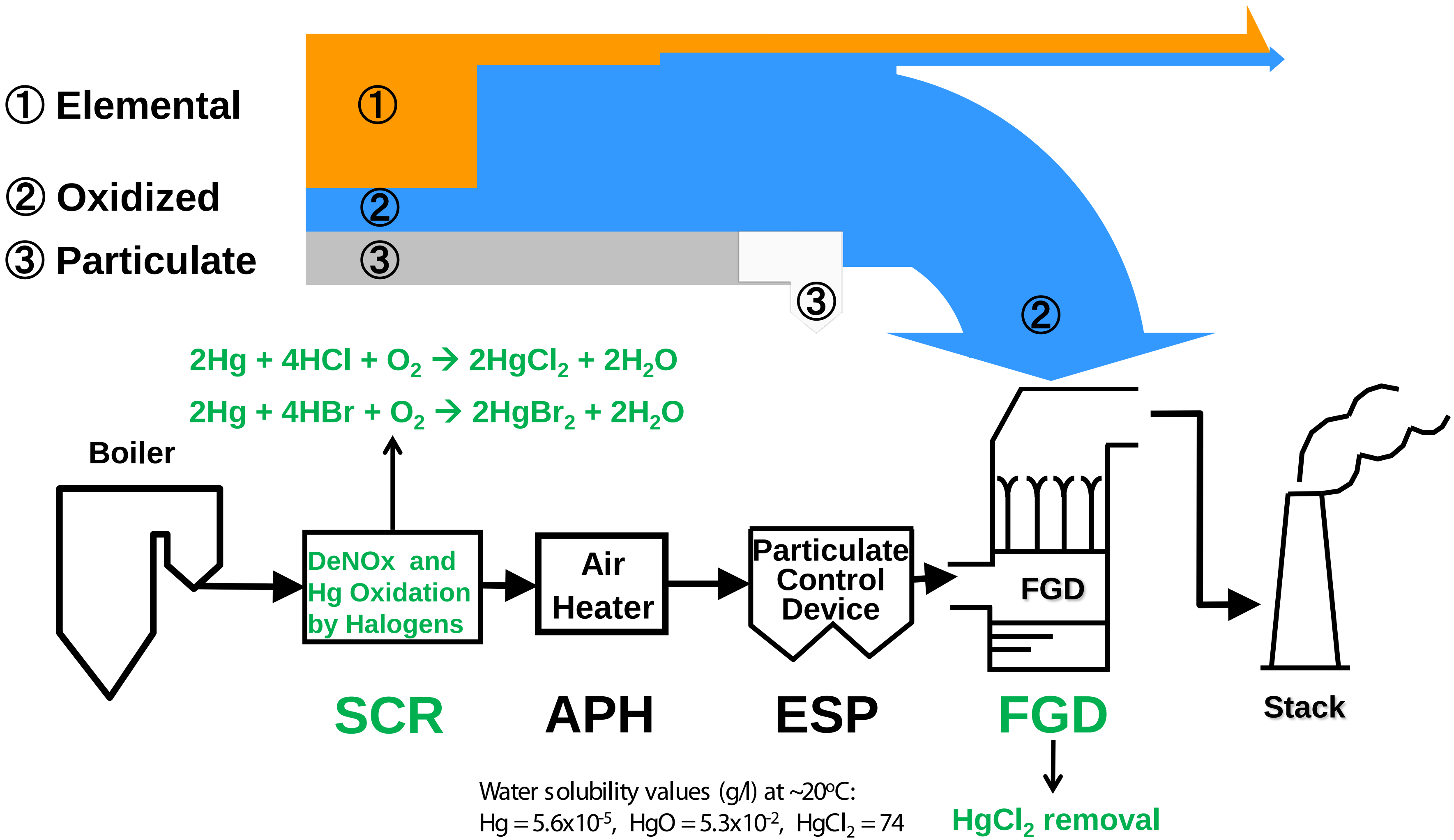
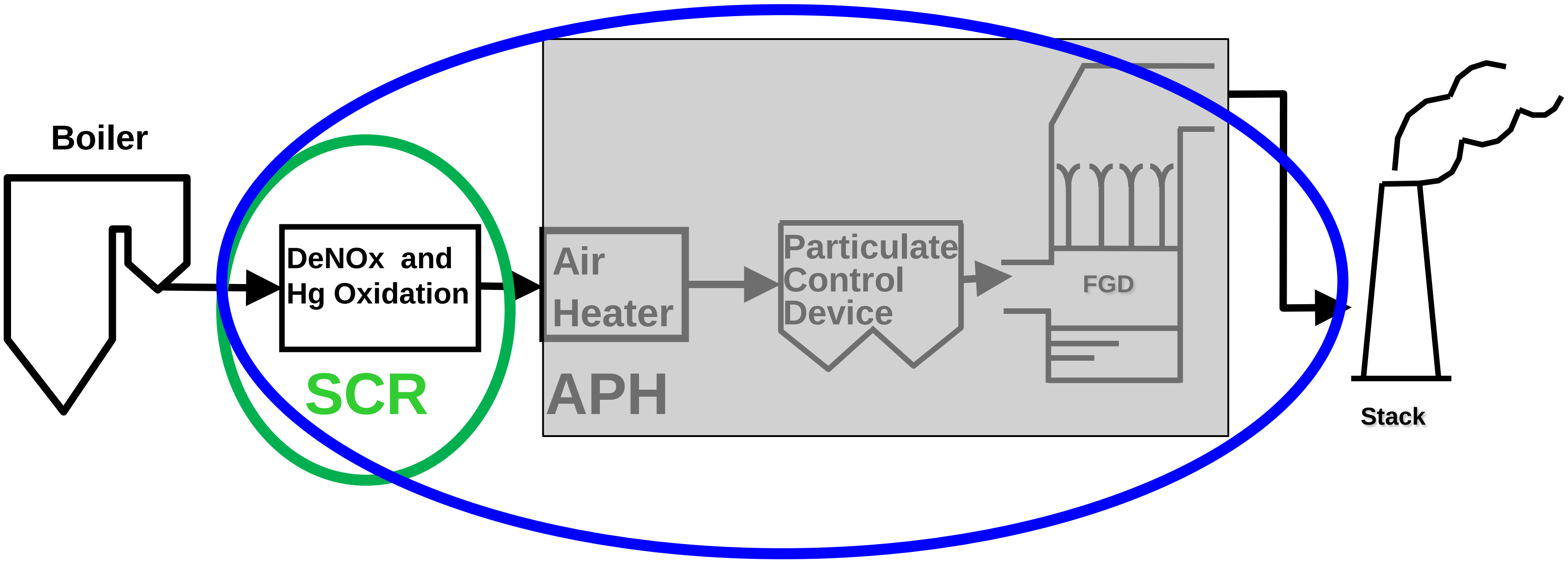


Water solubility values (g/l) at ~20°C:
Hg = 5.6×10^{-5}, HgO = 5.3×10^{-2}, $HgCl_2$ = 74

Key Differences for Hg vs. NOx

SCR is One Component of Overall System for Hg

- **DeNOx**
  - SCR Performance Requirements are well defined due to the dominant role of the SCR for NOx reduction
- **Hg**
  - Multiple systems may contribute to Hg control → SCR performance requirements are often not as well-defined yet may be essential for plant compliance



Catalyst Design Considerations

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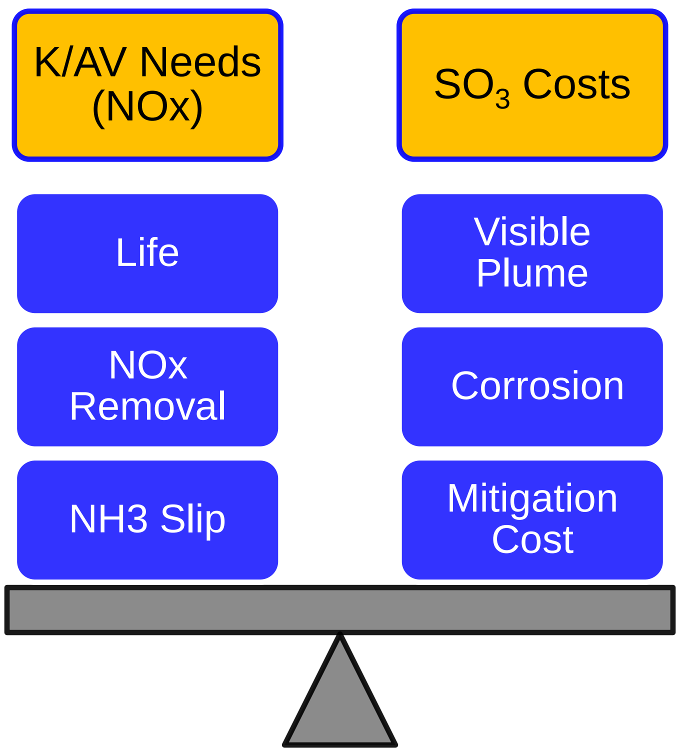
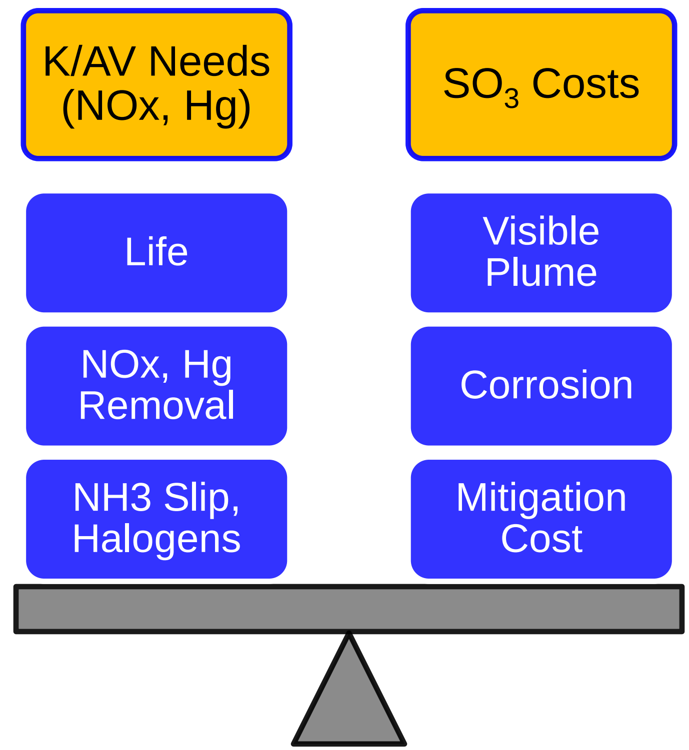
In Days Past:
Catalyst is formulated to achieve DeNOx requirements, while meeting SO_2 oxidation constraints.



Today:
Catalyst is formulated to achieve DeNOx and Hg oxidation requirements, while meeting SO_2 oxidation constraints.



Catalyst Design Considerations

NOx Removal

- Rate based or tonnage based?
- Stack based, plant based, fleet based?

Ammonia Slip

- TRI (Toxic Release Inventory)
- APH plugging
- Dust collection resistivity
- Ash sale criteria

SO_2 Oxidation

- Plume/Opacity
- Dust collection
- Cost of mitigation

Hg Oxidation

- May or may not drive design
- APC Equipment
- Halogens

Hg Control

Site Specific. Includes All or Some Components.

