

REINHOLD ENVIRONMENTAL Ltd.



2019 NO_x-Combustion-CCR Round Table Presentation

February 11 & 12, 2019, in Salt Lake City, Utah / Hosted by PacifiCorp

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Catalyst Deactivation Mechanisms Training Class

Chris DiFrancesco
Cormetech, Inc.

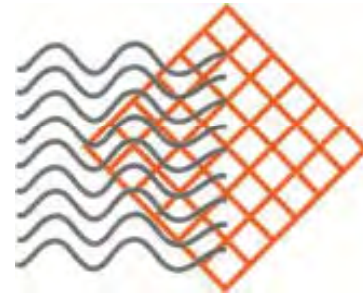
2019 NOx-Combustion-CCR Round Table

Overview

SCR Catalysts Deactivation Mechanisms



- **Background**
- **Primary deactivation mechanisms**
- **Regeneration to reverse deactivation mechanisms**



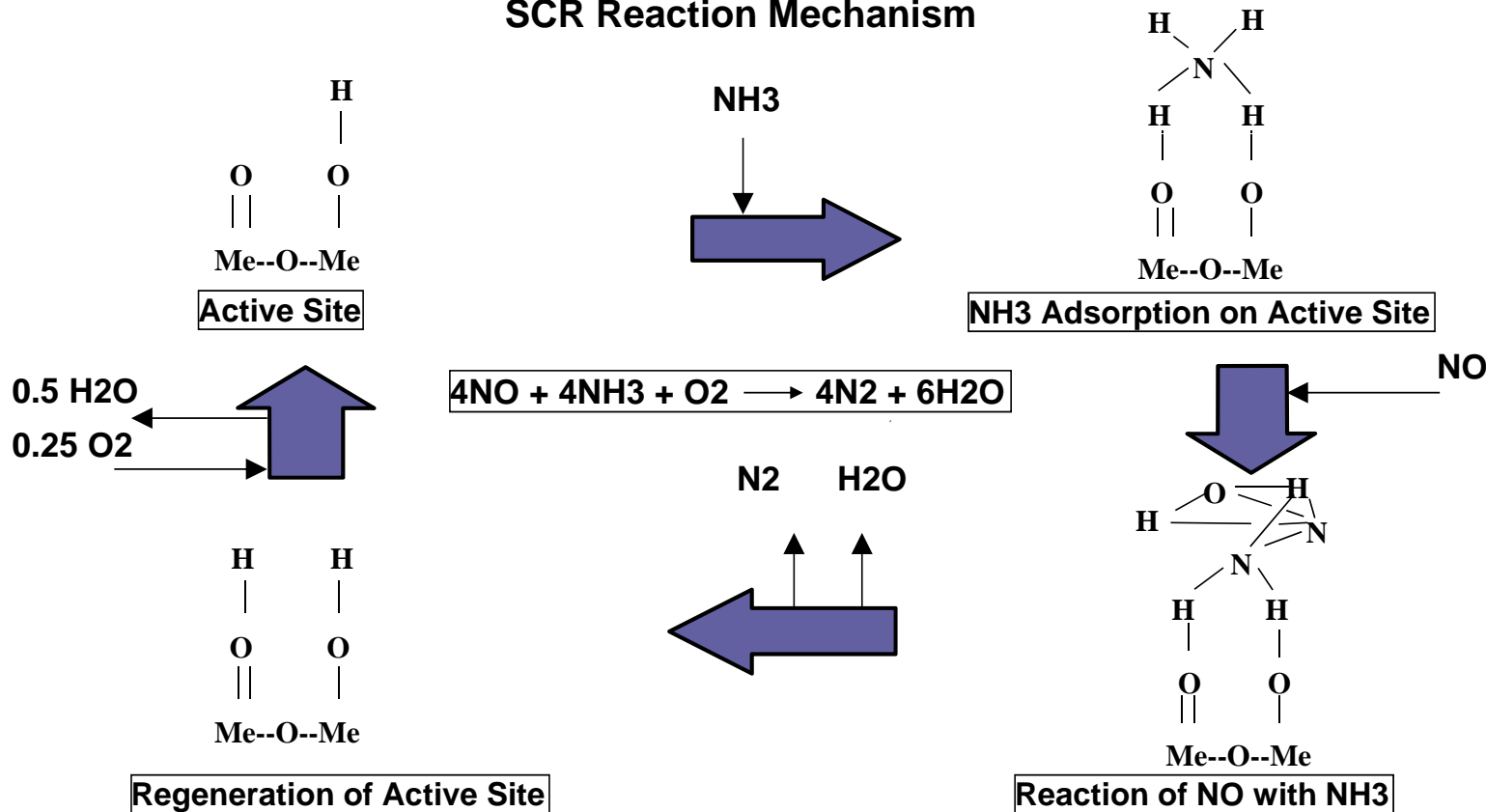
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Background

- What is deactivation?
- Why is understanding it important?

What is deactivation?

SCR Reaction Mechanism



Deactivation:

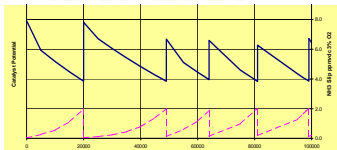
- Eliminates or hinders active sites**
 - Arsenic
 - Phosphorous
 - Alkaline metals
- Blocks reactants from reaching active sites**
 - Pore plugging (Calcium)
 - Catalyst channel plugging

*Active site and mechanism of the selective catalytic reduction of NO by NH₃ over V₂O₅: A periodic first-principles study. Phys. Chem. Chem. Phys., Issue 18, 2000.

SCR Catalyst Life-Cycle Management



Cycle primarily driven by catalyst deactivation



Monitoring & Addition/ Replacement Management

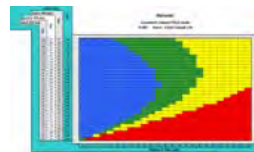
Design & Manufacture or Regenerate

Disposal or Recycle



Operation & Maintenance

Installation & Commissioning



On-line cleaning, In-situ Ice Blasting, coal & ash monitoring, and other deactivation mitigation steps

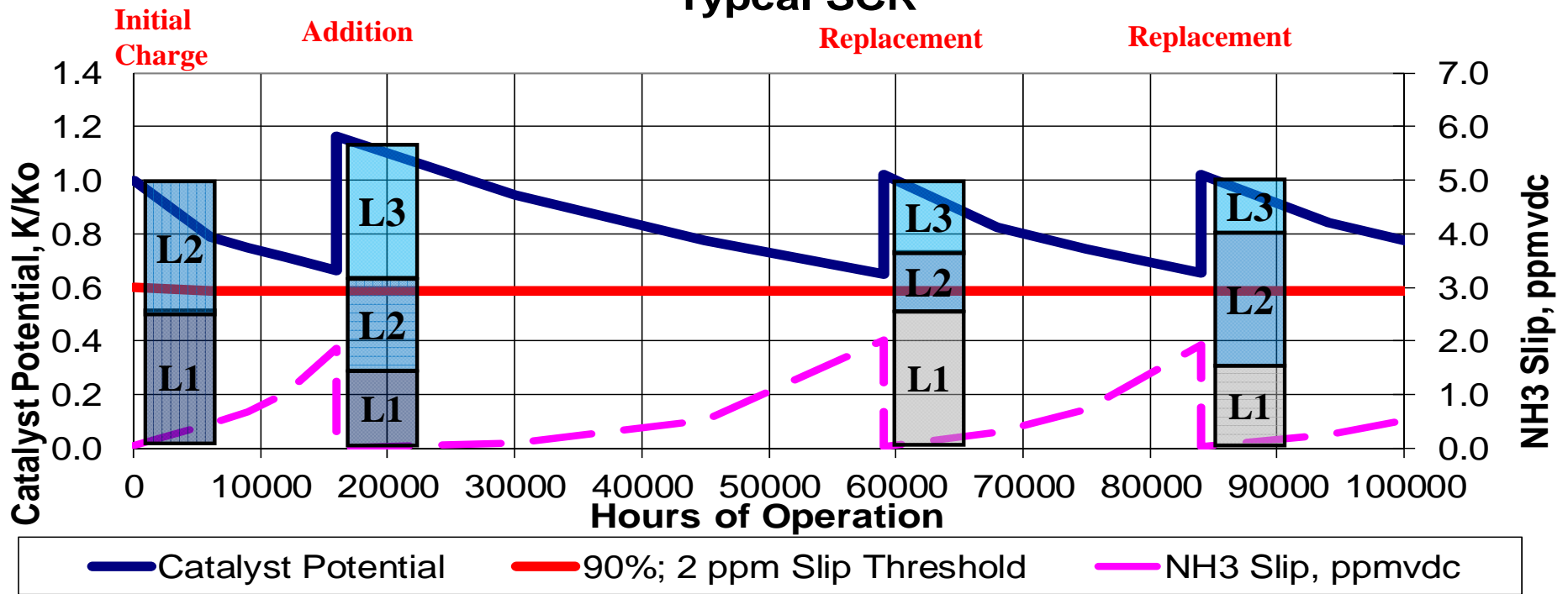


Impact on Catalyst Management



Significant catalyst potential added initially and over time to account for deactivation

