Ammonium bisulphate inhibition of SCR catalysts

by:

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Summary

As the limits for the amounts of NOx in the flue gas stack is lowered there has been an increased focus on operation of the SCR DeNOx at lower loads instead of shutting off the ammonia injection or by-passing the boiler economizer. Often the minimum operating temperature in SCR DeNOx is determined by the dew point of ammonium salts. It becomes critical at reduced boiler load to have accurate predictions of the dew point. Experimental simulations of a coal-fired SCR installation and an oil-fired installation have confirmed previously determined dew point correlations [1] for formation of ammonium salts. Due to capillary forces in the catalyst an effect of ammonium bisulphate, ABS, condensation is seen from approximately 28°C above the bulk gas phase dew point and the inhibition is reversible by thermal treatment. A new finding is a hysteresis effect meaning that regeneration to a certain inhibition level requires a somewhat higher temperature than the temperature at which this level is reached when the temperature is decreased from above the ABS dew point. A predictive ABS inhibition model developed at Haldor Topsøe satisfactorily describes the equilibrium inhibition levels and the dynamic behaviour of ABS inhibition.

The DNX® catalyst with its high porosity ensures optimal resistance against ABS condensation and together with the Haldor Topsøe design tools SCR DeNOx operation around the ABS dew point can be utilized to the maximum possible extent.
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List of symbols

\(a\) : Specific geometric surface area \([\text{m}^2/\text{m}^3]\) \\
\(F\) : Volumetric flow rate in the monolith \([\text{Nm}^3/\text{h}]\) \\
\(k_g\) : External mass transfer coefficient \([\text{Nm}^3/(\text{m}^2\cdot\text{h})]\) \\
\(k_i\) : Intrinsic reaction rate coefficient \([\text{Nm}^3/(\text{m}^2\cdot\text{h})]\) \\
\(k_{\text{NH3}}\) : Observed reaction rate coefficient \([\text{Nm}^3/(\text{m}^2\cdot\text{h})]\) \\
\(L\) : Reactor bed length \([\text{m}]\) \\
\(M\) : Molar mass \([\text{kg}/\text{mole}]\) \\
\(m\) : Mass \([\text{kg}]\) \\
\(v_0\) : Empty reactor velocity \([\text{Nm}/\text{h}]\) \\
\(P_i\) : Partial pressure of component \([\text{N/m}^2]\) \\
\(P_{\text{SO3,cat}}\) : \(\text{SO}_3\) partial pressure in pore system \([\text{N/m}^2]\) \\
\(p_{\text{v}}\) : ABS filled pore volume \([\text{m}^3/\text{kg}_{\text{cat}}]\) \\
\(R\) : Gas constant \([\text{J/(mole-K)}]\) \\
\(r_{\text{pore}}\) : Pore radius \([\text{m}]\) \\
\(T\) : Temperature \([\text{K}]\) \\
\(t\) : Time \([\text{h}]\) \\
\(x\) : Axial position \([\text{m}]\) \\
\(\alpha\) : Accessible surface area fraction \\
\(\eta_{\text{cat}}\) : Catalyst effectiveness factor \\
\(\rho_{\text{NH4HSO4}}\) : Density \([\text{kg/m}^3]\) \\
\(\sigma\) : Surface tension \([\text{N/m}]\)
Ammonium bisulphate dew point and SCR DeNOx performance

The minimum process temperature in SCR DeNOx with ammonia injection is determined by formation of ammonium salts. The injected NOx reducing agent, ammonia, reacts with the acid gases in the flue gas forming ammonia salts, i.e. ammonium chloride, NH₄Cl, ammonium bisulphate, NH₄HSO₄, and ammonium nitrate, (NH₄)₂NO₃. In most cases NH₄HSO₄ has the highest dew point but in waste incineration units with HCl concentrations of several hundred ppm NH₄Cl condensation determines the minimum temperature. In chlorine and sulphur free flue gases the minimum temperature is determined by the (NH₄)₂NO₃ dew point. SCR installations in coal fired power plants are normally operated at temperatures between 330°C and 430°C with ABS catalyst dew points typically between 280°C and 320°C. Below the dew point ammonia and sulphuric acid condenses as liquid ammonium bisulphate, NH₄HSO₄, in the catalyst pore structure which inhibits the performance. The bimolecular condensation reaction is written as:

\[
\text{NH}_3(g) + \text{H}_2\text{SO}_4(g) \rightarrow \text{NH}_4\text{HSO}_4(l)
\]

