REINHOLD ENVIRONMENTAL ®

2022 Reinhold/PCUG Round Table Presentation

Hosted by Duke Energy in the Charlotte Sheraton/Le Meridien Hotel, Charlotte, NC on June 27-28, 2022

CORMETECH
RELIABILITY. DELIVERED.

Low Temperature Operation

Reinhold Conference

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June 27, 2022

Review/Overview

- **Reaction Chemistry and Thermodynamics**
- **Cormetech Tmin Capability and Experience**
- **Design Considerations**
- **Case Studies**
- **Summary**

SCR Reaction Chemistry

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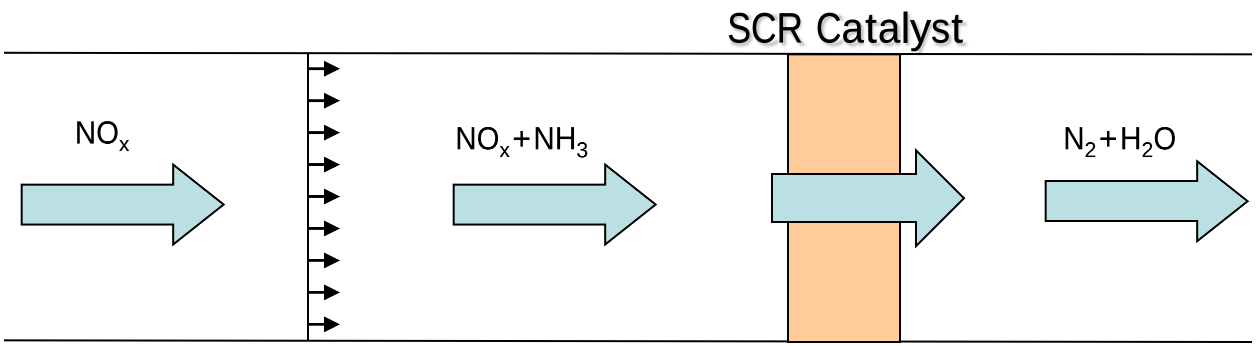
Desired Reactions (goal: maximize activity):

$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$		(NO_x Reduction)
$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$		(NO_x Reduction)
$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$		(NO_x Reduction)
$Hg + 2HCl + \frac{1}{2}O_2 \rightarrow HgCl_2 + H_2O$		(Hg Oxidation)



Undesired Reactions (goal: minimize activity):

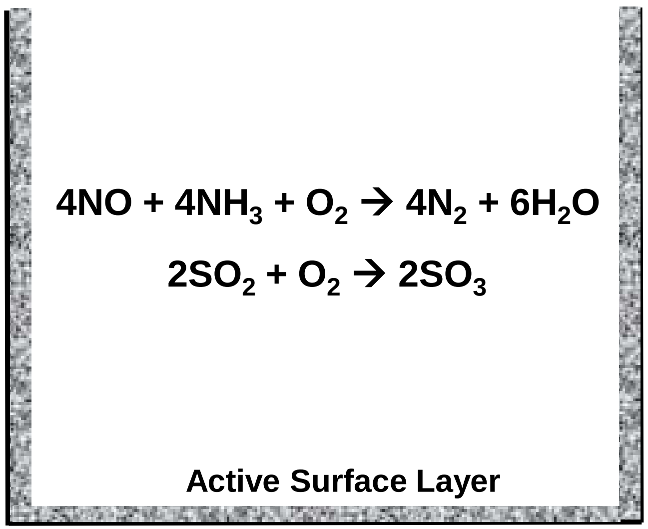
$SO_2 + \frac{1}{2} O_2 \rightarrow SO_3$		(SO_2 Oxidation)
$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$		(Ammonia Oxidation)
$NH_3 + SO_3 + H_2O \rightarrow NH_4SO_4$		(Ammonia Bisulfate)
$HgCl_2 + NH_3 + \frac{1}{4} O_2 \rightarrow Hg + 2\,HCl + \frac{1}{2} N_2 + \frac{1}{2} H_2O$		($HgCl_2$ Reduction by NH_3)
$HgCl_2 + SO_2 + H_2O \rightarrow Hg + 2\,HCl + SO_3$		($HgCl_2$ Reduction by SO_2)

ABS Deposition Controls Tmin

- ABS (ammonium bisulfate) deactivates SCR catalyst by filling and/or blocking pores
  - Effect is reversible: remove ABS by reheating above dew point

