

REINHOLD ENVIRONMENTAL Ltd.



**2013 NO<sub>x</sub>-Combustion Round Table  
& Expo Presentations**

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# SCR Catalyst Management into the 2020s

2013 Reinhold NO<sub>x</sub> Conference



Johnson Matthey

## Introduction/Objective

New industry trends call for revisiting catalyst management strategies

- MATS
- SCRs on Western Bituminous Fuel

The finalized Mercury and Air Toxics Standards (MATS) Rule creates an opportunity for plants to utilize their SCR for both Mercury and NO<sub>x</sub> removal

- How can plants most effectively meet all objectives?
- What role can SCR play?

Industry consensus: MATS compliance requires a comprehensive AQCS strategy

### MATS Limits for Existing Plants

>8300 Btu/lb	1.2 lb/TBtu
<8300 Btu/lb	11 lb/TBtu

## Agenda – Finding that Goldilocks scenario

- SCR Overview
- SCR Catalyst co-benefit
- Catalyst Management for Multi-pollutant compliance
- Surveillance Testing
- Operation and Maintenance Tips

## Economic Impact of Non-Conforming SCR

- Proper SCR Performance is necessary for units to meet emission permit requirements, limit air heater plugging and fly ash contamination from excess ammonia slip
  - Therefore, non-conforming SCR can cause a unit derate, forced outage or increase planned outage time/expenses
  - Unexpected decrease in Hg oxidation can increase cost of Hg compliance
- Obtaining and installing SCR catalyst can take a significant amount of time (days to weeks) and resources
  - ~\$10-90/MW-hr of lost revenue
  - Catalyst Cost
  - Cost of removal and installation of catalyst modules



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# Catalyst Management

## Catalyst Management Plan (CMP)

- Schedule for maintaining SCR catalytic potential for NO<sub>x</sub> reduction
- Process of adding, replacing, cleaning catalyst
- Tailored to fit unit performance based on activity monitoring
- If possible, adjusted to coincide with unit outage schedule

## Potential: Parameter that quantifies a catalyst's ability to reduce $\text{NO}_x$

$\text{NO}_x$  reduction in a catalyst layer depends on:

- Potential in the layer – catalyst activity, flue gas flow, total catalyst surface area
- $\text{NH}_3$  to  $\text{NO}_x$  ratio entering the layer

### 2 Concepts of Potential

- Theoretical Minimum required,  $P_{\min}$ , to achieve desired performance
- Measured Potential – laboratory testing of catalyst samples

## Theoretical Minimum Potential, $P_{\min}$

- $P_{\min}$ : requirement to achieve a target  $\text{NO}_x$  reduction with  $\text{NH}_3$  slip maintained below some limit
- $P_{\min} = f(\text{NO}_{x \text{ in}}, \text{NO}_{x \text{ out}}, \text{NH}_3 \text{ slip})$
- With added margin for . . .
  - Mal-distributions of  $\text{NH}_3$ - $\text{NO}_x$  mixing and flow
  - Unavailable catalyst surface due to channel plugging
  - Catalyst material lost to fly ash erosion

## Measured Potential

- Laboratory testing on a known catalyst quantity/geometry under defined flue gas conditions – Temperature, Flow, composition
- $\text{NO}_x$  reduction ( $\eta$ ) with  $\text{NH}_3/\text{NO}_x = 1.0$  measured across sample
- Catalyst activity ( $k$ ) is a proportionality constant relating  $\eta$  to the sample geometry and flow rate
- $k$  measured on fresh catalyst,  $k_0$ , and exposed/aged catalyst,  $k_t$
- Relative Activity,  $k/k_0$  (potential,  $P/P_0$ ) – Exposed catalyst vs fresh

