

REINHOLD ENVIRONMENTAL Ltd.



**2018 NO_x-Combustion Round Table
& Expo Presentation**

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

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RELIABILITY. DELIVERED.

SO_x and the SCR - How Sulfur Influences Catalyst Operation

Christopher Bertole

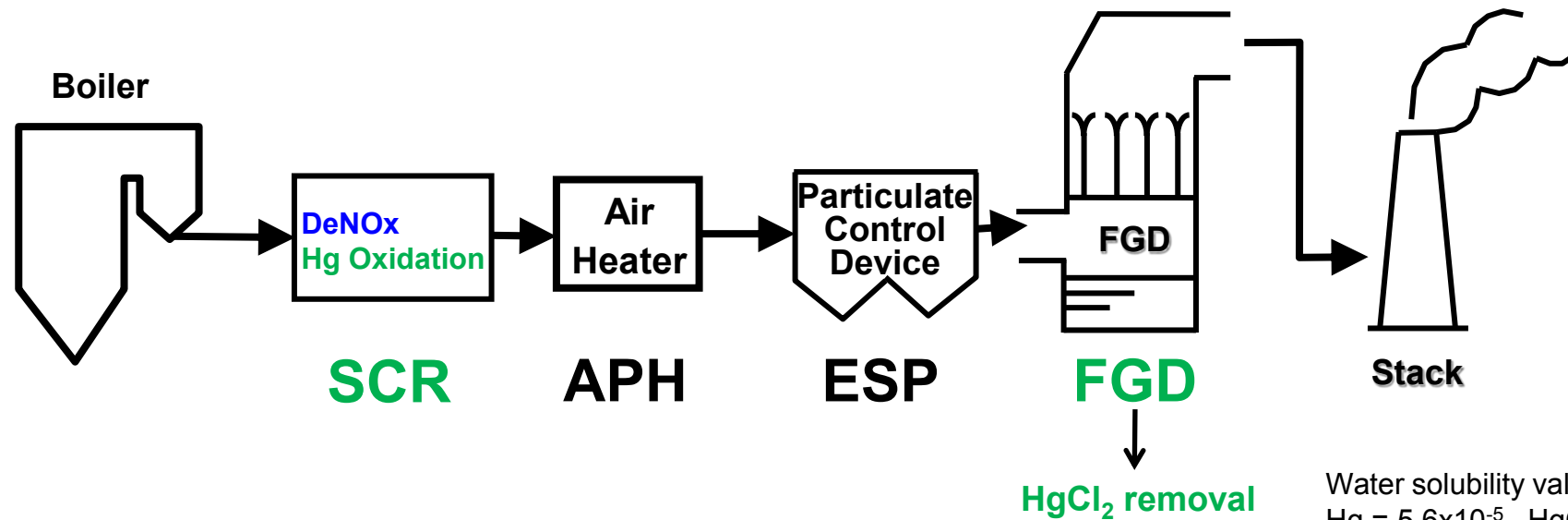
2018 Reinhold NO_x-Combustion-CCR Round Table

Introduction – SCR Functions



- Reduce NOx $4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$

- Oxidize Hg $2\text{Hg} + 4\text{HCl} + \text{O}_2 \rightarrow 2\text{HgCl}_2 + 2\text{H}_2\text{O}$
 $2\text{Hg} + 4\text{HBr} + \text{O}_2 \rightarrow 2\text{HgBr}_2 + 2\text{H}_2\text{O}$



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

Sulfur in Coal

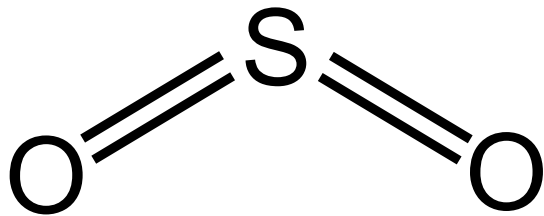


- Form
 - Inorganic sulfides [FeS_2 (pyrite)]
 - Inorganic sulfates [CaSO_4 , FeSO_4]
 - Organosulfur compounds
- Amount
 - Bituminous generally has higher sulfur content (<5wt%) than PRB (<2wt%)
- Release during combustion
 - ~100% of sulfur is volatilized from the burning char particle
 - Present in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

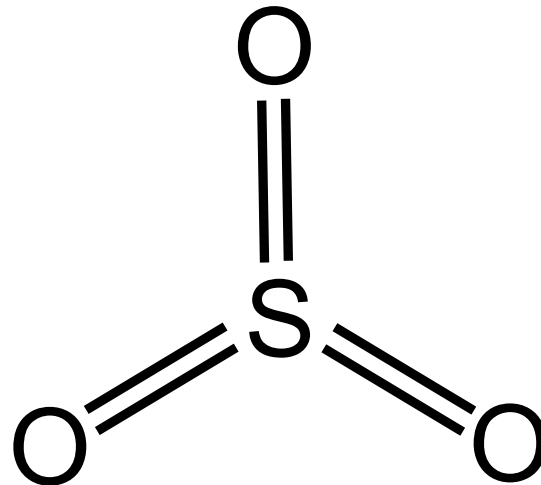
Sulfur in Flue Gas



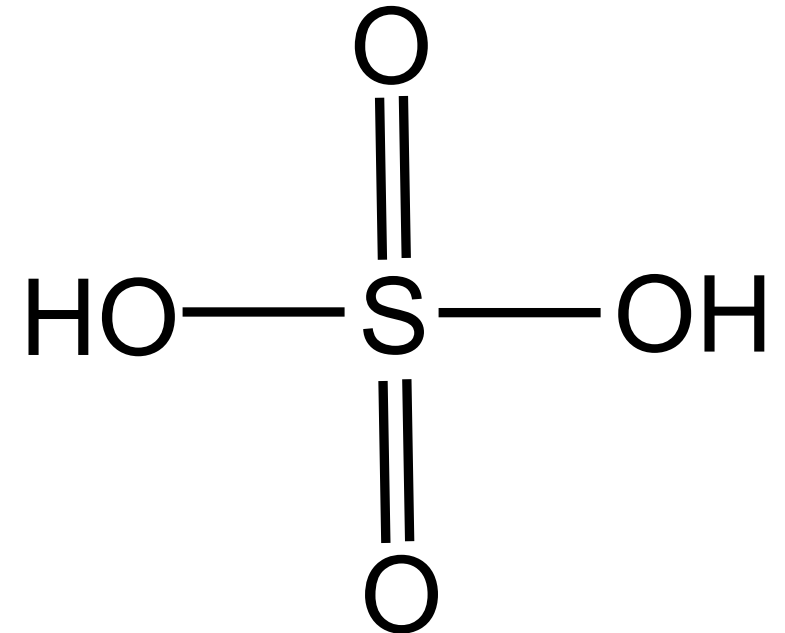
Sulfur Dioxide
(SO₂)
Boiling Point = -10°C



Sulfur Trioxide
(SO₃)
Boiling Point = 45°C

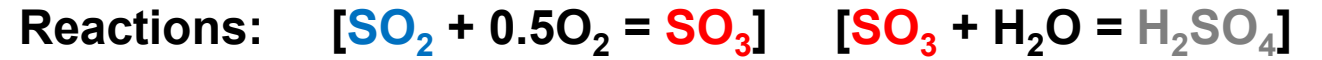


Sulfuric Acid
(H₂SO₄)
Boiling Point = 337°C



Distribution between these three species depends on temperature.

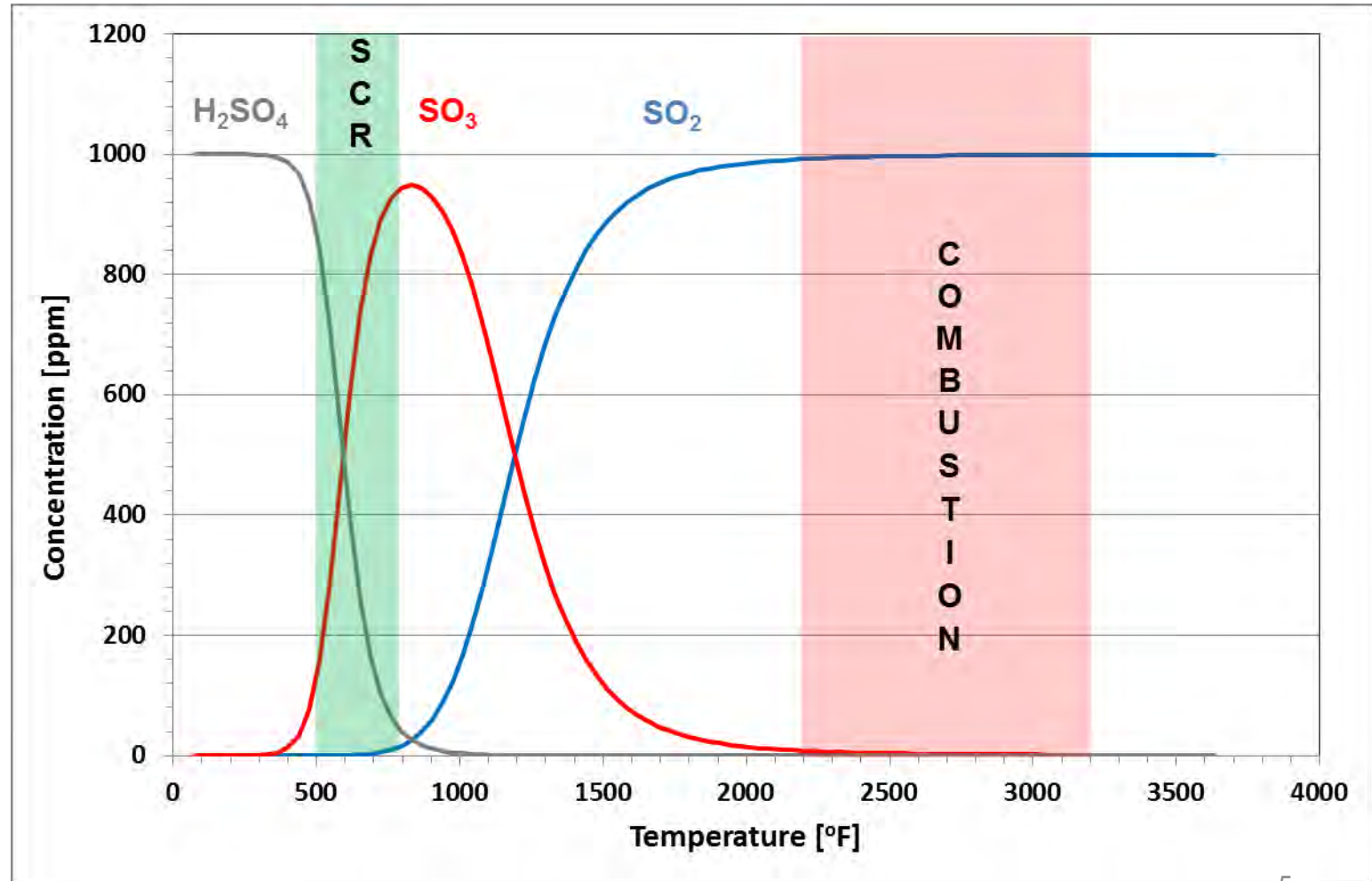
Thermodynamics



At Equilibrium

Combustion T range:
SO₂ favored.

SCR T range:
SO₃ / H₂SO₄ favored.



