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SCR Catalyst Deactivation for PRB-Firing Coal Utility Boilers

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Cormetech, Inc.

2013 Reinhold NOx-Combustion Round Table

Presentation Outline

- **Cormetech Experience**
- **Catalyst Deactivation from Ca, P, and Na**
  - Impact on Catalyst Activity
  - Mechanism: How They Deactivate Catalyst
  - Mechanism: Nature of the Deactivating Species
  - Impact of Staging
- **Potential Mitigation Options**

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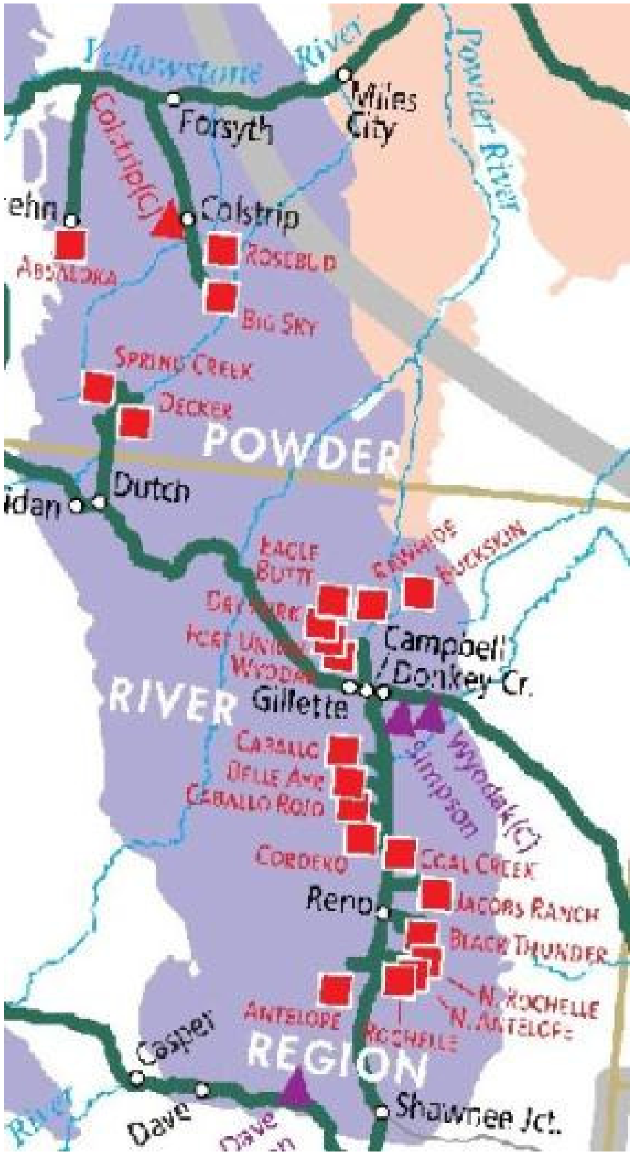
Cormetech Field Experience

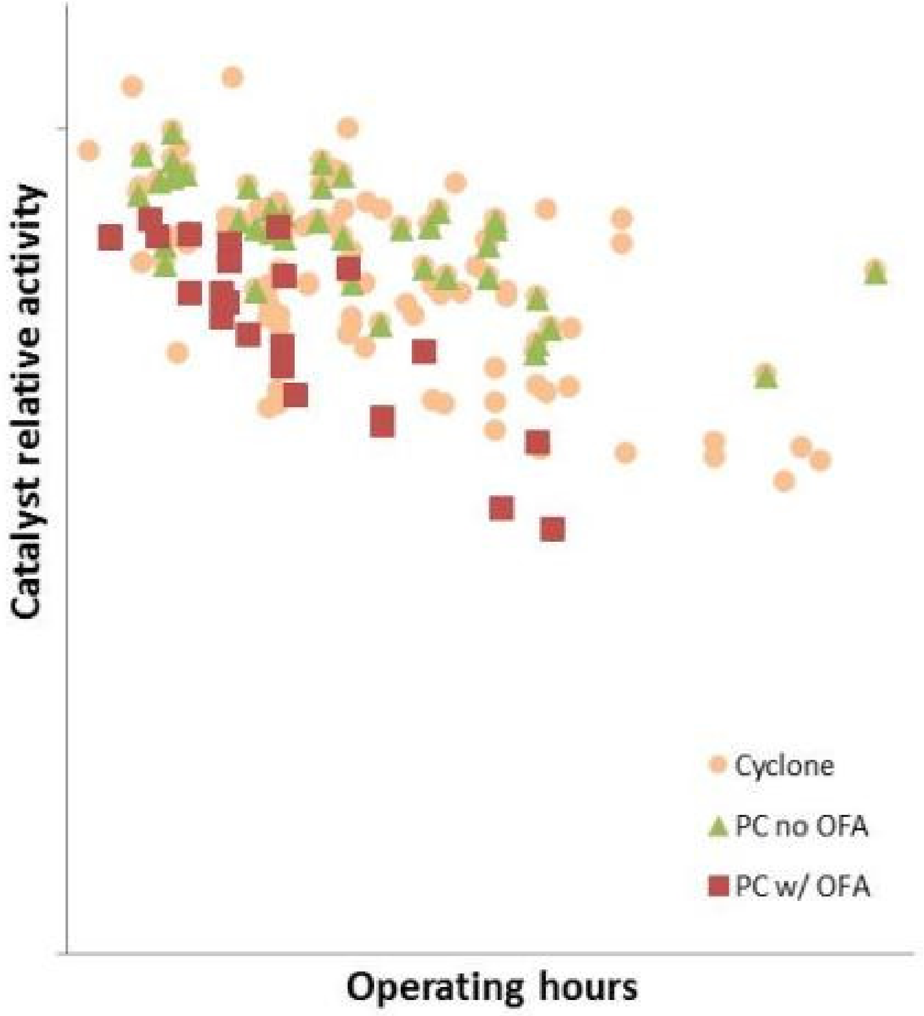
- More than 40 SCR units firing 100% PRB or high PRB blends.
- First unit started up in 2000.
- Longest running unit has >70,000 operational hours.
- 7, 8, and 9 mm pitch catalyst.



Catalyst Deactivation Data

PRB-Fired Applications

- **Wide range of measured catalyst deactivation rates.**
- **Staged combustion units can have high and low catalyst deactivation rates.**



Cormetech SCR Design Toolbox

Predicting K/Ko for PRB-Firing Units

- **Models**
  - Expected calcium and phosphorus accumulation rates
- **Unit specific / similar unit historical data**
- **Field experiment ash screening tests**
  - Methods validated by Cormetech in 2008-2010 at two staged units and one non-staged unit (all >500 MW PC units firing 100% PRB)
  - Characterization methods for sampled fly ash provide insight into the fly ash’s deactivation tendency for a given unit
  - Reviewed detailed results at 2012 NOx-Combustion Round Table
- **Slipstream reactor testing**

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Catalyst Deactivation Analysis

PRB-Fired Applications

- **PRB: Ca, P, and Na are the main catalyst deactivators**
  - Ca is primary deactivator ($CaSO_4$ blinds surface)
  - P can have a variable impact (P reacts with active sites)
  - Na is typically a minor contributor (Na reacts with active sites)
  - Elevated Fe_2O_3, SiO_2, and SO_3 are also typically observed
- **Review three examples to show deactivation "pie"**
  - All three examples are for staged combustion units
    - Two PC units and one cyclone unit
  - We applied a selective leaching method to remove the Ca and Na deactivation contributions, leaving the P deactivation untouched

Example 1

Staged Cyclone Unit

Selective leaching process removed calcium sulfate

Process did not affect phosphorus

Field Sample	K/Ko	Front Surface CaO Ratio vs. Fresh	Front Surface SO3 Ratio vs. Fresh	Average Surface P2O5 Ratio vs. Fresh	Expected K/Ko P2O5	Average Bulk Na2O+K2O Ratio vs. Fresh	Expected K/Ko Na2O+K2O
Untreated	0.68	2.1	5.3	4.6	0.93	1.0	1.00
Post Selective Leaching	0.89	1.0	1.1	6.1	0.92	1.0	1.00

- **Selective leaching process increased K/Ko from 0.68 to 0.89**
  - Post-leaching K/Ko is consistent with expected K/Ko from P_2O_5 content
- **~80% of field sample deactivation is from calcium blinding**
  - Phosphorus contributed ~20% to deactivation rate
  - Impact of alkali is negligible for this unit

Example 2

Staged PC Unit

Selective leaching process removed calcium sulfate

Process did not affect phosphorus

Field Sample	K/Ko	Front Surface CaO Ratio vs. Fresh	Front Surface SO3 Ratio vs. Fresh	Average Surface P2O5 Ratio vs. Fresh	Expected K/Ko P2O5	Average Bulk Na2O+K2O Ratio vs. Fresh	Expected K/Ko Na2O+K2O
Untreated	0.72	3.7	12.0	20.2	0.86	3.0	0.95
Post Selective Leaching	0.87	1.0	1.0	19.8	0.86	1.0	1.00

- **Selective leaching process increased K/Ko from 0.72 to 0.87**
  - Post-leaching K/Ko is consistent with expected K/Ko from P_2O_5 content
- **~40% of field sample deactivation is from calcium blinding**
  - Phosphorus contributed ~50% to deactivation rate
  - Impact of alkali on overall deactivation rate is ~10% for this unit

Example 3

Staged PC Unit

- **Data for two field samples from this unit are listed in table**
  - Selective leaching process was not done for these two field samples
  - Previous two examples validated for PRB application that the deactivation unaccounted for by P_2O_5 and alkali is due to calcium sulfate surface blinding

Field Sample	**K/Ko**	**Front Surface CaO Ratio vs. Fresh**	**Front Surface SO3 Ratio vs. Fresh**	**Average Surface P2O5 Ratio vs. Fresh**	**Expected K/Ko P2O5**	**Average Bulk Na2O+K2O Ratio vs. Fresh**	**Expected K/Ko Na2O+K2O**
Field Sample A No treatment	**0.71**	**5.6**	**19.6**	**13.5**	**0.87**	**1.0**	**1.00**
Field Sample B No treatment	**0.73**	**6.3**	**21.3**	**12.4**	**0.88**	**1.0**	**1.00**

- **~60% of measured deactivation is due to calcium blinding**
  - Phosphorus contributed ~40% to deactivation rate
  - Impact of alkali is negligible for this unit

