

REINHOLD ENVIRONMENTAL Ltd.



2017 NO_x-Combustion-CCR Round Table Presentation

February 27 & 28, 2017, in Cleveland, OH / Hosted by FirstEnergy

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State-of-the-Art Coal-Fired Performance Technology for Load Following Units



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2017 Reinhold NOx-Combustion Round Table

Training Session Overview

- **Background**
- **Operational Strategy**
- **Case Study:**
 - **Gibson Enhanced SCR Performance Testing**
- **Summary**

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SCR Catalyst Reactions

NO_x Reduction:



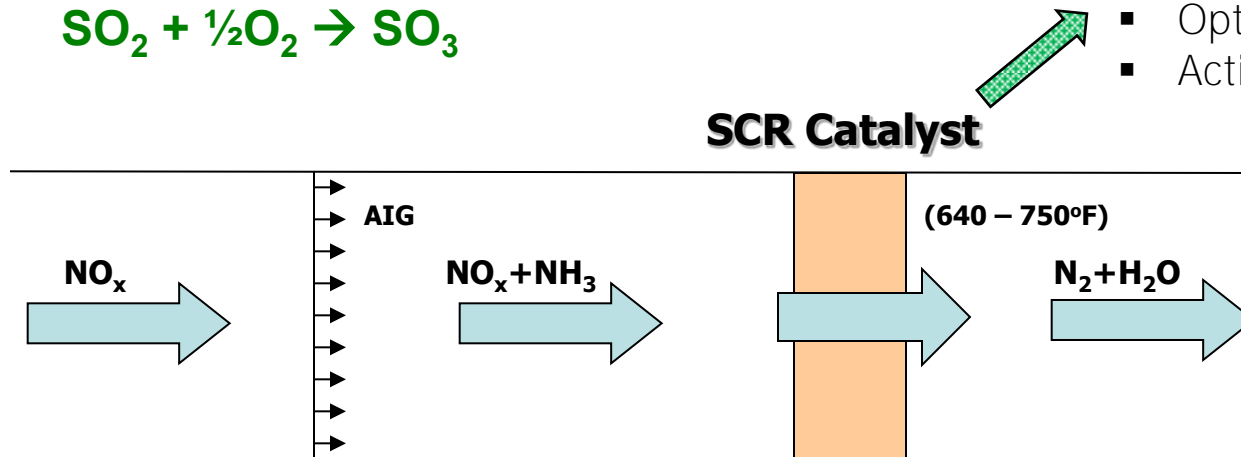
Hg Oxidation:



SO₂ Oxidation:



- V-W/Ti, or V-Mo/Ti
- Honeycomb, Plate
- Optimal: 640-750°F
- Active to 350°F



Catalyst “Surface Area”

Geometric Surface Area (A_p):

For example, 21 cell honeycomb:

$$A_p = 502 \text{ m}^2/\text{m}^3$$

$$SA = 1.6 \times 10^{-3} \text{ m}^2/\text{g}$$

$$\text{Cell opening} = \underline{6.4 \text{ mm}}$$



$$\text{Catalyst Potential} = K/AV = (K \times \text{Vol} \times A_p)/Q$$

N_2 BET Surface Area:

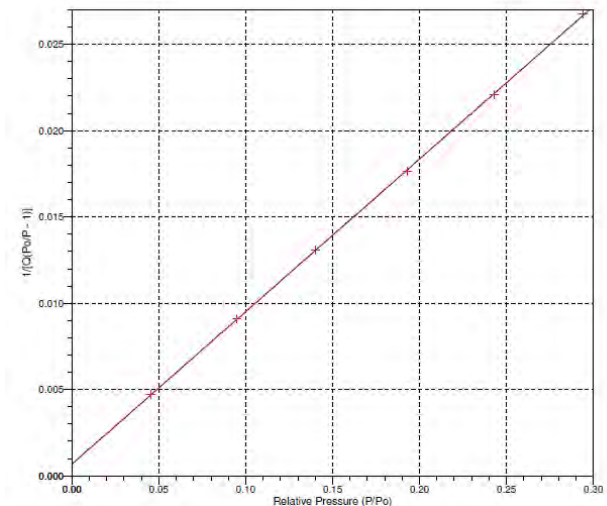
$$SA \sim 55 \text{ m}^2/\text{g}$$

$$\text{Pore diameter} = \underline{\sim 2-100 \text{ nm}}$$

Defines $K_{\text{intrinsic}}$ (+ metal oxide loadings)

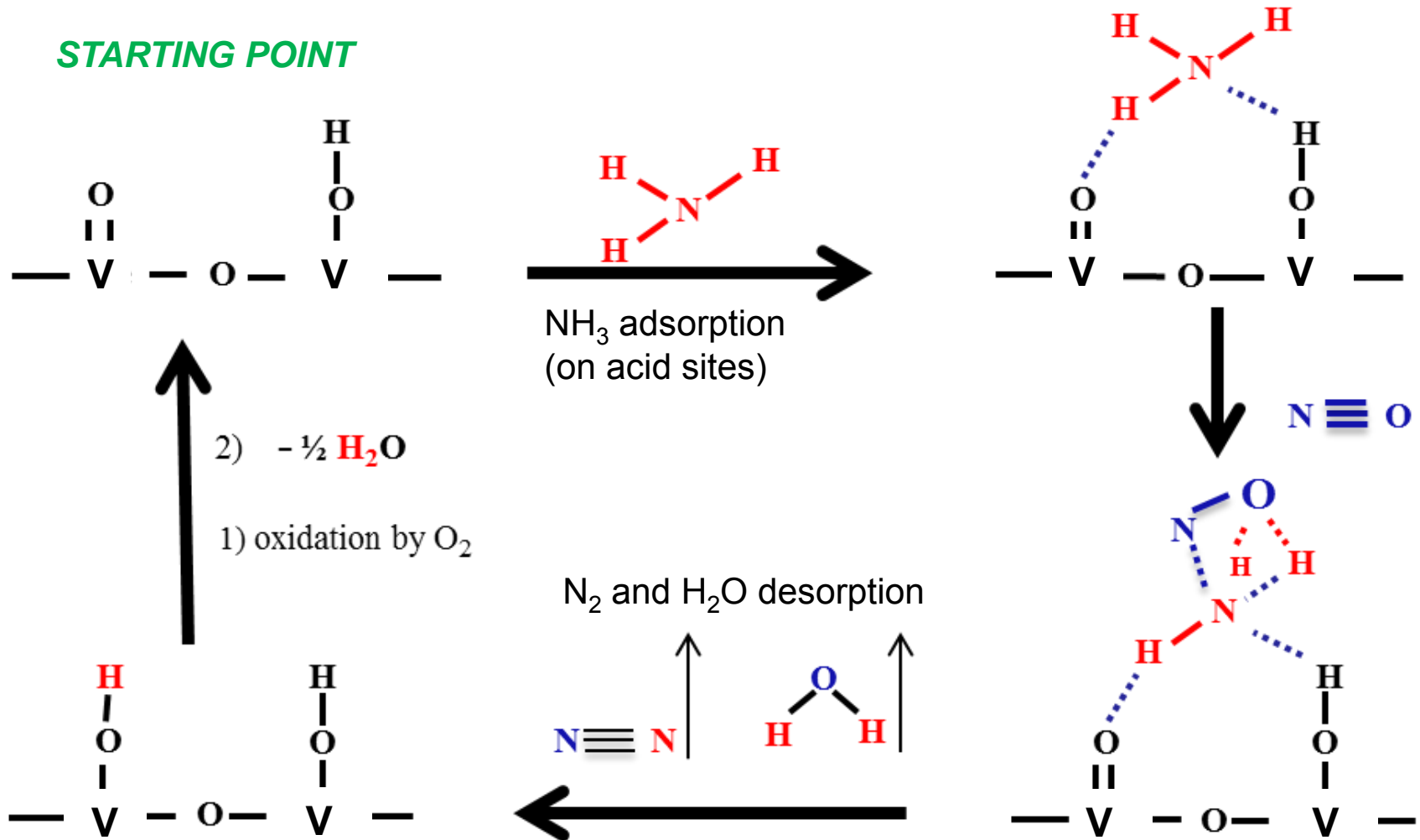


BET Surface Area Plot



DeNOx Catalytic Mechanism

The catalytic reactions occur on the BET-measured surface area of the V-W/Ti catalyst particles.



Question...

- If an SCR catalyst can have DeNOx activity down to 350°F, what is the issue with low load operation?
- The issue is: **SULFUR!**
- Sulfur in the coal combusts to SO_2 / SO_3 in the boiler
 - NH_3 , injected for the DeNOx reaction, can react with SO_3 / H_2SO_4 at low load SCR temperatures to form NH_4HSO_4
 - The formed NH_4HSO_4 (ABS, liquid) will cover the catalyst BET surface area, resulting in catalyst DEACTIVATION
- The good news is: this behavior can be managed to implement effective operational strategies for low load

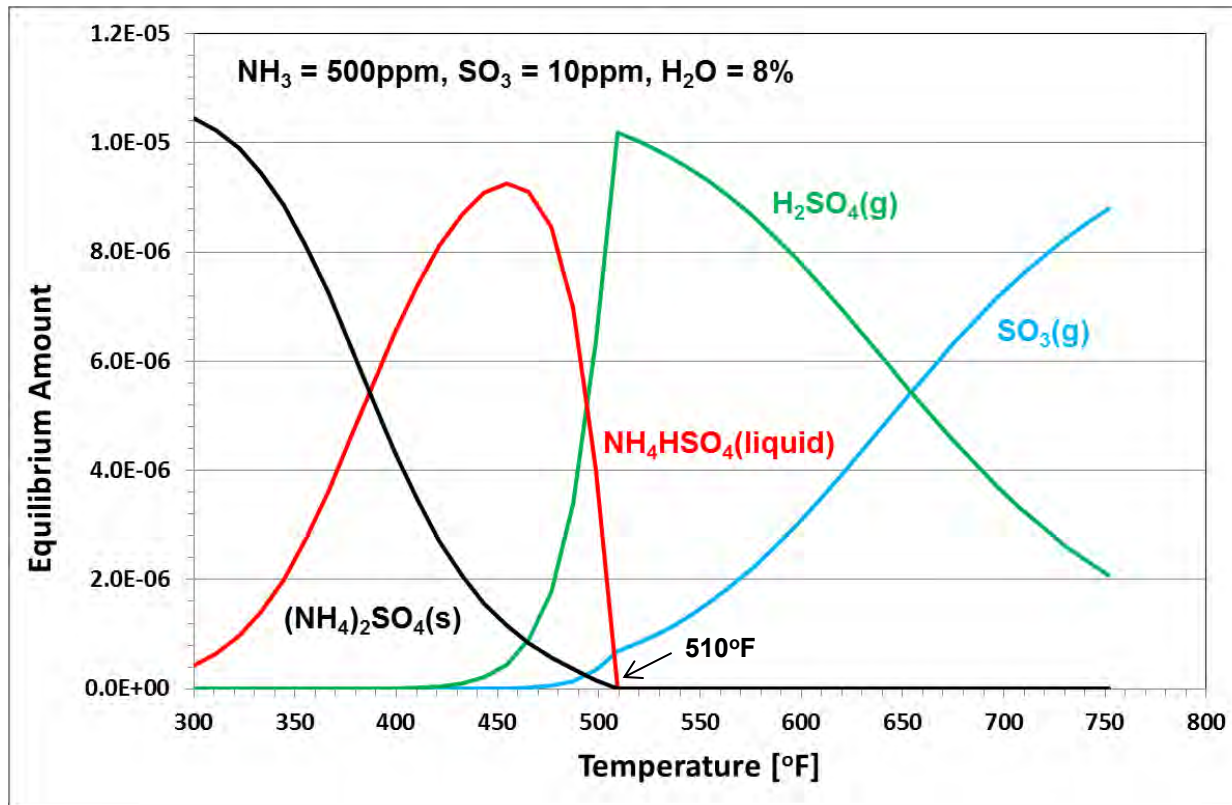
Bulk-Phase ABS and AS Properties

Ammonium Bisulfate (ABS)

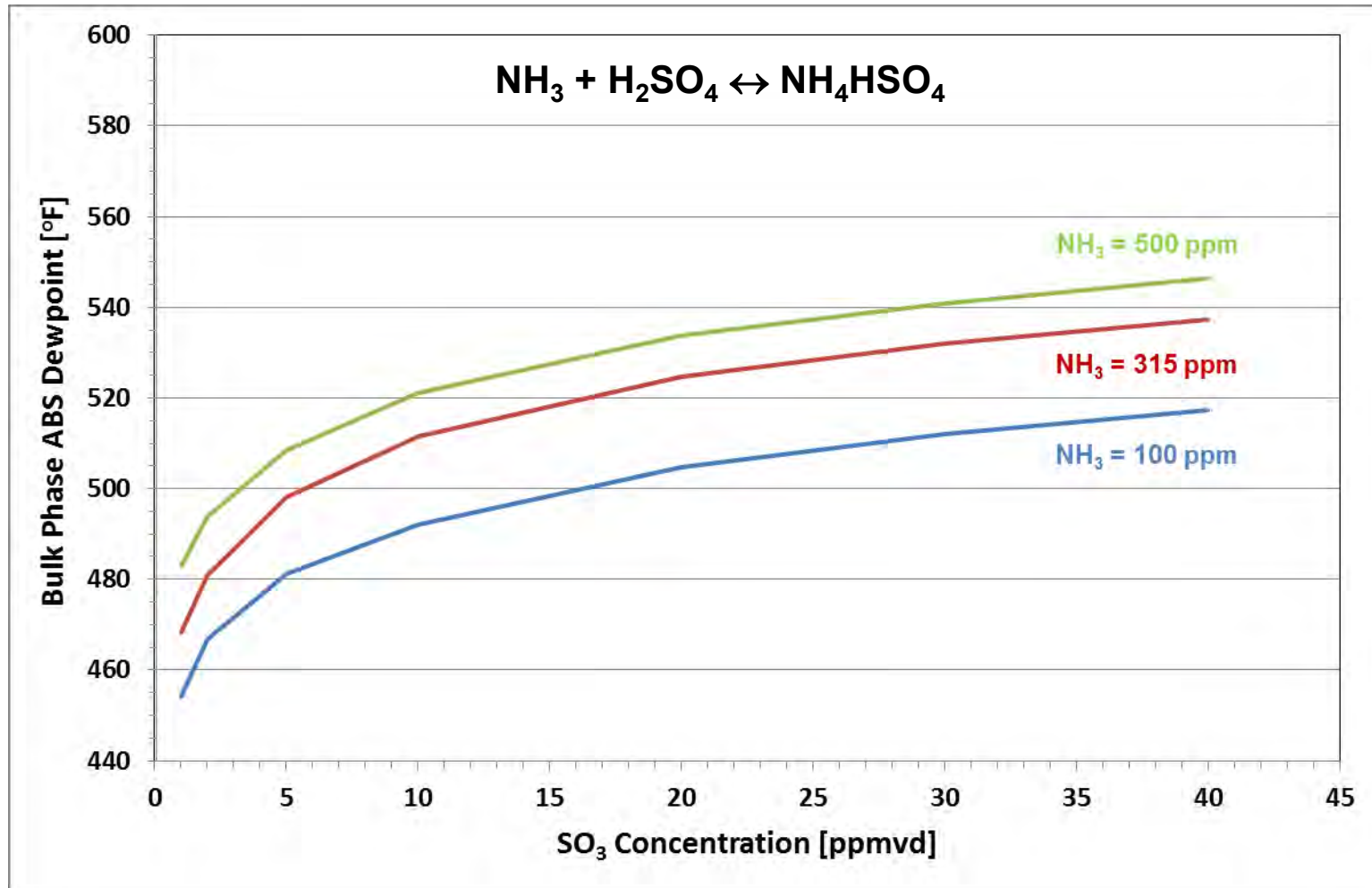
- $\text{NH}_3 + \text{H}_2\text{SO}_4 \leftrightarrow \text{NH}_4\text{HSO}_4$
- White sticky solid; corrosive
- $T_{\text{melting}} = 147^\circ\text{C}/297^\circ\text{F}$
- $T_{\text{boiling}} > 235^\circ\text{C}/455^\circ\text{F}$ (decomposes)

