

REINHOLD ENVIRONMENTAL Ltd.



**2013 NO<sub>x</sub>-Combustion Round Table  
& Expo Presentations**

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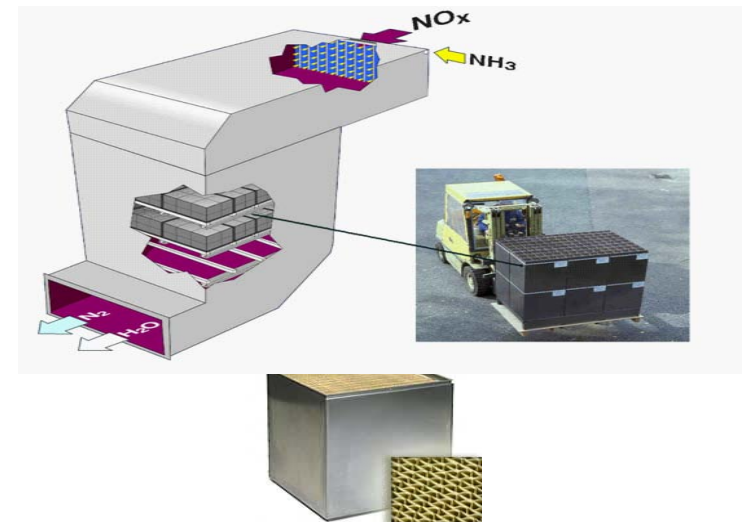
# Ammonium Bisulphate Inhibition of SCR Catalyst

RESEARCH | TECHNOLOGY | CATALYSTS

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# Reduced load operation in coal-fired power plants

- Increased gas turbine capacity and utilization (Flat load growth, low and sustainable NG prices)
- Base load natural gas substituted for base load coal
- Minimize economic impact during low demand periods
- Develop a comprehensive strategy for low load operation



# Optimization strategies for SCRs

- Optimise  $\text{NH}_3$  distribution
- Optimise flow distribution (temperature maldistribution)
- Add catalyst layer
- Boiler split / economizer bypass
- Low temperature  $\text{NH}_3$  injection strategy
  - Min. temperature determined by ABS dew point, ( $\text{SO}_3$ )

# SCR minimum operating temperature

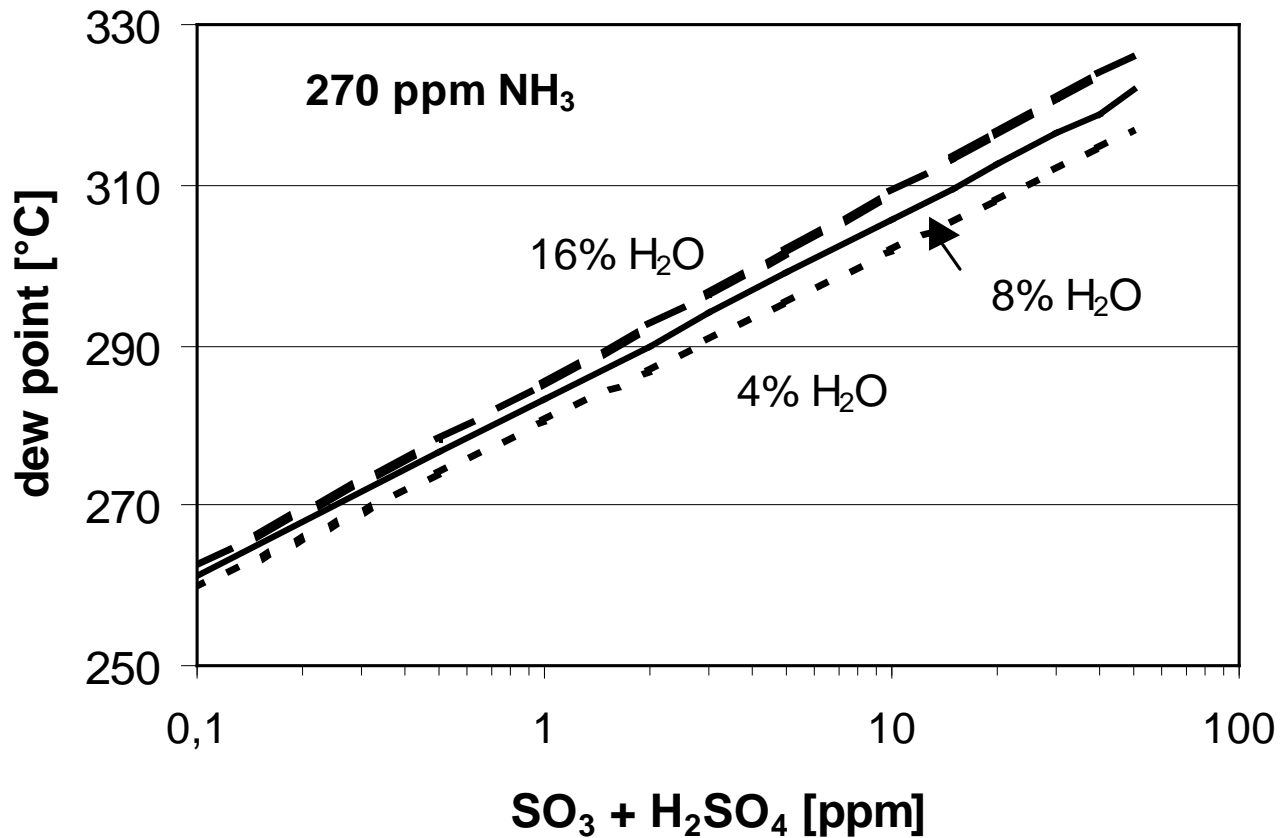
Given by the  $\text{SO}_3$  level due to condensation of ammonium bisulfate (ABS) in the catalyst pores.



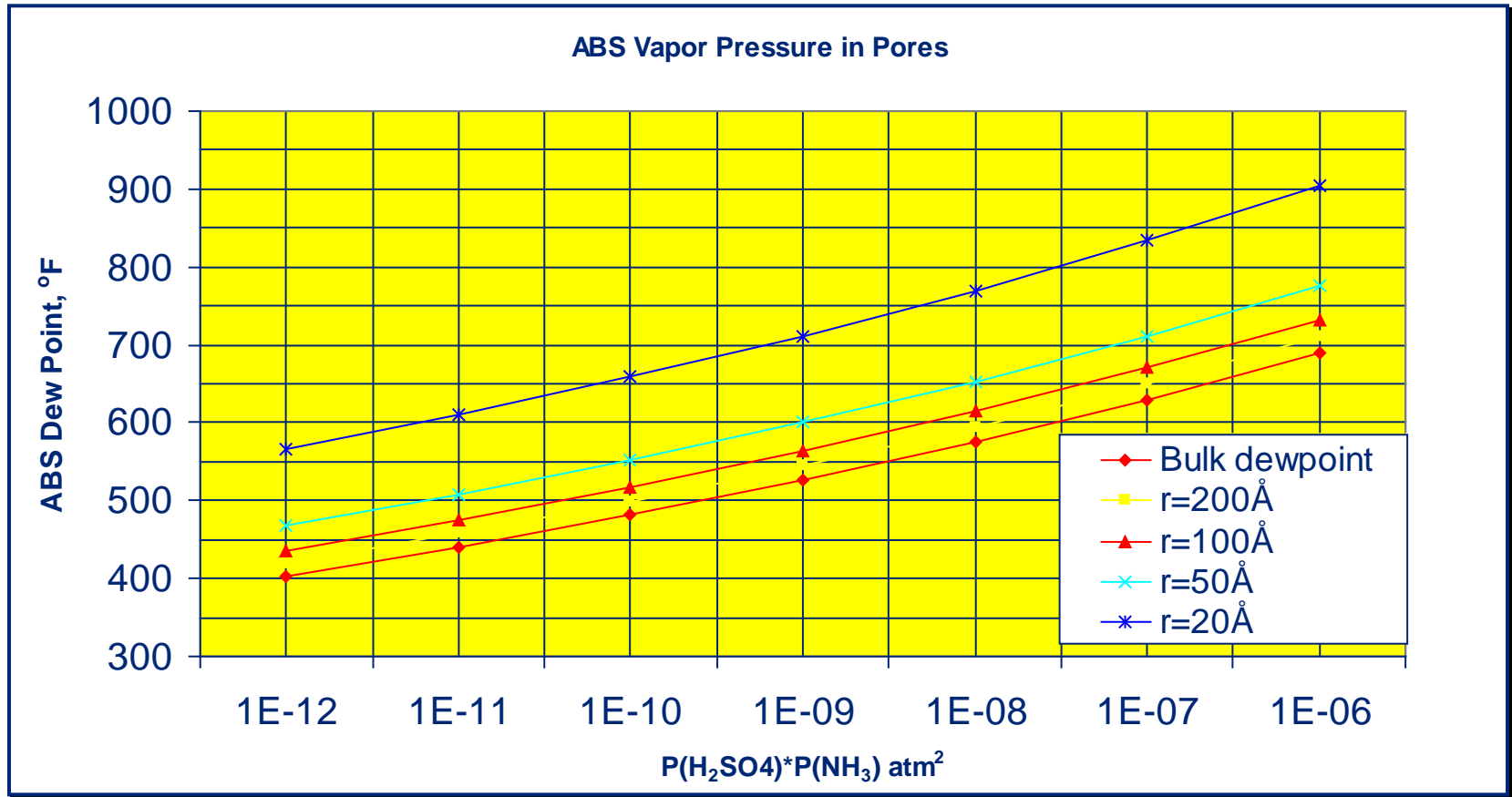
ABS inhibition

- depends on  $\text{NH}_3$
- $\text{H}_2\text{O}$
- $\text{SO}_3$
- Temperature
- Catalyst space velocity
- is reversible by heating