Summary

Catalyst Deactivation Analysis (PRB-Fired Units)

- **Ca, P, and Na are the catalyst deactivators**
  - Ca is a primary deactivator
  - P has a variable impact
  - Na is typically a minor contributor

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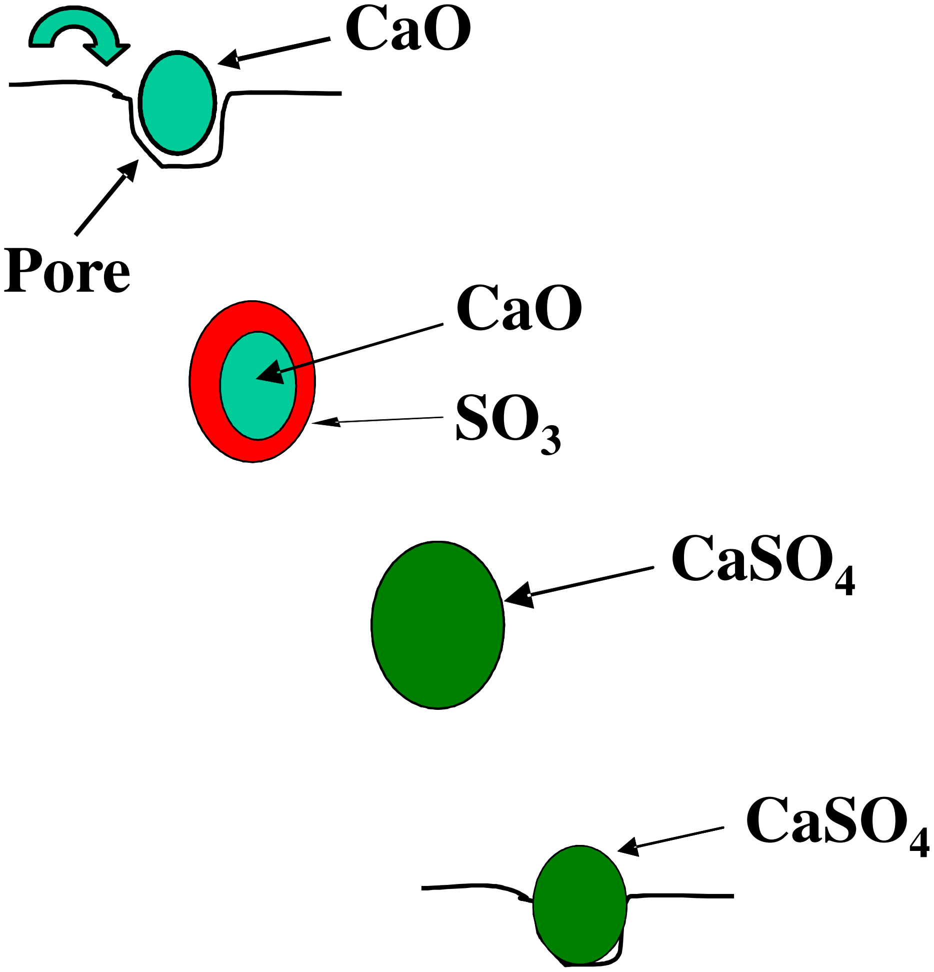
Calcium Deactivation

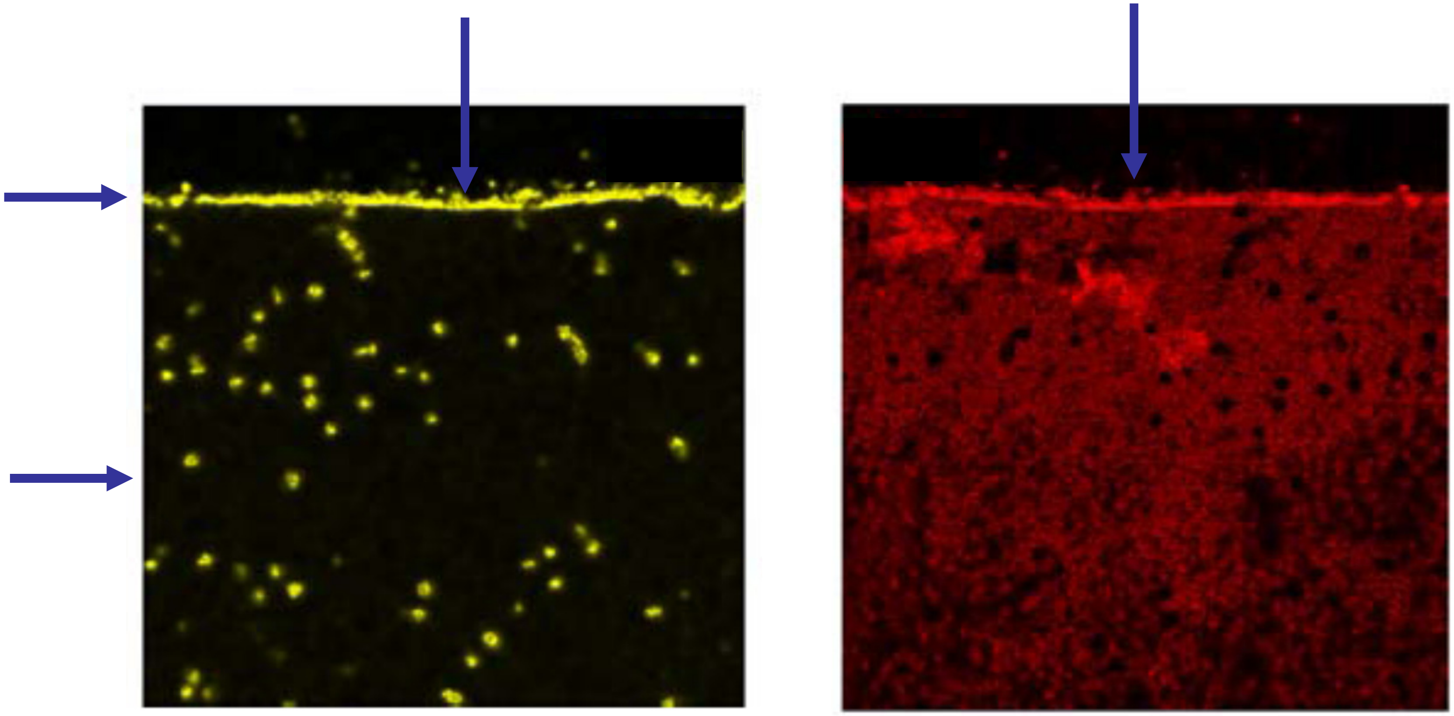
1. **Sub-micron CaO is caught in macro pore on catalyst.**
2. **SO_3 diffuses to CaO particle.**
3. **SO_3 and CaO react to form $CaSO_4$; particle expands ~14%.**
4. **$CaSO_4$ plugs pore. NH_3 & NO_x cannot diffuse to active sites.**



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

Calcium Deactivation

Thin $CaSO_4$ layer blinds catalyst surface



SEM-EDS Maps of Catalyst Cross-Section

Phosphorus Deactivation

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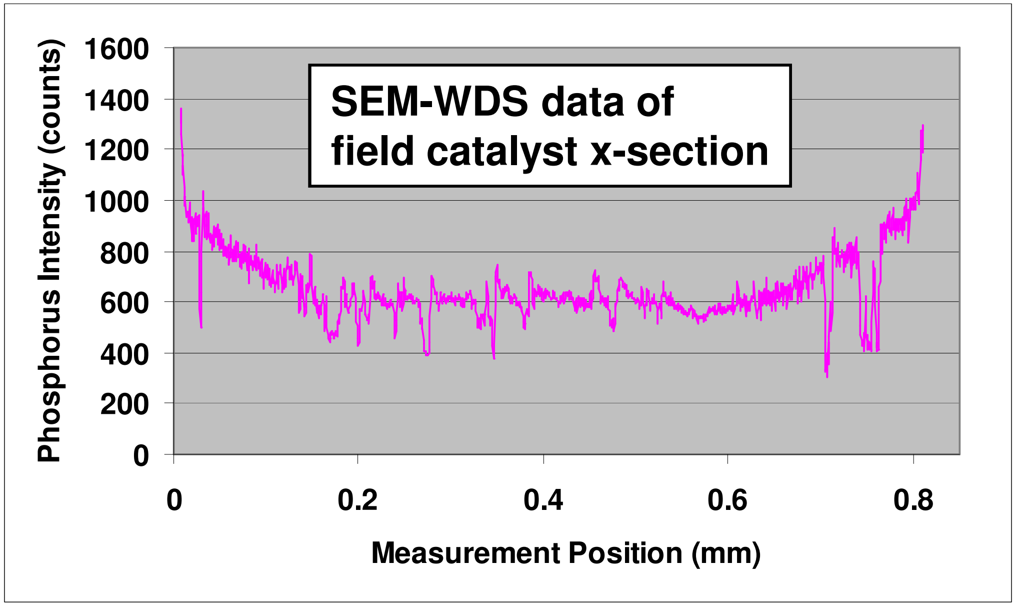
- **Phosphorus is a penetrating catalyst poison:**
  - Diffuses into catalyst bulk and chemically bonds to active sites
  - Wall x-section profile indicative of gaseous P (i.e., $H_3PO_{4(g)}$)
  - **Gaseous P is formed by SO_3 reaction with solid P in ash fume**



(P in ash) (SO$_3$ made in SCR)

$$Ca_3(PO_4)_{2(s)} + 3SO_{3(g)} + 3H_2O_{(g)}$$

$$\downarrow$$

$$CaSO_{4(s)} + 2H_3PO_{4(g)}$$

(gaseous P that deactivates SCR)

