REINHOLD ENVIRONMENTAL Ltd.

# 2019 NOx-Combustion-CCR Round Table Presentation

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

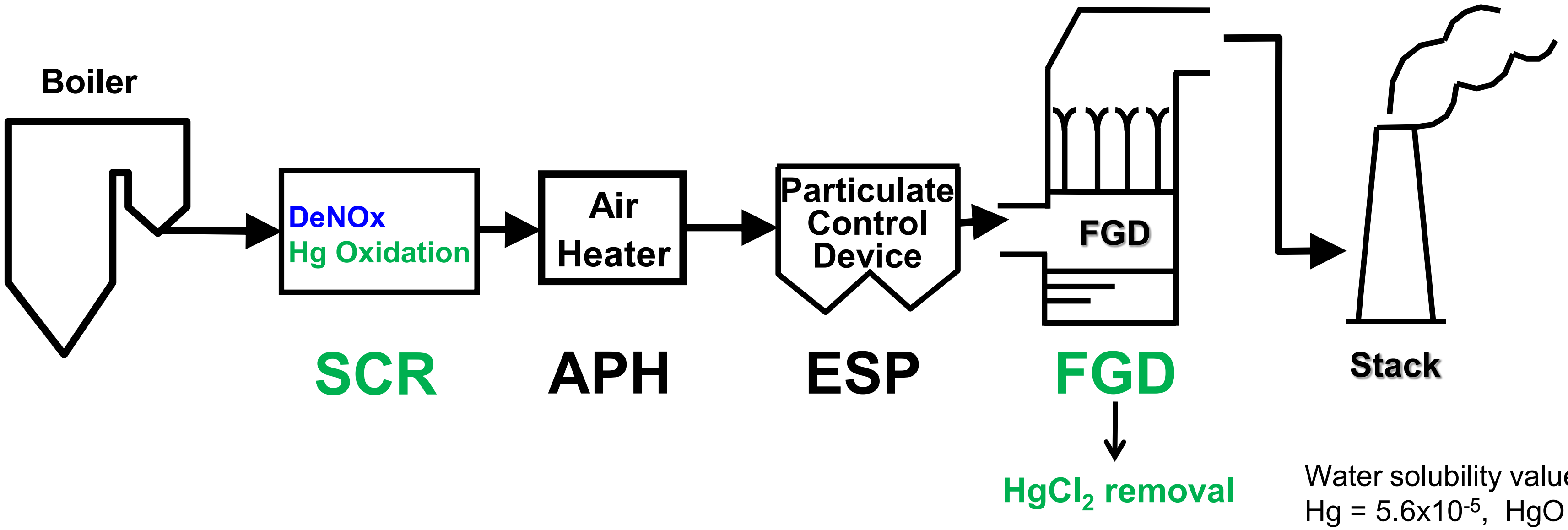
# SOx and the SCR - How Sulfur Influences Catalyst Operation

Christopher Bertole

2019 Reinhold NOx-Combustion-CCR Round Table

# Introduction – SCR Functions

- Reduce NOx $4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$
- Oxidize Hg $2Hg + 4HCl + O_2 \rightarrow 2HgCl_2 + 2H_2O$
  $2Hg + 4HBr + O_2 \rightarrow 2HgBr_2 + 2H_2O$




Water solubility values (g/l) at ~20°C:
Hg = $5.6 \times 10^{-5}$, HgO = $5.3 \times 10^{-2}$, $HgCl_2$ = 74

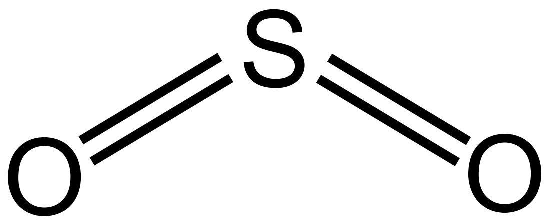
***Key: SCR on coal-fired boiler application must be able to perform with sulfur gases present.***

# Sulfur in Coal

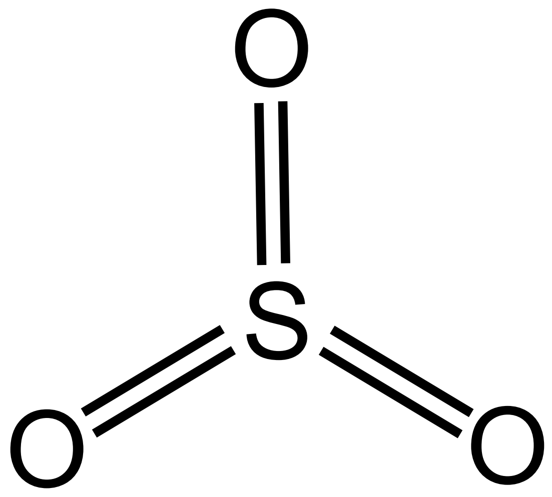
- **Form**
  - Inorganic sulfides [$FeS_2$ (pyrite)]
  - Inorganic sulfates [$CaSO_4$, $FeSO_4$]
  - Organosulfur compounds
- **Amount**
  - Bituminous generally has higher sulfur content (<5wt%) than PRB (<2wt%)
- **Release during combustion**
  - ~100% of sulfur is volatilized from the burning char particle.
  - Present in the flue gas in the oxidized state as…

# Sulfur in Flue Gas

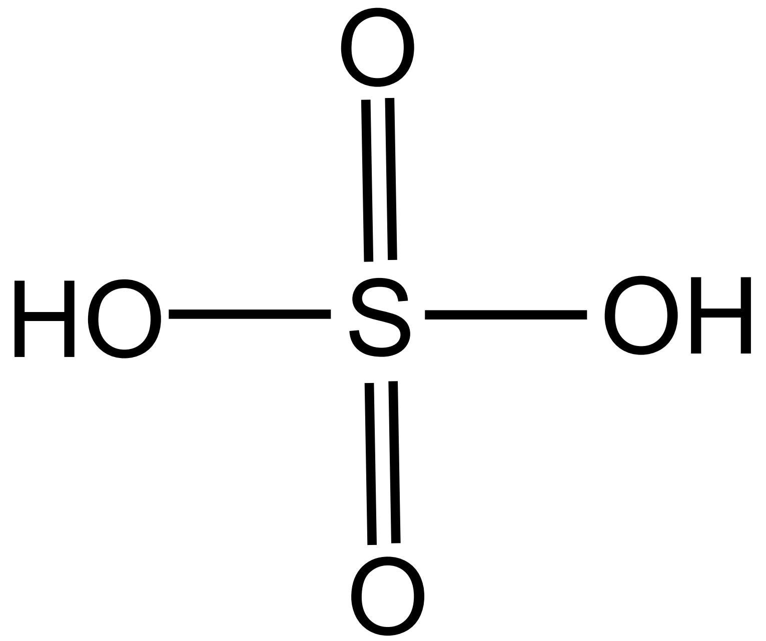
Sulfur Dioxide
($SO_2$)
Boiling Point = $-10^{o}C$




Sulfur Trioxide
($SO_3$)
Boiling Point = $45^{o}C$



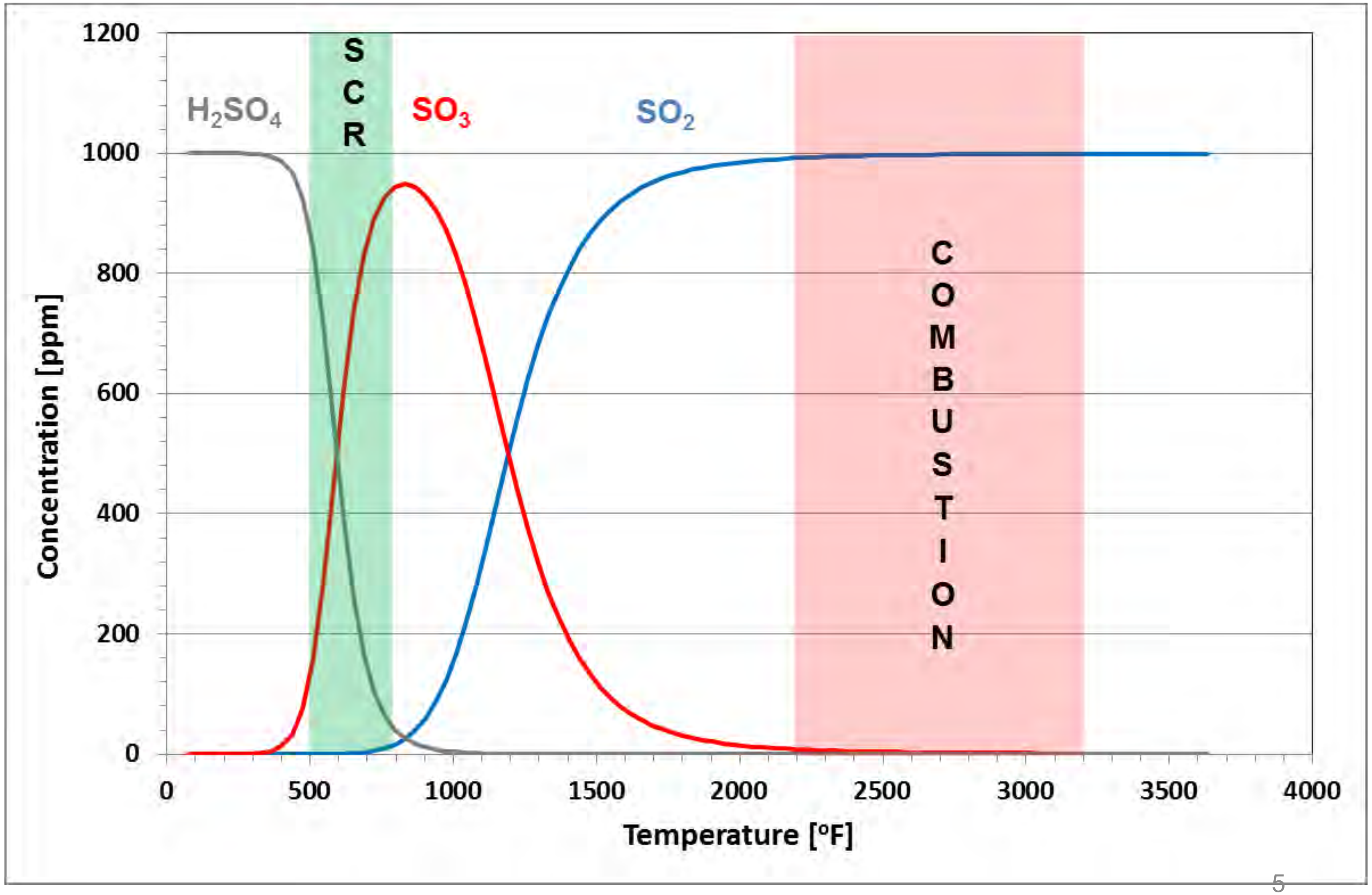

Sulfuric Acid
($H_2SO_4$)
Boiling Point = $337^{o}C$




***Distribution between these three species depends on temperature.***

# Thermodynamics

Reactions: [$SO_2 + 0.5O_2 = SO_3$] [$SO_3 + H_2O = H_2SO_4$]




<u>At Equilibrium</u>

**Combustion T range:**

$SO_2$ favored.

**SCR T range:**

$SO_3$ / $H_2SO_4$ favored.

# $SO_2$ Oxidation – Slow Reaction Kinetics

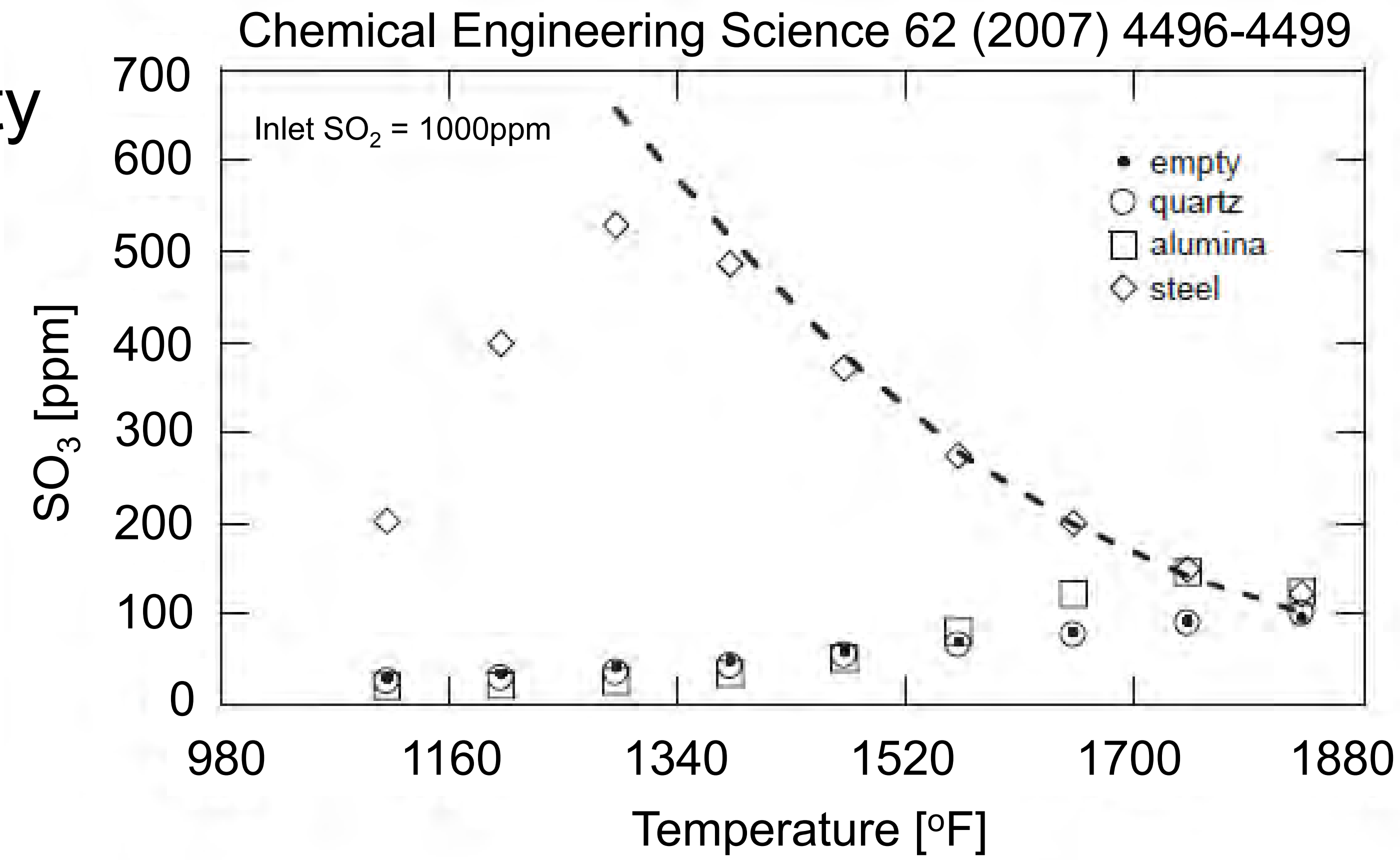
Reaction: [$SO_2 + 0.5O_2 = SO_3$]

## Gas Phase Reaction

- "empty": minimal reactivity

## Solid Catalyzed

- "quartz" and "alumina": minimal reactivity
- "steel": more reactive, but still only for >1000°F



# $SO_2$ Oxidation – Slow Reaction Kinetics

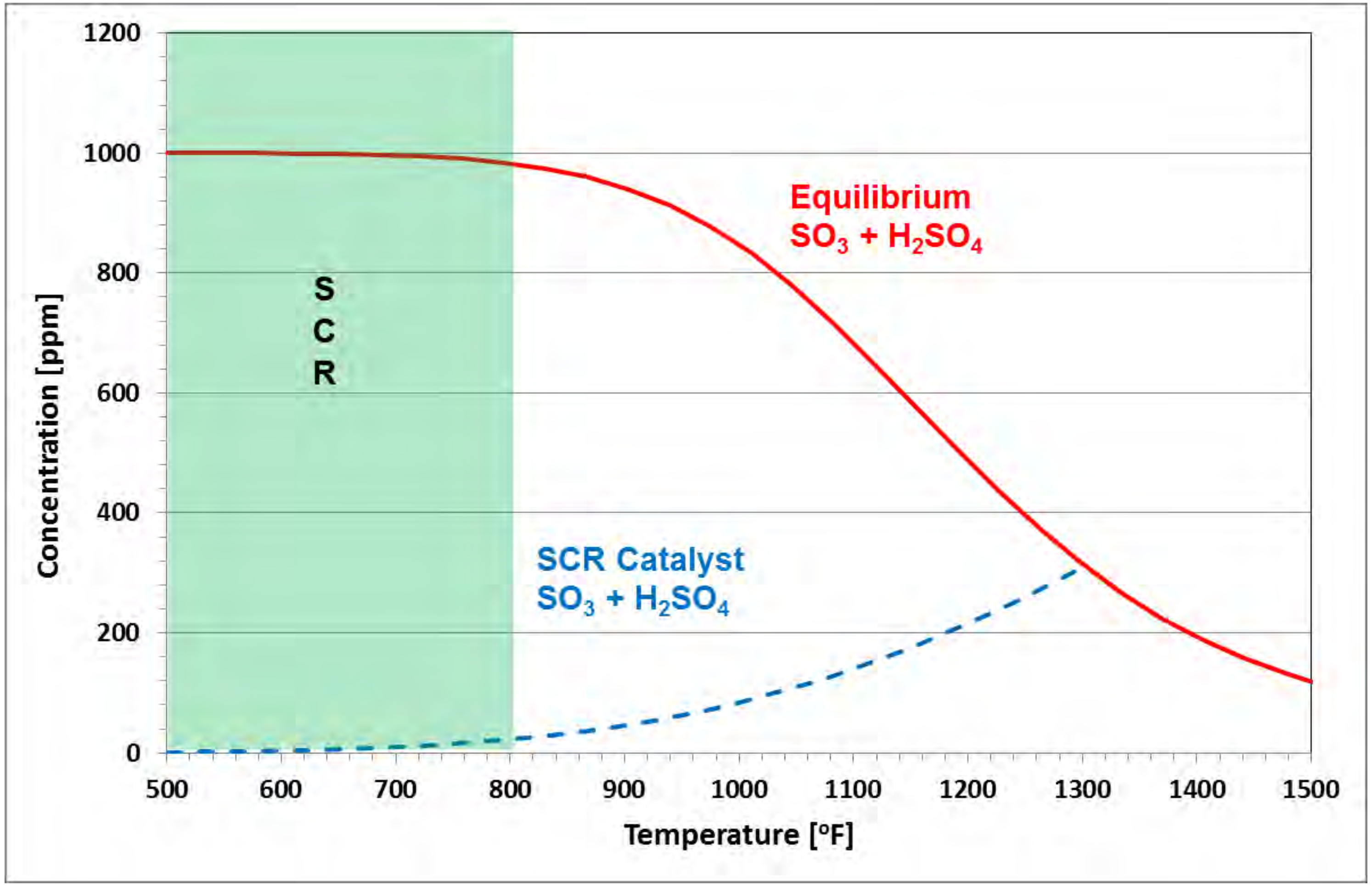
CORMETECH
RELIABILITY. DELIVERED.