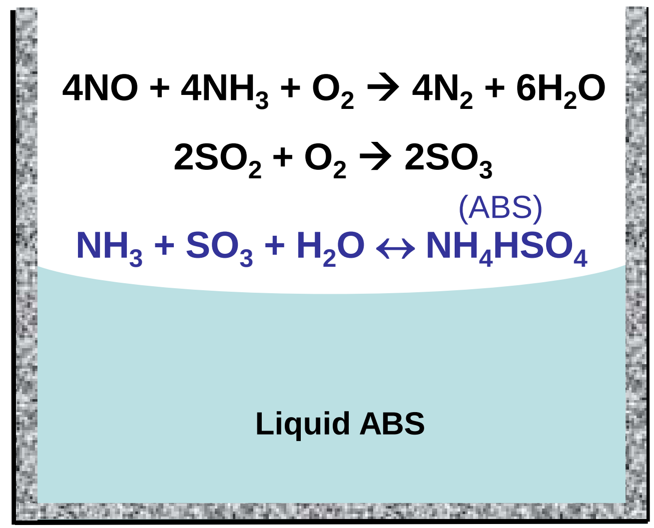
T > Dew Point

Catalyst Pore



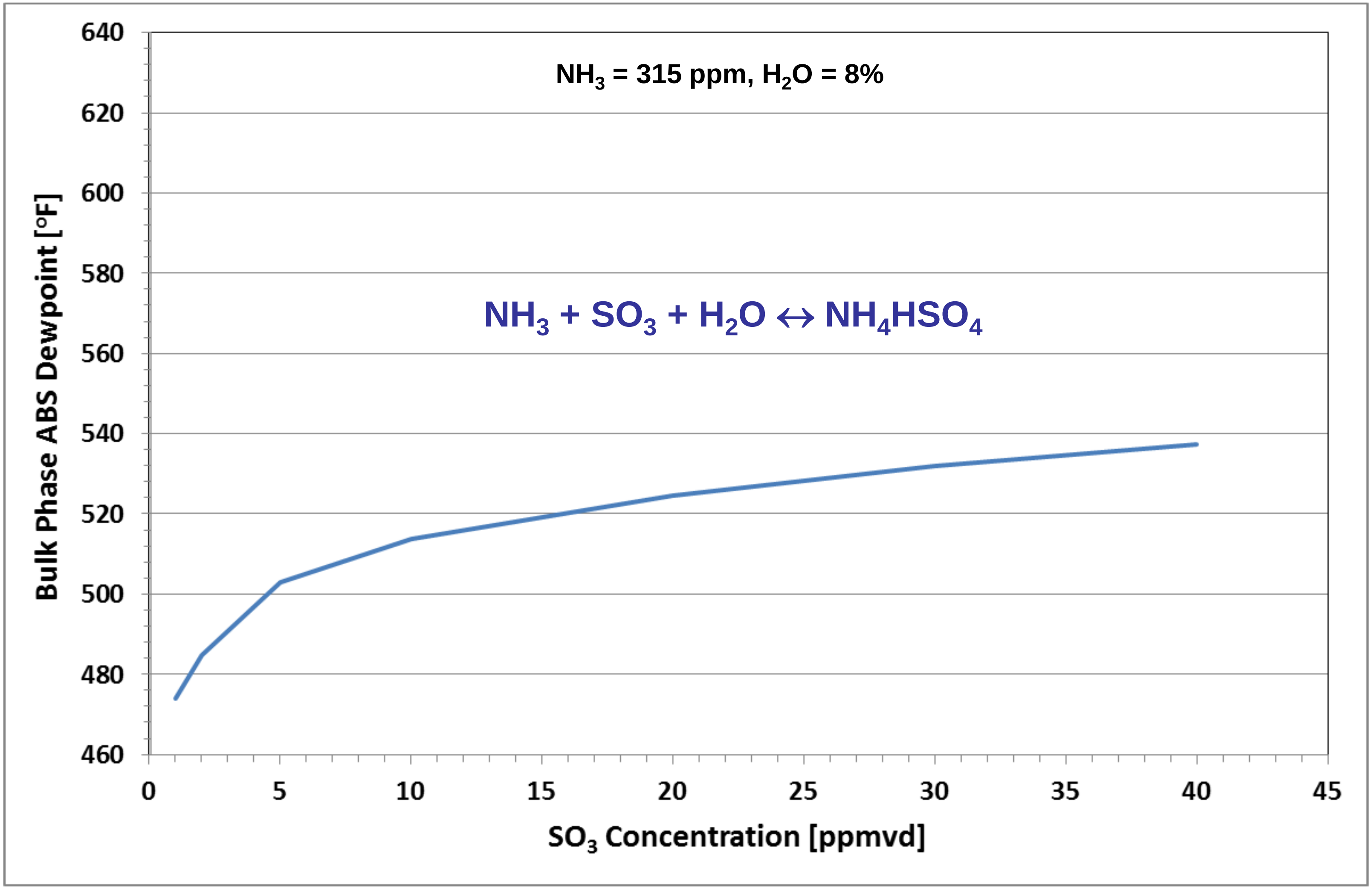
T < Dew Point

Catalyst Pore

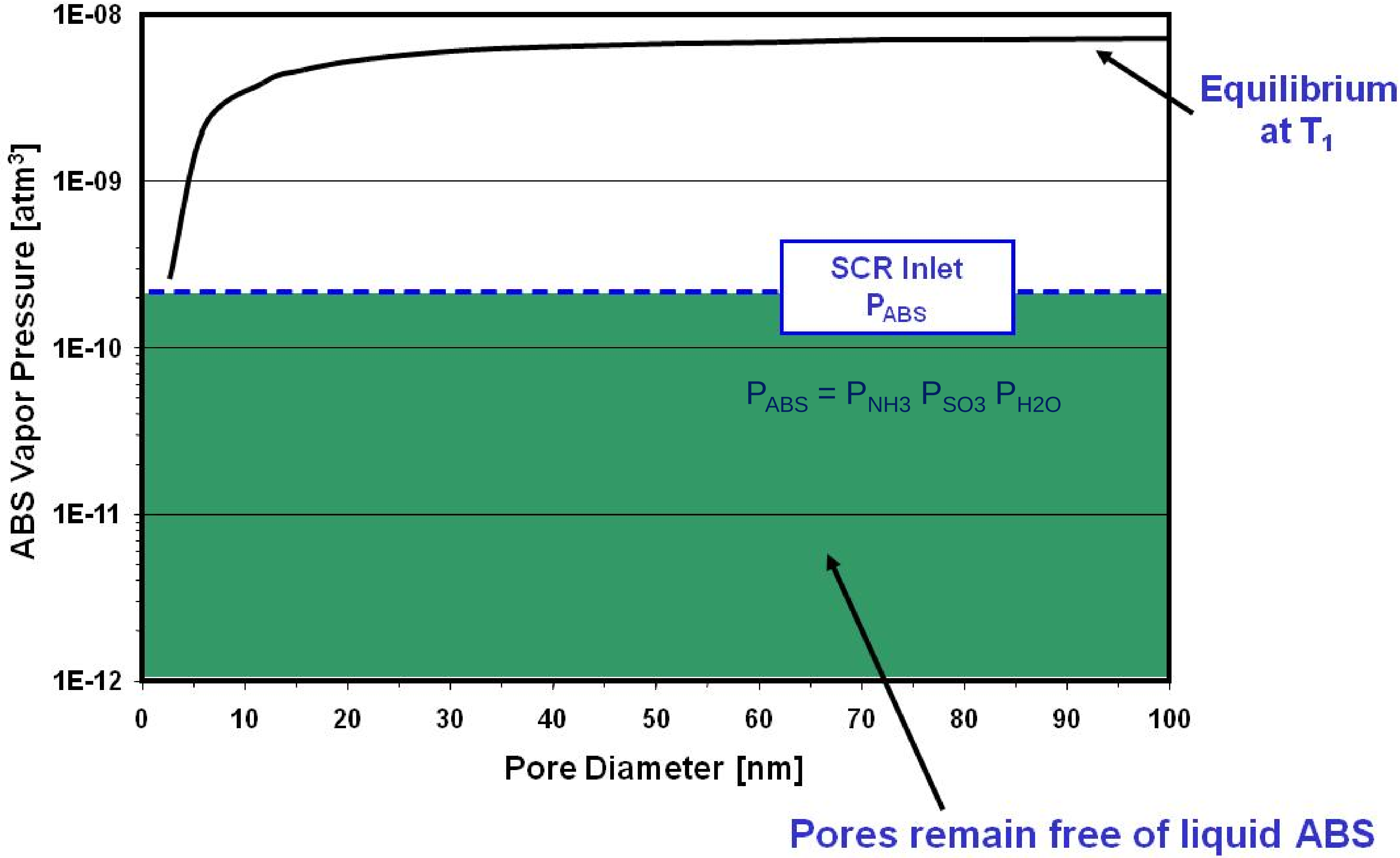


$$P_{ABS} = P_{NH3}\, P_{SO3}\, P_{H2O} = 1/K$$

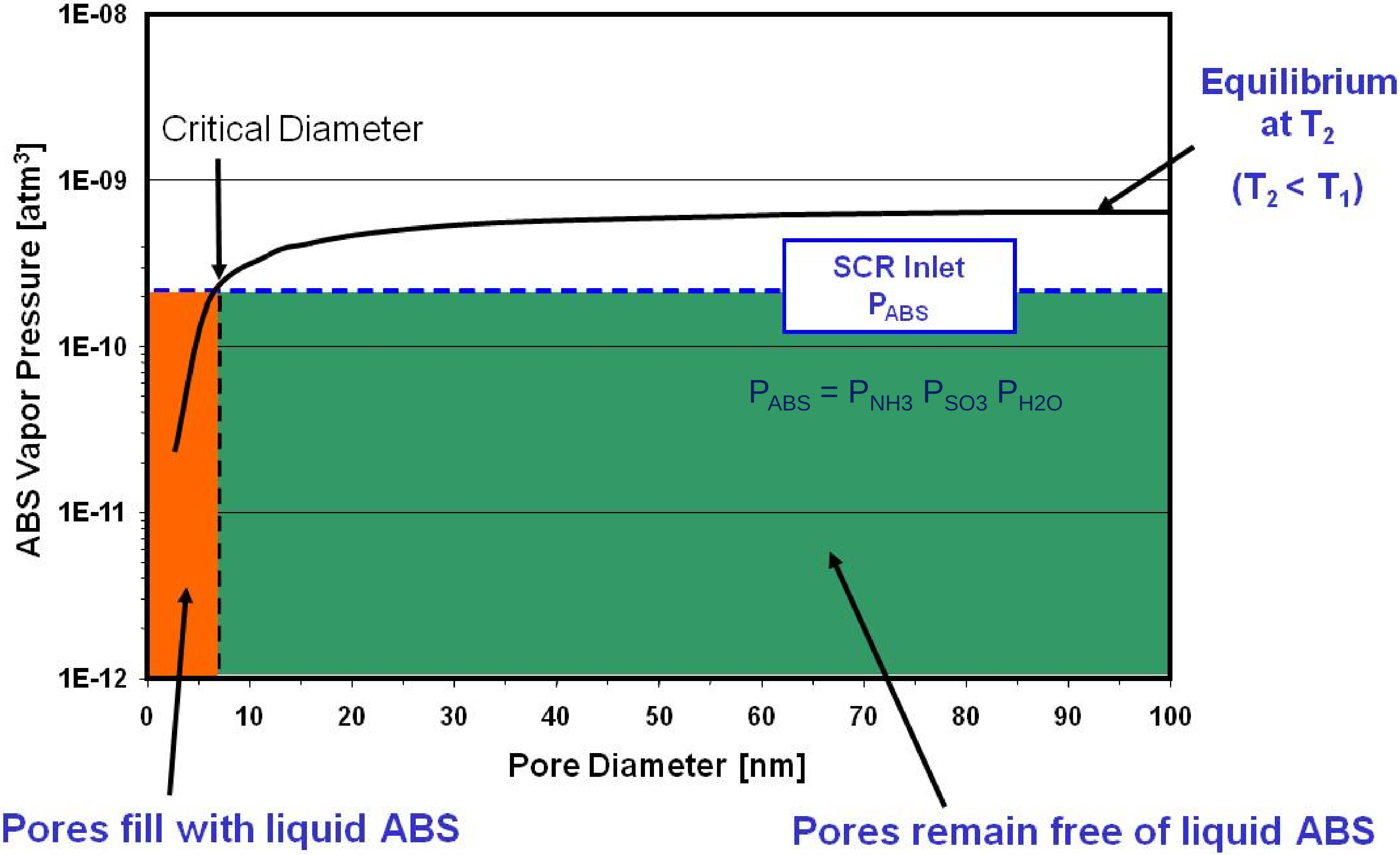
Bulk Phase ABS Dewpoint



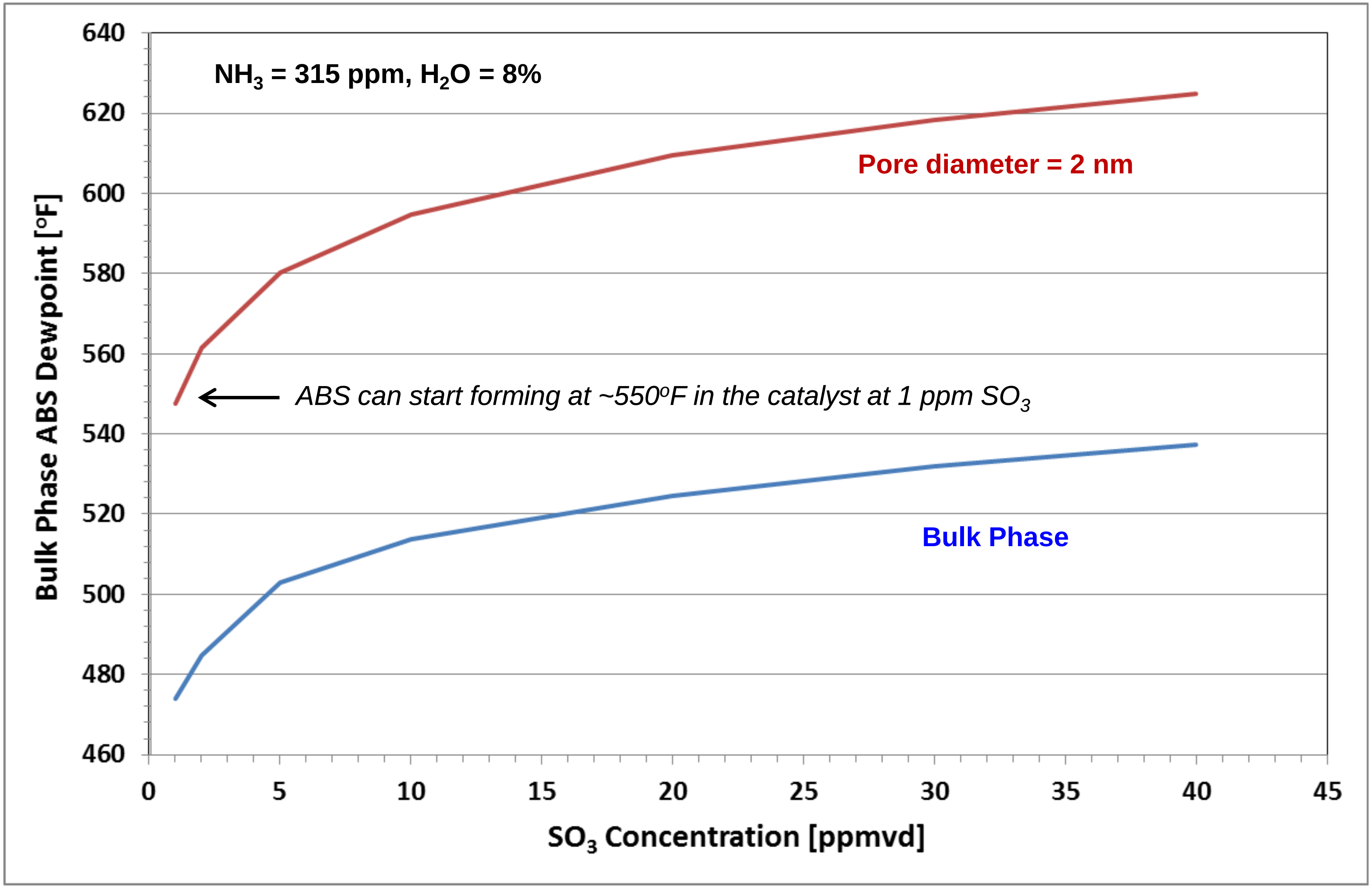
Pore Size Effect



Pore Size Effect

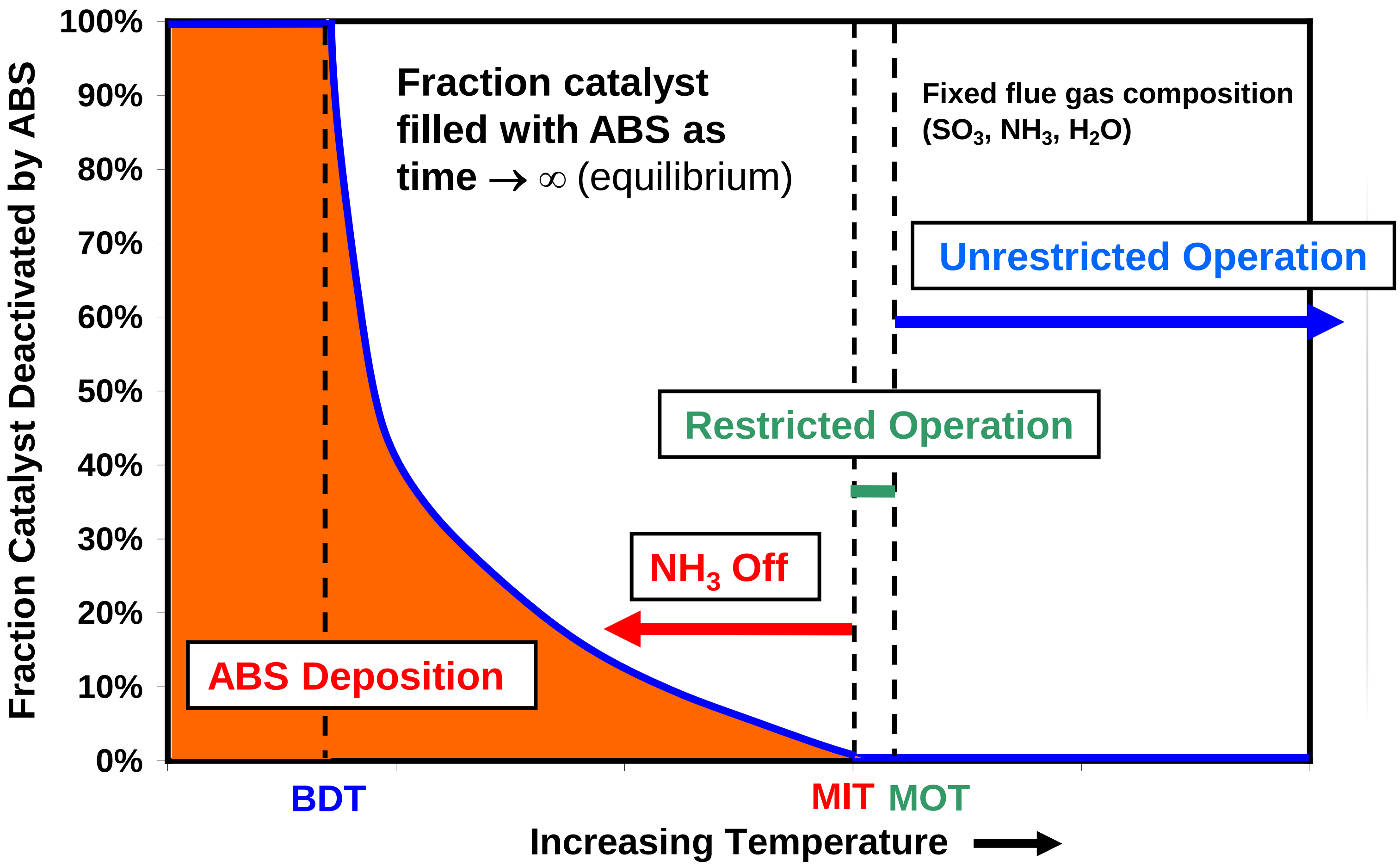


ABS Dewpoint Increase



Basic Approach

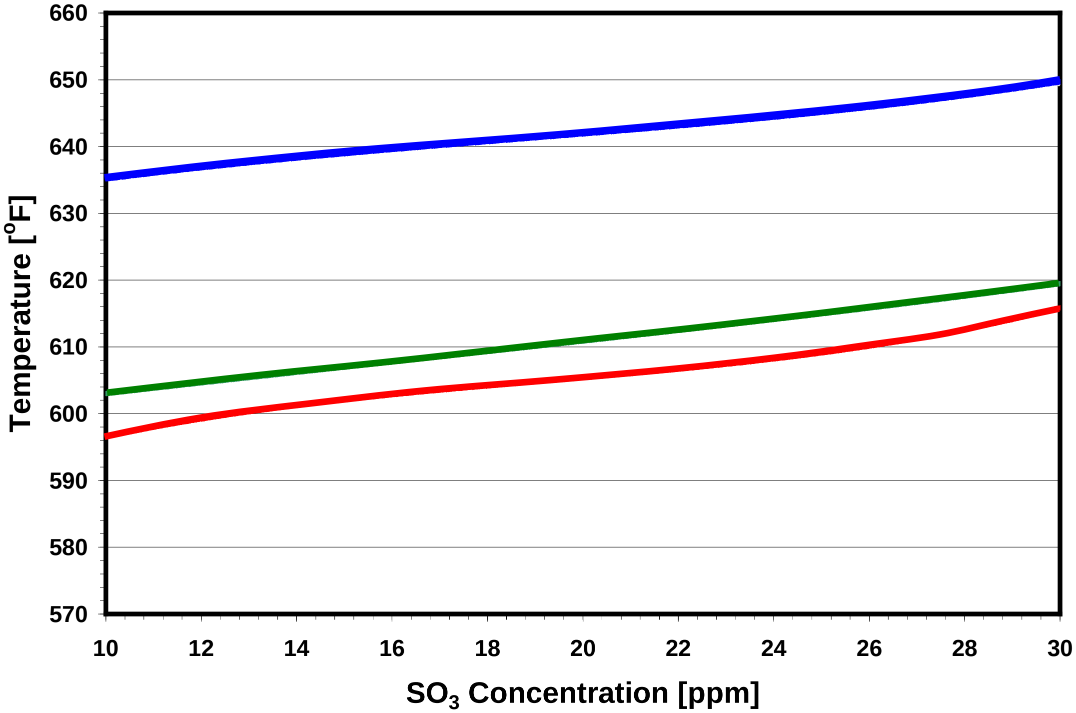
Avoids ABS Deposition



Cormetech "Tmin" Design Strategy

"Basic Approach":