Phosphorus Deactivation

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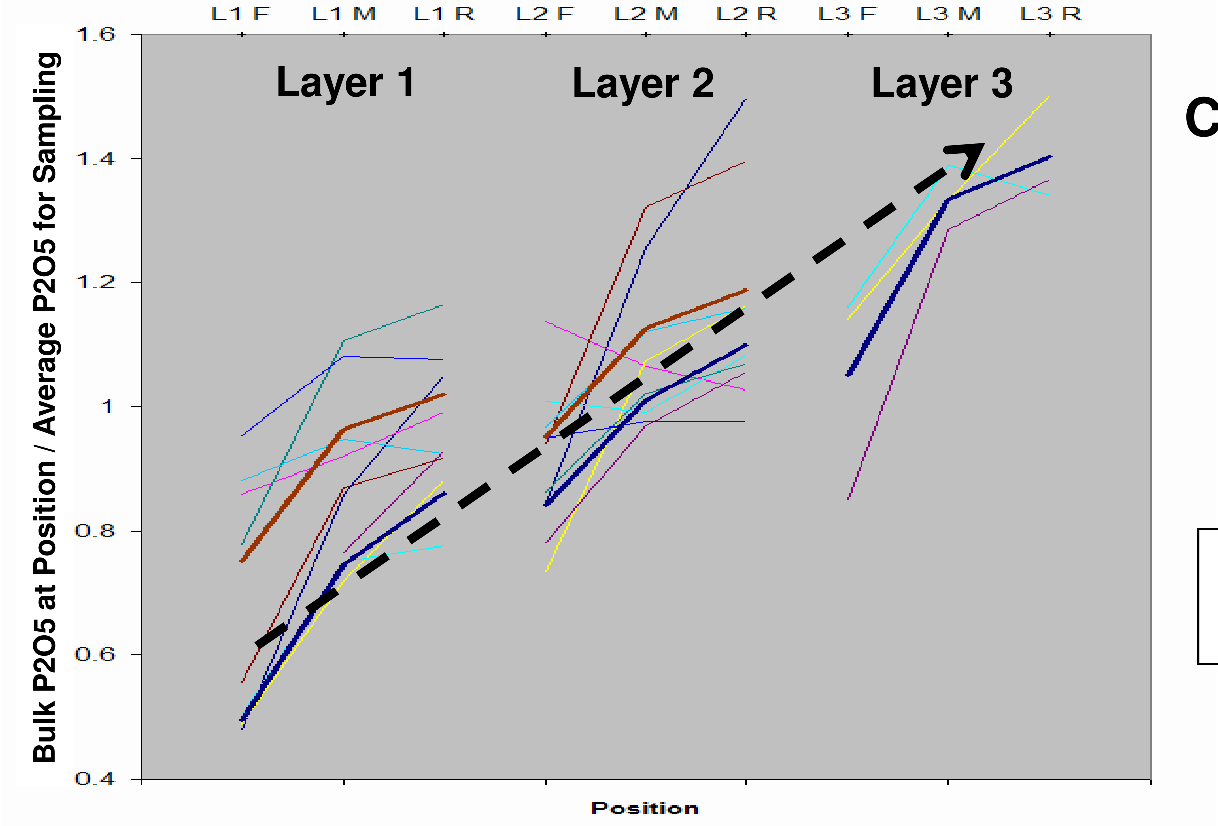
- **PRB: bulk P_2O_5 increases with catalyst length**
  - **Due to liberation of gaseous P from solid P in ash by SO_3**



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(gaseous P that deactivates SCR)

$$CaSO_{4(s)} + 2H_3PO_{4(g)}$$

This mechanism was validated by field and lab experiments.

Summary

Catalyst Deactivating Species in PRB-Fired Units

Deactivating Species	Source at SCR Inlet	Deactivation Mechanism
Ca	CaO solid particles in sub-micron ash. Formed through condensation of vaporized Ca in furnace.	CaO particles lodge in pore structure at catalyst wall surface, expand by sulfation, and block pore.
P	Solid particles with volatile P in sub-micron ash. Formed by reaction of vaporized P with condensed CaO in furnace.	Gas-phase P is released by reaction of ash with SO_3 produced in SCR; gas-phase P then 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.

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Overview

Deactivating Ca and P Species

- **Ca and P deactivators are present in sub-micron ash, formed by vaporization/condensation process**
  - **Ca** → sub-micron CaO adhesion in catalyst pores and sulfation
  - **P** → volatilization of P from sub-micron ash ($Ca_3(PO_4)_2$) by SO_3
    - **$Ca_3(PO_4)_2 + 3SO_3 + 3H_2O \rightarrow 3CaSO_4 + 2H_3PO_4$**
    - The amount of P release in the SCR is affected by the activity of the $Ca_3(PO_4)_2$ in the ash and the SO_3 concentration (influenced by catalyst and ash CaO)

Overview

Deactivating Ca and P Species

- **Ca and P deactivation are linked for PRB applications**
  - **P deactivation always coincides with Ca deactivation…**
    - Catalyst audit data and selective leaching test data
  - **Because the formation of the Ca and P deactivators are linked**
    - Ca in coal can vaporize and condense to form sub-micron CaO
    - Vaporized P reacts with the condensed CaO to form $Ca_3(PO_4)_2$

Overview

Deactivating Ca and P Species

- **Vaporization is not key factor affecting the deactivators**
  - **Ca and P vaporize in both staged and non-staged units**
    - But staged units can have higher deactivation rates from Ca and P than non-staged units
  - **Thus, post-vaporization chemistry must determine the activity of the CaO and $Ca_3(PO_4)_2$**
    - Staging lowers both peak combustion temperature and oxygen potential, which can affect thermo, kinetics, mass transfer
    - Staging leads to higher activity CaO and $Ca_3(PO_4)_2$ in the ash
    - Partial de-staging can have positive effect on lowering the catalyst deactivation rate
    - Mechanism was proposed in 2012 Reinhold presentation

Gaseous P is Formed in the SCR by SO_3 Reaction with Solid P in Ash Fume

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Overview of the data supporting this mechanism…

- P vaporizes from coal in staged and non-staged plants.
- Catalyst P length profile (increasing F → R) is opposite that of non-PRB SCR applications with P deactivation (decreasing F → R).
- Earlier study in scientific literature proposed this mechanism.
- Proposed reaction for P release has favorable thermodynamics.
- PRB fly ash contains Ca and P: $Ca_3(PO_4)_2$ formation is plausible. Ca-P particles have been previously detected in PRB ash fume.
- Lab: gaseous P can form by reacting PRB fly ash with SO_3.
- Field: P lost from the ash fume across the SCR is measurable.
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Gaseous P in SCR is formed by SO_3 reaction with solid P in ash fume.

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Phosphorus Vaporization

Coal Combustion

- **Phosphorus in PRB coal is mainly crandallite:**

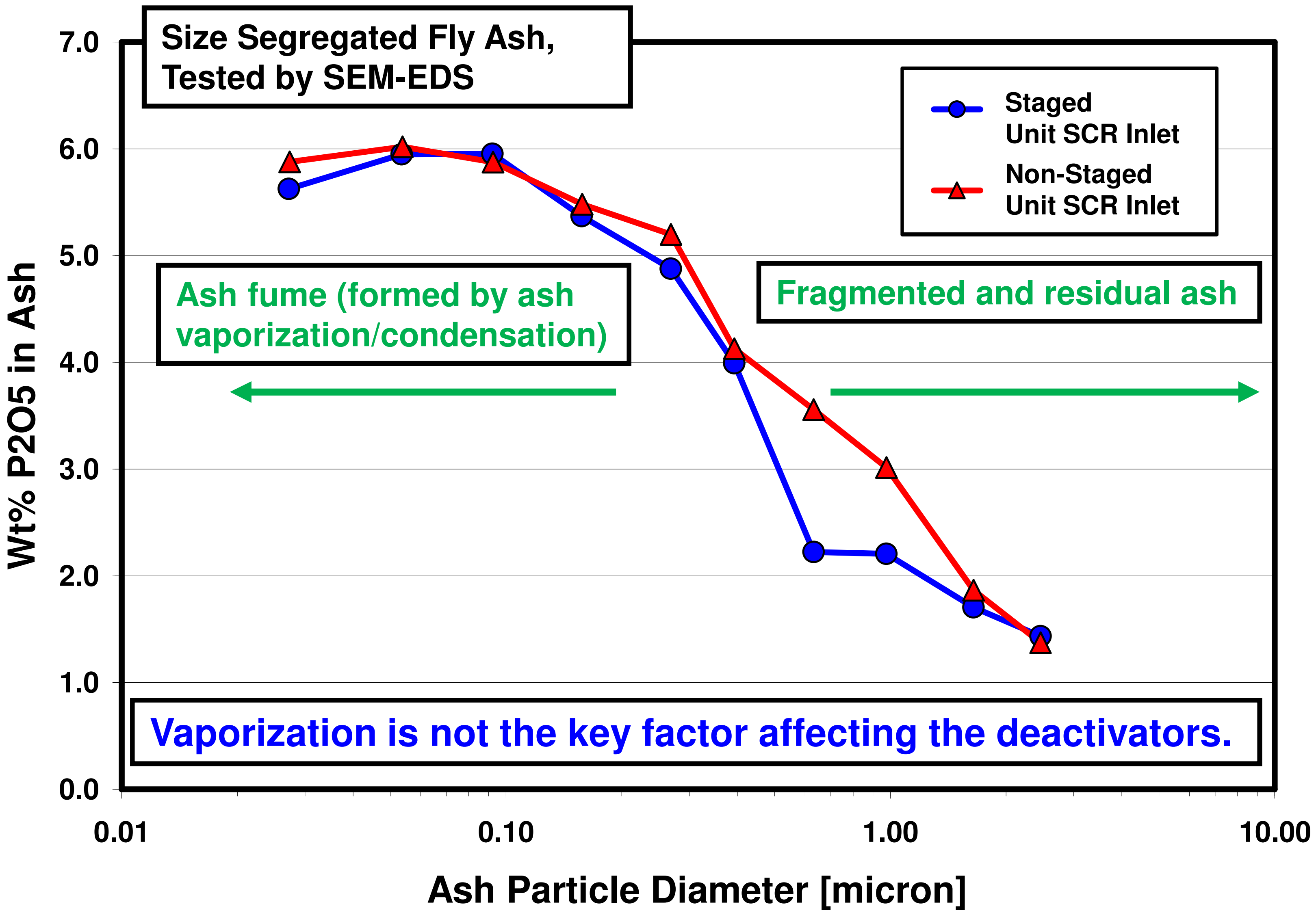
  $CaAl_3(PO_4)_2(OH)_5 \cdot (H_2O)$

- **Crandallite can vaporize in the burning char particle by the carbothermal reduction reaction:**

  $CaAl_3(PO_4)_2(OH)_5 . (H_2O) + SiO_2 + C \rightarrow 2P_{(g)} + CO_{(g)} + [CaAlSiO_3]$

- **The burning char particle is a reducing environment <u>under staged or non-staged</u> combustion conditions:**
  - **Phosphorus vaporizes in staged and non-staged units**
    - Data from low pressure impactor sampling confirms it (next slide)
    - Data show that the vaporized phosphorus reacts with the ash fume

Phosphorus Vaporizes in Staged and Non-Staged Combustion Units



Size Segregated Fly Ash, Tested by SEM-EDS

Ash fume (formed by ash vaporization/condensation)

Fragmented and residual ash

Vaporization is not the key factor affecting the deactivators.

