

# **REINHOLD ENVIRONMENTAL Ltd.**



## **2012 NO<sub>x</sub>-Combustion Round Table & Expo Presentation**

February 13-14, 2012, in Columbus, OH / Hosted by AEP

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# 2012 NOx-Combustion/PCUG Conference

## February 14, 2012

### Maximizing Your SCR System's Fuel and Dispatch Flexibility



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# Presentation Topics

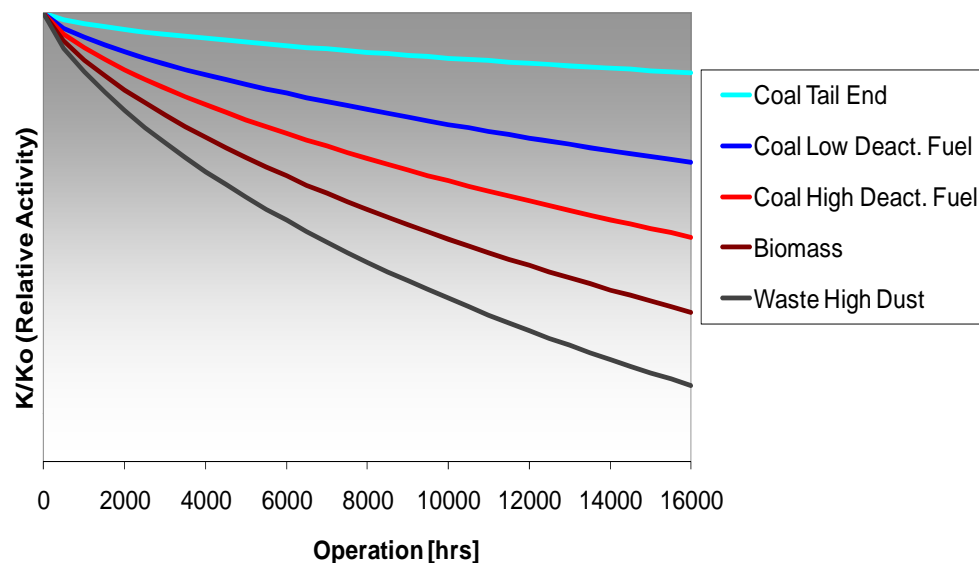
- Catalyst Deactivation Mechanisms for PRB Applications
- PRB Fueled Unit Catalyst Deactivation Trends
  - Various Catalyst Types and Compositions
  - Various Types of Combustion
- Deactivation Rate and the Catalyst Design Process
- Assessing Catalyst Designs to Minimize Project Risk
- Alternate Example Designs



# Catalyst Deactivation Mechanisms

- Catalyst Poisons:

- Arsenic
- Potassium
- Phosphorus
- Sodium
- Cadmium
- Lead
- Copper
- Other Elements



- Fouling by Solid Compounds

- Gypsum (Calcium Sulfate) and Other Solid Compound Deposition
- Ammonium Bisulfate (Avoided by Keeping Above Permissive Temperatures)

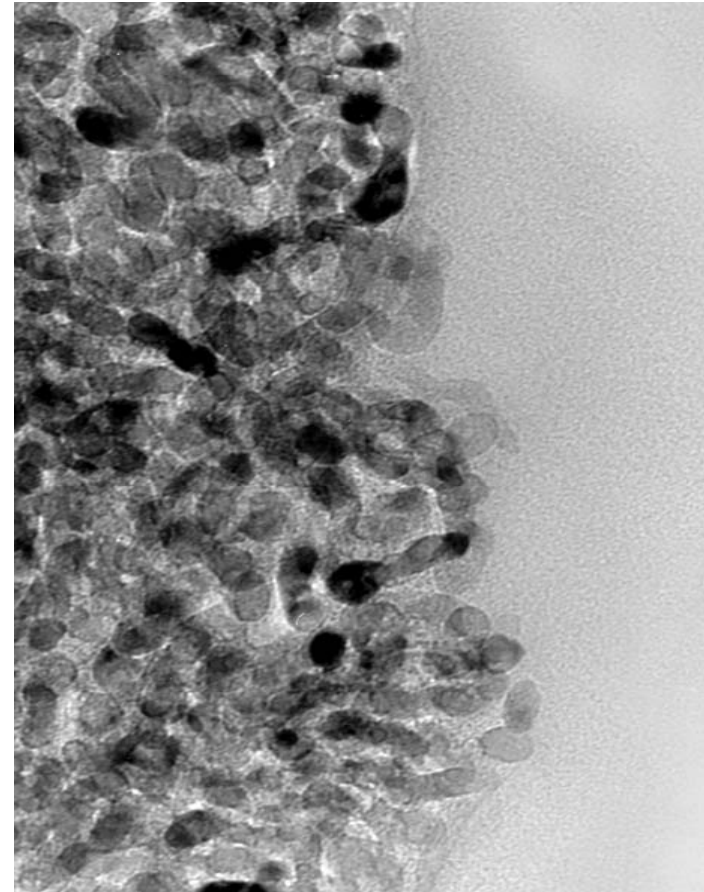
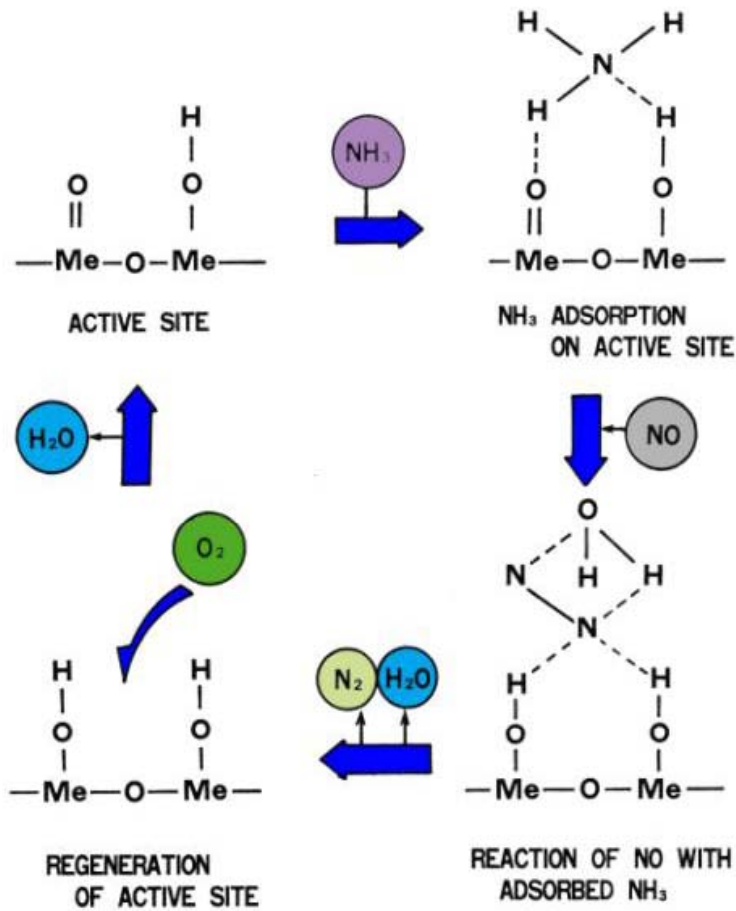
- Deactivation Occurs During...

- Normal SCR Operation
- Startups and Shutdowns as Unit Goes Through Acid Dew Point

