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SCR Catalyst Deactivation Mechanism for PRB-Firing Coal Utility Boilers

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2012 NOx-Combustion Round Table

Presentation Outline

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

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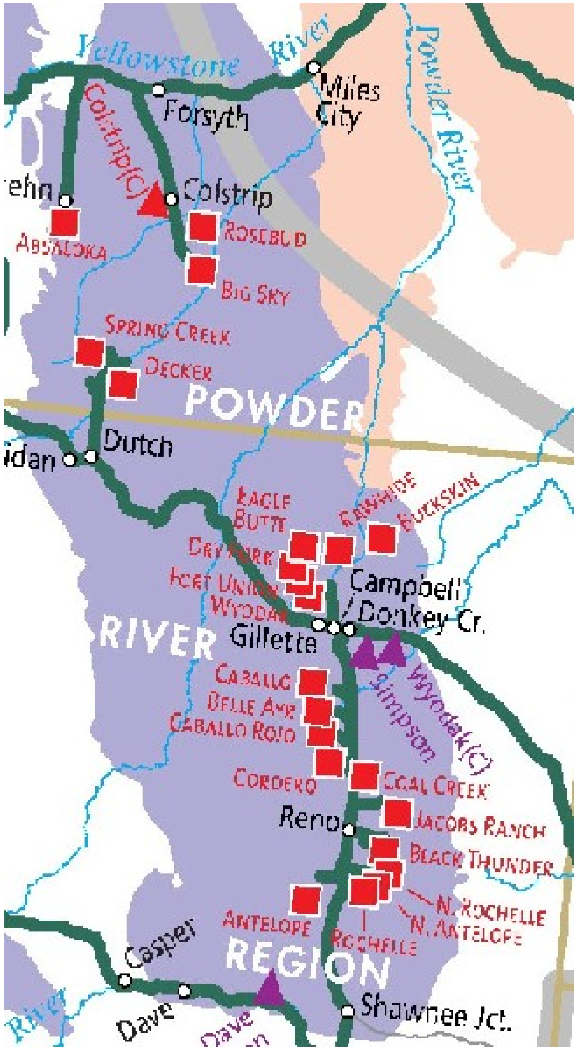
Cormetech PRB Experience

- **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

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- **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)**:
    - SO_3 reaction with fly ash in lab to test gaseous P_2O_5 generating potential
  - **Size segregated fly ash (DLPI)**:
    - P mass balance across SCR to gage vaporization loss
    - SO_3 reaction with fly ash disks in lab to test gaseous P_2O_5 generating potential
- **Slipstream reactor testing (t ~ 3k-8k h)**

Catalyst Deactivation Audit Data

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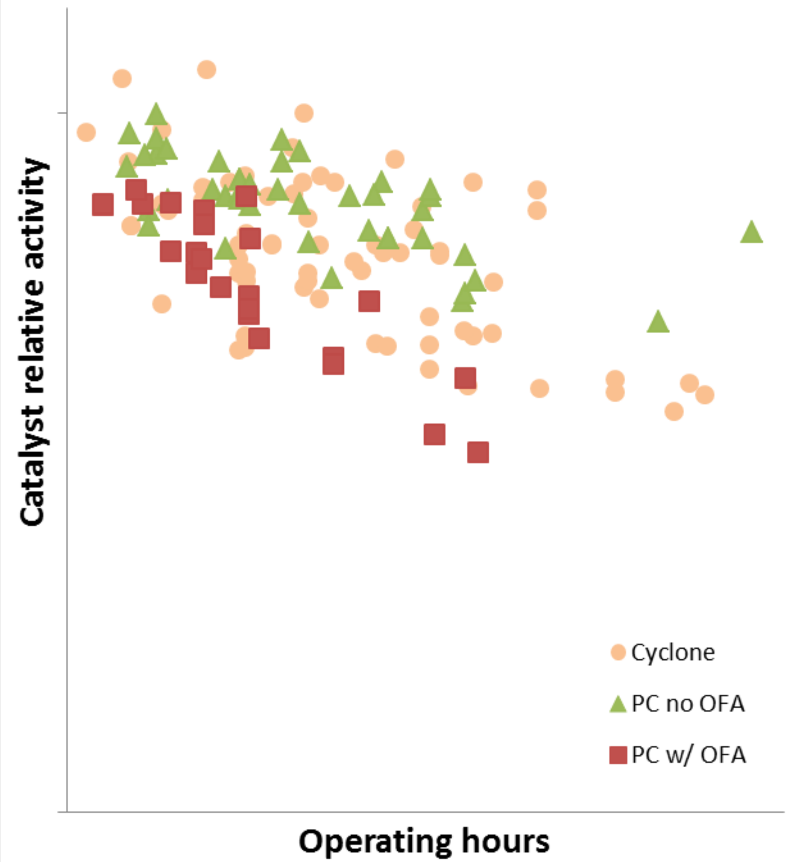
- **Wide range of measured catalyst deactivation rates**
  - Calcium blinding is primary mode
  - Phosphorus impact is variable (<10% to ~50% of K/Ko loss)
  - Elevated Na_2O, Fe_2O_3, SiO_2, and SO_3 also typically observed
  - "Staged" combustion units can have high or low deactivation rates



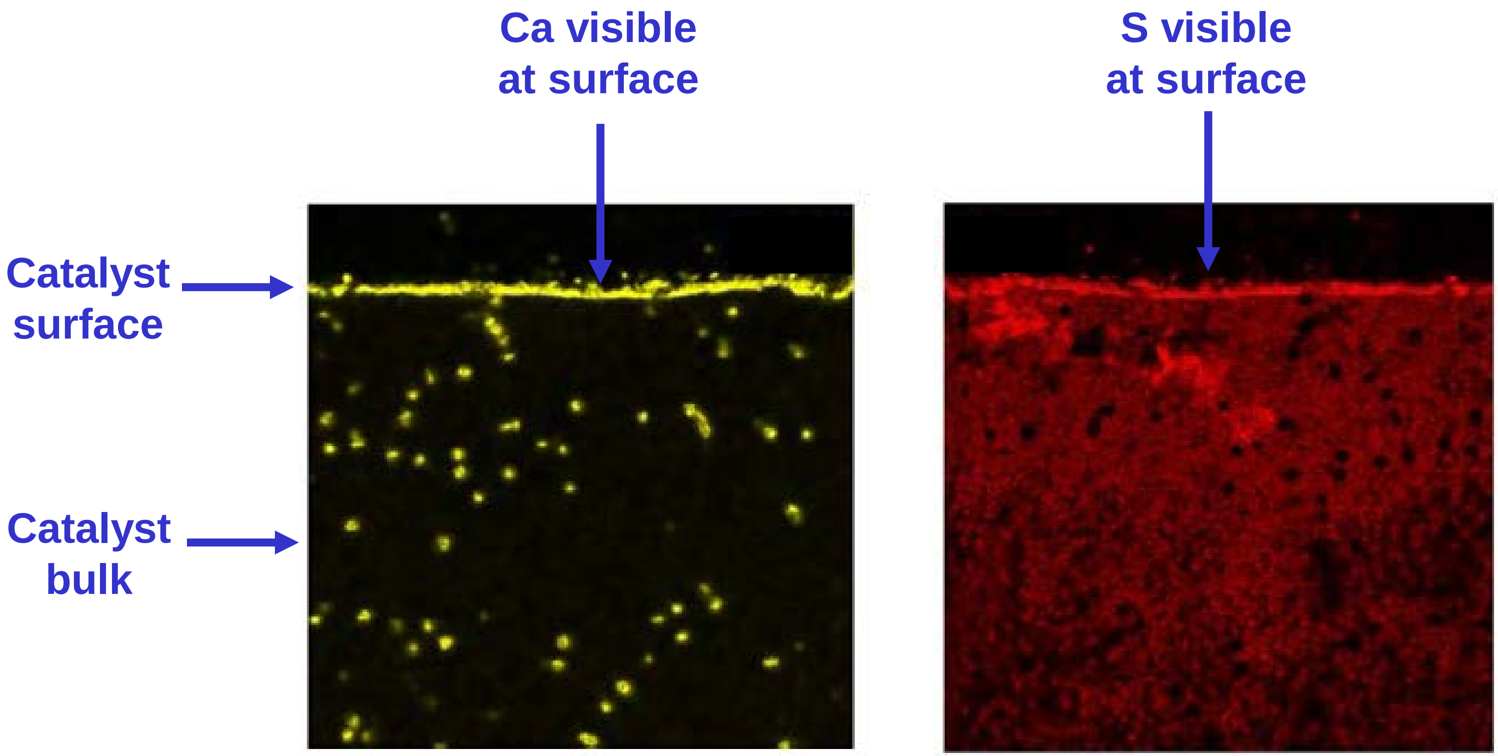
Catalyst Deactivation Species
PRB-Fired Applications