Catalyst Management Plan 2 Initial Plus 1 Spare Layer Typical SCR



Primary Deactivation Mechanisms

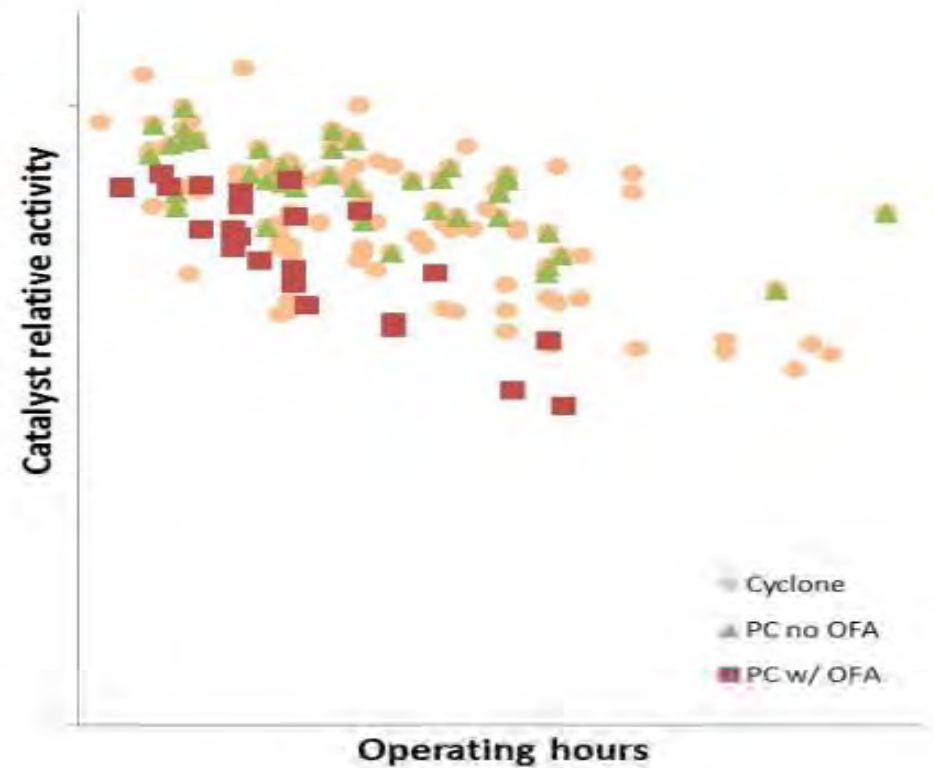


- **Calcium & Phosphorous**
 - Pore plugging due to calcium oxide in ash
 - Why does P poisoning increase along catalyst length?
 - What does this tell us about the root cause of high P poisoning?
 - How can we mitigate?
- **Arsenic**
 - What form poisons catalyst?
 - Why do some coals result in higher As poisoning than others?
 - How can we mitigate?
- **Alkaline metals**
 - Sources of alkaline metals, including additives
- **Catalyst Channel Plugging**
 - Ash is in a very dilute phase, so why does catalyst plug?
 - How can we mitigate?

Calcium and Phosphorous Deactivation



- **Primary deactivation mechanisms for PRB-Fired Applications**
- **Wide range of measured catalyst deactivation rates**

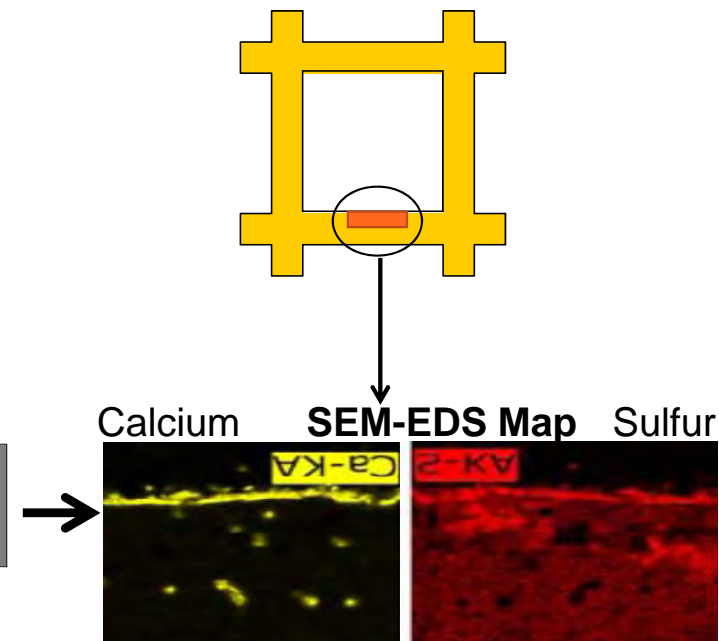
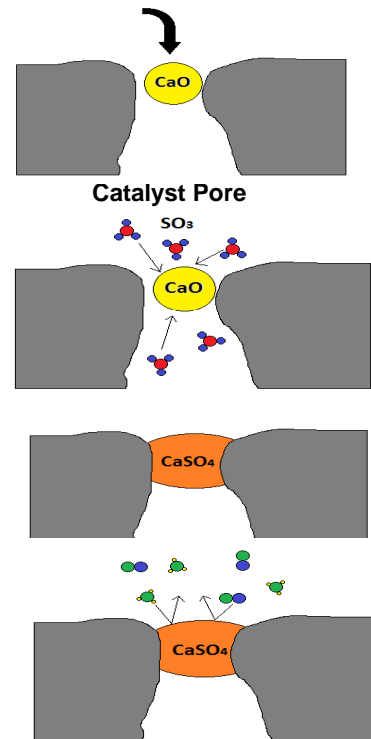


Calcium Deactivation Mechanism



PRB and Bituminous Units

1. Sub-micron CaO formed during coal combustion.
2. Sub-micron CaO is caught in macro-pore of catalyst surface.
3. SO₃ in flue gas diffuses to CaO particle.
4. SO₃ and CaO react to form CaSO₄. Particle swells by ~14%.
5. CaSO₄ plugs pore: NH₃ and NO_x are blocked from active sites.



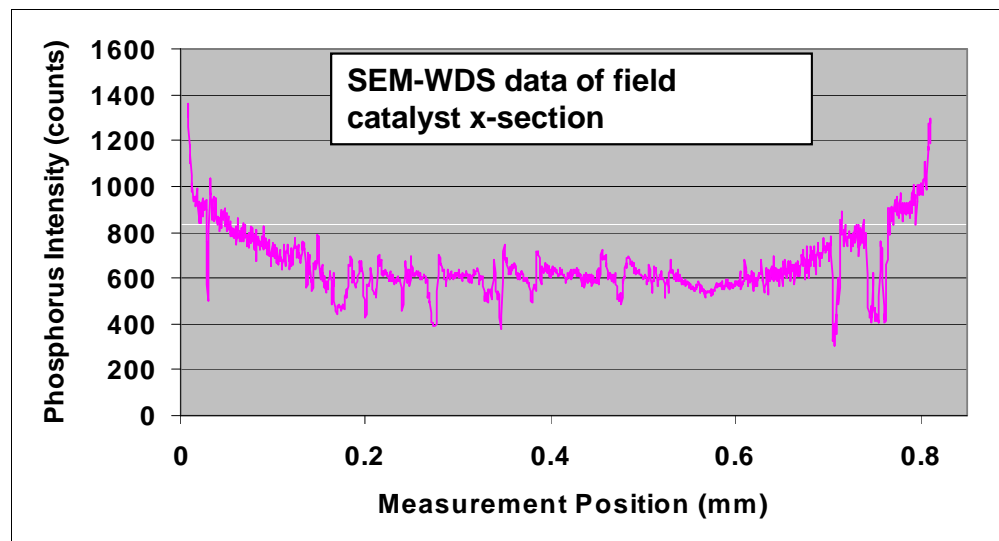
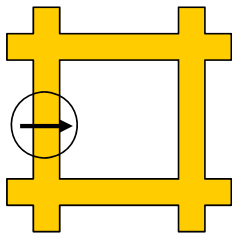
May be accounted for in design based on amount of calcium in the coal