# Catalyst Chemical Cycle

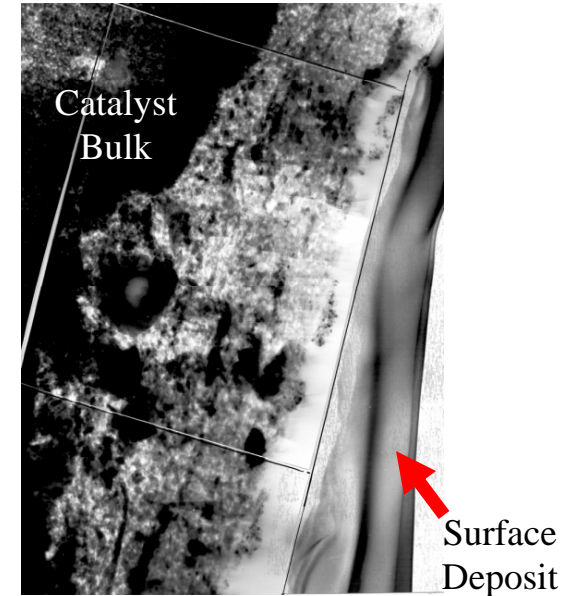
## Catalyst Chemical Cycle

## Active Sites



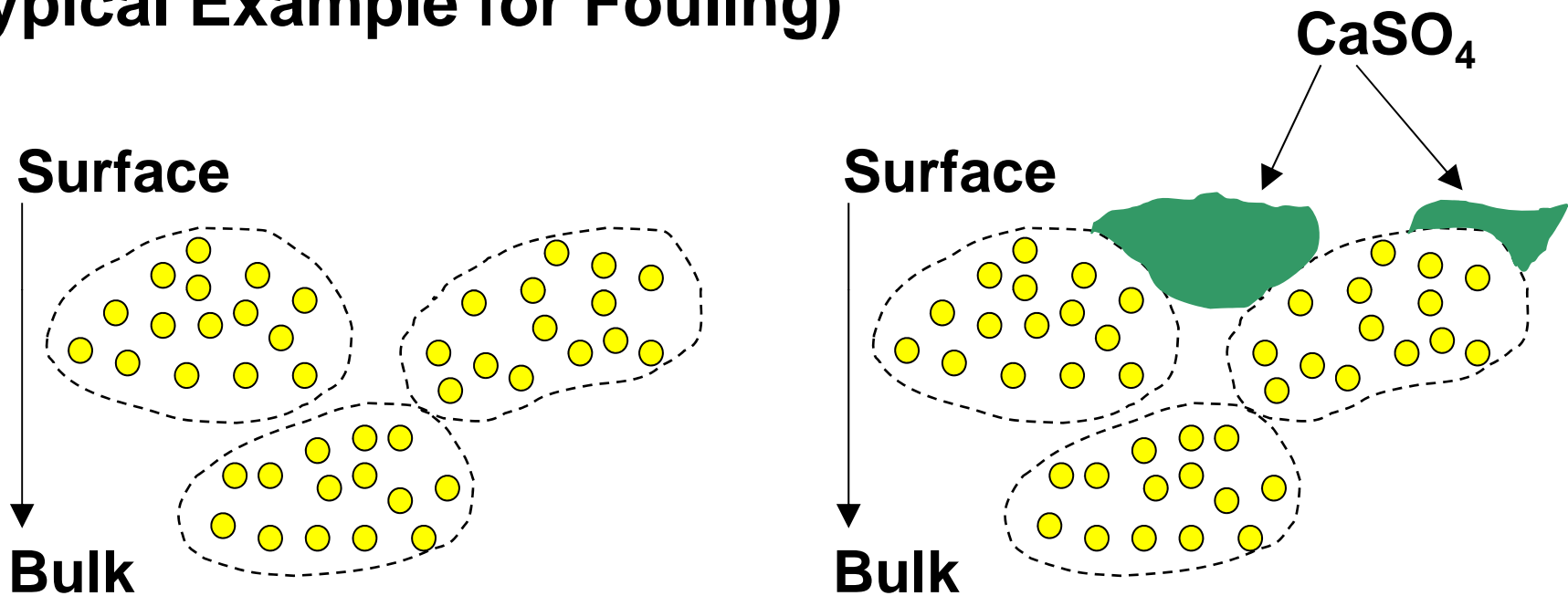
# PRB Deactivation Mechanisms

- Catalyst Fouling
  - Calcium Sulfate Formation on Catalyst Surface
  - Blinding of Active Pore Sites
- Phosphorus Deactivation
  - Pore Blocking and Pore Condensation by Polyphosphates
    - ◆ Carbothermic Reduction Creates P Bearing Inorganic Compounds (Proposed by B&W 2010)
    - ◆ Gaseous Phosphorous Oxidized with  $O_2$  to  $P_nO_m$  (i.e.,  $P_4O_{10}$ ) or w/ $H_2O$  vapor -- Phosphoric Acid
    - ◆ Higher Temperatures Phosphoric Acid Forms Polyphosphoric Acid and w/Alkali Compounds Polyphosphates
  - Risk Increases With “Deep Staging” with Low  $O_2$  and Higher CO



# Catalyst Deactivation Mechanisms:

## Calcium Deterioration (Typical Example for Fouling)



FRESH CATALYST

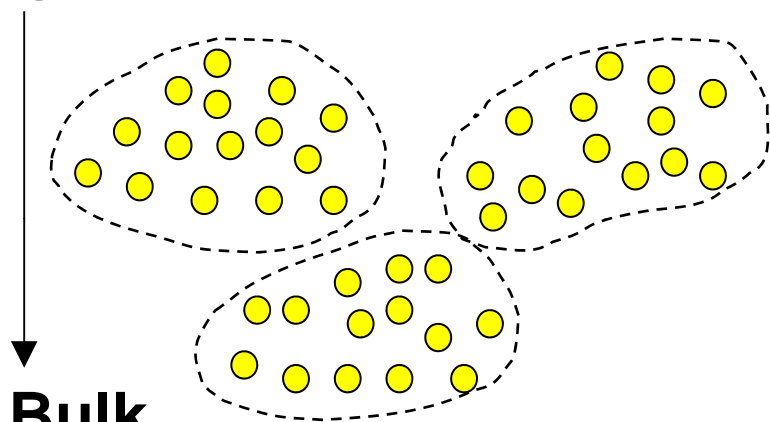
CALCIUM DETERIORATION

Gypsum: formed from  $\text{SO}_3$  and  $\text{CaO}$  (ash) blocks the access of the gas to the active centers.

# Catalyst Deactivation Mechanisms:

## Phosphorus Deterioration

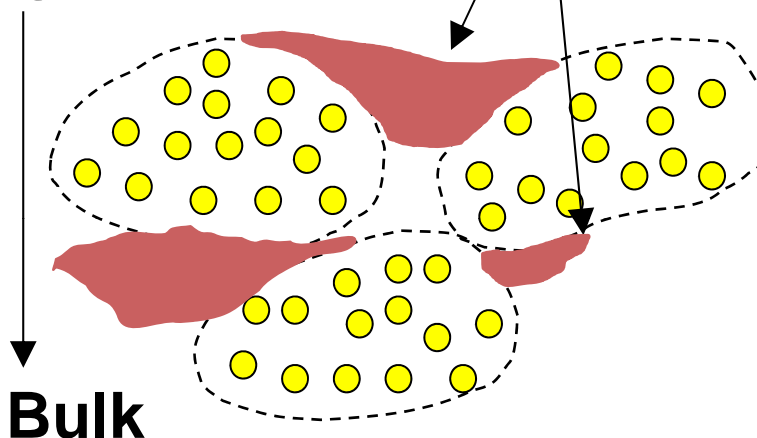
Surface



FRESH CATALYST

## Polyphosphates

Surface

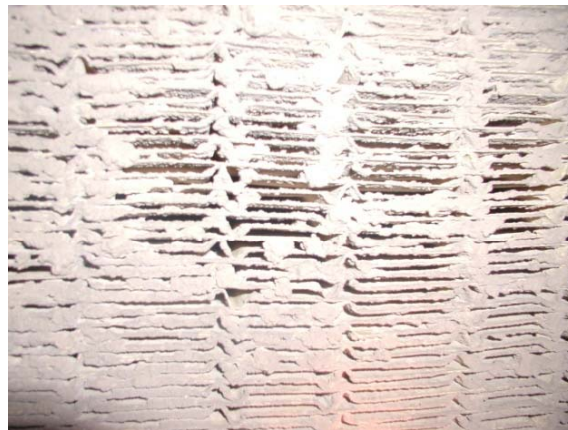
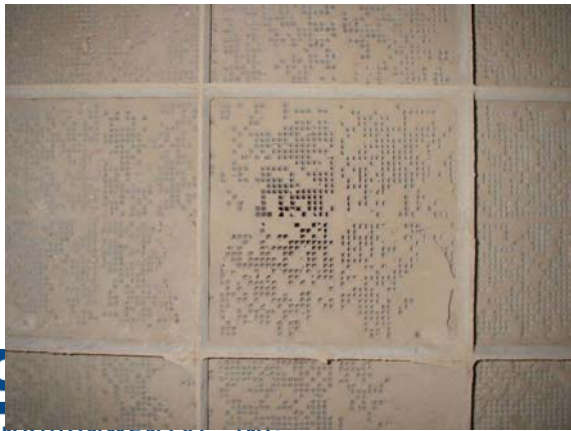


PHOSPHORUS DETERIORATION

- Increased Air Staging or Poor Combustion Results in Carbothermic Reduction of Phosphorus Compounds Increasing Catalyst Deactivation
- Pore Condensation and Pore Blocking by Polyphosphoric Acid Aerosols / Sub-micron Particles of Polyphosphates
- Changes the Nature of Acid Sites on the Catalyst by Forming P-OH Acid Sites with a Lower Acid Strength Than the Acid Sites Formed as V-OH

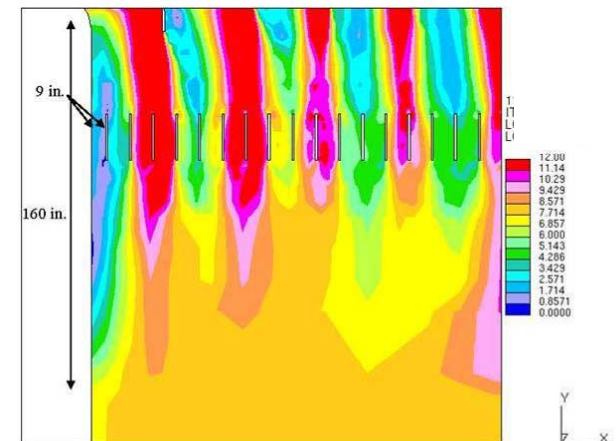
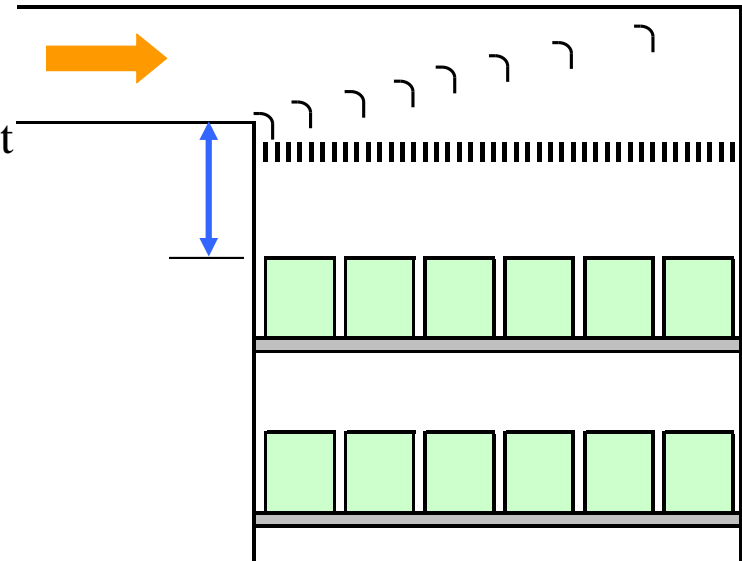
# PRB Deactivation Mechanisms

- Catalyst Pluggage
  - High Angle of Repose Ash
  - Pluggage Reduces Surface Area Available for Reaction
  - Pluggage Can Be A Result From Several Sources
    - ◆ Improper Pitch
    - ◆ Large Particle Ash (LPA)
    - ◆ High Unburned Carbon
    - ◆ High Ash Loading
    - ◆ Poor Flow/Ash Distribution Designs
    - ◆ Reactor Design



# Minimizing Potential Pluggage Begins With Reactor and LPA Design

- Reactor Configuration
  - Ensure Proper Distance Exists From Crossover Duct Down to Top of 1<sup>st</sup> Catalyst Layer (~13 feet)
  - Minimize Internal Structures
- Flow Modeling Critical to...
  - Confirm Adequate Freeboard Above Top Catalyst Layer
  - Confirm Support Beam Shadowing Effects on Second Layer
  - Confirm Proper Flow and Ash Distribution
  - Confirm Vertical Flow Into Catalyst
- Ensure Catalyst Cleaning Acoustic Energy is Adequately Distributed
- Incorporate Large Particle Ash (LPA) Collection and Removal Device Upstream of Catalyst

