REINHOLD ENVIRONMENTAL Ltd.

2016 NOx-Combustion-CCR Round Table Presentation

February 1 & 2, 2016, in Orlando, FL / Hosted by OUC

Low Load SCR Operation

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2016 Reinhold NOx – Combustion Roundtable
February 2, 2016

Agenda

- Background
- What is the ABS formation (condensation) temperature?
- ABS capillary condensation
- Additional factors impacting site specific SCR MOT
- Ongoing EPRI R&D
- Summary

Background

- Increased coal unit cycling
- Economic unit operation often requires deeper minimum load operation
  - SCR system often represents minimum load constraint
    - ABS condensation temperature is principle basis of catalyst OEMs minimum operating temperature (MOT)
  - SCR constraints site specific
    - Some units have flue gas temperature control
      - Associated boiler efficiency penalty
    - SCR NOx reduction requirements on some units may allow reduced SCR NSR at reduced load
- For units in need of expanded reduced load capability, significant potential benefits associated with dynamic methodology to assess MOT

Potential Cost Benefits Associated with Lower SCR MOT

- Reduced load capability during negative power pricing time periods
  - Insufficient duration to offset start-up costs by taking unit off-line
  - Assume additional 100 MW reduced load feasibility
    - Typically represents 10 – 30 F change in SCR inlet temperature
  - Time periods when bid power price is less than generation cost
    - Assume $10/MW-hr negative cost differential
    - 100 MW lower load provides $1,000/hr reduced loss
      - 88 weekly hours of deeper reduced load operation potential during slack load periods of Mon – Thu (10 pm – 6 am) and Fri 10 pm to Mon 6 am
      - Weekly loss reduction of $88,000

Reduced load operation during time periods of negative power pricing can provide significant reduction in operating losses

Order of Magnitude Unit Start-Up Costs

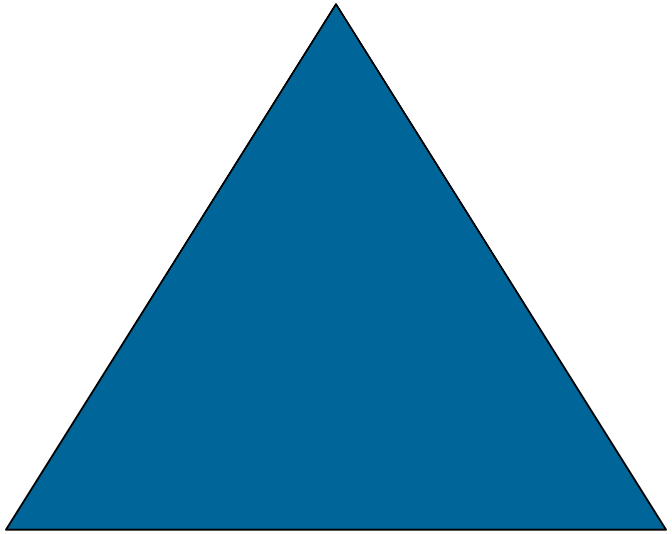
- Typical start-up costs for nominal 500 MW coal-fired unit
  - 25,000 gallons fuel oil at $2.50/gallon ($62,500)
  - 12 hours coal mill operation at 25 tph with coal cost of $30/ton ($9,000)
  - Auxiliary power
  - Ancillary boiler costs (boiler water, accelerated boiler wear, etc.)
  - Dispatch costs
  - Order of magnitude unit start-up costs of ~$80k - $120k

Typically operate unit at loss for short periods of time rather than incur operating start-up costs associated with taking unit off-line

Range of Perspectives

Utility

- Comply with environmental mandates
- Minimize operational cost impacts
- Maximize operational flexibility



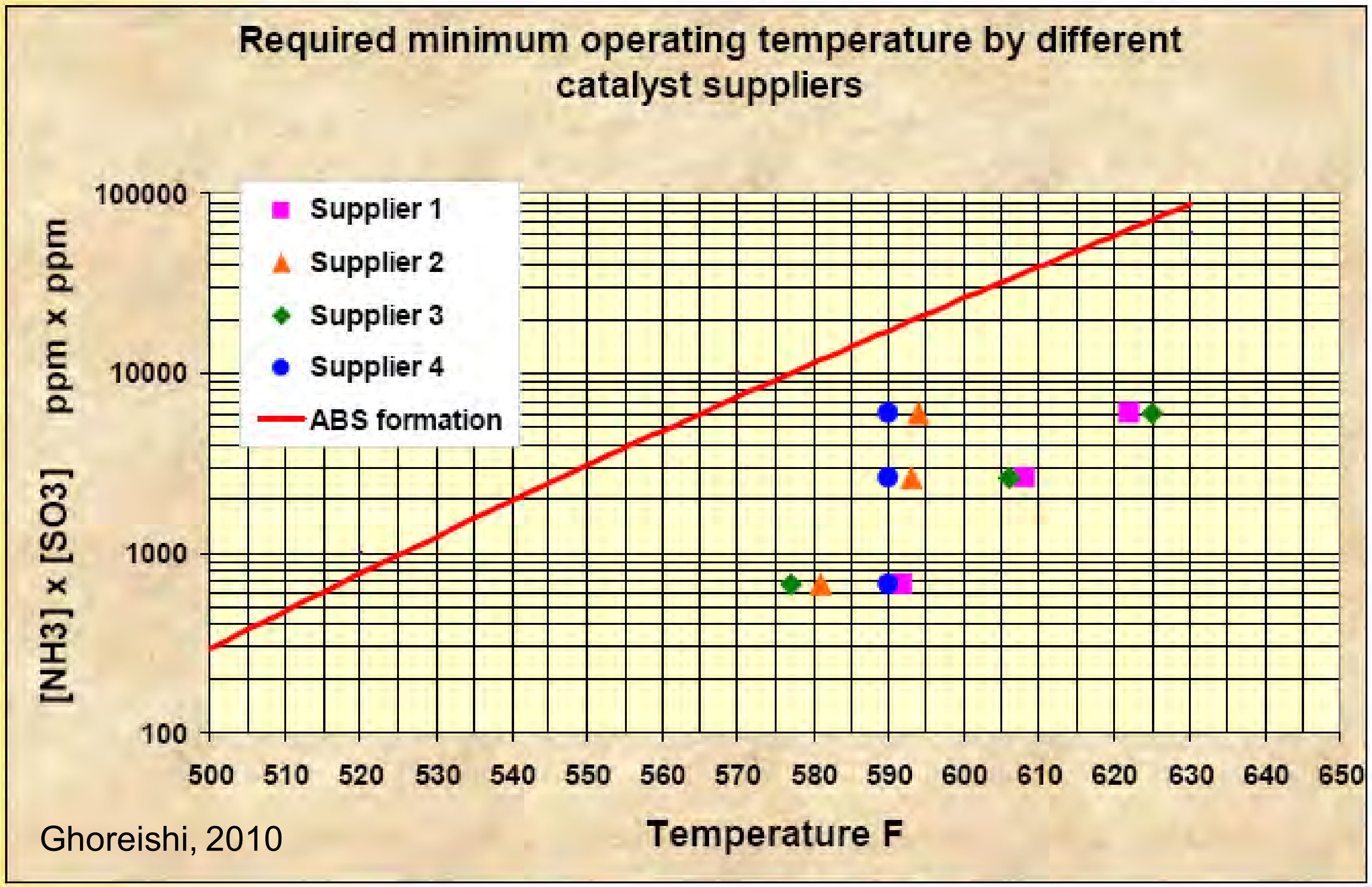
Catalyst OEM

- Maintain competitive catalyst performance guarantees and pricing
- Minimize risk associated with guarantees

EPRI

- Provide objective engineering R&D
- Conduct experiments that provide data for establishing dynamic MOT calculation methodology

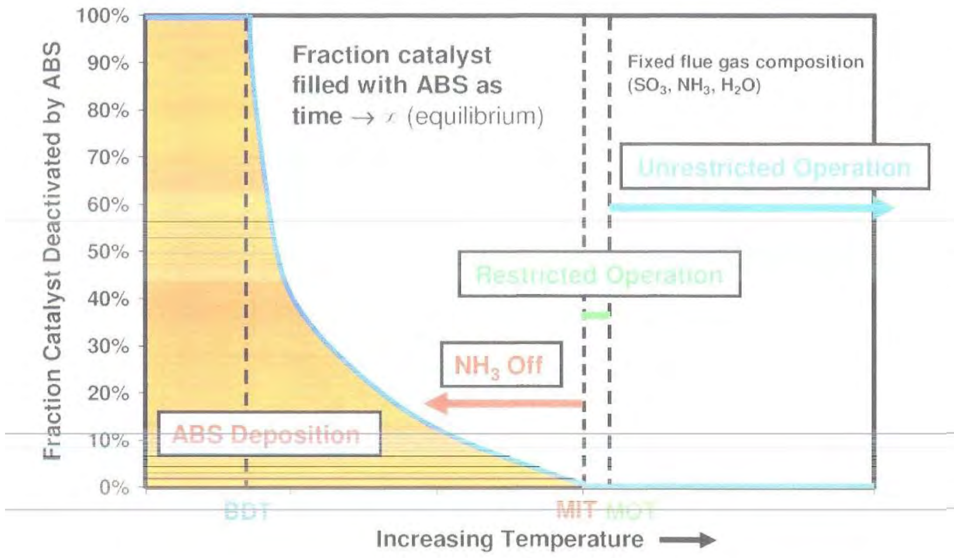
Range in SCR Minimum Operating Temperatures