$$k = -AV \ln (1 - \eta)$$

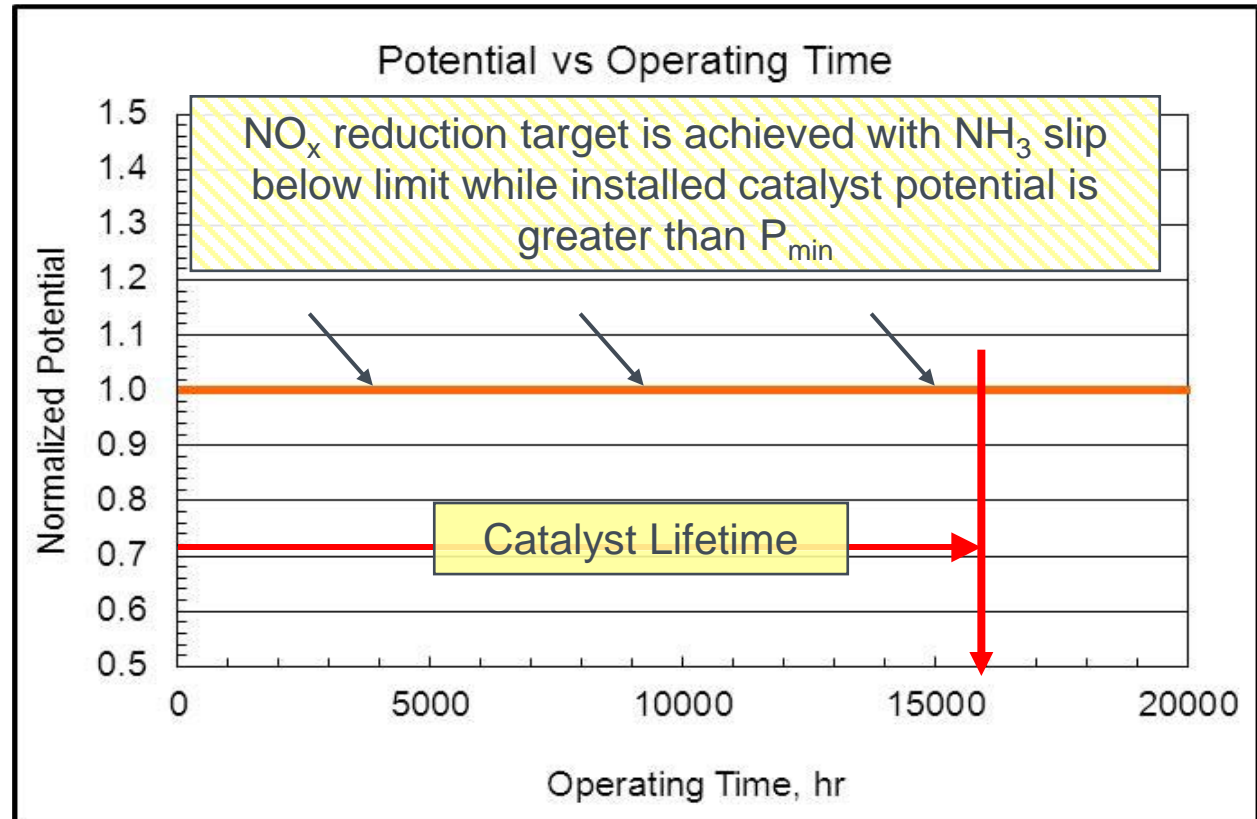
$$P = \frac{k}{AV}$$

$$AV = \frac{V_{fg}}{\text{Tot SA}_{\text{cat}}}$$

$$P = -\ln (1 - \eta)$$

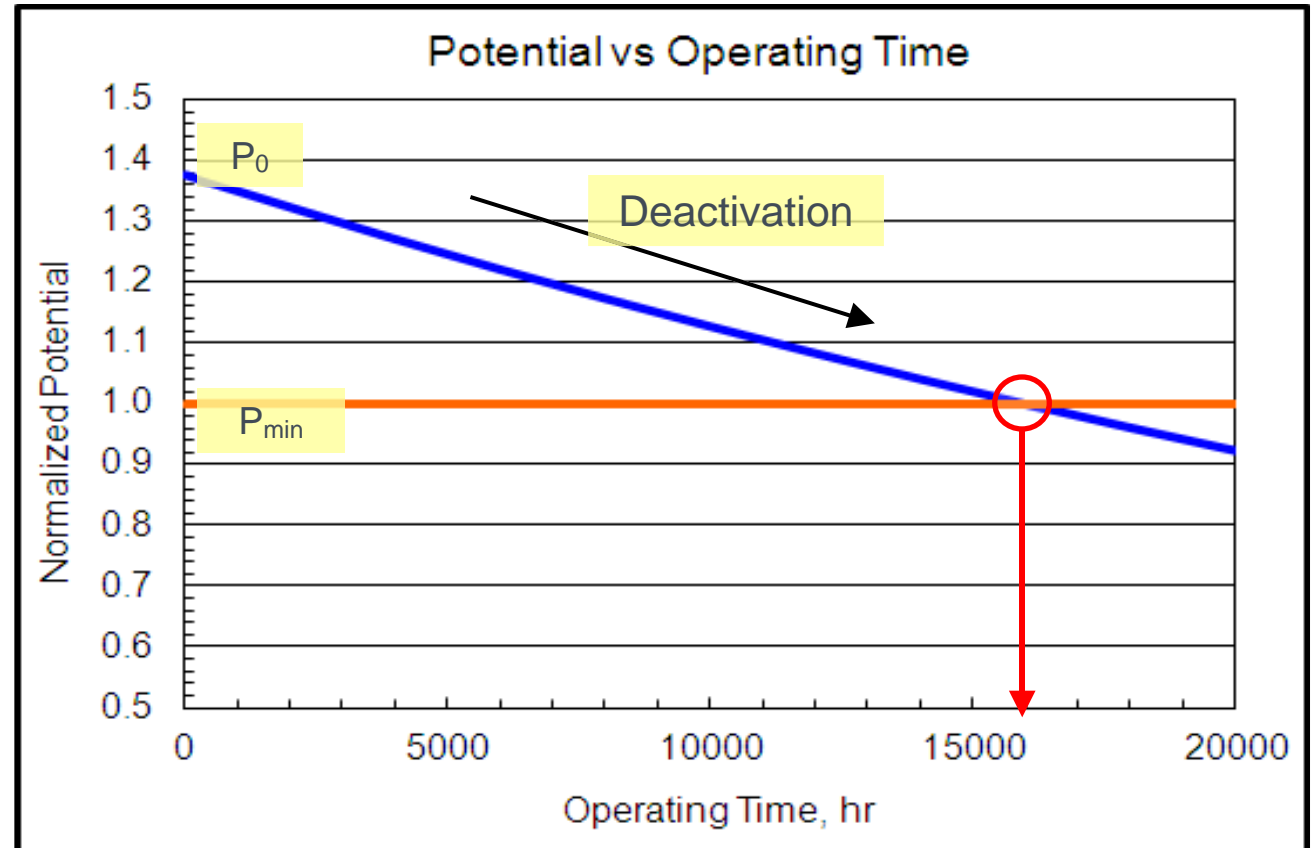
## Practical Example – Minimum Potential

- $\text{NO}_{x\text{in}} = 300$  ppmvd
- $\text{NO}_{x\text{out}} = 30$  ppmvd
- 90%  $\text{NO}_x$  reduction
- $\text{NH}_3$  slip  $\leq 2$  ppmvd
- $P_{\text{min}} = 1.0$  (Normalized)
- Catalyst lifetime = 16,000 hr

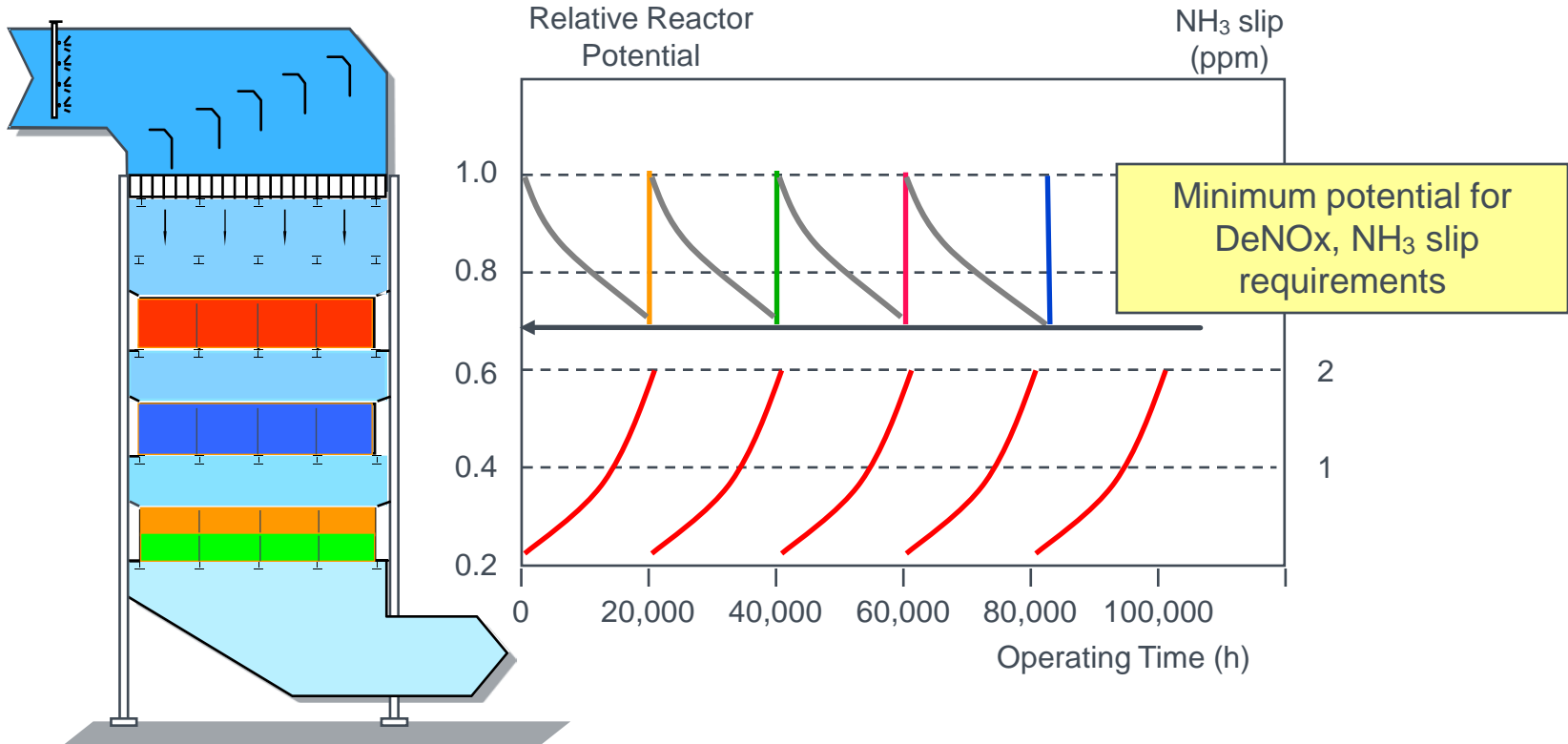


## Initial Potential, $P_0$

- Operating Life: 16000 hr
- $P_{\min} = 1.0$
- Relative potential at 16,000 hours:  $P/P_0 = 0.73$
- Initial potential installed:  $P_0 = 1.38$



# CMP, 2 + 1 Example



# Fuel Comparison

	Eastern Bituminous	PRB	Western Bituminous
Calcium	Low	High	Medium
Ash Loading	Medium	Medium	Medium - High
Sulfur Content	High	Low	Low - Medium
Sensitivity to Ammonia Slip	High	Low	No Field Data
Primary Deactivation Mechanisms	Arsenic	Ca Masking, Alkali Metals, Phosphorous	No Field Data

