Low Flue Gas Temperature SCR Operation

Cormetech, Inc.
Scot Pritchard
Chris Bertole, PhD

The risk of ammonium bisulfate (ABS) formation and resultant SCR catalyst deactivation is a cause for SCR operating restrictions for coal fired utility boilers when running at low load (reduced flue gas temperature). Cormetech has performed significant work in this area to assist utilities in expanding their SCR operating range thus maximizing NOx reduction and minimizing cost. This presentation will address work performed to date and keys for implementation.

January 23-24, 2006

CORMETECH

SCR Minimum Operating Temperature

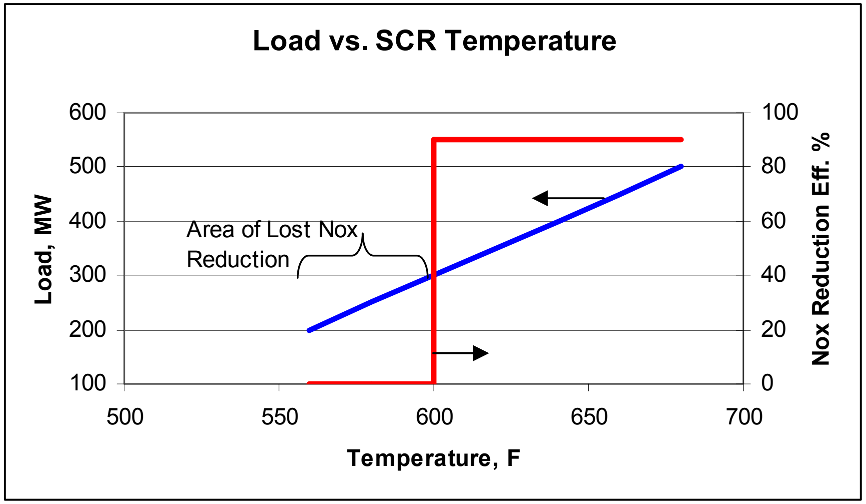
- **Background**
  - Drivers, Chemistry and Thermodynamics
- **Current Design Approach**
  - MIT, MOT, RT
- **Cyclical Operation**
  - Strategy
  - Case Study

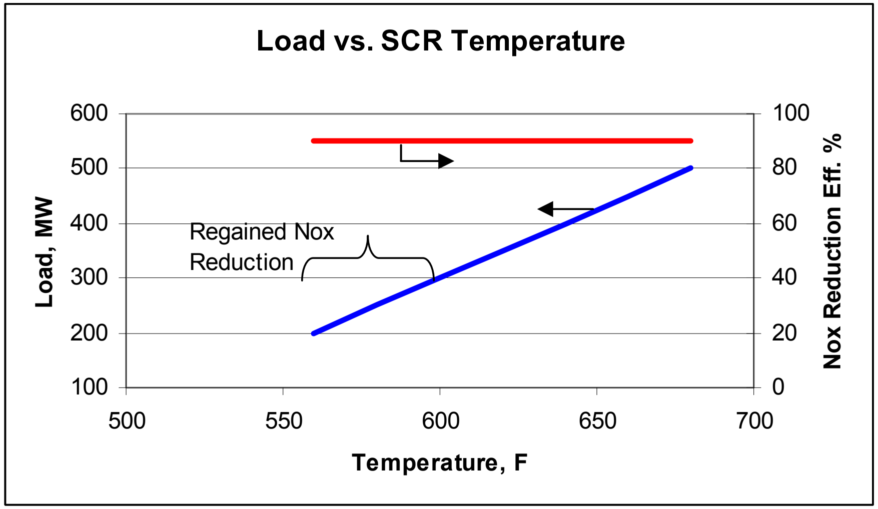
Background

- Ammonia Bisulfate formation temperature limits can restrict operation of the SCR at lower loads (lower temperature)
- Restricted operation is necessary to avoid risk of temporary catalyst deactivation and a mismatch with the removal requirements OR use of economizer bypass or other temperature control method
- However, there is opportunity to stretch the operation range of the SCR given proper understanding of unit operation and catalyst response