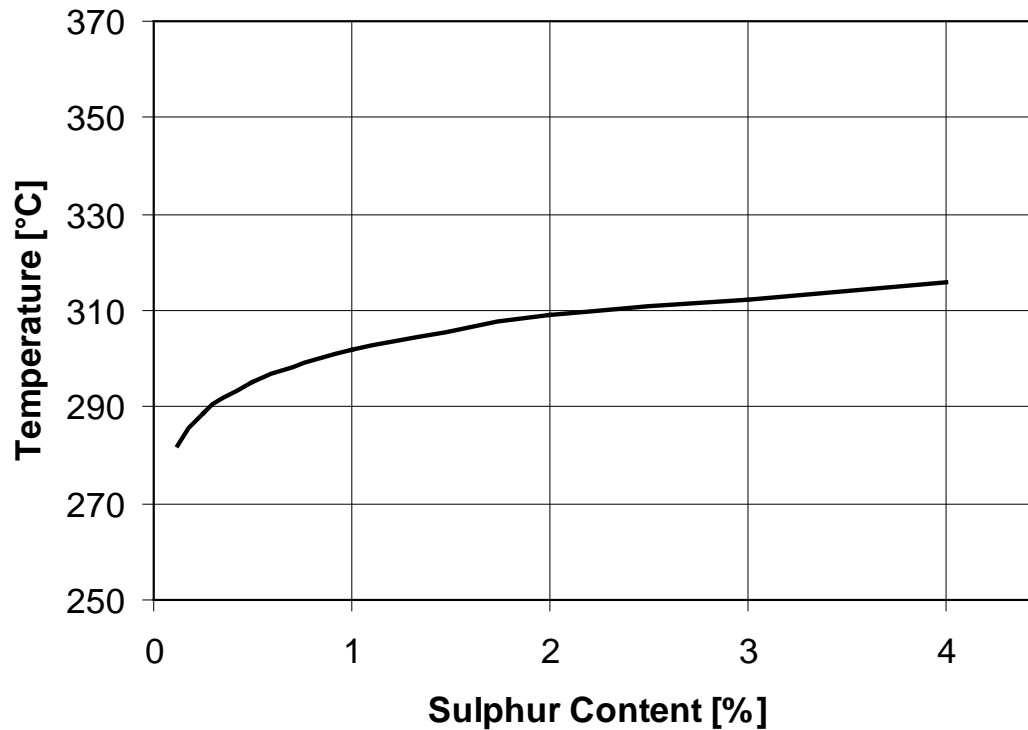
# DNX<sup>®</sup> ABS dew point $k_{\text{NH}_3}/k_{\text{NH}_3,0} \approx 0.95$



# Effect of pore size on dew point temperature



# Minimum temperature guideline in large diesel engines



# ABS dew point

- Matsuda et al. bulk dew point by Clausius-Clapeyron type equation where P are partial pressures in the gas phase
- The influence of capillary forces is described by Kelvin equation where  $r_{\text{pore}}$  is the pore size that is just filled with ABS at given gas composition and temperature and  $\sigma$  is the surface tension of ABS

$$\ln(P_{\text{NH}_3} \cdot P_{\text{H}_2\text{SO}_4})_{\text{eq,bulk}} = 27.97 - \frac{26671}{T[\text{K}]}$$

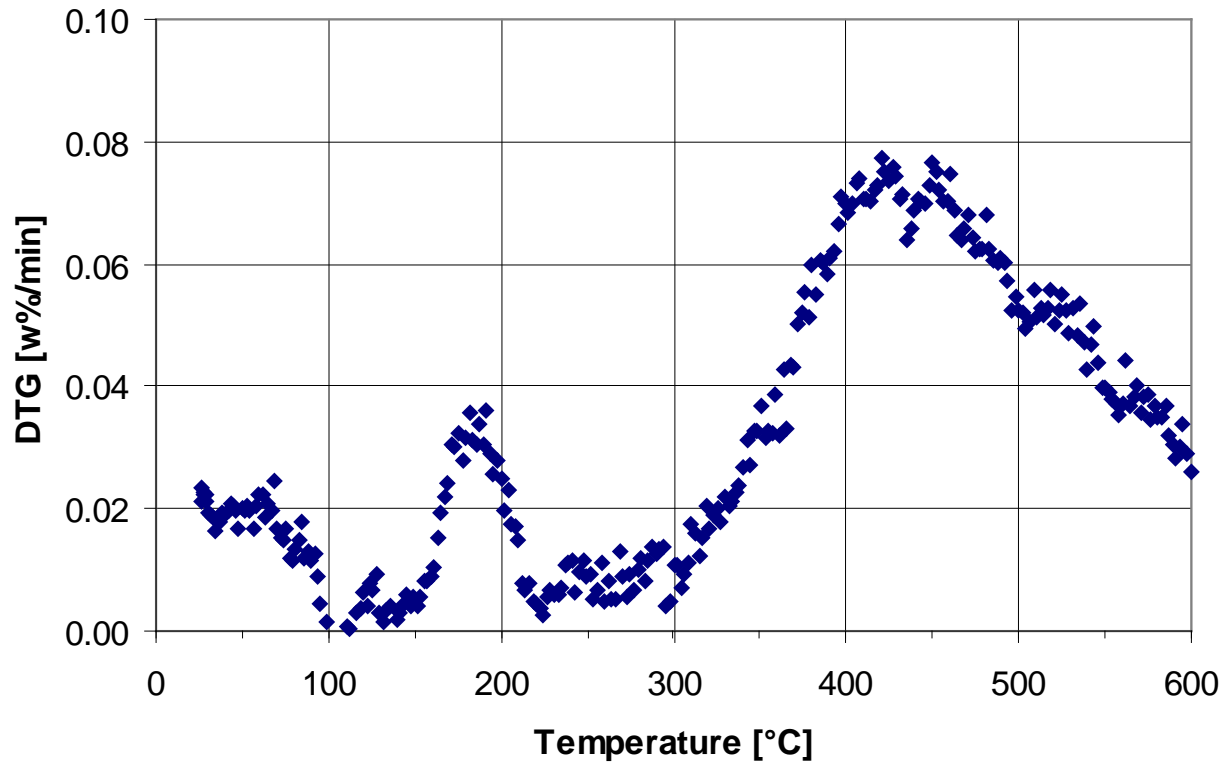
$$\ln \frac{(P_{\text{NH}_3} \cdot P_{\text{H}_2\text{SO}_4})_{\text{eq,pore}}}{(P_{\text{NH}_3} \cdot P_{\text{H}_2\text{SO}_4})_{\text{eq,bulk}}} = - \frac{2 \cdot \sigma \cdot M}{\rho \cdot r_{\text{pore}} \cdot R \cdot T}$$

# Formation of ABS downstream the catalyst

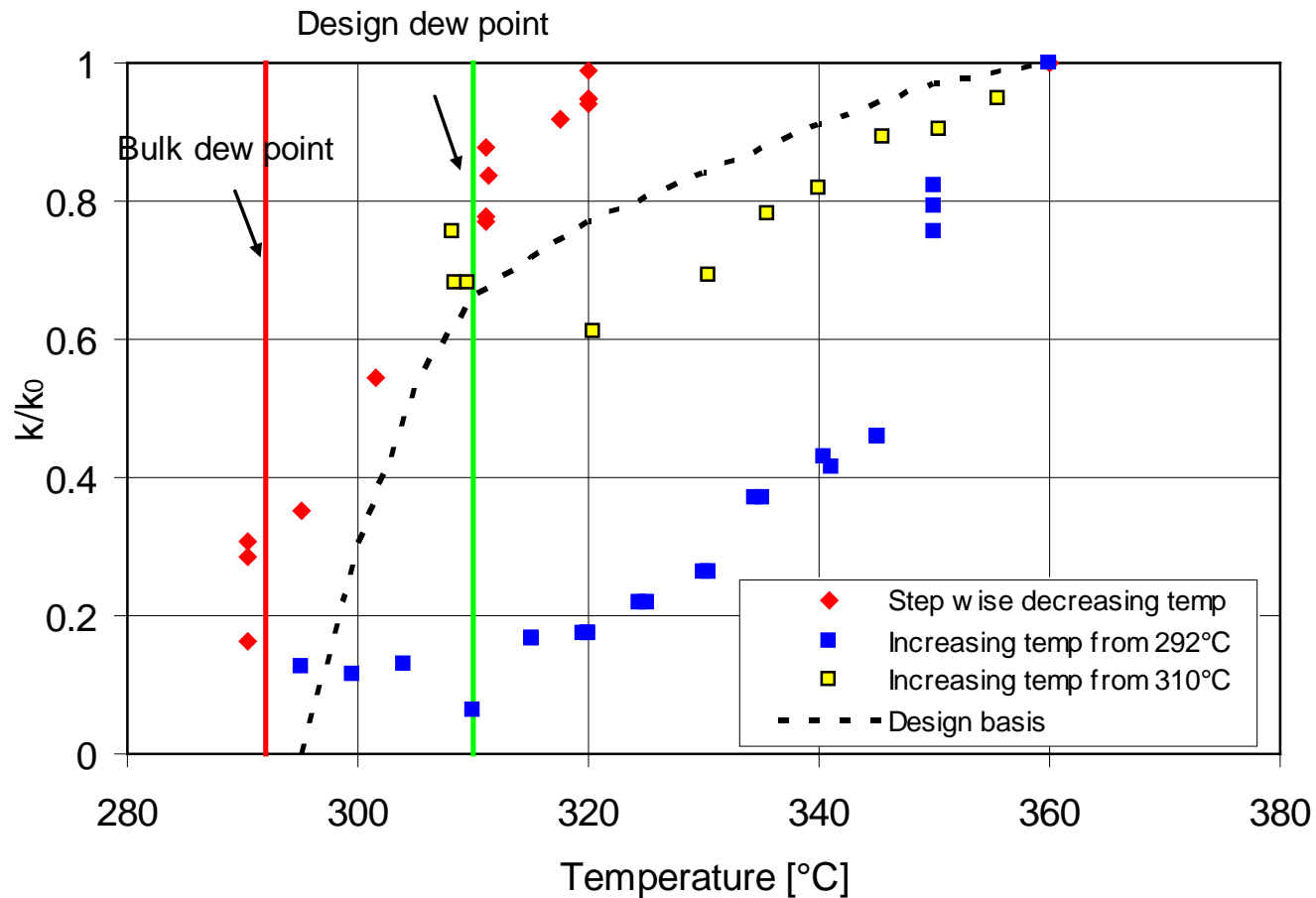
- Sub cooling in the downstream segment.
  - Reverse effect of capillary condensation
  - Adsorption on particles
- Temperatures of metal surfaces compared to ABS dew point.



