

# **REINHOLD ENVIRONMENTAL Ltd.**



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

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# SCR Catalyst Deactivation Mechanism for PRB-Firing Coal Utility Boilers

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2012 NO<sub>x</sub>-Combustion Round Table

# Presentation Outline



- **SCR Design Approach for PRB Units**
- **Field Experiments → Mechanistic Insight**
- **Practical Application**

# Presentation Outline

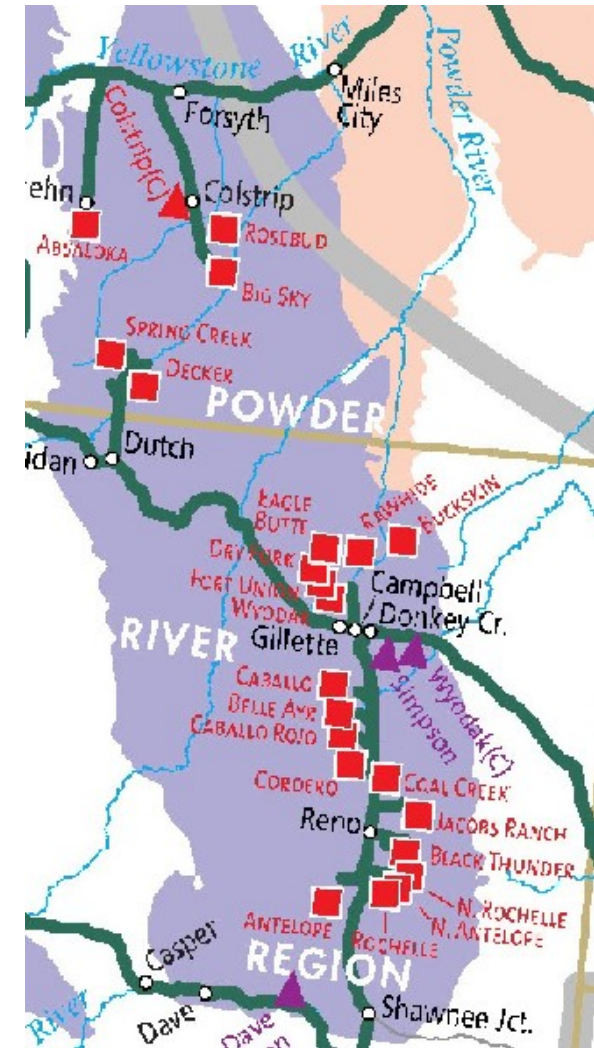


- **SCR Design Approach for PRB Units**
- **Field Experiments → Mechanistic Insight**
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# Cormetech PRB Experience



- **More than 40 SCR units firing 100% PRB or high PRB blends**
- **First unit began operation in early 2000**
- **Longest running unit has >68,000 operational hours**
- **7, 8, and 9 mm pitch catalyst**



# Catalyst Design Tools

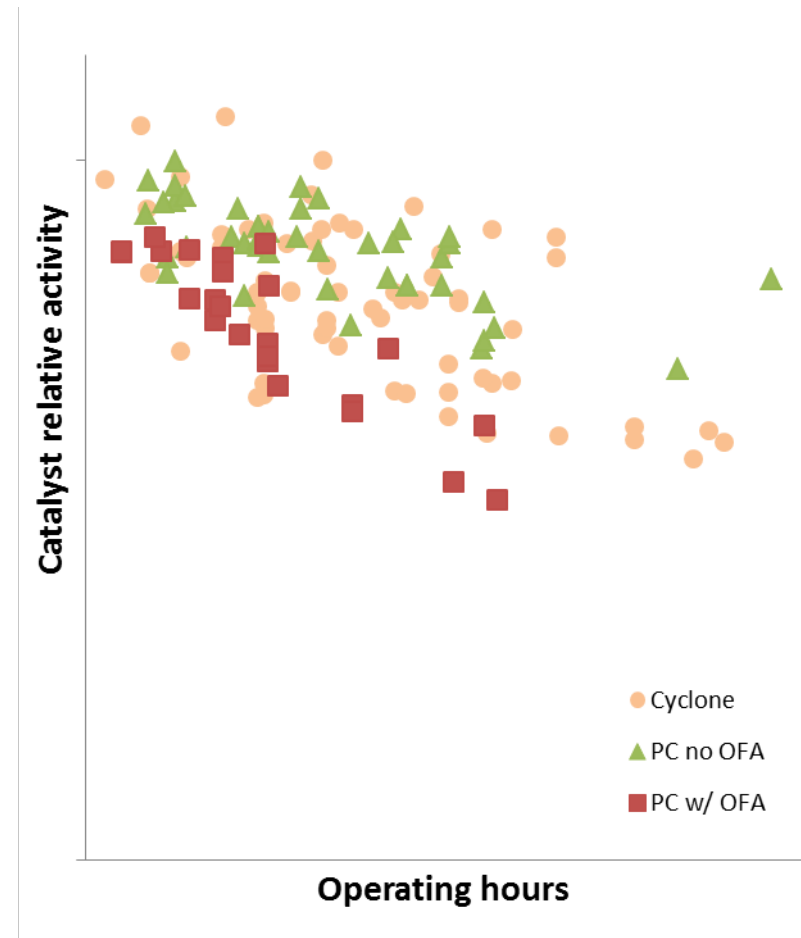
## Predicting K/Ko for PRB-Firing Units



- **Models**
  - Expected calcium and phosphorus accumulation rates
- **Unit specific / similar unit historical data**
- **Fly ash sampling and characterization (t ~ 24 - 100 h)**
  - Provides insight into deactivation tendency of the fly ash for a unit
  - Methods were developed during Cormetech's field experimentation
  - **Bulk fly ash (isokinetic):**
    - $\text{SO}_3$  reaction with fly ash in lab to test gaseous  $\text{P}_2\text{O}_5$  generating potential
  - **Size segregated fly ash (DLPI):**
    - P mass balance across SCR to gage vaporization loss
    - $\text{SO}_3$  reaction with fly ash disks in lab to test gaseous  $\text{P}_2\text{O}_5$  generating potential
- **Slipstream reactor testing (t ~ 3k-8k h)**

# Catalyst Deactivation Audit Data

- **Wide range of measured catalyst deactivation rates**
  - Calcium blinding is primary mode
  - Phosphorus impact is variable (<10% to ~50% of K/Ko loss)
  - Elevated  $\text{Na}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{SiO}_2$ , and  $\text{SO}_3$  also typically observed
  - “Staged” combustion units can have high or low deactivation rates



# Catalyst Deactivation Species

## PRB-Fired Applications



<b>Deactivating Species</b>	<b>Source</b>	<b>Deactivation Mechanism</b>
<b>Ca</b>	<b>CaO-rich particles in sub-micron ash fume</b>	<b>Particles lodge in pore structure at catalyst wall surface, expand by sulfation, and block pore</b>
<b>P</b>	<b>Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>-rich particles in sub-micron ash fume</b>	<b>Release of gas-phase P by reaction with SO<sub>3</sub> produced in SCR; gas-phase P diffuses into catalyst wall, and reacts with active sites</b>
<b>Na</b>	<b>Water-Soluble Na in Ash</b>	<b>Na transfers from ash to catalyst, migrates into catalyst wall, and reacts with active sites</b>