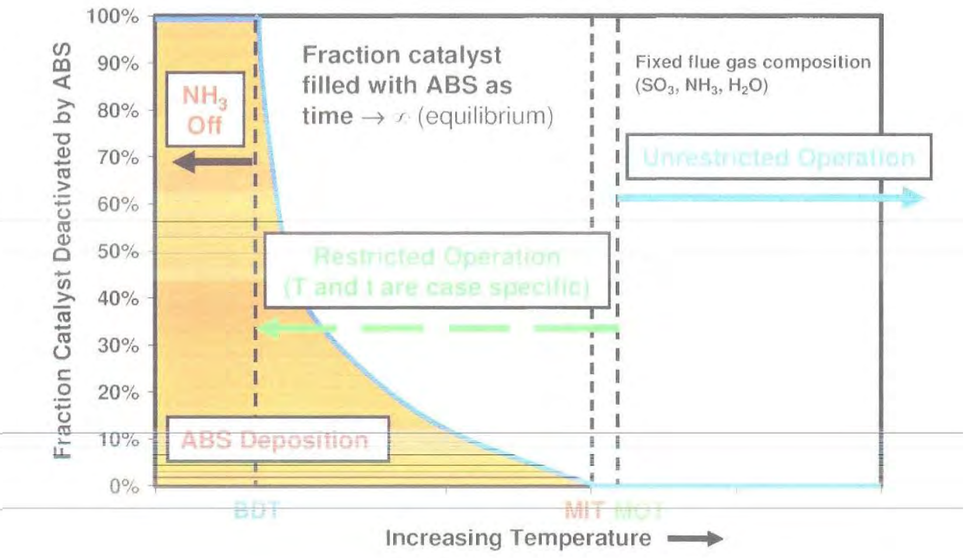
Inconsistent temperature margin between reported ABS formation line and MOT used by different catalyst suppliers

Catalyst Vendor 'Basic' and 'Enhanced' Approach

Basic Approach



Enhanced Approach



- Eliminates ABS as source of catalyst deactivation
- Operation within set guidelines
  - Predicated on ABS capillary condensation temperature
  - Margin for temperature variability

- Operation within capillary condensation region for limited time
  - Site specific determination
  - Recover catalyst activity with SCR operation above recovery temp

(Bertole, Reinhold Environmental Conference, 2007)

Underscores importance of accurate ABS condensation temperature and need for dynamic MOT determination

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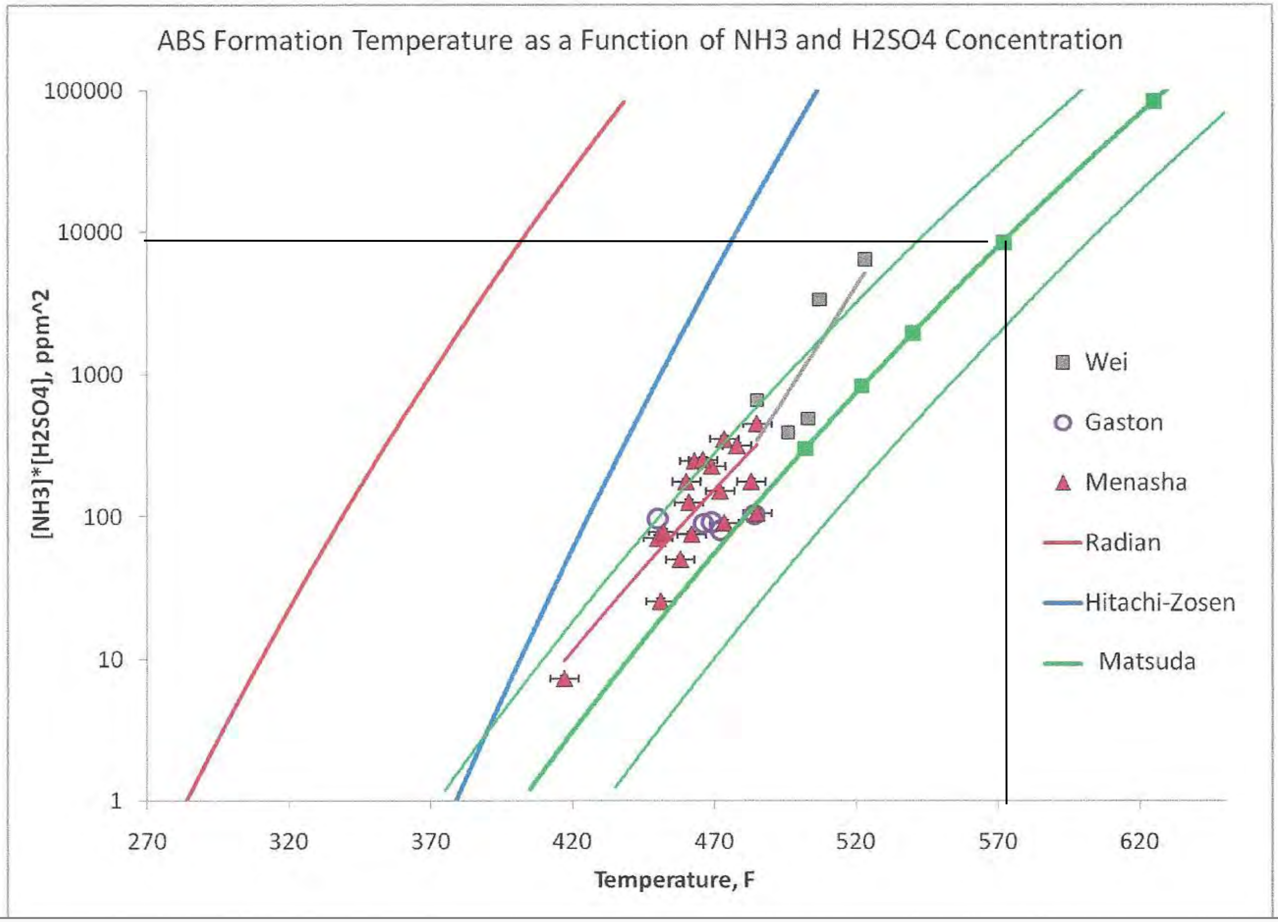
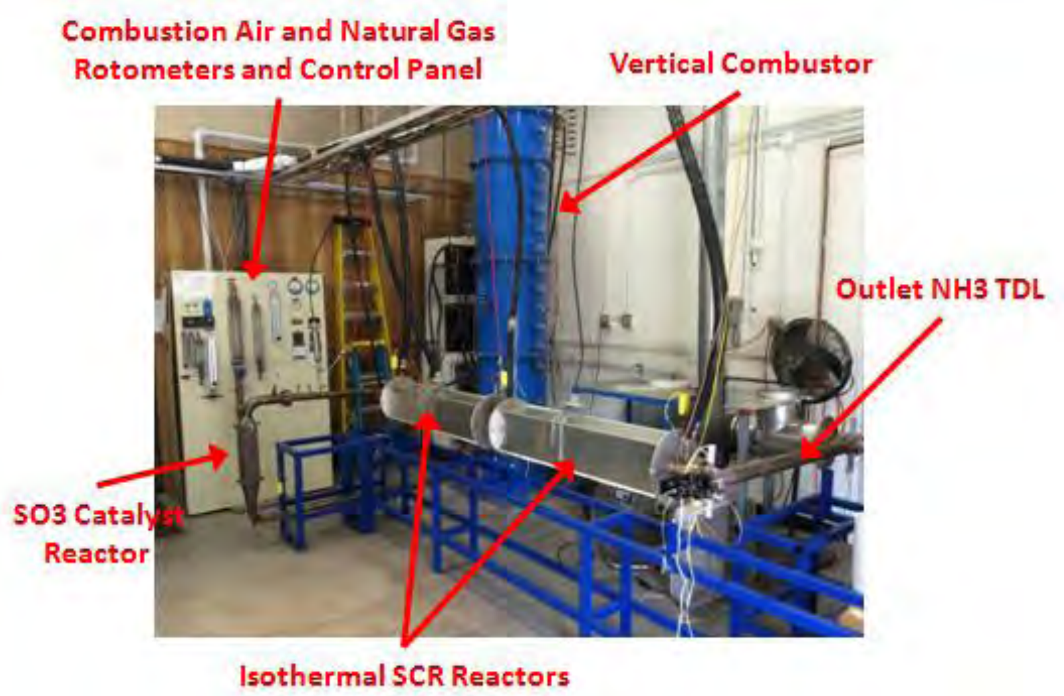
Range of ABS Formation Temperature Correlations



What is the ABS formation temperature?

