REINHOLD ENVIRONMENTAL Ltd.

2016 NOx-Combustion-CCR Round Table Presentation

February 1 & 2, 2016, in Orlando, FL / Hosted by OUC

SCR Catalyst Deactivation by P and Ca in Utility Boilers Firing PRB Coals

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2016 Reinhold NOx-Combustion-CCR Round Table

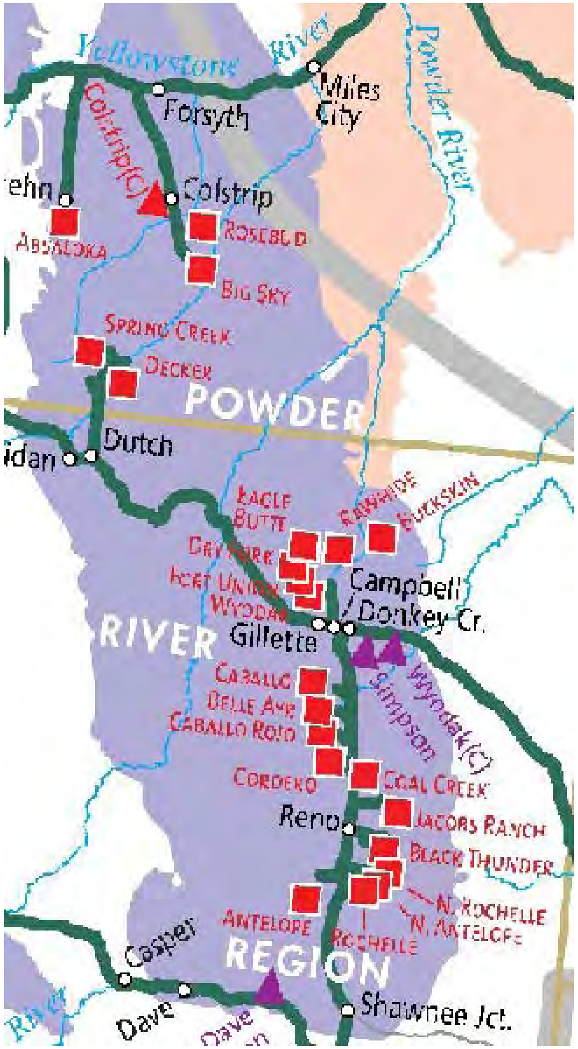
Presentation Outline

CORMETECH

- **Cormetech Experience**
- **Catalyst Deactivation from Ca, P**
  - Deactivation Mechanisms
  - Formation Processes
- **Impacts of Firing Stoichiometry**
- **Catalyst Management Tools**
- **Applications**
  - Case Study
  - Catalyst Design and Management Considerations

Cormetech Experience

- **More than 40 SCR units firing 100% PRB or high PRB blends.**
- **First unit started up in 2000.**
- **Longest running unit has >70,000 operational hours.**
- **Extensive research to understand PRB deactivation mechanism**



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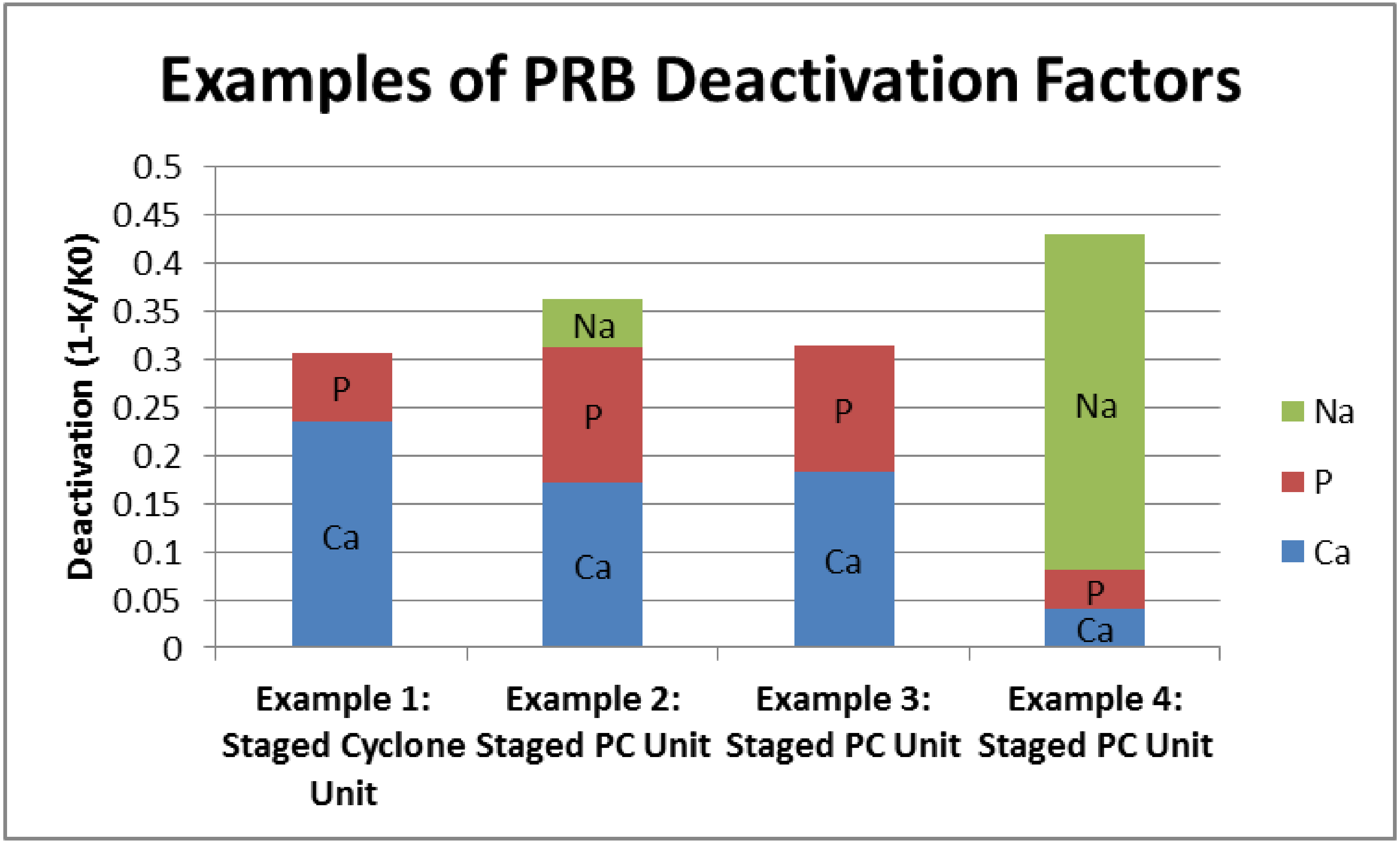
Deactivation Mechanisms for PRB Coals

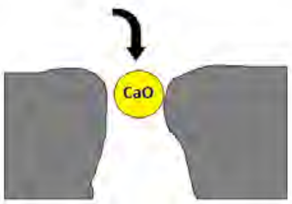
- **Ca is the primary deactivator**
  - – $CaSO_4$ blinds the catalyst surface
- **P can have a variable impact**
  - – P reacts with catalyst active sites
- Na is typically a minor contributor
  - – Na reacts with catalyst active sites
- Elevated Fe_2O_3, SiO_2, and SO_3 are also typically observed

Actual Field Data

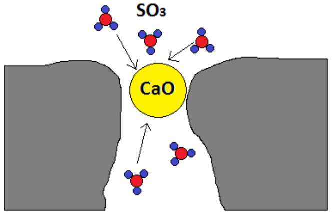


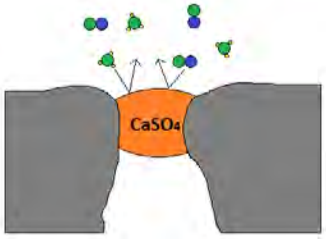
Calcium Deactivation Mechanism

1. Sub-micron CaO is caught in macro-pore of catalyst.
2. SO_3 diffuses to CaO particle.
3. SO_3 and CaO react to form $CaSO_4$. Particle swells by ~14%.
4. $CaSO_4$ plugs pore: NH_3 and NO_x are blocked from active sites.