## SCR and Mercury Oxidation

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

## Reactions of Hg

Desired Reactions – Hg oxidation

- $\text{Hg} + 2 \text{HCl} + \frac{1}{2} \text{O}_2 \rightarrow \text{HgCl}_2 + \text{H}_2\text{O}$
- $\text{Hg} + \text{SO}_3 + \frac{1}{2} \text{O}_2 \rightarrow \text{HgSO}_4$
- $2 \text{HCl} + \frac{1}{2} \text{O}_2 \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$
- $\text{Hg} + \text{Cl}_2 \rightarrow \text{HgCl}_2$

Other Reactions

- $\text{Cl}_2 + \text{SO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{HCl} + \text{SO}_3$
- $3 \text{HgCl}_2 + 2 \text{NH}_3 \rightarrow 3 \text{Hg} + 6 \text{HCl} + \text{N}_2$
- $\text{HgCl}_2 + \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{Hg} + 2 \text{HCl} + \text{SO}_3$

## NOx Reactions

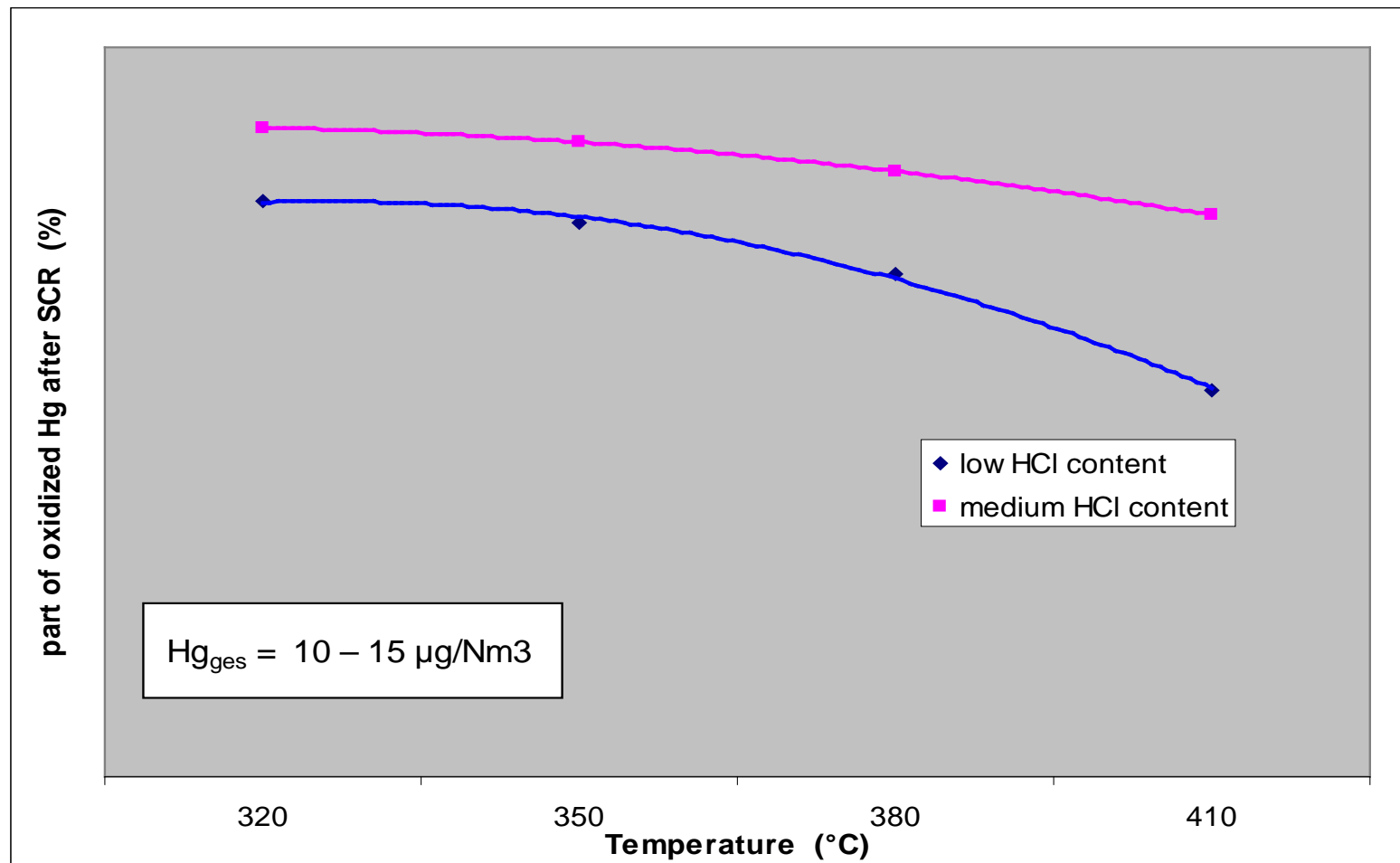
- $4 \text{NO} + 4 \text{NH}_3 + \text{O}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O}$
- $2 \text{NO}_2 + 4 \text{NH}_3 + \text{O}_2 \rightarrow 3 \text{N}_2 + 6 \text{H}_2\text{O}$

## Sulfur and Ammonia Reactions

- $2 \text{SO}_2 + \text{O}_2 \rightarrow 2 \text{SO}_3$
- $\text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{HSO}_4$  (ABS)
- $\text{NH}_4\text{HSO}_4 + \text{NH}_3 \rightarrow (\text{NH}_4)_2\text{SO}_4$  (AS)
- $2 \text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{SO}_4$  (AS)

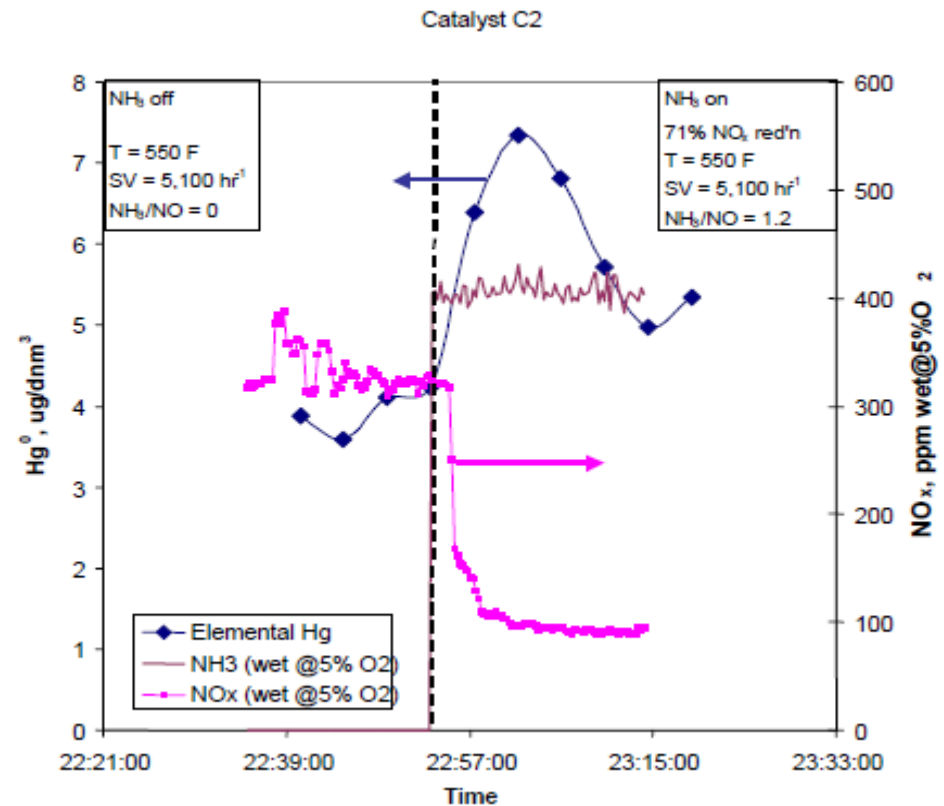
	Eastern Bituminous	PRB	Western Bituminous
Mercury Oxidation	High	Low	No Field Data