SO₂ Oxidation – Slow Reaction Kinetics

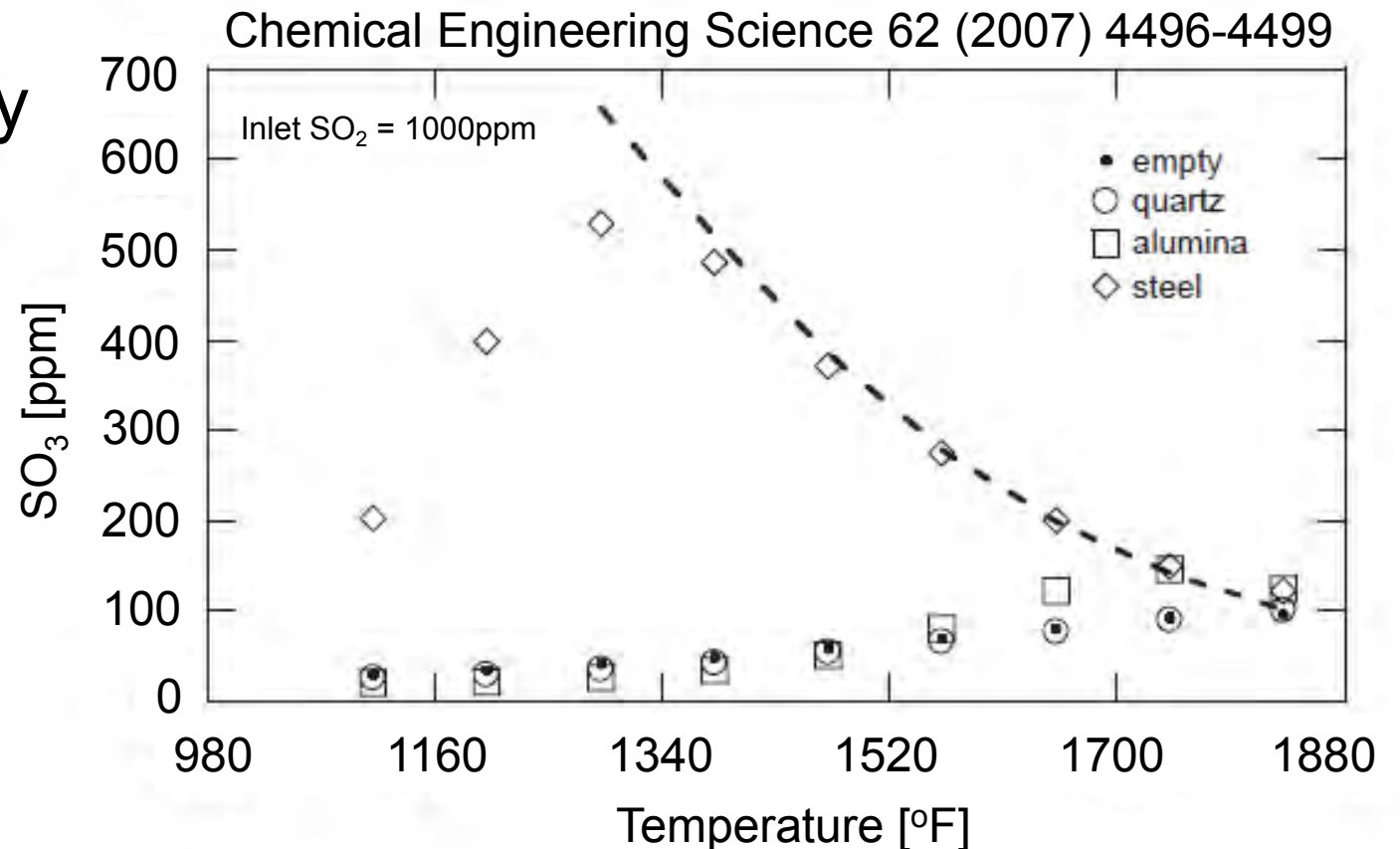


Gas Phase Reaction

- “empty”: minimal reactivity

Solid Catalyzed

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



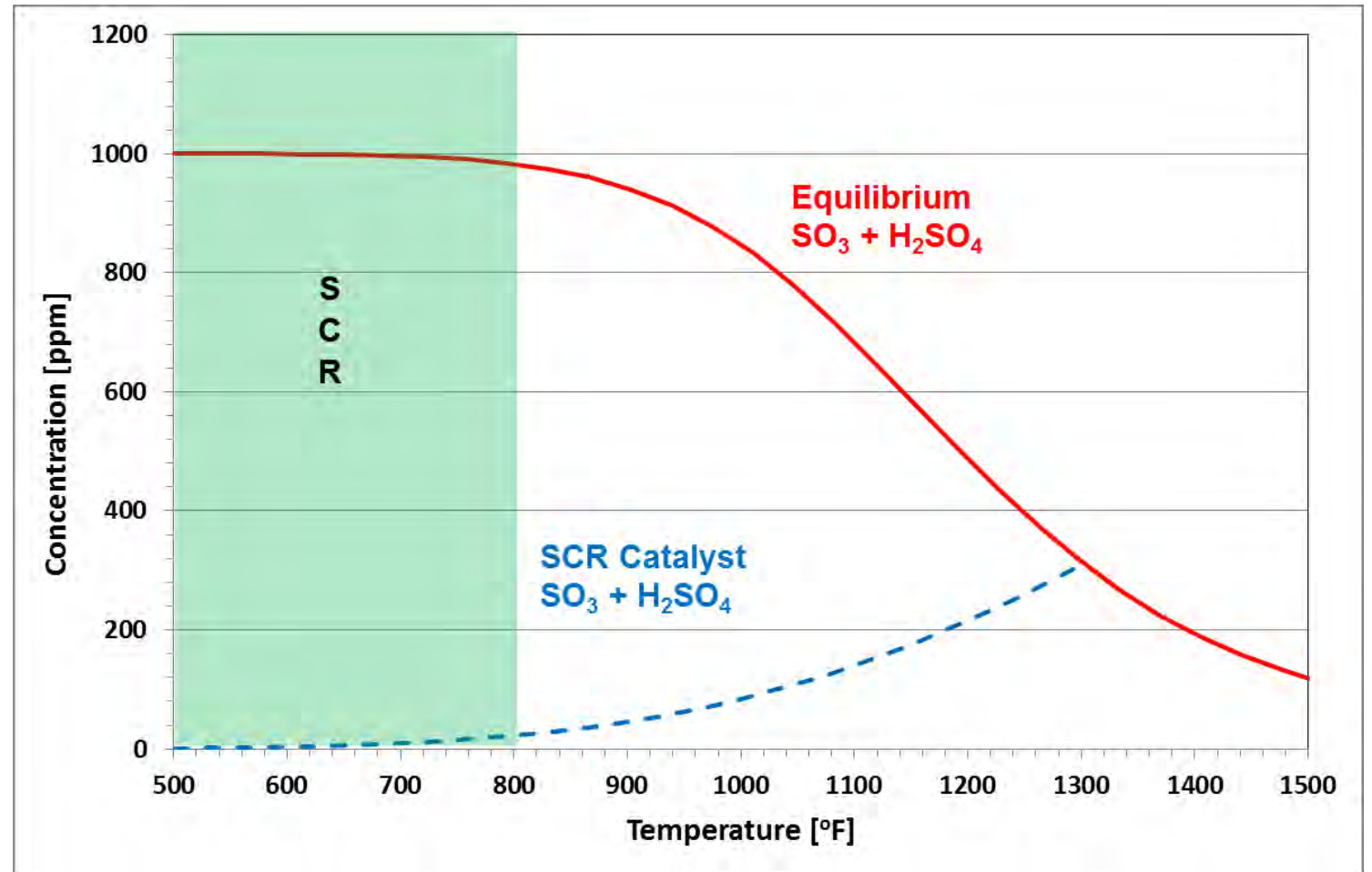
SO₂ Oxidation – Slow Reaction Kinetics



In the SCR

SO₂ oxidation rate over the SCR catalyst is kinetically limited.

Very far away from reaching equilibrium.



SOx and the SCR: Workshop Overview



- How do SO_2/SO_3 affect the ability of the SCR catalyst to function for DeNOx and Hg oxidation?
- How does the SCR affect BOP operations with respect to sulfur?

SO_x and the SCR: Workshop Overview



- How do SO₂/SO₃ affect the ability of the SCR catalyst to function for DeNO_x and Hg oxidation?
 - Adsorption on the catalyst.
 - Positive impact on DeNO_x.
 - Slightly negative impact on Hg oxidation.
 - Increases phosphorus accumulation rate for PRB.
 - Reacts with NH₃ at low temperatures to form ABS salts in the pores and cause a reversible deactivation.
- How does the SCR affect BOP operations with respect to sulfur?

SO₂/SO₃ Interaction with SCR Catalyst

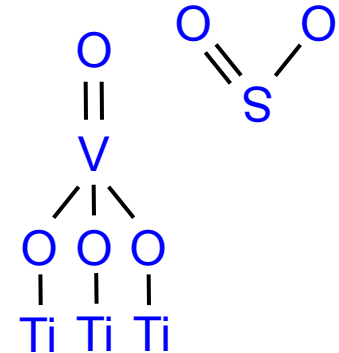


- Adsorption of SO_x onto the V-W/Ti SCR catalyst surface

- **No significant SO₂ adsorption**

- Applied Catalysis B: Environmental 19 (1998) 103-117 & references therein

- SO₂ reacts from the gas phase with catalyst-bound oxygen to form SO₃

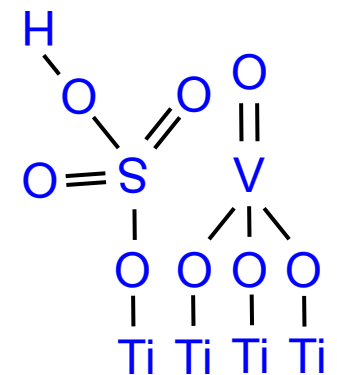


- **Strong SO₃ adsorption**

- Applied Catalysis B: Environmental 92 (2009) 30-40

- SO₃ adsorbs onto TiO₂ sites to form TiO₂-SO₄ sites

- It does not adsorb onto the VO_x or WO_x active sites for SCR



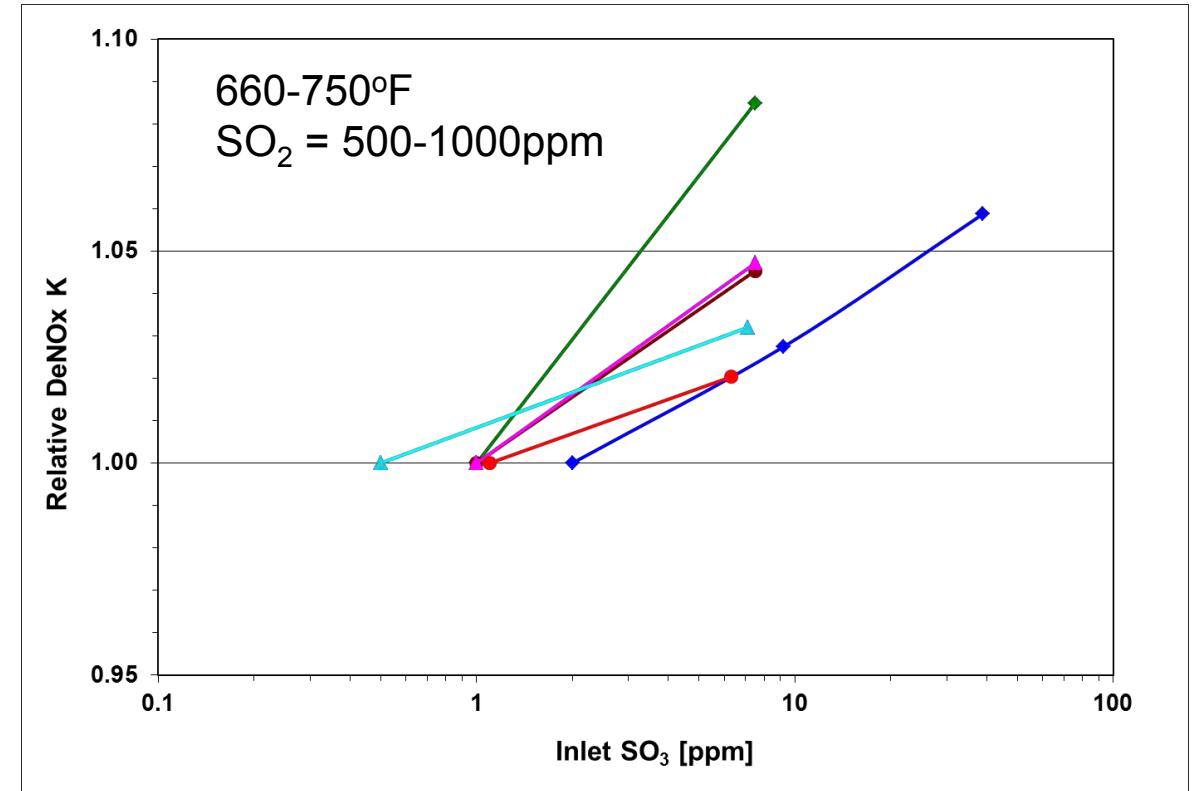
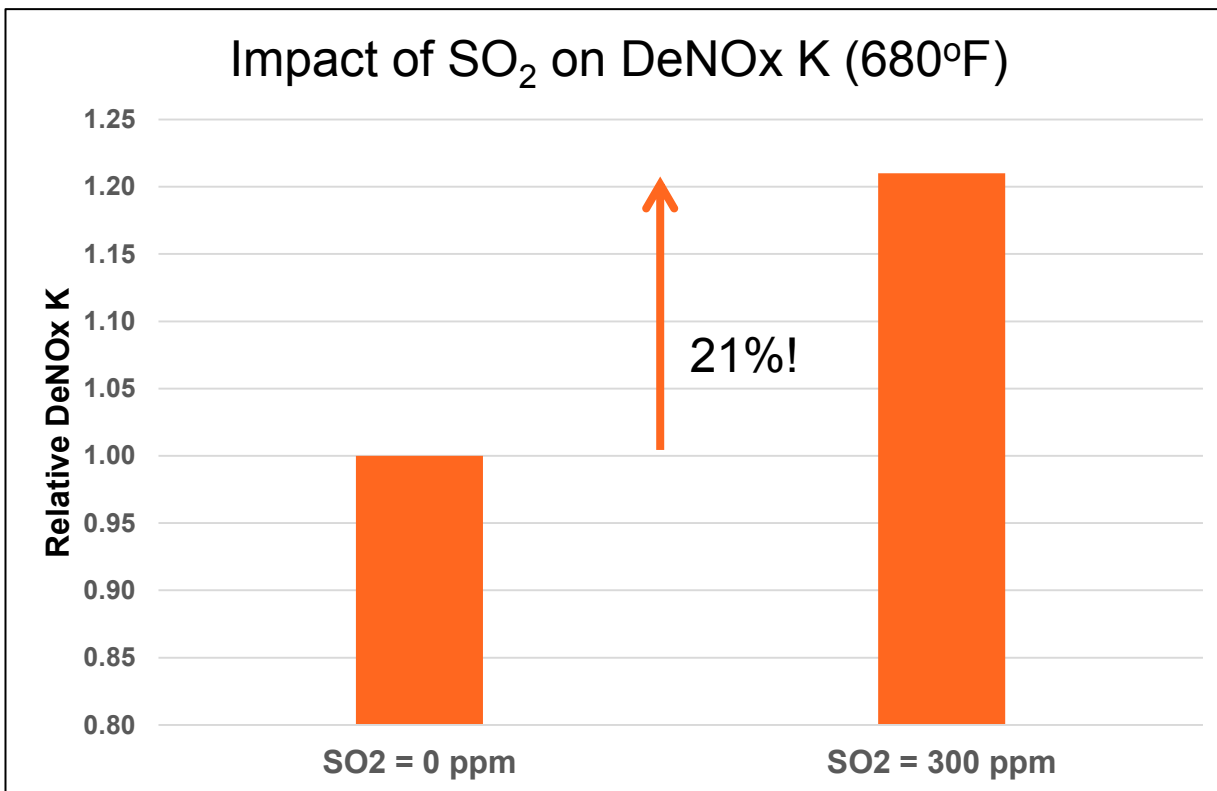
Sulfur Stability and Enhanced Activity



- V-W/Ti catalyst is a good catalyst for coal-fired boilers because...
 - It's sulfur stable!
 - SO_3 does not interact V_2O_5 or WO_3
 - $\text{TiO}_2\text{-SO}_4$ decomposes at relatively low temperatures and does not inhibit SCR activity
 - Other commercially applied SCR catalysts (e.g., Cu/zeolites, Fe/zeolites) are not sulfur stable and can be used only for low sulfur gas or diesel units
- DeNOx activity of V-W/Ti SCR catalyst is in fact enhanced by sulfur
 - Sulfate increases the density of Bronsted acid sites on the catalyst
 - Leads to higher NH_3 coverage

Sulfur Impact on SCR Activity

- SO₂ injection for de-sulfated catalyst has largest K impact.
- SO₃ co-injection with SO₂ yields further increase in K.

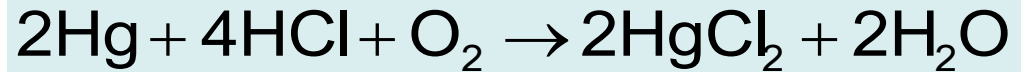


Need to consider sulfur's impact on catalyst potential when assessing the conversion of coal units to gas firing.