Background

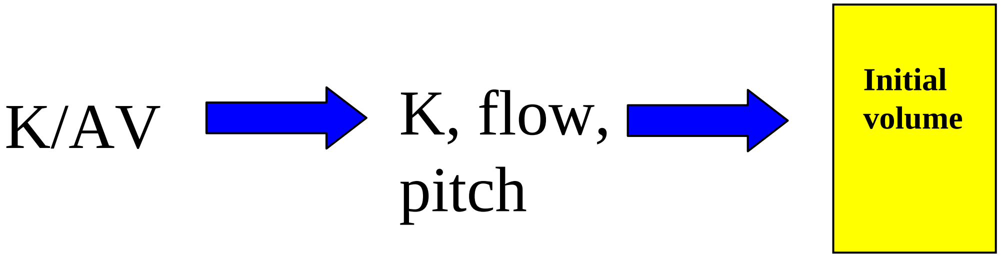
- Shutting off ammonia at low loads can be a significant cost
- Having to use or install an econ bypass can be costly
- 200 hours at loads between 200-300 MW when ammonia is not injected on a 500 MW plant with a baseline of 0.55 lb/mmbtu and 90% reduction can be worth over $200,000 (ref. $2000/ton NOx credit value)





Catalyst Design Requirements

1. Determine minimum catalyst potential requirement
   f(Noxin, Efficiency, and NH_3 slip)
   K/AV where:
   K = f(T,formulation), [formulation = f(SO_2 conv.)]
   AV = flow/(vol m^3 * m^2/m^3)
2. Determine initial catalyst activity K – f(T, form.)
3. Know gas flow (Nm^3/hr)
4. Select catalyst pitch – 7 mm, Ap = 539 m^2/m^3



