

REINHOLD ENVIRONMENTAL Ltd.



# **2017 NO<sub>x</sub>-Combustion-CCR Round Table Presentation**

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W. S. Hinton & Associates  
Research and Consulting Engineers

**2017 NO<sub>x</sub>-Combustion-CCR/PCUG Conference**  
**Renaissance Cleveland Hotel**  
**Cleveland, OH**

# MERCURY OXIDATION IMPACTS AS CATALYST AGES

(MANAGING CATALYST FOR MERCURY OXIDATION)

**W. Scott Hinton, Ph.D., P.E.**

W.S. HINTON & ASSOCIATES  
203. W. Jackson St.  
Tel: 850-261-5239  
email: [shinton@wshinton.com](mailto:shinton@wshinton.com)

# Agenda

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- 1. Review of catalyst management for deNOx.**
- 2. Review of factors affecting mercury oxidation in relation to catalyst management.**
- 3. Managing the SCR for mercury oxidation.**

# Equation Review - DeNOx

## DeNOx Activity

The deNOx activity is a laboratory-measured metric utilized in modeling. This is not the reactor design equation.

$$K_{\text{deNOx}} \text{ (m/hr)} = -AV \cdot \ln(1 - \% \text{deNOx})$$

## Theoretical DeNOx Potential

The deNOx potential is calculated according using the following equation. It uses lab measured activity, and implies a direct proportionality to AV.

$$P_{\text{lab}} = -\ln(1 - \text{deNOx Eff.}) = K_{\text{deNOx}} / AV$$

## Actual DeNOx Potential

The actual deNOx potential takes into account fouling as follows.

$$P_{\text{actual}} = P_{\text{lab}} (1 - \% \text{Fouling})$$

# Equation Review – Mercury Oxidation

## Mercury Oxidation Rate

This is a calculated parameter based on Hg speciation. It is specific to the actual conditions (flow, constituents, halogens, temperature, etc.) and can be done in the field or in the lab.

$$\text{Hg Oxidation Rate (\%)} = (\% \text{Hg}^0_{\text{in}} - \% \text{Hg}^0_{\text{out}}) / \% \text{Hg}^0_{\text{in}}$$

## Mercury Oxidation Activity

This is simply a mathematical transformation for convenience. It is specific to the conditions. Although it implies that the K-value is directly proportional to AV, this is not correct.

$$K_{\text{Hg}}(\text{m/hr}) = -AV * \ln(1 - \text{HgRate}(\%))$$

## Mercury Oxidation Potential

As above, this is simply a convenient mathematical transformation. Again, although it implies that the K-value is directly proportional to AV, this is not correct.

$$P_{\text{Hg}} = -\ln(1 - \text{HgRate}(\%)) = K_{\text{Hg}}/AV$$

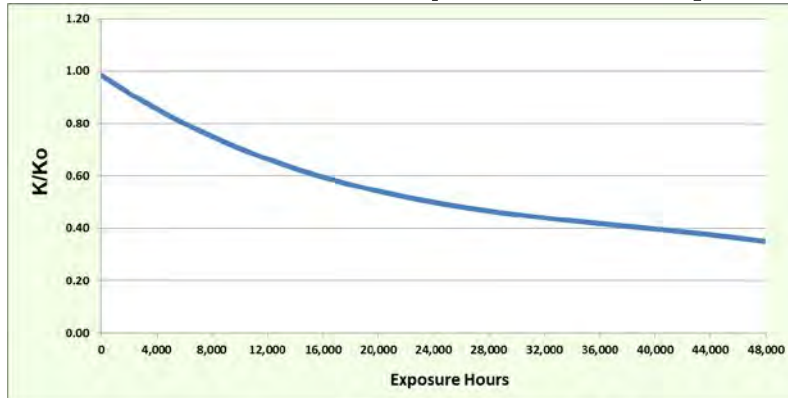
## Fouling-Related Mercury Oxidation Potential

The actual Hg oxidation potential must take into account the change in AV due to fouling using empirical expressions as a function of conditions (NH<sub>3</sub>, halogens, etc.)