Deactivating Species	Source	Deactivation Mechanism
Ca	CaO-rich particles in sub-micron ash fume	Particles lodge in pore structure at catalyst wall surface, expand by sulfation, and block pore
P	$Ca_3(PO_4)_2$-rich particles in sub-micron ash fume	Release of gas-phase P by reaction with SO_3 produced in SCR; gas-phase P diffuses into catalyst wall, and reacts with active sites
Na	Water-Soluble Na in Ash	Na transfers from ash to catalyst, migrates into catalyst wall, and reacts with active sites

Catalyst Deactivation Mechanism

Calcium Deactivation

- **SEM-EDS data of $CaSO_4$ catalyst blinding layer**



Catalyst Deactivation Mechanism

Phosphorus Deactivation

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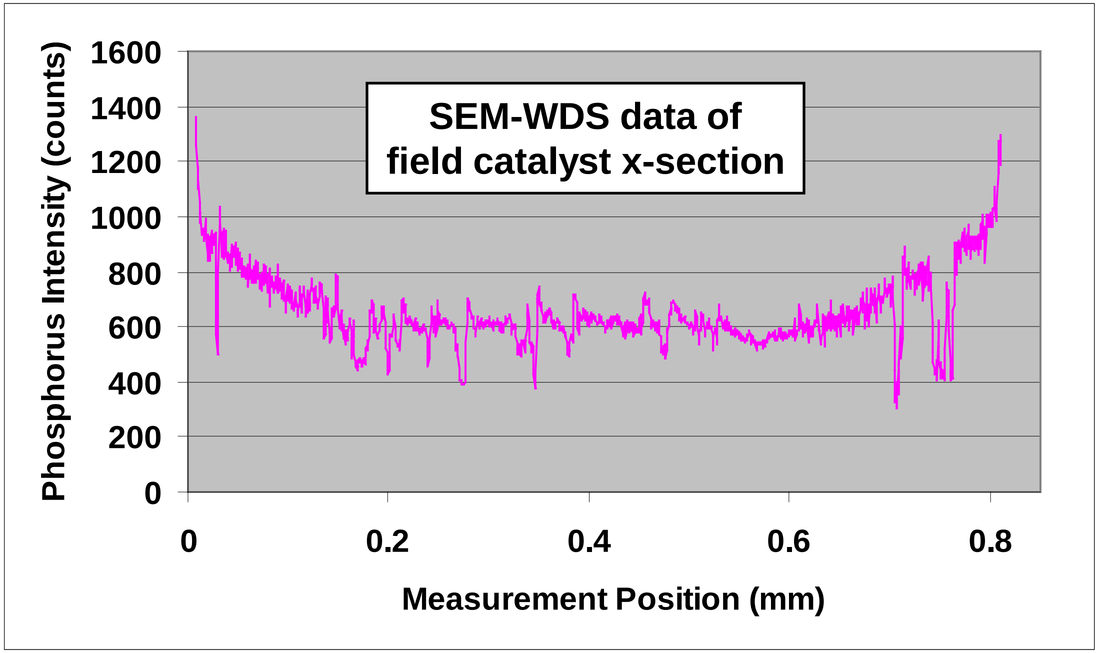
- **Phosphorus is a penetrating catalyst poison:**
  - Diffuses into catalyst bulk and chemically bonds to active sites
  - Wall x-section profile indicative of gas-phase P (i.e., $H_3PO_{4(g)}$)



Catalyst Deactivation Mechanism
Phosphorus Deactivation

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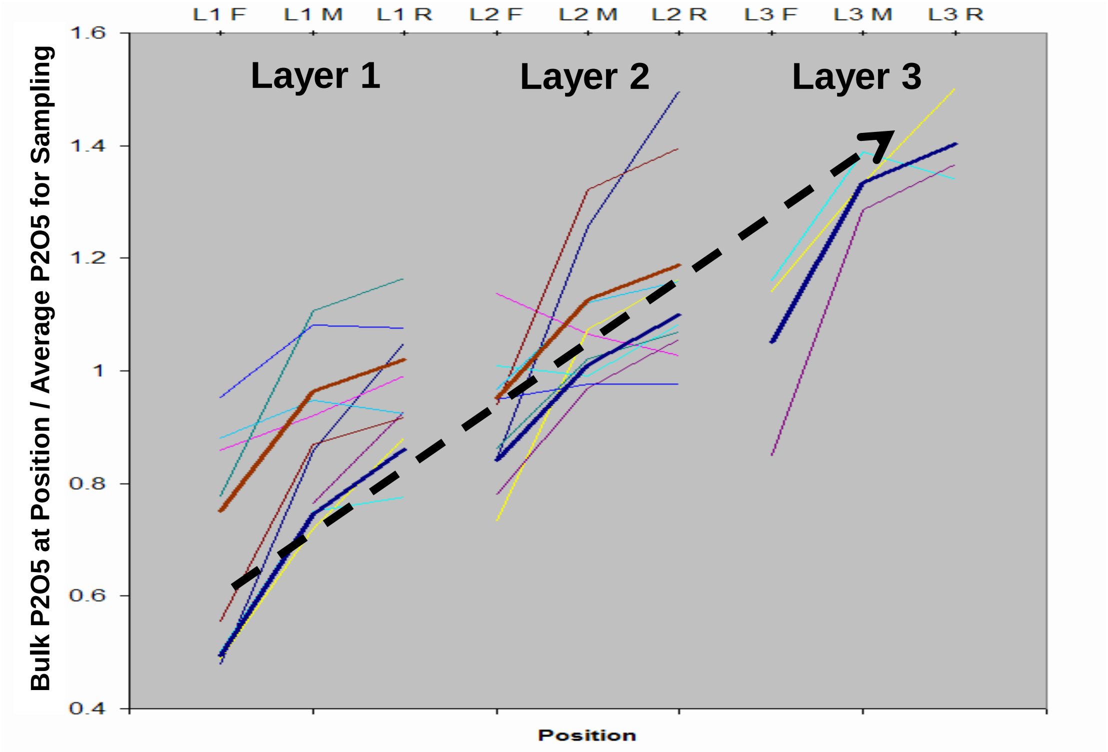
- **PRB: Bulk P_2O_5 typically increases with catalyst length**
  - Unexpected behavior for a gas phase poison



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Field Experiments Overview

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- **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, NOx
- **Field experiments provided key mechanistic insights**

Gas Phase P Measurements

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

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		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_2O_5 accumulation observed in the catalyst audit samples

Phosphorus Volatilization from Ash

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Thermodynamics for Reaction of Metal Phosphates with SO_3

Reaction	300°C delta G [kJ]	400°C delta G [kJ]
Ca3(PO4)2 + 3SO3(g) + 3H2O(g) = 3CaSO4 + 2H3PO4(g)	-125.7	-71.7
2FePO4 + 3SO3(g) + 3H2O(g) = Fe2(SO4)3 + 2H3PO4(g)	35.5	70.6
2AlPO4 + 3SO3(g) + 3H2O(g) = Al2(SO4)3 + 2H3PO4(g)	107.4	164.4
Mg3(PO4)2 + 3SO3(g) + 3H2O(g) = 3MgSO4 + 2H3PO4(g)	61.9	117.6