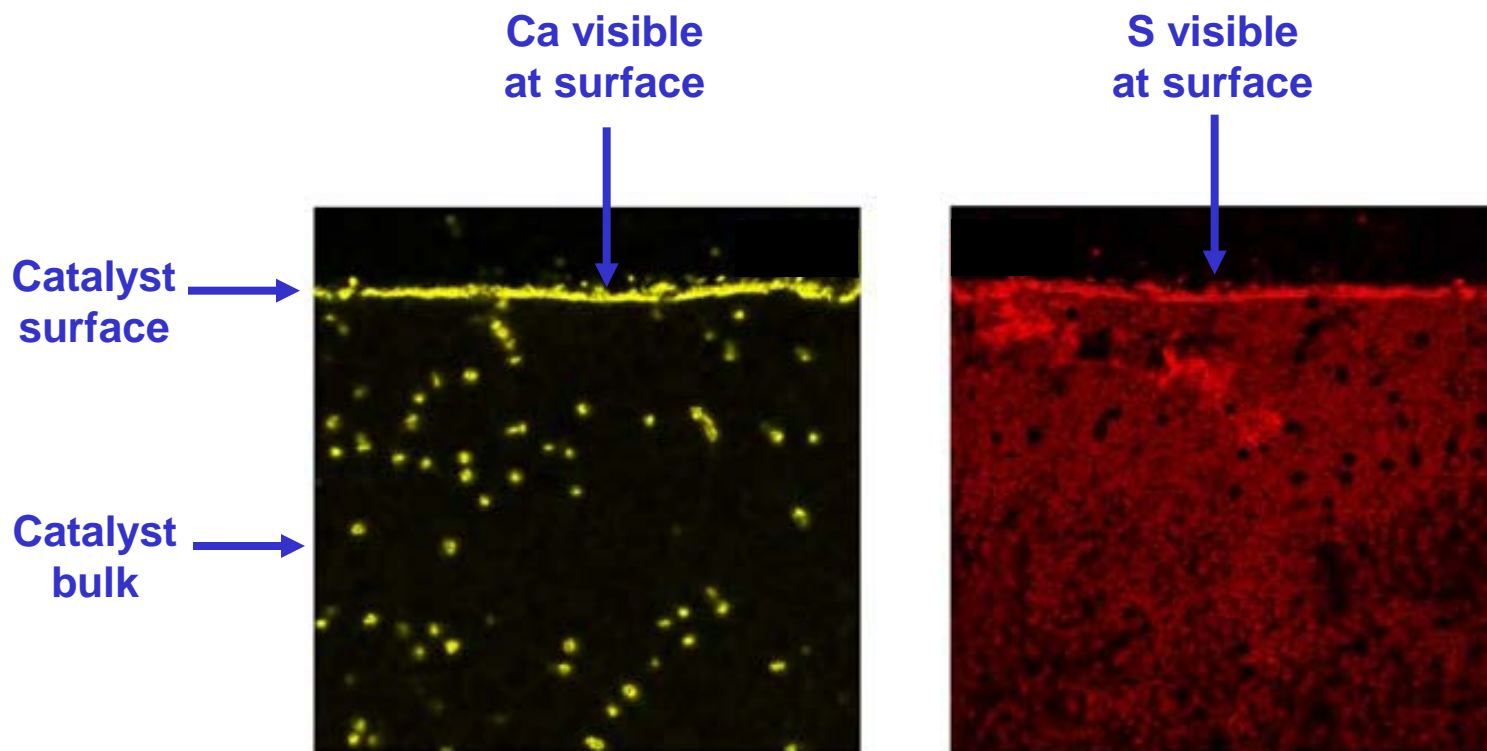
# Catalyst Deactivation Mechanism

## Calcium Deactivation



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- **SEM-EDS data of  $\text{CaSO}_4$  catalyst blinding layer**

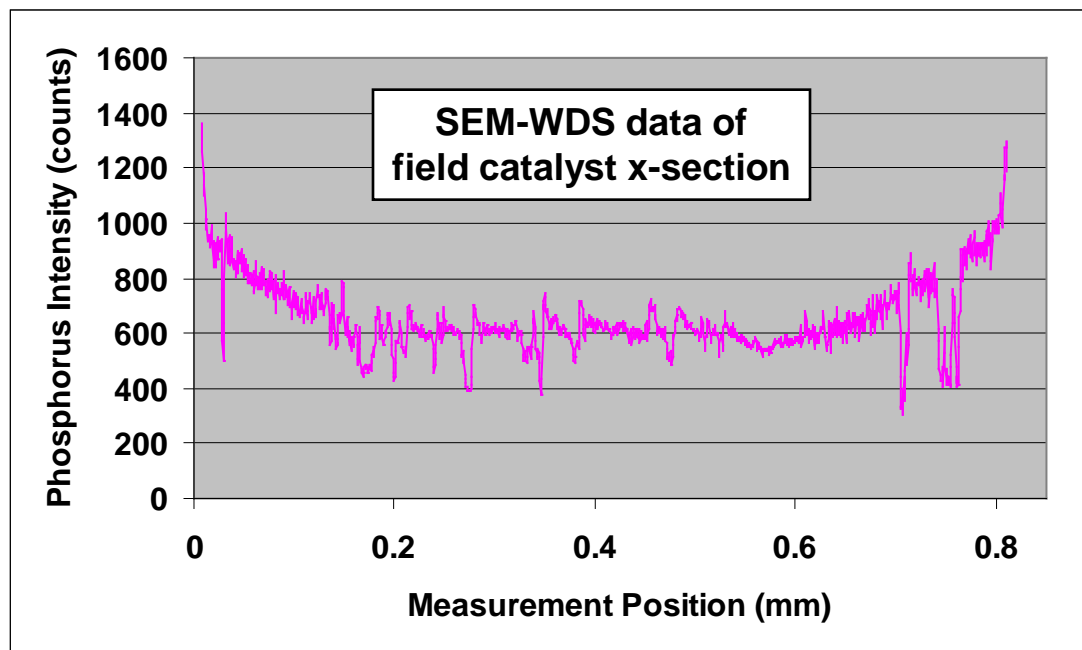


# Catalyst Deactivation Mechanism



## Phosphorus Deactivation

- **Phosphorus is a penetrating catalyst poison:**
  - Diffuses into catalyst bulk and chemically bonds to active sites
  - Wall x-section profile indicative of gas-phase P (i.e.,  $\text{H}_3\text{PO}_{4(g)}$ )

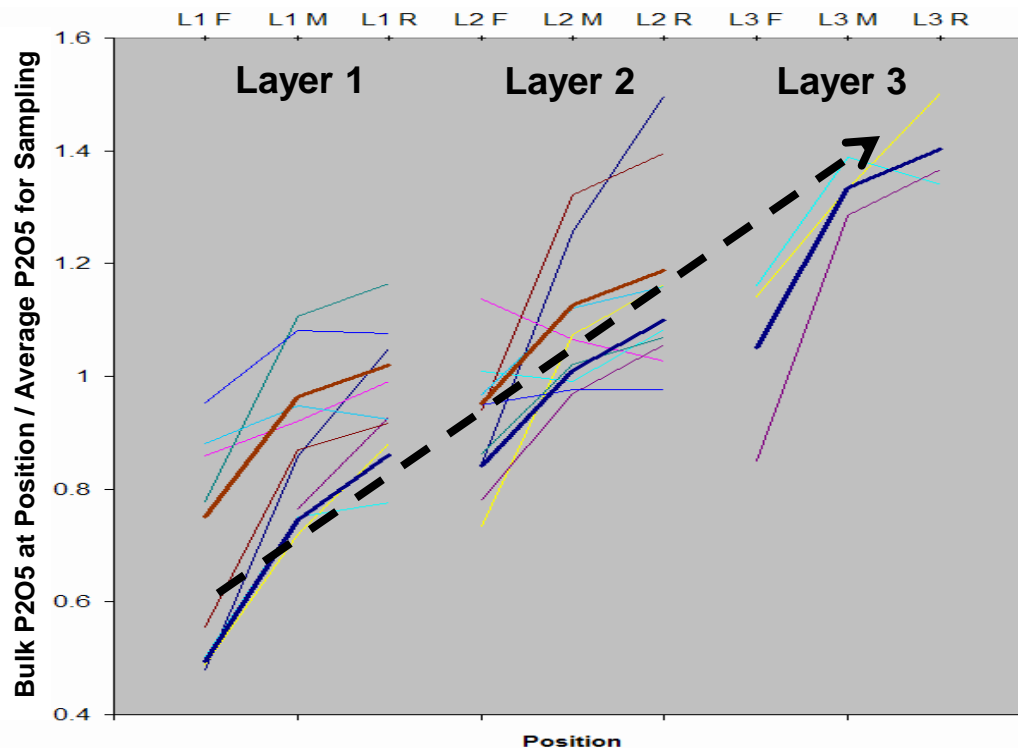


# Catalyst Deactivation Mechanism



## Phosphorus Deactivation

- **PRB: Bulk  $P_2O_5$  typically increases with catalyst length**
  - Unexpected behavior for a gas phase poison



# Presentation Outline



- **SCR Design Approach for PRB Units**
- **Field Experiments → Mechanistic Insight**
- **Practical Application**

# Field Experiments Overview



- **Ran field tests at three Plant sites (2008 – 2010)**

- All Plants are >500 MW PC units firing 100% PRB

Plant	Staged Combustion?	SCR Catalyst Deactivation Rate	Relative Contribution of Ca vs. P to Deactivation
A	YES	HIGH	balanced Ca and P
B	NO	LOW	low deactivation rate
C	YES	MEDIUM - HIGH	mainly Ca, some P

- **Factors studied:**

- Coal mine, load (full and partial), degree of combustion staging

- **Sampling methods:**

- Coal, isokinetic and size-segregated fly ash, gas phase P, NO<sub>x</sub>

- **Field experiments provided key mechanistic insights**

# Gas Phase P Measurements



Plants A (SCR Inlet and Outlet) and B (SCR Inlet)

		Testing Day 1 Data		Testing Day 2 Data	
Unit Catalyst Deactivation Rate		SCR Inlet P2O5(g) [ppbvd]	SCR Outlet P2O5(g) [ppbvd]	SCR Inlet P2O5(g) [ppbvd]	StDev P2O5(g) [ppbvd]
Plant A	High	2.7	3.5	2.1	2.1
Plant B	Low	1.4 ± 0.5	not measured	3.9 ± 0.7	not measured