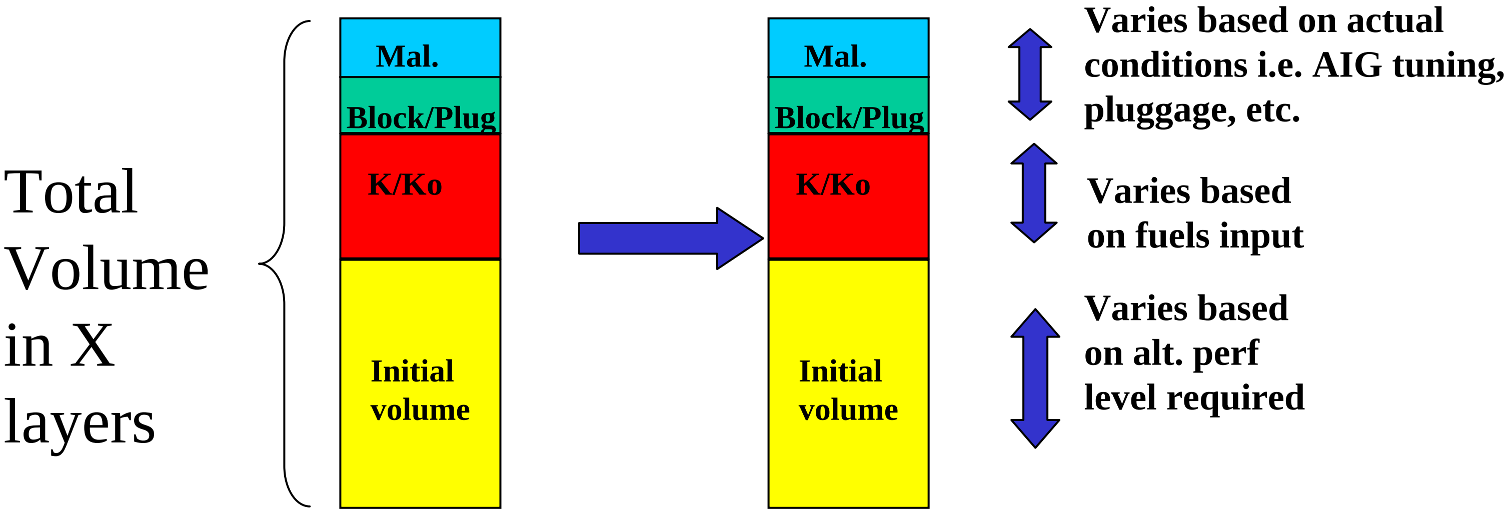
K/AV

K, flow, pitch

Initial volume

Catalyst Design Requirements

5. Determine margin required for:
   - fuels (K/Ko) → life
   - blockage/pluggage
   - maldistribution (NH_3:NOx, temp., flow)
6. Iterate solution based on margin impact on formulation and K
7. Evaluate Impact on Hg speciation



Total Volume in X layers

Mal.

Block/Plug

K/Ko

Initial volume

Mal.

Block/Plug

K/Ko

Initial volume

Varies based on actual conditions i.e. AIG tuning, pluggage, etc.

Varies based on fuels input

Varies based on alt. perf level required

Chemistry

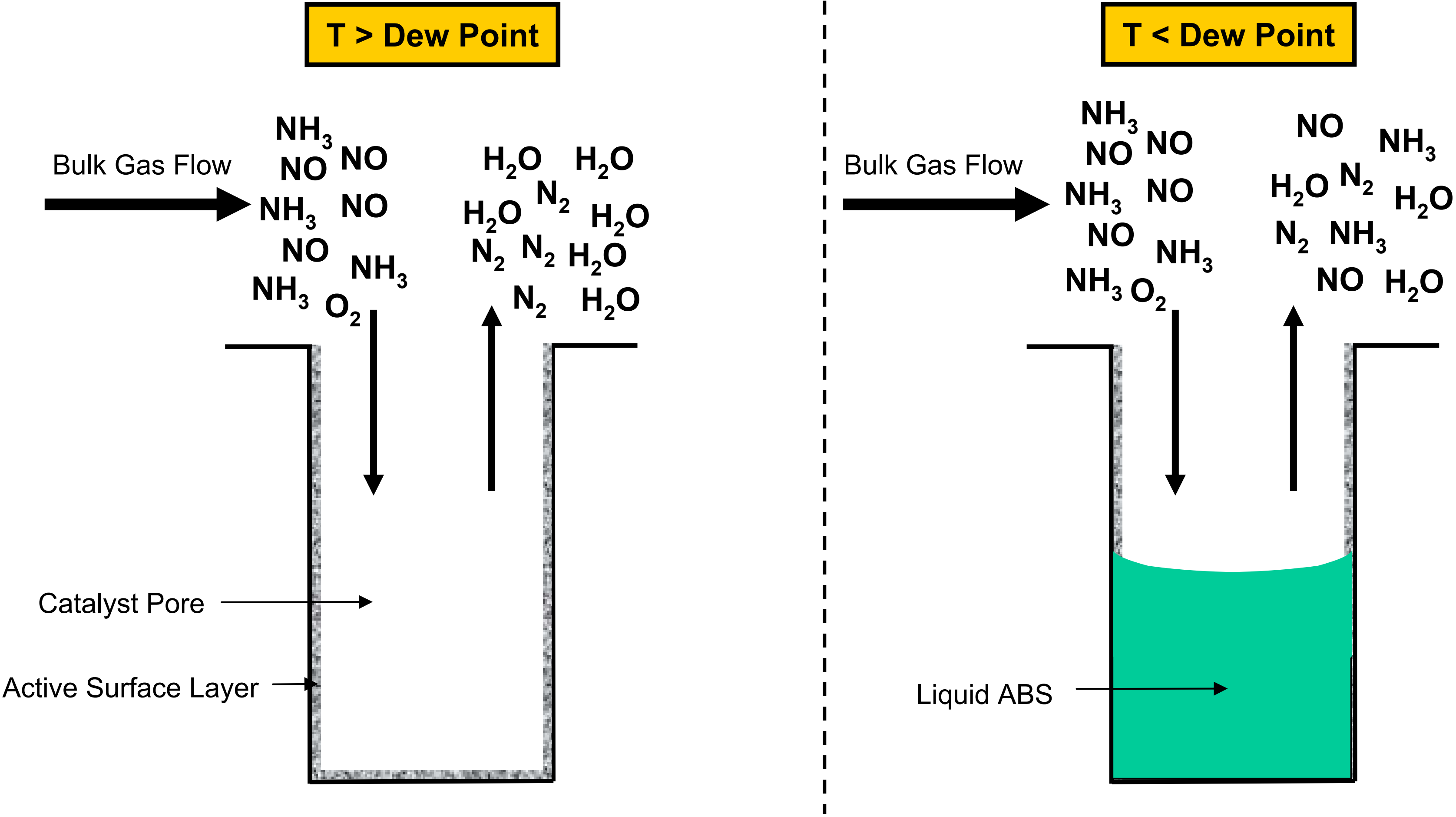
- SO_3 and H_2SO_4 in the flue gas creates potential for salt formation when NH_3 is injected
- At low NH_3 partial pressures:
  - $NH_{3(g)} + H_2SO_{4(g)} \leftrightarrow NH_4HSO_{4(l)}$ *(ammonium bisulfate, or ABS)*
  - $NH_{3(g)} + SO_{3(g)} + H_2O_{(g)} \leftrightarrow NH_4HSO_{4(l)}$
- At higher NH_3 partial pressures:
  - $2\ NH_4HSO_{4(l)} \leftrightarrow (NH_4)_2SO_{4(s)} + H_2SO_{4(g)}$ *(ammonium sulfate)*
  - $NH_3 + NH_4HSO_{4(l)} \leftrightarrow (NH_4)_2SO_{4(s)}$
  - $2\ NH_3 + H_2SO_{4(g)} \leftrightarrow (NH_4)_2SO_{4(s)}$
  - $2\ NH_3 + SO_{3(g)} + H_2O_{(g)} \leftrightarrow (NH_4)_2SO_{4(s)}$

