

Retrofit of SCR-Systems - Formation mechanisms of SO₃-aerosols and implications on the Flue Gas Cleaning System

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0. Abstract

The retrofit of DeNOx-systems has been accomplished in nearly all German power plants during the nineteen-eighties as an implementation of the respective prescriptions of the environmental legislation (13. BImSchV). Since then, many years of experience have been accumulated at E.ON Engineering regarding the operation, the efficiency and the impact on the total flue gas cleaning system. Especially the often-reported opacity problems occurring after the retrofit of DeNOx-systems still remain to be an issue of key-interest.

This paper shall contribute to the general understanding of formation mechanisms of SO₃ in its different states, its concentration profiles along the flue gas path and the specific effects related to SO₃ or sulphuric acid observed in the individual components of the boiler and flue gas cleaning system. Results obtained in several measuring campaigns in power stations in Germany as well as in the United States are shown and discussed. The dependencies on specific process conditions such as sulphur content of coal, the catalyst type, air heater setpoint temperatures and the general configuration of the plant are discussed.

As sulphuric acid as a conditioning agent has an important effect also on the efficiency of electrostatic precipitators, the relevant test results are specifically reviewed in this respect.

1. Introduction

In the late eighties and early nineties, when most of the German SCR-systems went into service, electrostatic precipitators all of a sudden came back into the focus of many power station operators. It was observed, that after commissioning of the retrofitted high-dust-SCR's the opacity increased significantly and a clearly visible plume could be seen in some locations as well. As this phenomenon – as any other non-water vapour emission from the stack - was spontaneously attributed to the particulate control, ESP-OEM's were confronted with calls from upset power plant operators to immediately rectify this "obvious problem of the ESP".

Extensive investigations started and resulted in the identification of the real source of this phenomenon: the increased sulphur dioxide conversion in the newly installed SCR-catalysts and subsequently generated aerosols in the downstream components of the flue gas system.

After this first discovery, another conclusion was drawn: If a significant amount of SO₃ was generated in the catalyst, this could be beneficial for the particulate removal in the ESP, practically acting as system inherent conditioning device [1]. However, the ESP-OEM's were not all of one opinion and many debates took place about the effectiveness if any of such conditioning. Apart from that, quite some ESP-supply contracts were won or lost due to the different evaluation and consideration of those findings among the OEM's and operators.

During the following years after the SCR-retrofits, many investigations in this matter were carried out and today, these findings are and will be most valuable for the implementation of SCR-technology in other countries such as the USA and any other future candidate for NOx-mitigation measures.

In the following, the above aspects and various SO₃-measuring campaigns are reviewed again regarding the mechanisms discovered and conclusions are made regarding the conditioning effect on the ESP.

2. Formation mechanisms of SO₃

Furnace and boiler

Primarily, sulphur is oxidised to gaseous species such as SO₂ and SO₃, whereas SO₂ is the predominant oxide. This exothermic reaction is very rapid and occurs near the burner zone. As the flue gas cools down along the convective region of the boiler, the rate of SO₃-production increases significantly. SO₃-production via gas-phase processes is nearly completed before the flue gas enters the economizer [2].

The conversion rate of SO₃-production in the furnace can be conservatively estimated to be in the range of 0,65% and is virtually independent of the coal type, however strongly dependent on the excess air level (figure 1).

In addition, fly ash components such as iron oxides deposited on the tube surfaces in the economizer region catalyse SO₂ via molecular oxygen. This is a very site specific factor due to its dependency on soot blowing regimes, available surface areas, etc. and can not be generalised. Boiler conversion rates found in recent tests in North American power stations fired with both low and high sulphur coals yielded total boiler conversion rates of 0,9 to > 1,4 %.

SCR-Reactors

In EON-owned power stations as well as in those of other utilities, the most commonly installed configuration of a SCR-system is the High-Dust-SCR (figure 2).

As the SO₃-conversion is an unwanted side-reaction due to its follow-up reaction products and the aerosol issue, its maximum rate ranging from 0,25 to 1,25% usually is a guarantee value the SCR-manufacturers are committed to.

The conversion is mainly depending on the SO₂-concentration present, the flue gas flow per catalyst volume (the so-called area velocity AV), the flue gas temperature and of course the chemical composition of the catalyst with the vanadium content playing the major role (figure 3).