- Avoids ABS deposition on the catalyst
- No catalyst margin added for ABS-induced deactivation



RT = recovery temperature

MOT = minimum operating T

MIT = minimum injection T for NH_3

Basic Approach

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Simple operating recommendations

- Temperatures (MIT, MOT, RT)
- Time allowances

Protects catalyst life

- Eliminates ABS as a source of deactivation

Reduces impact of transient emissions

- Minimizes SO_3 and NH_3 spikes during heating transient

Drivers

For Expanded Low Temperature SCR Operation

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Maintenance

- Condenser cleaning
- Fan / boiler water feed pump outages
- Mills out of service

Load cycling of coal-fired boilers

- Night and weekend operation
- Shoulder seasons
- Increased power production by gas turbines, renewables
- Efficiency: no longer wanting to use economizer bypass
- Operating unit on gas/ maintaining and maintaining compliance when switching to coal

Load cycling durations can vary

- Overnight or Weekend
- Newer: No time limit (∞)

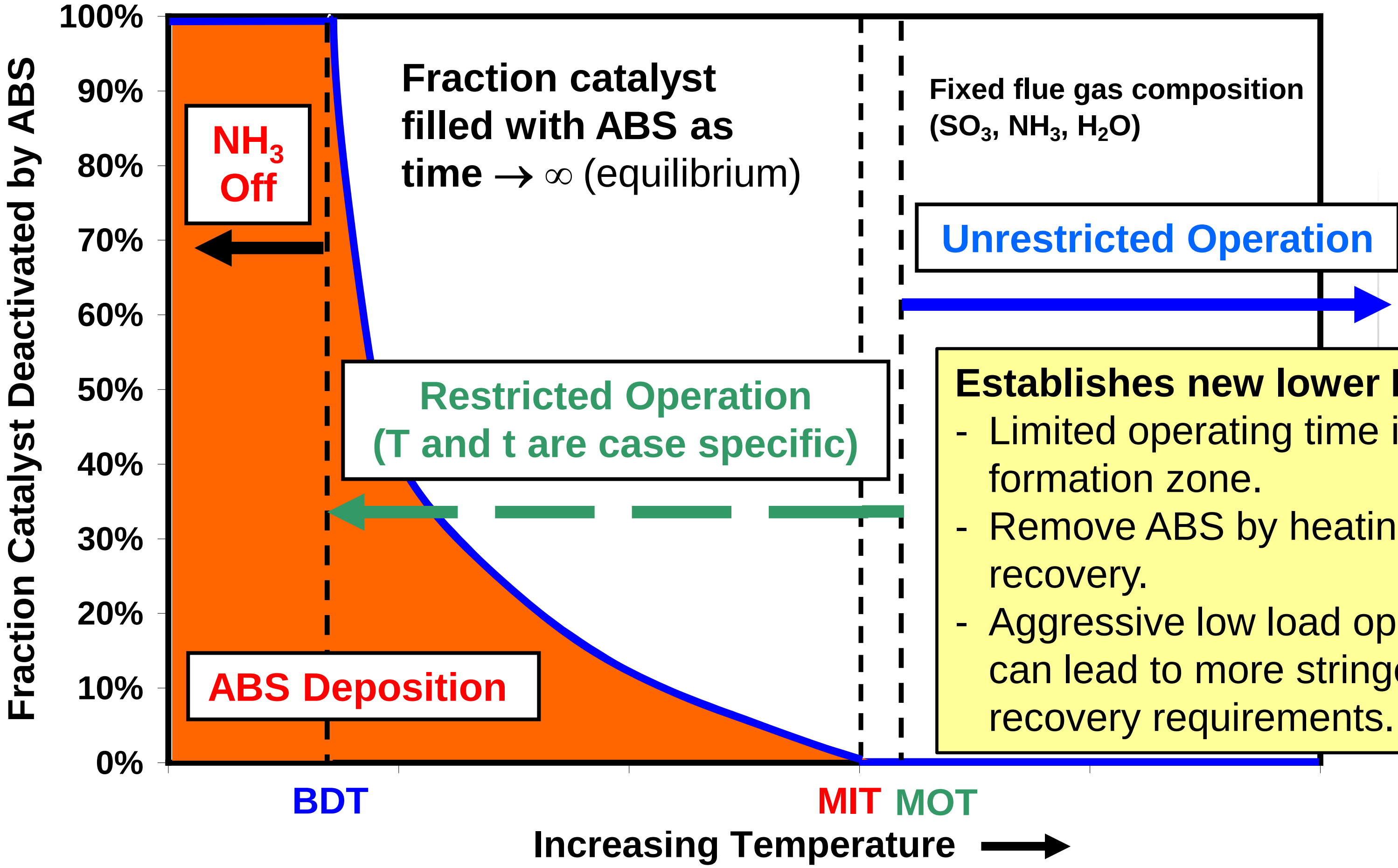
Minimize NOx emissions as much as possible with no dispatch limitations.

Cormetech Tmin Design Strategy

- **"Enhanced Approach":**
  - **Operate down toward the bulk ABS dew point**
    - **Allow controlled amount of ABS deposition and deactivation**
    - **Recover catalyst potential by reheating above recovery temperature**
  - **Increases flexibility to manage emissions at low load**
    - Requires understanding unit's operation and catalyst's response at both full and low load conditions
      - **Catalyst:**
        - » DeNOx kinetics, ABS deposition/removal kinetics, ABS thermo
      - **Unit:**
        - » Temperature, flue gas flow rate, flue gas composition
    - Case specific evaluation is necessary

Enhanced Approach

Manages ABS Deposition in Catalyst



Establishes new lower MIT

- Limited operating time in formation zone.
- Remove ABS by heating recovery.
- Aggressive low load operation can lead to more stringent recovery requirements.

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18 years of field operating experience

2004: first application in full-size boiler (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 the Power-Gen International Conference, 2006

2005: TVA implemented Enhanced Approach across SCR fleet

Bertole, C.J., Pritchard, S., Giles, J., SCR Operation at Low Flue Gas Temperature, presented at the Power-Gen International Conference, 2006

Currently used in 60+ boilers (multiple users)

Catalyst deactivation rates from field audits have been consistent with fuels fired: no additional deactivation from ABS observed

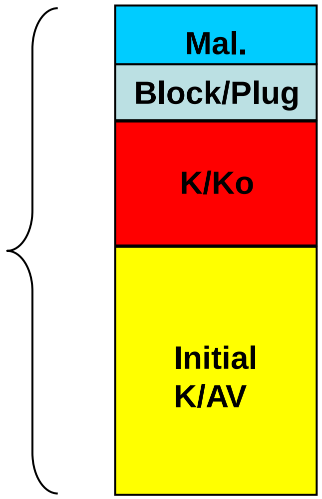
Cormetech's Toolbox

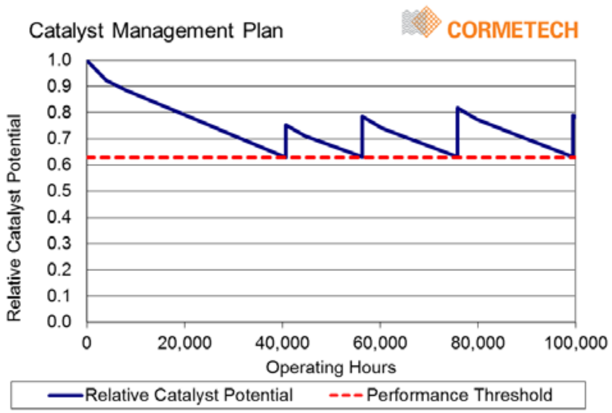
Applying the Enhanced Approach

- **Models for engineering analysis**
  - Thermodynamic and kinetic model
  - Transient deactivation and recovery model
    - Incorporates thermodynamics (ABS equilibrium) and kinetics in dynamic model
    - Predicts DeNOx, SO_3, and NH_3 transient responses
  - Evaluate the feasibility of multiple desired operating scenarios
  - The impact of SO_3 mitigation additives on catalyst ABS response
- **Lab validation testing**
  - Characterize catalyst and/or DSI material for model baselining
  - Verify modeling output
  - Large testing database (model development and experience)
- **Field implementation**

Design Considerations

Total
K/AV in
X layers





- **MR = 1 equation → K/AV = - ln (1 – DeNOx)**
- **For low load and recovery conditions:**

Transient K/AV must be ≥ K/AV required to meet DeNOx, NH_3 slip

- Thus: $K/K_{full\ load}$ must be ≥ $AV/AV_{full\ load}$

Also, need to consider transient SO_3 & NH_3 spikes during recovery

During Low Load Operation

- **As boiler load is reduced:**
  - Flue gas temperature and flow rate both decrease
  - Impact: DeNOx K ↓ (bad) and AV ↓ (good)
- **DeNOx K decreases due to:**
  - Kinetic effect of temperature
  - ABS pore plugging and deactivation
- **DeNOx and NH_3 slip performance cannot be met if:**
  - $K/K_{full\ load}$ slips below $AV/AV_{full\ load}$
  - **Alternatives:**
    - 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

Case – Wide Ranging Fuels Mix

SO_2 @ ppm 800-3200 ; SO_3 @ 8-32 ppm

Average NOx levels

Ask:

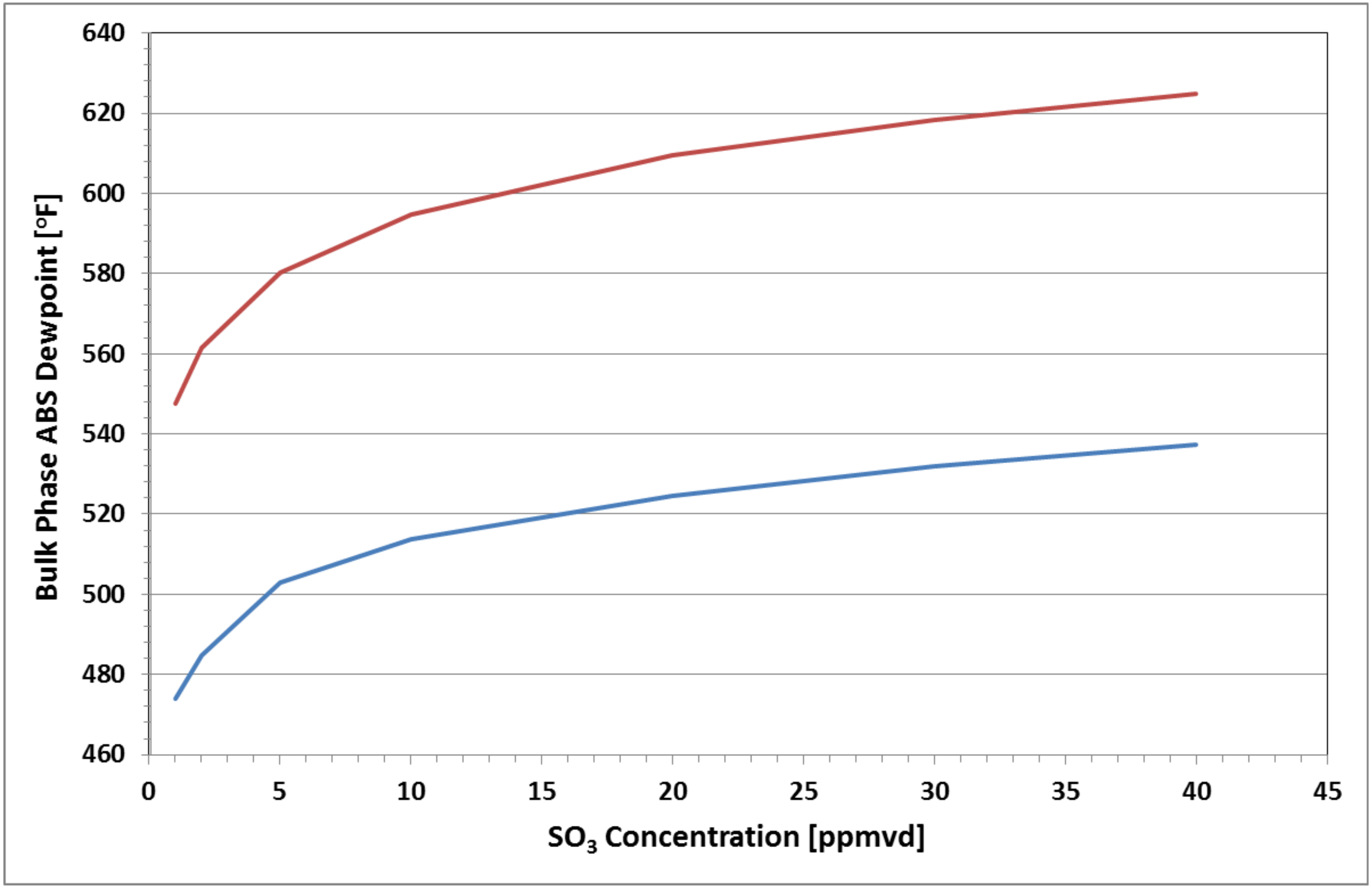
Lowest operating load possible

No time limit at lower load

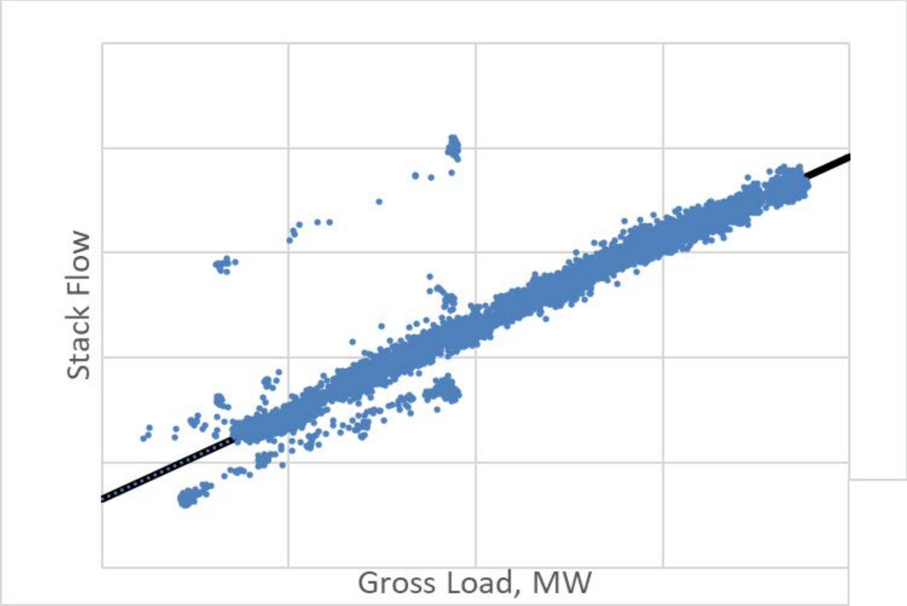
Curtailment of NOx reduction likely – that's 'OK'

