Reinhold Environmental Ltd.

2007 NOx Round Table & Expo Presentation

February 5-6, 2007 in Cincinnati, OH

Low Flue Gas Temperature SCR Operation

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Presentation Overview

- **Background:**
  - Reaction Chemistry
  - Catalyst Design
- **Cormetech Tmin Design Strategy:**
  - Basic Approach
  - Enhanced Approach
- **Case Studies:**
  - Duke Energy Belews Creek Unit 2
  - Tennessee Valley Authority Fossil Units

Reaction Chemistry

- **NOx reduction**

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

- **SO_2 oxidation**

  $2SO_2 + O_2 \Rightarrow 2SO_3$

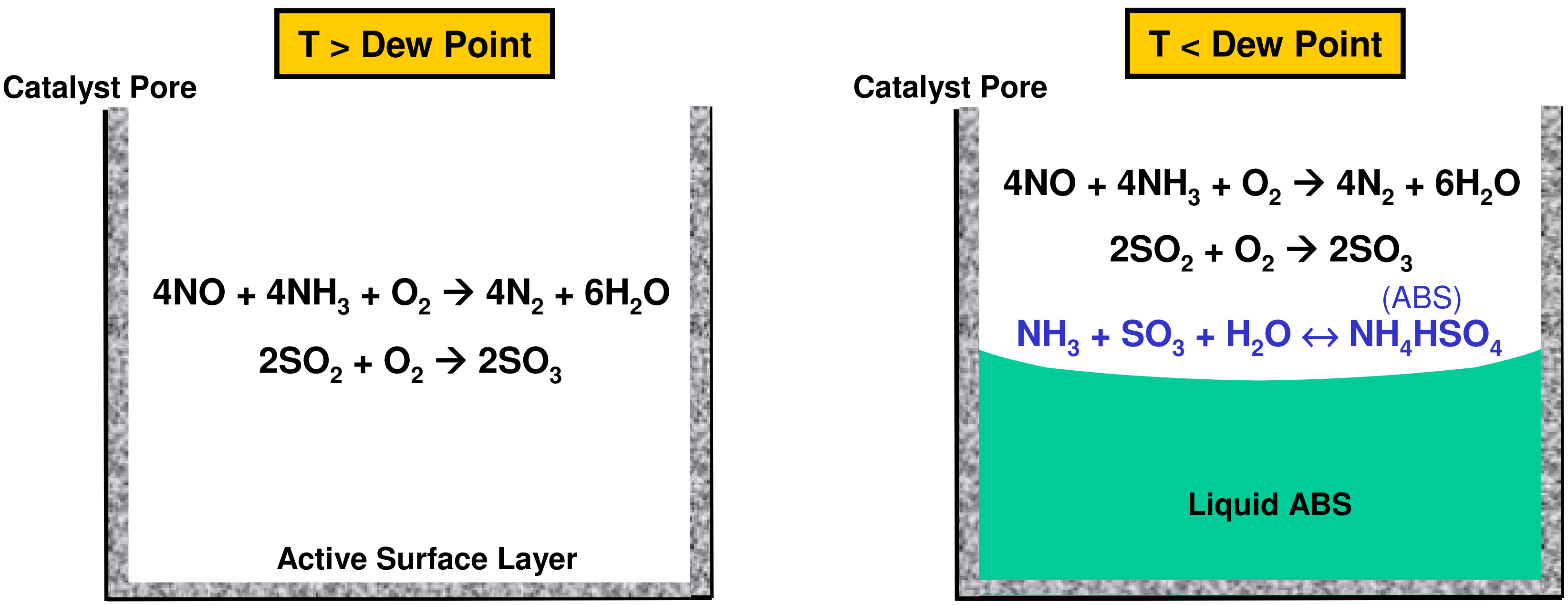
- **Salt formation at low temperature**

  $NH_{3(g)} + SO_{3(g)} + H_2O_{(g)} \Leftrightarrow NH_4HSO_{4(l)}$ *(ammonium bisulfate, ABS)*

  $2NH_{3(g)} + SO_{3(g)} + H_2O_{(g)} \Leftrightarrow (NH_4)_2SO_{4(s)}$ *(ammonium sulfate, AS)*

ABS Deposition Controls SCR Tmin

- ABS deactivates SCR catalyst by filling and/or blocking pores, inhibiting access to the catalyst's active sites
  - Effect is reversible: remove ABS by reheating above dew point