- **In SCR temperature range: solid $Ca_3(PO_4)_2$ has a thermodynamically-favored reaction pathway for releasing gas phase phosphorus by reaction with SO_3**
- **$Ca_3(PO_4)_2$ is a condensed reactive phosphorus (CRP)**

Laboratory Data

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Confirmation of Thermodynamic Calculations

- **We generated gas phase phosphorus in lab testing by reacting gaseous SO_3 (at SCR conditions) with:**
  - **Pure $Ca_3(PO_4)_2$ (confirmed the thermo)**
  - **Isokinetic bulk fly ash (SCR inlet) from Plants A, B, and C:**

Plant	Unit Catalyst Deactivation Rate	Unit Operation	Average H3PO4(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 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

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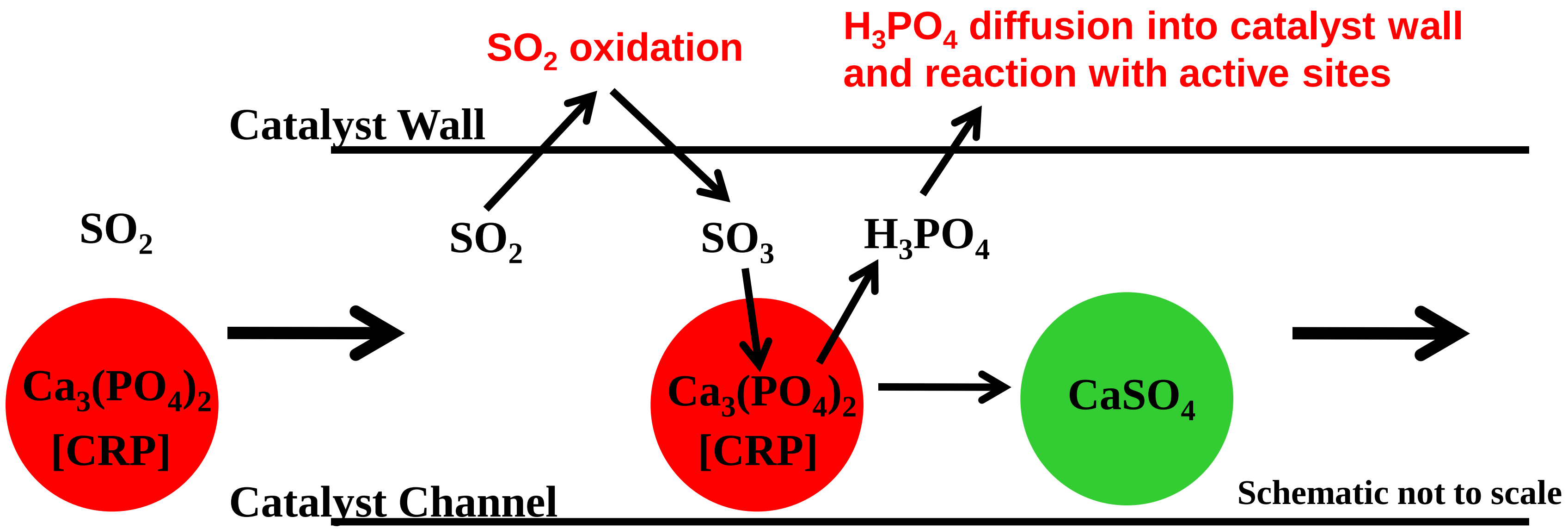

- **SO_3 concentration increases with catalyst length, increasing the amount of gaseous P released**
  - Explains why bulk P in catalyst increases with catalyst length
  - <u>Amount of P released will depend on</u>: saturation vapor pressure of P over the CRP (solid solution) and effective SO_3 concentration

Field Catalyst Data

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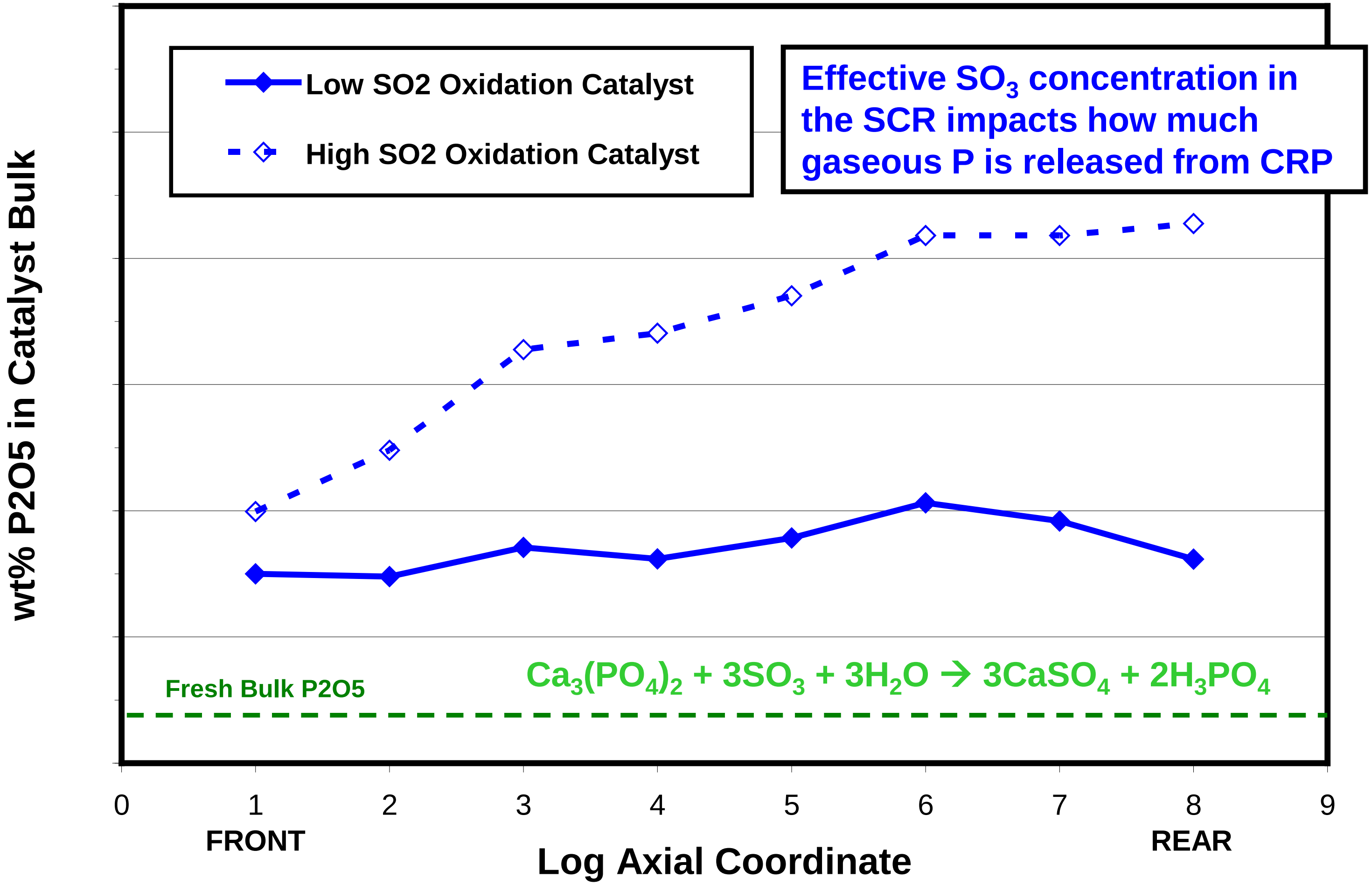
Loaded two ½ catalyst samples (low and high SO_2 oxidation rate catalyst) in single sample tray and loaded it into a <u>Plant A</u> SCR module for field aging.