Catalyst Pore

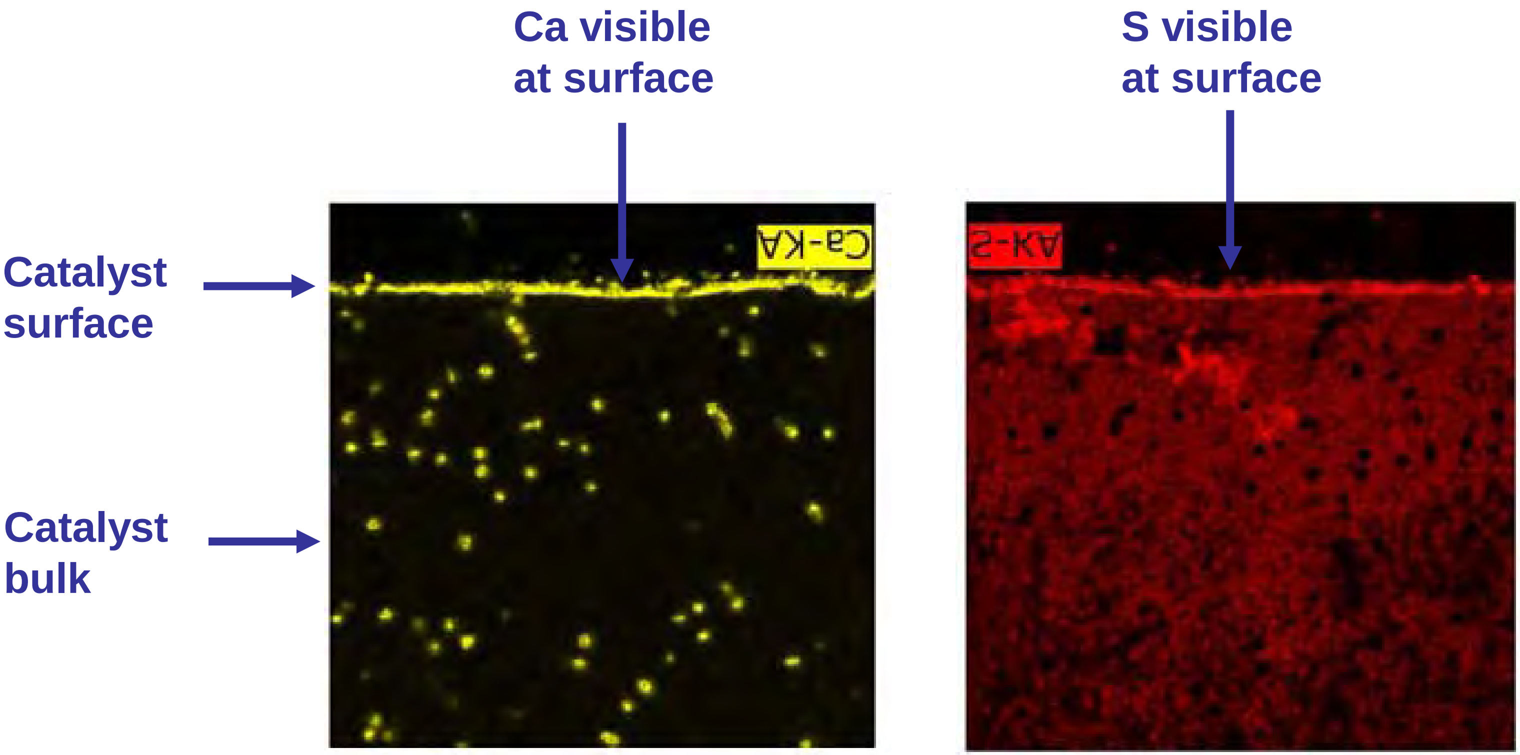




Step 1 is rate limiting step – depends on availability and adhesion of CaO particle in pore

Calcium Deactivation Mechanism Cont'd

- Thin layer of $CaSO_4$ blinds the catalyst surface



Ca visible at surface

S visible at surface

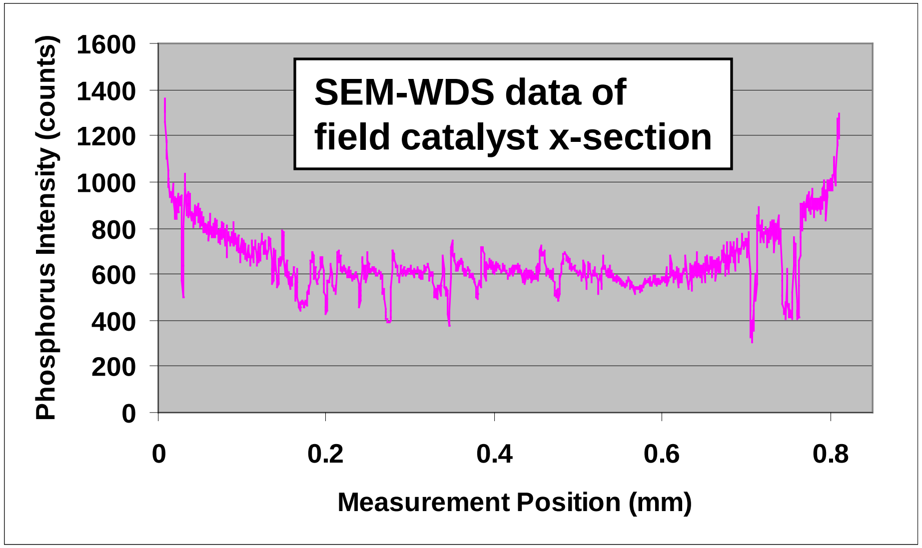
Catalyst surface

Catalyst bulk

SEM-EDS Maps of Catalyst Cross-Section

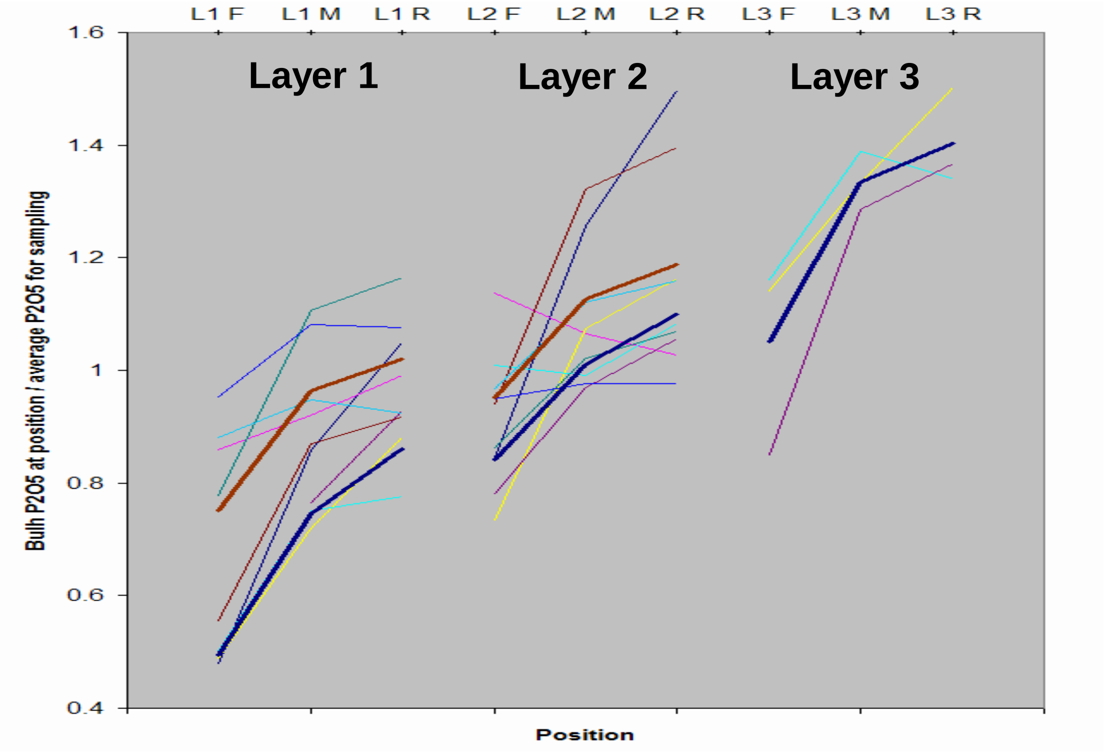
Phosphorus Deactivation Mechanism

- Phosphorus is a penetrating poison
  - – Diffuses into the catalyst bulk and chemically bonds with active sites
  - – P species is gas phase, e.g. H_3PO_4