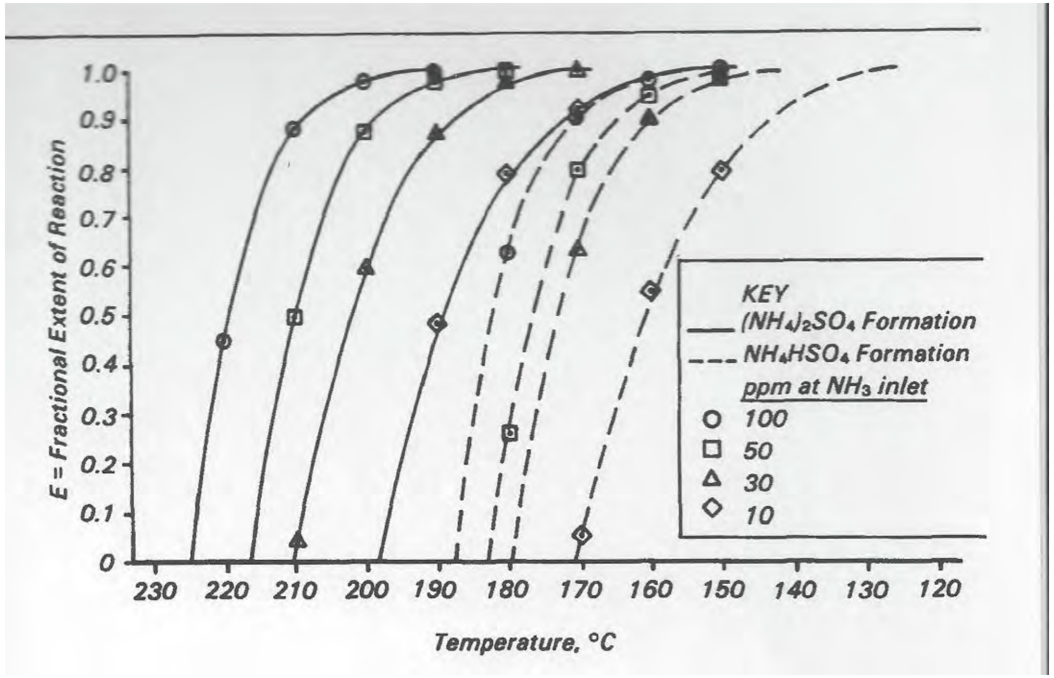
EPRI Research Approach

- Review literature and experimental basis for determining ammonium bisulfate (ABS) formation temperature
- Conduct lab tests
- Based on assessments, establish methodology for calculating site specific minimum operating temperature (MOT)
- Conduct field tests to demonstrate and validate methodology



Radian ABS Formation Study in Air Preheaters

- Burke and Johnson, *Ammonium Sulfate and Bisulfate Formation in Air Preheaters*, EPA-600/57-82-025a, August 1982
- Conducted thermodynamic and kinetic analysis of NH_3 and SO_3 reactions
  - While ammonium sulfate found to be thermodynamically favored, ammonium bisulfate kinetically favored
  - Calculations conducted for 10 ppm SO_3 and range of NH_3 from 10 – 100 ppm
  - Limited laboratory experiments
- Suggested reaction path
  - $SO_{3(g)} + H_2O_{(g)} = H_2SO_{4(g)}$
  - $NH_{3(g)} + H_2SO_{4(g)} = NH_4HSO_{4(l)}$
  - a $NH_4HSO_{4(l)}$ + b NH3 = (a-b) $NH_4HSO_{4(l)}$ + b $(NH_4)_2SO_{4(l)}$



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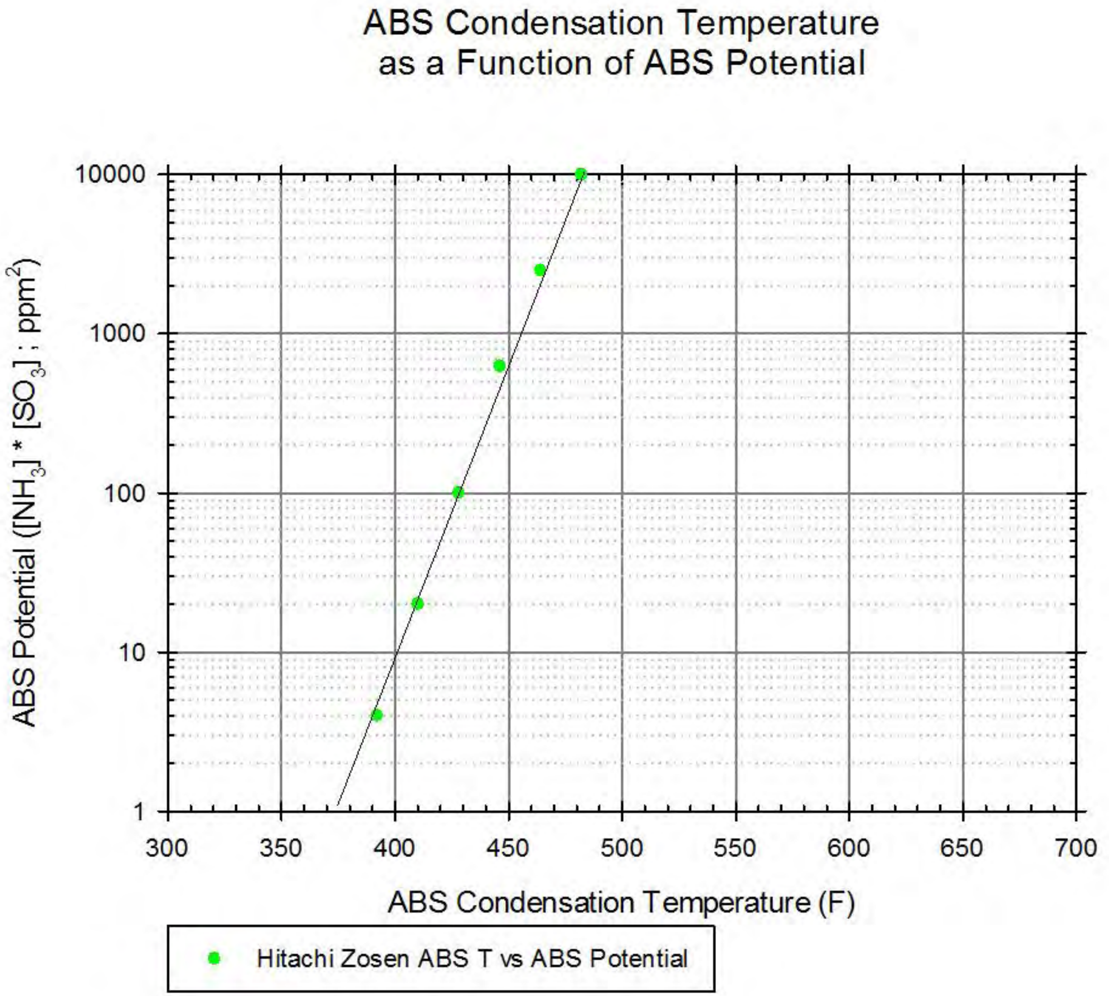
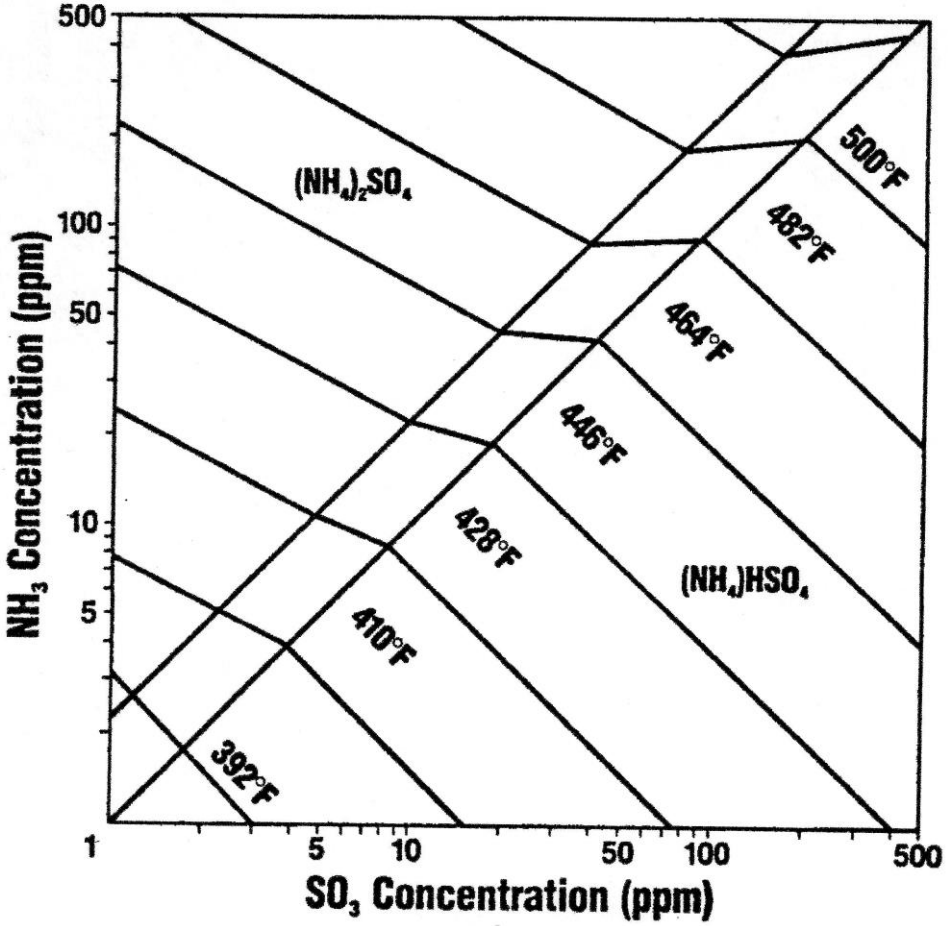
Hitachi Zosen ABS Phase Diagram