At SCR DeNOx temperatures gaseous sulphuric acid is in equilibrium with SO₃ and the ABS dew point therefore depends on water content, ammonia content and SO₃ concentration:

\[
\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4
\]

Ammonium bisulphate has a melting point of 147°C. Formation of ammonium sulphate (NH₄)₂SO₄ is thermodynamically more favourable but analysis of condensed salts has shown that (NH₄)₂SO₄ is only formed in limited amounts due to kinetic limitations [2,3].

ABS inhibition is reversible and ABS is readily evaporated by increasing the catalyst temperature. The bulk dew point in the SCR reactor inlet is typically around 290°C (554°F) but the observed dew point is higher due to capillary forces in the micro pore structure. The ABS dew point decreases through the SCR reactor since NH₃ is consumed in the SCR reaction. According to Matsuda [1] the bulk dew point is as a good approximation given by the Clausius-Clapeyron equation:

\[
\ln \left( \frac{P_{\text{NH}_3} \cdot P_{\text{H}_2\text{SO}_4}}{P_{\text{eq, bulk}}} \right) = 27.97 - \frac{26.671}{T[K]}
\]

where \( P_{i} \) [atm] are partial pressures in the gas phase. The influence of the capillary forces is given by the Kelvin equation:

\[
\ln \left( \frac{P_{\text{NH}_3} \cdot P_{\text{H}_2\text{SO}_4}}{P_{\text{eq, pore}}} \right) = \frac{2 \cdot \sigma \cdot M}{\rho \cdot r_{\text{pore}} \cdot R \cdot T}
\]
where \( r_{\text{pore}} \) is the pore size that is just filled with ABS at a given gas composition and temperature and \( \sigma \) is the surface tension of ABS. Other sources [2,3] have reported vapour pressures that are significantly lower compared to the Matsuda numbers. These numbers are based on observations of ammonium bisulphate and ammonium sulphate fouling of heat exchange surfaces. Depending on the process parameters such as gas velocity, gas passing area, gas temperature, metal temperature and particle concentrations a major part of the ammonium bisulphate formed will pass through the heat exchanger as aerosols. Another factor is super cooling. Both capillary condensation and super cooling are the result of a relatively high surface energy or surface tension of the condensing phase. These factors may result in lower observed dew points that are more relevant to heat exchanger surfaces. As a comparison the Clausius-Clapeyron equation derived from the data generated by Ando et al. [3] becomes:

\[
\ln\left(\frac{P_{\text{NH}_3 \ [atm]} \cdot P_{\text{H}_2\text{SO}_4 \ [atm]}}{P_{\text{eq,bulk}}}\right) = 41.6 - \frac{30,900}{T[K]}
\]

The catalyst activity is directly related to the extent of pore condensation which means that ABS inhibition increases gradually as the temperature is lowered towards the bulk dew point. Model predictions show that 10 ppm \( \text{SO}_3 \) (\( \text{SO}_3 + \text{H}_2\text{SO}_4 \)), 200 ppm \( \text{NH}_3 \) and 8% \( \text{H}_2\text{O} \) condense as ABS in pores smaller than approximately 40 Å. Operation below the bulk dew point is not an option except for very low \( \text{SO}_3 \) concentrations in a low dust SCR installation since ABS will condense not only inside the catalyst pores but also at the catalyst surface creating a sticky surface which could over time lead to pluggage of the catalyst.