## SCR Catalyzed

Even more reactive, but still…

$SO_2$ oxidation rate over SCR catalyst is kinetically limited.

Very far away from away from reaching equilibrium.



# SOx and the SCR: Workshop Overview

- How does the SCR impact BOP operations with respect to sulfur?
- How does sulfur affect SCR catalyst performance?

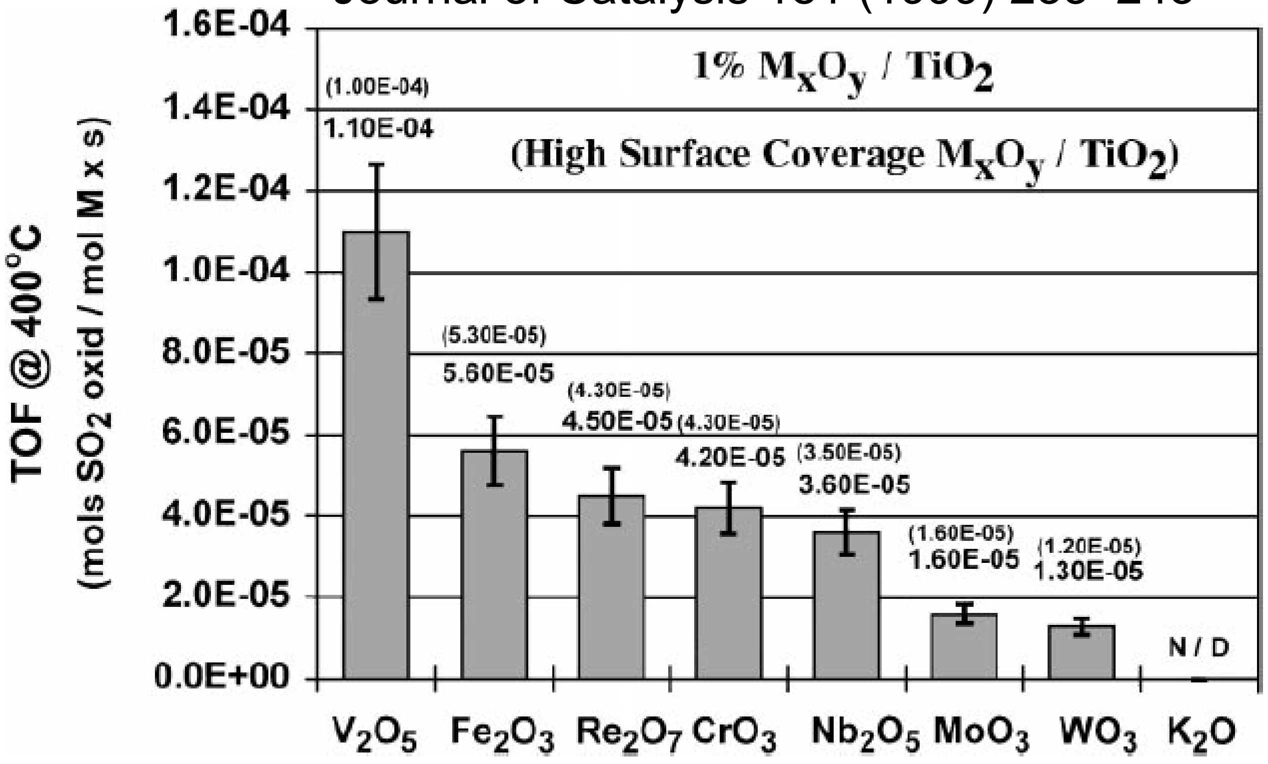
# Catalytic $SO_2$ Oxidation

- SCR catalyst enables: $SO_2 + 0.5\ O_2 \rightarrow SO_3$

$V_2O_5$ is a very active catalyst for $SO_2$ oxidation.

It is the main active metal oxide used in sulfuric acid synthesis catalyst.

Journal of Catalysis 181 (1999) 233–243



# BOP Impacts from SCR $SO_2$ Oxidation

- Potential Plant operating issues from the higher $SO_3$:
  - Air preheater fouling (ABS).
  - Heat rate limitation.
  - Changes in ash resistivity affecting ESP removal efficiency.
  - Stack opacity concerns (i.e., blue plume).

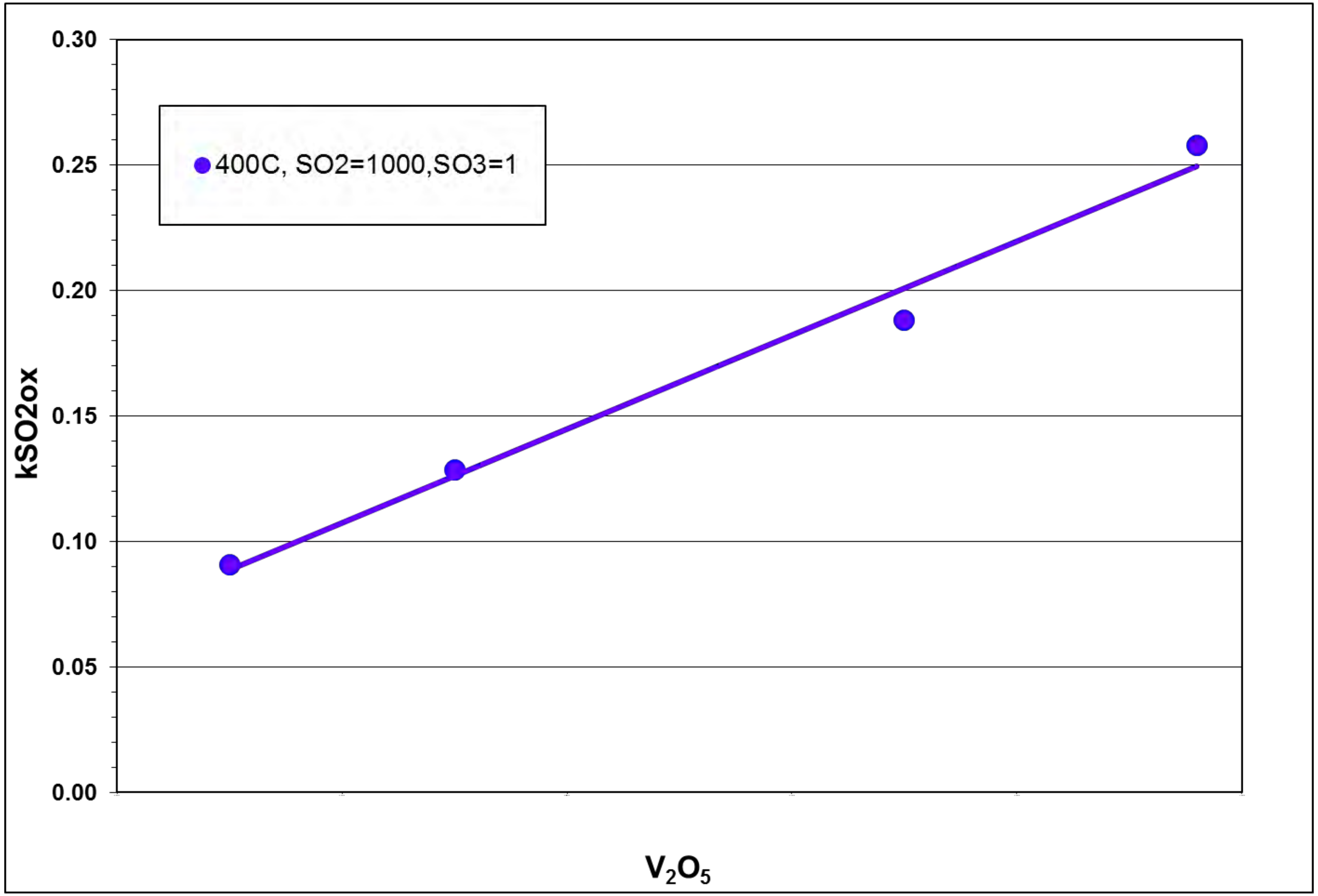
# SCR $SO_2$ Oxidation: Steady State Aspects

- Steady state = stable load.
- $SO_2$ oxidation rate is impacted by:
  - Catalyst formulation.
  - Temperature and flue gas composition.
  - Catalyst geometry.
  - Impact of regeneration.

# $SO_2$ Oxidation: Impact of $V_2O_5$ Loading

Factors strongly impacting the $SO_2$ oxidation activity:

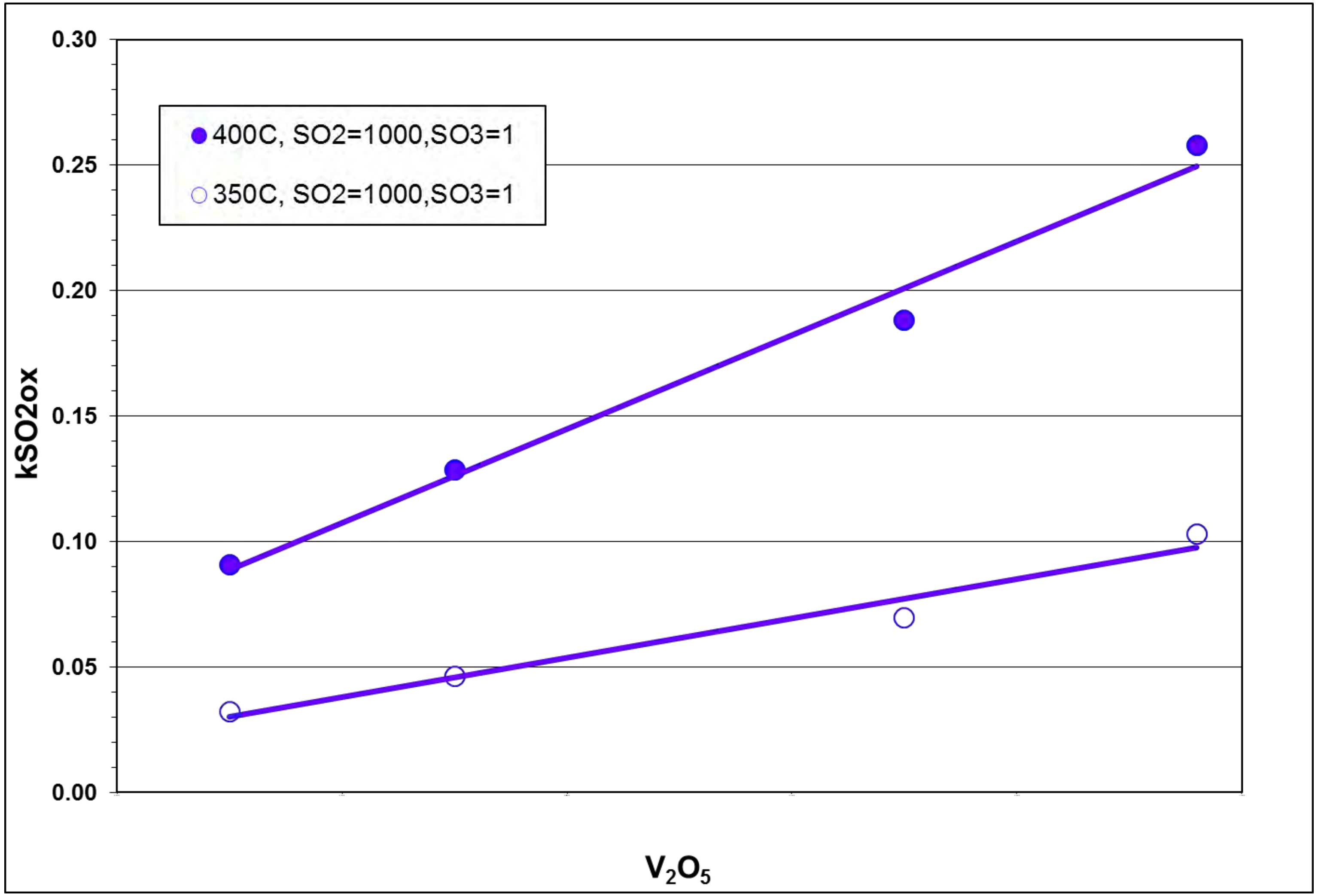
- $V_2O_5$ loading.



# $SO_2$ Oxidation: Impact of Temperature

Factors strongly impacting the $SO_2$ oxidation activity:

- $V_2O_5$ loading.
- Temperature.

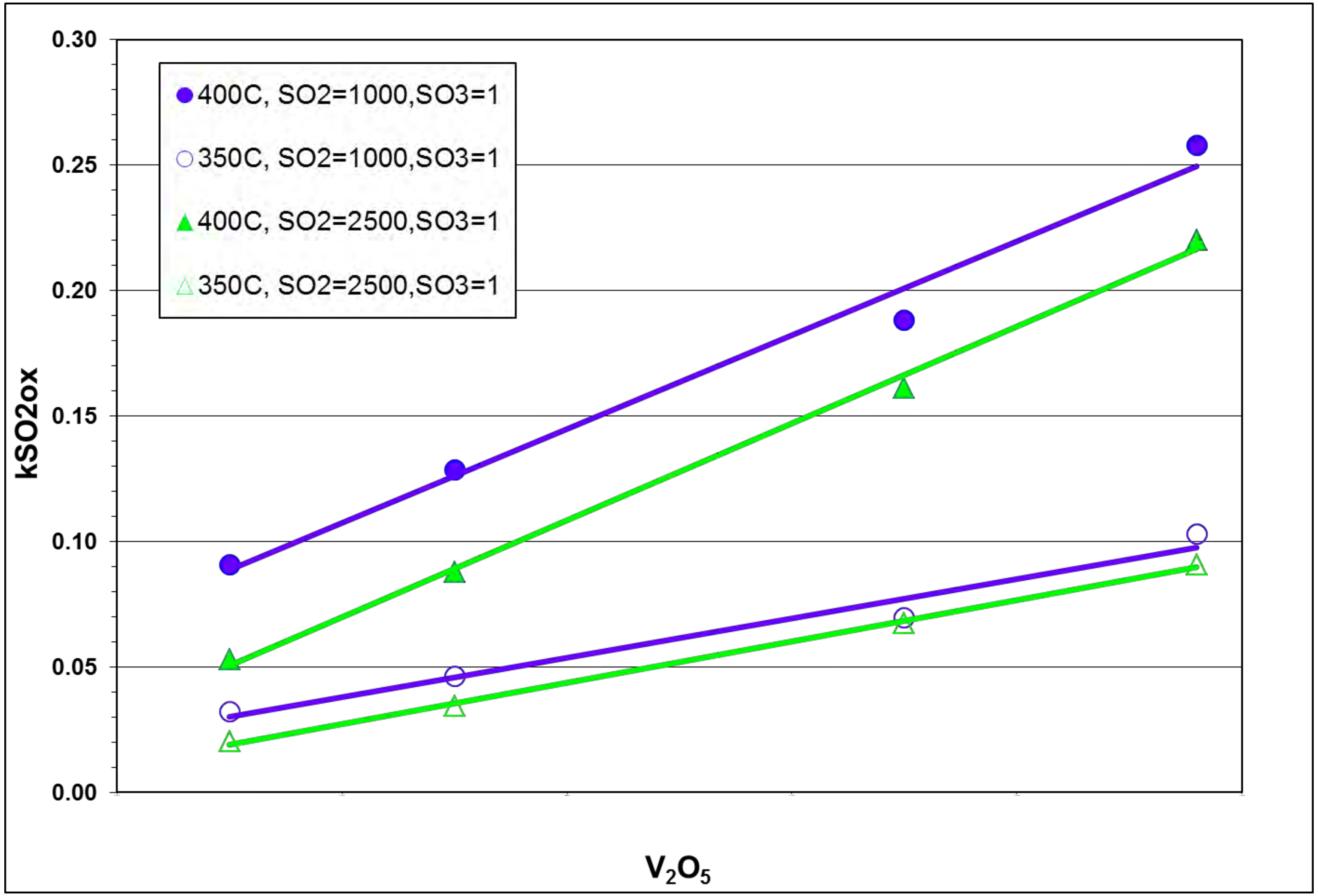


# $SO_2$ Oxidation: Impact of $SO_2$ Concentration

Factors strongly impacting the $SO_2$ oxidation activity:

- $V_2O_5$ loading.
- Temperature.
- $SO_2$ concentration.