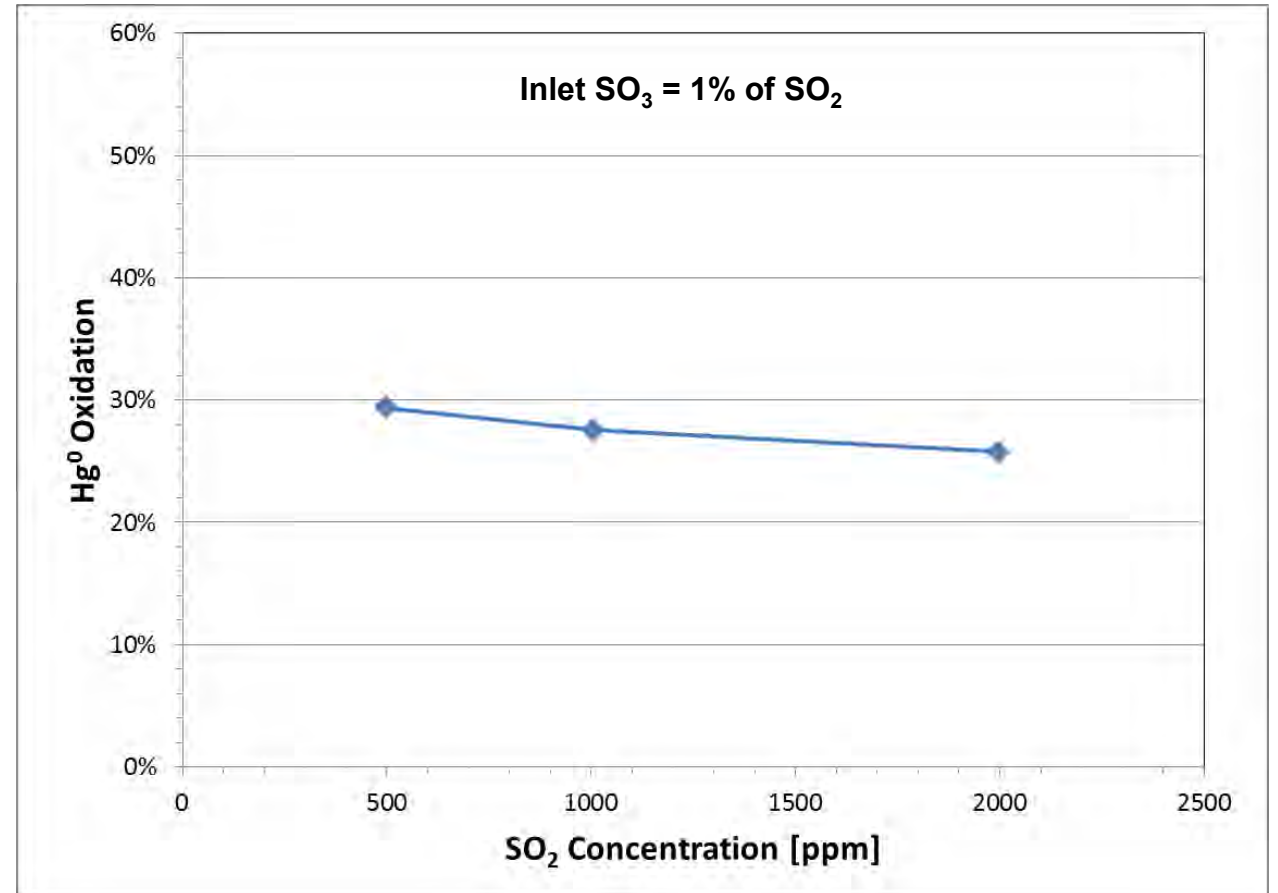
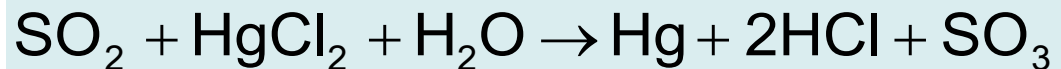
Sulfur Impact on Hg Oxidation Activity



Desired reaction:



SO₂ has a minor inhibiting effect on Hg oxidation through reduction of Hg²⁺



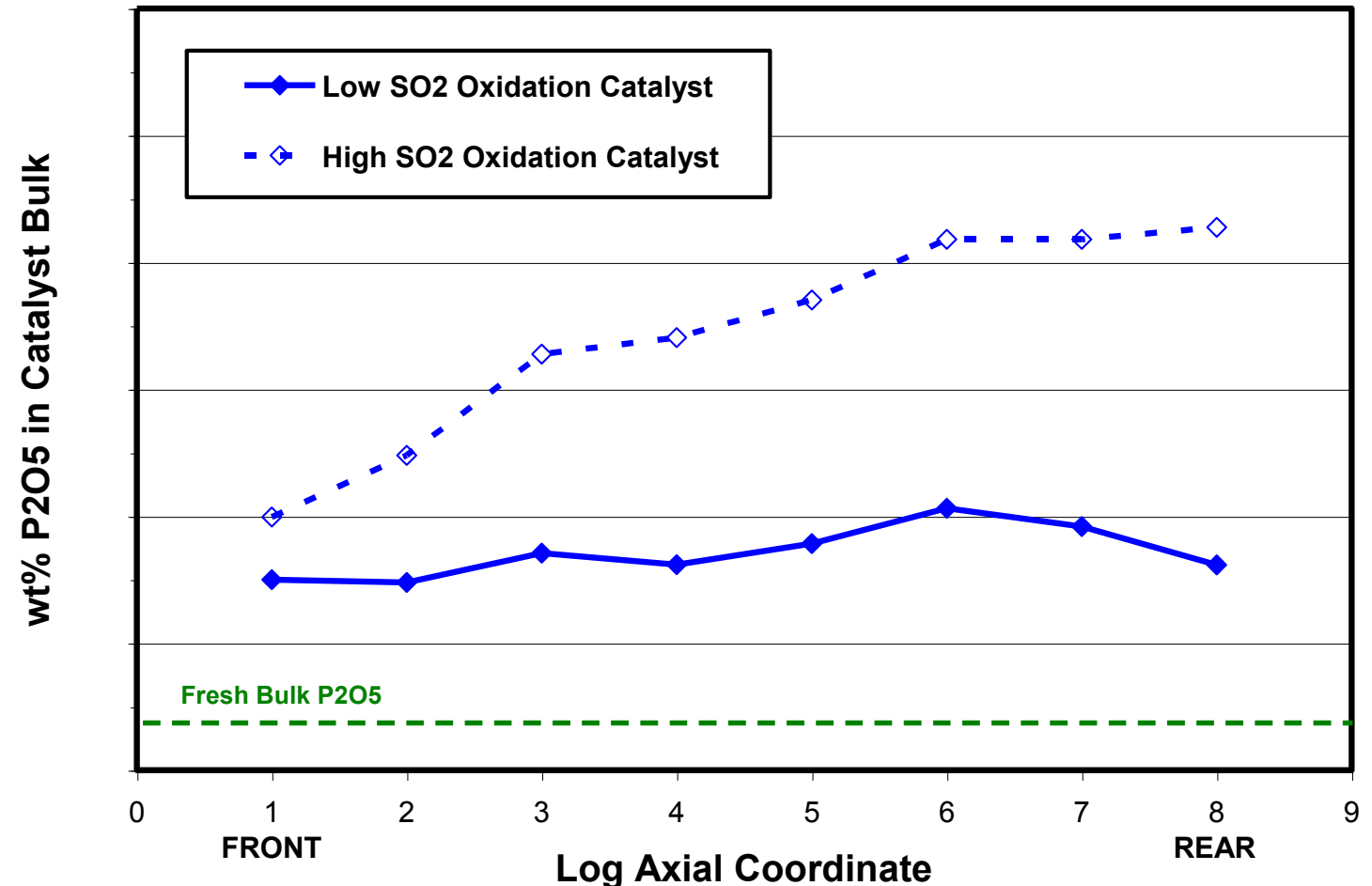
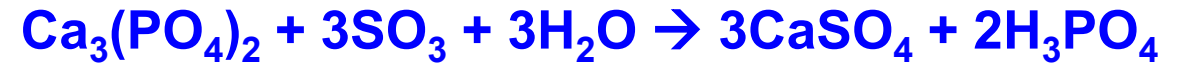
750°F, 3.5% O₂, 11% H₂O, HCl = 11 ppm, 350 ppm NO, 0.2 MR, CO = 100 ppm

SO₂ Oxidation in the SCR Affects Catalyst Phosphorus Accumulation Rate for PRB



Staged combustion PRB-firing boilers can exhibit high SCR deactivation rates due to Ca and P deposition.

The gaseous P that causes catalyst deactivation forms from SO₃ reacting with Ca₃(PO₄)₃ in the fly ash within the SCR itself.



Sulfur Impact on SCR at Low Load



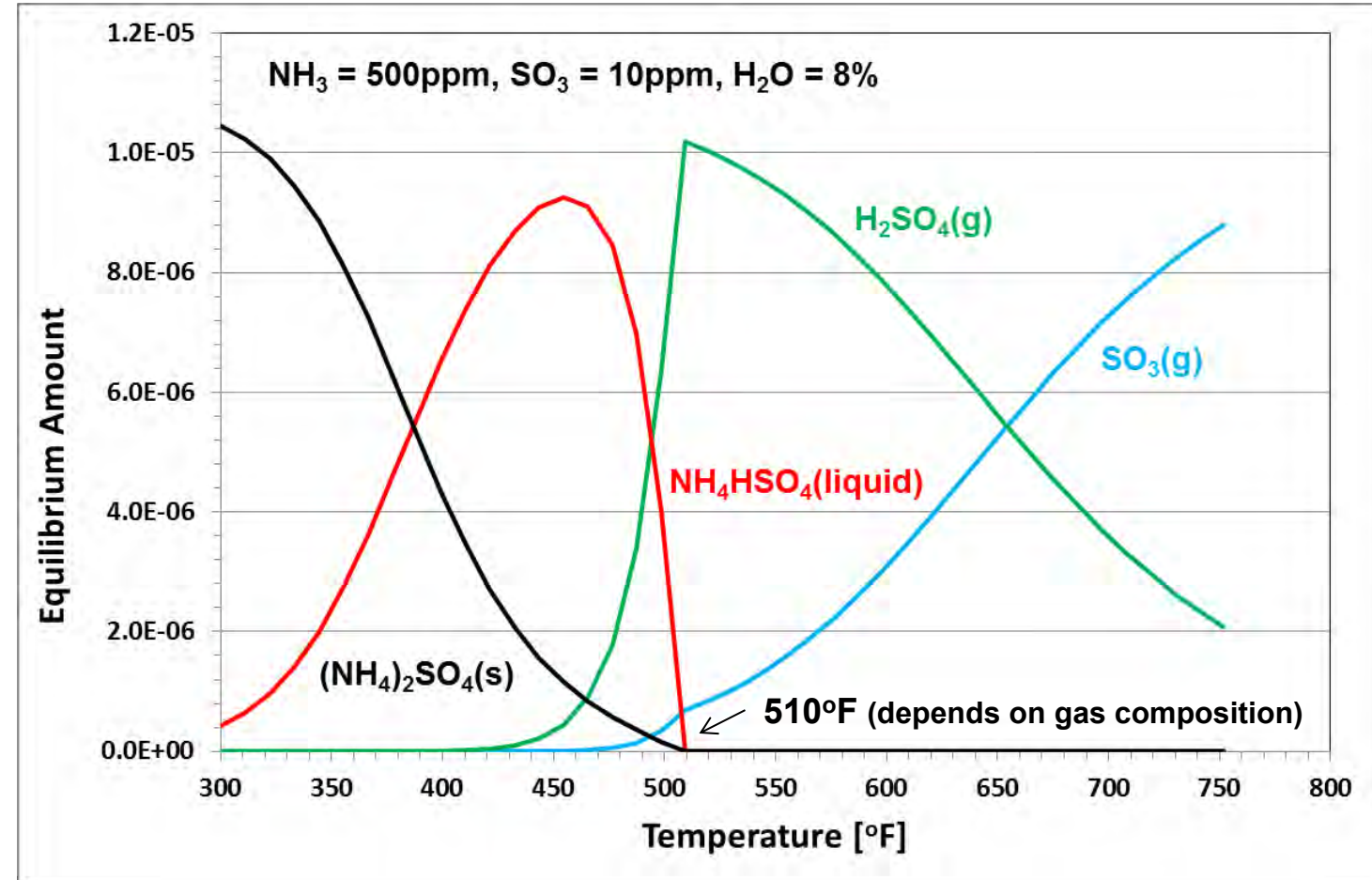
Ammonium Bisulfate (ABS)

- $\text{NH}_3 + \text{H}_2\text{SO}_4 \leftrightarrow \text{NH}_4\text{HSO}_4$
- White sticky solid; corrosive
- $T_{\text{melting}} = 147^\circ\text{C} / 297^\circ\text{F}$
- $T_{\text{boiling}} > 235^\circ\text{C} / 455^\circ\text{F}$ (decomposes)

Ammonium Sulfate (AS)

- $2\text{NH}_3 + \text{H}_2\text{SO}_4 \leftrightarrow (\text{NH}_4)_2\text{SO}_4$
- White solid
- $T_{\text{melting}} = 235\text{-}280^\circ\text{C} / 455\text{-}536^\circ\text{F}$
(forms liquid ABS and/or decomposes)

Bulk Phase Equilibrium Curve



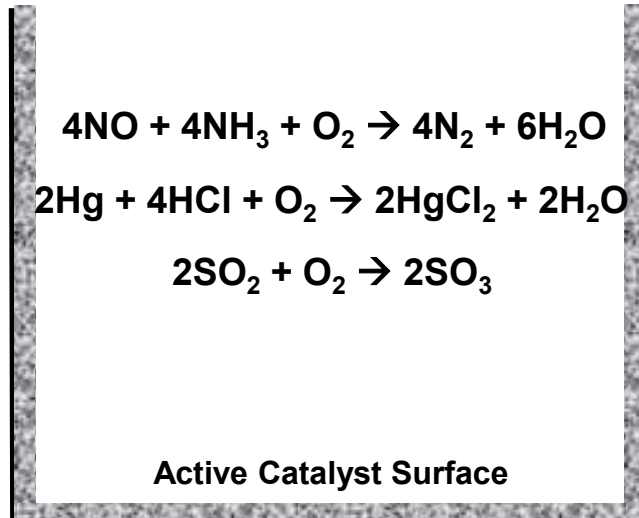
ABS Deposition Controls SCR T_{min}



- ABS deactivates SCR catalyst by blocking pores.
 - Effect is reversible: reheating above dew point removes ABS.