# Hg Oxidation in Catalyst – Effects of Temperature and Cl



## Key Characteristics of Mercury Oxidation

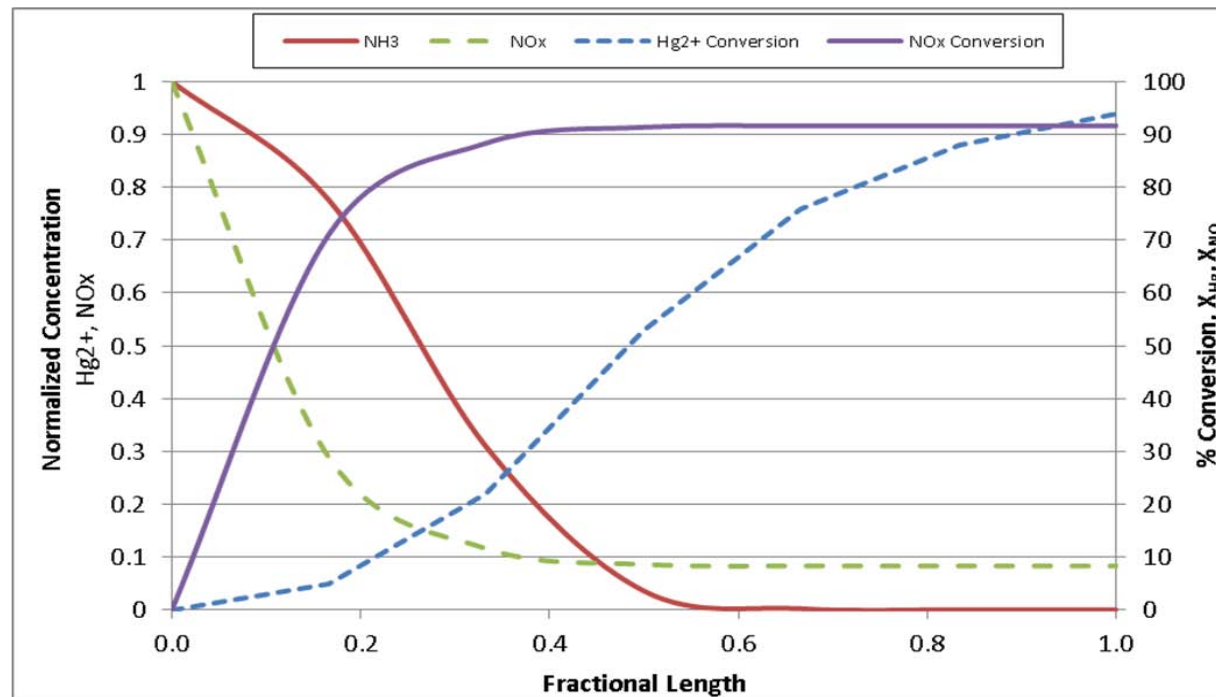
- Ammonia has ability to inhibit mercury adsorption on the catalyst
  - Decreases mercury oxidation when this occurs
  - Reaction not independent with respect to ammonia
  - Some data show that at very high halogen concentrations, mercury oxidation did not decrease to the extent predicted (Hinton 2012)



Source: Senior (2004)

# Key Characteristics of Mercury Oxidation

- As ammonia is consumed within the SCR reactor, the oxidation of mercury increases