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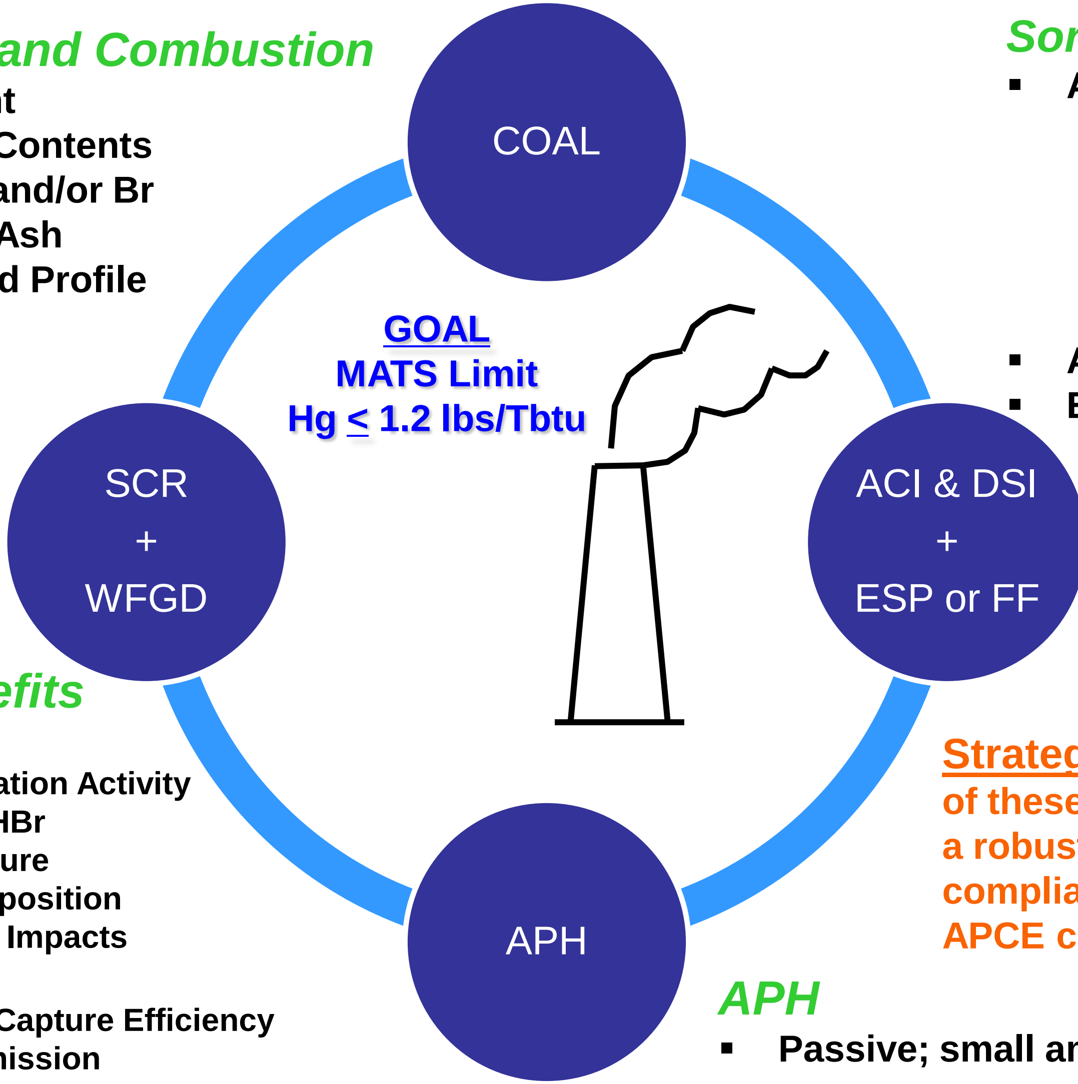
Coal Type and Combustion

- Hg Content
- Cl and Br Contents
- Added Cl and/or Br
- LOI in Fly Ash
- Boiler Load Profile

Sorbents + ESP or FF

- ACI (+ DSI):
  - Hg Capacity
  - Temperature
  - SO_3 Concentration
  - HCl and HBr
  - Sorbent Injection Rate
  - DSI for SO_3 Mitigation
- Amended Silicates
- ESP or FF:
  - ACI, DSI Capture
  - Ash Capture (Hg on LOI)



SCR Co-Benefits

- SCR:
  - Hg^0 Oxidation Activity
  - HCl and HBr
  - Temperature
  - Gas Composition
  - Seasonal Impacts
- WFGD:
  - Hg^{2+} Net Capture Efficiency
  - Hg^0 Reemission

Strategy: Utilize all or some of these components to deliver a robust control plan for MATS compliance. Currently installed APCE can influence selection.

APH

- Passive; small amount of Hg Oxidation

Catalyst Management - Field

- **Inspection/Maintenance**
  - **Catalyst**
  - **Ash Layout/Plugging**
  - **Ammonia Injection System**
  - **Ductwork**
  - **Expansion Joints**
  - **Cleaning Equipment**
- **Performance**
  - **Testing**
  - **NH_3 Balancing**
- **Manage Potential**
  - **DeNOx & Hg Oxidation**

Catalyst Potential, K/AV

DeNOx

$$\frac{K_{DeNOx}}{AV} = -\ln\left[1-\eta_{DeNox}\right]$$

$$\eta_{DeNOx} = \text{DeNOx efficency}$$

$$K = \text{DeNOx Activity}$$

Defined at MR=1.0

Independent of layer position

Hg Oxidation

$$\frac{K_{HgOx}}{AV} = -\ln\left[1-\eta_{HgOx}\right]$$

$$\eta_{HgOx} = \textit{fraction of } Hg^0 \textit{ oxidation}$$

$$K = \text{Hg Oxidation Activity}$$

Defined as simplified first order reaction

Highly dependent on conditions

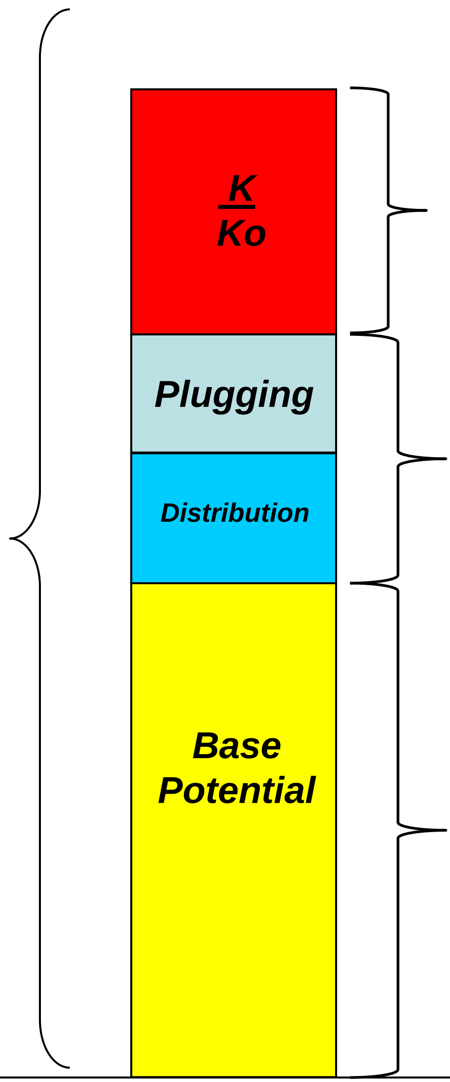
Dependent on layer position (NH_3 level)

Can change as layers above are replaced or deactivate

Breakdown of Design Potential

DeNOx Potential

Total Potential



Deactivation
- Fuel
- Operating Mode

Scale Up
- Plugging
- Maldistribution
  (NH_3, NOx, Velocity, etc.)

Performance Requirements
- % NOx removal
- Slip
- SO_2 Oxidation

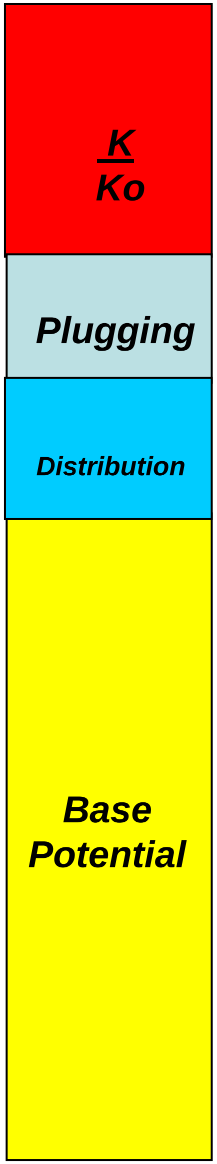
Flue Gas Conditions
- Inlet NOx
- Flow rate
- Temperature

Hg Oxidation Potential

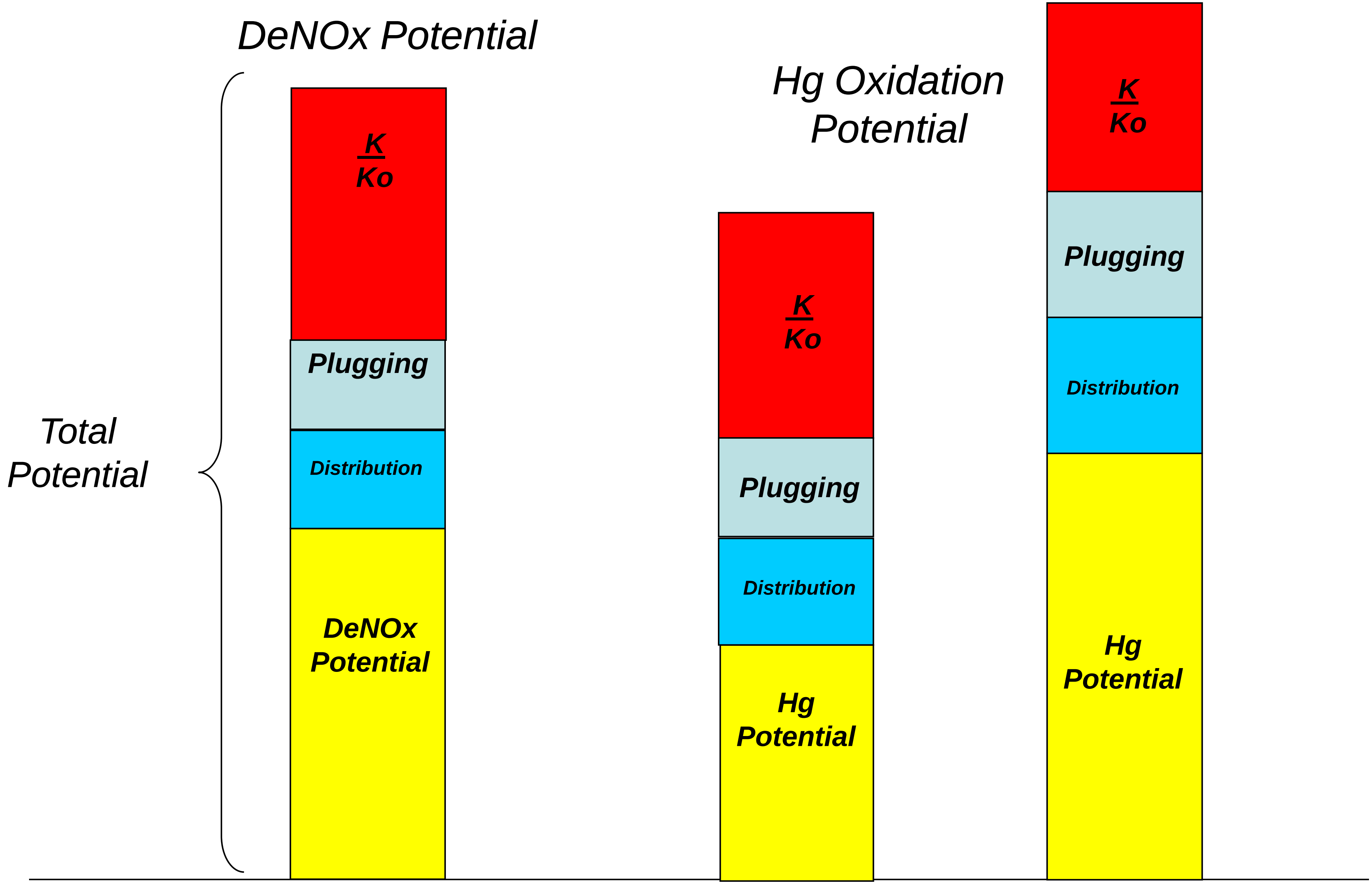
- *Catalyst type*
- *HCl level*
- *Layer position (NH_3)*
- *Temperature*
- *Not equivalent to DeNOx K/Ko*

- *SCR Hg Oxidation required*
- *Dependent on Hg in Coal*

- *HCl level in Coal*
- *Layer position (NH_3 level)*
- *DeNOx target (NH_3 level)*
- *Br addition*



