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

**Christopher Bertole**

CORMETECH

**Chad Donner**

DUKE ENERGY

2017 Reinhold NOx-Combustion Round Table

# Training Session Overview

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

# Training Session Overview

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

# SCR Catalyst Reactions

## NOx Reduction:

$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$

$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$

$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$

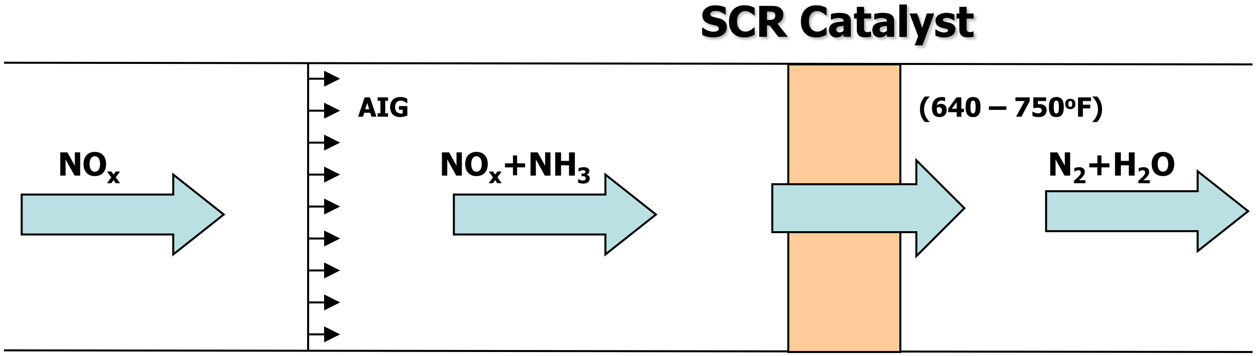
## Hg Oxidation:

$Hg + 2HCl + \frac{1}{2}O_2 \rightarrow HgCl_2 + H_2O$

## $SO_2$ Oxidation:

$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$

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



# Catalyst “Surface Area”

## Geometric Surface Area (Ap):

**For example, 21 cell honeycomb:**

**Ap = 502 $m^2/m^3$**
**SA = 1.6 x $10^{-3}$ $m^2/g$**
**Cell opening = <u>6.4 mm</u>**

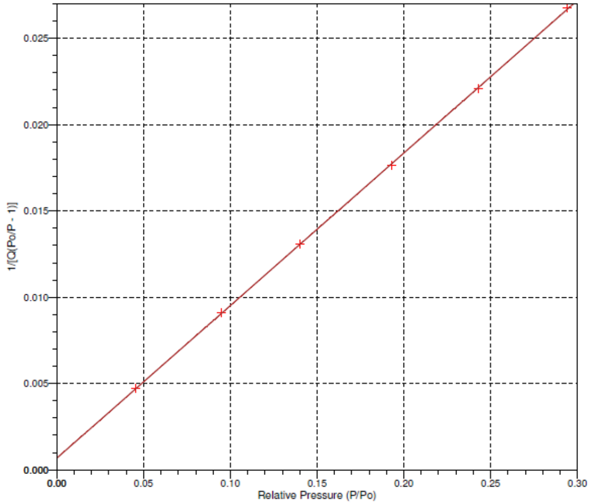
Catalyst Potential = K/AV = (K x Vol x Ap)/Q

## $N_2$ BET Surface Area:

**SA ~ 55 $m^2/g$**
**Pore diameter = <u>~2-100 nm</u>**

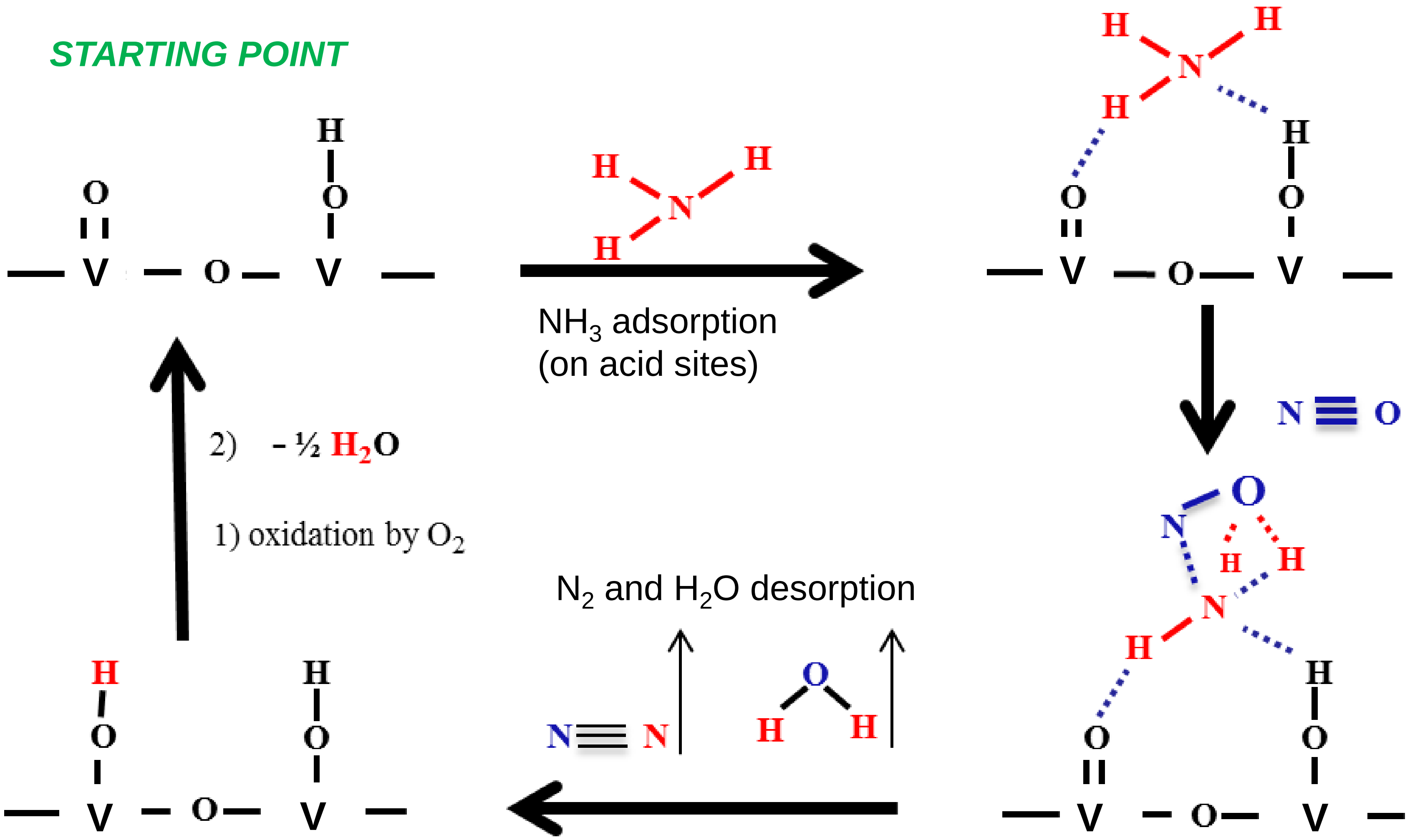
Defines $K_{intrinsic}$ (+ metal oxide loadings)

*BET Surface Area Plot*



# DeNOx Catalytic Mechanism

***The catalytic reactions occur on the <u>BET-measured surface area</u> 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**

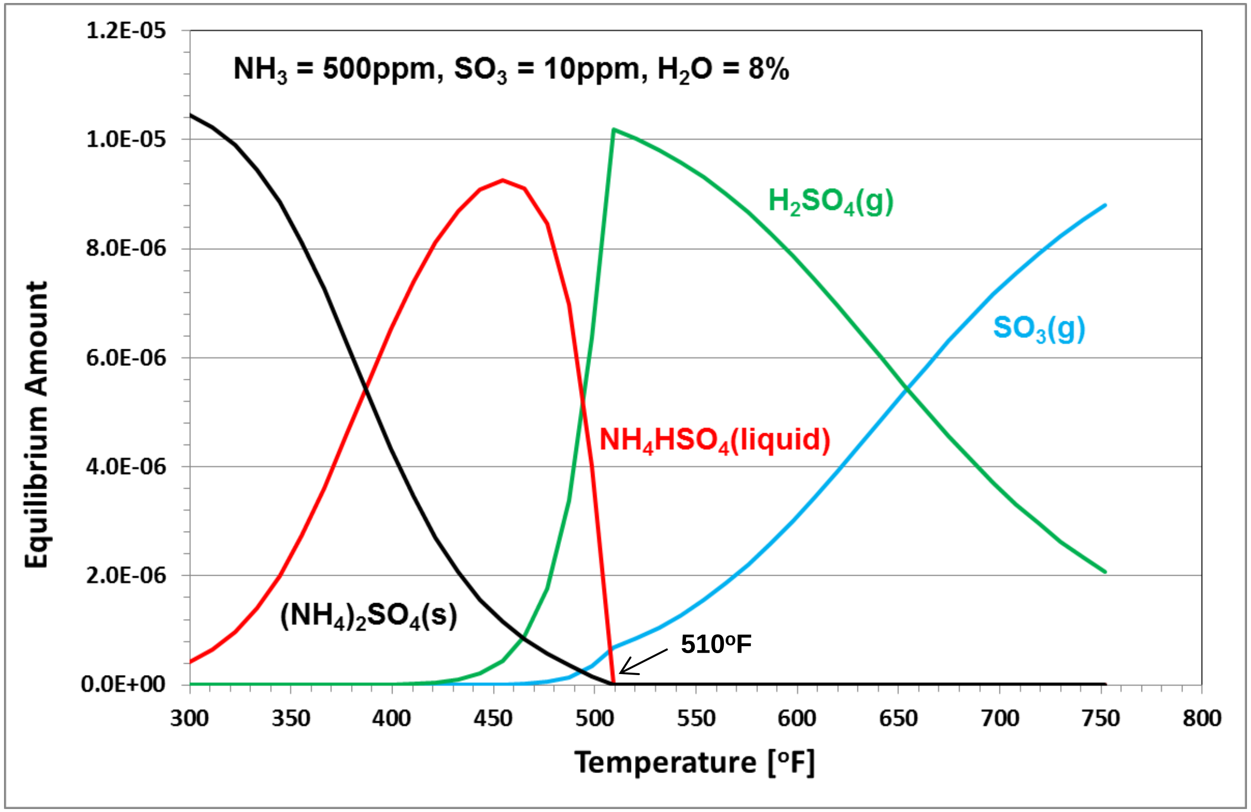
# Bulk-Phase ABS and AS Properties

**Ammonium Bisulfate (ABS)**

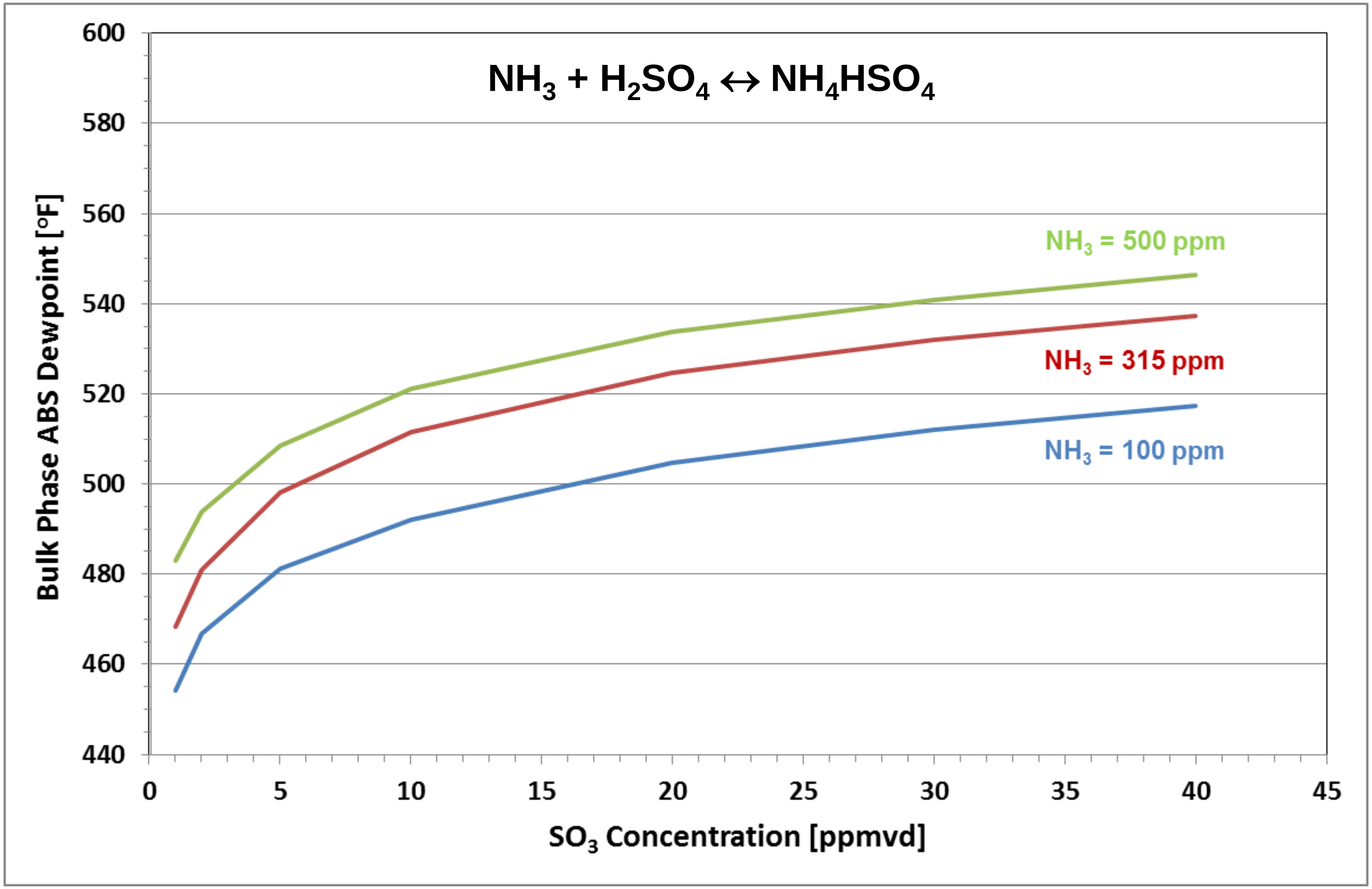
- **$NH_3 + H_2SO_4 \leftrightarrow NH_4HSO_4$**
- White sticky solid; corrosive
- $T_{melting}$ = 147°C/297°F
- $T_{boiling}$ > 235°C/455°F (decomposes)