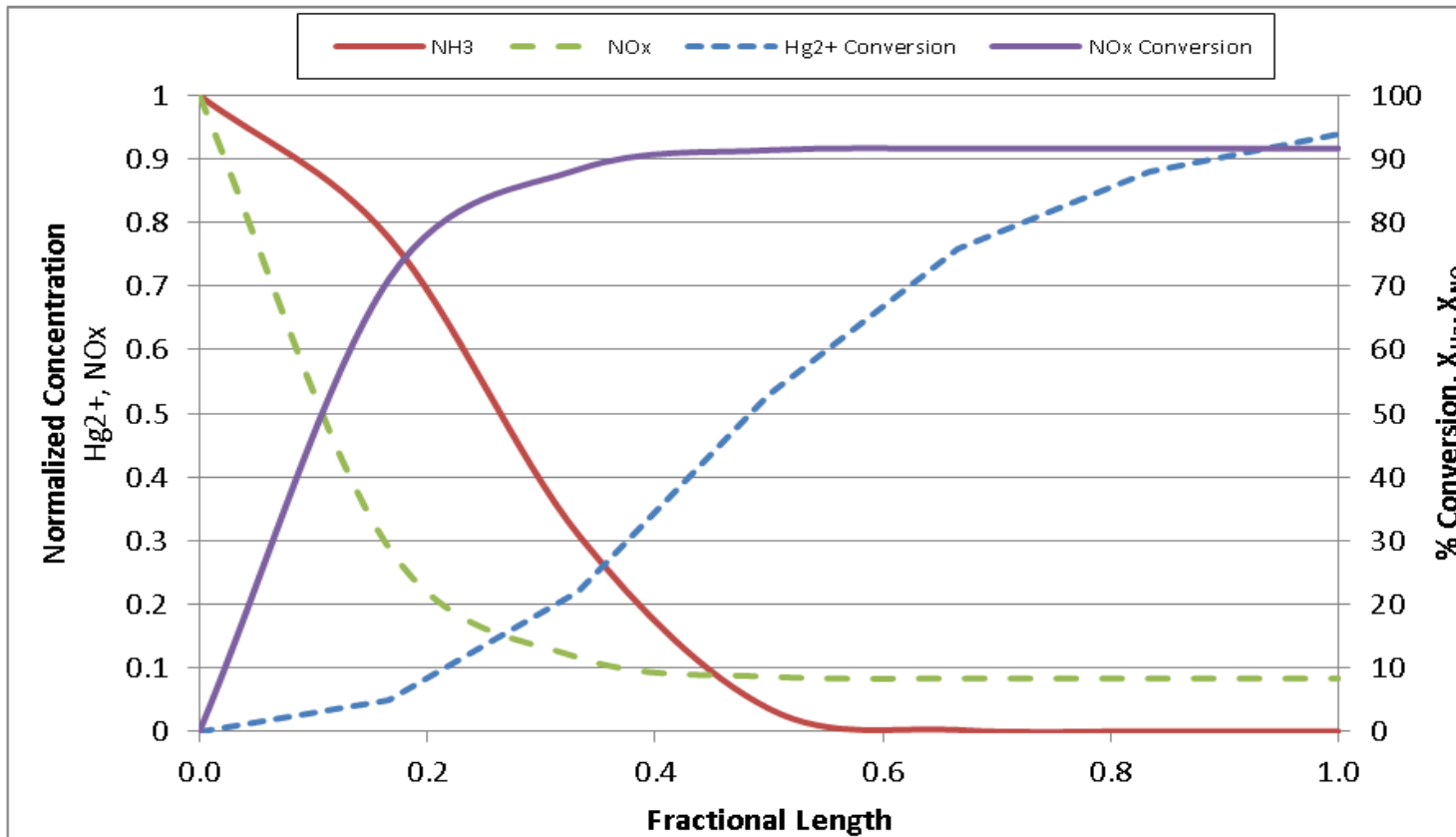


# Catalyst Management and Mercury Oxidation

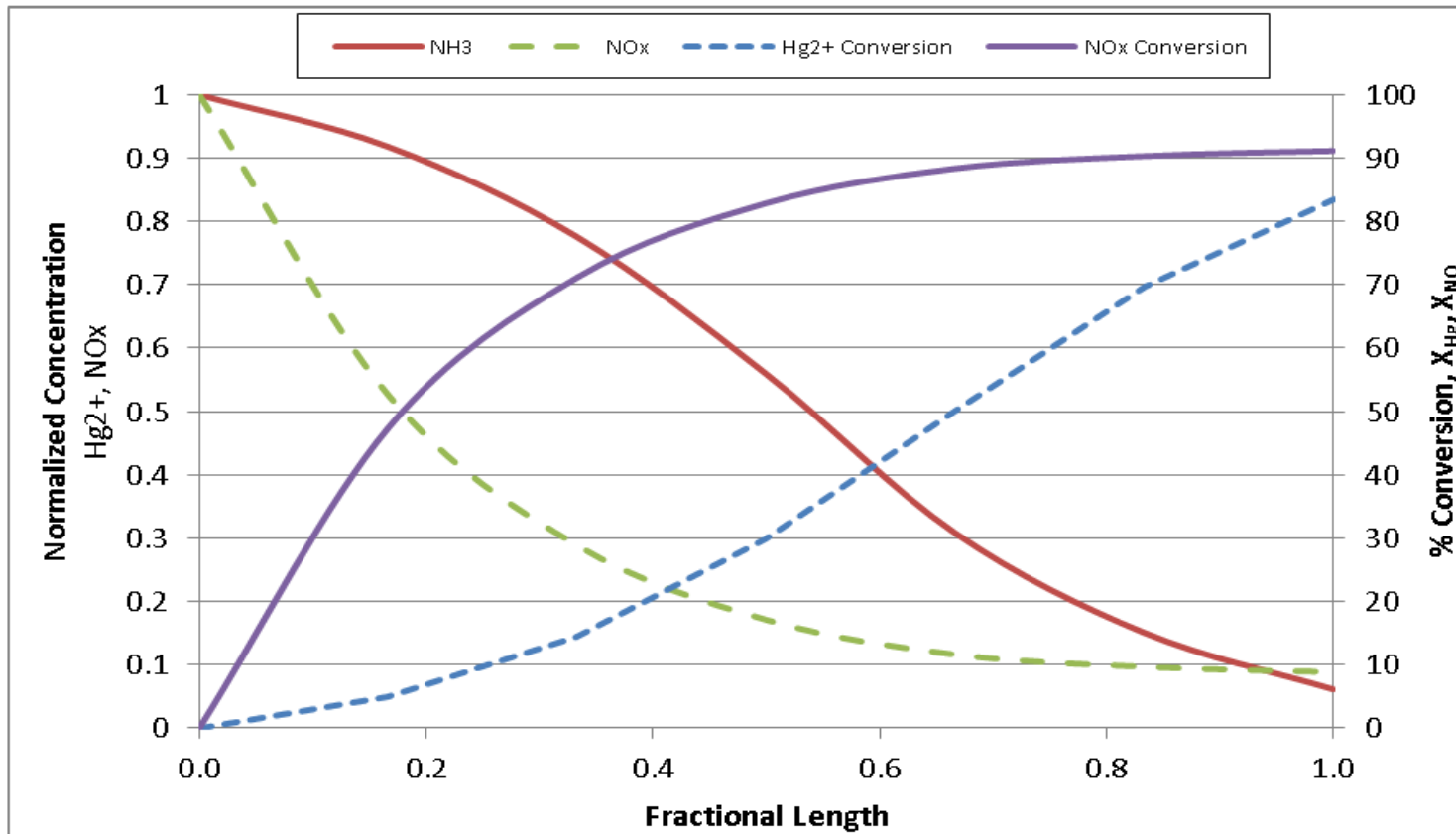
NOx reduction and Hg Oxidation compete

- NOx conversion can be maintained by increasing ammonia flow, allowing plant operators to maintain NOx outlet requirements
- Hg oxidation can be increased by decreasing NOx requirement
- Hg oxidation favored in lower catalyst layers as NH<sub>3</sub> is depleted
- Both can be increased by adding catalyst
  - Trade-offs – SO<sub>2</sub> conversion, pressure drop
- Many plants will start managing catalyst based on mercury oxidation potential
- At constant NOx reduction, Hg oxidation will decrease over time