To set the $V_2O_5$ loading: balance activity for DeNOx and Hg oxidation with $SO_2$ oxidation rate.

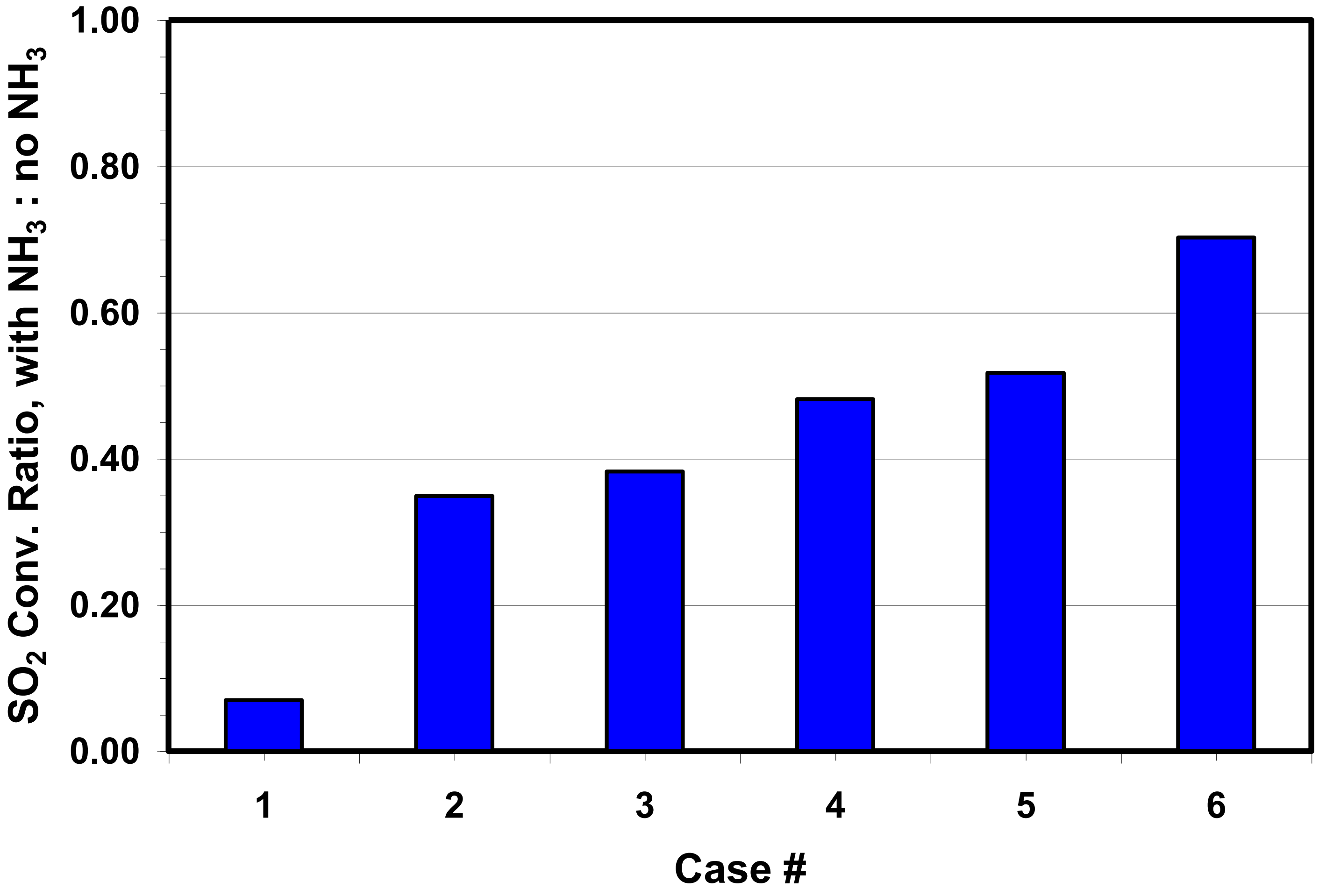


# $SO_2$ Oxidation: Impact of $NH_3$

$NH_3$ can strongly inhibit the $SO_2$ oxidation rate.

Extent of the inhibition will depend on:

- $NH_3$ concentration.
  - Inlet NOx, DeNOx.
  - Layer position.
- Temperature.
- Catalyst formulation.

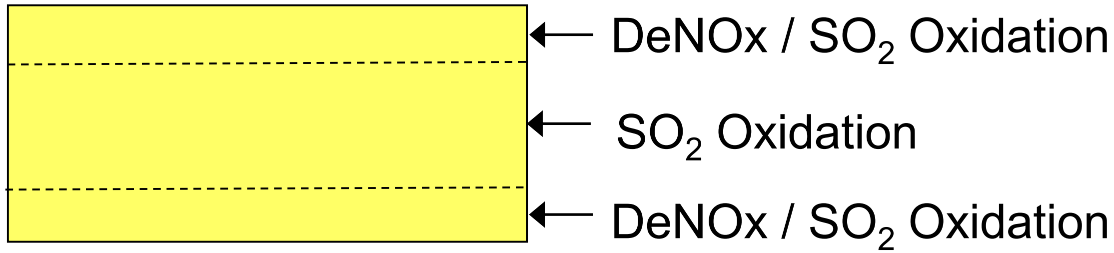


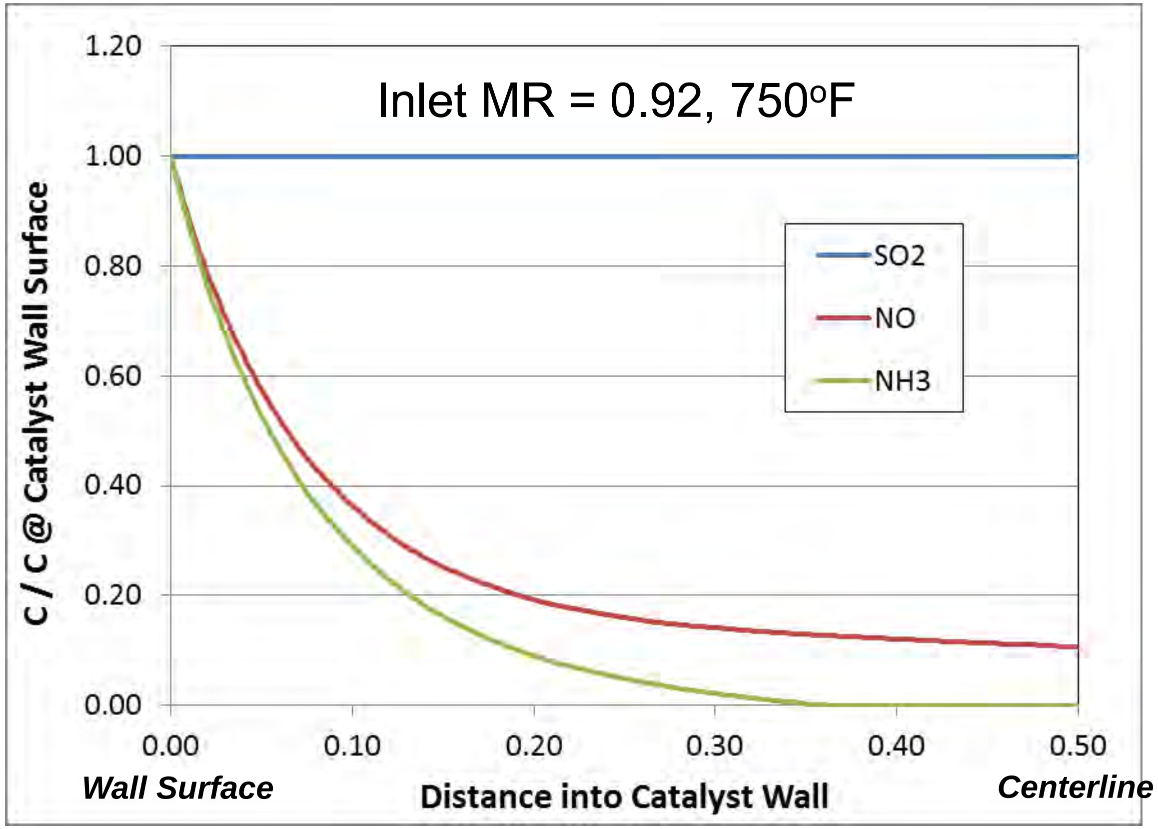
# $SO_2$ Oxidation is Kinetically Limited

Slow $SO_2$ oxidation reaction occurs throughout wall.

Fast DeNOx reaction occurs near surface of wall.

**Catalyst Wall Cross-section:**



# Impact of Catalyst Geometry

- Smaller pitch / higher geometric surface area catalyst improves the trade-off between DeNOx and $SO_2$ oxidation.
- Effective system design (reduce ash sloughing) and maintenance practices will mitigate plugging risk.

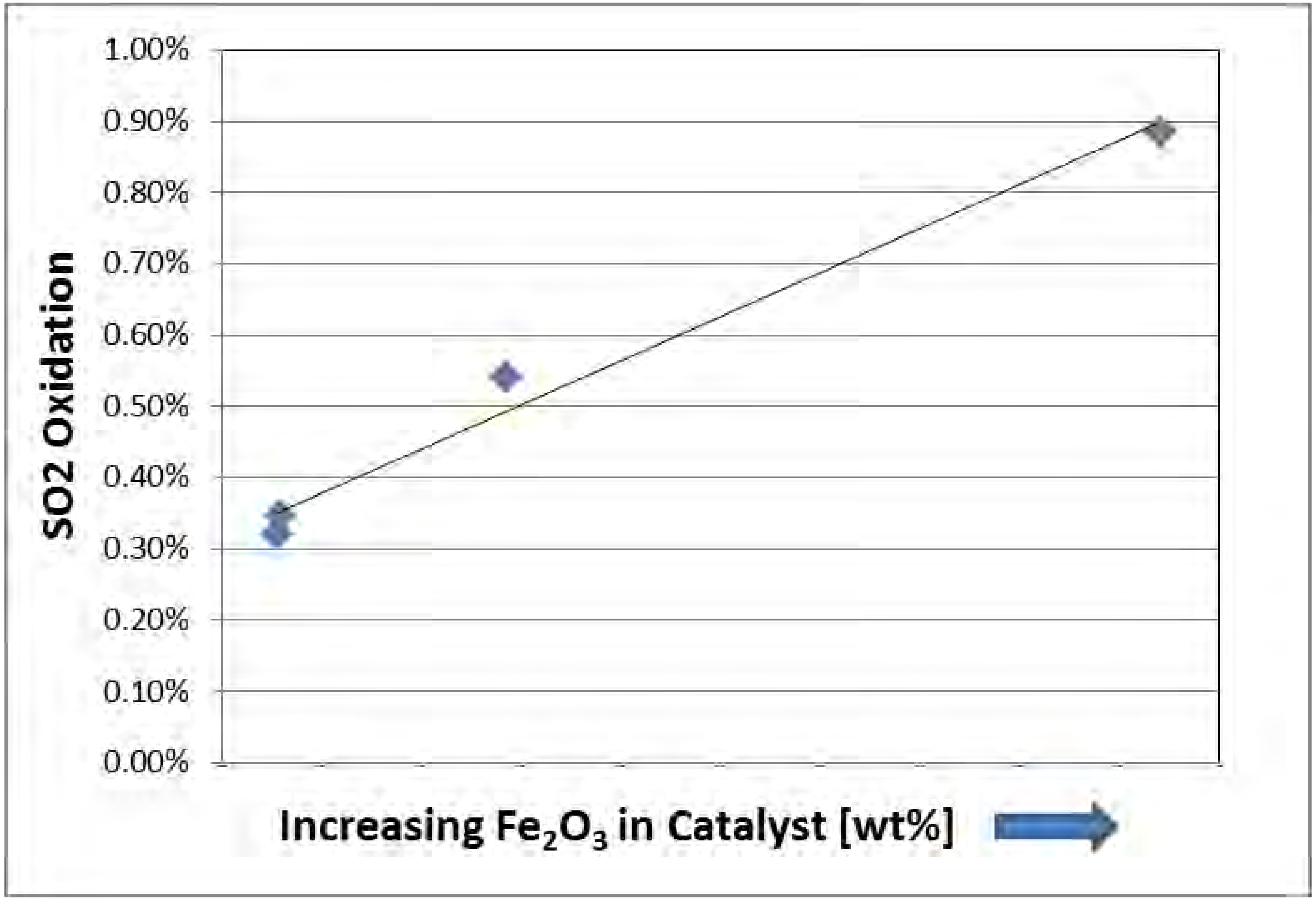
| Type | Pitch [mm] | Relative Volume (20 Cell = 1.00) | $SO_2$ Oxidation (20 Cell = 1.0%) |
|---|---|---|---|
| 16 Cell | 9 | 1.39 | 1.9% |
| 18 Cell | 8 | 1.14 | 1.7% |
| 20 Cell | 7 | 1.00 | 1.0% |
| 21 Cell | 7 | 1.00 | 0.5% |
| 22 Cell | 7 | 1.00 | 0.4% |

Constant DeNOx and $NH_3$ slip for all cases

# Impact of Regeneration

Regeneration can lead to increased iron oxide level in the SCR catalyst (from exposed steel in plates).

Iron oxide is active for $SO_2$ oxidation.



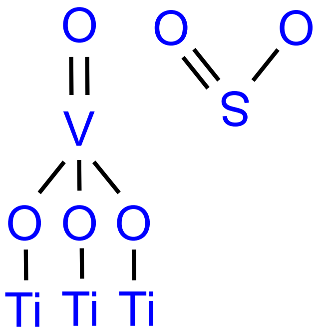
# SOx and the SCR: Workshop Overview

- How does the SCR impact BOP operations with respect to sulfur?
  - Catalytic $SO_2$ oxidation: increase in $SO_3$ across SCR.

- How does sulfur affect SCR catalyst performance?

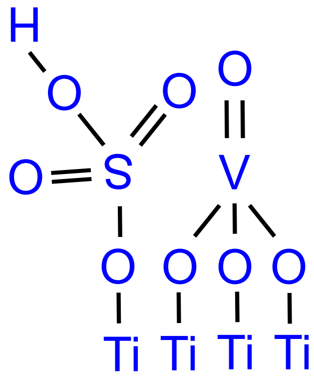
# Sulfur Interaction with SCR Catalyst

- Adsorption of SOx onto the V-W/Ti SCR catalyst surface.



  - **No significant $SO_2$ adsorption.**
    - Applied Catalysis B: Environmental 19 (1998) 103-117 & references therein.
  - $SO_2$ reacts from the gas phase with catalyst-bound oxygen to form $SO_3$.

  - **Strong $SO_3$ adsorption.**
    - Applied Catalysis B: Environmental 92 (2009) 30-40.
  - $SO_3$ adsorbs onto $TiO_2$ sites to form $TiO_2$-$SO_4$ sites.
    - It does not adsorb onto the $VO_X$ or $WO_X$ active sites for SCR.

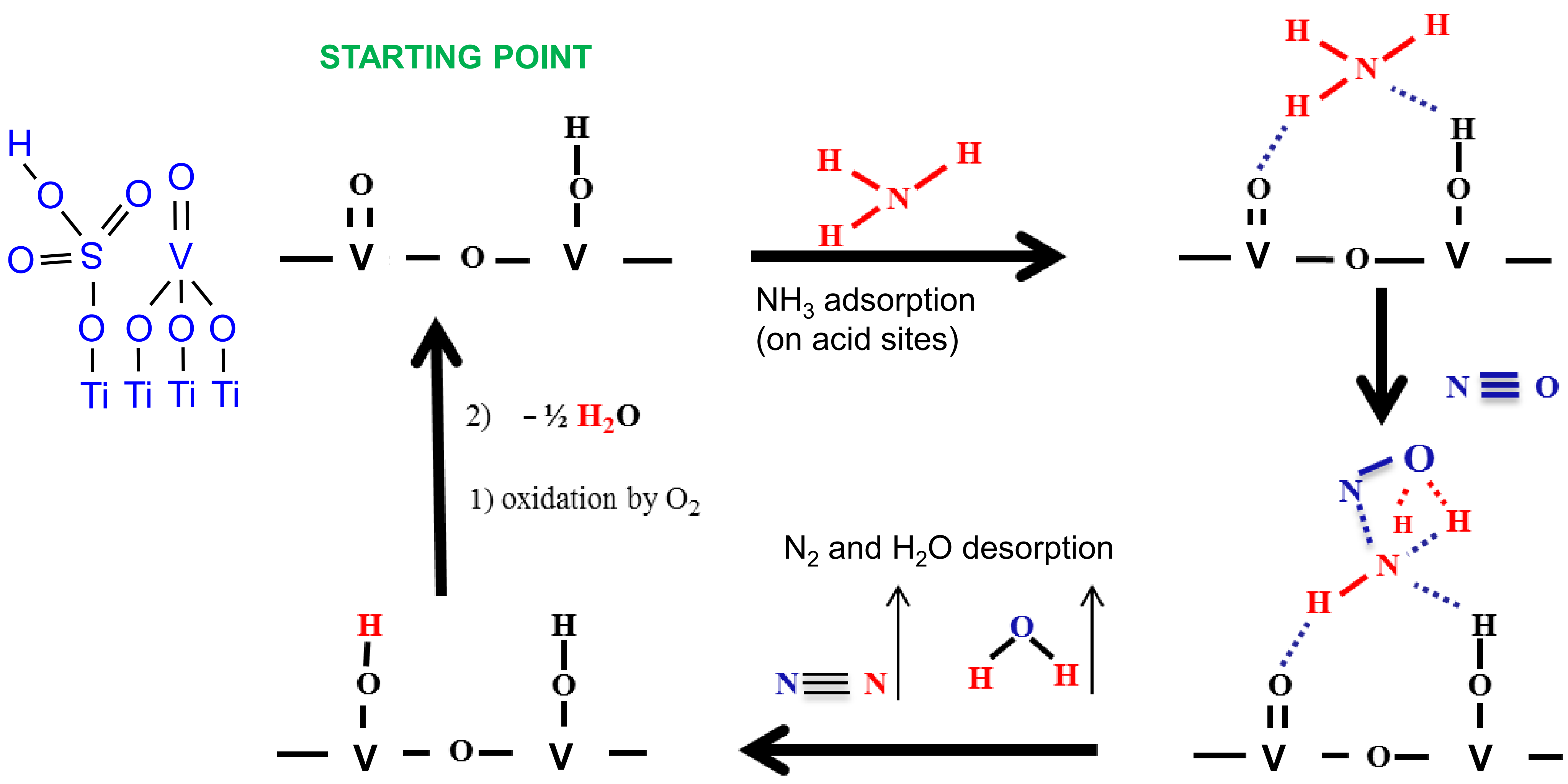


# Sulfur Stability and Enhanced Activity

- **V-W/Ti is a good SCR catalyst for coal-fired boilers because...**
  - *It's sulfur stable!*
    - $SO_3$ does not interact $V_2O_5$ or $WO_3$.
    - $TiO_2$-$SO_4$ decomposes at relatively low temperatures and does not inhibit SCR activity.
  - Other commercial SCR catalysts (e.g., Cu/zeolites, Fe/zeolites) are not sulfur stable and can only be used for low sulfur gas or diesel units.

