Method for Enhanced Low Load SCR Operation

Christopher J. Bertole, Ph.D.

Extended Abstract #81

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Overview

- **Introduction**
- **Enhanced Approach Method**
- **Data and Model Simulations**
- **Summary**

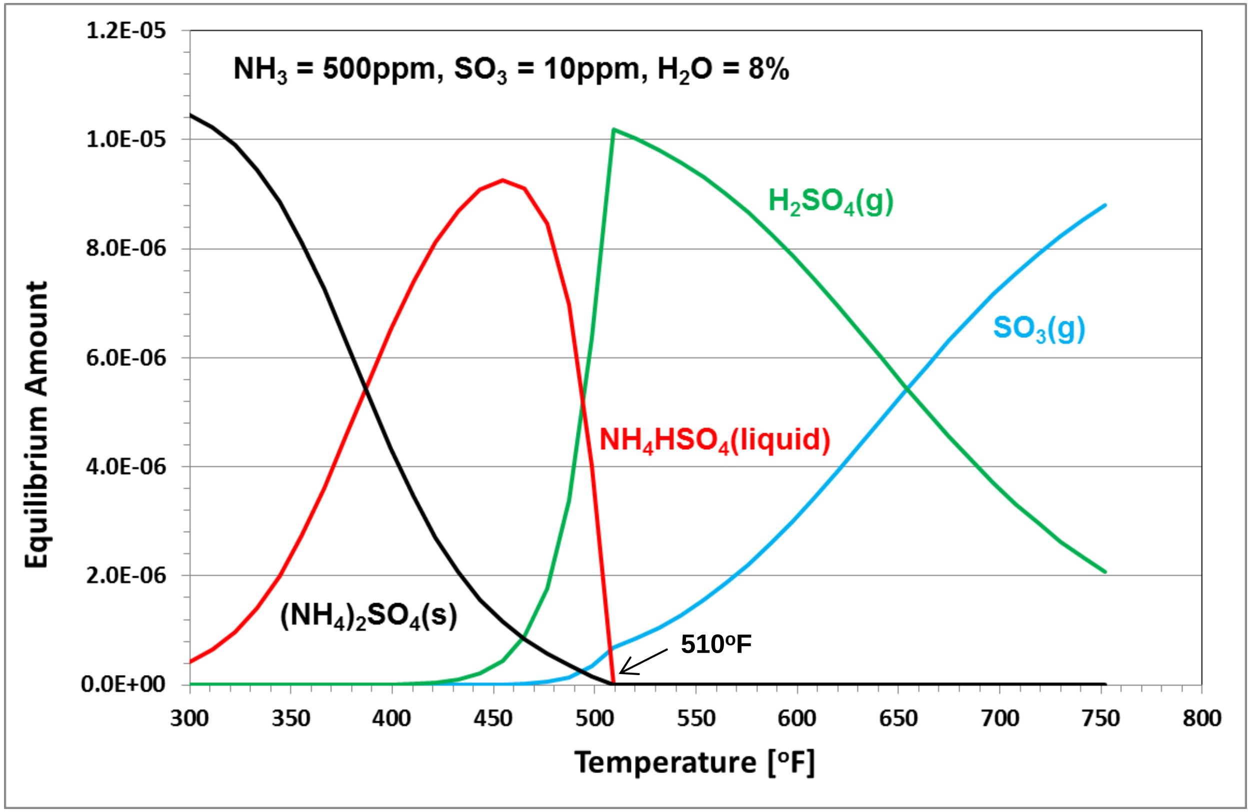
Properties of ABS and AS

Ammonium Bisulfate (ABS)

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

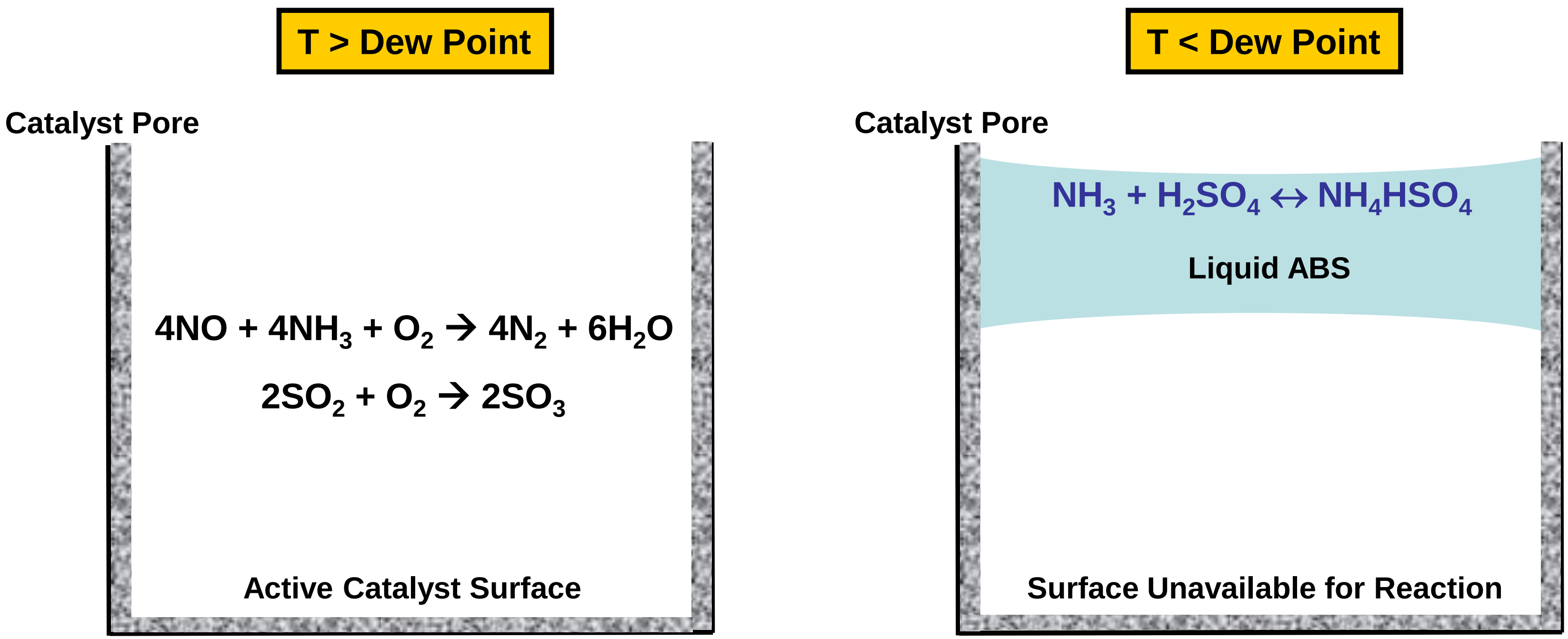
Ammonium Sulfate (AS)