The equation from Matsuda et al. [1] is very accurate in the prediction of the bulk dew point. The bulk dew point has been determined experimentally in the laboratory by identifying the temperature point with total catalyst inhibition. An overview of bulk dew point predictions and experimental observations are shown in Figure 1.

![Figure 1: Relation between predicted and observed bulk dew points calculated according to Matsuda et al.](image-url)
A thermo-gravimetric analysis (TGA) of an SCR DeNOx sample with ABS in the pore structure shows the characteristics of ABS. The catalyst sample was operated below the ABS dew point until steady state was achieved. Then SO$_3$, ammonia and water dosing was stopped instantaneously and the sample was quenched in air. Subsequent TGA analysis of the catalyst sample revealed the following characteristics about ABS (Figure 2): Below 100°C water physisorbed during cooling and handling of the sample is released. ABS is hygroscopic at lower temperatures and chemisorbed water evaporates between 160°C and 210°C. Above 310°C ABS and sulphuric acid (SO$_3$ and water) evaporate from the sample. The physical behaviour in the TGA analysis is a bit different from real SCR DeNOx flue gas conditions in that the inlet gas does not contain sulphur trioxide, ammonia and water. Some of the ABS is released at temperatures well above the dew point since the time is too short at the lower temperatures to regenerate the catalyst completely.

![Figure 2: Thermogravimetric analysis (TGA) of SCR deNOx catalyst with ammonium bisulphate condensed in the pore structure. The sample is heated by 2°C/min. Derivative thermogravimetric curves (DTG) are shown as a function of temperature.](image)

**Laboratory experiments**

Laboratory reactor experiments have been carried out with process conditions that correspond to a typical oil-fired boiler operating case and a typical coal-fired boiler operating case, using a Topsøe low-dust type catalyst, DNX-LD, and a high-dust type catalyst, DNX-HD, respectively. The laboratory reactor is an isothermal reactor with compensation for heat loss. The reactor cross section has dimensions of 45 mm × 45 mm. 500 mm monolith catalyst was loaded in the reactor. The catalyst height is larger in a typical full scale installation and the experiments therefore show the behaviour in the first part of a typical catalyst installation. The test conditions are listed in Table 1.
Table 1: Experimental Conditions

<table>
<thead>
<tr>
<th></th>
<th>Coal-fired boiler</th>
<th>Oil-fired boiler</th>
</tr>
</thead>
<tbody>
<tr>
<td>DNX type</td>
<td>HD</td>
<td>LD</td>
</tr>
<tr>
<td>NOx [ppm]</td>
<td>300</td>
<td>150</td>
</tr>
<tr>
<td>NH₃/NOₓ</td>
<td>0.9</td>
<td>0.8</td>
</tr>
<tr>
<td>lₗcat [m]</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>SO₂ [ppm]</td>
<td>3000</td>
<td>300</td>
</tr>
<tr>
<td>SO₃ [ppm]</td>
<td>30</td>
<td>3</td>
</tr>
<tr>
<td>O₂ [%]</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>H₂O [%]</td>
<td>8</td>
<td>12</td>
</tr>
<tr>
<td>v₀ [Nm/s]</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Tₚ design dew point [°C]</td>
<td>317</td>
<td>287</td>
</tr>
<tr>
<td>Tₚ bulk dew point [°C]</td>
<td>292</td>
<td>262</td>
</tr>
</tbody>
</table>

v₀ denotes the linear gas velocity in the (empty) reactor and NH₃/NOₓ is the ammonia-to-NOx ratio in the feed gas. The design dew point is the temperature where a typical installed catalyst volume in full scale (NHSV = 4000 h⁻¹) has approximately 95% residual activity.