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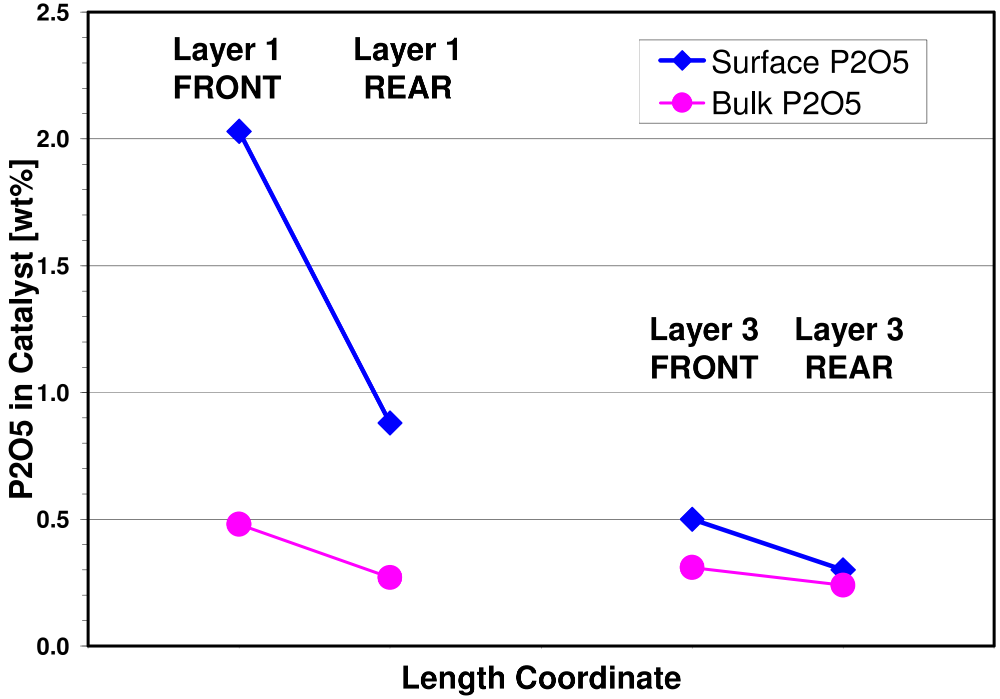
P Accumulation in Non-PRB Units Shows Expected Length Profile

- **For oil/diesel firing SCR applications with phosphorus contamination: P decreases with increasing catalyst length**
- **NH_3 does not inhibit H_3PO_4 adsorption onto SCR catalyst**

Cormetech SCR Catalyst Field Samples,
Boiler firing heavy oil (number 6).



SAE Paper, P. Chavannaavar (Caterpillar)
2012-01-1299 (On-Road Diesel SCR Catalyst Field Sample)

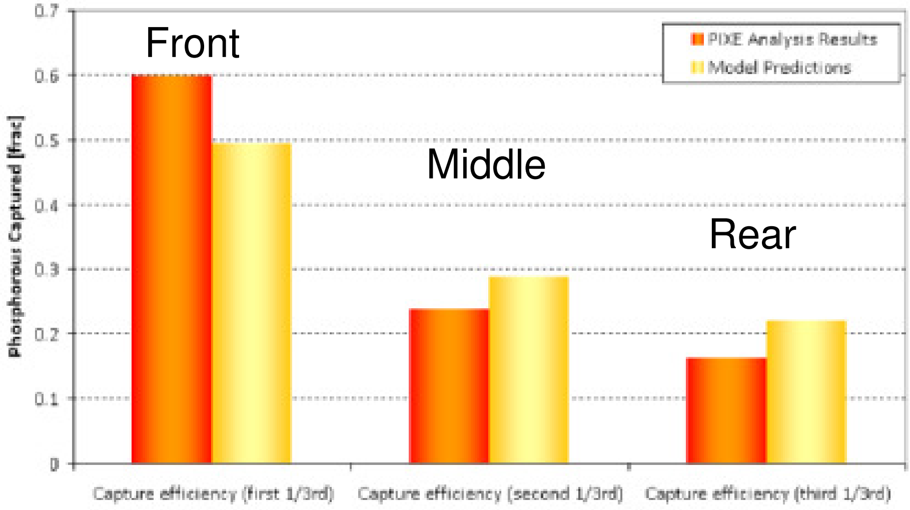


Figure 6. Model predictions versus field aged results for deposition of phosphorus on City Bus application

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Biomass Co-Combustion Study

Hard Coal + Sewage Sludge/ Meat Bone Meal

- **Reference: Beck et al. Fuel 84 (2005) 1911**
- **Full-scale SCR testing**
  - Measured higher gaseous H_3PO_4 concentration at SCR outlet vs. SCR inlet, which suggests that a release of particulate bound phosphorus into the gas phase occurred within the SCR
- **Beck proposed the following reaction in the SCR:**
  - **$Me_3(PO_4)_2(s) + 3H_2SO_4(g) \rightarrow 3MeSO_4(s) + 2H_3PO_4(g)$**
    - $Me_3(PO_4)_2 = Ca_3(PO_4)_2$, $AlPO_4$, and/or $FePO_4$ (Beck et al. Fuel 86 (2007) 632)
  - Thermodynamic calculations were not presented to gage feasibility, but reaction proposal would produce a bulk P_2O_5 increase with catalyst length

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Phosphorus Volatilization from Ash

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**

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TEM-EDS Study of PRB Ash Detected $Ca_3(PO_4)_2$ in the Ultrafine Particles

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Chen et. Al, Environmental Science and Technology 39 (2005) 1144

50 kW lab combustor.

Analyzed ash fraction <2.5 μm by TEM-EDS and electron diffraction.

For PRB ash: identified $Ca_3(PO_4)_2$ particles in the ash fume (<100 nm) by TEM-EDS (Table 3) and electron diffraction (Figure 9).

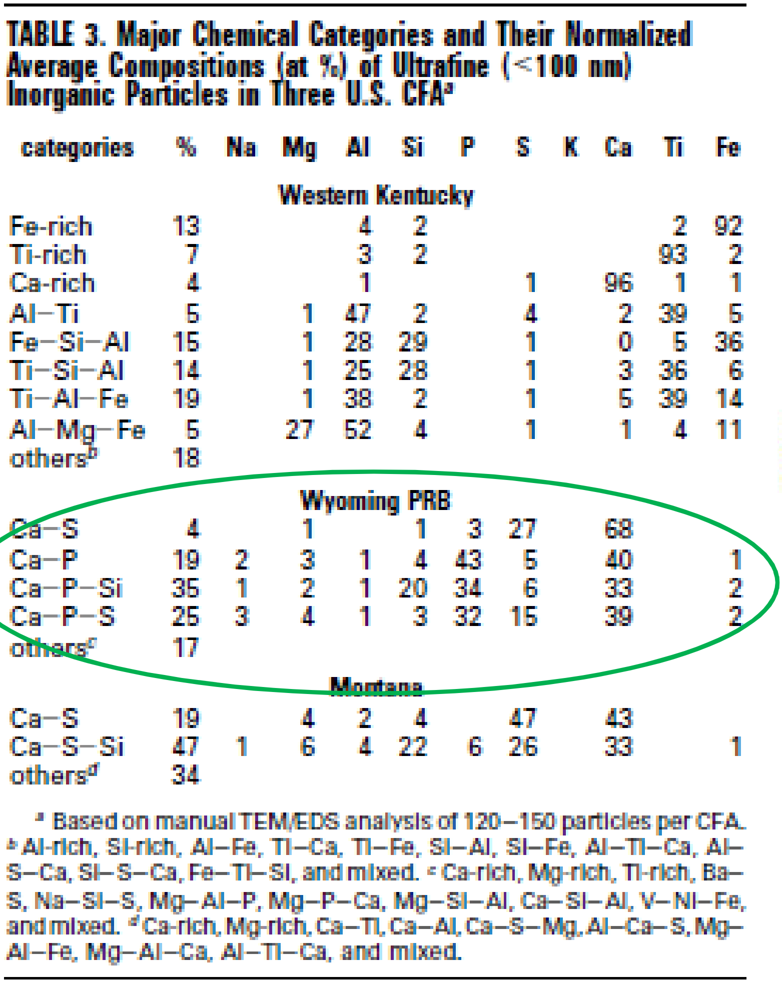

TABLE 3. Major Chemical Categories and Their Normalized Average Compositions (at %) of Ultrafine (<100 nm) Inorganic Particles in Three U.S. CFA[a]

categories	%	Na	Mg	Al	Si	P	S	K	Ca	Ti	Fe
Western Kentucky											
Fe-rich	13			4	2					2	92
Ti-rich	7			3	2					93	2
Ca-rich	4			1			1		96	1	1
Al–Ti	5		1	47	2		4		2	39	5
Fe–Si–Al	15		1	28	29		1		0	5	36
Ti–Si–Al	14		1	25	28		1		3	36	6
Ti–Al–Fe	19		1	38	2		1		5	39	14
Al–Mg–Fe	5		27	52	4		1		1	4	11
others[b]	18										
Wyoming PRB											
Ca–S	4		1		1	3	27		68		
Ca–P	19	2	3	1	4	43	5		40		1
Ca–P–Si	35	1	2	1	20	34	6		33		2
Ca–P–S	25	3	4	1	3	32	15		39		2
others[c]	17										
Montana											
Ca–S	19		4	2	4		47		43		
Ca–S–Si	47	1	6	4	22	6	26		33		1
others[d]	34										

[a] Based on manual TEM/EDS analysis of 120–150 particles per CFA. [b] Al-rich, Si-rich, Al–Fe, Ti–Ca, Ti–Fe, Si–Al, Si–Fe, Al–Ti–Ca, Al–S–Ca, Si–S–Ca, Fe–Ti–Si, and mixed. [c] Ca-rich, Mg-rich, Ti-rich, Ba–S, Na–Si–S, Mg–Al–P, Mg–P–Ca, Mg–Si–Al, Ca–Si–Al, V–Ni–Fe, and mixed. [d] Ca-rich, Mg-rich, Ca–Ti, Ca–Al, Ca–S–Mg, Al–Ca–S, Mg–Al–Fe, Mg–Al–Ca, Al–Ti–Ca, and mixed.