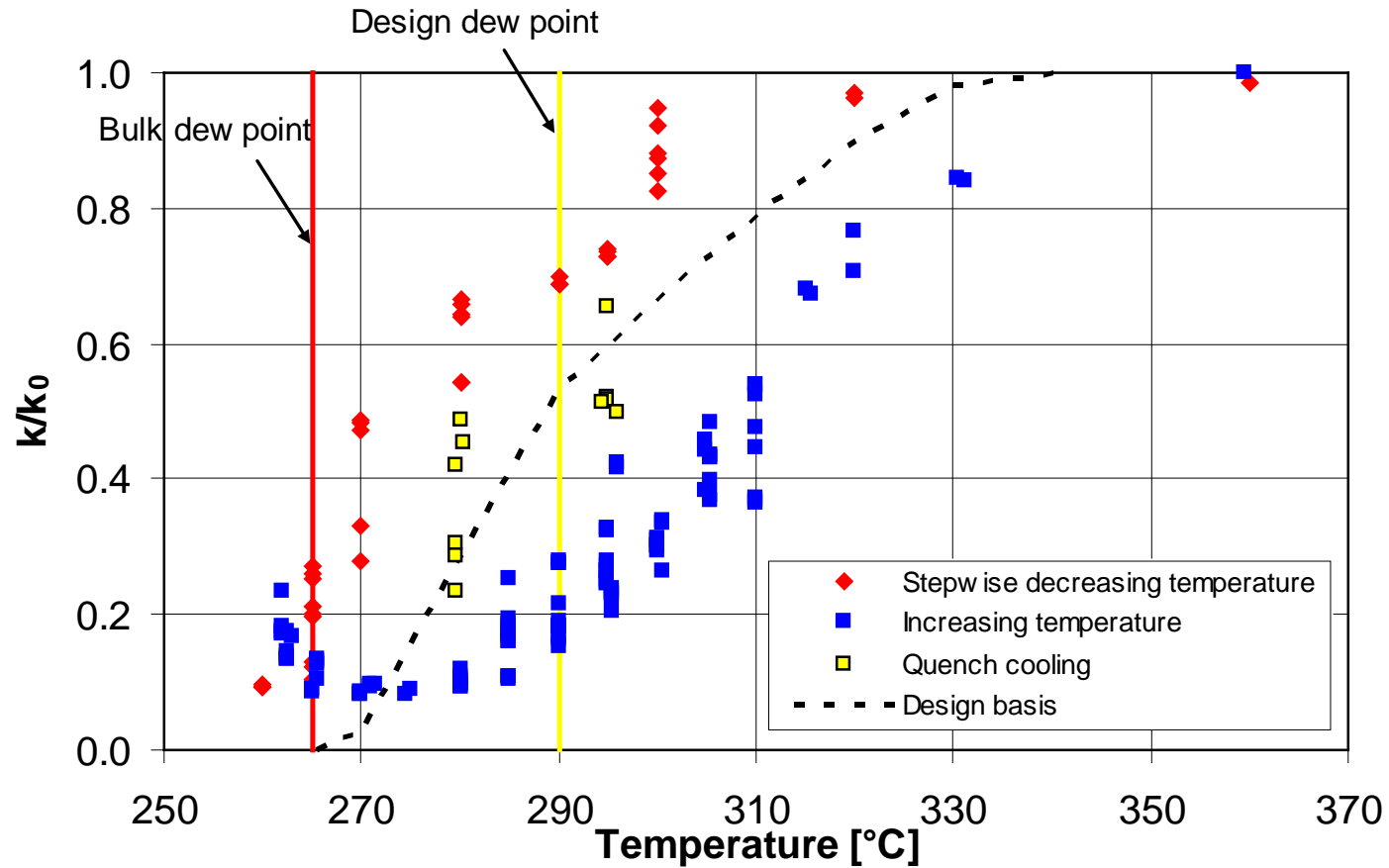
# Thermogravimetric analysis (TGA) of ABS



# SCR ABS inhibition in coal-fired boiler



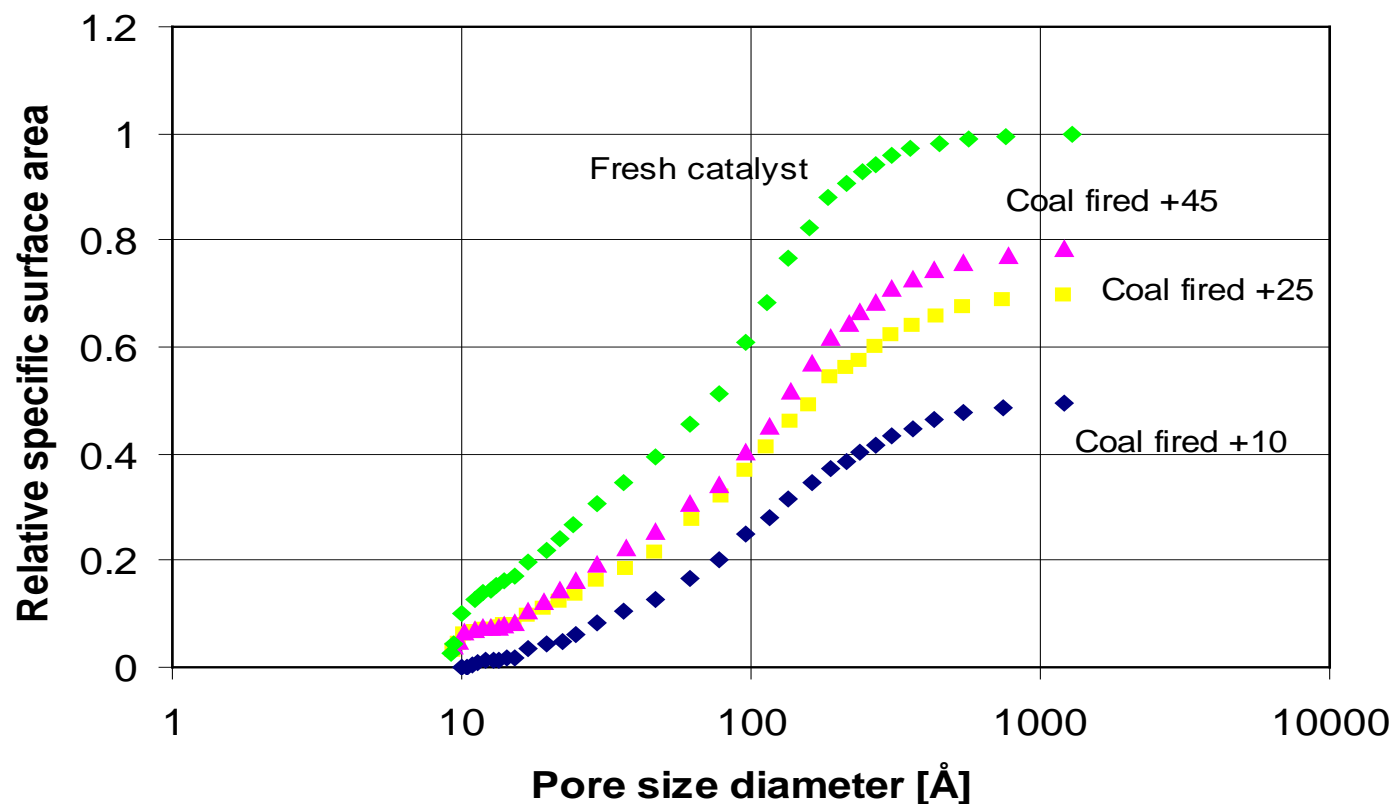
# SCR inhibition in oil-fired boiler



# Characterisation of inhibited catalyst

Position in catalyst [mm], from top	S [%w]	NH <sub>4</sub> <sup>+</sup> [%w]	N/S molar ratio	Relative Specific surface QBET	Relative Nitrogen pore volume	Relative Specific surface HBET
0	2.70	0.48	0.32	-	-	-
100	1.37	0.34	0.46	0.49	0.73	0.50
250	0.82	0.12	0.28	0.69	0.93	0.42
350	0.67	0.07	0.22	-	-	-
500	0.62	0.06	0.19	0.78	1.00	0.71
ABS	23.1	9.92	0.77	-	-	-
Ref	0.01-0.05	-	N.A.	1.00	1.00	1.00

# Effect of ABS on specific surface area



Cumulative specific surface area measured by nitrogen adsorption. The samples were taken at different distances, 10 cm, 25 cm and 45 cm, respectively, from the leading edge of the catalyst.