- **Plants A and B: no significant measured difference for gas phase P concentration at the SCR inlet**
  - Also: the measured values are too low to account for the rate of bulk P<sub>2</sub>O<sub>5</sub> accumulation observed in the catalyst audit samples

# Phosphorus Volatilization from Ash



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## Thermodynamics for Reaction of Metal Phosphates with SO<sub>3</sub>

Reaction	300°C	400°C
	delta G [kJ]	delta G [kJ]
$\text{Ca}_3(\text{PO}_4)_2 + 3\text{SO}_3(\text{g}) + 3\text{H}_2\text{O}(\text{g}) = 3\text{CaSO}_4 + 2\text{H}_3\text{PO}_4(\text{g})$	-125.7	-71.7
$2\text{FePO}_4 + 3\text{SO}_3(\text{g}) + 3\text{H}_2\text{O}(\text{g}) = \text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_3\text{PO}_4(\text{g})$	35.5	70.6
$2\text{AlPO}_4 + 3\text{SO}_3(\text{g}) + 3\text{H}_2\text{O}(\text{g}) = \text{Al}_2(\text{SO}_4)_3 + 2\text{H}_3\text{PO}_4(\text{g})$	107.4	164.4
$\text{Mg}_3(\text{PO}_4)_2 + 3\text{SO}_3(\text{g}) + 3\text{H}_2\text{O}(\text{g}) = 3\text{MgSO}_4 + 2\text{H}_3\text{PO}_4(\text{g})$	61.9	117.6

- In SCR temperature range: solid  $\text{Ca}_3(\text{PO}_4)_2$  has a thermodynamically-favored reaction pathway for releasing gas phase phosphorus by reaction with SO<sub>3</sub>
- $\text{Ca}_3(\text{PO}_4)_2$  is a condensed reactive phosphorus (CRP)

# Laboratory Data

## Confirmation of Thermodynamic Calculations

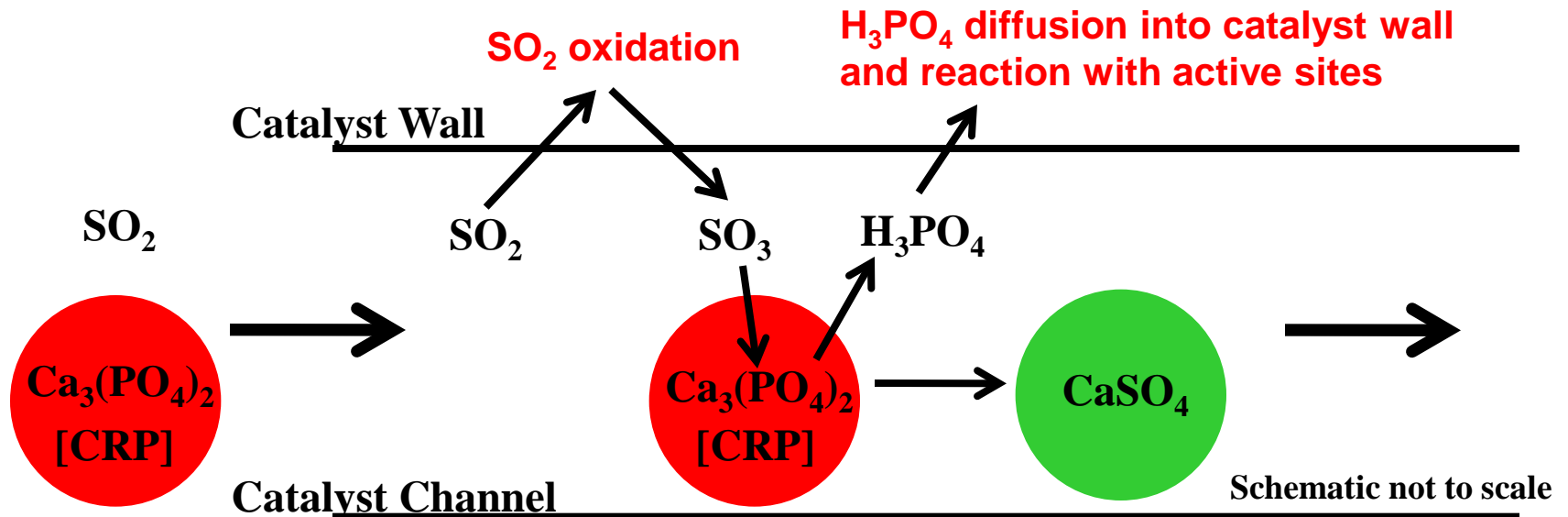
- We generated gas phase phosphorus in lab testing by reacting gaseous  $\text{SO}_3$  (at SCR conditions) with:
  - Pure  $\text{Ca}_3(\text{PO}_4)_2$  (confirmed the thermo)
  - Isokinetic bulk fly ash (SCR inlet) from Plants A, B, and C:

Plant	Unit Catalyst Deactivation Rate	Unit Operation	Average $\text{H}_3\text{PO}_4(\text{g})$ Generated in Test Relative to Plant A
Plant A	High	Staged Operation	1.00
Plant B	Low	Non-Staged	0.31

Table: Lab test data for  $\text{SO}_3$  reaction with fly ash from Plants A and B to generate gas phase P

Catalyst audit data:  
Plant A catalyst has 3x higher bulk accumulation rate for phosphorus than Plant B catalyst.

# Phosphorus Release Mechanism

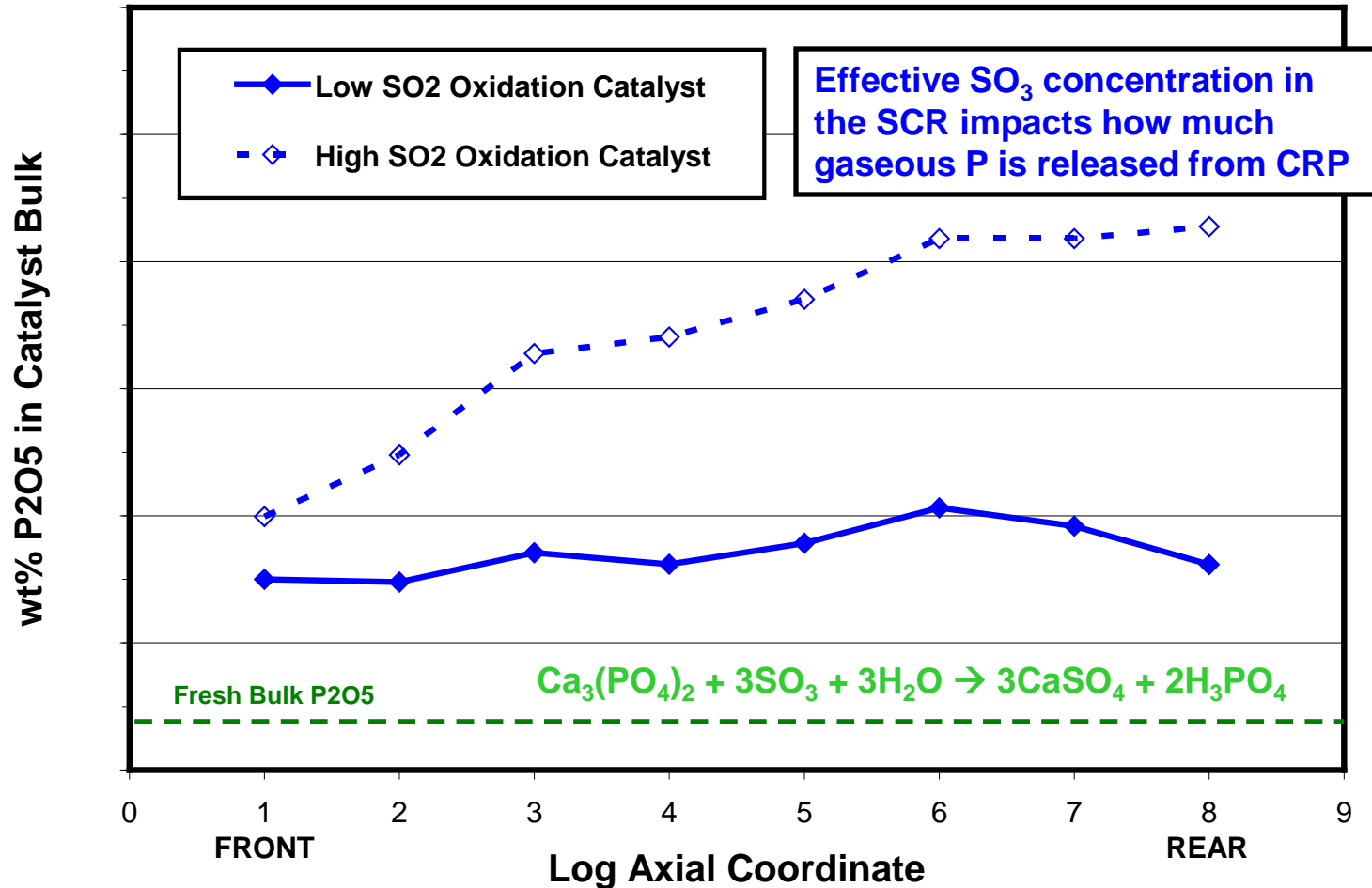


- **SO<sub>3</sub> concentration increases with catalyst length, increasing the amount of gaseous P released**
  - Explains why bulk P in catalyst increases with catalyst length
  - Amount of P released will depend on: saturation vapor pressure of P over the CRP (solid solution) and effective SO<sub>3</sub> concentration