$$P_{\text{Hg-actual}} = P_{\text{Hg-clean}} \times (1 - \% \text{Fouling})$$

# Primary Factors Affecting Catalyst Management for DeNOx

## 1. Deactivation Rate (fuel and operations dependent)

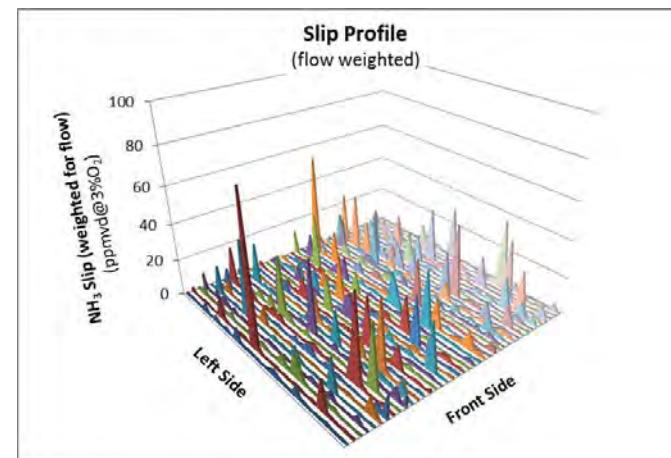


## 2. Required Performance – deNOx, inlet NOx, slip, SO<sub>2</sub> conversion, etc.

## 3. Fouling/sootblowing.

## 4. Reactor “Health” – NH<sub>3</sub>/NOx, flow, and temperature distributions.

## 5. Temperature and load.



# Base Case – Typical Management Plan

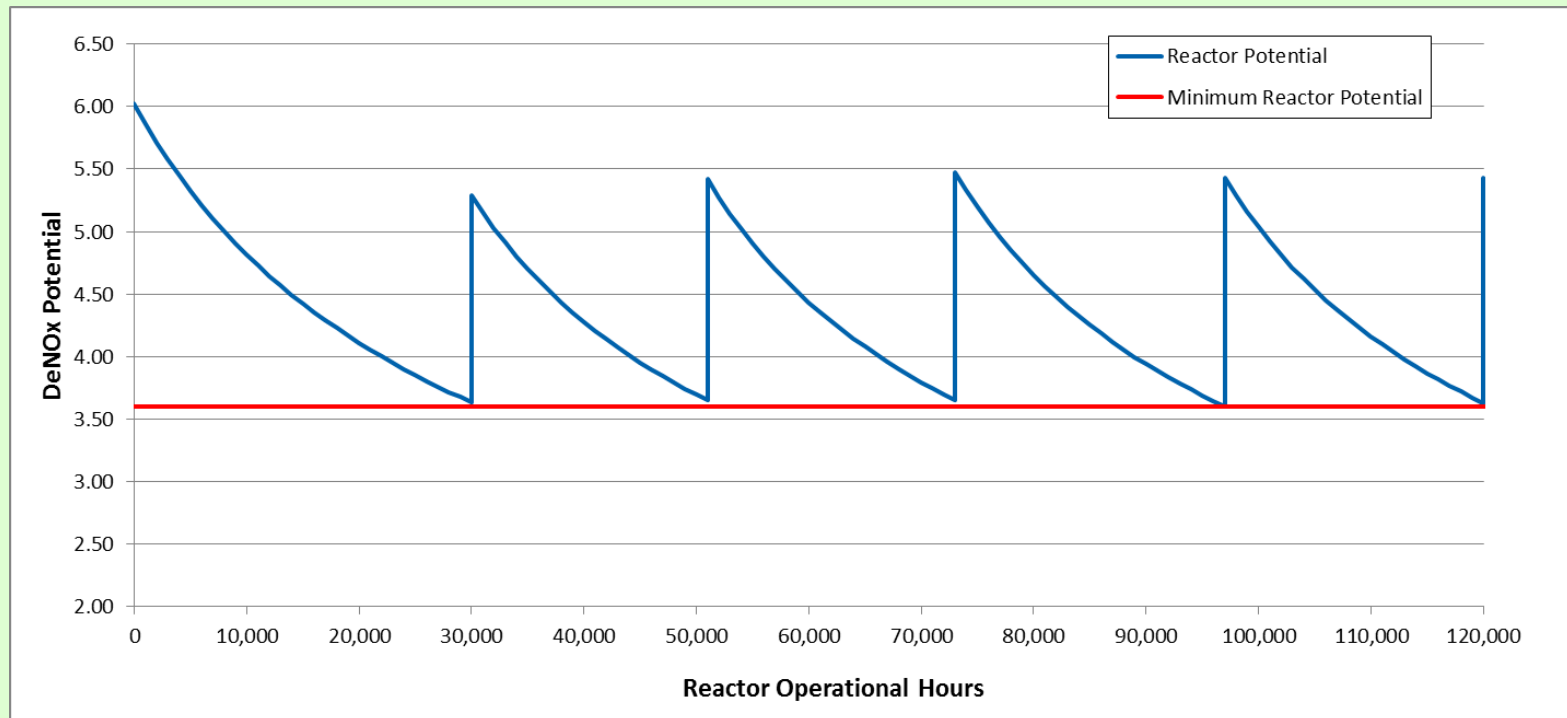
## Base Case:

300 ppm NO<sub>x</sub>  
90% deNO<sub>x</sub>  
10% RMS Flow  
5% RMS NH<sub>3</sub>/NO<sub>x</sub>

No Fouling

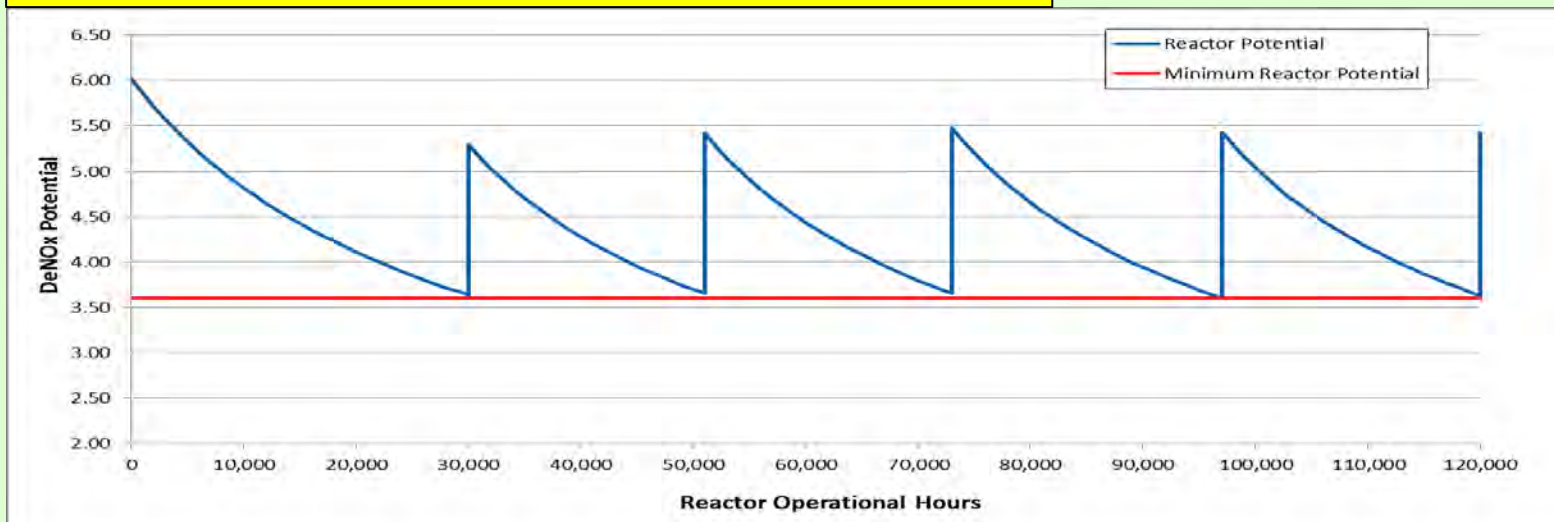
## Deactivation:

Moderate  
P/P<sub>o</sub> = 0.6 after 16,000 hrs.