The activity relative to fresh catalyst activity has been measured at various temperatures around the ABS dew point where the temperature has been either decreased or increased in steps of 5°C. The coal fired case results are shown in Figure 3. The steady state activity relative to the fresh catalyst activities k/k₀ is given as a function of temperature. When the temperature is lowered towards the bulk dew point inhibition is observed from 28°C above the bulk dew point. When the catalyst is heated a hysteresis effect is seen since reactivation is slower than inhibition. It is actually necessary to the bring the catalyst up above 350°C (60°C above the bulk dew point) in order the fully regenerate the catalyst. The Haldor Topsøe design basis predicts an inhibition level that is an average between the observed level at decreasing temperature and increasing temperature. Regeneration of a fully inhibited catalyst follow a curve that is quite different from the regeneration of a catalyst exposed to the design dew point temperature. But in practical operation one should never operate the catalyst close the dew point until 100% inhibition is reached.

The oil fired experiment showed a tendency that inhibition levels also depended to some extent on the cooling rates. Inhibition was stronger when the catalyst was quench cooled, i.e. temperature was lowered to the design dew point from 360°C, compared step wise (5°C) cooling, cf. Figure 4. During the cooling transient pore condensation develop in pores that are larger than the pores where ABS condenses at steady state conditions. Steady state is, however, never reached as a result of the hysteresis phenomena, which means that once formed the condensate is more difficult to remove.
**Figure 3:** Steady state activity at operation close to the ABS bulk dew at typical coal fired conditions, cf. Table 1.

**Figure 4:** Steady state activity at operation close to the ABS bulk dew at typical HFO fired conditions, cf. Table 1.
Before extracting the DNX-HD element from the reactor the temperature was lowered to the design dew point (310°C) and given enough time to reach the steady state inhibition level. The elements were then characterized in order to describe the nature of the NH$_4$HSO$_4$ pore filling. The sample was analyzed for ammonium content and sulphur content. The pore volume distribution and specific surface area was measured by multi point (QBET) and single point (HBET) nitrogen adsorption/desorption. Degassing temperature was set to 150°C for 48 hours in order to detain the ABS in the pore structure. The results are listed in Table 2 and Figure 5. Up to 2.7w% sulphur are accumulated in the catalyst. The molar nitrogen to sulphur ratio, N/S ratio, is lower than the stoichiometry in NH$_4$HSO$_4$ (N/S = 1.0), which is explained by an absorption capacity of sulphuric acid in liquid ABS and sulphur adsorption in the catalyst. The back ground sulphur absorbed on the catalyst is 100 – 500 ppmw. In spent catalyst the background content is often higher due to the sulphation of fly ash accumulated in the catalyst.

### Table 2: DNX-HD Experiment

<table>
<thead>
<tr>
<th>Position in catalyst [mm], from top</th>
<th>S [%w]</th>
<th>NH$_4^+$ [%w]</th>
<th>N/S molar ratio</th>
<th>Relative specific surface QBET</th>
<th>Relative Nitrogen pore volume</th>
<th>Relative specific surface HBET</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.70</td>
<td>0.48</td>
<td>0.32</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100</td>
<td>1.37</td>
<td>0.34</td>
<td>0.46</td>
<td>0.49</td>
<td>0.73</td>
<td>0.50</td>
</tr>
<tr>
<td>250</td>
<td>0.82</td>
<td>0.12</td>
<td>0.28</td>
<td>0.69</td>
<td>0.93</td>
<td>0.42</td>
</tr>
<tr>
<td>350</td>
<td>0.67</td>
<td>0.07</td>
<td>0.22</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>500</td>
<td>0.62</td>
<td>0.06</td>
<td>0.19</td>
<td>0.78</td>
<td>1.00</td>
<td>0.71</td>
</tr>
<tr>
<td>ABS</td>
<td>23.1</td>
<td>9.92</td>
<td>0.77</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ref</td>
<td>0.01-0.05</td>
<td></td>
<td>N.A.</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

A piece of ABS taken from a cold surface in the reactor was analyzed and this sample had a N/S ratio of 0.77. The average ratio in the catalyst is 0.29.