# Field Catalyst Data



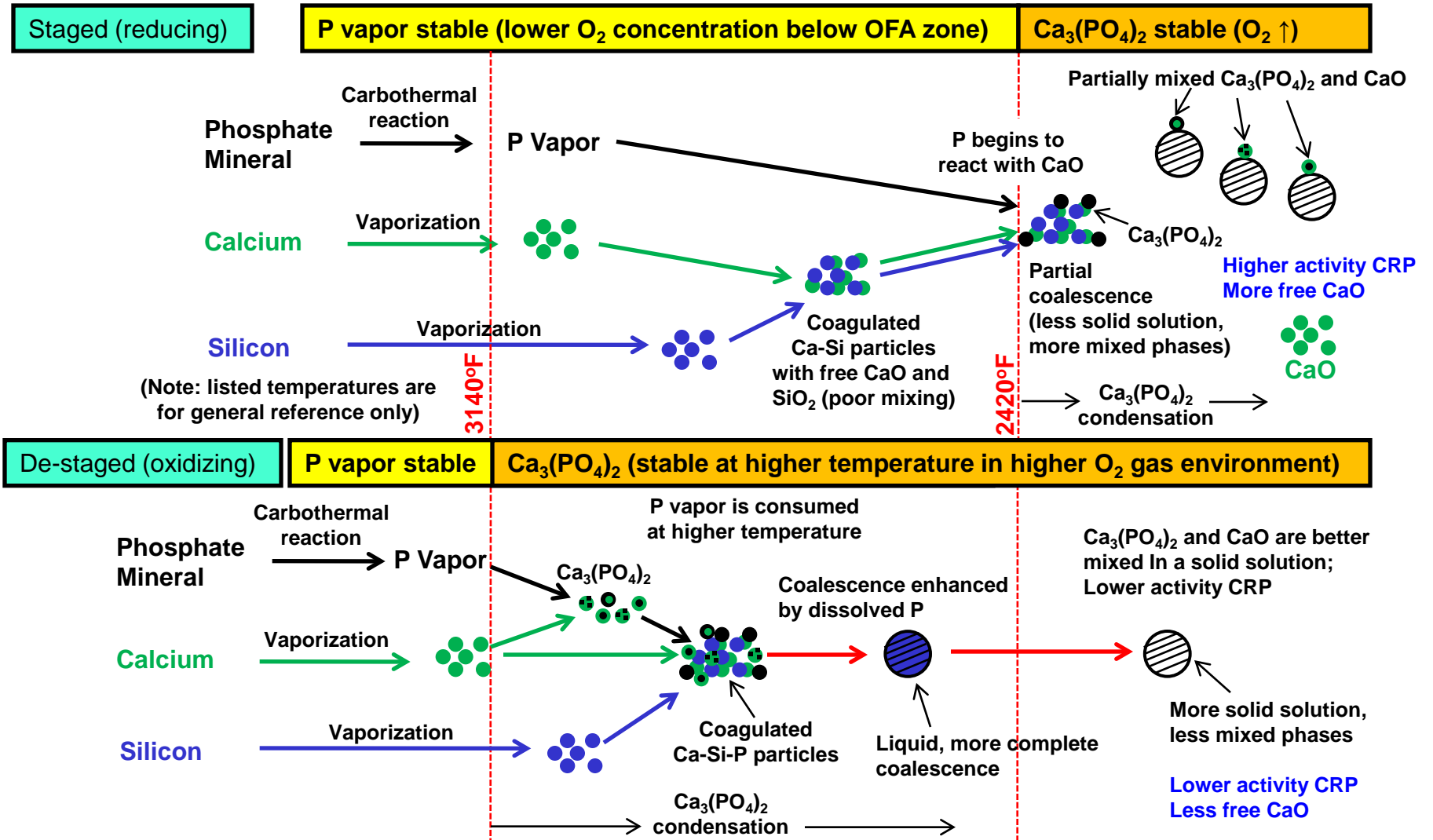
Loaded two ½ catalyst samples (low and high SO<sub>2</sub> oxidation rate catalyst) in single sample tray and loaded it into a Plant A SCR module for field aging.



# Proposed CRP Formation Mechanism



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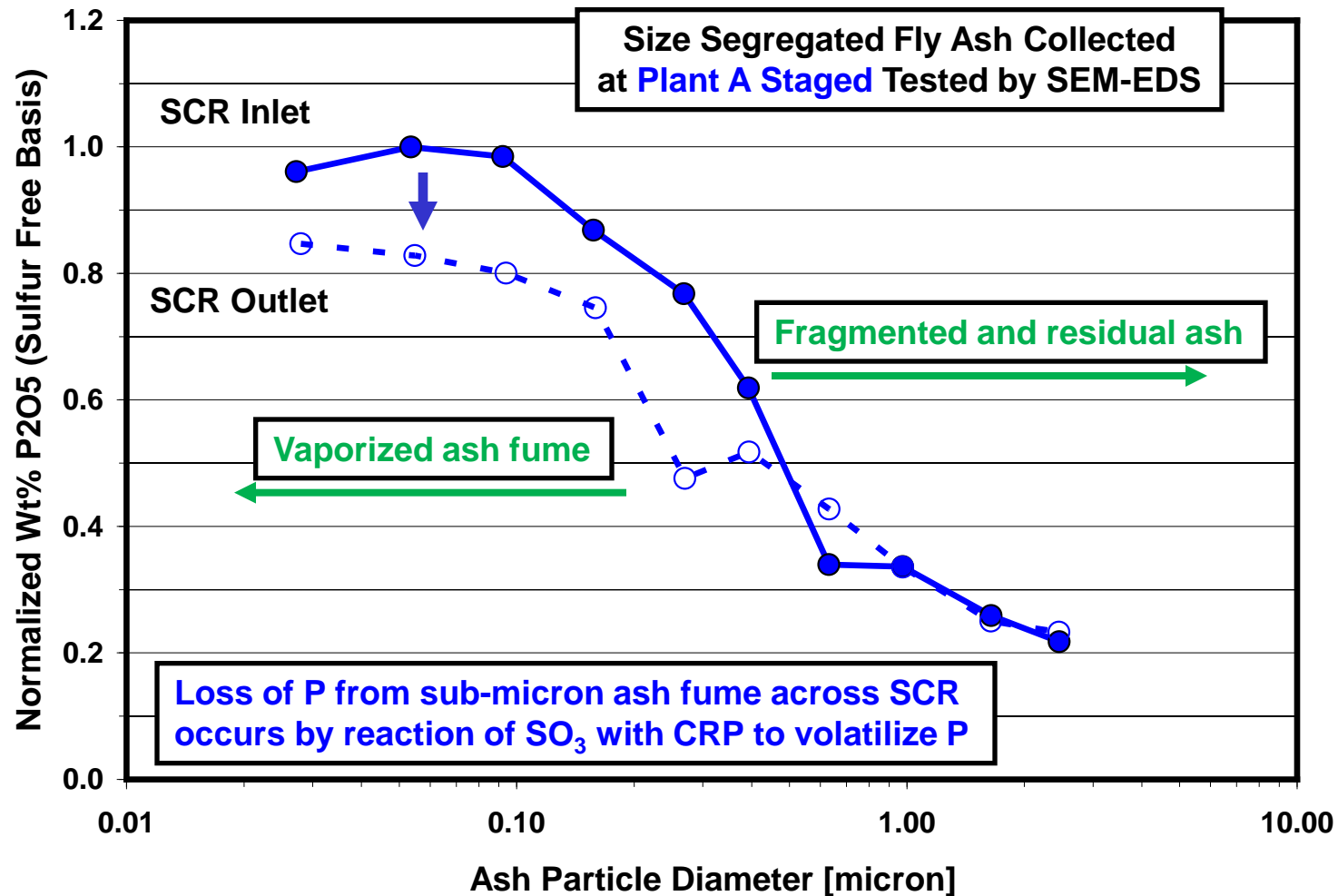


