REINHOLD ENVIRONMENTAL Ltd.

2018 NOx-Combustion Round Table & Expo Presentation

February 19-20, 2018, in St. Louis, MO / Hosted by Dynegy

Catalyst Deactivation Mechanisms

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Cormetech, Inc.

2018 NOx-Combustion-CCR Round Table

The “New” CORMETECH

CORMETECH RELIABILITY. DELIVERED.

Nov. 2017 CORMETECH CLEANER AIR THROUGH INNOVATION + STEAG SCR-Tech An Environmental Services Company

steag + EnergyCapital Partners

CORMETECH RELIABILITY. DELIVERED.

- New catalyst
- Regenerated catalyst
- Hybrid Systems
- Cradle to grave services
- Turnkey catalyst replacement
- Catalyst testing
- Mercury management

- Total field service offering
- Total SCR management
- Customized process solutions
- Ammonia storage systems
- Ammonia slip catalyst
- PAC addition to FGD’s
- Ash sweepers

- Acoustic cleaners
- Ice blasting
- SCR Design
- LPA screens
- SNCR design
- CO / VOC catalyst
- Flow modeling

Total Lifecycle Management

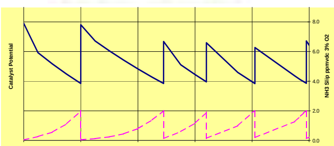
Overview

- **Background**
- **Primary deactivation mechanisms**
  - Calcium & Phosphorous
  - Arsenic
  - Alkaline metals
  - Catalyst Channel Plugging
- **For each mechanism**
  - Chemical/physical mechanism
  - Factors
  - Mitigation
- **Regeneration**

Background

Catalyst Life-Cycle Management

Cycle primarily driven by catalyst deactivation



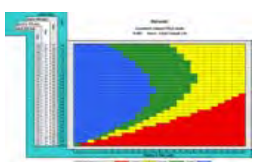
On-line cleaning,
In-situ Ice Blasting,
coal & ash monitoring,
and other deactivation
mitigation steps