Phosphorous Deactivation Mechanism



PRB Units

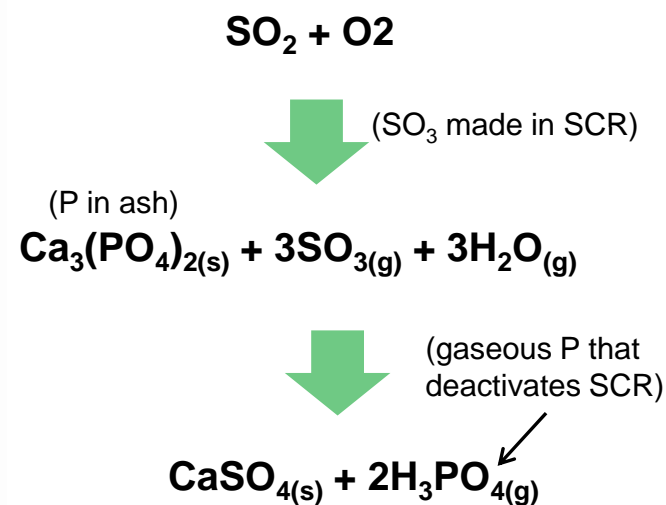
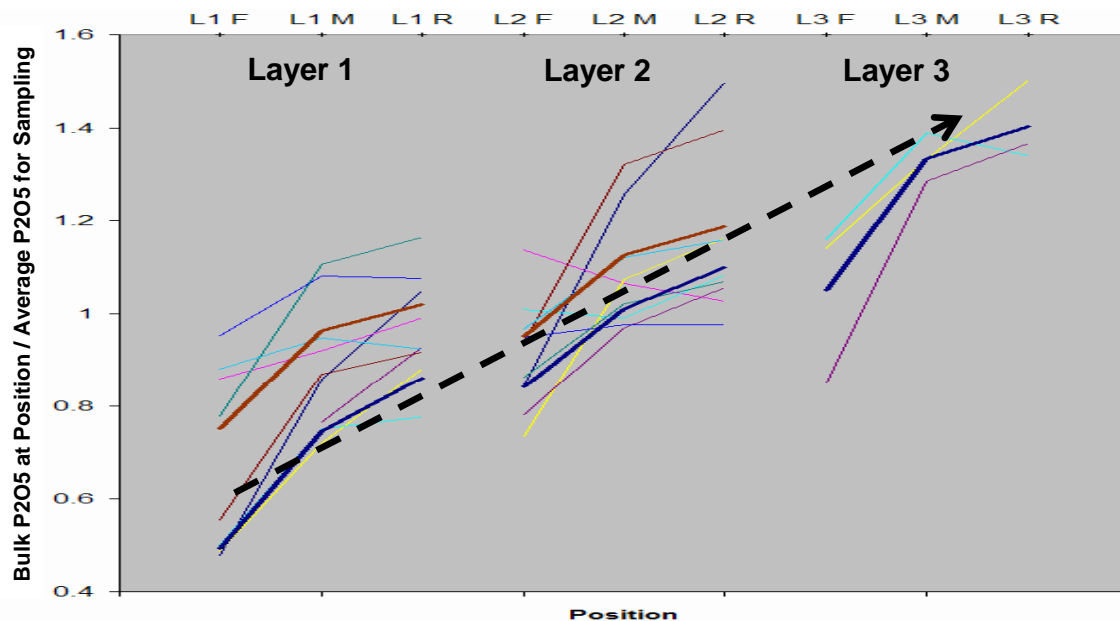
- **Phosphorus is a penetrating poison**
 - Diffuses into the catalyst bulk and chemically bonds with active sites
 - Profile in catalyst wall indicates P species is gas phase, e.g. H_3PO_4



Phosphorous Deactivation Mechanism



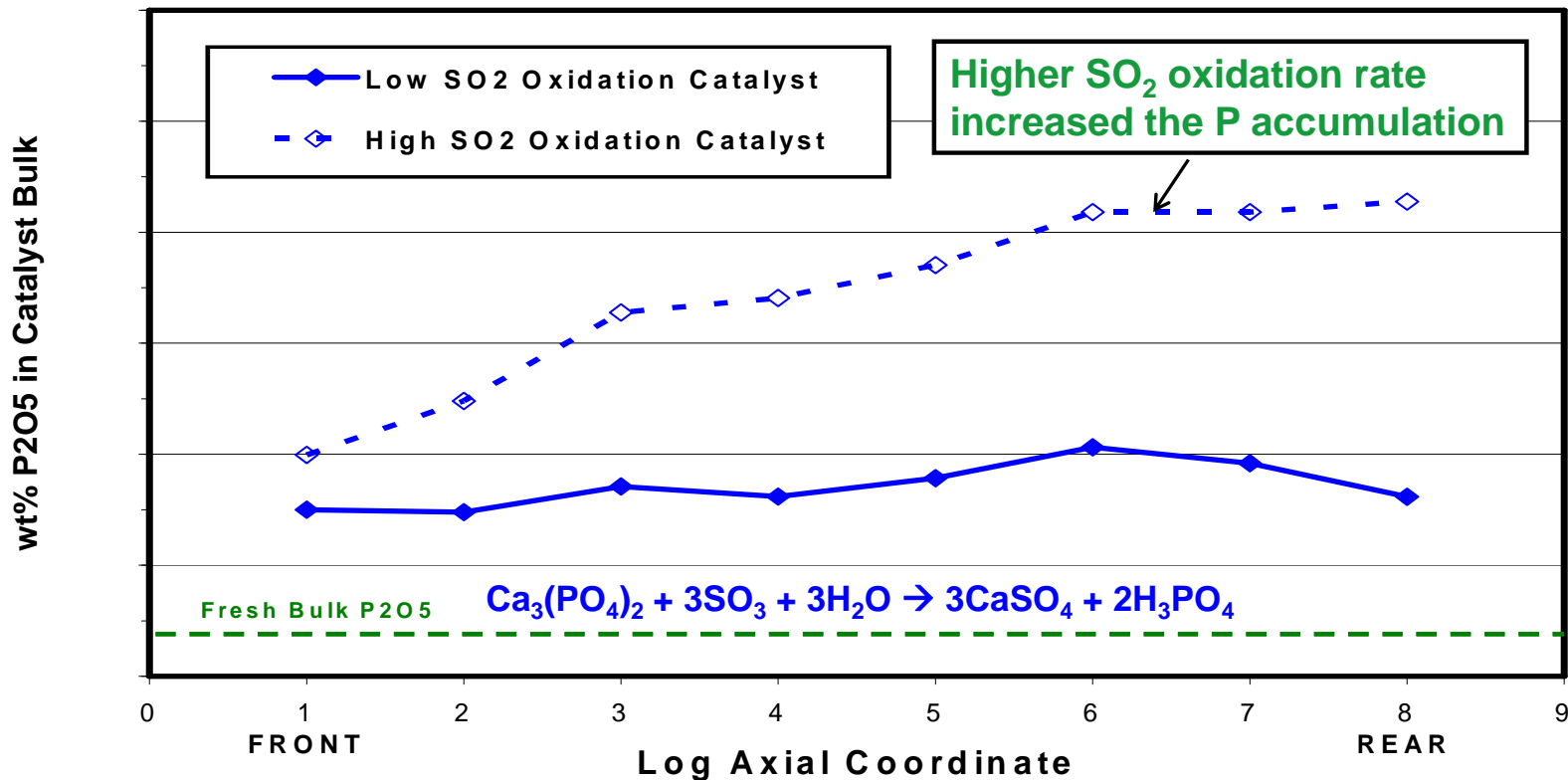
- PRB with staged combustion: bulk P_2O_5 in catalyst increases with catalyst length
 - Due to liberation of gaseous P from solid P in ash by SO_3 made in SCR