Breakdown of Design Potential



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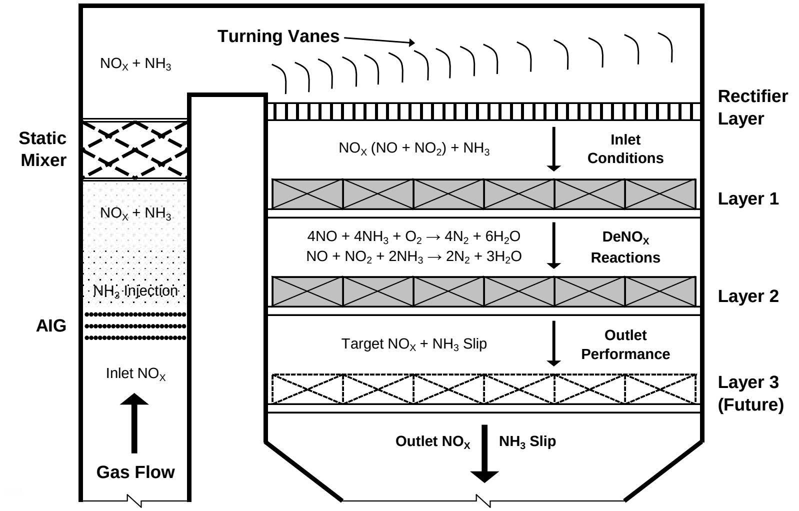
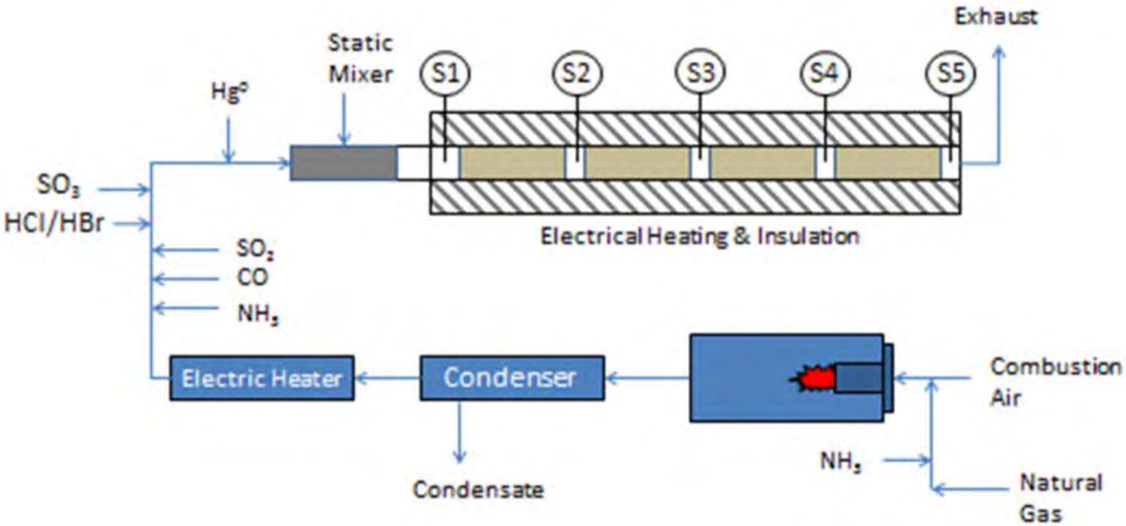
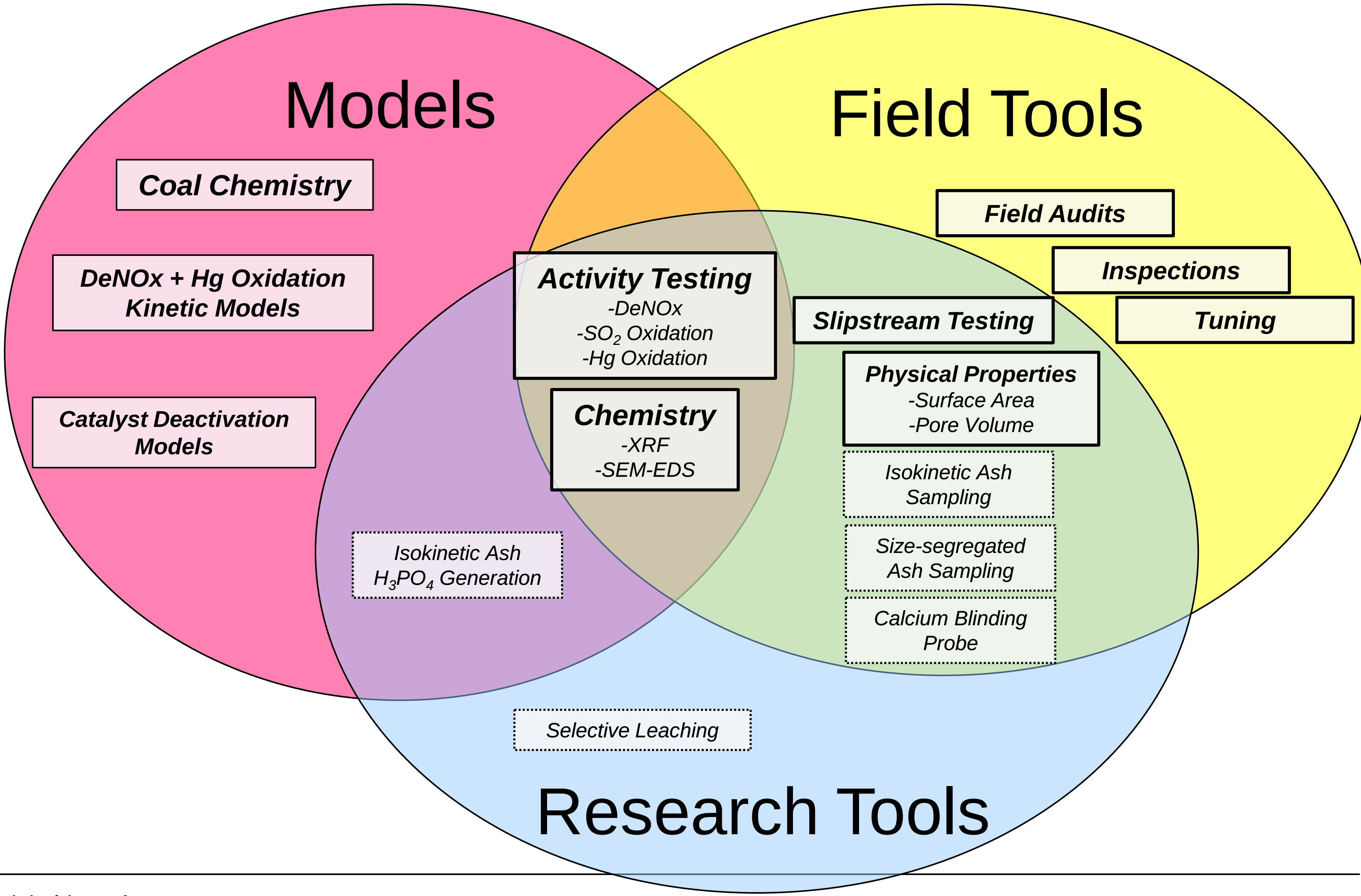
  - **Tools**
  - Case Study





Catalyst Management Tools



Measuring Catalyst Performance

- **Measure DeNOx**
  - Inlet and Outlet NOx: CEMS (Chemiluminescence)
  - NH_3 Slip: Wet Impinger/IC, FTIR
- **Measure SO2 Oxidation**
  - SO_2: CEMS (UV)
  - SO_3: Controlled condensation
- **Lab-scale catalytic reactors**
  - Micro reactor
  - Bench reactor
- **Field (full scale reactor)**
  - SCR inlet and outlet NOx measurements
    - Operating condition changes & transients
    - Representative sampling
  - Stack NOx measurements
    - Final system performance

Measuring Catalyst Performance

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- **Measure Hg^0 and Hg^{2+}**
  - CEMS
  - Sorbent traps
  - Ontario-Hydro
- **Lab-scale catalytic reactors**
  - Micro reactor
  - Bench reactor
- **Field (full scale reactor)**
  - SCR inlet and outlet measurements
    - Particulate challenge (high dust difficult to measure)
    - Operating condition changes & transients
    - Representative sampling
  - Stack measurements
    - Final system performance
    - SCR contribution combined

Reactor Test Capabilities

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Semi-Bench

DeNox Activity(gas)
High NO2
DP
CO Oxidation

Full Bench

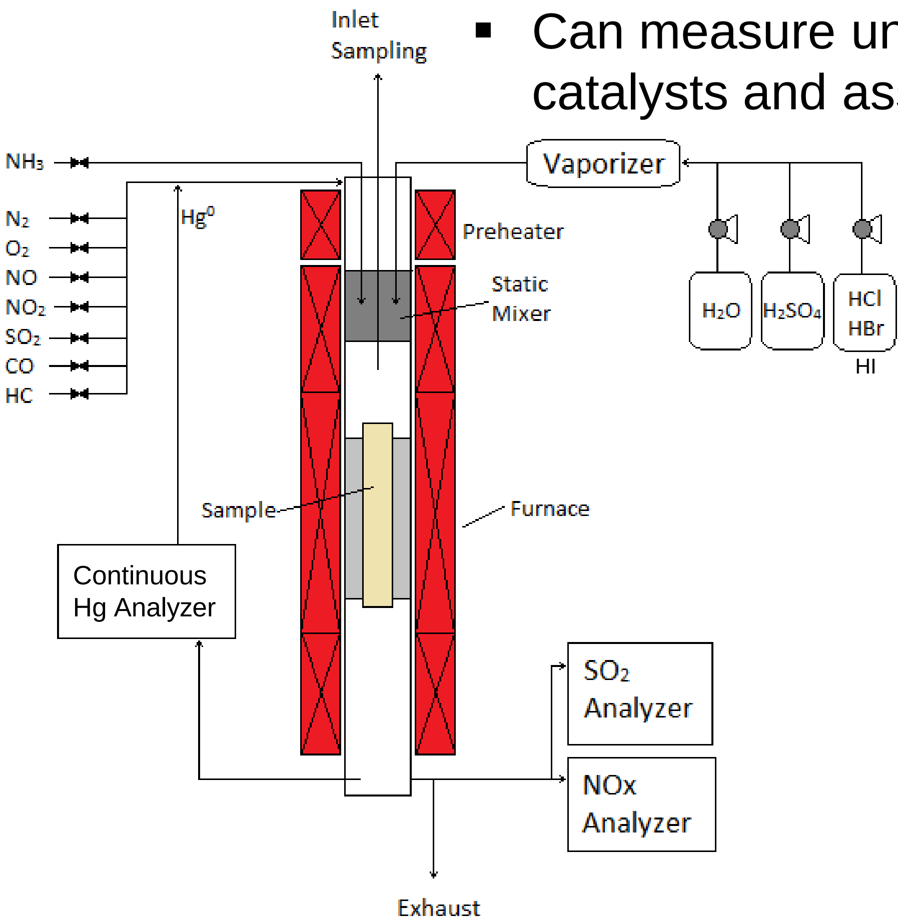
DeNox Activity (gas/coal)
SO2 Oxidation
DP
Mercury Oxidation

Micro

DeNox Activity (gas/coal)
SO2 Oxidation
Mercury Oxidation
CO Oxidation
High NO2

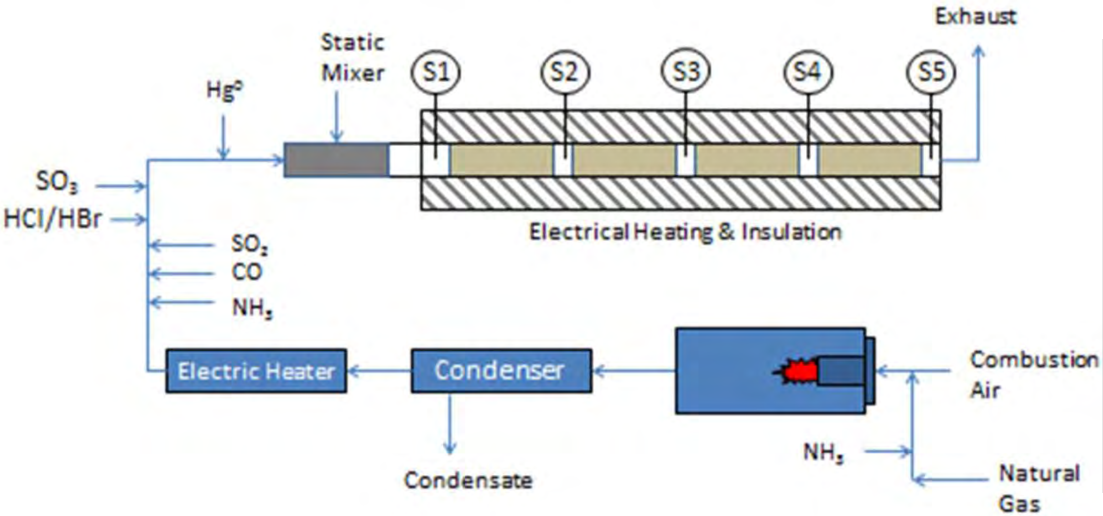
Micro Reactor

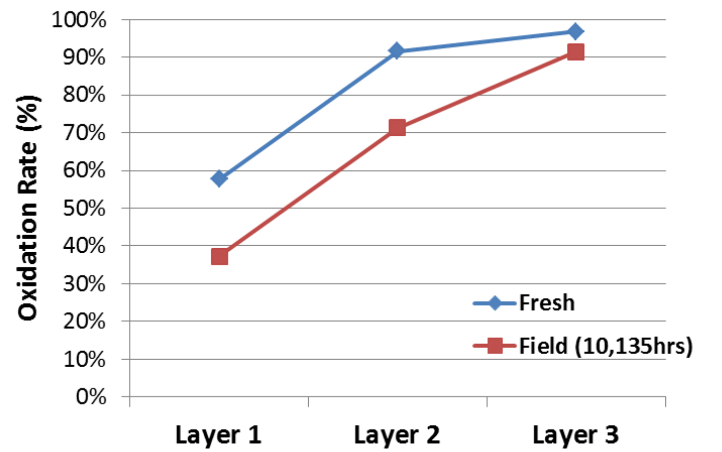
- Example shown is fully-automated for efficient data collection.
  - Well suited for parametric studies
  - Can measure under a full range of conditions to develop catalysts and assist with management strategies.



Bench Reactor

- **Bench is well-suited for field audit testing**
  - **Full size element (Full cross-section, Full length)**
    - Catalyst poisons not evenly distributed throughout log.
  - **Multi-layer system test**
    - System and individual layer performance in a single test
- Can test honeycomb, plate, corrugated (or any combination).
- Full range of flue gas conditions including HCl and HBr injection.