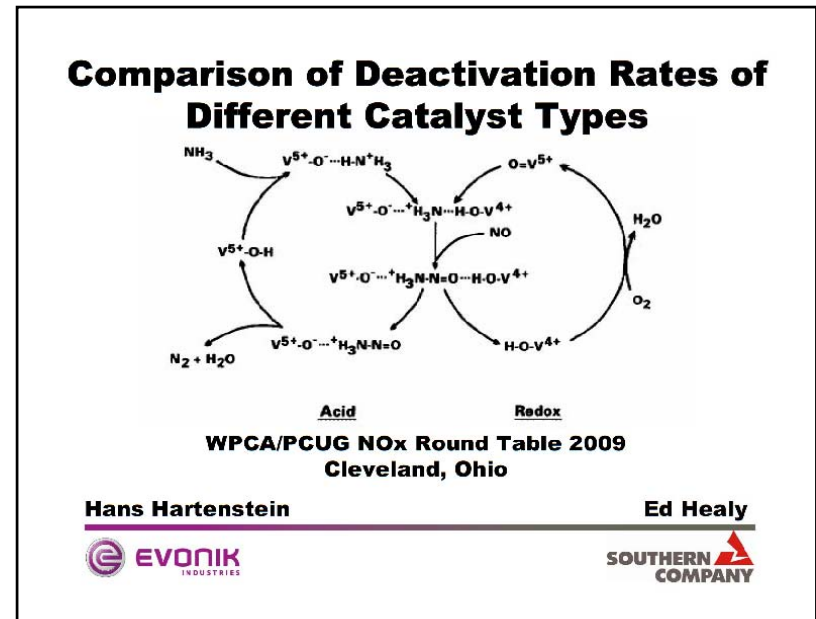


# Catalyst Deactivation

- Vanadia–Titania Type Catalyst Deactivates **Independent** of....
  - Catalyst Type and Geometry
  - Catalyst Composition
- 25+ Years of Experience With Testing Catalyst From All Suppliers Confirms Conclusion
  - Reference Also Paper Presented by the Southern Company and Evonik (now Steag) at the 2009 Reinhold Round Table
- Deactivation Resistance Comes From Providing Adequate Reactor Potential

**Web Address for Paper:**

<http://www.reinholdenvironmental.com/public/47bc6d6a7e8f479388a20d66579738f8/Hans%20Hartenstein%20presentation%20Deactivation%202009.pdf>



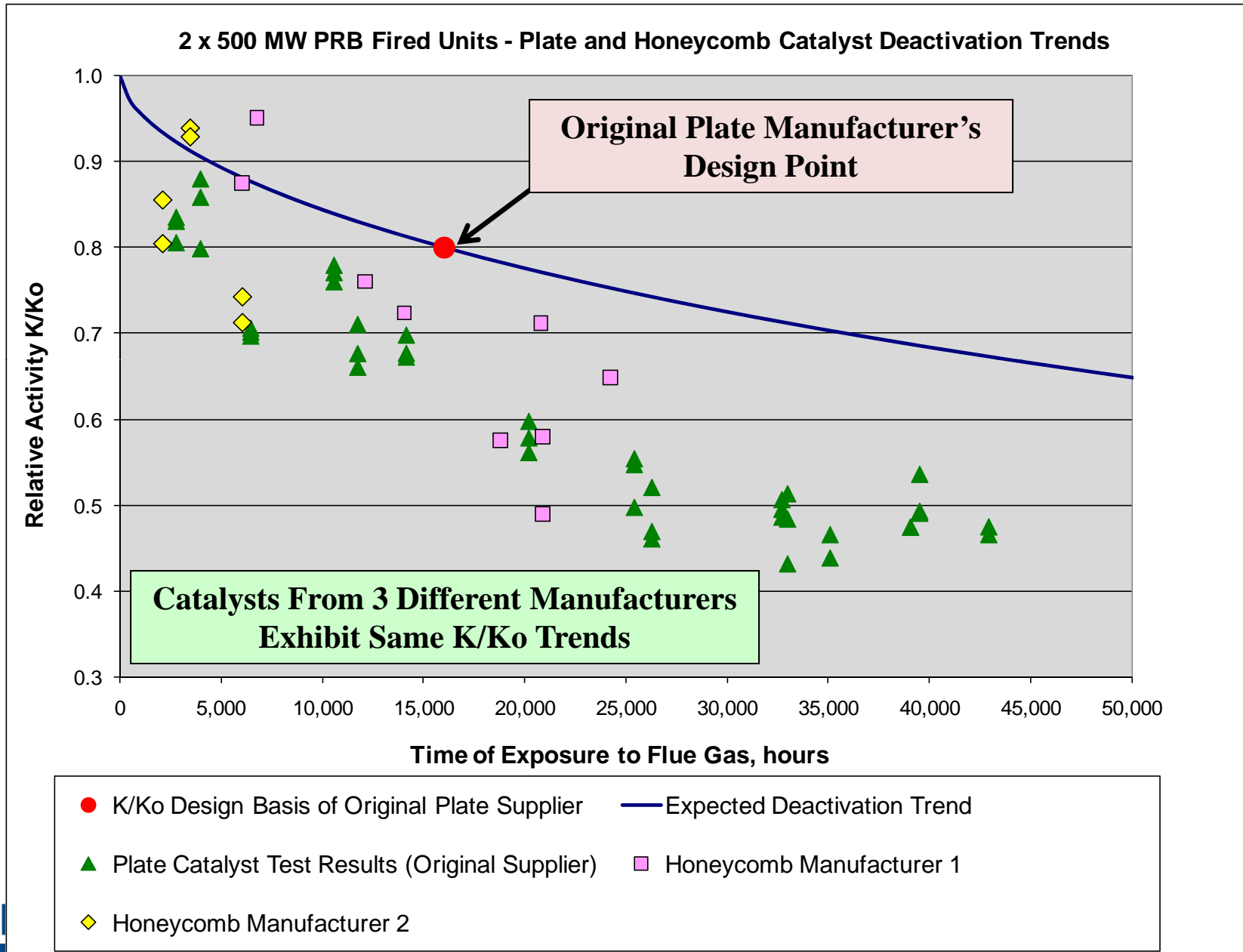
# Fresh (New) Catalyst Constituents

Catalyst Chemical Compound	Honeycomb Catalyst	Plate Catalyst	Corrugated Fiber
Vanadium ( $V_2O_5$ )	up to 3%	up to 3%	up to 3%
Titania ( $TiO_2$ )	~80%	~80%	~70%
Tungsten ( $WO_3$ )	5 to 10%	5 to 10% (1)	5 to 10%
Molybdenum ( $MoO_3$ )	0%	5 to 10% (1)	0%
Silica ( $SiO_2$ )	~8%	~8%	~17%

Note: (1) Plate type catalyst utilizes either tungsten or molybdenum.

The Predominant Variable Constituent Modulated is Vanadium to Achieve  $SO_2$  to  $SO_3$  Conversion Rate Objectives

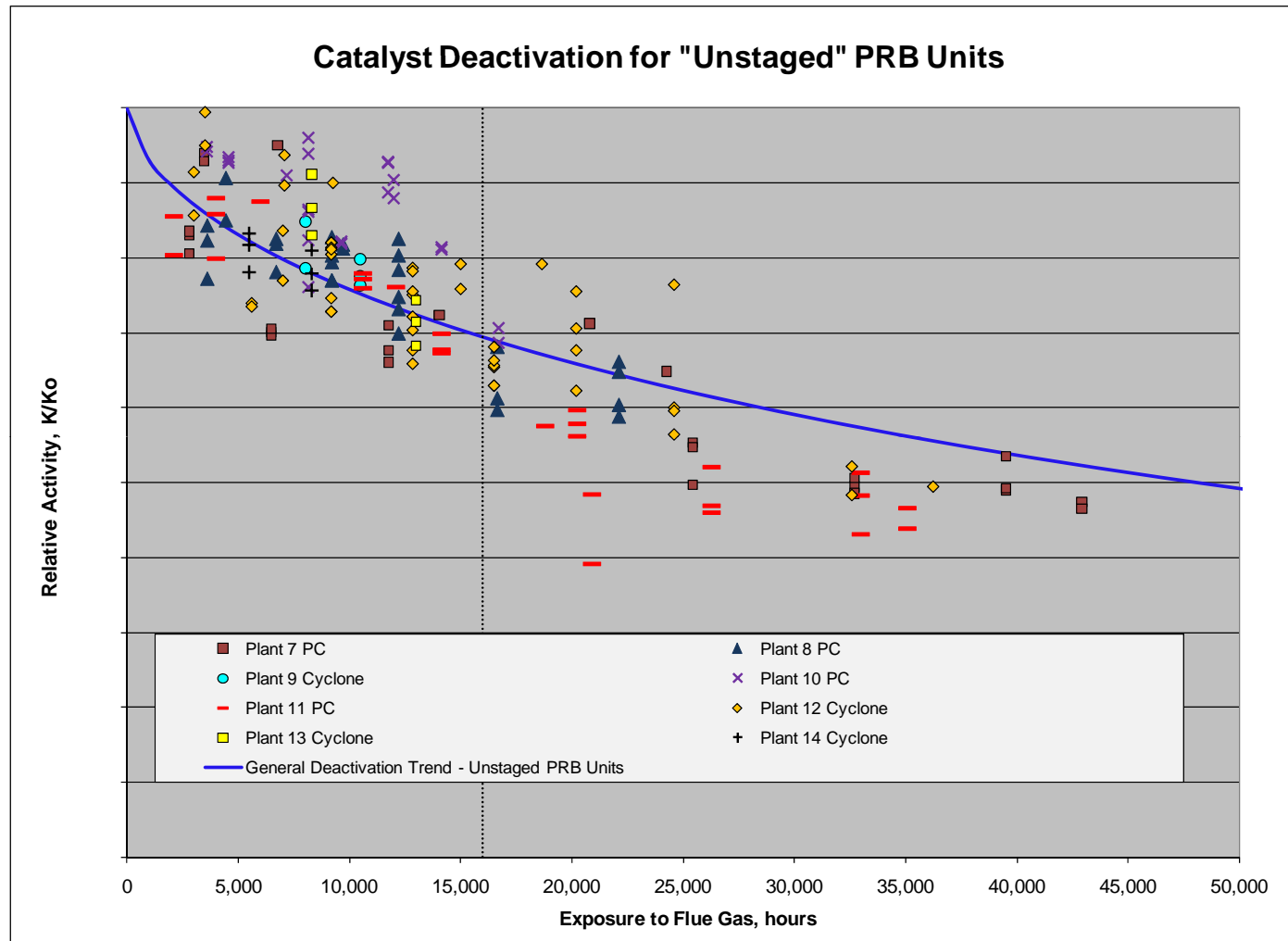
# Plate and Honeycomb Deactivation Trends - PRB Units