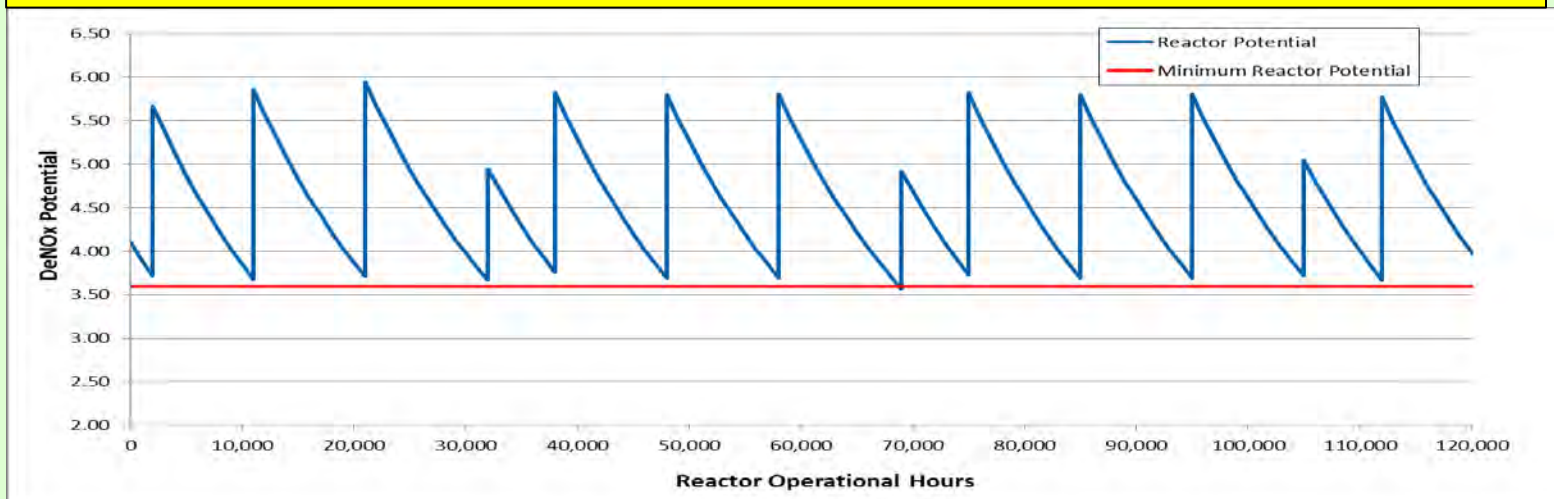


# Example Effect of Fouling on Management Plan

## Base Case: No Fouling (5 Management Events)



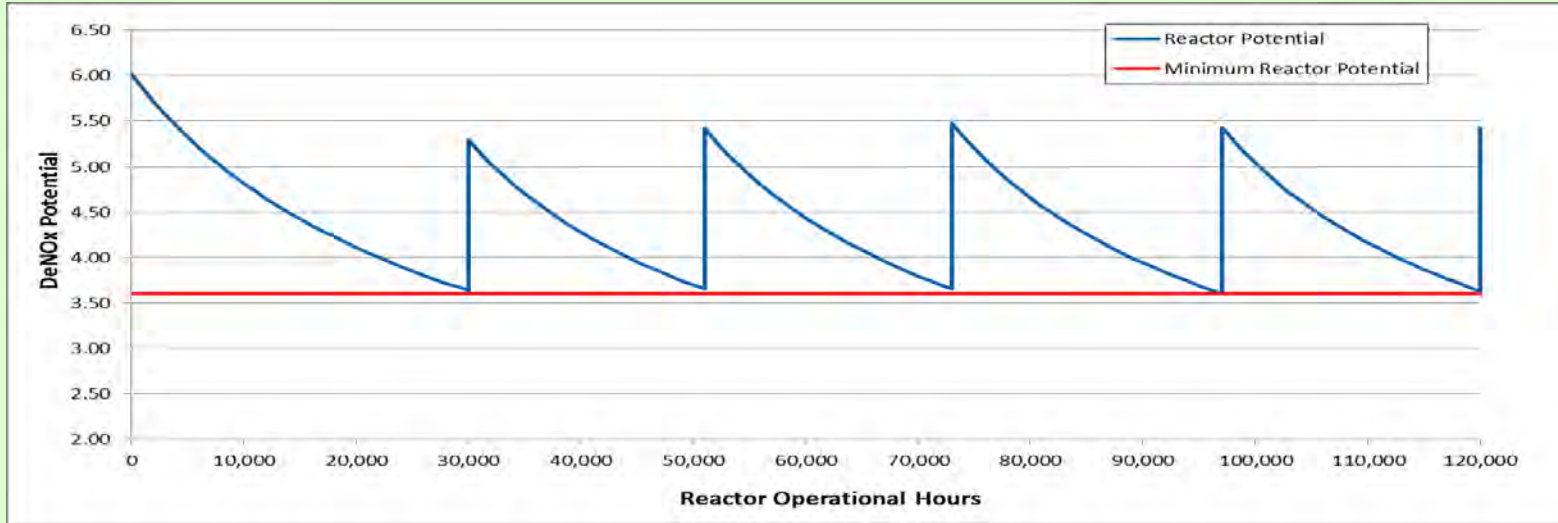
## High Fouling Case: 15% Fouling/Yr. (12 Events Management Events)



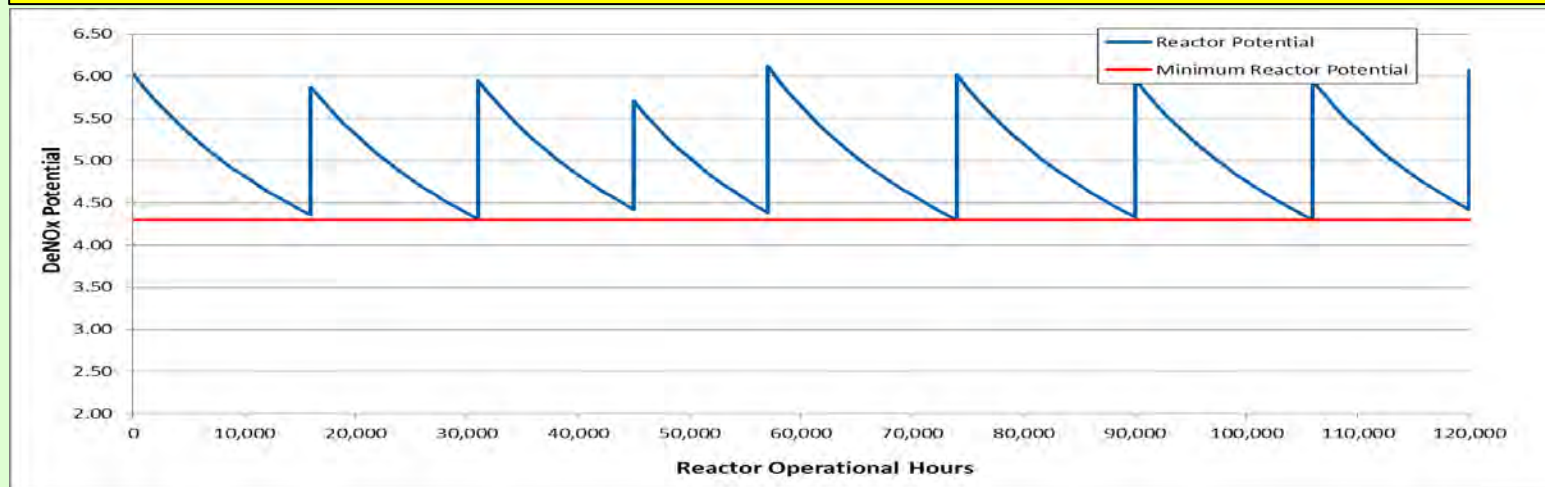
# Example Effect of Maldistributions on Management Plan

(effect of maldistributions is strongly a function of overall deNO<sub>x</sub>)

**Base Case: 5% RMS NH<sub>3</sub>/NO<sub>x</sub>; 10% RMS Flow (5 management events)**



**Poor Distributions Case: 8% RMS NH<sub>3</sub>/NO<sub>x</sub>; 15% RMS Flow (8 management events)**



# MERCURY OXIDATION AGING EFFECTS

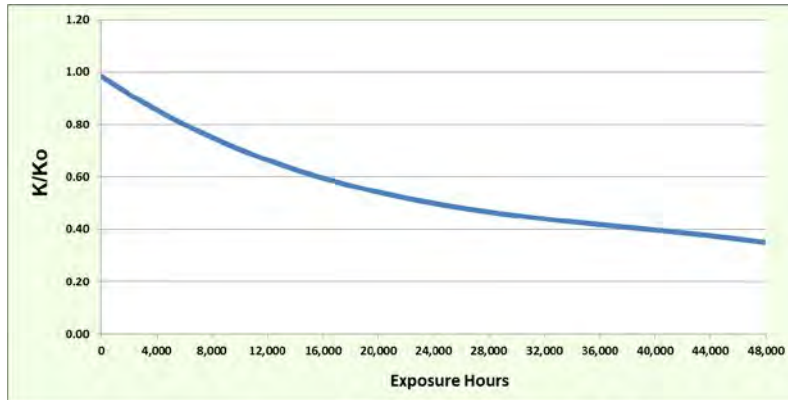
Catalyst performance declines over time in a rough qualitatively similar manner to deNOx deactivation.

Mercury oxidation decline is much more complicated, however, and many parameters have an effect.

In terms of managing this decline (i.e. catalyst management), many factors must be considered.