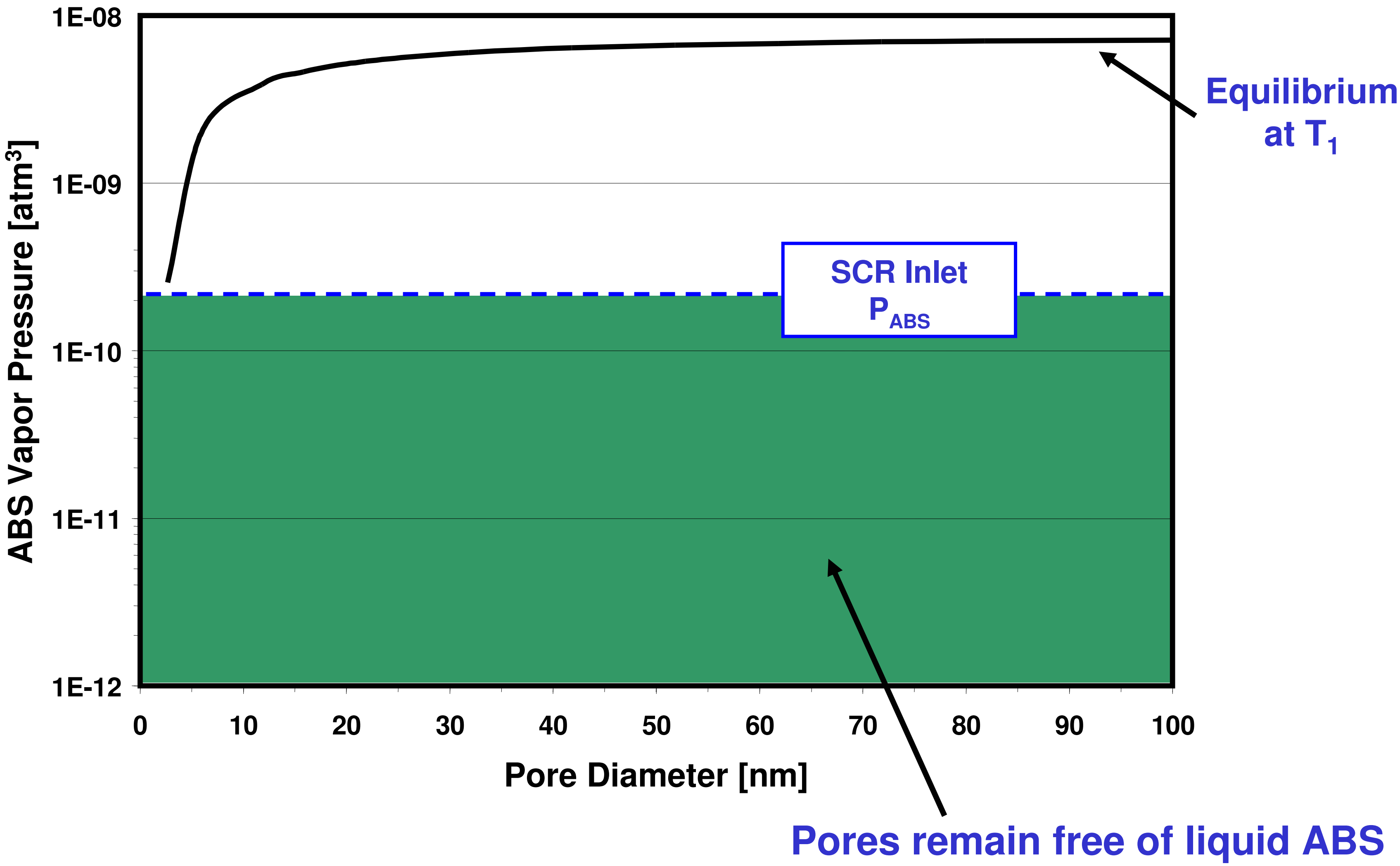


$$P_{ABS} = P_{NH3} P_{SO3} P_{H2O} = 1/K$$

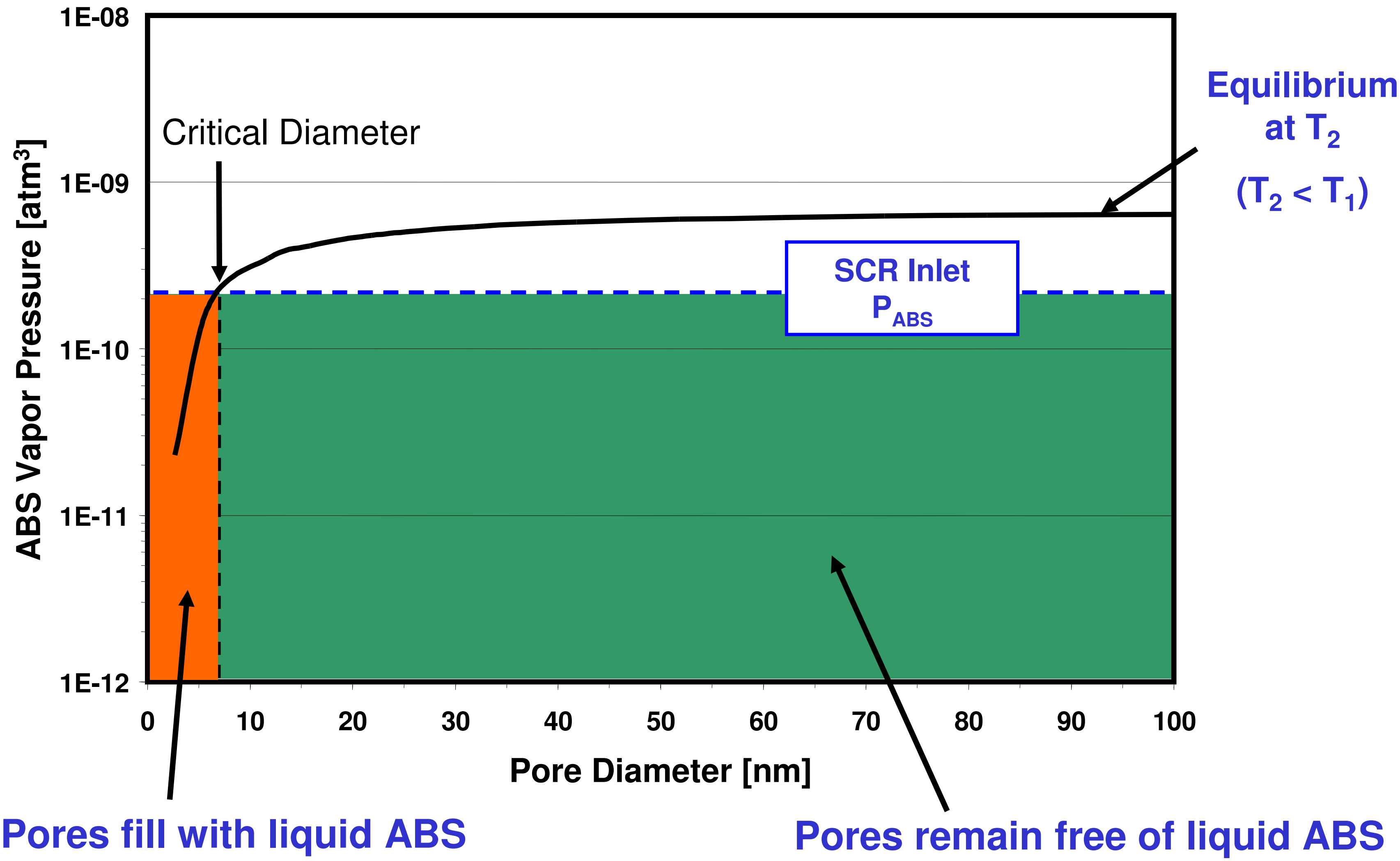
Capillary Condensation

- Liquid ABS forms in SCR catalyst pores above the bulk phase dew point temperature (BDT)
  - Thomson's theory of capillary condensation (Kelvin equation):
    - $\ln (P/P_{sat\ vap\ bulk\ liquid}) = -(2\ \sigma\ V_l) / (r\ R\ T)$
      - σ = ABS surface tension, V_l= ABS molar volume, R = gas constant, T = temperature, and r = pore radius
  - Smaller catalyst pores result in:
    - larger vapor pressure reduction of liquid ABS
    - higher ABS dew point → ABS formation at higher temperature