# PRB Fired Units Deactivation Trends

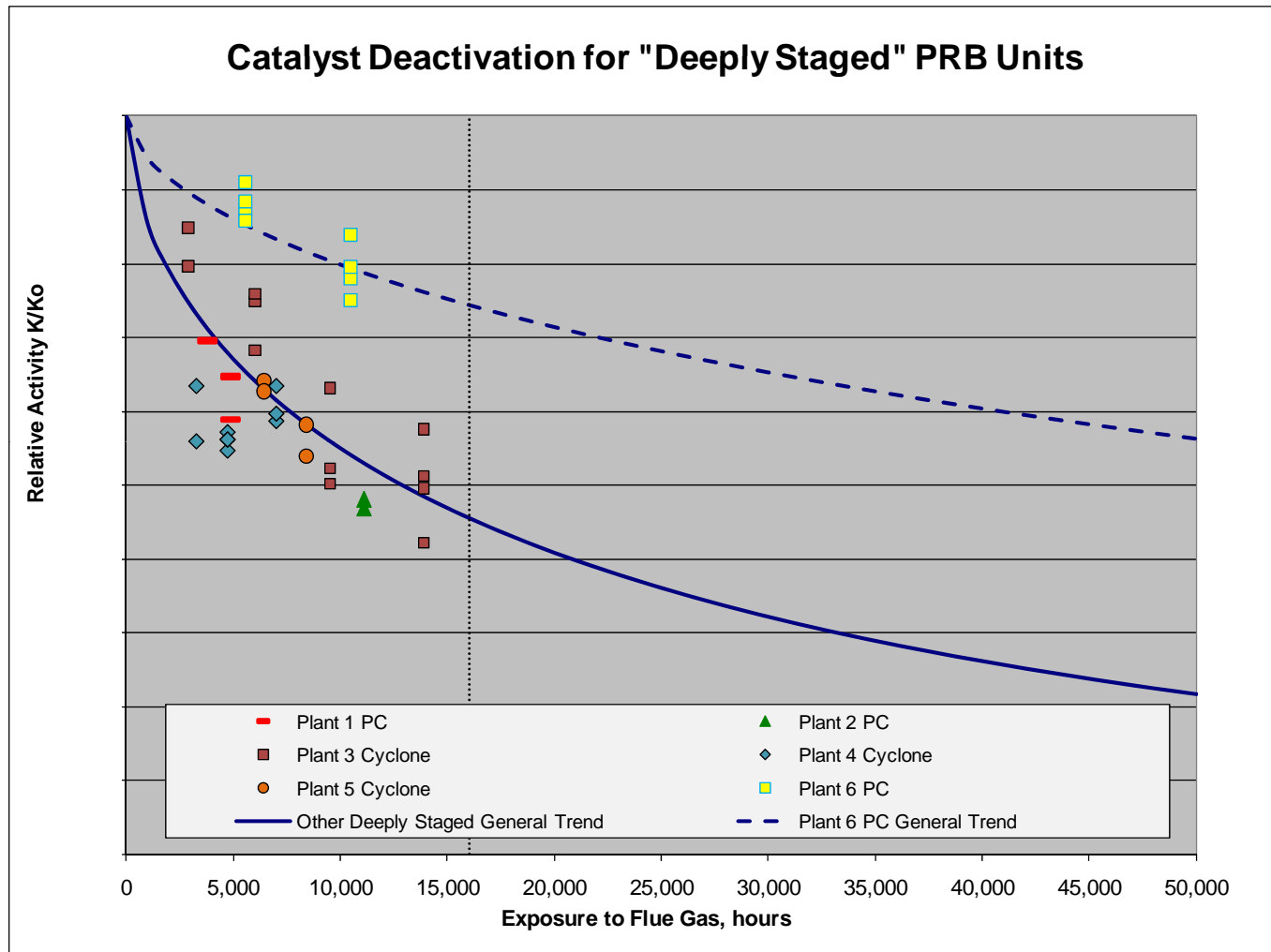
- Two Groups of Results Discussed
  - Group 1 – “Unstaged” Combustion
    - ◆ Minimal or No Overfire Air (OFA)
    - ◆ Typified by “Good Combustion” Higher O<sub>2</sub> and Low CO
    - ◆ NO<sub>x</sub> Concentration Typically Higher Than Staged Combustion
  - Group 2 – “Deep Staged” Combustion
    - ◆ Use of Low NO<sub>x</sub> Burners with Air Staging (e.g., OFA)
    - ◆ Very Low Combustion NO<sub>x</sub>
    - ◆ Poor Combustion (Intermittent or Steady State)
    - ◆ High CO Available Promotes Carbothermic Reduction of Phosphorus-Bearing Inorganic Compounds

# Group 1: “Unstaged” PRB Unit Catalyst Activity Test Results



- “Unstaged” PRB Units Indicate a K/Ko @ 16,000 hours of 0.6 to 0.7
- Wide Variation of Results Dependent on Fuel Quality and Combustion Parameters

## Group 2: “Deeply Staged” PRB Unit Catalyst Activity Test Results



- “Deeply Staged” PRB Units Typically Indicate a K/Ko @ 16,000 hours of 0.4 to 0.55
- Plant 6 Exhibits a Different Trend – Seems to be Exception



# Reactor Potential

$$P = K / Av$$



P = Reactor Potential

K = Catalyst Activity, Nm<sup>3</sup>/m<sup>2</sup>h or Nm/h

Av = Area Velocity, Nm/h

(normal gas flow, Nm<sup>3</sup>/h divided by total installed catalyst surface area, m<sup>2</sup>)



The Magnitude of Reactor Potential Determines  
the Amount of SCR System Performance Possible  
(DeNOx & Ammonia Slip Control)

# Area Velocity ( $A_v$ )

$$A_v = Q_{fg} / A_{cat} = Q_{fg} / (V_{rcat} \times SSA)$$

Where:  $Q_{fg}$  = flue gas flow rate, Nm<sup>3</sup>/h

$A_{cat}$  – catalyst geometric surface area, m<sup>2</sup>

$V_{rcat}$  = reactive catalyst volume available, m<sup>3</sup>

$SSA$  = catalyst specific surface area, m<sup>2</sup>/m<sup>3</sup>

# Volume Calculation

## Considering Edge Hardening

$$V_{rcat} = V_{cat} \times (l_{cat} - l_{eh}) \div l_{cat}$$

Where:  $V_{cat}$  = total catalyst volume, m<sup>3</sup>

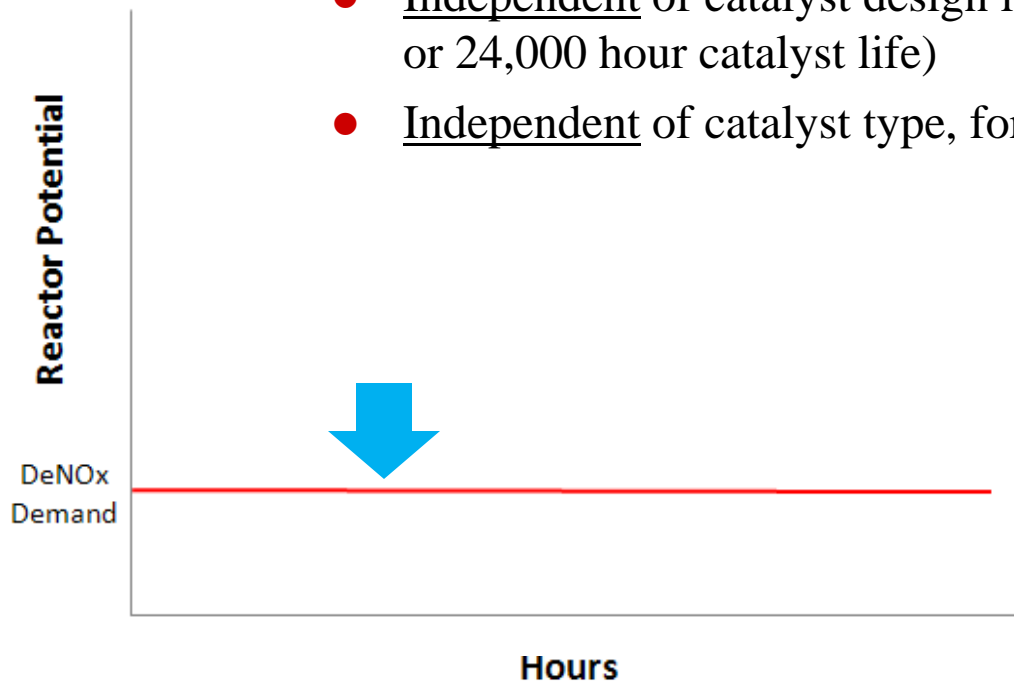
$l_{cat}$  = catalyst element total length, m