Developed in Japan, no English translation of development found

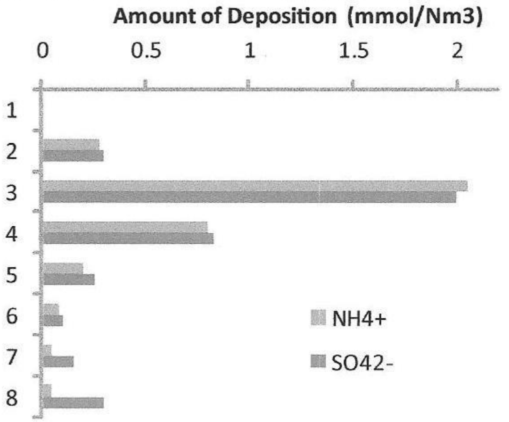


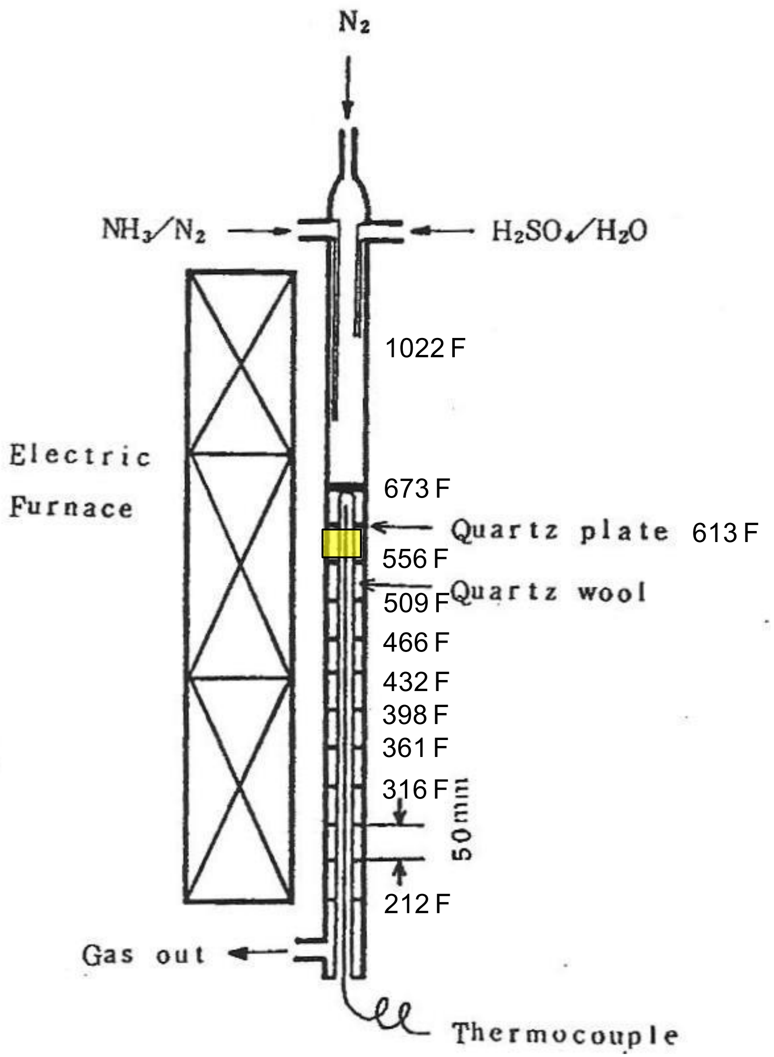
A.Saleem, M. Galgano, and S. Inaba, "*Hitachi-Zosen DeNOx Process for Fossil Fuel-Fired Boiler*", Proceedings of the Second NOx Control Technology Seminar, Denver, CO. 1978

Matsuda* Experiment

- Results shown for 20-hour experiment with 83.3 ppm NH_3 and 100 ppm SO_3
- Chemical analysis showed first ABS formation in Zone '2' with axial temperature gradient of 613 – 556 F
  - Formation *assumed* to occur at 572 F
    - Implies minimum range of formation of +/- 28 F based on axial temperature gradient
  - No accounting for lower wall temperature or potential radial temperature gradient

Region	C	F	NH_4^+/SO_4^{2-} (Mole Ratio)
1	356 - 323	673 - 613	---
2	323 - 291	613 - 556	0.91
3	291 - 265	556 - 509	1
4	265 241	509 - 466	0.95
5	241 - 222	466 - 432	0.77
6	222 - 203	432 - 398	0.26
7	203 - 183	298 - 361	0.14
8	183 - 158	361 - 316	0.11

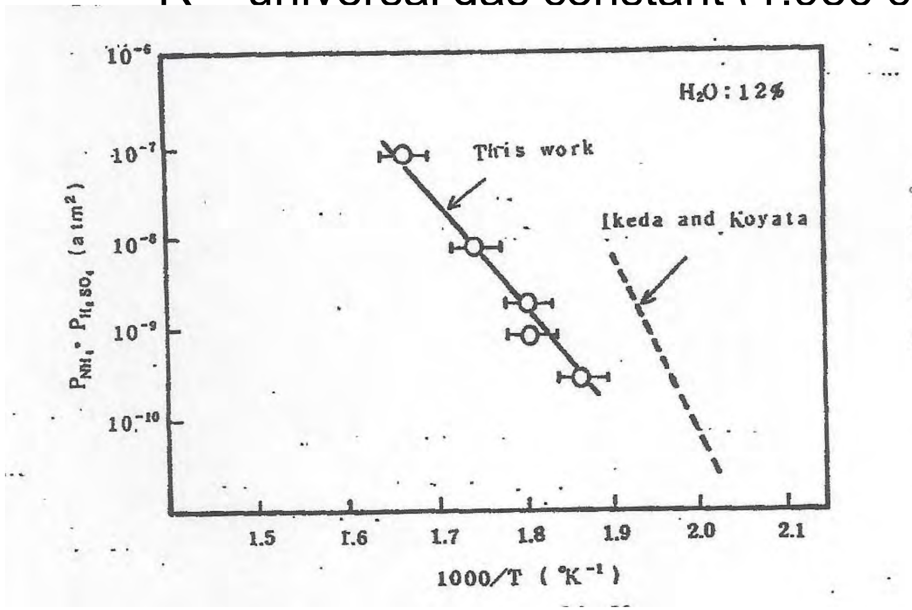




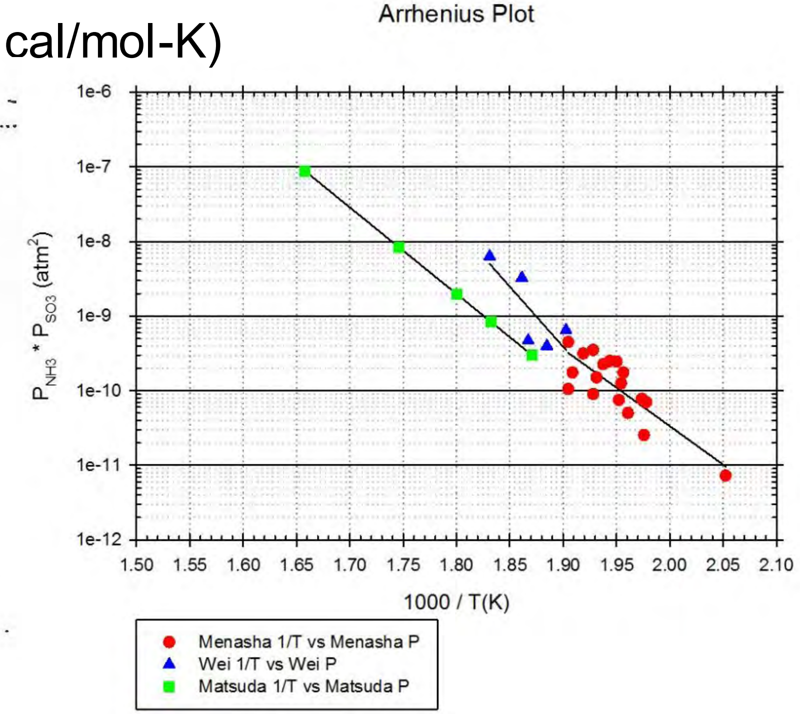
*(Ind. Eng. Chem. Prod. Res. Dev,, 1982, 21, 48-52)

Matsuda* Experiment Results

- ABS condensation temperature results provide estimate of 'pre-exponential' factor based on Arrenhius plot
  - Only five data points with broad range of error bars
  - Assumed 100% of reaction follows one step H_2SO_4 reaction path
- $P_{NH3} * P_{SO3} = 1.41 * 10^{12} \exp(-53{,}000 / RT)$
  - P_{NH3} and P_{SO3} gaseous concentration in atmospheres
  - R = universal gas constant (1.986 cal/mol-K)