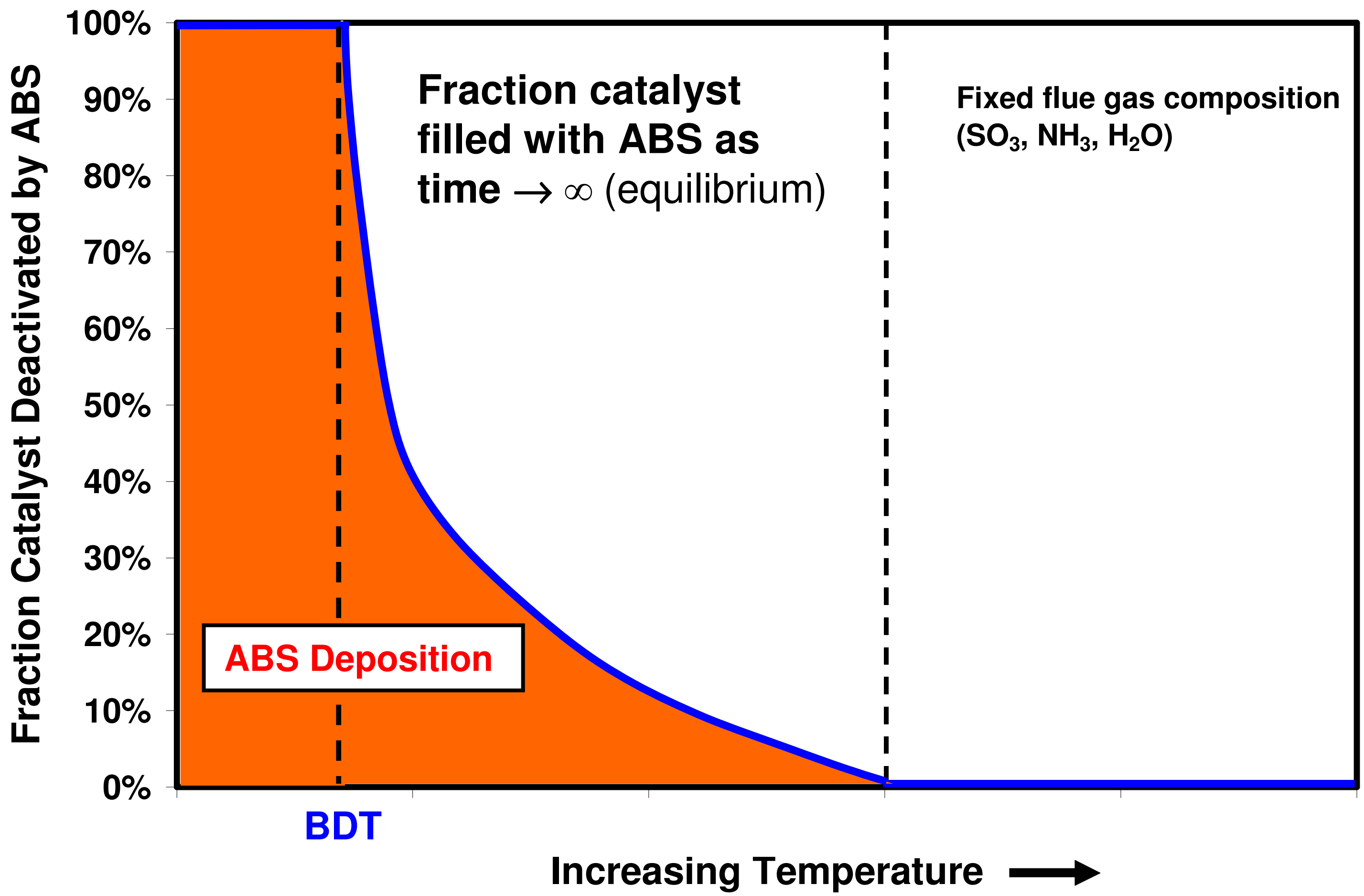
Effect of Pore Size on ABS Vapor Pressure



Effect of Pore Size on ABS Vapor Pressure



Impact of Temperature on ABS Formation



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Catalyst Design Refresher

1. **Determine minimum catalyst potential (K/AV)**
   - K/AV = f (NOx in, DeNOx, NH_3 slip)
   - K = f (temperature, gas composition, catalyst formulation)
   - formulation = f(SO_2 conversion)
   - AV = flow / (catalyst volume m^3 * Ap m^2/m^3)
2. **Select catalyst pitch (e.g., 7 mm, Ap = 539 m^2/m^3)**

K/AV → K, flow, pitch → **Initial volume**

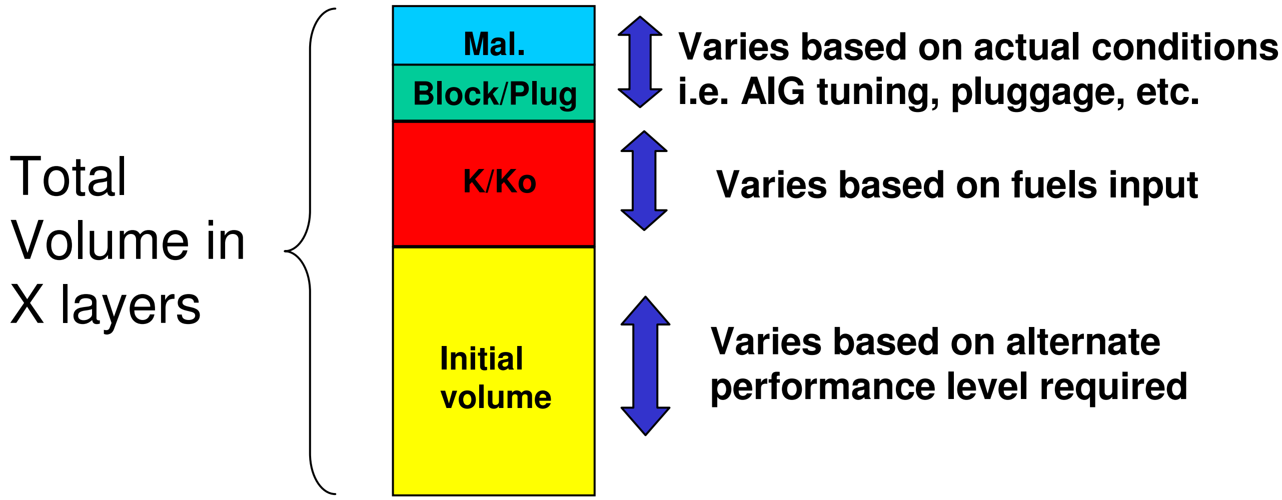
Catalyst Design, cont'd

3. Determine margin required for:

- Fuels (K/Ko) → life
- Blockage/ pluggage
- Maldistribution (NH_3/NOx, flow, temperature)