Monitoring & Addition/ Replacement Management

Design & Manufacture or Regenerate

Installation & Commissioning

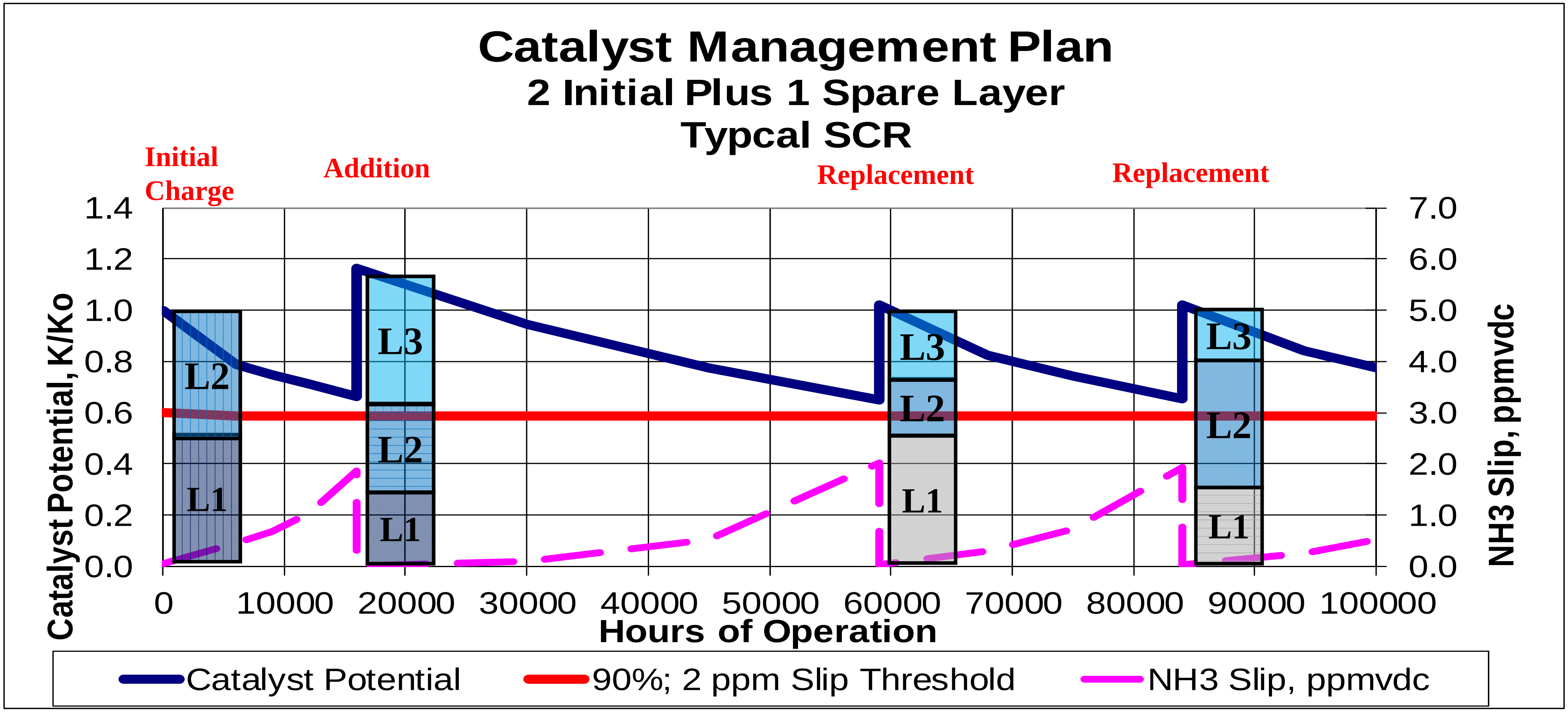
Operation & Maintenance



Regenerate or Dispose

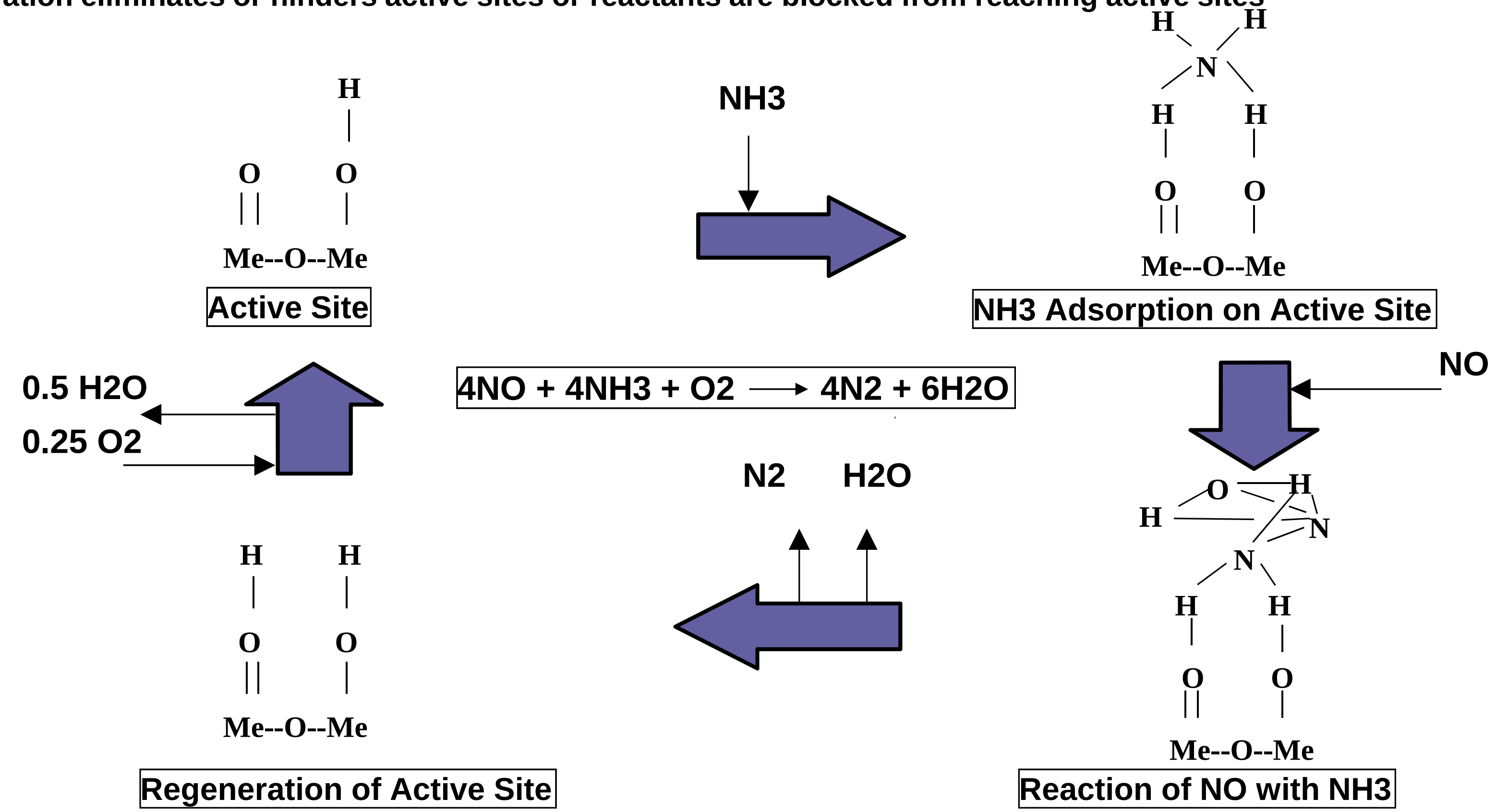
Impact on Catalyst Management

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



Reaction Mechanism

Deactivation eliminates or hinders active sites or reactants are blocked from reaching active sites



*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.

Primary Deactivation Mechanisms

- Calcium & Phosphorous
- Arsenic
- Alkaline metals
- Catalyst Channel Plugging

Understanding:

- Chemical/physical mechanism
- Factors

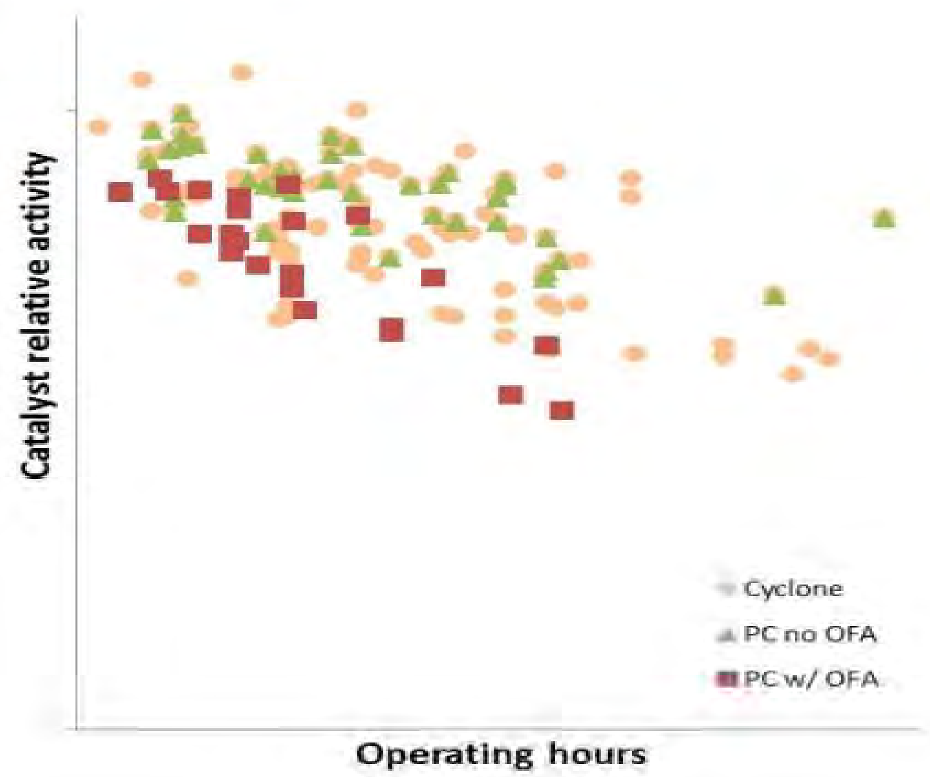
Leads to:

- Mitigation

Calcium and Phosphorous Deactivation

- **Primary deactivation mechanisms for PRB-Fired Applications**

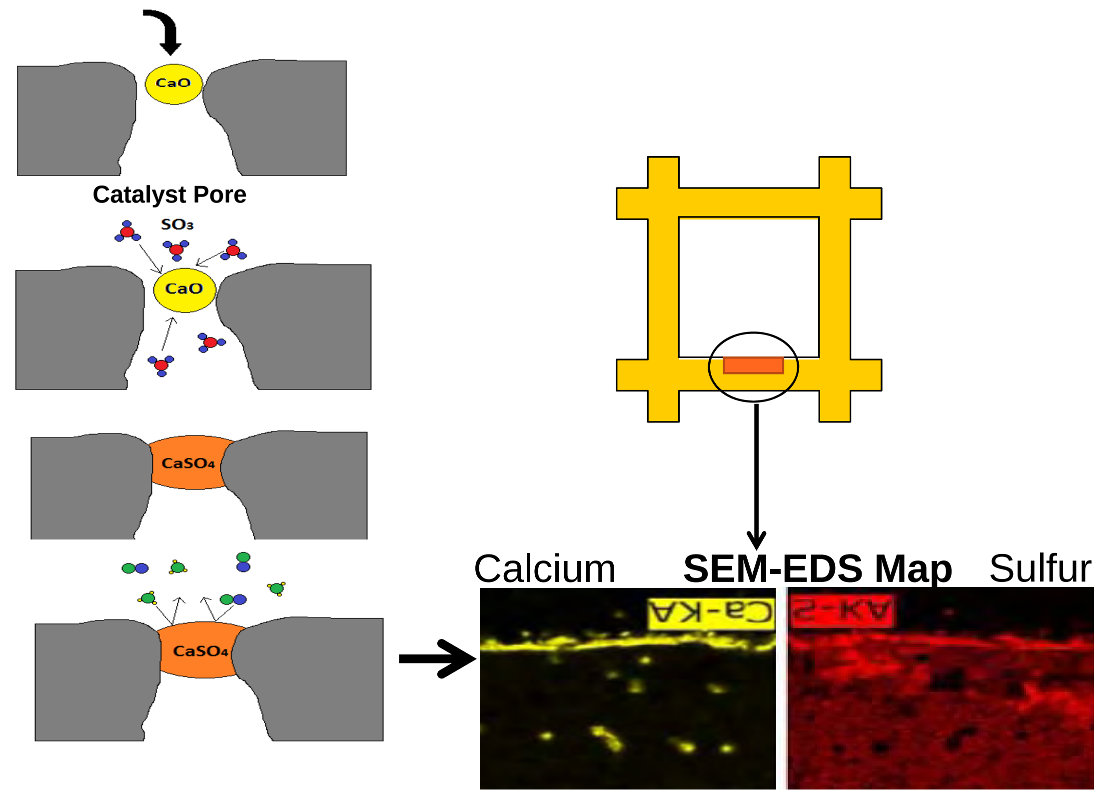
- **Wide range of measured catalyst deactivation rates**



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.**
3. **SO_3 diffuses to CaO particle.**
4. **SO_3 and CaO react to form $CaSO_4$. Particle swells by ~14%.**
5. **$CaSO_4$ plugs pore: NH_3 and NO_x are blocked from active sites.**