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



ABS Deposition Controls SCR Tmin

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

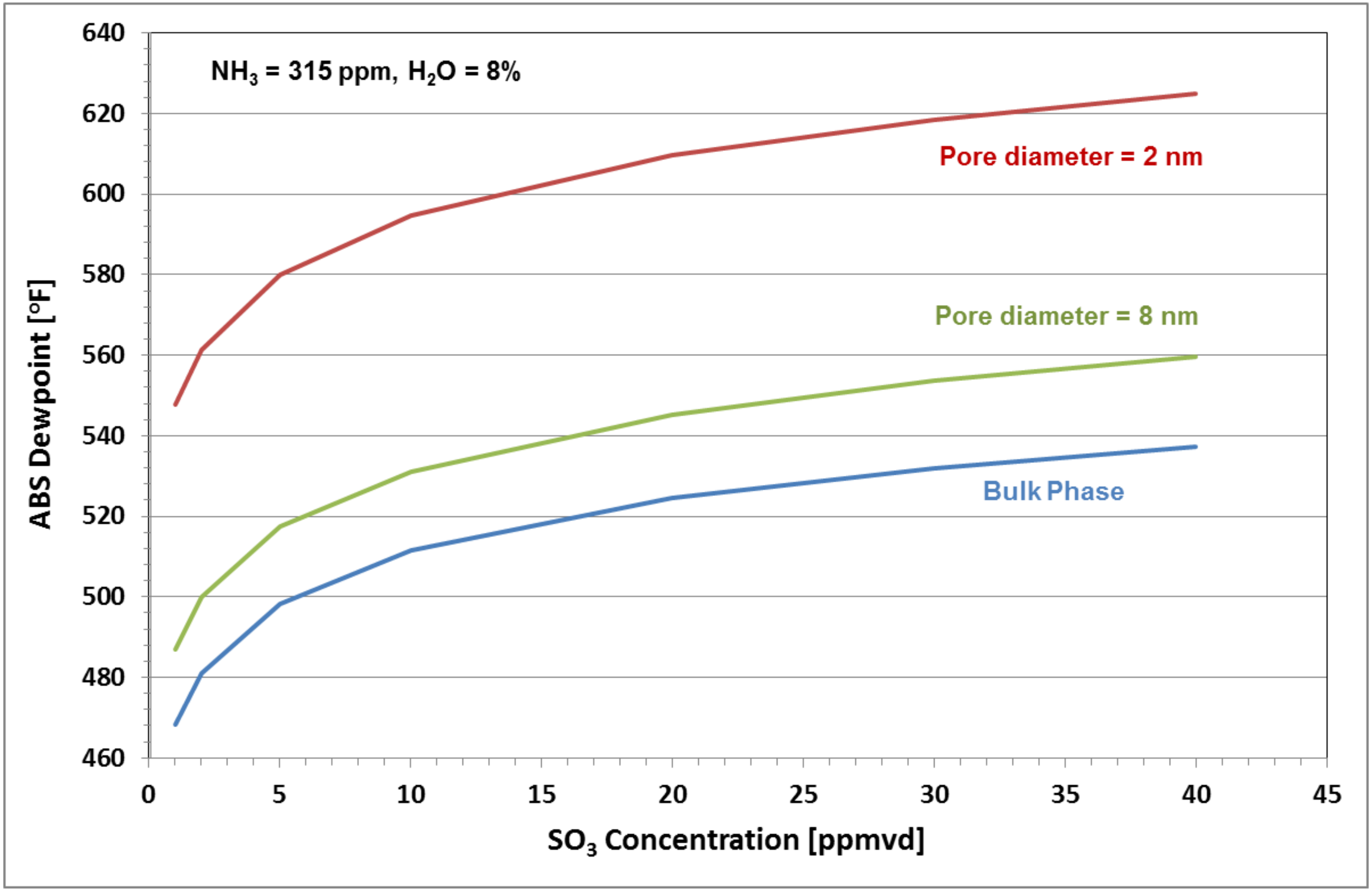


Capillary Condensation

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

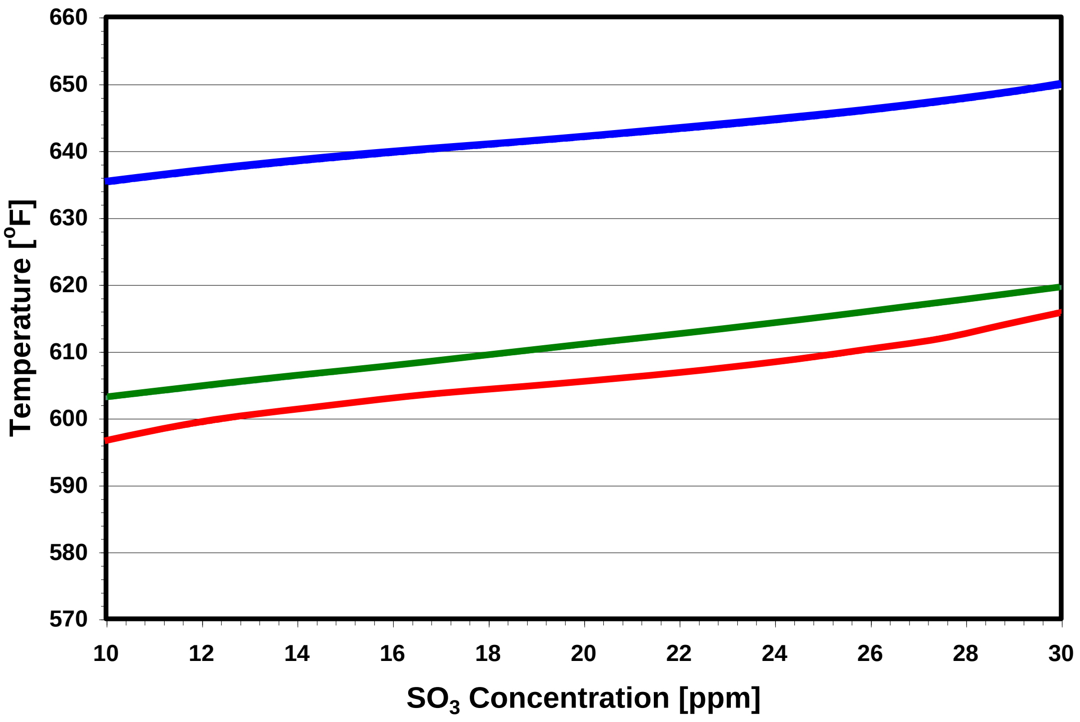
Impact of Pore Size on ABS Dew Point

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



Tmin: Basic Approach

- **1990's: "Basic Approach"**
  - Avoid ABS deposition in the SCR catalyst.
  - Simple operating guidelines.