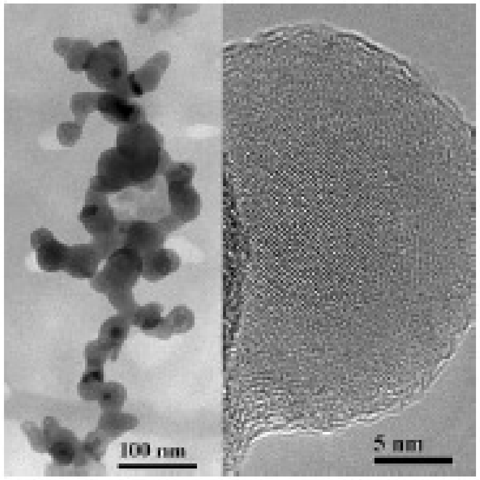

FIGURE 8. Fractal-like ultrafine Ca phosphates with primary particle size 30–50 nm (left). High-mag image of the primary particles (right) (Wyoming PRB CFA).

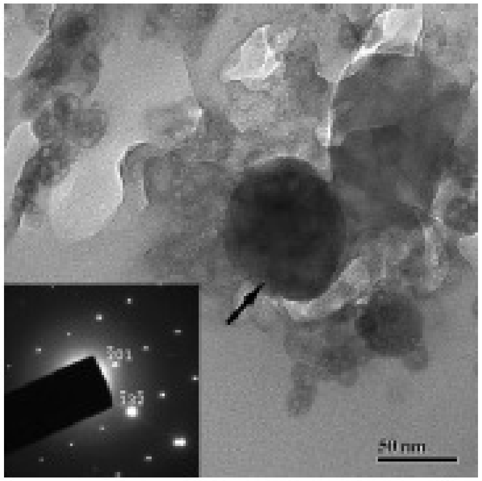

FIGURE 9. Micrograph and SAED pattern of a spherical $Ca_3(PO_4)_2$ particle (Wyoming PRB CFA).

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Phosphorus Volatilizes from Ash

Laboratory Data for Isokinetic Bulk Fly Ash

- **We generated gas phase phosphorus in lab testing by reacting gaseous SO_3 (at SCR conditions) with:**
  - **Pure $Ca_3(PO_4)_2$**
  - **Isokinetic bulk fly ash (SCR inlet) from PRB-firing plants:**

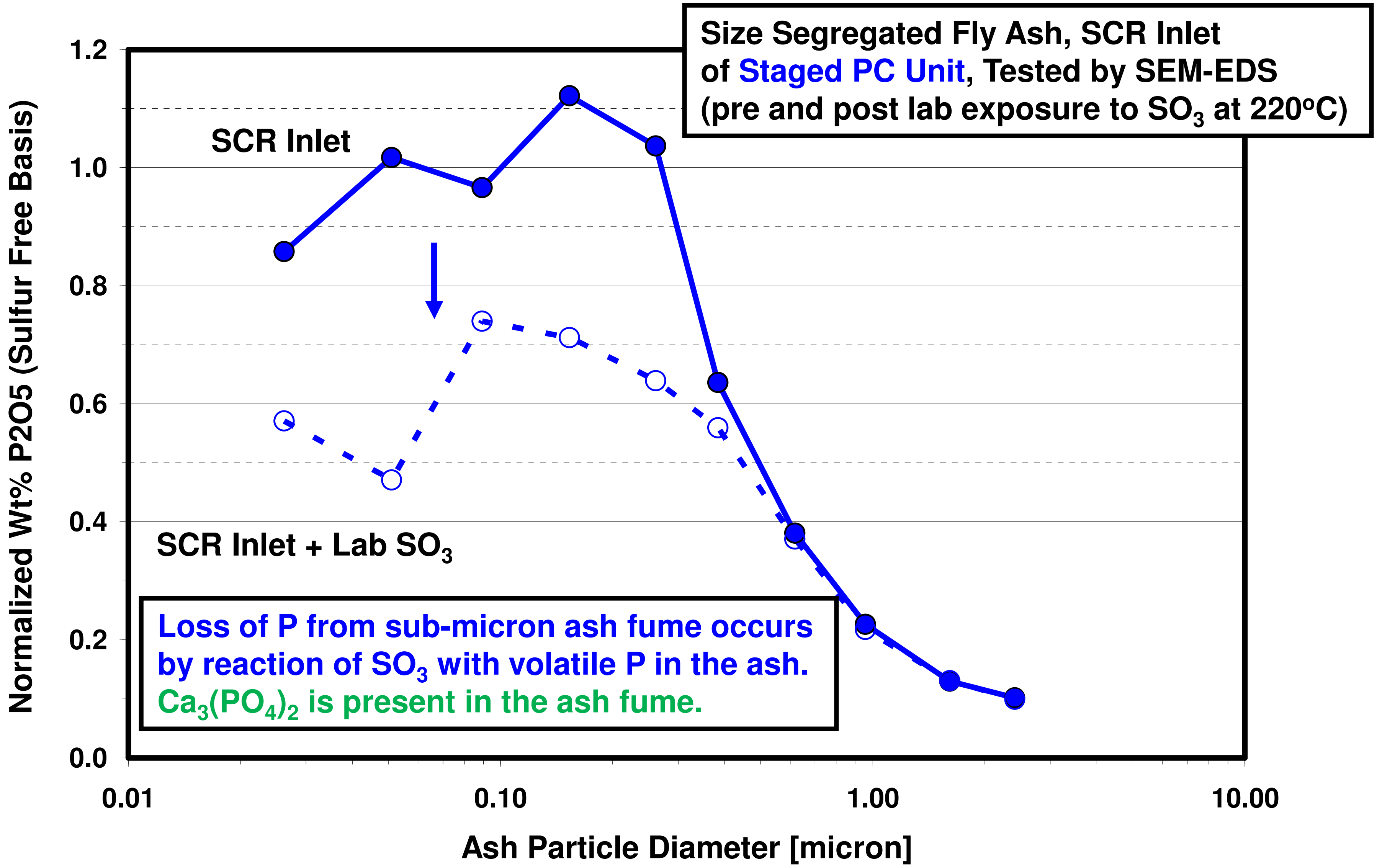
Plant	Unit Catalyst Deactivation Rate	Unit Operation	Average H3PO4(g) Generated in Test Relative to Plant A
Plant A	High	Staged Operation	1.00
Plant B	Low	Non-Staged	0.31

Table: Lab test data for SO_3 reaction with fly ash from Plants A and B to generate gas phase P.

Plant A catalyst has 3x higher bulk accumulation rate for phosphorus than Plant B catalyst.

Phosphorus Volatilizes from Ash

Laboratory Data for Size Segregated Fly Ash (Low Pressure Impactor)



Size Segregated Fly Ash, SCR Inlet of Staged PC Unit, Tested by SEM-EDS (pre and post lab exposure to SO_3 at 220°C)

Loss of P from sub-micron ash fume occurs by reaction of SO_3 with volatile P in the ash. $Ca_3(PO_4)_2$ is present in the ash fume.

Gaseous P is Formed in the SCR by SO_3 Reaction with Solid P in Ash Fume

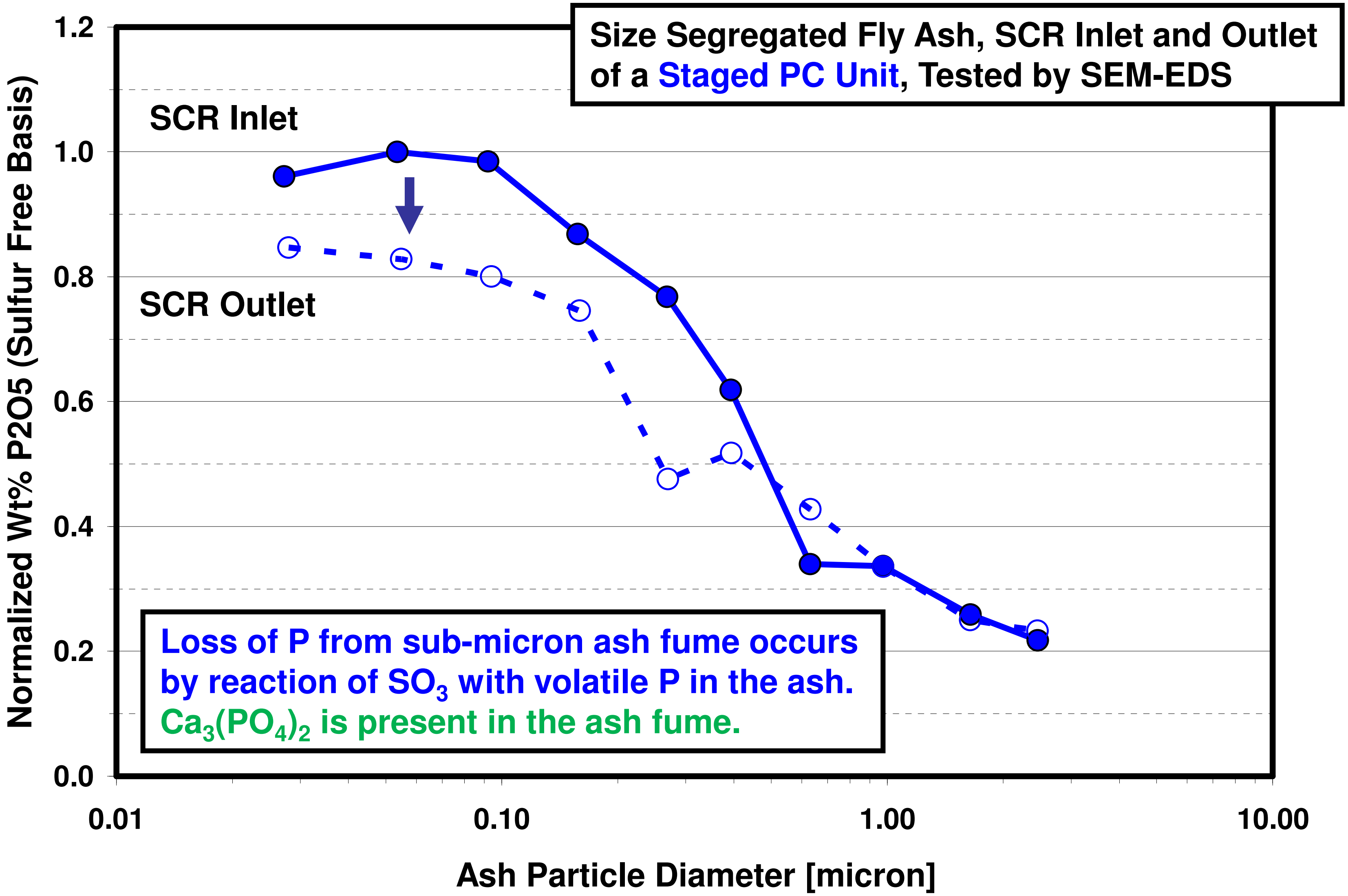
Overview of the data supporting this mechanism…