# Primary Factors Affecting Catalyst Management for Mercury Oxidation

## 1. Deactivation Rate (fuel, operations, layer location dependent)



## 2. Fouling/sootblowing.

## 3. Temperature, load, halogens.

## 4. Layer location (local ammonia conditions).

## 5. Minor; moderate changes in deNOx set point, maldistributions.

# Options for Determining Mercury Oxidation Deactivation Rate

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- 1. Test samples in the lab similar to current deNOx deactivation approach.**
- 2. Relate mercury oxidation deactivation to deNOx deactivation.**

# Option 1. Test samples in the lab

**Approach: Periodically retrieve field samples and measure mercury oxidation on bench, semi-bench or micro-scale reactors.**

## Concerns

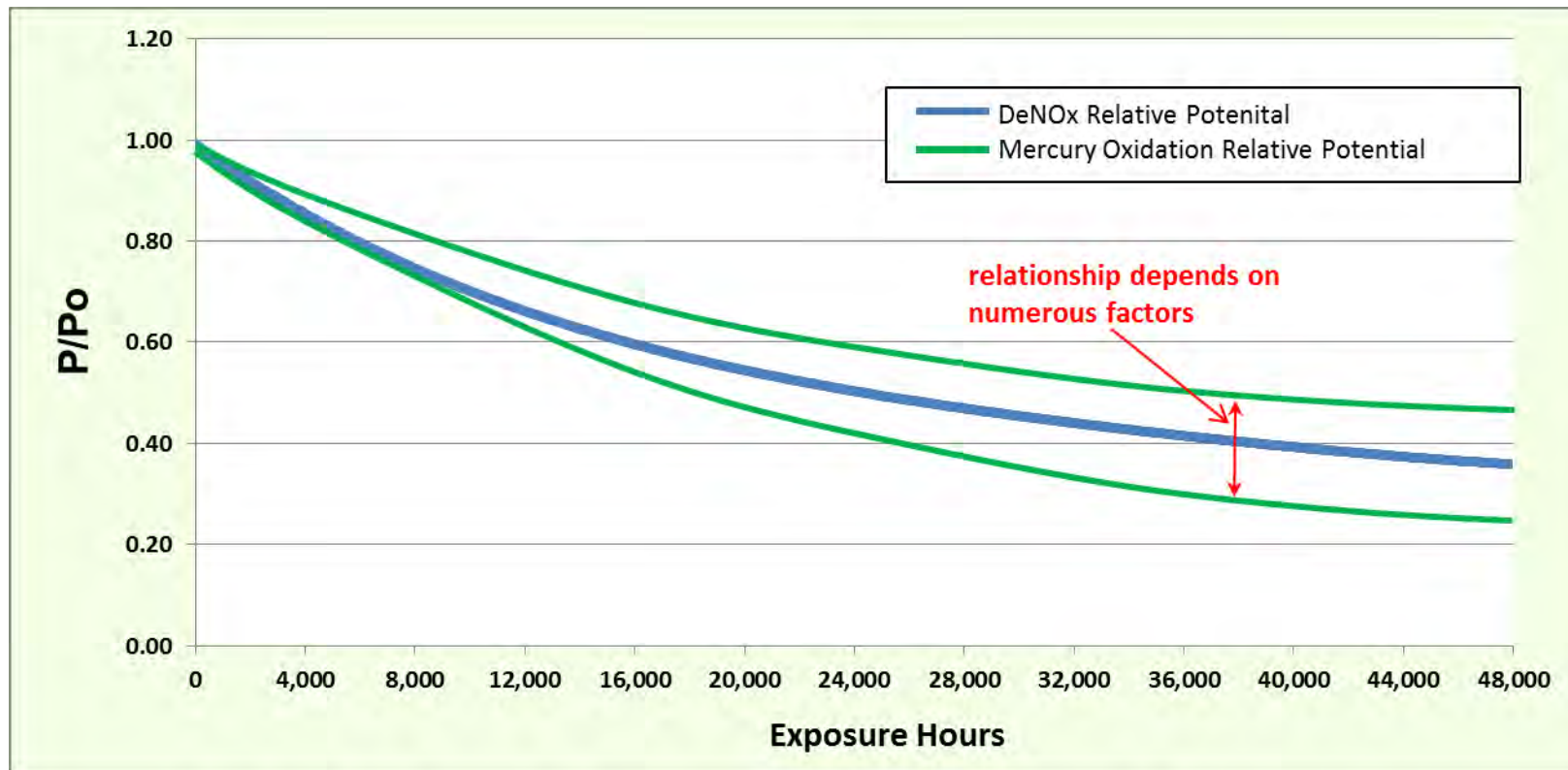
1. What conditions should be used?
2. How do you relate the tested conditions to the field conditions?
3. Lab testing is expensive and takes time.
4. How do the different test rig scales affect the data?

*\*\*\*Photos courtesy; Fossil Energy Research Corp.*



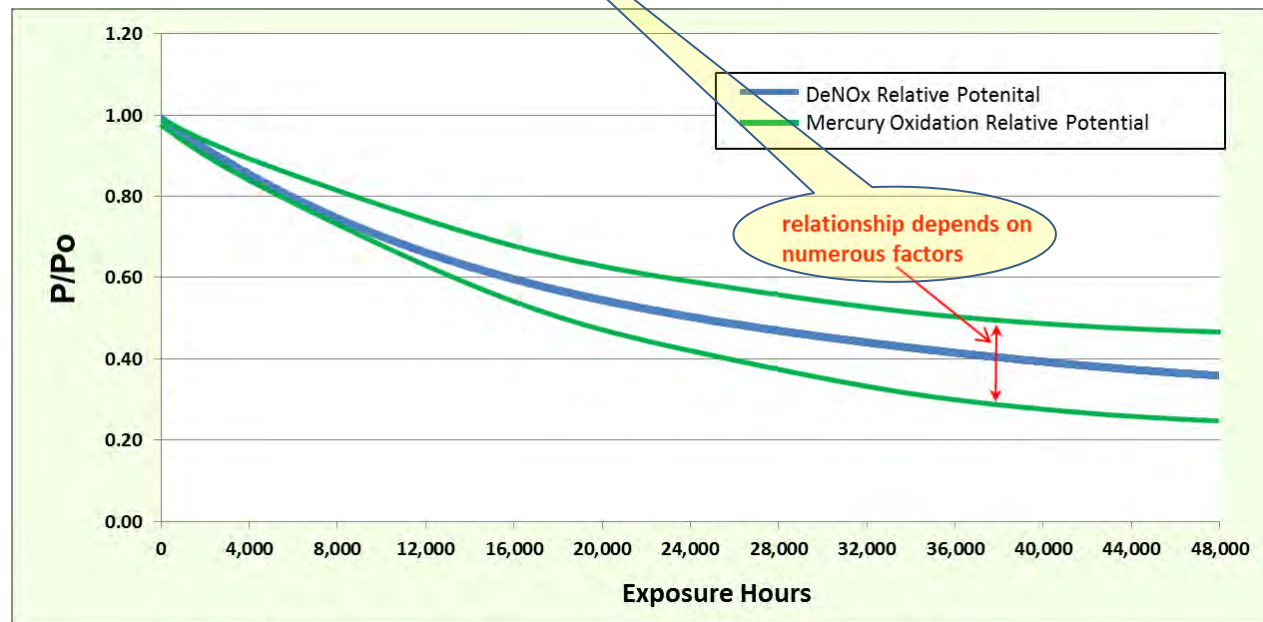
# Option 2. Relate mercury oxidation deactivation to deNOx deactivation