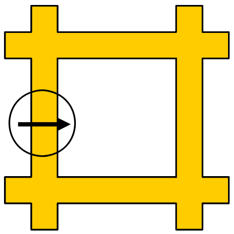


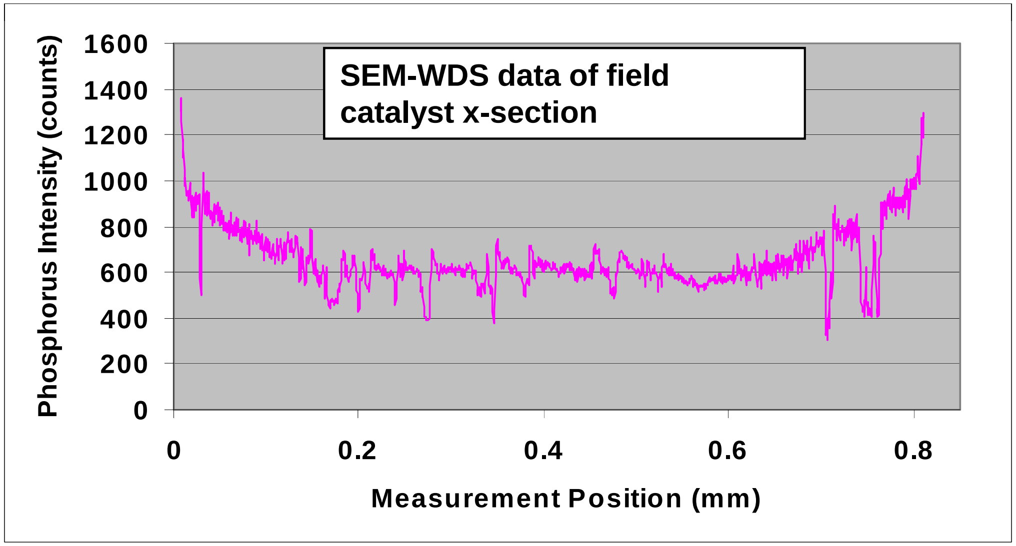
Rate depends on amount of sub-micron CaO available in flue gas.

Phosphorous Deactivation Mechanism

PRB Units

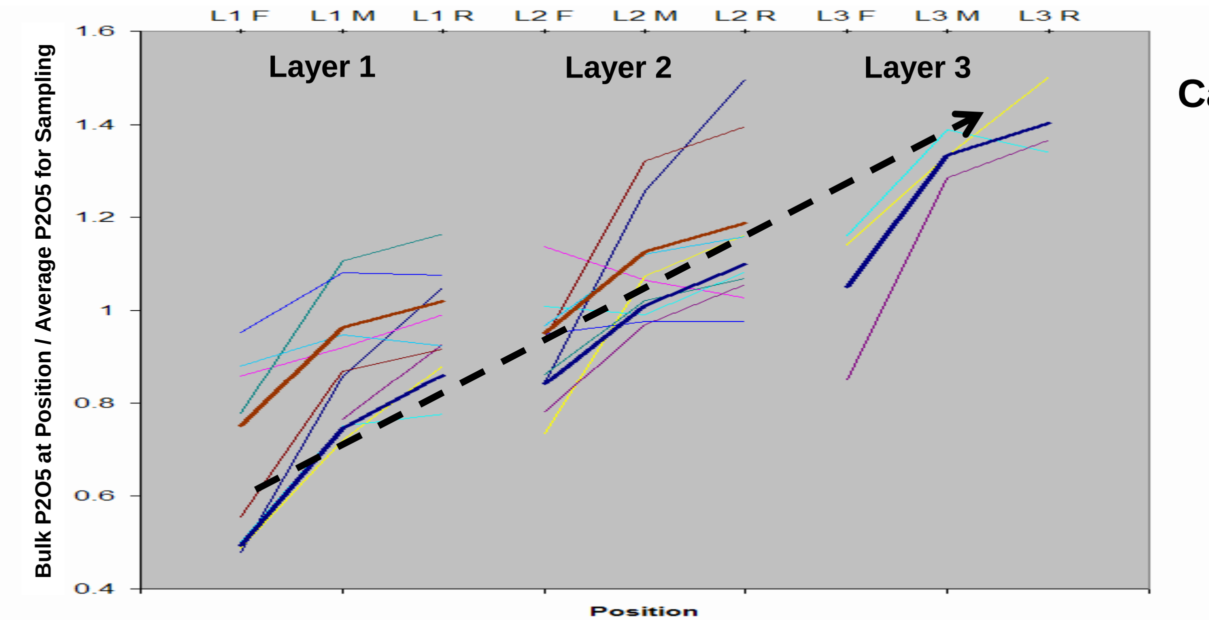
- **Phosphorus is a penetrating poison**
  - Diffuses into the catalyst bulk and chemically bonds with active sites
  - Profile in catalyst wall indicates P species is gas phase, e.g. H_3PO_4





Phosphorous Deactivation Mechanism

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



(P in ash) (SO3 made in SCR)

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

(gaseous P that deactivates SCR)