# ABS inhibition: time – temperature history

Oil Fired Catalyst Sample						
	Sample Position from leading edge	S [%w]	NH <sub>4</sub> <sup>+</sup> [%w]	N/S molar ratio	Relative Specific surface area	Relative N <sub>2</sub> pore volume
Design Temp. Operation <sup>1)</sup>	+ 0	4.7	0.76	0.29	0.47	0.57
Bulk Dew point operation <sup>2)</sup>	+ 0	2.6	0.45	0.31	0.47	0.62

- 1) Catalyst was analyzed after quench cooling to the design dew point and steady state operation
- 2) Catalyst was reinstalled in reactor, regenerated and quenched cooled to bulk dew point and then heated to the design dew point and analyzed

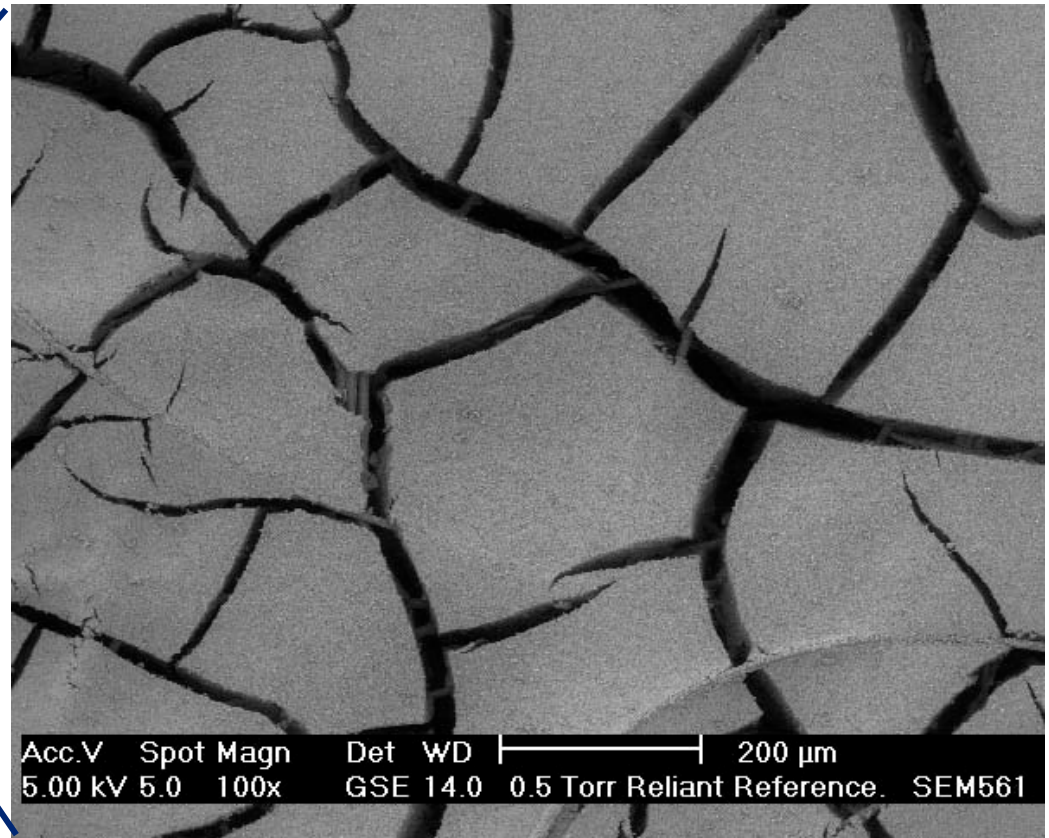
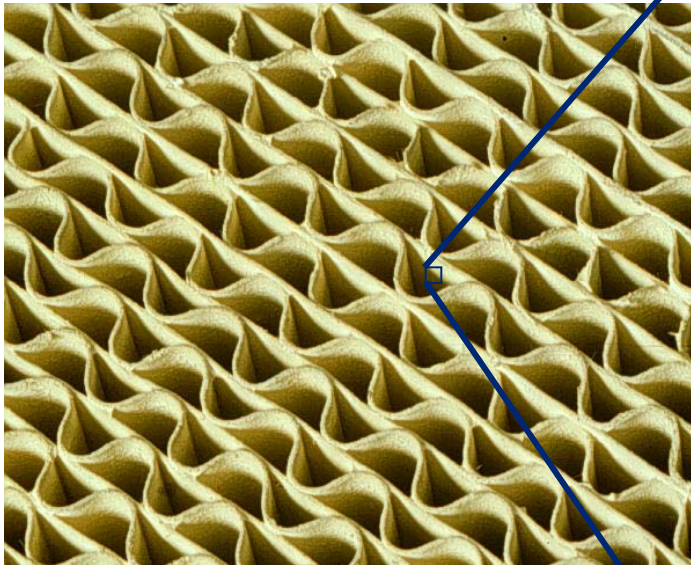
The accumulation of S and NH<sub>4</sub> at steady state depends to some degree on temperature – time history of the catalyst

# Possible causes of hysteresis effect

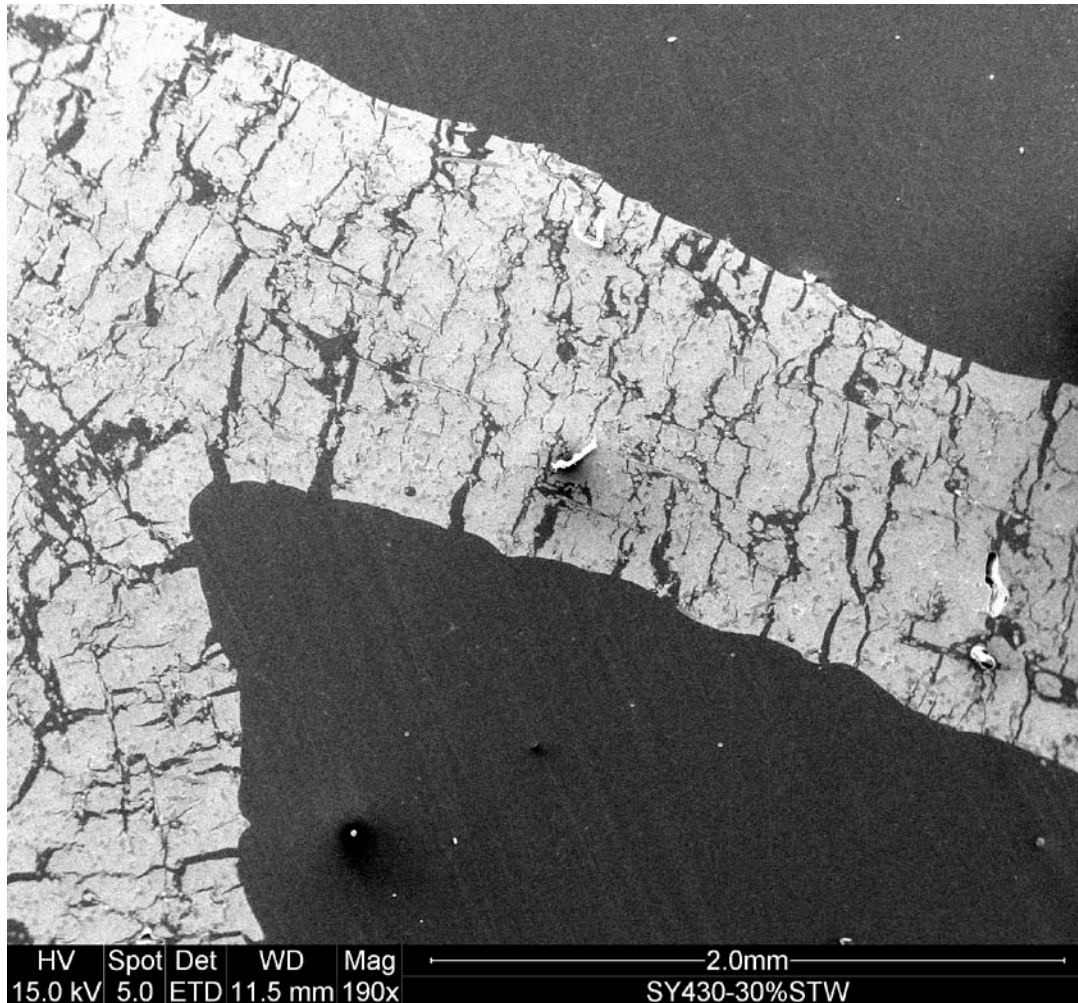
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- Decrease in vapor pressure of accumulated ABS
  - Interaction between condensed salts and the catalyst
  - Formation of  $(\text{NH}_4)_2\text{SO}_4$  due to abundant gas phase ammonia
  - Accumulation of sulfuric acid