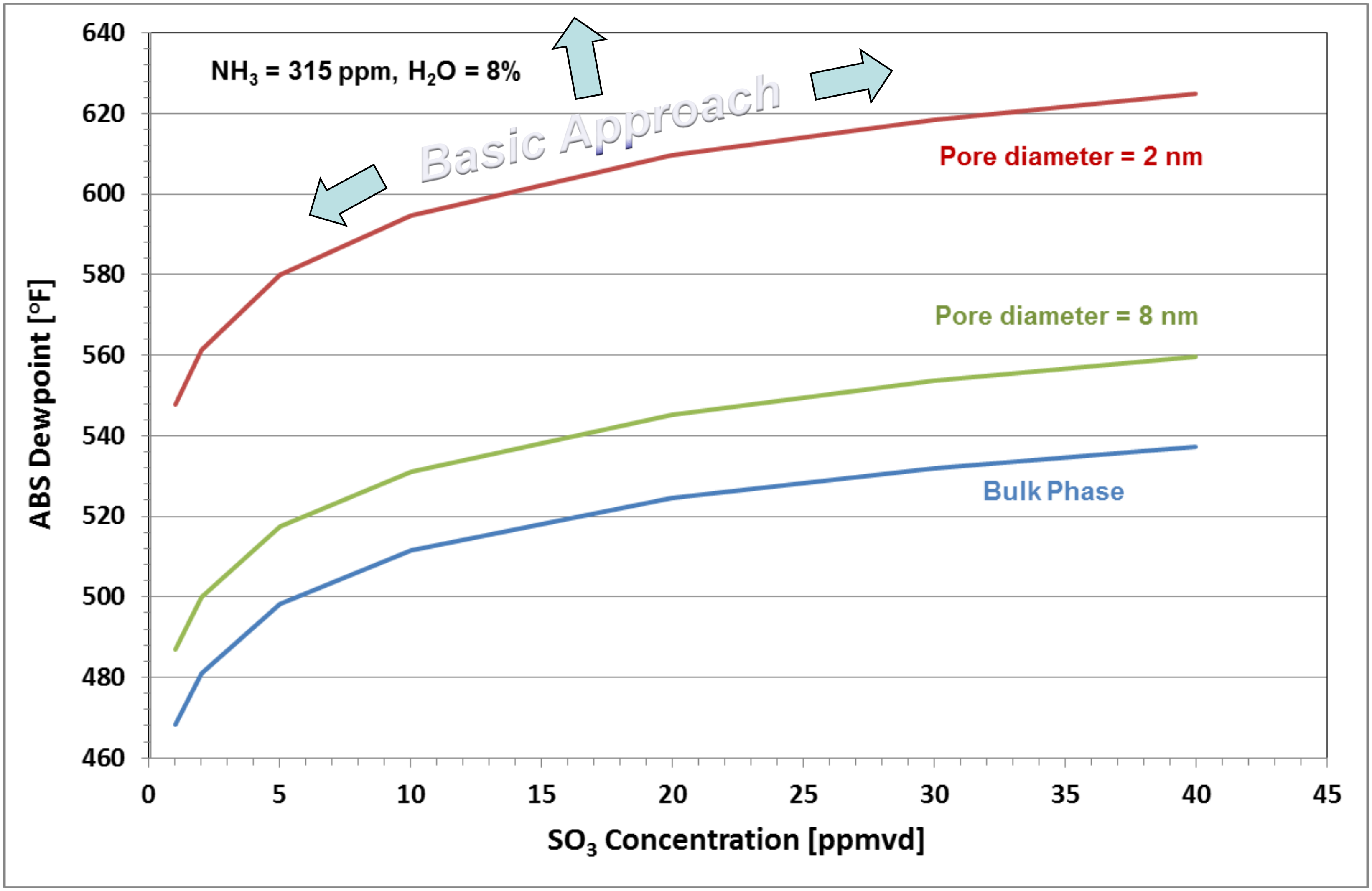


RT = recovery temperature (T)

MOT = minimum operating T

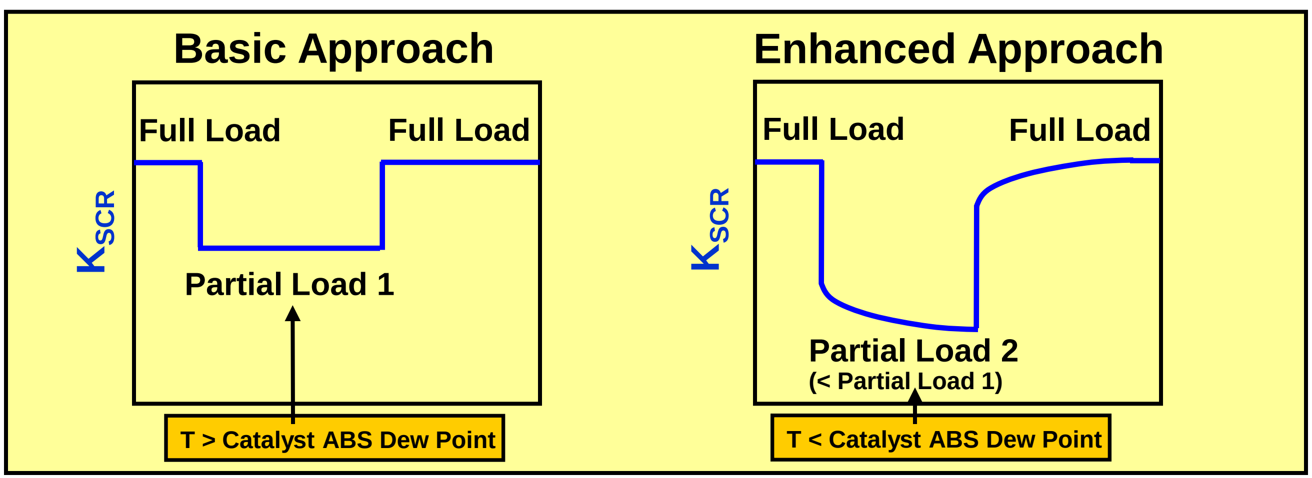
MIT = minimum injection T for NH_3

Basic Approach Avoids ABS Deposition



Tmin: Enhanced Approach

- **2000's: Development of the "Enhanced Approach"**
  - Operate down towards the ABS dew point
  - 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

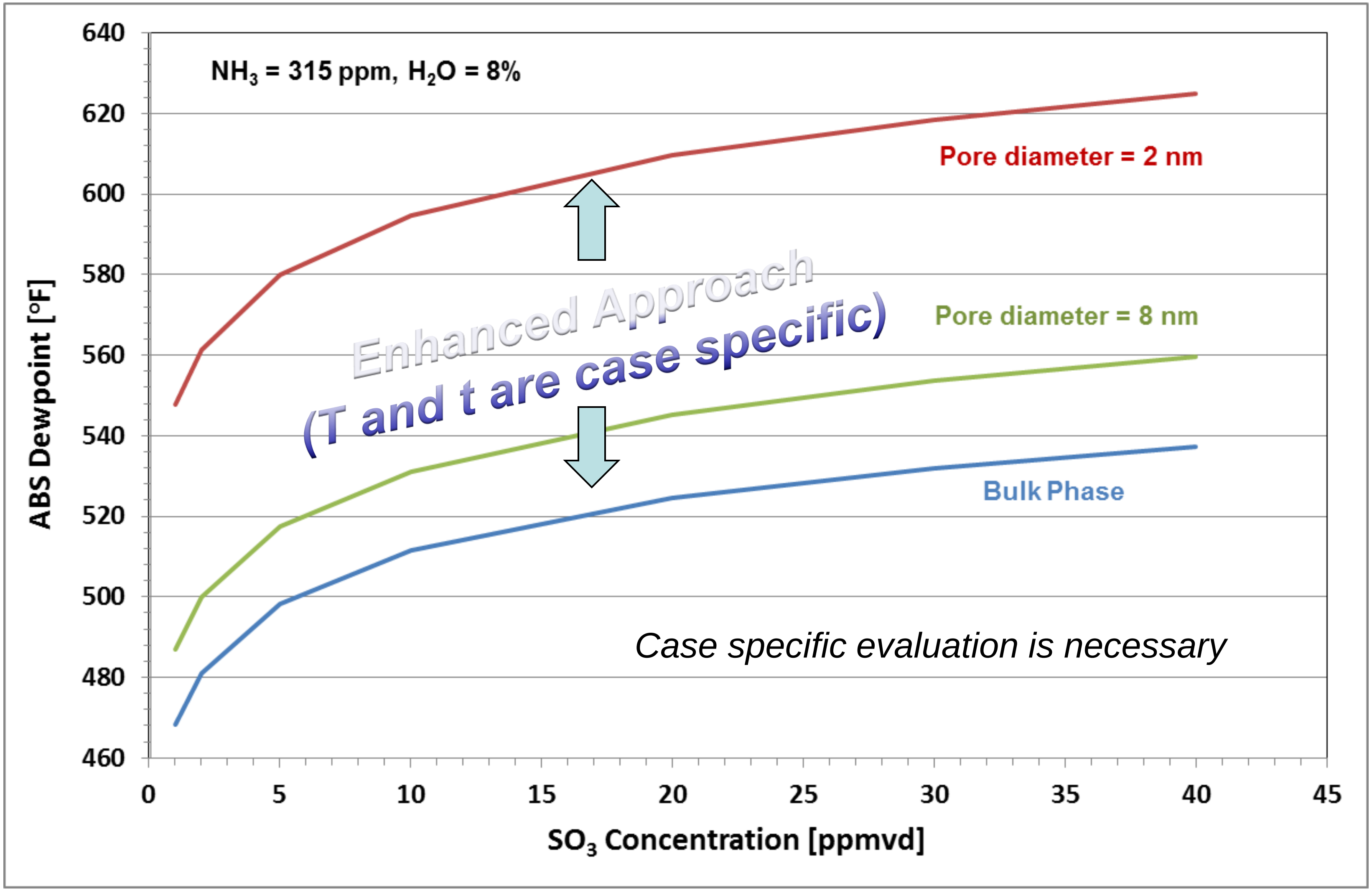


Tmin: Enhanced Approach

- **"Enhanced Approach" increased low load flexibility**
  - **Drivers:**
    - **Load Cycling** (weekend, overnight, shoulder seasons)
    - **Unit Maintenance** (condenser cleaning, boiler feed pump and fan malfunctions)
    - **Avoid Installation of Economizer By-Pass**
  - **+12 years of operating experience (since 2004)**
    - Enhanced Approach in-use at >20 boilers
    - Catalyst deactivation rates from field audits have been consistent with fuels fired
      - *No additional deactivation from ABS observed*
  - **Cormetech Publications:**
    - **Duke Belews Creek 2:** Whitaker, W., DiFrancesco, C., Ake, T., Langone, J., Successful Year-Round SCR Operation at Duke Energy's Belews Creek Power Plant, presented at Power-Gen International Conference, 2006
    - **TVA SCR Fleet:** Bertole, C.J., Pritchard, S., Giles, J., SCR Operation at Low Flue Gas Temperature, presented at Power-Gen International Conference, 2006