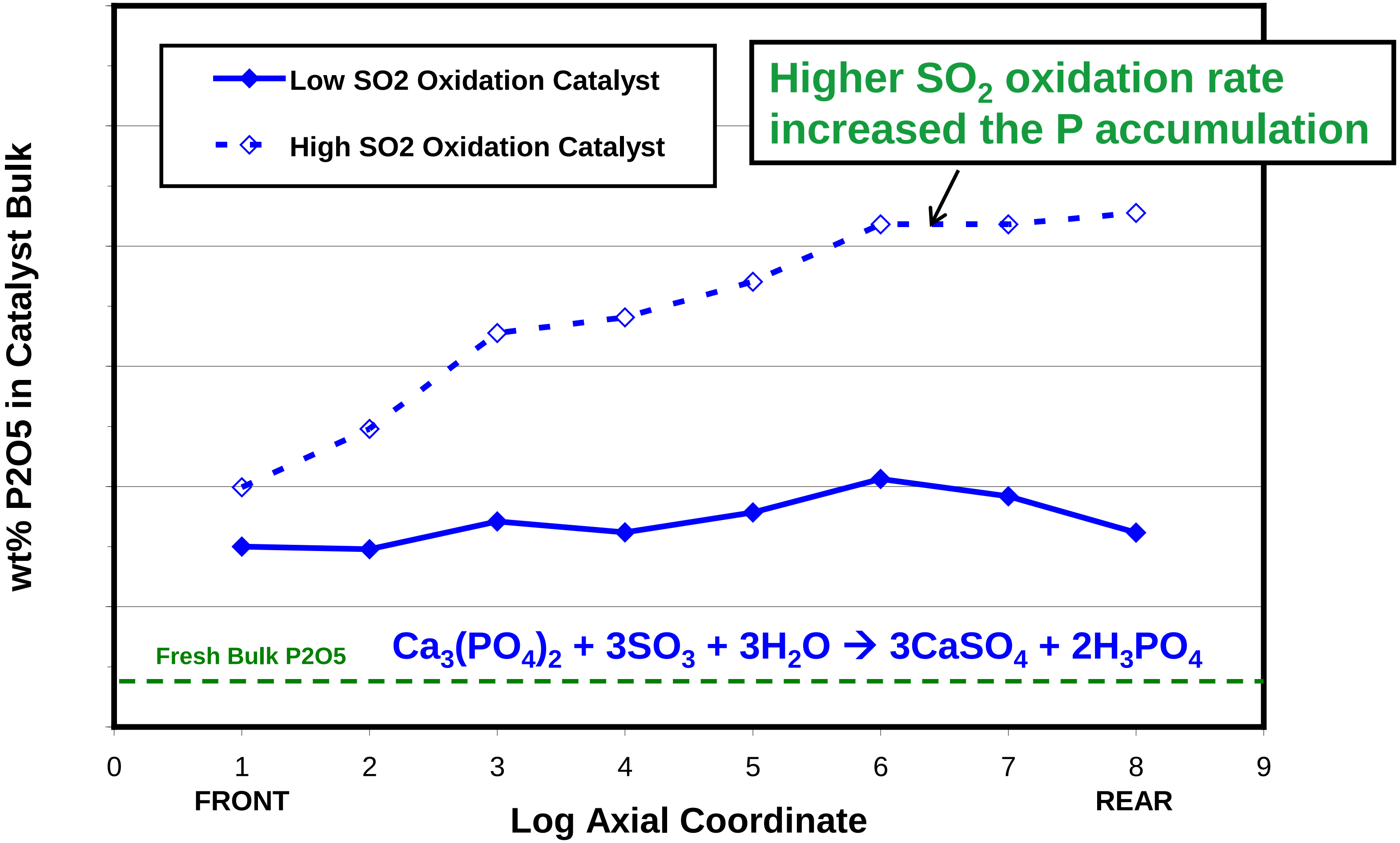
Phosphorus Deactivation Mechanism Cont'd

- **Bulk P_2O_5 increases vs. catalyst length**
  - – Due to liberation of gaseous P from solid P in the ash by SO_3 produced in the catalyst



Effect of SO_2 Oxidation on P Deactivation

Loaded two ½ catalyst samples (low and high SO_2 oxidation rate catalyst) in single sample tray and loaded it into a Staged PC Unit SCR module for aging.



Higher SO_2 oxidation rate increased the P accumulation

$Ca_3(PO_4)_2 + 3SO_3 + 3H_2O \rightarrow 3CaSO_4 + 2H_3PO_4$

Phosphorus Deactivation Mechanism Cont'd

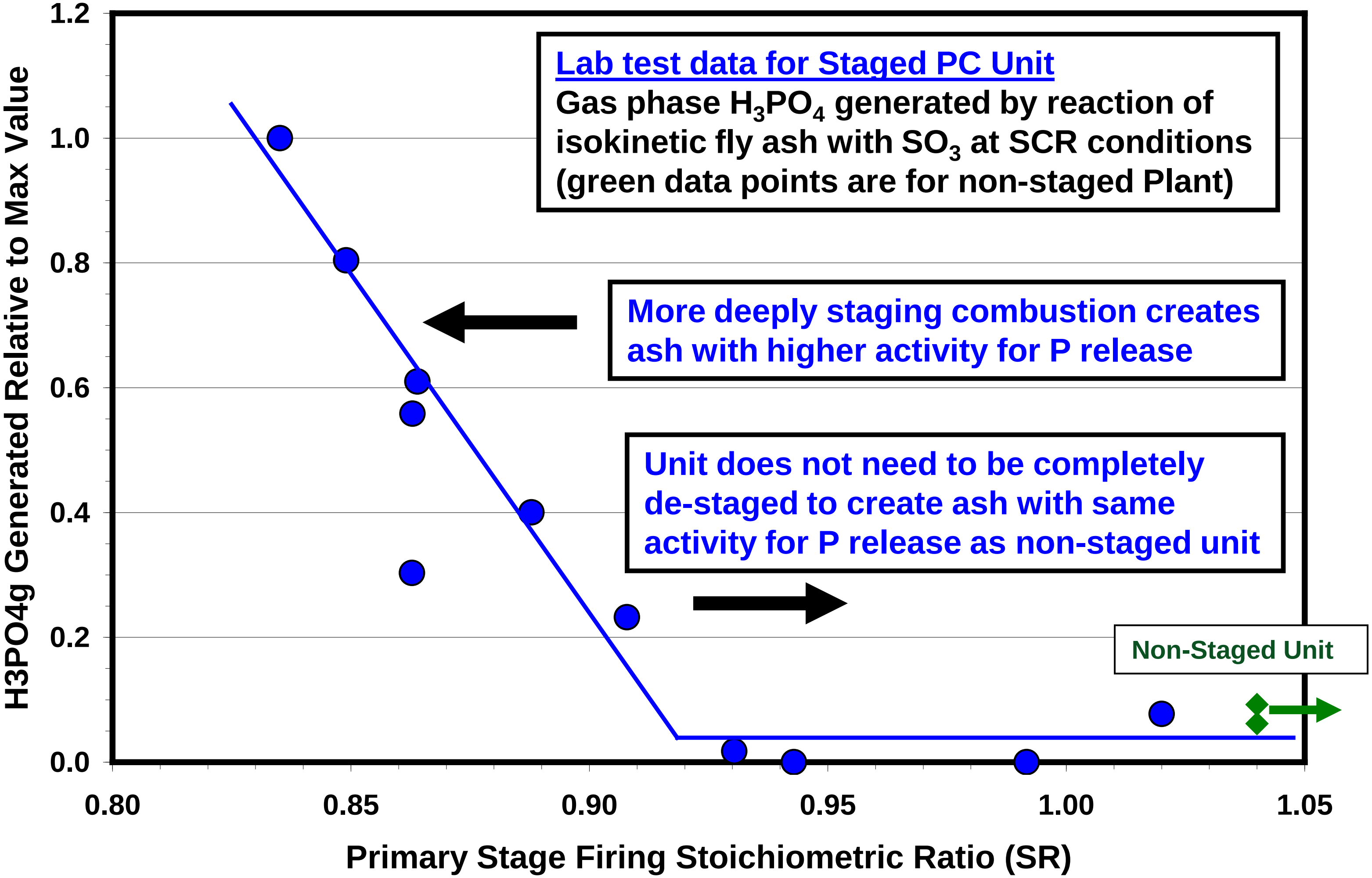
- Gaseous phosphorus is formed by reaction of SO_3 with solid P in the ash fume
  - $Ca_3(PO_4)_{2\,(s)} + 3SO_{3\,(g)} + 3H_2O_{(g)} \xrightarrow{\text{yields}} 3CaSO_{4\,(s)} + 2H_3PO_{4\,(g)}$