SO3 Impact on Gaseous P Generation



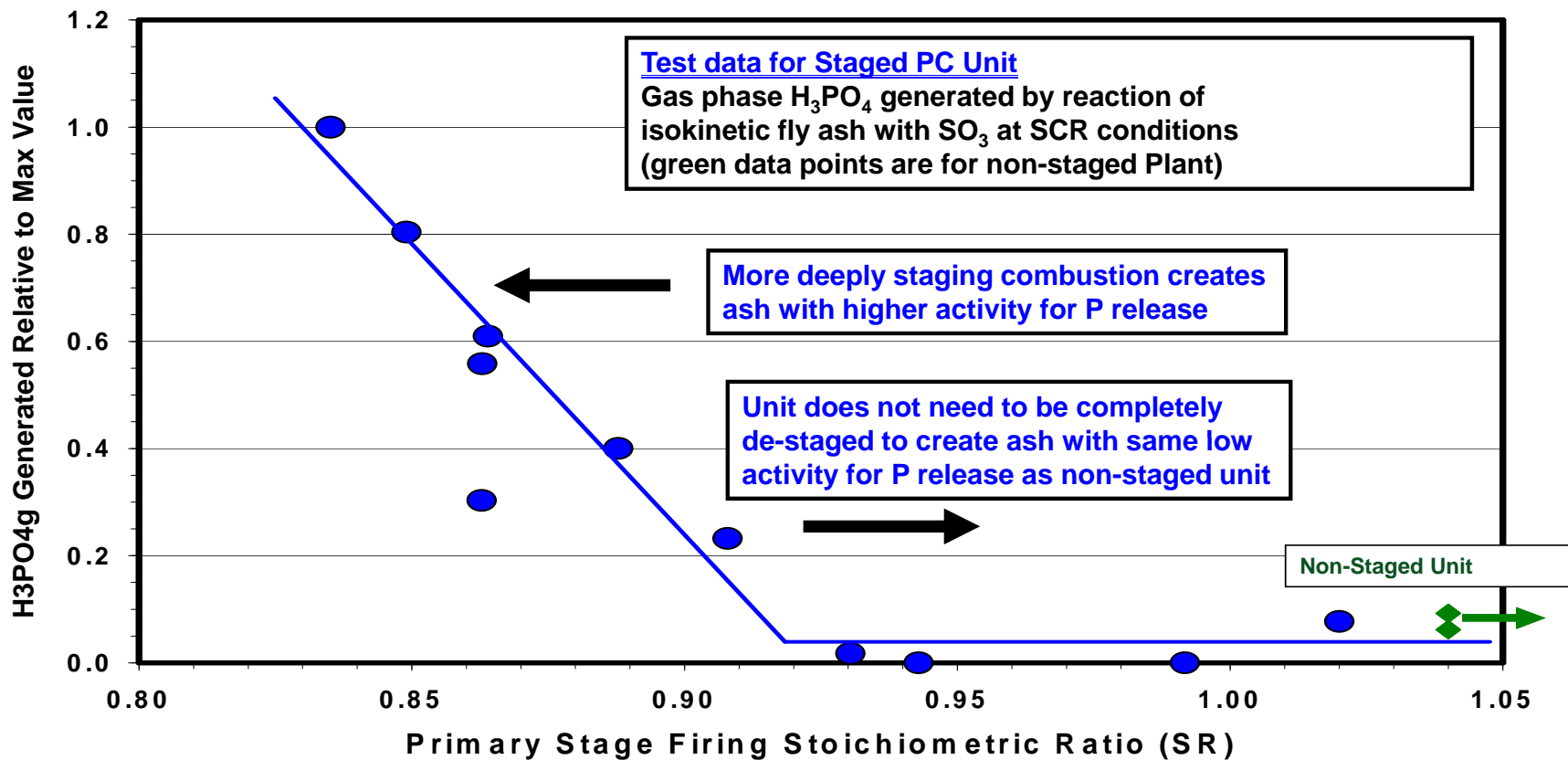
Two ½ cross-section catalyst samples (one with low and one with high SO₂ oxidation rate) in single sample tray and loaded it into a **Staged PC PRB Unit** SCR module for aging.



Combustion De-Staging Impact on Gaseous P Generation



- Degree of staging determines the amount of reactive $\text{Ca}_3(\text{PO}_4)_s(\text{s})$ in flue gas



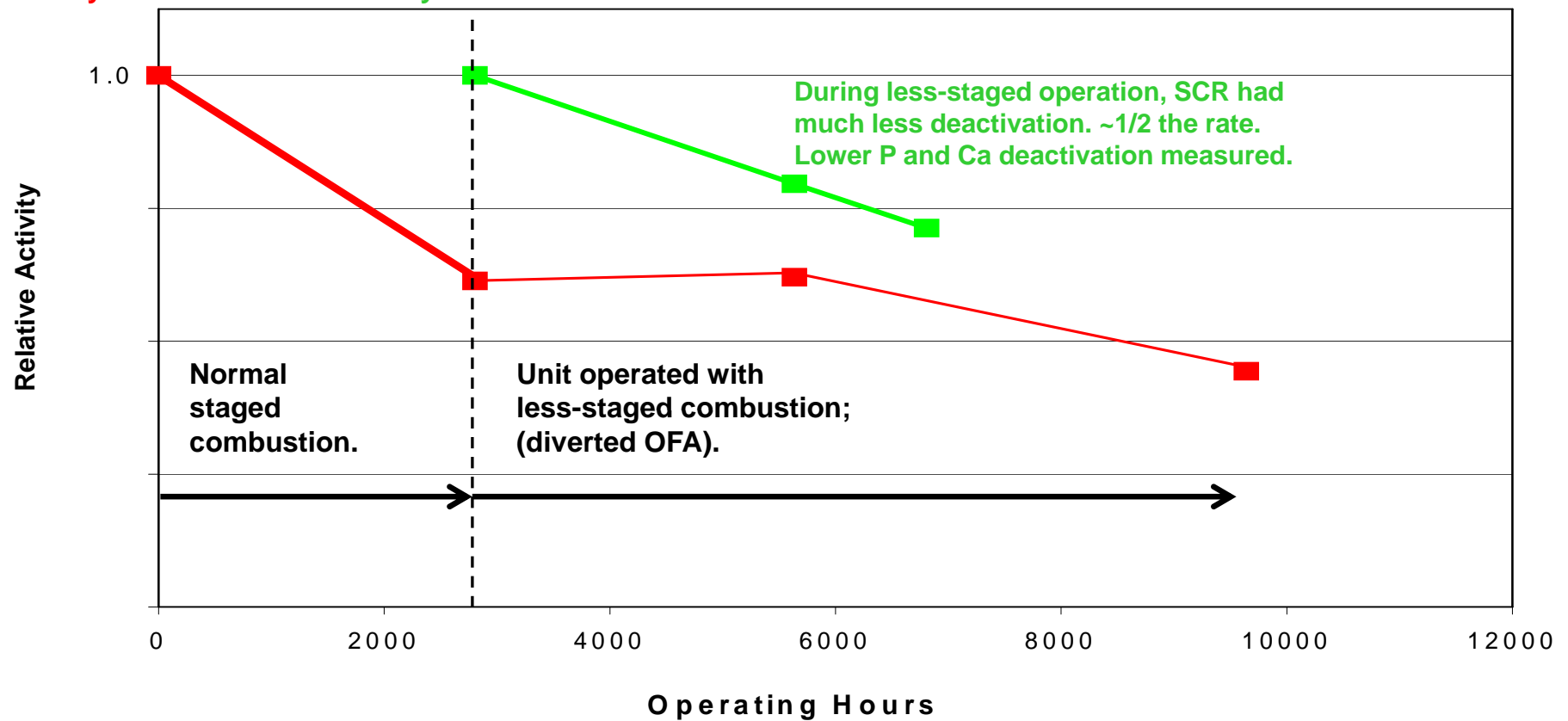
Combustion De-Staging Impact on Gaseous P Generation



Slipstream sample results allowed for frequent sampling. Less P and Ca deactivation

Catalyst Load 1

Catalyst Load 2



Mitigation of P and Ca Deactivation by De-Staging



- **Case-by-case Cost Benefit Analysis**
 - **Costs:**
 - More reactor potential required to achieve higher DeNO_x at higher inlet NO_x
 - Does not need to be completely de-staged, i.e. non-staged
 - Higher NH₃ usage rate
 - **Benefits:**
 - Less change in catalyst potential over time (fewer catalyst management actions)
 - Potential lower LOI
 - Potential reduction in boiler tube wastage

For more information on Ca & P Deactivation:

SCR Catalyst Deactivation for PRB-Firing Coal Utility Boilers by Chris Bertole at 2013 Reinhold NO_x Combustion Round Table

SCR Catalyst Deactivation by P and Ca in Utility Boilers Firing PRB Coals by Rutherford and MacInnes 2016 Reinhold NO_x Combustion-CCR Round Table