Enhanced Approach

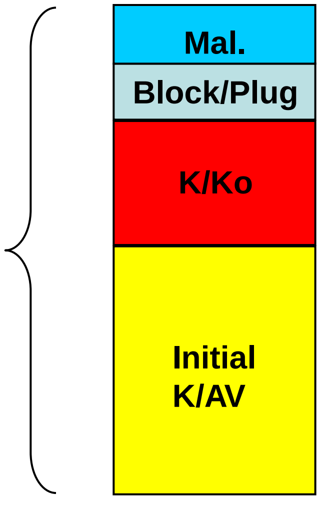
Manage ABS Deposition in Catalyst: Transient Cycling



Design Considerations

Applying the Enhanced Approach

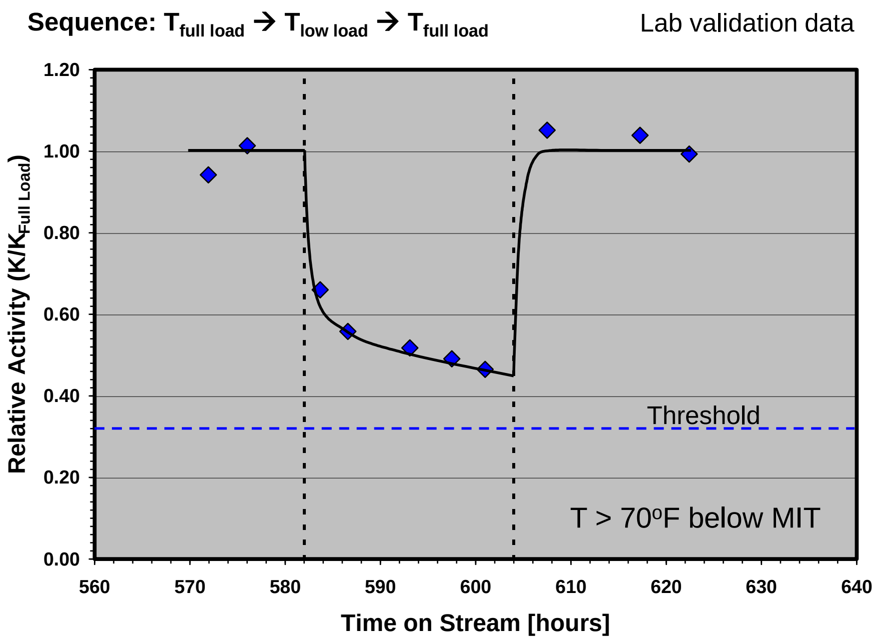
Total K/AV in X layers



- **<u>For the low load and recovery conditions:</u>**
  - Transient K/AV must be $\geq$ K/AV required to meet DeNOx, NH_3 slip
    - Thus: $K/K_{full\ load}$ must be $\geq$ $AV/AV_{full\ load}$
  - Need to consider transient SO_3 & NH_3 spikes during recovery
  - *Must understand the unit's operation and catalyst's response at both full and low load conditions (case specific evaluation)*

During Low Load Operation

- **DeNOx and NH_3 slip performance <u>cannot be met</u> if:**
  - $K/K_{full\ load}$ decreases below $AV/AV_{full\ load}$ (i.e., below threshold)
  - **Options to consider to mitigate:**
    - Increase NH_3 slip, or reduce DeNOx efficiency
    - Settle at a higher low load temperature (don't go as low!)
    - Reheat catalyst above recovery temperature



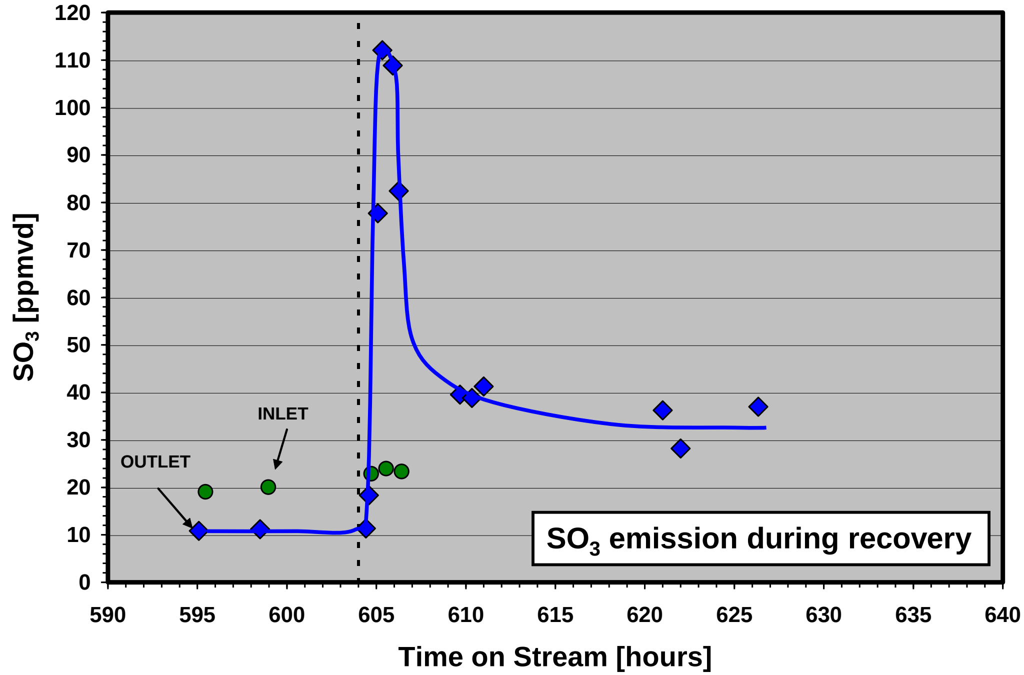
Scenario OK!

During Recovery Phase

- **DeNOx and NH_3 slip performance is at risk if:**
  - K has not fully recovered to pre-cycle level
  - **Options to consider to mitigate:**
    - Increase NH_3 slip, or reduce DeNOx efficiency during recovery
    - Go to a higher recovery temperature to assist ABS removal
    - Settle at a higher low load temperature (don't go as low!)
- **Potential for increased SO_3 and NH_3 slip emissions**
  - Due to (1) NH_3 & SO_3 desorption and (2) ABS elimination

SO_3 Emission During Recovery Phase

Sequence: $T_{full\ load}$ → $T_{low\ load}$ → $T_{full\ load}$ Lab validation data



- **Options to consider to reduce spikes**:
  - **Minimize NH_3 slip spike** by reducing NH_3 flow rate during reheat
  - **Minimize NH_3 slip and SO_3 spikes** by slowing T ramp rate
  - Don't deposit as much ABS at low load (e.g., operate at a lower DeNOx, or higher temperature, or reduce total time at low load)

Current Day: Pushing the Boundaries…

- **2016: Move the low load limits even lower…**
  - **Drivers:**
    - Coal units are increasingly load following due to increased supply from renewables (wind and solar)
    - Regulations (i.e., CSAPR) forcing higher total NOx reduction
  - **Goal:**
    - Keep SCR in-service at low boiler load points to operate profitably during periods of low demand, to be ready for peak demand calls
      - Run at lower SCR temperatures,
      - For longer times,
      - While maintaining high DeNOx…
  - **Example: Duke Energy Plant Gibson study**
    - Chad Donner, “Sorbent Injection for Low Load Operating Flexibility”, 2016 Reinhold APC/PCUG Conference → included Cormetech lab test