P in Ash

SO_3 made in SCR

Gas phase P that deactivates catalyst

Impact of Staging on H_3PO_4 Generation Potential



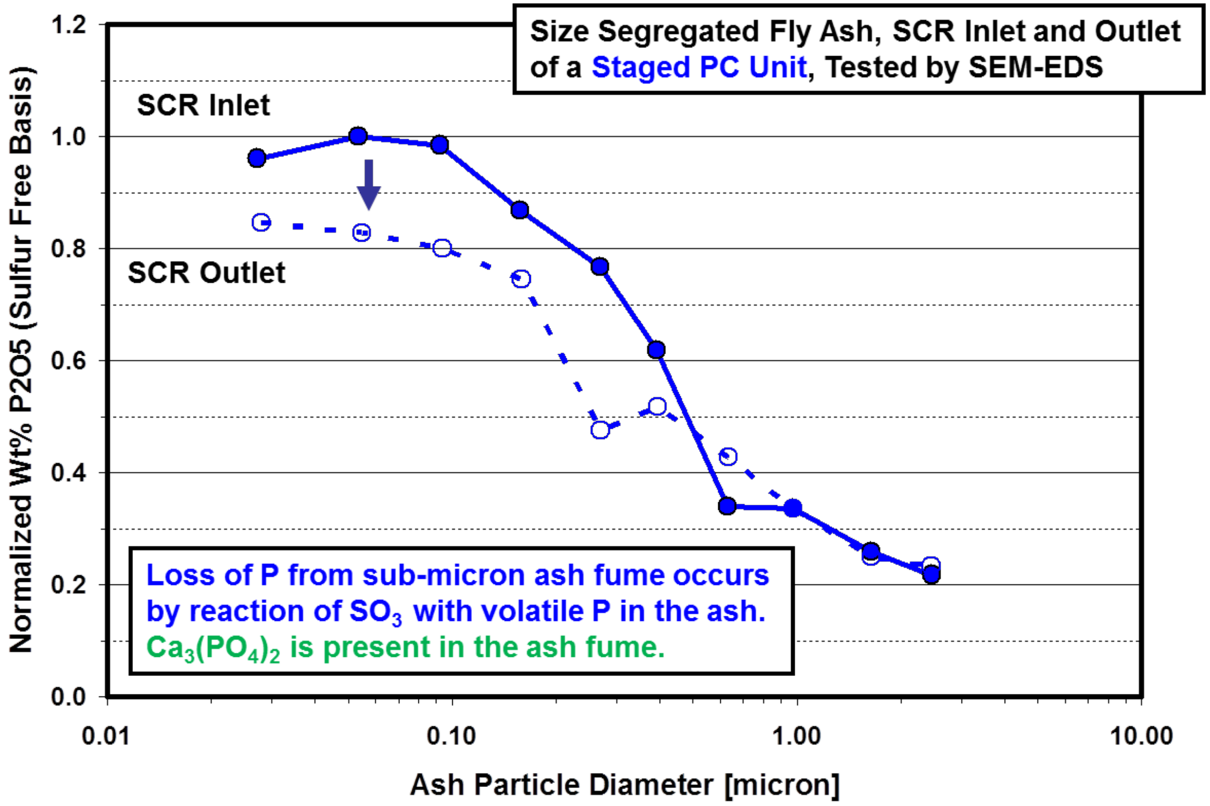
Lab test data for Staged PC Unit
Gas phase H_3PO_4 generated by reaction of isokinetic fly ash with SO_3 at SCR conditions (green data points are for non-staged Plant)

More deeply staging combustion creates ash with higher activity for P release

Unit does not need to be completely de-staged to create ash with same activity for P release as non-staged unit

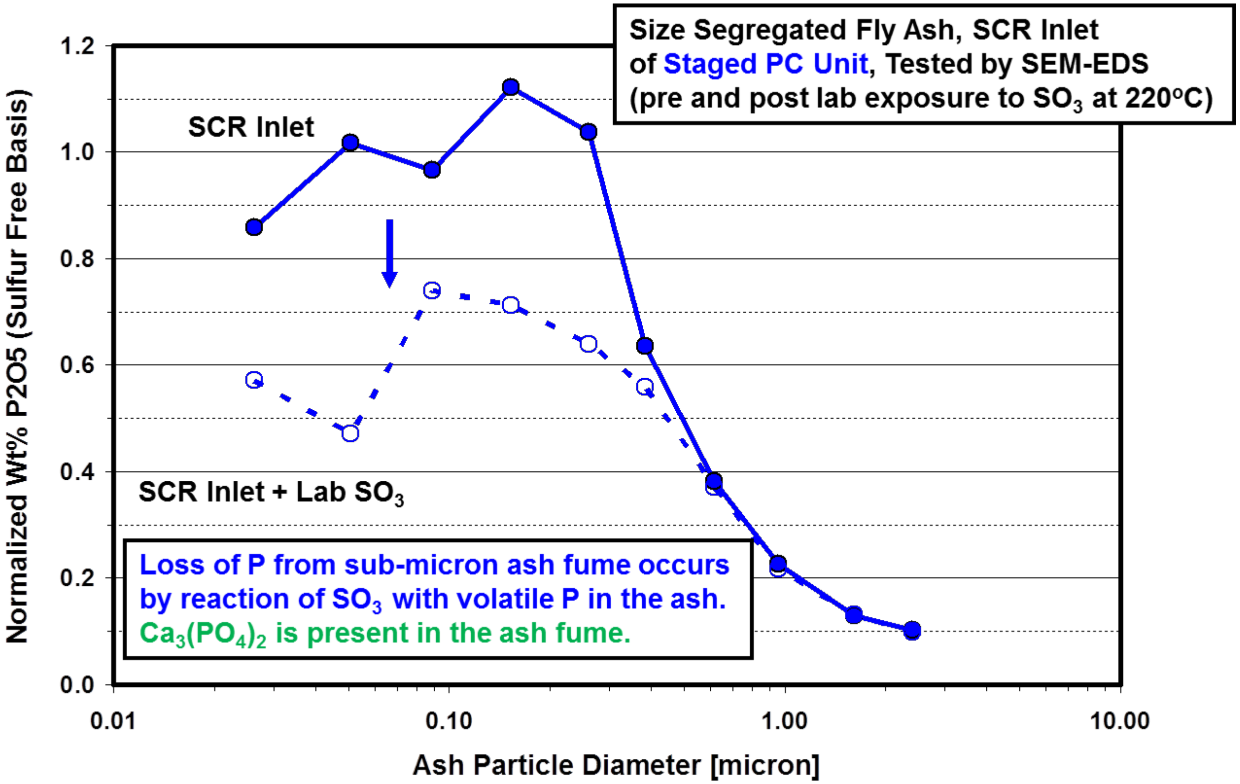
Ash P Analysis

- Size-segregated ash samples pulled from field
- Loss of P is sub-micron particles across SCR