The cumulative specific surface area shows how accessible surface area in the catalyst is lowered when ABS condenses in the micro pore structure. It is also seen that the surface area reduction is largest at the leading edge of the catalyst.
Figure 5: Cumulative specific surface area measured by nitrogen adsorption. The samples were taken from different distances, 10 cm, 25 cm and 45 cm, from the leading edge of the catalyst.

In the oil-fired boiler simulation the catalyst was extracted after operation at the design dew point and a sample was taken from the leading edge for chemical analysis \(^1\). The catalyst was reintserted in the reactor. The catalyst was then regenerated and the temperature was subsequently decreased quickly to the bulk dew point. When complete inhibition was obtained the temperature was increased to the design dew point and the catalyst was then extracted and analyzed again \(^2\).

### Table 3: DNX-LD experiment

<table>
<thead>
<tr>
<th>Sample position from leading edge</th>
<th>S [%w]</th>
<th>NH(_4^+) [%w]</th>
<th>N/S molar ratio</th>
<th>Relative specific surface area</th>
<th>Relative N(_2) pore volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Design temp. operation (^1)</td>
<td>+ 0</td>
<td>4.7</td>
<td>0.76</td>
<td>0.29</td>
<td>0.47</td>
</tr>
<tr>
<td>Bulk dew point operation (^2)</td>
<td>+ 0</td>
<td>2.6</td>
<td>0.45</td>
<td>0.31</td>
<td>0.47</td>
</tr>
</tbody>
</table>

The results show that the accumulated amounts of sulphur and ammonium at steady state to some extent depend on the temperature-time history of the catalyst. A quench cooling to the
bulk dew point followed by an increase in temperature to the design dew point results in smaller amounts of accumulation compared to quench cooling directly to the design dew point. This indicates an effect of pore blocking in the outer pores of the pore structure as a part of the ABS inhibition mechanism. As in the DNX-HD experiment the nitrogen/sulphur ratio in the catalyst is around 0.30.

The decrease in vapour pressure of accumulated ABS could be explained by several mechanisms. One explanation could be that interactions between the condensed salt and the catalyst change the vapour pressure. Other explanations could be formation of \((\text{NH}_4\text{)}_2\text{SO}_4\) by reaction with gas phase ammonia. The ammonium sulphate has been shown to have a lower vapour pressure [2]. However, this explanation is not in line with the observed decrease in nitrogen/sulphur ratio in the catalyst. Finally, accumulation of sulphuric acid could play a role in the vapour pressure change.

**ABS inhibition model**

A design model that predicts the effect of ABS inhibition including the dynamic behaviour has been developed at Haldor Topsøe.

![Figure 6: ABS deactivation mechanism. Bulk-phase \(\text{SO}_3\) and \(\text{NH}_3\) condense in the catalyst pores where the SCR DeNOx reactions take place.](image)
The model consists of a number of differential equations describing the conversion of ammonia and NO\textsubscript{x} coupled with the uptake and release of SO\textsubscript{3} from ABS which means that one molecule of NH\textsubscript{3} is released for every molecule SO\textsubscript{3} that is released. In the model SO\textsubscript{3} is calculated as SO\textsubscript{3}'\textsuperscript{,} which is the sum of H\textsubscript{2}SO\textsubscript{4} and SO\textsubscript{3}. The catalyst has been sectionalized in the gas-flow direction and the pore condensation is assumed constant in these sections. The change in pore condensation is calculated in time steps based on the calculated gas phase outlet SO\textsubscript{3} concentration in each section. The model does not take SO\textsubscript{3} reactions with fly ash in the bulk or in the pores into account.