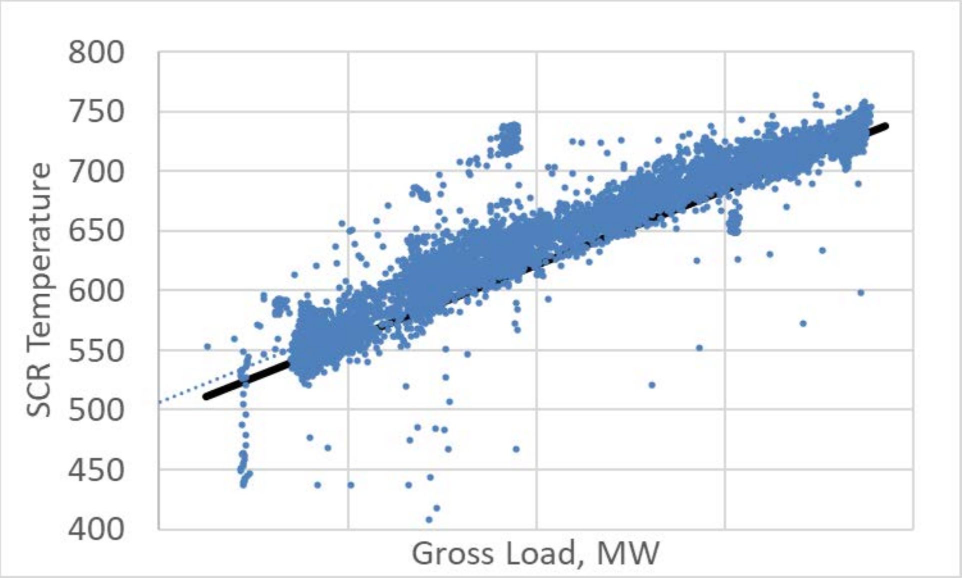
Maintain ammonia slip ≤ 2

Case - Wide Ranging Fuels Mix Operating Data

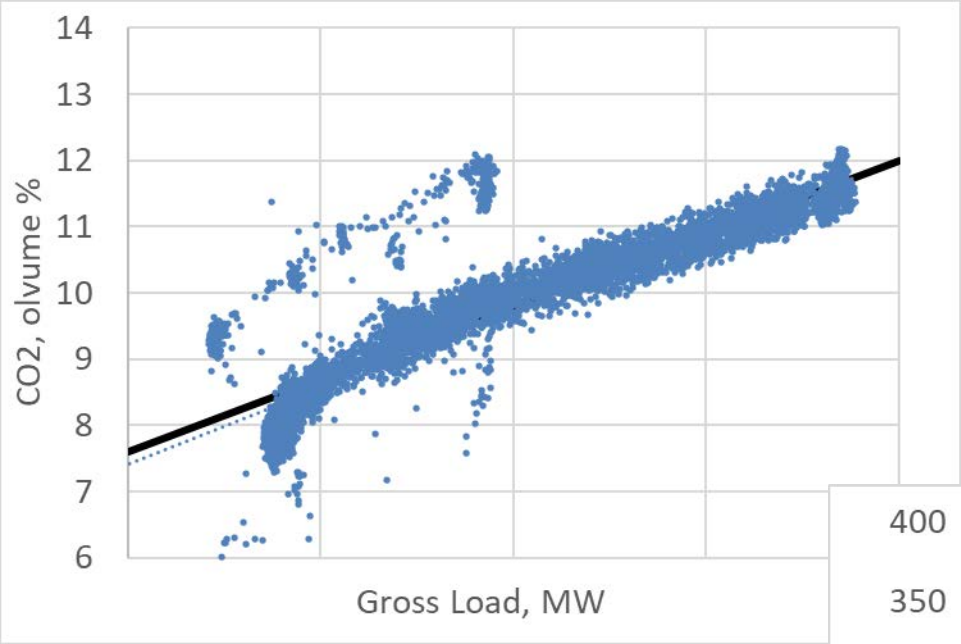


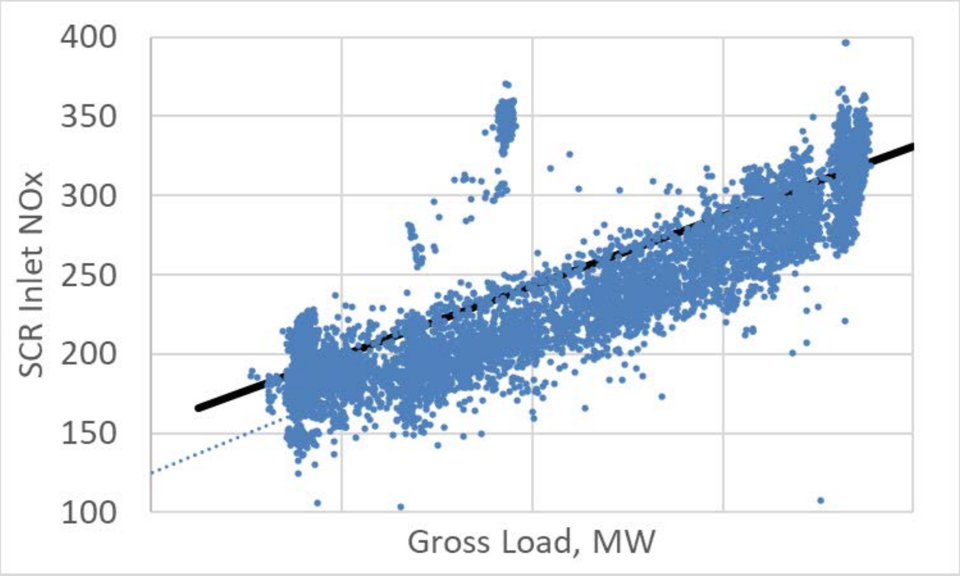
Case - Wide Ranging Fuels Mix Operating Data





Case - Wide Ranging Fuels Mix Operating Data





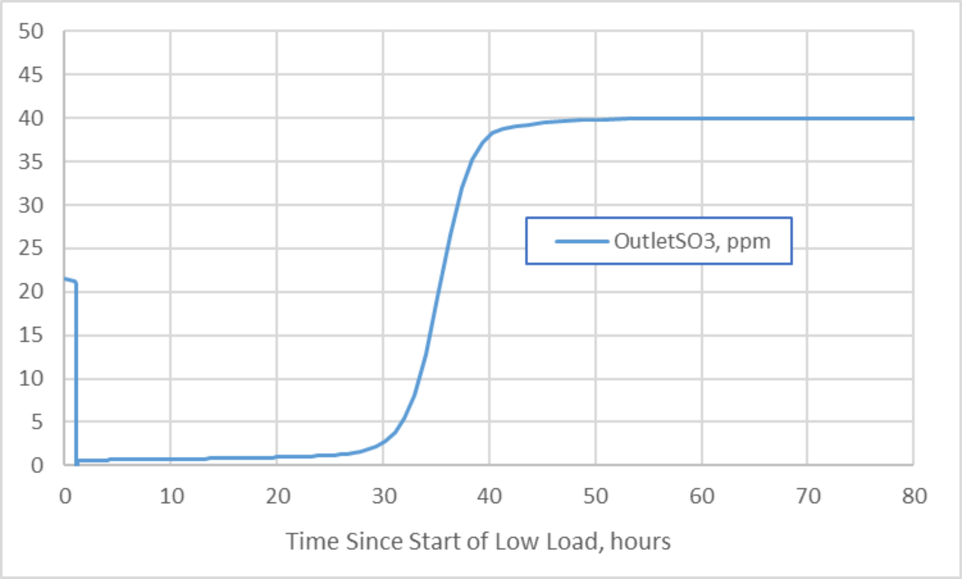
Case - Wide Ranging Fuels Mix Model Inputs

Parameter	Low Loads for Study				Above ABS formation	Full load
	low low	low	mid	high		
Gross MW	130	200	275	350	400	800
NOx Inlet based on ref load	184	199	216	232	243	307
Temp based on ref load F	536	558	582	605	621.0	748
Temp based on ref load C	280	292	305	318	327.2	398
Relative AV $[AV/AV_{FL}]$	0.302	0.375	0.453	0.531	0.531	1
O2, Vol% wet	7.0	6.3	5.7	5.2	4.9	3
O2, Vol% dry	7.6	6.9	6.3	5.7	5.4	3.3
H2O, Vol%	8.0	8.2	8.5	8.7	8.5	8.3

	Range of Constituent for Study			
SO2	800	1600	2400	3200
SO3	8	16	24	32

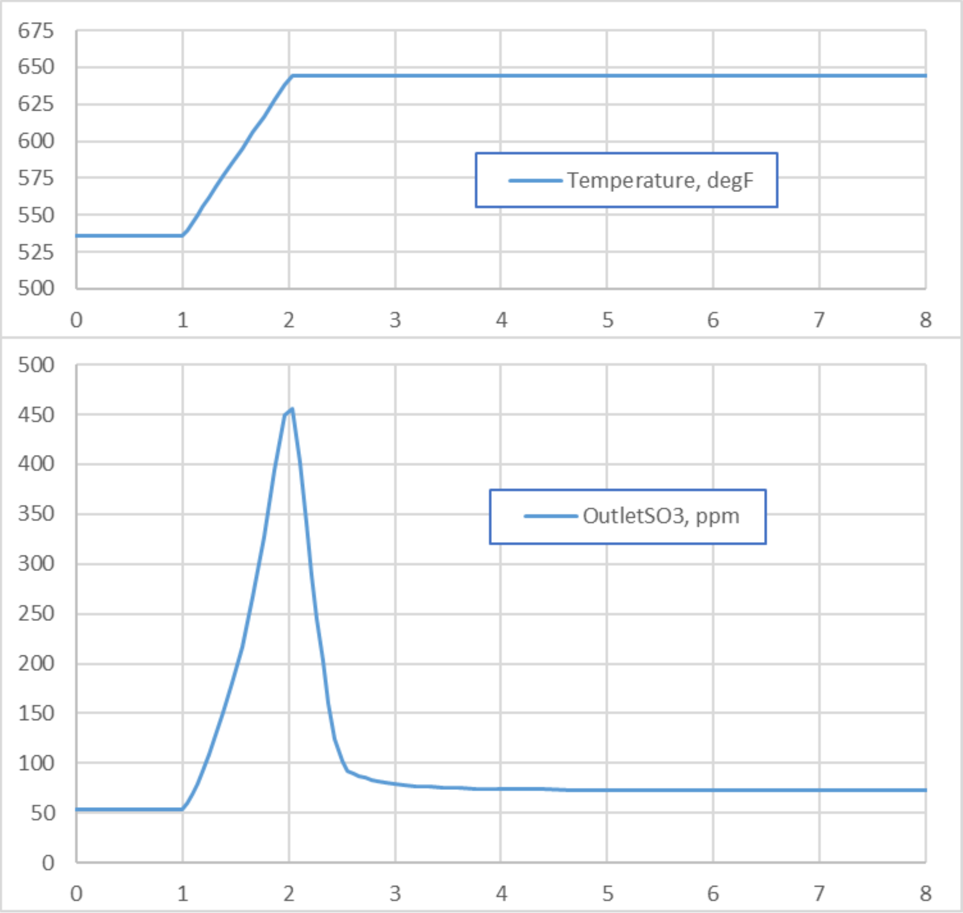
Case - Wide Ranging Fuels Mix Model Results

SCR Outlet SO_3 at start of Low Load
(Case: 2400 ppm SO_2, 536 ^oF)