At SCR Conditions, ABS is the Main Concern

- Ammonium bisulfate (ABS) deposition:
  - $NH_{3(g)} + SO_{3(g)} + H_2O_{(g)} \leftrightarrow NH_4HSO_{4(l)}$
  - $K = 1 / [\, P^{eq}_{NH3}\, P^{eq}_{SO3}\, P^{eq}_{H2O} \,] = 1 / [\, P_{ABS}^{eq,\text{ or sat vap}} \,]$
- ABS deposition is controlled by thermodynamics:
  - $P_{ABS} = P_{NH3}\, P_{SO3}\, P_{H2O}$ (ABS does not exist in the vapor phase)
  - if $P_{ABS} > P_{ABS}^{\text{sat vap}}$, ABS will deposit
    - occurs when operating T is below dew point T
    - micro pores → capillary condensation raises dew point T

ABS Deactivates SCR Catalyst by Pore Plugging

$[NH_3(g) + SO_3(g) + H_2O(g) \leftrightarrow NH_4HSO_4(l)]$



T > Dew Point

Bulk Gas Flow

NH_3 NO NO NH_3 NO NO NH_3 NH_3 O_2

H_2O H_2O N_2 H_2O H_2O N_2 N_2 H_2O N_2 H_2O

Catalyst Pore

Active Surface Layer

T < Dew Point

Bulk Gas Flow

NH_3 NO NO NH_3 NO NO NH_3 NH_3 O_2

NO NH_3 H_2O N_2 H_2O N_2 NH_3 NO H_2O

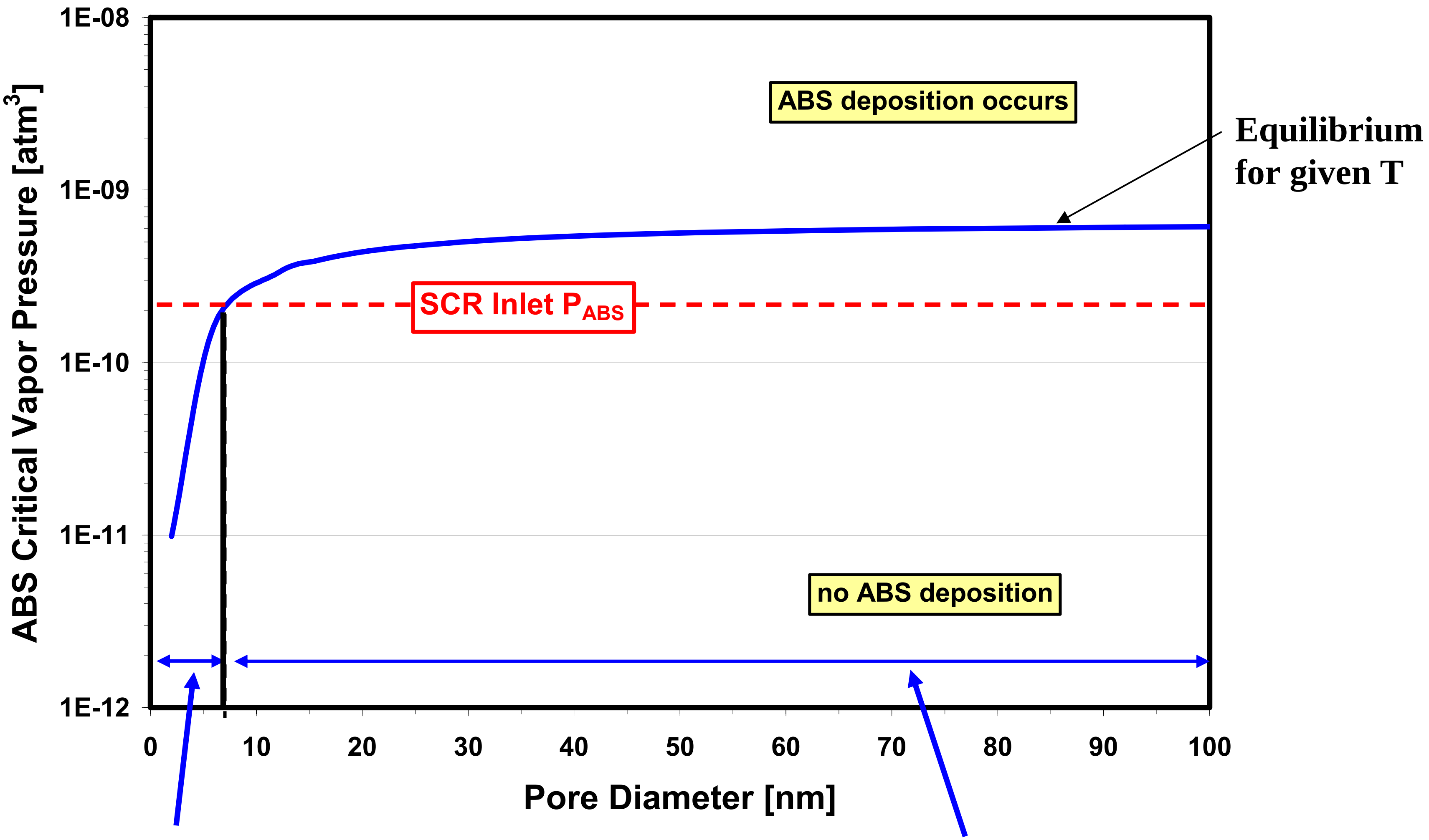
Liquid ABS

January 23-24, 2006

Capillary Condensation Occurs in Catalyst Pores

- Liquid ABS forms in SCR catalyst pores at a temperature above the saturation point due to capillary condensation
  - Vapor pressure of liquid over the curved surface in a pore is lower than over a flat surface, due to thermodynamics
  - Thomson's theory of capillary condensation (Kelvin equation):
    - $\ln (P/P_{\text{sat vap bulk liquid}}) = -(2\ \sigma\ V_l) / (r\ R\ T)$
      - σ = ABS surface tension, V_l= ABS molar volume, R = gas constant, T = temperature, and r = pore radius
  - Thus, smaller catalyst pores result in:
    - Liquid ABS vapor pressure reduction
    - Higher ABS dew point → ABS formation at higher temperature