\[
\begin{align*}
\frac{dR_{NH_3}(x,t)}{dx} + \frac{k_{NH_3} \cdot a}{v_0} \cdot R_{NH_3}(x,t) - \frac{dP_{SO_3}(x,t)}{dx} &= 0, \quad 0 \leq x \leq l, \quad t \geq 0, \quad R_{NH_3}(0,t) = R_{NH_3,0}(t) \\
\frac{dP_{SO_3}(x,t)}{dx} - \frac{k_g \cdot a}{v_0} \cdot (P_{SO_3;cat}(t) - P_{SO_3}(x,t)) &= 0, \quad 0 \leq x \leq l, \quad t \geq 0, \quad P_{SO_3}(0,t) = P_{SO_3;0}(t) \\
\frac{dP_{NO}(x,t)}{dx} + \frac{dP_{SO_3}(x,t)}{dx} - \frac{dP_{NH_3}(x,t)}{dx} &= 0, \quad 0 \leq x \leq l, \quad t \geq 0, \quad P_{NO}(0,t) = P_{NO,0}
\end{align*}
\]

where the pore system partial pressure \(P_{SO_3;cat}\) is a function of the pore volume blocked by ABS, bulk species concentrations at the section inlet and the temperature.

\[
P_{SO_3;cat}(t) = f(pv(t), P_{SO_3;0}, P_{NH_3,0}, P_{NO,0}, T), \quad t \geq 0
\]

The change in blocked pore volume with time for each section is calculated as:

\[
\left. \frac{d(pv)}{dt} \right|_i = \frac{\left( P_{SO_3;cat}(t) - P_{SO_3}(0,t) \right) \cdot F \cdot M_{NH_3HSO_4}}{R \cdot T \cdot P_{NH_3HSO_4}} \cdot \frac{1}{m_{cat,section}}, \quad pv(0) = pv_0, \quad t \geq 0
\]

The intrinsic rate constant is assumed to be proportional to the fraction of accessible surface area:

\[
k_i = a \cdot k_{i,0}
\]

The observed reaction rate constant \(k_{NH_3}\) is then calculated taking the relative influence of intrinsic chemical reaction and diffusion into account:

\[
k_{NH_3} = \left( \frac{1}{k_g} + \frac{1}{k_i \cdot \eta_{cat}} \right)^{-1}
\]

The diffusion coefficient for ammonia and NO\textsubscript{x} is assumed independent of the ABS condensation in the pore structure.
As shown earlier in Figures 3 and 4, the prediction of the equilibrium ABS inhibition corresponds to experimental observations. The observed dynamic behaviour is also reasonably well described as illustrated in Figure 7. A model simulation of the DNX-HD coal-fired experiment inhibition shows that the model predicts a larger amount of ABS in the pore system compared to analysis of the extracted catalyst, cf. Table 4. This indicates that the ABS does not solely affect the intrinsic activity but also the effective diffusion coefficient. Presumably the reason is that the activity is overestimated for a given amount of pore condensation. The agreement between pore volume measurements and the ABS filled pore volume estimated from chemical analysis is reasonable.

![Graph](image)

**Figure 7**: Deactivation and regeneration predictions compared to experimental observations for a DNX-LD (120mm) with 13 ppm SO$_3$ and 300 ppm NOx. Left: 294°C/328°C cycle operation. Right: 350°C regeneration.

**Table 4**: DNX-HD experiment, ABS pore volume [µl/g] in catalyst

<table>
<thead>
<tr>
<th>Position [mm] from top</th>
<th>From QBET analysis</th>
<th>S analysis</th>
<th>N analysis</th>
<th>Model prediction</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>53</td>
<td>54</td>
<td>17</td>
<td>74</td>
</tr>
<tr>
<td>250</td>
<td>14</td>
<td>17</td>
<td>4</td>
<td>64</td>
</tr>
<tr>
<td>500</td>
<td>~0</td>
<td>14</td>
<td>2</td>
<td>54</td>
</tr>
</tbody>
</table>
Haldor Topsøe industrial experience

Possibility of operation below and near the ABS dew point has a number of advantages. In coal-fired boilers the SCR can be operated at reduced load at temperature close to the bulk dew point for several days. Operation below the bulk dew point should never take place since the catalyst surface becomes sticky and initiates irreversible fly ash deposition. In tail end flue gases, i.e. after particulate removal, with very low concentrations of dust and SO₃, operation near or below the bulk ABS dew point is possible for an extended period (months). This is of relevance to e.g. installations on waste incineration plants. An option for regeneration using a duct burner or steam has to be available.