**Approach: Use deNOx deactivation as a surrogate for mercury oxidation deactivation; relate the two using empirical data.**



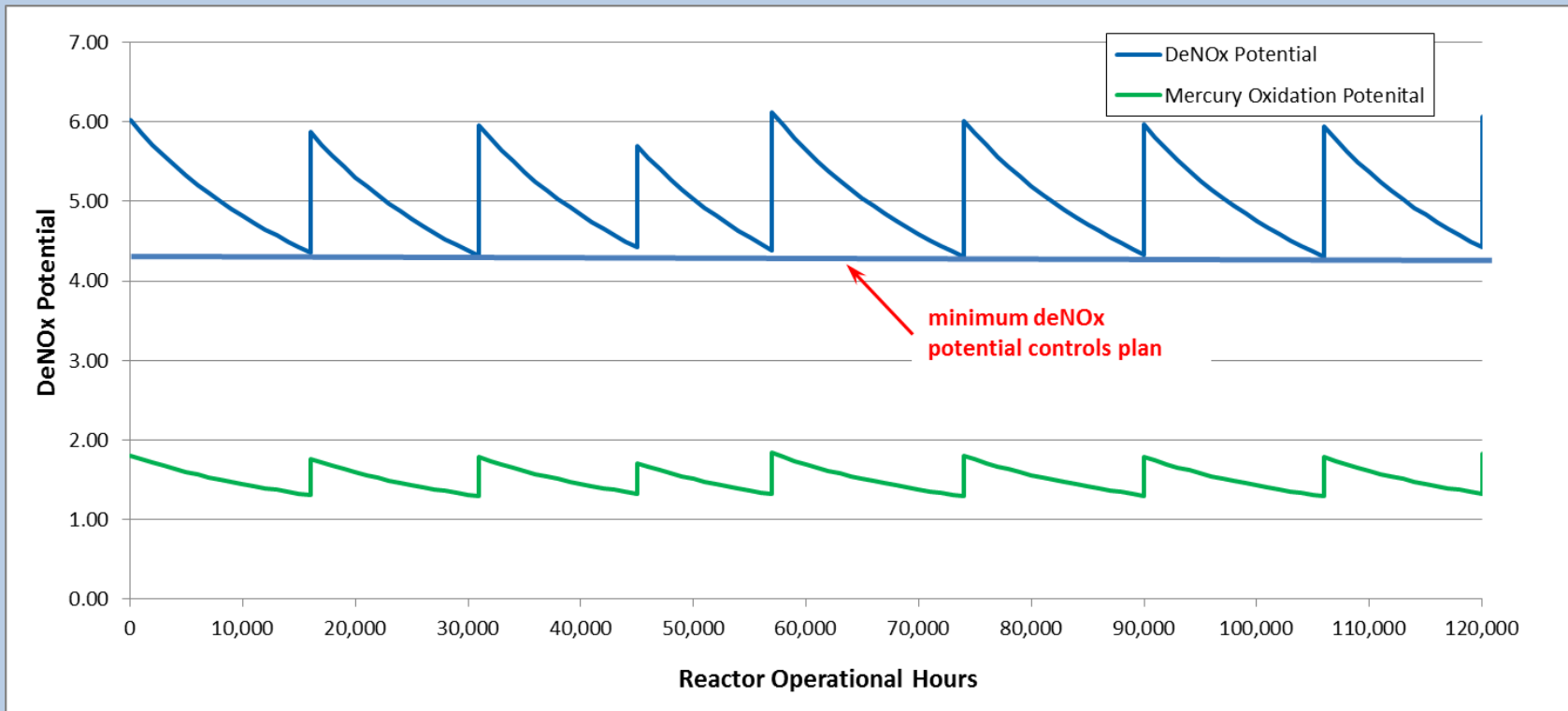
# Factors affecting the relationship of relative activity for deNOx and mercury oxidation

1. Overall operating conditions; temperature, halogens, other constituents?
2. Layer specific conditions; ammonia level
3. Catalyst design; geometry, formulation, OEM/Regen., conventional/advanced.