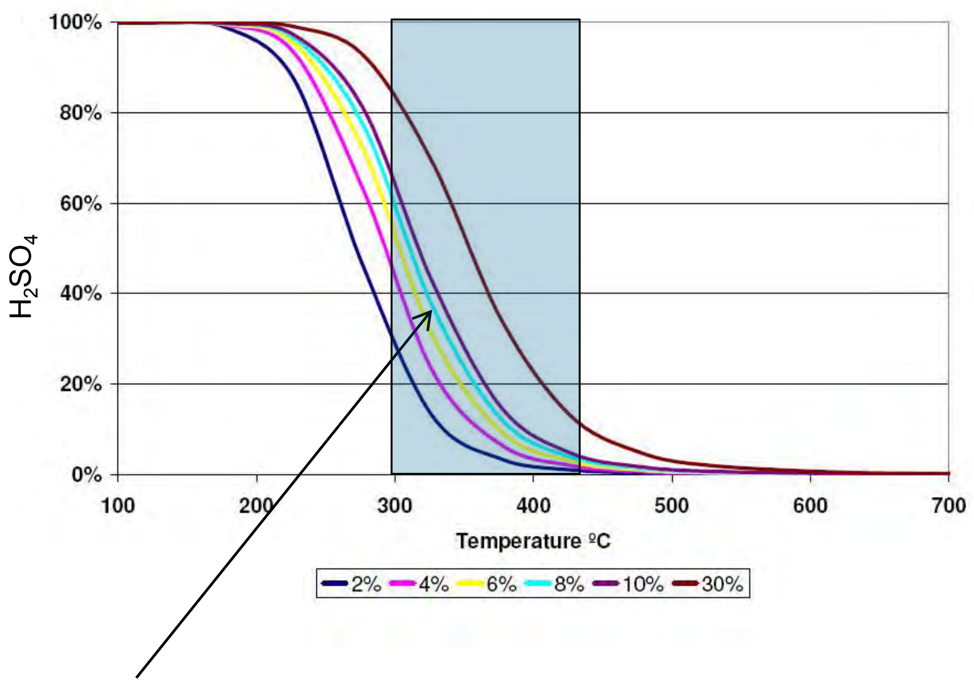


*(Ind. Eng. Chem. Prod. Res. Dev, 1982, V21, 48-52)



Ammonium Bisulfate Formation

Fraction of SO_3 Present as H_2SO_4 as a Function of Moisture Content



•Typical SCR Operating Temperature Regime

Chemical Reactions Forming ABS

- One step reaction
  - $NH_3 + H_2SO_4 = NH_4HSO_4$ (l)
    - ΔH_{298} = -53 kcal/mole
- Two step reaction
  - $SO_3 + H_2O = H_2SO_4$
    - ΔH_{298} = -25 kcal/mole
  - $NH_3 + H_2SO_4 = NH_4HSO_4$ (l)
    - Overall ΔH_{298} = -78 kcal/mole
- At typical coal-fired boiler SCR operating temperatures of 300 – 425 C (570 – 800 F), most ABS formed via $NH_3 + H_2SO_4$

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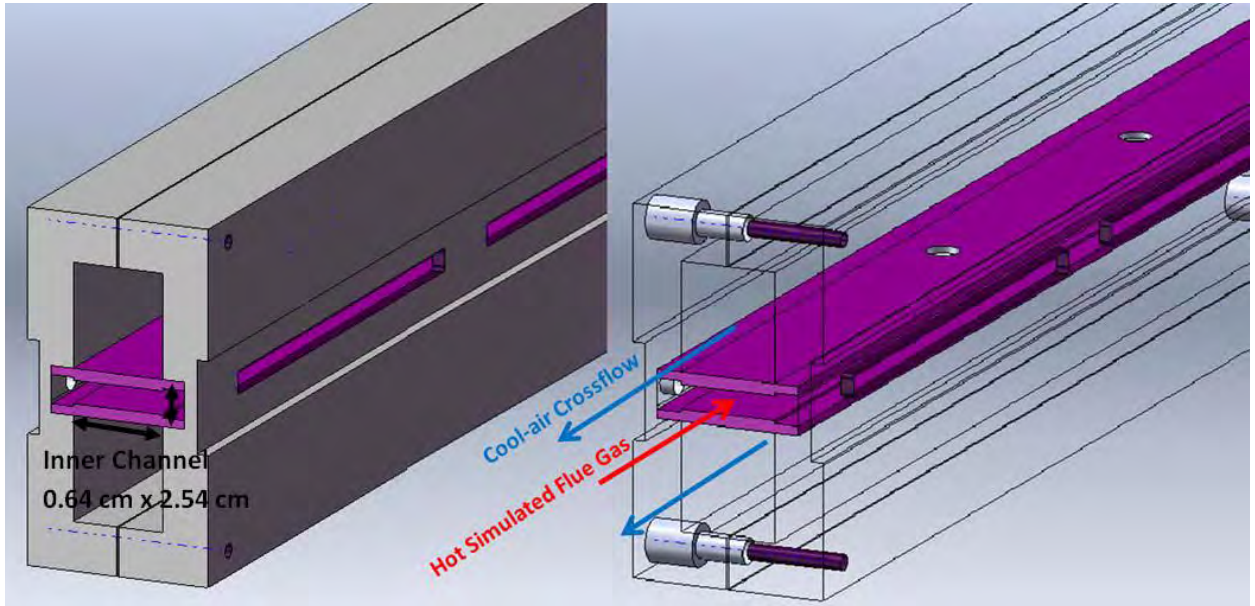
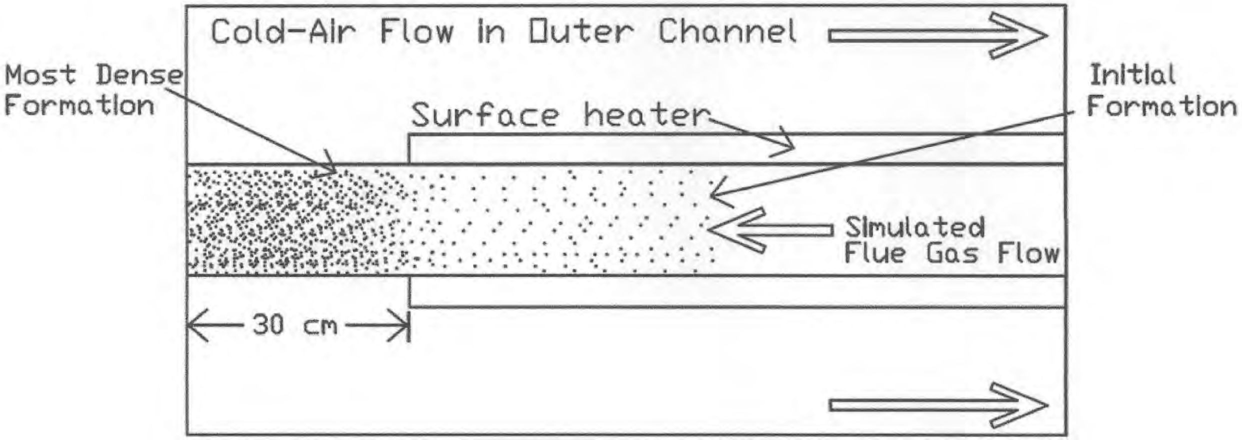
UCI* Experiments and Results

- EPRI Technology Innovation funded experiments at UC Irvine
  - Conducted over range of NH_3 and SO_3 concentrations more typical of SCR or air heater
  - Wei (2007) conducted 5 tests using LAND acid dew point meter
  - Menasha (2010) conducted 18 tests using a simulated air heater channel
    - Reported temperature uncertainty of 2.5 K (4.5 F)
    - Slight scatter in formation temperature data may be attributable to presence of small seed particles