**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)

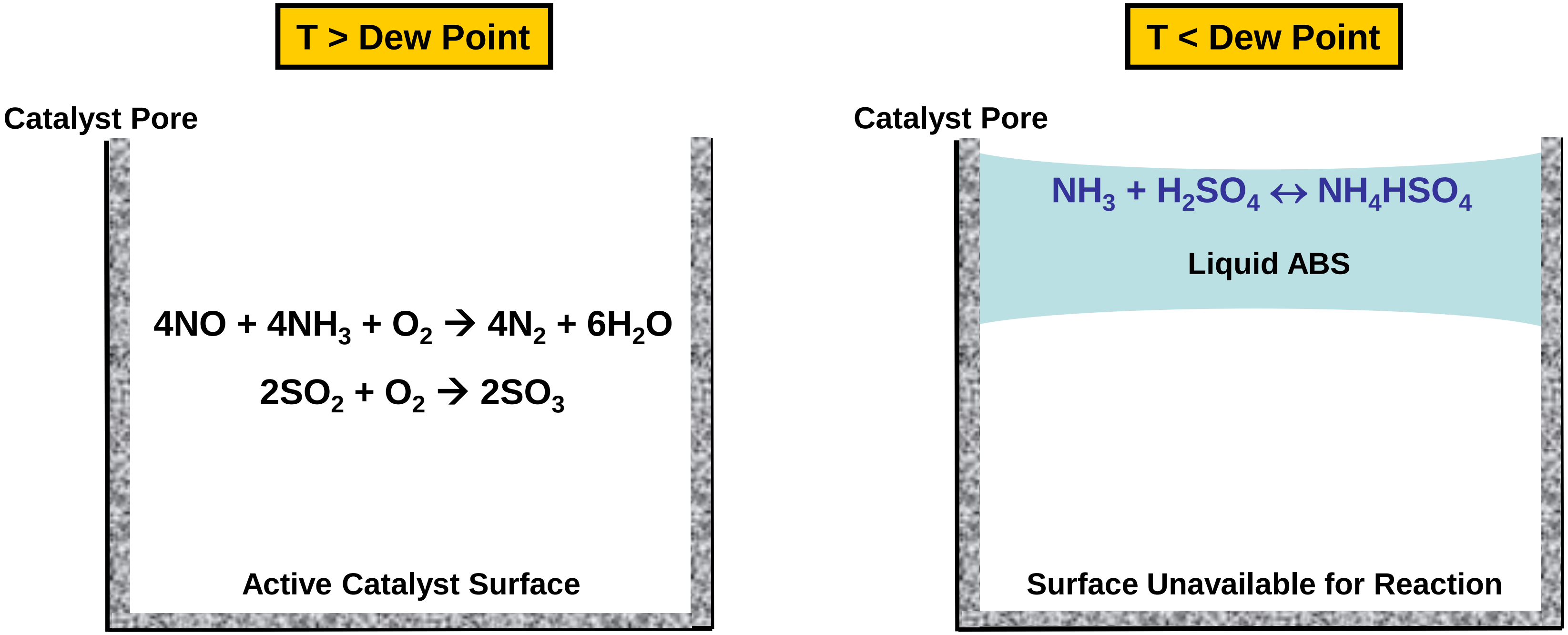


# Bulk-Phase ABS Equilibrium Curves



# ABS Deposition Controls SCR Tmin

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



**T > Dew Point**

**Catalyst Pore**

$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$

$2SO_2 + O_2 \rightarrow 2SO_3$

**Active Catalyst Surface**

**T < Dew Point**

**Catalyst Pore**

$NH_3 + H_2SO_4 \leftrightarrow NH_4HSO_4$

**Liquid ABS**

**Surface Unavailable for Reaction**

# Capillary Condensation

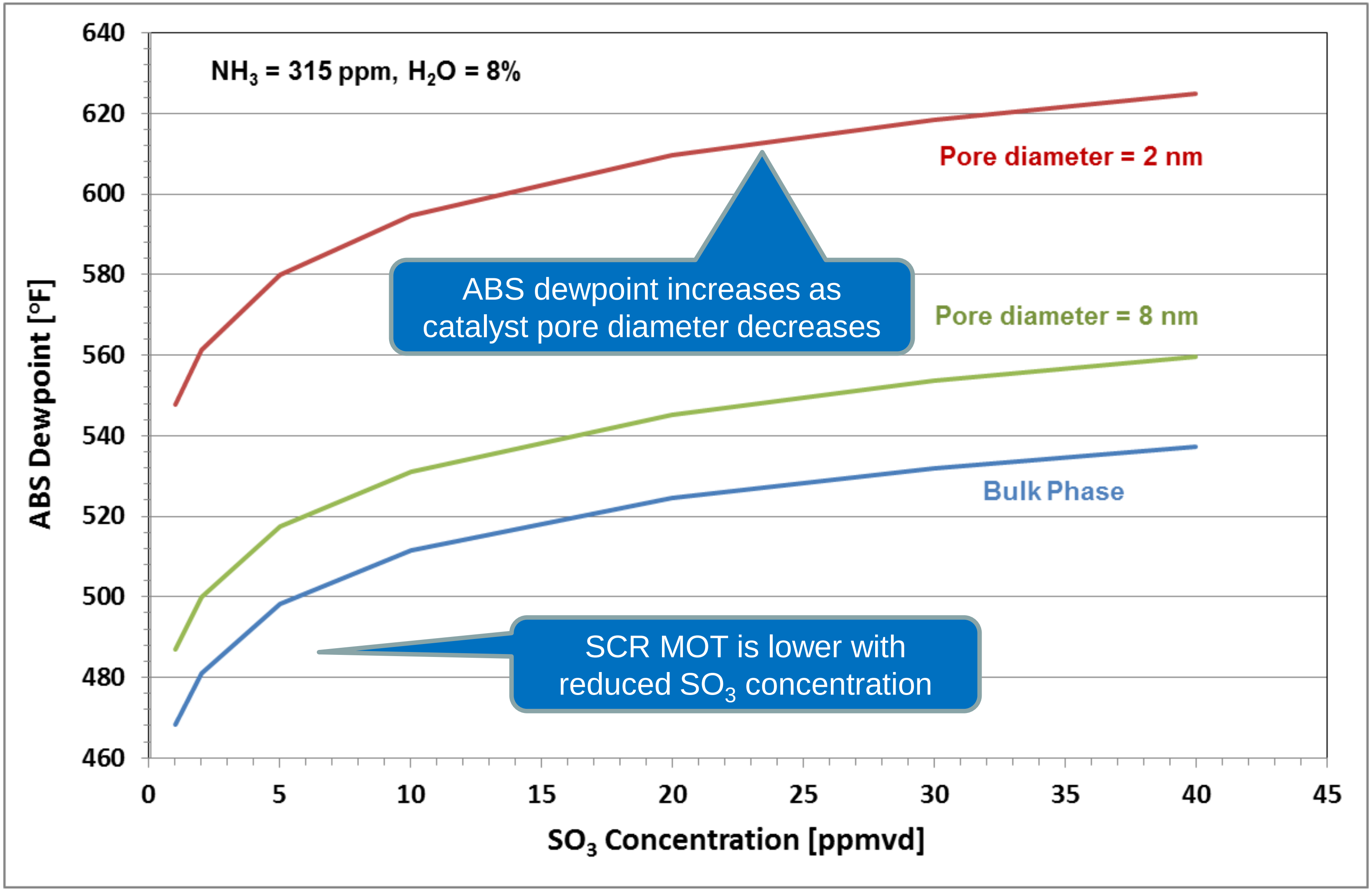
- **Liquid ABS forms in SCR catalyst pores above the bulk phase dew point temperature (BDT)**
  - **Kelvin equation**:
    - $$\ln\left(\frac{\text{P vap in pore}}{\text{Psat vap bulk liquid}}\right) = -\frac{2\,\sigma\,V_l}{r\,R\,T}$$
    - $\sigma$ = ABS surface tension, $V_l$= ABS molar volume, R = 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 → ABS formation at higher temperature

# Impact of Pore Size on ABS Dew Point

CORMETECH

DUKE ENERGY.

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



ABS dewpoint increases as catalyst pore diameter decreases

SCR MOT is lower with reduced SO$_3$ concentration

# Toolbox

## Predict Catalyst Response to ABS Formation

CORMETECH
DUKE ENERGY.

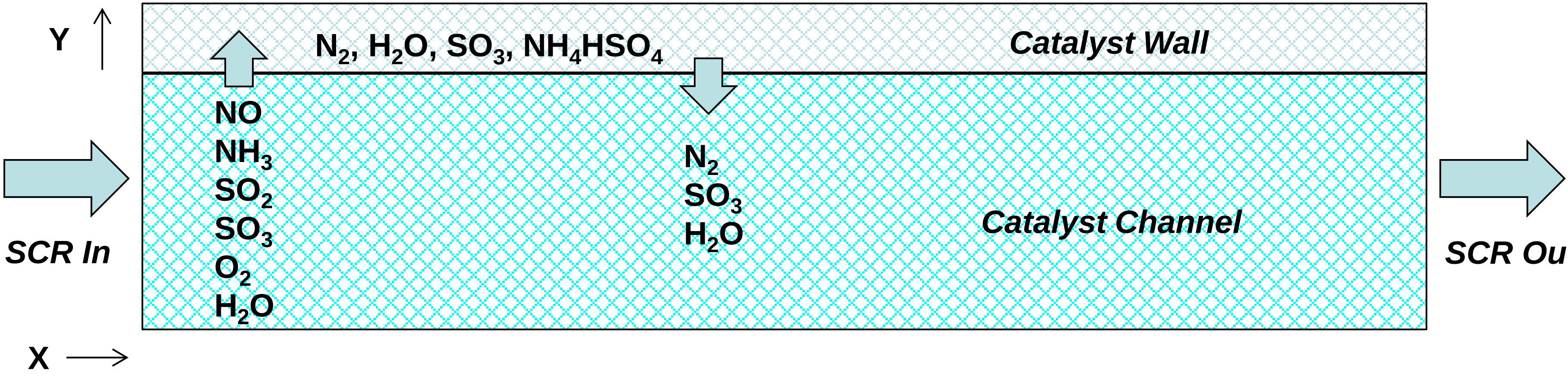
### Transient model

- Predict deactivation and recovery (DeNOx, $SO_3$, $NH_3$ transients)
- Evaluate feasibility of desired operating scenarios and iterate

**Reactions in Catalyst Wall:**

$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$ $SO_2 + \frac{1}{2} O_2 \rightarrow SO_3$

$NH_3 + H_2SO_4 = NH_4HSO_4$



**FEM model: account for internal / external mass transfer, intrinsic kinetics, $SO_3$/$NH_3$ 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

**Bench**

**Micro**

# Example: Lab Catalyst Test

**Ran test cycle on micro reactor.**

| Step 1 | |
|---|---|
| Temperature [°F] | **637** |
| NOx [ppmvd] | 226 |
| Molar Ratio | 0.98 |
| $SO_2$ [ppmvd] | 800 |
| $SO_3$ [ppmvd] | 28 |

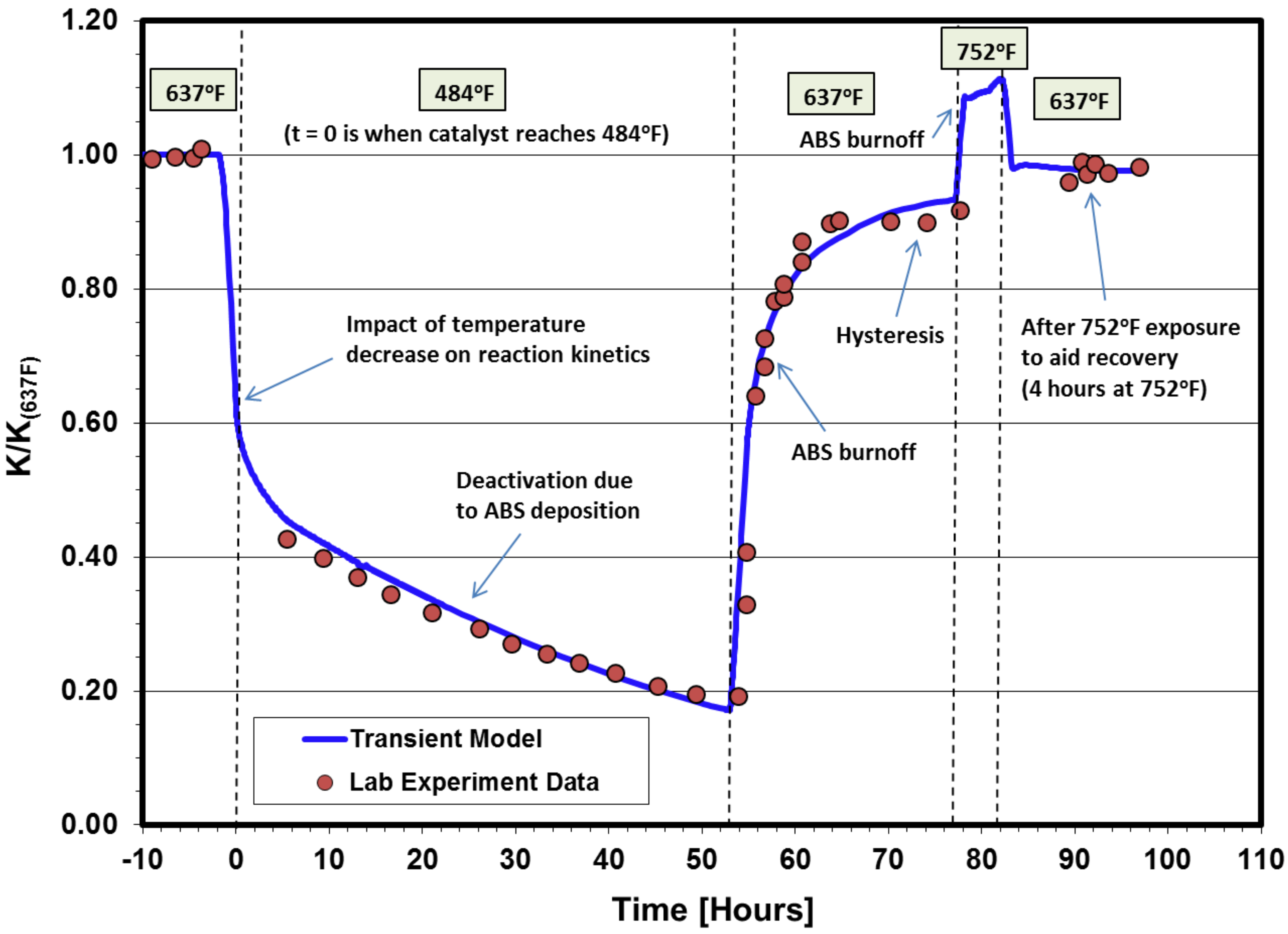
| Step 2 | |
|---|---|
| Temperature [°F] | **484** |
| NOx [ppmvd] | 226 |
| Molar Ratio | 0.98 |
| $SO_2$ [ppmvd] | 100 |
| $SO_3$ [ppmvd] | 4.2 |

| Step 3 | |
|---|---|
| Temperature [°F] | **637** |
| NOx [ppmvd] | 226 |
| Molar Ratio | 0.98 |
| $SO_2$ [ppmvd] | 800 |
| $SO_3$ [ppmvd] | 28 |

| Step 4 | |
|---|---|
| Temperature [°F] | **752** |
| NOx [ppmvd] | 226 |
| Molar Ratio | 0.98 |
| $SO_2$ [ppmvd] | 800 |
| $SO_3$ [ppmvd] | 28 |