Arsenic Deactivation Mechanism



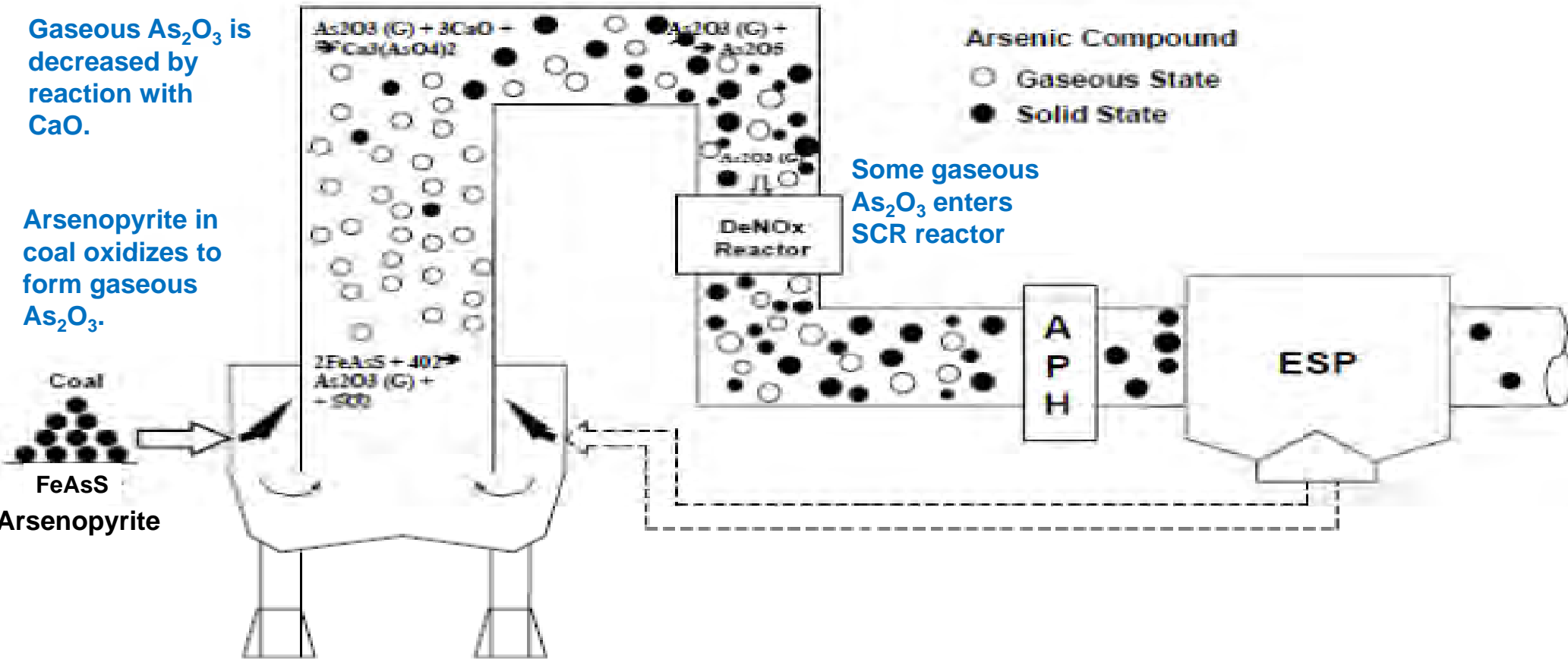
Gaseous As_2O_3 is decreased by reaction with CaO .

Arsenopyrite in coal oxidizes to form gaseous As_2O_3 .

Arsenic Compound

- Gaseous State
- Solid State

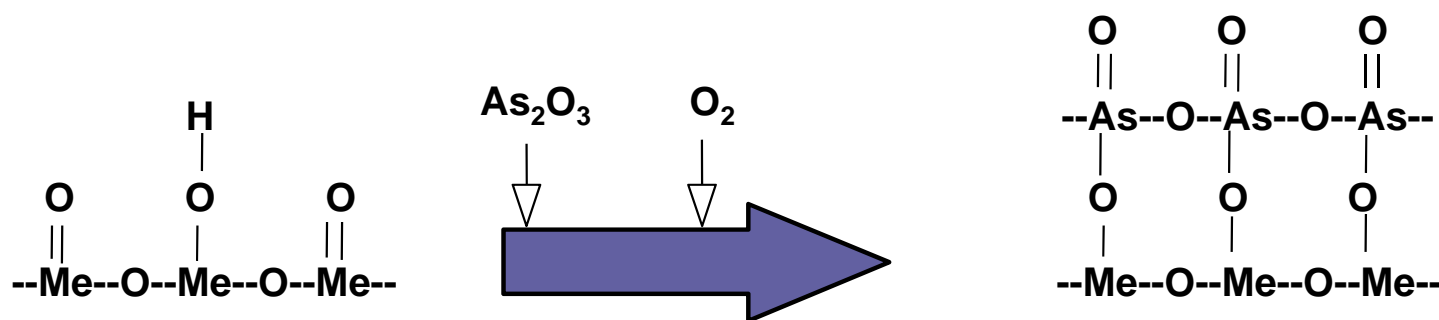
Some gaseous As_2O_3 enters SCR reactor



Arsenic Deactivation Mechanism



Gaseous As_2O_3 oxidizes and reacts with active sites, but not all active sites*

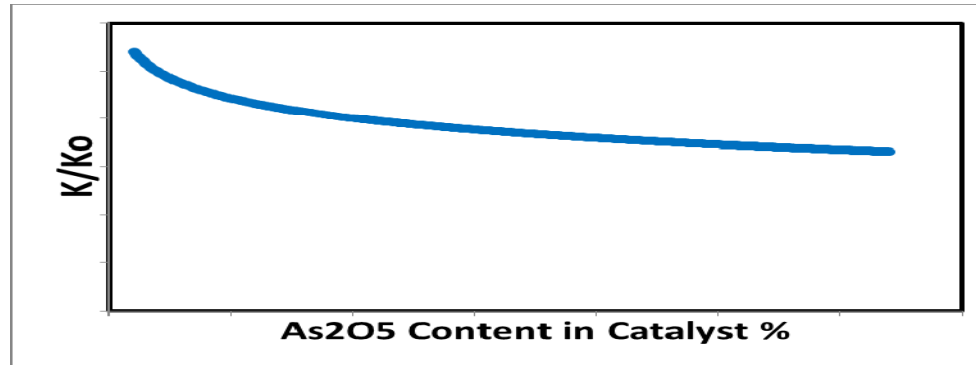


*(Catalysis Today (1998) 25-35)