$l_{eh}$  = length of edge hardening applied  
to each catalyst element, m

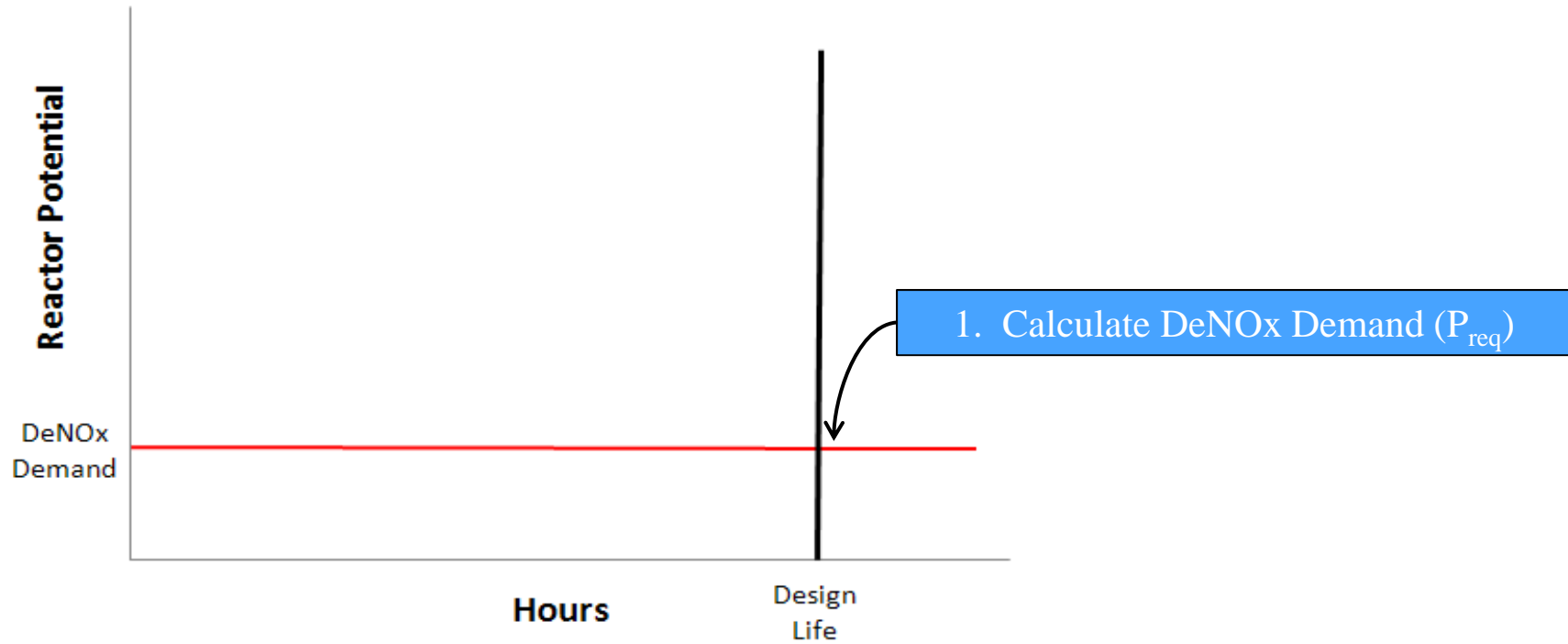
When no edge hardening is used:  $V_{rcat} = V_{cat}$

# DeNOx Demand

- DeNOx Demand ( $P_{req}$ ) = The reactor potential required to meet NOx removal and ammonia slip requirements
- Calculated based on NO<sub>x</sub> removal requirements, NH<sub>3</sub> slip, and SCR reactor pluggage and distributions (velocity, NH<sub>3</sub>/NO<sub>x</sub>, temperature)
- Independent of catalyst design life (i.e. same value for 16,000 or 24,000 hour catalyst life)
- Independent of catalyst type, formulation or manufacturer

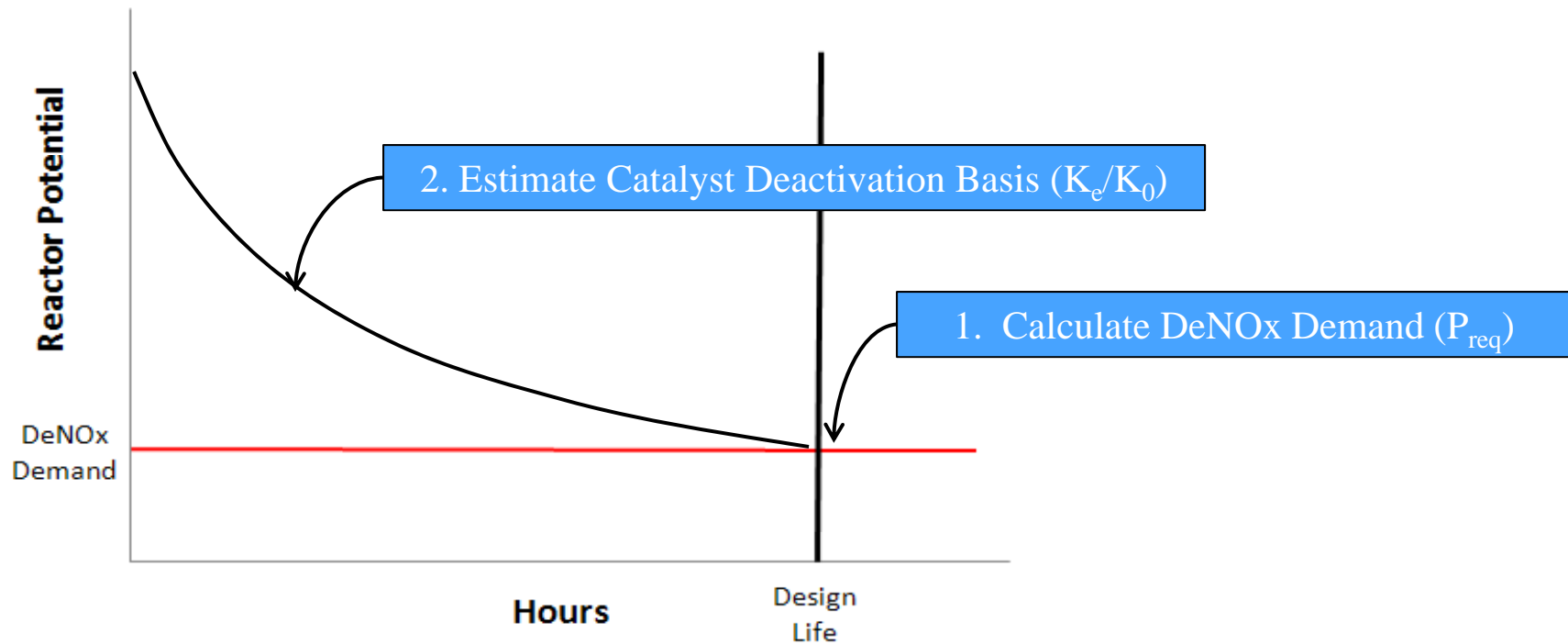


# Catalyst Design Process



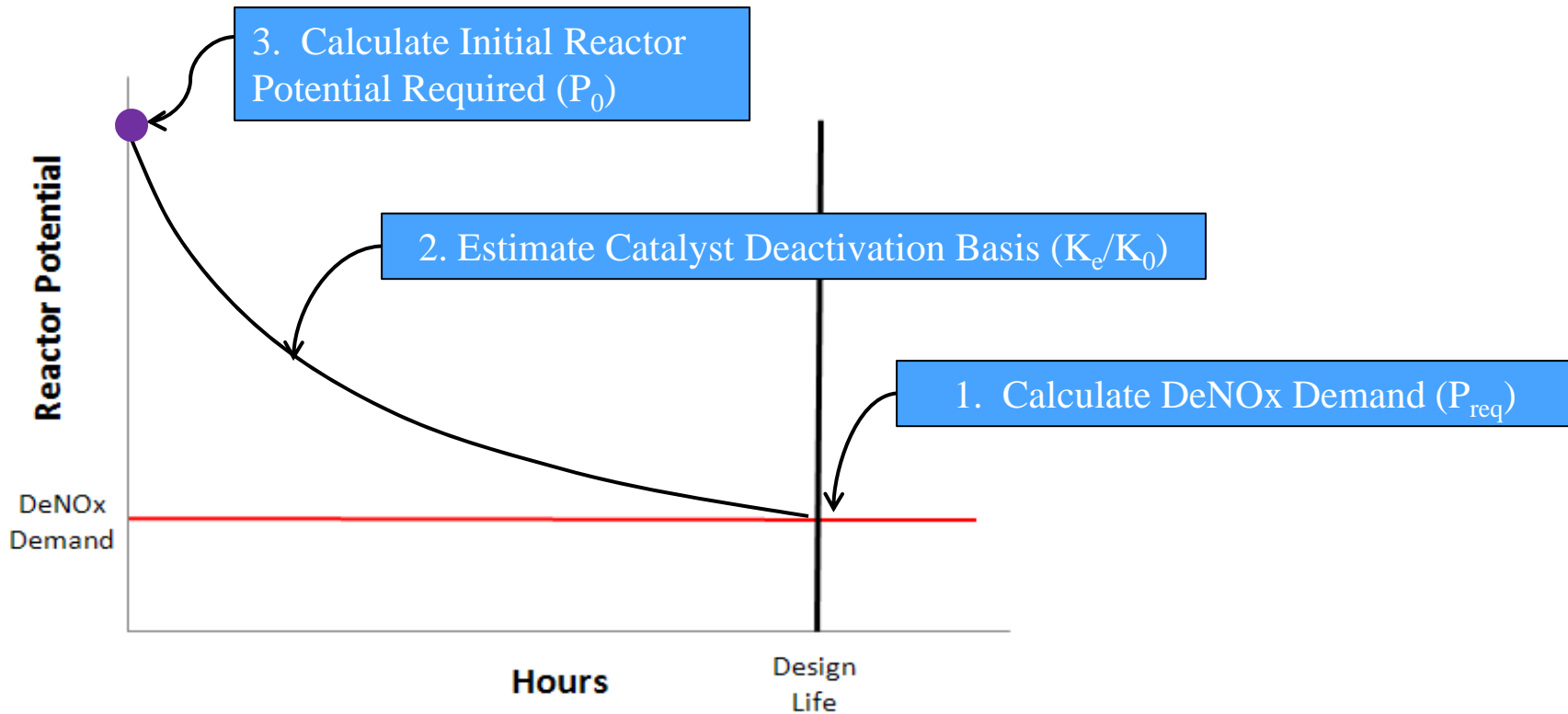
1. Calculate DeNOx demand ( $P_{req}$ ) required