The Toolbox
Applying the Enhanced Approach

Lab testing for validation

- Characterize catalyst for model baselining
- Verify modeling output
- Large testing database

Bench

Micro

The Toolbox

Applying the Enhanced Approach

CORMETECH

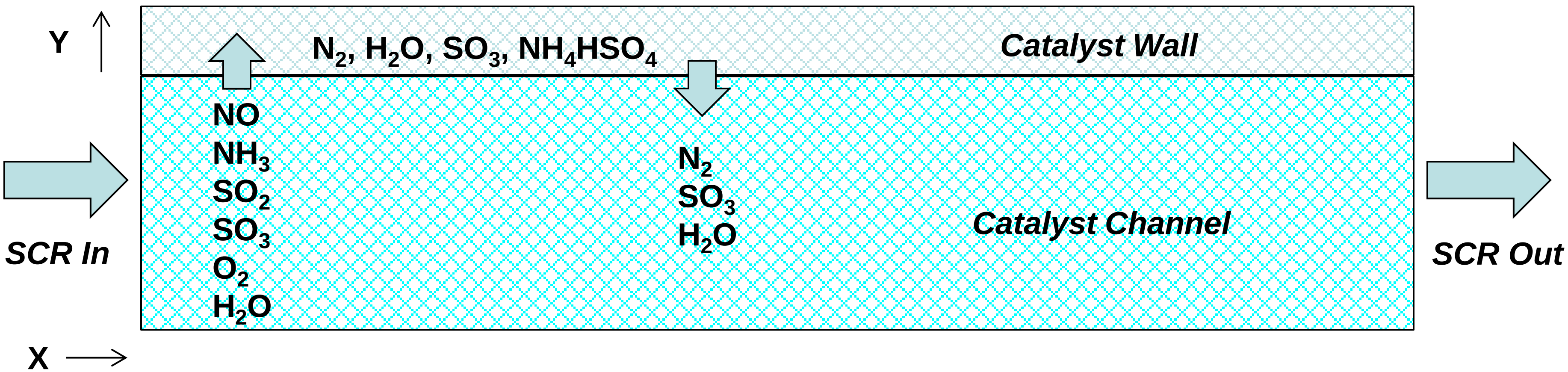
Transient model for engineering analysis

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

Reactions in Catalyst Wall:

$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$ $SO_2 + ½ O_2 \rightarrow SO_3$

$NH_3 + H_2SO_4 = NH_4HSO_4$



FEM model: accounts for internal / external mass transfer, intrinsic kinetics, SO_3/NH_3 adsorption, and ABS pore plugging/removal (thermo, kinetics).

Solve a set of 15 simultaneous PDEs to generate a solution.

Example: Lab Catalyst Test

Ran test cycle on Cormetech micro reactor. 6.9mm pitch catalyst sample.

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

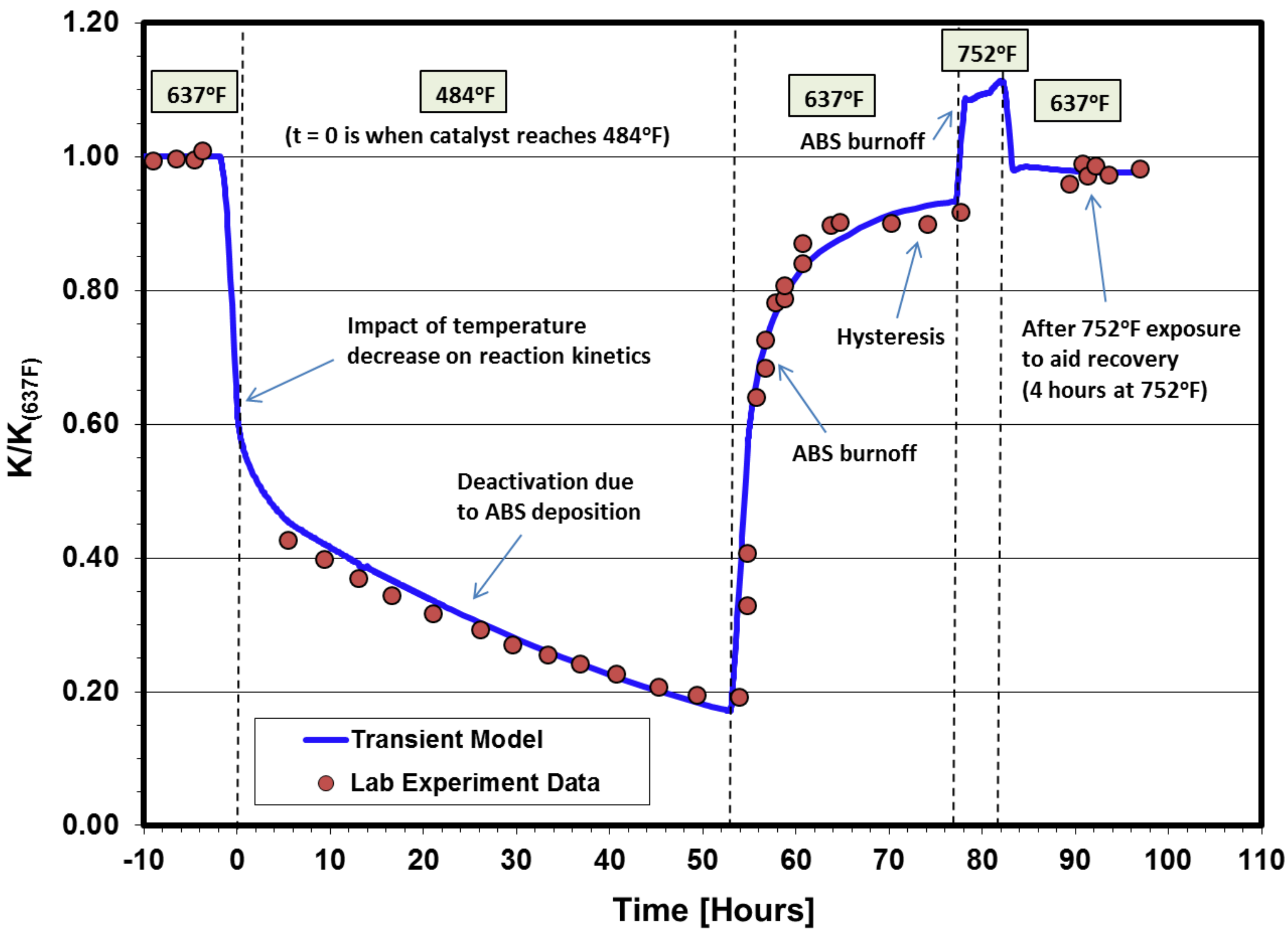
Step 4

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

Lab Catalyst Test: Model vs. Lab Data



Duke Energy Plant Gibson Study

CORMETECH

Ran test cycle on Cormetech bench reactor using Gibson catalyst samples.