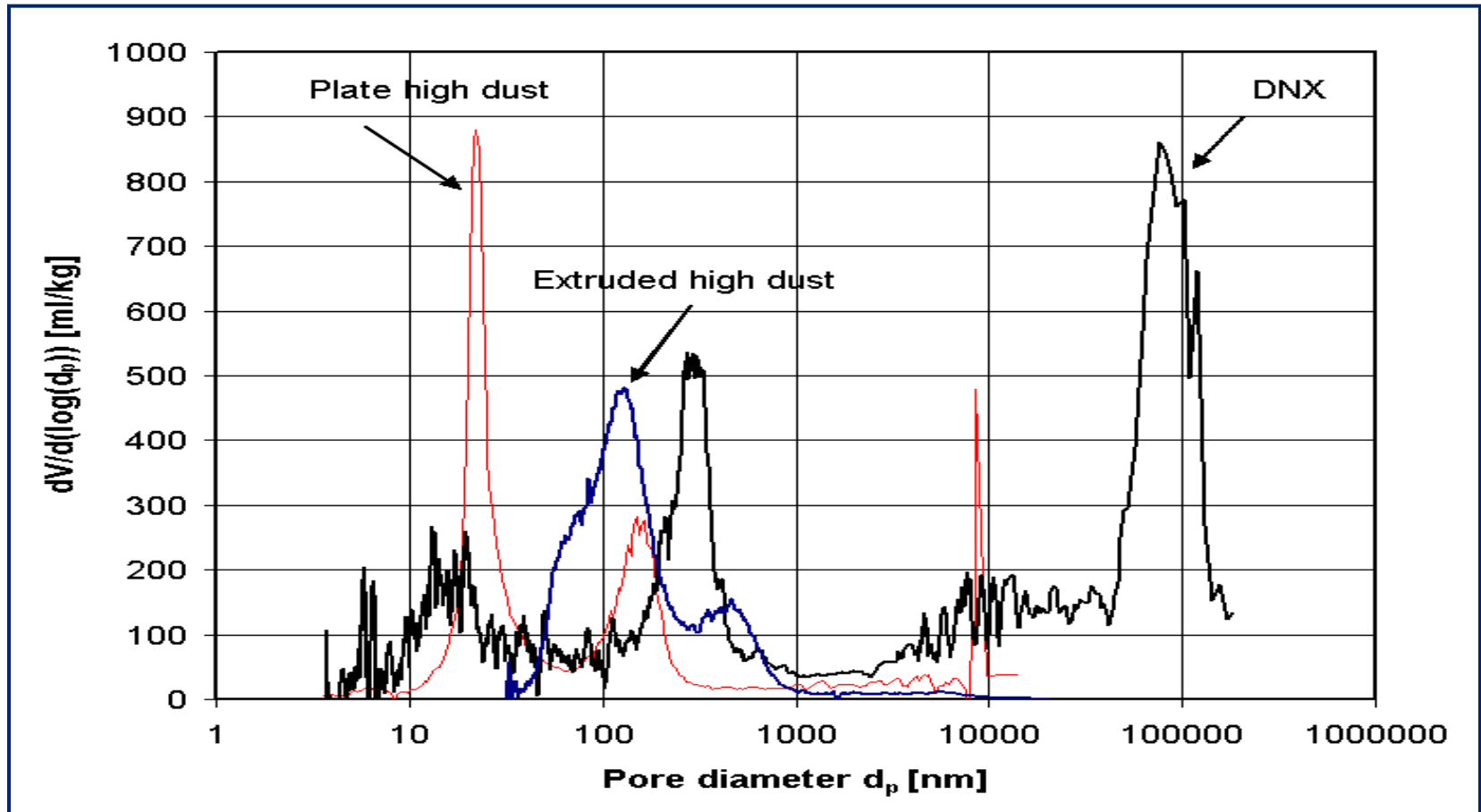
# Effect of macro pores on ABS inhibition



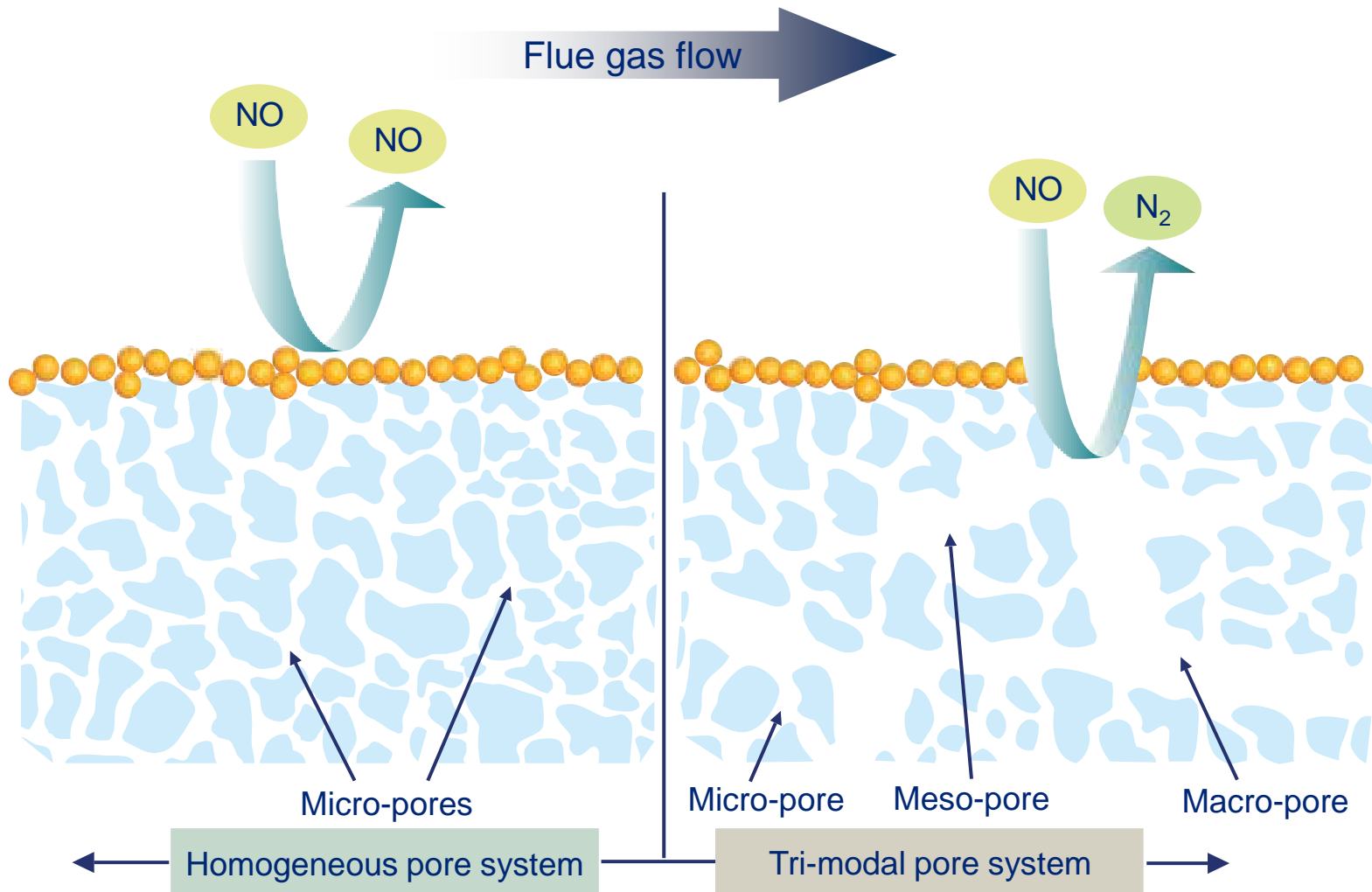
# Wall cross section of porous SCR catalyst