- P vaporizes from coal in staged and non-staged plants.
- Catalyst P length profile (increasing F → R) is opposite that of non-PRB SCR applications with P deactivation (decreasing F → R).
- Earlier study in scientific literature proposed this mechanism.
- Proposed reaction for P release has favorable thermodynamics.
- PRB fly ash contains Ca and P: $Ca_3(PO_4)_2$ formation is plausible. Ca-P particles have been previously detected in PRB ash fume.
- Lab: gaseous P can form by reacting PRB fly ash with SO_3.
- Field: P lost from the ash fume across the SCR is measurable.
- Field: changing the SCR catalyst SO_2 oxidation rate has a measurable impact on the P accumulation rate.

Gaseous P in SCR is formed by SO_3 reaction with solid P in ash fume.

Phosphorus Volatilizes from Ash

Field Data for Size Segregated Fly Ash (Low Pressure Impactor)



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SCR SO_2 Oxidation Affects Catalyst Phosphorus Accumulation Rate

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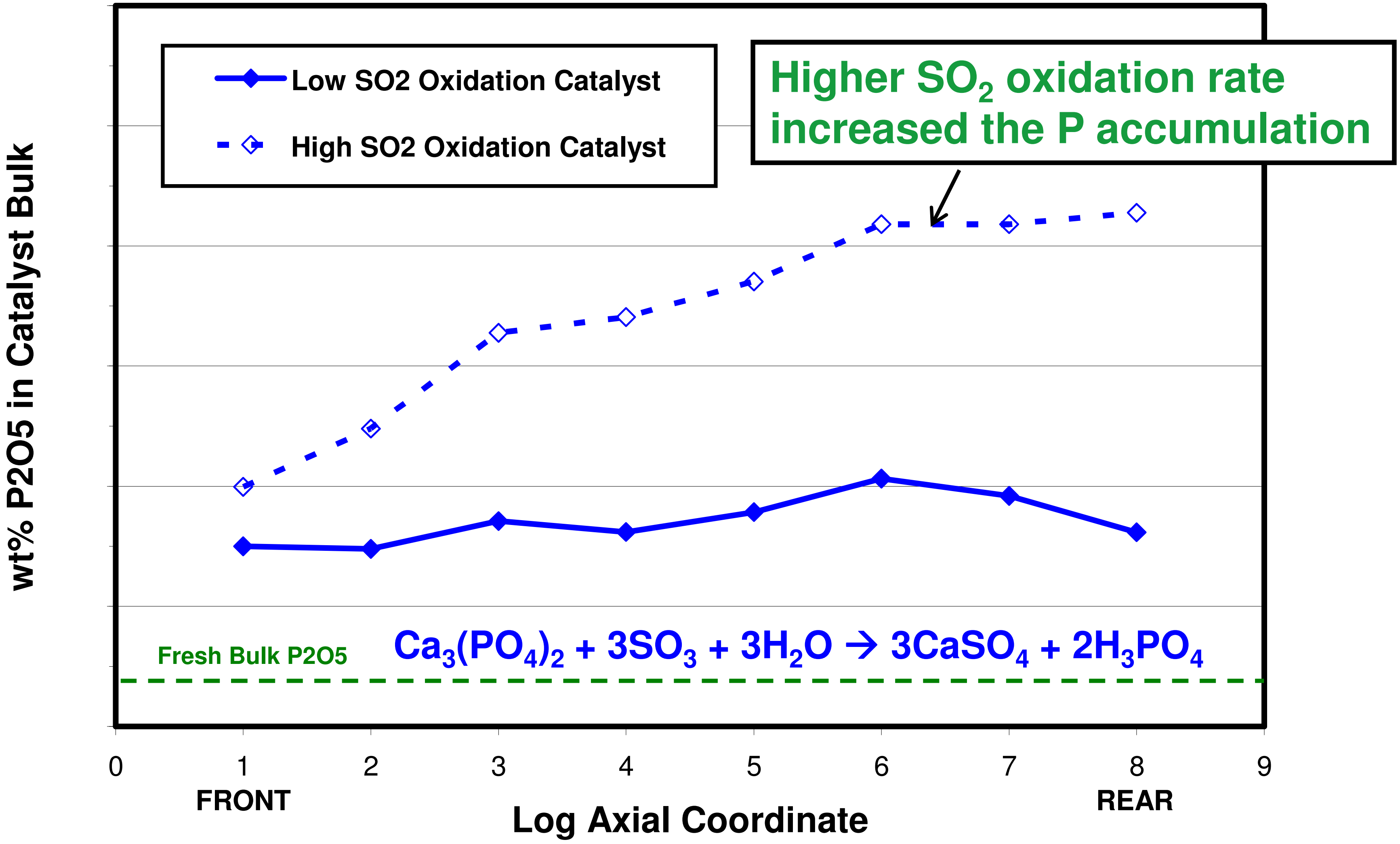
Loaded two ½ catalyst samples (low and high SO_2 oxidation rate catalyst) in single sample tray and loaded it into a Staged PC Unit SCR module for aging.



Higher SO_2 oxidation rate increased the P accumulation

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

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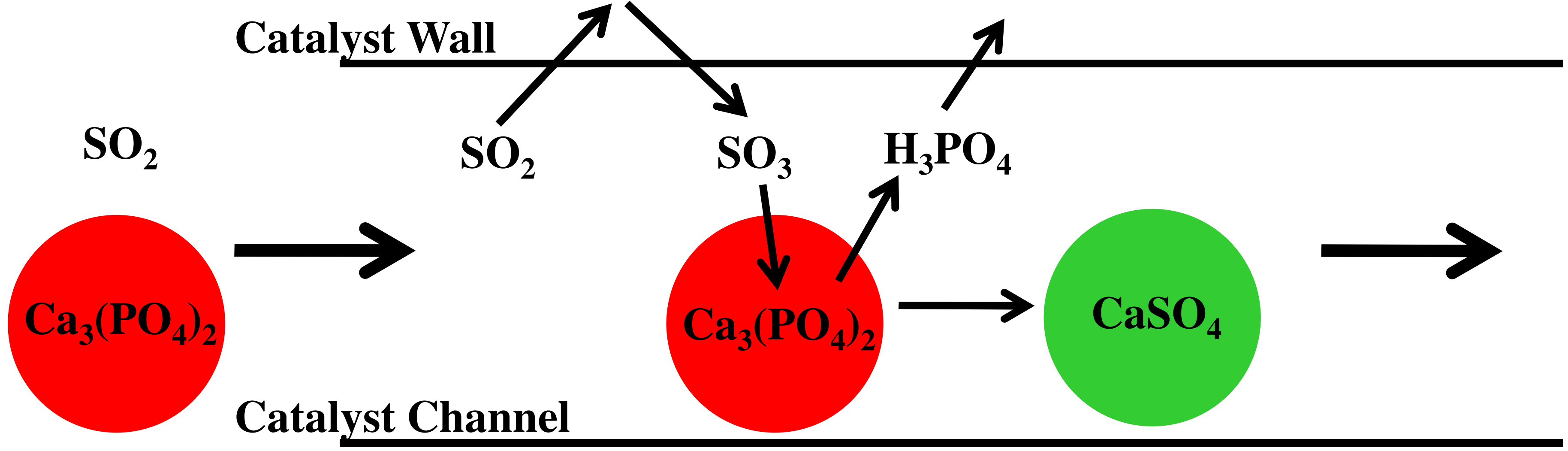
Phosphorus Release Mechanism

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



SO_2 oxidation

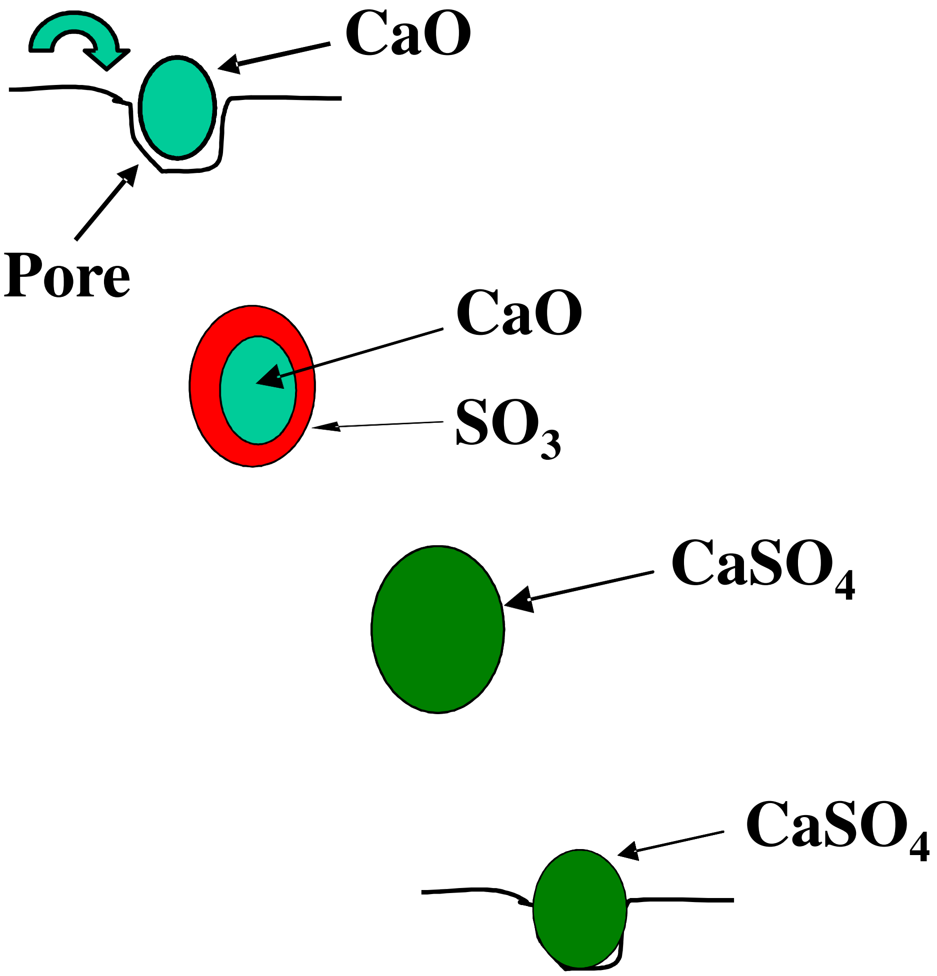
H_3PO_4 diffusion into catalyst wall and reaction with active sites