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

SO3 Impact on Gaseous P Generation

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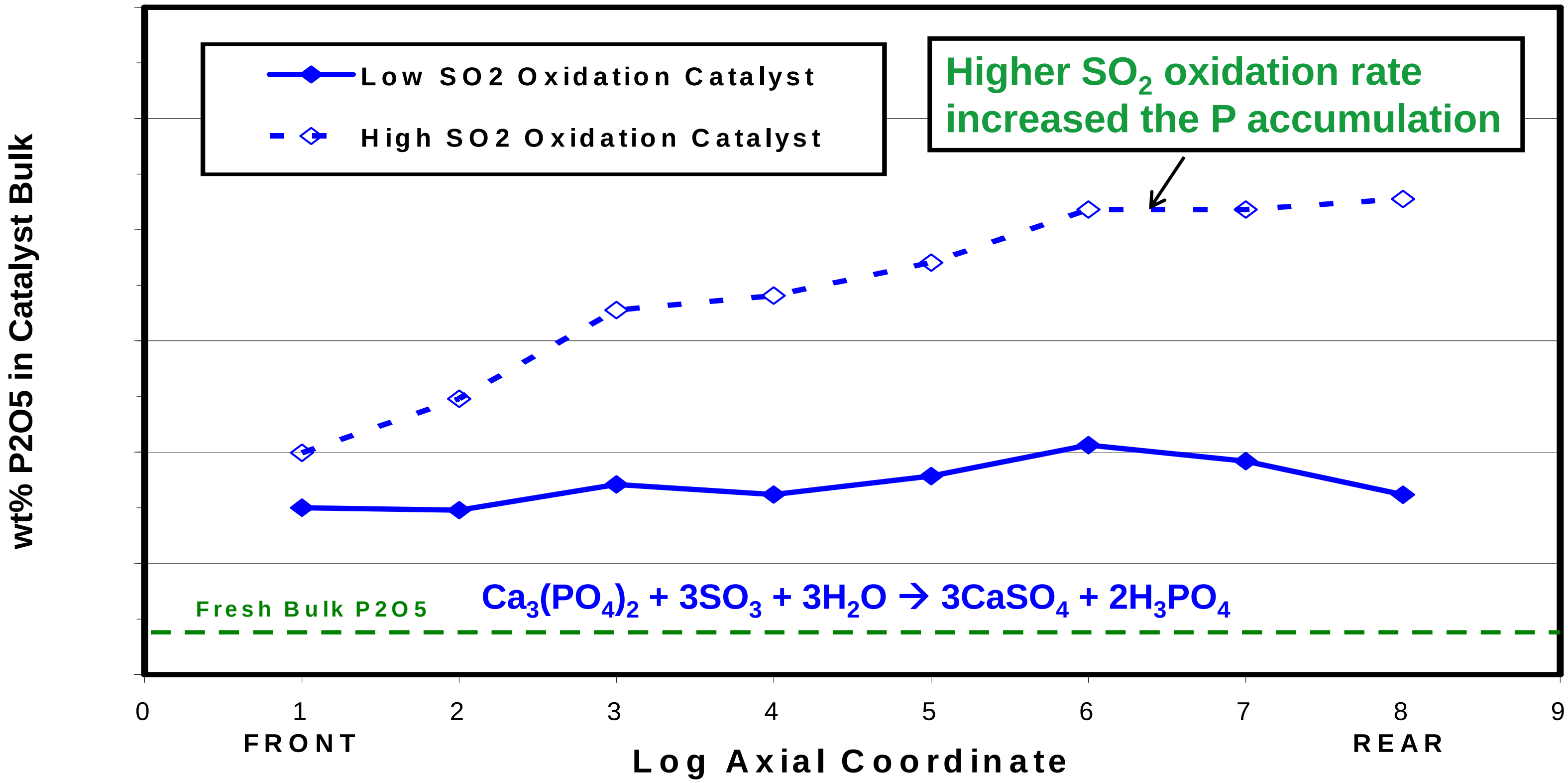
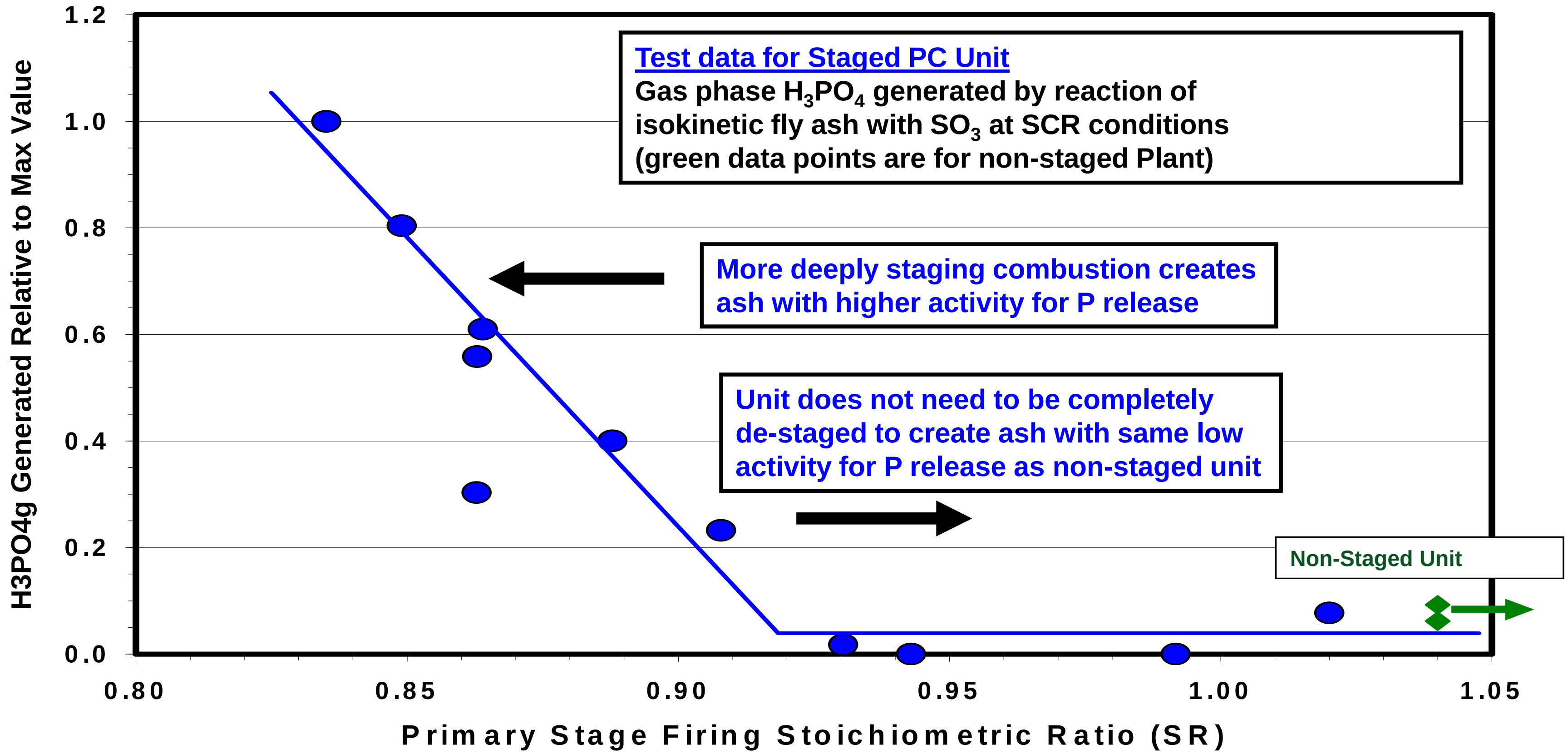
Two ½ cross-section catalyst samples (one with low and one with high SO_2 oxidation rate) in single sample tray and loaded it into a Staged PC PRB Unit SCR module for aging.

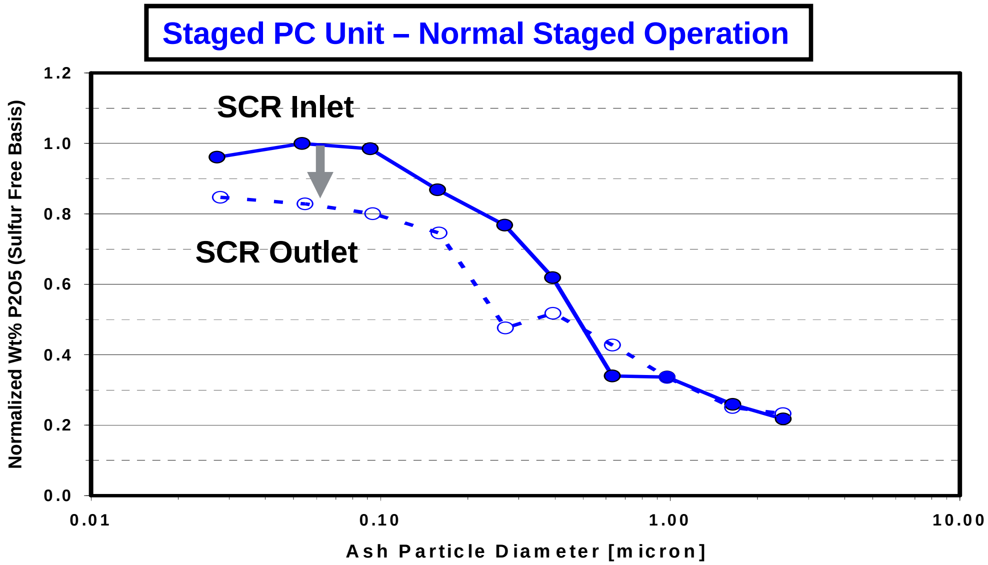


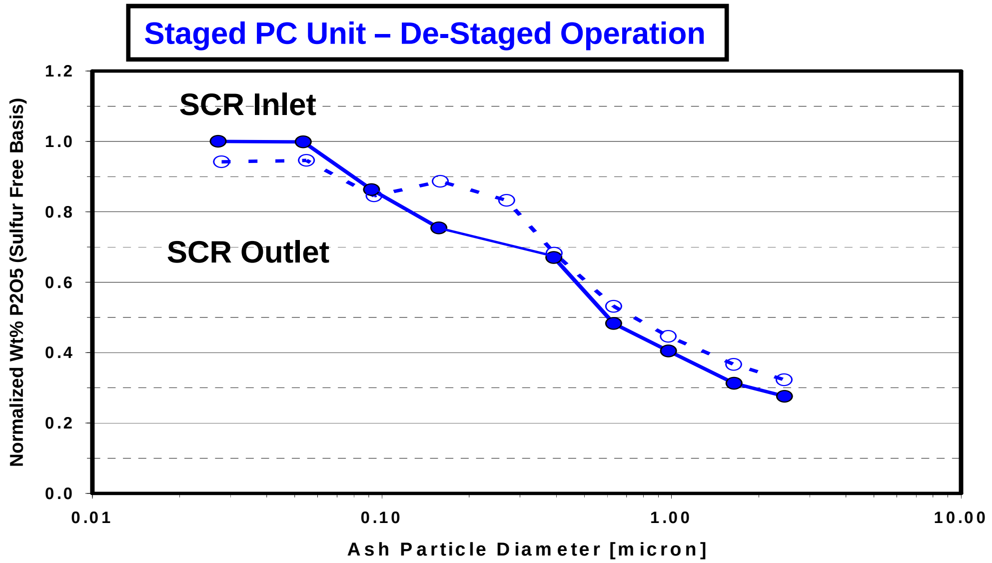
Combustion De-Staging Impact on Gaseous P Generation