# Tri-modal pore size distribution



# Benefits of a meso- and macro-pore

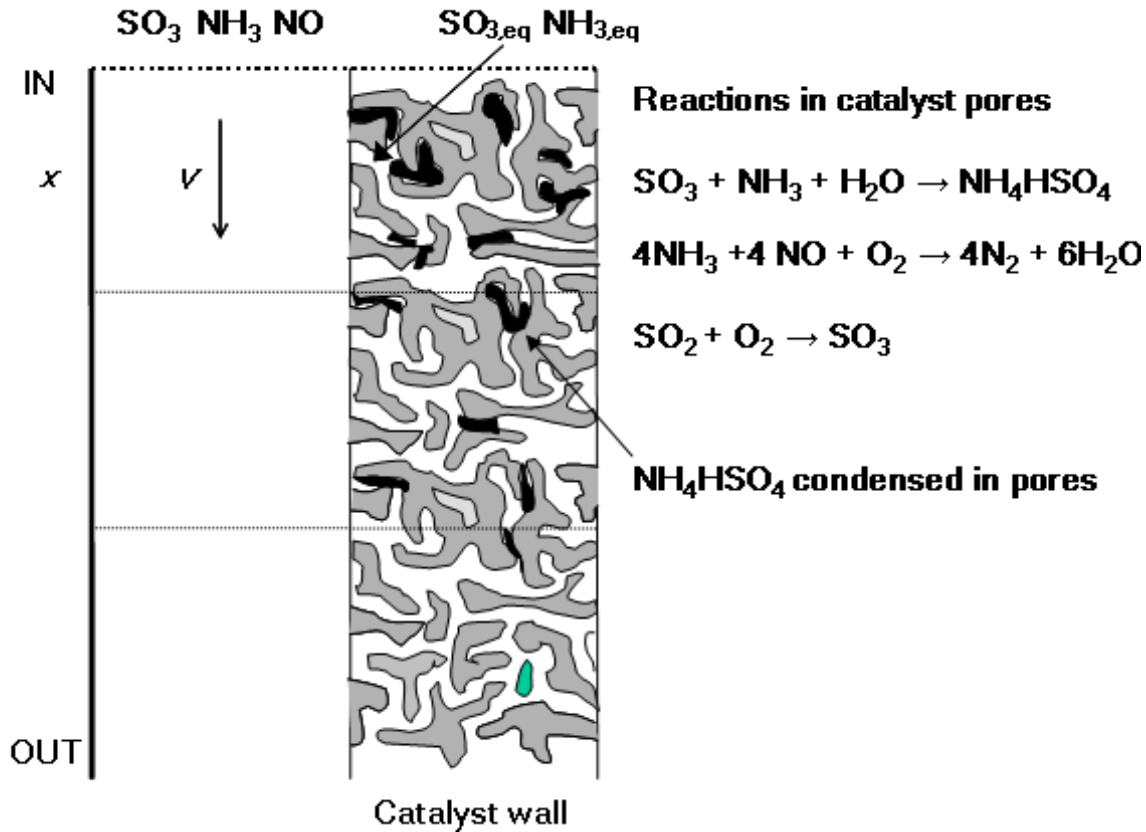


# Pore distribution tri-modal catalyst

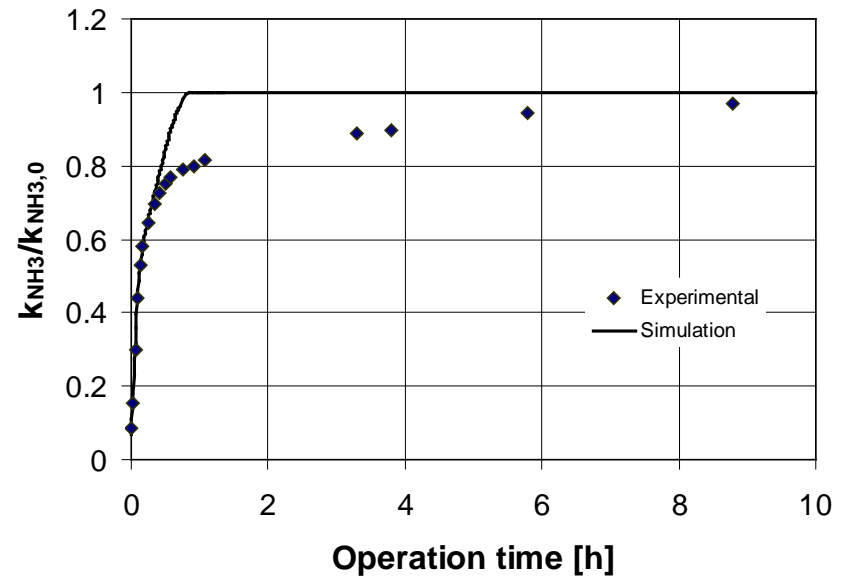
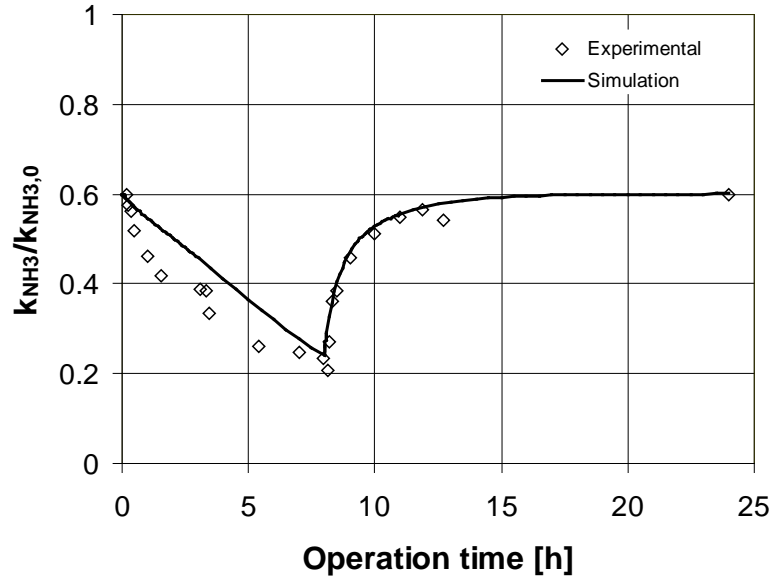
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- Pore Volume > 600 ml/kg
  - 1/3 of pores greater than 2000nm (Macro)
  - 1/3 of pores 100nm – 2000nm (Meso)
  - 1/3 of pores less than 100nm (Micro)

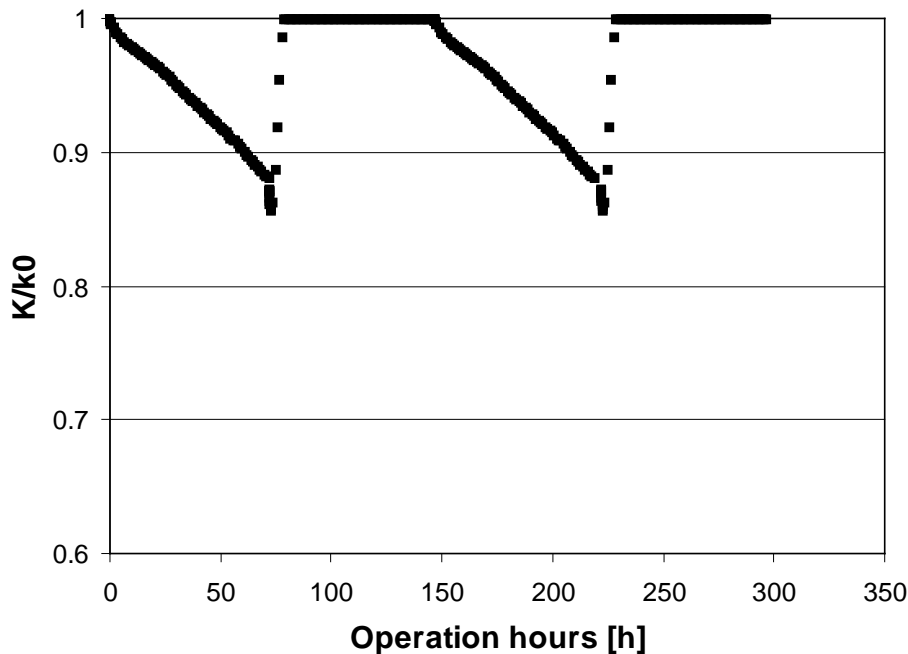
# Topsøe predictive ABS inhibition model