Pore Size Effect on ABS Sat. Vapor Pressure



Pores will fill with liquid ABS

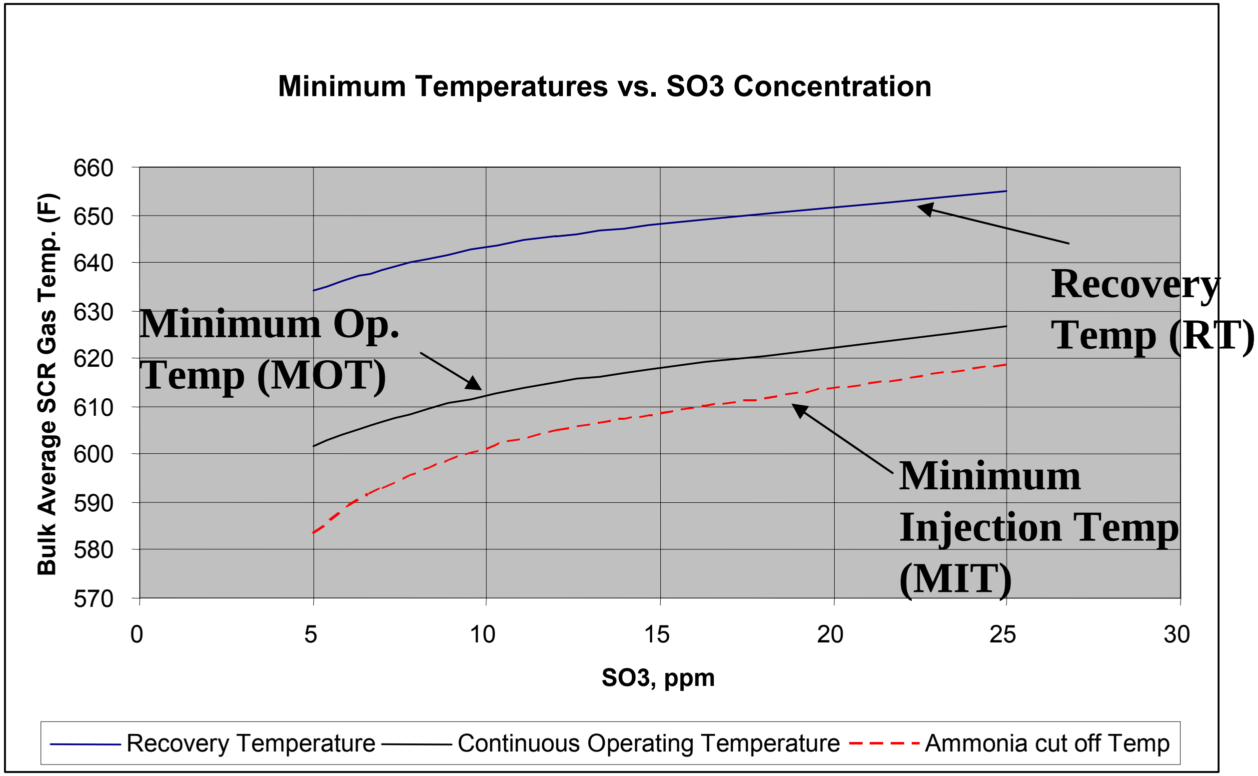
Pores remain free of liquid ABS

Thus, ABS Partial Pressure Controls SCR Tmin

- ABS deposition limits SCR operation at low temperature
  - Liquid ABS deactivates SCR catalyst by filling and/or blocking pores, inhibiting access to the catalyst’s active sites
  - Catalyst retains activity in pores not filled
  - Higher P_{ABS} = higher ABS dew point T = higher Tmin
  - Thus, higher NH_3, SO_3, or H_2O will result in higher Tmin