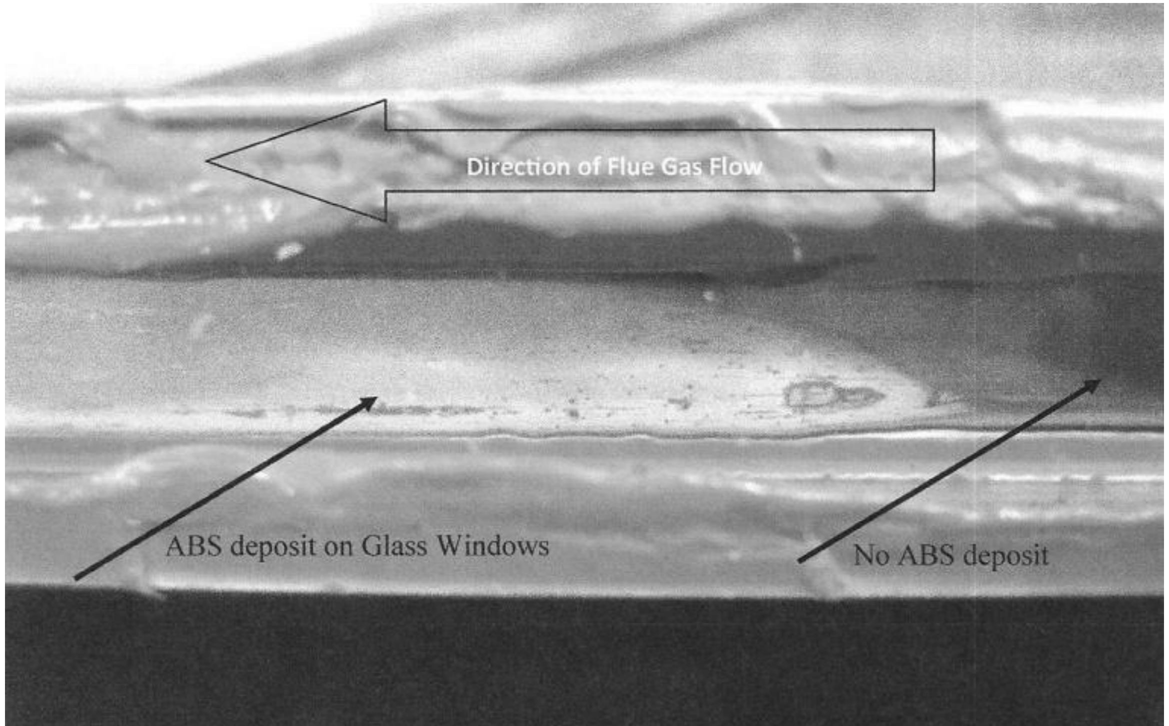




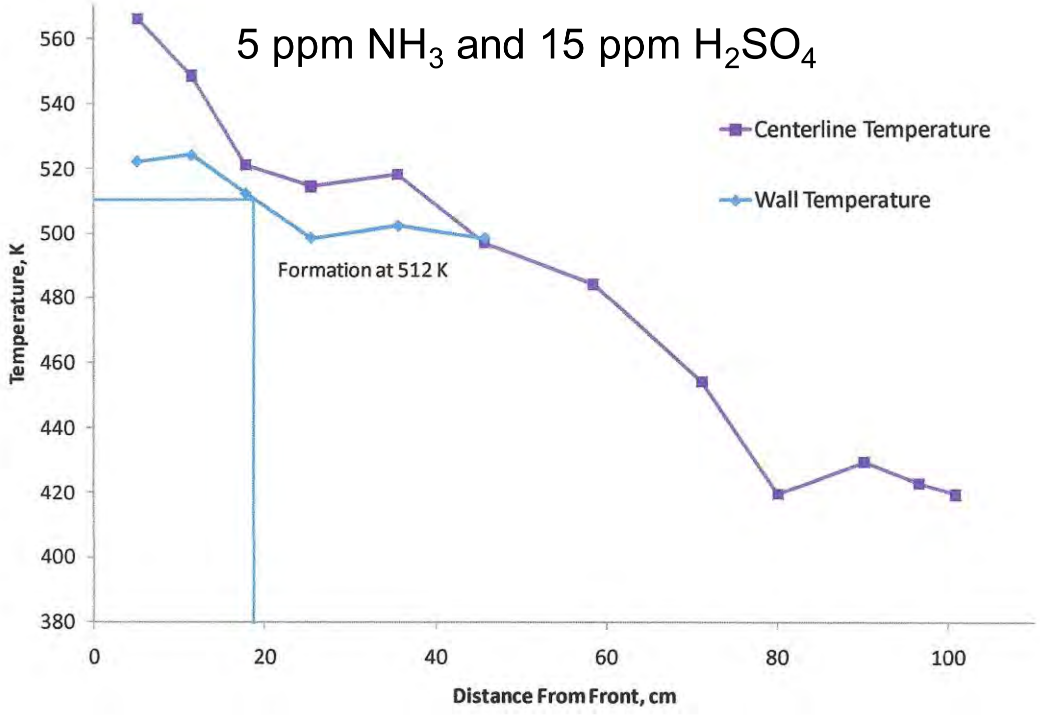
*(Fuel, 2011, V90, p. 2445-2453)
(Wei, EPRI 2007 SCR Workshop)

UCI* Air Heater Experiment and Results

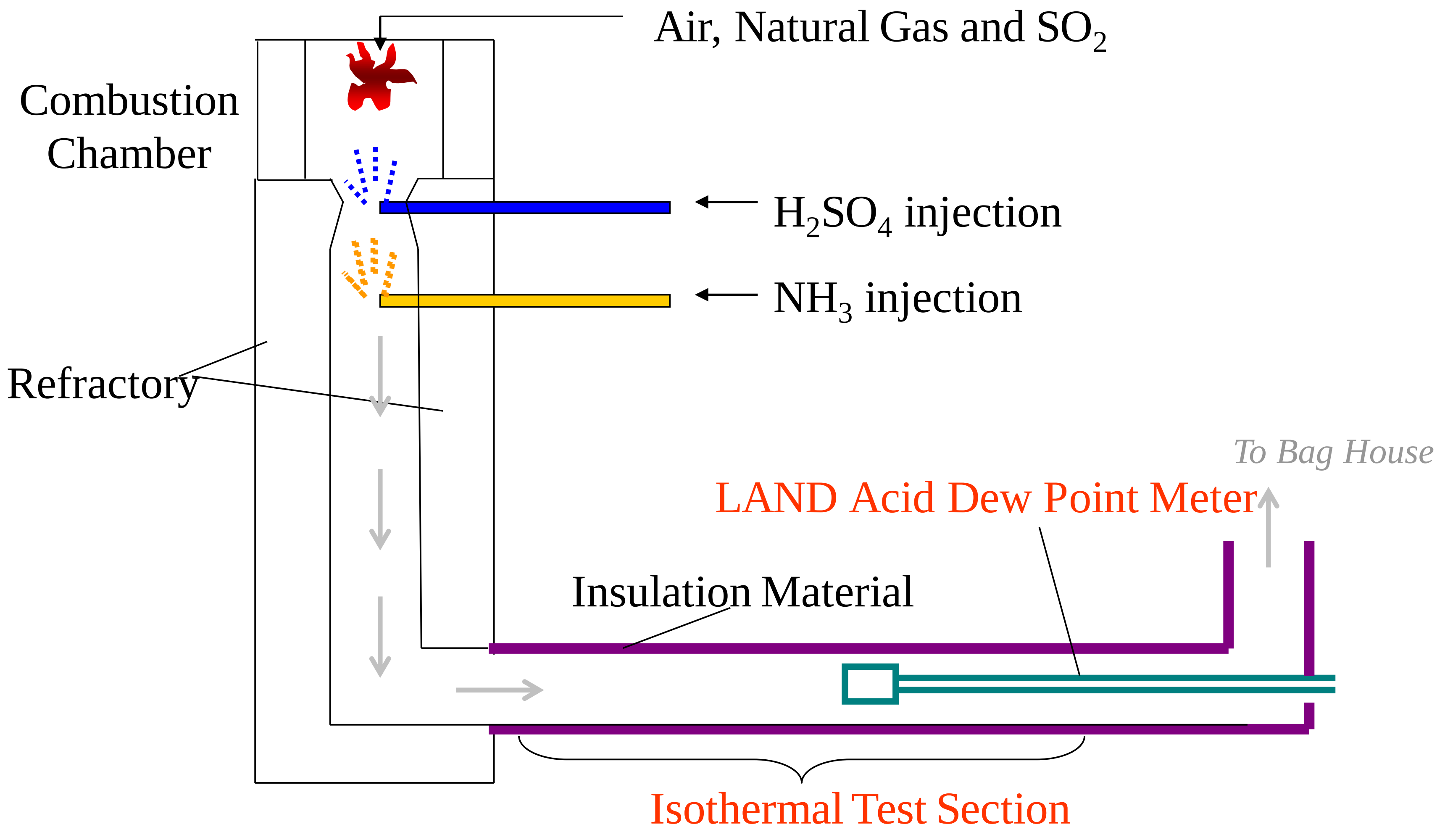
- Broader experimental data set at lower concentration range provides more accurate calculation of pre-exponential factor and activation energy
  – $P_{NH3} * P_{SO3} = 2.97 * 10^{13} \exp(-54,947 / RT)$



*(Fuel, 2011, V90, p. 2445-2453)