# ABS inhibition model

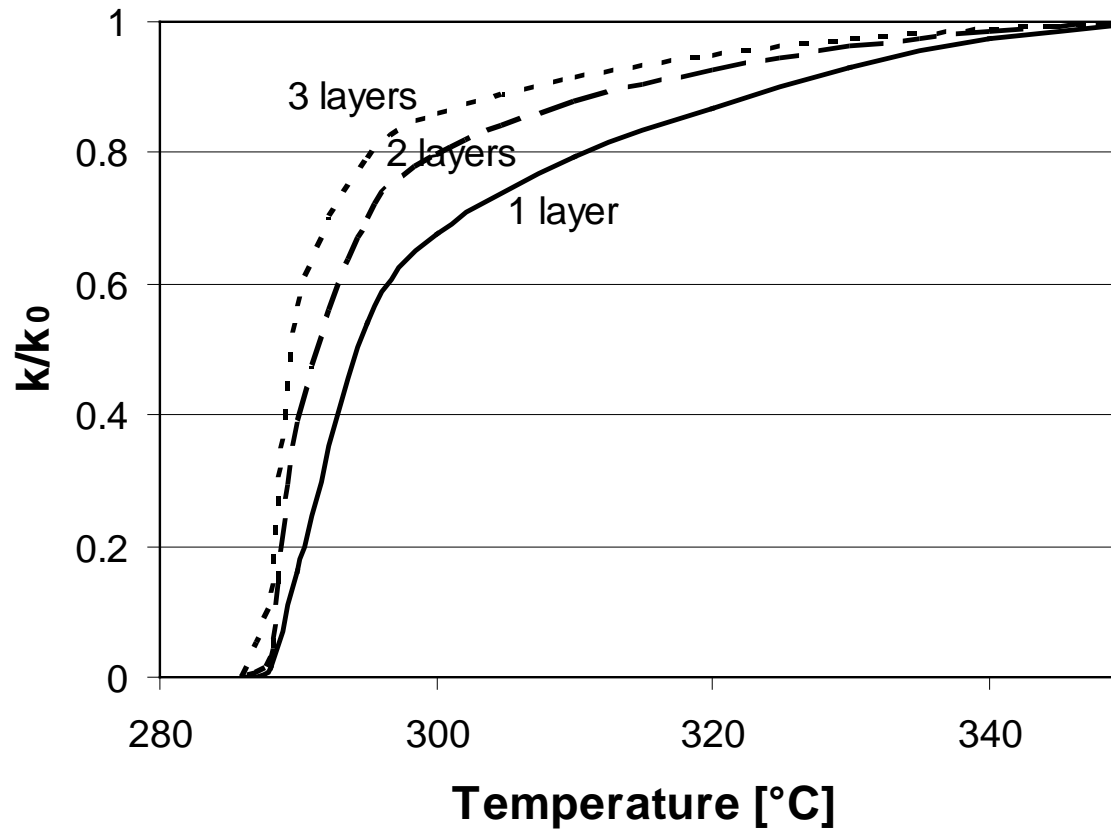


# Reduced load operation experience

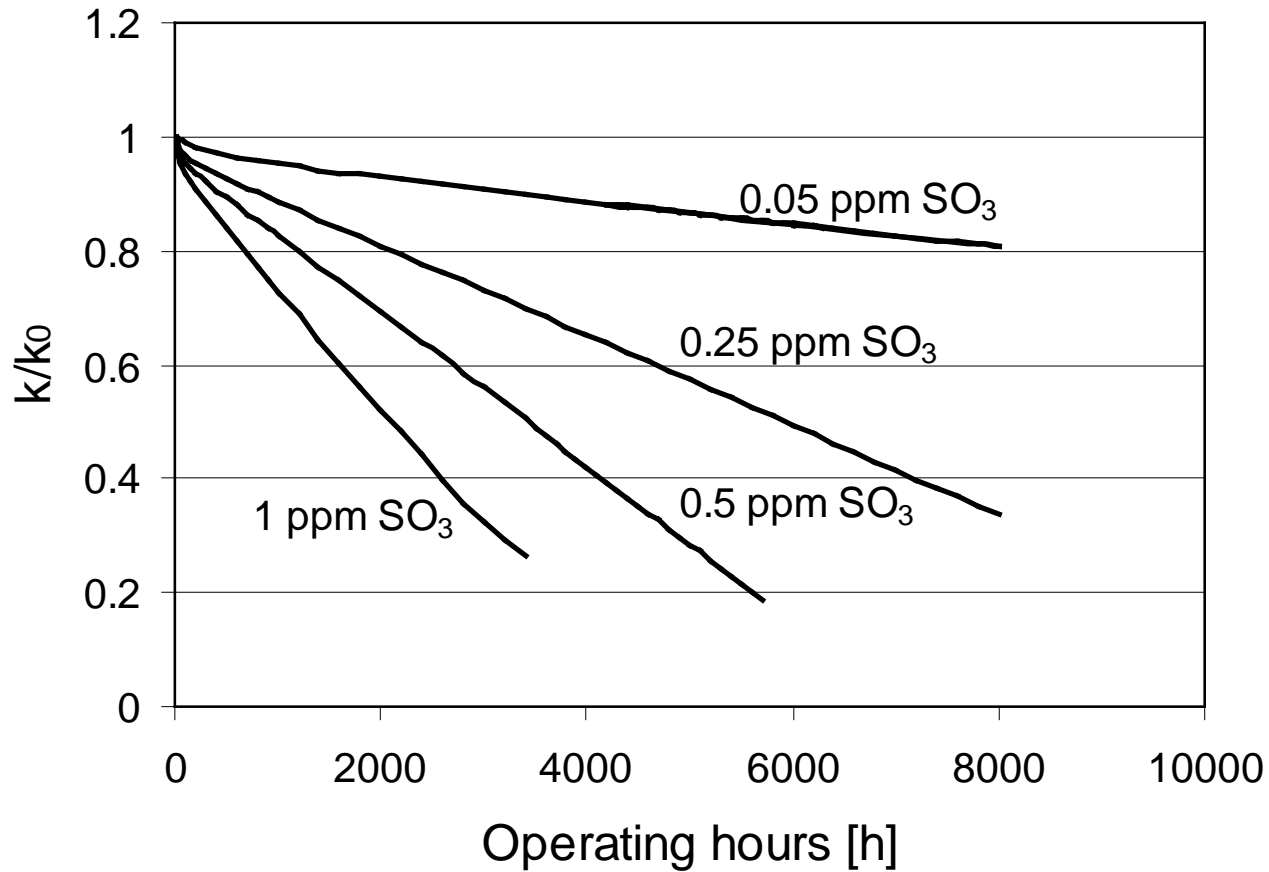


- Predicted relative SCR DeNOx activity in 554°F/662°F cyclic operation in a coal-fired boiler with 265 ppm NOx, 90% NOx removal, space velocity 1700 Nm<sup>3</sup>/m<sup>3</sup>/h and 16 ppm SO<sub>3</sub> at 554°F. The bulk dew point is 547°F. Regeneration takes place at 100% load conditions and 662°F.

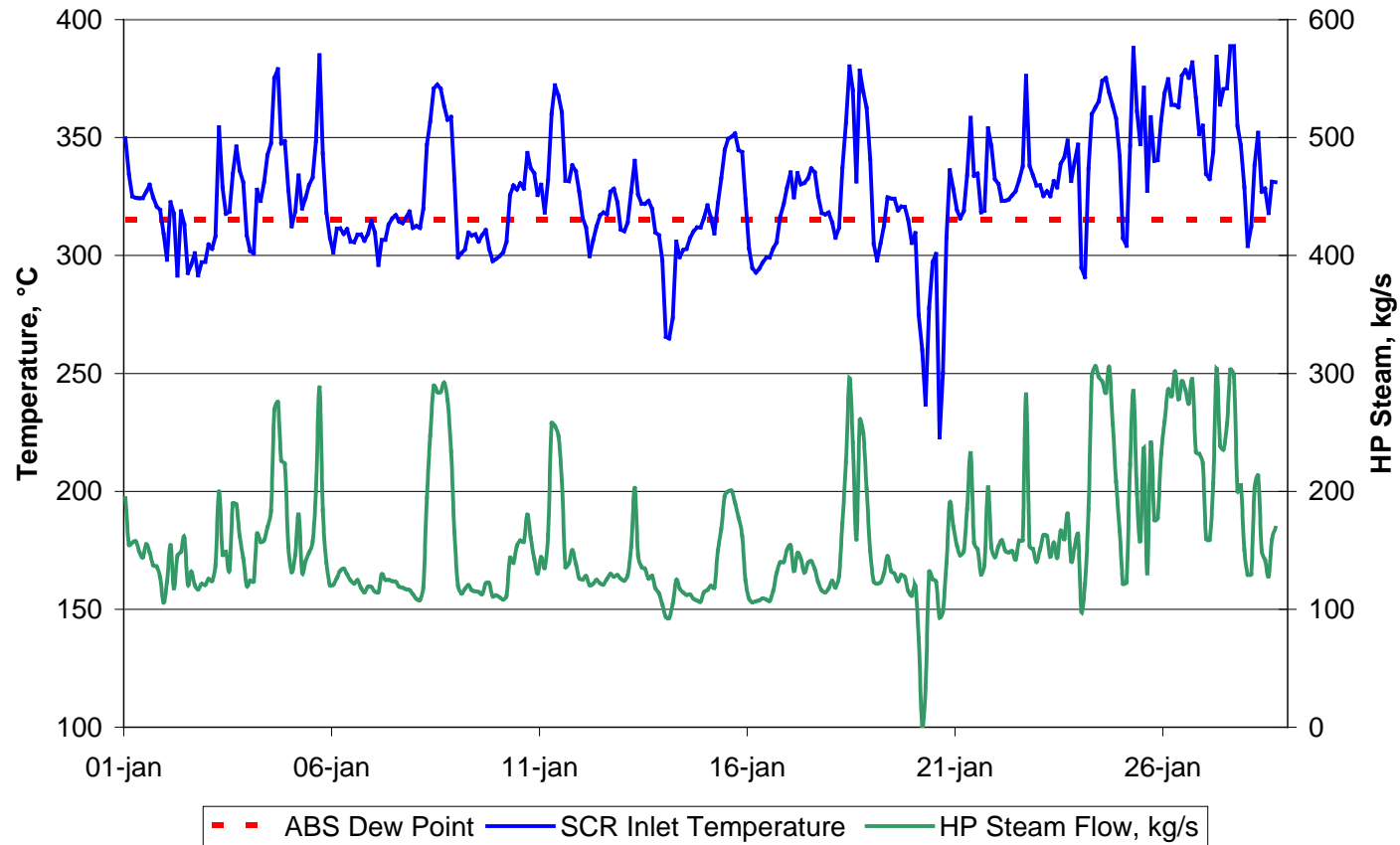
# Effect of additional SCR DeNOx layers



# Tail-end DeNOx



# Reduced load operation at Esbjerg Power Station



Ref: Dong Energy

# NH<sub>3</sub> injection strategy (Studstrup)

- Assume 1% conversion of SO<sub>2</sub> at SCR inlet.
- 18°F temperature margin to Matsuda dew point.
- Calculate minimum allowable ammonia injection temperature.
- Strategy was based on output of design tool “Model”

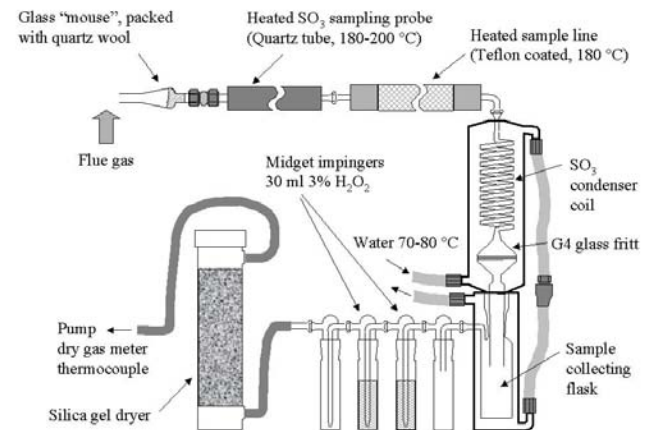


- Minimum temperature can be reduced.
- Accounts for coal sulphur content.

# SO<sub>3</sub> measurement

- Controlled condensation
  - Gas sampling & condensation with controlled nucleation. SO<sub>3</sub> determined by wet chemical analysis.
- Continuous methods
  - Evaporation of condensed phase detected by electrical conductivity. SO<sub>3</sub> determined from dew point.