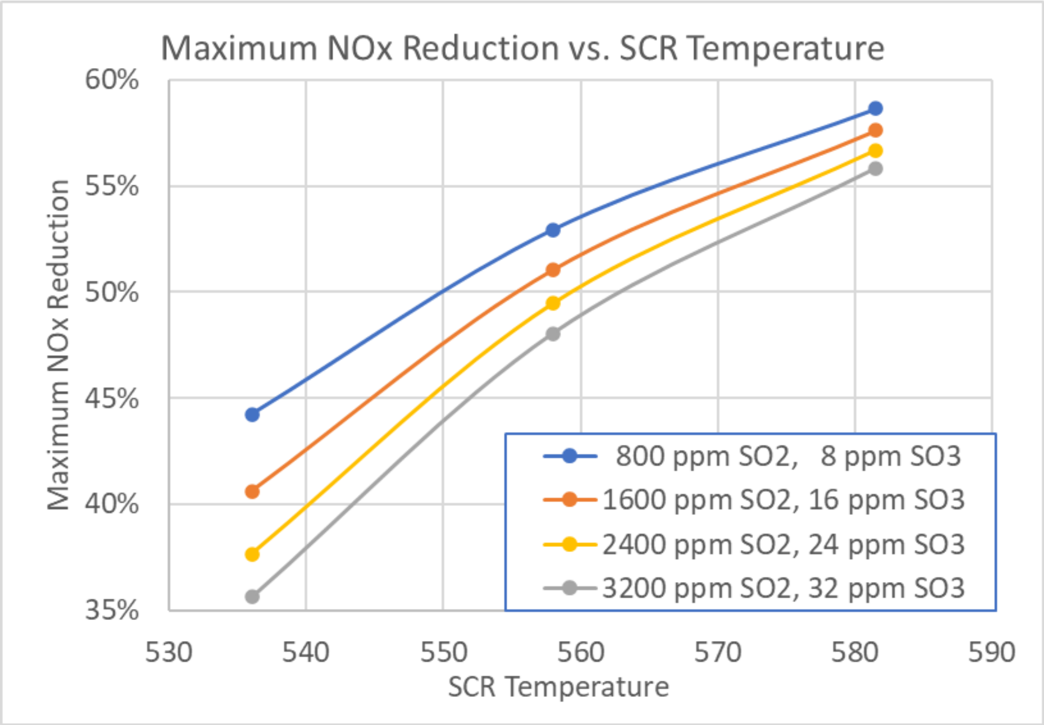
Case - Wide Ranging Fuels Mix Model Results

SCR Outlet SO_3 during recovery to full load (Case: 3200 ppm SO_2, 536 ^oF)



Case - Wide Ranging Fuels Mix Model Results

Limited NOx reduction allowance



Case - Wide Ranging Fuels Mix Implementation

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- *When SO_3 at SCR inlet is very high, then operating below ~550-580 becomes an issue and lower deNOx is likely the solution.*
- *Slowing the load ramp rate during recovery will reduce the magnitude of the SO_3 spike.*
- *Reducing the NH_3 injection rate and/or lowering the DeNOx efficiency during the first few hours of recovery will reduce the potential to form ABS in downstream equipment*

Case - PRB

SO_2 @ 200 ppm; SO_3 @ 2 ppm

Higher NOx levels

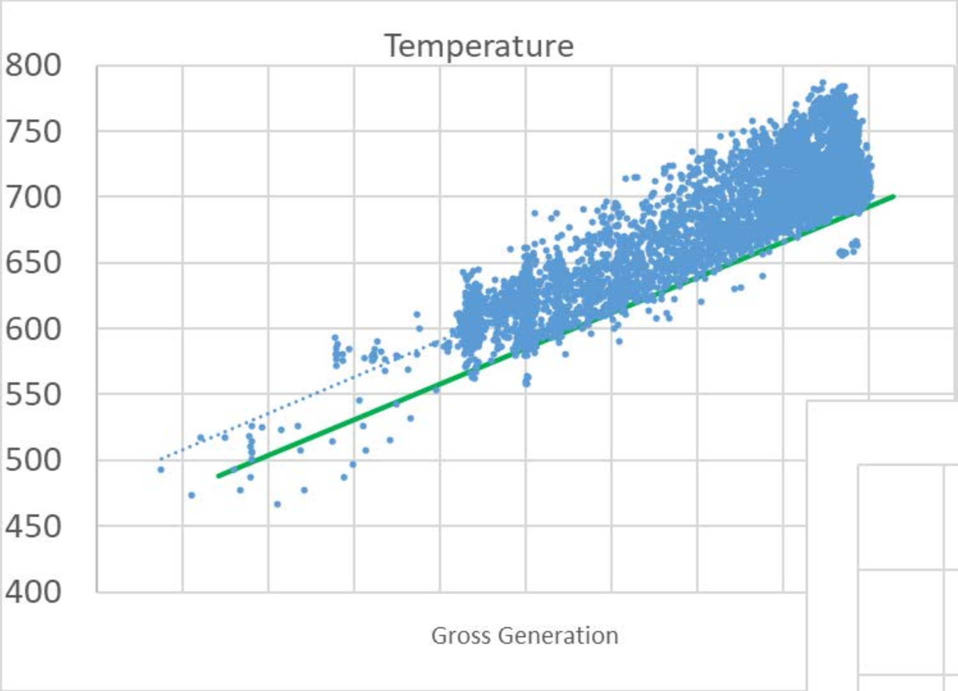
Ask:

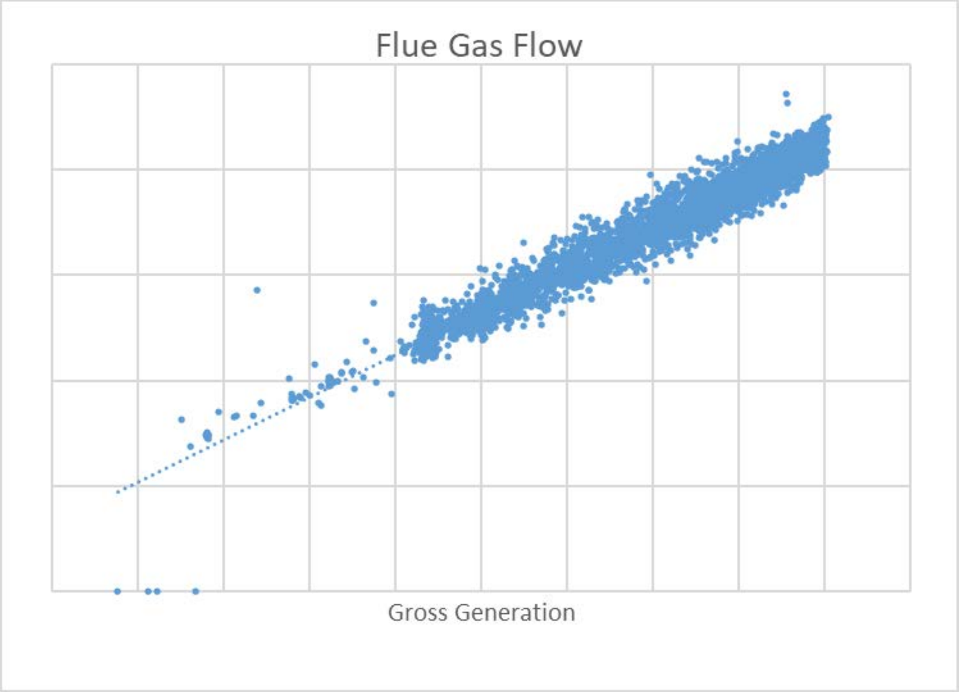
Lowest operating load possible

No time limit at lower load

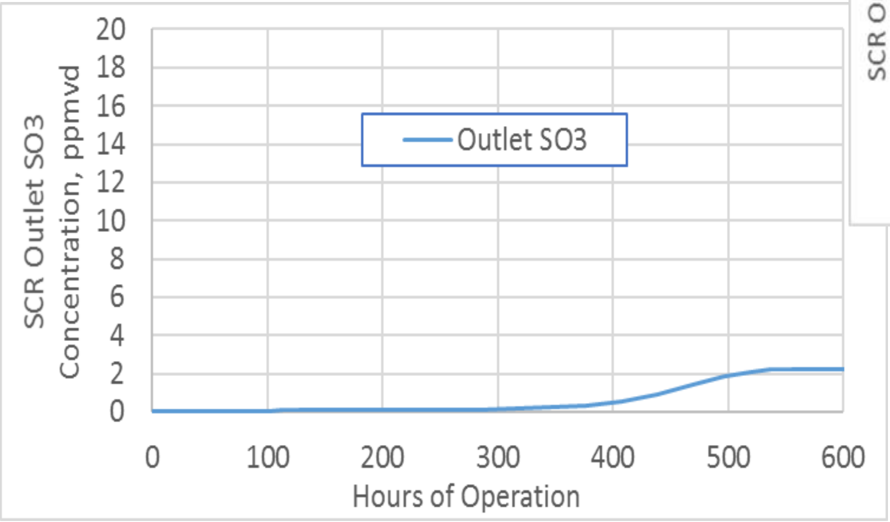
If possible, no curtailment of NOx reduction

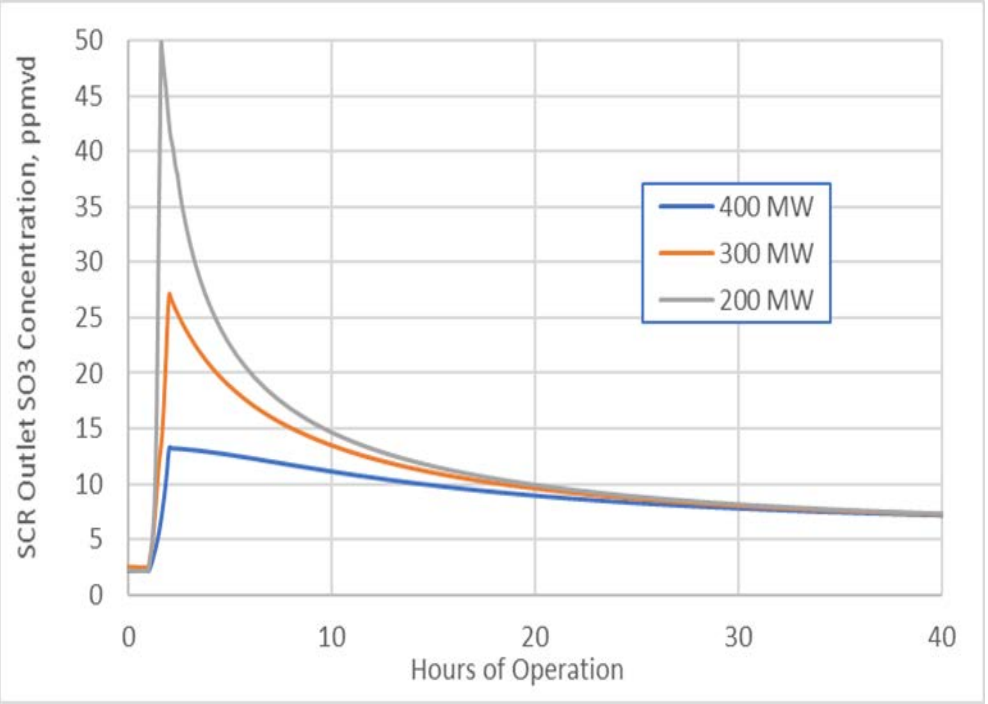
Case - PRB
Operating Data





Case - PRB
Model Results

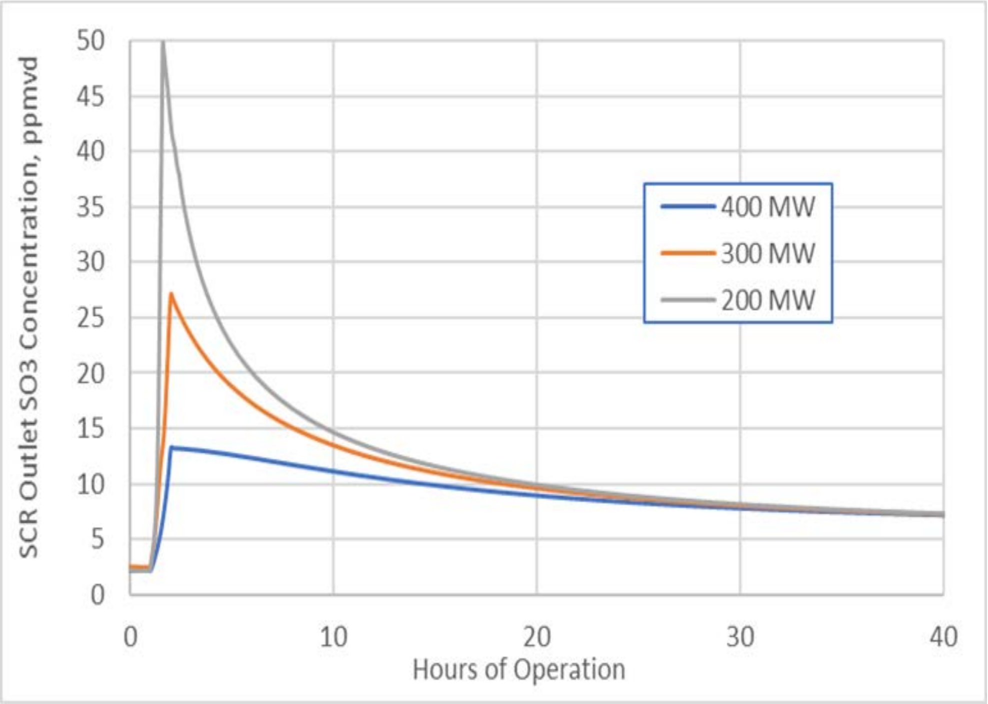


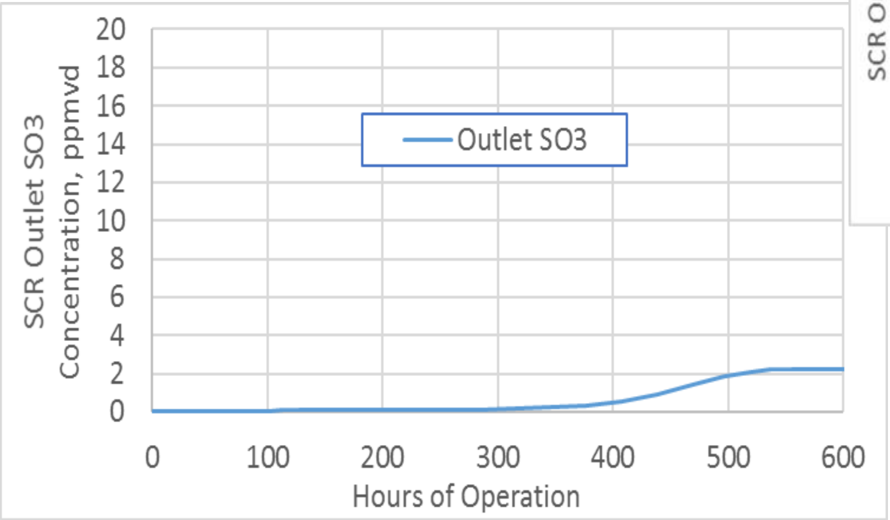


Case - PRB Implementation

Continuous operation to average bulk temperature of 530 F with up to 4 hours down to 518 F before ammonia shut off