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)

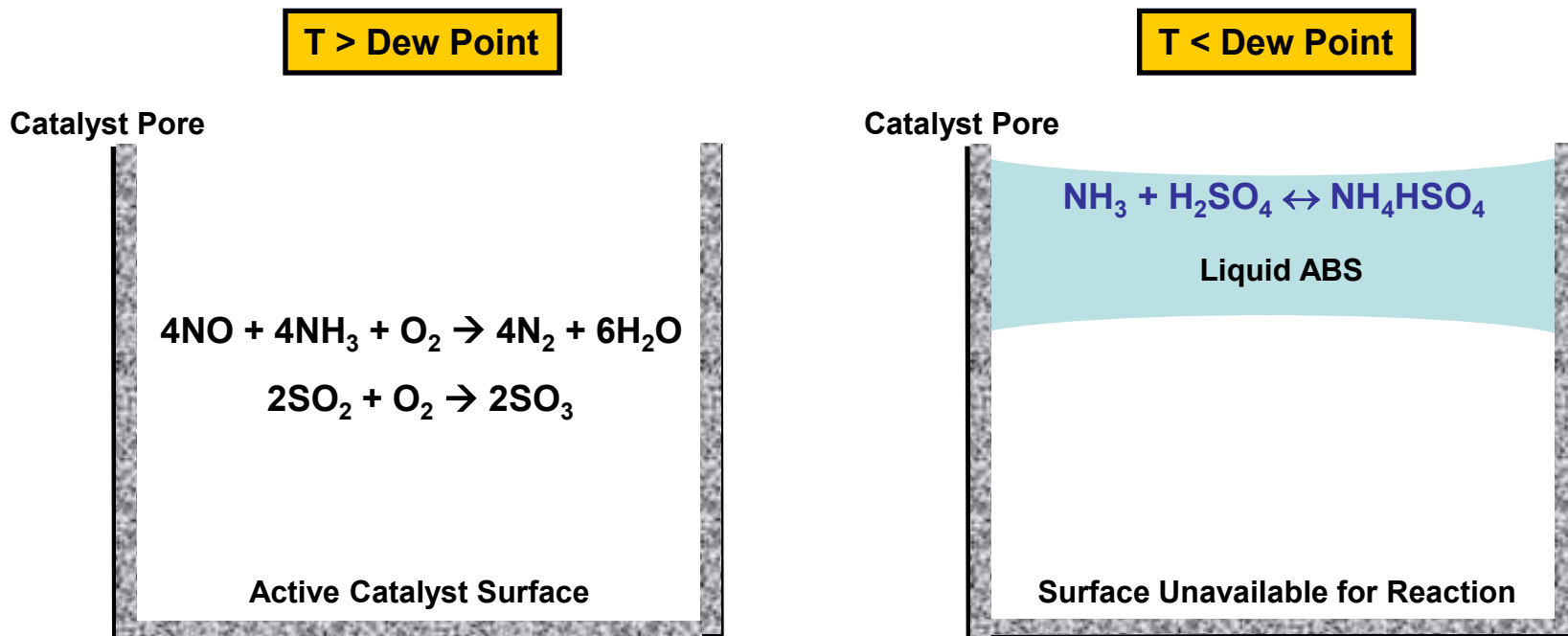


Bulk-Phase ABS Equilibrium Curves



ABS Deposition Controls SCR Tmin

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

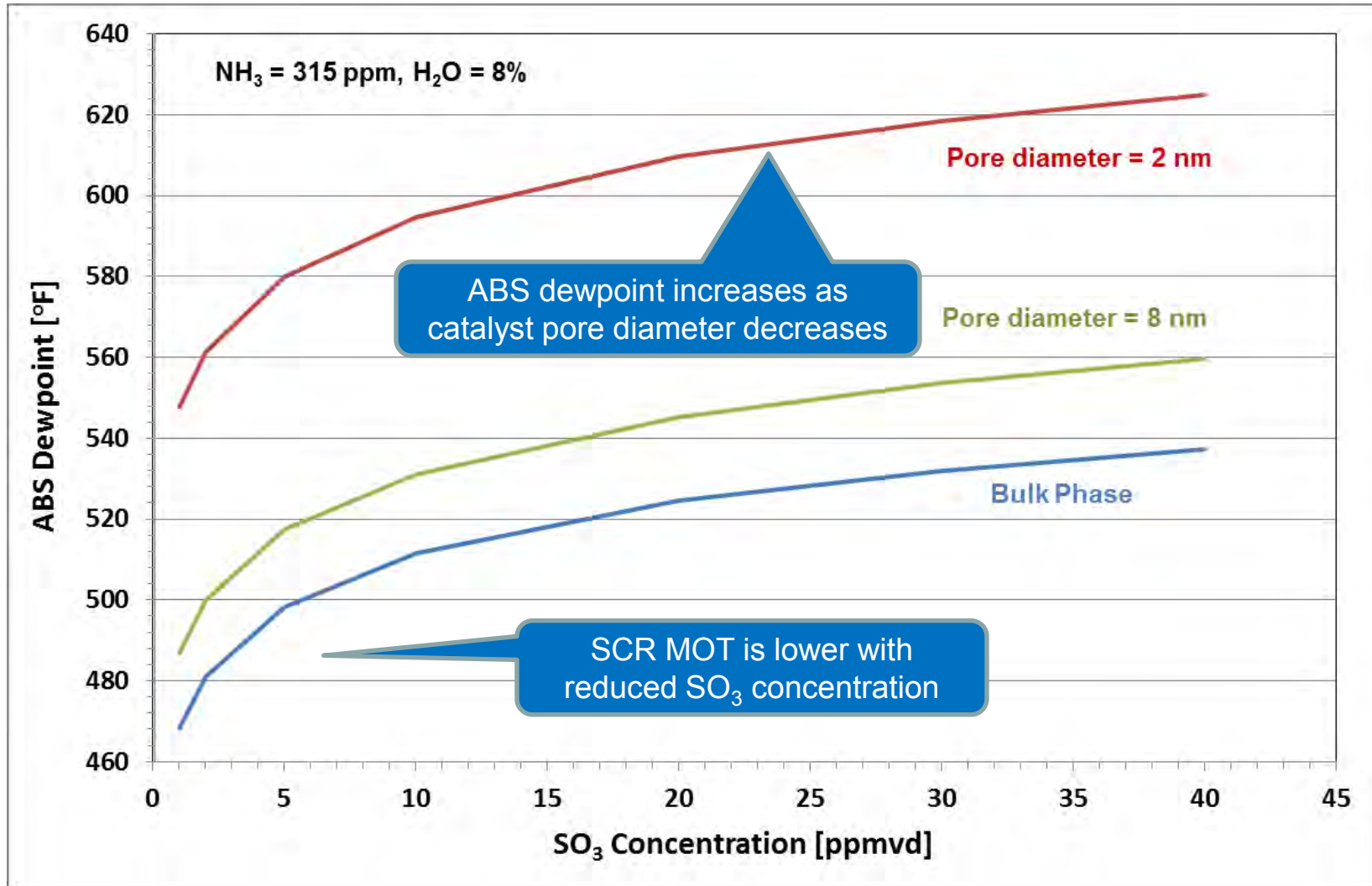


Capillary Condensation

- **Liquid ABS forms in SCR catalyst pores above the bulk phase dew point temperature (BDT)**
 - **Kelvin equation:**
 - $\ln \left(\frac{P \text{ vap in pore}}{P_{\text{sat vap bulk liquid}}} \right) = - \frac{2 \sigma V_l}{r R T}$
 - σ = ABS surface tension, V_l = ABS molar volume, R = gas constant, T = temperature, and r = pore radius
 - **Smaller catalyst pores (i.e., radius < 10nm) result in:**
 - Larger vapor pressure reduction of liquid ABS
 - Higher ABS dew point \rightarrow ABS formation at higher temperature

Impact of Pore Size on ABS Dew Point

Kelvin equation calculates critical diameter above which no condensation will occur.



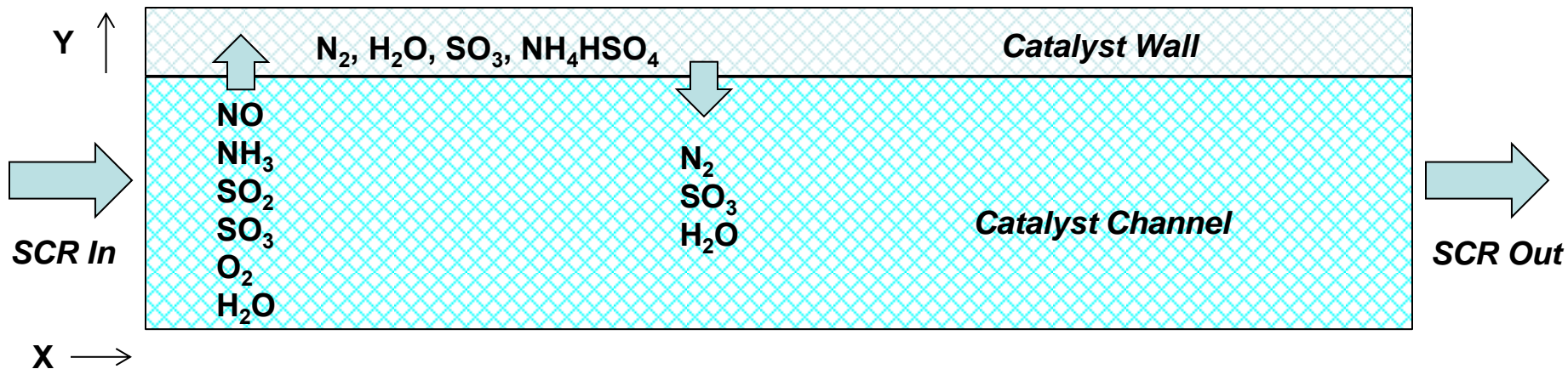
Toolbox

Predict Catalyst Response to ABS Formation

Transient model

- Predict deactivation and recovery (DeNO_x, SO₃, NH₃ transients)
- Evaluate feasibility of desired operating scenarios and iterate

Reactions in Catalyst Wall:



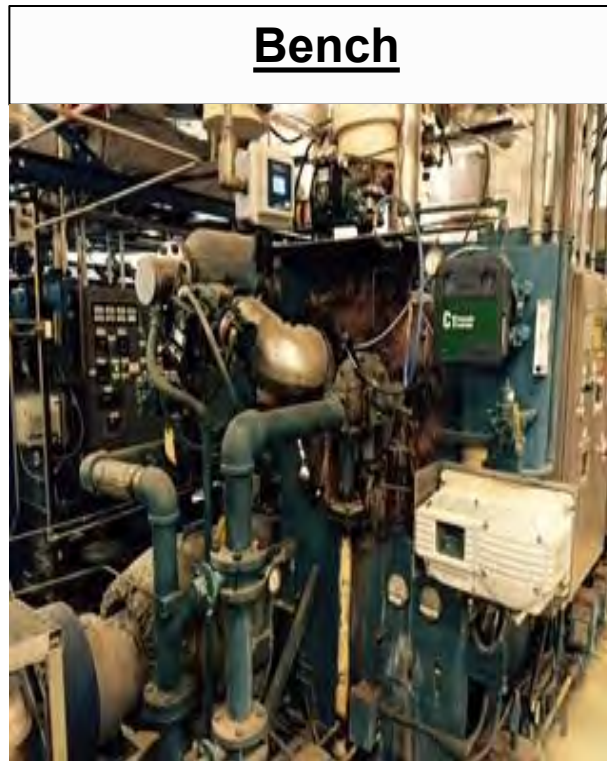
FEM model: account for internal / external mass transfer, intrinsic kinetics, SO₃/NH₃ adsorption, and ABS pore plugging/removal (thermo, kinetics).