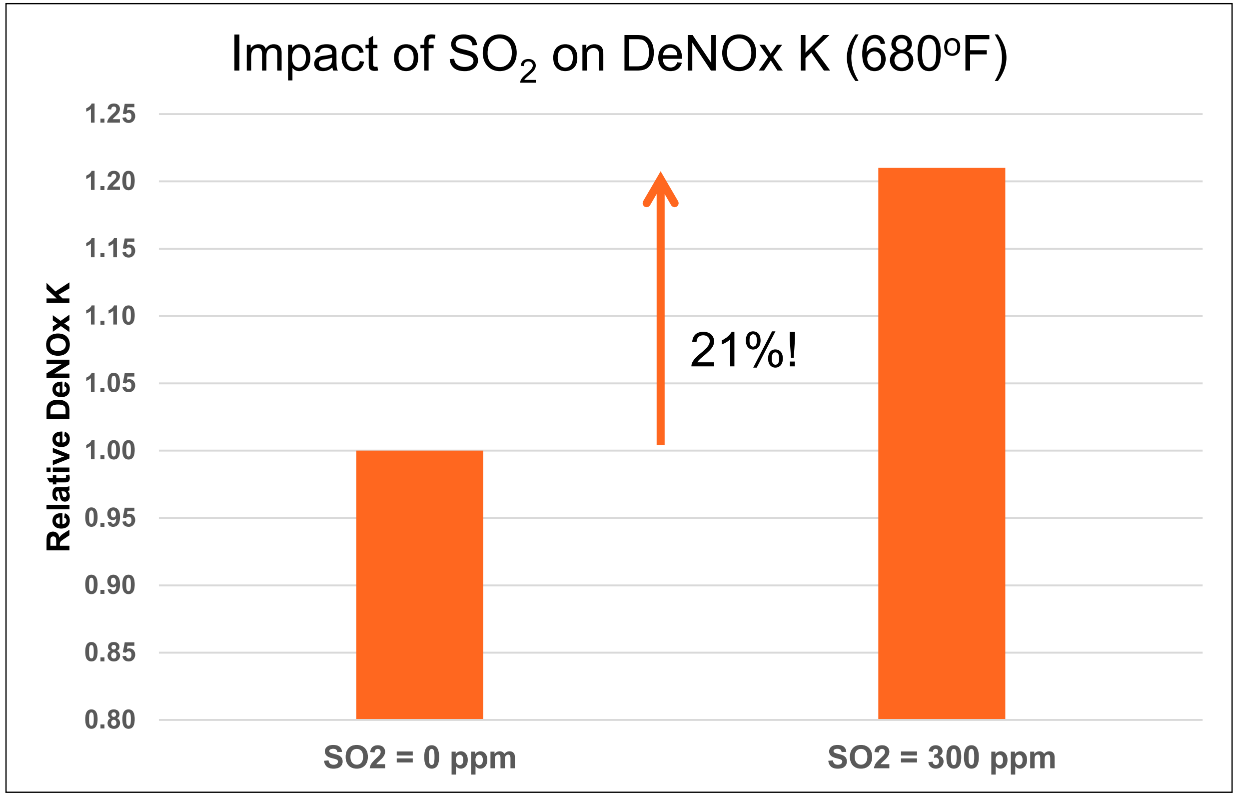
- **DeNOx activity of V-W/Ti SCR catalyst is enhanced by sulfur!**
  - Sulfate increases the density of Bronsted acid sites on the catalyst.
    - Leads to higher $NH_3$ coverage.

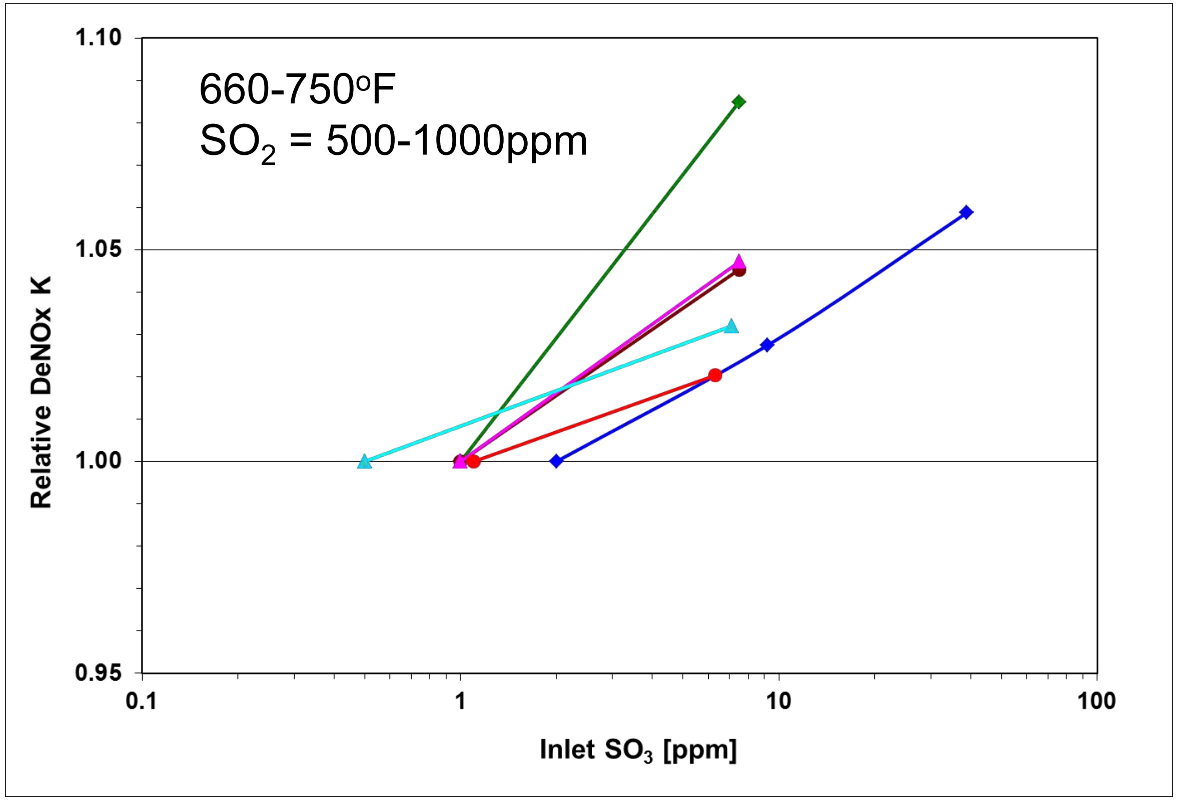
# DeNOx Reaction Mechanism



# Positive Impact on DeNOx

- $SO_2$ injection for de-sulfated catalyst has largest K impact.
- $SO_3$ co-injection with $SO_2$ yields further increase in K.




Need to consider sulfur's impact on catalyst potential when assessing the conversion of coal units to gas firing.

# Small Impact on Hg Oxidation

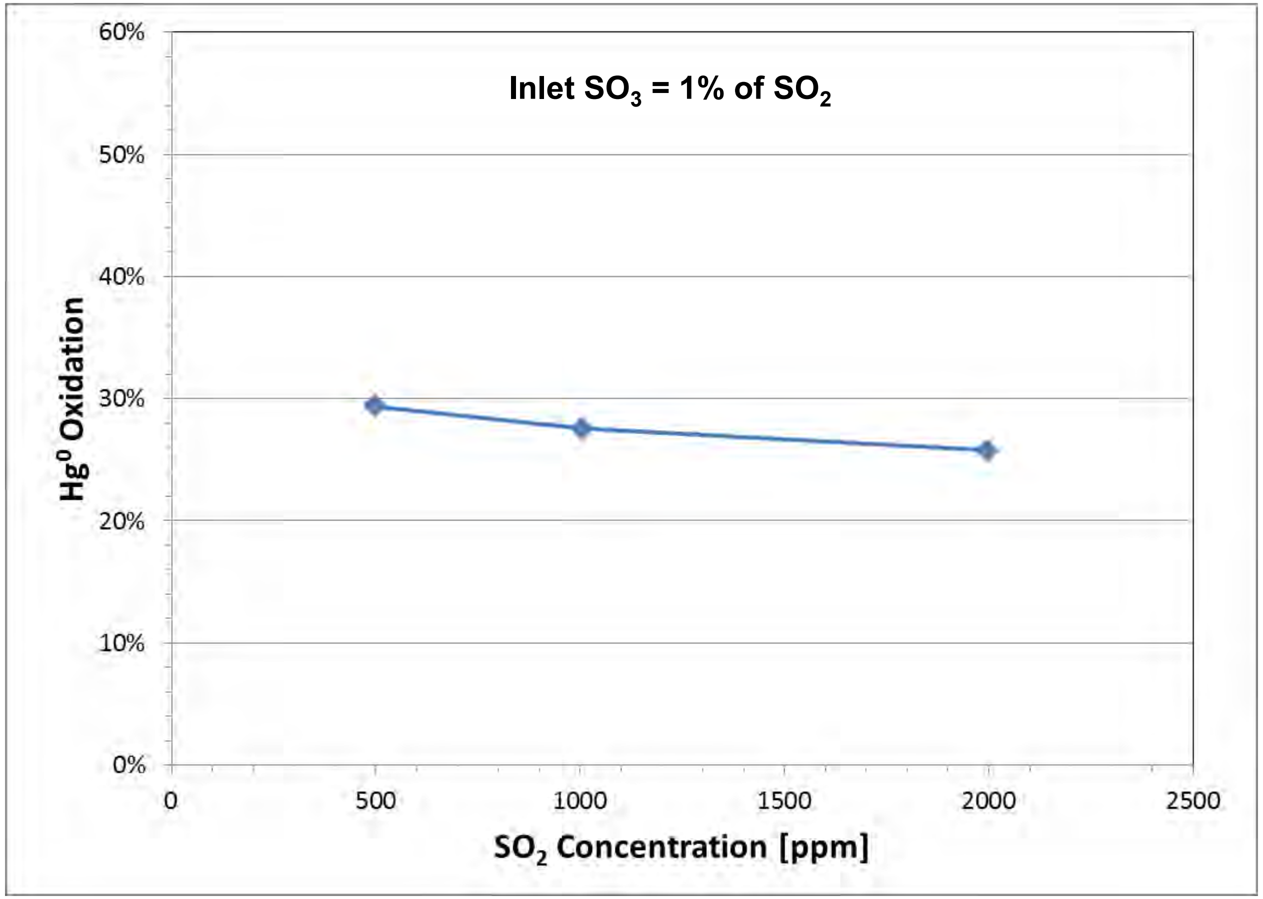
CORMETECH
RELIABILITY. DELIVERED.

Desired reaction:

$$2Hg + 4HCl + O_2 \rightarrow 2HgCl_2 + 2H_2O$$

$SO_2$ has a minor inhibiting effect on Hg oxidation through reduction of $Hg^{2+}$

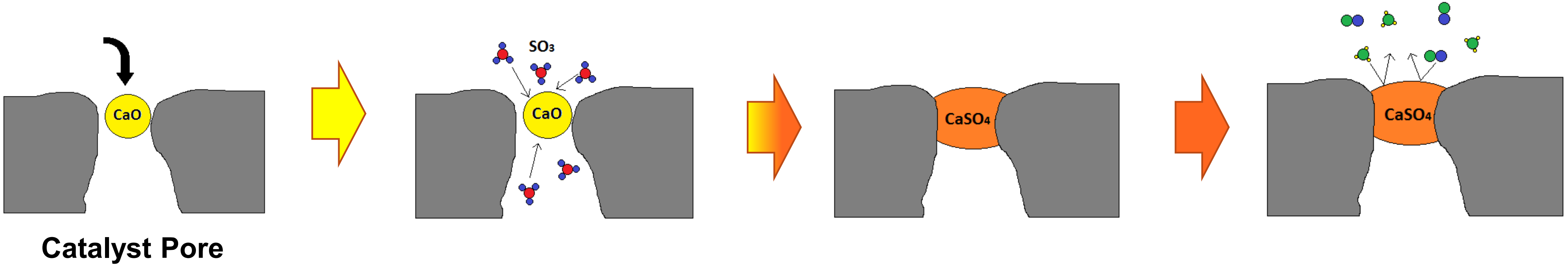
$$SO_2 + HgCl_2 + H_2O \rightarrow Hg + 2HCl + SO_3$$



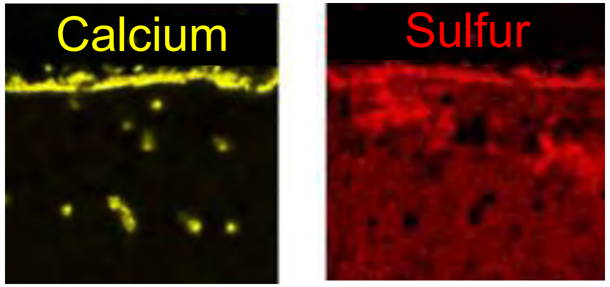

750°F, 3.5% $O_2$, 11% $H_2O$, HCl = 11 ppm, 350 ppm NO, 0.2 MR, CO = 100 ppm

# Sulfur Participation in Catalyst Deactivation Mechanisms

**PRB** boilers can exhibit high SCR deactivation rates due to **Ca** and P.




**SEM-EDS Maps**

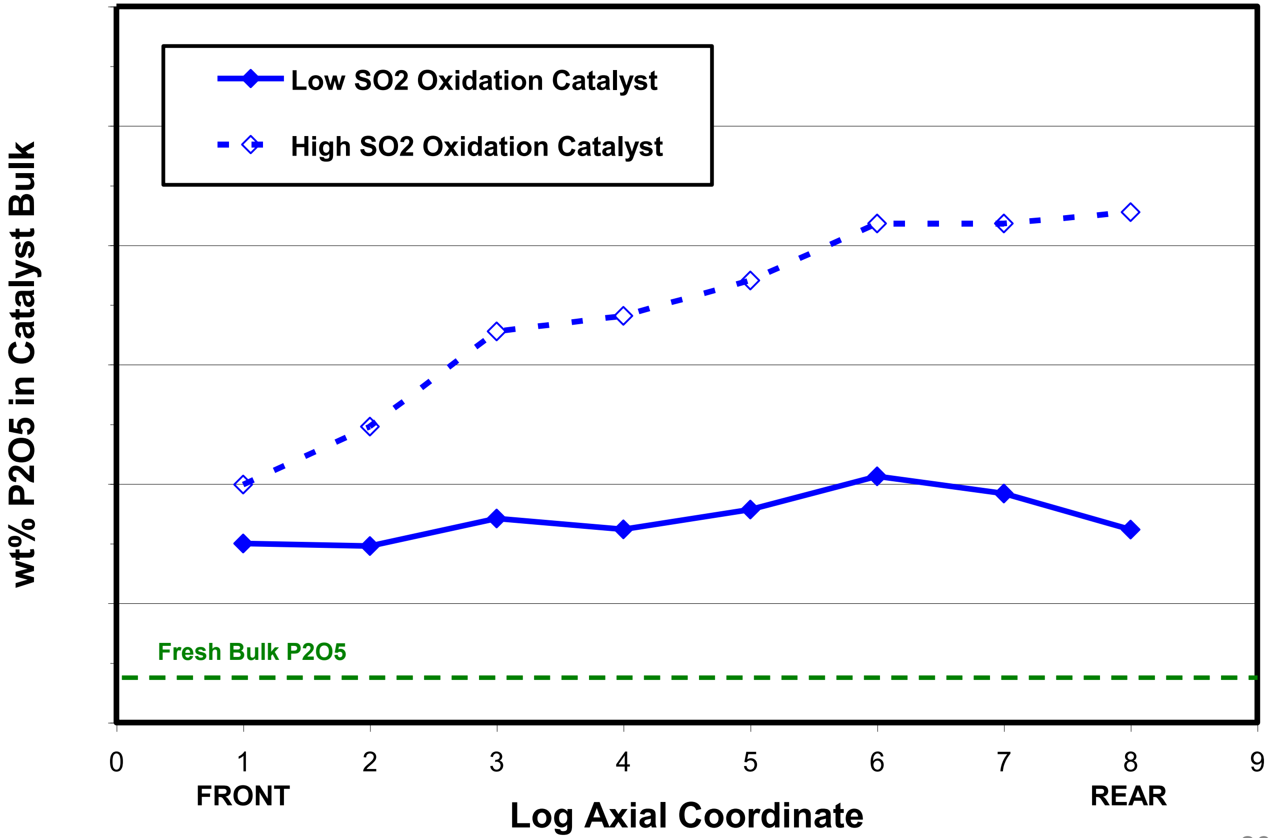


# Sulfur Participation in Catalyst Deactivation Mechanisms

**PRB** boilers can exhibit high SCR deactivation rates due to Ca and **P**.

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

**Gaseous P (i.e., $H_3PO_4$)** that causes catalyst deactivation forms from $SO_3$ reacting with $Ca_3(PO_4)_3$ in the fly ash in the SCR itself.