Although the conversion rates appear low in absolute terms, the SCR-reactor might cause an increase of 50% or even a doubling of the inlet concentration of the SO₃ present at the SCR-inlet.

However, the SCR-system also contributes to a certain extent to the neutralisation of the SO₃ generated by utilising another – unwanted – side effect: the NH₃-slip. A minor fraction of the NH₃ injected upstream the SCR to react with the NO_x sneaks through the reactor and combines with SO₃ to form ammonium sulphate and ammonium bisulfate. Especially the latter can contribute significantly to plugging and corrosion of air heaters [3].

3. Role of the air heater

Temperature stratification

The majority of the power stations use rotary regenerative air heaters to transfer heat from the combustion exhaust gases to the combustion air flowing to the furnace. Due to its design, a considerable variation in temperature occurs at the outlet duct toward the ESP. Figure 4 shows temperature profiles across the duct after a Ljungström-type air heater for two different set-points. The measuring data for the lower setpoint has been extrapolated for the last two sampling ports maintaining the temperature difference found on the other ports (dotted line).

The “cold-end” or rather the “cold side” of the air heater with a difference of more than 30K compared to the “hot side” is clearly reflected. Similar findings and obvious consequences on ash resistivity and electrical behaviour of ESP-bus-sections have been reported in other publications [4]. A significant impact on ESP-operation can be assumed especially if the sectionalisation across the flow direction is not sufficient.

SO₃-capture in the air heater

Depending on the air heater setpoint, which rather represents a mean outlet temperature, and the subsequent temperature distribution both in flow direction as well as along the circumference of the air heater, the water vapour present in the flue gas easily reacts with the gaseous and hygroscopic SO₃ to form H₂SO₄-vapour. Condensation of sulphuric acid occurs, when and where local metal temperatures in the air heater passages drop below the acid dewpoint – the so-called cold-end-corrosion in air heaters is a consequence of this phenomenon.

Temperature and SO₃-profiles taken at different air heater setpoints during a measuring campaign in an US-American power station firing high volatile bituminous coal with sulphur contents between 3,2 and 3,8% a.r. are shown in figures 5 and 6.

High airheater setpoint

Figure 5 with a setpoint of 185°C shows a concentration of approx. 66 ppmV of gaseous SO₃ at the outlet of the economizer. The respective temperature profile taken in the air heater outlet duct (blue line) has a difference of approx. 35K between the hottest and the coldest sample port whereas the inlet temperature distribution entering from the economizer can be assumed to be quite even at 360°C. Subsequently, a corresponding SO₃-profile – given as total SO₃, i.e. gaseous and aerosol - is established which is depicted in the red curve. However, no SO₃-aerosols were detected.

It can be concluded, that the balance between the SO₃-inlet load and the concentration exiting the air heater was condensed in the air heater. As condensation surface, the air heater plates and the particles are available, however, to quantify the individual collection rate of each is rather difficult. In total, around 9% of the SO₃ were captured on the hot outlet side of the air heater and approx. 58% on the cold outlet side.

Considering the given conditions, we would assume, that the cold air heater plates would represent a better option for condensation due to the clear temperature difference, whereas the particles experienced the same temperature curve as the gaseous phase, thus not offering a significant driving force to condensate besides acting as condensation nuclei.

Other extensive investigations in this matter have examined the processes responsible for the combination of sulphuric acid and ash particles [5]. Generally, two mechanisms are contributing: adsorption and condensation. The adsorption already starts above acid dewpoint and mainly depends on acid concentration and temperature. For the condensation, the particles act as condensation nuclei, thus the particle size is another main factor.

A high percentage of alkali constituents such as calcium and magnesium oxides in the fly ash add to an increased acid capture [6]. In such case, the acid reacts with the alkalis thus neutralising the acid, which then is not having any conditioning effect on the fly ash resistivity.

Low airheater setpoint

Following above tests with high air heater outlet temperatures, another test was conducted lowering the setpoint to 163°C (figure 6). Again, the profile of the total SO₃-concentration after the air heater is matching with the temperature profile, which shows a difference of more than 30K from the cold to the hot side. During those tests at 8% average H₂O-content present in the flue gas, an increasing SO₃-aerosol concentration towards the cold side of the duct was found. SO₃-capture increased to 15% on the hot outlet side and more than 70% on the cold outlet side.