Implement over several stages





Case – NG Operation Coal Application

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SO_2 @ 5 ppm; SO_3 @ 0.1 ppm

NOx levels – Review as a part of study

Ask:

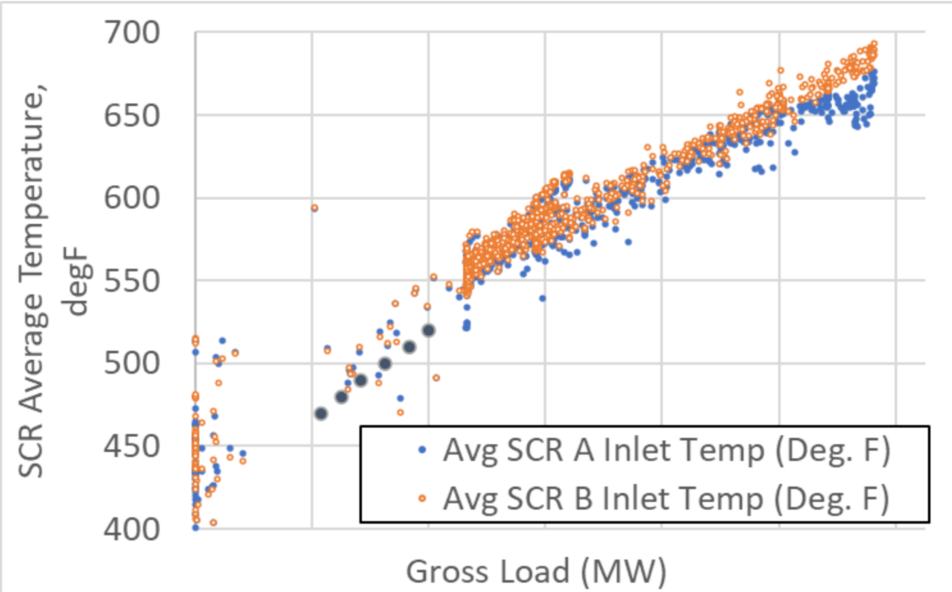
Lowest operating load (temperature) possible on natural gas

No time limit at lower load

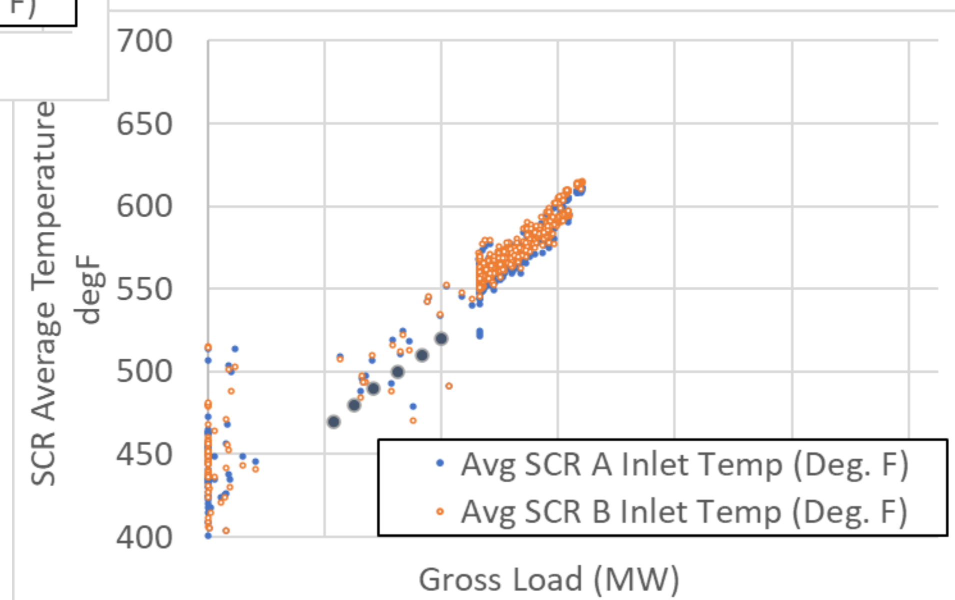
If possible, no curtailment of NOx reduction

Verify previous lab model results and REMOVE previous time

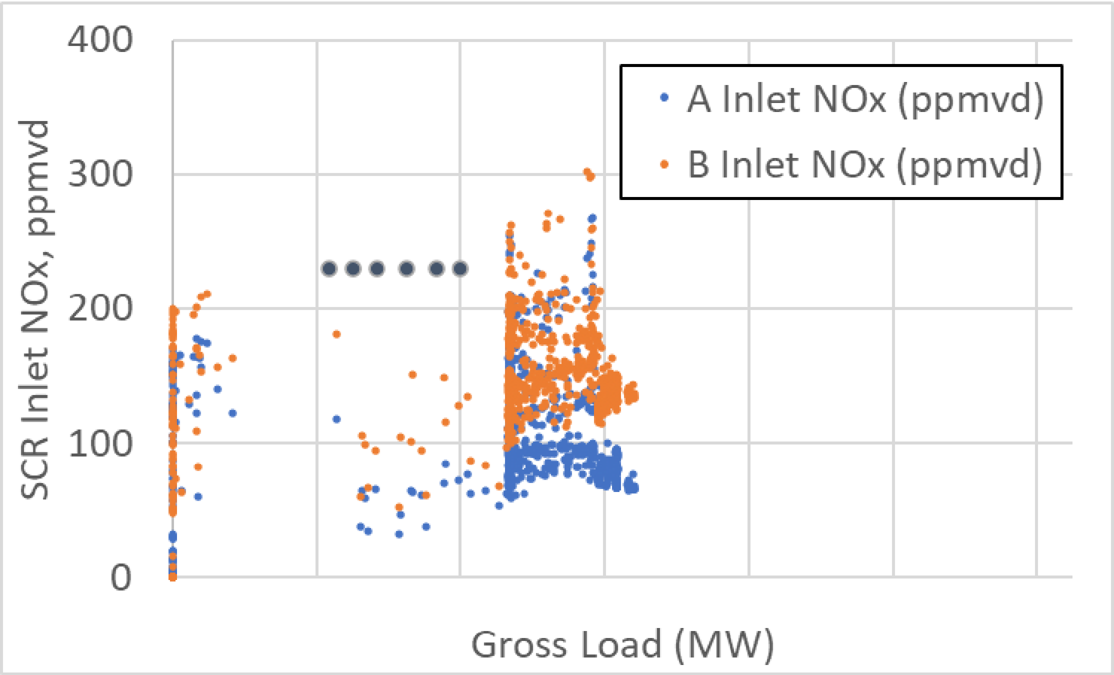
Case - NG Operation Coal Application Operating Data



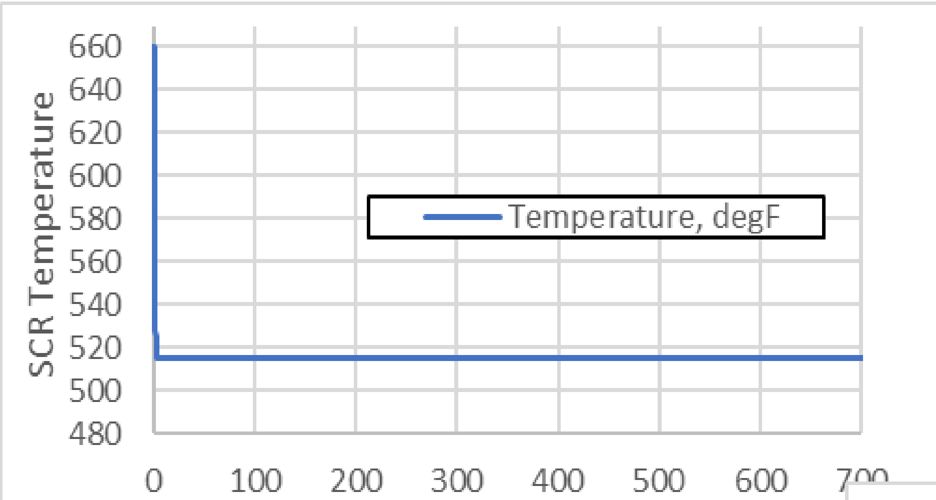
Natural Gas only operation

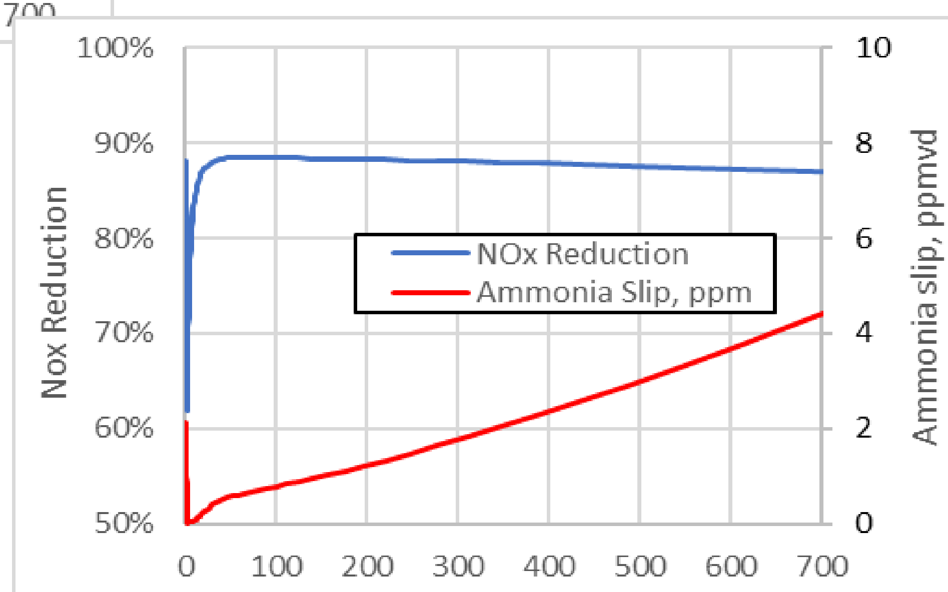


Case - NG Operation Coal Application Operating Data



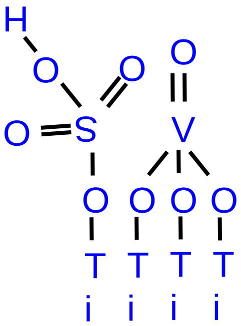
Case - NG Operation Coal Application Model Results

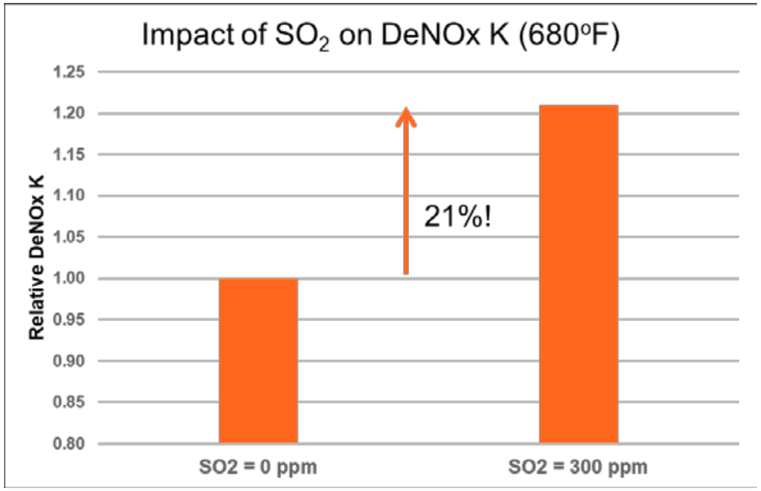




Adsorbed Sulfate Promotes Activity

- Adsorbed sulfate: good for DeNOx activity.
  - Formed by SO_3 adsorption on catalyst.
  - Sulfate enhances surface acidity → promotes NH_3 adsorption.