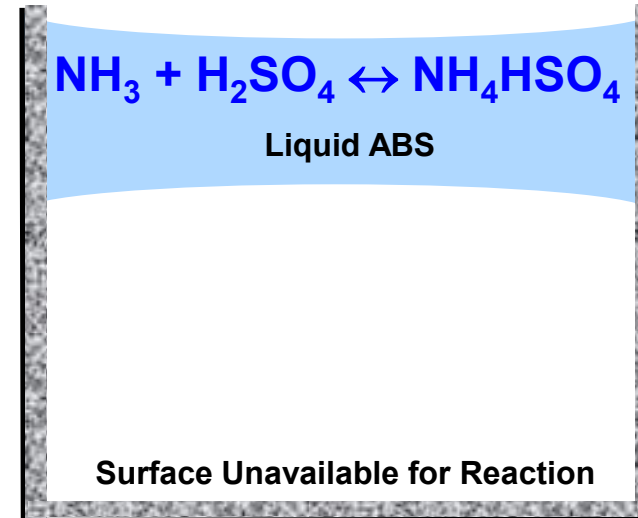
T > Dew Point

Catalyst Pore



T < Dew Point

Catalyst Pore



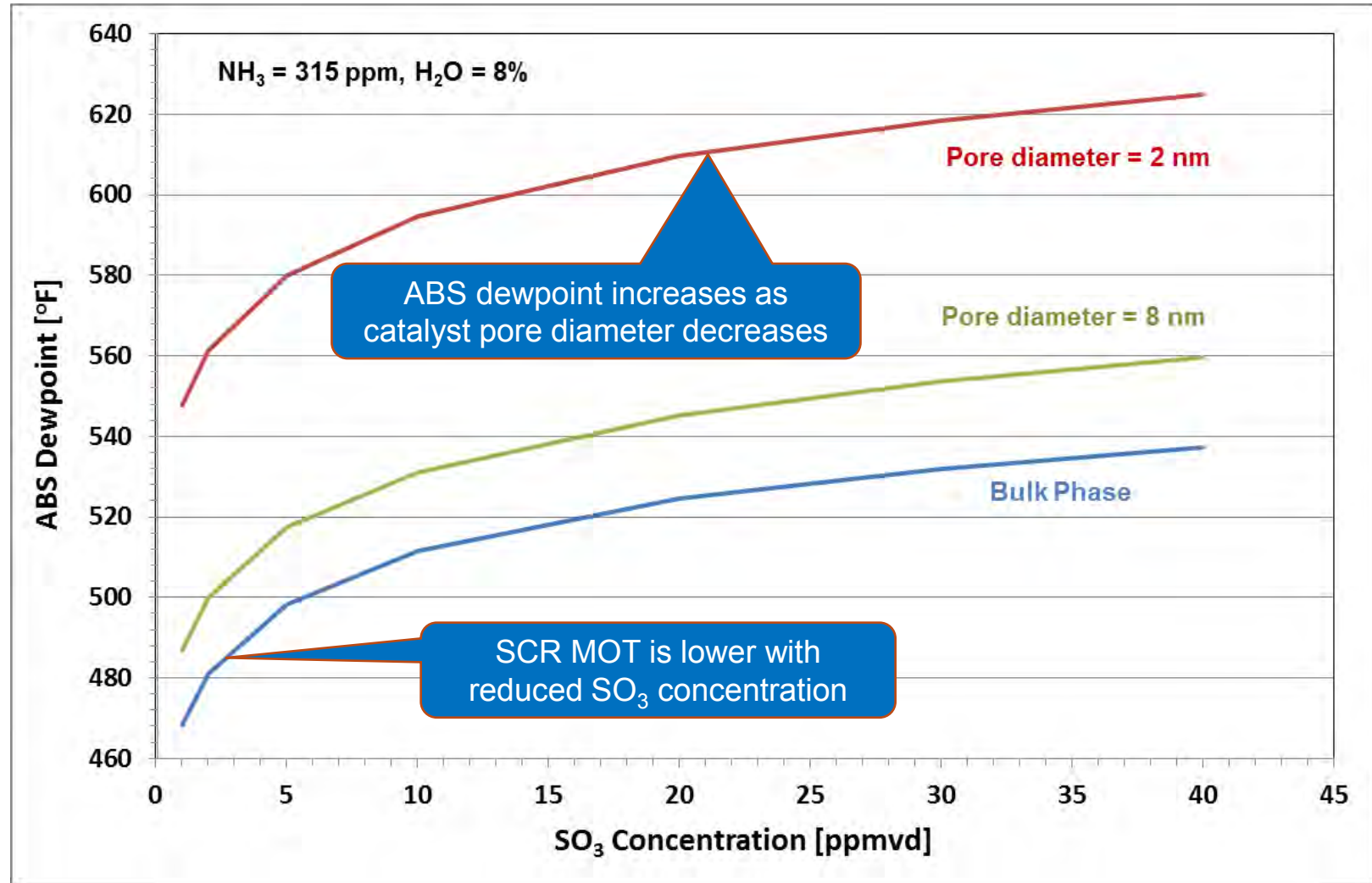
Impact of Catalyst Micro Pores on ABS



Kelvin equation

$$\ln \left(\frac{P \text{ vap in pore}}{P_{\text{sat vap bulk liquid}}} \right) = - \frac{4 \sigma V_1}{d R T}$$

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

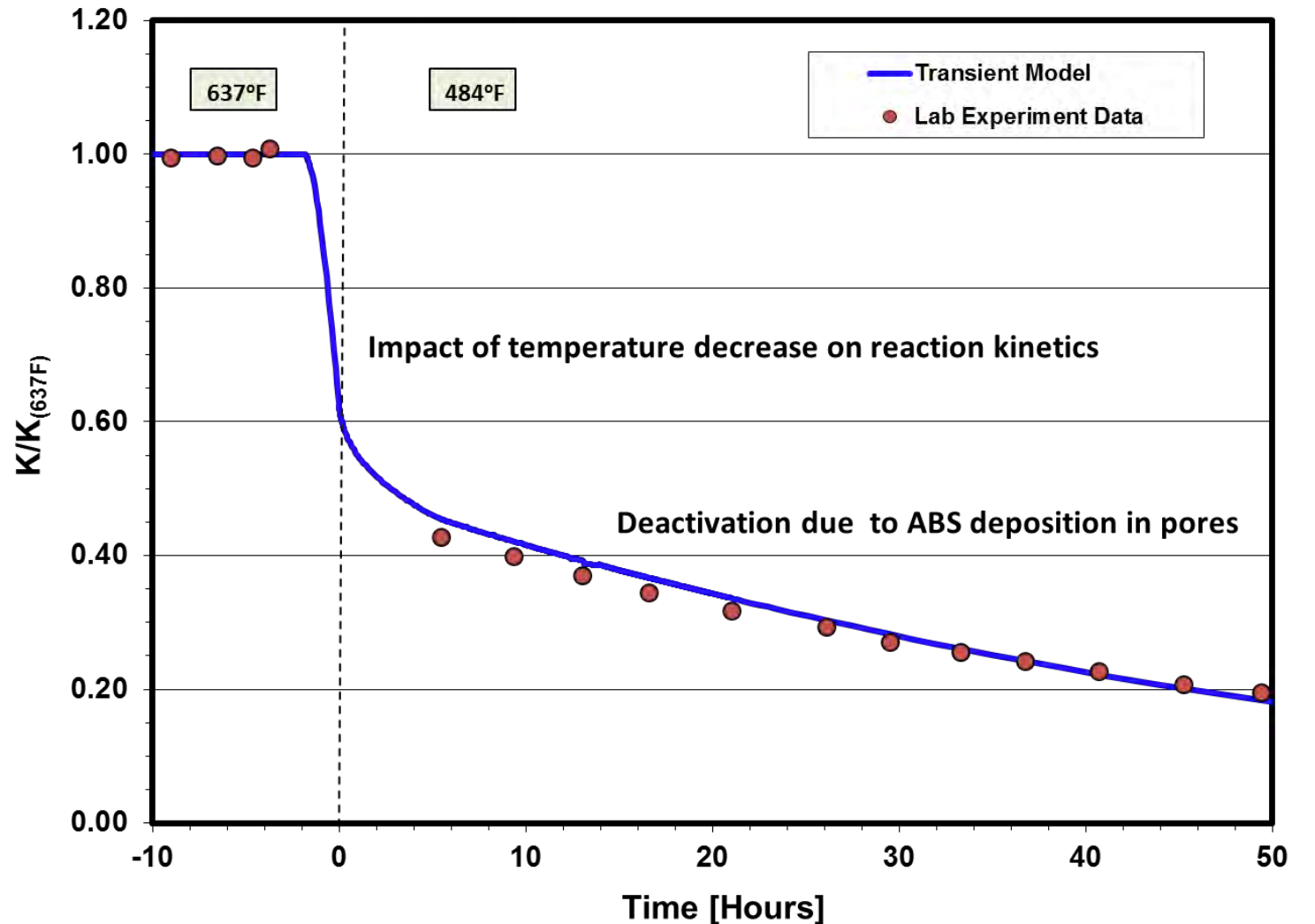


ABS Deposition Deactivates Catalyst



ABS blocks catalyst active sites in pores and results in activity loss.

Effect is reversible: heating the catalyst above the recovery temperature will remove the ABS.



Enhancing Low Load SCR Operation



- CORMETECH's tools and expertise (modeling, lab testing and field support) can help extend an SCR's low load operating range
 - Evaluate different scenarios (time, temp., SO₃, DeNO_x, NH₃ slip, DSI)
 - Generate transient responses for DeNO_x, NH₃ slip and outlet SO₃
- DSI to lower inlet SO₃ can further extend operation at low load
 - C. Bertole (CORMETECH), C. Donner (DUKE ENERGY) presentation at 2017 Reinhold NO_x-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

SO_x and the SCR: Workshop Overview



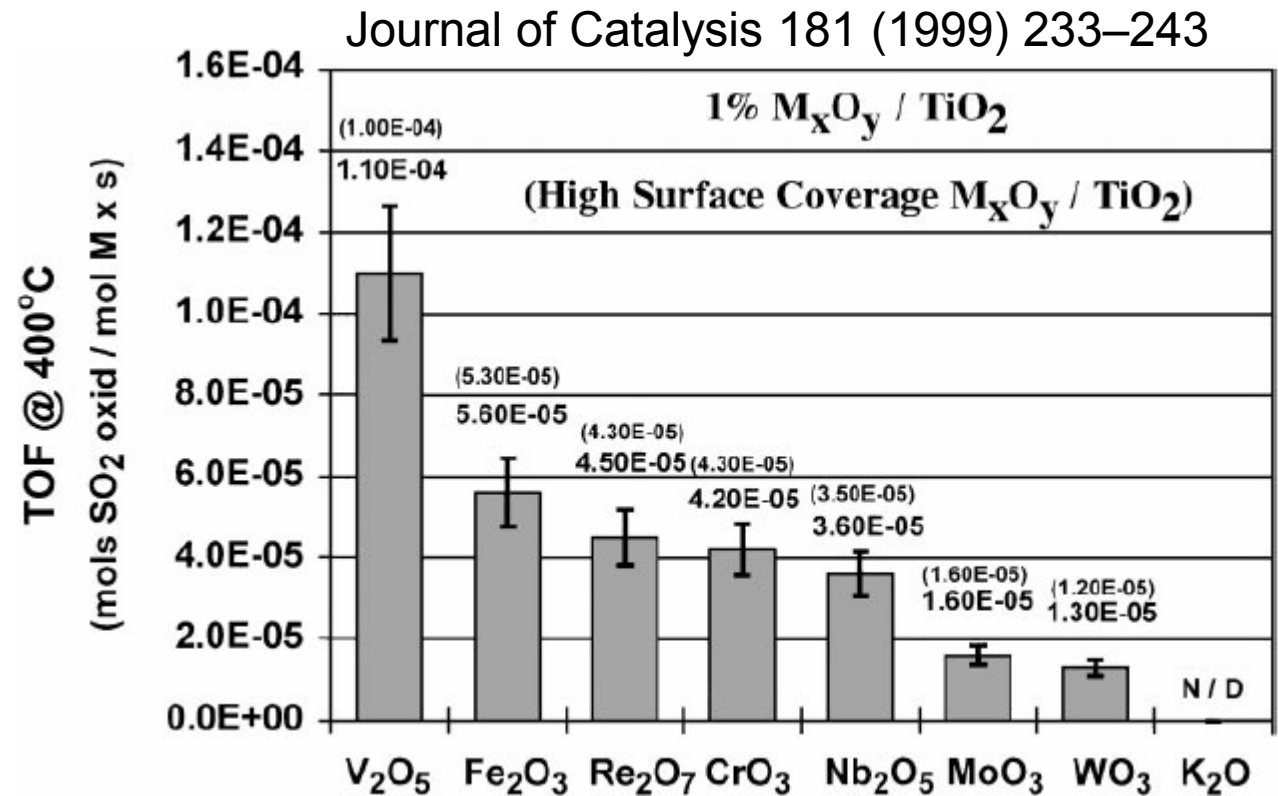
- How do SO₂/SO₃ affect the ability of the SCR catalyst to function for DeNO_x and Hg oxidation?
- How does the SCR affect BOP operations with respect to sulfur?
 - Catalytic SO₂ oxidation increases the SO₃ concentration in the flue gas across the SCR.
 - Steady state and transient behaviors.

Catalytic SO₂ Oxidation



- SCR catalyst enables: $\text{SO}_2 + 0.5 \text{O}_2 \rightarrow \text{SO}_3$

V₂O₅ is a very active catalyst for SO₂ oxidation. It is the main active metal oxide used in sulfuric acid synthesis catalyst.