Toolbox

Characterize Catalyst Response to ABS Formation

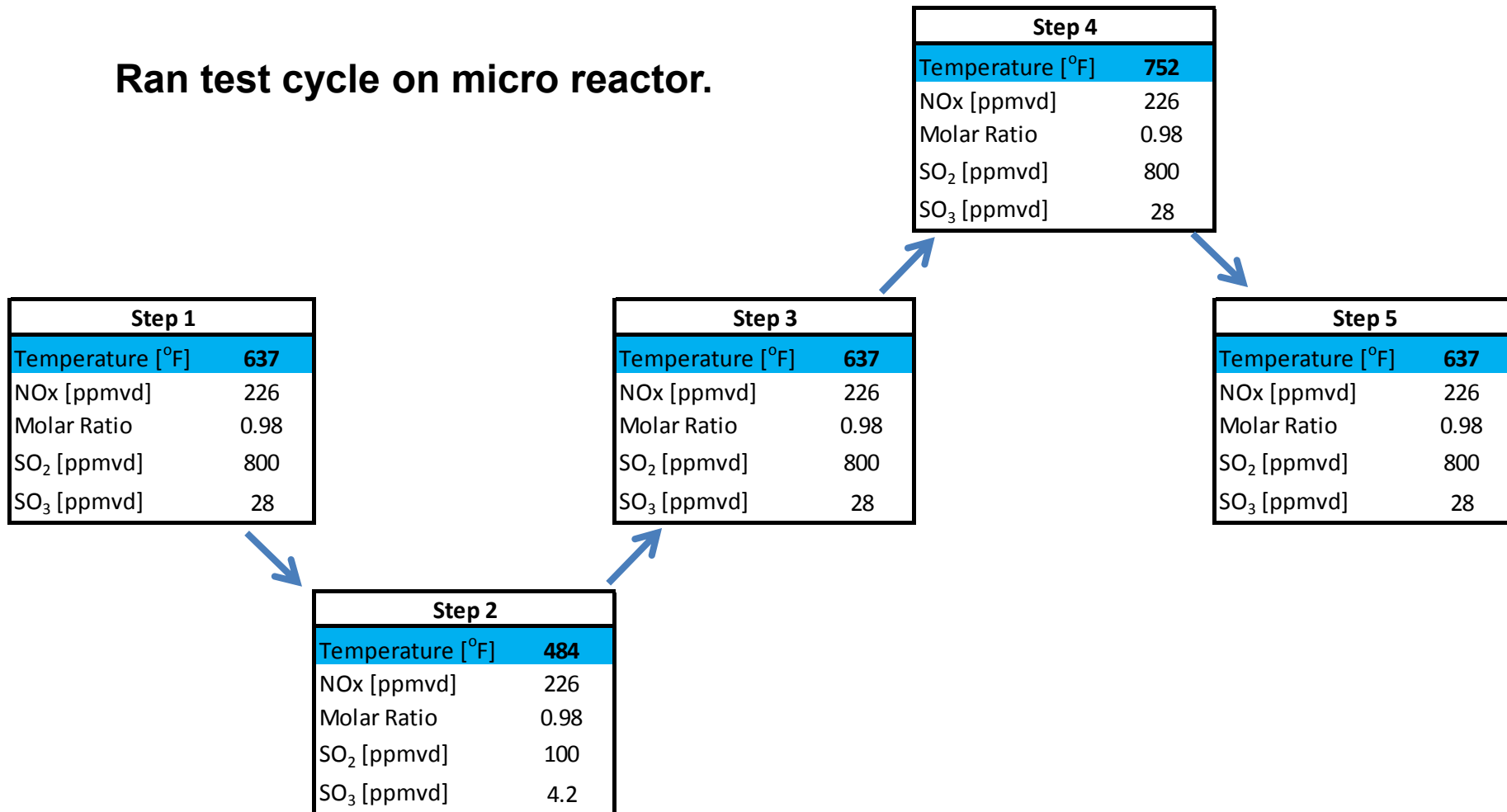
Lab testing

- Characterize catalyst for model baselining
- Verify modeling output

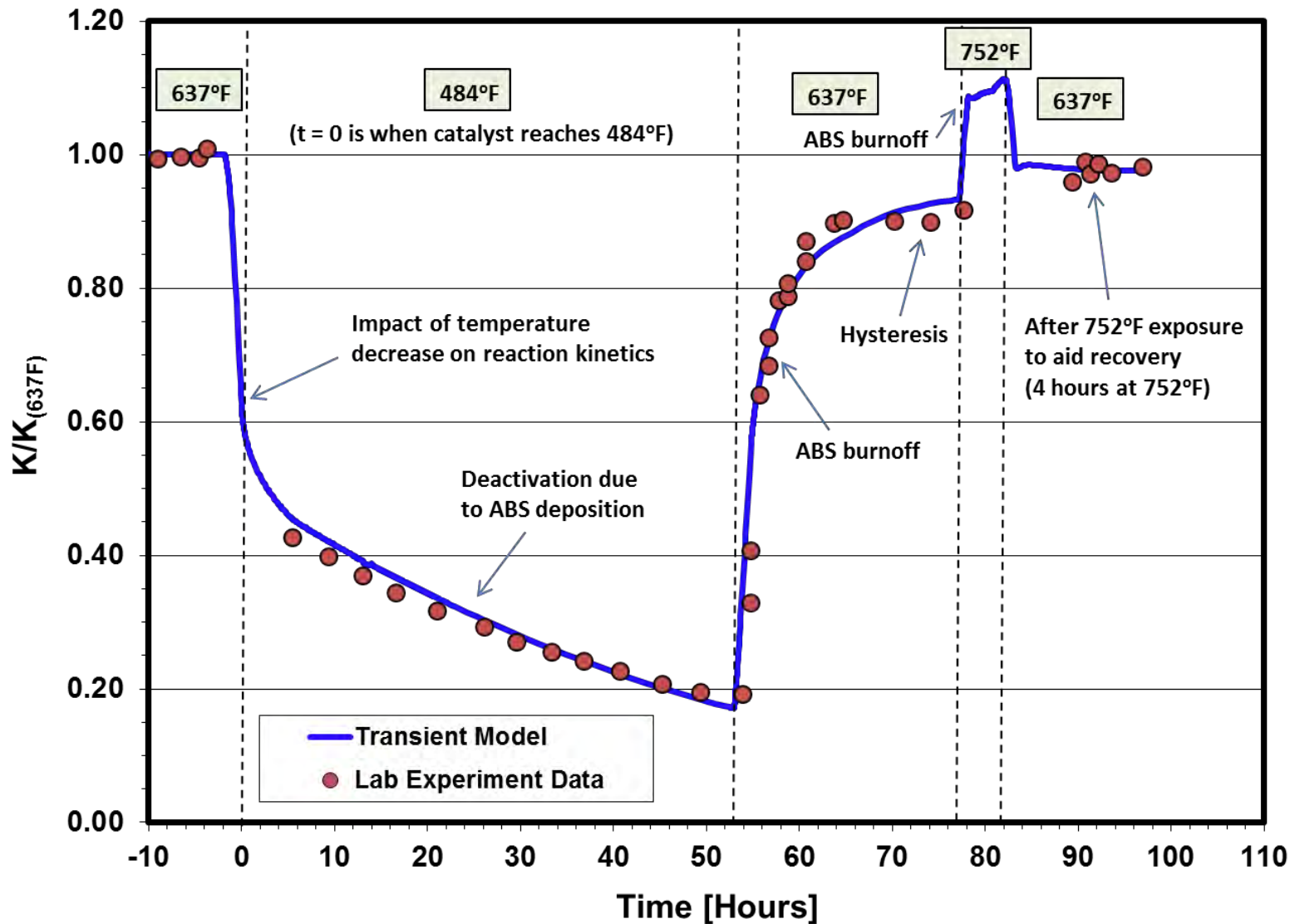


Example: Lab Catalyst Test

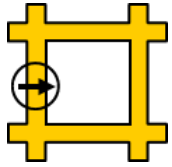
Ran test cycle on micro reactor.



Catalyst Test: Model vs. Lab Data

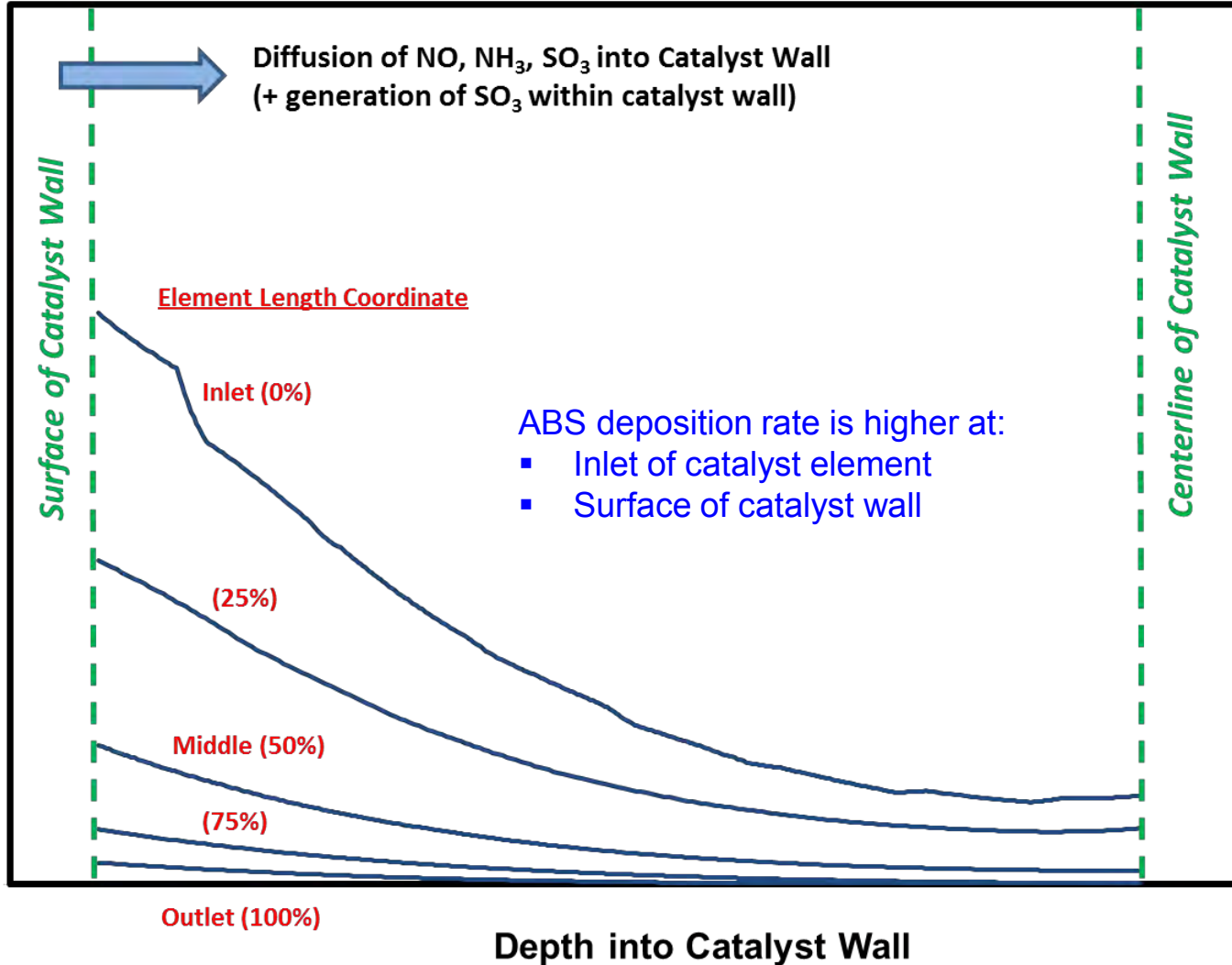


Model: ABS Profile in Catalyst Wall

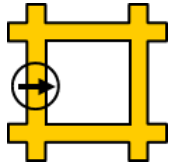


$t = 2$ hour point in low load “step 2”

Amount ABS Deposited in Catalyst Pores

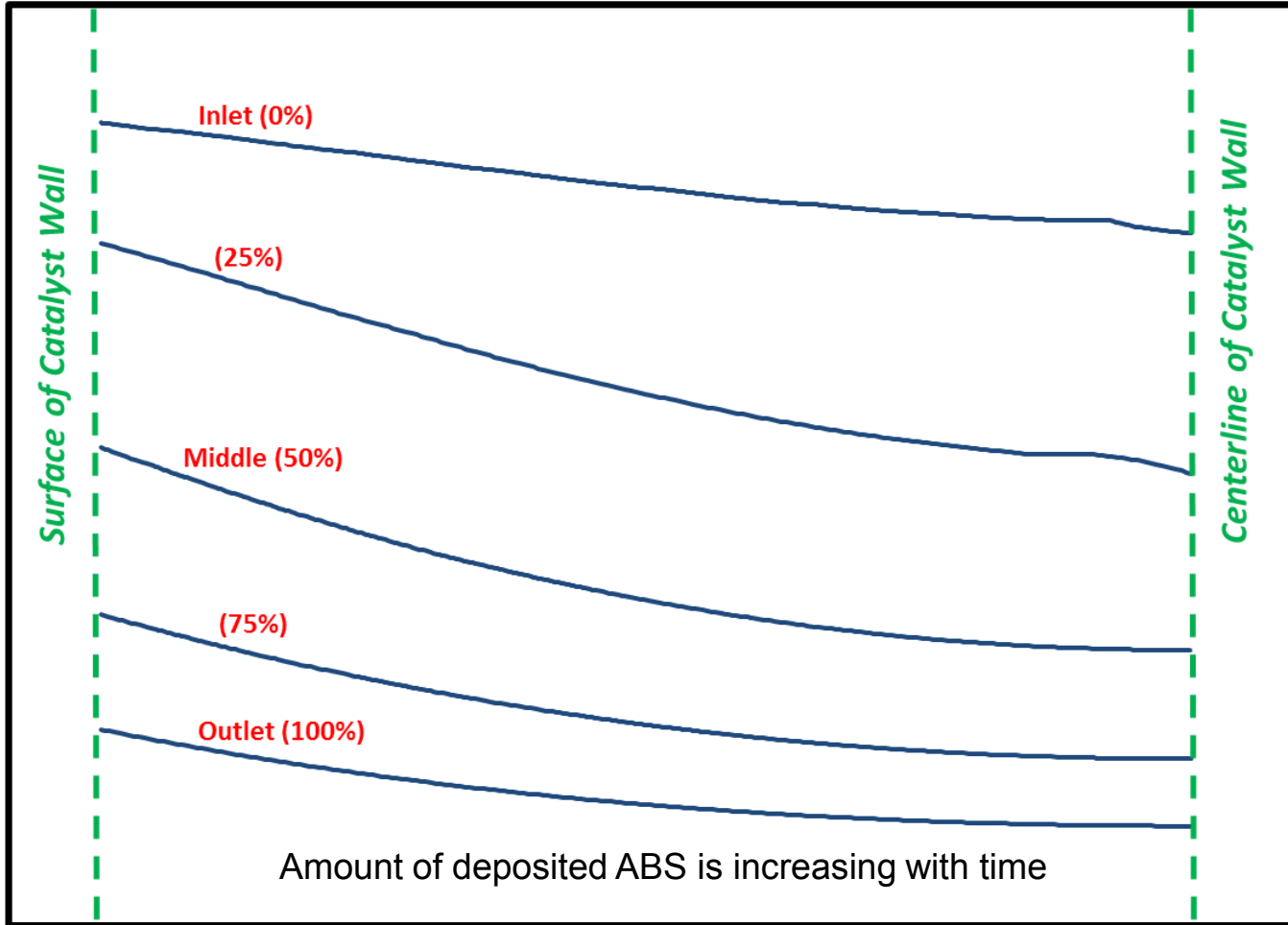


Model: ABS Profile in Catalyst Wall



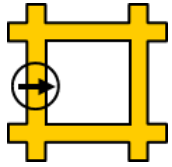
$t = 17$ hour point in low load “step 2”

Amount ABS Deposited in Catalyst Pores



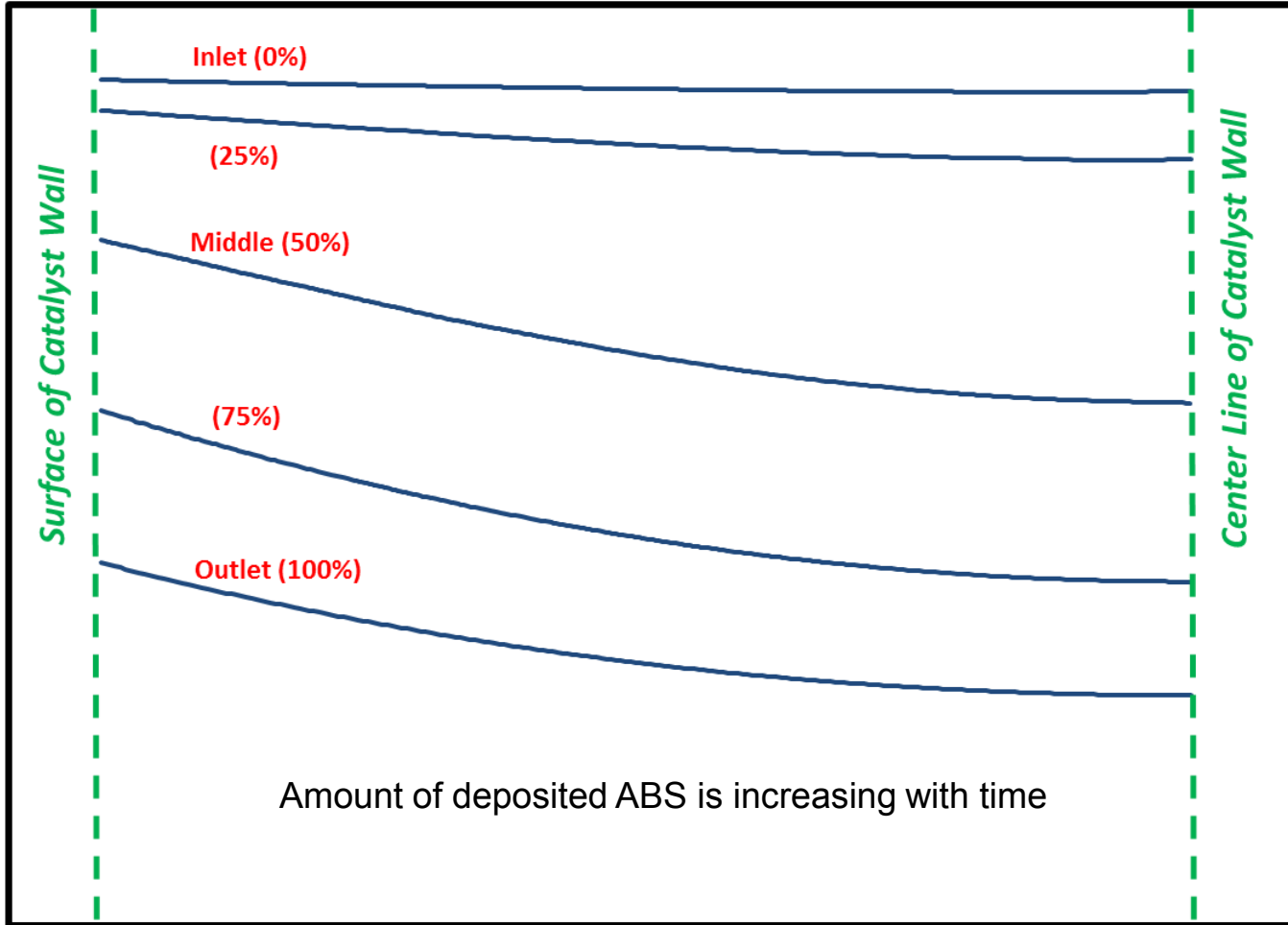
Depth into Catalyst Wall

Model: ABS Profile in Catalyst Wall



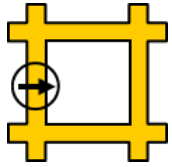
Amount ABS Deposited in Catalyst Pores

$t = 32$ hour point in low load “step 2”