# Sulfur Participation in Catalyst Deactivation Mechanisms

CORMETECH
RELIABILITY. DELIVERED.

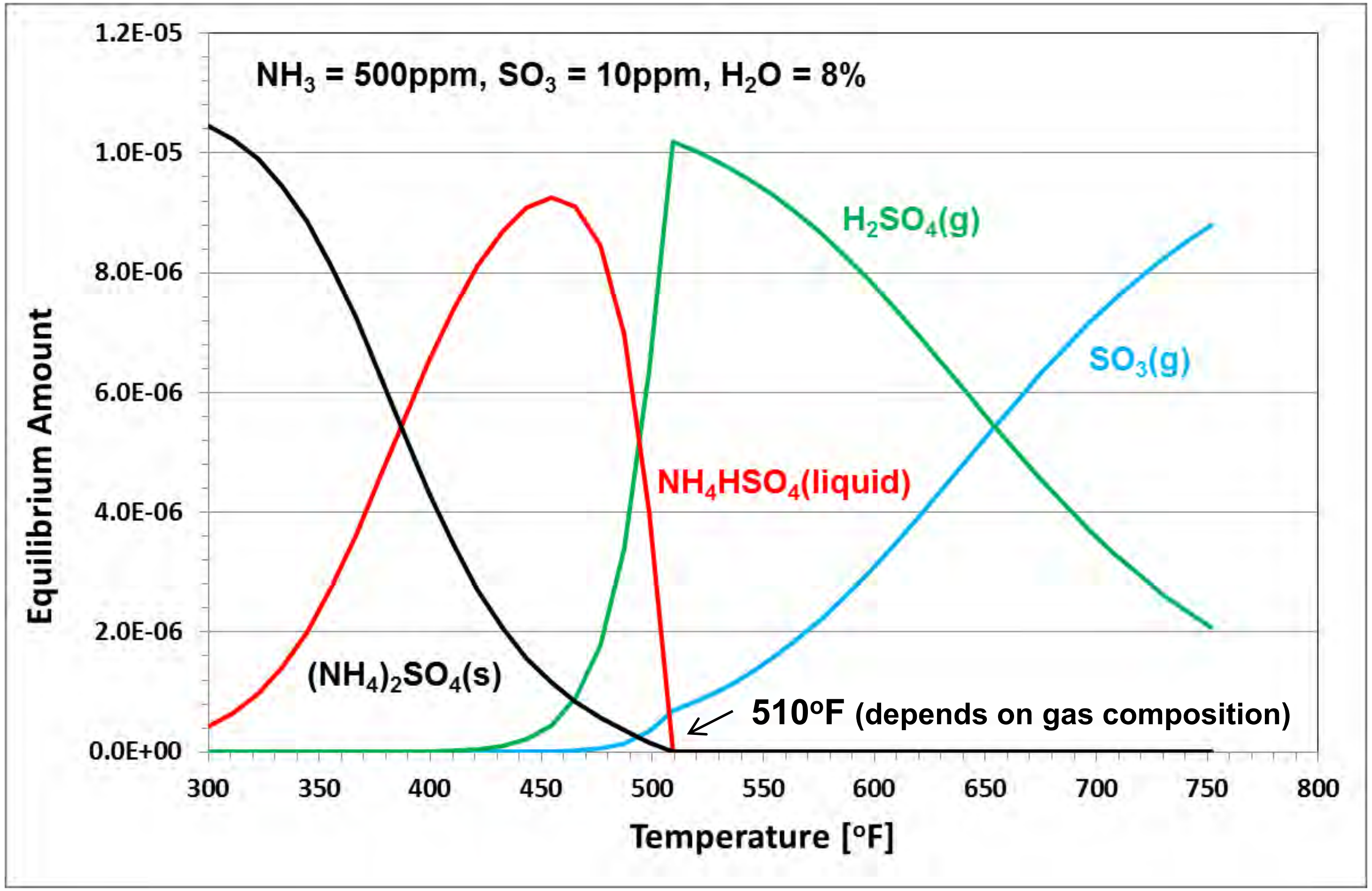
## Ammonium Bisulfate (ABS)

- **$NH_3 + H_2SO_4 \leftrightarrow NH_4HSO_4$**
- White sticky solid; corrosive
- $T_{melting}$ = 147°C / 297°F
- $T_{boiling}$ > 235°C / 455°F (decomposes)

## Ammonium Sulfate (AS)

- **$2NH_3 + H_2SO_4 \leftrightarrow (NH_4)_2SO_4$**
- White solid
- $T_{melting}$ = 235-280°C / 455-536°F (forms liquid ABS and/or decomposes)

Bulk Phase Equilibrium Curve

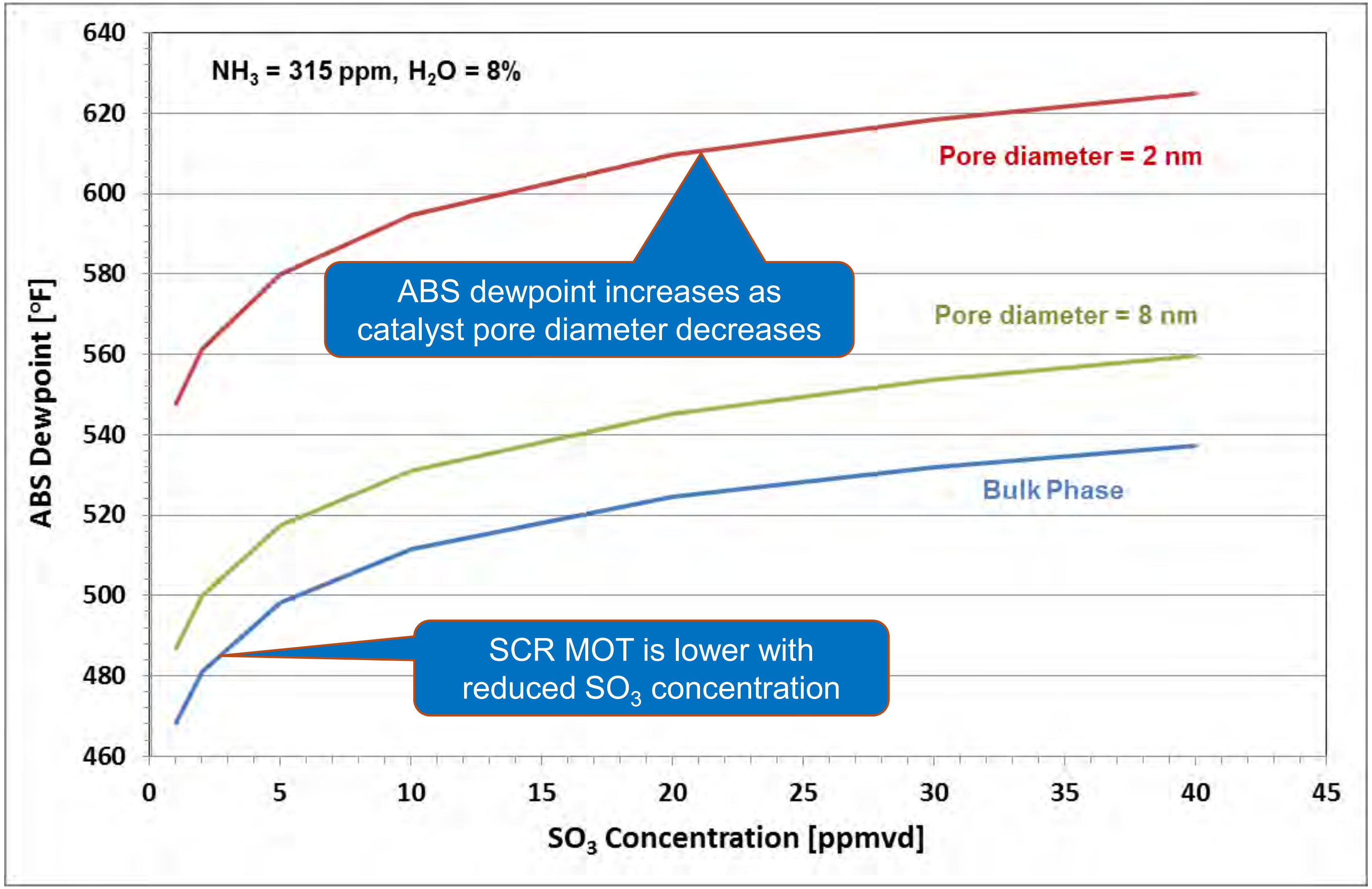


# Impact of Catalyst Micro Pores on ABS

<u>Kelvin equation</u>

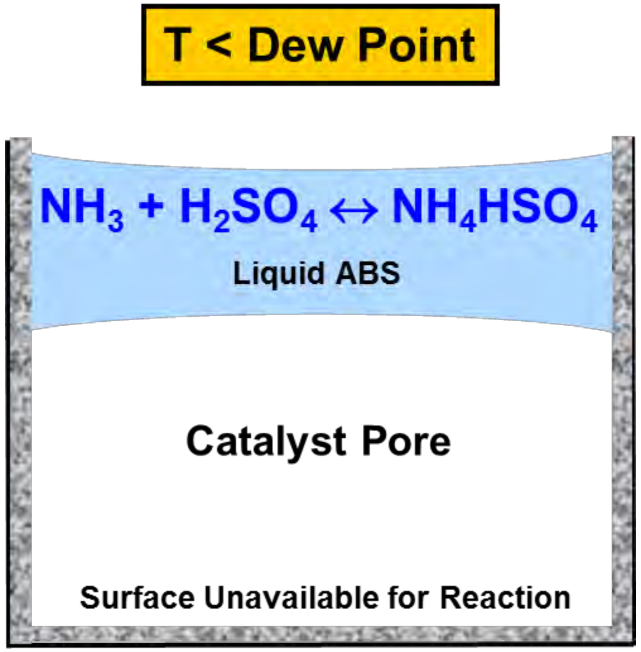
$$\ln\left(\frac{\text{P vap in pore}}{\text{Psat vap bulk liquid}}\right) = -\frac{4\,\sigma\,V_l}{d\,R\,T}$$

Calculates critical pore diameter above which no ABS condensation will occur.

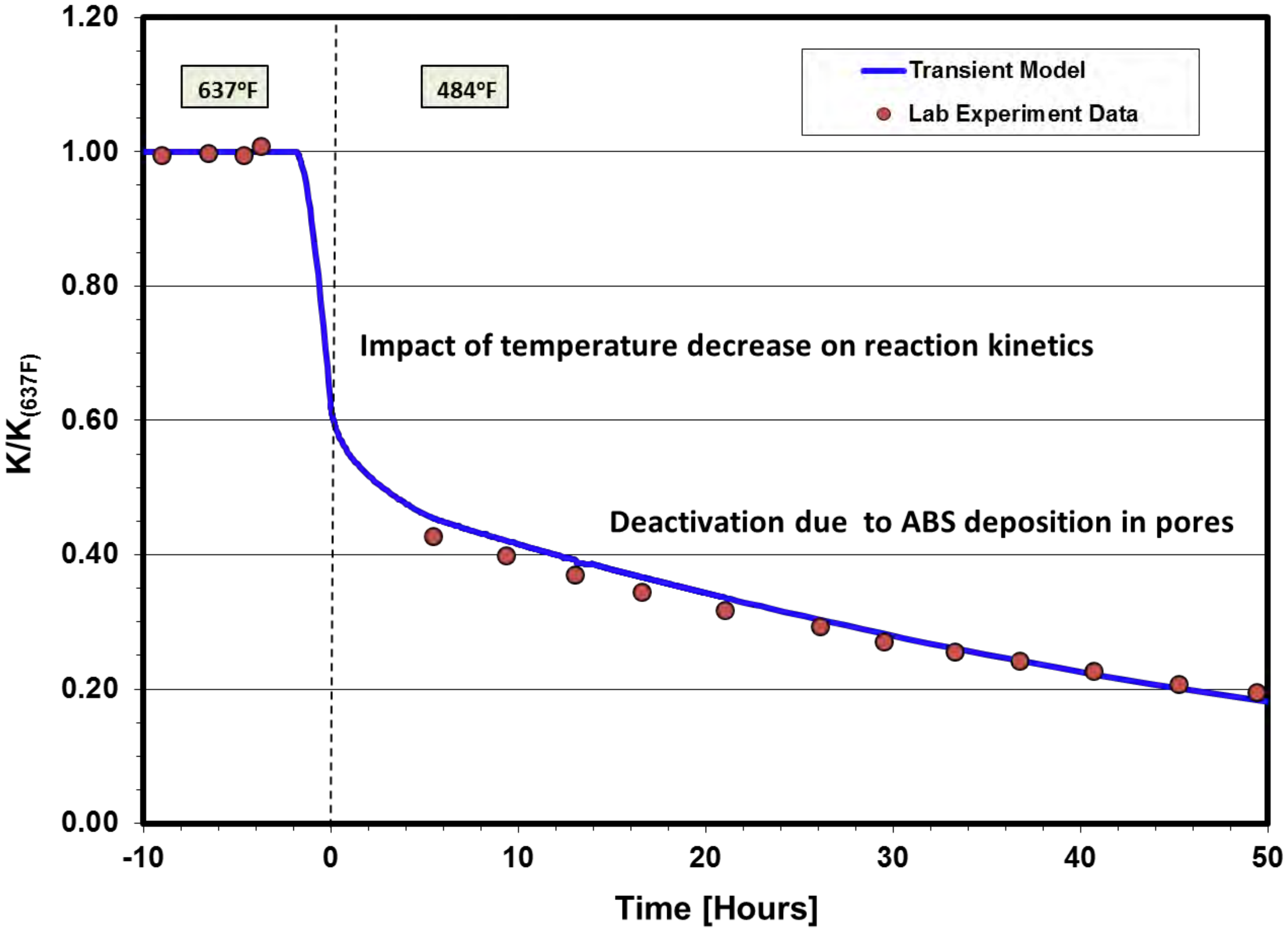


# ABS Deposition Deactivates Catalyst

ABS blocks active sites.




*Effect is reversible: heat catalyst above recovery temperature to remove ABS.*



# Enhancing Low Load SCR Operation

CORMETECH
RELIABILITY. DELIVERED.

- **CORMETECH can help extend an SCR's low load operability.**
  - Tools and expertise: modeling, lab testing, field support.
  - Evaluate scenarios (time, temp., $SO_3$, DeNOx, $NH_3$ slip, DSI).
  - Generate transient responses for DeNOx, $NH_3$ slip and outlet $SO_3$.

- **DSI to lower inlet $SO_3$ can further extend operation at low load.**
  - C. Bertole (CORMETECH), C. Donner (DUKE ENERGY) presentation at 2017 Reinhold NOx-Combustion Round Table: "State-of-the-Art Coal-Fired Performance Technology for Load Following Units".
  - Case specific: balance the enhanced low load operation with the risk of faster catalyst deactivation from sorbent accumulation.

# SOx and the SCR: Workshop Overview

- How does the SCR impact BOP operations with respect to sulfur?
  - Catalytic $SO_2$ oxidation: increase in $SO_3$ across SCR.

- How does sulfur affect SCR catalyst performance?
  - Adsorbs on the catalyst as sulfate.
  - Positive impact on DeNOx.
  - Slightly negative impact on Hg oxidation.
  - Leads to calcium sulfate surface blinding for PRB.
  - Increases phosphorus accumulation rate for PRB.
  - Reacts with $NH_3$ at low temperatures to form ABS salts in the pores and cause a reversible deactivation.

# SOx and the SCR: Workshop Overview

- How does the SCR impact BOP operations with respect to sulfur?
  - Catalytic $SO_2$ oxidation: increase in $SO_3$ across SCR.
  - Transients: dynamics of $SO_3$ / ABS storage and release from the catalyst.

- How does sulfur affect SCR catalyst performance?
  - Adsorbs on the catalyst as sulfate.
  - Positive impact on DeNOx.
  - Slightly negative impact on Hg oxidation.
  - Leads to calcium sulfate surface blinding for PRB.
  - Increases phosphorus accumulation rate for PRB.
  - Reacts with $NH_3$ at low temperatures to form ABS salts in the pores and cause a reversible deactivation.

# SCR $SO_2$ Oxidation and ABS: Transient Aspects

CORMETECH
RELIABILITY. DELIVERED.

- **Transient = load cycling:**
  - Dynamics of $SO_3$ / ABS storage and release from the catalyst.
    - Strong $SO_3$ adsorption onto $TiO_2$, but not on V or W.
    - Weak $SO_2$ adsorption.
    - ABS formation in micro pores (below dew point).

- **Review:**
  - $SO_3$ coverage on catalyst as function of temperature / $SO_3$ concentration.
  - Aging time for $SO_2$ oxidation testing.
  - Temperature cycling transients (heat / cool) “without” and “with” $NH_3$.
  - SOx cycling transients: impact of sulfate on DeNOx activity (non-ABS).