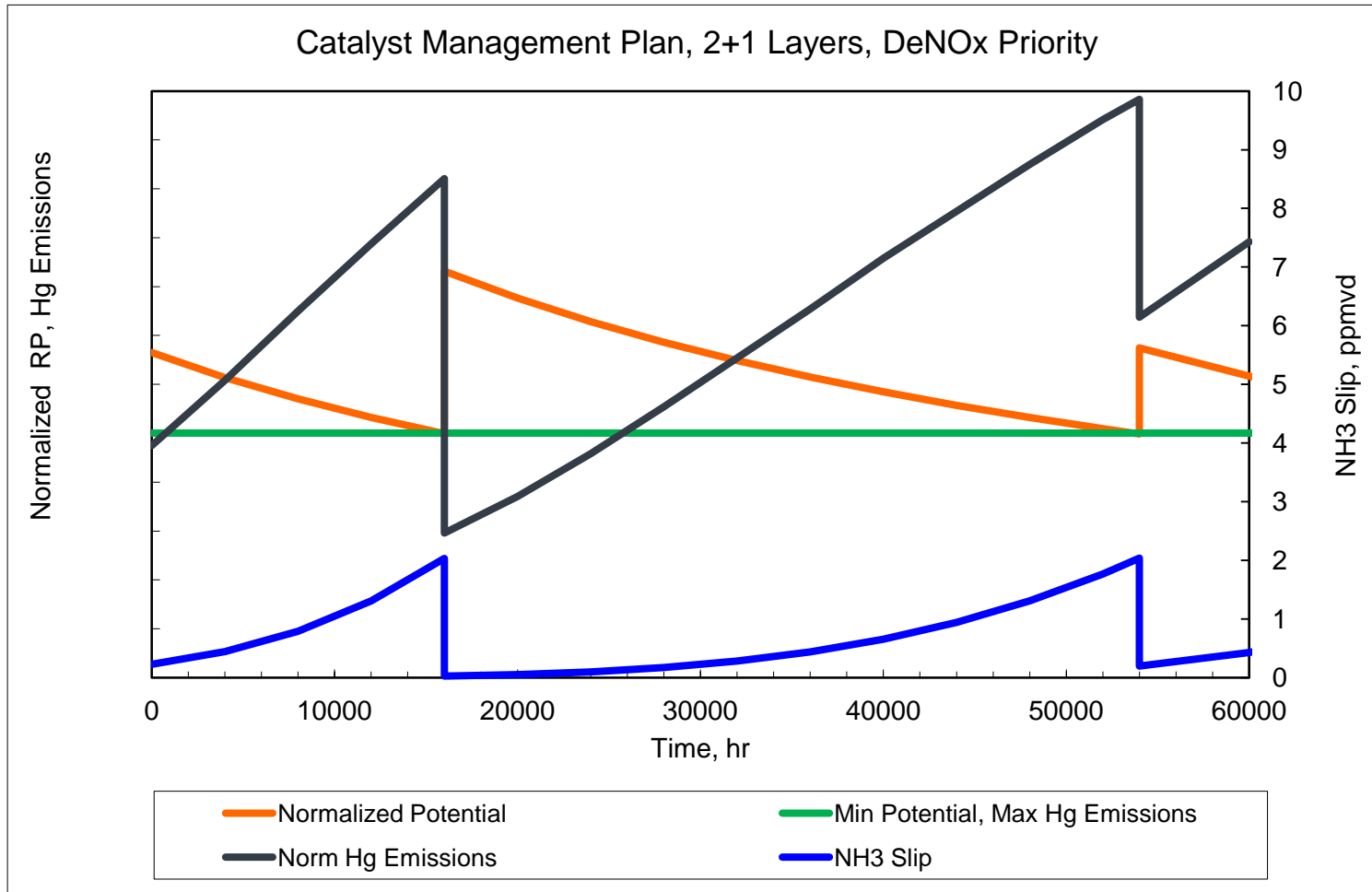
## Effect of Catalyst Aging - New



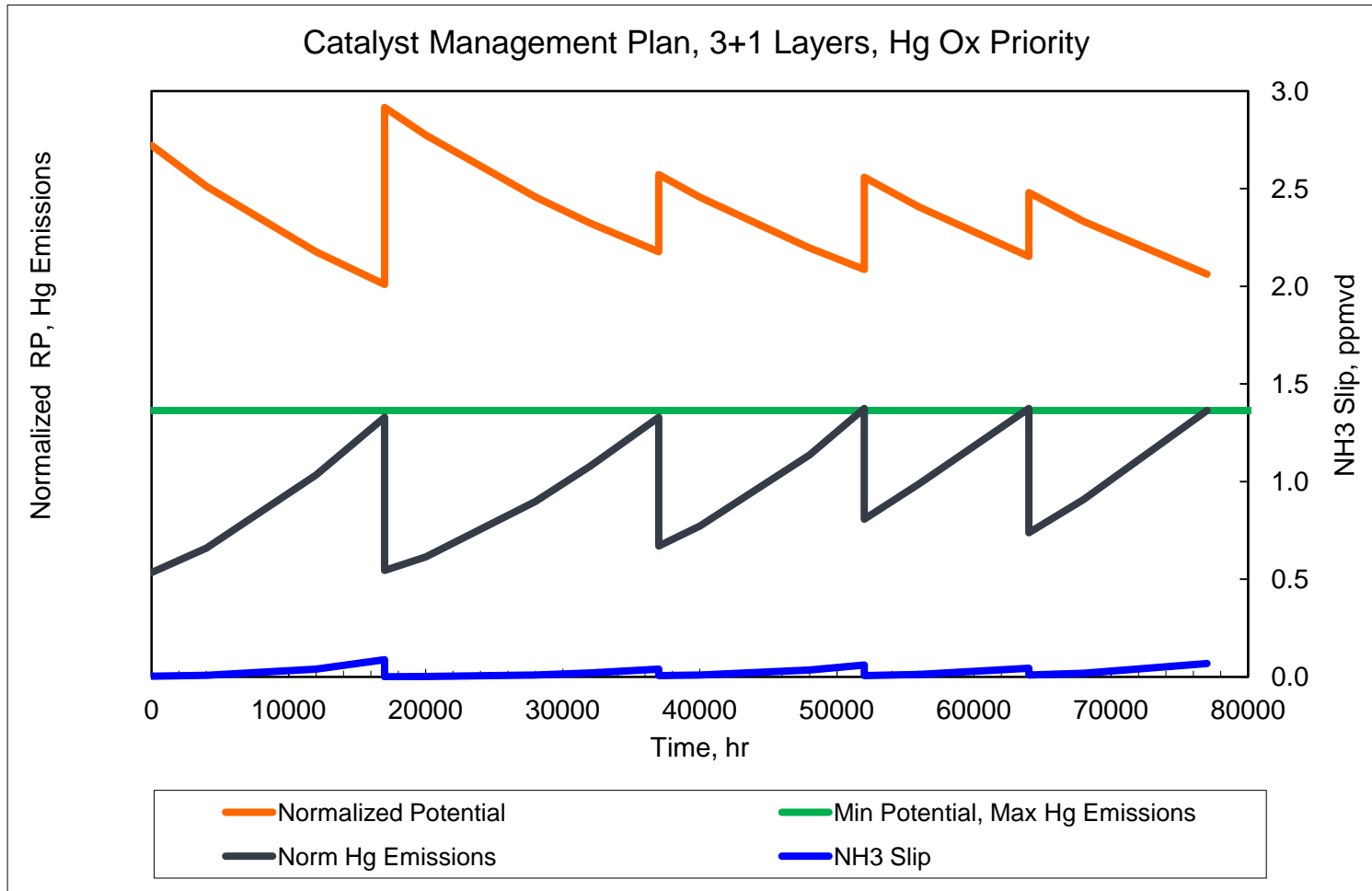
## Effect of Catalyst Aging - Exposed



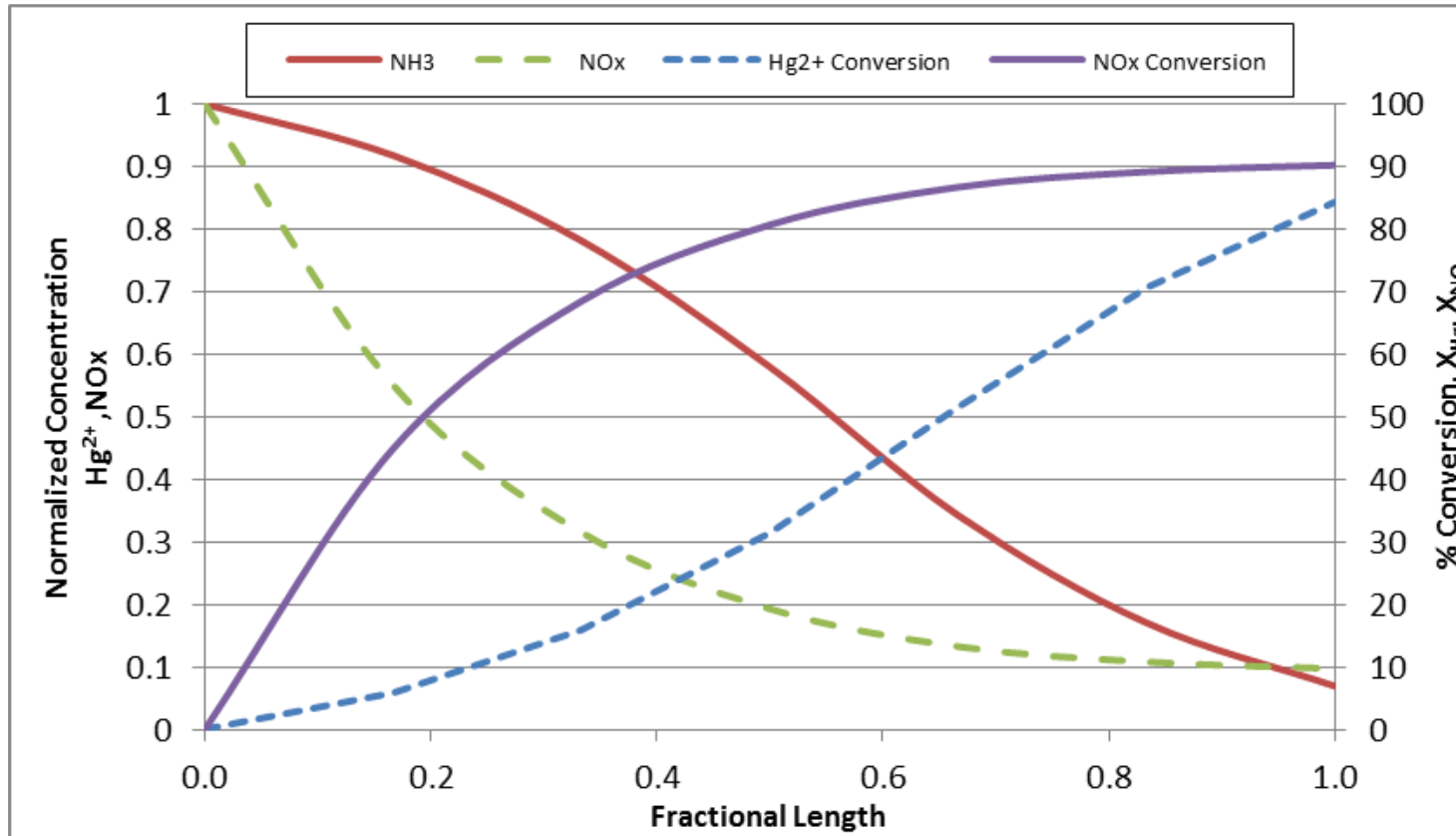
# CMP for DeNOx and Mercury



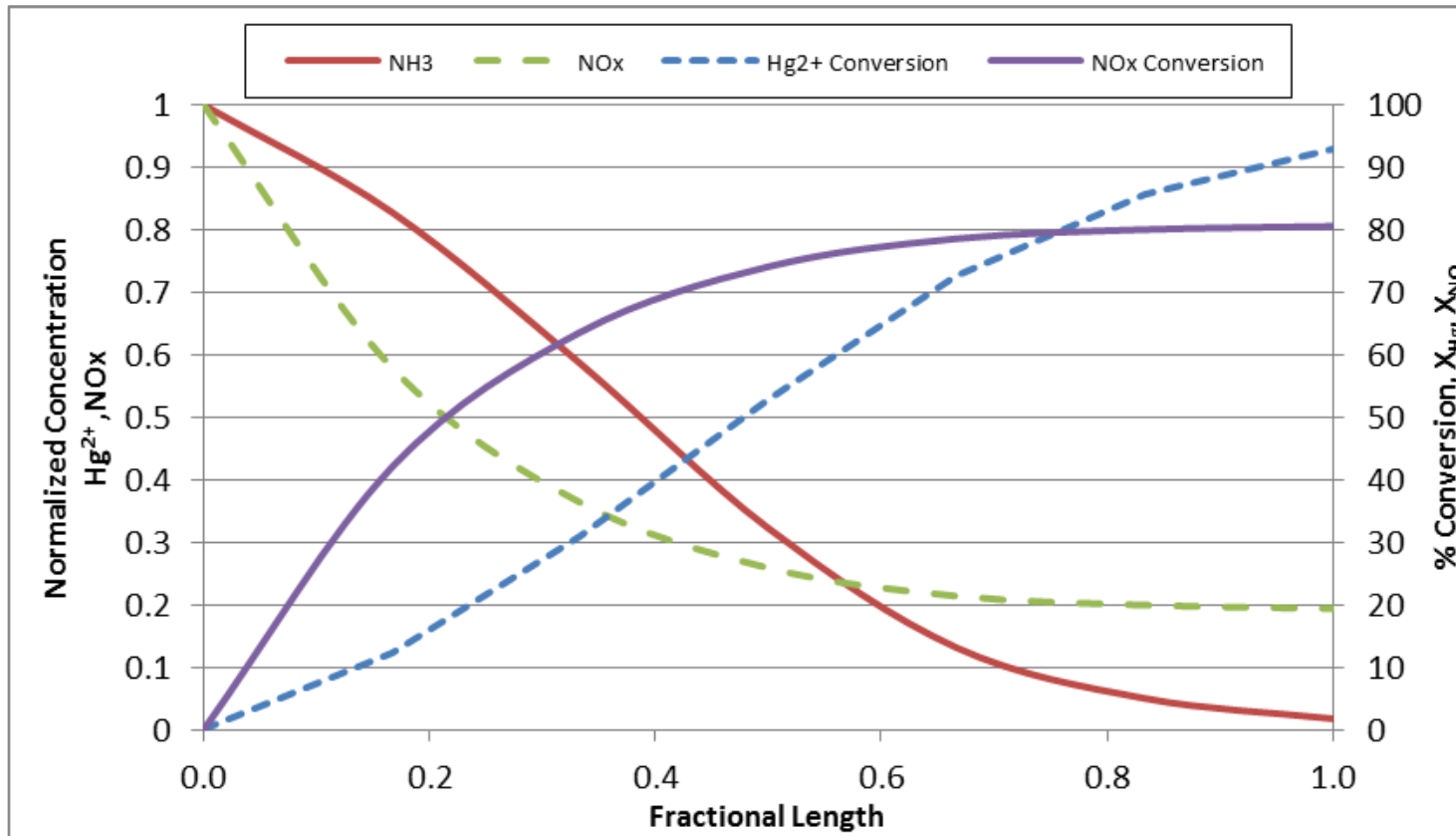
# CMP for DeNOx and Mercury



# 90% NO<sub>x</sub> Conversion



## 80% NO<sub>x</sub> Conversion – All other parameters constant



## Economics of decreased oxidation

Oxidized Mercury with 80% NO<sub>x</sub> Reduction = ~0.020 lb/hr

Oxidized Mercury with 90% NO<sub>x</sub> Reduction = ~0.018 lb/hr

Difference: ~0.002 lb/hr (16 lb/yr)

Annual differential cost of ACI: \$176,000 – \$480,000

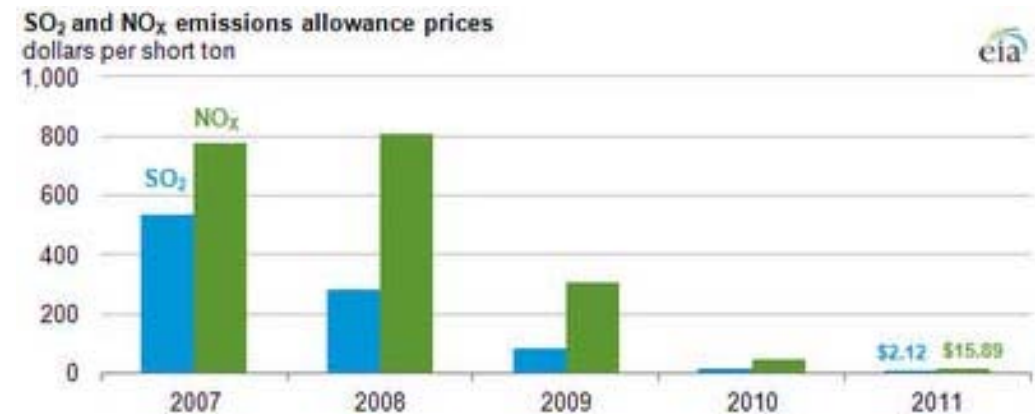
Design Parameters	
Coal Heating Value	~11350 BTU/lb
Trace Hg	0.09 mg/kg