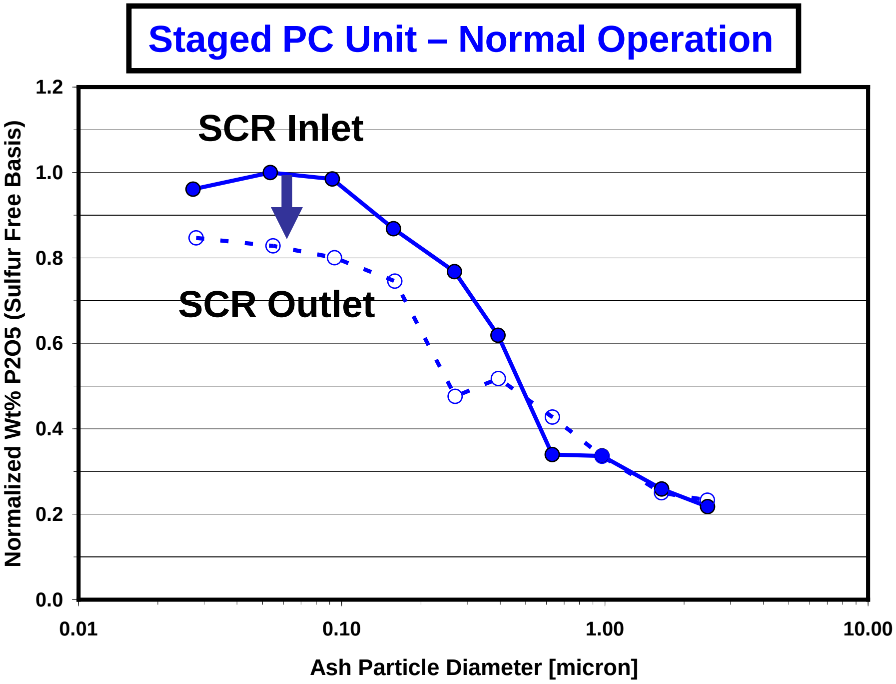


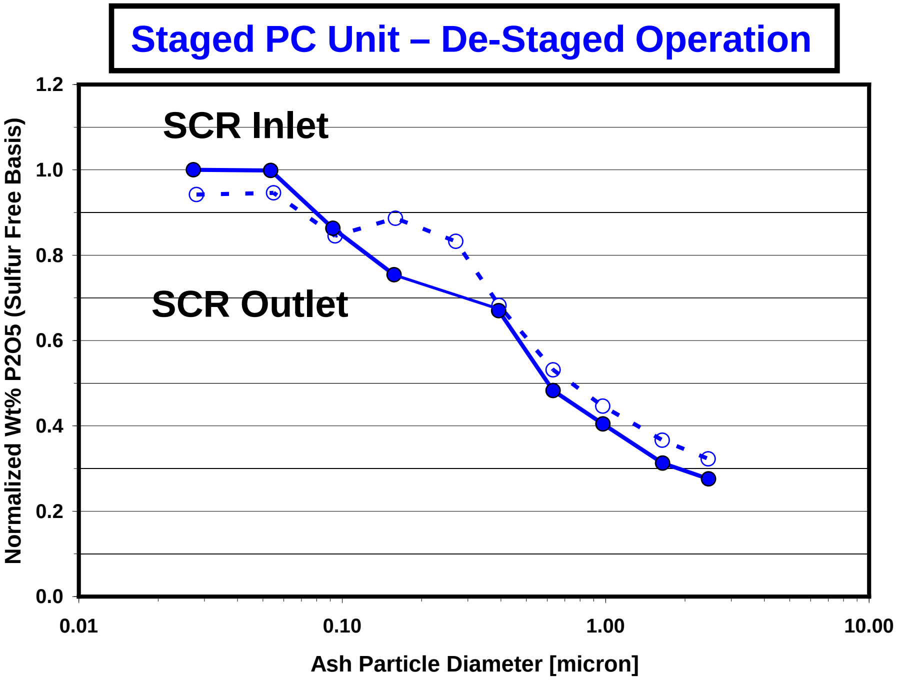
Ash P Analysis

- Loss of P in sub-micron particles when reacted with SO_3.



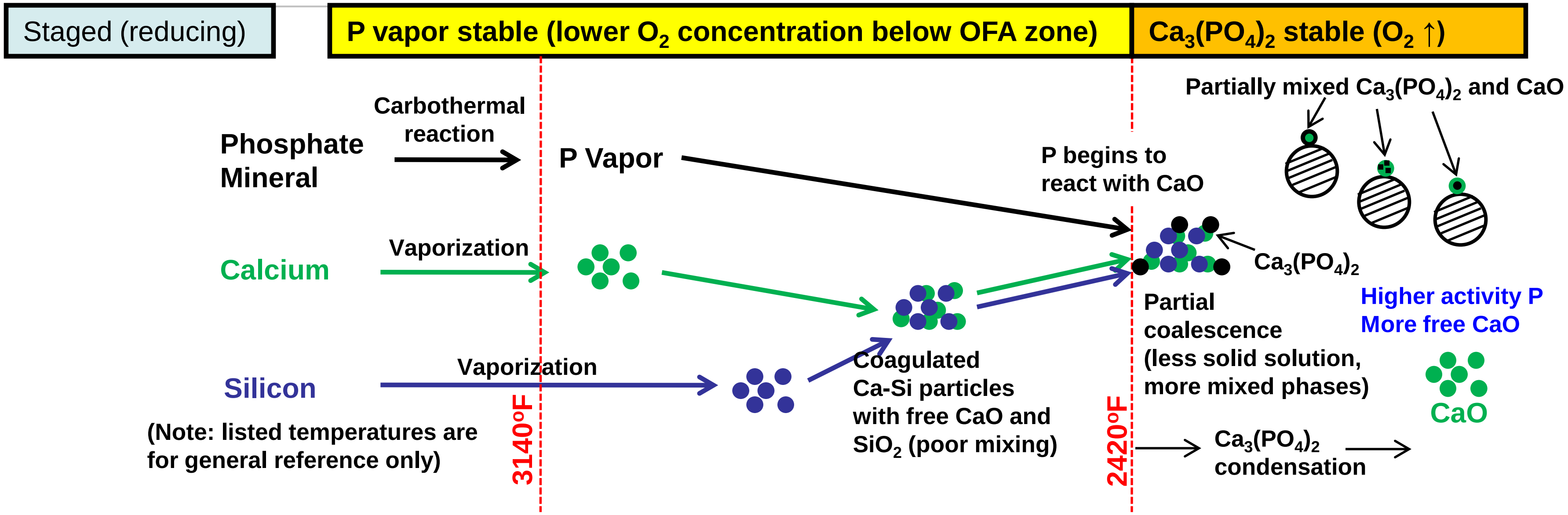
Ash P Analysis





- **Operating the unit de-staged reduced the amount of P lost from the ash fume across the SCR (i.e., reduces the activity of the $Ca_3(PO_4)_2$ in the ash fume)**

Hypothesis of Ca and P Particle Formation



Staged (reducing)

P vapor stable (lower O_2 concentration below OFA zone)

$Ca_3(PO_4)_2$ stable (O_2 ↑)

Phosphate Mineral

Carbothermal reaction

P Vapor

P begins to react with CaO

Partially mixed $Ca_3(PO_4)_2$ and CaO

$Ca_3(PO_4)_2$

Calcium

Vaporization

Silicon

Vaporization

Coagulated Ca-Si particles with free CaO and SiO_2 (poor mixing)

Partial coalescence (less solid solution, more mixed phases)

Higher activity P
More free CaO

CaO

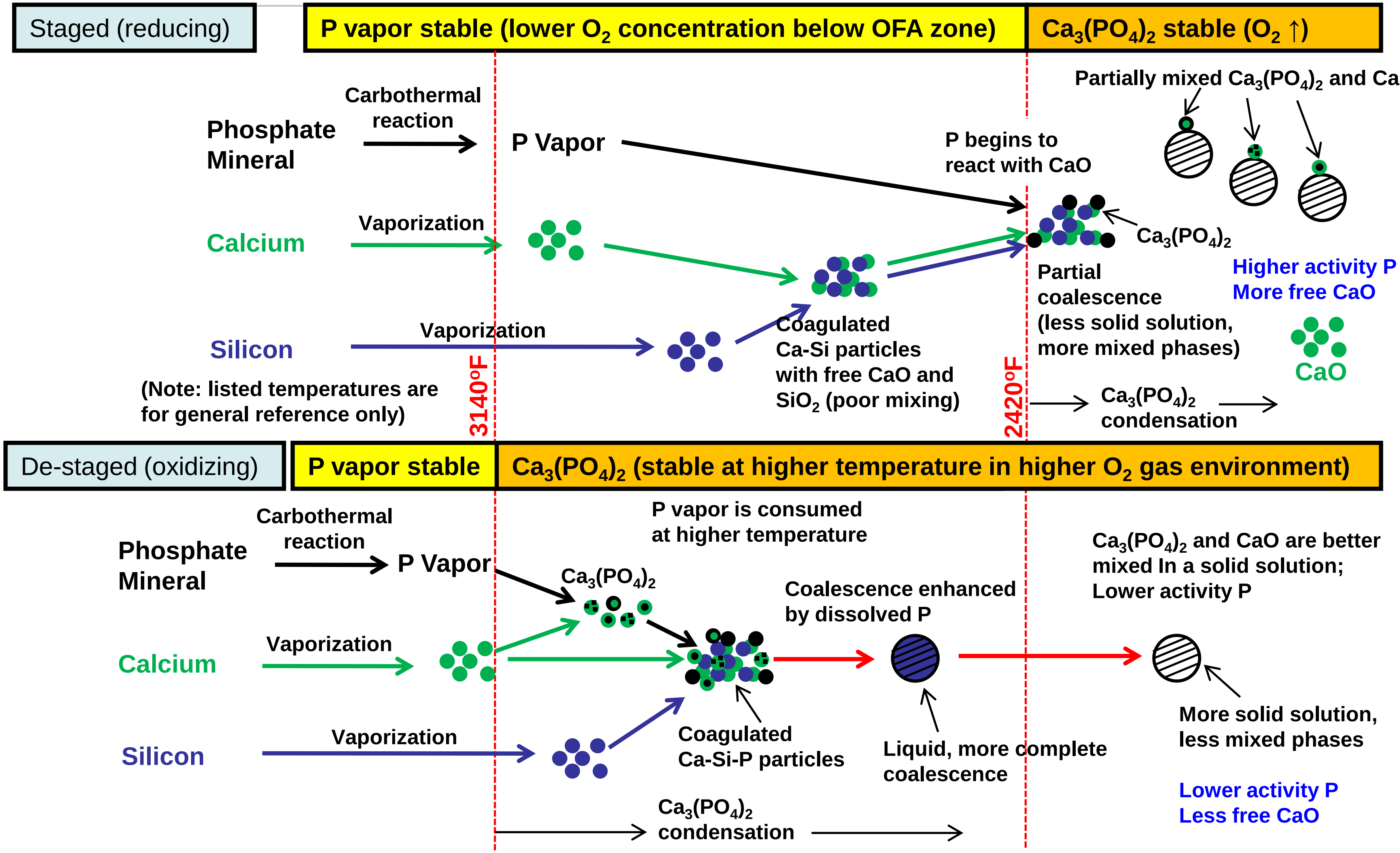
$Ca_3(PO_4)_2$ condensation

3140°F

2420°F

(Note: listed temperatures are for general reference only)