## HTAS controlled condensation

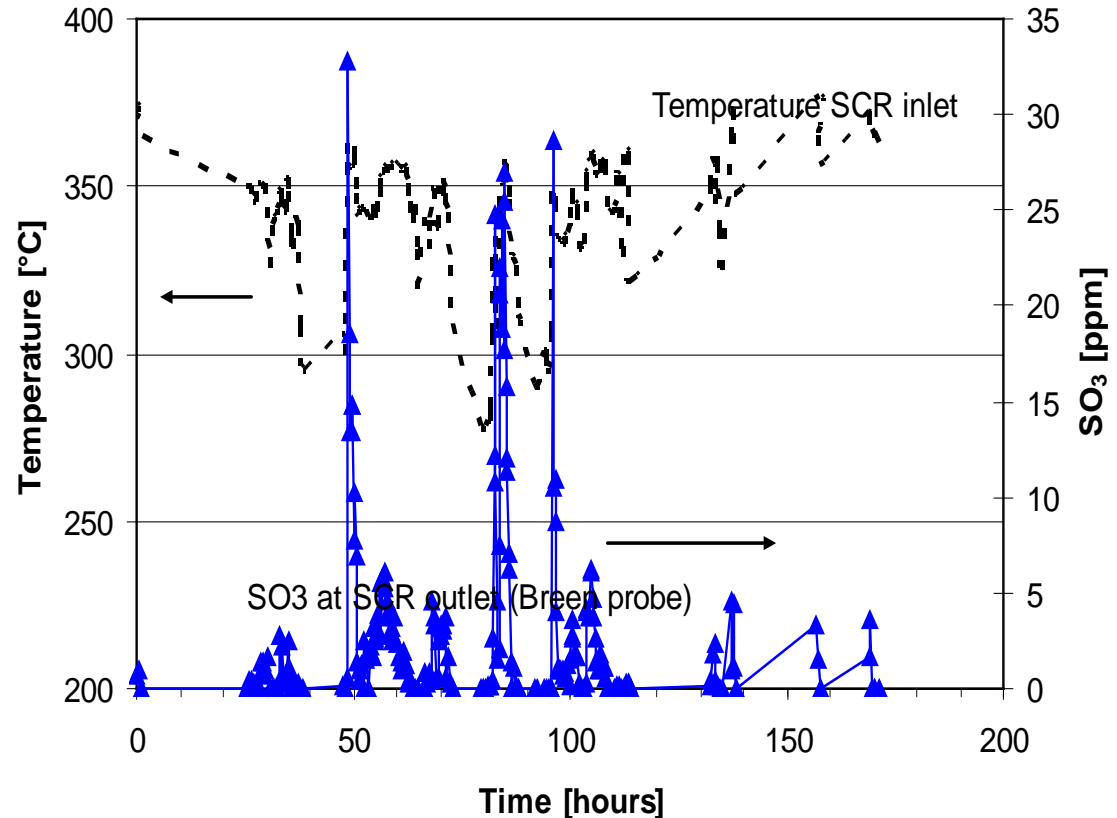


## Probe from Breen Energy Solutions



# Reduced load at Studstrup

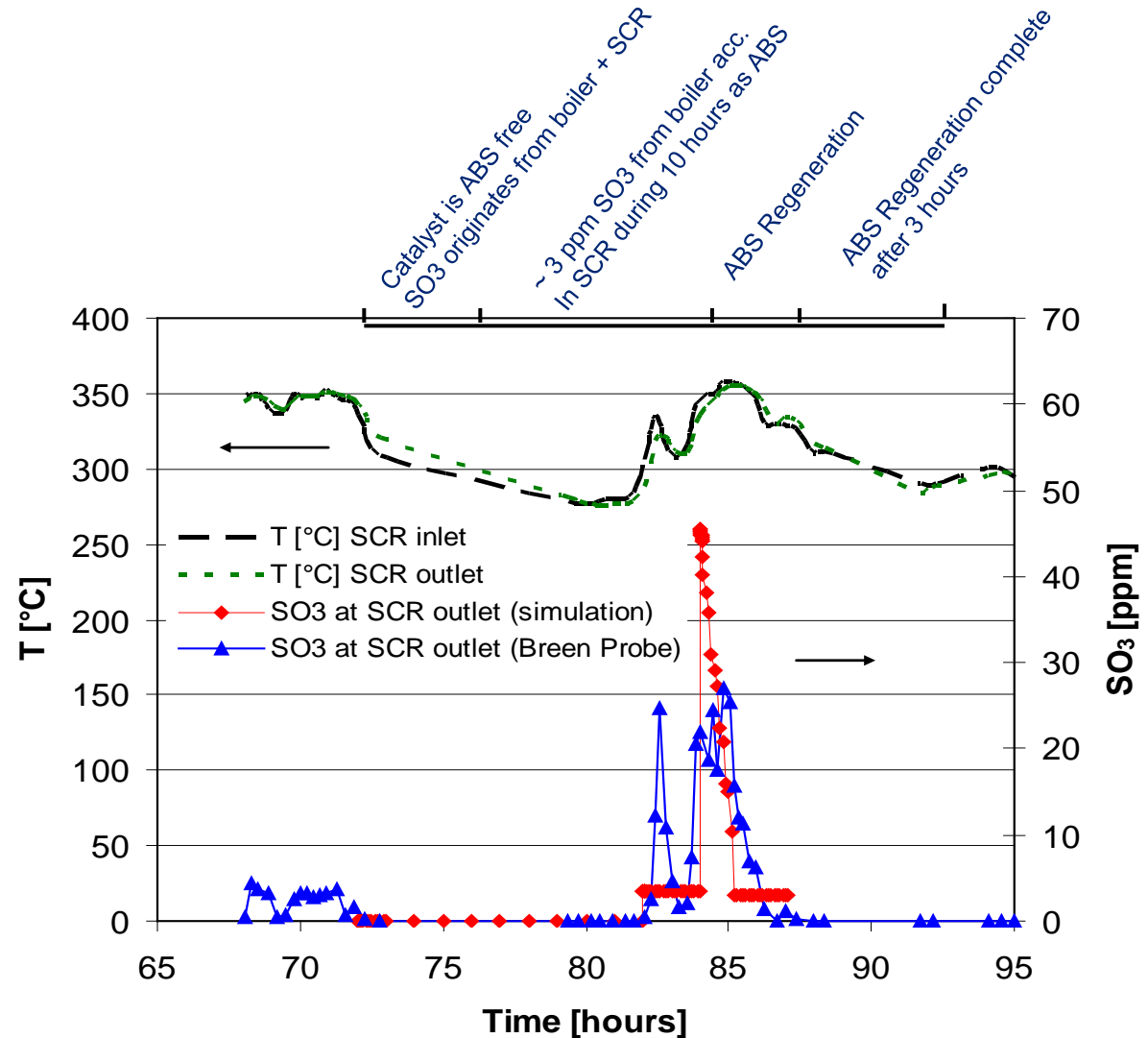
- 350 MWt power plant unit.
- ~ 3 ppm  $\text{SO}_3$  at SCR inlet.
- Reduced load operations in the range 280 - 300°C for 10 hours followed by heating to 350°C.
- $\text{SO}_3$  measured at SCR outlet using a Breen probe.



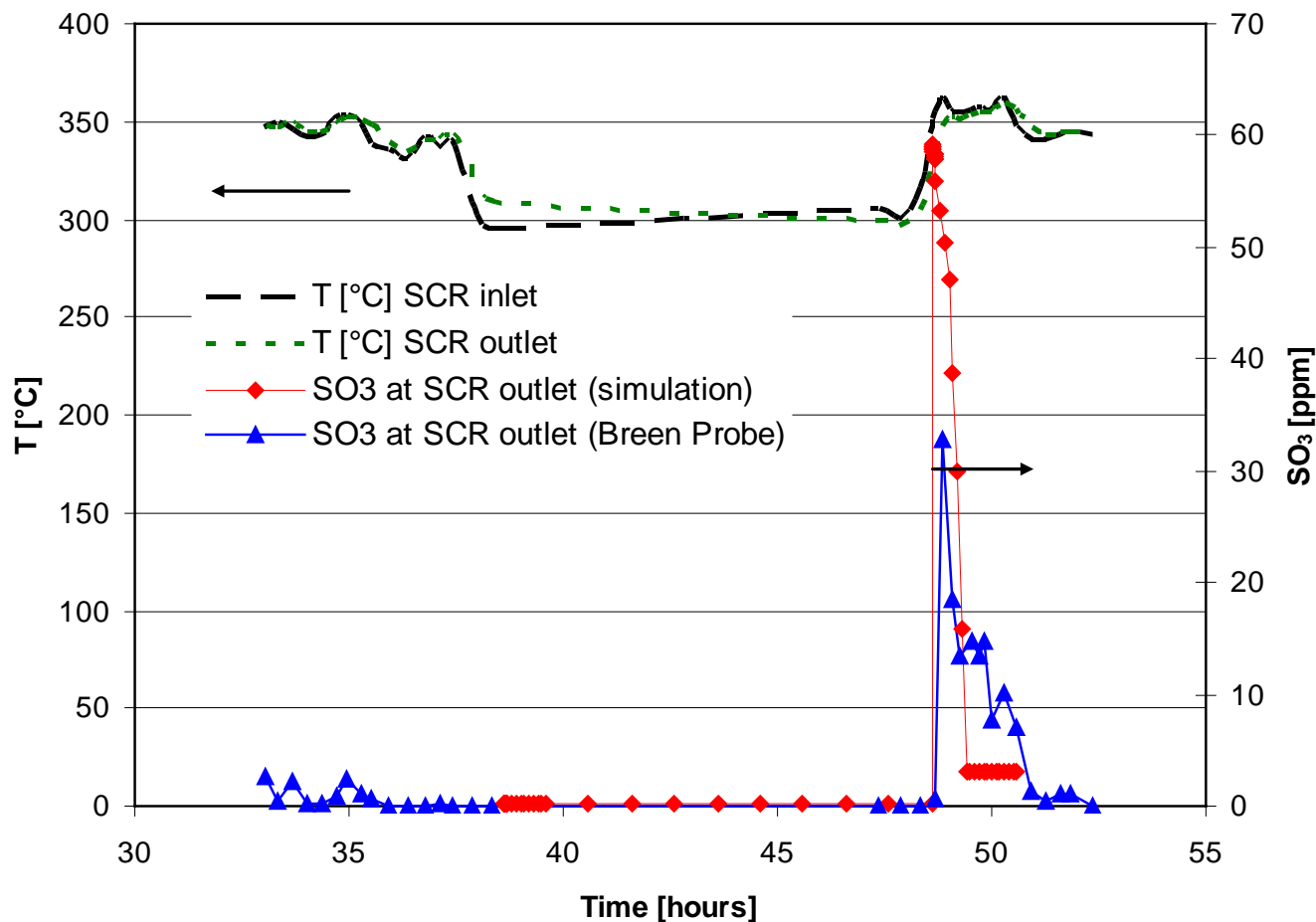
Ref: Dong Energy

# Breen Probe and Topsøe ABS model

- Regeneration experiment
  - Baseline operation
  - ABS accumulation
  - Regeneration
- 3 ppm SO<sub>3</sub> from the boiler.
- After 10 hours 0.007 ml/gcat ABS is accumulated.
- ABS regeneration complete after 3 hours



# Breen Probe and Topsøe ABS model



# Conclusions

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- SCR can successfully be operated below the pore dew point for extended periods of time
- ABS condensed in the catalyst pores can be evaporated during catalyst “regeneration” to original activity
- A hysteresis effect is observed between ABS inhibition and catalyst “regeneration”
- Actual ABS inhibition is somewhat dependent on the time – temperature history of the catalyst
- SO<sub>3</sub> concentration increases considerable during catalyst “regeneration”
- Predictive model describes well the dynamic behavior