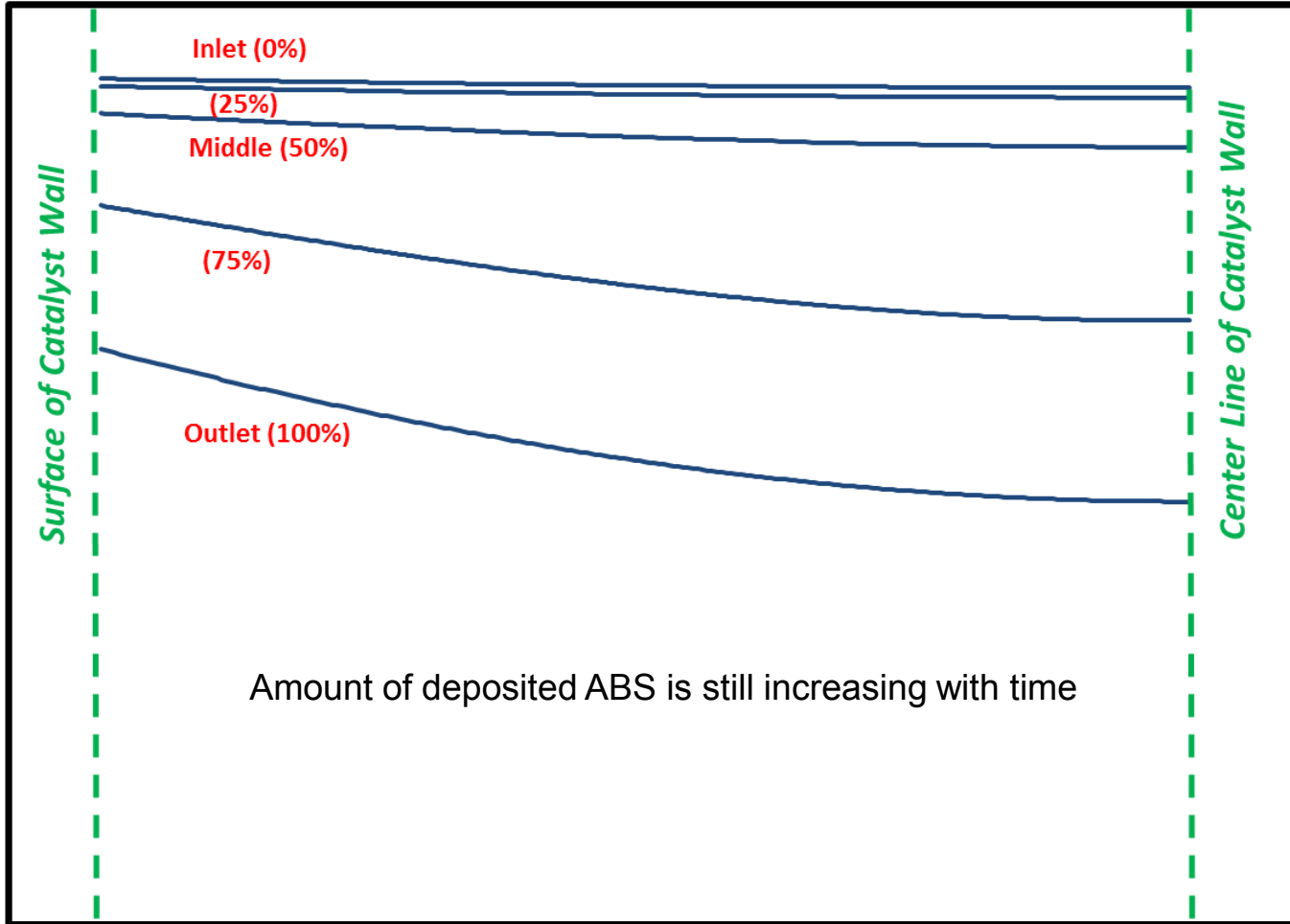
Depth into Catalyst Wall

Model: ABS Profile in Catalyst Wall



Amount ABS Deposited in Catalyst Pores

$t = 51$ hour point in low load “step 2”



Depth into Catalyst Wall

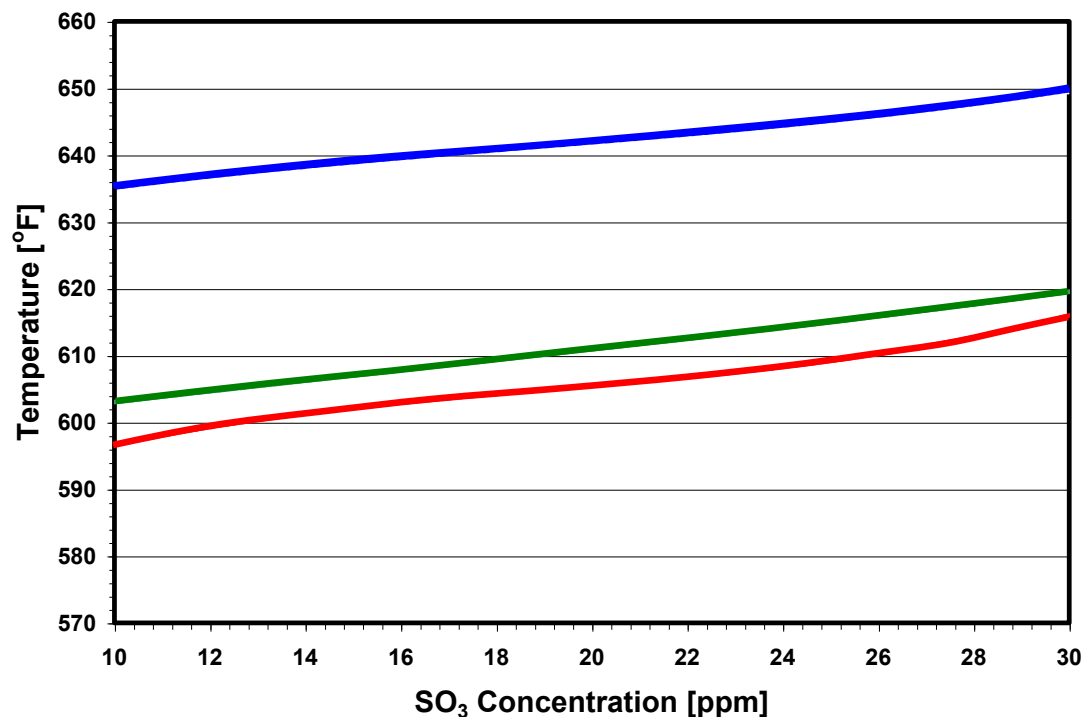
Training Session Overview

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 - **Gibson Enhanced SCR Performance Testing**
- **Summary**

Tmin: Basic Approach

- “Basic Approach”

- Avoid ABS deposition in the SCR catalyst.
- Simple operating guidelines.

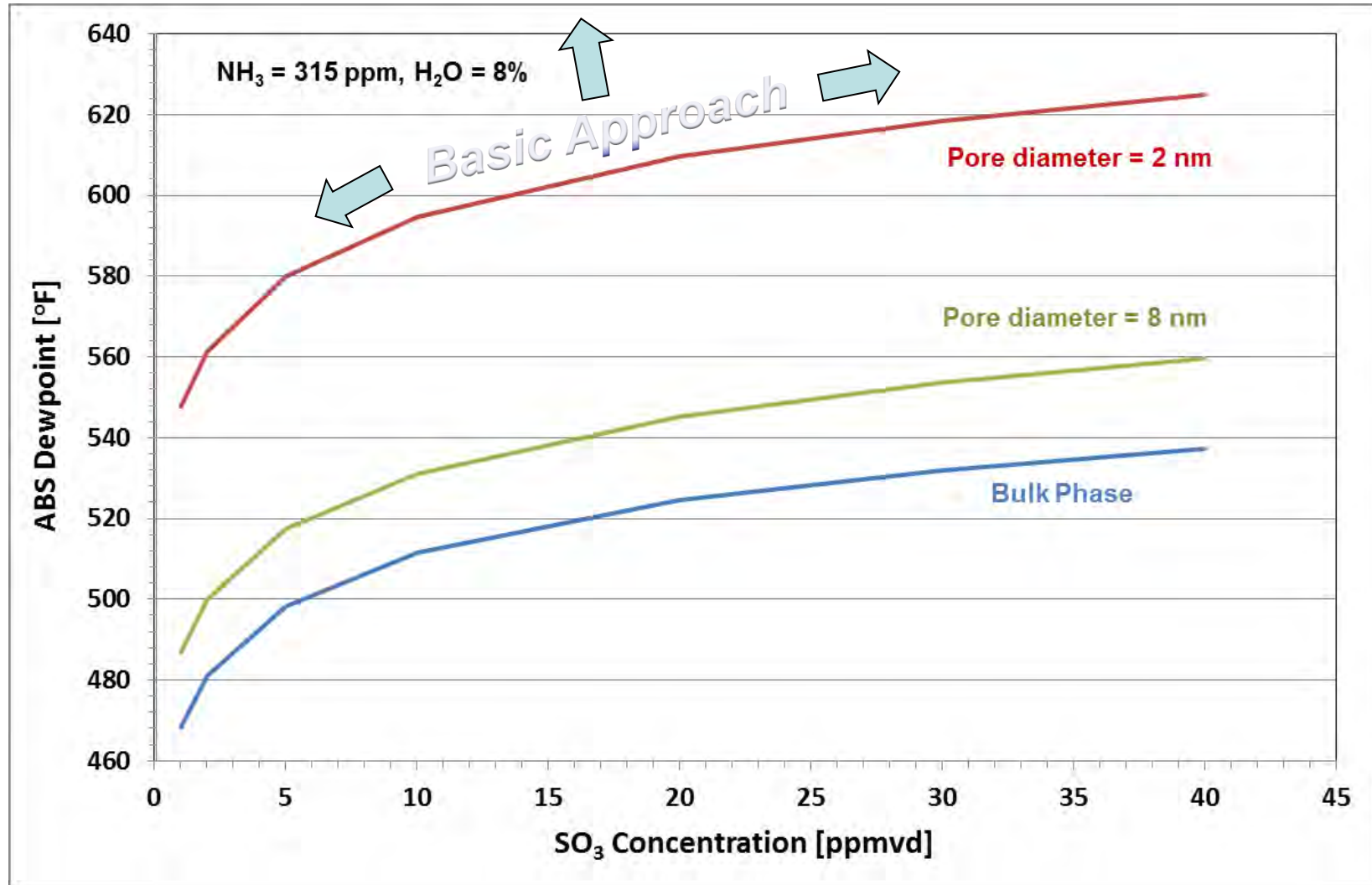


RT = recovery temperature (T)