Factors Impacting DeNOx and SO_2 Oxidation

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Factor	DeNOx Correlation with Increasing Factor Value	Note
Temperature	↑	
O_2	↑	
H_2O	↓	
SO_2/SO_3	↑	
Catalyst V_2O_5	↑	SO2 to SO3 conversion limits formulation

Factor	SO_2 Oxidation Correlation with Increasing Factor Value	Note
Temperature	↑	
O_2	↑	
Inlet SO_3	↓	
NH_3	↓	
Catalyst V_2O_5	↑	SO2 to SO3 conversion limits formulation

Factor Impacting Hg Oxidation
Positive Correlations

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Factor	Hg Oxidation Correlation with Increasing Factor Value	Note
HCl	↑	Strong interdependence with T and concentration
HBr	↑	Strong interdependence with T and concentration
HI	↑	Strong interdependence with T and concentration
O_2	↑	
Catalyst surface area	↑	Determined by layer length and Ap/pitch selection
Catalyst V_2O_5	↑	
Advanced catalysts	↑	Improve Hg ox at constant DeNOx and SO_2 ox
Hg^0	O	No impact: kinetics are first order in Hg^0

Factor Impacting Hg Oxidation
Negative Correlations

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Factor	Hg Oxidation Correlation with Increasing Factor Value	Note
Hg^{2+}	○ ↓	Impact depends on re-reduction activity
Temperature	↓	Strong interdependence with HCl, HBr, NH_3, catalyst
NH_3	↓	Strong interdependence with T, HCl, HBr, catalyst
NO	↓	Impact is cross-correlated through NH_3
H_2O	↓	
SO_2	↓	
SO_3	↓	
CO	↓	Strong interdependence with T, HCl, HBr, catalyst
Hydrocarbons	↓	
Catalyst Age	↓	Strong interdependence with catalyst type

SCR Hg Mass Balance

- **At the SCR inlet, Hg is present in three forms:**

$$Hg_{in}^{total} = Hg_{in}^{0} + Hg_{in}^{2+} + Hg_{in}^{particulate}$$

Particulate Hg is not affected by the SCR

- **Hg mass balance across SCR (at steady state):**

$$Hg_{in}^{0} + Hg_{in}^{2+} = Hg_{out}^{0} + Hg_{out}^{2+}$$

$$2Hg + 4HCl + O_2 \rightarrow 2HgCl_2 + 2H_2O$$

- **Quantify Hg oxidation by the SCR:**

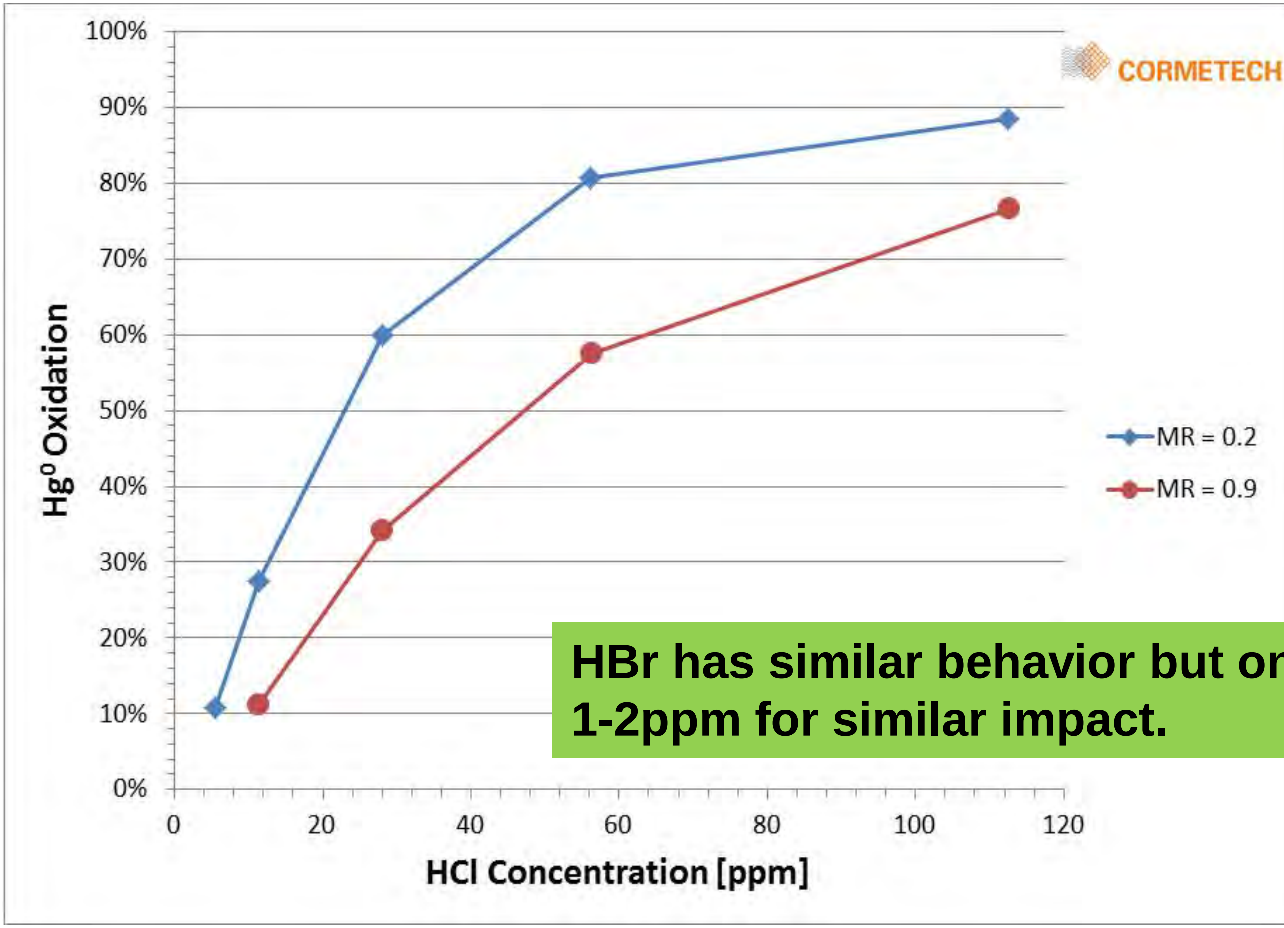
$$\eta_{HgOx} = \frac{Hg_{in}^{0} - Hg_{out}^{0}}{Hg_{in}^{0}}$$

$$\%\ Oxidized = \frac{Hg_{out}^{2+}}{Hg_{out}^{0} + Hg_{out}^{2+}}$$

Impact of HCl and NH_3

Hg Oxidation Activity

The kinetic data are consistent with a mechanism where HCl adsorbs on the catalyst. NH_3 can significantly inhibit Hg oxidation activity.



HBr has similar behavior but only takes 1-2ppm for similar impact.

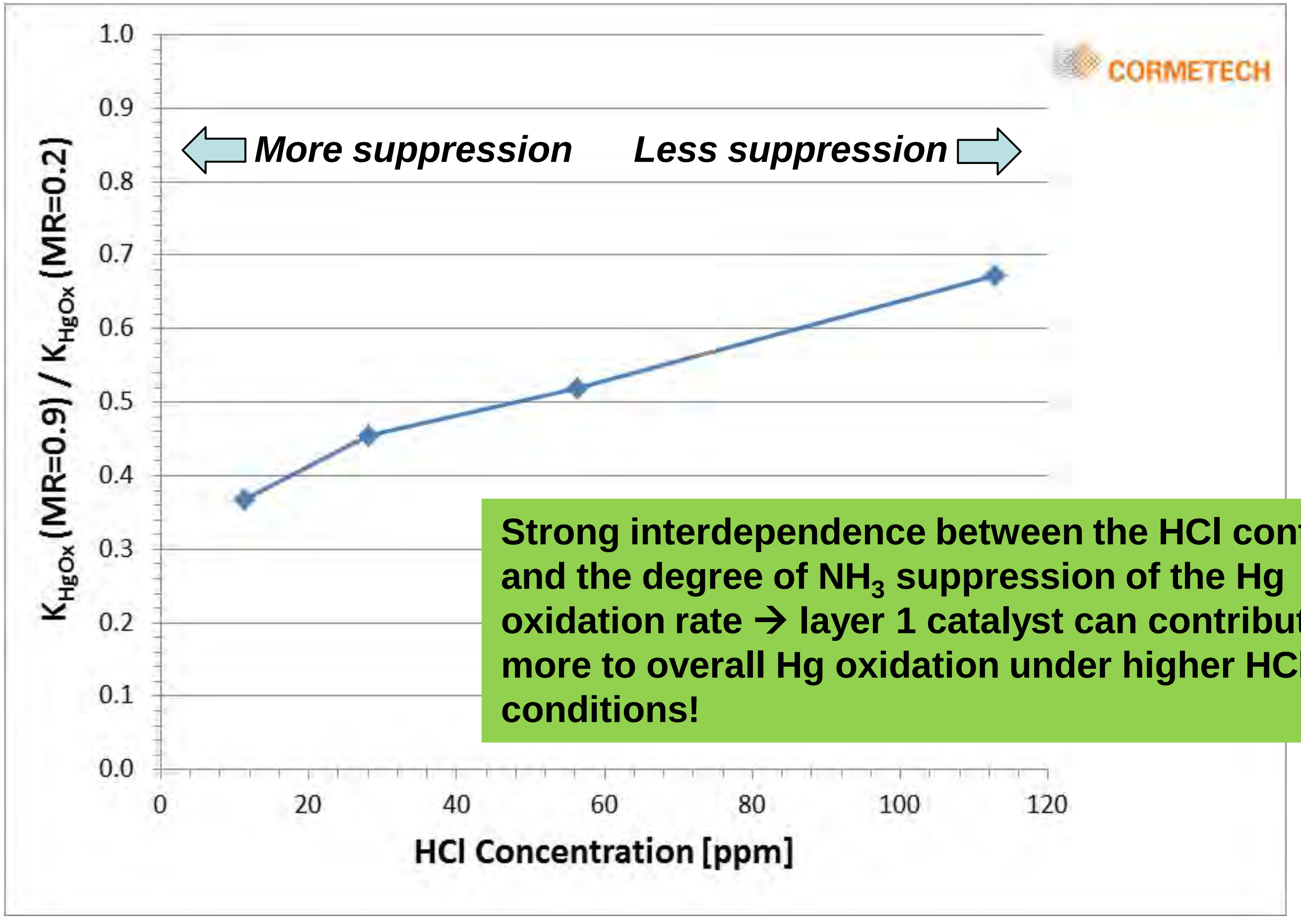
400°C, 3.5% O_2, 11% H_2O, 350 ppm NO, 1000 ppm SO_2, 10 ppm SO_3, 100 ppm CO; MR = Inlet Molar Ratio

Impact of HCl on NH_3 Inhibition

Hg Oxidation Activity

There is a strong Interdependence between the HCl concentration and the degree of NH_3 suppression of the Hg oxidation rate.

K ratio on y-axis!



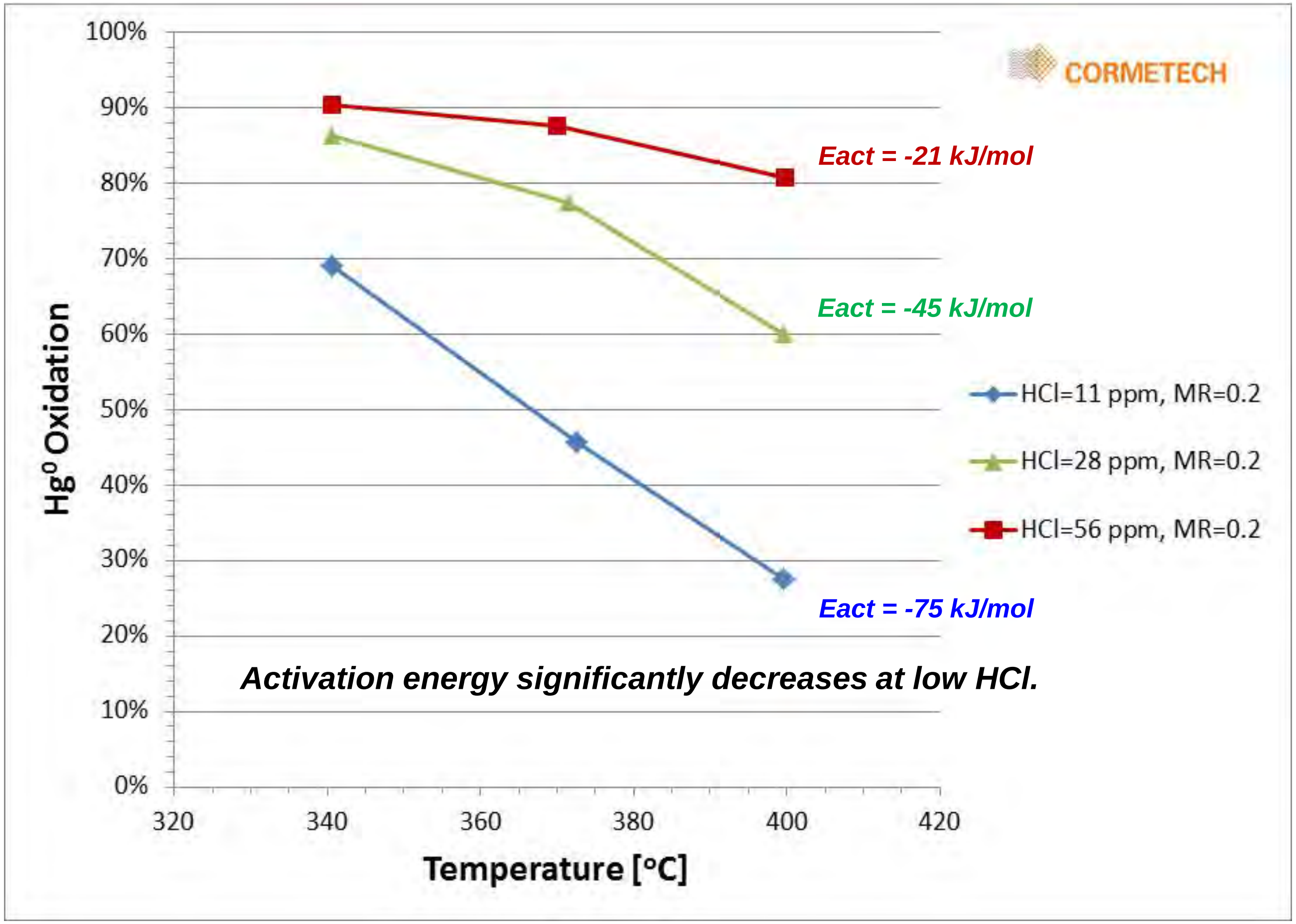
Strong interdependence between the HCl content and the degree of NH_3 suppression of the Hg oxidation rate → layer 1 catalyst can contribute more to overall Hg oxidation under higher HCl conditions!