Hypothesis of Ca and P Particle Formation



Staged (reducing)

P vapor stable (lower O_2 concentration below OFA zone)

$Ca_3(PO_4)_2$ stable (O_2 ↑)

Phosphate Mineral — Carbothermal reaction → **P Vapor** → P begins to react with CaO → $Ca_3(PO_4)_2$

Calcium — Vaporization →

Silicon — Vaporization →

Coagulated Ca-Si particles with free CaO and SiO_2 (poor mixing)

Partial coalescence (less solid solution, more mixed phases)

Partially mixed $Ca_3(PO_4)_2$ and CaO

Higher activity P
More free CaO

CaO

$Ca_3(PO_4)_2$ condensation

(Note: listed temperatures are for general reference only)

3140°F

2420°F

De-staged (oxidizing)

P vapor stable

$Ca_3(PO_4)_2$ (stable at higher temperature in higher O_2 gas environment)

Phosphate Mineral — Carbothermal reaction → **P Vapor**

P vapor is consumed at higher temperature

$Ca_3(PO_4)_2$

Calcium — Vaporization →

Silicon — Vaporization →

Coagulated Ca-Si-P particles

Coalescence enhanced by dissolved P

Liquid, more complete coalescence

$Ca_3(PO_4)_2$ and CaO are better mixed In a solid solution; Lower activity P

More solid solution, less mixed phases

Lower activity P
Less free CaO

$Ca_3(PO_4)_2$ condensation

Summary of Ca and P Deactivating Species

- Ca and P deactivators are present in the sub-micron ash, formed by vaporization/ condensation processes
  - Ca → sub-micron CaO adhesion and sulfation in catalyst pores
    - Dependent on fuel chemistry and combustion conditions
  - P → volatilization of P from sub-micron ash ($Ca_3(PO_4)_2$) by SO_3
    - The amount of P released is dependent on the activity of the $Ca_3(PO_4)_2$ in the ash and the SO_3 concentration
    - Interacts with CaO in ash
    - Dependent on catalyst design, fuel chemistry, and combustion conditions

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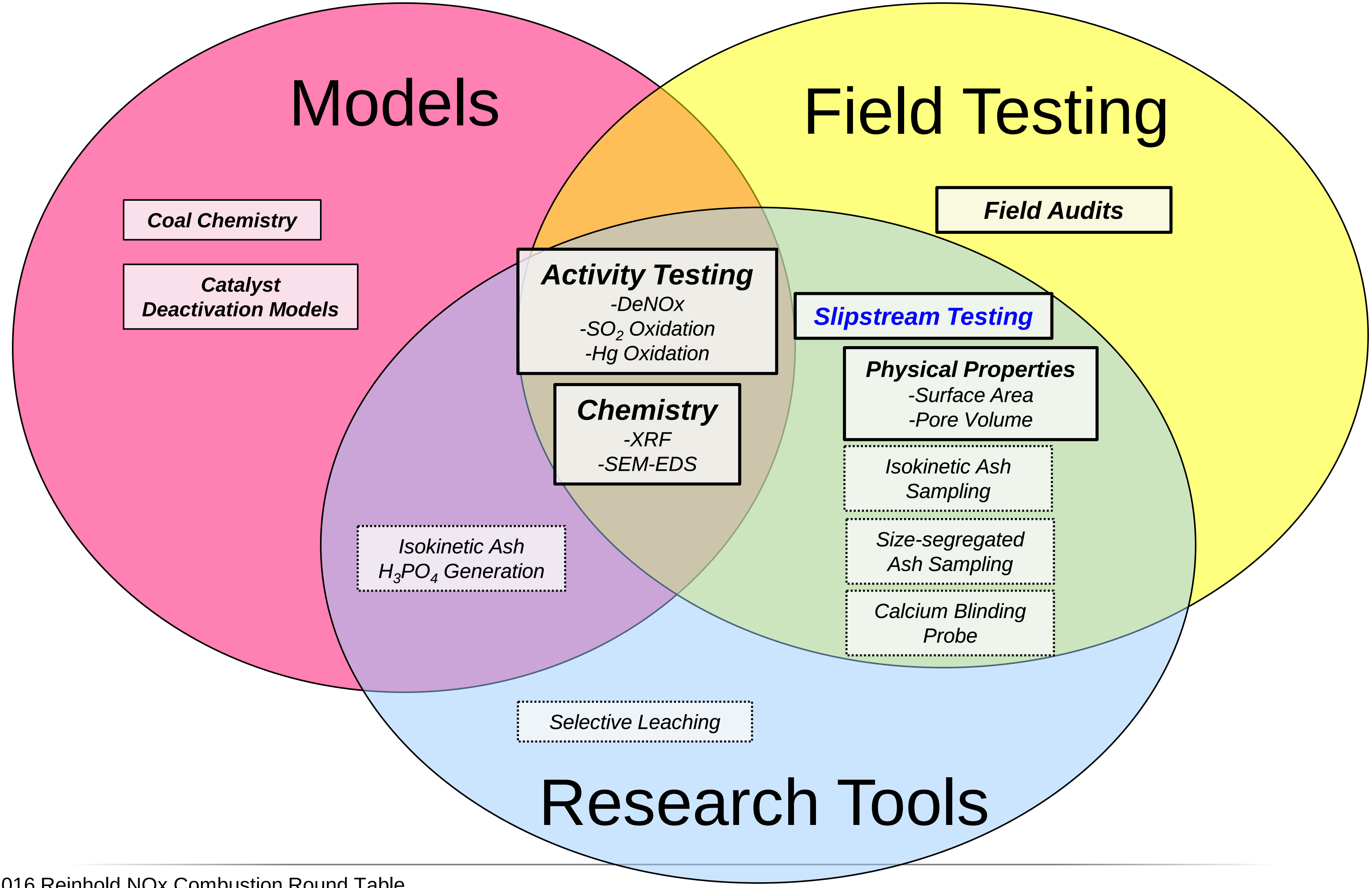
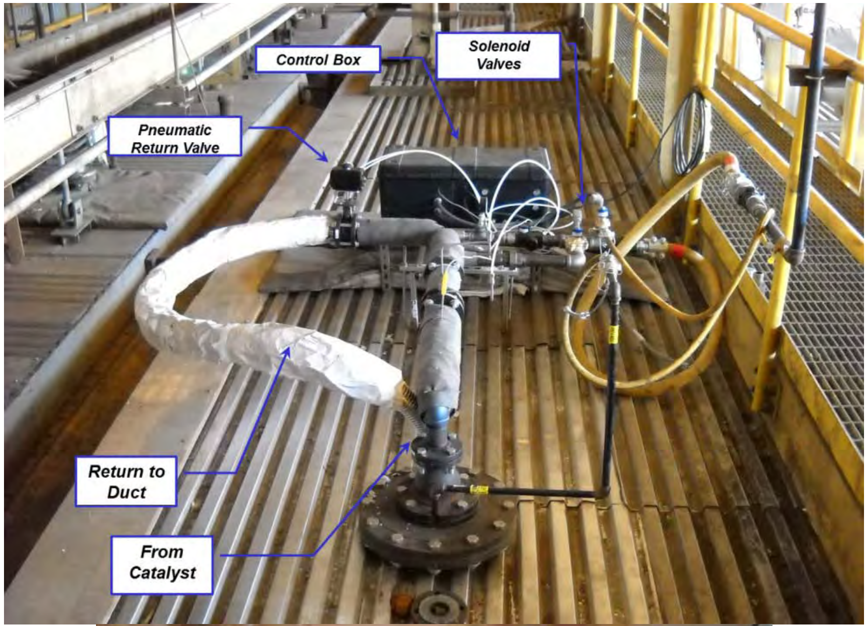
Catalyst Management Tools