Combustion De-Staging Impact on Gaseous P Generation

SCR-inlet and SCR-outlet, particle size segregated ash analysis

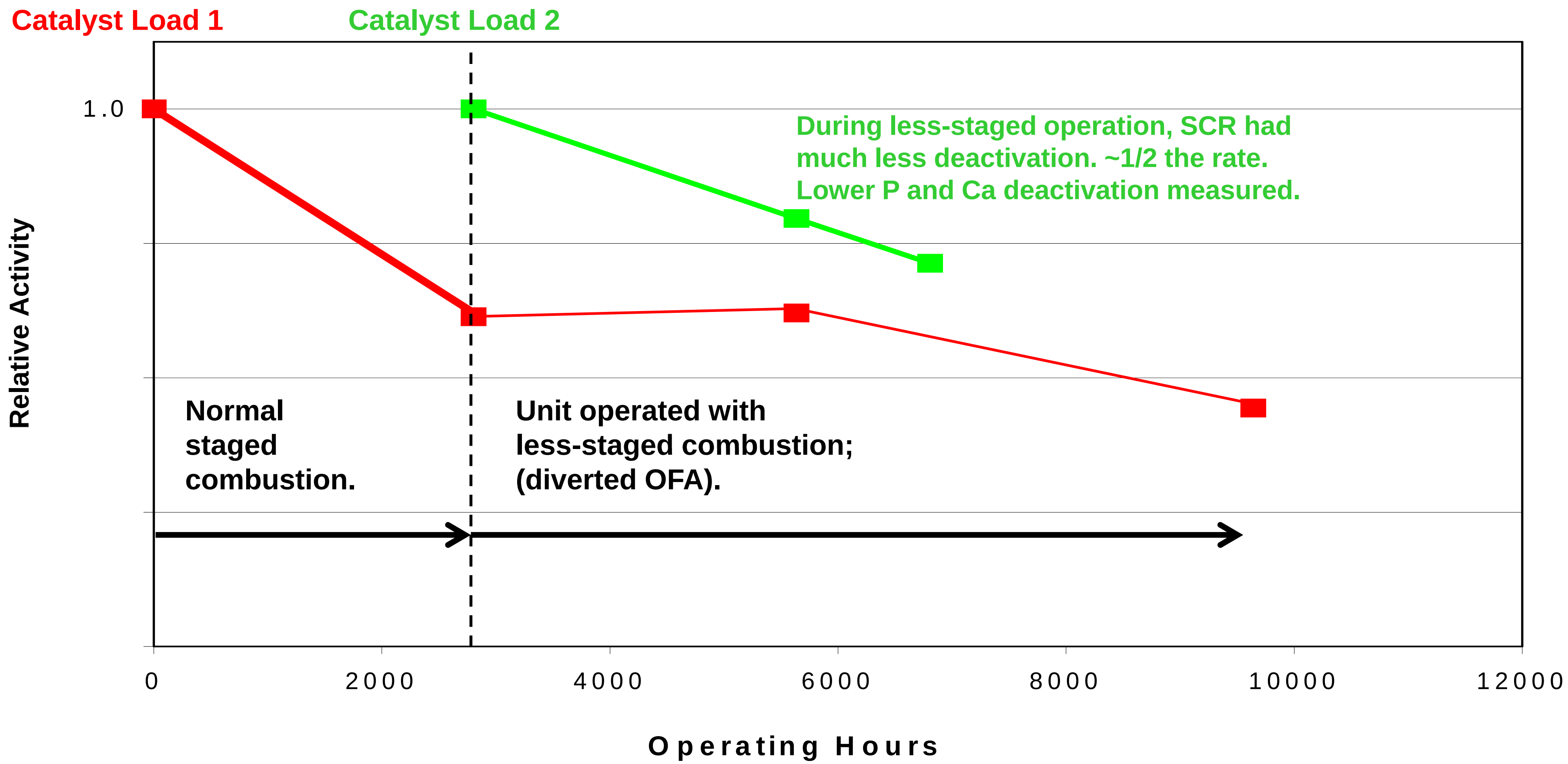




- **Operating the unit de-staged reduced the amount of P lost from the ash fume across the SCR (i.e., reduces the activity of the $Ca_3(PO_4)_2$ in the ash fume)**

Combustion De-Staging Impact on Gaseous P Generation

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



Mitigation of P and Ca Deactivation by De-Staging

- **Case-by-case Cost Benefit Analysis**
  - **Costs:**
    - More reactor potential required to achieve higher DeNOx at higher inlet NOx
      - Does not need to be completely de-staged, i.e. non-staged
    - Higher NH_3 usage rate
  - **Benefits:**
    - Less change in catalyst potential over time (fewer catalyst management actions)
    - Potential lower LOI
    - Potential reduction in boiler tube wastage

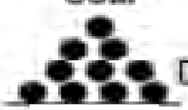
For more information on Ca & P Deactivation:
SCR Catalyst Deactivation for PRB-Firing Coal Utility Boilers by Chris Bertole at 2013 Reinhold NOx Combustion Round Table
SCR Catalyst Deactivation by P and Ca in Utility Boilers Firing PRB Coals by Rutherford and MacInnes 2016 Reinhold NOx Combustion-CCR Round Table

Arsenic Deactivation Mechanism

Gaseous As_2O_3 is decreased by reaction with CaO.

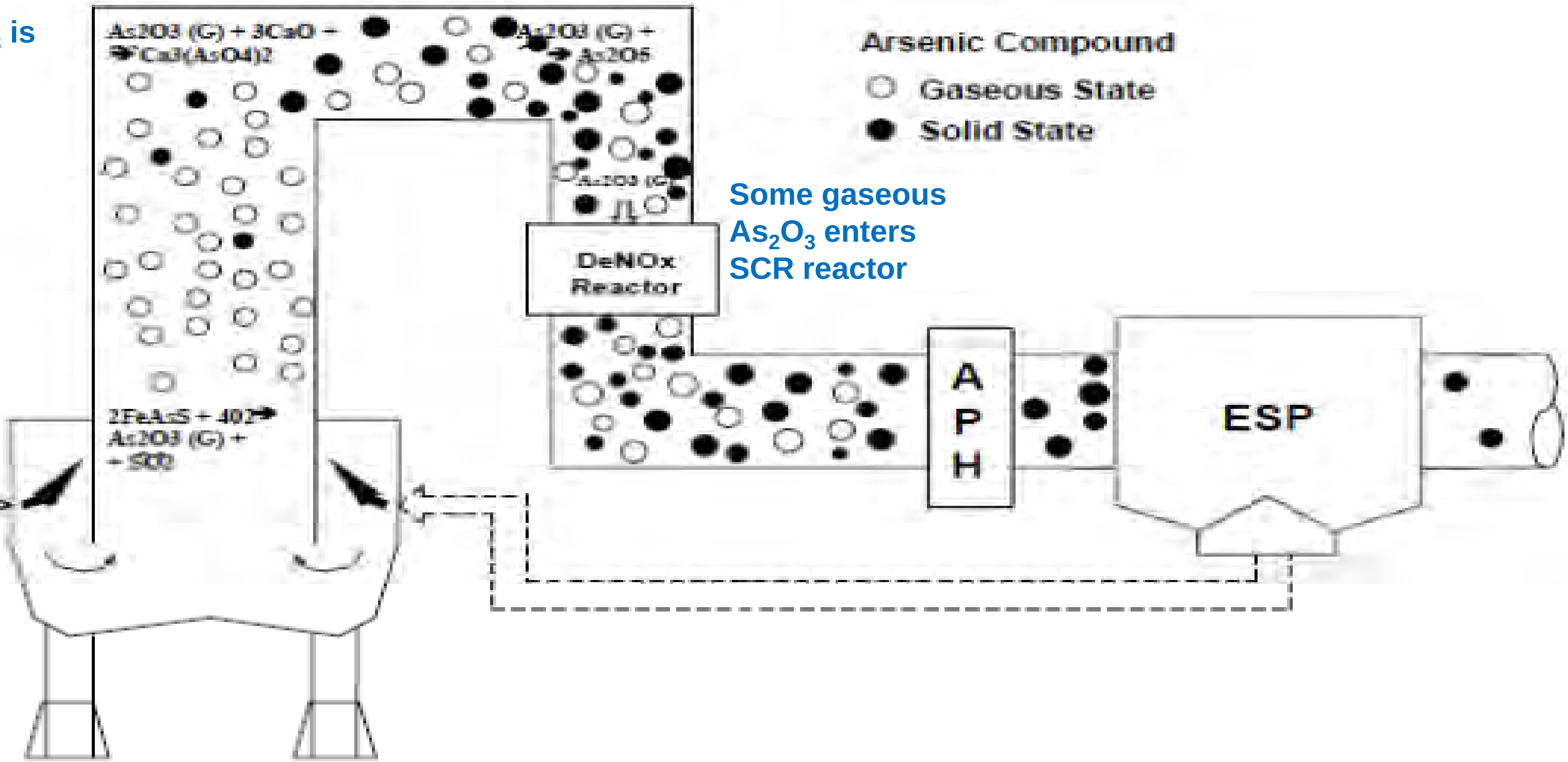
Arsenopyrite in coal oxidizes to form gaseous As_2O_3.