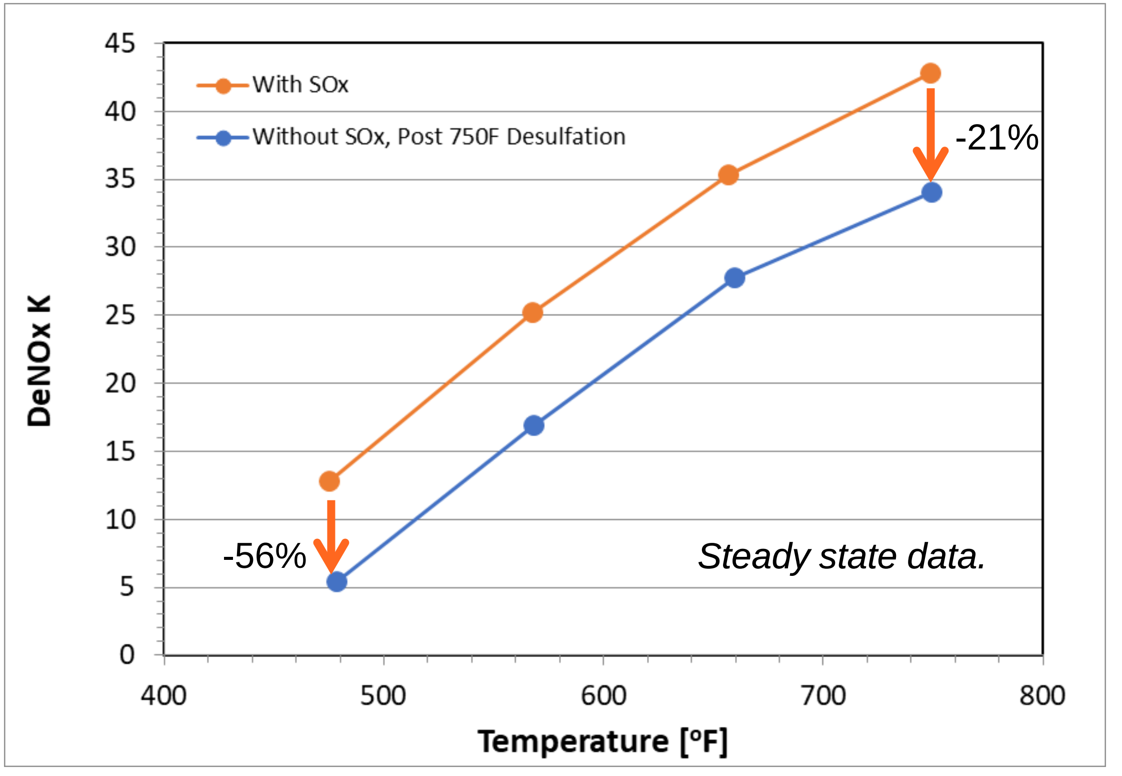


SO_3 Impact on DeNOx Activity: Sulfated vs. De-Sulfated Catalyst States

Data set for two "states":

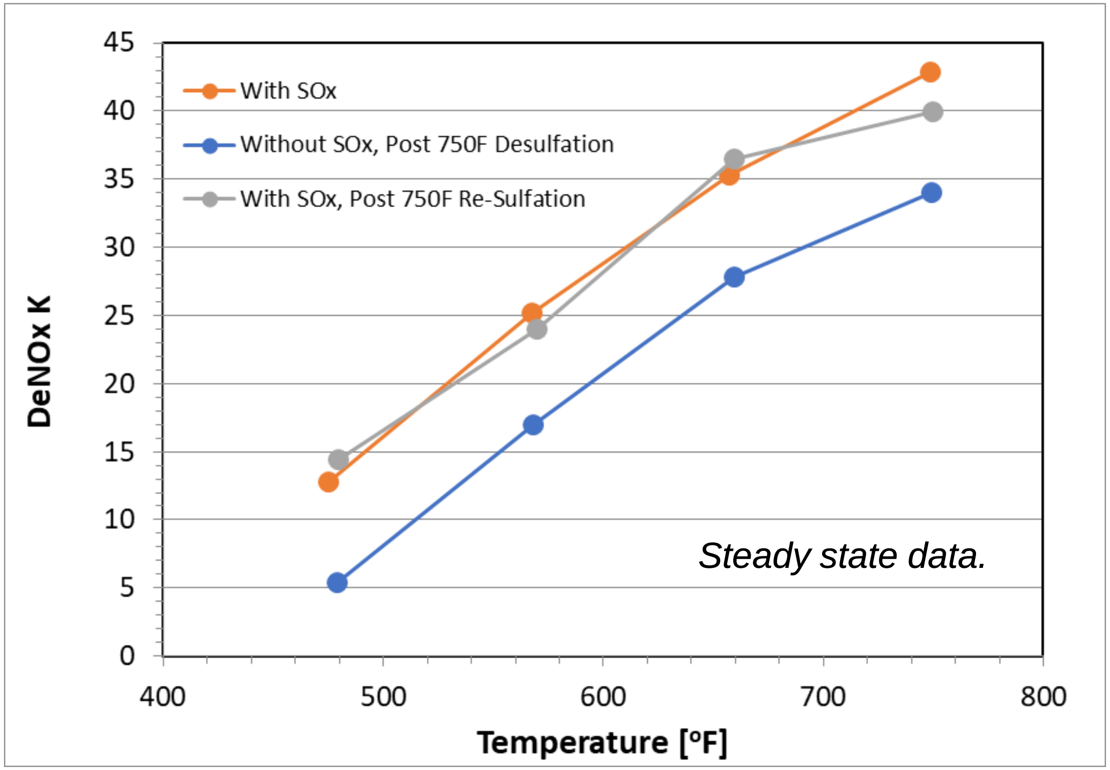
- After 750ºF aging "with SOx" to fully sulfate.
- After 750ºF soak "without SOx" to fully desulfate.

Sulfate has a big impact!



SO_3 Impact on DeNOx Activity: Impact of Re-Sulfation

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



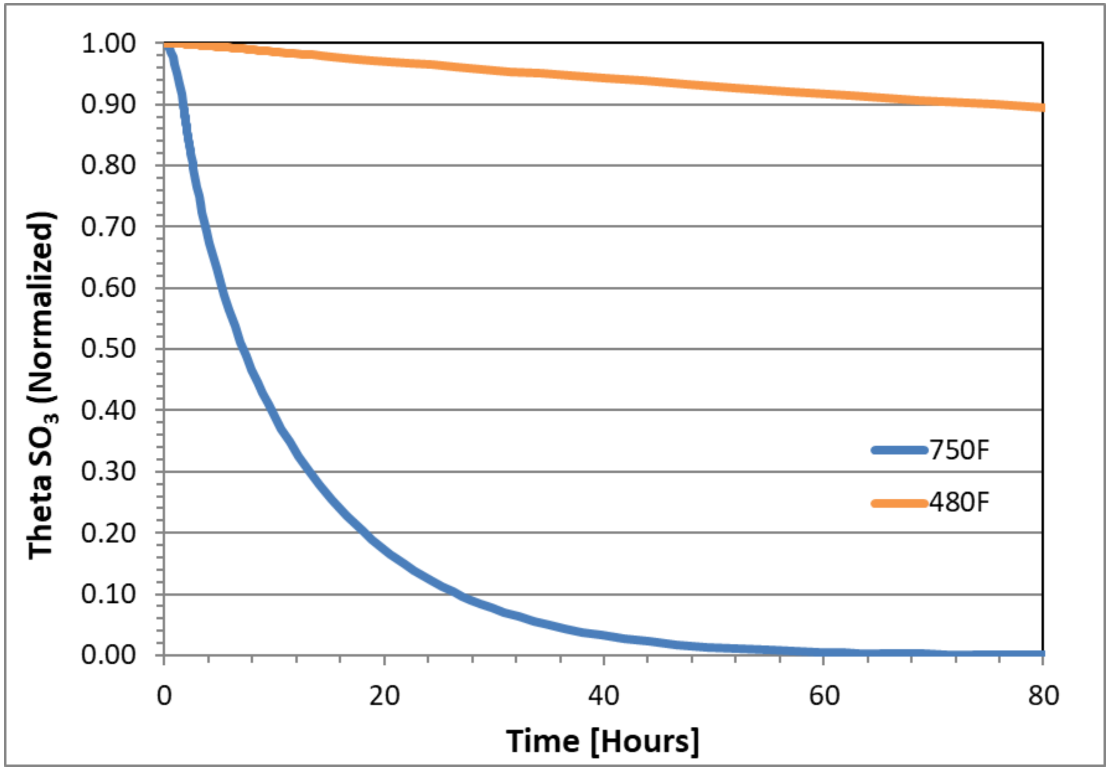
Simulation: Sulfate Desorption Transient
Fully Sulfated State → No SOx Flow

At 750ºF:

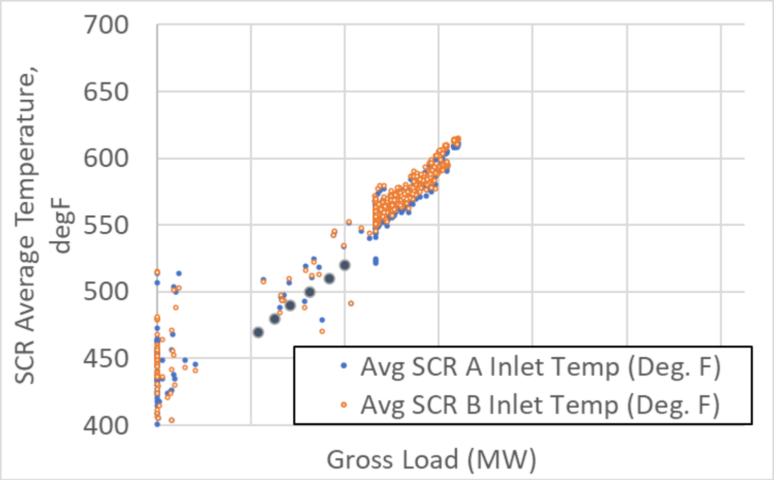
Sulfate desorption is fast.

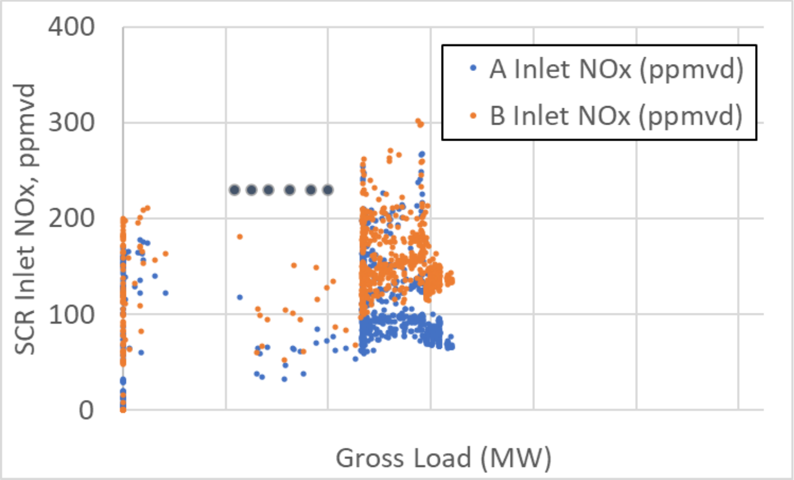
At 480ºF:

Sulfate desorption is slow.



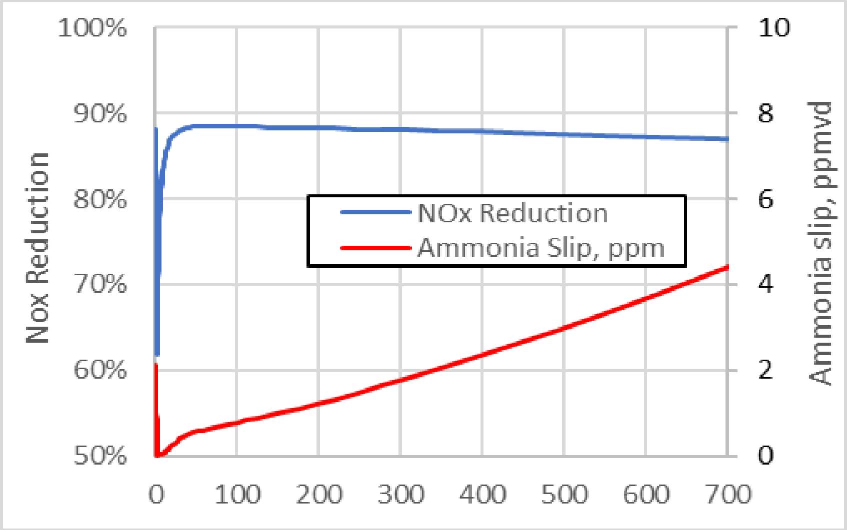
Case - NG Operation Coal Application Implementation



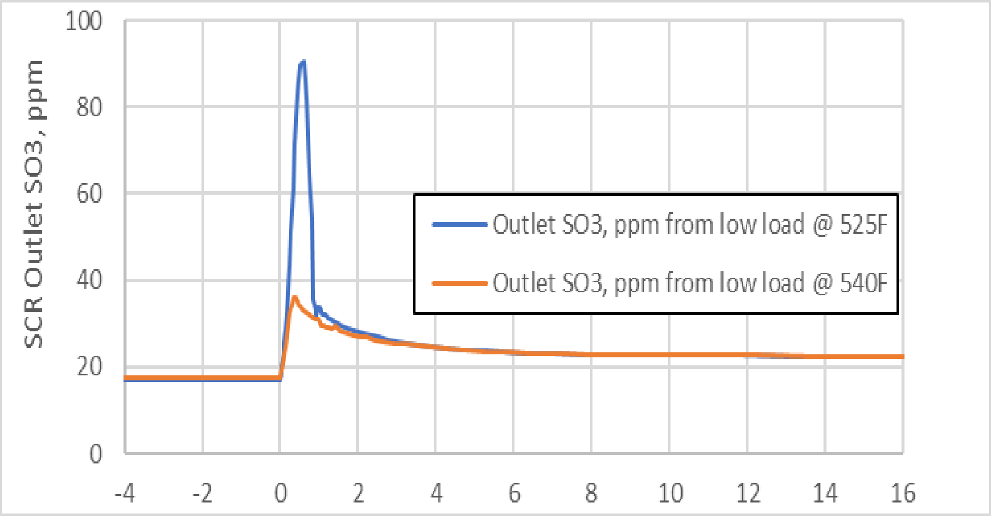


'Risk Mitigation'