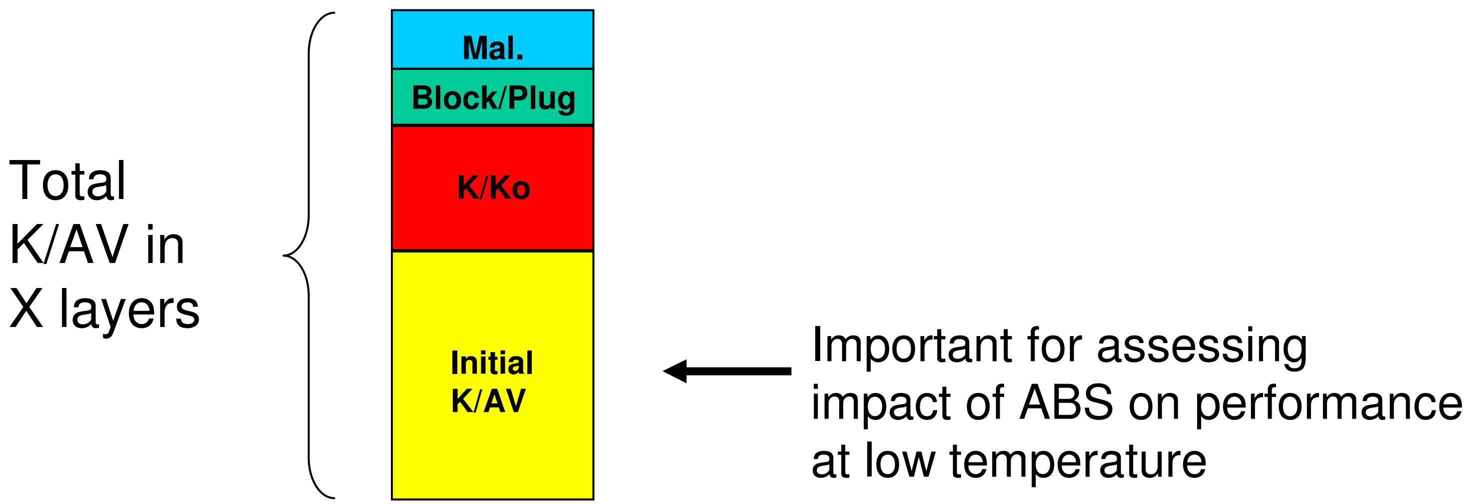
4. Iterate solution

- Margin impact on K, SO_2 conversion, catalyst formulation



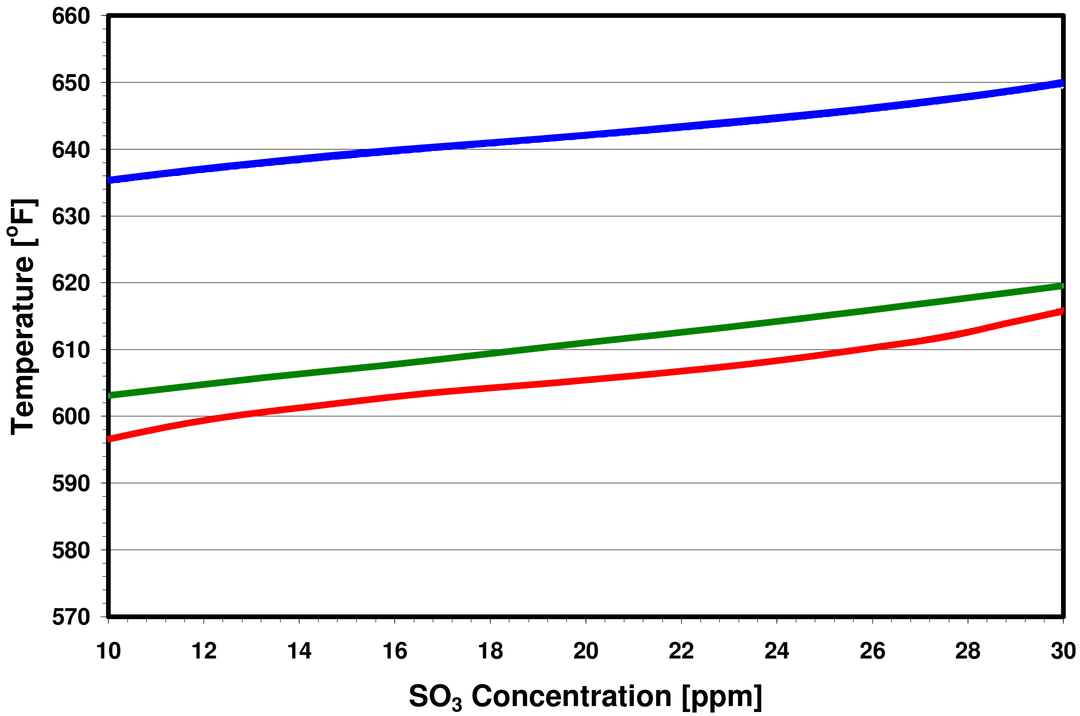
Catalyst Design, cont'd 2

- **In terms of catalyst potential (K/AV):**



Cormetech Tmin Design Strategy

- **Basic Approach:**
  - Avoids risk of ABS deposition on the catalyst
  - No catalyst margin added for ABS-induced deactivation

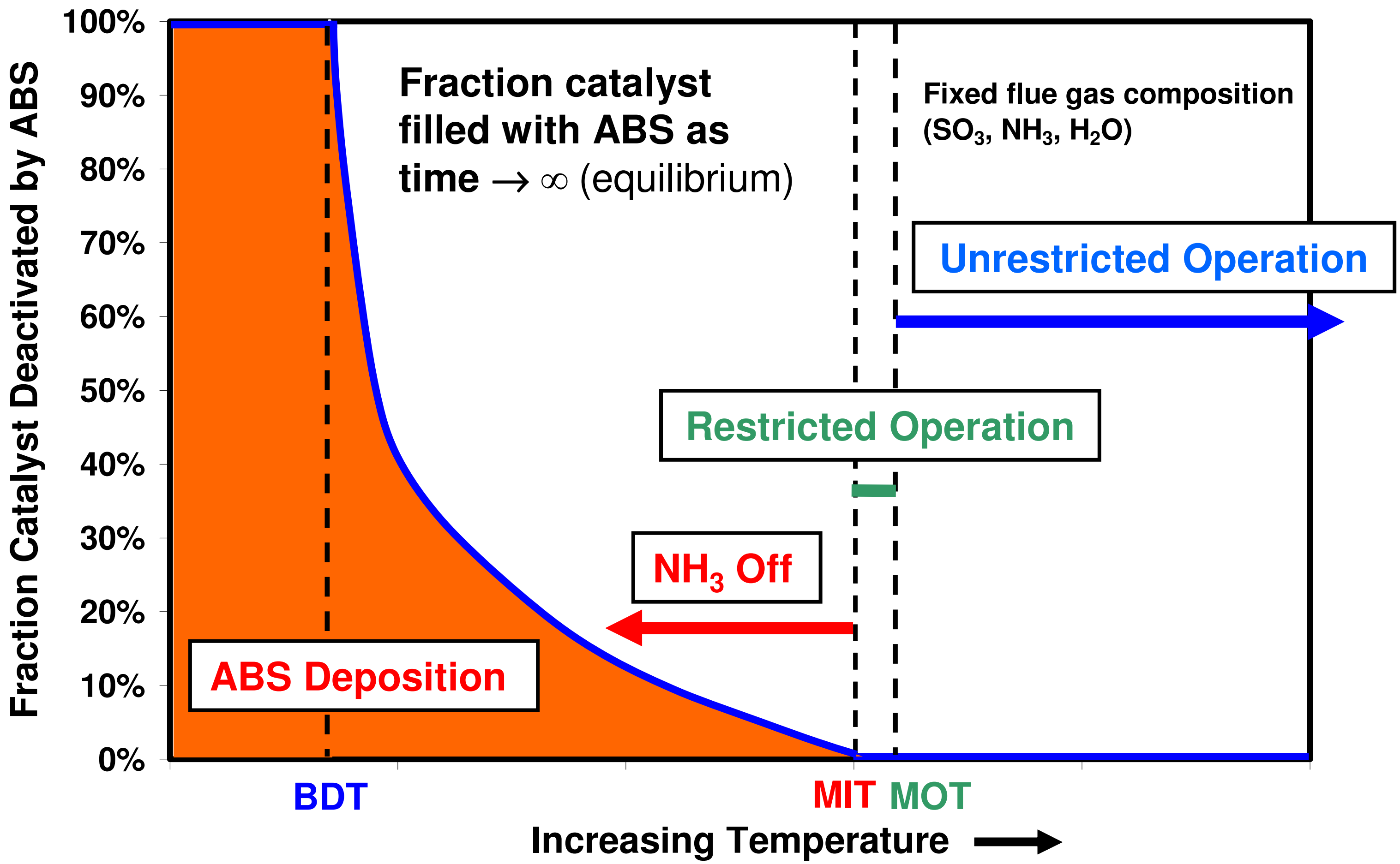


RT = recovery temperature

MOT = minimum operating T

MIT = minimum injection T for NH_3

Basic Approach: Avoids ABS Formation



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Summary of the Basic Approach