400ºC, 3.5% O_2, 11% H_2O, 350 ppm NO, 1000 ppm SO_2, 10 ppm SO_3, 100 ppm CO; MR = Inlet Molar Ratio

Impact of Temperature (MR=0.2)

Hg Oxidation Activity

Listed activation energy values are for the overall Hg oxidation reaction. Values are negative because the rate decreases as temperature increases.

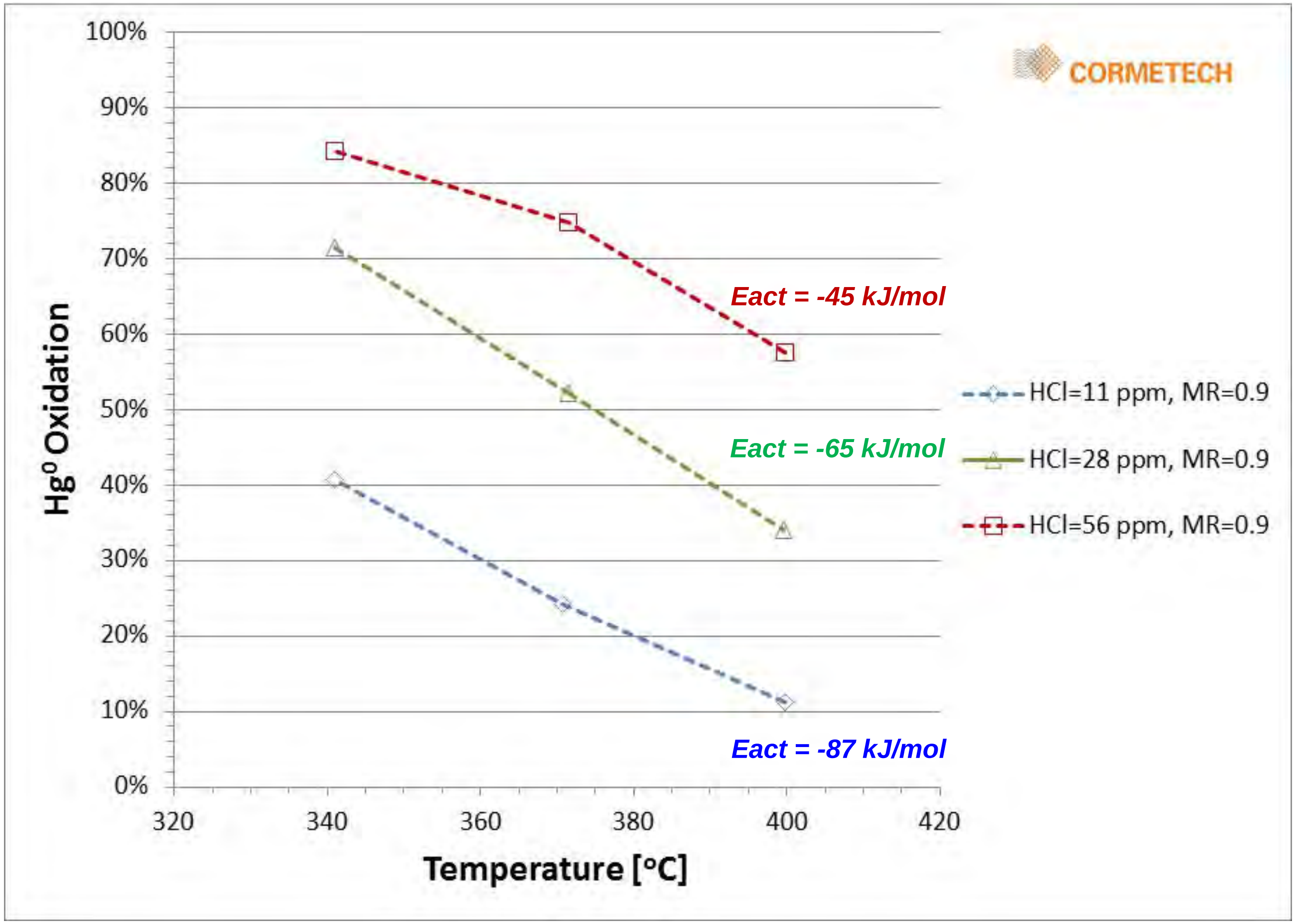


3.5% O_2, 11% H_2O, 350 ppm NO, 1000 ppm SO_2, 10 ppm SO_3, 100 ppm CO; MR = Inlet Molar Ratio

Impact of Temperature (MR=0.9)

Hg Oxidation Activity

With high inlet NH_3, the activation energy decreases for constant HCl, which indicates that NH_3 inhibition can become more pronounced at high temperature.

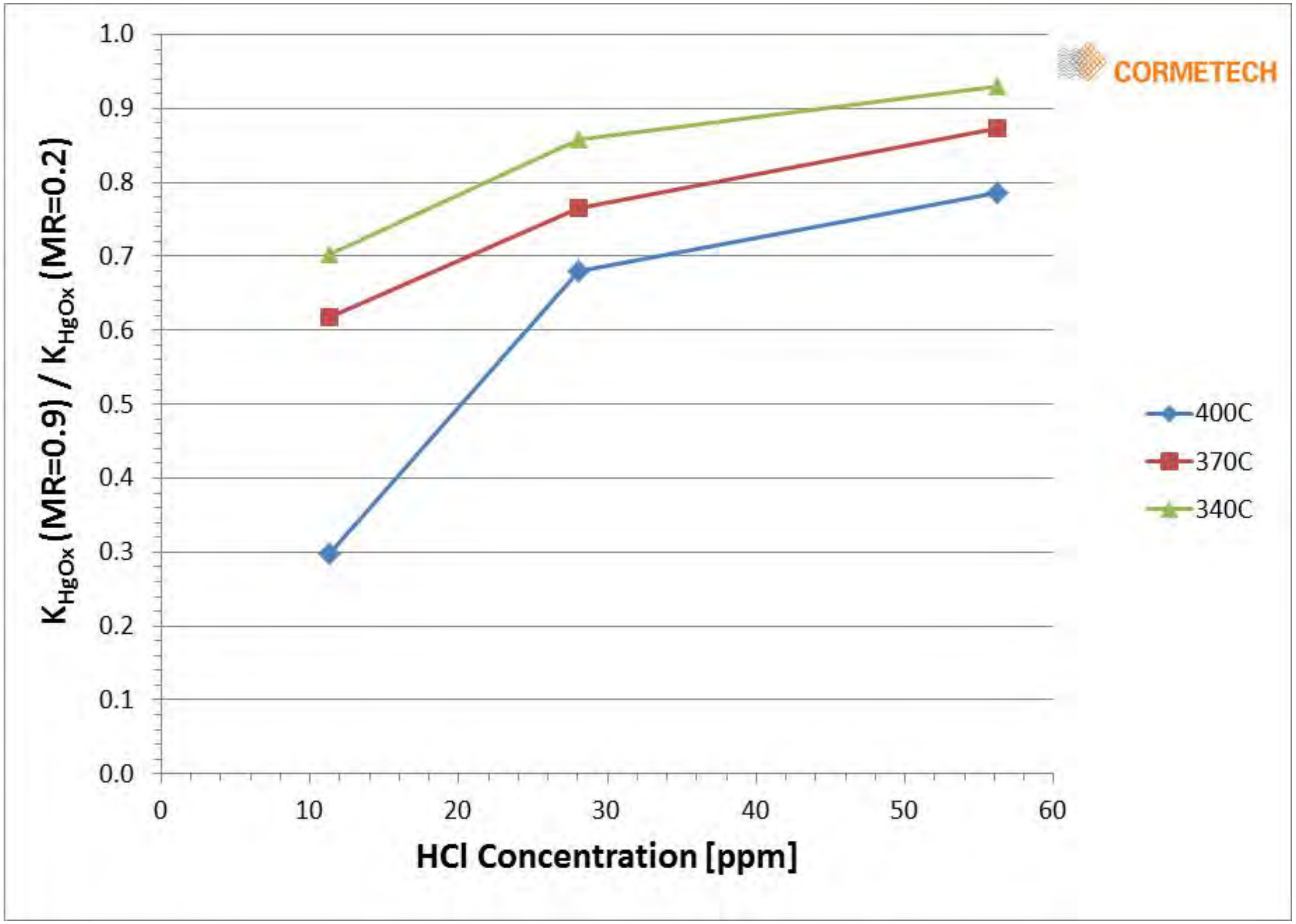


3.5% O_2, 11% H_2O, 350 ppm NO, 1000 ppm SO_2, 10 ppm SO_3, 100 ppm CO; MR = Inlet Molar Ratio

Impact of Temperature

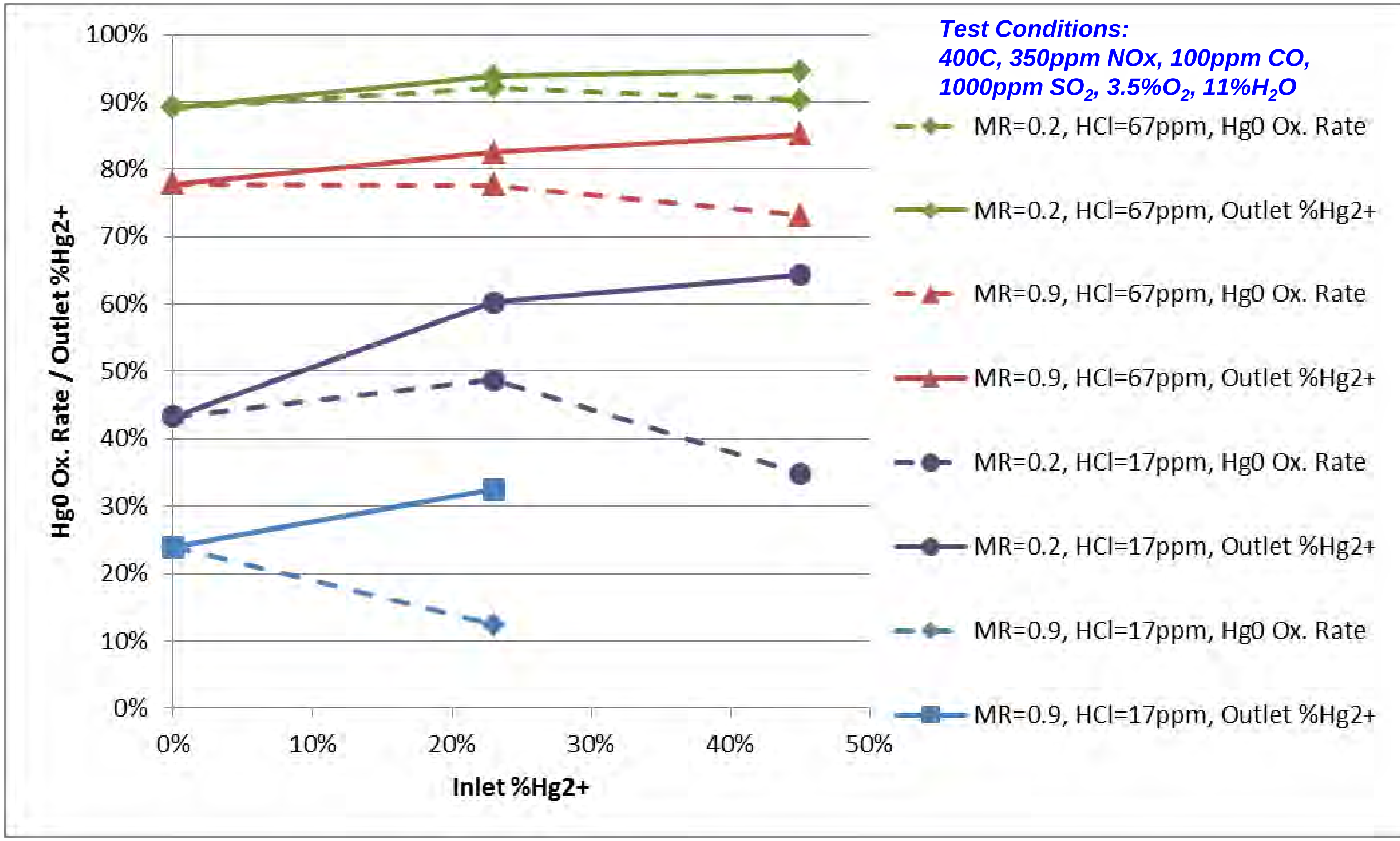
Hg Oxidation Activity

Increasing HCl can reduce the amount of NH_3 suppression across the temperature range.