Step 1	
Temperature [°F]	**720**
NOx [ppmvd]	280
Molar Ratio	0.86
SO_2 [ppmvd]	2700
SO_3 [ppmvd]	3.5

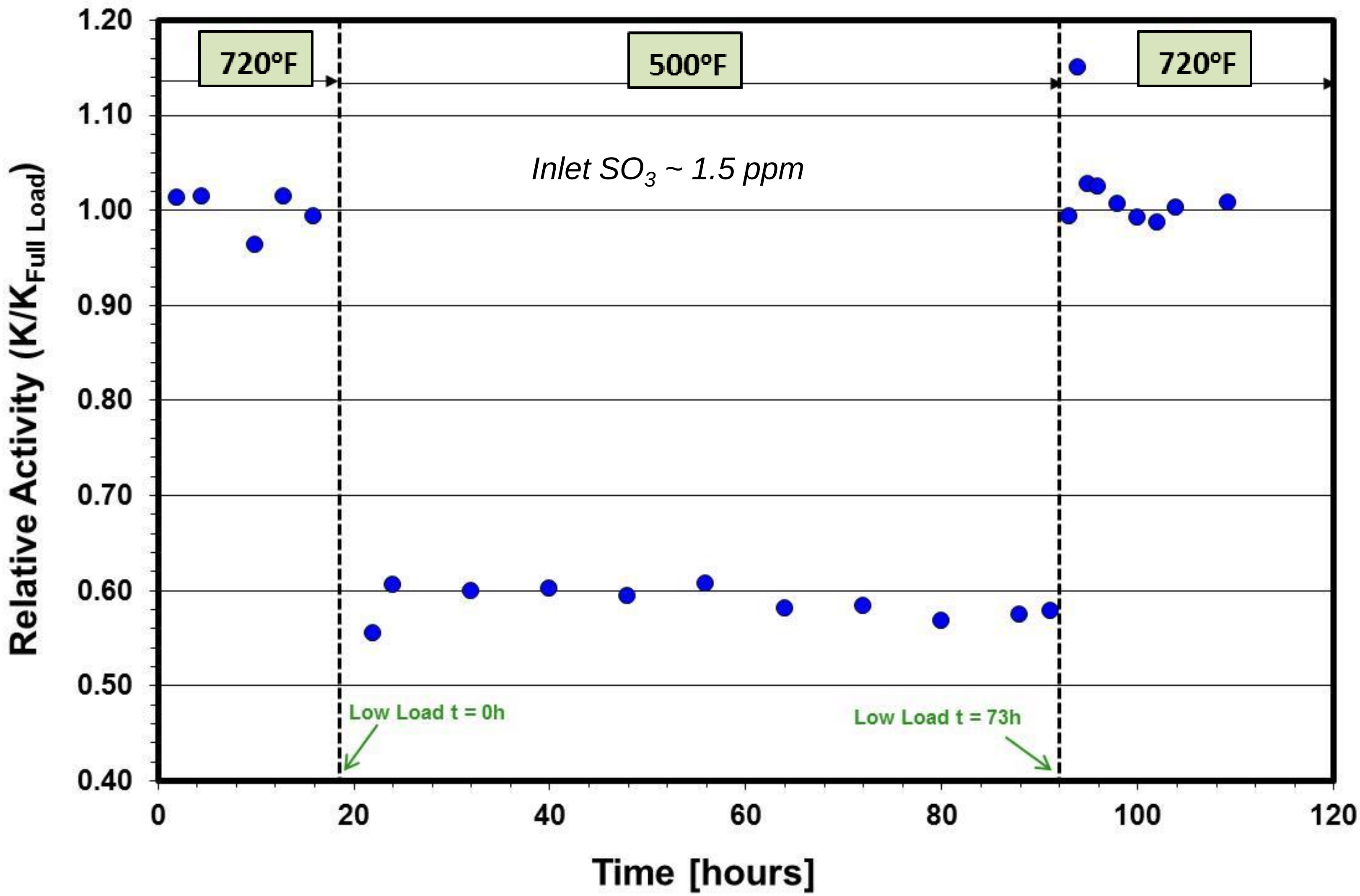
Step 2	
Temperature [°F]	**500**
NOx [ppmvd]	230
Molar Ratio	0.86
SO_2 [ppmvd]	2700
SO_3 [ppmvd]	1.5

Step 3	
Temperature [°F]	**720**
NOx [ppmvd]	280
Molar Ratio	0.86
SO_2 [ppmvd]	2700
SO_3 [ppmvd]	3.5

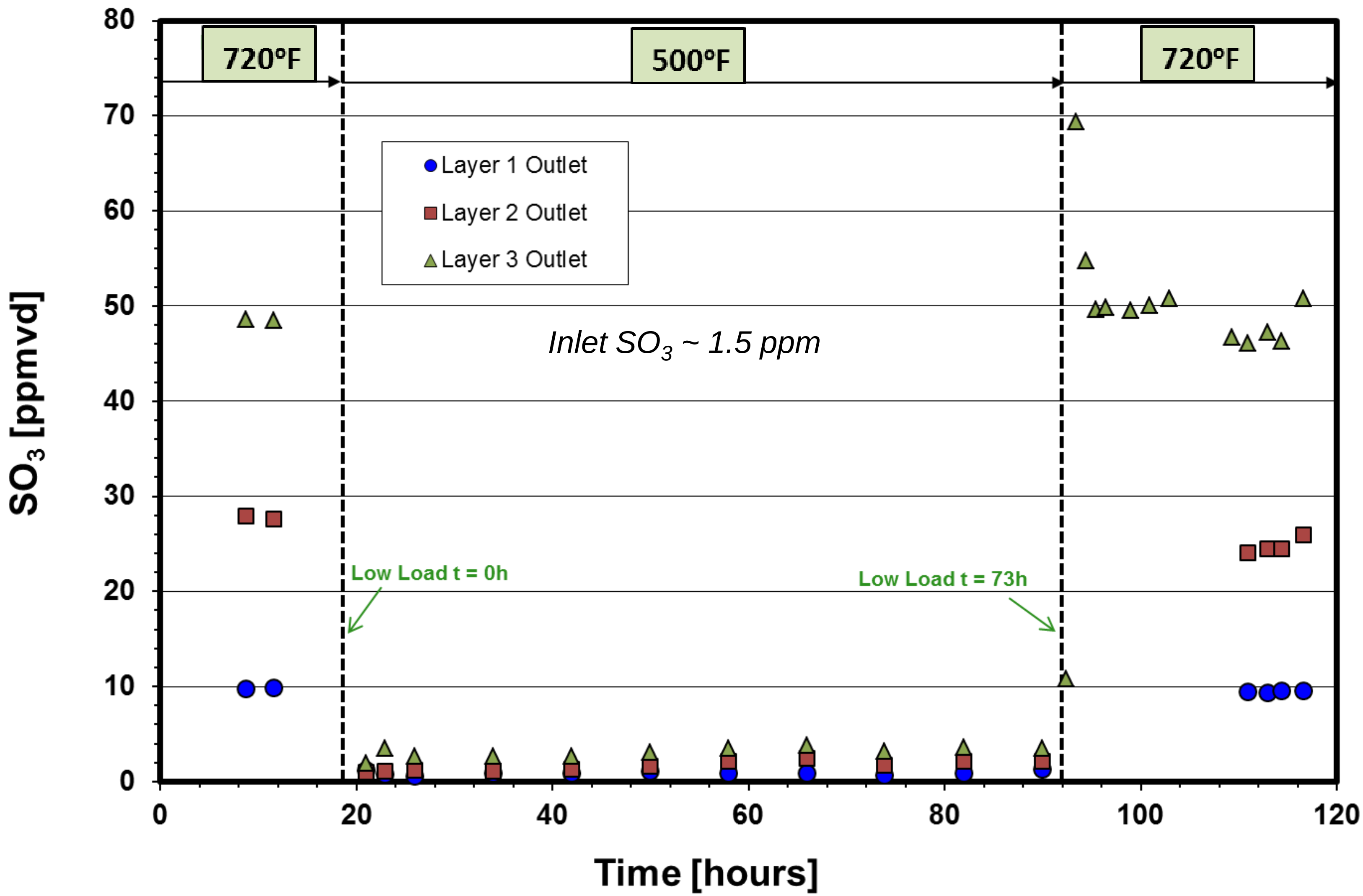
Low inlet SO_3 operating condition due to DSI system at Gibson.