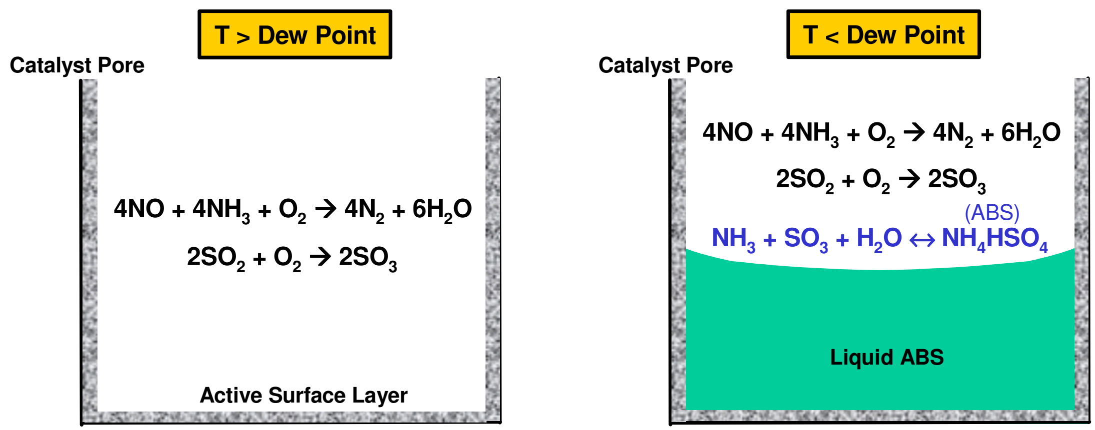
- **Simplifies operating recommendations**
  - Temperatures (MIT, MOT, RT)
  - Time allowances
  - Operate plant within set guidelines
- **Protects catalyst life**
  - Eliminates ABS as a source of deactivation
- **Reduces impact of transient emissions**
  - Minimizes SO_3 and NH_3 spikes during heating transient

Drivers for Lower Temperature SCR Operation

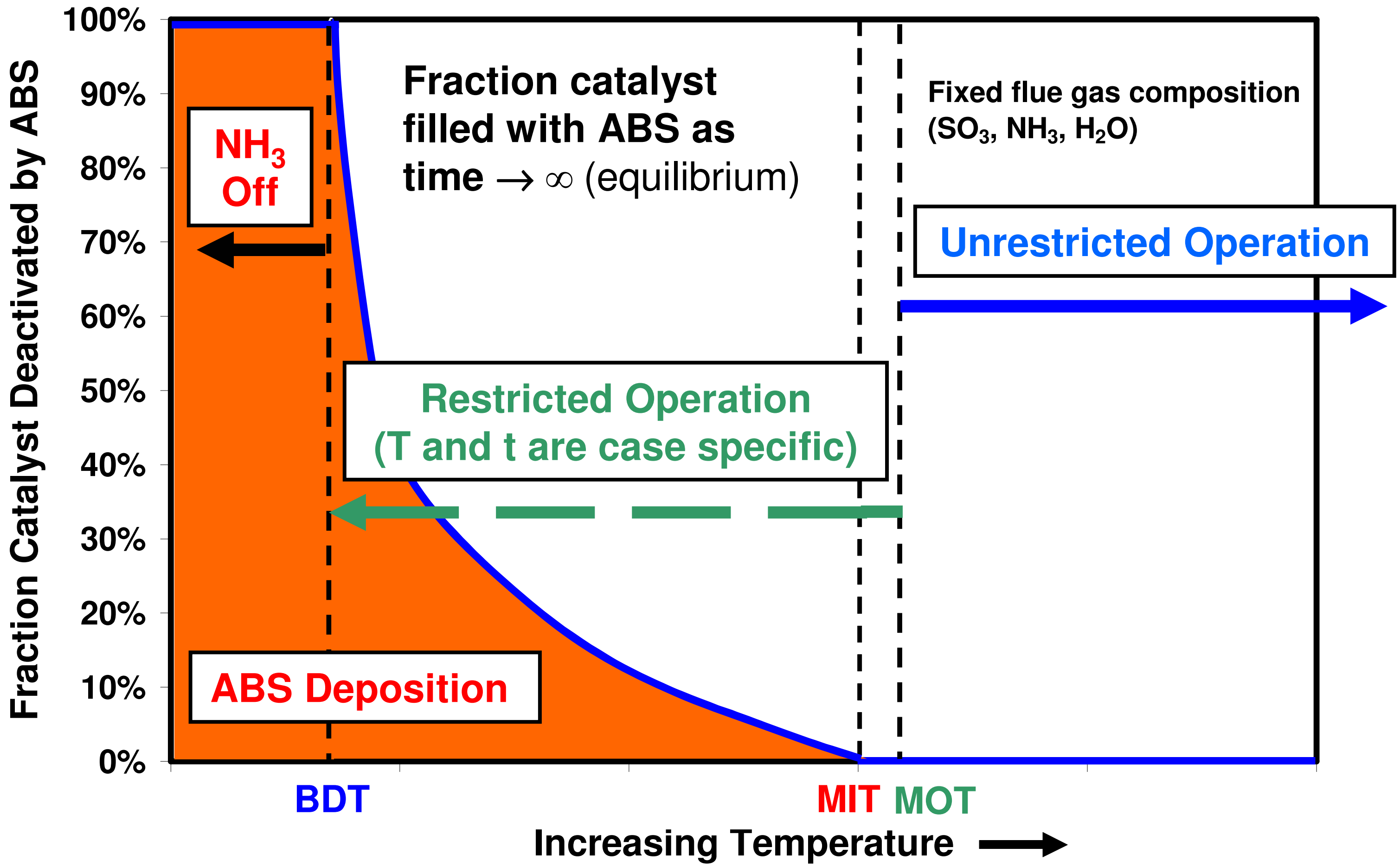
- **Load cycling**
  - Weekend, overnight, and/or shoulder seasons
- **Unit maintenance**
  - Short or long term impacts
    - Condenser cleaning
    - Boiler feed pump, heater, and/or fan malfunctions
- **Avoid installation or use of an economizer by-pass**
- These factors push the SCR to operate at lower temperature, but run up against Tmin concerns (ABS)

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
    - Requires understanding unit's operation and catalyst's response
  - Successfully implemented in >14 boilers