# CRP Exists in Sub-Micron Ash Fume



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CRP is Formed by Vaporization/Condensation Process in Furnace

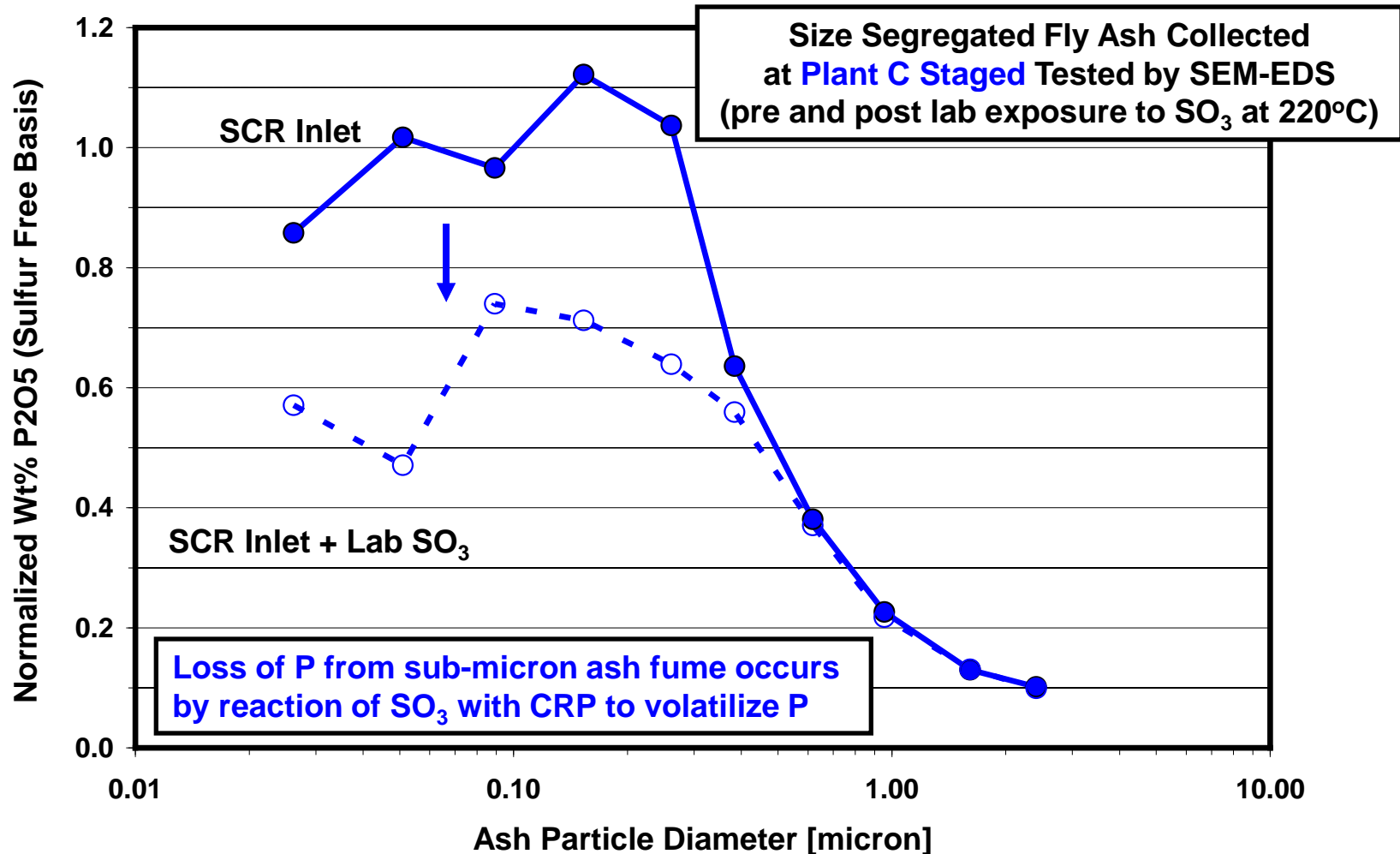


# CRP Exists in Sub-Micron Ash Fume



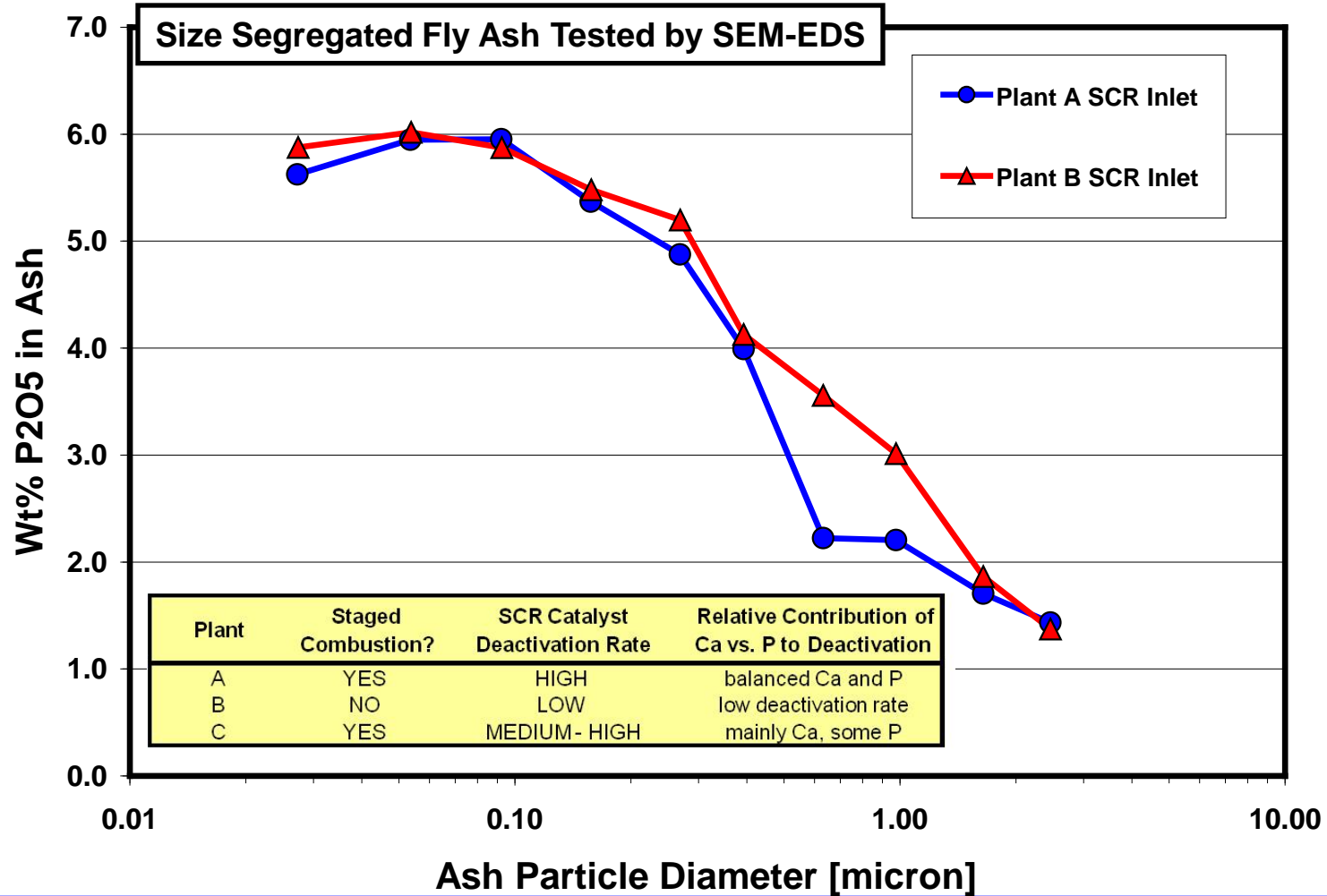
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CRP is Formed by Vaporization/Condensation Process in Furnace