Slipstream Reactor

- Small reactor that exposes DeNOx catalyst to flue gas (no NH_3 injection)
- Can be installed on any unit, even without existing SCR.
- Runs continually (unattended), and measures real life, real-time deactivation rate of the unit.
- **Most robust tool for characterizing deactivation of a specific unit.**



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Application of Knowledge

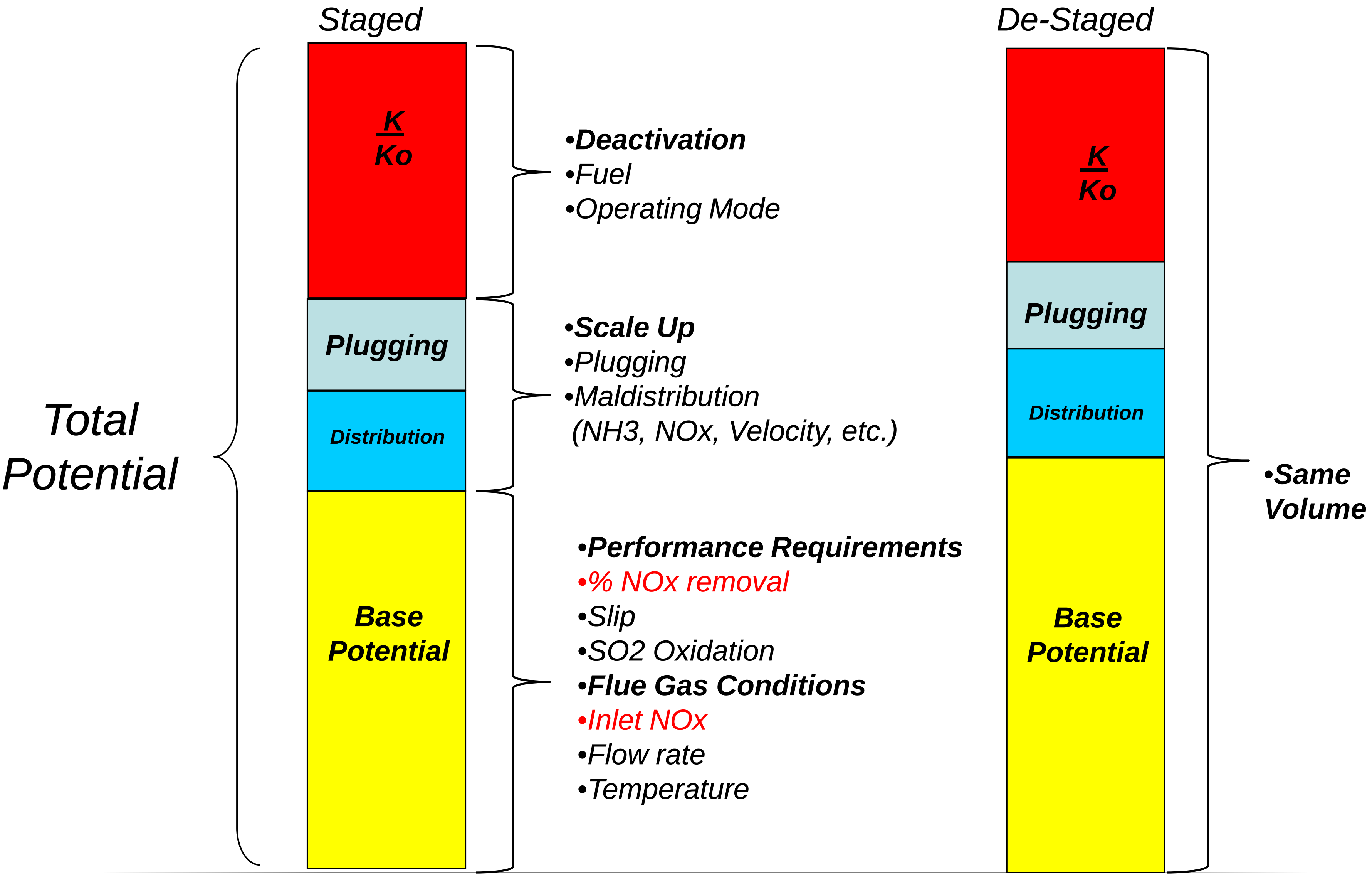
- Discuss Application in General Terms & Look at a Case Study:
  - 1980's Vintage Boiler with Modern Low NOx Burner/Overfire Air System

  - Assess Impact of Increasing Boiler Outlet NOx from 0.16 lb/MMBtu to 0.20 lb/MMBtu
    - Understand the Rates of Catalyst Deactivation
    - Understand Implications of Higher Potential Requirements
    - Sum Up the Positives & Negatives

Application

- Considerations & Directional Impacts Associated with De-Staging Combustion System
  - Increase in Ammonia Consumption Rate
    - Technical – Capacity of Ammonia Equipment [- Impact]
    - Cost of Higher Ammonia Consumption [- Impact]
  - Lower Catalyst Usage Over Lifetime [+ Impact]
  - Boiler Tube Corrosion [Directional Impact +]
  - Hg Oxidation [Directional Impact -]
  - Additives
    - Phosphorus Mitigation [+ Impact]
    - Mercury Control [- Impact]

Application



- ***Deactivation***
- *Fuel*
- *Operating Mode*

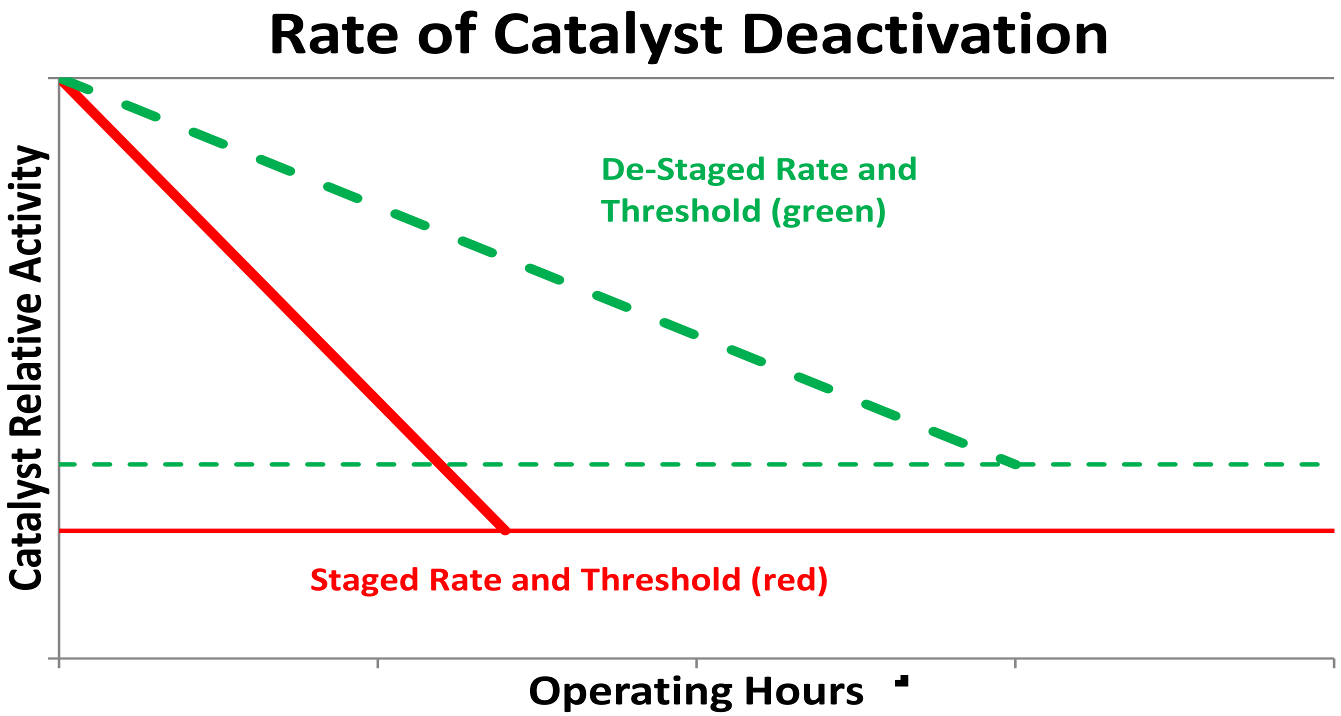
- ***Scale Up***
- *Plugging*
- *Maldistribution*
  (NH3, NOx, Velocity, etc.)