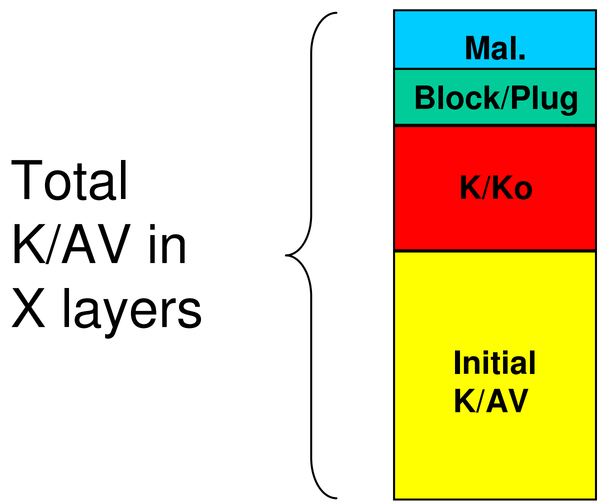


Enhanced Approach



Design for Enhanced Approach

- **Evaluate, for low load and recovery conditions:**
  - Real time K/AV vs. K/AV required to meet DeNOx, NH_3 slip
  - Impact of transient SO_3 and NH_3 spikes during recovery



Low Load Considerations

- **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:
    - Reduce DeNOx efficiency, or increase NH_3 slip
    - Reheat catalyst above recovery temperature

Recovery Phase Considerations

- **Potential for slow K recovery (lag K/AV requirement)**
  - Options (if slow): reduce DeNOx efficiency, increase NH_3 slip
- **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

Application of the Enhanced Approach

- **Evaluate and balance:**
  - Plant operating needs
  - Severity of low load condition
    - 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

➢ <u>Engineering analysis, lab validation test, field implementation</u>

Cormetech Capability

- **Enhanced approach requires good understanding of catalyst's and unit's responses**
- **At low load:**
  - Kinetic effect of temperature (activation energy)
  - ABS pore plugging and deactivation
    - Thermodynamics: max extent to which catalyst will fill with ABS
    - Kinetics: rate at which catalyst will fill with ABS
- **During recovery at full load:**
  - Rate of activity recovery = f (T, cycle duration, gas comp)
  - Transient SO_3 and NH_3 emissions
- **Extensive testing conducted by Cormetech to understand and model these phenomena (testing at Cormetech, MHI, and University collaboration)**

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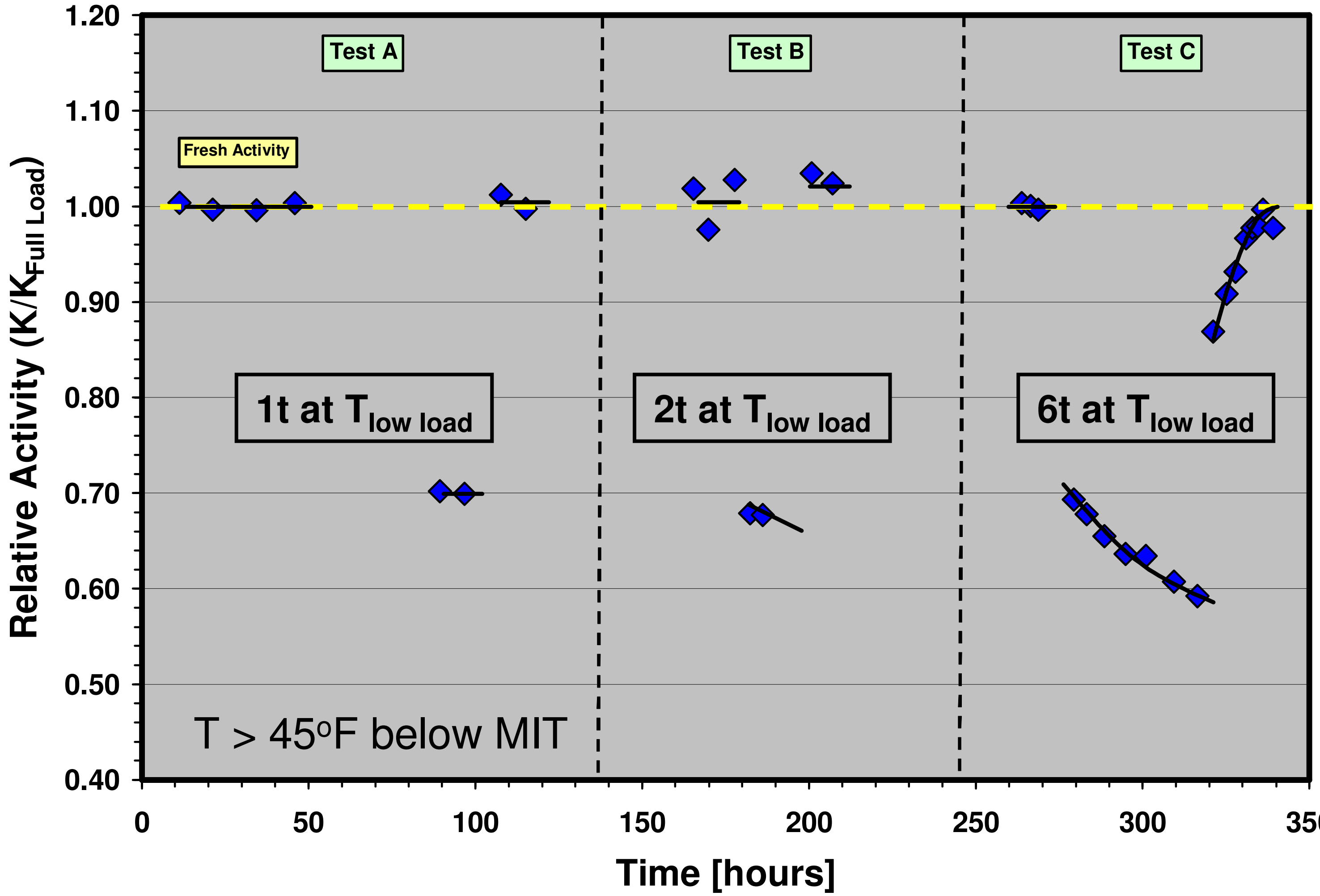
Example 1: DeNOx Activity Data