# SCR Inlet P in Ash Data for Plants A & B CORMETECH

## Staged vs. Non-Staged Combustion has Little Impact on P Vaporization



# Carbothermal Reduction Process

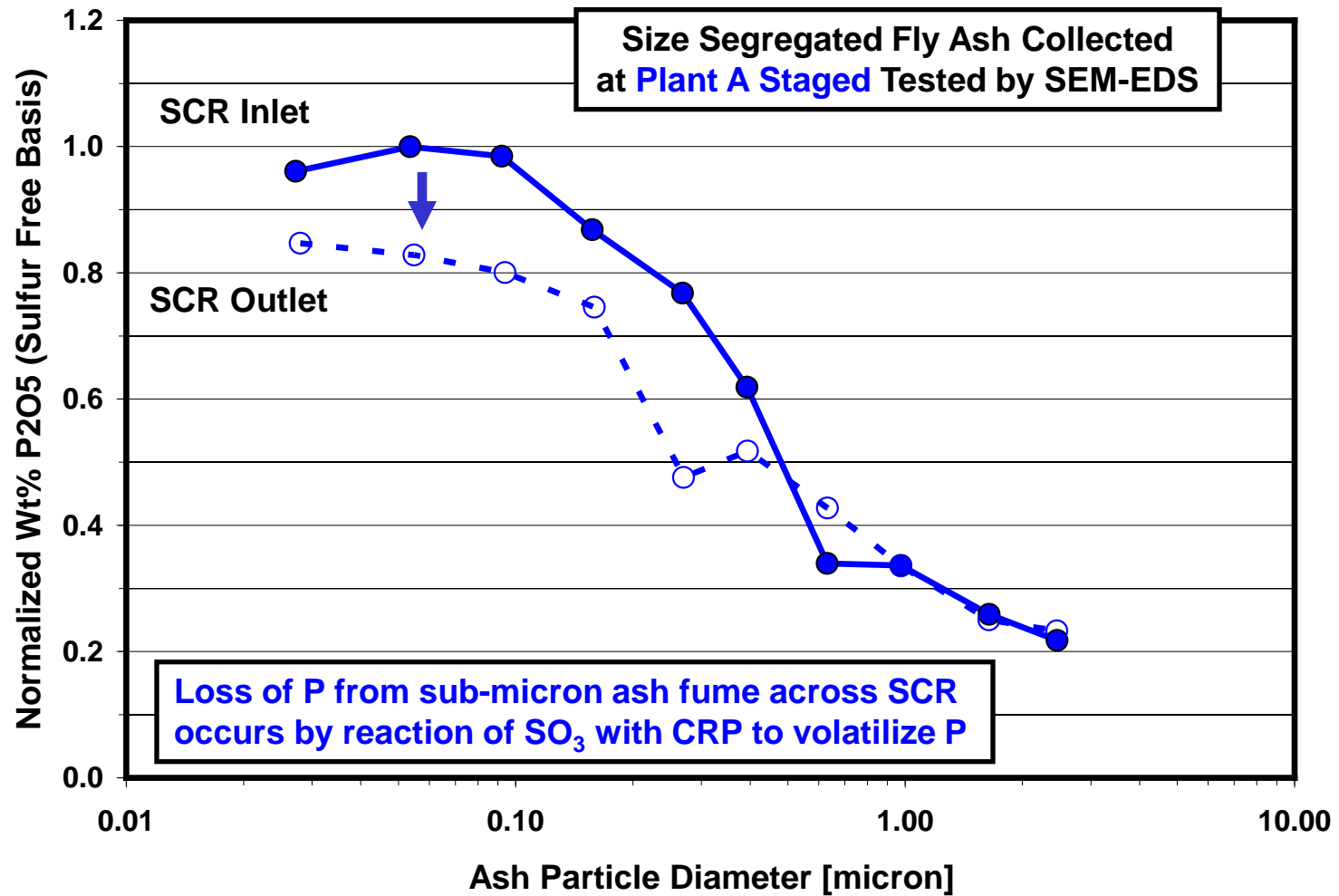


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## Mechanism of Phosphorus Vaporization from Coal

- Phosphorus in PRB coal is mainly crandallite (a mineral phosphate):  $\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot (\text{H}_2\text{O})$
- Crandallite can vaporize in the burning char particle by reaction with C and  $\text{SiO}_2$  releasing gas phase P in furnace (process is called carbothermal reduction):
  - $\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot (\text{H}_2\text{O}) + \text{SiO}_2 + \text{C} \rightarrow 2\text{P}_{(g)} + \text{CO}_{(g)} + [\text{CaAlSiO}_3]$
- The burning char particle is a reducing environment under staged or non-staged combustion conditions
- Key for CRP formation are the reactions that occur after phosphorus is vaporized from the char particle