Potential Impacts of SCR SO₂ Oxidation



- Potential Plant operating issues from higher SO₃:
 - Air preheater fouling (ABS)
 - Heat rate limitation
 - Changes in ash resistivity affecting ESP removal efficiency
 - Stack opacity concerns (i.e., blue plume)

SO₂ Oxidation and SO₃: Steady State and Transient Behaviors



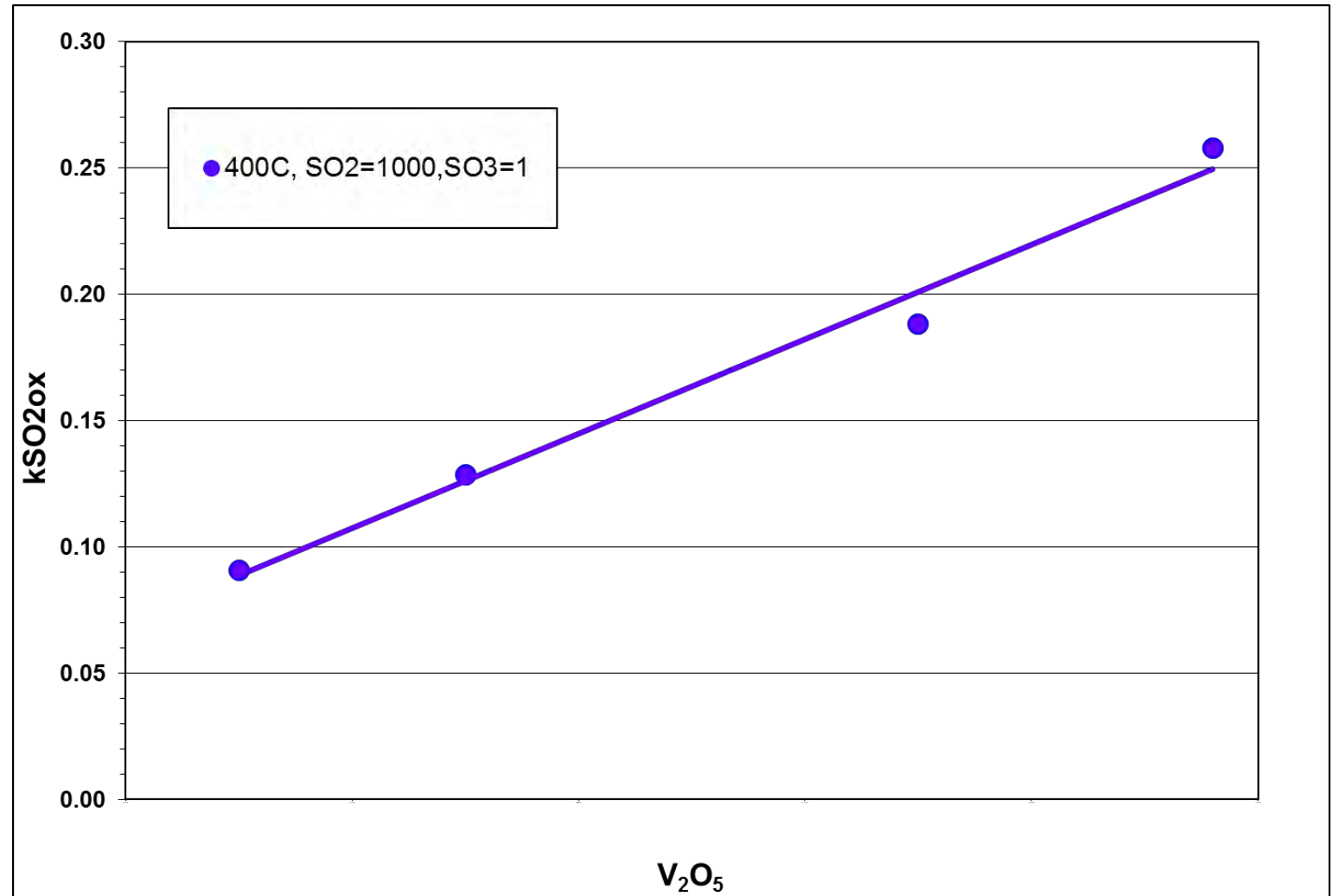
- Steady state (stable load): SO₂ oxidation rate
 - Catalyst formulation
 - Temperature and flue gas composition
 - Catalyst geometry
 - Impact of regeneration
- Transient (load cycling): SO₃ / ABS storage and release

Impact of V_2O_5 Loading



Factors strongly impacting the SO_2 oxidation activity:

- V_2O_5 loading

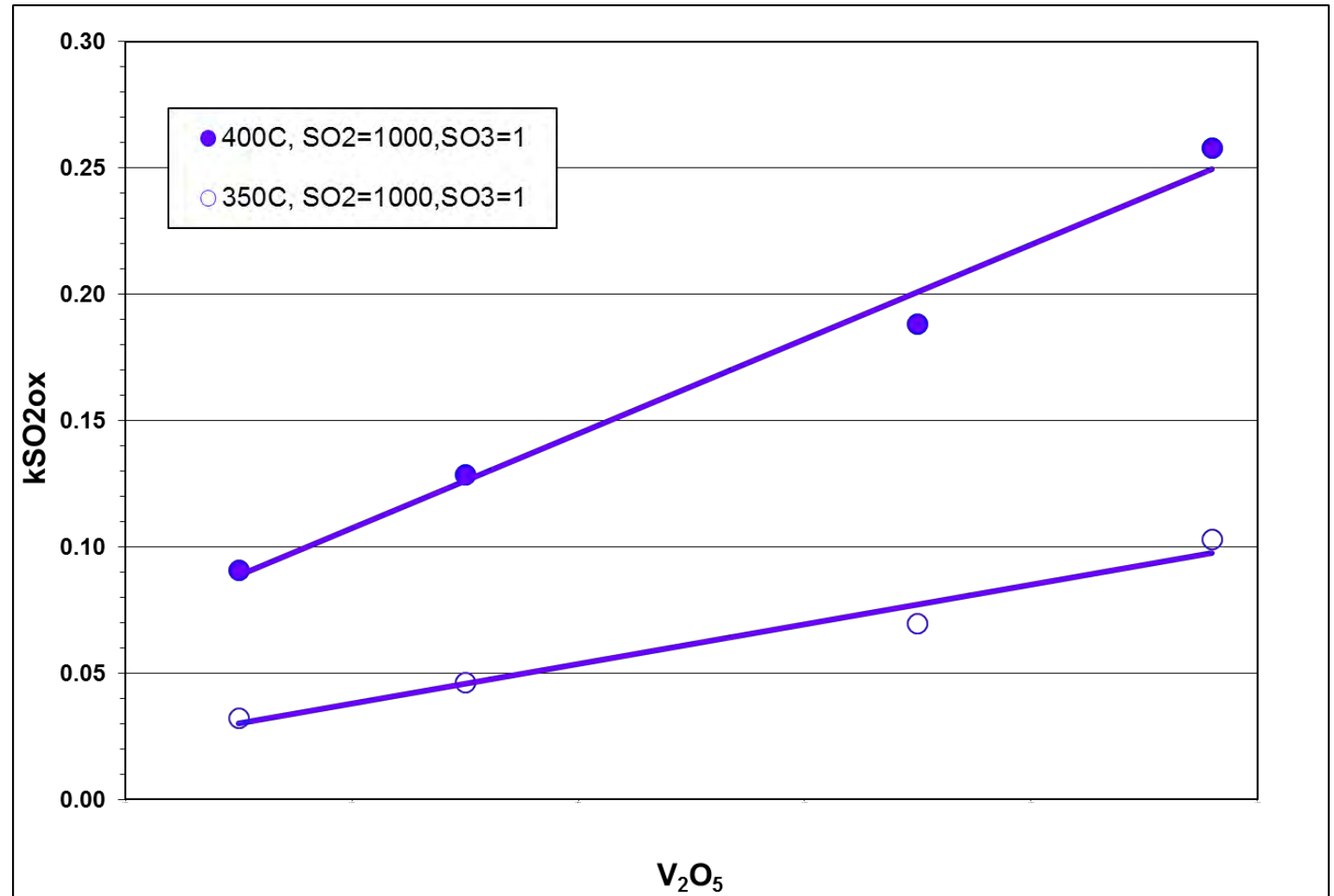


Impact of Temperature



Factors strongly impacting the SO_2 oxidation activity:

- V_2O_5 loading
- Temperature

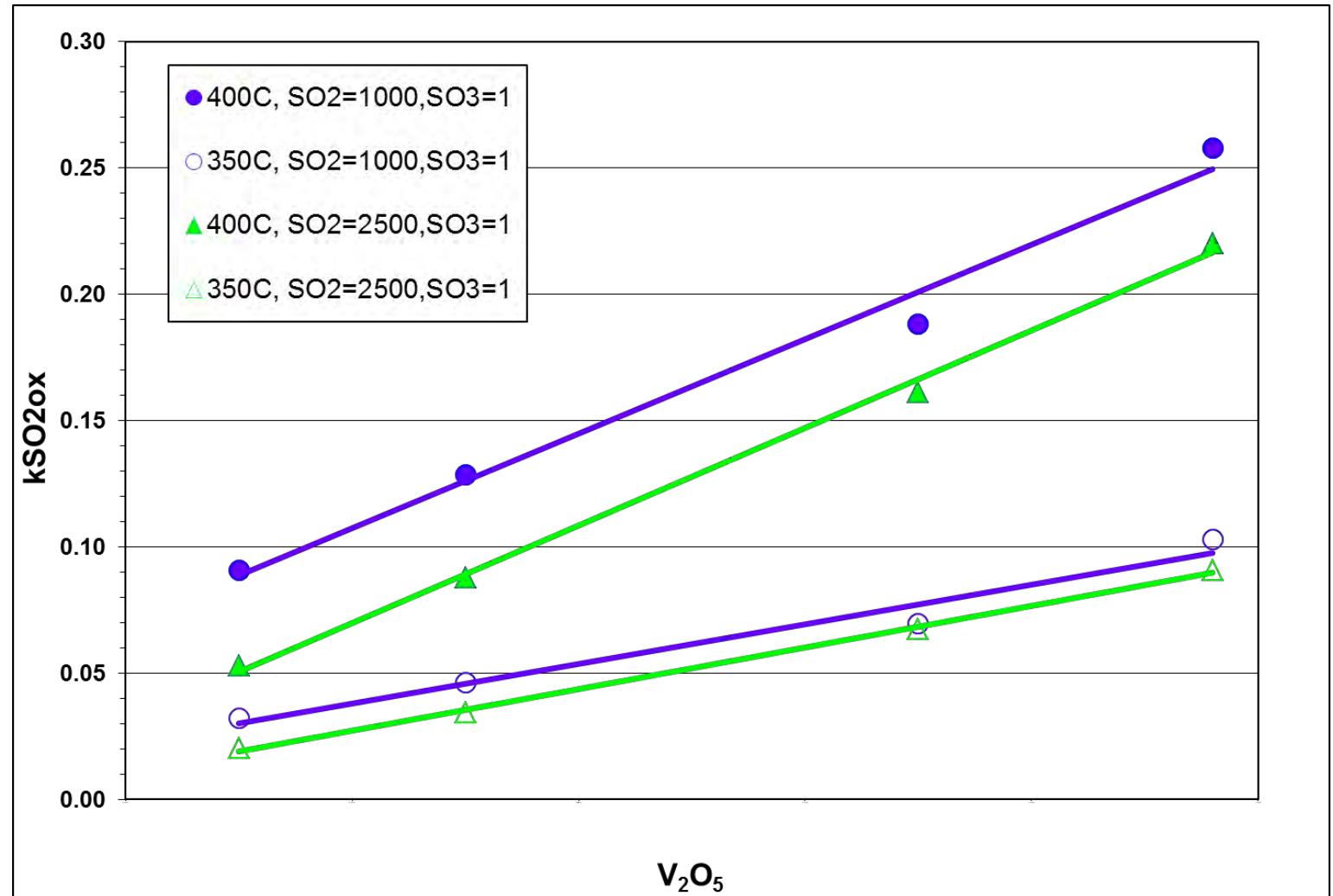


Impact of SO₂ Concentration

Factors strongly impacting the SO₂ oxidation activity:

- V₂O₅ loading
- Temperature
- SO₂ concentration

To set the V₂O₅ loading: balance activity for DeNO_x and Hg oxidation with SO₂ oxidation rate.



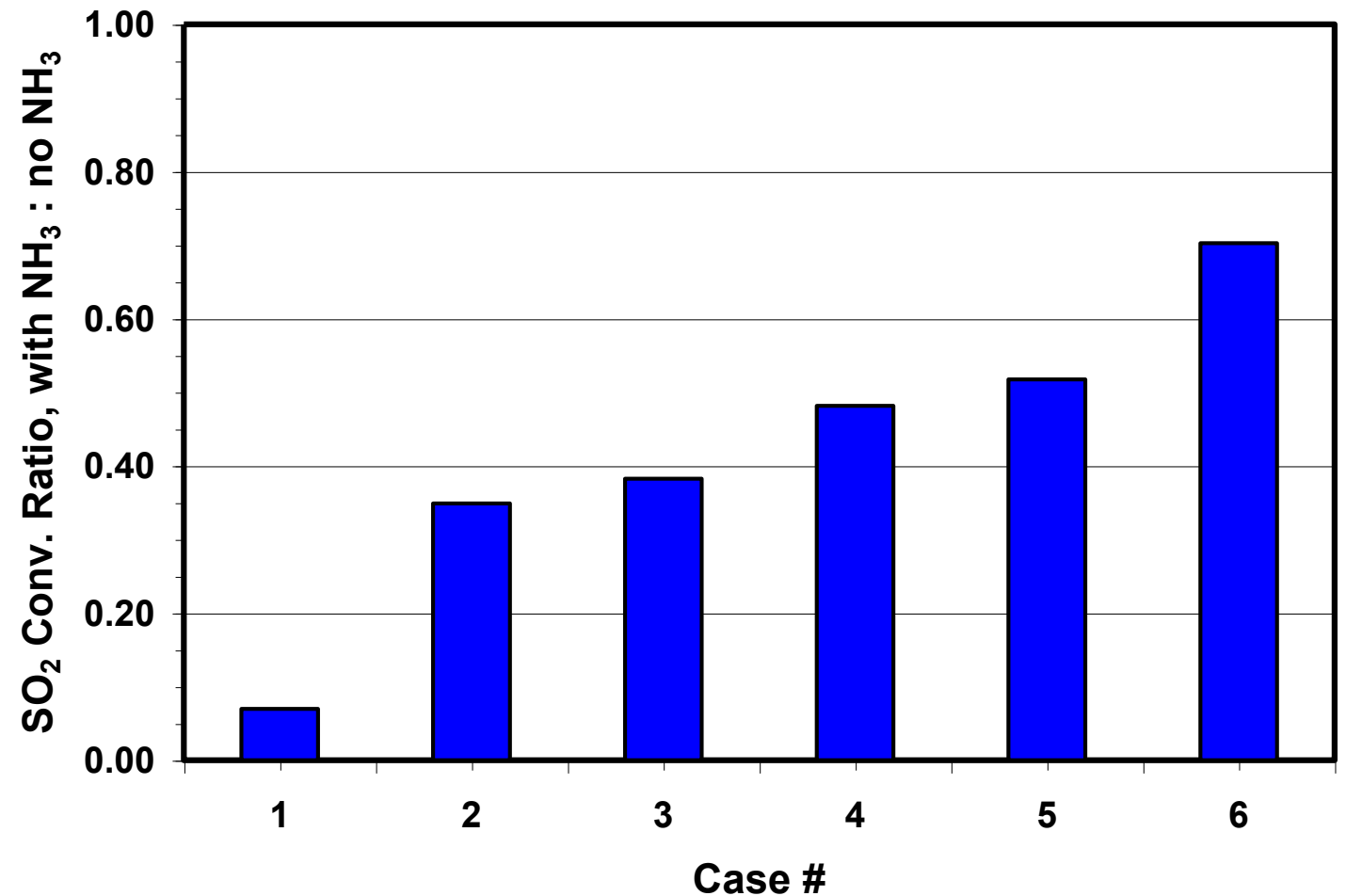
Impact of NH₃



NH₃ can strongly inhibit the SO₂ oxidation rate.