# $SO_3$ Catalyst Adsorption Model

**Adsorption:** $SO_3 + \underline{\quad} \xrightarrow{ka} \underline{SO_3}$

*Rate adsorption = ka $P_{SO3}$ $(1 - \theta_{SO3})$*

**Desorption:** $\underline{SO_3} \xrightarrow{kd} \underline{\quad} + SO_3$

*Rate desorption = kd $\theta_{SO3}$*

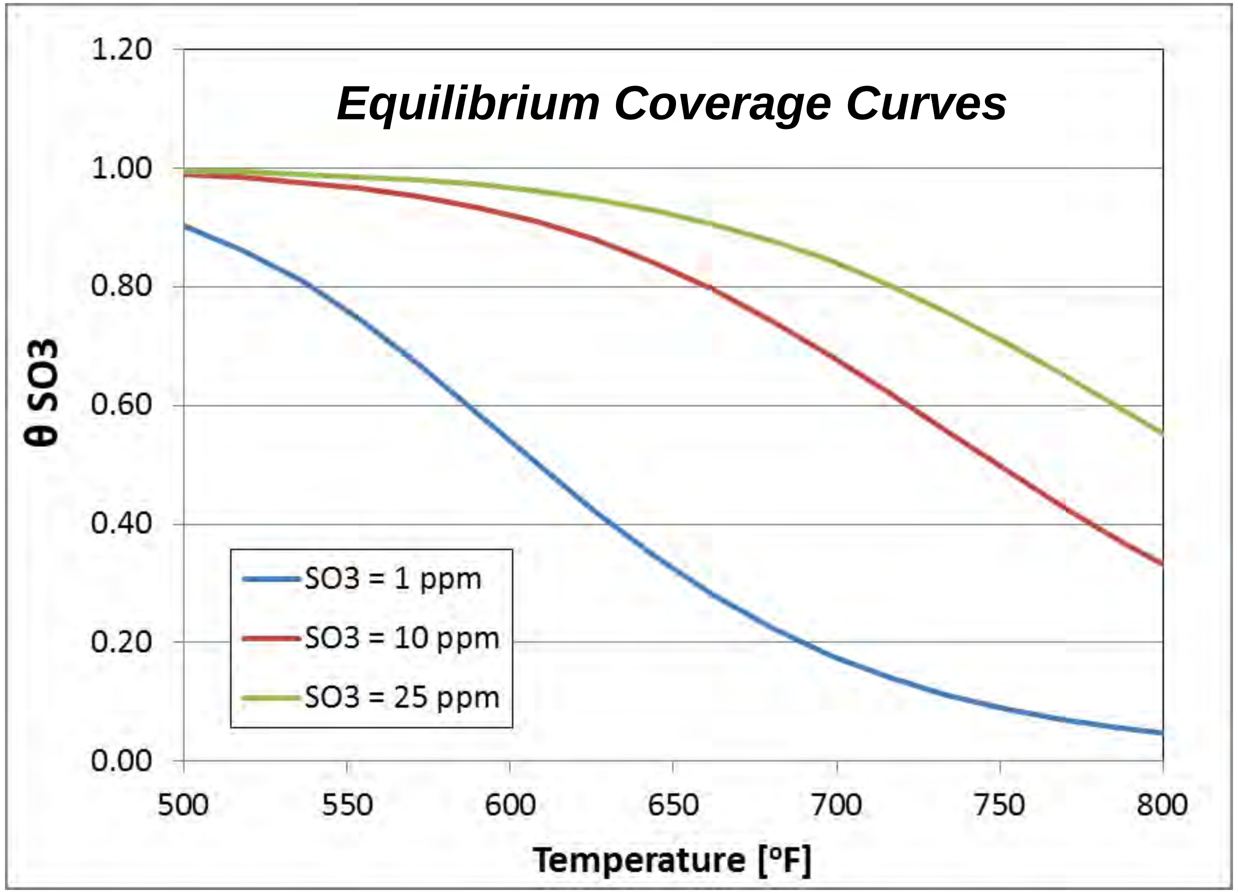
**At equilibrium:**

rate adsorption = rate desorption

$$ka\, P_{SO3} (1 - \theta_{SO3}) = kd\, \theta_{SO3}$$

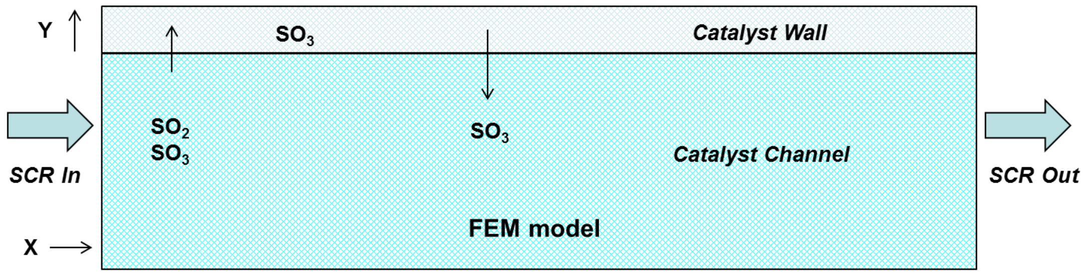
$$\theta_{SO3} = ka / kd\, P_{SO3} / (1 + ka / kd\, P_{SO3})$$

$\theta_{SO3}$ = fractional coverage of $SO_3$



# Transient $SO_2$ Oxidation Model

Mass Balance Equations




$C_{SO2}$ (gas phase):

$$\frac{\partial C_{SO2}}{\partial t} + u_x \frac{\partial C_{SO2}}{\partial x} = D_{SO2}\left(\frac{\partial^2 C_{SO2}}{\partial x^2} + \frac{\partial^2 C_{SO2}}{\partial y^2}\right) + \{-k_{rSO2} C_{SO2}\}\rho_{cat}$$

$C_{SO3}$ (gas phase):

$$\frac{\partial C_{SO3}}{\partial t} + u_x \frac{\partial C_{SO3}}{\partial x} = D_{SO3}\left(\frac{\partial^2 C_{SO3}}{\partial x^2} + \frac{\partial^2 C_{SO3}}{\partial y^2}\right) + \{k_{rSO2} C_{SO2} - k_{aSO3}(1-\theta_{SO3})\Omega_{SO3} + k_{dSO3}\theta_{SO3}\Omega_{SO3}\}\rho_{cat}\Omega_{SO3}$$

$\theta_{SO3}$ (adsorbed $SO_3$ on catalyst surface):

$$\frac{\partial \theta_{SO3}}{\partial t} = D_{\theta SO3}\left(\frac{\partial^2 C_{\theta SO3}}{\partial x^2} + \frac{\partial^2 C_{\theta SO3}}{\partial y^2}\right) + \{+k_{aSO3}(1-\theta_{SO3}) - k_{dSO3}\theta_{SO3}\}\rho_{cat}\Omega_{SO3}$$

# Simulation vs. Actual Data: $SO_2$ Oxidation Test

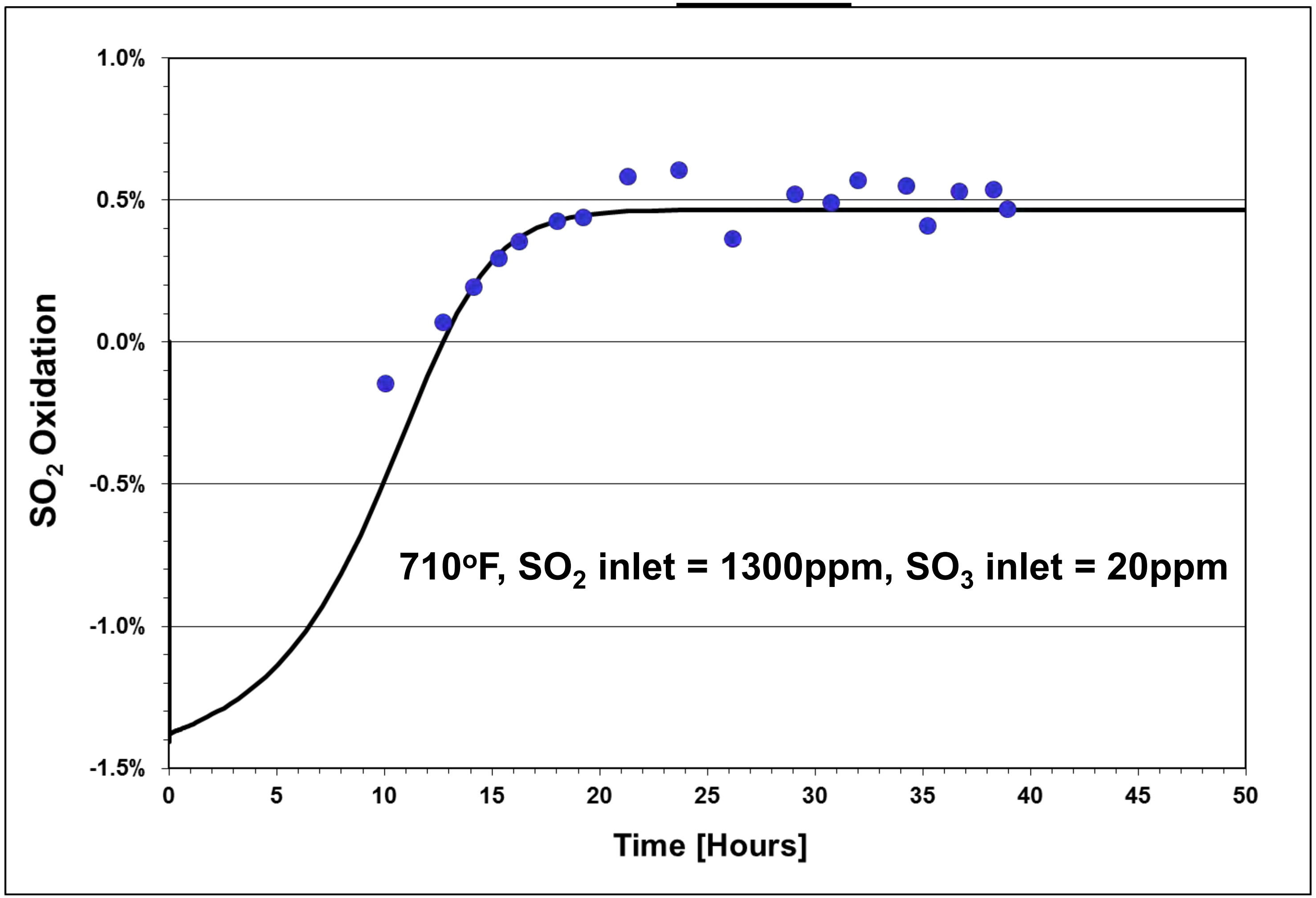
CORMETECH
RELIABILITY. DELIVERED.

Transient is due to $SO_3$ adsorbing onto the catalyst.

Steady state is achieved once the catalyst reaches the stable $SO_3$ coverage for the condition.

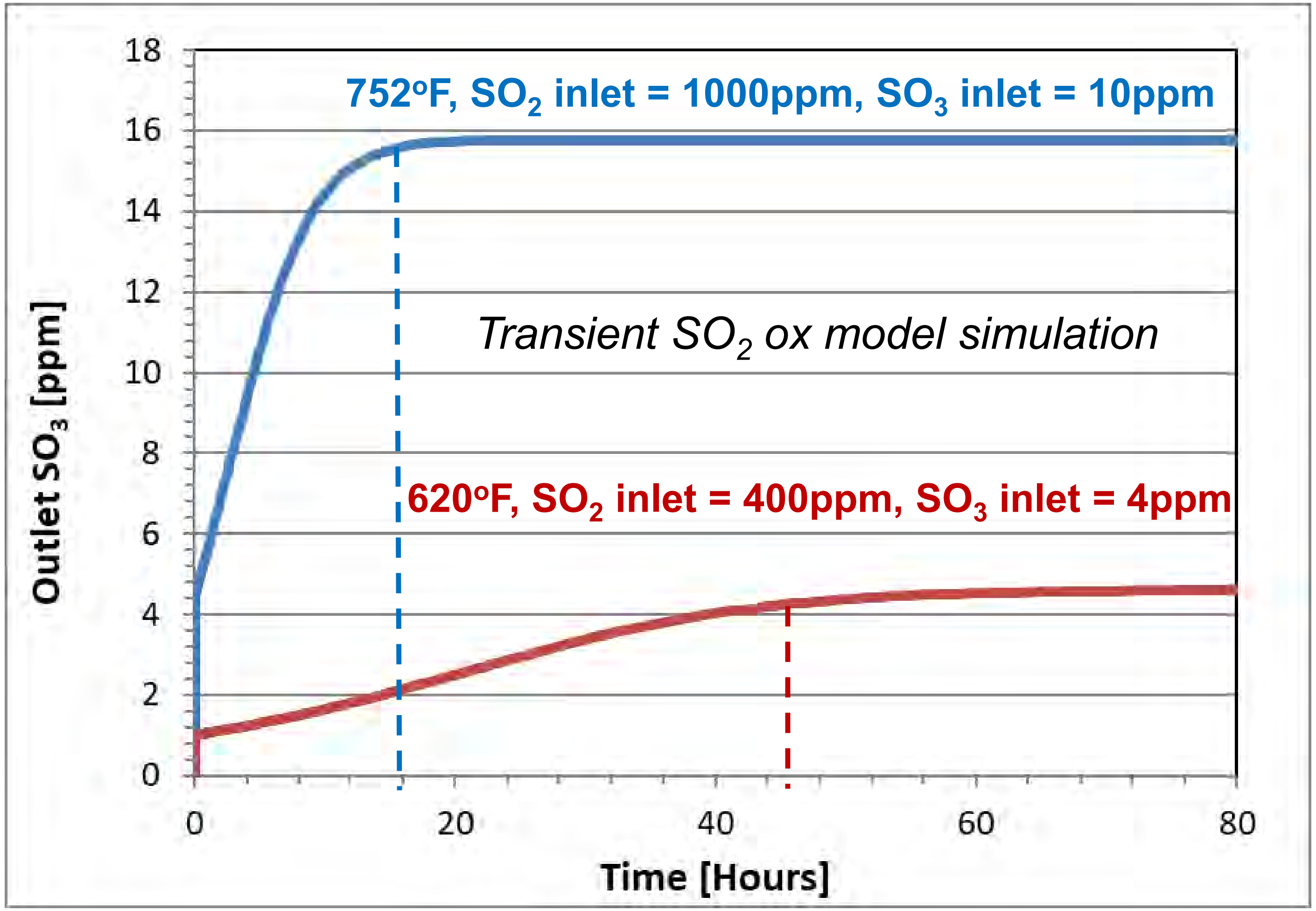
Model predicts trend well.

**SOx flow was turned on at time = 0h.**



# Simulation:
# Aging Time Depends on Test Condition

SOx flow was turned on at time = 0h.




Aging time to reach steady state will depend on testing condition and initial state of the catalyst.

- Temperature
- Inlet $SO_2$ and $SO_3$
- AV
- Fresh or field catalyst

# Simulation:
# Load Cycles (without $NH_3$)

Equilibrium $SO_3$ coverage is a strong function of temperature.

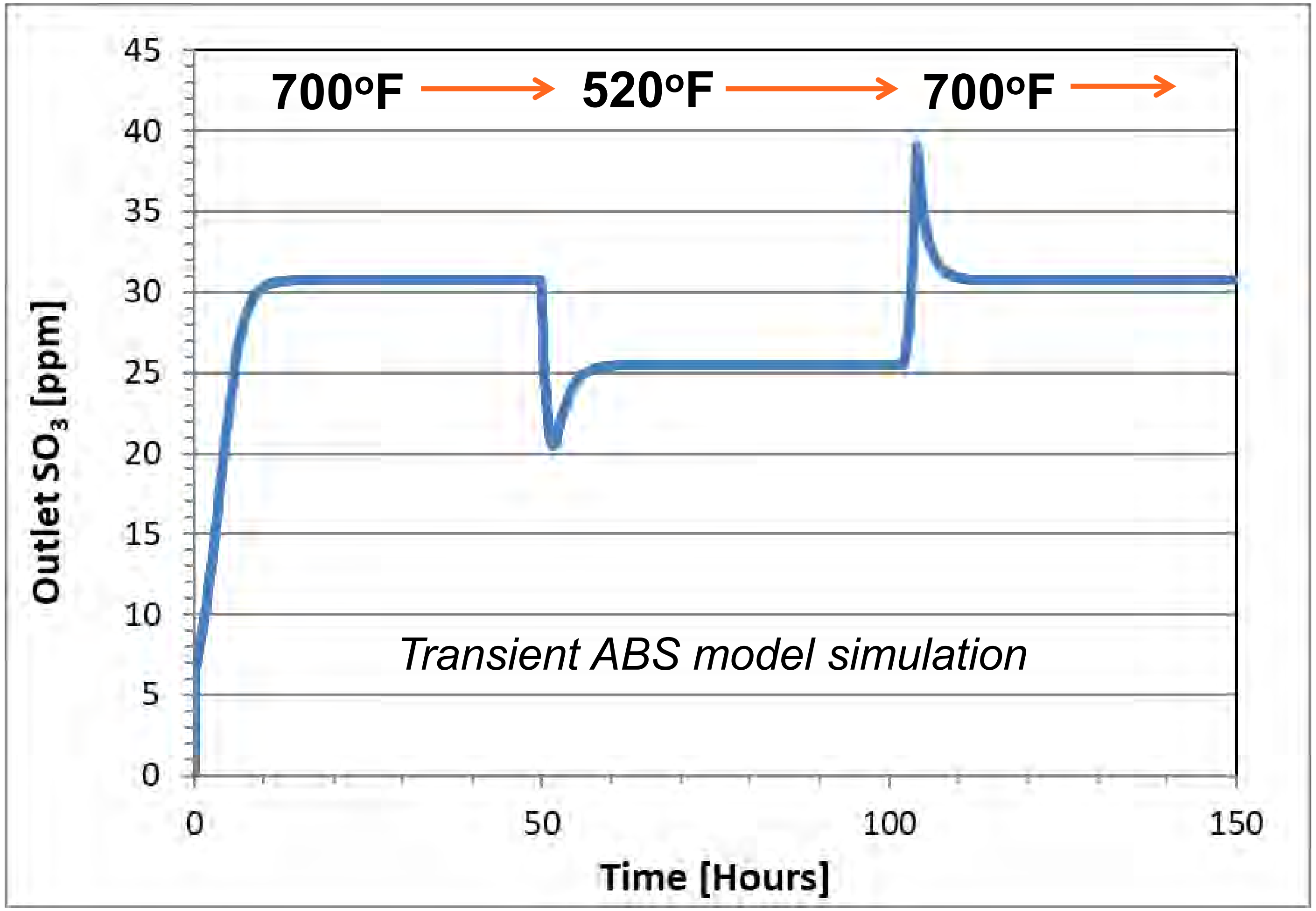
Decreasing temperature:

- Yields $SO_3$ dip, then stable.