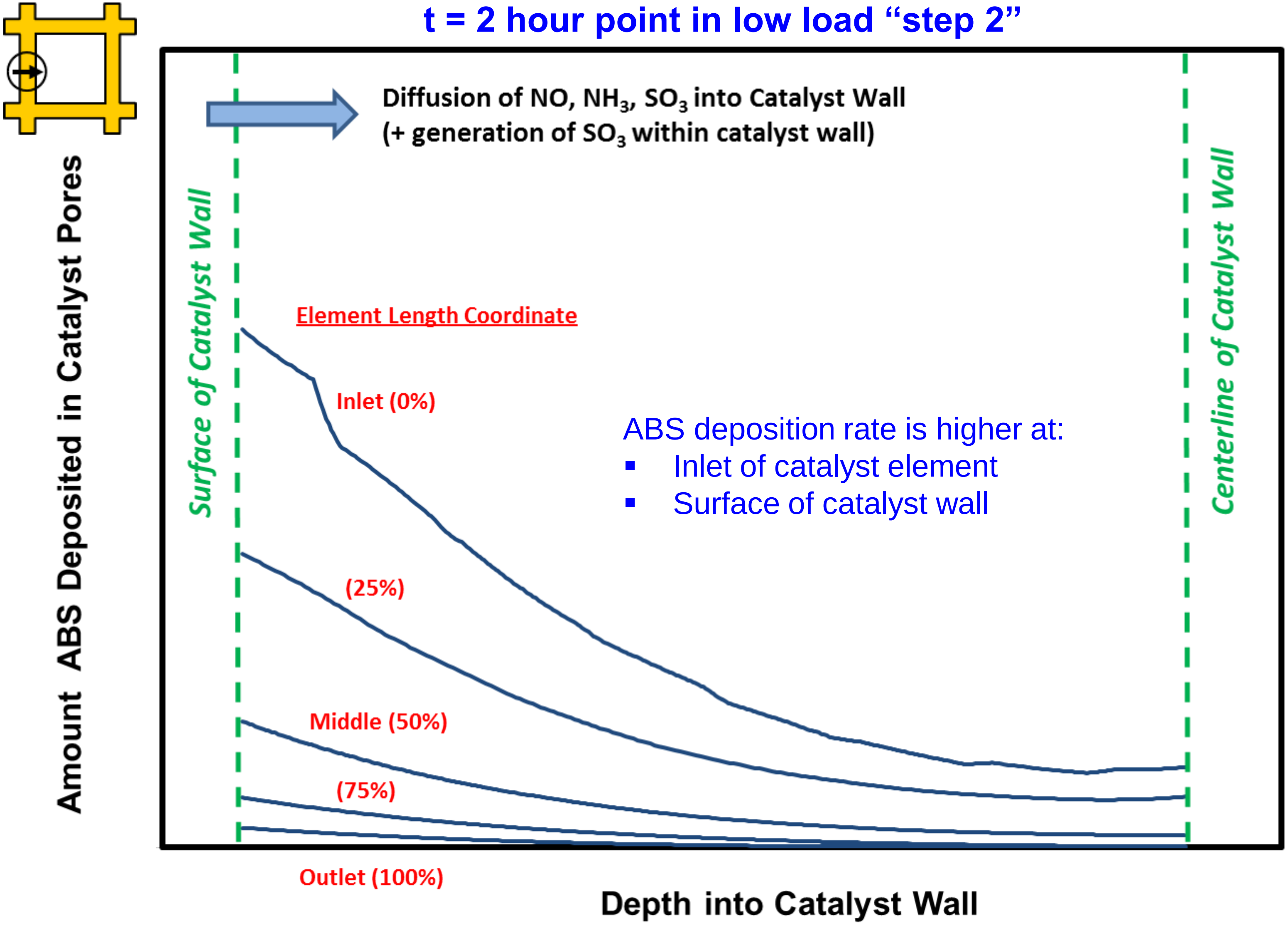
| Step 5 | |
|---|---|
| Temperature [°F] | **637** |
| NOx [ppmvd] | 226 |
| Molar Ratio | 0.98 |
| $SO_2$ [ppmvd] | 800 |
| $SO_3$ [ppmvd] | 28 |

# Catalyst Test: Model vs. Lab Data



# Model: ABS Profile in Catalyst Wall

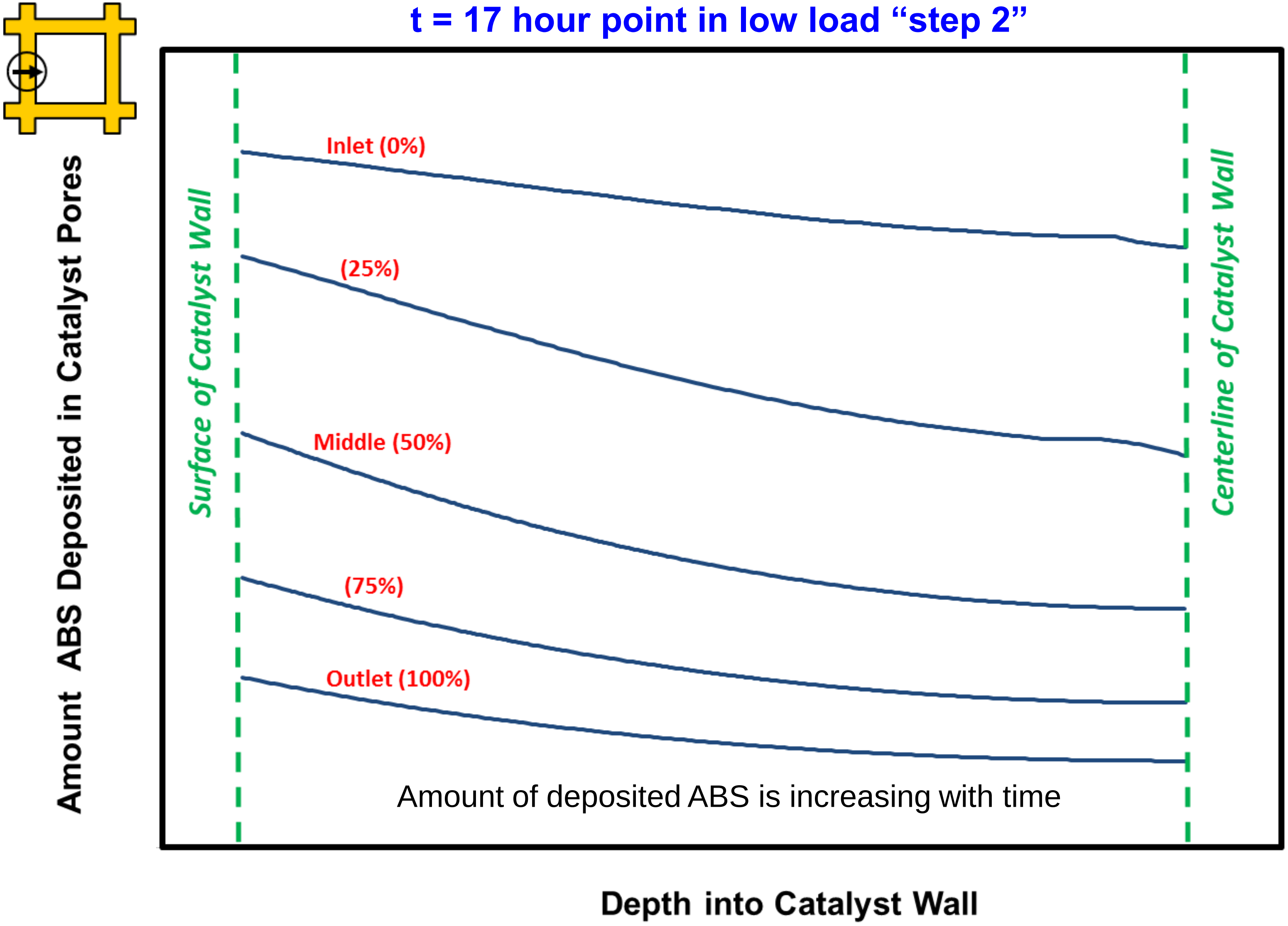
**t = 2 hour point in low load “step 2”**



ABS deposition rate is higher at:

- Inlet of catalyst element
- Surface of catalyst wall

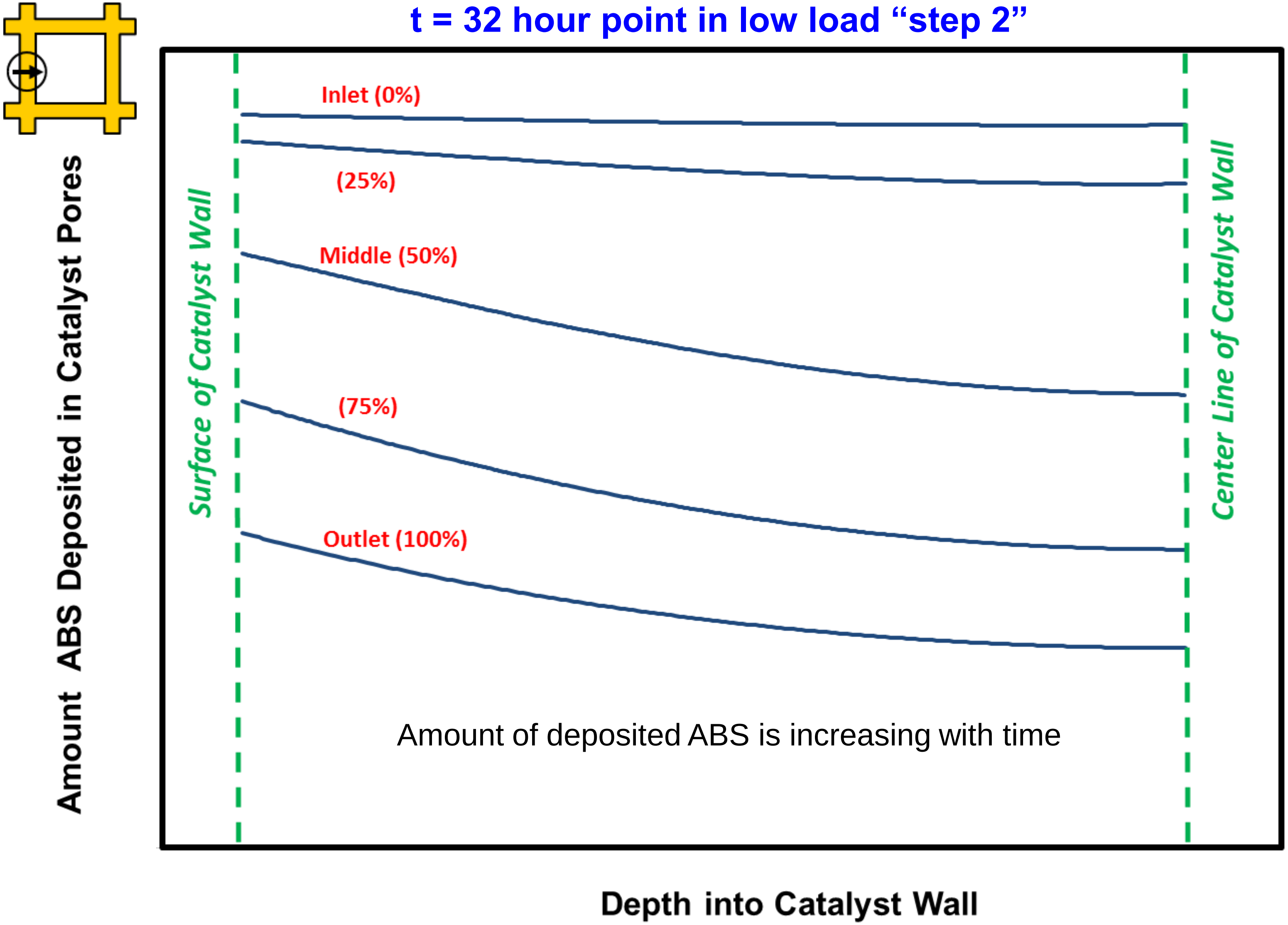
# Model: ABS Profile in Catalyst Wall



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

Amount of deposited ABS is increasing with time

# Model: ABS Profile in Catalyst Wall

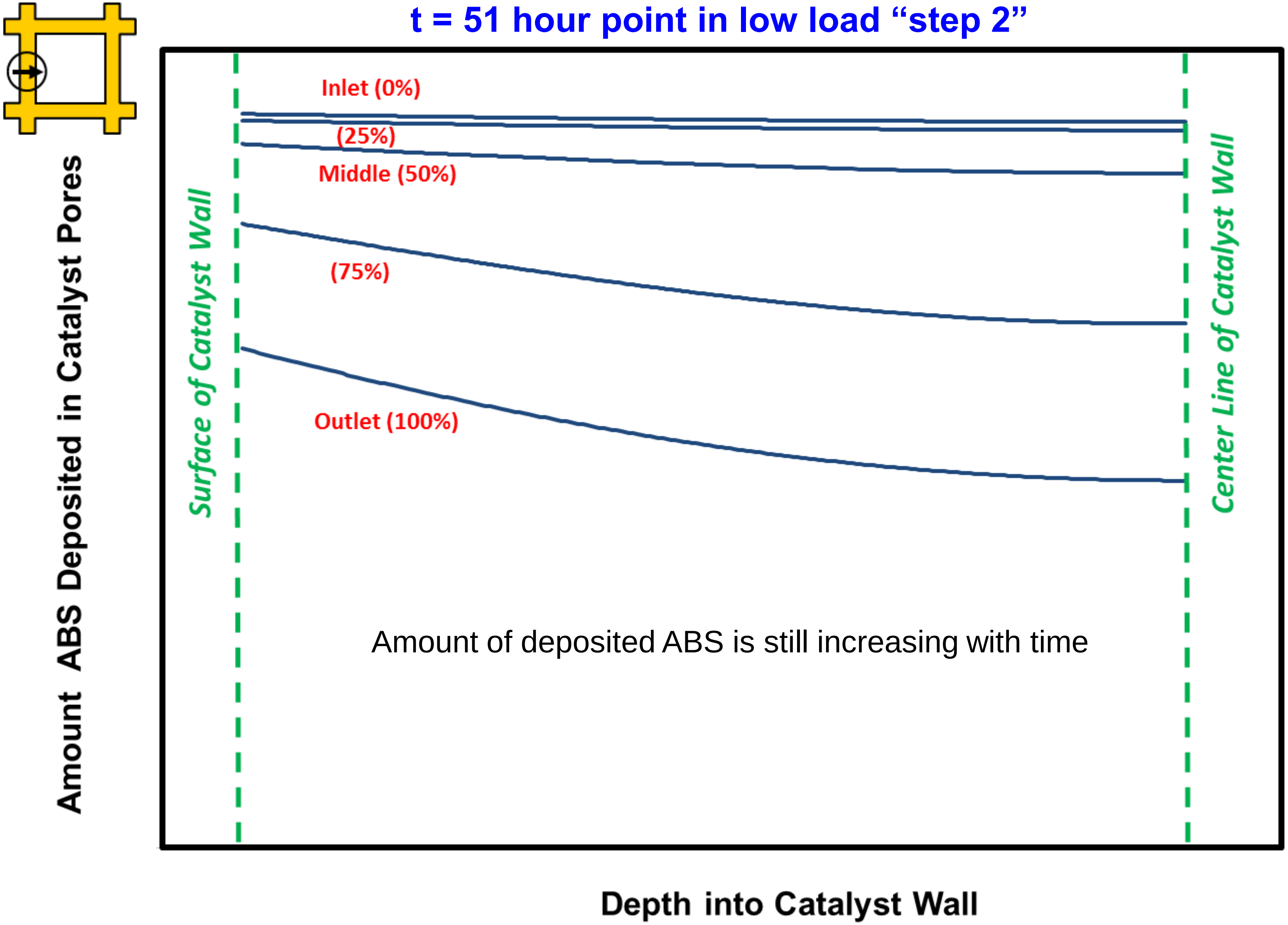


t = 32 hour point in low load “step 2”

Amount of deposited ABS is increasing with time

# Model: ABS Profile in Catalyst Wall

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



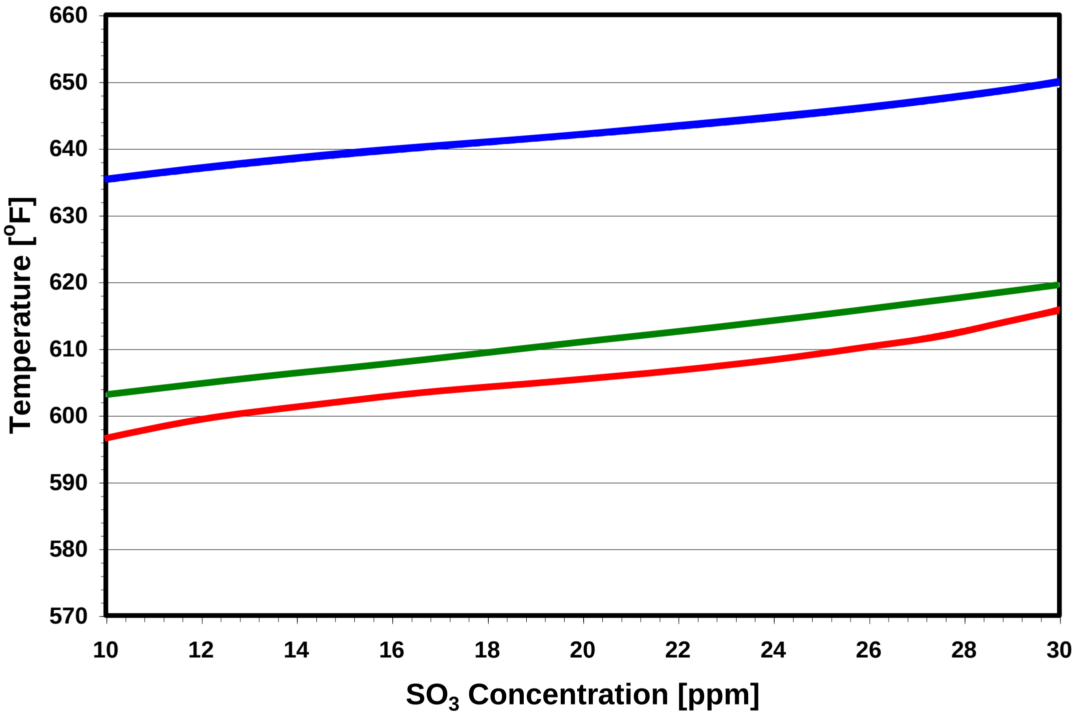
Amount of deposited ABS is still increasing with time

# Training Session Overview

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

# Tmin: Basic Approach

- **“Basic Approach”**
  - Avoid ABS deposition in the SCR catalyst.
  - Simple operating guidelines.

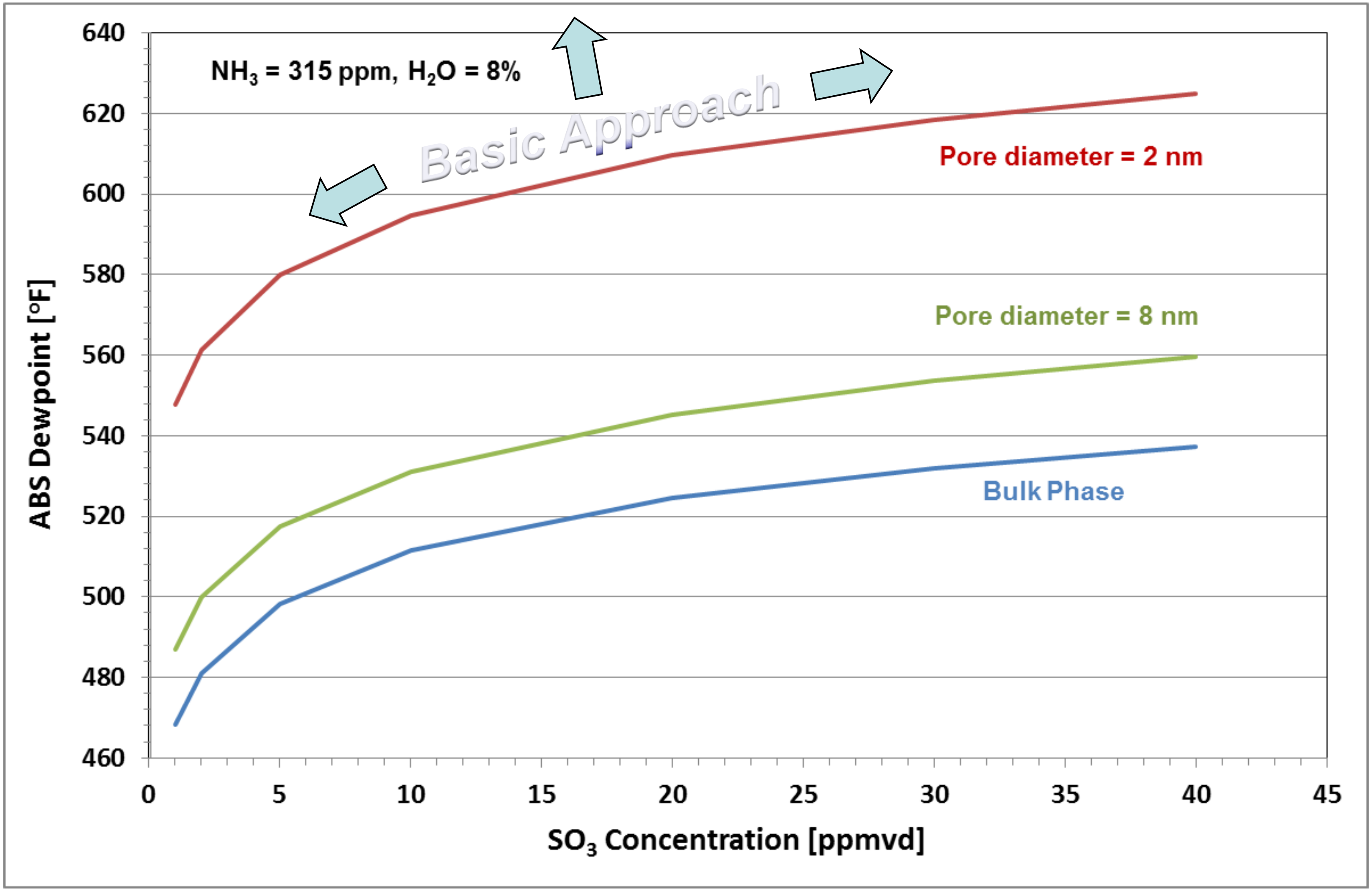


**RT** = recovery temperature (T)

**MOT** = minimum operating T

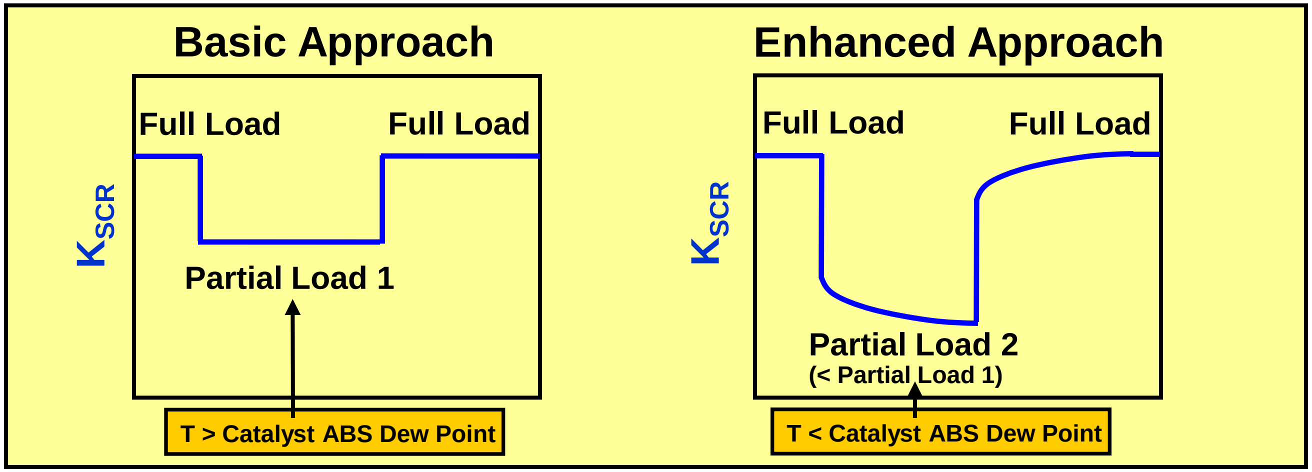
**MIT** = minimum injection T for $NH_3$