Coal



FeAsS

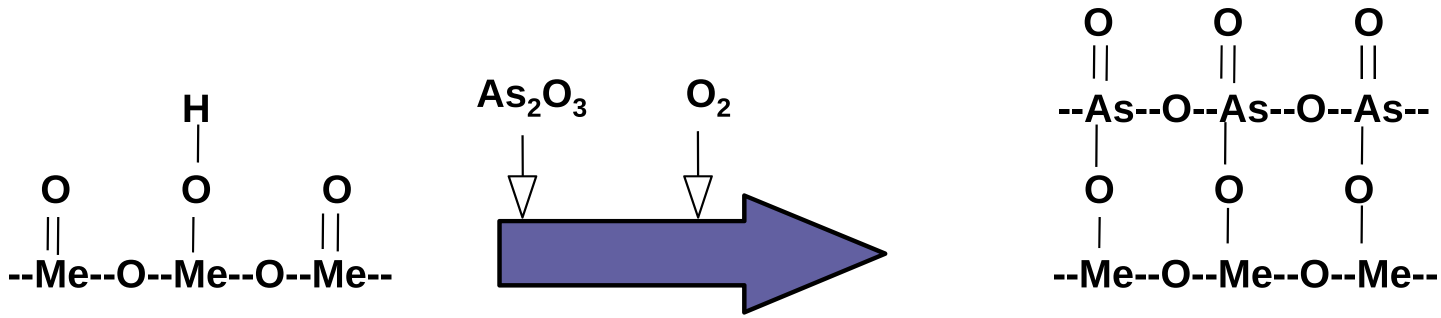
Arsenopyrite



Some gaseous As_2O_3 enters SCR reactor

Arsenic Deactivation Mechanism

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



*(Catalysis Today (1998) 25-35)

Deactivation Due to Arsenic

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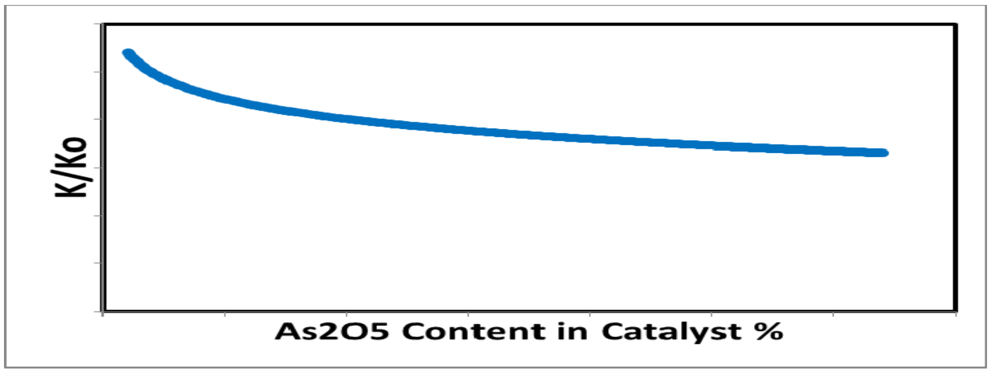
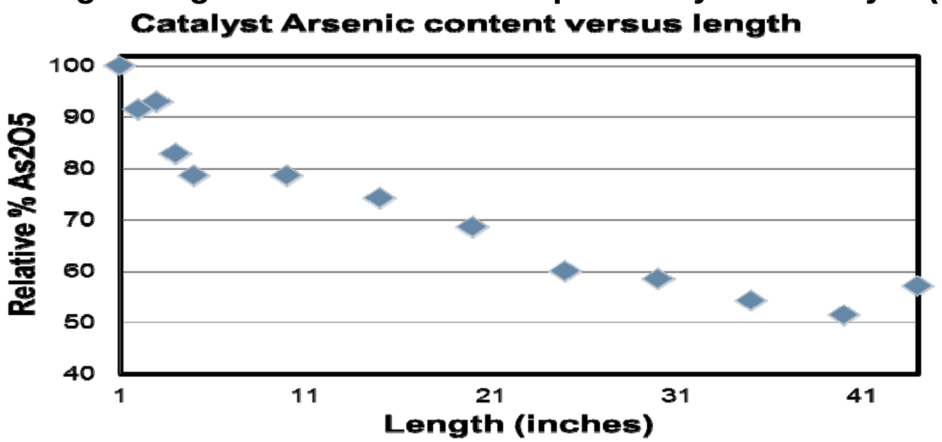
Deactivation levels off as As_2O_5 saturates available sites:

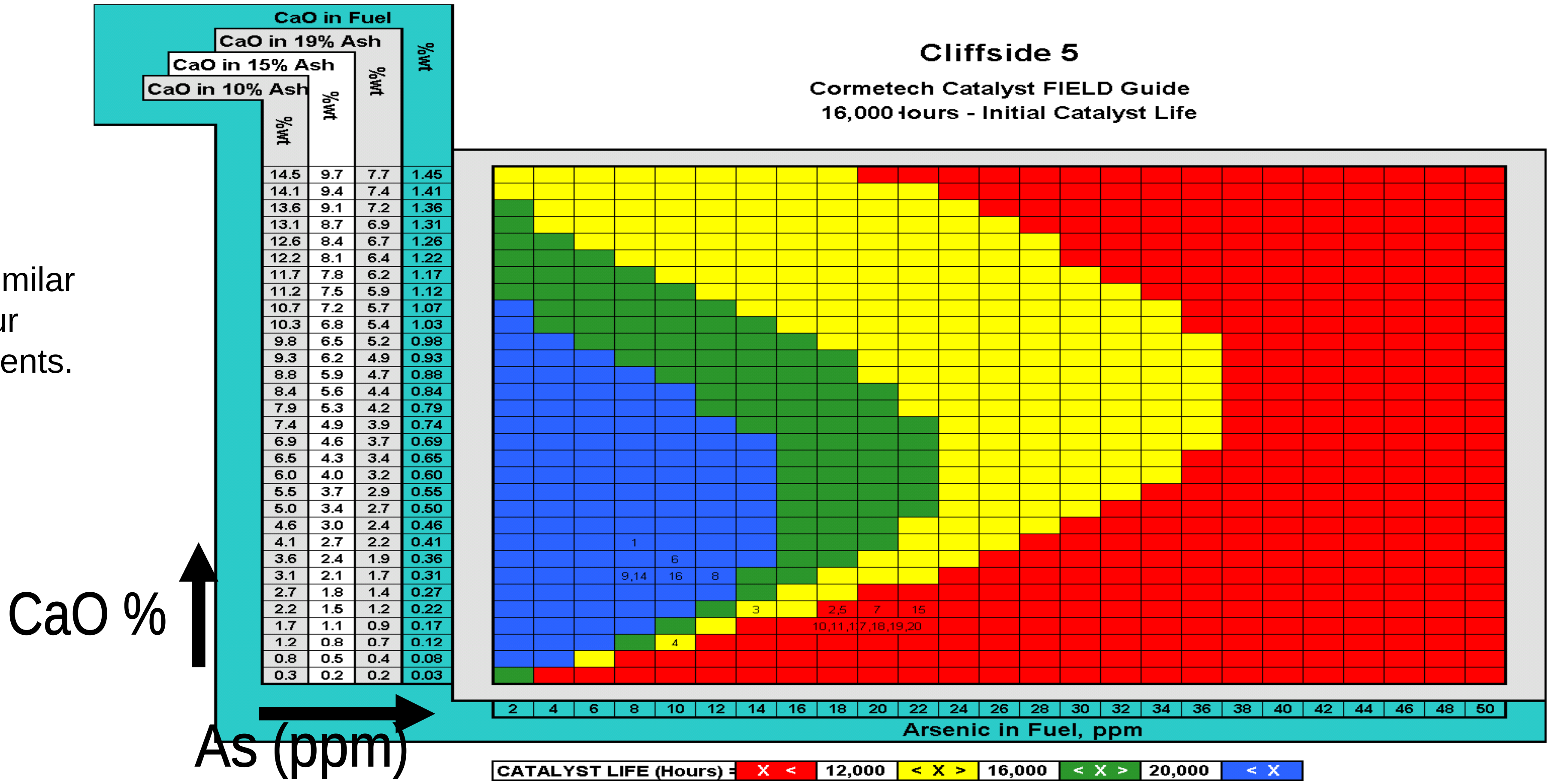


As_2O_5 content decreases with length as gaseous arsenic is captured by the catalyst (typical example):



Impact of Coal Composition

At similar sulfur contents.



Mitigation of Arsenic Deactivation

Limestone Addition

- **Addition of Limestone ($CaCO_3$) to coal forms solid non-poisoning form**
  - $CaCO_3 \rightarrow CaO + CO_2$
  - As_2O_3 (g) + 3CaO (s) + O_2 (g) $\rightarrow$ $Ca_3(AsO_4)_2$ (s)
  - Successful experience in Japan, EU, and US
- **Case Studies**
  - Duke Cliffside
    - Initial report: Mega Symposium May 2003 by Duke Energy, Riley Power, and Cormetech
  - SCE&G Wateree Station
    - Limestone addition in operation since 2012.

Mitigation of Arsenic Deactivation

Limestone Addition – Duke Cliffside

- **Typical arsenic content of coal is ~10ppm, but with some coals reaching 20ppm.**
- **Limestone addition installed in 2002**
- **In operation continuously since then**
- **Rate: 6 pounds of limestone per ton of coal**
  - No change since start of operation
- **Original two (2) top layers of catalyst still is service at ~67,000 operating hours**
  - Arsenic levels still far from saturation

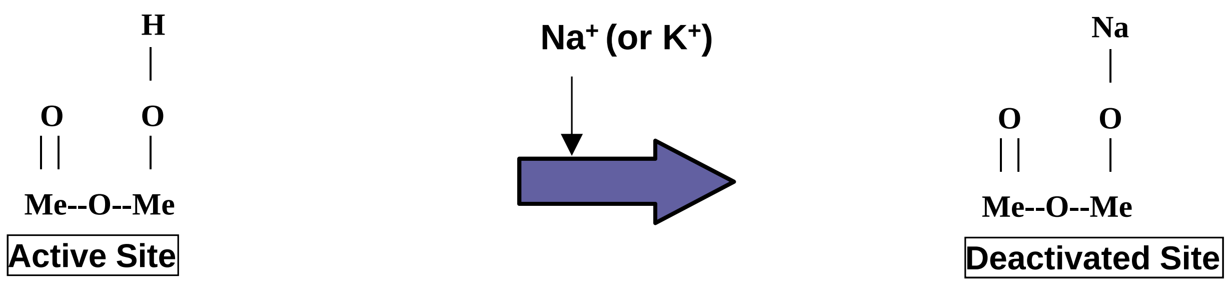
Mitigation of Arsenic Deactivation

Limestone Addition – SCE&G Wateree Station

- **Limestone addition started in 2012**
- **LSFO WFGD provided readily available, low cost, limestone source**
- **Reported by Andrew Walker at 2013 Cormetech Users' Group Meeting:**
  - Material flow
    - Limestone is a very unforgiving material
    - Flop gate must be cleaned regularly
    - Angle of repose is critical in designing a successful system
  - No boiler fouling/slagging
  - No adverse impact on ash sales
  - Increasing CaO in ash from 1.1% to 4.3%
    - <6,500 ton/yr, < $200,000/yr, cost in fuel base
  - Following catalyst test indicated greatly reduced deactivation rate
- **2018 Update: Reduced deactivation consistent with FIELD Guide™.**

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

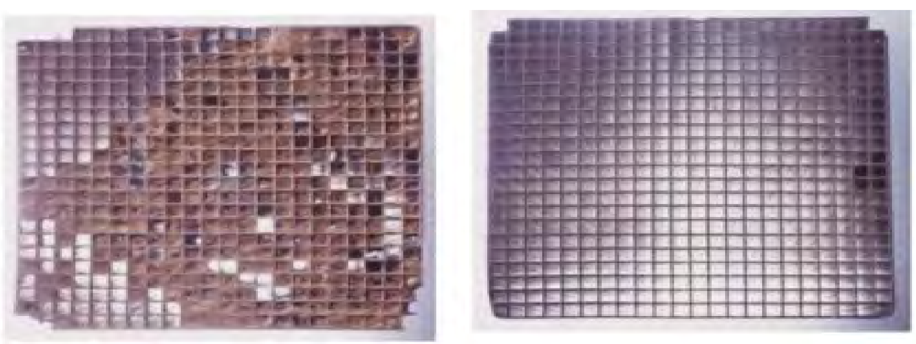
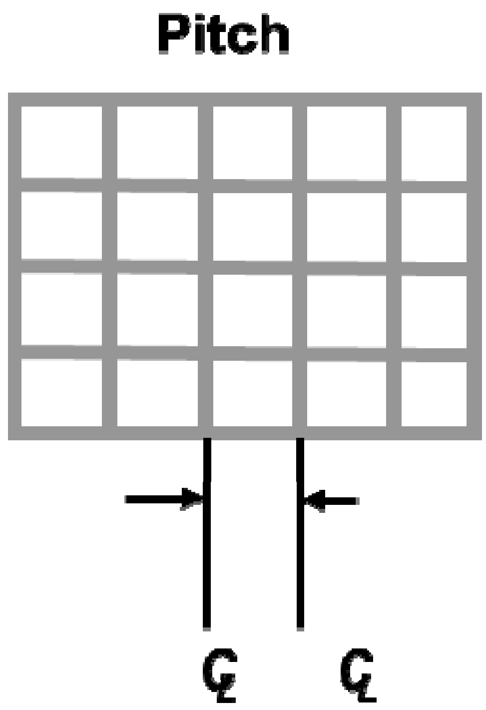


Plate Type

Catalyst Plugging Mechanisms

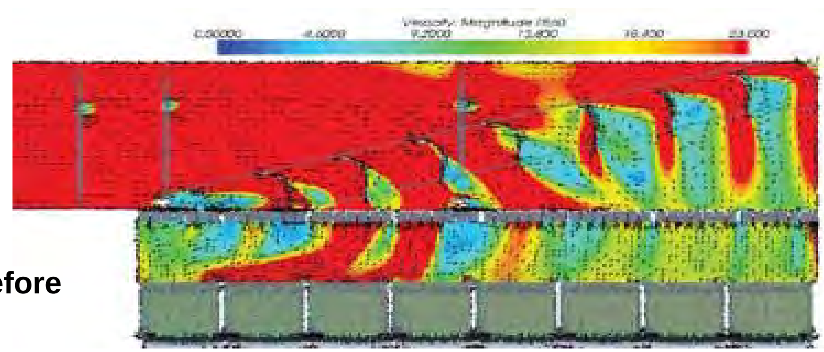
- **Large Particle Ash (LPA)**
  - Ash diameter near size of catalyst catalyst pitch or larger (Pitch typically 5.7 – 9.5 mm)
- **Collection of ash on upstream reactor surfaces and subsequent sloughing**
  - “Avalanche” will plug catalyst
    - Dense phase flow
  - Units w/ higher ash loadings are more 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