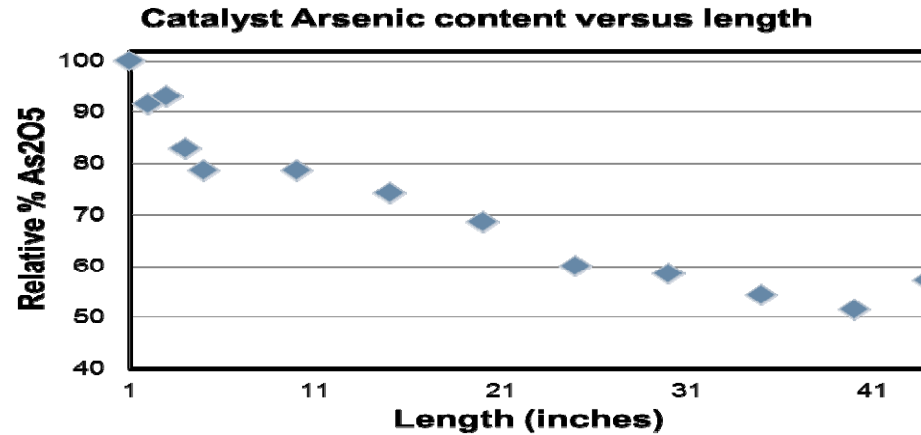
Deactivation Due to Arsenic



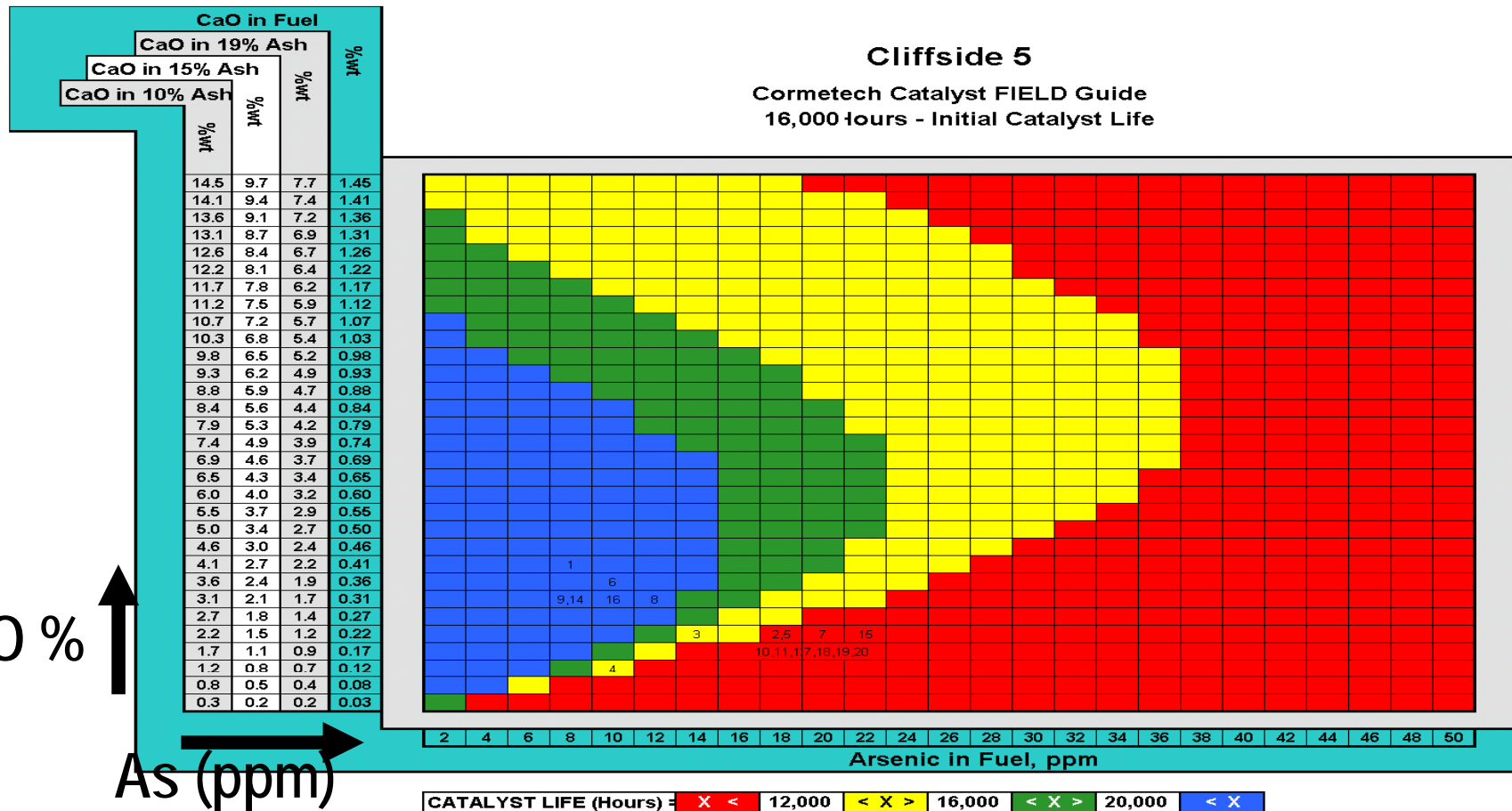
Deactivation levels off as As_2O_5 saturates available sites:



As_2O_5 content decreases with length as gaseous arsenic is captured by the catalyst (typical example):



Impact of Coal Composition



Mitigation of Arsenic Deactivation



Limestone Addition

- **Addition of Limestone (CaCO_3) to coal forms solid non-poisoning form**
 - $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$
 - $\text{As}_2\text{O}_3 (\text{g}) + 3\text{CaO} (\text{s}) + \text{O}_2 (\text{g}) \rightarrow \text{Ca}_3(\text{AsO}_4)_2 (\text{s})$
 - Successful experience in Japan, EU, and US
- **Examples of successful long-term experience**
 - Duke Cliffside
 - Limestone addition in operation since 2002.
 - Original top 2 layers was still in service as of ~67K hours
 - SCE&G Wateree Station
 - Limestone addition in operation since 2012.
 - Reduced deactivation consistent with FIELD Guide™

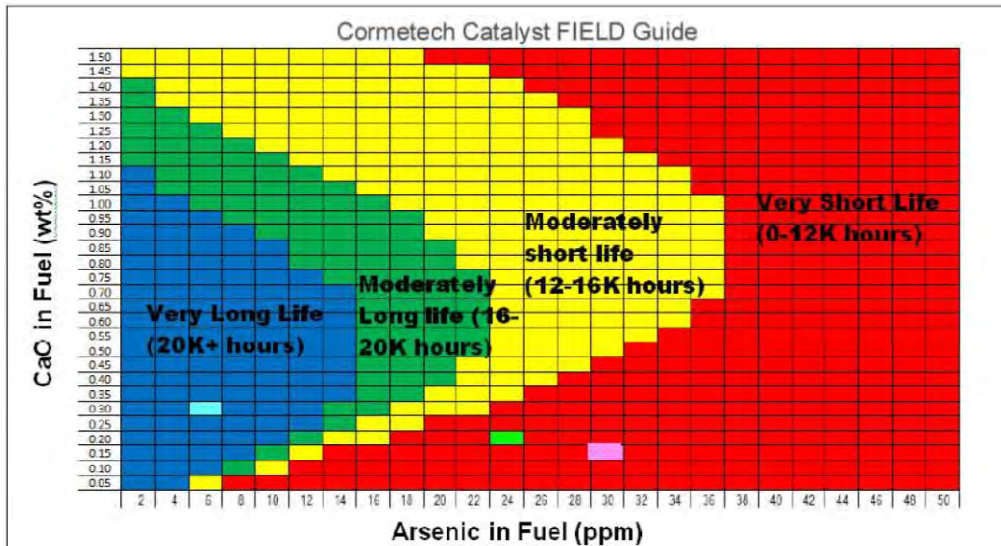
Mitigation of Arsenic Deactivation



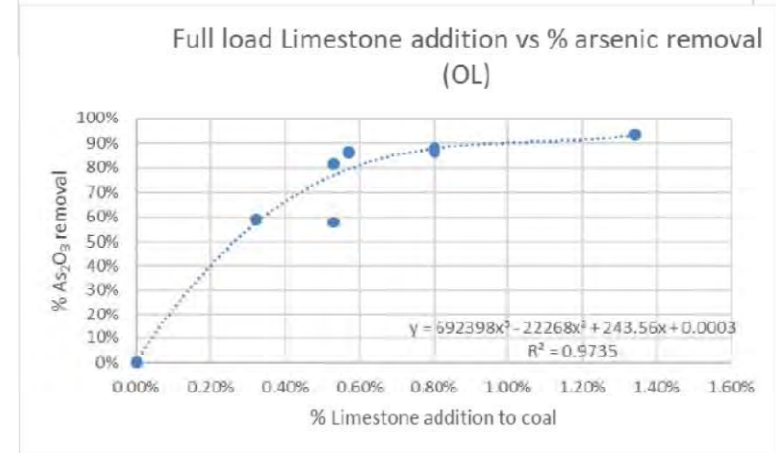
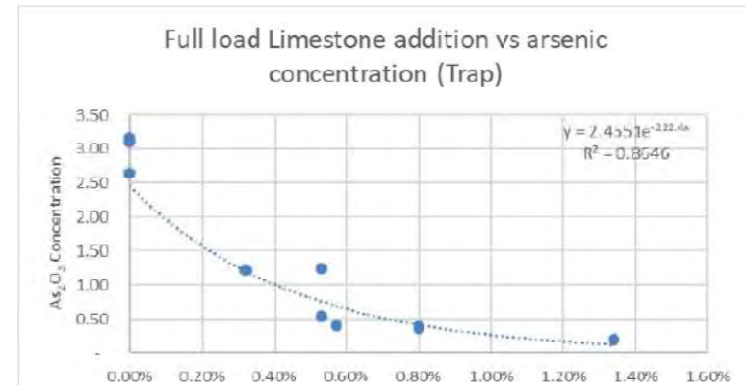
Mitigating Arsenic Poisoning of SCR Catalyst from Burning Gibson IB Coal

Jason Bookout (Technical Services)
February 19th 2018

2018 NO_x-Combustion-CCR
Round Table

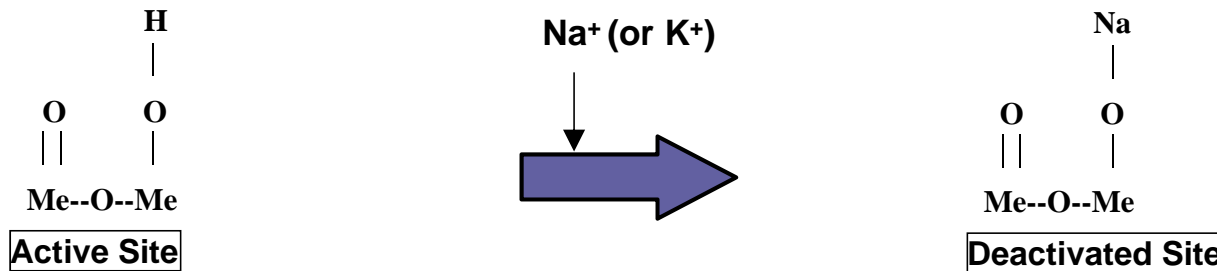


Arsenic in flue gas measured by sorbent trap ($\mu\text{g}/\text{m}^3$)



Alkali Deactivation Mechanism

- **Ash fume (sub-micron particles) accumulates on the catalyst surface, K and Na from salts in the ash can penetrate into the catalyst bulk**
 - PRB: typically Na Bit: typically K
 - K and Na react with catalyst active sites, and migrate into the catalyst wall



- **Na can also accumulates due to DSI (Dry Sorbent Injection) intended to reduce SO₃ upstream of the SCR.**
 - Need to consider trade-offs (SO₃ reduction benefit vs catalyst impact)
 - Change in deactivation may not be significant on units with pre-existing high deactivation rates.