Proposed CRP Formation Mechanism

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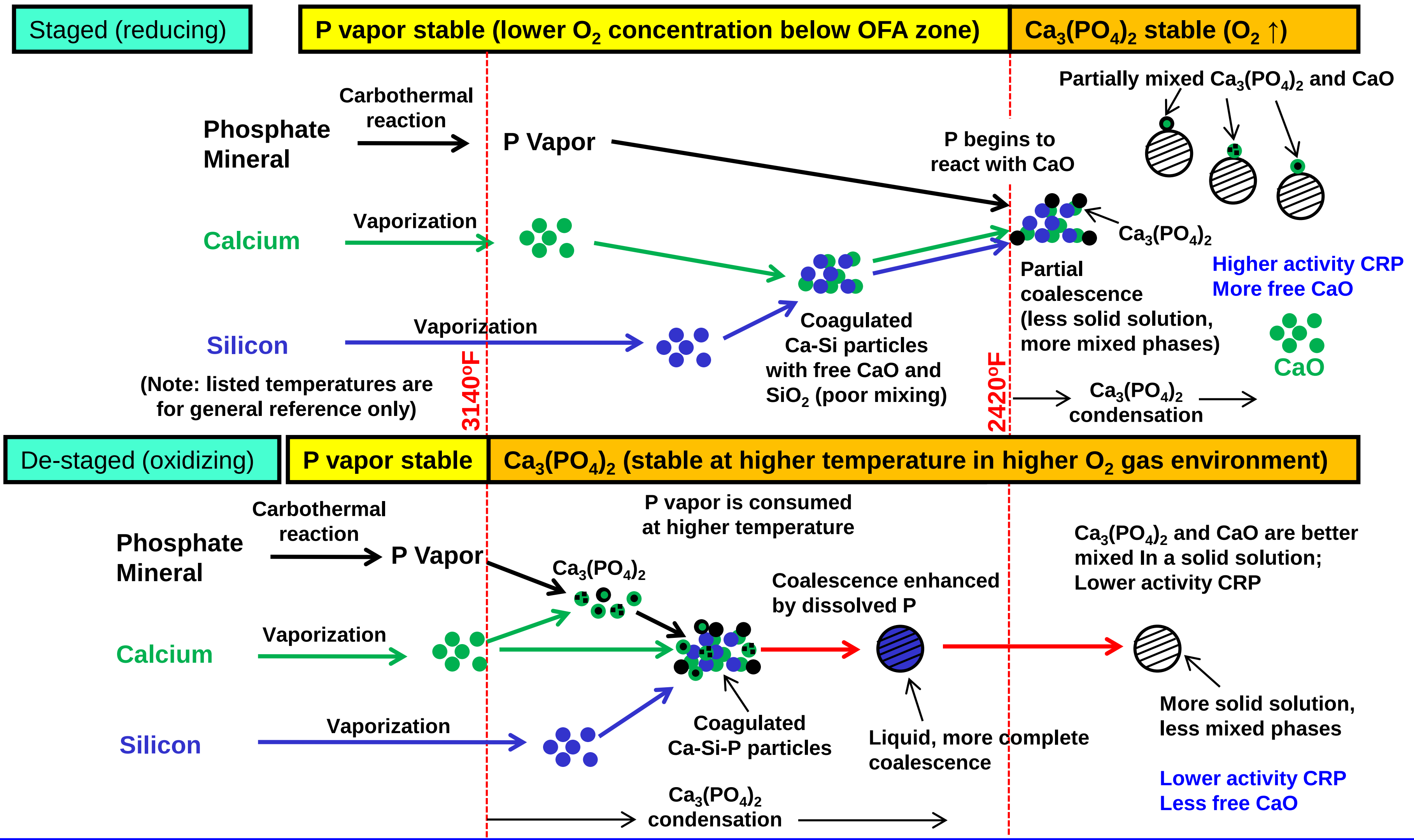

CRP Exists in Sub-Micron Ash Fume

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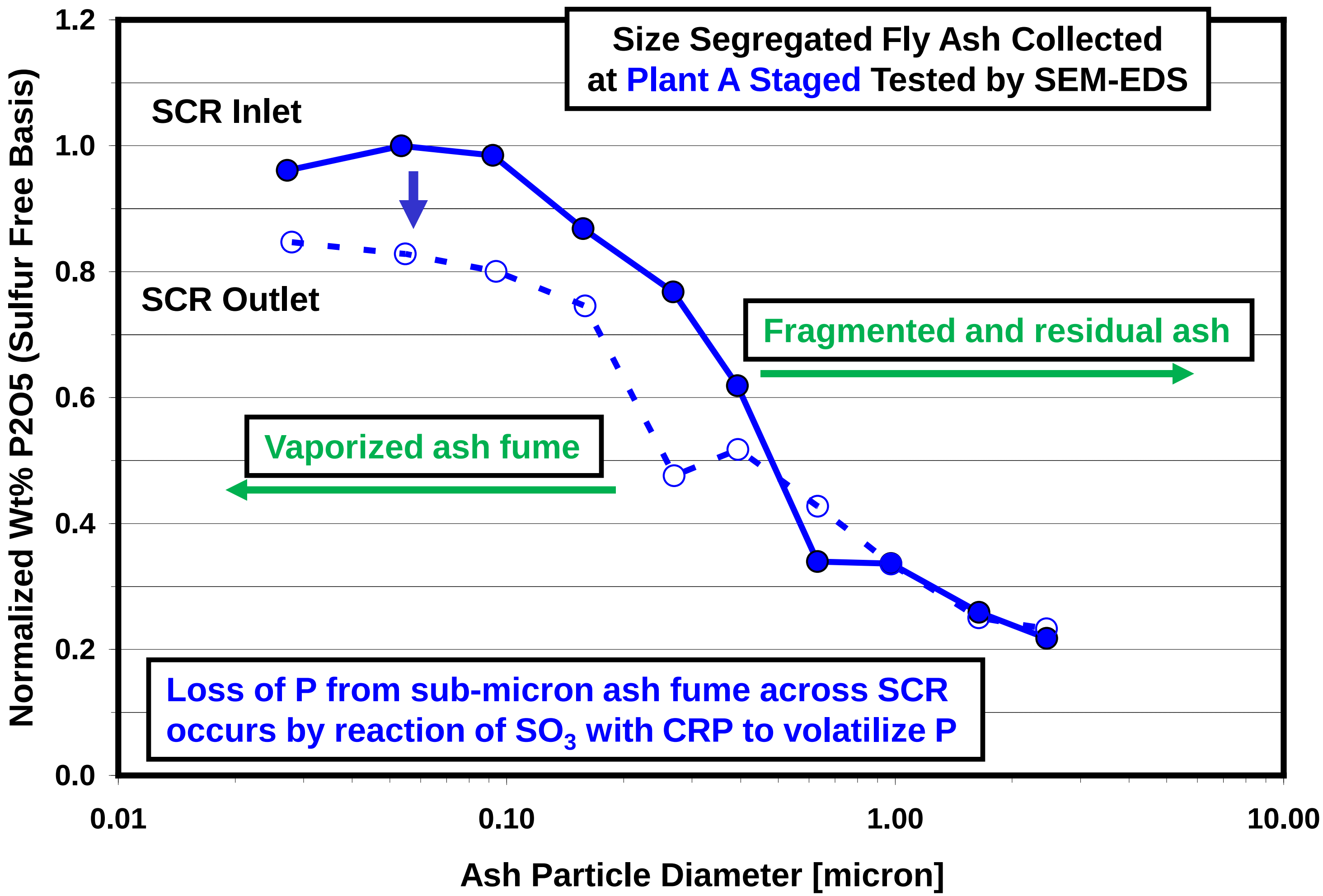
CRP is Formed by Vaporization/Condensation Process in Furnace