Extent of the inhibition will depend on:

- NH₃ concentration
 - Inlet NO_x, DeNO_x
 - Layer position
- Temperature
- Catalyst formulation



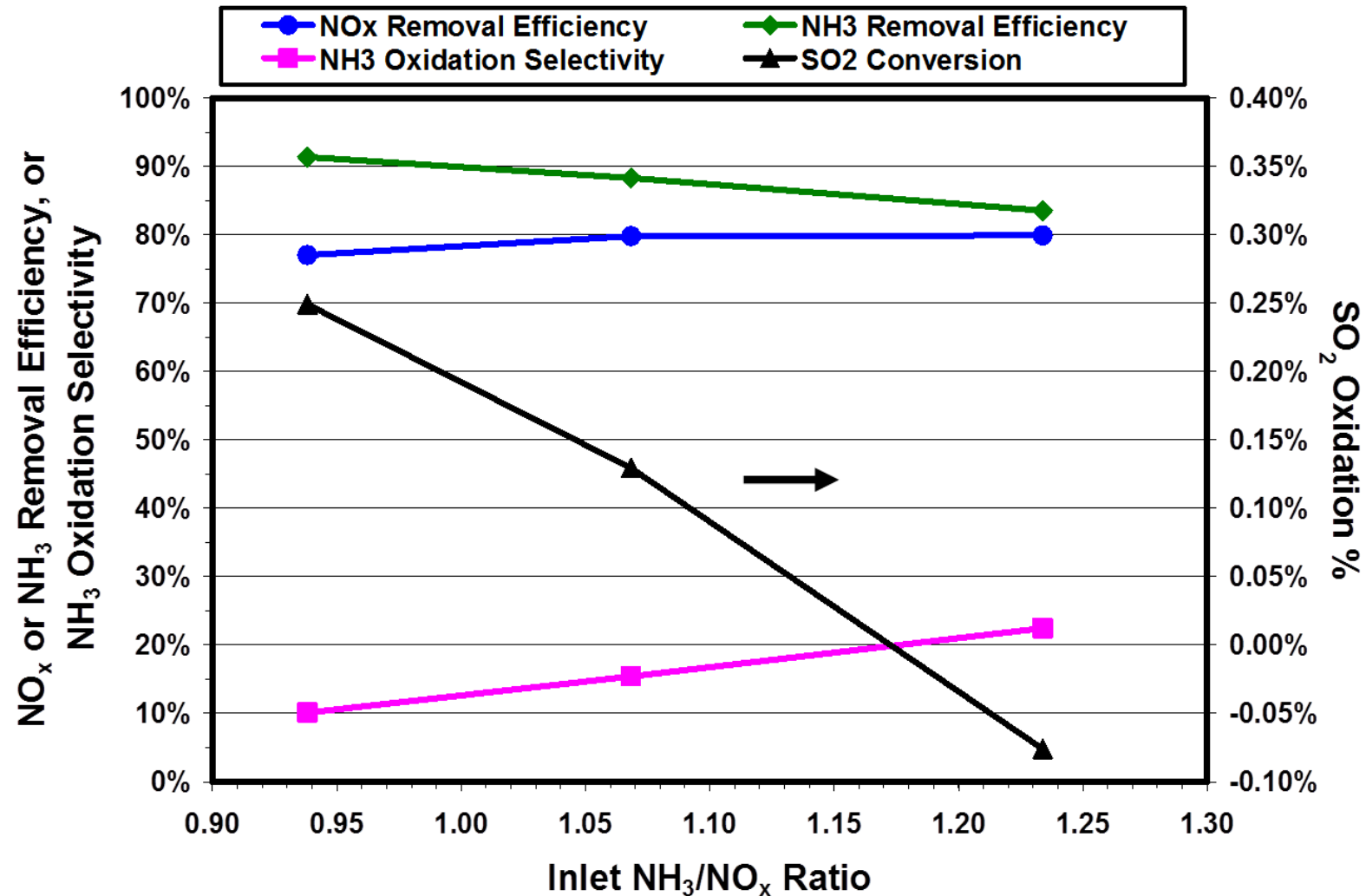
SDA Product: Selective Decomposition of Ammonia



SDA catalyst adds NH_3 oxidation activity to SCR.

It can reduce sensitivity to MR maldistribution, or achieve ultra-high De NO_x , through NH_3 over-injection.

Possible to achieve a negative SO_2 oxidation over an SDA catalyst layer.



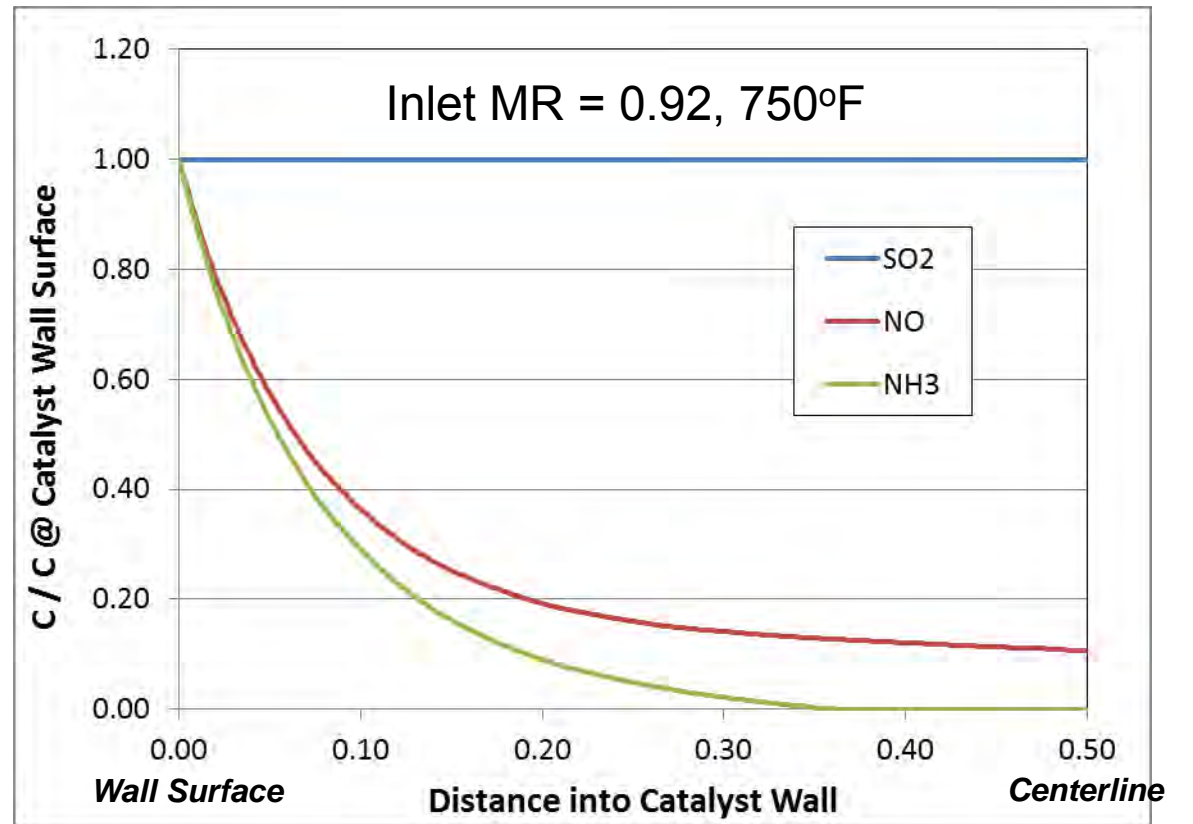
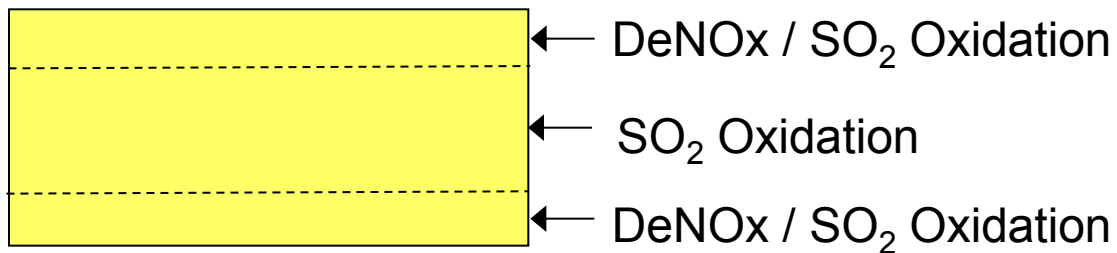
SO₂ Oxidation is Kinetically Limited



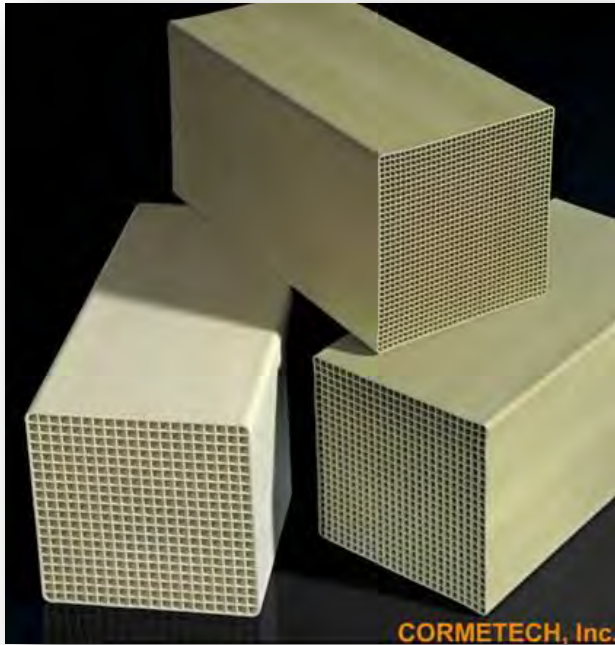
Fast DeNOx reaction occurs near surface of wall.

Slow SO₂ oxidation reaction occurs throughout wall.

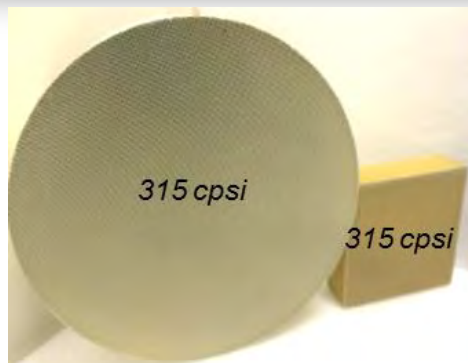
Catalyst Wall Cross-section:



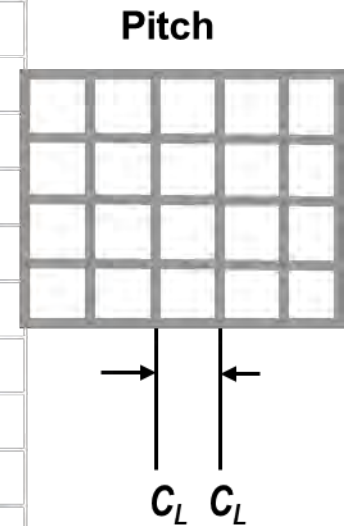
Selection of Catalyst Geometry



CORMETECH
Dust Buster™



Cells	Pitch (mm)	CPSI	Flue Gas
16	9.2	7	<i>Dirtier</i>
18	8.2	9	
20	7.4	11	
21	7.1	13	
22	6.9	14	
23	6.4	15	
25	5.9	18	
35	4.2	35	
40	3.7	48	
45	3.3	58	
55	2.7	86	
70	2.1	140	
108	1.4	315	
*	1.3	400	<i>Cleaner</i>



* Undergoing pre-production trials

High Open Area = Low DP

Impact of Catalyst Geometry



- Smaller pitch / higher geometric surface area catalyst improves the trade-off between DeNOx and SO₂ 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%

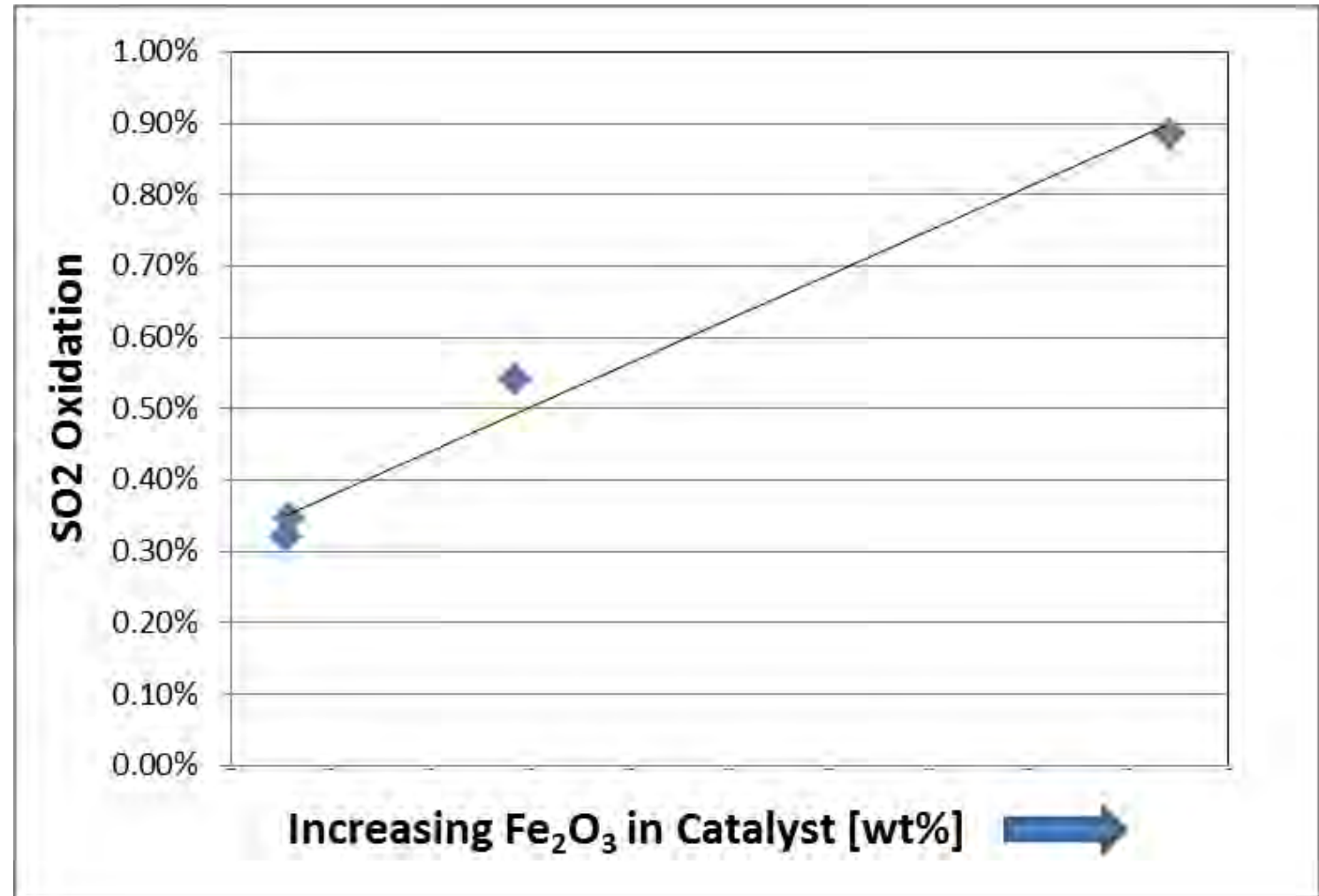
Constant DeNOx and NH₃ slip for all cases

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 SO₂ oxidation.