Boiler Heat Input	~2500 MBTU/Hr
Cost of ACI Hg Removal (low)	\$11,000/lb Hg
Cost of ACI Hg Removal (high)	\$30,000/lb Hg

## NO<sub>x</sub> Reduction vs. Mercury Oxidation

Recent decrease in NO<sub>x</sub> allowance price could play a role in plant's MATS compliance strategy

- Little benefit in reducing more NO<sub>x</sub> than required

Balancing priorities of NO<sub>x</sub> reduction and Hg oxidation strategy for future



# Catalyst Upkeep

# Surveillance Testing

- Many SCR users sample catalyst annually for NO<sub>x</sub> performance
- 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
- In addition, SO<sub>2</sub> measurements, and physical composition techniques can be performed

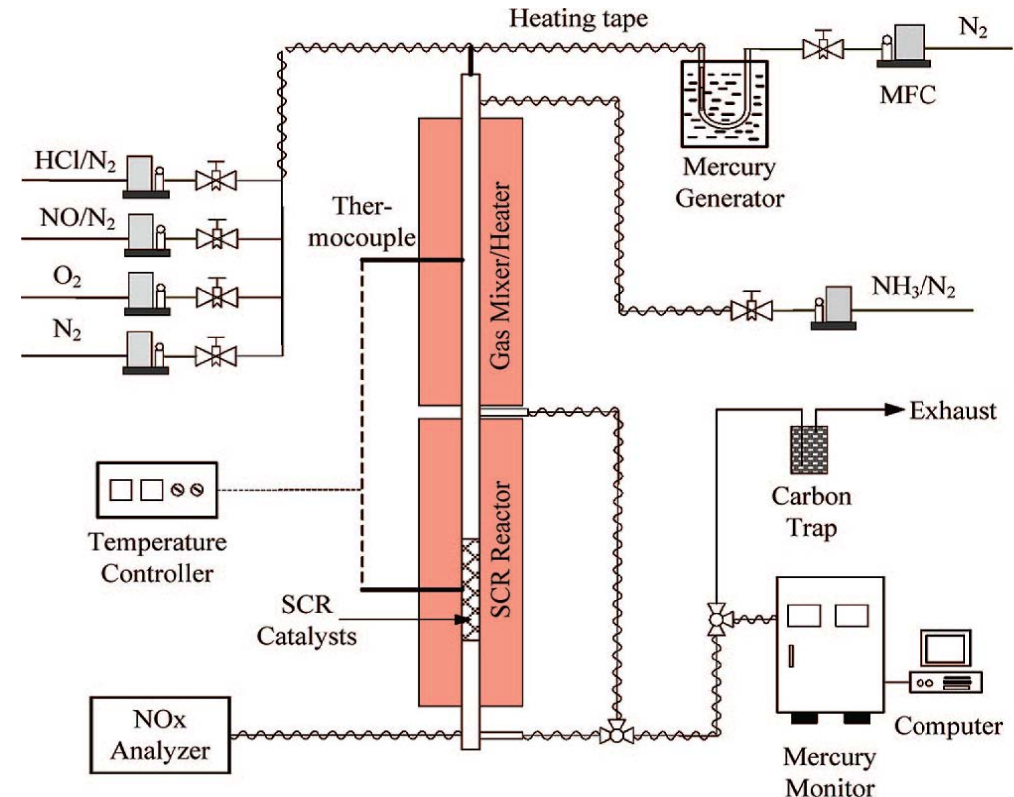
In the future, periodic Hg oxidation testing anticipated