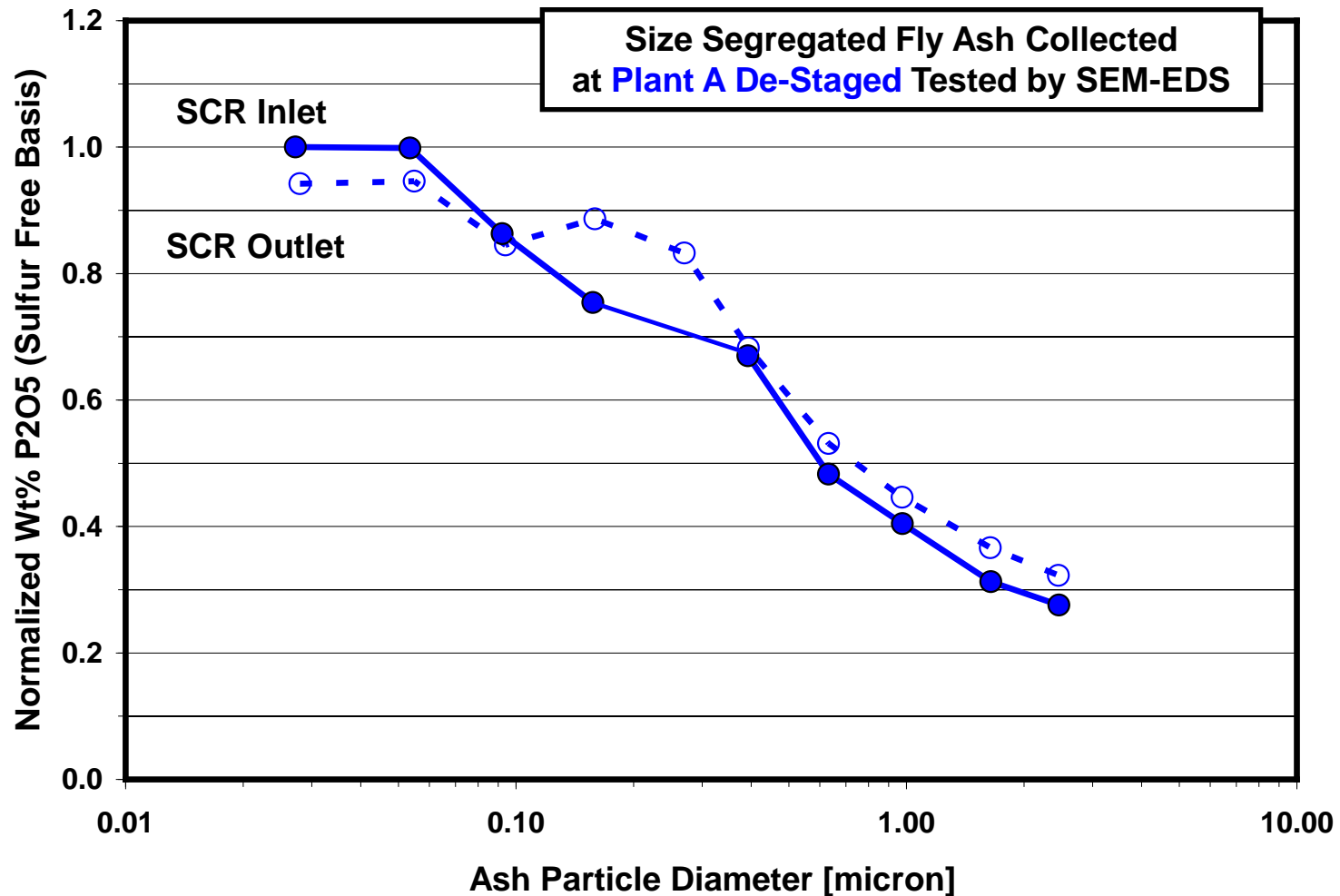
# Plant A – Staged Combustion



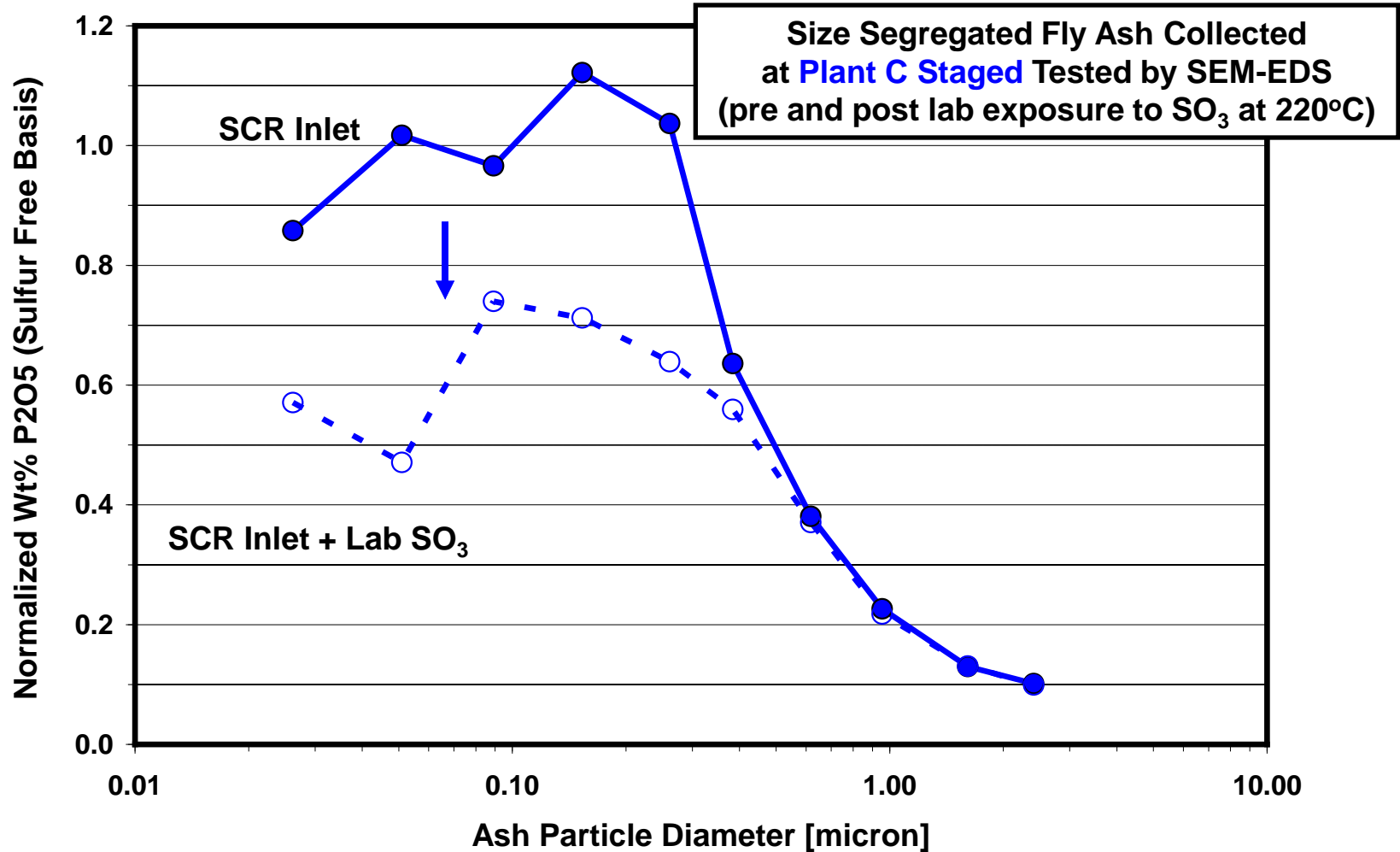
# De-Staging Reduces CRP Activity



## Lower Amount of P Loss Across SCR for Plant A Operating De-Staged



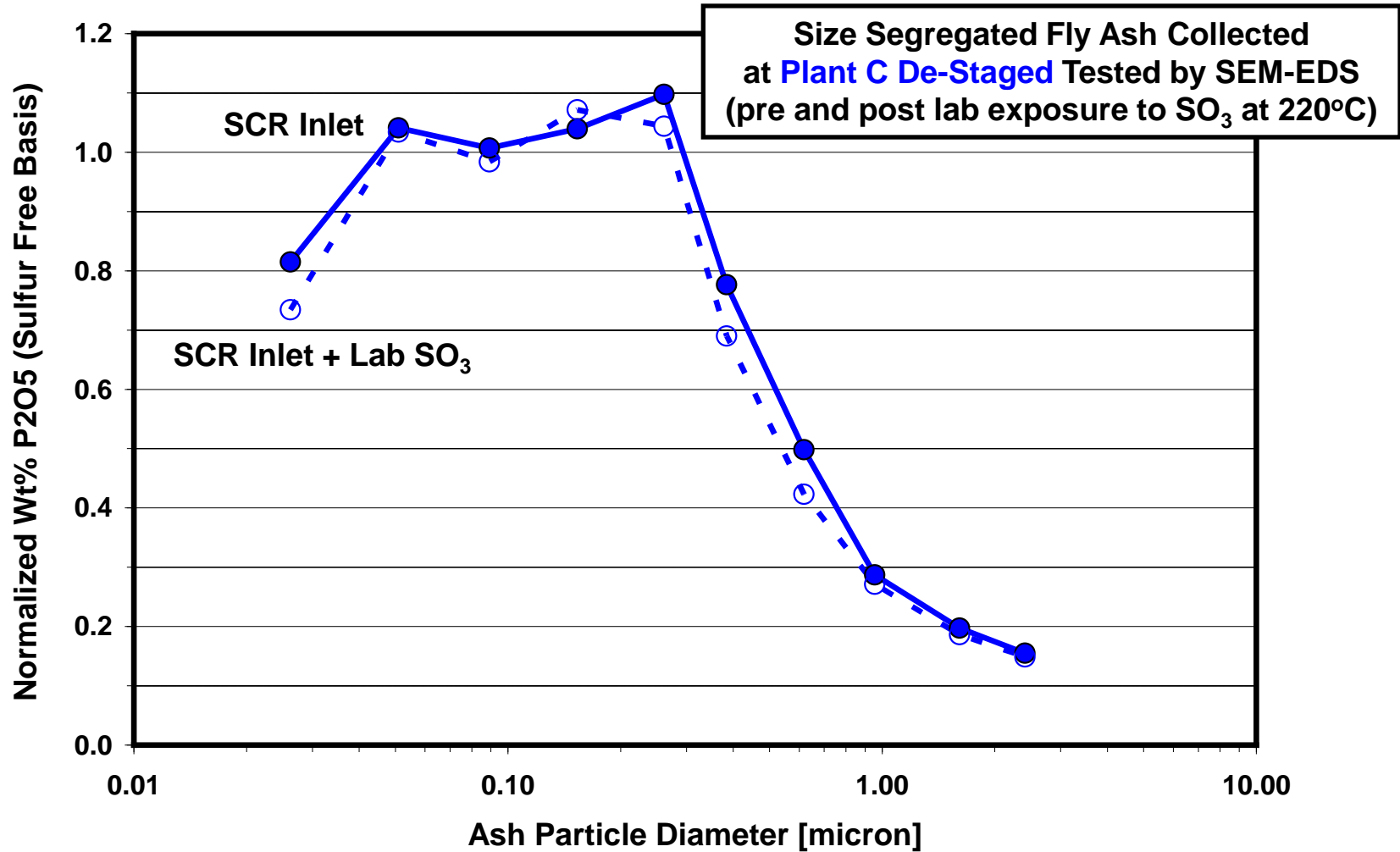
# Plant C – Staged Combustion



# De-Staging Reduces CRP Activity



## Lower Amount of P Loss for Plant C Operating De-Staged

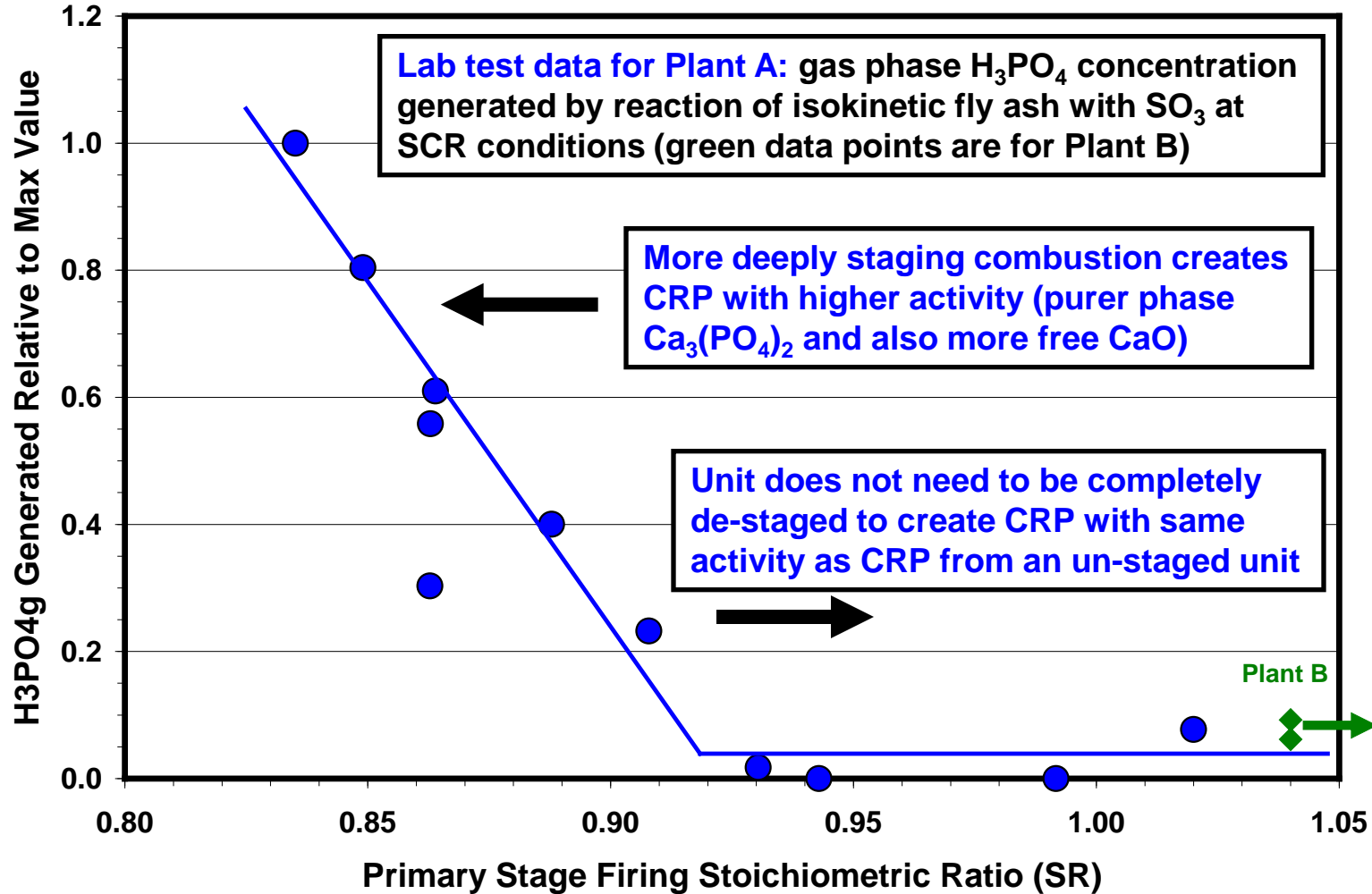


# Bulk Fly Ash Data: Impact of Staging



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CRP Activity = Saturation Vapor Pressure of P over Solid CRP



# Mechanism Summary



- **Free CaO and CRP exist in the sub-micron ash fume:**
  - P, Ca, and Si vaporize from the burning coal char particle
  - CRP formation is driven by the condensation reactions that occur post-vaporization between gaseous P and condensed free CaO
- **Staged combustion:**
  - Cooler combustion & lower O<sub>2</sub> in the primary combustion zone
    - Less coalescence/mixing of condensed CaO and SiO<sub>2</sub> particles
    - Gaseous P condenses in OFA zone as surface enriched Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>
    - More free CaO and higher activity CRP → higher deactivation rate
- **Partially de-staged and non-staged combustion:**
  - Hotter combustion & higher O<sub>2</sub> in the primary combustion zone
    - More coalescence/mixing of CaO/SiO<sub>2</sub> particles (calcium silicate)
    - Gaseous P condenses as diluted Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and may react with SiO<sub>2</sub> to form phosphate glasses
    - Less free CaO and lower activity CRP → lower deactivation rate

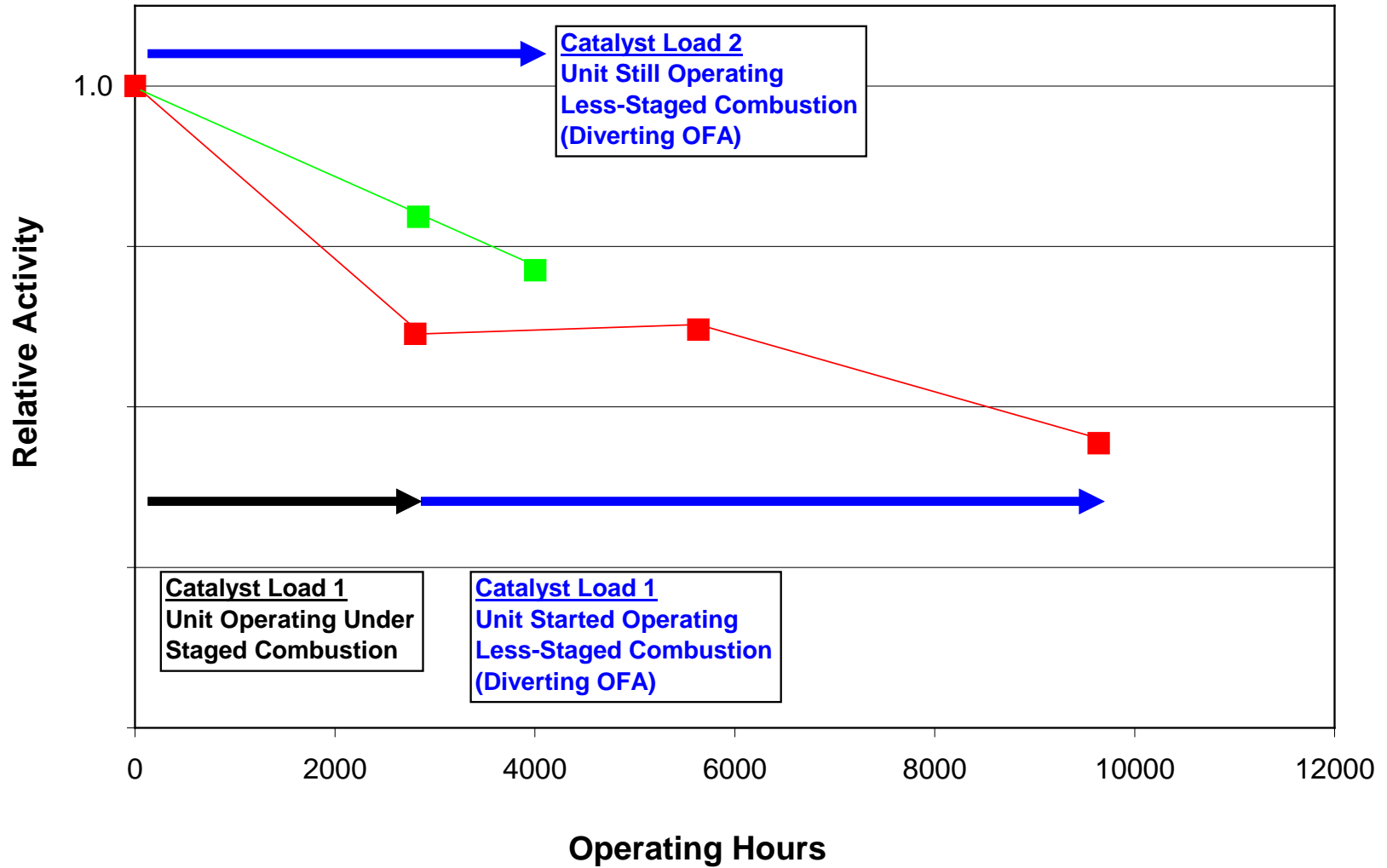