Increasing temperature:

- Yields $SO_3$ spike, then stable.

**$SO_2$ inlet = 2500ppm, $SO_3$ inlet = 25ppm, MR = 0**

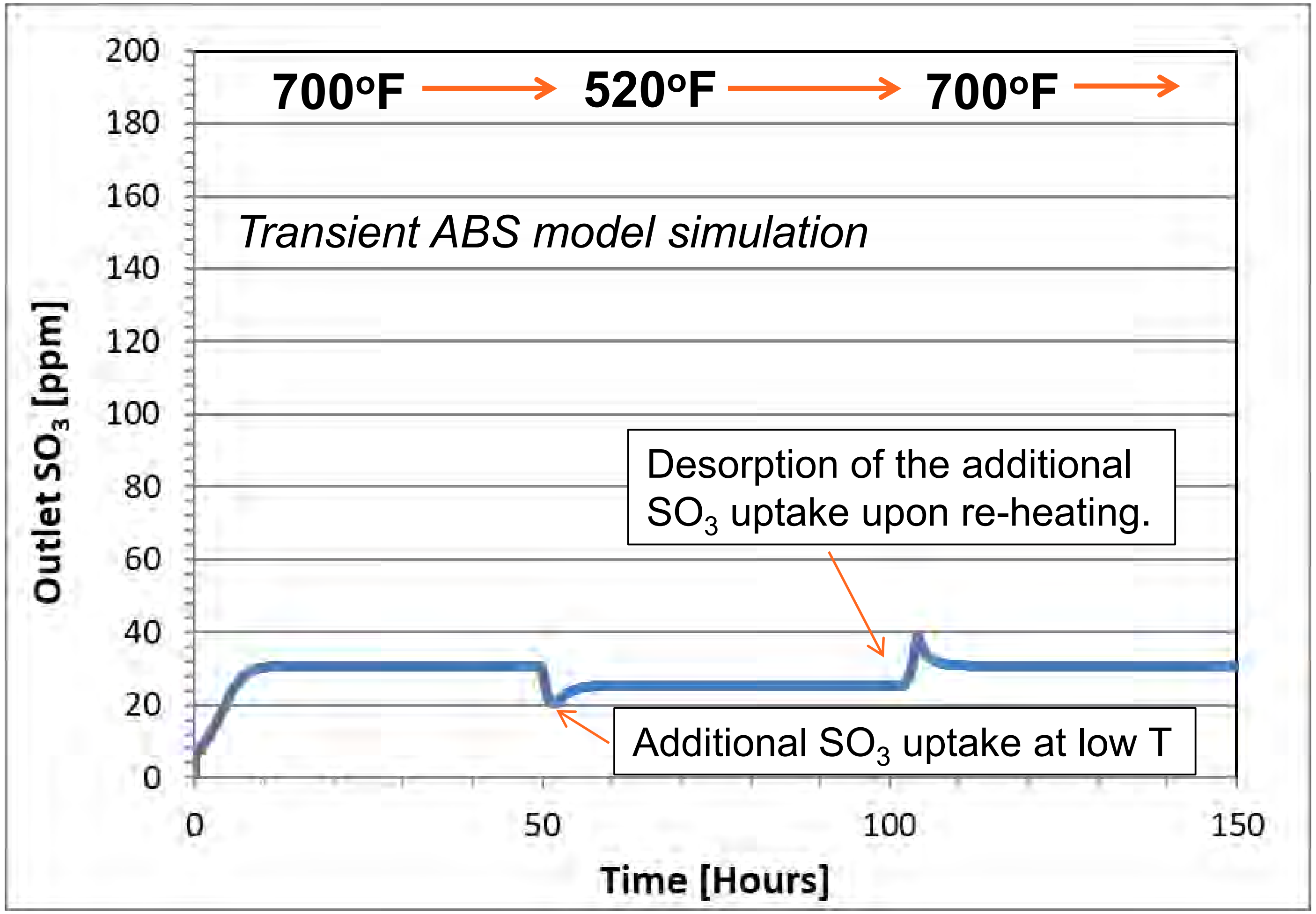


# Simulation:
# Load Cycles (without $NH_3$)

**Without $NH_3$ injection:**

Transients are due to changes in $SO_3$ adsorption/desorption equilibria on the catalyst at the different temperatures.

**$SO_2$ inlet = 2500ppm, $SO_3$ inlet = 25ppm, MR = 0**



# Simulation: Load Cycles (with $NH_3$)

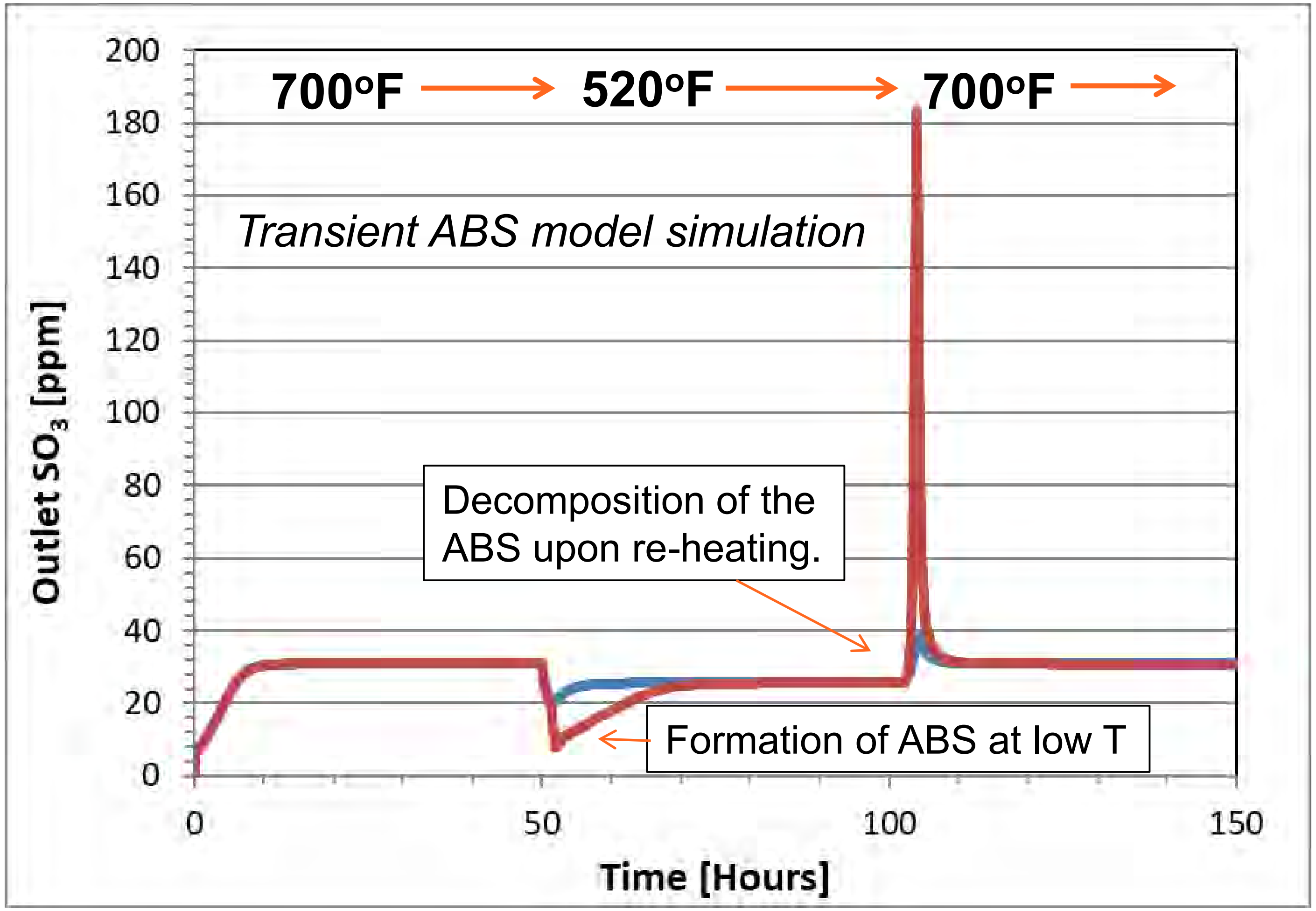
**With $NH_3$ injection:**

Transients are due to changes in $SO_3$ adsorption/desorption equilibria on the catalyst at the different temperatures

+

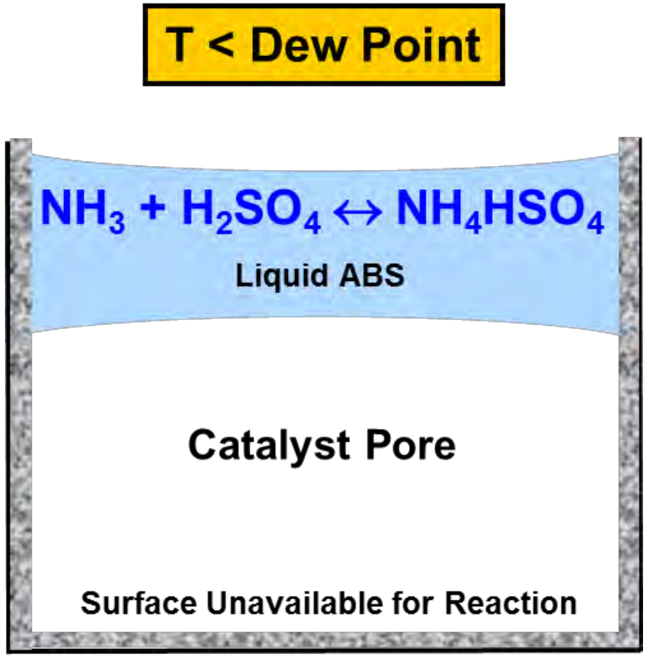
ABS formation/decomposition.

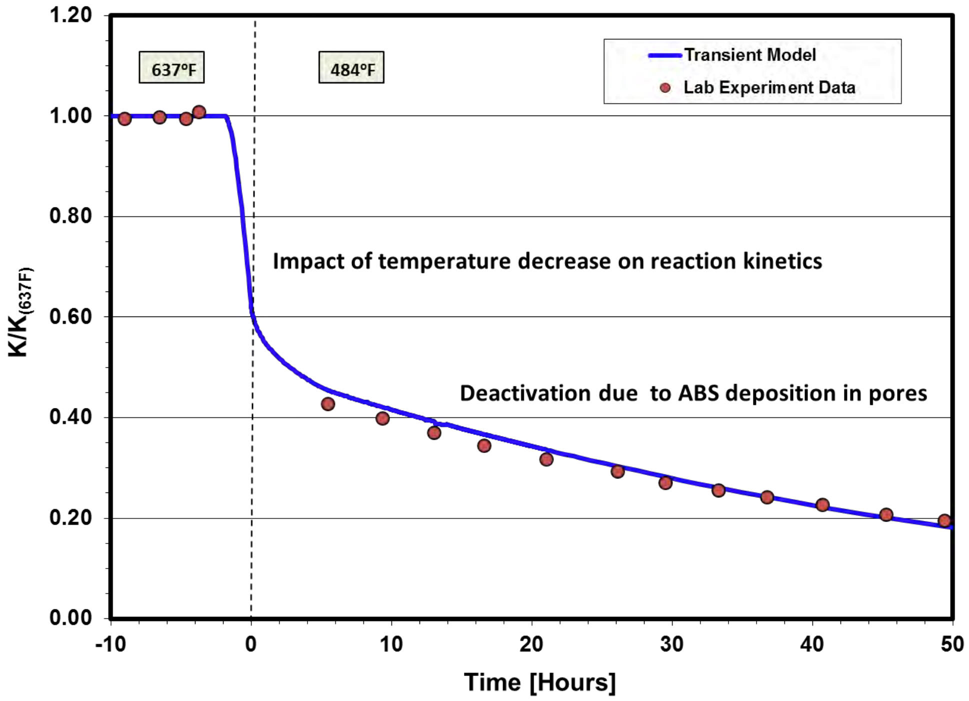
**$SO_2$ inlet = 2500ppm, $SO_3$ inlet = 25ppm, MR = 0.92**



# ABS Deposition Deactivates Catalyst

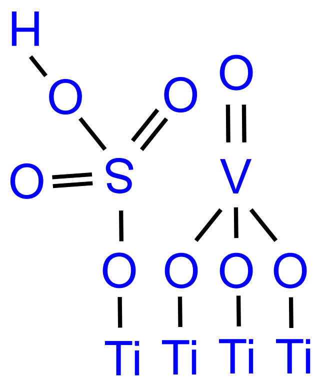
- **Deposited ABS: bad for DeNOx activity.**
  - Blocks pores → reactants (NOx, $NH_3$) can't reach catalyst active sites.

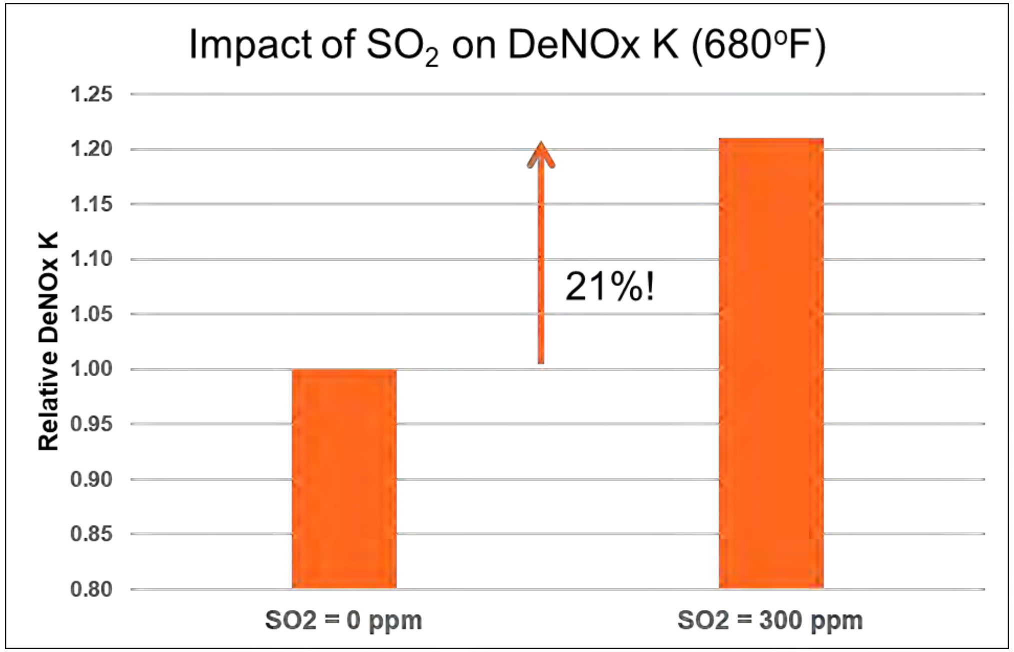


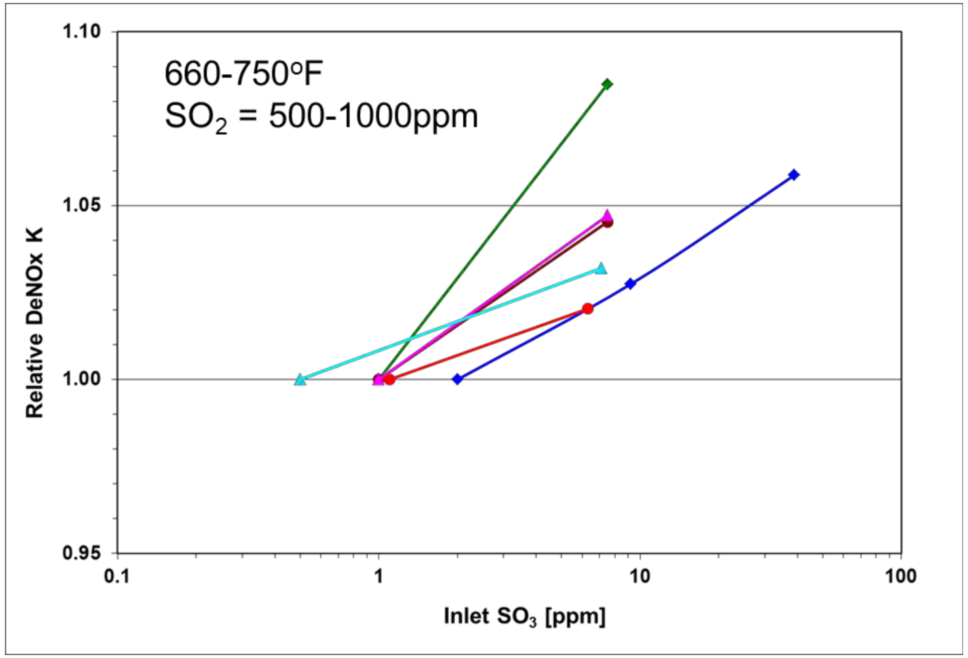



# Adsorbed Sulfate Promotes Activity

- **Adsorbed sulfate: good for DeNOx activity.**
  - Formed by $SO_3$ adsorption on catalyst.
  - Sulfate enhances surface acidity → promotes $NH_3$ adsorption.
  - What is the impact of transients?