- **SO_3 concentration increases with catalyst length, releasing gaseous P from the ash fume**
  - This effect drives the increase in bulk P along the catalyst length
  - **<u>Amount of P released in the SCR thus depends on</u>:**
    - Activity of the $Ca_3(PO_4)_2$ in the ash fume
    - SO_3 concentration (influenced by catalyst and ash CaO)

Calcium Deactivation

Surface Blinding

1. Sub-micron CaO is caught in macro pore on catalyst.
2. SO_3 diffuses to CaO particle.
3. SO_3 and CaO react to form $CaSO_4$; particle expands ~14%.
4. $CaSO_4$ plugs pore. NH_3 & NO_x cannot diffuse to active sites.



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

Presentation Outline

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- **Cormetech Experience**
- **Catalyst Deactivation from Ca, P, and Na**
  - Impact on Catalyst Activity
  - Mechanism: How They Deactivate Catalyst
  - Mechanism: Nature of the Deactivating Species
  - **Impact of Staging**
- **Potential Mitigation Options**

Impact of Staging

Affects the Activity of the $Ca_3(PO_4)_2$ for P Release

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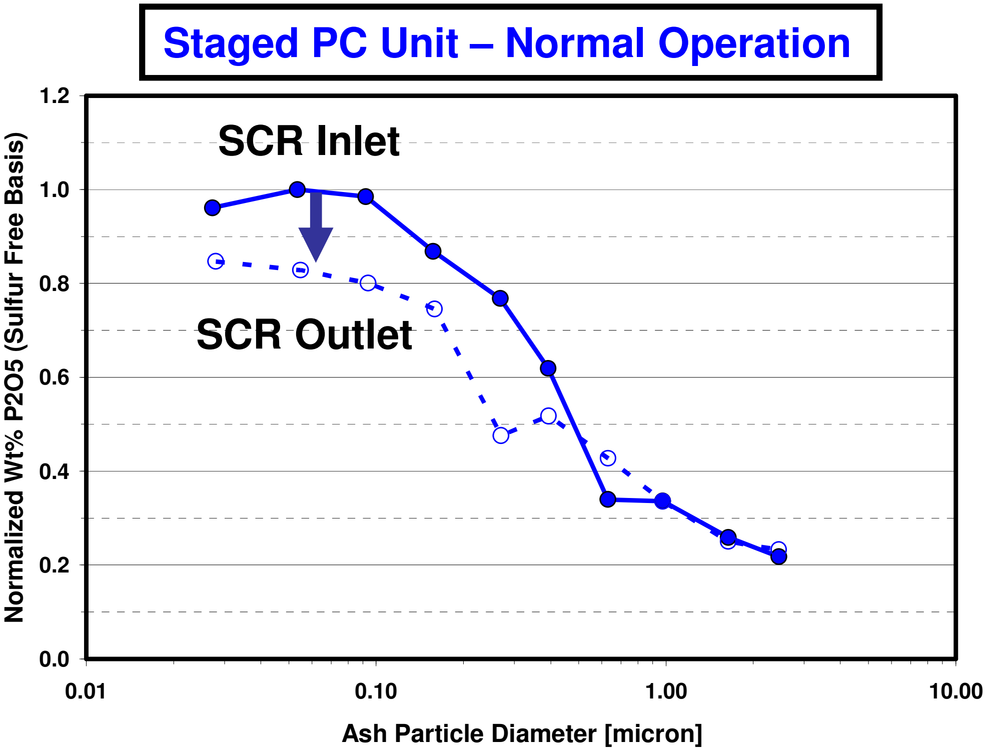
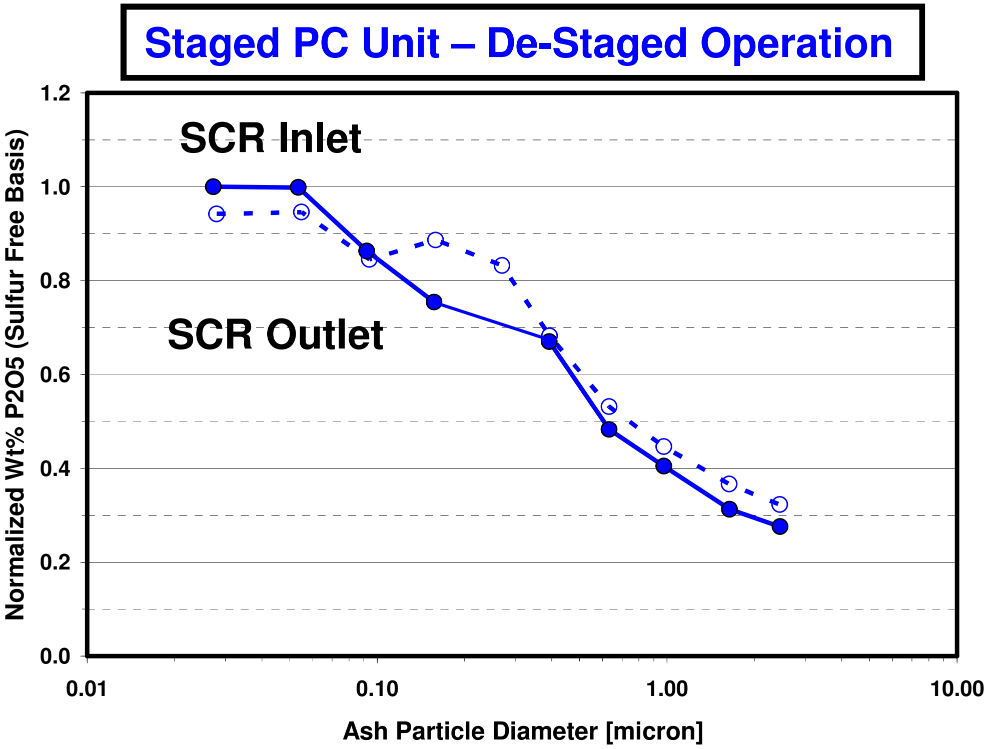