3.5% O_2, 11% H_2O, 350 ppm NO, 1000 ppm SO_2, 10 ppm SO_3, 100 ppm CO; MR = Inlet Molar Ratio

Impact of Inlet Hg^{2+}



- Higher inlet Hg^{2+} reduces the Hg^0 oxidation rate due to reverse reactions.
- Highest impact will be at high temperatures, in the presence of reducing agents (NH_3, CO, SO_2), and lower HCl
- Testing at low inlet Hg2+ relative to the field condition should give a conservative measurement of outlet %Hg2+.

Advanced Catalyst

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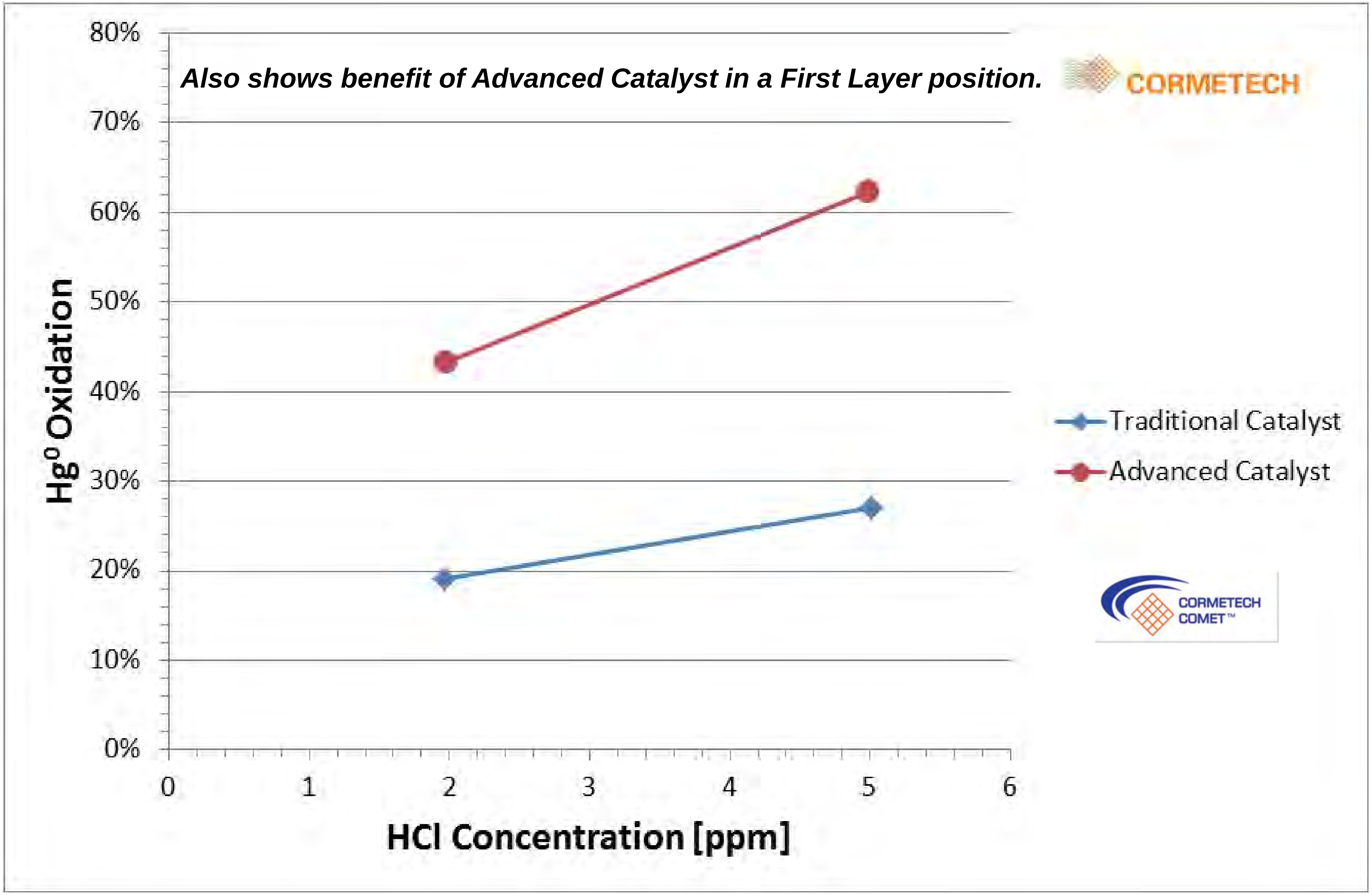
- **Depending on your SCR Hg oxidation requirement traditional catalyst may be able to meet your needs.**
- **But, for challenging conditions, such as…**
  - Lower HCl, and/or
  - Higher temperature, and/or
  - Higher concentration of reducing agents (NH_3, CO, SO_2)
- **…we can modify catalyst formulation and processing to improve Hg oxidation relative to DeNOx and SO_2 oxidation**

Advanced Catalyst: Low HCl



370°C, 250 ppm NO, 0.9 MR, 4% O_2, 14% H_2O, 400 ppm SO_2, 4 ppm SO_3, 100 ppm CO

Advanced Catalyst: NH_3 Impact

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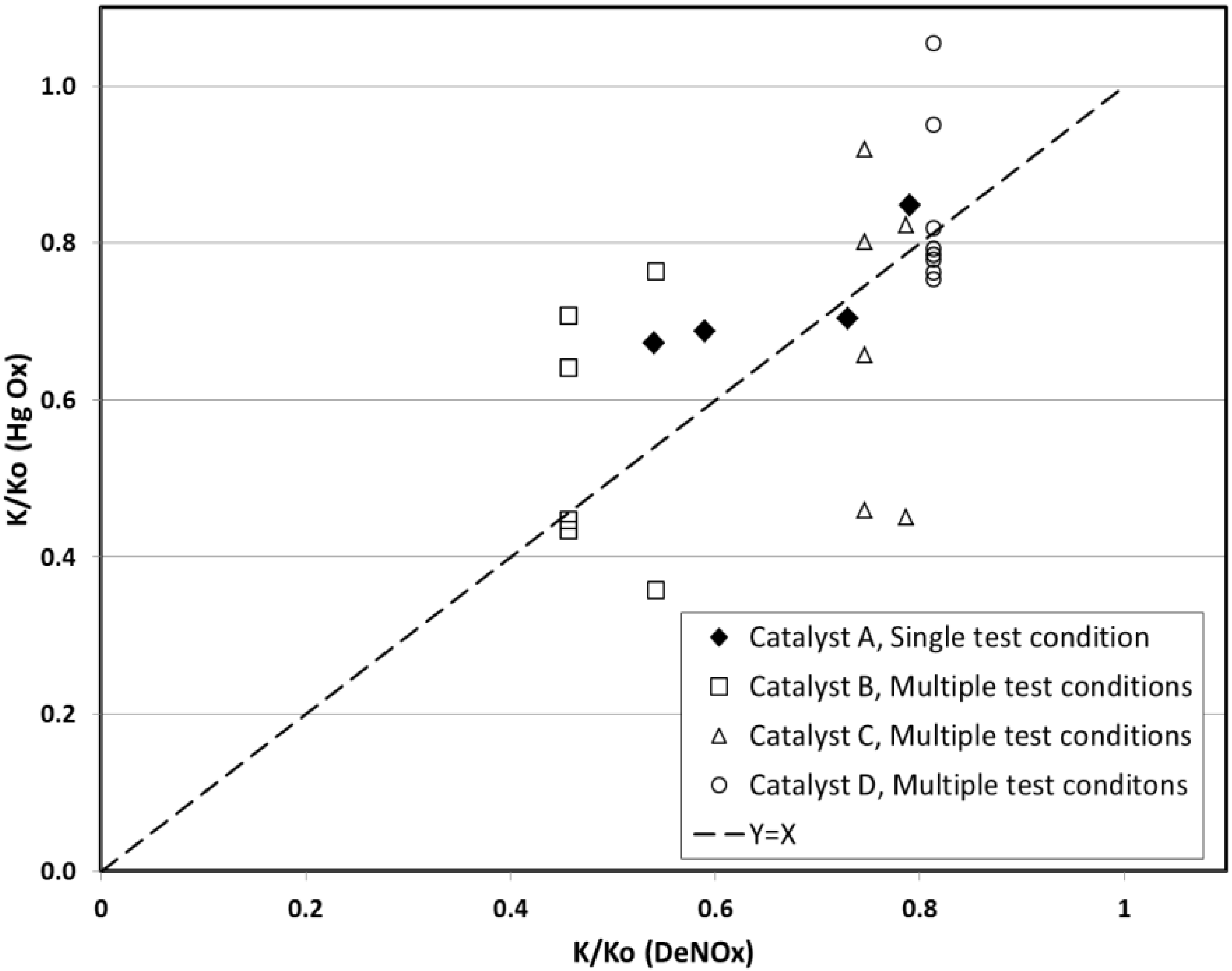
Advanced Catalyst also has a performance benefit in the First Layer position for higher HCl cases.

Single Layer Performance Example					
Position	**Case**	**MR**	**HCl [ppm]**	**Layer Hg Ox**	**Hg Ox Delta Advanced vs. Traditional**
Layer 1	Traditional Catalyst	1.0	58	53%	
Layer 1	Advanced Catalyst	1.0	58	72%	18%

371°C, 305 ppm NO, 1.0 MR, 4.3% O_2, 8.5% H_2O, 850 ppm SO_2, 8 ppm SO_3, 100 ppm CO.

COMET™ catalyst can significantly improve Hg oxidation in the upper layers of the SCR

Catalyst Deactivation
Correlation with DeNOx Deactivation

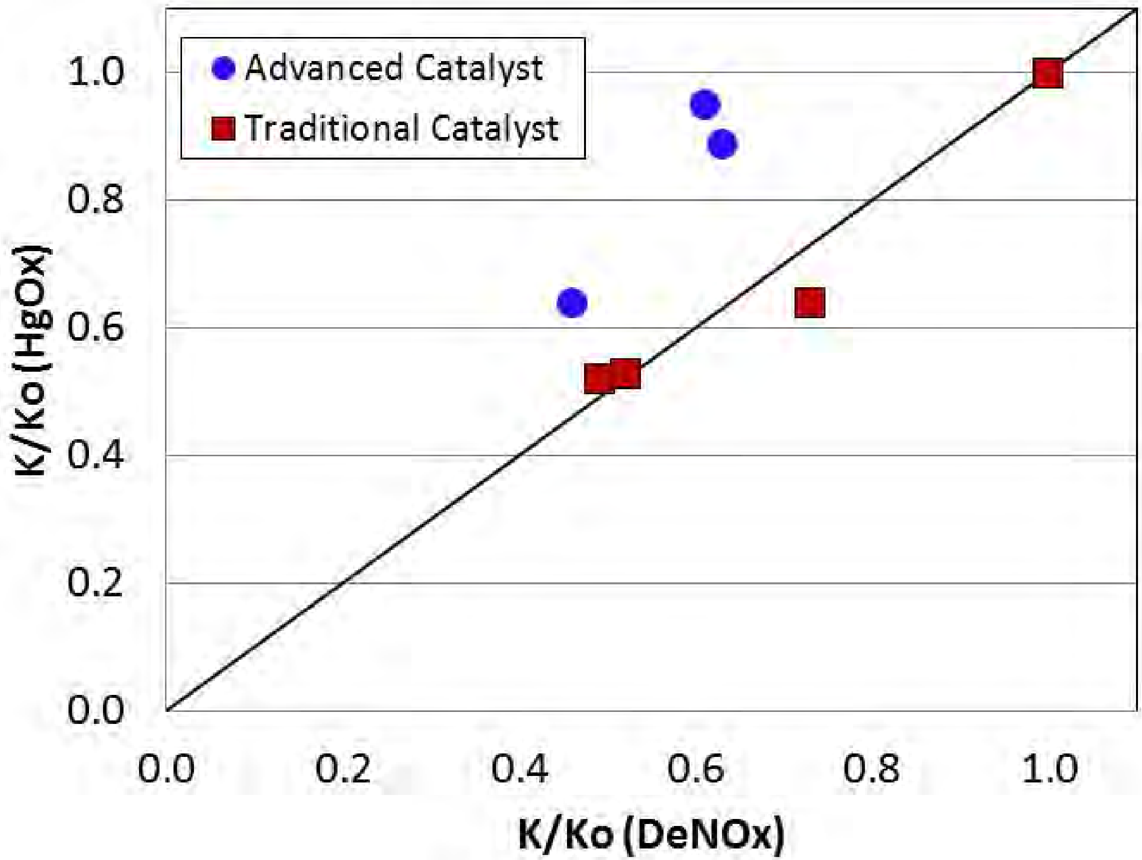


Hg oxidation deactivation generally correlates with DeNOx deactivation.