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# Partial De-Staging Impact Data

## PC Unit Firing 100% PRB



# Mitigation Cost/Benefit Analysis

Requires Case Specific Evaluation



- **Partial de-staging?**

- **Costs:**

- More K/AV required to achieve higher DeNO<sub>x</sub>
    - Higher NH<sub>3</sub> usage rate
    - Combustion modification capability and engineering

- **Benefits:**

- Lower catalyst deactivation rate (for Ca & P) → lower overall K/AV
    - Reduce catalyst volume (lower DP) and/or extend catalyst life

- **Lower SO<sub>2</sub> oxidation catalyst?**

- **Costs:**

- Loss of initial K due to formulation change → more volume/DP

- **Benefits:**

- Lower catalyst deactivation rate (for P, but not Ca)

- **Other options?**

# Summary

- **More than 40 SCR units firing 100% PRB or high PRB blends**
- **Wide range of measured catalyst deactivation rates**
- **Deactivation models, Unit specific / similar unit historical data, Fly ash sampling and characterization, and Slipstream reactor testing are used to manage the uncertainty of deactivation rates**
- **Field experiments provided key mechanistic insights**
  - Gas phase P is generated within the SCR by reaction of CRP [ $\text{Ca}_3(\text{PO}_4)_2$ ] with  $\text{SO}_3$
  - More deeply staging combustion creates CRP with higher activity (purer phase  $\text{Ca}_3(\text{PO}_4)_2$  and also more free CaO) that leads to more severe catalyst deactivation.
  - Unit does not need to be completely de-staged to create CRP with same activity as CRP from an un-staged unit
- **SCR catalyst test data has shown the beneficial impact of modest de-staging on deactivation rate**

# QUESTIONS?