Current Design Approach for Tmin

- MIT → temperature where ABS first condenses in catalyst
  - Function of NH_3, H_2O, and SO_3 (specific to each plant)
- MOT = MIT with margin
  - Max. 100 hours between MIT and MOT, equiv. hours above RT



January 23-24, 2006

Current Design Approach for Tmin

- Motivations for standardized approach:
  - – Simplify operating recommendations
    - Frequency, time, temperature
  - – Minimize risk of ABS formation
    - Multiple frequency operation (recovery risk) i.e. 0.999^{X}
      - – No margin for ABS K/Ko (minimize catalyst volume for job)
  - – Time of recovery vs. operation capability
    - Achievable recovery temperature
    - Emissions limits (recovery considered to be too slow to be useful)
  - – Limitation: Tmin is set more conservatively and can restrict operation

Tmin Impact Assessment for Individual Plants

- Impact of low temperature operation influenced by:
  - Cycling frequency (full and part load temp)
    - Extent of load cycling/ weekend operation/ maintenance
- Clear benefit of lowering Tmin:
  - Larger SCR turndown ratio → NOx reduction at lower loads
  - Greater operation flexibility
  - Potential elimination of temperature control
- Consider system operation options to reduce Tmin:
  - Lower inlet SO_3 and/or NH_3
    - Reduce inlet NO_x and/or efficiency
    - Fuels and/or fuel additives (current and future)

Modified Design Approach for Tmin

- Continuous, long term SCR operation below the dew point temperature will deactivate the catalyst
  - But: ABS can be driven off catalyst and the activity recovered if the catalyst is heated to a “recovery temperature”, or RT

- **Temperature cycling:**
  - Operate below “standard” MIT for a specified time interval
  - Allow ABS to deactivate part of the catalyst
  - Drive off accumulated ABS and restore activity above RT
  - Allows short term operation below MIT on a repeated basis

Recent Experience and Current Capability

- Several laboratory studies have been performed for the operating conditions of specific plants with subsequent full scale successful implementation
  - Plants currently evaluated on a case-by-case basis
  - Assessment input criteria
    - Cycling frequency
    - Gas flow, SO_3, H_2O, and NH_3 (DeNOx, inlet NO_x, NH_3slip) at full and low load conditions, and expected ranges
    - Spatial distribution of temperature
    - Boiler transient information (temperature/flow vs. time)
      - Assess SO_3 and NH_3 peak emission concern
    - Routinely achievable recovery temperature

Considerations for Tmin Assessments

- Low load:
  - Rate and extent of catalyst deactivation as a function of temperature and cycle duration
  - Catalyst activity decrease is due to a combination of
    - kinetic effect of temperature
    - ABS pore plugging and deactivation
    - Performance cannot be met if $K/K_{\text{full load}}$ slips below $AV/AV_{\text{full load}}$ (reduce efficiency)

Considerations for Tmin Assessments

- Full load/ recovery phase:
  - Rate of activity recovery as a function of temperature and cycle duration
  - Potential for increased SO_3 and NH_3 slip emissions
    - Due to ABS elimination
    - Can 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
      - continued need to focus on NH_3 slip control to avoid APH fouling

Considerations for Tmin Assessments

- Thus, optimal strategy is a balance between:
    - length of time at low load conditions (and the extent of deactivation)
    - performance recovery upon return to full load conditions (may have to reduce efficiency during recovery)

Summary – Activity Data

- Short time period at low load (tests A and B):
  - Activity decrease mainly due to kinetic effect
  - Minimal ABS deactivation
  - Fast recovery upon return to RT
- Longer time period at low load (test C):
  - Activity decrease due to kinetic and ABS deactivation effects
    - Small micro pores fill first → activity will level off once pores below the critical radius are filled
  - Longer recovery time likely due to ABS elimination from pores
    - Rate is still feasible for consideration

Thank You

Questions?

Scot Pritchard
919-595-8708
Pritchardsg@cormetech.com
Cormetech, Inc