Sequence: $T_{full\ load}$ → $T_{low\ load}$ → $T_{full\ load}$

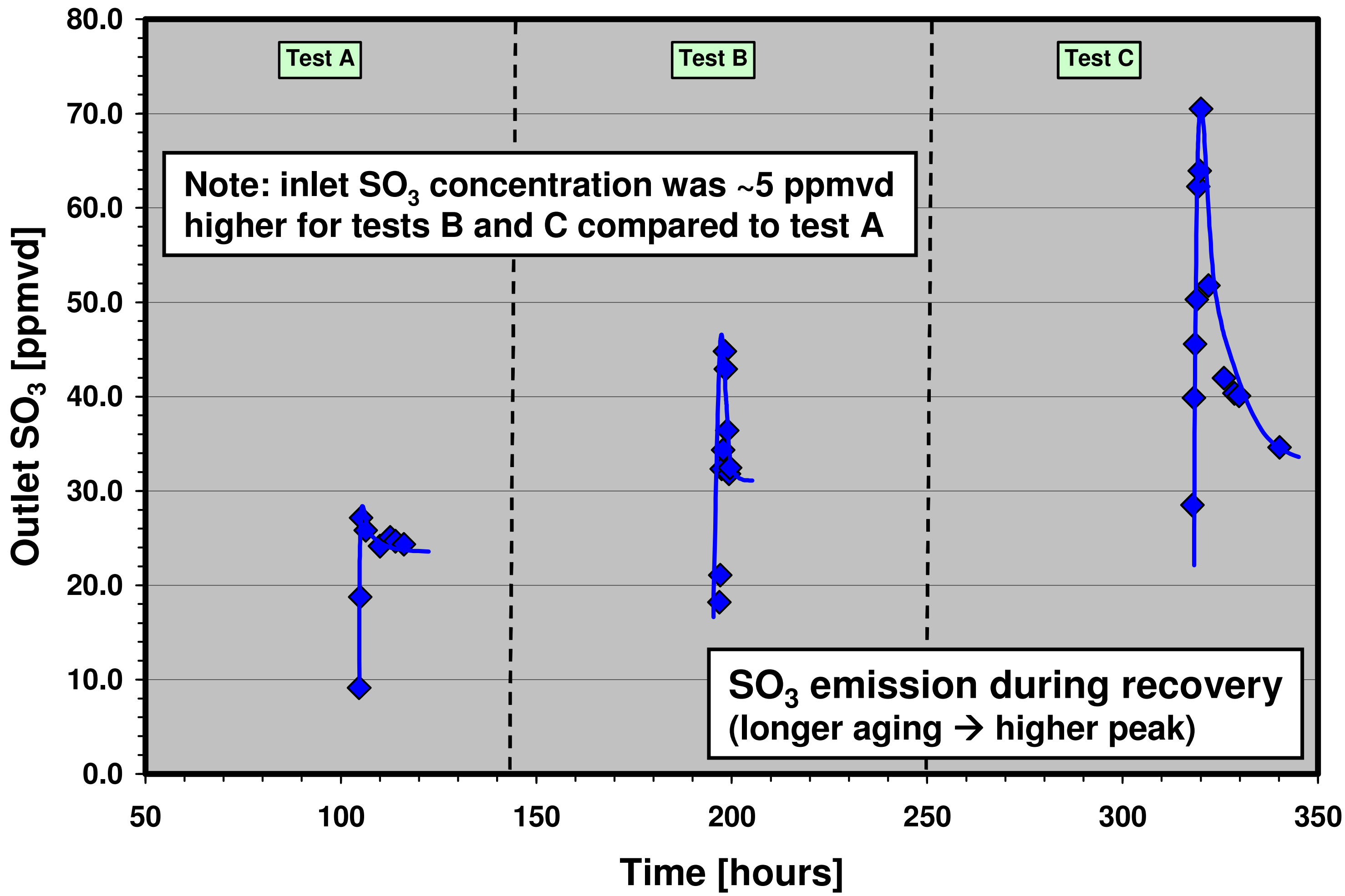
Lab validation data



Example 1: SO_3 Emission Data

Sequence: $T_{full\ load}$ → $T_{low\ load}$ → $T_{full\ load}$

Lab validation data



Case Study: Duke Energy Belews Creek Unit 2

- **Unit 2 operating temperature just above NH_3 MIT**
  - Prohibited operation of SCR at low loads
- **Low load conditions necessary for:**
  - Turbine valve tests
  - Load cycling: decreases in power demand
  - Other planned and unplanned maintenance
- **Solution: operate in Enhanced mode**
  - >50^{o}F below MIT
  - Validated through lab and field testing

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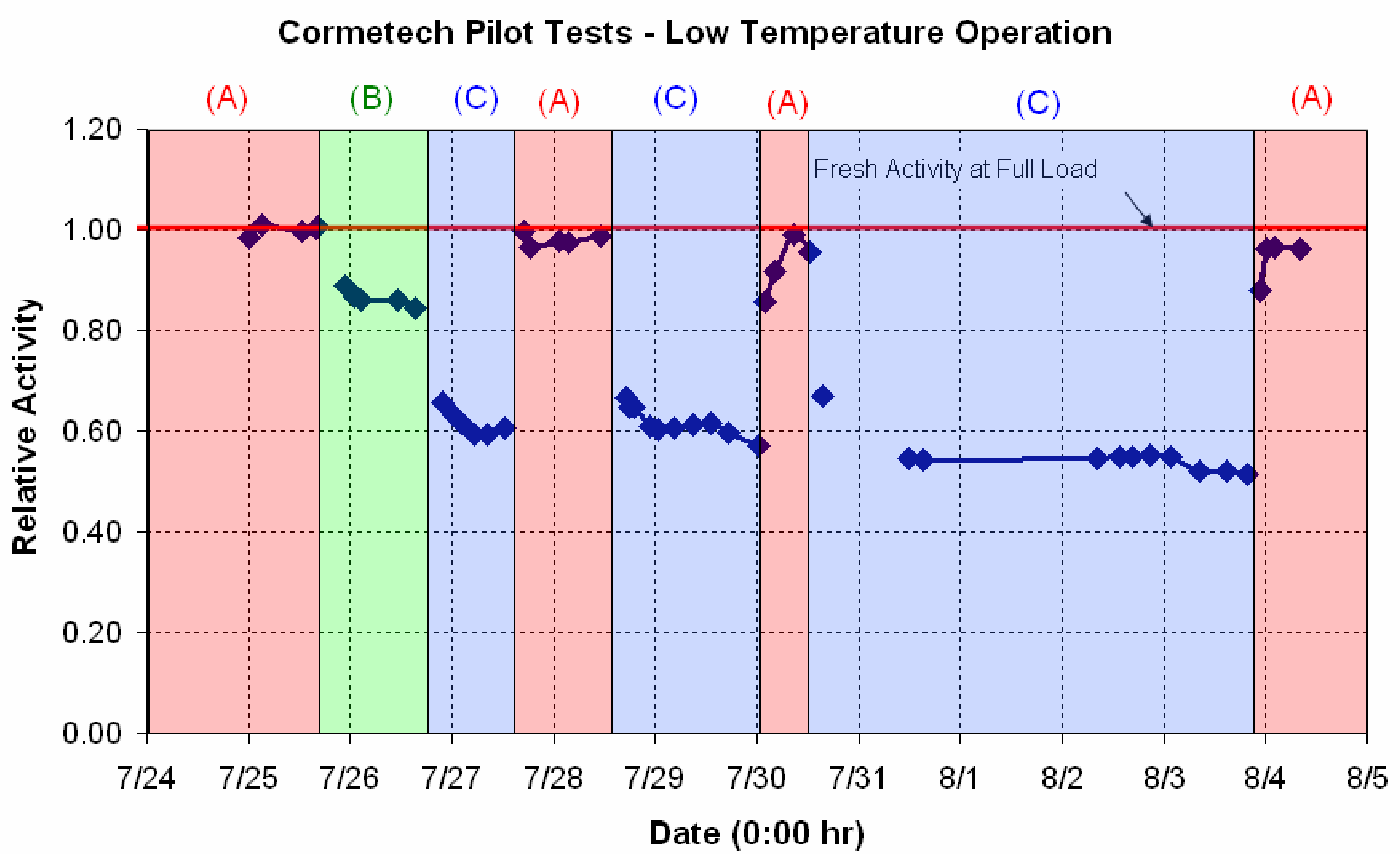
Lab Validation: Belews Creek Unit 2



(A) Operation at full load temperature. (B) Operation at 25 °F below minumum injection temperature.