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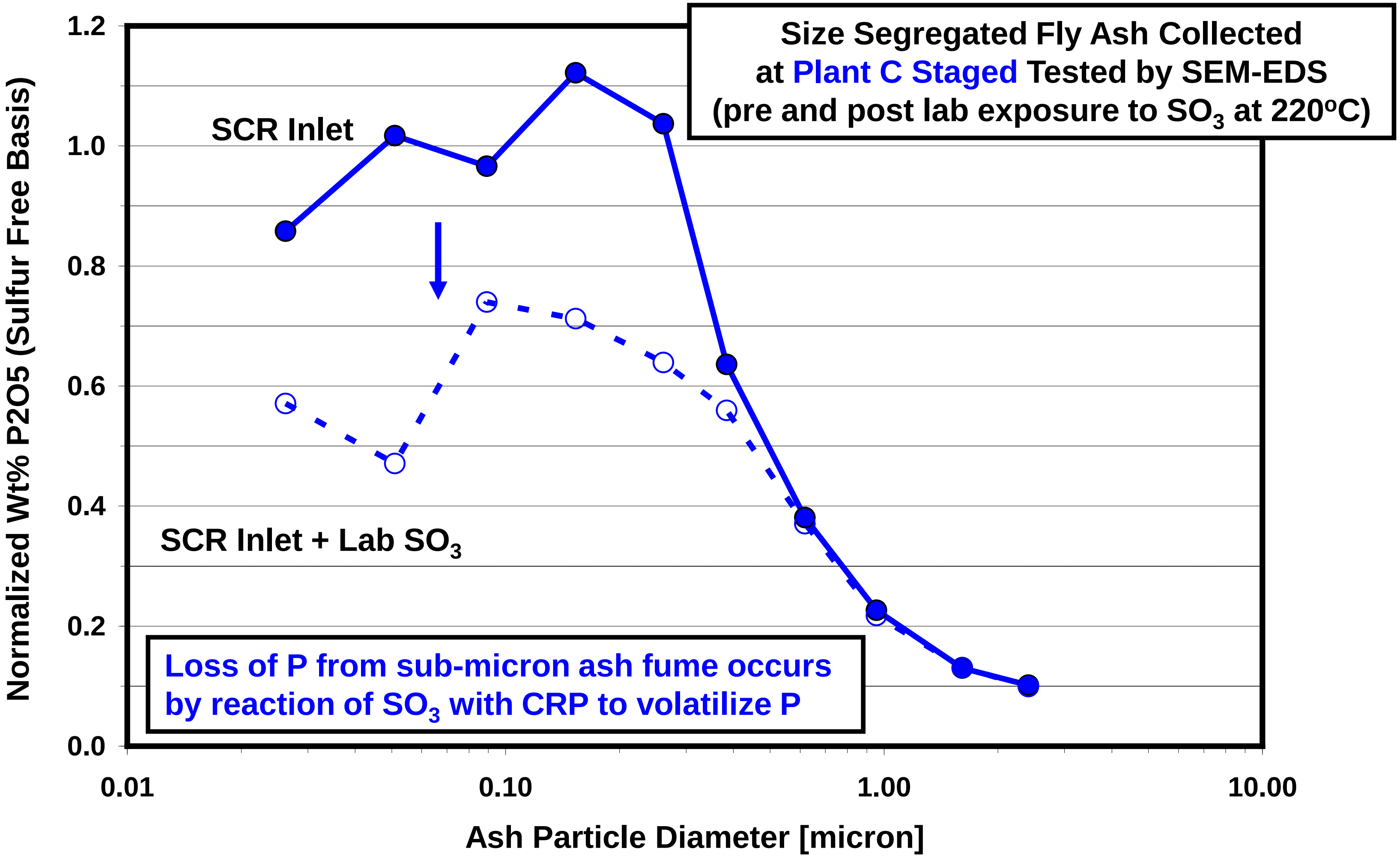

SCR Inlet P in Ash Data for Plants A & B

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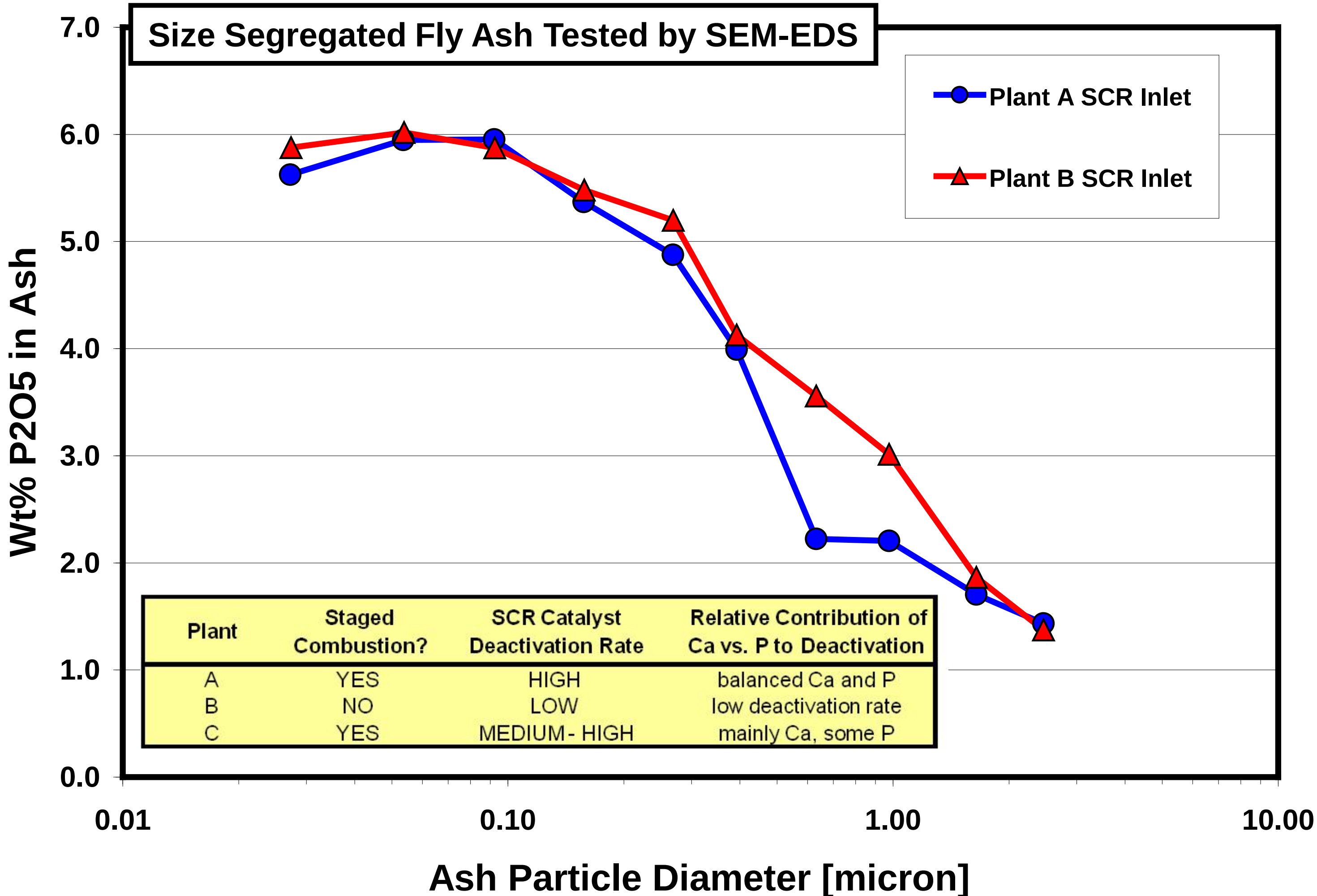
Staged vs. Non-Staged Combustion has Little Impact on P Vaporization