# Creating a Joint Catalyst Management Scheme

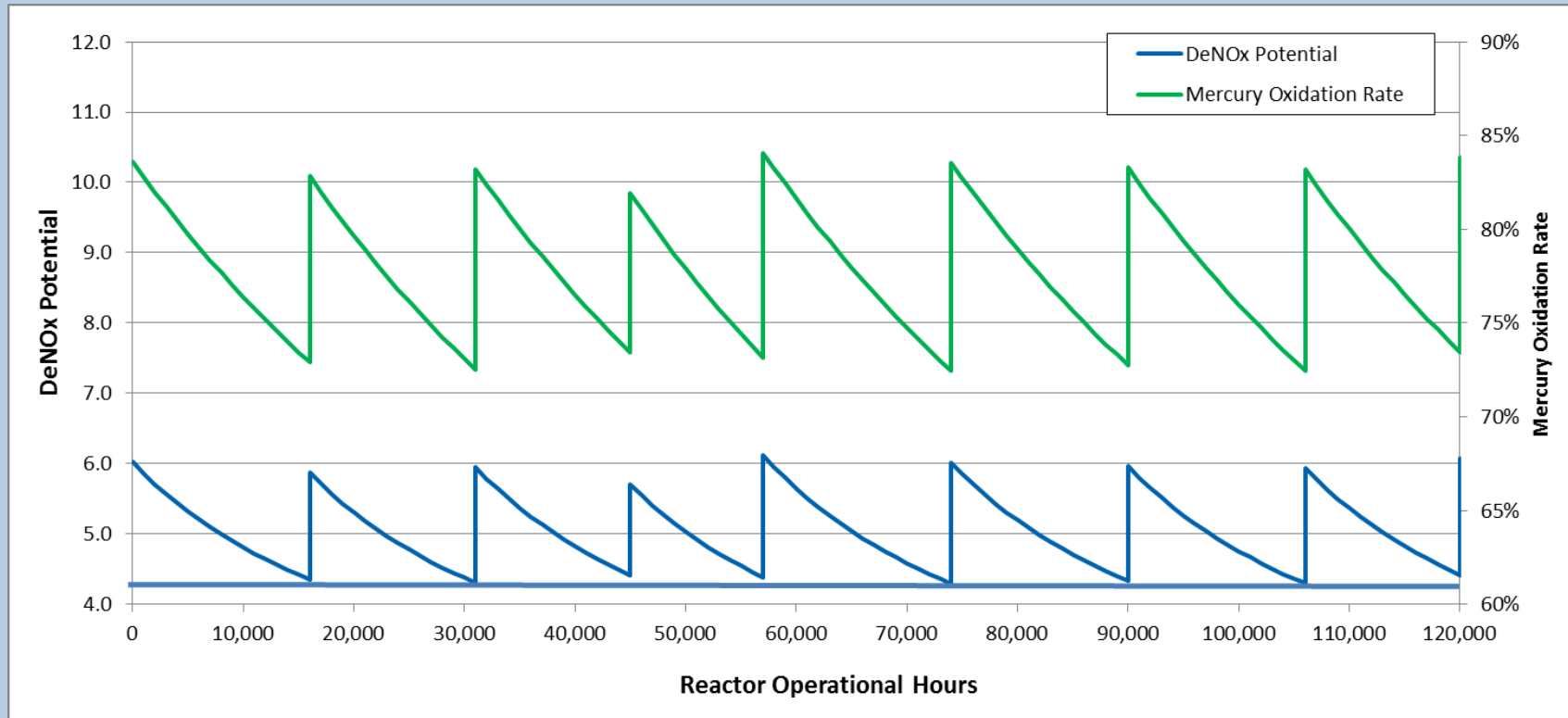
## Example 1: Controlled by deNOx



# Creating a Joint Catalyst Management Scheme

## Example 1: Controlled by deNOx

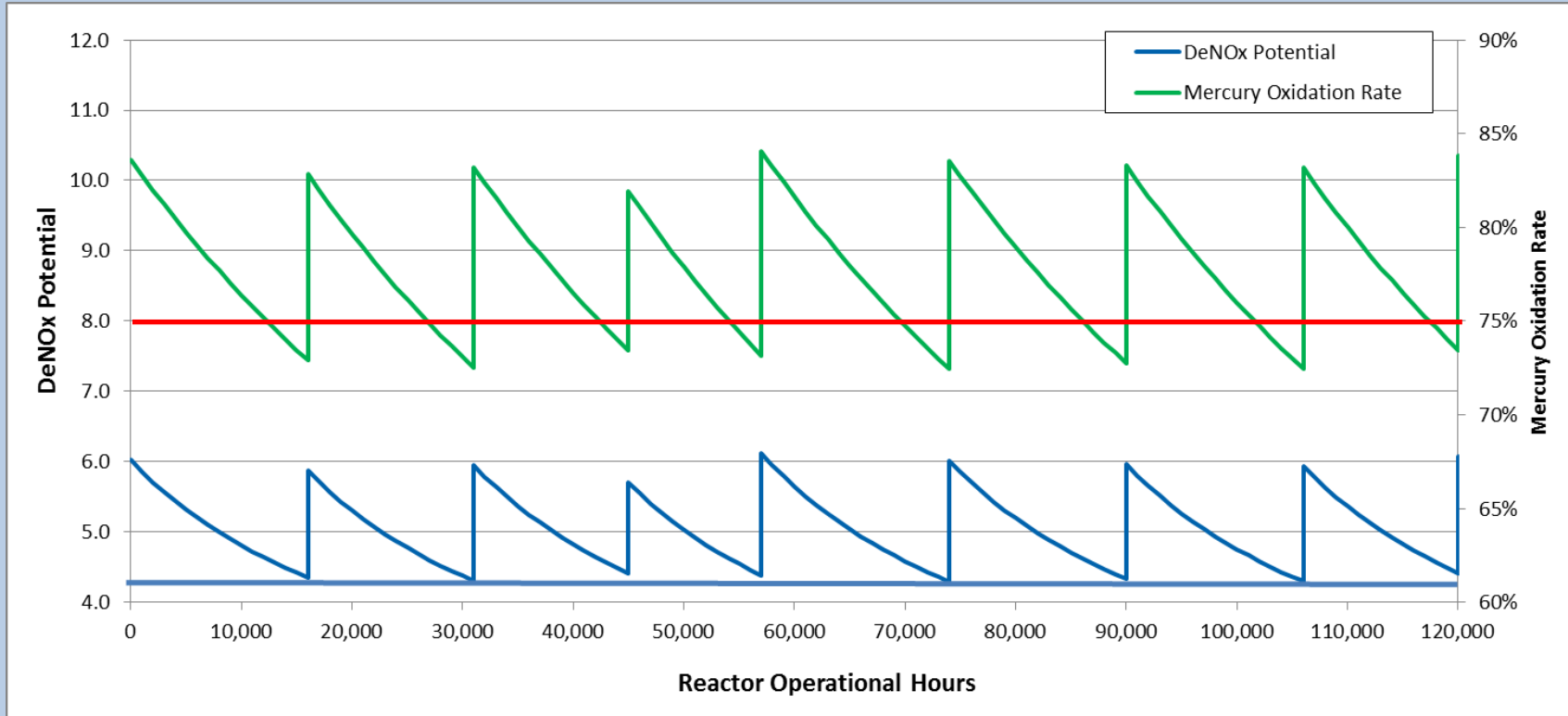
Alternate Plot: "Read off" mercury oxidation as a function of age.



# Creating a Joint Catalyst Management Scheme

## Example 2: controlled by mercury oxidation

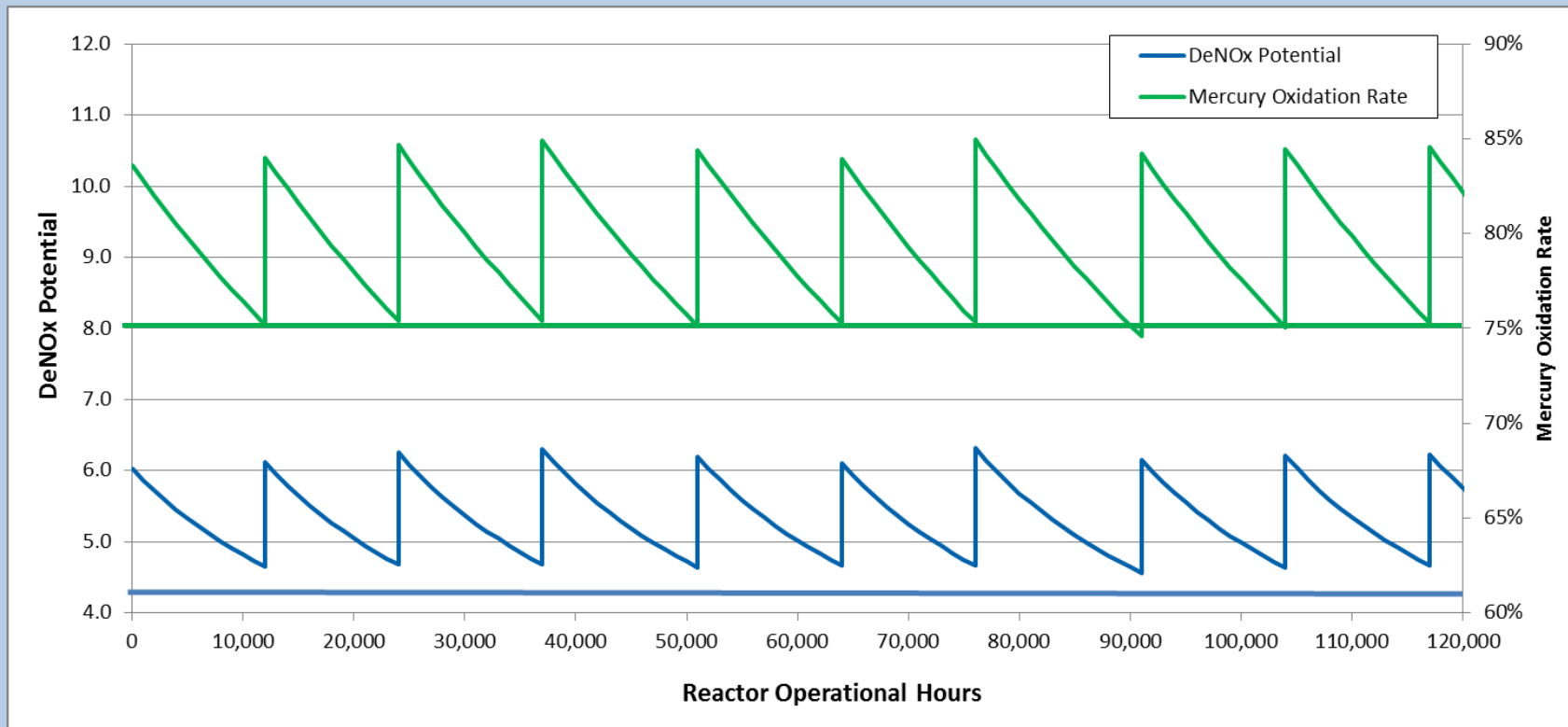
Example: Control mercury oxidation rate to a minimum of 75%