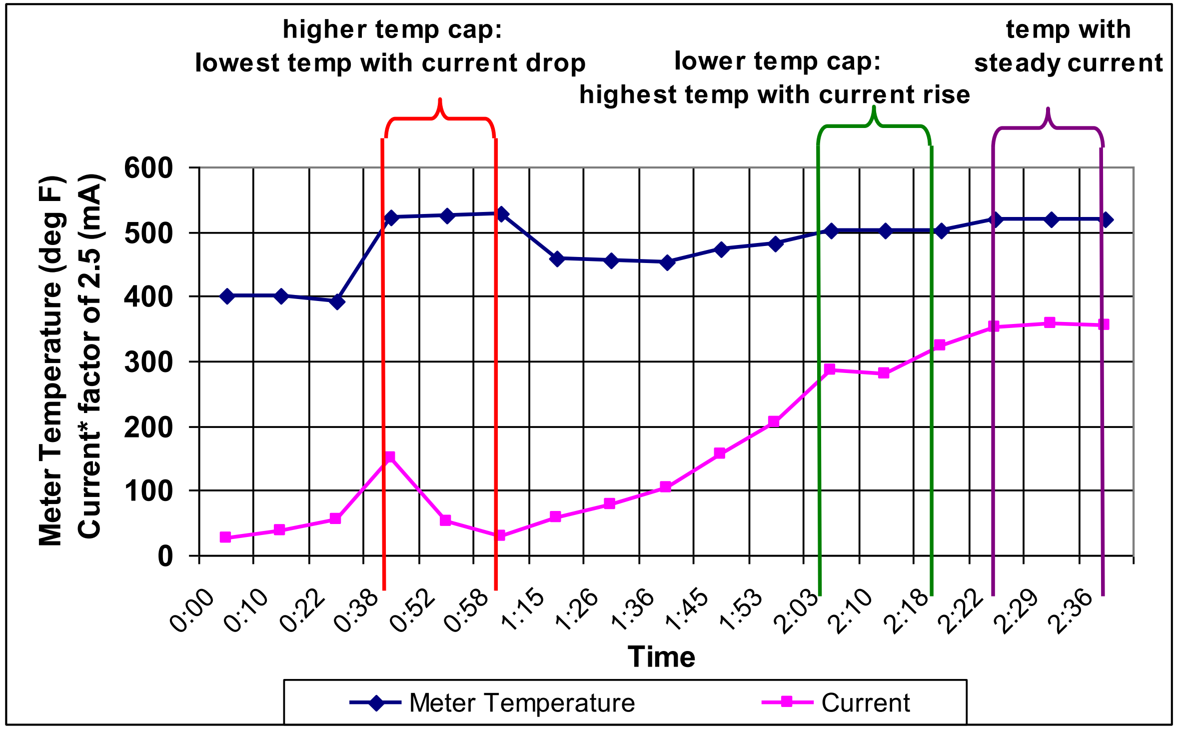


UCI* Experiment (Wei) with LAND Acid Dew Point Meter



*(Wei, EPRI 2007 SCR Workshop)

LAND Acid Dew Point Test Approach



Temp selection rules:
At each temperature:
Decrease in current
→ evaporation
Increase in current
→ condensation
Steady current
→ dewpoint temp

- Determine preliminary temperature range from curves
- Maintain probe at each temp within the range for 20 ~ 30 min and select the next test temperature accordingly

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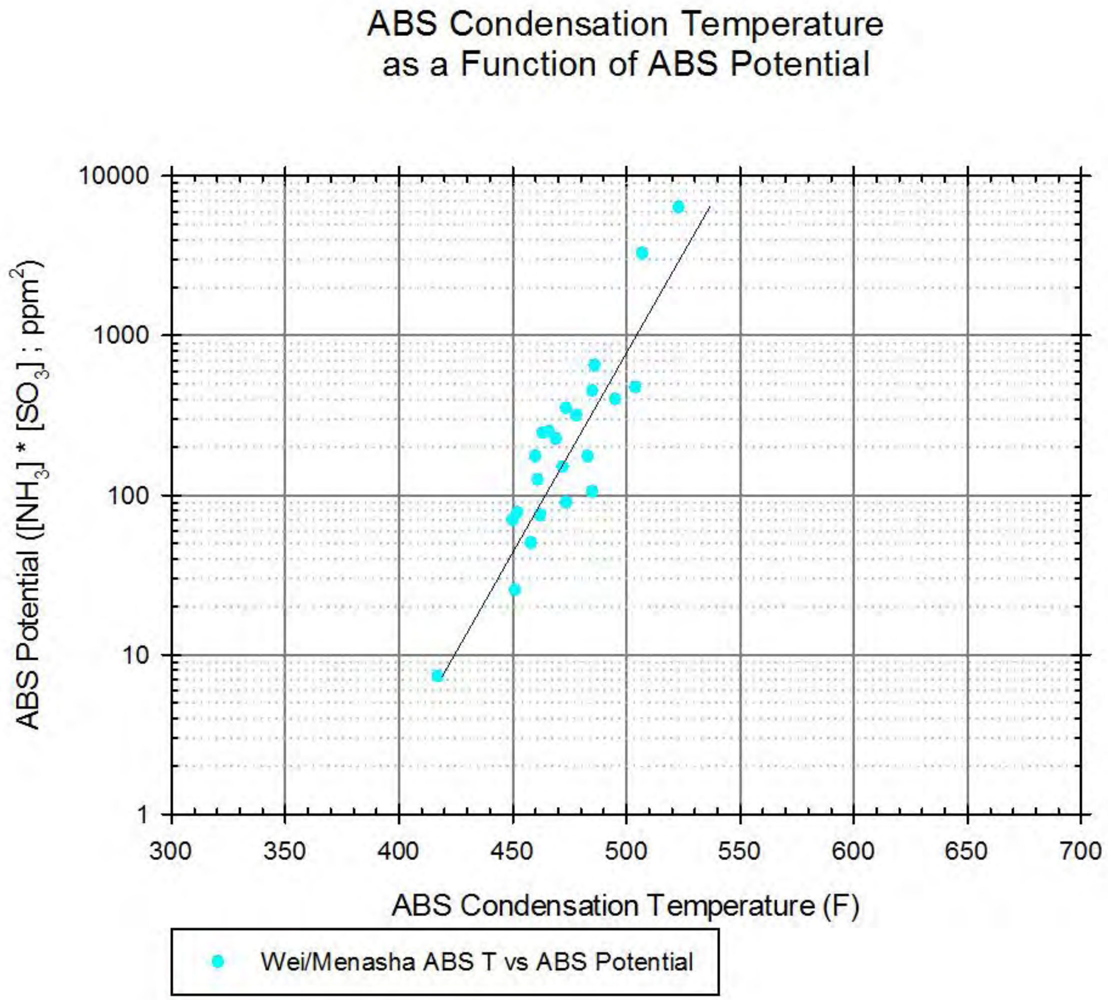
UCI Experimental Results Summary



Consistent ABS condensation temperature results obtained from two experimental approaches

Comparison of Calculated ABS Condensation Temperature UCI vs Matsuda

ABS Formation Potential (ppm^2)	Matsuda ABS (F)	UCI ABS (F)	Delta (F)
5,000	560	533	27
2,500	545	520	25
1,000	527	503	24
500	513	490	23
250	499	477	22
100	482	462	20

- ABS formation potential = [NH_3] * [SO_3]
  - For typical medium to high sulfur coal = 2,500 – 5,000 ppm^2
  - For typical low sulfur PRB = 100 – 250 ppm^2

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Comparison of UCI and Matsuda Results

- Matsuda results for experiment with 83.3 ppm NH_3 and 100 ppm SO_3 showed first ABS formation in Zone ‘2’ with axial temperature gradient of 613 – 556 F
  - Formation assumed to occur at 572 F
    - No rationale provided for temperature selection
  - Potential for Zone ‘2’ condensation to have occurred near cooler wall
- For same condition, UCI results calculate ABS formation at 544 F
  - UCI temperature falls within Zone ‘3’ which exhibited greatest condensation

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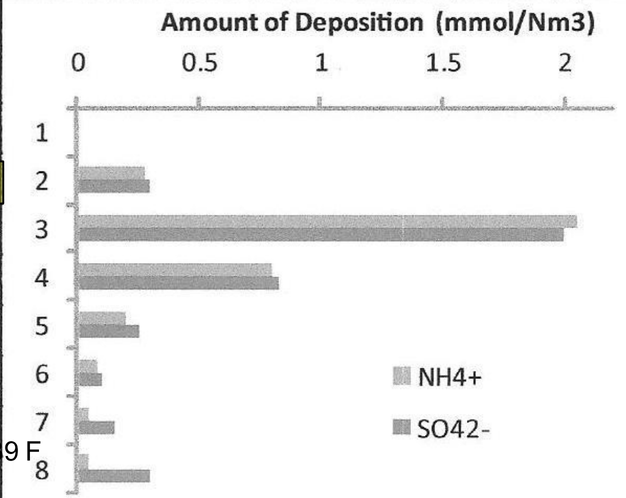
39 F