MOT = minimum operating T

MIT = minimum injection T for NH₃

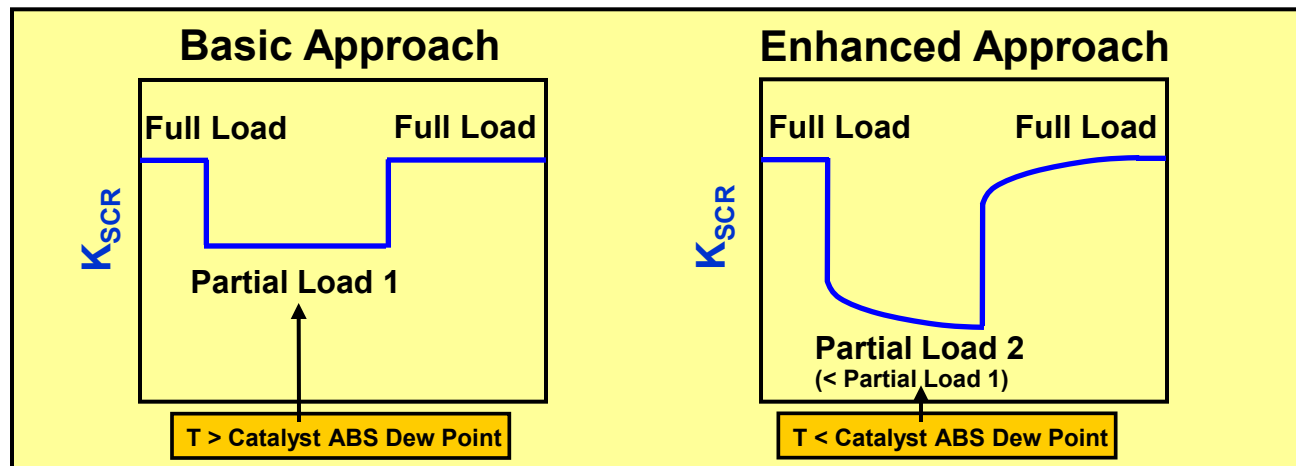
Basic Approach Avoids ABS Deposition



Tmin: Enhanced Approach

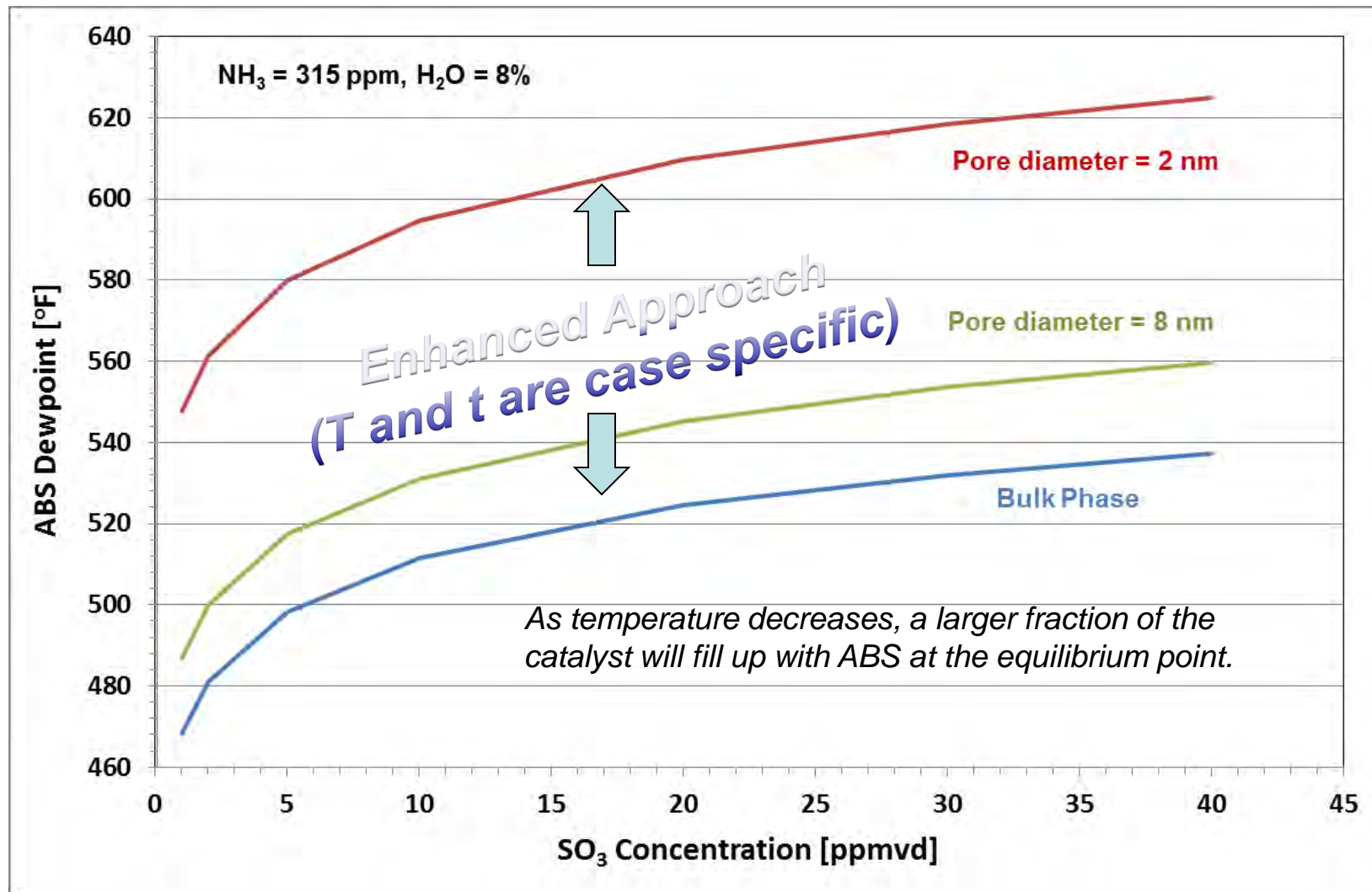
- **“Enhanced Approach”**

- Operate down towards the ABS dew point (but not below!)
- Allow a controlled amount of ABS deposition in the SCR catalyst during low temperature operation, and then...
- Recover the full catalyst potential by reheating the catalyst above the recovery temperature and driving off the ABS



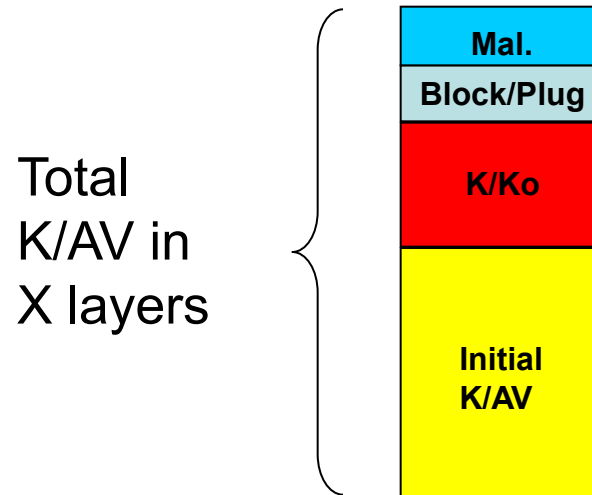
Enhanced Approach

Manage ABS Deposition in Catalyst: Transient Cycling



Design Considerations

Applying the Enhanced Approach



- **For the low load and recovery conditions:**

- Transient K/AV must be \geq K/AV required to meet DeNO_x, NH₃ slip
 - Thus: $K/K_{\text{full load}}$ must be $\geq AV/AV_{\text{full load}}$
- Need to consider transient SO₃ & NH₃ spikes during recovery

Developing an Operational Strategy

- **Factors impacting catalyst ABS amount at low load:**

Factor	Factor Direction	Potential Impact on ABS Amount
Temperature	↓	↑
Inlet SO ₃ (coal type, DSI)	↑	↑
DeNOx	↑	↑
Time	↑	↑

Developing an Operational Strategy

- **Factors impacting catalyst recovery (ABS removal):**

Factor	Consideration
Achievable Recovery Temperature	Higher recovery temperature can avoid the hysteresis and more quickly remove the deposited ABS.
Time at Recovery Temperature	Longer hold time at recovery temperature will help the removal of the deposited ABS.
Emission Spikes (SO ₃ , NH ₃)	SO ₃ and NH ₃ emission spikes can occur during recovery, due to desorption of the adsorbed ABS, SO ₃ , and NH ₃ .
Temperature Ramp Rate	Lowering the ramp rate can reduce the amplitude of the SO ₃ and NH ₃ emission spikes during recovery.
NH ₃ Injection Rate	Lowering the NH ₃ injection rate can reduce the NH ₃ emission spike during recovery (use it for DeNO _x).
Use of DSI	If available, DSI can be used to mitigate the SO ₃ emission spike during recovery.
DeNO _x and NH ₃ Slip	If recovery is not complete, risk is to run at reduced DeNO _x and/or higher NH ₃ slip.

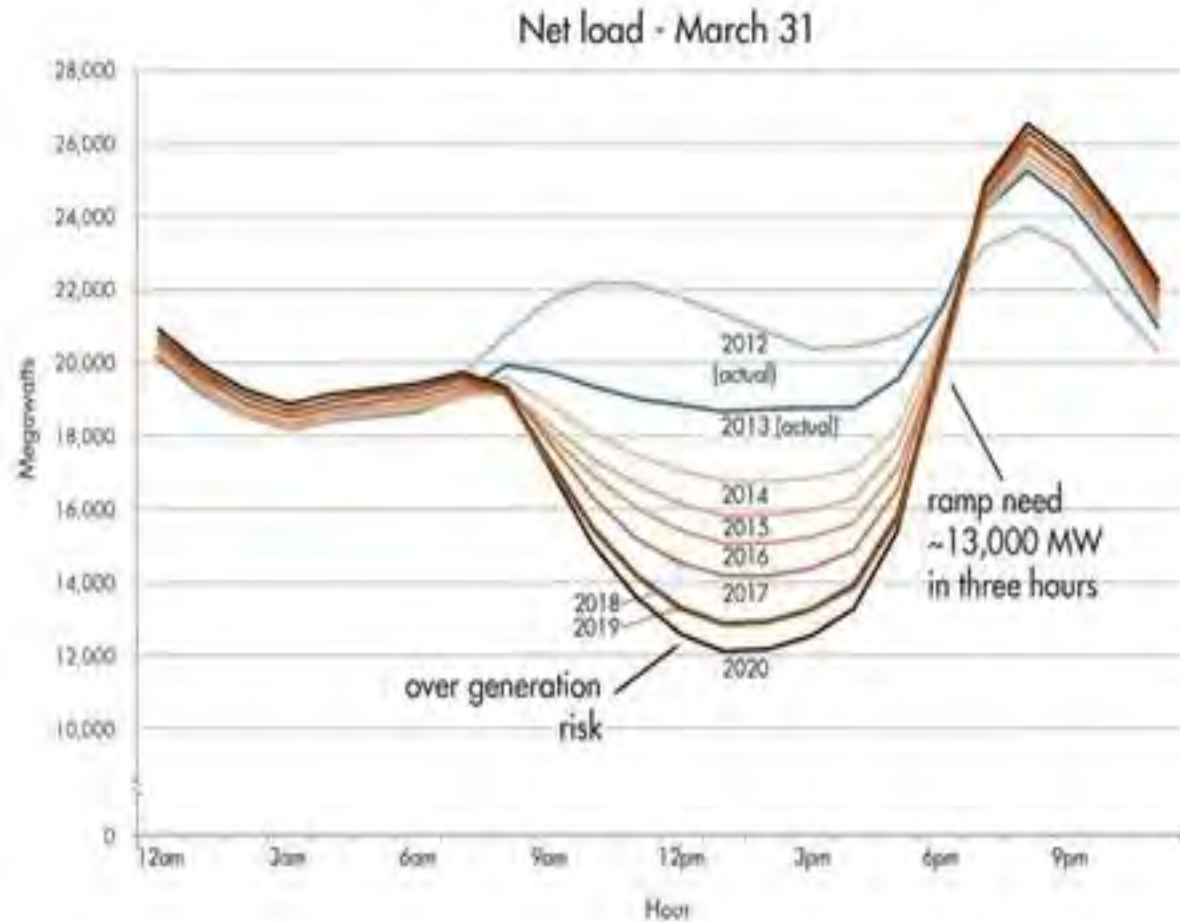
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Drivers for Low Load Operation

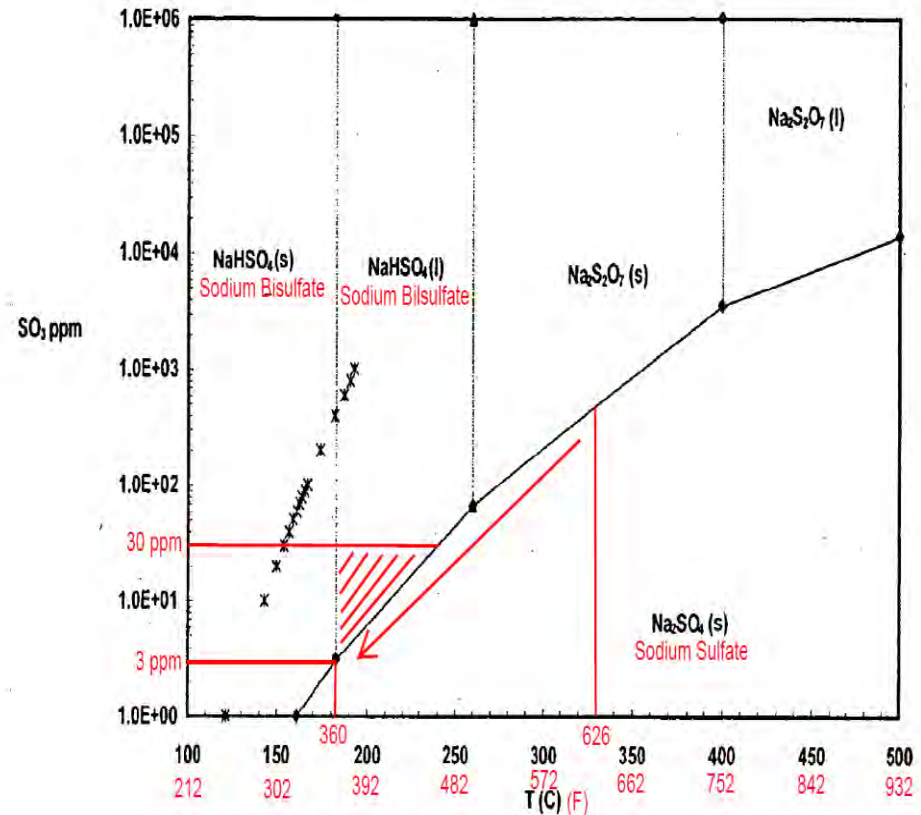
- **Solar and wind have created large amounts of peak generation that are priority.**
- **Coal must now load follow to a degree and be more nimble for turndown and ramp rate.**
- **New Ozone season limits will require pushing the SCR's harder and keeping them in service longer.**



California ISO Projected Demand Response Curve

SBS System Background

- Liquid sodium bisulfate forms between ~360-500°F with this temperature range occurring in the air heater and possibly in the air heater outlet duct.
- The preferential reaction is to form solid sodium sulfate at higher temperatures, however sodium sulfate will continue to react with residual SO_3 so a high level of control (<3 ppm) is needed to prevent conversion to the liquid sodium bisulfate.
- This was the primary reason URS relocated their process to the higher temperature region and maintains a high rate of control to capture residual SO_3 from the SCR.
- Pre-SCR SO_3 control can also be achieved using hydrated lime DSI without risk of liquid byproduct, however, high rates of control (90+%) can be difficult to achieve using DSI.



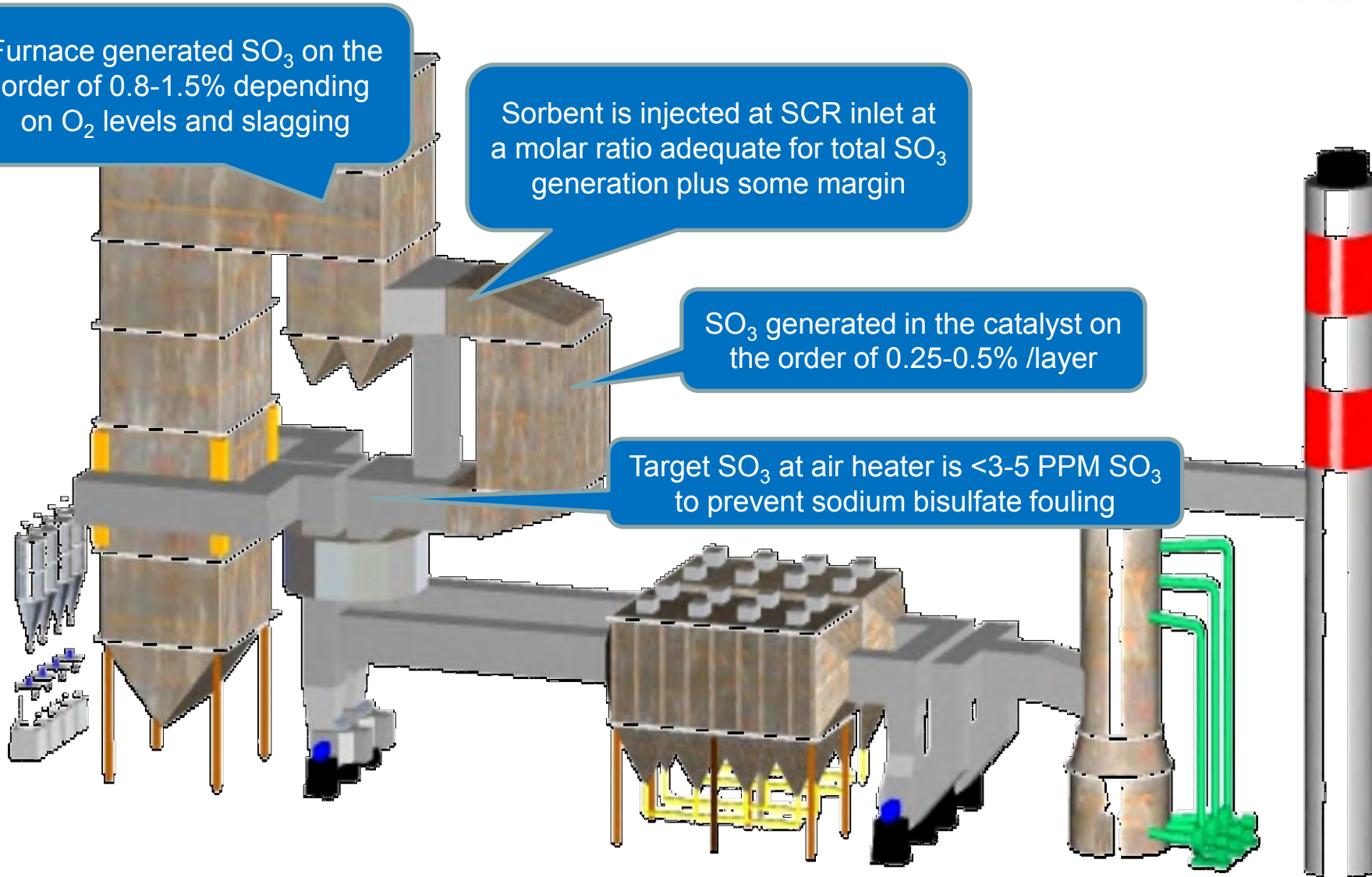
SBS System Background

Furnace generated SO_3 on the order of 0.8-1.5% depending on O_2 levels and slagging