Carbothermal Reduction Process

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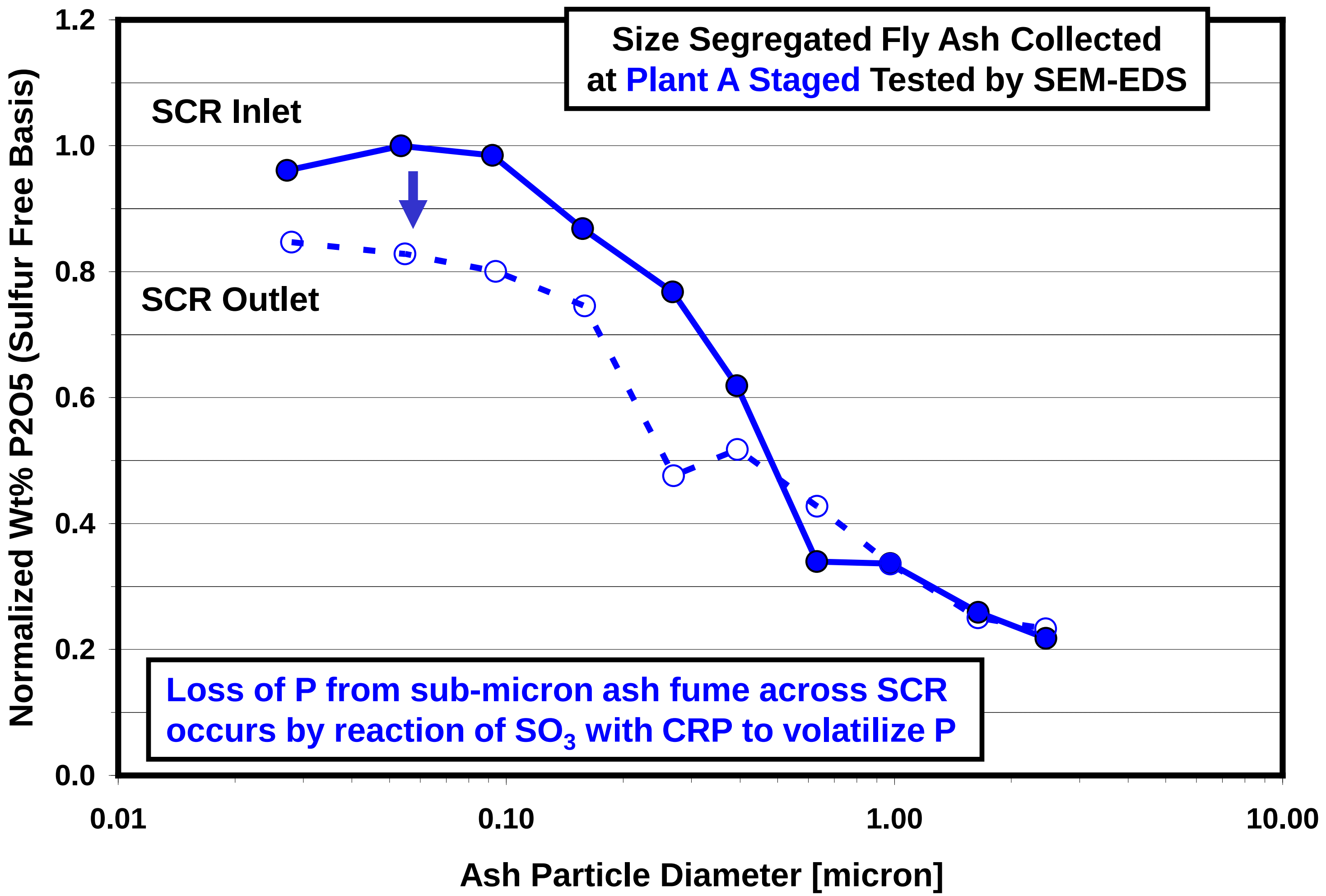
Mechanism of Phosphorus Vaporization from Coal

- **Phosphorus in PRB coal is mainly crandallite (a mineral phosphate): $CaAl_3(PO_4)_2(OH)_5\cdot(H_2O)$**
- **Crandallite can vaporize in the burning char particle by reaction with C and SiO_2 releasing gas phase P in furnace (process is called carbothermal reduction):**
  - **$CaAl_3(PO_4)_2(OH)_5.(H_2O) + SiO_2 + C \rightarrow 2P_{(g)} + CO_{(g)} + [CaAlSiO_3]$**
- **The burning char particle is a reducing environment <u>under staged or non-staged</u> 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

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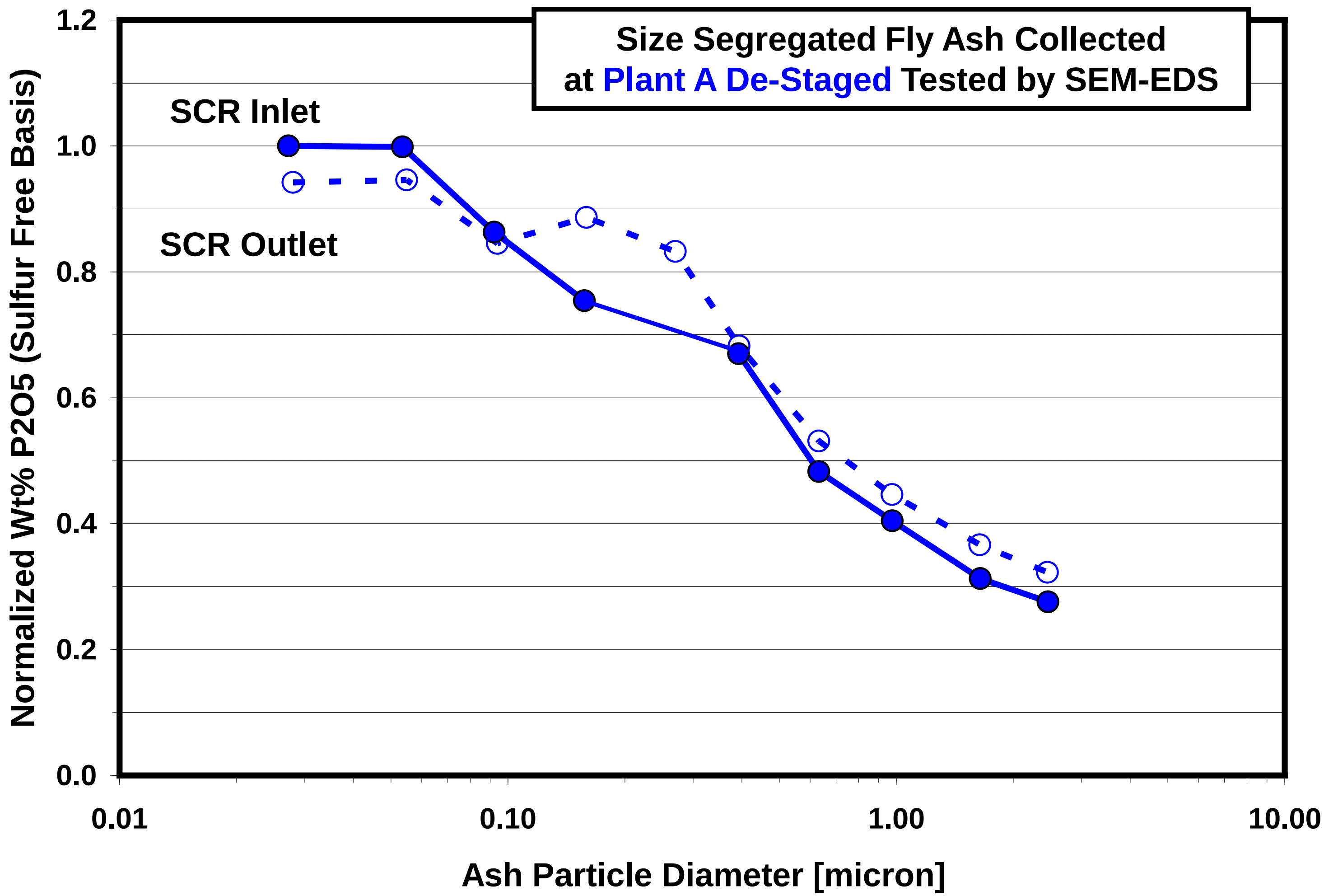
Lower Amount of P Loss Across SCR for Plant A Operating De-Staged