(C) Operation at 65 °F below minimum injection temperature (MIT).

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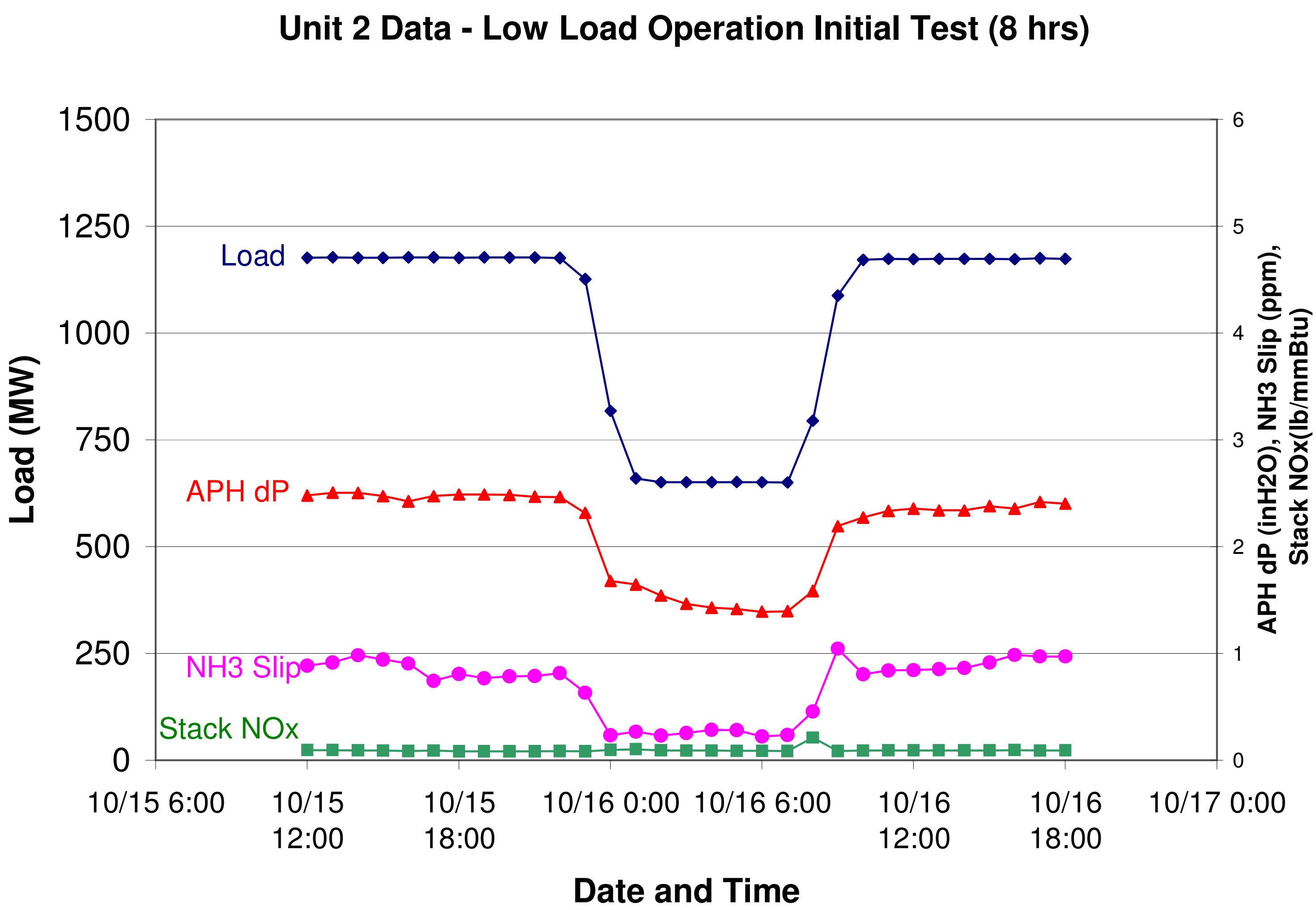
Field Implementation: Belews Creek Unit 2

- **Lab validation tests:**
  - K decrease at low load due to T decrease and ABS formation
  - K decrease < flow decrease: DeNOx potential is maintained
  - Complete recovery of catalyst activity at full load
- **SCR control logic implemented in October 2004**
- **Field results:**
  - High NOx removal rates during extended low load operation
  - Complete recovery of catalyst activity
  - No adverse impact on APH DP observed
  - 2005 field audits: deactivation rates consistent with fuel usage

Field Validation Test: Belews Creek Unit 2



Belews Creek Unit 2 - Summary

- **Operation at low load is routine**
- **Combined 2005 and 2006 ozone seasons:**
  - 1800 hours of operation at low load
  - 2200 tons of NOx removed during low load

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Case Study: TVA Fossil Units

- **Drivers for lower temperature SCR operation:**
  - Increase load cycling capability
  - Maximize tons NOx removed
- **Enhanced Mode strategies implemented in 2005 at:**
  - Cumberland Fossil Unit (CUF 1&2)
  - Bull Run Fossil Unit (BRF 1)
  - Kingston Fossil Unit (KIF 1-4)
  - Widows Creek Fossil Unit (WCF 7&8)
  - Each Unit employs Cormetech SCR Catalyst

Field Implementation: TVA Fossil Units

- **Lab validation tests:**
  - Complete recovery of catalyst activity
  - SO_3 and NH_3 spike in first 2 hours at recovery temperature
- **SCR control logic implemented in April 2005**
- **Field results:**
  - High NOx removal rates during extended low load operation
  - Complete recovery of catalyst activity
  - Did not observe SO_3 and NH_3 spikes (likely dampened by APH)
  - No adverse impact on APH DP or stack opacity observed
  - 2005 field audits: deactivation rates consistent with fuel usage

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Financials: TVA Fossil Units

- Using the new low temperature operating guidelines based on the Enhanced Approach netted an additional NOx reduction of **974 tons** system wide

UNIT	TONS NOx SAVED	COST SAVINGS
BRF 1	135	$359,078
CUF 1	609	$1,457,091
CUF 2	140	$383,604
KIF 1-4	56	$137,241
WCF 7-8	34	$79,054
TOTAL	974	$2,416,086

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2006 Operation: TVA Fossil Units

- **Based on the positive 2005 results, Cormetech and TVA worked to further increase the low temperature operating performance of the SCRs:**
  - Allowable low temperature operating time before recovery
  - Achievable NO_x removal rates at low load
  - Operation at even lower temperatures

Summary

- **Cormetech's Enhanced Approach**
  - Provides increased flexibility for low temperature SCR operation, without adverse effect on the catalyst, air pre-heater, or stack opacity
  - Demonstrated at Duke Belews Creek and TVA Fossil Units

Summary, cont'd

- **Applying the Enhanced Approach requires a good understanding of catalyst's and unit's responses to load changes:**
  - Catalyst:
    - DeNOx kinetics, ABS deposition/removal kinetics and thermo
  - Unit:
    - Temperature, flue gas flow rate and composition

Acknowledgements

- **Duke Energy Belews Creek Steam Station**
  - Wayne Whitaker
- **Tennessee Valley Authority**
  - Joe Giles

Thank You!

Questions?