Staged PC Unit – Normal Operation



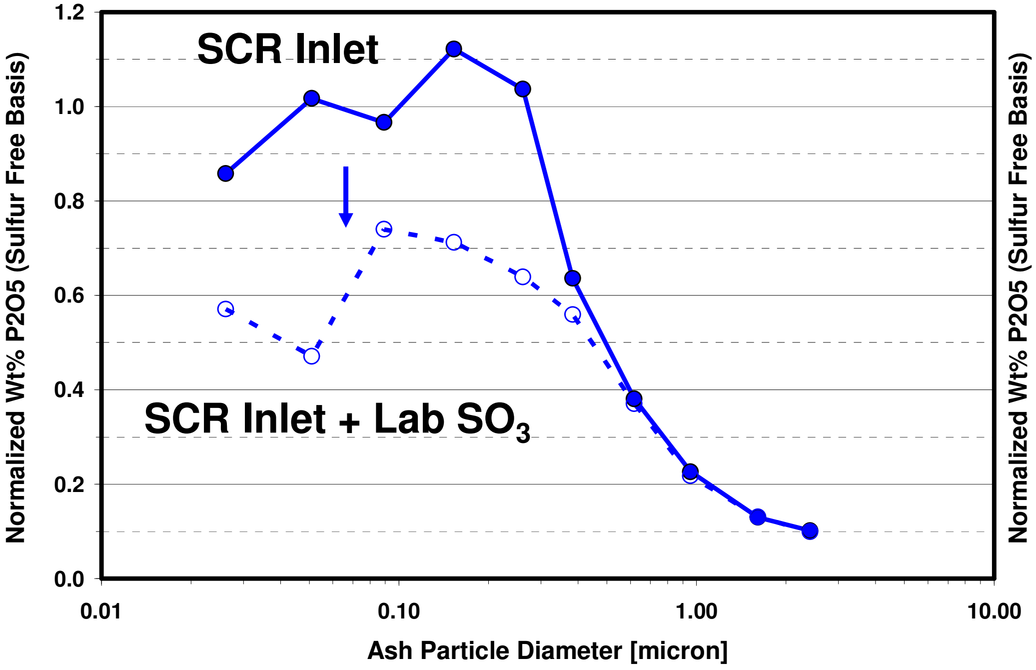
Staged PC Unit – De-Staged Operation

- **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)**

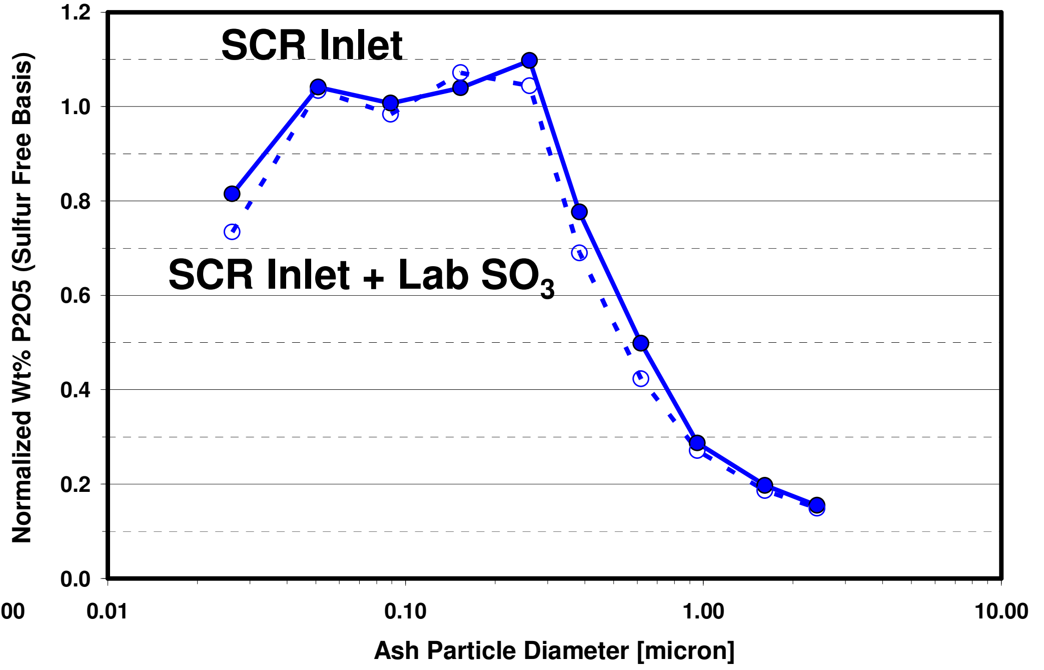
Impact of Staging

Affects the Activity of the $Ca_3(PO_4)_2$ for P Release

Staged PC Unit – Normal Operation



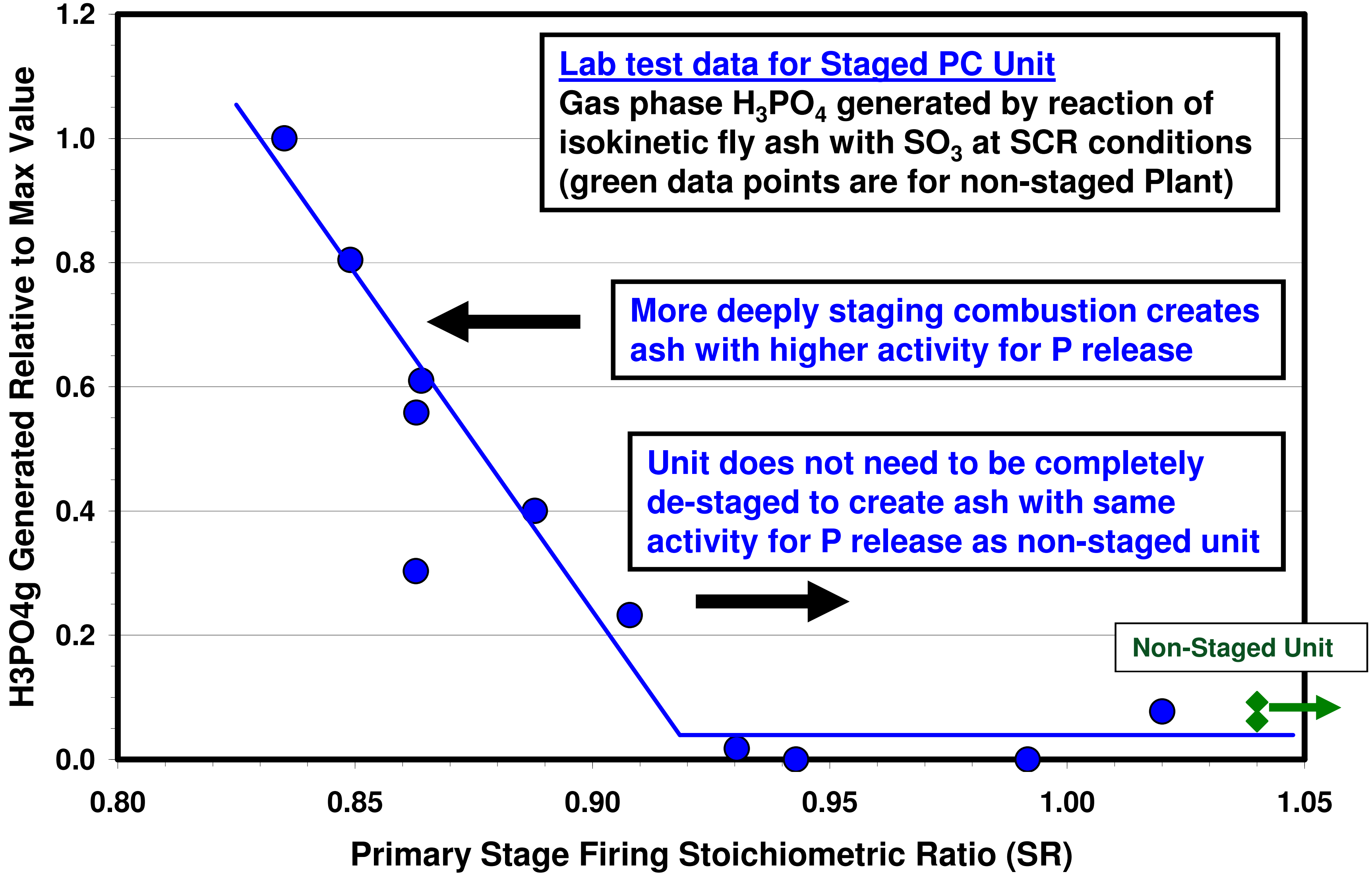
Staged PC Unit – De-Staged Operation



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

Impact of Staging

Affects the Activity of the $Ca_3(PO_4)_2$ for P Release



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

Summary

Impact of Staging on Deactivating Species

- **Staging can lead to higher activity $Ca_3(PO_4)_2$ and CaO**
  - **P → volatilization of P from sub-micron ash ($Ca_3(PO_4)_2$) by SO_3**
    - $Ca_3(PO_4)_2 + 3SO_3 + 3H_2O \rightarrow 3CaSO_4 + 2H_3PO_4$
    - Staging can increase the amount of P that can be volatized from the ash (i.e., it has higher activity)
  - **Ca → sub-micron CaO adhesion in catalyst pores and sulfation**
    - Staging can increase the activity of the CaO in the ash (from catalyst audit data: staging can lead to more Ca blinding)
  - **Partial de-staging can have positive effect on lowering the catalyst deactivation rate**

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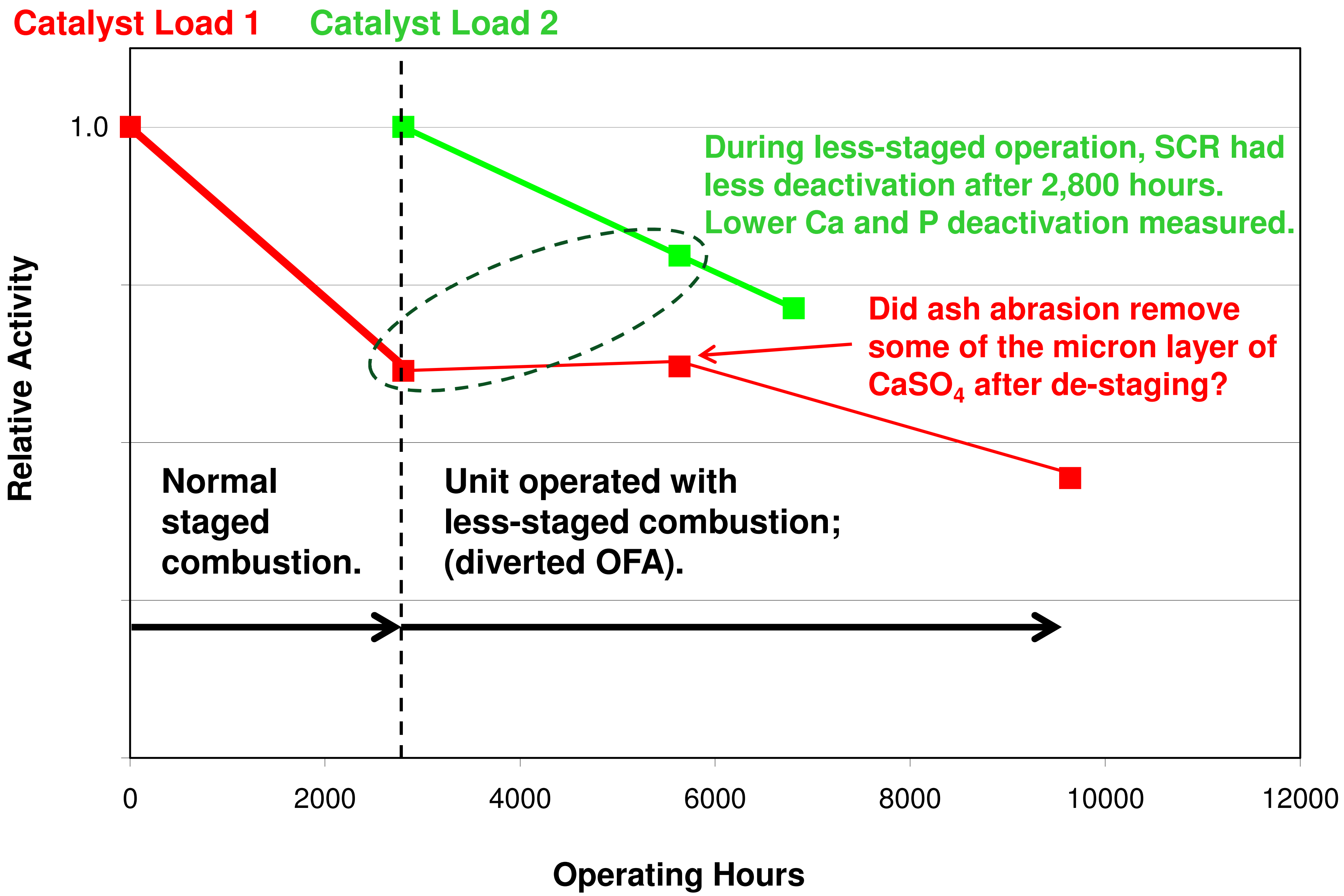
Partial De-Staging Impact

PC Unit Firing 100% PRB



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?

Normal staged combustion.

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

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? Such as additives?**

Summary

- More than 40 SCR units firing 100% PRB or high PRB blends.
- 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. The gaseous P that deactivates the catalyst forms in the SCR by the reaction: $Ca_3(PO_4)_2 + 3SO_{3(g)} + 3H_2O_{(g)} \rightarrow 3CaSO_4 + 2H_3PO_{4(g)}$
- 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.

Thank You!

Questions?