# Catalyst Design Process



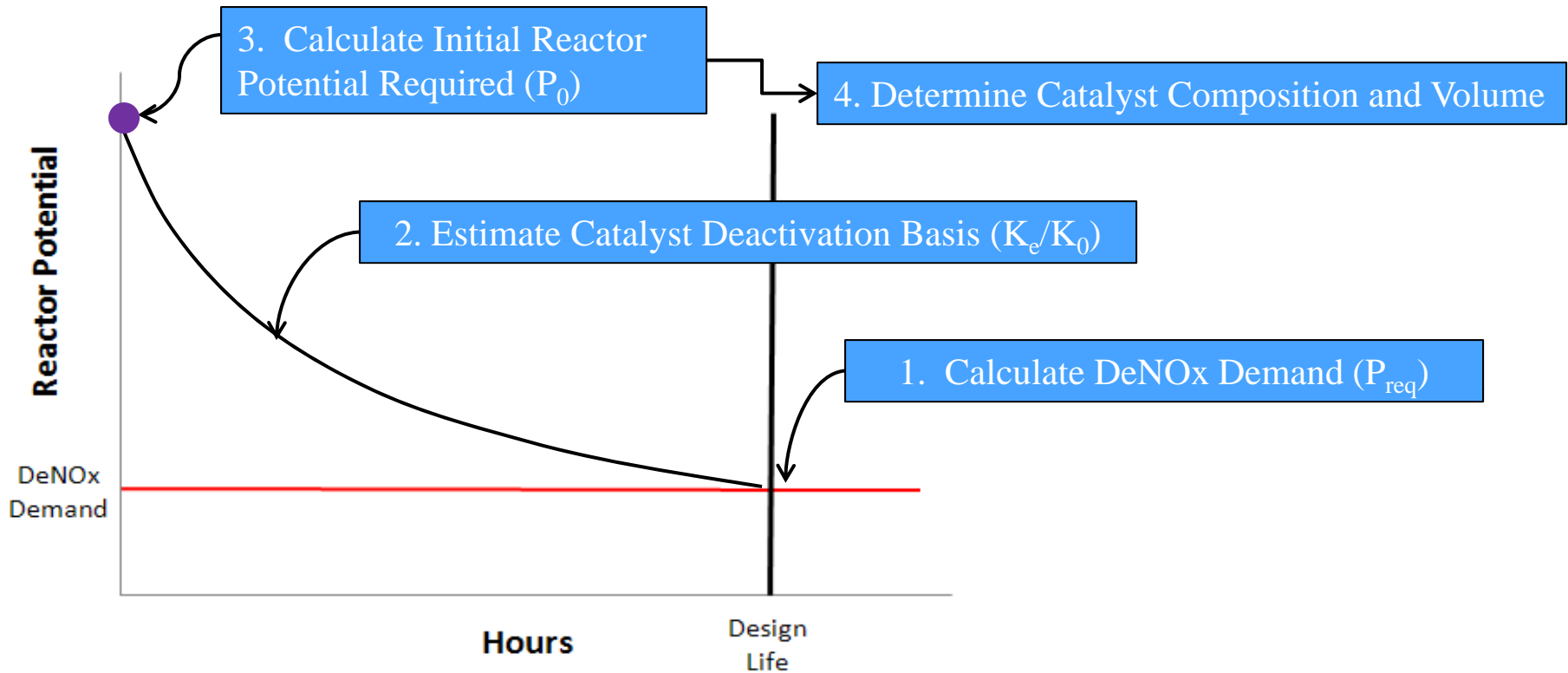
1. Calculate DeNOx demand ( $P_{req}$ ) required
2. Estimate catalyst deactivation basis ( $K_e/K_0$ ) based on fuel quality, combustion practices, unit duty, and design life

# Catalyst Design Process



1. Calculate DeNOx demand ( $P_{req}$ ) required
2. Estimate catalyst deactivation basis ( $K_e/K_0$ ) based on fuel quality, combustion practices, unit duty, and design life
3. Calculate initial reactor potential [  $P_0 = P_{req}/(K_e/K_0)$  ]

# Catalyst Design Process



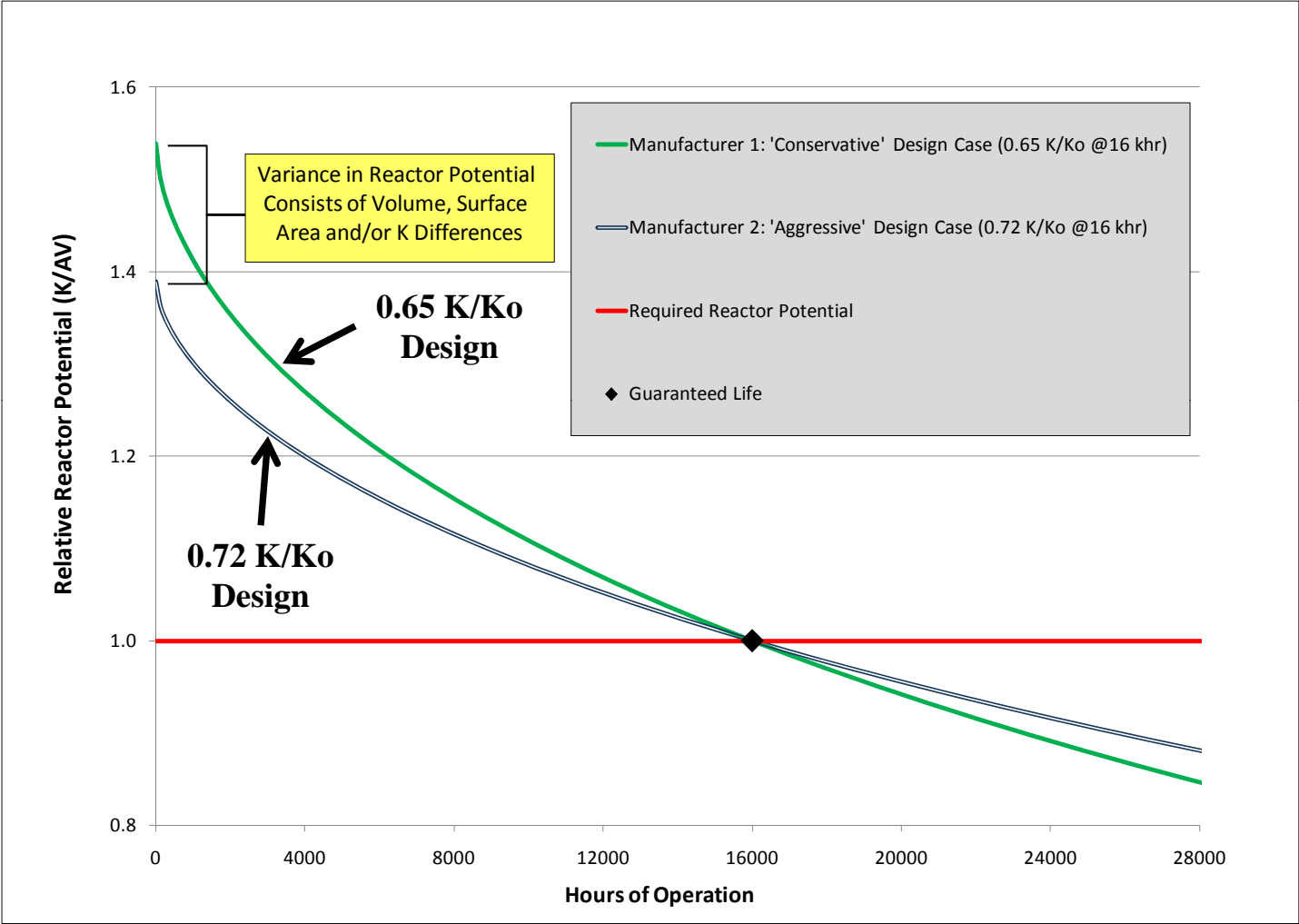
1. Calculate DeNOx demand ( $P_{req}$ ) required
2. Estimate catalyst deactivation basis ( $K_e/K_0$ ) based on fuel quality, combustion practices, unit duty, and design life
3. Calculate initial reactor potential [  $P_0 = P_{req}/(K_e/K_0)$  ]
4. Catalyst volume determined based on  $P_0$ , SO<sub>2</sub>:3 conversion rate requirement, and catalyst geometry

# Why is Estimating Catalyst Deactivation So Important

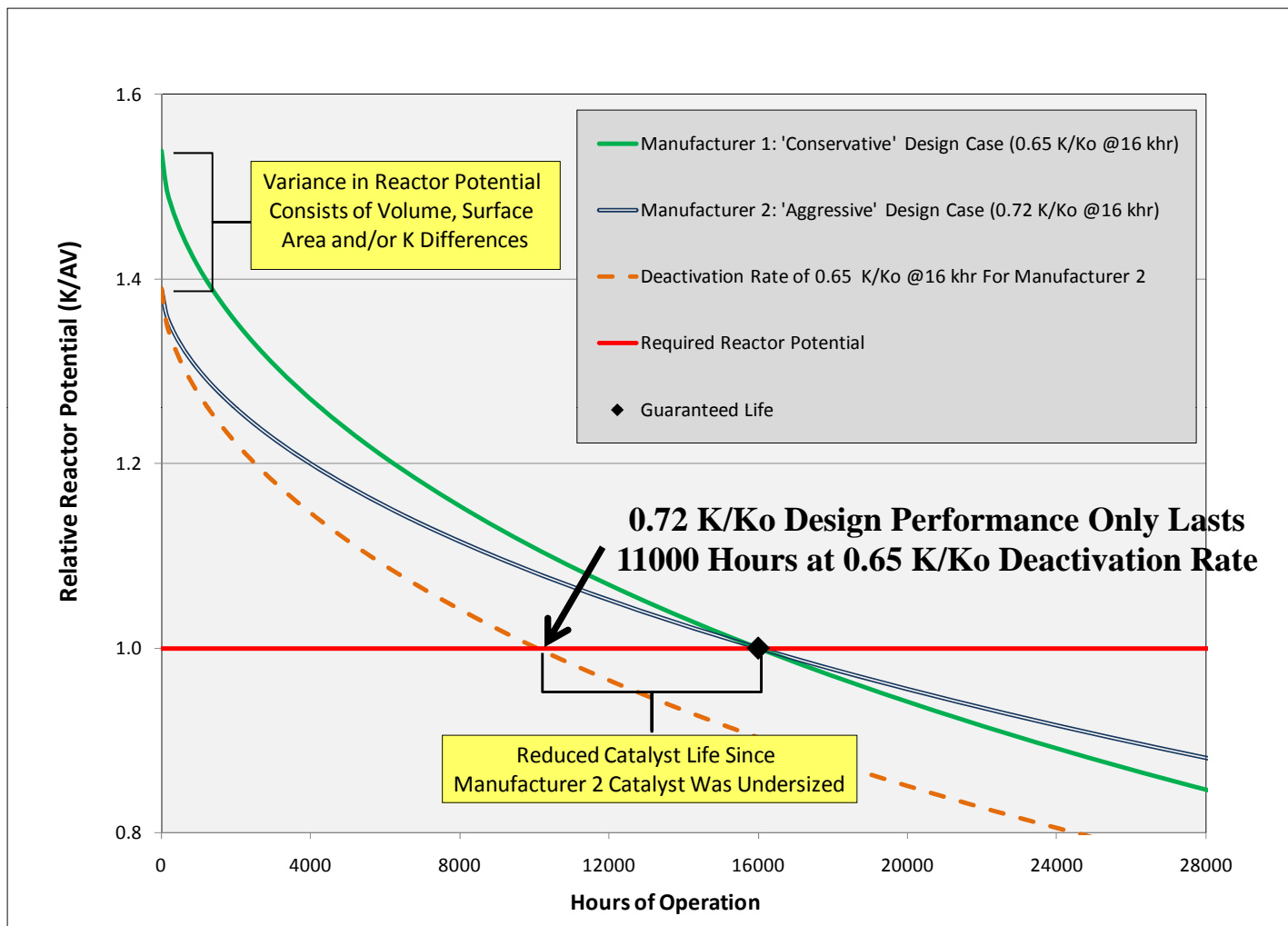
- If Deactivation is Underestimated
  - Catalyst is Undersized
  - Incapable of Meeting NO<sub>x</sub> Removal and Ammonia Slip Performance at Some Point During the Guarantee Period
  - Deficient Performance is Either Tolerated or an Early Outage (Unscheduled) is Required for Catalyst Addition
  - Catalyst Management Costs are Underestimated
- Understanding and Managing Reactor Potential Critical to Minimize Risk
- Examples Help to Illustrate Risk