## Surveillance Testing – Predicting Field Performance

- NO<sub>x</sub> reduction
  - Lab testing can be used to predict field performance
- SO<sub>2</sub> to SO<sub>3</sub> oxidation
  - Lab testing can not be used to predict field performance
    - Fly Ash adsorption of SO<sub>3</sub> in field
    - NH<sub>3</sub> reaction with SO<sub>3</sub> to form ABS
- Hg Oxidation
  - No industry standard lab testing protocol
  - Applicability to field performance still being determined

# Hg Oxidation Lab Testing

- Often volume to area scaling issues
- Potential use
  - Parametric studies
  - Catalyst screening
  - Catalyst surveillance
  - Guarantee testing
- Matching ammonia profile along catalyst length is very important with regards to correlating to field results



Representative Lab schematic

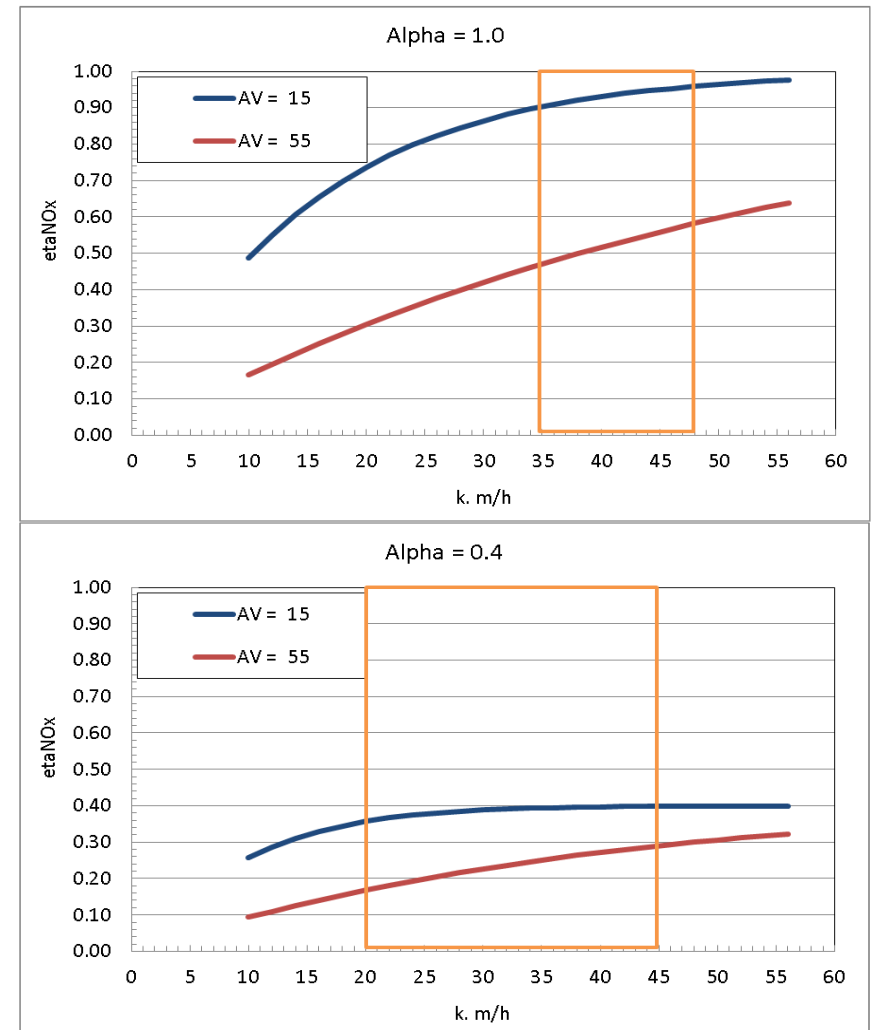
Source: He et al. (2009)

## Relationship between AV, LV and Ammonia Profile

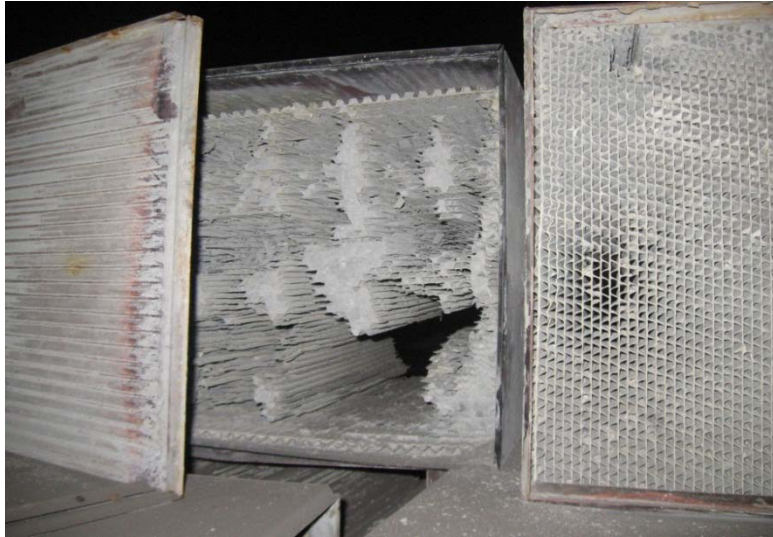
- Matching the ammonia profile in lab reactors can be difficult
  - Full layer area velocity (residence time) and linear velocity can not always be matched simultaneously
  - NO<sub>x</sub> activity dependent on linear velocity, not area velocity
  - Ammonia Profile dependent on area velocity
- Desired to have boundary conditions (inlet NH<sub>3</sub> concentration and outlet NH<sub>3</sub> concentration) as close to field as possible

## Relationship between AV, LV and Ammonia Profile

- At lower AV, outlet  $\text{NH}_3$  is less dependent on  $\text{NO}_x$  activity
- At lower  $\text{NH}_3/\text{NO}_x$  inlet, outlet concentration is approximately constant over expected activity range
- One potential method to approximating ammonia profile may be to match field AV and  $\text{NH}_3/\text{NO}_x$ 
  - Absolute ammonia and  $\text{NO}_x$  concentration should be representative of what catalyst will be seeing



## Don't Forget Catalyst Maintenance!



### SCR Catalyst is an asset

- Use soot-blowers, sonic horns, maintain correct SCR environment
- Learn from SCR operating experience
- Follow catalyst operating manual --- Avoid Headaches!
- Poorly maintained catalyst loses its ability to be regenerated

## Takeaways

- Future catalyst requirements will be more rigorous– Catalyst Management will become more onerous
- Mercury Oxidation will be transient – not only over the SCR but through the entire system
- NOx reaction and Hg reaction compete
- Utilization of more catalyst layers provides greater flexibility
- Mercury lab testing protocol and subsequent correlation to field performance are not currently available



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Thank You!

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