In coal fired boilers the SCR DeNOx activity can be maintained at a relatively high level during cyclic operation if the boiler is operated at reduced load for a limited time. The activity decreases around 15% during 72 hours at typical coal fired SCR conditions with 16 ppm SO₃. As low-temperature operation typically occurs at reduced load, the reduced activity is sufficient to maintain the desired NOx removal efficiency.

![Figure 8: Predicted relative SCR deNOx activity in 290°C/350°C cyclic operation in a coal fired boiler with 265 ppm NOₓ, 90% NOx removal, space velocity 1700 Nm³/m³/h and 16 ppm SO₃ at 290°C. The bulk dew point is 286°C. Regeneration takes place at 100% load conditions and 350°C.](image)

The effect of operating close to the dew point can be minimized by increasing the amount of catalyst. In Figure 9 the effect of additional catalyst layers on the overall steady state catalyst activity is shown. The relative activity loss close to the bulk dew point is lower the higher the
design NOx conversion of the SCR unit since most of the ammonia is converted in the first layer. A catalyst with high porosity as the DNX catalyst also reduces the effect of ABS close to the dew point because the catalyst can accommodate more ABS.

![Figure 9](image)

**Figure 9**: Effect of number of SCR layers on ABS inhibition on relative activity in the SCR close to the ABS dew point.

In tail-end SCR units with low SO3 levels ABS may build up only slowly over time. In Figure 10 the DeNOx activity is given as a function of operating hours for a typical tail-end installation. With 0.5 ppm SO3 70% of the DeNOx activity is retained after 2000 hrs.

One difficulty in designing SCR units for operation close to the dew point in real plants is the uncertainty in the estimation of the SO3 concentration. When measured in high-dust SCR’s the SO3 concentration is often underestimated due to SO3 capture in the sample line fly ash filter [4].

Operation below the design dew point, which is the minimum temperature where more than 95% activity compared to the fresh catalyst activity is retained at space velocity 4000 h⁻¹, and close to the bulk dew point has been demonstrated in full scale. Figure 10 shows SCR temperature and steam production during one month at a coal fired power plant. The SCR temperature is below the design dew point during approximately 30% of the time. During such periods NOx conversion was not impeded.
**Figure 10:** Predicted development in SCR activity as a function of SO₃ concentration in a tail-end unit. NHSV = 2800 h⁻¹, 250 ppm NOx, 80% deNOx and 260°C.

**Figure 11:** Example of temperature variation during one month in full scale SCR SO₃ level is 10-20 mg/Nm³ which gives a design minimum temperature of approximately 315°C.
Conclusion

The known dew point correlations for the formation of ammonium bisulphate have been confirmed by NOx conversion experiments that verified the steady state catalyst activity approaching zero as the temperature approaches the predicted ABS bulk dew point. Due to capillary forces in the pore system an effect of ABS on the catalyst efficiency is observed from approximately 28°C (50°F) above the bulk dew point. The steady state and transient behaviour of ABS inhibition is satisfactorily described by an inhibition model developed at Haldor Topsøe A/S. A new finding is a hysteresis effect meaning that regeneration to a certain inhibition level requires a somewhat higher temperature than the temperature at which this level is reached when the temperature is decreased from above the ABS dew point. Even when ammonia injection is stopped it is difficult to remove the last part of ABS in the catalyst pore structure below 350°C.

The DNX® catalyst providing a high porosity ensures optimal resistance to ABS inhibition and applying the Haldor Topsøe design tools, safe SCR DeNOx operation close to the ABS dew point can be utilized to the maximum possible extent.

References