# “Unstaged” Catalyst Design Comparison of Two Catalyst Manufacturer Designs

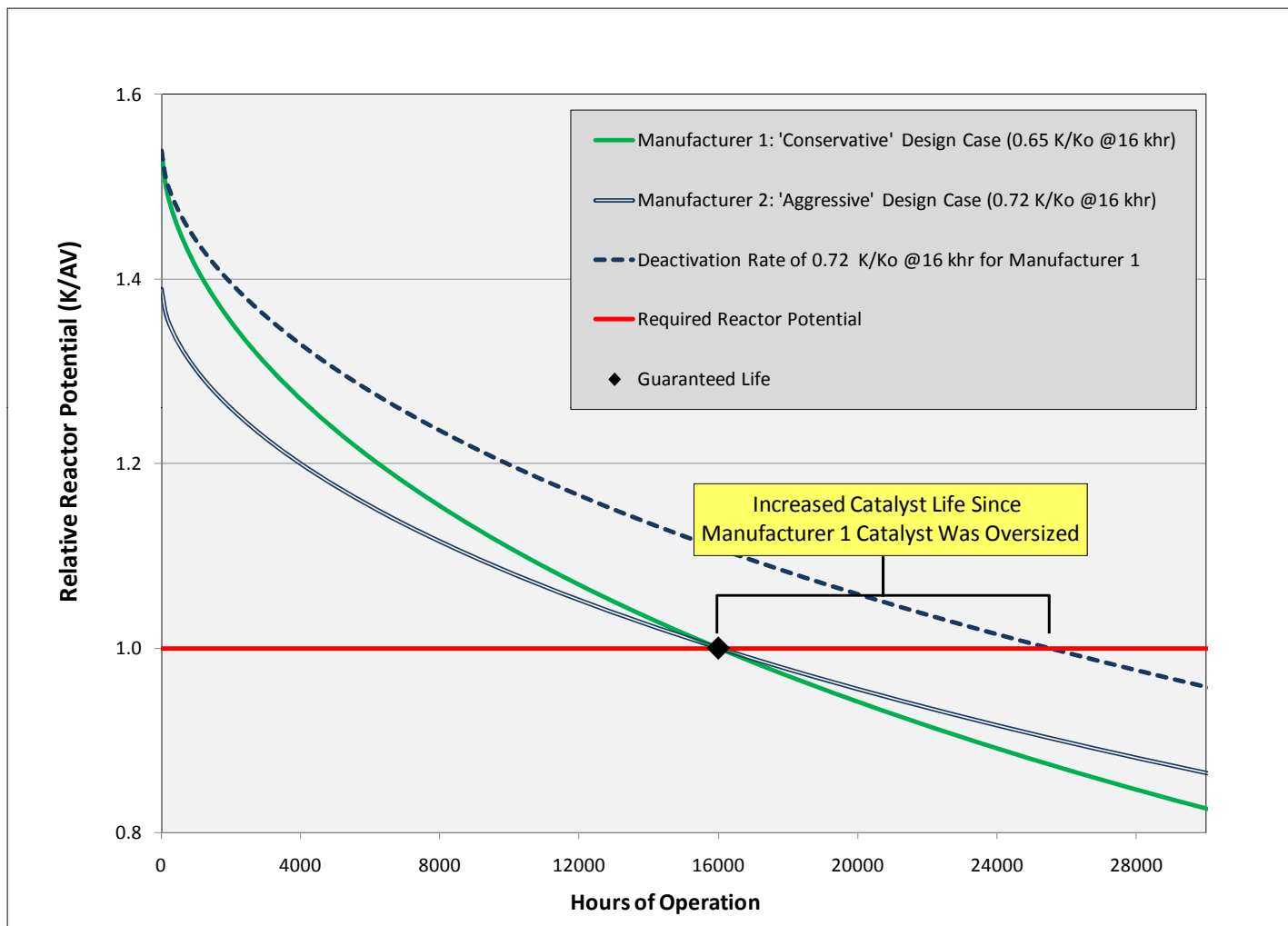


# “Unstaged” Catalyst Design Comparison – Case 1 High Deactivation



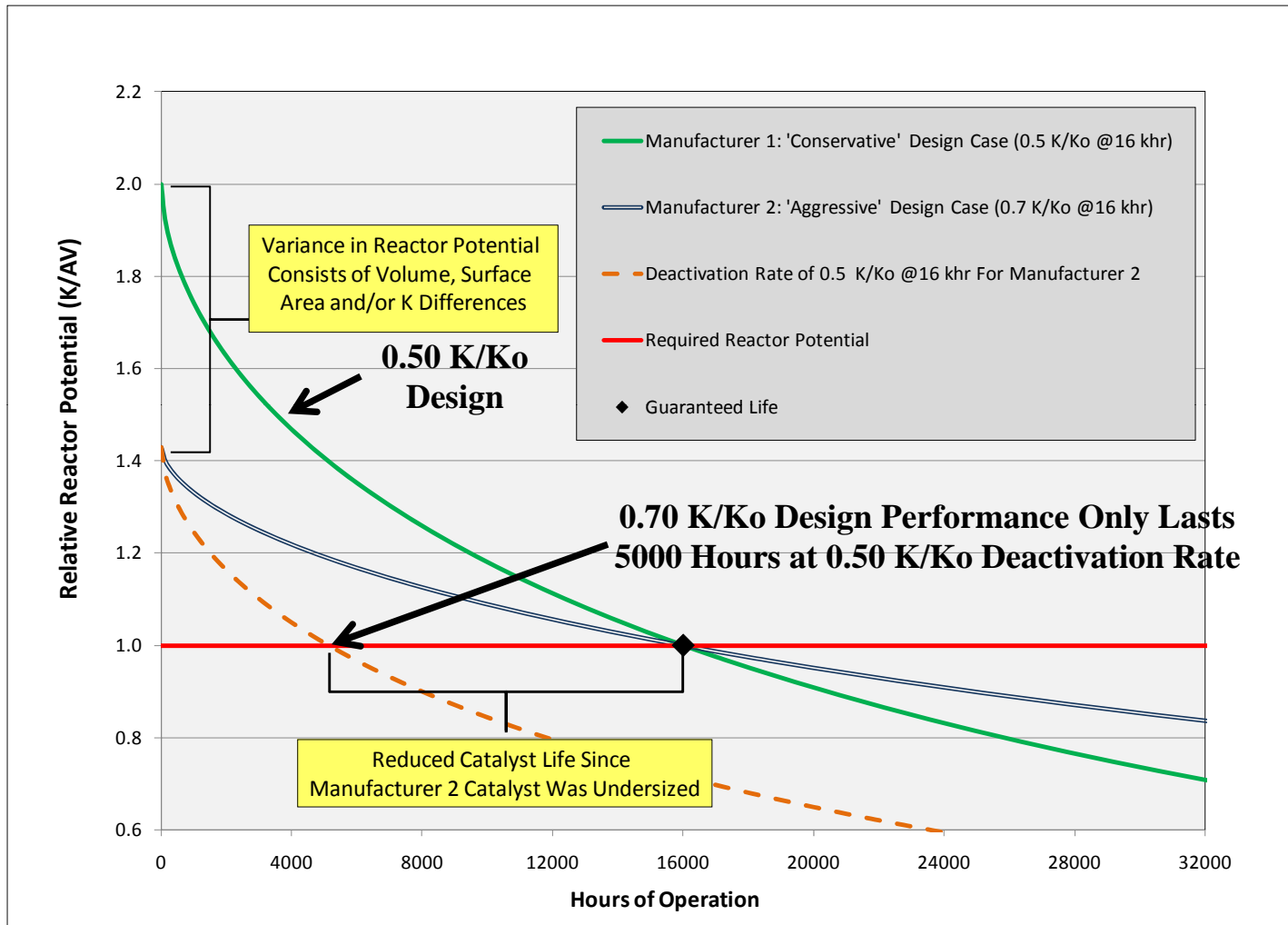
- A Catalyst Designed for a Deactivation Rate  $K/K_o = 0.72$  @ 16khr Will Require a Catalyst Addition at Approximately 11,000 Hours if a Deactivation Rate  $K/K_o = 0.65$  Occurs (see dashed line above)