# Basic Approach Avoids ABS Deposition



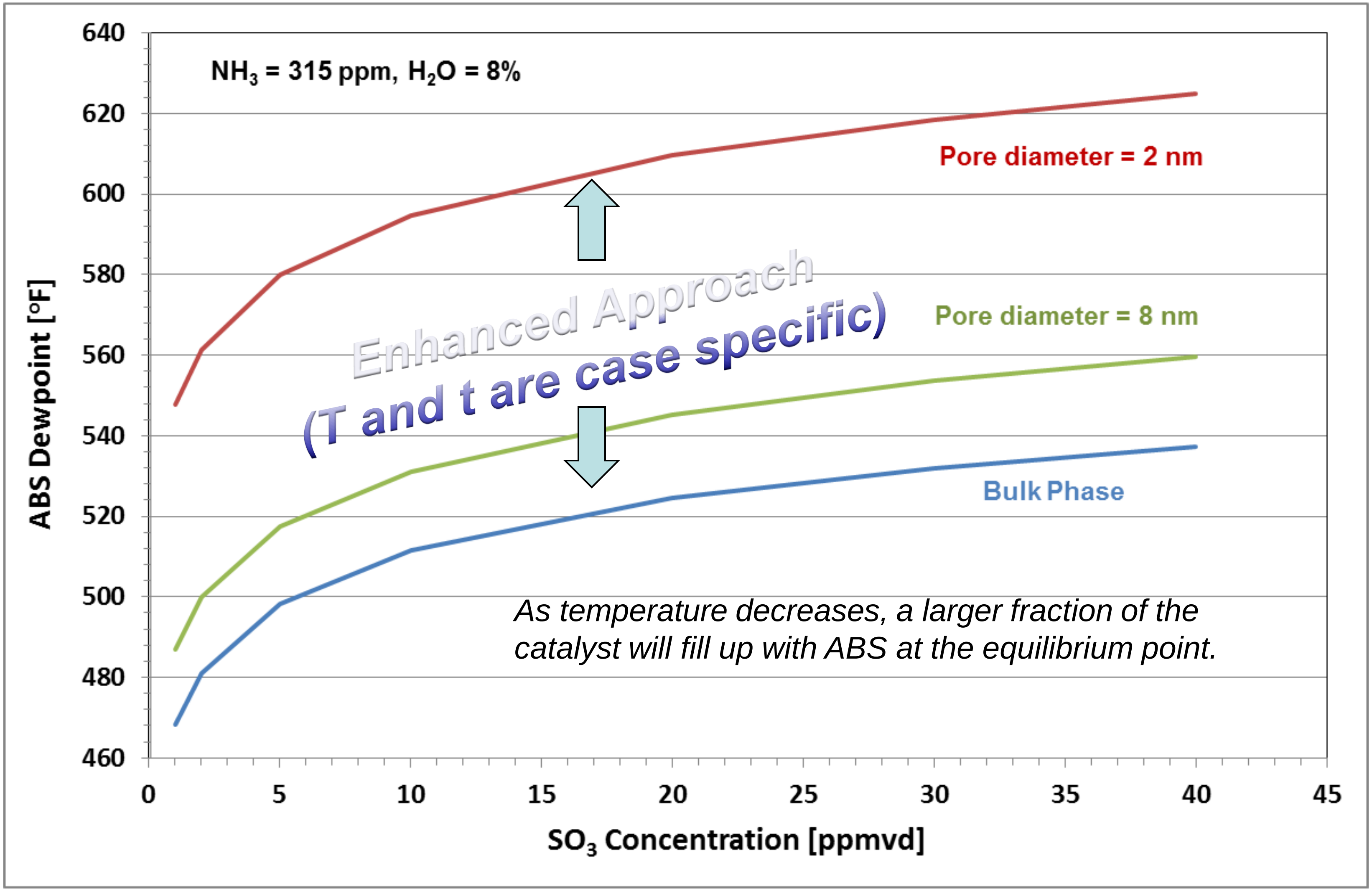
# Tmin: Enhanced Approach

- **“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

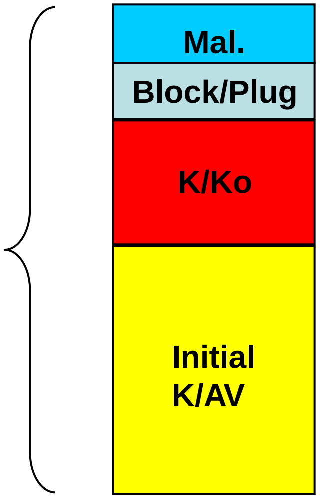
## Manage ABS Deposition in Catalyst: Transient Cycling



*As temperature decreases, a larger fraction of the catalyst will fill up with ABS at the equilibrium point.*

# Design Considerations

## Applying the Enhanced Approach



- **For the low load and recovery conditions:**
  - Transient K/AV must be $\geq$ K/AV required to meet DeNOx, $NH_3$ slip
    - Thus: $K/K_{\text{full load}}$ must be $\geq AV/AV_{\text{full load}}$
  - Need to consider transient $SO_3$ & $NH_3$ 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):**

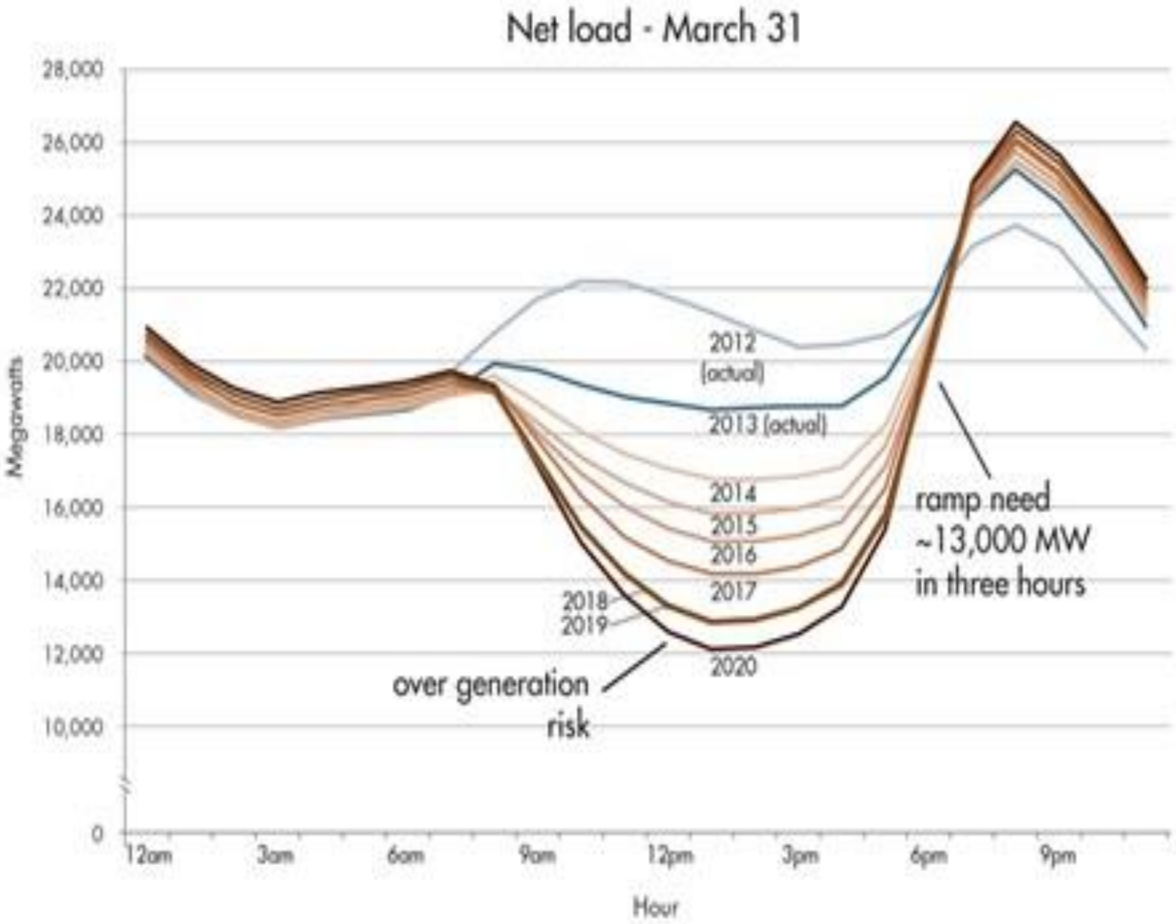
| Factor | Consideration |
|---|---|
| Achievable Recovery Temperature | Higher recovery temperature can avoid the hysteresis and more quickly remove the deposited ABS. |
| Time at Recovery Temperature | Longer hold time at recovery temperature will help the removal of the deposited ABS. |
| Emission 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 DeNOx). |
| Use of DSI | If available, DSI can be used to mitigate the $SO_3$ emission spike during recovery. |
| DeNOx and $NH_3$ Slip | If recovery is not complete, risk is to run at reduced DeNOx and/or higher NH3 slip. |

# Training Session Overview

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

# Drivers for Low Load Operation

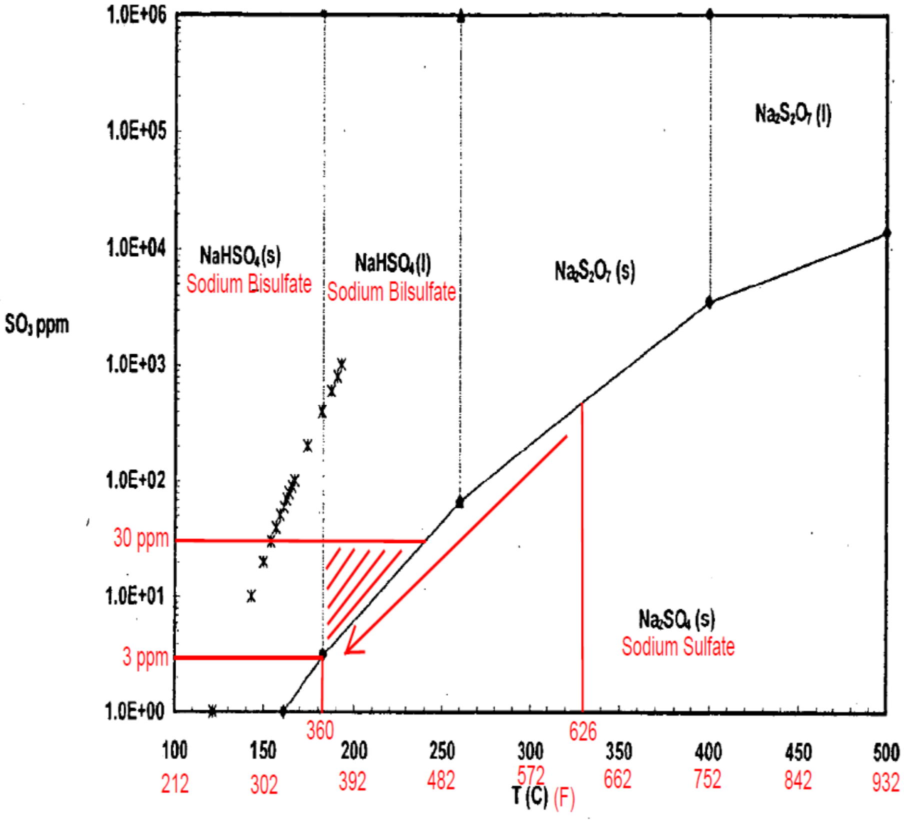
- **Solar and wind have created large amounts of peak generation that are priority.**
- **Coal must now load follow to a degree and be more nimble for turndown and ramp rate.**
- **New Ozone season limits will require pushing the SCR's harder and keeping them in service longer.**



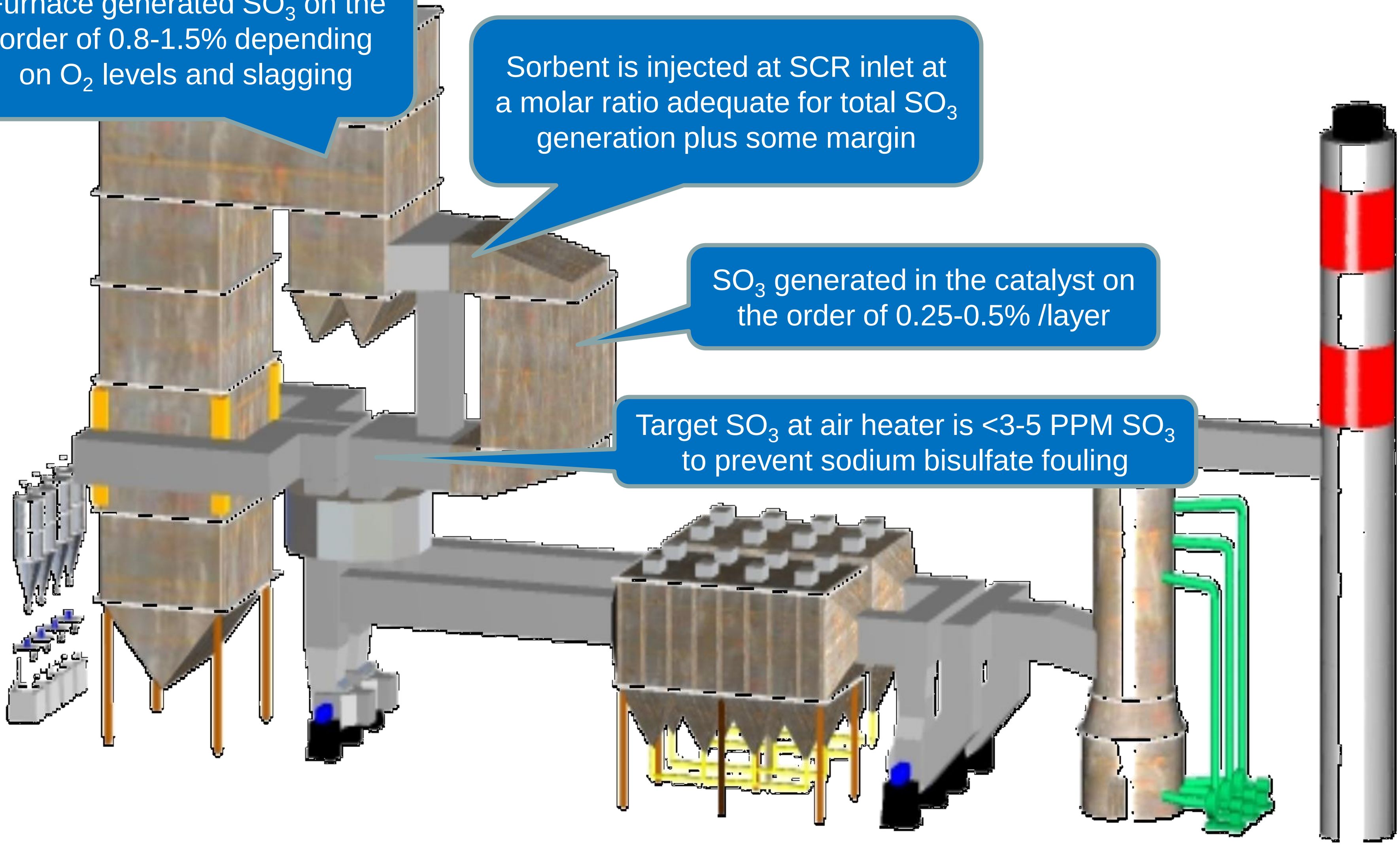
*California ISO Projected Demand Response Curve*

# SBS System Background

- Liquid sodium bisulfate forms between ~360-500ºF 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

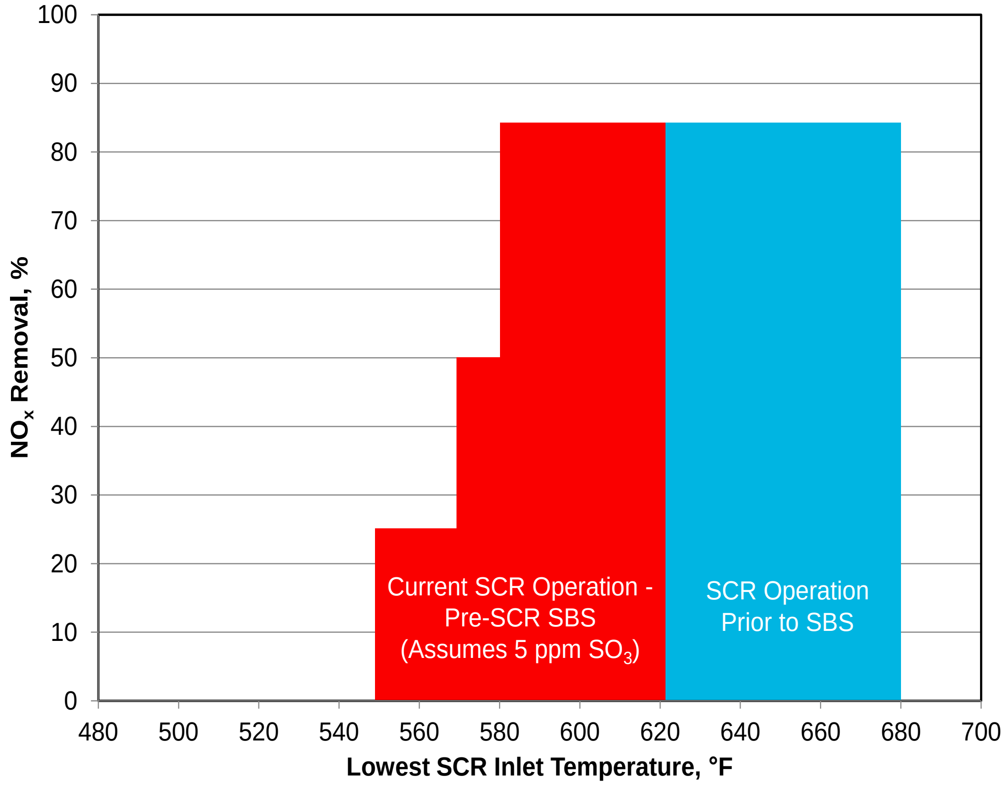
# Gibson: Reduced Catalyst MOT

- **Options considered for low load SCR operation**
  - Reduce the $NH_3$ at the SCR inlet by reducing inlet NOx (gas co-firing) or NOx 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 NOx removal at full load.