Sorbent is injected at SCR inlet at a molar ratio adequate for total SO_3 generation plus some margin

SO_3 generated in the catalyst on the order of 0.25-0.5% /layer

Target SO_3 at air heater is <3-5 PPM SO_3 to prevent sodium bisulfate fouling

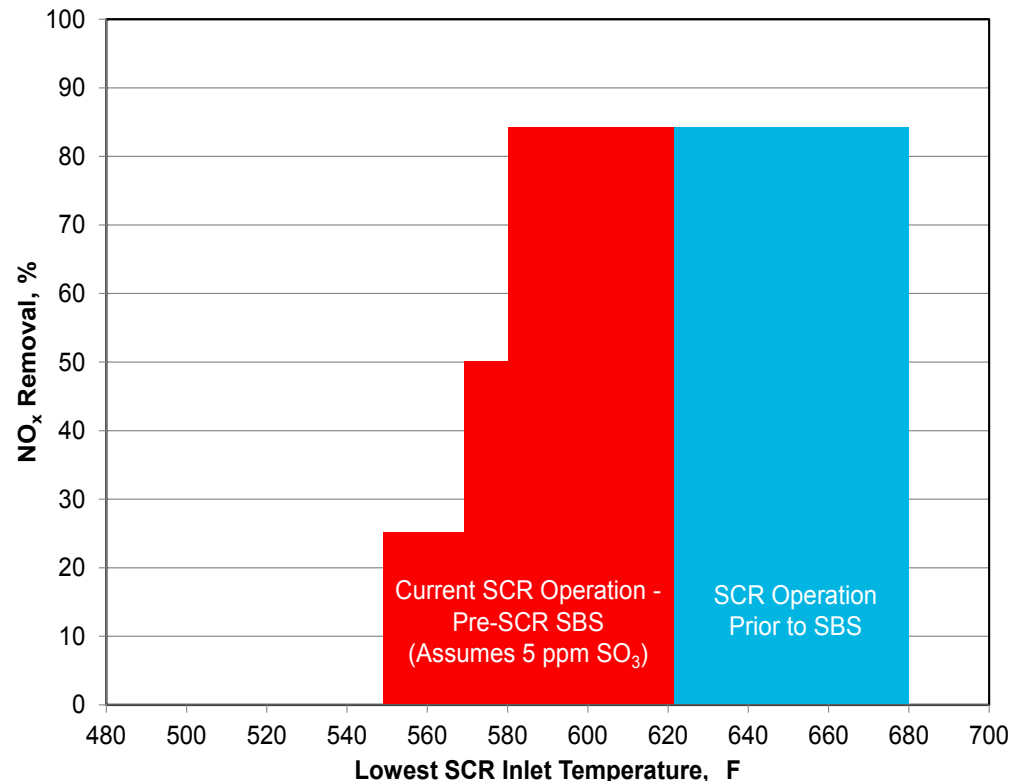


Gibson: Reduced Catalyst MOT


- **Options considered for low load SCR operation**
 - Reduce the NH_3 at the SCR inlet by reducing inlet NO_x (gas co-firing) or NO_x removal rate.
 - Increase the SCR inlet temperature at low load by economizer modifications and/or bypass systems either water/gas.
 - Would result in a full time or part-time heat rate penalty depending on the technology chosen.
 - **Enhanced Approach:** restrict the operating time below the MOT to limit the amount of ABS formed, then operate at a set time at full load to “burn-off” the ABS.
 - Manage an ABS Inventory Calculation. Effective method for expanding the low load operation range for a unit.
 - Remove the SO_3 prior to the SCR to low levels, which can greatly reduce the MOT without heat rate penalty. Added benefits: reduced APH fouling and enhanced NO_x removal at full load.

Gibson Plant Overview

- Five Units:
 - 675 MWg, 4.0-6.0 lb/Mmbtu coal
- High-dust Foster Wheeler SCR's designed for 3 layers of catalyst and 85% NO_x removal
 - Historically had poor distribution
- Horizontal shaft air heaters with cold side ESP's
- SBS was installed post AH in 2005 and relocated Pre-SCR from '09-'14
 - Original MOT was 622°F and was modified to 550°F with tiered NO_x removal at low load based on the assumption of 5 ppm SO₃
 - Min load was changed from 440 MWg to 280 MWg

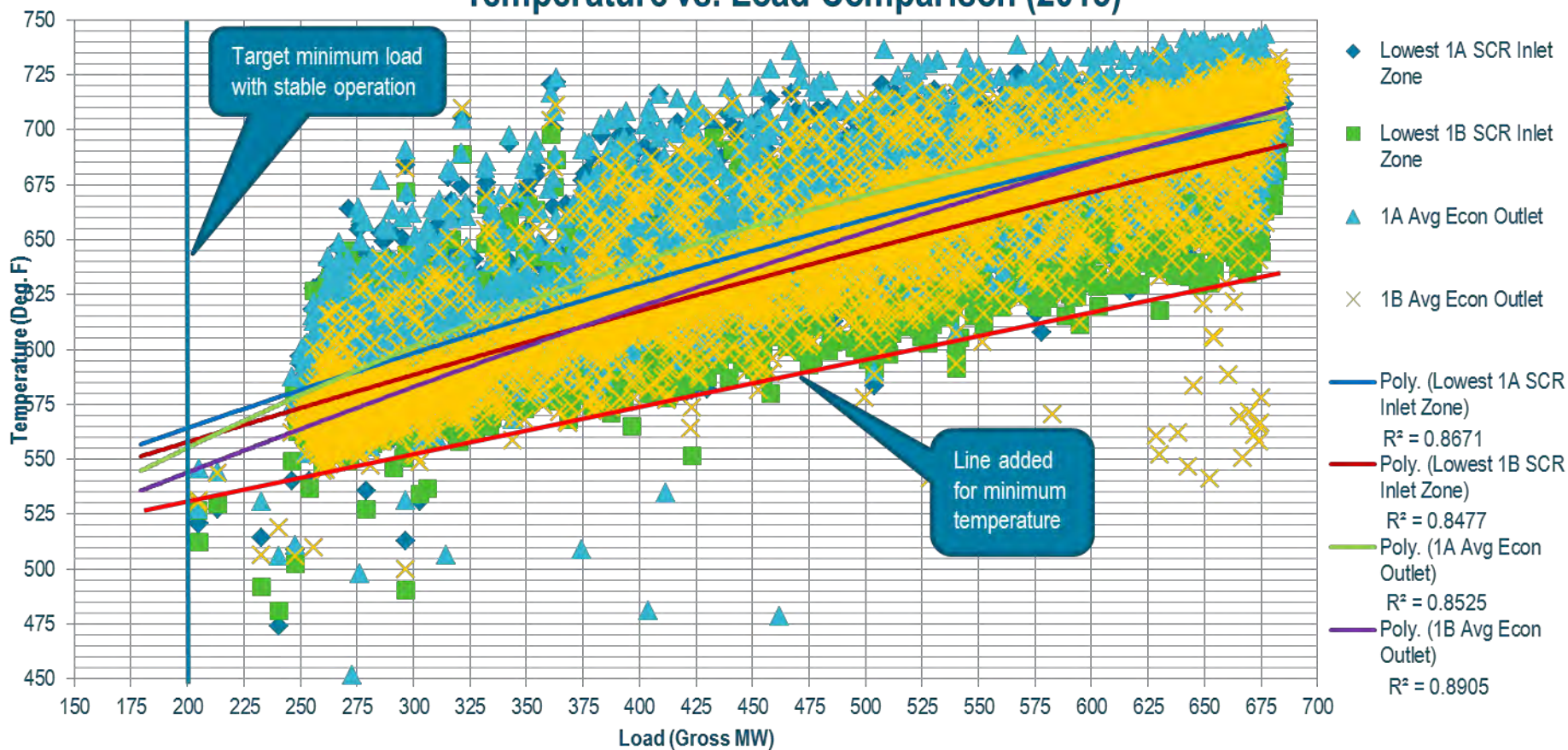


Testing Overview/Goals

- **Laboratory catalyst testing performed by CORMETECH.**
 - Demonstrated 72-hour operation to simulate a holiday weekend at full 85% NO_x removal at 500°F flue gas temp.
- **Two-week test program on Gibson Unit 1 (July 2016).** 
 - AECOM performed gas testing with modified CCS procedure to validate SO₃ concentrations around the SCR at full and low load.
 - Breen probes for condensable monitoring.
- **Used CORMETECH transient modeling coupled with the field and lab data to determine reasonable operating parameters.**
- **Field test objectives and goals:**
 - Quantify the boiler and SCR SO₂ conversion at full and low load.
 - Evaluate operation at elevated NH₃ slip and increased NO_x removal.
 - Evaluate operation at reduced air heater gas outlet temperatures.
 - Measure SO₃ and Na compounds in the primary air stream for NH₃ dilution to possibly eliminate the in duct heat exchanger.
 - Evaluate the feasibility of permanently blanking the economizer bypass duct to eliminate an O&M burden.
 - Run a full scale 72 hour test at 200MWg to simulate a long holiday weekend.

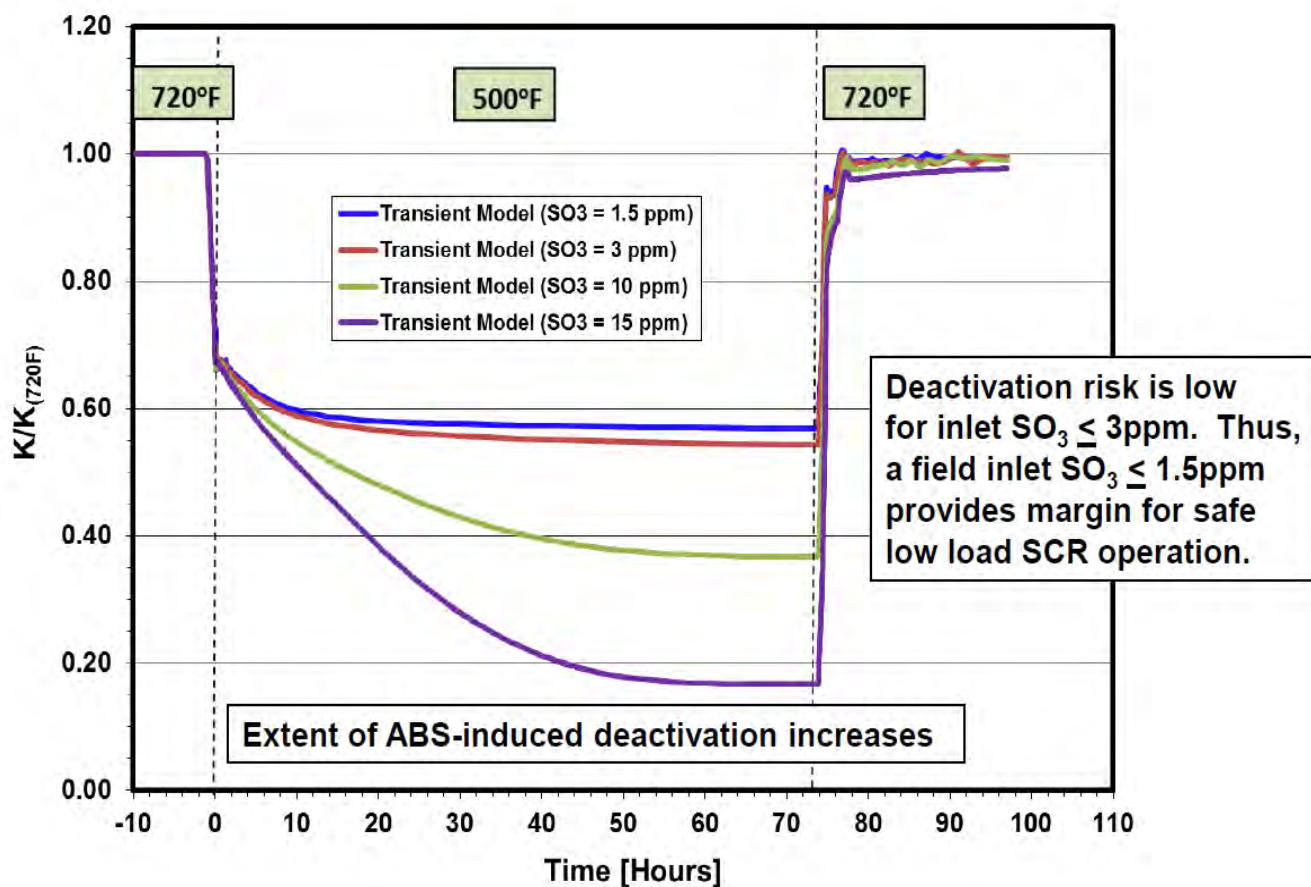
Testing Overview/Goals

Temperature vs. Load Comparison (2015)



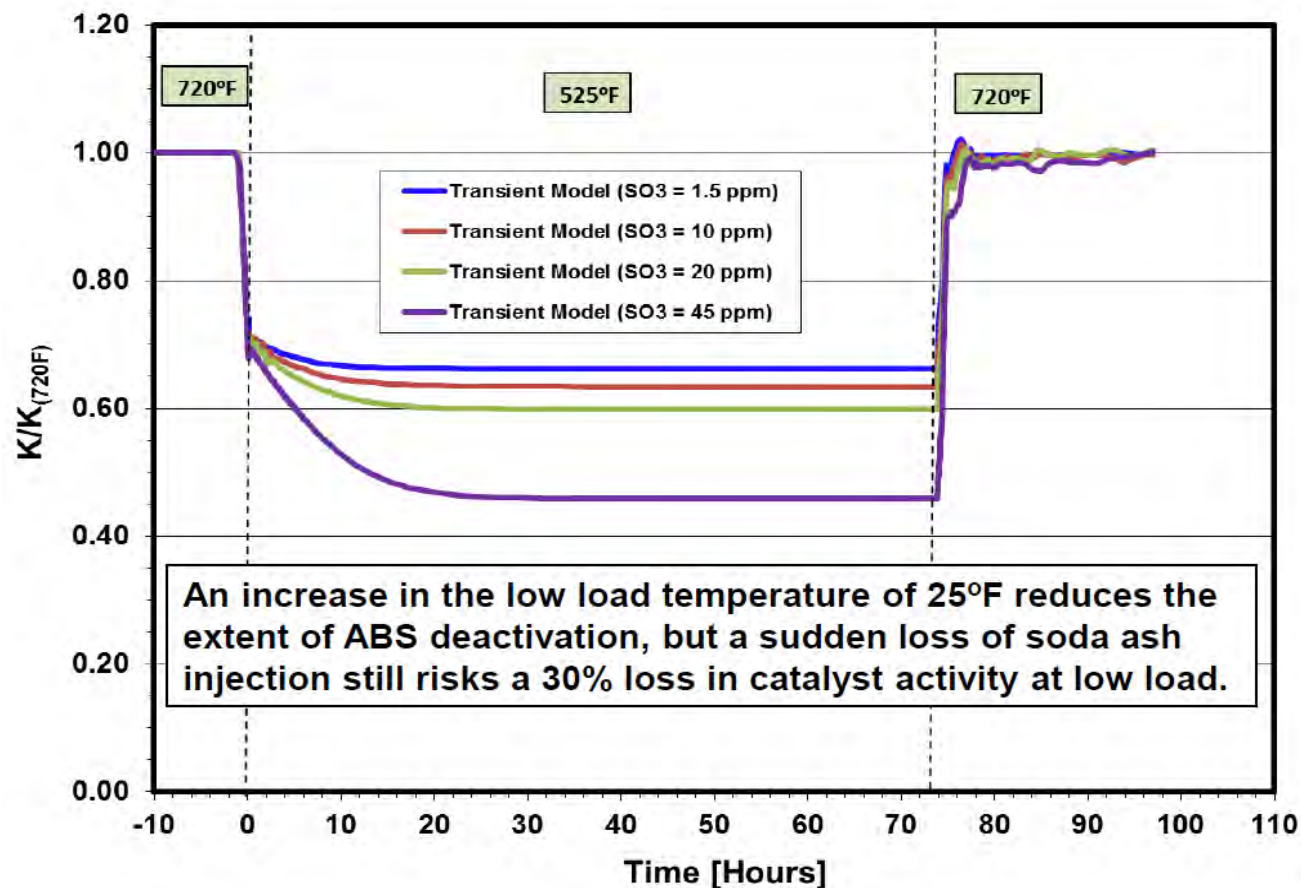
Transient Modeling Results

- Sensitivity analysis with varying SO_3 levels shows very little ABS accumulation at 1.5ppm SO_3 (indicated by the flat line).
- Field data collected confirms these low SO_3 values and are slightly less providing additional margin
- Model was run at an aggressive 500°F to provide additional margin.