- ***Performance Requirements***
- *% NOx removal*
- *Slip*
- *SO2 Oxidation*
- ***Flue Gas Conditions***
- *Inlet NOx*
- *Flow rate*
- *Temperature*

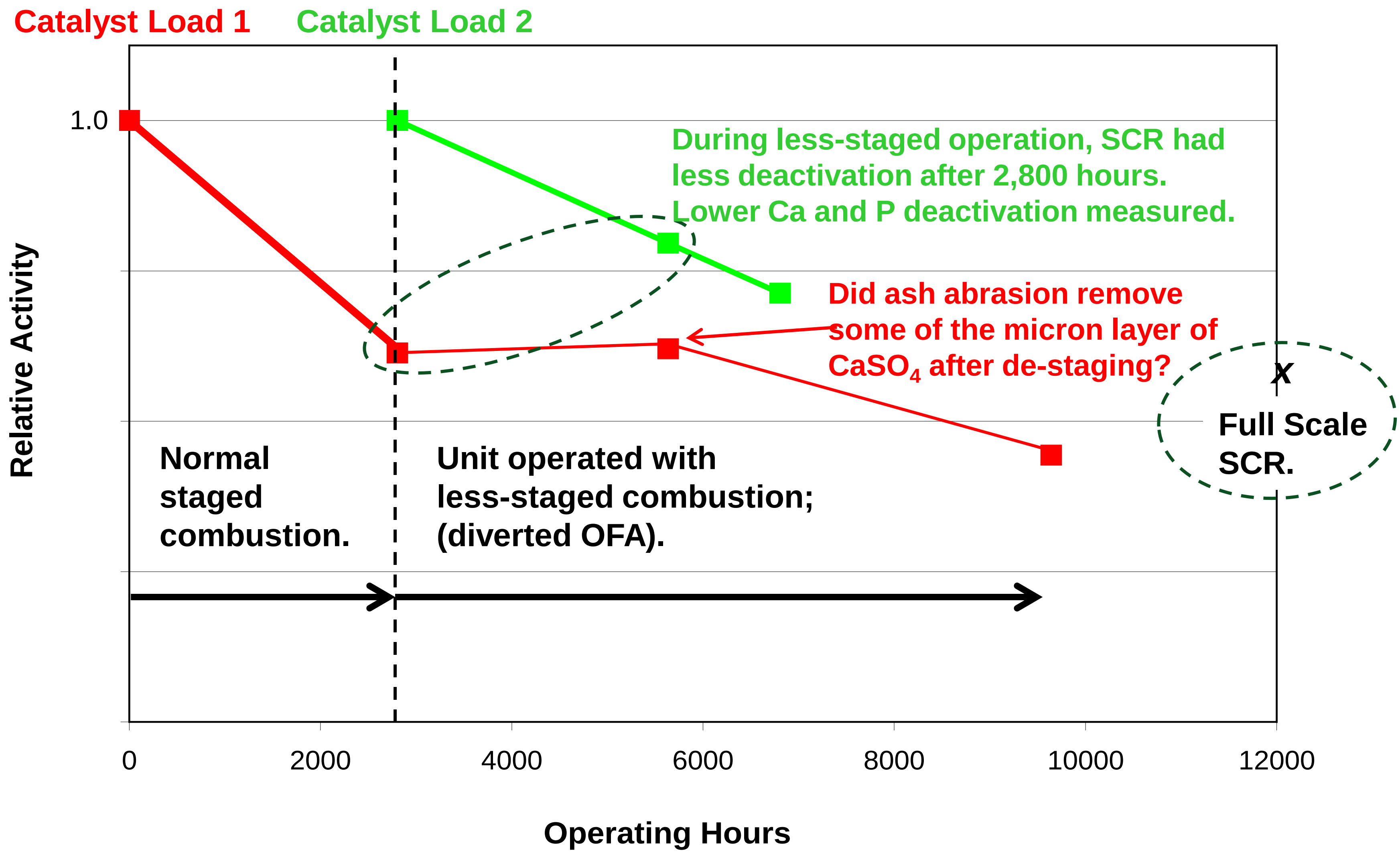
- ***Same Volume***

Application

- Essential that the Deactivation Rate Benefit be More Than Enough to Offset the Higher Base Potential Requirement



Case Study



During less-staged operation, SCR had less deactivation after 2,800 hours. Lower Ca and P deactivation measured.

Did ash abrasion remove some of the micron layer of $CaSO_4$ after de-staging?

Full Scale SCR.

Normal staged combustion.

Unit operated with less-staged combustion; (diverted OFA).

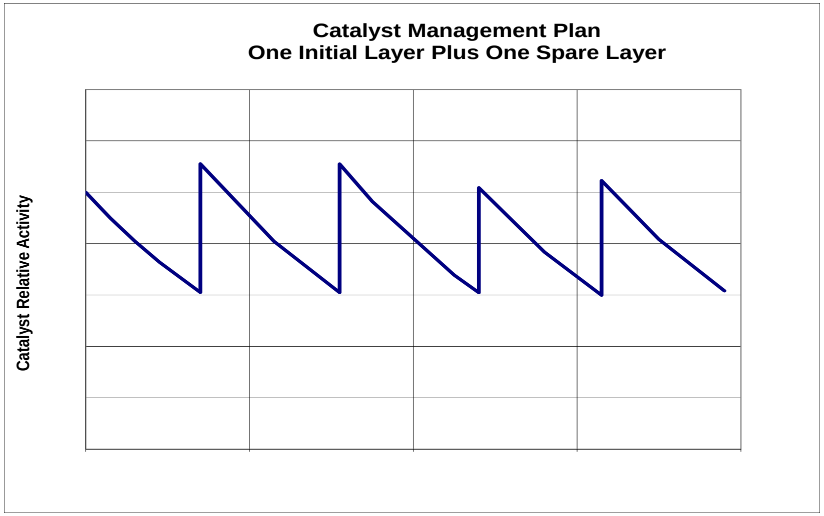
Application

- Cost Benefit Analysis
  - **Costs:**
    - More K/AV required to achieve higher DeNOx
    - Higher NH_3 usage rate
    - Combustion modification capability and engineering
  - **Benefits:**
    - Lower catalyst deactivation rate (for Ca & P)
    - Reduce catalyst volume (lower DP) and/or extend catalyst life

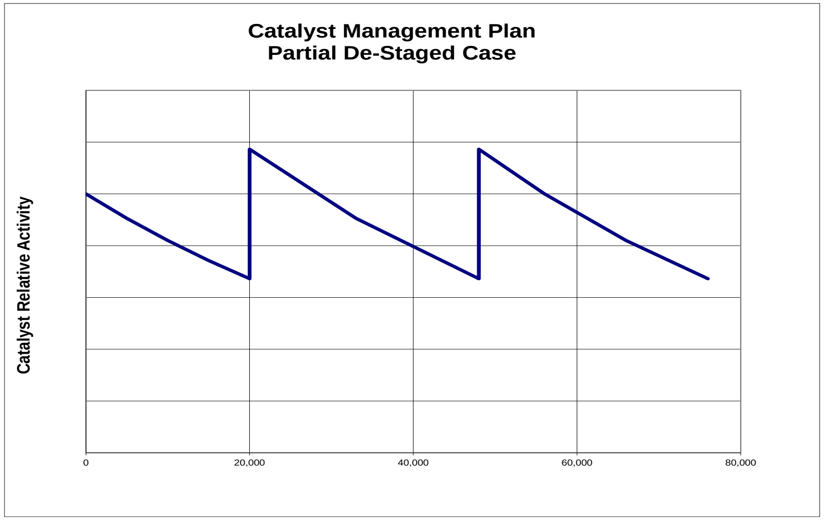
Application

- **Primary Cost → Ammonia Consumption**
  - **Est. $1.5 – 2 MM over 10 Years**
    - **Based on $300-$400/Ton of Anhydrous Ammonia**

- **Primary Benefit → Catalyst Savings**
  - **Est. $4 – 5 MM over 10 Years**



Catalyst Management Plan
One Initial Layer Plus One Spare Layer



Catalyst Management Plan
Partial De-Staged Case

Summary

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- **Wide range of measured catalyst deactivation rates, resulting from Ca, P, and Na poisoning.**
- **Detailed understanding of deactivation mechanism built from catalyst audit and controlled field experiments.**
- **Sub-micron CaO and $Ca_3(PO_4)_2$ are the key deactivating agents.**
- **Deactivation models, Unit specific / similar unit historical data, Fly ash sampling and characterization, and Slipstream reactor testing are tools to manage the uncertainty of deactivation rates. They can also be used to assess the effectiveness of potential mitigation options.**
- **De-staging the firing system can optimize the SCR lifecycle costs.**

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Questions?