# Gibson Plant Overview

CORMETECH
DUKE ENERGY.

- 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% NOx 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 622ºF and was modified to 550ºF with tiered NOx removal at low load based on the assumption of 5 ppm $SO_3$
  - Min load was changed from 440 MWg to 280 MWg

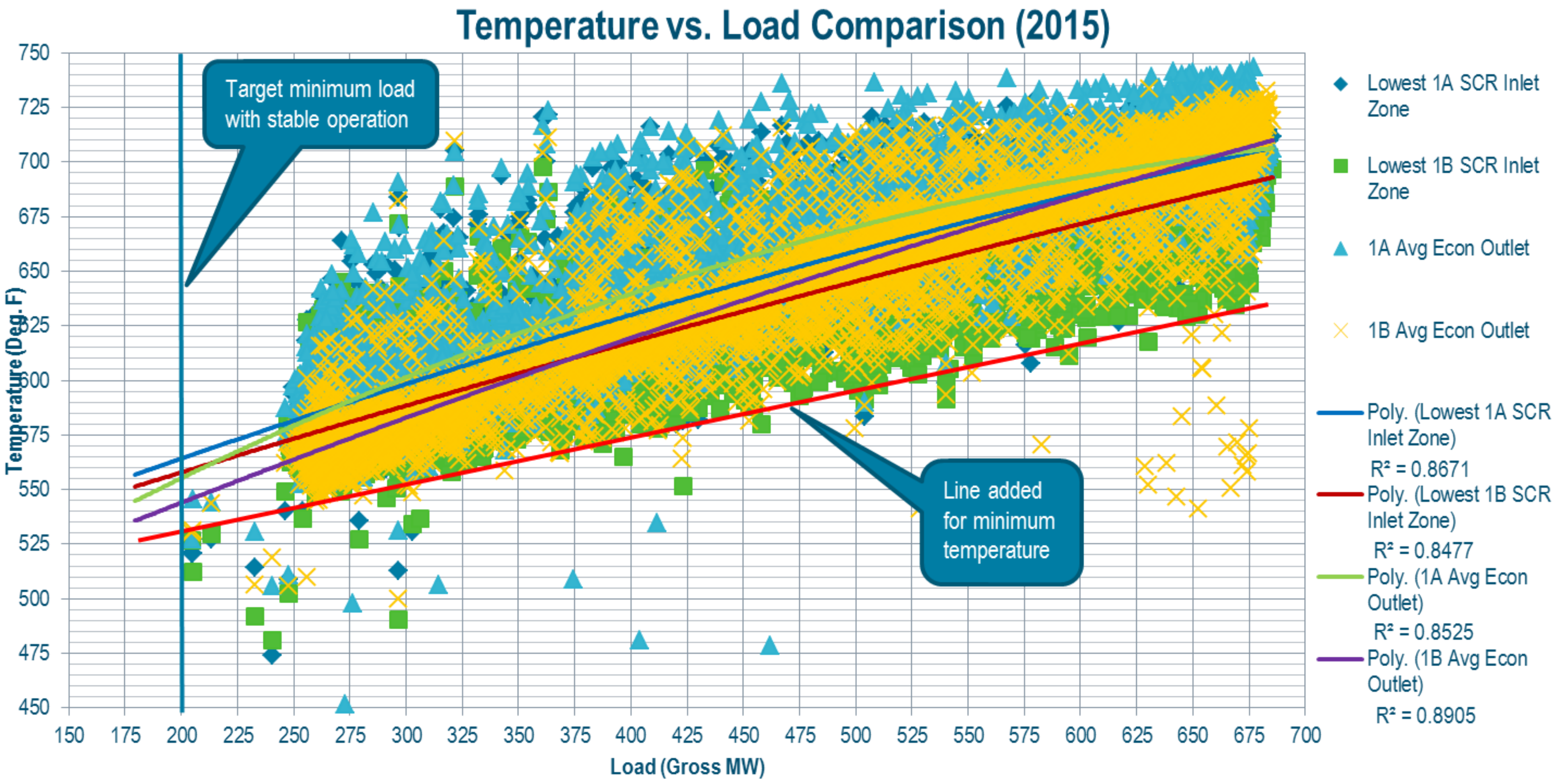


# Testing Overview/Goals

- **Laboratory catalyst testing performed by CORMETECH.**
  - Demonstrated 72-hour operation to simulate a holiday weekend at full 85% NOx removal at 500$^{o}$F flue gas temp.
- **Two-week test program on Gibson Unit 1 (July 2016).**
  - AECOM performed gas testing with modified CCS procedure to validate $SO_3$ 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 $SO_2$ conversion at full and low load.
  - Evaluate operation at elevated $NH_3$ slip and increased NOx removal.
  - Evaluate operation at reduced air heater gas outlet temperatures.
  - Measure $SO_3$ and Na compounds in the primary air stream for $NH_3$ 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

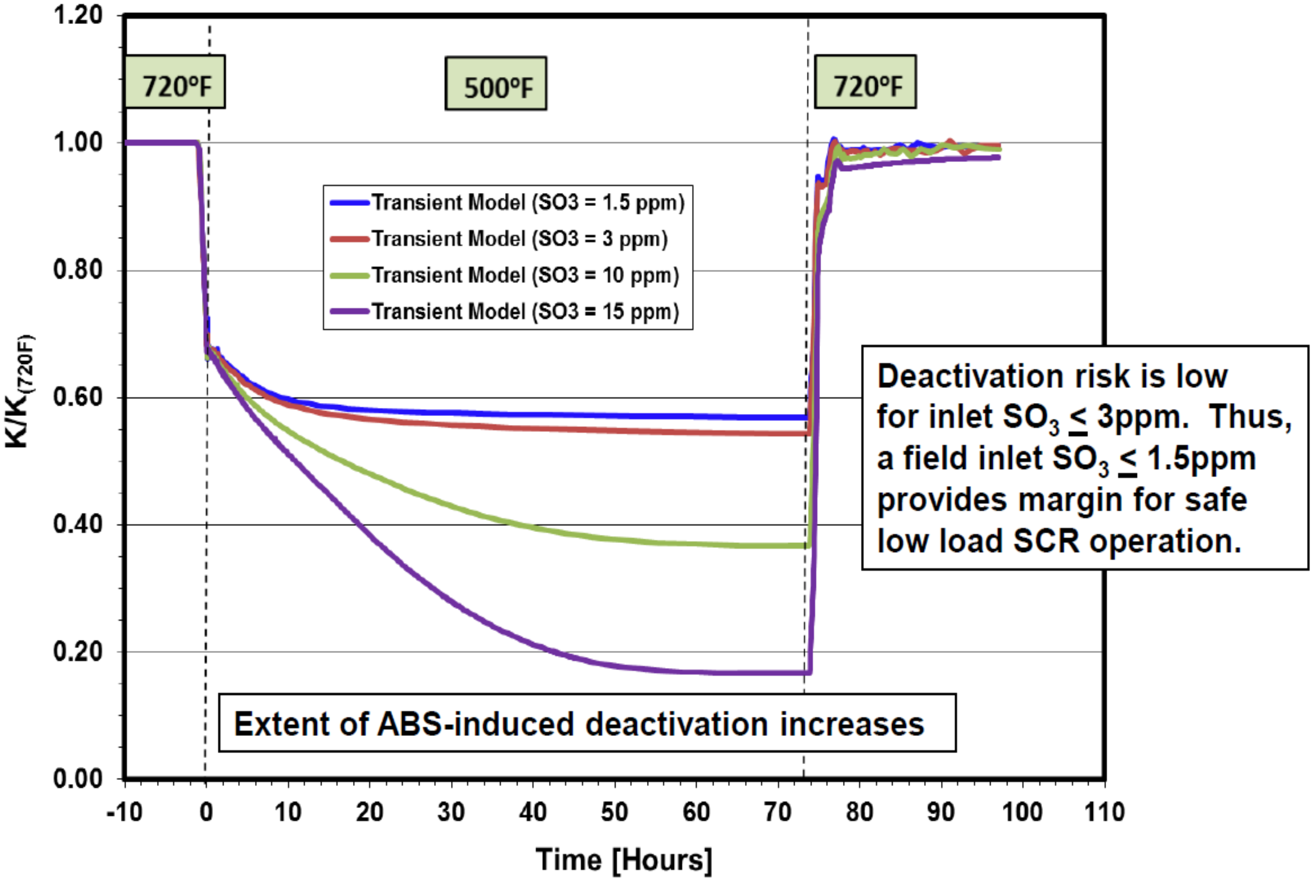


Target minimum load with stable operation

Line added for minimum temperature

# 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.

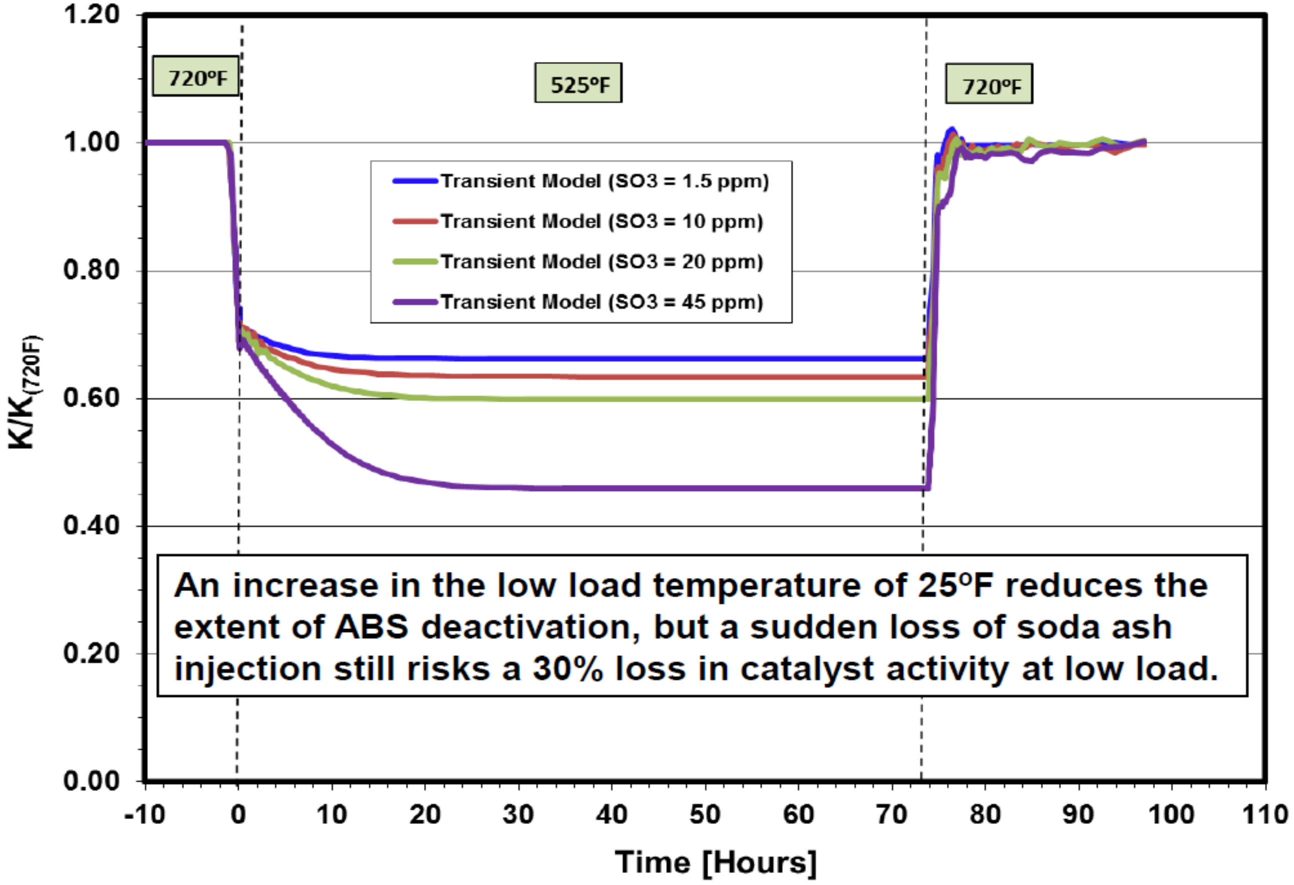


**Deactivation risk is low for inlet $SO_3 \leq$ 3ppm. Thus, a field inlet $SO_3 \leq$ 1.5ppm provides margin for safe low load SCR operation.**

**Extent of ABS-induced deactivation increases**

# 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 <u>less than 30 minutes</u> without SBS would not pose significant risk to the catalyst.