# Creating a Joint Catalyst Management Scheme

## Example 2: controlled by mercury oxidation

Controlling to 75% mercury oxidation increases catalyst events from 8 to 9.5  
Excess deNOx potential is present throughout the life cycle

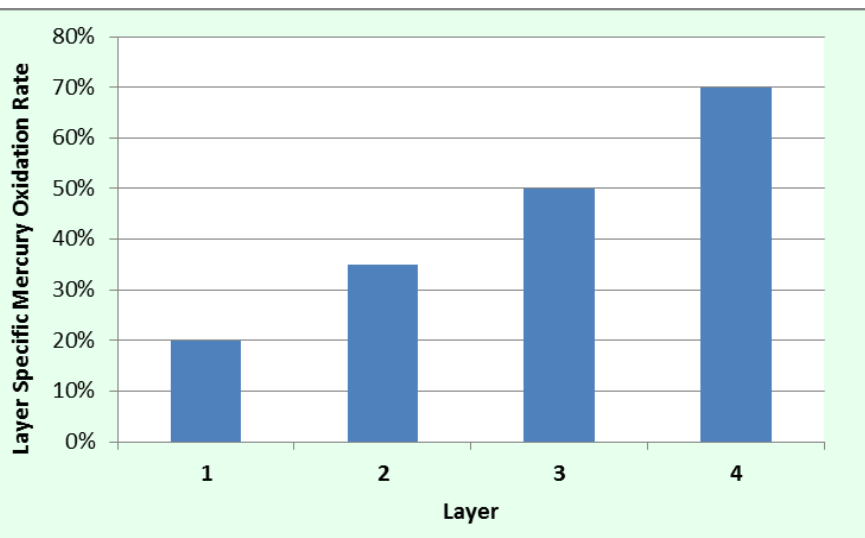


# Major Considerations When Managing for Mercury Oxidation

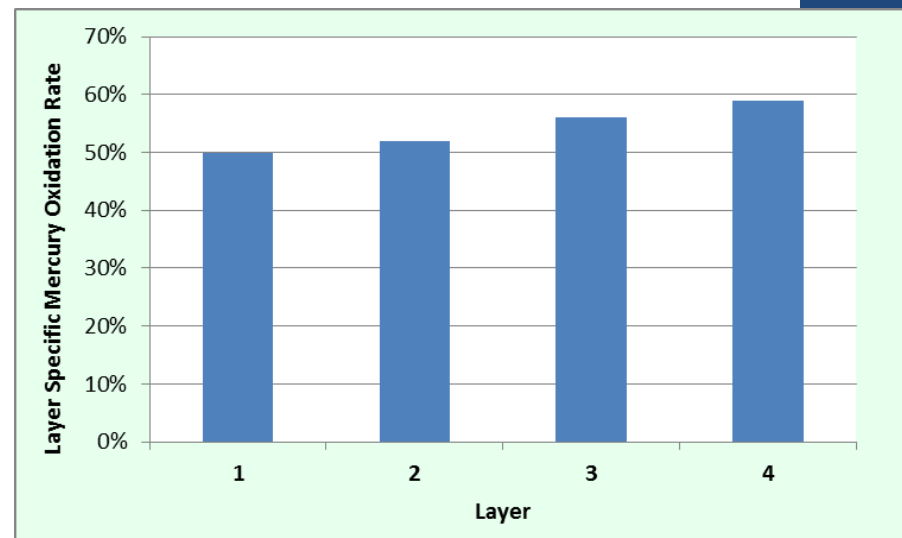
1. Reactor must be treated on a layer by layer basis – ammonia profile strongly affects layer-specific mercury oxidation.

The ammonia impact is strongly affected by halogens

Example: Low halogen environment.

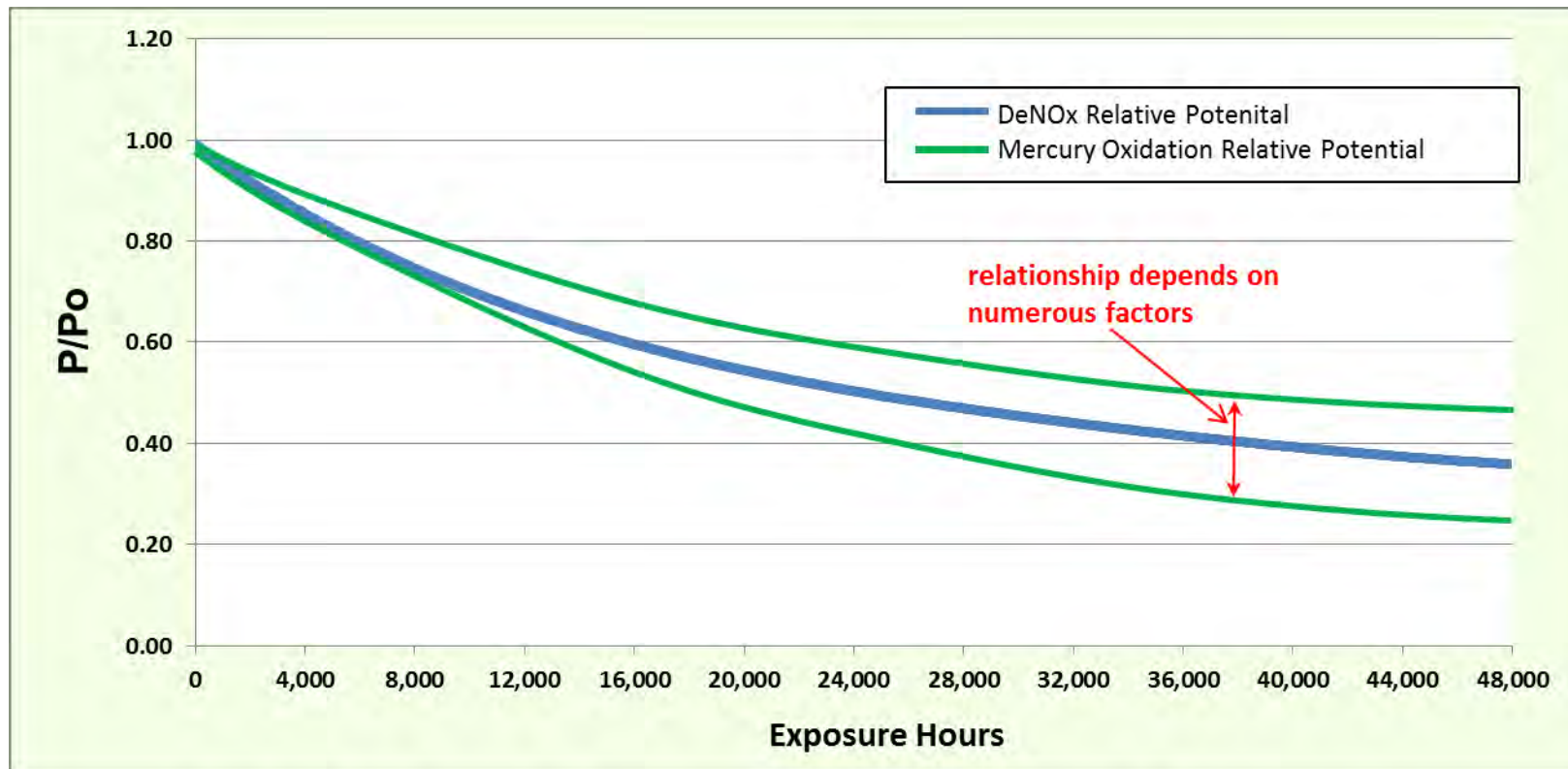


Example: High halogen (bromine) environment.