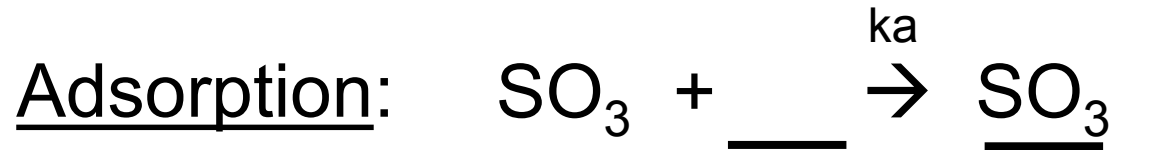


Dynamic / Transient



- Transient (load cycling):
 - Dynamics of SO_3 storage and release from the catalyst
 - Strong SO_3 adsorption onto TiO_2 , but not on V or W.
 - Weak SO_2 adsorption.
- 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 .

SO₃ Catalyst Adsorption Model



$$\text{Rate adsorption} = k_a P_{\text{SO}_3} (1 - \theta_{\text{SO}_3})$$



$$\text{Rate desorption} = k_d \theta_{\text{SO}_3}$$

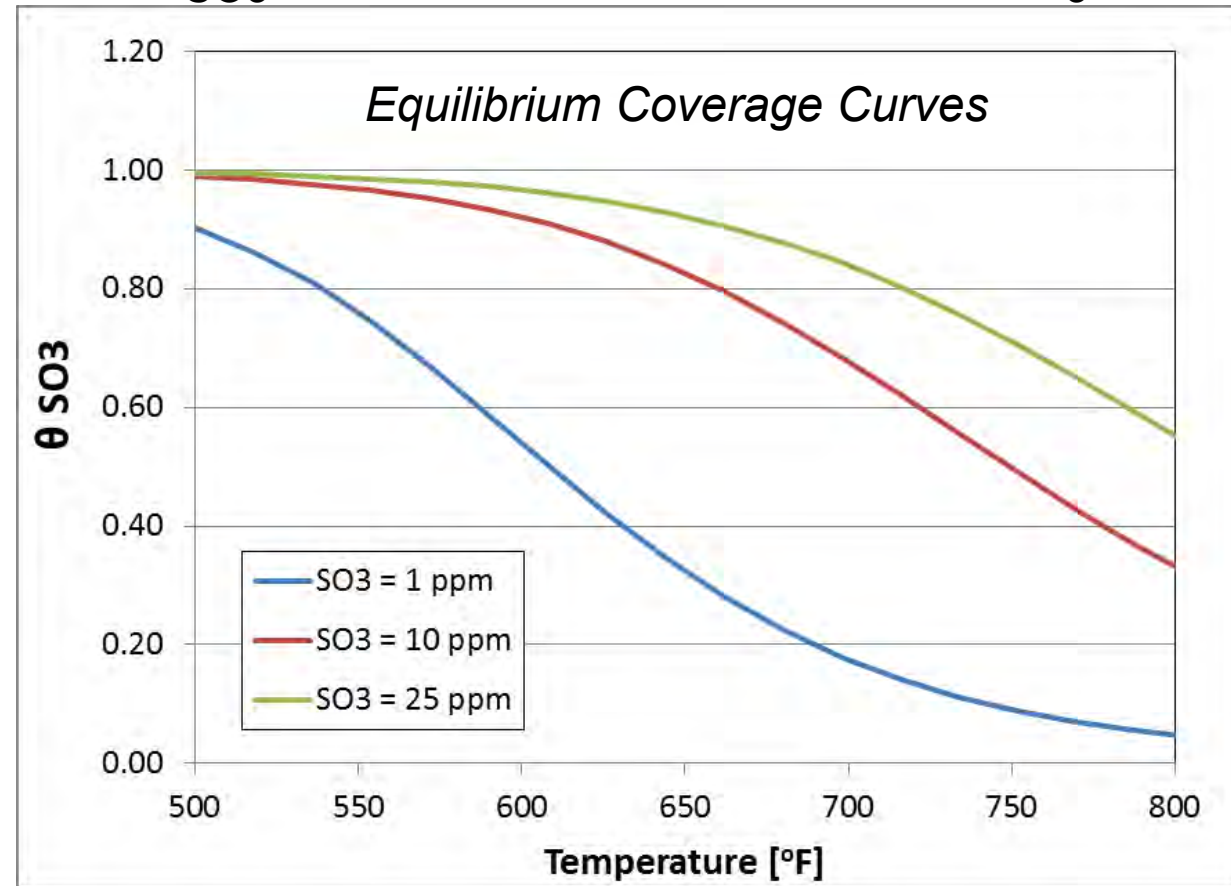
At equilibrium:

rate adsorption = rate desorption

$$k_a P_{\text{SO}_3} (1 - \theta_{\text{SO}_3}) = k_d \theta_{\text{SO}_3}$$

$$\theta_{\text{SO}_3} = k_a / k_d P_{\text{SO}_3} / (1 + k_a / k_d P_{\text{SO}_3})$$

θ_{SO_3} = fractional coverage of SO₃



Transient SO₂ Oxidation Model



Mass Balance Equations

C_{SO_2} (gas phase):

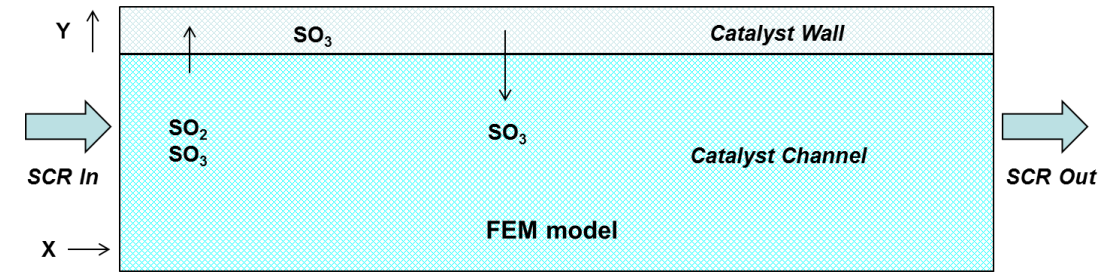
$$\frac{\partial C_{SO_2}}{\partial t} + u_x \frac{\partial C_{SO_2}}{\partial x} = D_{SO_2} \left(\frac{\partial^2 C_{SO_2}}{\partial x^2} + \frac{\partial^2 C_{SO_2}}{\partial y^2} \right) + \{-k_{rSO_2} C_{SO_2}\} \rho_{cat}$$

C_{SO_3} (gas phase):

$$\frac{\partial C_{SO_3}}{\partial t} + u_x \frac{\partial C_{SO_3}}{\partial x} = D_{SO_3} \left(\frac{\partial^2 C_{SO_3}}{\partial x^2} + \frac{\partial^2 C_{SO_3}}{\partial y^2} \right) + \{k_{rSO_2} C_{SO_2} - k_{aSO_3} (1 - \theta_{SO_3}) \Omega_{SO_3} + k_{dSO_3} \theta_{SO_3} \Omega_{SO_3}\} \rho_{cat} \Omega_{SO_3}$$

θ_{SO_3} (adsorbed SO₃ on catalyst surface):

$$\frac{\partial \theta_{SO_3}}{\partial t} = D_{\theta SO_3} \left(\frac{\partial^2 \theta_{SO_3}}{\partial x^2} + \frac{\partial^2 \theta_{SO_3}}{\partial y^2} \right) + \{+k_{aSO_3} (1 - \theta_{SO_3}) - k_{dSO_3} \theta_{SO_3}\} \rho_{cat} \Omega_{SO_3}$$



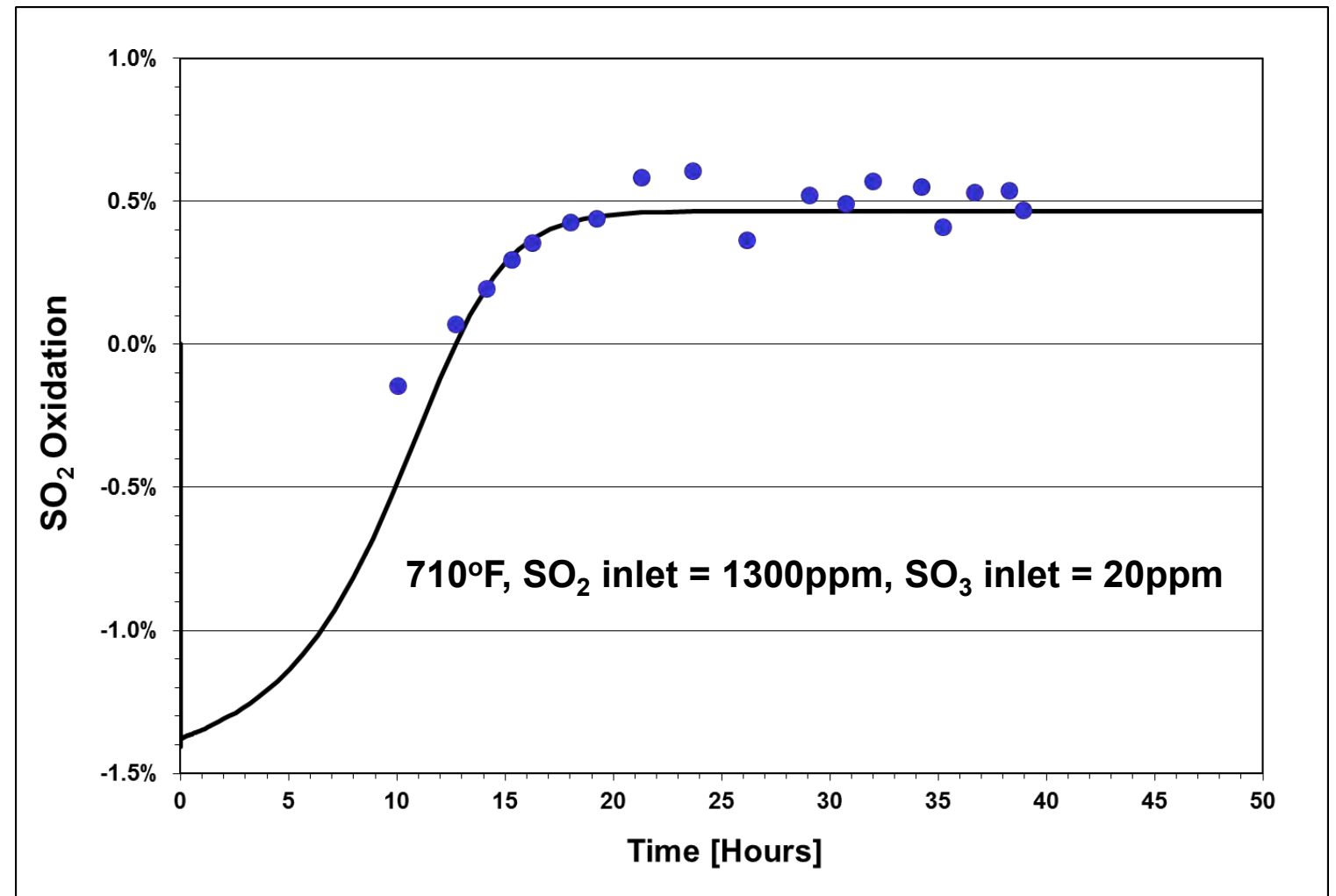
SO₂ Oxidation Testing



Transient is due to SO₃ adsorbing onto the catalyst.

Steady state is achieved once the catalyst reaches the stable SO₃ coverage for the condition.

Model predicts trend well.

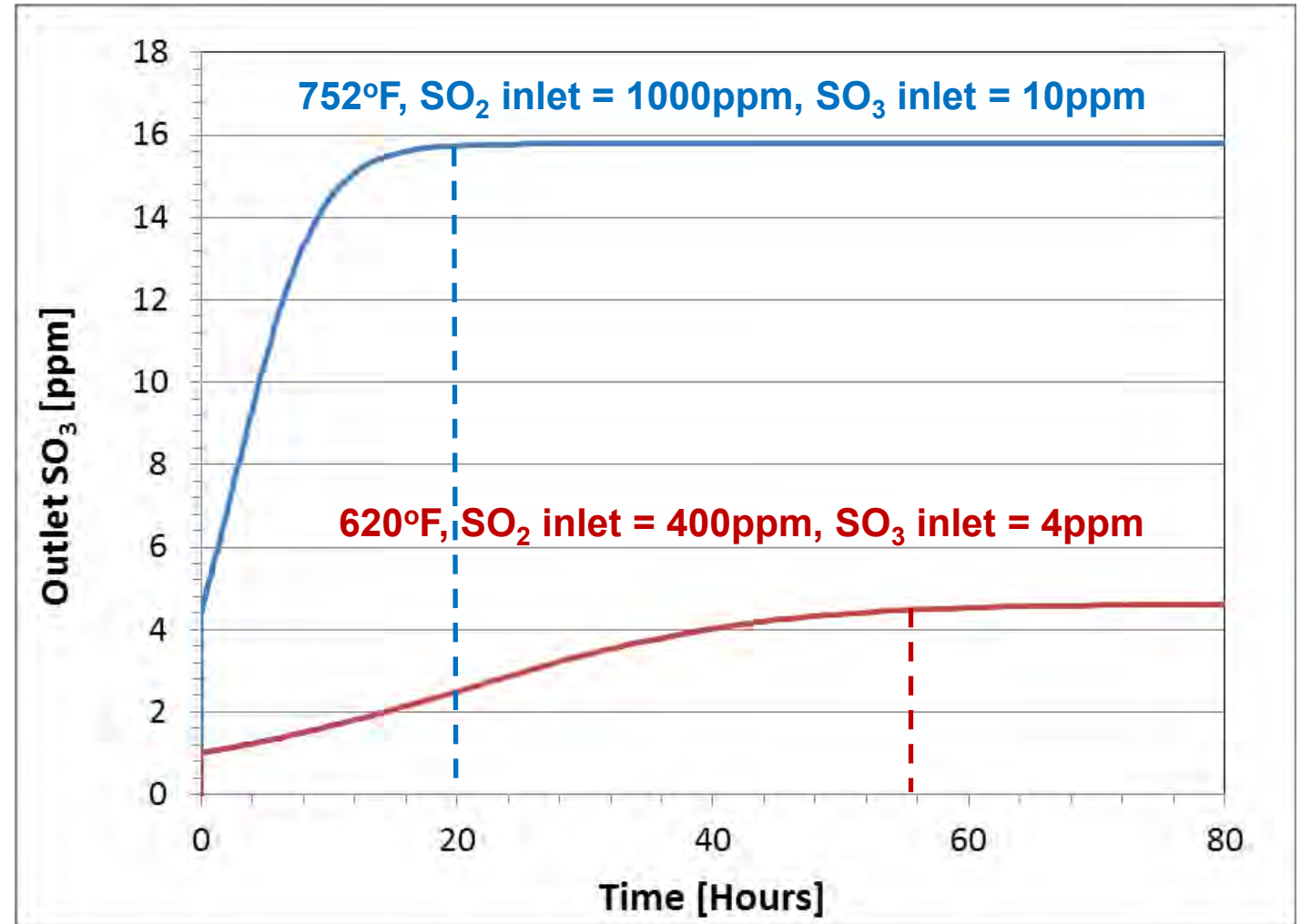


Transient Model Simulation



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



Temperature Transient



Equilibrium SO_3 coverage is a strong function of temperature.