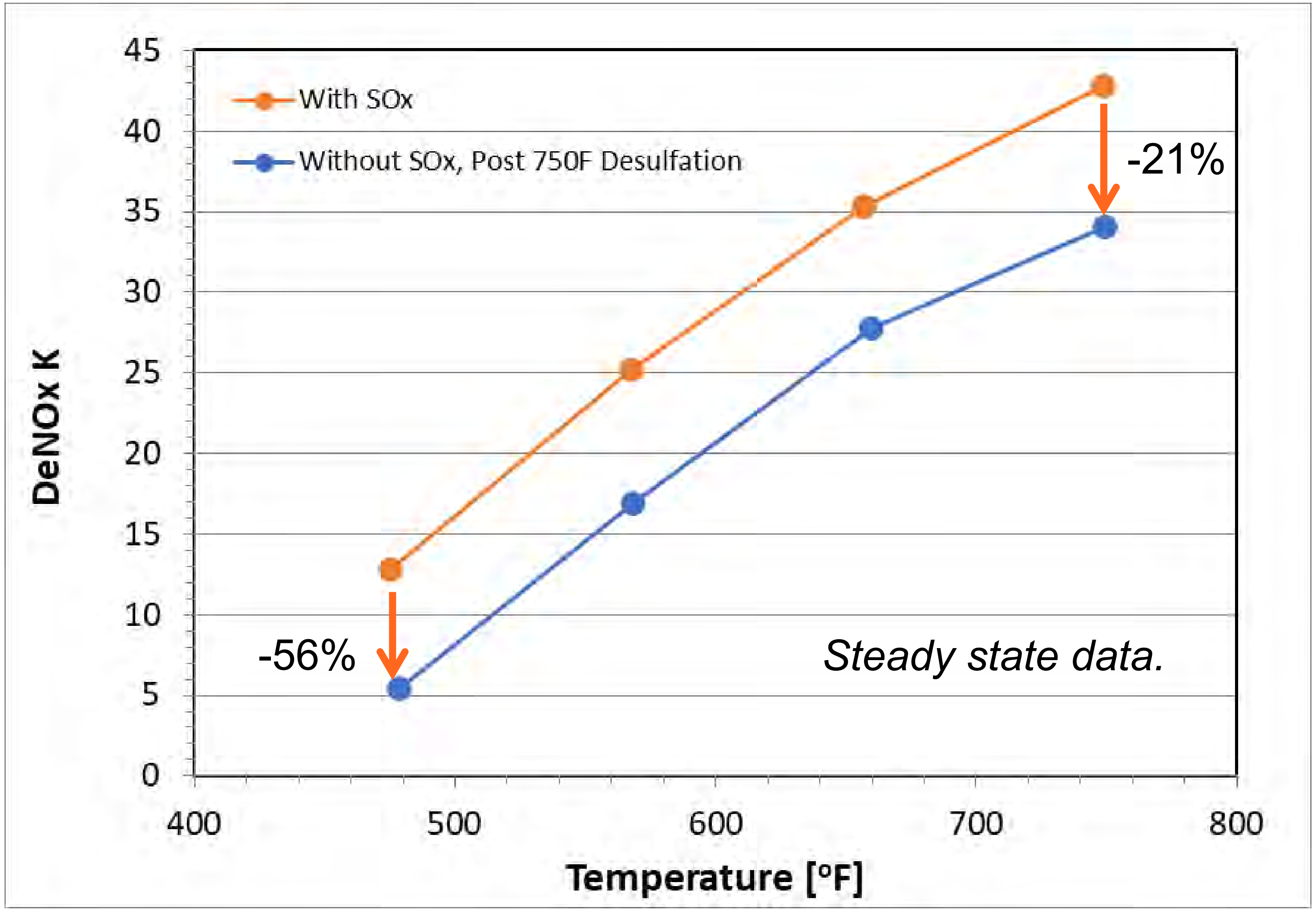



# $SO_3$ Impact on DeNOx Activity: Sulfated vs. De-Sulfated Catalyst States

Data set for two "states":

- After 750°F aging "with SOx" to fully sulfate.
- After 750°F soak "without SOx" to fully desulfate.

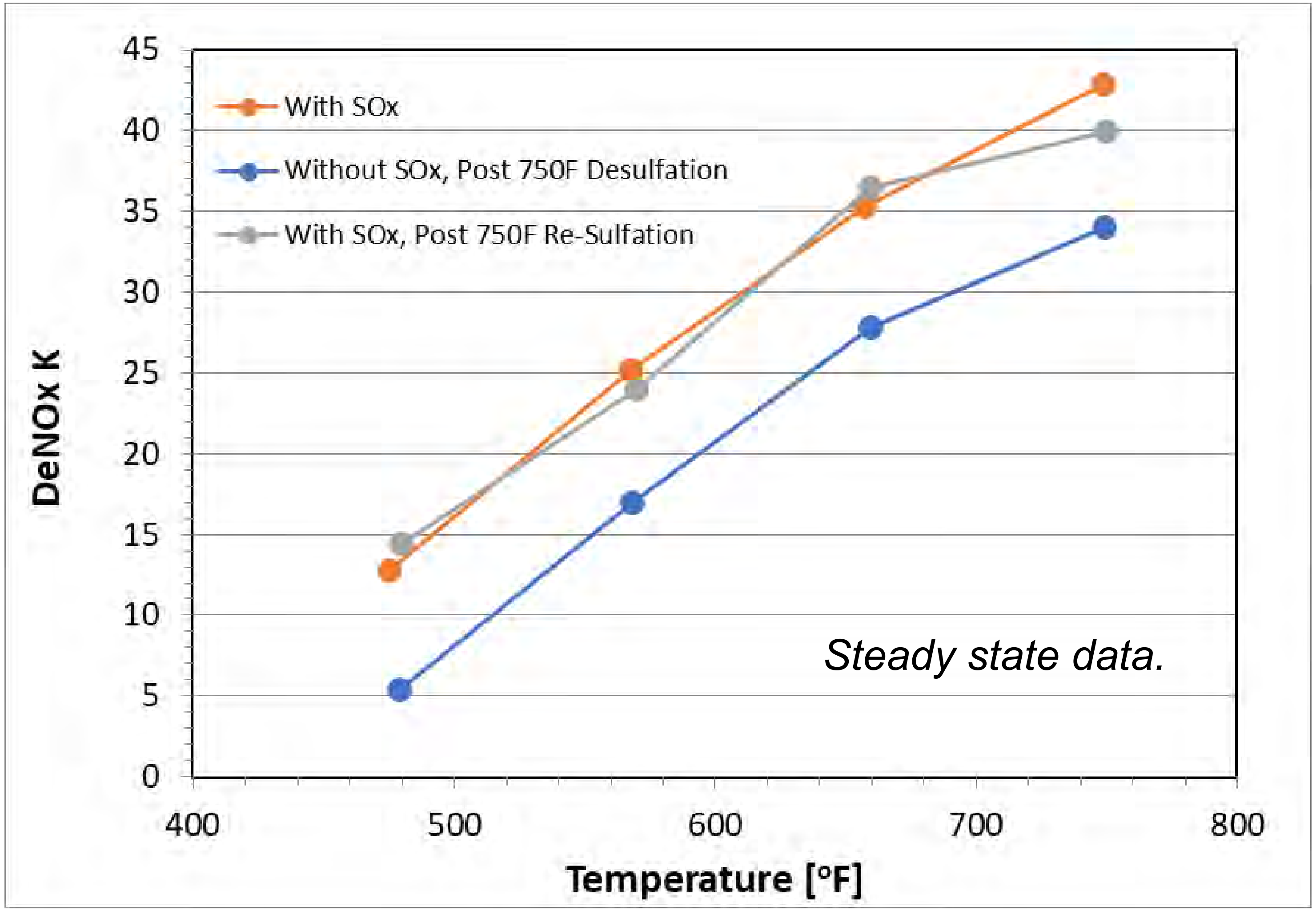
Sulfate has a big impact!



# $SO_3$ Impact on DeNOx Activity: Impact of Re-Sulfation

CORMETECH
RELIABILITY. DELIVERED.

Aging catalyst again at 750°F "with SOx" restores the DeNOx activity.



# Simulation: Sulfate Desorption Transient Fully Sulfated State → No SOx Flow

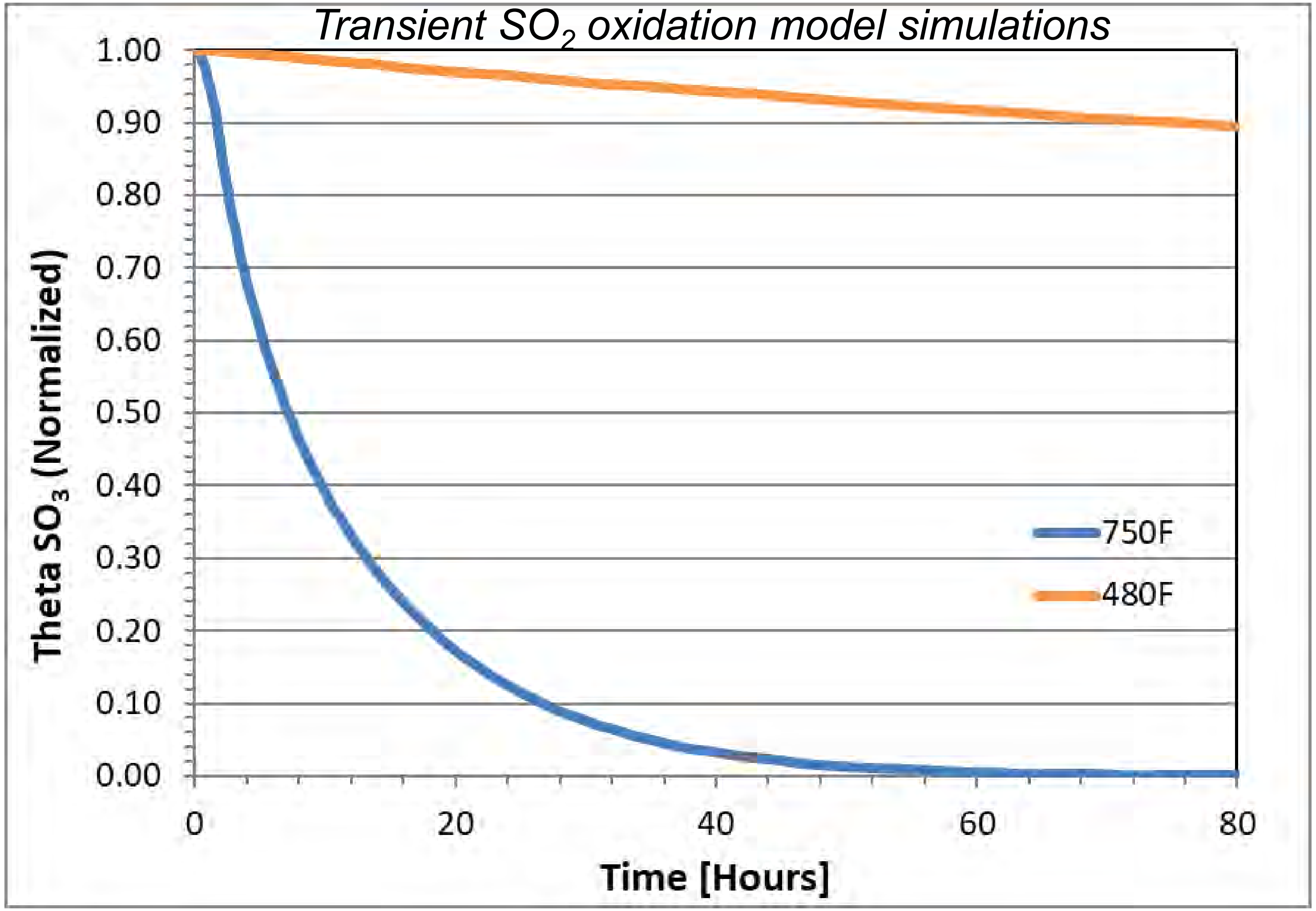
**At 750°F:**

Sulfate desorption is fast.

**At 480°F:**

Sulfate desorption is slow.

Do the sulfate transients predict DeNOx transients after turning off SOx flow?

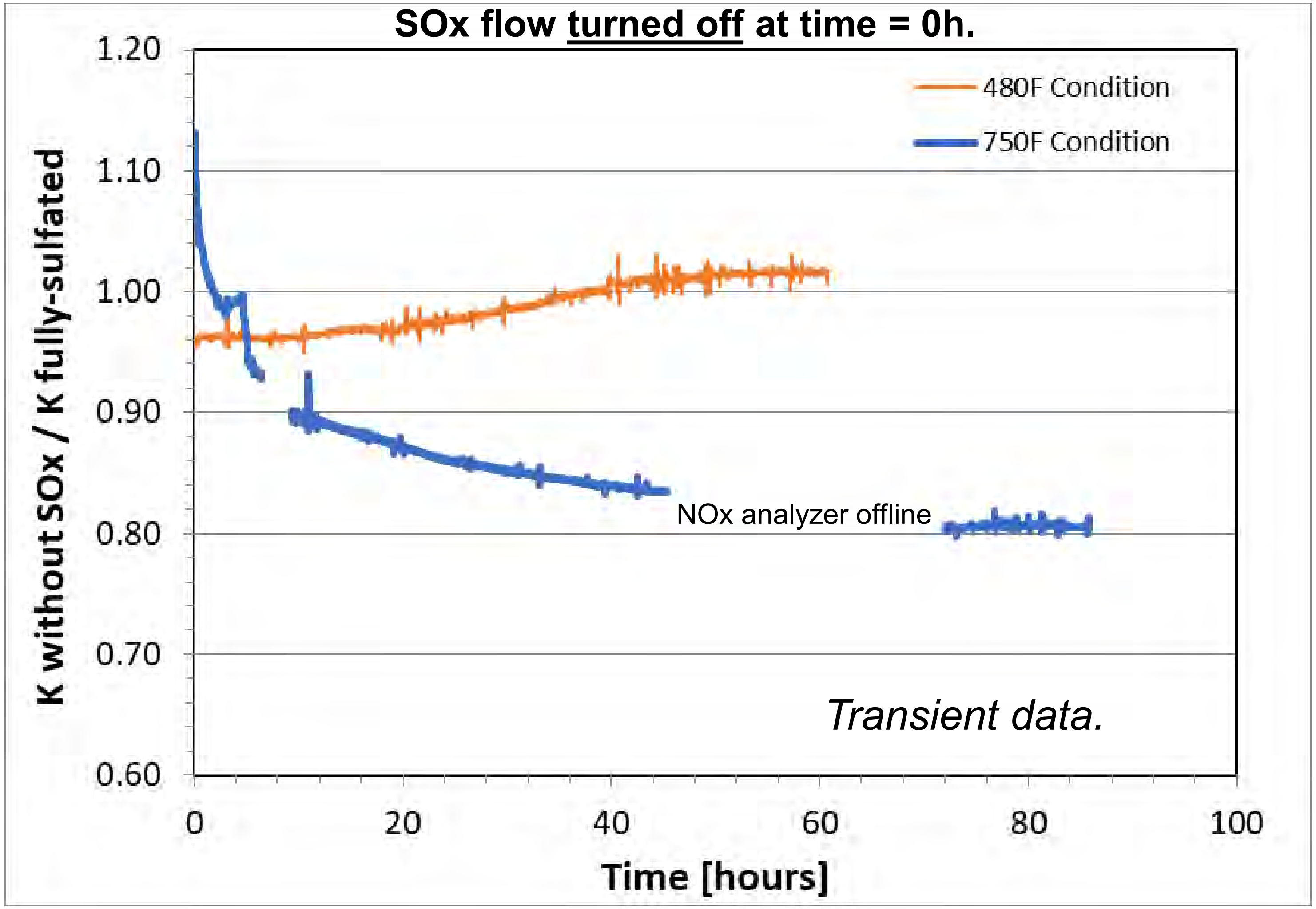


# Test Data: DeNOx Transient
# Fully Sulfated State → No SOx Flow

**At 750°F:** fast sulfate desorption leads to rapid DeNOx activity loss.

**At 480°F:** slow sulfate desorption  sustains high DeNOx activity for longer.

$SO_2$ ox transient model can predict the catalyst DeNOx responses for different operating scenarios.



# SOx and the SCR: Summary

- How does the SCR impact BOP operations with respect to sulfur?
  - Catalytic $SO_2$ oxidation: increase in $SO_3$ across SCR.
  - Transients: dynamics of $SO_3$ / ABS storage and release from the catalyst.

- How does sulfur affect SCR catalyst performance?
  - Adsorbs on the catalyst as sulfate.
  - Positive impact on DeNOx.
  - Slightly negative impact on Hg oxidation.
  - Leads to calcium sulfate surface blinding for PRB.
  - Increases phosphorus accumulation rate for PRB.
  - Reacts with $NH_3$ at low temperatures to form ABS salts in the pores and cause a reversible deactivation.

**CORMETECH has the tools to help in these evaluations.**

# Thank You.

Dr. Christopher Bertole

bertolecj@cormetech.com