Total SO₃-capture

The total SO₃-capture found in several investigations carried out in German and US-American power stations ranged between 35 and 70% as average values, depending on the air heater setpoint. Results from a test campaign in an US-American power station firing low-sulphur bituminous coal for two different air heater setpoints are given in figure 7.

However, when discussing the total SO₃-capture, it should always be kept in mind, that above profiles are most likely to be present in all similar installations and can lead to significant disturbances in terms of corrosion etc. which might not be expected when looking at the total value alone.

The amount of acid condensed on the air heater plates will partly undergo evaporation as soon as the heating elements are exposed to the combustion air entering the furnace or be removed during soot blowing (figure 8).

4. SO₃-balance

In order to assess the SO₃-load along the flue gas system as a baseline study before a SCR-retrofit as well as to evaluate possible SO₃-mitigation methods, various tests have been carried out during the last decade in European and US-American power stations. Some results are shown in figure 9. Power station A1 is an US-American unit firing a blend of pet coke and bituminous coal, A2 the same station firing 100% bituminous coal with approx. 3% sulphur and power station B is a German unit firing local coal with approx. 1% sulphur.

It should be noted, that the obviously increased boiler SO₂-conversion rate when firing 100% bituminous coal in case A2 compared to the lower rate while firing a blend of pet coke and coal in A1 can be explained with the pet-coke ash deposits having high vanadium contents still present on the economiser surface.

All tests of SO₃-concentrations were carried out at the same time on the locations given in the chart. It is obvious, that a significant capture of SO₃ takes place along the air heater/ESP path. However, due to the limited test programme, no tests were carried out directly after the air heater. It can also be seen, that aerosols were captured also in the wet scrubber FGD-system at a rate between 25 and 50%.

More insight into the variations of SO₃ in this specific part of the flue gas system is presented by investigations carried out by EON Engineering in an US-American power station C firing low-sulphur West Virginia coal (0,5 – 0,6% S) but without SCR. Those results are matching those found in early 1990 in Germany (power station D), where tests were initiated to investigate about the SO₃-aerosol problem after a SCR-retrofit had taken place (figure 10) [7].

Similar SO₃-removal rates were found compared to the above tests and it should be noted, that even in the case of no SCR present with correspondingly low SO₃-concentrations at the boiler outlet, the SO₃-removal in the air heater was between 40 and 70% depending on air heater set-points between 170°C and 185°C.

The most interesting result is, that the concentrations of SO₃ found after the ESP on the same level as those at the outlet of the air heater. It can be concluded, that no further reaction of the remaining SO₃ out of the gas phase was taking place, i.e. no condensation or adsorption of sulphuric acid on the fly ash.

In other words, no further conditioning of the fly ash took place except such attributable to the processes in the air heater described above.

5. Opacity

It can be concluded from the explanations above, that the air heater can be considered to be an acid trap. Its efficiency is depending on and limited by the outlet temperature as well as the uniformity of the temperature profile.

During some of the tests described above, the opacity has been recorded as a function of different air heater setpoints and subsequent aerosol levels in the flue gas. The results while firing high sulphur, high volatile bituminous coal are shown in figure 11. It should be recalled, that opacity as an optical measurement does not distinguish between the cause of any light scatter

ing or extinction. Both liquid and solid particles are contributing to the opacity reading.

All results with SCR in operation are within a close range between 13,3 and 16,5% for the different air heater setpoints. Opacity in the common duct after ESP decreased slightly in two cases by 2 – 3%-points when increasing the air heater setpoint. However, during another test run, the opacity slightly increased by less than 1%-point after making a similar change regarding the setpoints. During SCR-bypass operation the opacity dropped significantly to levels less than 5% comparable to those prevailing before the retrofit of the SCR.

For all air heater setpoint temperatures tested, the predicted fly ash resistivity using the Southern Research Institute Model 1 [8] indicated VSA-resistivity values on the left side of the maximum, i.e. increasing temperatures cause an increase also in ash resistivity (figure 12). One should expect a decrease of ESP-efficiency and subsequent increase in opacity if all other parameters are constant. One possible explanation for above findings can be found in the different contribution of aerosols and ash to the total opacity as shown in figure 13.

When aerosols were eliminated by increasing the temperature, the “ash-related” opacity increased due to the increased ash resistivity but to a total level lower than before caused by the combination of fly ash and aerosol.