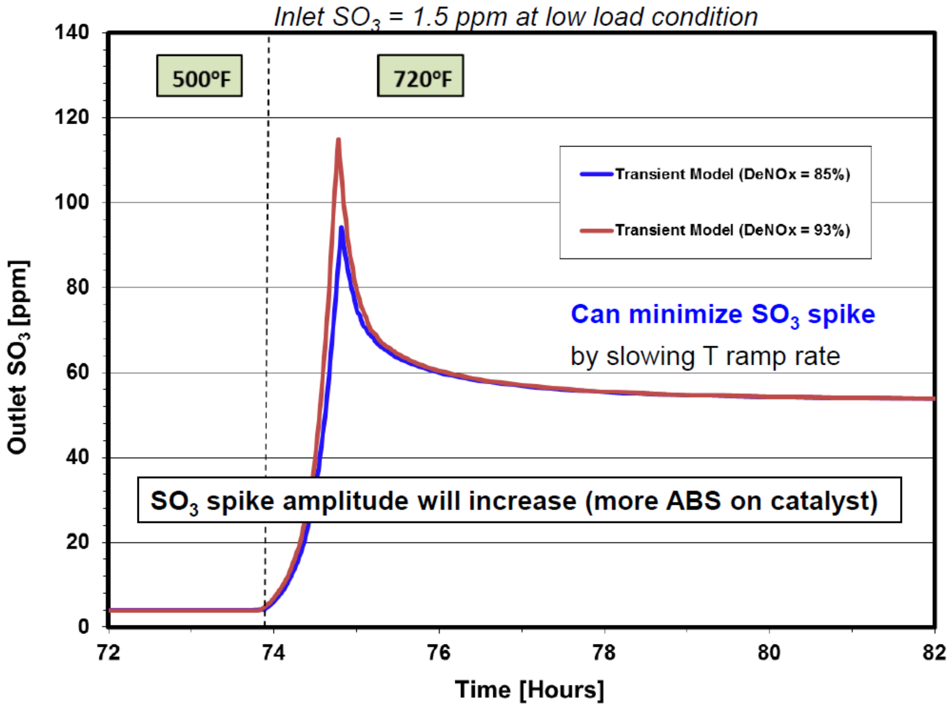
An increase in the low load temperature of 25°F reduces the extent of ABS deactivation, but a sudden loss of soda ash injection still risks a 30% loss in catalyst activity at low load.

# Transient Modeling Results

CORMETECH

DUKE ENERGY

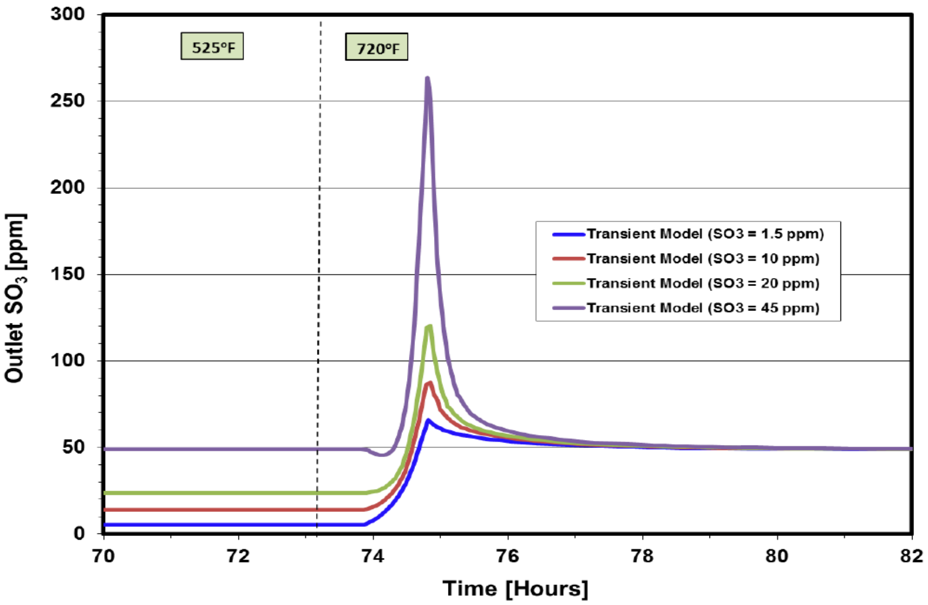
- $SO_3$ will spike on load ramp as ABS breaks down into $SO_3$ and $NH_3$.
- Amplitude is indicative of the quantity of ABS accumulation in the catalyst.
- Can minimize spikes by increasing SBS during load ramp and/or reducing load ramp rate.


*Inlet $SO_3$ = 1.5 ppm at low load condition*

**Can minimize $SO_3$ spike**

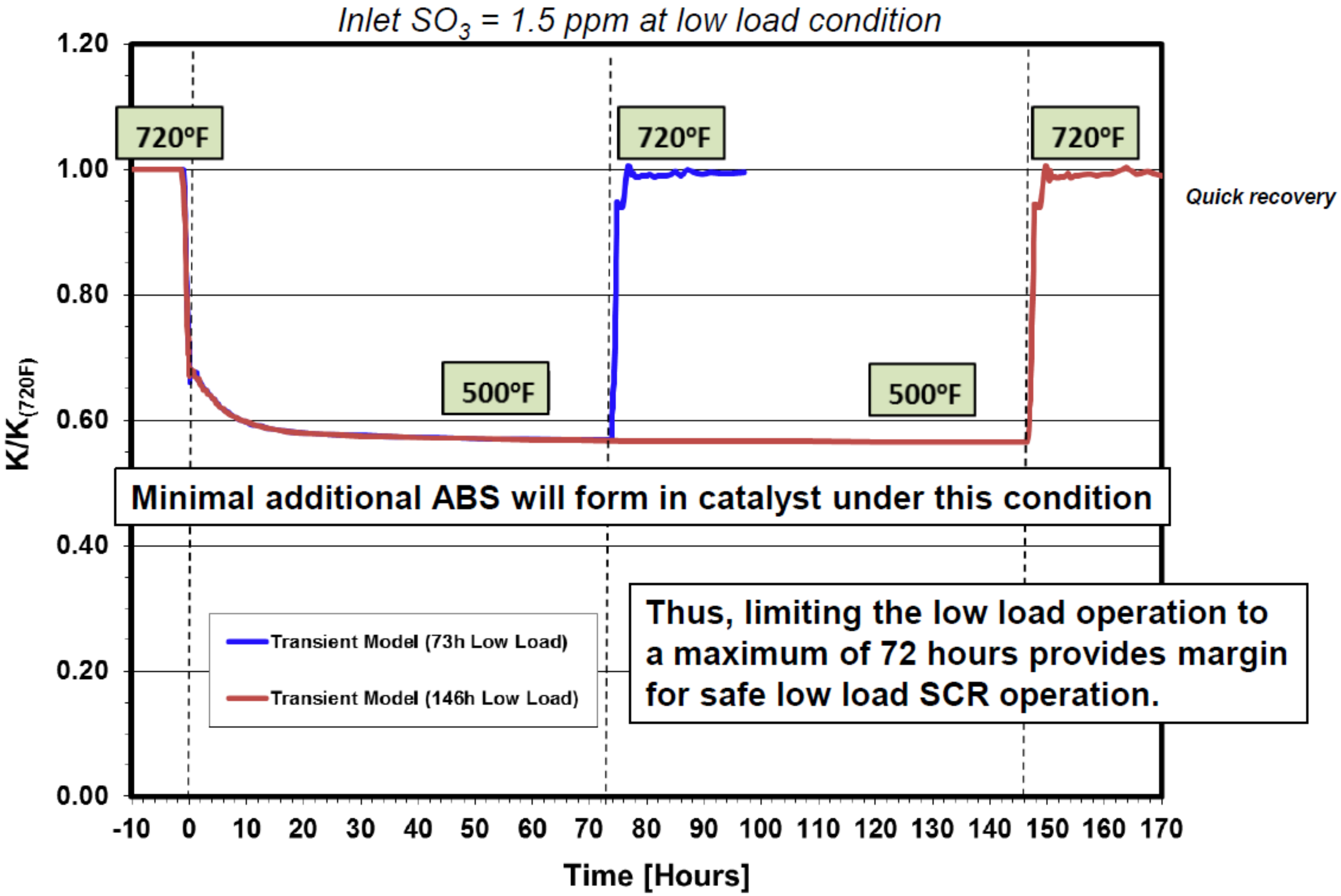
by slowing T ramp rate

**$SO_3$ spike amplitude will increase (more ABS on catalyst)**



# Transient Modeling Results

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

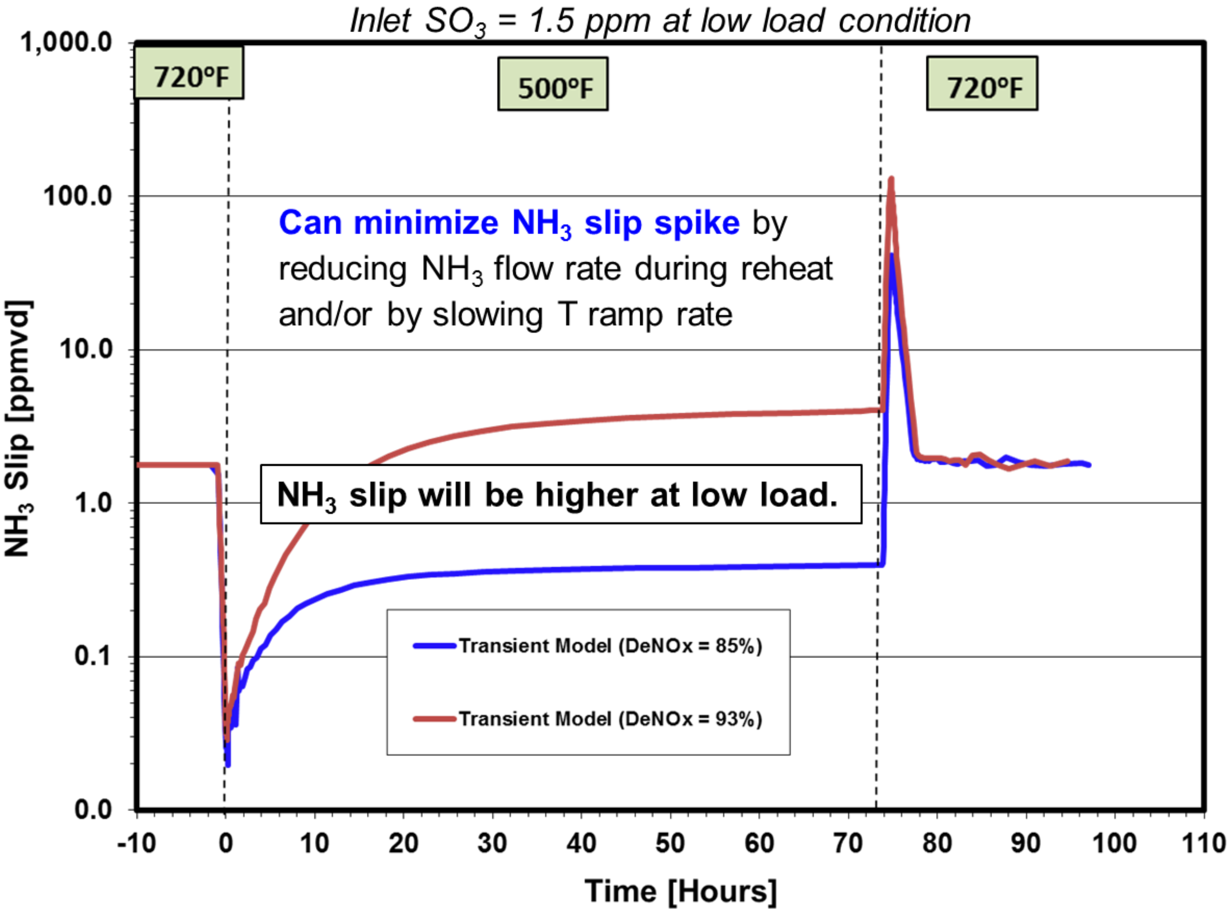


**Minimal additional ABS will form in catalyst under this condition**

**Thus, limiting the low load operation to a maximum of 72 hours provides margin for safe low load SCR operation.**

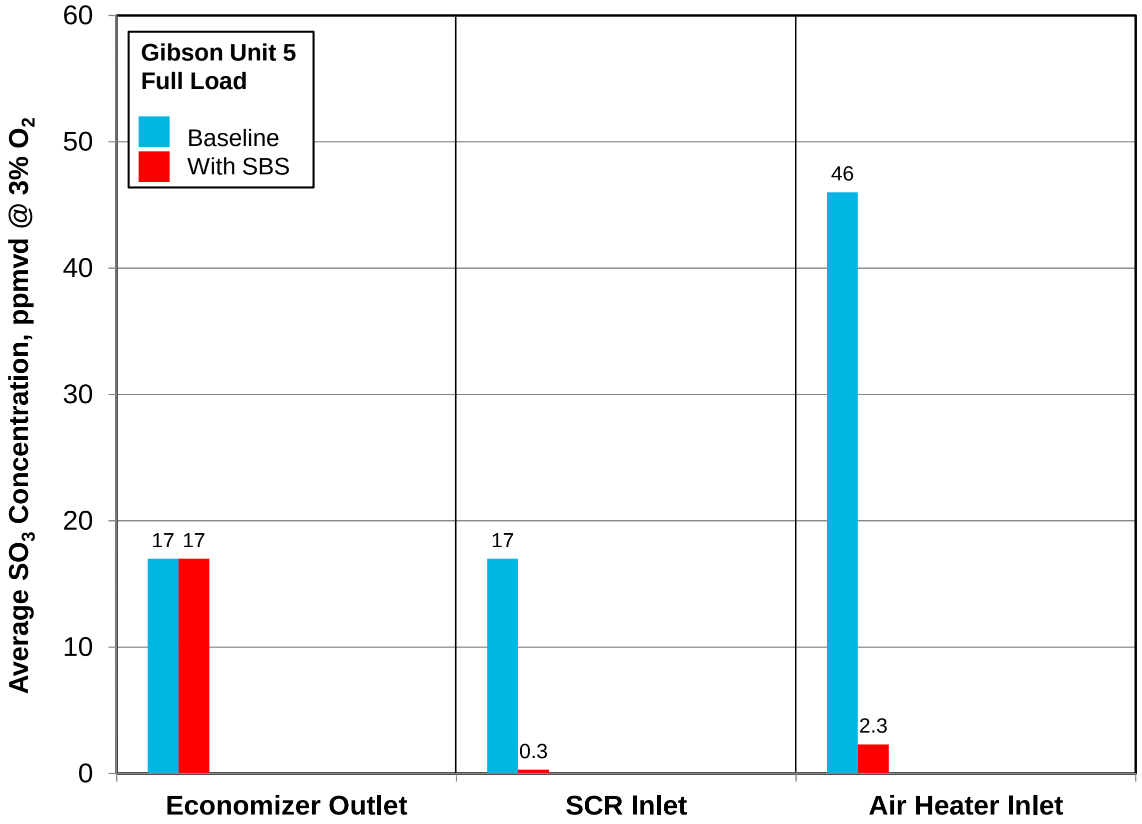
# Transient Modeling Results

- Additional sensitivity testing was performed for 93% NOx removal during enhanced low load.
- Ammonia slip increases greater for low load than full load due to the NOx reaction kinetics working against our favor due to temperature.
- Ammonia will spike similar to $SO_3$ on load ramp due to the decomposition of ABS, $NH_3$ can be reduced during load ramp to minimize the affect.