- *NOx reduction may be well below model*
- *Unit must operation 1+ week on NG only*
- *Temporary slip levels likely not an issue*
- *Recovery is quick when returning to coal*



Case – Revalidation of Lab Study



Case - Flat SCR Temperature Profile

SO_2 @ 1600 ppm; SO_3 @ 16 ppm

Low to medium NOx levels

86% DeNOx at full load, 74% DeNOx at low load

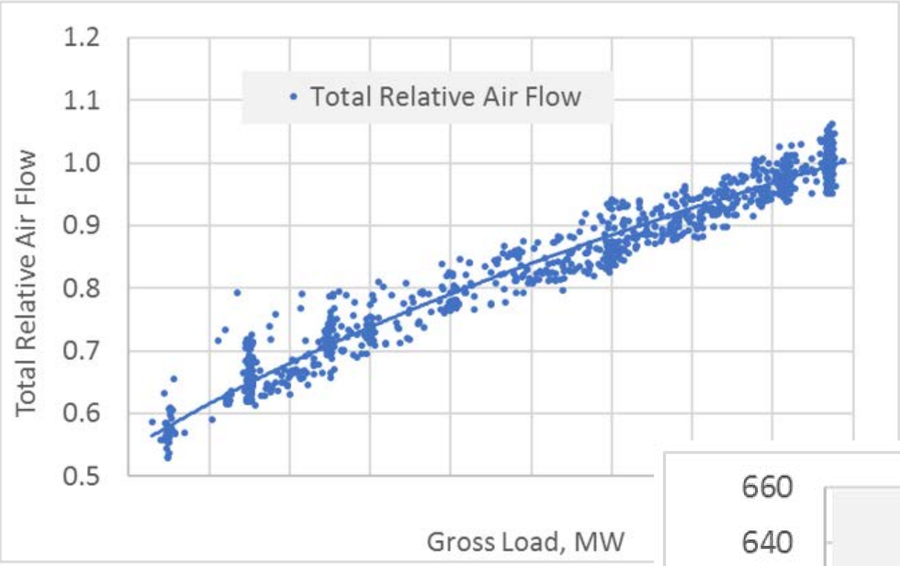
Ask:

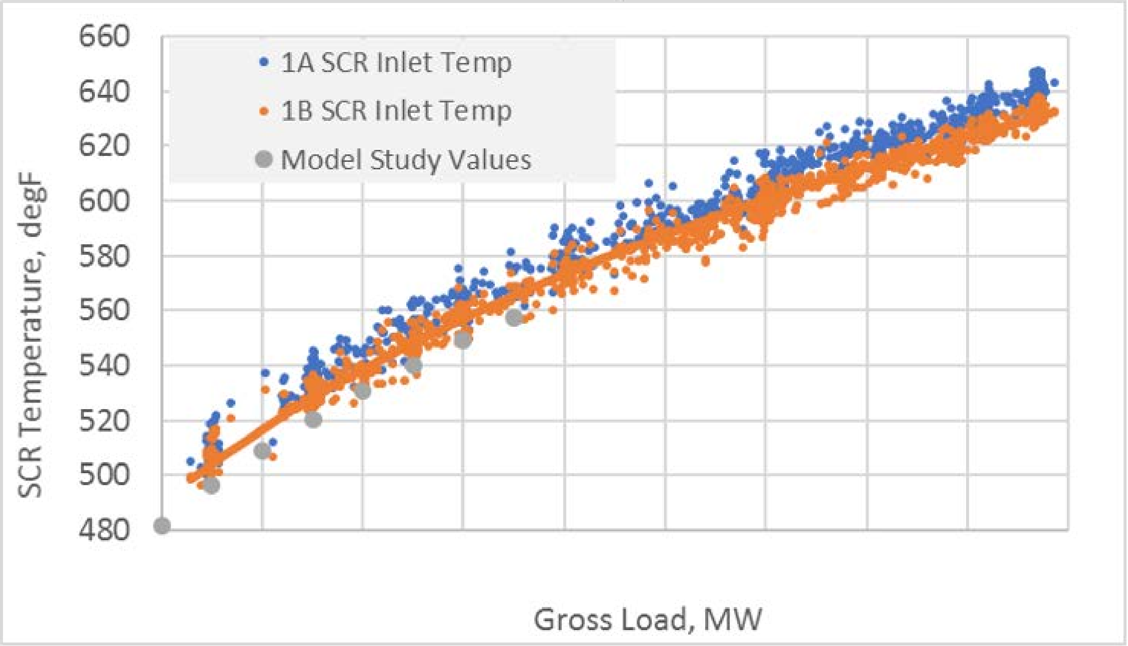
Lowest operating load possible

No time limit at lower load

If possible, no curtailment of NOx reduction

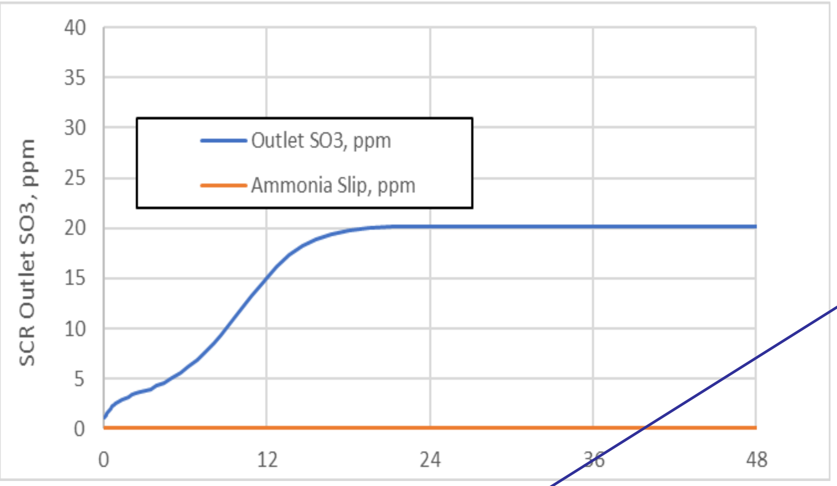
Case – Flat SCR Temperature Profile Operating Data

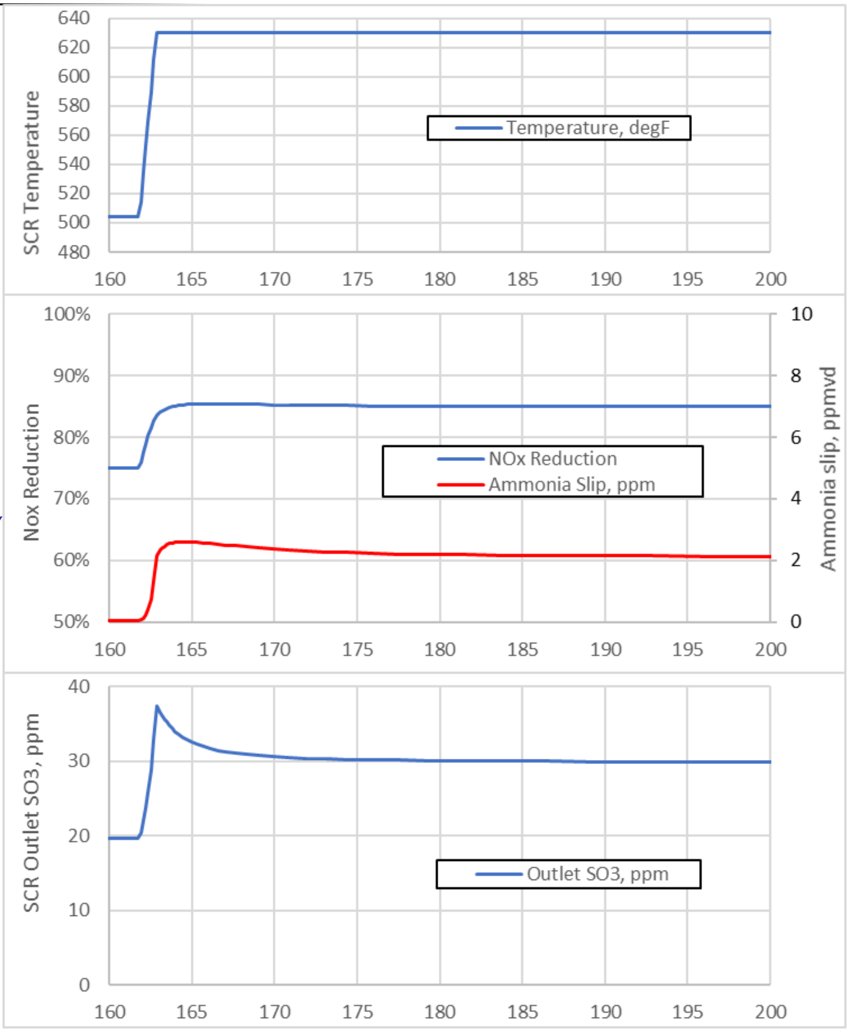




Case - Flat SCR Temperature Profile Model Results

SCR Outlet SO_3 & NH_3 at start of Low Load (Average Temperature 510 ^oF)

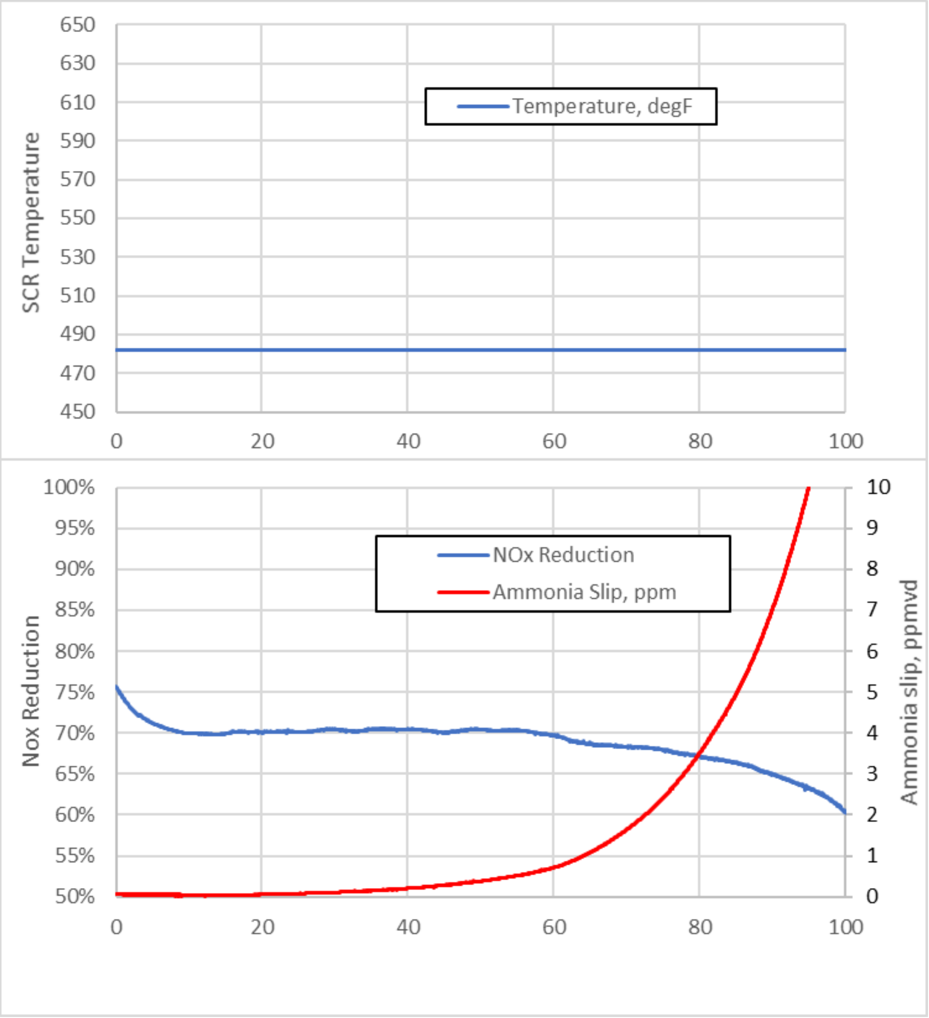




SCR DeNOx, ammonia slip and outlet SO_3 at end of Low Load (Average Temperature 510 ^oF)

Case - Flat SCR Temperature Profile Model Results

SCR Outlet SO_3 & NH_3 at start of Low Load
(Average Temperature 487 ºF)



Case - Flat SCR Temperature Profile Implementation

Continuous operation to average bulk temperature of 510 F

Watch for:

- *Higher SO_3 Levels*
- *NH_3 levels (that is, inlet NO_x and $deNO_x$ levels).*

Recovery Phase Considerations

- **Potential for slow K recovery (lag K/AV requirement)**
  - Options (if slow): reduce DeNOx efficiency, increase NH_3 slip, reduce amount of time at low load condition
- **Potential for increased SO_3 and NH_3 slip emissions**
  - Due to ABS elimination
  - Minimize NH_3 slip spike by reducing NH_3 flow rate, and NH_3 and SO_3 spikes by lowering temperature ramp rate
  - In practice: SO_3 appears to be condensed in APH, limiting spike in stack emission
  - Focus on NH_3 slip control to avoid APH fouling

Summary

- **Enhanced Approach increases flexibility for meeting NOx reduction requirements at low load conditions**
- **Evaluate and balance**

  Plant operating needs

  Severity of low load condition

  Fuel (sulfur), temperature, length of time, extent of deactivation

  Capability for performance recovery upon return to full load

  Achievable temperature

  Rate of activity recovery

  Transient SO_3 and NH_3 emissions

- ❑ Engineering & modeling evaluation, lab validation testing (as necessary), and field implementation

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