Catalyst Channel Plugging



Plugging blocks access of flue gas to active sites within channels

- **Ash flows in a highly dilute phase (<25 ppm by volume even at 100 g/Nm³) and ash particles are small compared to catalyst openings, so it should flow through catalyst readily...**
- **...but of course, catalyst can and does plug**

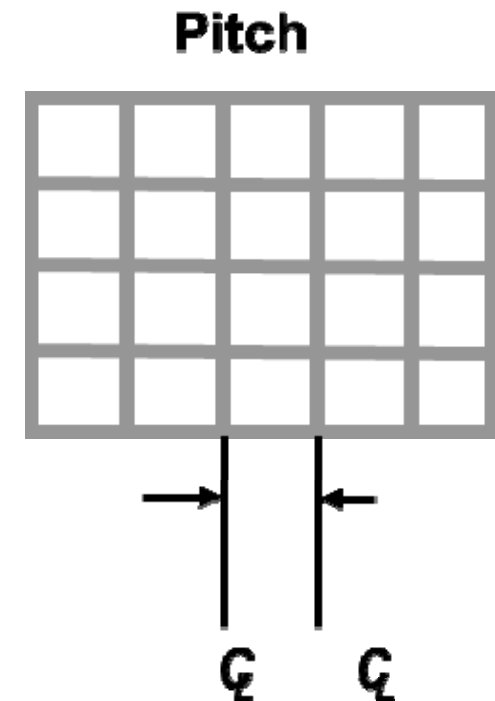
Honeycomb Type

Plate Type



Catalyst Plugging Mechanisms

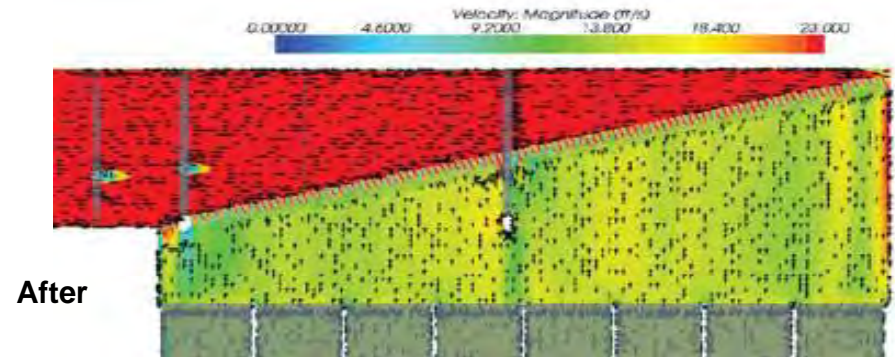
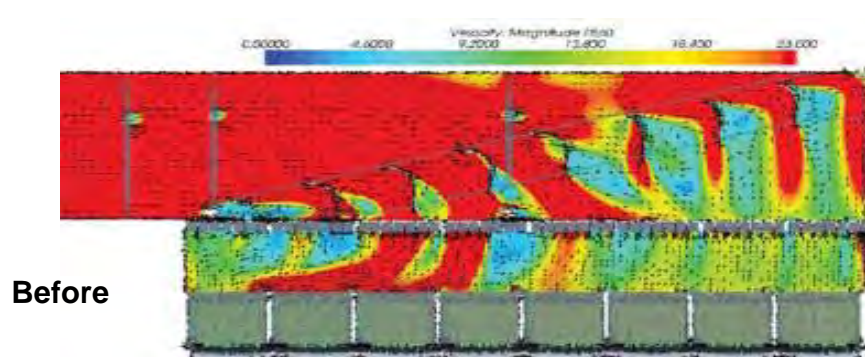
- **Large Particle Ash (LPA)**
 - Ash diameter near size of catalyst pitch or larger (Pitch typically 5.7 – 9.5 mm)
- **Collection of ash on upstream reactor surfaces and subsequent sloughing**
 - “Avalanche” will plug catalyst
 - Dense phase flow
 - Units w/ higher ash loadings are more susceptible
- **Poor ash flow (low velocity and/or recirculation zones, angular flow)**
 - Sticky ash may start to bridge on catalyst – usually localized
 - Units w/ higher ash loadings are more susceptible



Plugging Mitigation – Reactor Design



- **Reactor Design**
 - Flow path design
 - Flow / ash distribution correction devices
 - Prevention of ash accumulation on reactor surfaces
- **Reactor re-designs have been successful in addressing root-cause (Power Magazine October 2013):**



Plugging Mitigation – LPA Screens

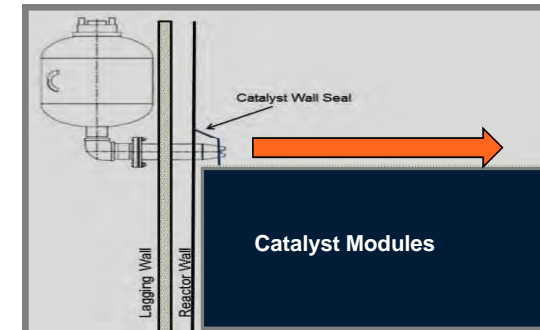
- Removes LPA upstream of catalyst
- Pleated design
 - Lower pressure drop
 - Less erosion
 - Self cleaning



Plugging Mitigation – Ash Sweeper



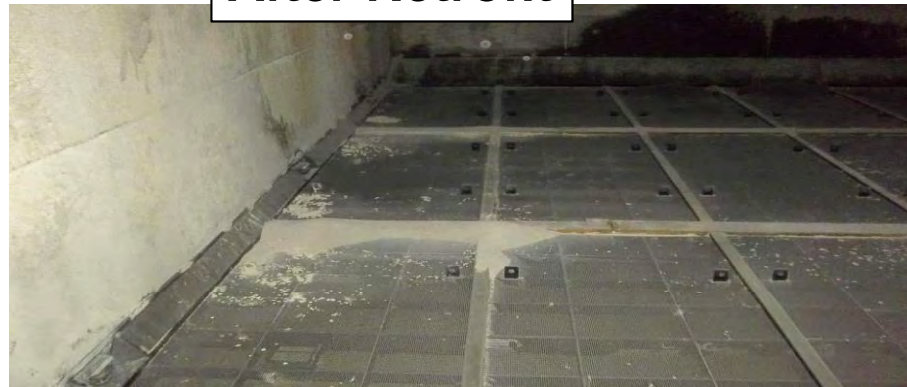
- Uses burst of air to re-entrain ash piles
- System Effectiveness
 - Near the walls
 - Top of the modules (module screen and above.)



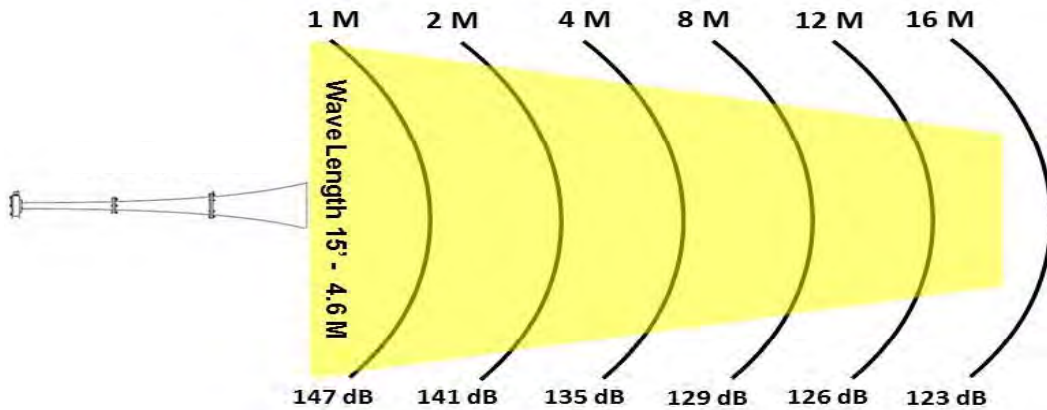
Before Retrofit



After Retrofit



Plugging Mitigation – Acoustic Cleaners



- Uses sonic waves for ash agitation



Plugging Mitigation – Ash Dispersion



Dust Buster™ Ash Dispersion Technology reduces density of ash flow, preventing plugging.