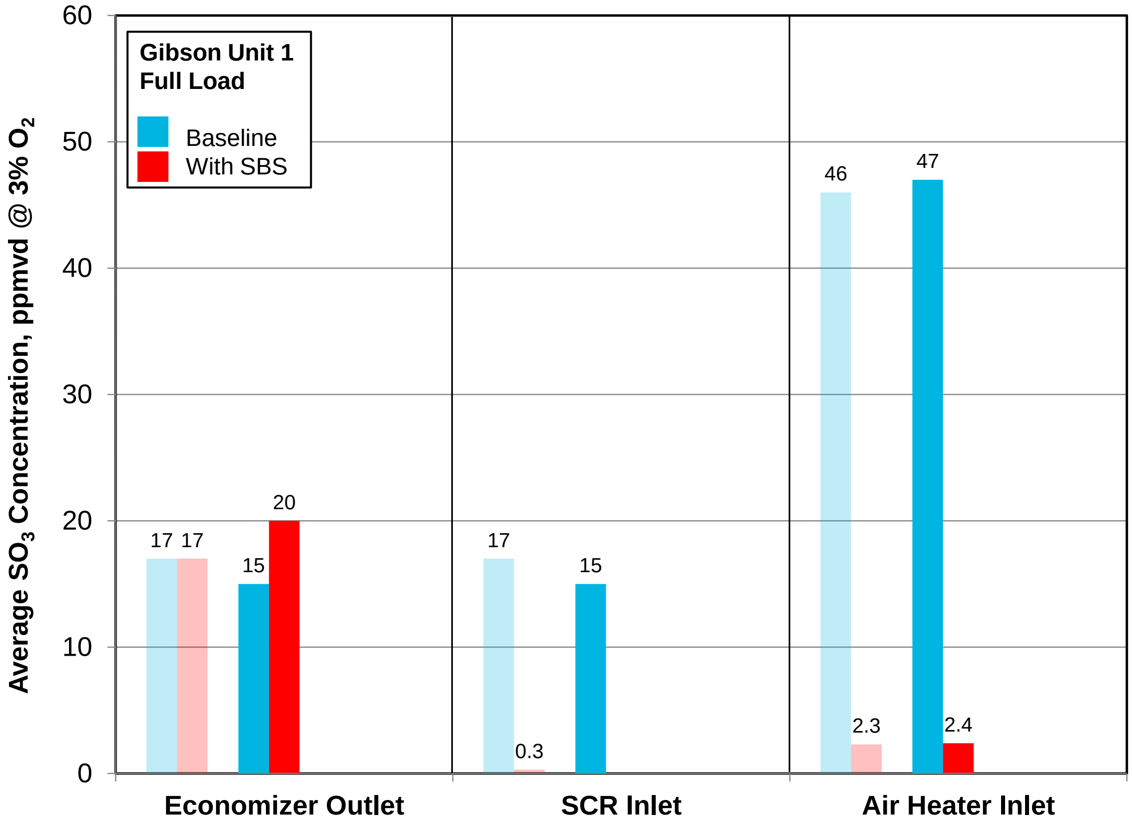
# Full Scale Testing

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



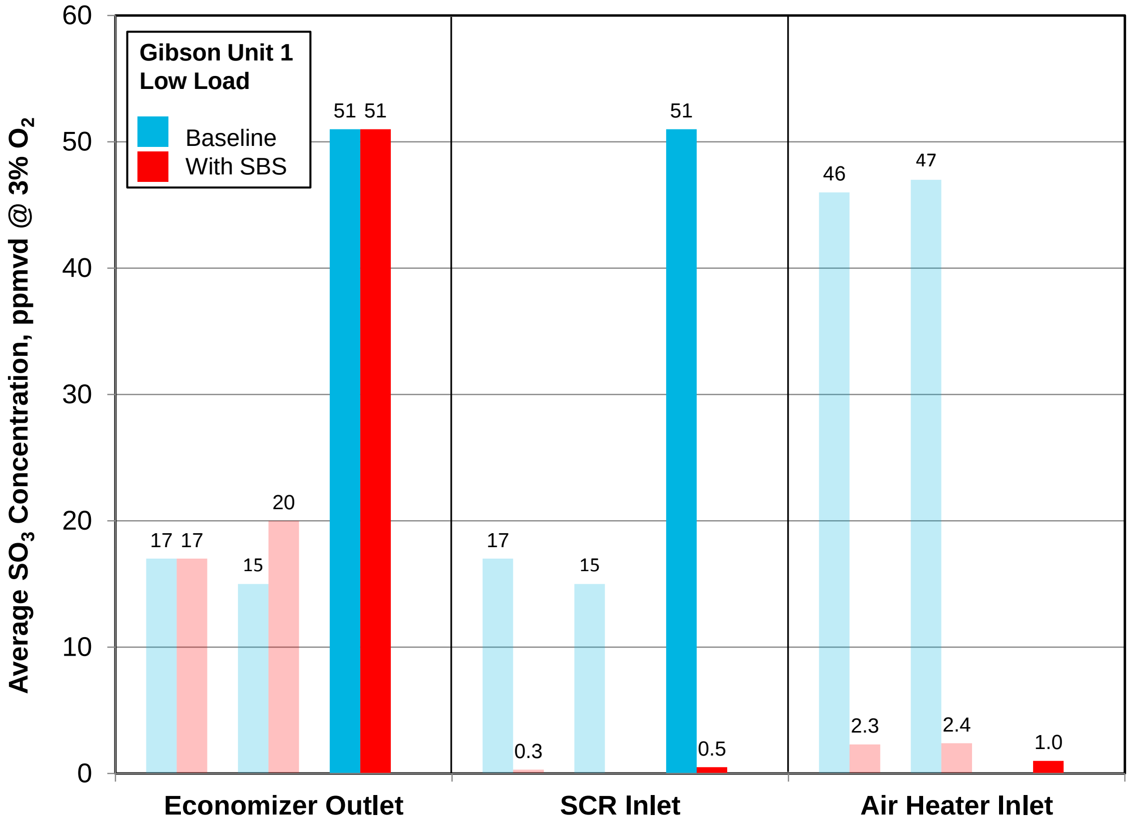
# Full Scale Testing

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



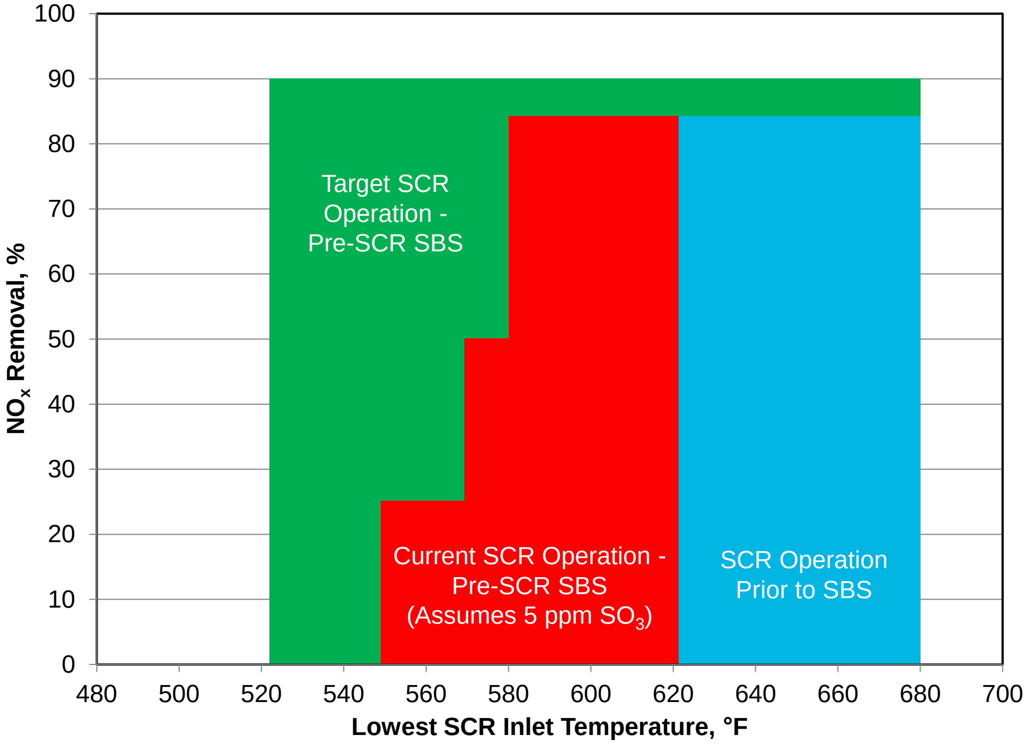
# Full Scale Testing

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

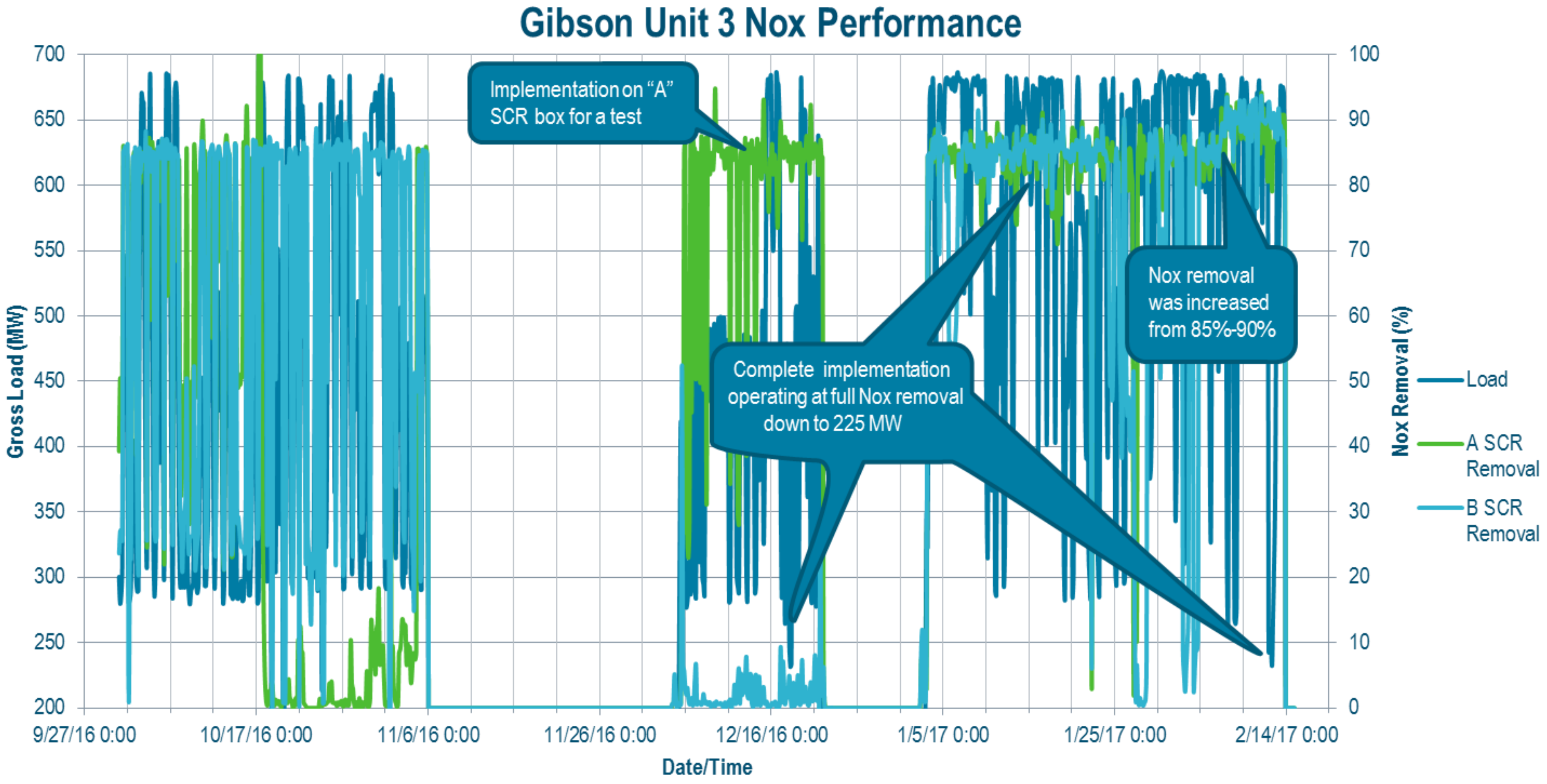


# Gibson Summary

- 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 NOx 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



Gibson Unit 3 Nox Performance

Implementation on "A" SCR box for a test

Complete implementation operating at full Nox removal down to 225 MW

Nox removal was increased from 85%-90%

# Summary

- **We reviewed tools that can provide flexibility for meeting NOx reduction requirements at low load conditions.**
- **Evaluate & balance (using modeling, lab, and field tests):**
  - **Plant operating needs…**
    - DeNOx and $NH_3$ slip goals
    - Dispatch
  - **With the severity of the low load condition…**
    - Temperature, length of time, extent of deactivation
    - Utilization of DSI to reduce inlet $SO_3$
  - **And the capability for performance recovery on return to full load.**
    - Achievable load and temperature
    - Rate of activity recovery
    - Transient $SO_3$ and $NH_3$ emissions

# Questions?