Plant C – Staged Combustion

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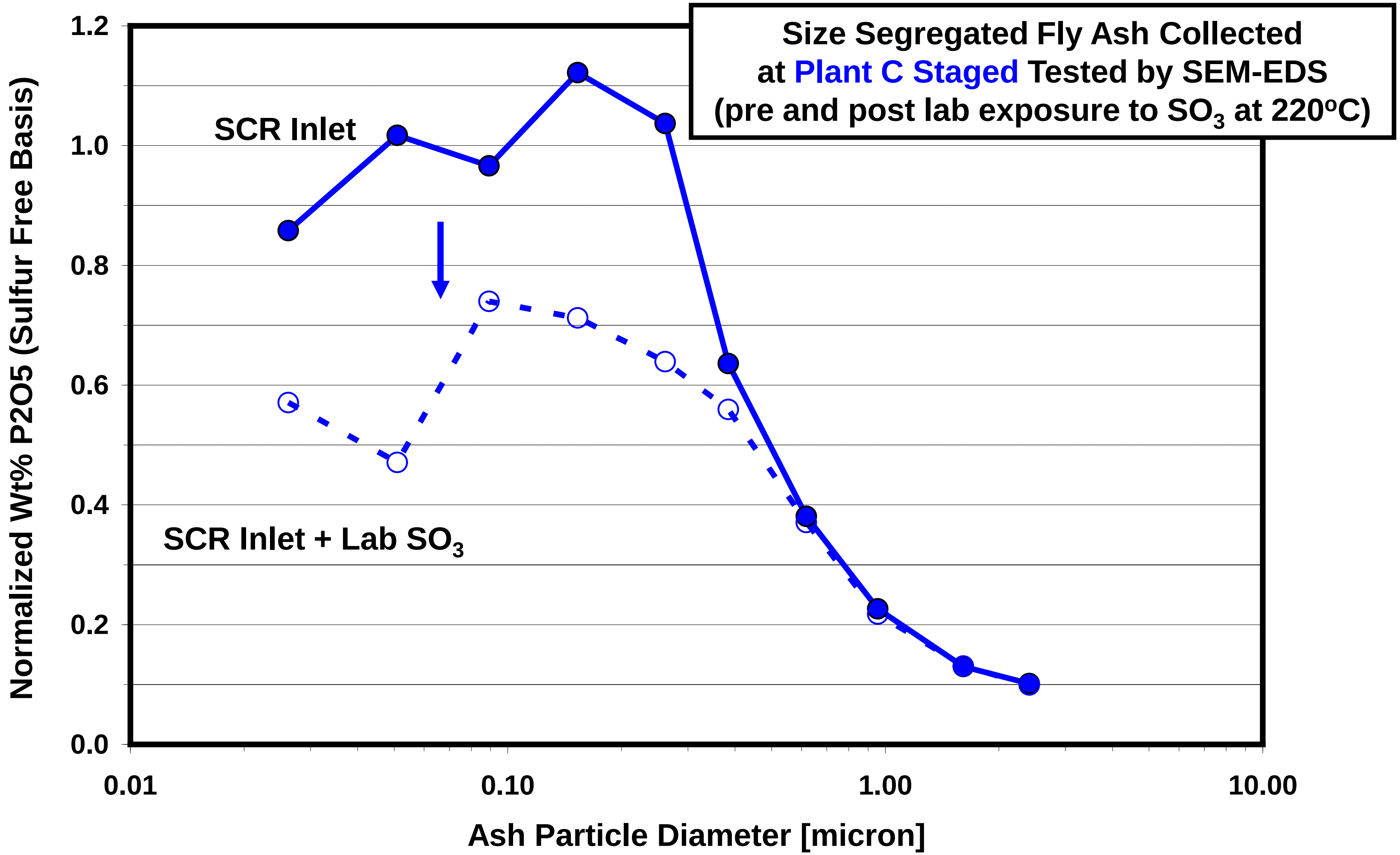

De-Staging Reduces CRP Activity

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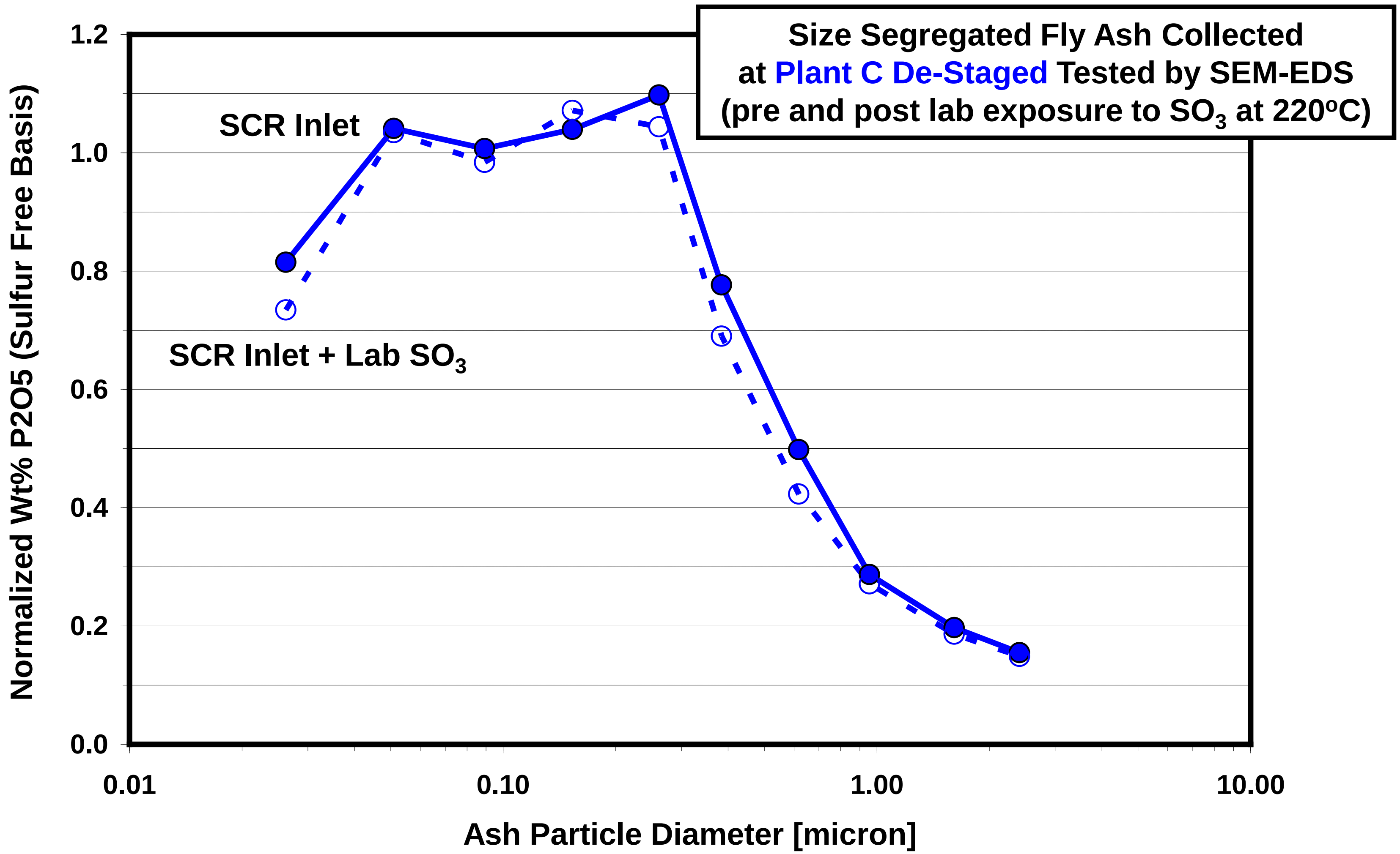
Lower Amount of P Loss for Plant C Operating De-Staged