Lab Test

Large
Offset
From
Catalyst
Face

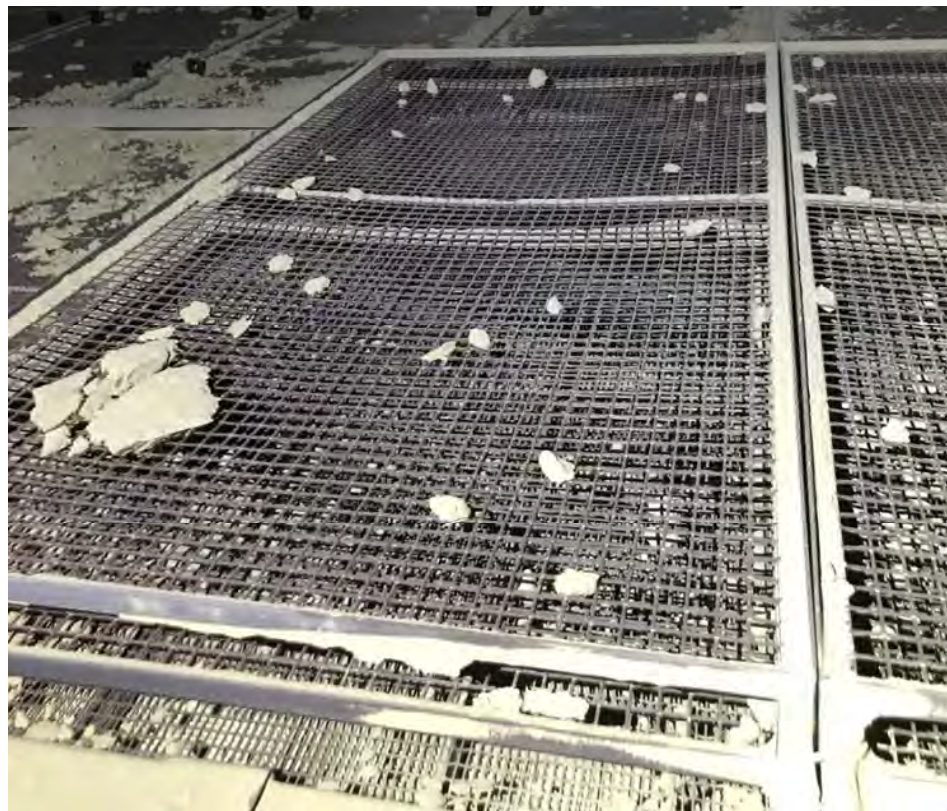


Dense
Phase
Ash Flow
From Sloughing

More
Dilute
Phase
Ash Flow

Patent Pending

Plugging Mitigation – Ash Dispersion



- Multi-layer ash dispersion screens installed in area of ash sloughing from overhead beam in center of reactor.
- Catalyst below screen pack has very little plugging

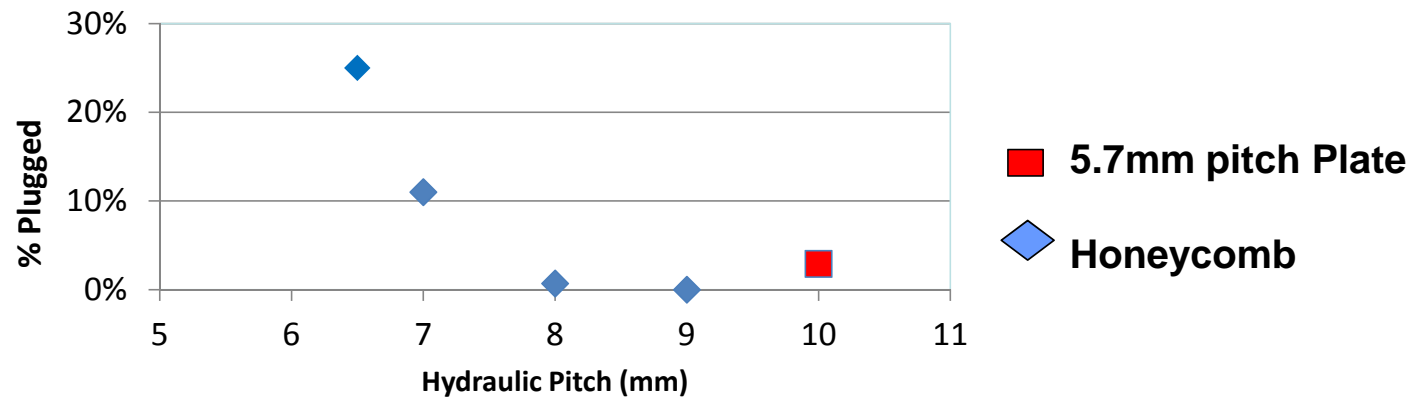
Module with screen pack installed.

Catalyst Considerations



• Catalyst Pitch Impact

- With sub-optimal reactor designs, larger pitch catalyst is less susceptible to plugging regardless of type
- Example: Sticky ash drop testing to simulate sloughing or piling due to sub-optimal reactor design:



Catalyst Considerations



- **Catalyst pitch selection**

- Good reactor design/re-design and/or ash accumulation mitigation devices allow the use of high surface area catalyst (e.g. 7mm pitch honeycomb), maximizing catalyst potential per layer and minimizing lifecycle costs
 - Best value in \$/potential
 - Minimizes change-out frequency
- However, sub-optimal reactor designs may utilize large pitch catalyst to prevent plugging.
 - Throughout entire layer
 - Or in areas susceptible to localized plugging, i.e. Hybrid
 - Potentially combined with ash accumulation mitigation devices
 - In severe cases, even the largest pitches can't solve all problems

Dust Buster™ Catalyst



Innovative catalyst for difficult coal-fired applications

- **Very high ash loading (e.g. > 40 g/Nm³ of flue gas)**
- **And/or sub-optimal reactor design:**
 - Ash collection zones in reactor
 - Poor ash distribution in reactor
- **Localized use or entire layer**
- **Available in 1350mm continuous layers**
 - Avoids plugging between sub-layers

CORMETECH
Dust Buster™



Dust Buster™ Catalyst



- **Operating in 8 units**
 - including demo modules, partial (hybrid) and full layers

Standard Module
(adjacent to boiler wall)



Module with Dustbuster™
(at boiler wall adjacent to standard module)
No significant plugging after 22 months of operation



In-situ Ice Blasting

- The Process
 - A mechanical method to remove SCR catalyst pluggage
 - No residue added to ash
 - No loss of catalyst material loss or performance
 - Works on all catalyst types



Patent: 8,268,743

Regeneration

- **Reverses the catalyst deactivation mechanisms**
 - Remove plugging and poisons
 - Replenish active sites
- **Can normally match the original catalyst's performance**
- **Some plate catalyst can present regeneration issues**
 - SO₃ ppm increase (% SO₂ Conversion) is most common issue due to corrosion of mesh
- **Regeneration can also change the original catalyst formulation to better meet current plant operating conditions**
- **If catalyst is no longer regenerable, recycling may be an option to avoid landfill disposal.**



Summary



- **Catalyst deactivation poisons active sites or blocks reactants from getting to them**
- **Solid calcium oxide fume reacts with sulfur trioxide to plug pores blocking reactants**
 - Can be predicted and accounted for based on calcium in coal
- **Gaseous phosphorous completely poisons active sites**
 - In staged units, P increase with catalyst length from release of gaseous P from calcium phosphate in ash
 - Depends on amount of reactive calcium phosphate formed during staged combustion
 - Can be mitigated with de-staging but must consider cost-benefit
- **Gaseous arsenic poisons certain active sites**
 - Decreases with catalyst length and saturates
 - Highly dependent on As and Calcium in the coal
 - Can be mitigated by limestone addition to reduce gaseous arsenic
- **Alkaline metals completely poison active sites**
 - Need to consider cost-benefit of DSI used to reduce SO₃
- **Plugging eliminates access to active sites**
 - Plugging due to sub-optimal reactor design
 - Can be mitigated by reactor redesign, mitigation devices, catalyst selection
- **Regeneration is used to reverse deactivation mechanisms and extend life-cycle**
- **Understanding above is key to effective life-cycle management**

Thank You