UCI results potentially more consistent with Matsuda experiment

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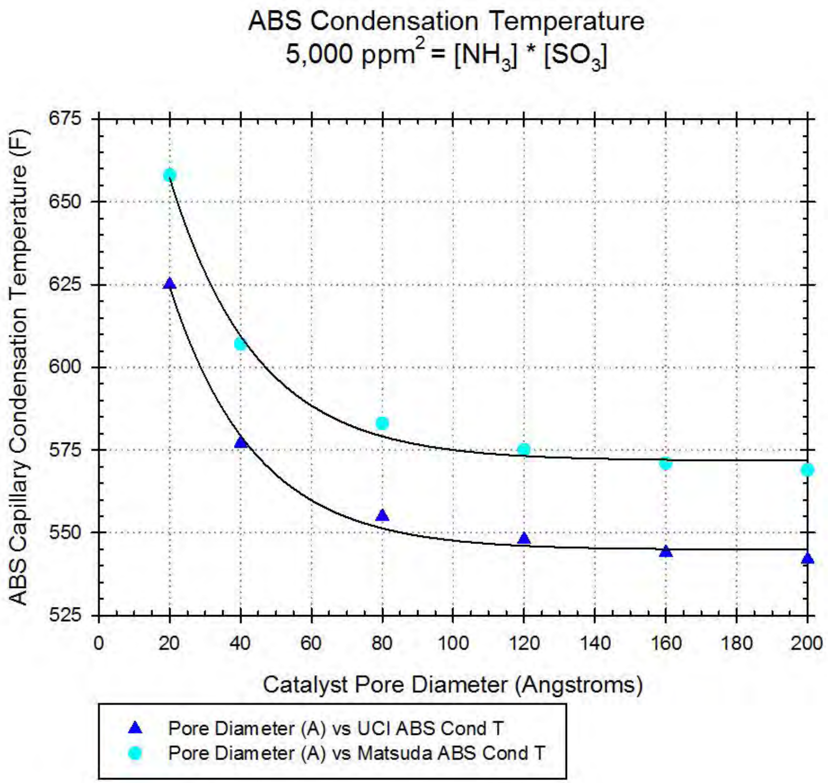
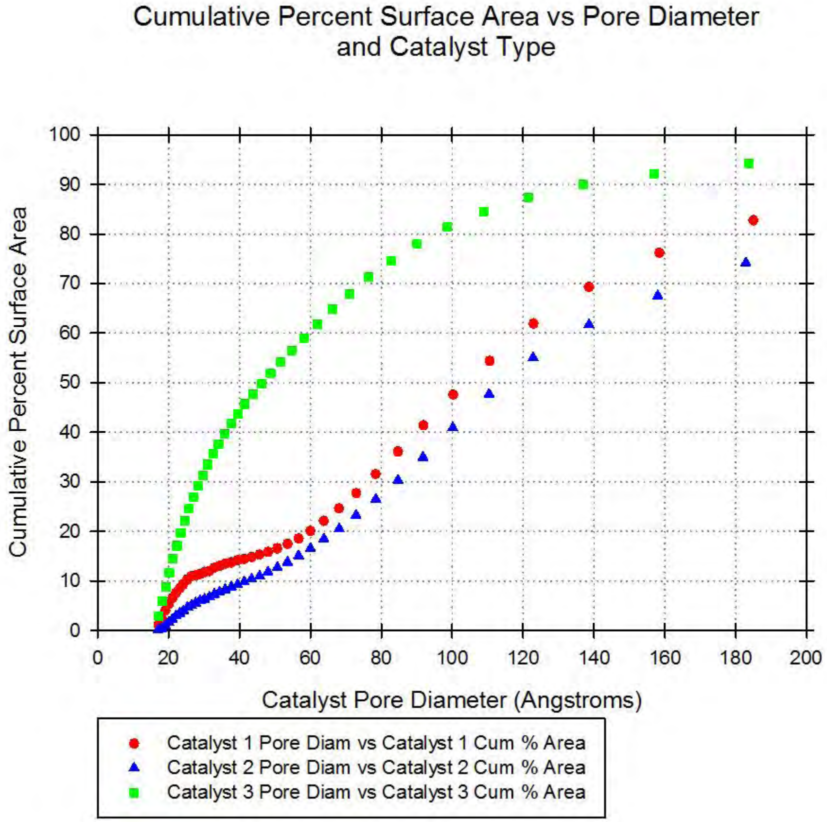
ABS Capillary Condensation Temperature

- ABS capillary condensation in catalyst pores occurs at higher temperatures
- Thomson's theory of capillary condensation used to calculate ABS formation in micro pores
  - $\ln (P/P_{eq}) = 2 \sigma M / \rho \gamma R T$
    - Surface tension (σ) = 150 dyn/cm^2
    - Density (ρ) = 1.78 g/cm^3 for ABS
    - Pore size (γ) = cm
  - $\ln (P/P_{eq}) = 2.33 * 10^{-4} (cm^{-1} K^{-1}) / \gamma T$

Catalyst Pore Diameter (A)	Matsuda Capillary ABS (F)	UCI Capillary ABS (F)	Delta (F)
20	658	625	33
40	607	577	30
80	583	555	28
120	575	548	27
160	571	544	27
200	569	542	27

ABS Capillary Condensation Temperature - SCR Catalyst





SCR catalyst surface area impacted from ABS condensation a function of catalyst pore size distribution

Calculation of ABS Capillary Condensation Temperature Based on Estimated Concentrations

- Calculate ABS capillary condensation temperature as a function of first catalyst layer impacted
  - Calculation based on pore size associated with 10% of overall pore surface area
  - Sensitivity analysis to assess impact associated with 10% higher NOx and 20% higher SO_3 levels
  - Analysis also examines changes in second catalyst layer capillary condensation temperature

			10% of Pore Surface Area		
	NH_3	SO_3	NH_3*SO_3	Pore Radius	T_{Cap}
	ppm	ppm	ppm^2	A	F
Baseline Minimum Load Operating Conditions	200	25	5000	20	577
Sensitivity Test Case (+10% Nox ; +20% SO3)	220	30	6599	20	583
SCR Layer 2 (Assumed 50% deNOx Layer 1)	100	25	2500	20	563
Sensitivity Test Case (+10% Nox ; +20% SO3)	110	30	3300	20	569

For 5,000 ppm^2 and catalyst pore radius of 20 A, ~10% of first layer surface area impacted at 575 – 580°F

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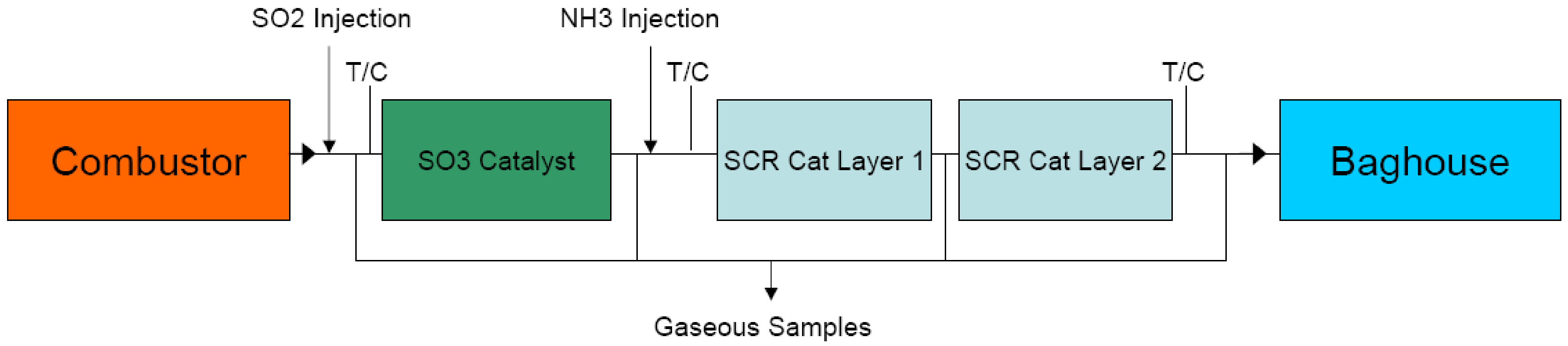
Additional Factors Impacting SCR MOT

- Dynamic SCR MOT methodology can address:
  - Range of coals fired and associated sulfur levels
  - Higher SCR inlet SO_3 levels at reduced loads of interest
    - Potential impact of enhanced SO_2 oxidation due to increased excess oxygen for steam temperature control
- Dynamic methodology only provides estimate of single temperature
  - Need to assess potential gradients across SCR inlet
  - Use of bluff body and/or static mixers
  - Number, location, and representativeness of SCR inlet temperature measurements
  - Frequency of SCR tuning and potential variability of SCR NSR
    - Need to identify typical range of SCR inlet temperature and/or ABS potential (e.g. $[NH_3] * [SO_3]$)

Summary of Literature Review of ABS Formation Temperature

- Literature over the years has suggested a broad range of potential ABS condensation temperatures
  - ABS formation temperature a function of [NH_3] and [SO_3]
- Empirical evidence has generally supported Matsuda results **prior** to UCI lab investigations
  - Review of experimental method and assumptions suggest Matsuda experiment and resultant equation has error of +28 F on average
  - Error carries over to calculation of ABS capillary condensation temperature
- UCI lab investigation provides more accurate methodology with measured ABS condensation reaction activation energy supported by literature
- Results suggest a lower SCR catalyst minimum operating temperature is feasible

Laboratory Tests



- Lab based project addressing fundamental questions:
  - Confirmation of which experiment (UCI or Matsuda) best estimates ABS condensation temperature?
  - To what extent does ABS capillary condensation affect just the top catalyst layer, or all layers?
  - How long can the SCR operate at a calculated MOT and maintain requisite performance?
  - How long does it take to recover at different temperatures?
    - Catalyst recovery often referenced in terms of full load operation

Summary

- SCR often represents constraint to minimum load operation
- Significant savings associated with moderate reductions in SCR minimum operating temperature
  - Review of literature and new data suggests ABS condensation temperature lower than previously thought
  - UCI data sets appear to provide the most accurate estimate of ABS condensation temperature
- Dynamic SCR MOT calculation approach developed
  - EPRI lab research being conducted to support the above
    - Looking to work with catalyst vendors and utilities to develop broad based assessment and industry accepted approach

Together…Shaping the Future of Electricity