Bulk Fly Ash Data: Impact of Staging

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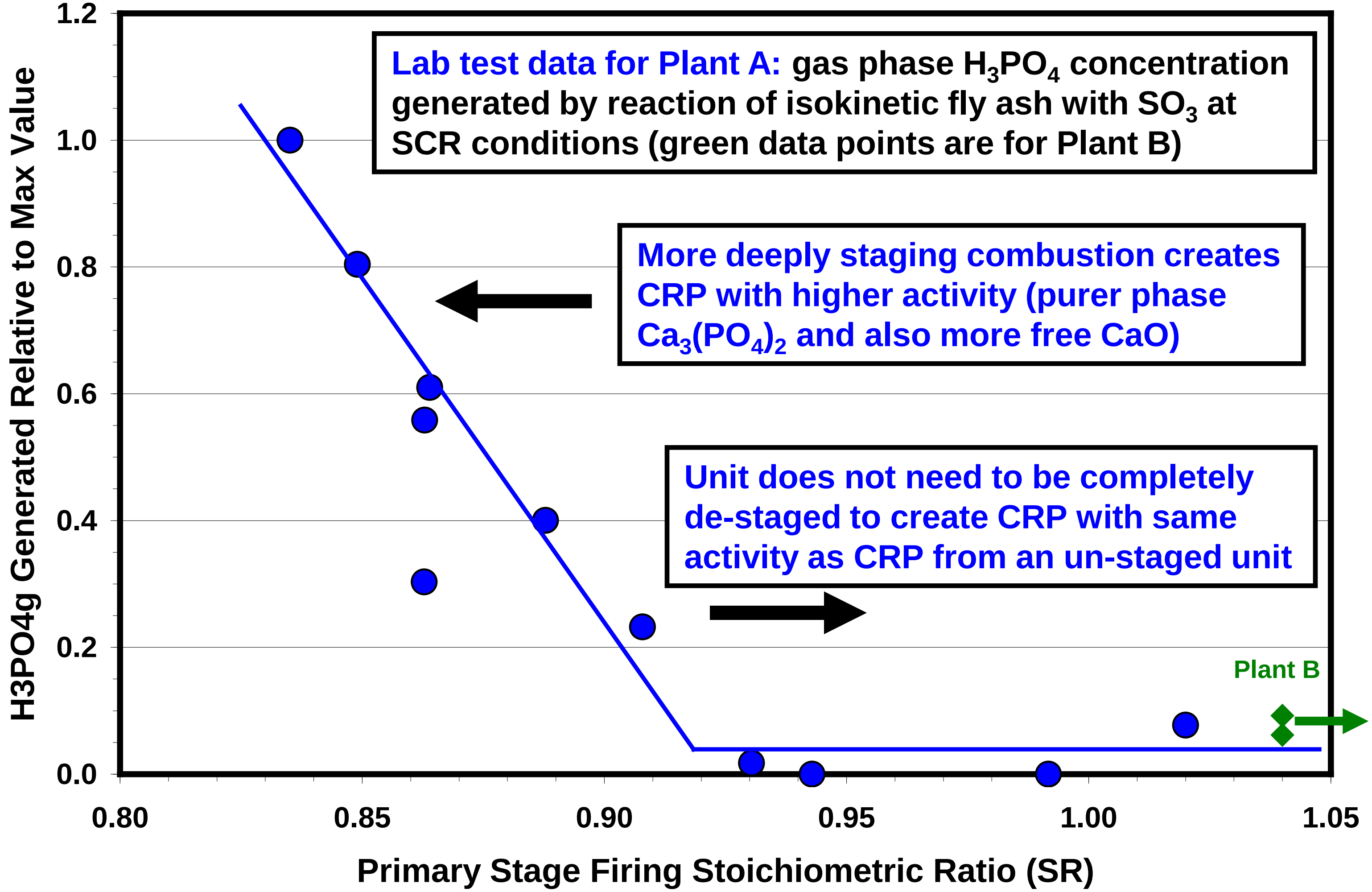
CRP Activity = Saturation Vapor Pressure of P over Solid CRP



Mechanism Summary

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- **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_2 in the primary combustion zone
    - Less coalescence/mixing of condensed CaO and SiO_2 particles
    - Gaseous P condenses in OFA zone as surface enriched $Ca_3(PO_4)_2$
    - More free CaO and higher activity CRP → higher deactivation rate
- **Partially de-staged and non-staged combustion:**
  - Hotter combustion & higher O_2 in the primary combustion zone
    - More coalescence/mixing of CaO/SiO_2 particles (calcium silicate)
    - Gaseous P condenses as diluted $Ca_3(PO_4)_2$ and may react with SiO_2 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

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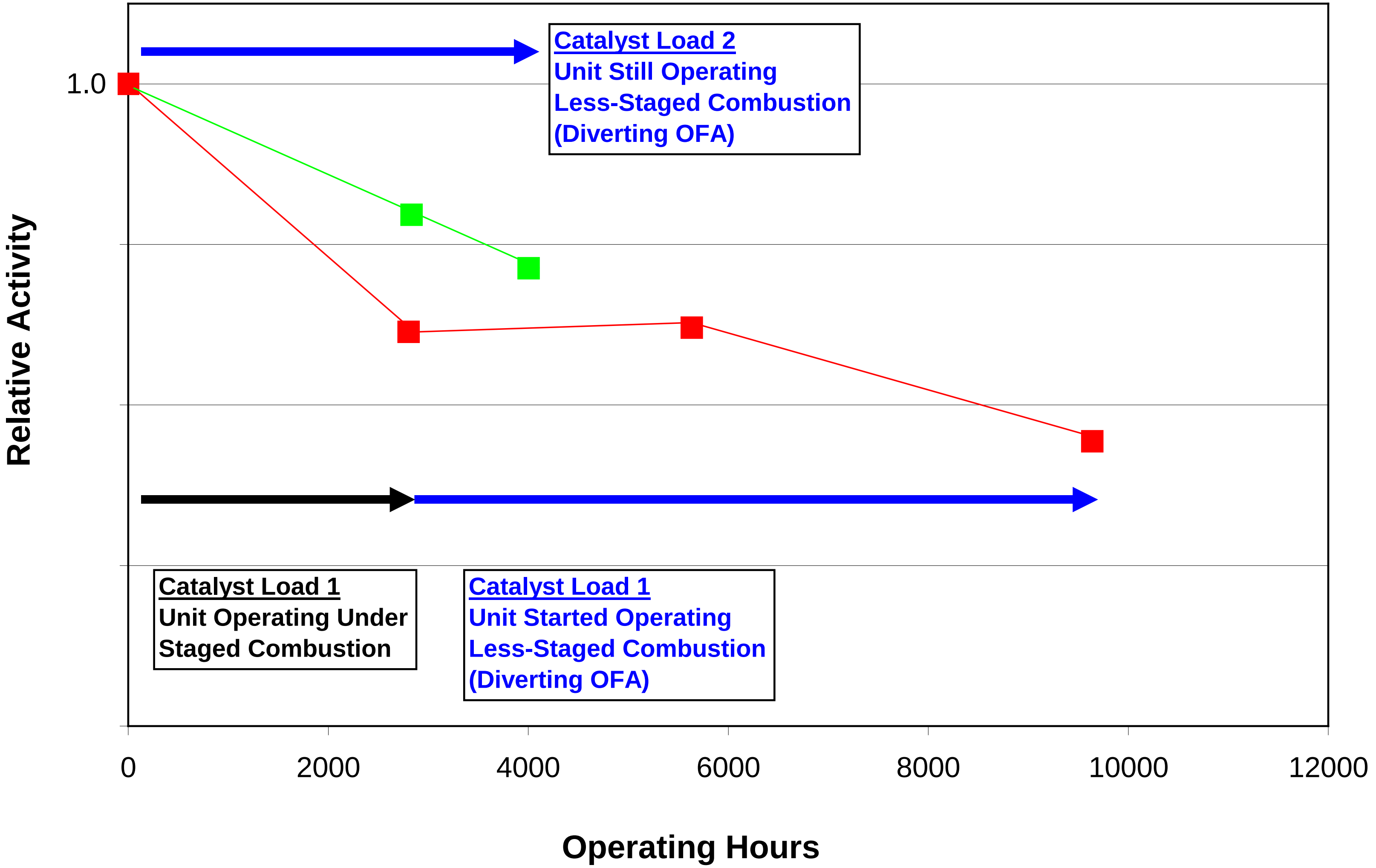

Mitigation Cost/Benefit Analysis

Requires Case Specific Evaluation

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- **Partial de-staging?**
  - **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) → lower overall K/AV
    - Reduce catalyst volume (lower DP) and/or extend catalyst life
- **Lower SO_2 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

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- **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 [$Ca_3(PO_4)_2$] with SO_3
  - More deeply staging combustion creates CRP with higher activity (purer phase $Ca_3(PO_4)_2$ 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?