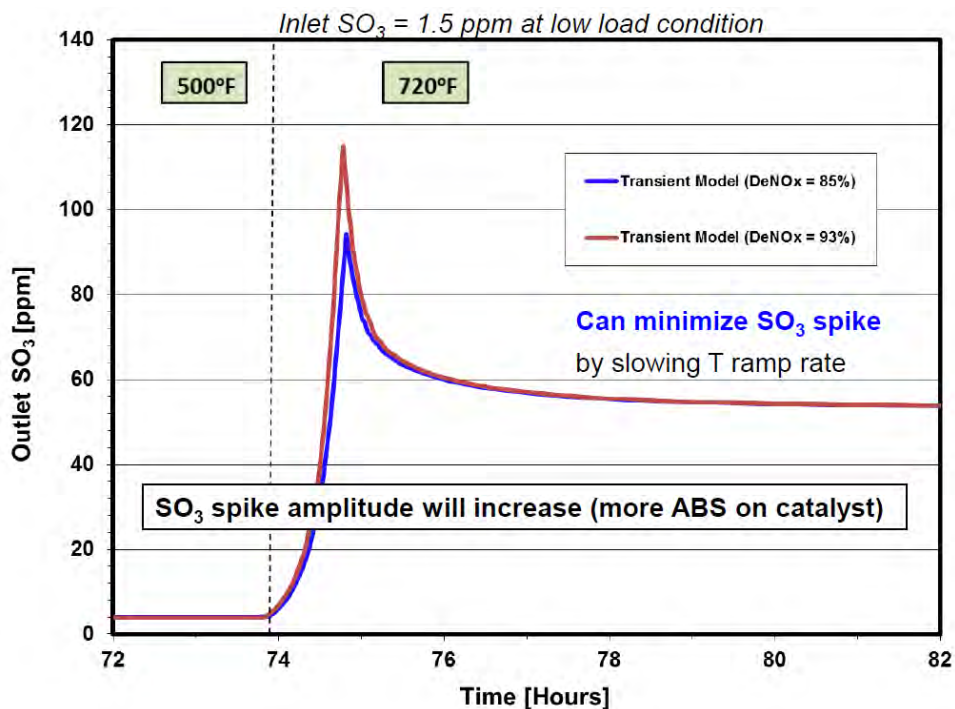
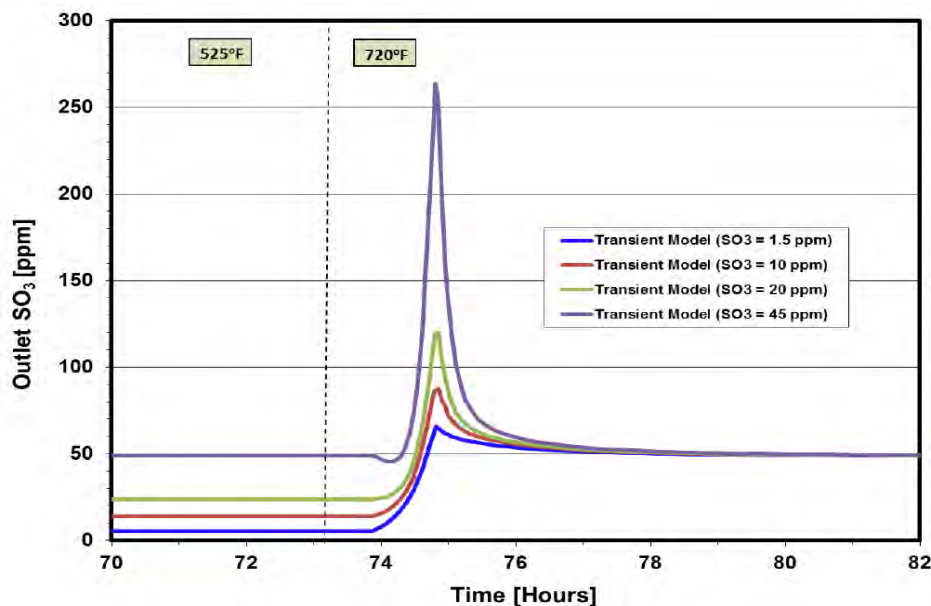
Transient Modeling Results

- Transient model was run again at 525°F to represent expected operations.
- Typical operating temperatures reduce the extent of ABS deactivation.
- Modeling was also performed to simulate a loss of SBS injection.
- Operating for less than 30 minutes without SBS would not pose significant risk to the catalyst.



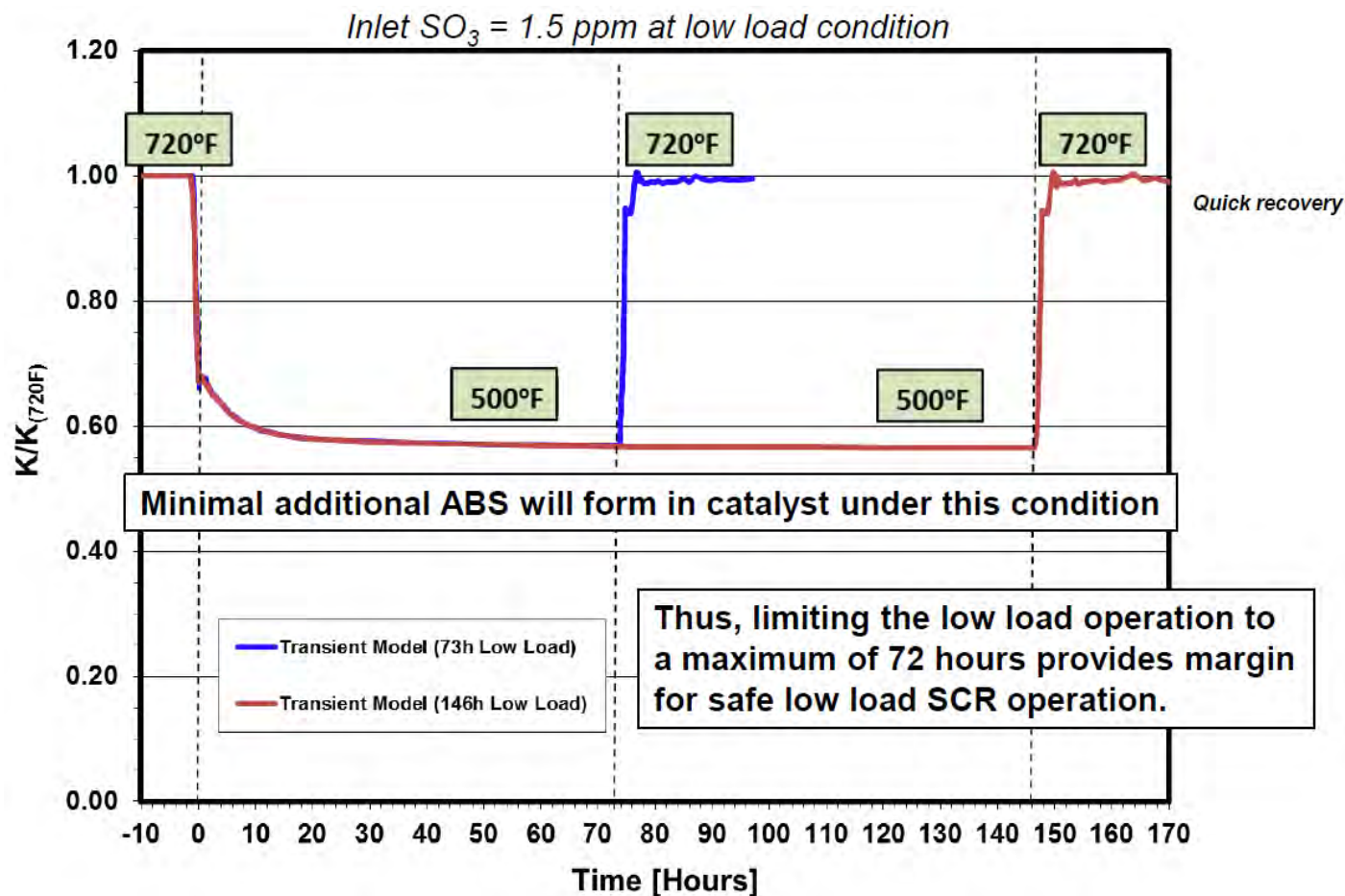
Transient Modeling Results

- SO_3 will spike on load ramp as ABS breaks down into SO_3 and NH_3 .
- Amplitude is indicative of the quantity of ABS accumulation in the catalyst.
- Can minimize spikes by increasing SBS during load ramp and/or reducing load ramp rate.



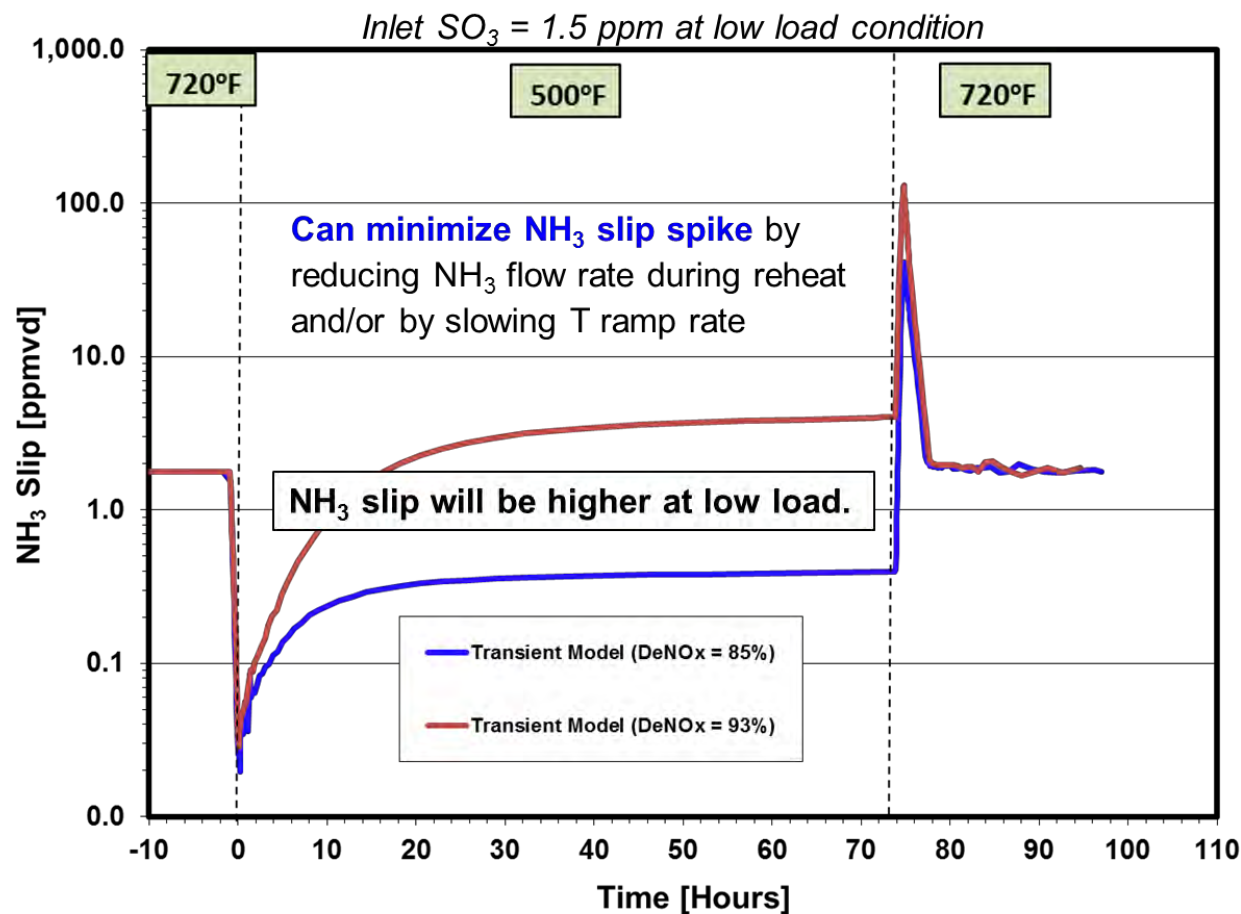
Transient Modeling Results

- Minimal additional impact is seen with the effect of time as long as SO_3 mitigation is maintained.