The extent of deactivation for the two reactions may not be equivalent:

K/Ko (Hg Ox) is sensitive to operating conditions (especially NH_3, HCl, temperature, and catalyst type).

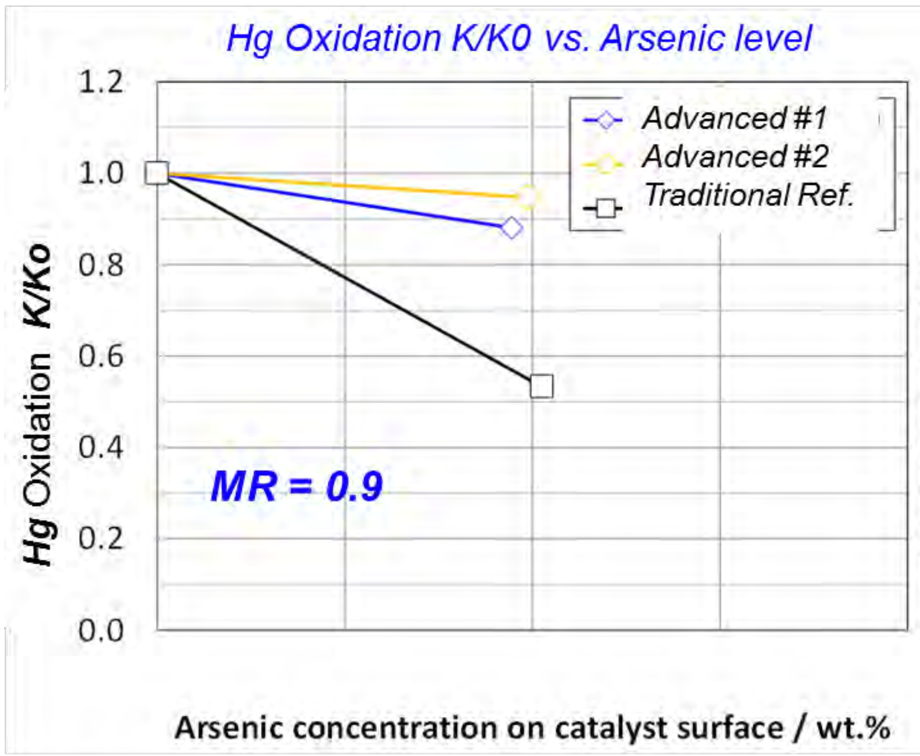
Advanced Catalyst: K/Ko

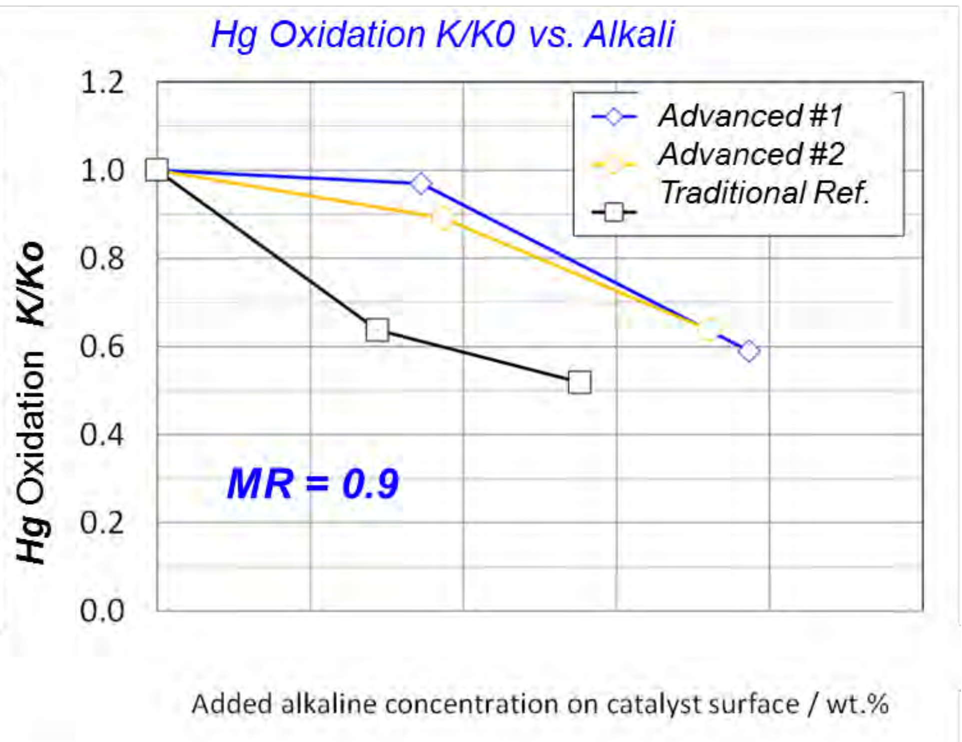


400°C, 350 ppm NO, 0.9 MR, 3.5% O_2, 12% H_2O, 1000 ppm SO_2, 10 ppm SO_3, 100 ppm CO, 56 ppm HCl

Advanced Catalyst Deactivation

- Arsenic and Alkali poisoning
  - Hg Oxidation deactivation resistance is higher for COMET™ catalyst
  - Difference in deactivation rate is greatest at higher ammonia levels





Test condition: 400C, 3.5%O2, 12% H2O, 350ppmvd NOx ,1000ppmvd SO2, 100ppmvd CO, 56ppmvd HCl, MR = 0.9,

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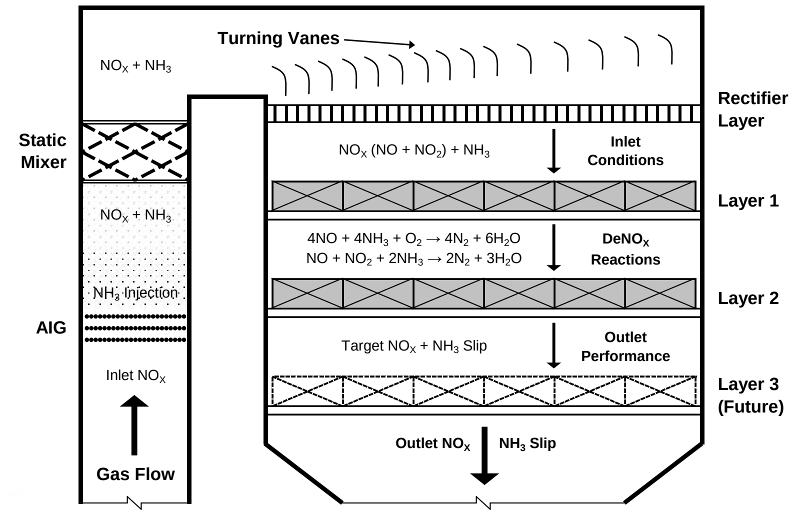
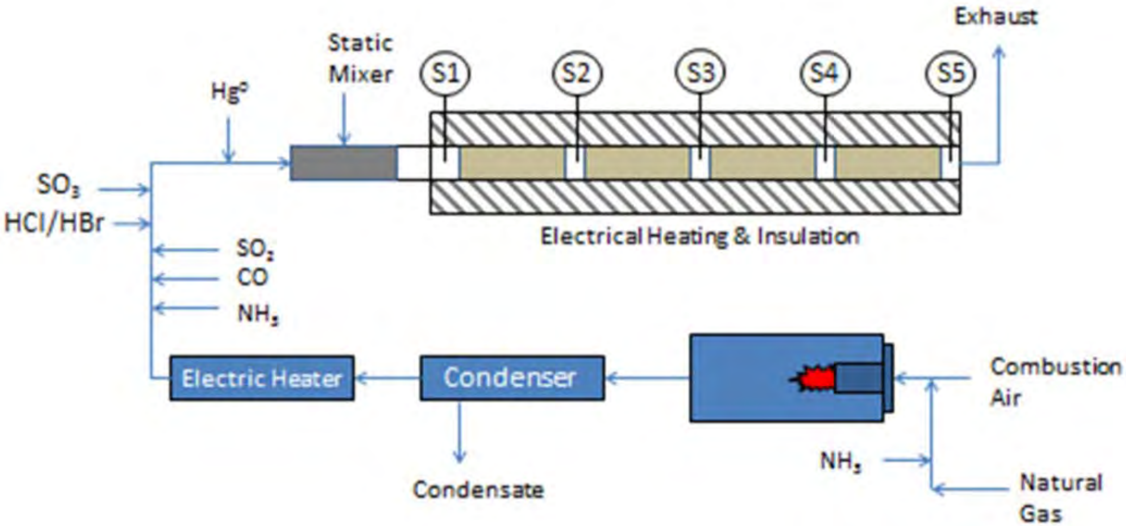
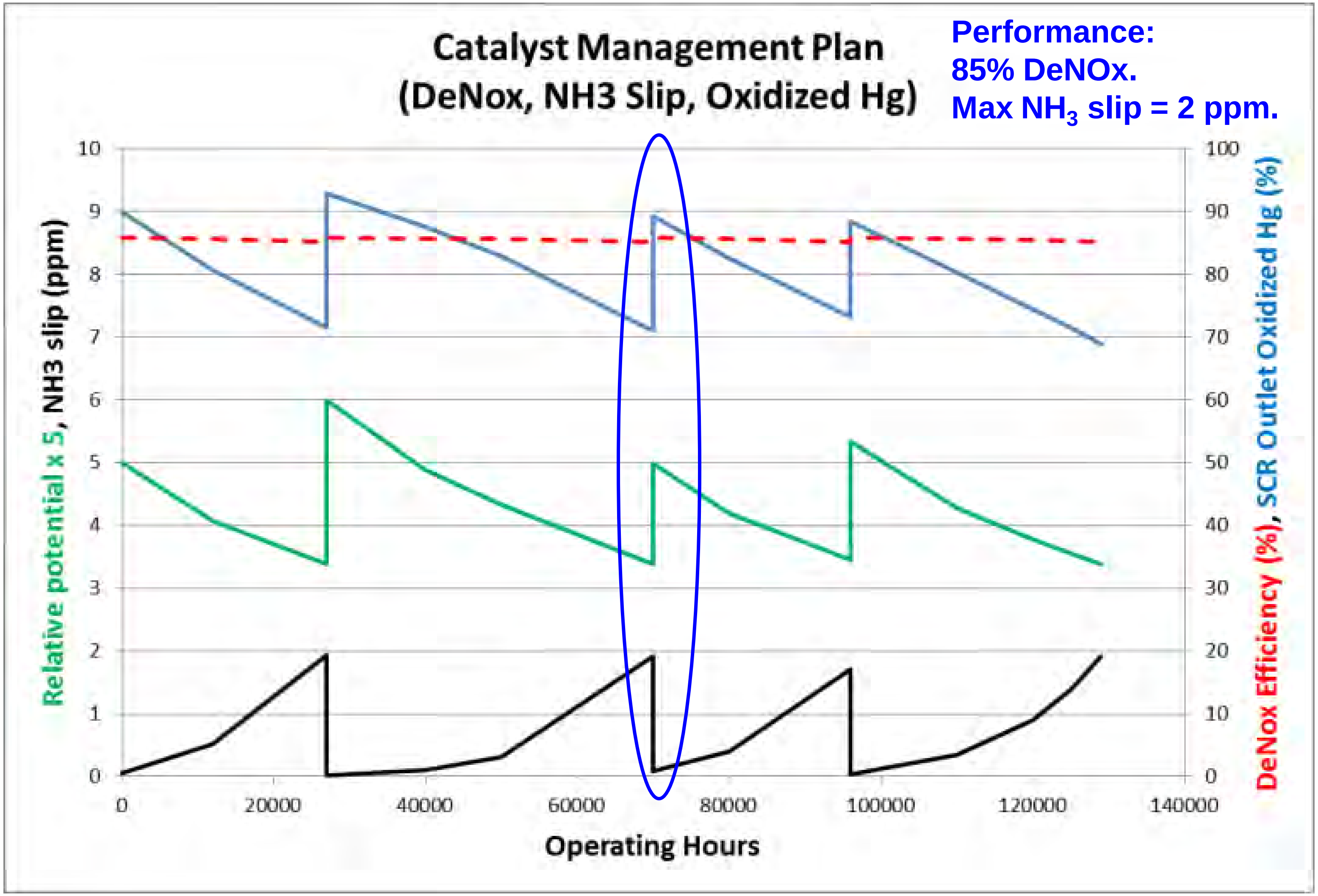