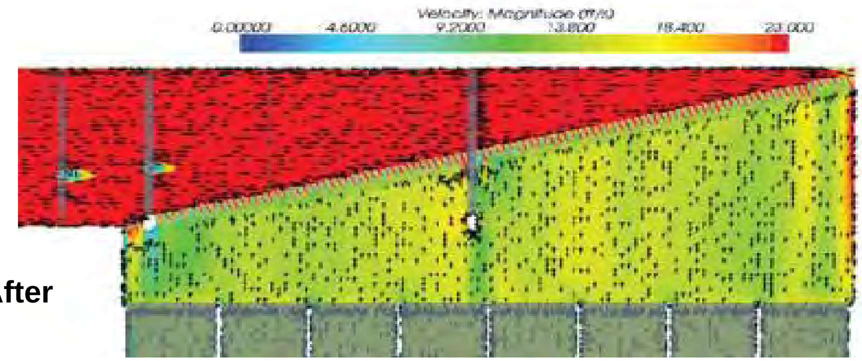
Plugging Mitigation – Reactor Design

- **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):**

Before



After

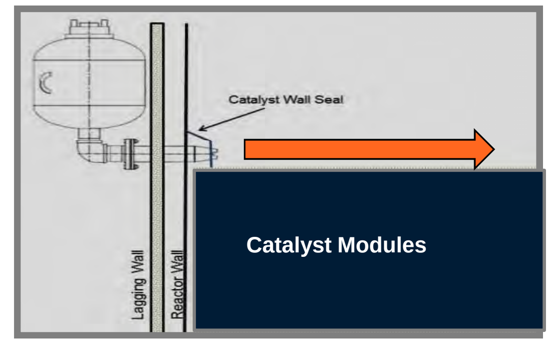


Plugging Mitigation – LPA Screens

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

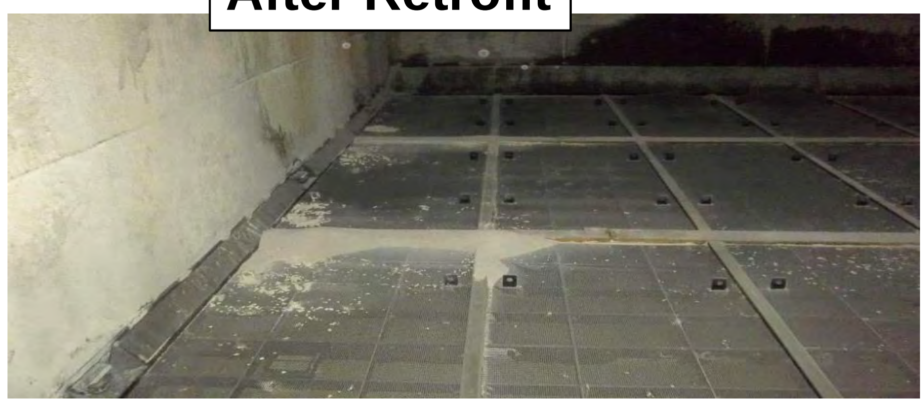
Plugging Mitigation – Ash Sweeper

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

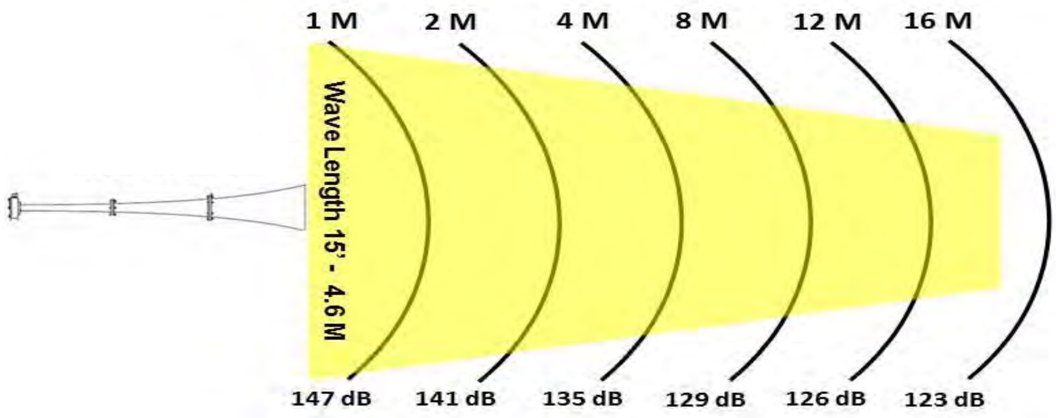


Before Retrofit

After Retrofit



Plugging Mitigation – Acoustic Cleaners



- **Uses sonic waves for ash agitation**

Plugging Mitigation – Ash Dispersion

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

Lab Test

Dense Phase Ash Flow From Sloughing

Large Offset From Catalyst Face

More Dilute Phase Ash Flow

Patent Pending

Plugging Mitigation – Ash Dispersion

Recent field installation with multi-layer dispersion technology.

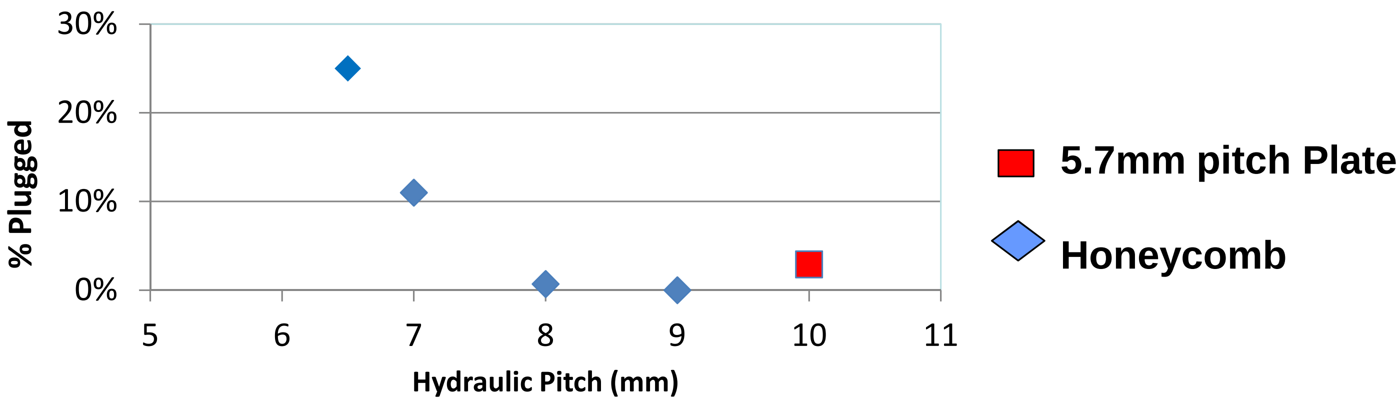
Localized use
in area with ash
sloughing upstream.

Augments
other on-line
cleaning systems

Patent Pending

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:**
  - Large 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

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

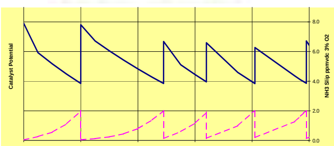
Patent: 8,268,743

Regeneration

- **Reverses the catalyst deactivation mechanisms**
  - Remove plugging and poisons
  - Replenish active sites
- **Can normally match the original catalyst's performance**
- **Regenerating "original" catalyst to meet "current" catalyst formulation may not be possible in some cases**
- **Some plate catalyst can present significant regeneration issues**
  - SO3 ppm increase (% SO_2 Conversion) is most common issue
- **Regeneration can also change the original catalyst formulation to better meet current plant operating conditions**

Summary

Cycle primarily driven by catalyst deactivation



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Monitoring & Addition/ Replacement Management

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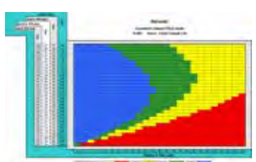
Regenerate or Dispose

Catalyst deactivation understanding leads to:
Deactivation mitigation
&
Optimized catalyst management

Minimizing life-cycle costs

Operation & Maintenance



Installation & Commissioning

Thank You