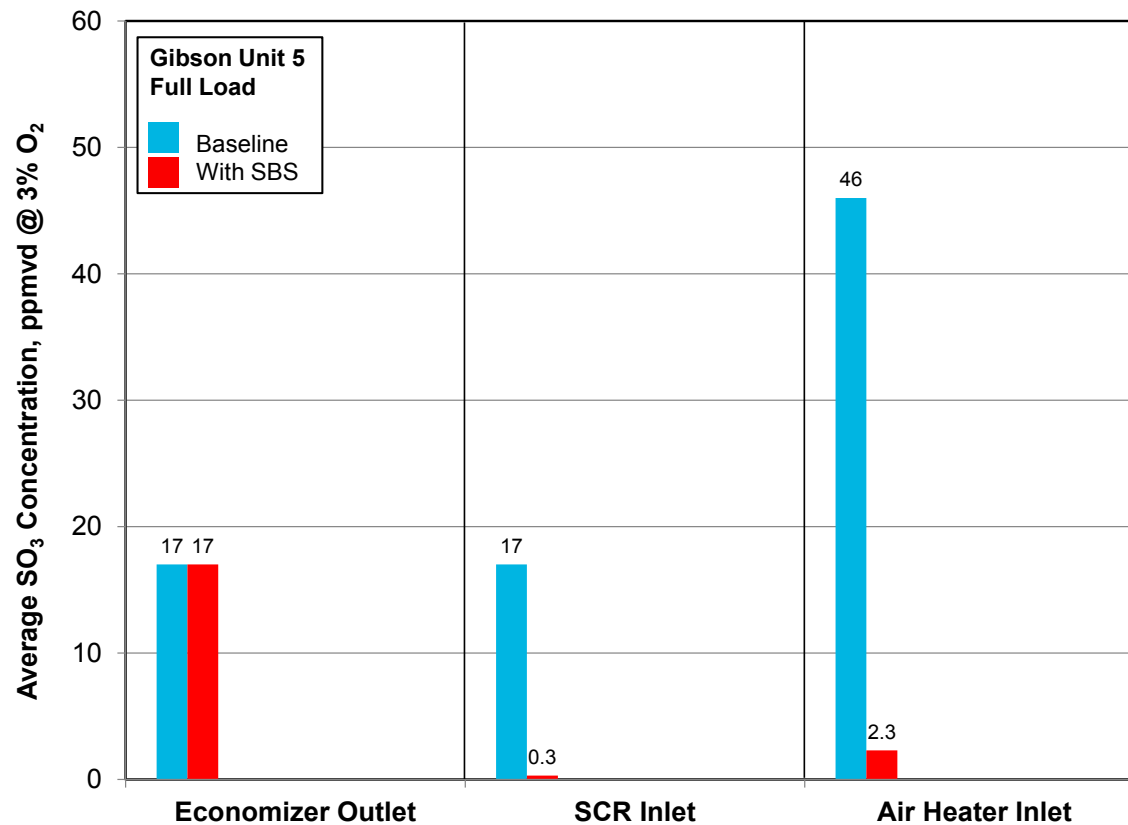
Transient Modeling Results

- Additional sensitivity testing was performed for 93% NO_x removal during enhanced low load.
- Ammonia slip increases greater for low load than full load due to the NO_x reaction kinetics working against our favor due to temperature.
- Ammonia will spike similar to SO₃ on load ramp due to the decomposition of ABS, NH₃ can be reduced during load ramp to minimize the affect.



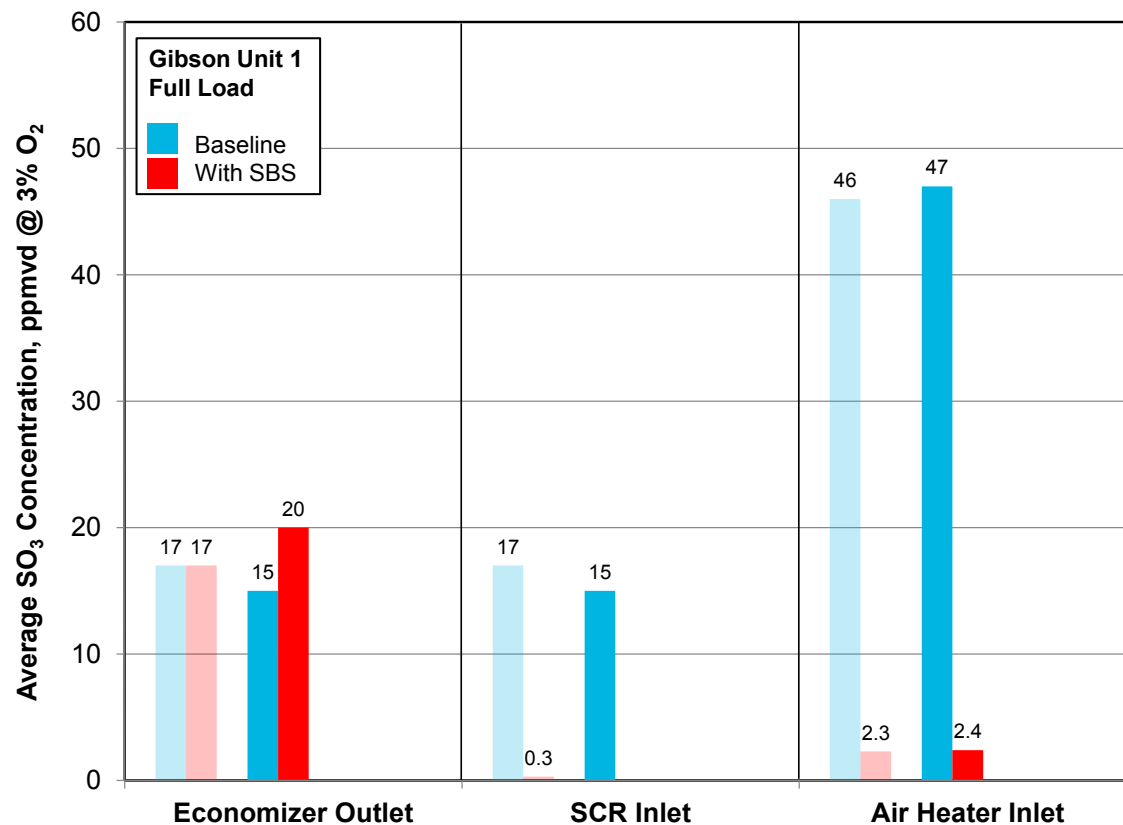
Full Scale Testing

Gibson Unit 5 full load test data from 2009 shows very low SCR inlet SO_3 .



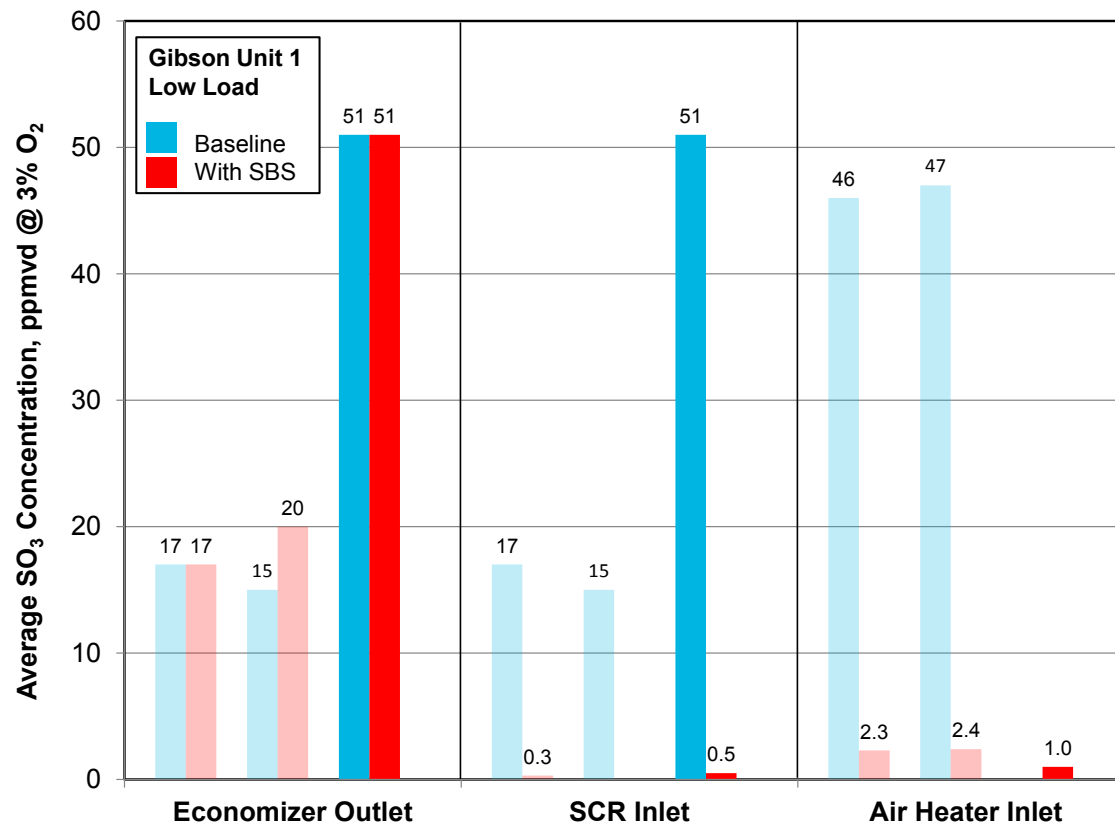
Full Scale Testing

Gibson Unit 1 full load test data from 2016 very similar to the Unit 5 data.



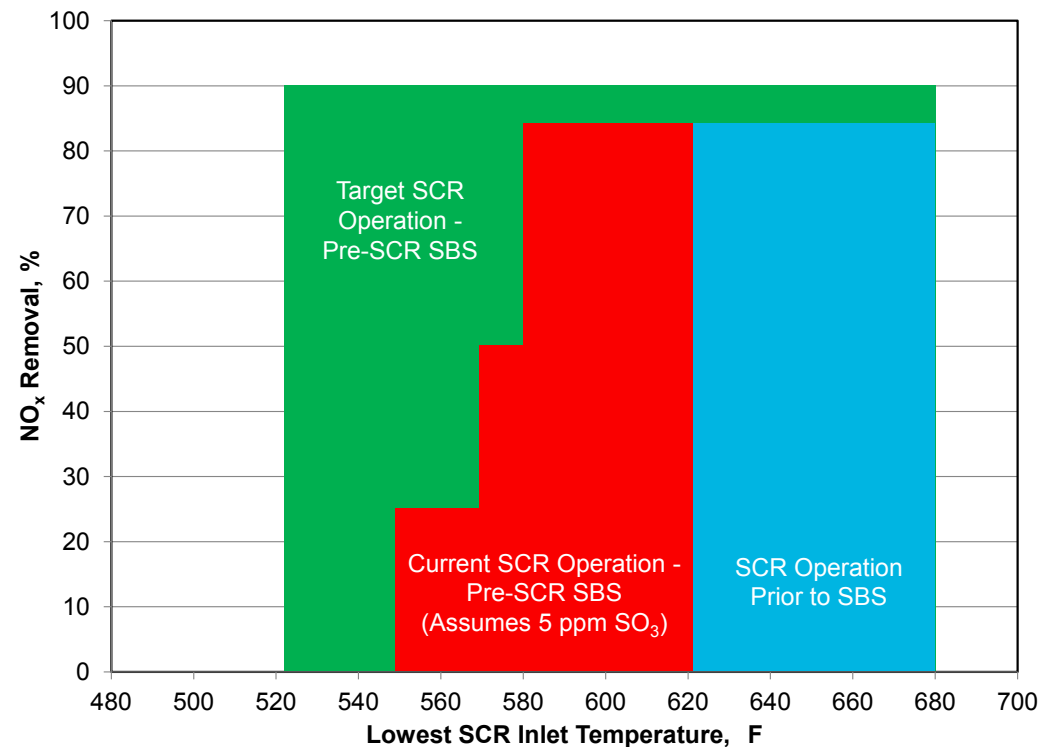
Full Scale Testing

Gibson Unit 1 low load test data shows very low inlet SO_3 and the effect of high O_2 on boiler SO_3 .

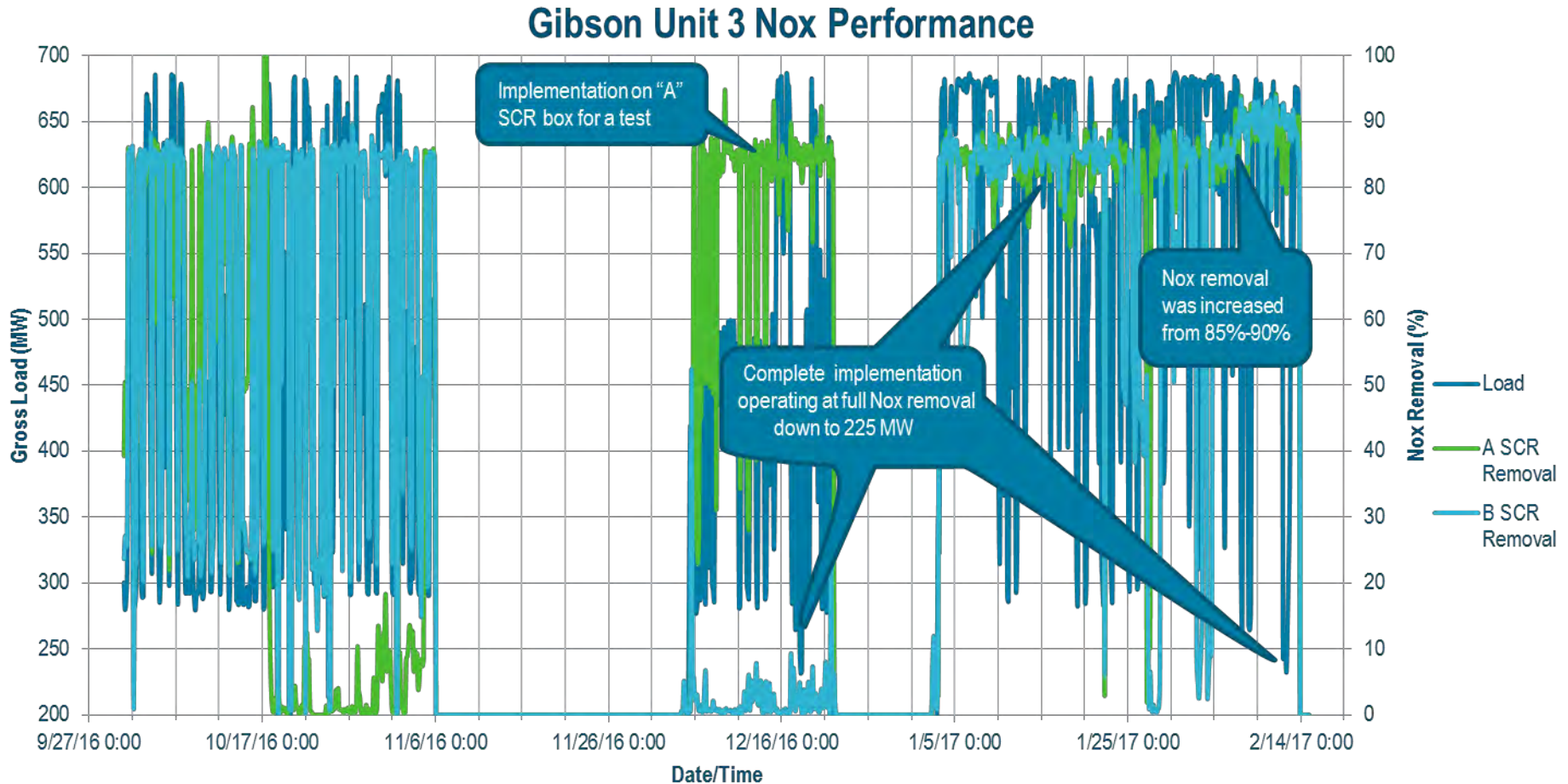


Gibson Summary

- Field testing resulted in SO_3 numbers lower than the lab testing providing confidence in the enhanced operation mode.
- Recommendation was made to further modify the low load constraints from 280 MWg to 220 MWg with full NO_x removal.
- Economizer outlet SO_3 was much higher than expected due to the very low load and high O_2 .
- Approach will be implemented across remaining Gibson Units with minimal additional testing.



Gibson Summary



Summary

- **We reviewed tools that can provide flexibility for meeting NO_x reduction requirements at low load conditions.**
- **Evaluate & balance (using modeling, lab, and field tests):**
 - **Plant operating needs...**
 - DeNO_x and NH₃ slip goals
 - Dispatch
 - **With the severity of the low load condition...**
 - Temperature, length of time, extent of deactivation
 - Utilization of DSI to reduce inlet SO₃
 - **And the capability for performance recovery on return to full load.**
 - Achievable load and temperature
 - Rate of activity recovery
 - Transient SO₃ and NH₃ emissions

Questions?