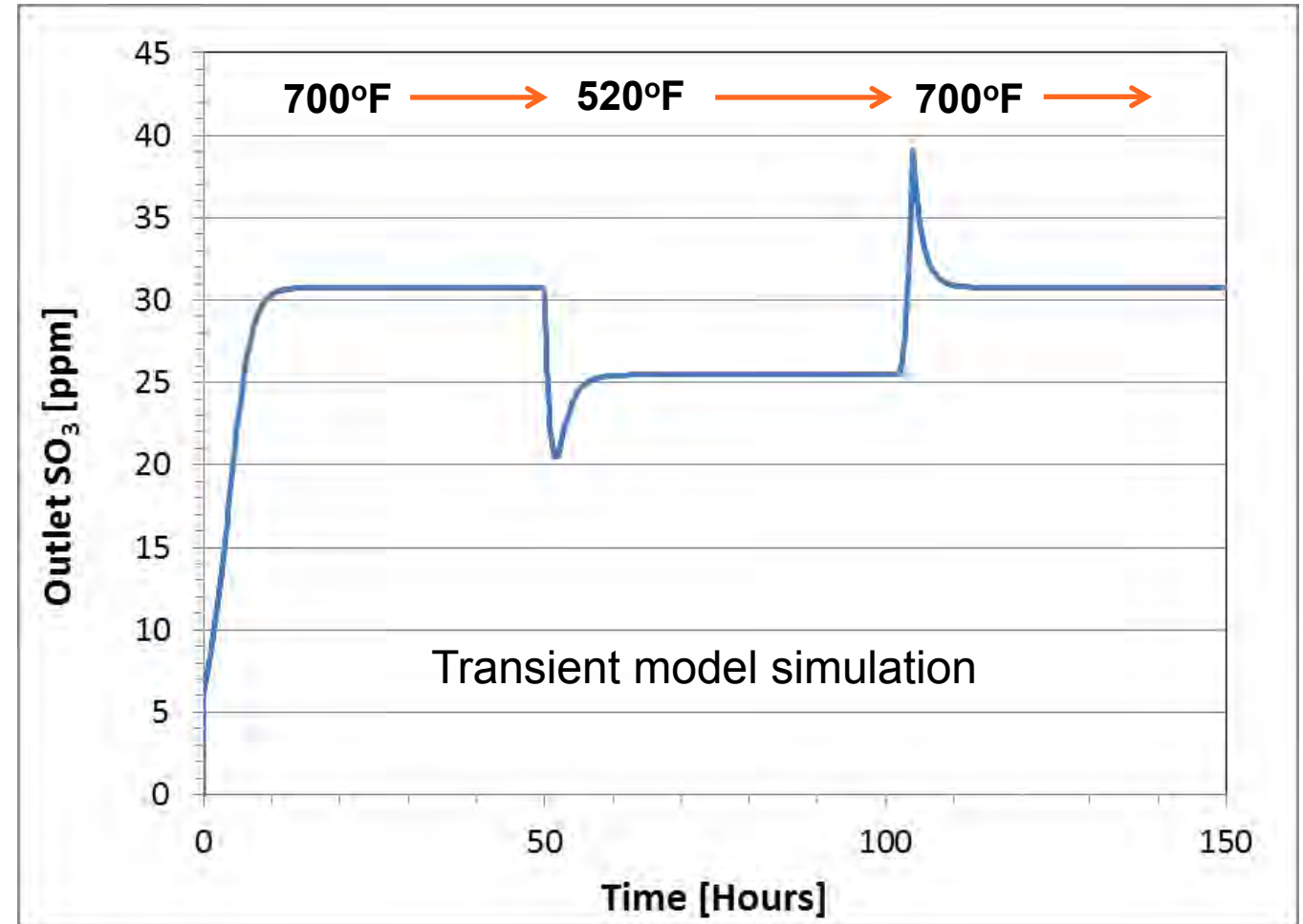
Decreasing temperature:

- Yields SO_3 dip, then stable.

Increasing temperature:

- Yields SO_3 spike, then stable.

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



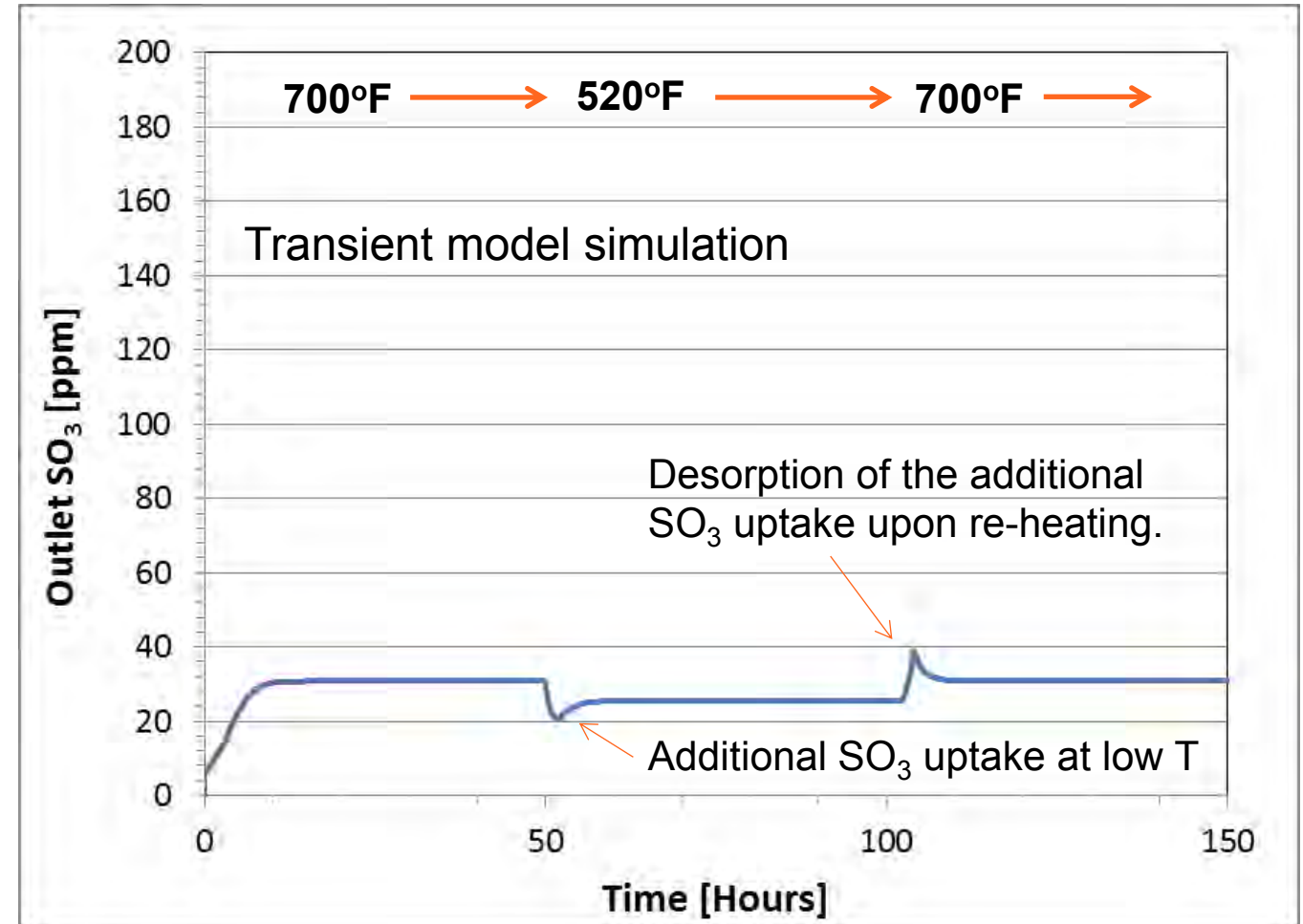
Transient SO₂ Oxidation & ABS Model



SO₂ inlet = 2500ppm, SO₃ inlet = 25ppm, MR = 0

Without NH₃ injection:

Transients are due to changes in SO₃ adsorption/desorption equilibria on the catalyst at the different temperatures.



Transient SO₂ Oxidation & ABS Model

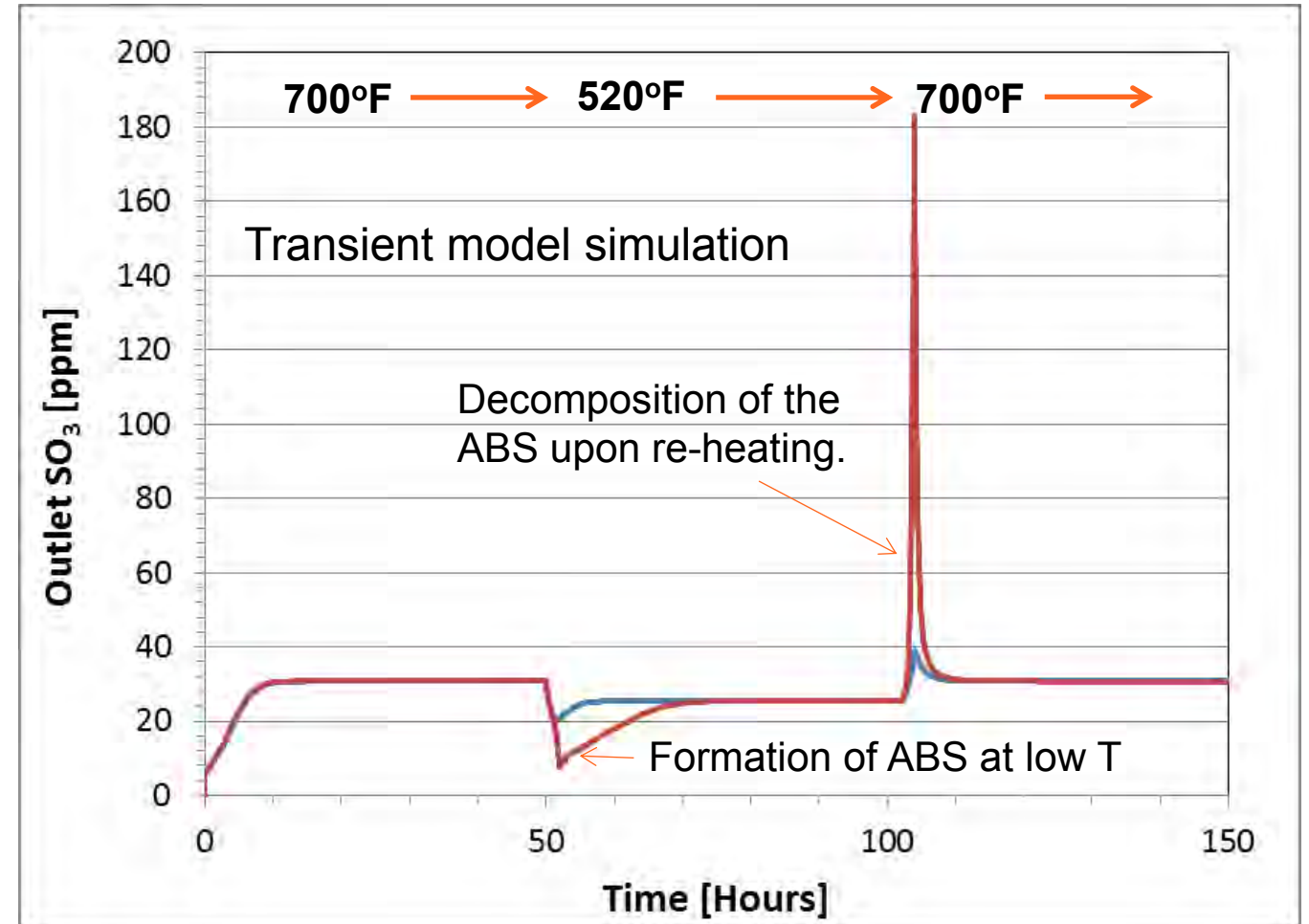


SO₂ inlet = 2500ppm, SO₃ inlet = 25ppm, MR = 0.92

With NH₃ injection:

Transients are due to changes in SO₃ adsorption/desorption equilibria on the catalyst at the different temperatures

+
ABS formation/decomposition.



Summary



- SO_2/SO_3 affects the SCR catalyst:
 - Positive impact on DeNOx.
 - Slightly negative impact on Hg oxidation.
 - Increases the phosphorus accumulation rate on the catalyst for PRB.
 - Reacts with NH_3 at low temperatures to form ABS salts in the pores and cause a reversible deactivation (removable by catalyst reheat).
- The SCR affects BOP operations with respect to SO_3 :
 - Catalytic SO_2 oxidation increases the SO_3 concentration in the flue gas.
 - Steady state and transient effects (SO_3 desorption, ABS decomposition).
- CORMETECH has the tools to help in these evaluations.

Thank You.