# “Unstaged” Catalyst Design Comparison – Case 2 Low Deactivation



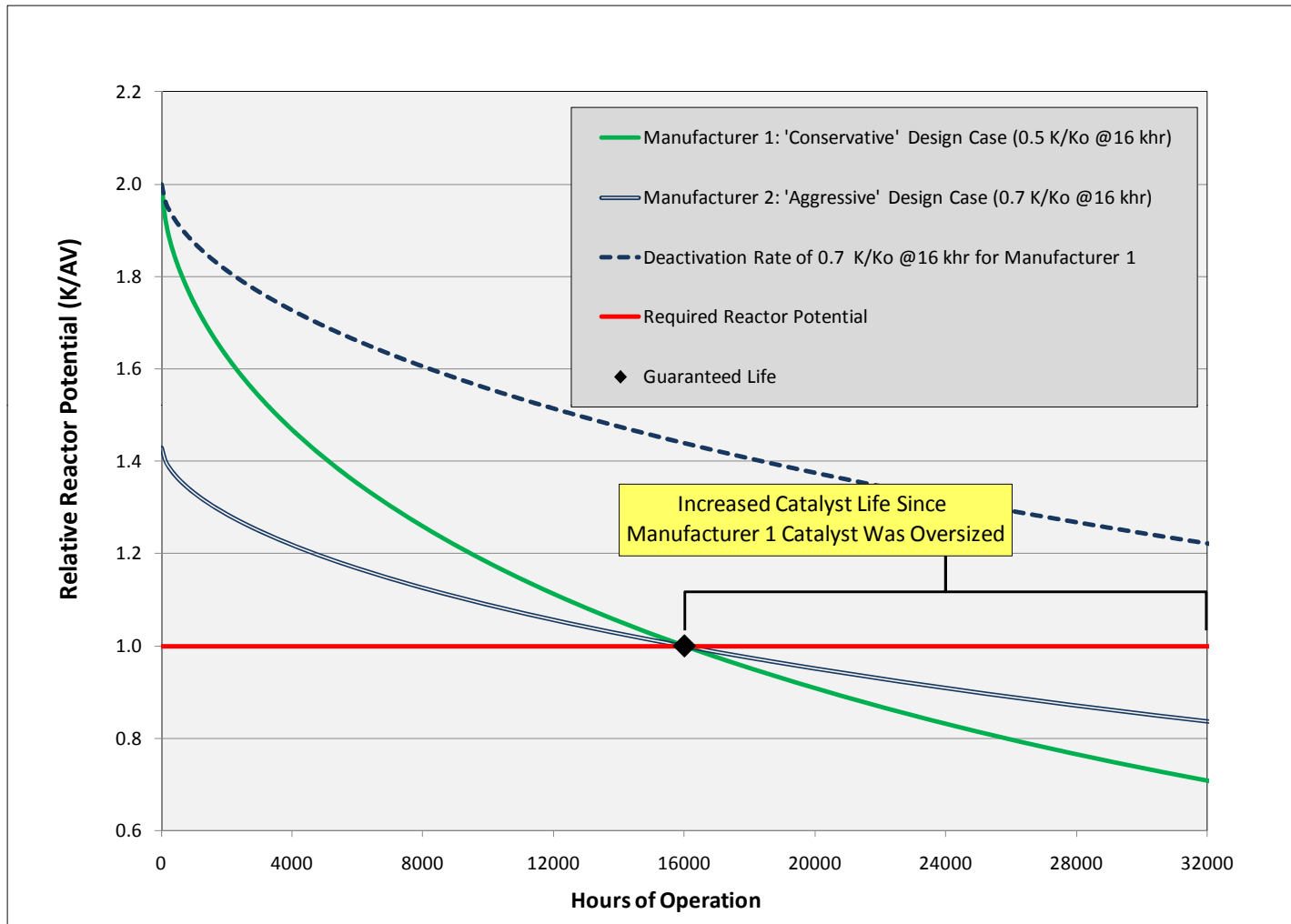
- A Catalyst Designed for a Deactivation Rate  $K/K_o = 0.65$  @ 16khr Will Not Require a Catalyst Addition Until Approximately 26,000 Hours if a Deactivation Rate  $K/K_o = 0.72$  Occurs (see dashed line above)

# “Deeply Staged” Catalyst Design Comparison – Case 1 High Deactivation



- A Catalyst Designed for a Deactivation Rate  $K/K_o = 0.70$  @ 16khr Will Require a Catalyst Addition at Approximately 5000 Hours if a Deactivation Rate  $K/K_o = 0.50$  Occurs (see dashed line above)

# “Deeply Staged” Catalyst Design Comparison – Case 2 Low Deactivation

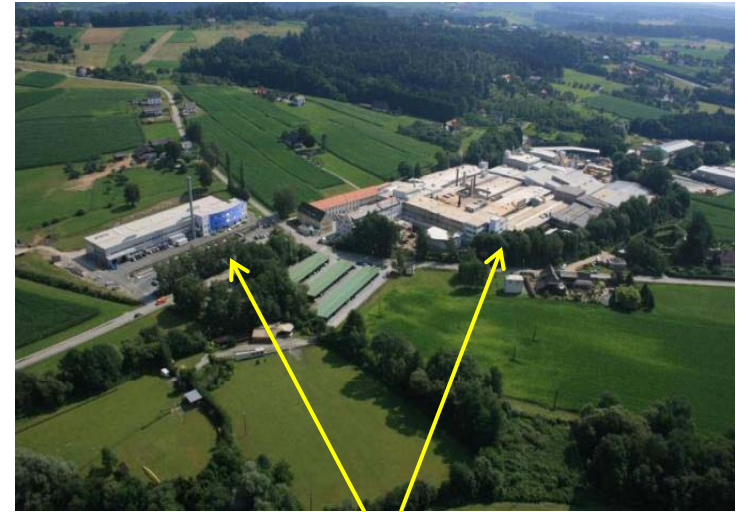
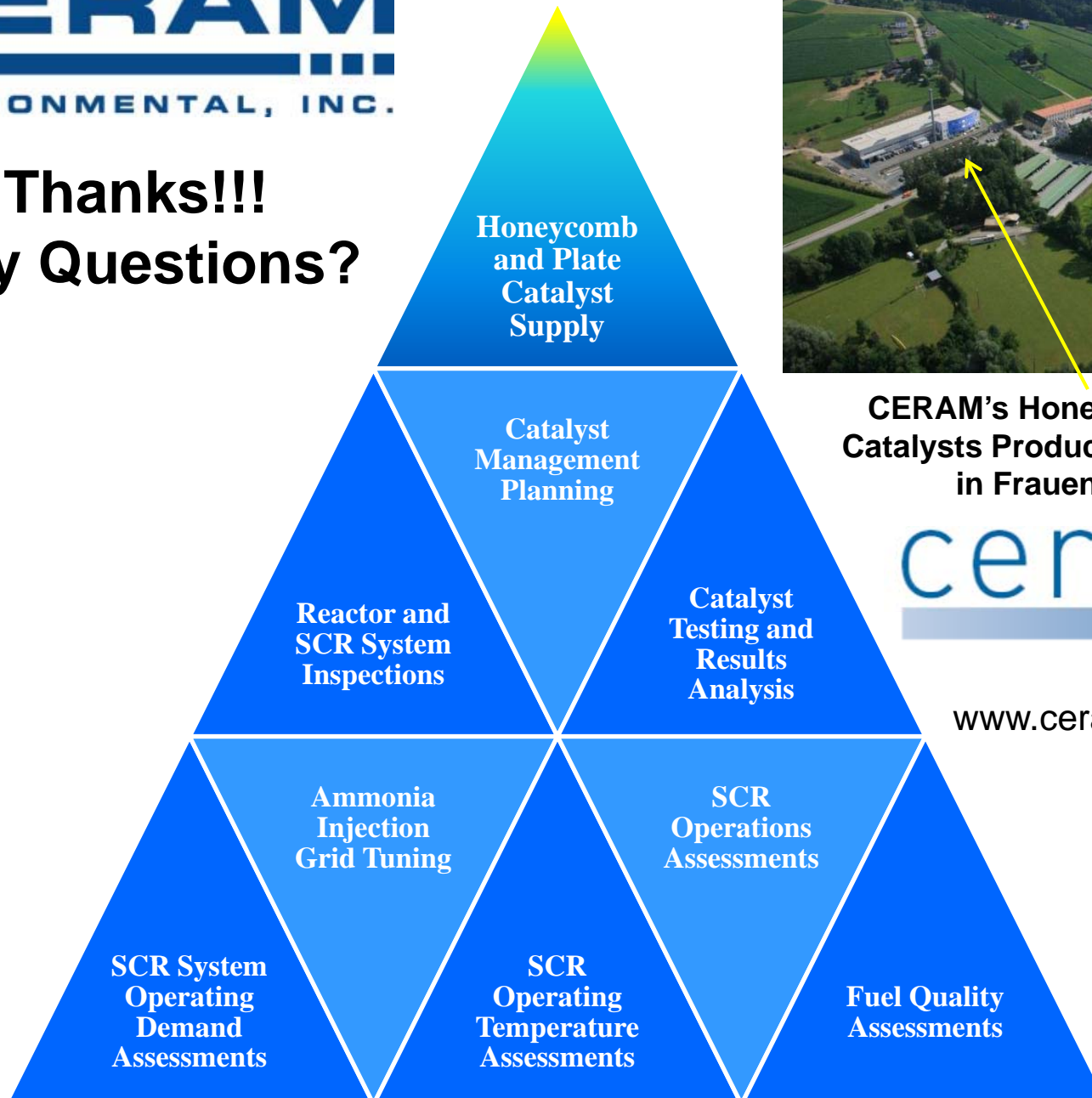


- A Catalyst Designed for a Deactivation Rate  $K/K_o = 0.50$  @ 16khr Will Not Require a Catalyst Addition Until More Than 32,000 Hours if a Deactivation Rate  $K/K_o = 0.70$  Occurs (see dashed line above)

# Conclusions

- PRB Fired Unit Catalyst Deactivation is Very Site Specific
- Dependent on...
  - Fuel Phosphorus Levels
  - Combustion Quality
    - ◆ Increased Staging and/or High CO Increases Deactivation Rate
    - ◆ De-Staging Unit Possible (Higher Inlet NO<sub>x</sub> & NH<sub>3</sub> Cost)
- All Catalyst Compositions and Types Deactivate Similarly
  - There Are No Demonstrated “Poison Resistant” Catalysts
- Reactor Potential Sizing Is Extremely Important and MUST Consider the Required DeNO<sub>x</sub> Demand and Design Deactivation Rate
- Catalyst Designs Should be Scrutinized to Determine Reactor Potential
- Owners Should Take an Active Role in Assuring Catalyst is Designed Properly to Achieve Outage Objectives – Avoid Surprises!

**Thanks!!!  
Any Questions?**



**CERAM's Honeycomb and Plate Catalysts Production Plant Located in Frauental, Austria**



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