Desired low load run time = 72 hours

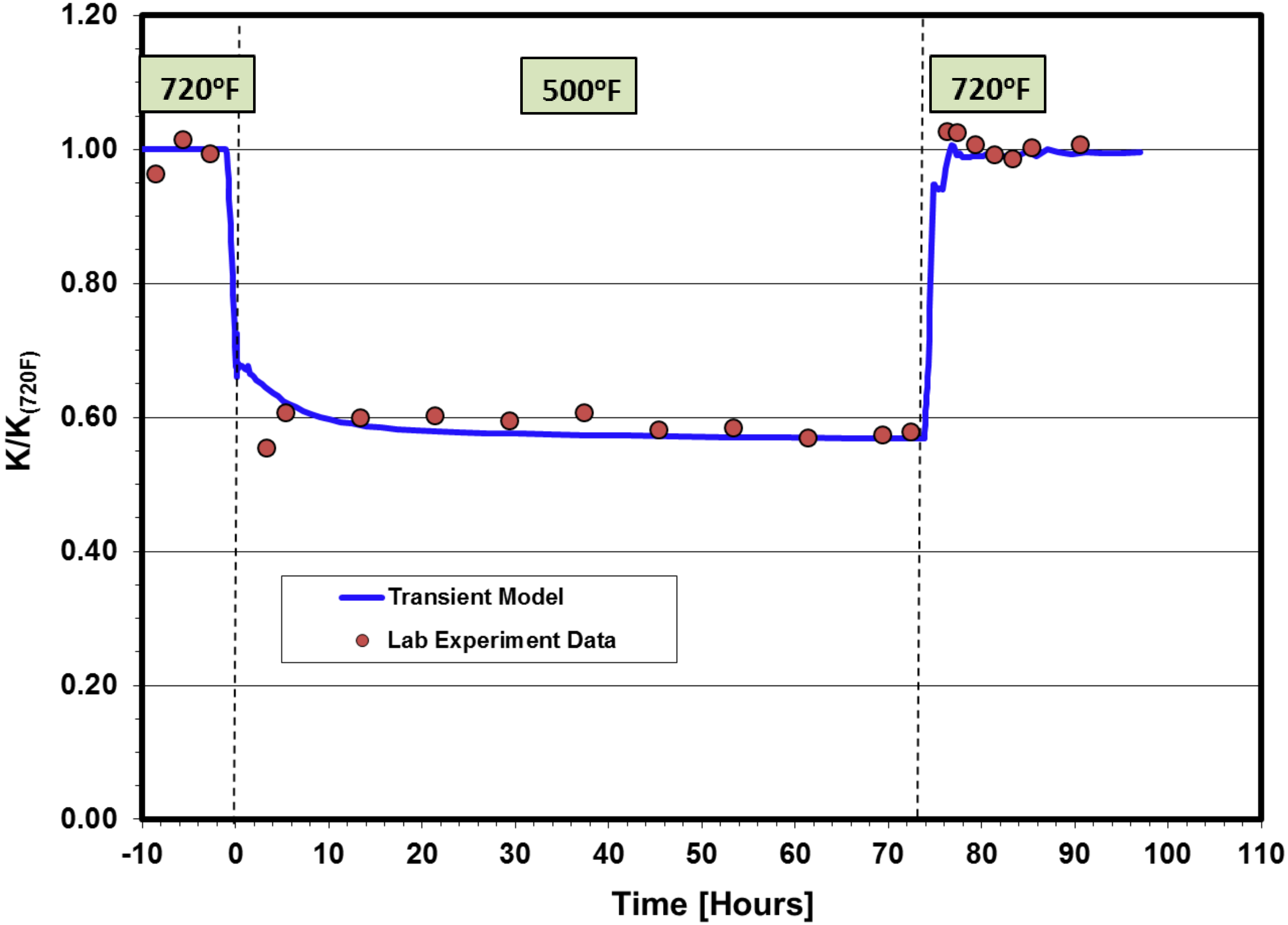
Duke Energy Plant Gibson Study



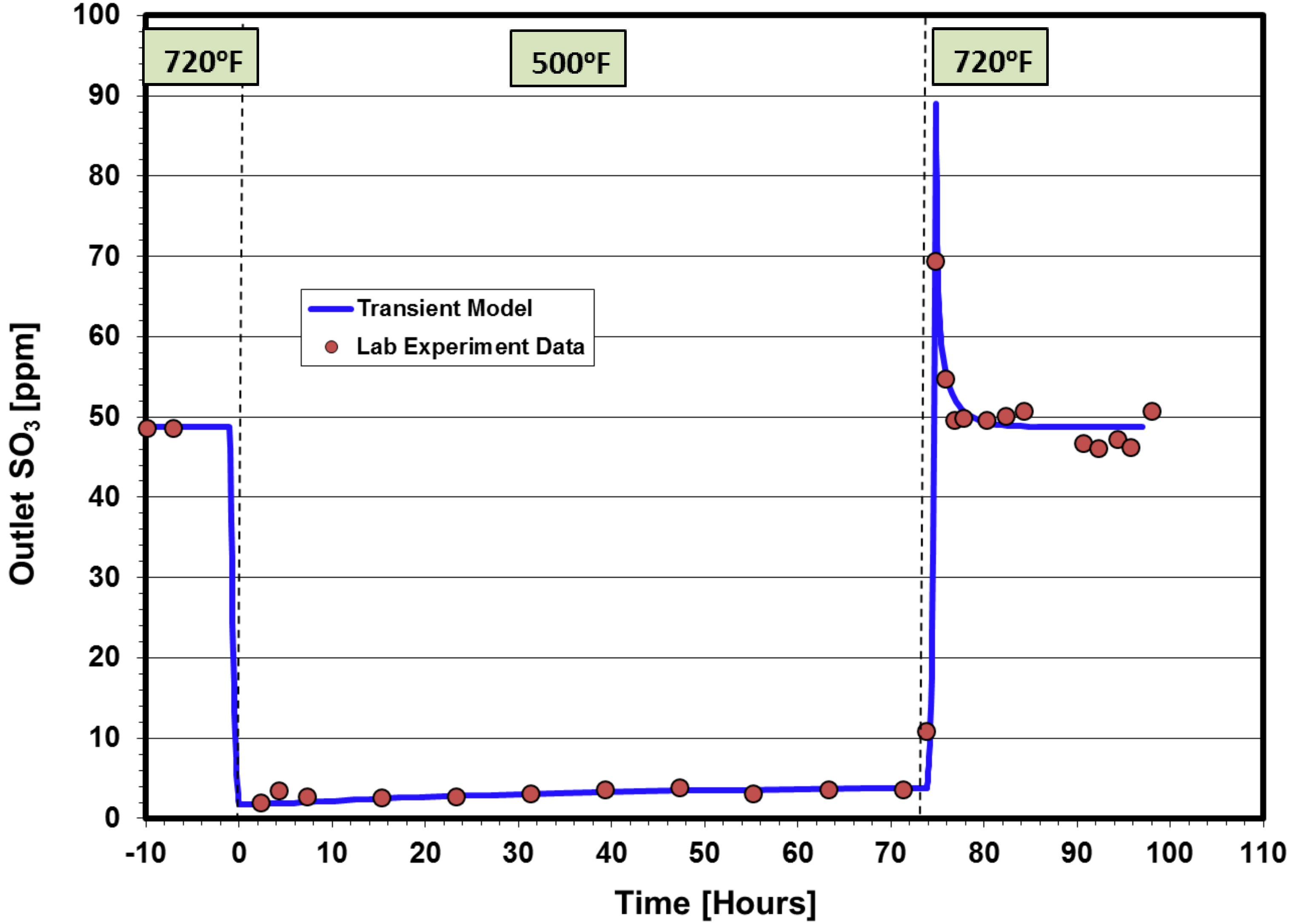
Duke Energy Plant Gibson Study



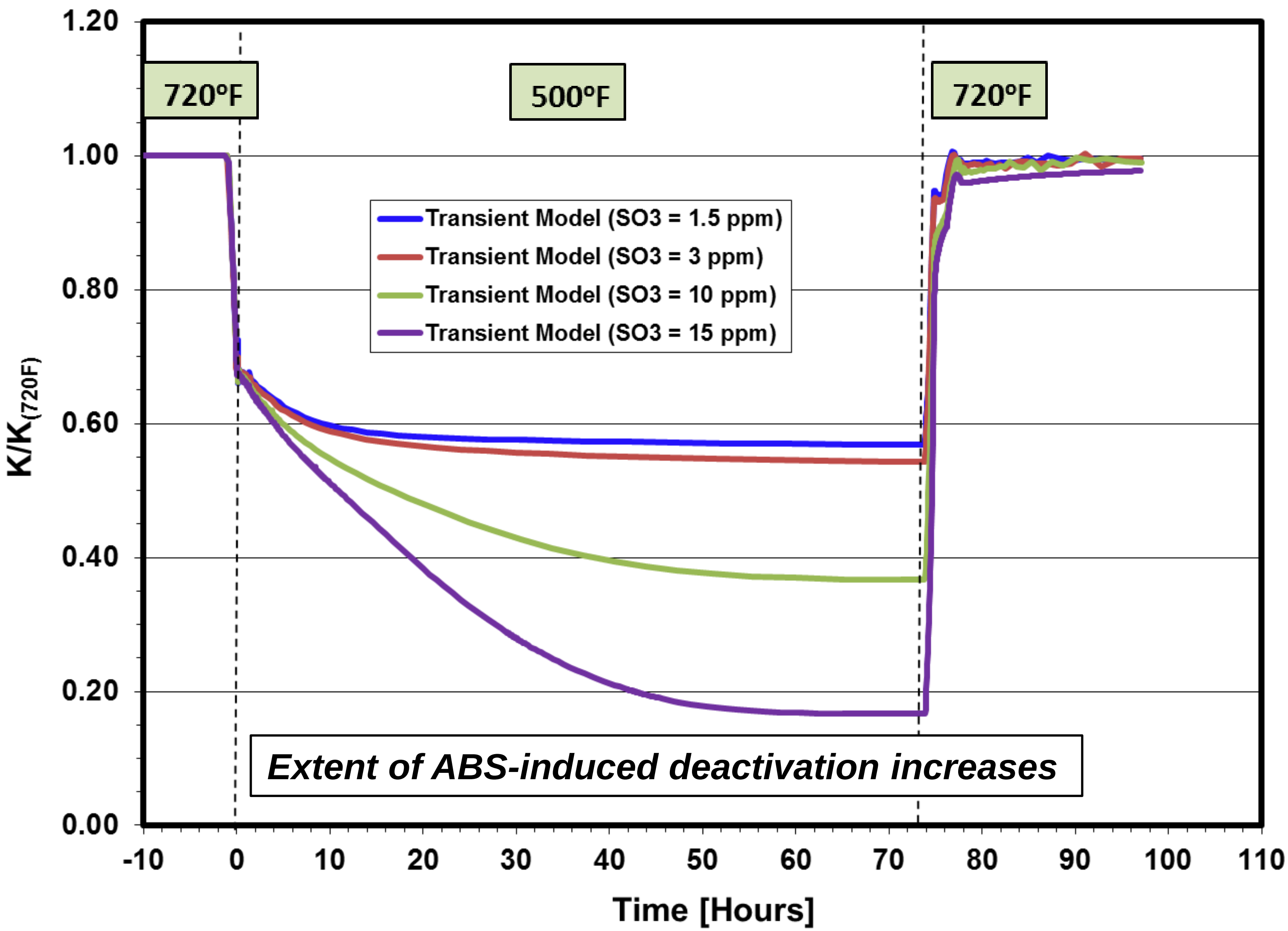
Model Fit: DeNOx K Ratio



Model Fit: Outlet SO_3

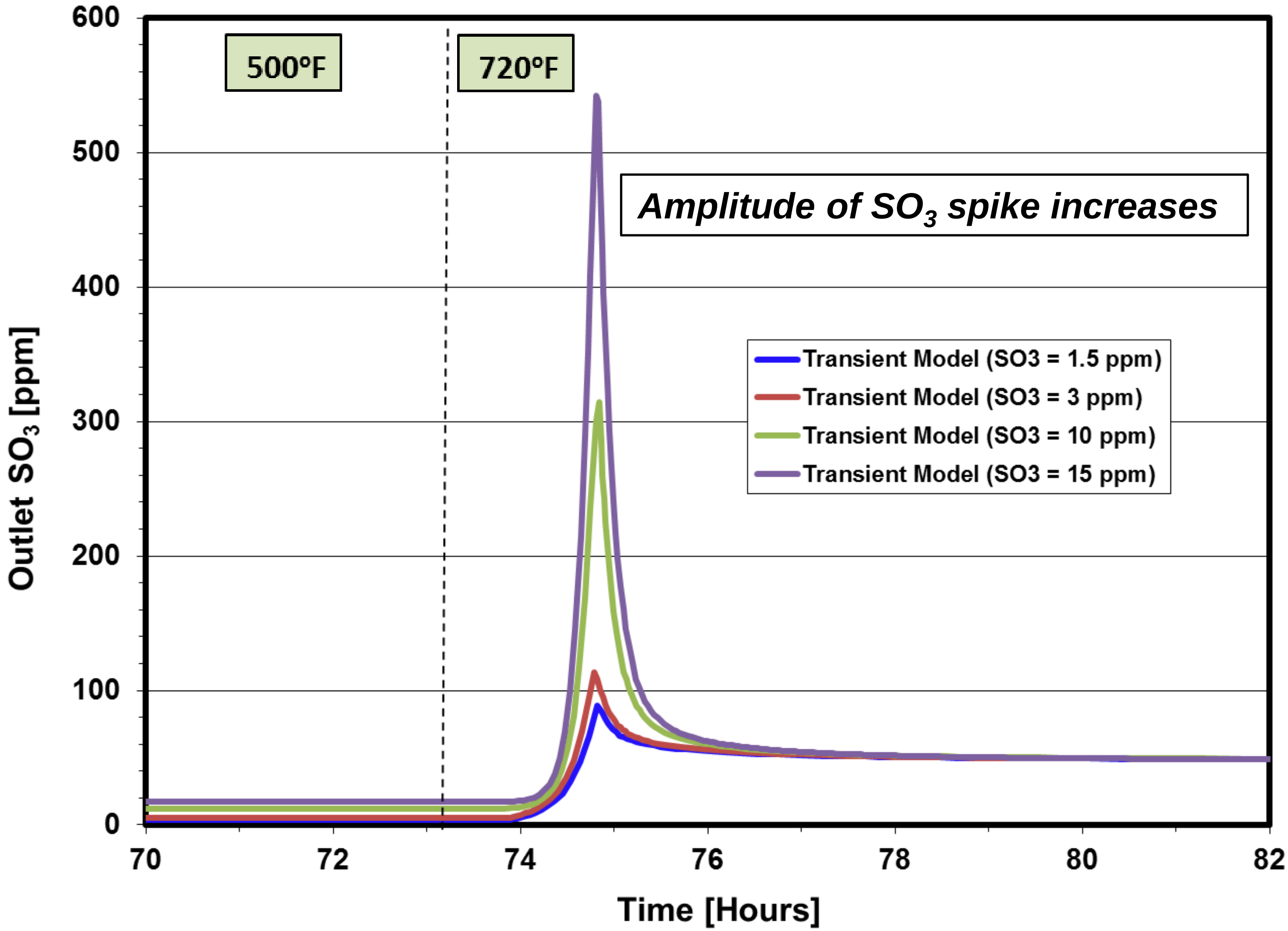


What if Actual Inlet SO_3 is Higher?



What if Actual Inlet SO_3 is Higher?

CORMETECH



Summary

CORMETECH

- **Enhanced Approach provides flexibility for meeting NOx reduction requirements at low load conditions**
- **Key is to evaluate and balance:**
  - **Plant operating needs…**
  - **With the severity of the low load condition…**
    - Temperature, length of time, extent of deactivation
  - **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

➢ <u>Model simulation, along with lab validation testing, are useful tools to evaluate different low load operating scenarios for a specific Plant</u>

Thank You!

Questions?

Christopher J. Bertole, Ph.D.

bertolecj@cormetech.com