# Major Considerations When Managing for Mercury Oxidation

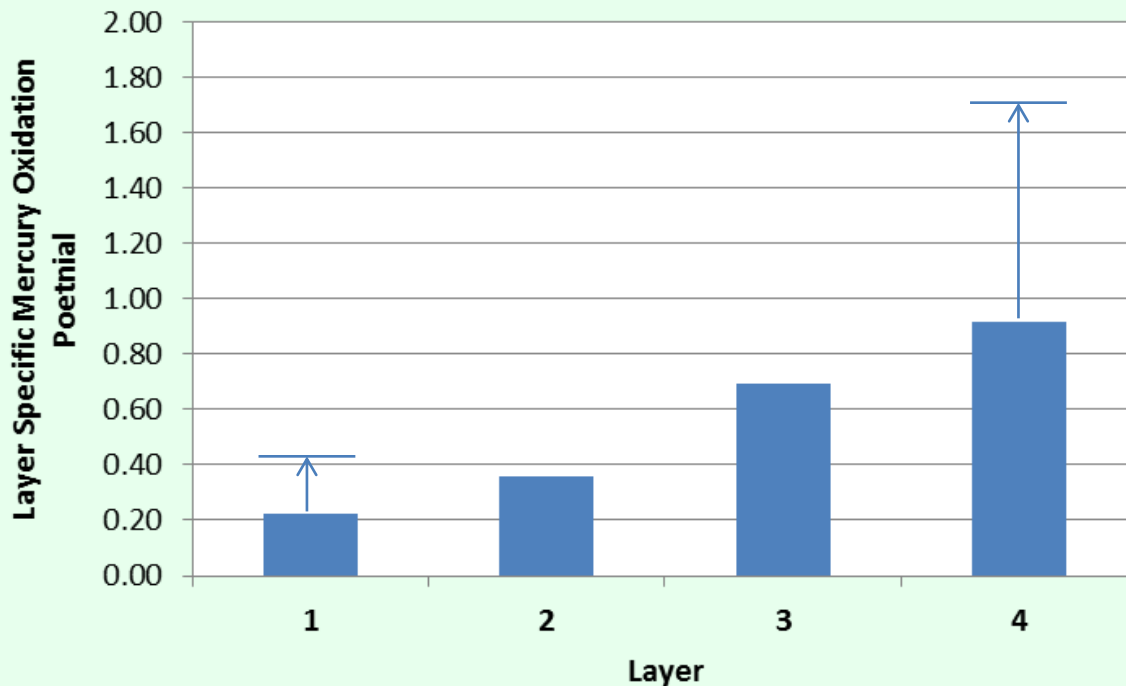
2. The specific layer location and flue gas conditions affects how the deNOx deactivation relates to mercury oxidation deactivation. (In other words, the relationship between deNOx deactivation and mercury oxidation deactivation will differ for each layer.)



# Major Considerations When Managing for Mercury Oxidation

- Simply replacing the layer with the lowest deNOx potential is not necessarily the optimal approach for managing for mercury oxidation.

Due to the ammonia effect, adding potential to a lower location has more effect than adding potential to an upper location. However, “trickle-down” effect due to the change in ammonia profile must be considered.



Example: All layers have same activity with  $P/P_o = 0.5$  for deNOx and Hg. Replacing L1 adds 0.2 points to  $P_{Hg}$ , while replacing L4 adds 0.9 points. However, this does not consider trickle-down.

# Major Considerations When Managing for Mercury Oxidation

## 4. Advanced catalysts

1. **Advanced catalysts are designed to enhance mercury oxidation, as compared to conventional catalysts, especially under lower-halogen conditions.**
2. **Must account for any trade-offs (cost, lower deNO<sub>x</sub> activity, higher SO<sub>2</sub> conversion).**
3. **Influence of ammonia is impacted with advanced catalyst use, this can affect how the catalyst is managed.**
4. **The exact benefits, and under what conditions, are still being evaluated.**

# Major Considerations When Managing for Mercury Oxidation

5. Must have a robust mercury oxidation model to effectively understand each layer's contribution to overall mercury oxidation, supporting management decisions.

**There are too many factors to be able to intuitively manage for mercury oxidation with any degree of quantitative certainty. Even qualitative management can be difficult without a model.**

# CONCLUSIONS

- **Lots of progress is being made in understanding mercury oxidation. The industry now has the required tools, which are constantly being refined, to predict mercury oxidation with a reasonable degree of certainty.**
- **Work is on-going to answer specific targeted questions.**
- **Mercury oxidation isn't simple, but with the right tools it can be understood.**

# EPRI Resources

## Protocol for Laboratory Testing of SCR Catalyst: 2nd Edition

**Product ID:** 1014256

**Date Published:** 21-Dec-2007

**Pages:** 82

**Sector Name:** Generation

**Document Type:** Technical Results

## SCR Catalyst Mercury Oxidation Laboratory Testing Guideline – Industry Version

**Product ID:** 3002005087

**Date Published:** 03-Mar-2015

**Pages:** 60

**Sector Name:** Generation

**Document Type:** Technical Results

## Guidelines for Speciated Mercury Field Measurements

**Product ID:** 3002006098

**Date Published:** 09-Dec-2015

**Pages:** 130

**Sector Name:** Generation

**Document Type:** Technical Results

## PRE-SW: Catalyst React (CatReact), v3.0 - Beta

**Product ID:** 3002009618

**Date Published:** 20-Dec-2016

**Sector Name:** Generation

**Document Type:** Software

# Things to keep an eye on...



1. Continued updates from catalyst manufacturers related to mercury oxidation deactivation and performance associated with field management cases.
2. Advanced catalyst developments and performance in field applications.
3. EPRI advanced catalyst performance trials using pilot scale facilities.
4. EPRI age-related performance tracking using laboratory measurements.
5. EPRI round-robin testing for bench-scale deNO<sub>x</sub> and SO<sub>2</sub> conversion measurements.
6. EPRI round-robin testing for laboratory mercury oxidation testing.
7. New developments in trap technology for field testing, including speciated mercury, ammonia, halogens, etc.



W. Scott Hinton, Ph.D., P.E.

***W.S. HINTON & ASSOCIATES***

203 W. Jackson St.

Pensacola, FL 32501

Office: 850-936-0037

Cell: 850-261-5239

email: [shinton@wshinton.com](mailto:shinton@wshinton.com)