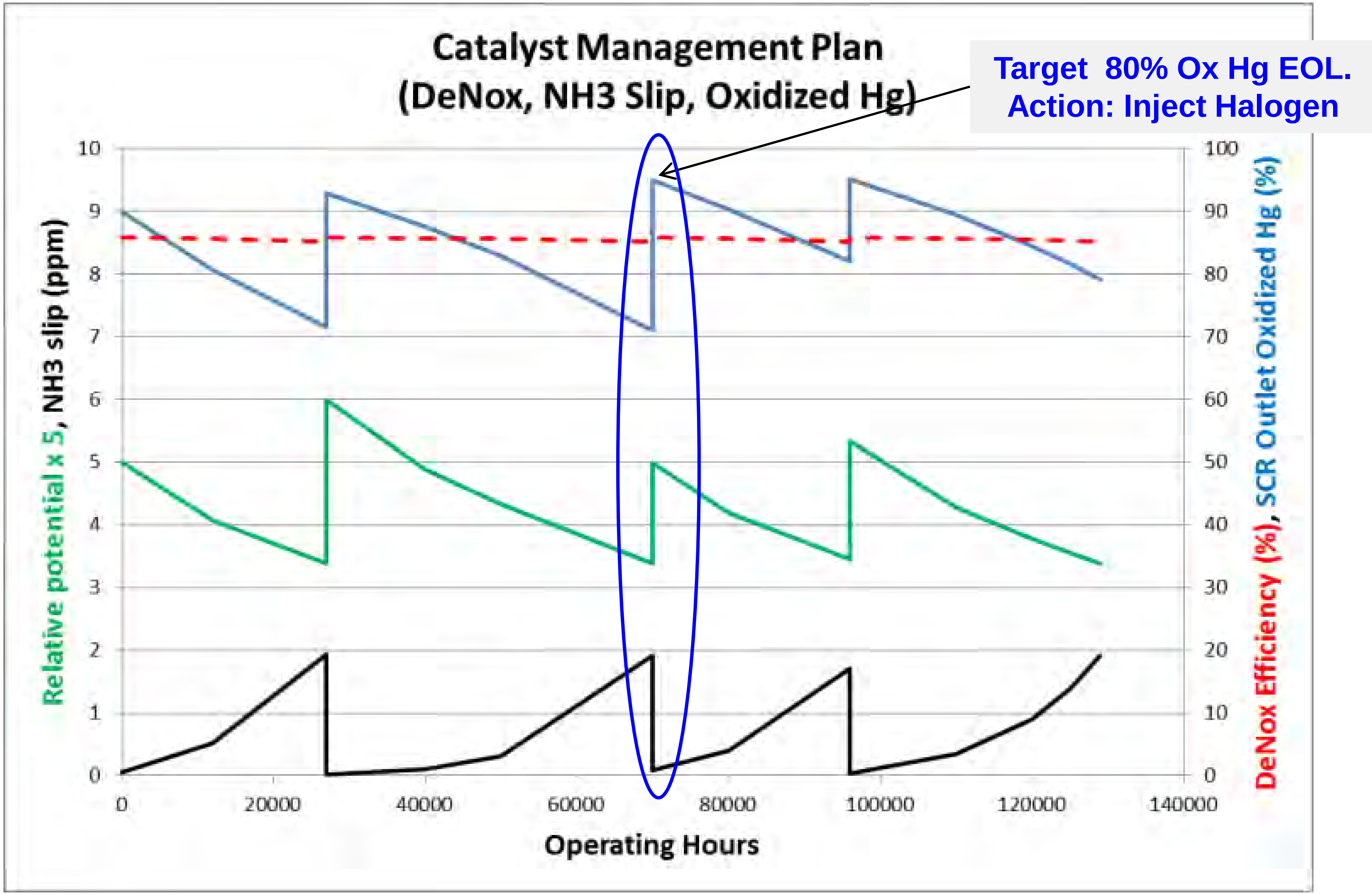
Catalyst Management

- **Case Study**
  - 2+1 design
  - SCR is at 70,000 hours operation: time for an action
  - What options to consider?

Case Study 1
w/ DeNOx Potential & Hg Oxidation



Case Study 1
w/ DeNOx Potential & Hg Oxidation



Case Study 1

w/ DeNOx Potential & Hg Oxidation

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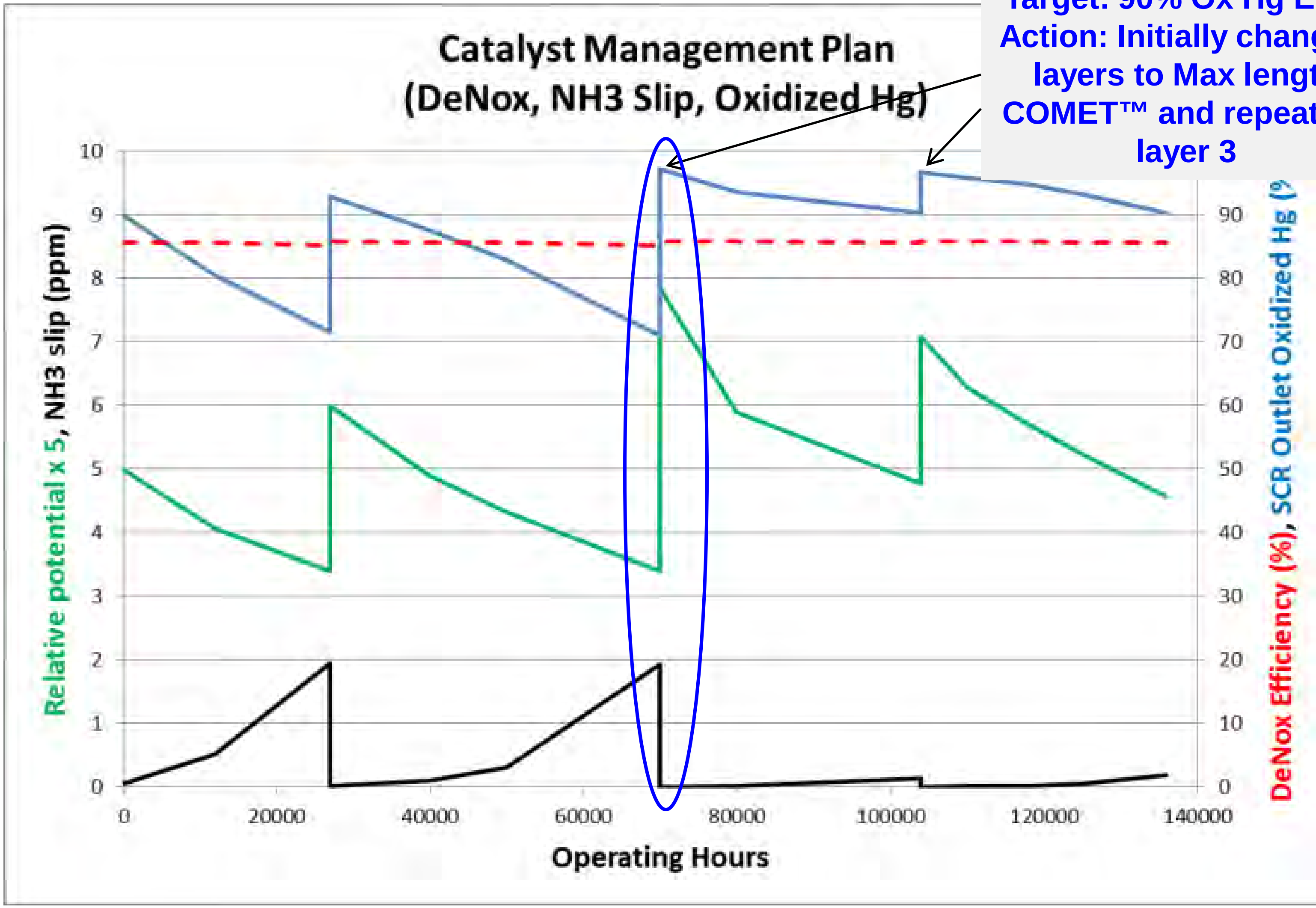
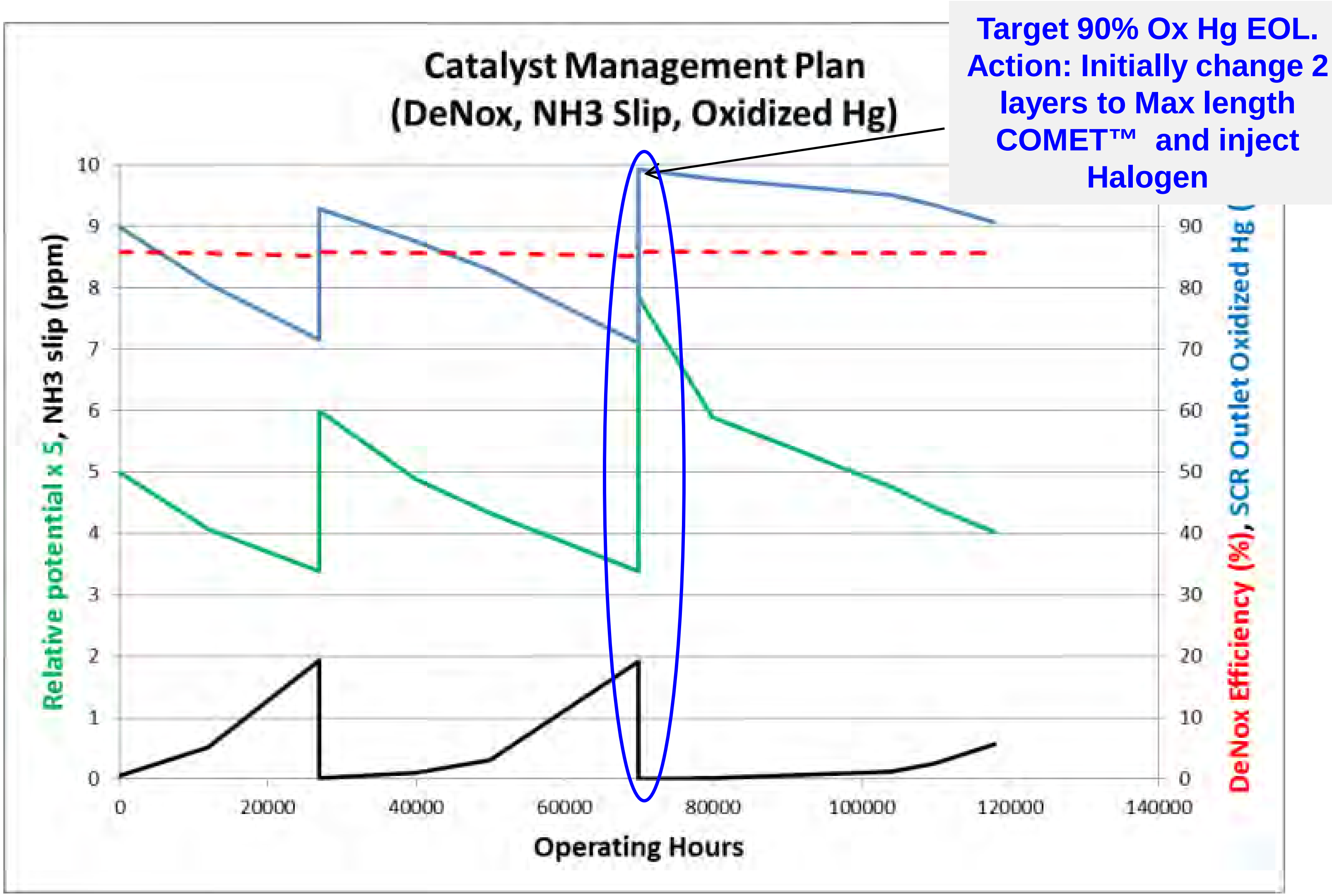


Target: 90% Ox Hg EOL. Action: Initially change 2 layers to Max length COMET™ and repeat for layer 3

Case Study 1

w/ DeNOx Potential & Hg Oxidation



Summary

- **Catalyst management for Hg oxidation and DeNOx are interdependent.**
- **SCR Hg oxidation is influenced by multiple factors**
  - Layer dependency
  - More factors in setting design conditions
  - Interdependencies between factors
  - Impacts of catalyst type & formulation
- **Cormetech has and integrated approach to optimize the SCR for Hg oxidation, maintain NOx reduction and manage SO_2 oxidation.**
  - Predictive modeling
  - Lab testing
  - Field experience
  - Product solutions

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Thank You!

Questions?