Since the tests have been made with the SO₃-issue as a primary concern, further relevant ESP-operating parameters unfortunately have not been recorded, and thus an explanation of the contradictory findings in another test (figure 11 - test 3) is not easy if not impossible. Nevertheless, all opacity readings are within a very close range, even small variations in ash chemistry or other operation parameters might have caused this result also under consideration of above explanations.

Aerosol generation in FGD-systems

Above explanations apply to the generation of aerosols in the air heater, which are likely to appear directly downstream of the ESP. However, in all German power stations as well as in those of many other utilities in Europe, FGD-systems are located downstream the particulate collection device. Usually, so-called gas-gas-heaters are installed upstream the FGD, which mostly are similar devices as the regenerative air heaters discussed above. This heat exchanger cools the flue gas down to approx. 80°C before entering the FGD and reheats the desulphurised flue gas to approx. 80°C after leaving the FGD.

Regardless of having such gas-gas-heater or cooling the flue gas in the FGD, the flue gas is rapidly quenched down to a temperature lower than the acid dewpoint of the remaining sulphuric acid (figure 14). Complete condensation of the acid in the gas-gas-heater accompanied by aerosol generation is the consequence [7]. The FGD captures about 20 – 50% of the aerosols, thus the flue gas exiting to the stack still carries a considerable aerosol load, which can also be increased by re-evaporation of condensed acid on the gas-gas-heater plates on the clean gas side.

It should be noted as well, that the opacity monitored at the stack can have several contributors: the fly ash having escaped both ESP and FGD, aerosols generated somewhere along the flue gas system and - depending on the operating conditions - various kinds of particles generated in the FGD-process, i.e. droplets, salts and gypsum particles. Thus, utmost care and extensive investigations on all above aspects are required when searching for suitable measures to minimise opacity.

6. Conclusions

Above test campaigns have shown, that the air heater plays a key role in how much SO₃ will be present in the downstream flue gas cleaning equipment. It furthermore determines, in which state this SO₃ – gaseous and/or as aerosol - will be present by setting the outlet temperature.

The question, whether the additional SO₃ generated by a retrofitted SCR-system is useful and contributing in conditioning the fly ash in the classical sense can not be answered straight away from the above results. However, some indications can be given which in total should lead to a negative answer:

- The driving force of normal add-on SO₃-conditioning plants is the condensation of the hot acid-air-gas mixture shortly after being injected into the relatively cold flue gas flow forming an acid film on the fly ash [9]. Those controlled conditions are not prevailing in an air heater or anywhere else downstream the SCR-reactor, where the cold heat exchanger plates represent the main driver for acid condensation. It can therefore be assumed, that acid deposition on the ash by condensation is not the main cause of SO₃-capture in the air heater.
- There certainly is some capture of sulphuric acid on the fly ash in the air heater. Considering the concentration and temperature profiles given in the figures above, it is obvious, that this results in an uneven distribution of “conditioned” and “unconditioned” ash.
- Furthermore, at the hot outlet side of the air heater, where ash resistivity can be expected to be higher, the least reduction of SO₃, i.e. only marginal “conditioning” would take place, whereas on the cold outlet side, the opposite conditions would prevail.
- According to the test results, no further reaction out of the gas phase – condensation or adsorption – took place after leaving the air heater.

In addition, one should mention that of course in the past many plants with SCR-systems have been retrofitted with true SO₃-conditioning systems downstream the air heater, especially after switching fuels to low-sulphur coals.

Another important conclusion relates to the discussion of opacity and the ongoing issue of PM₁₀ and PM_{2,5}:

- For future investigations regarding the opacity impact of SO₃-aerosols the particulate matter needs to be determined parallel to the SO₃-testing.
- The contribution of each particle type – ash and SO₃-aerosol – needs to be determined in order to fully understand the individual impact on opacity and to determine suitable mitigation methods.

Specifically when SO₃-mitigation methods such as alkali injection upstream the ESP are implemented, the ESP-collection will be affected. The evaluation of such effects is virtually impossible, if no difference is made between the aerosol and ash contribution to opacity.

7. References

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- [10] Personal communication with Gutberlet, Dieckmann, Albrecht of EON Engineering GmbH; February, March 2004
- [11] Various test reports of EON Engineering GmbH; 2001 – 2004; not published

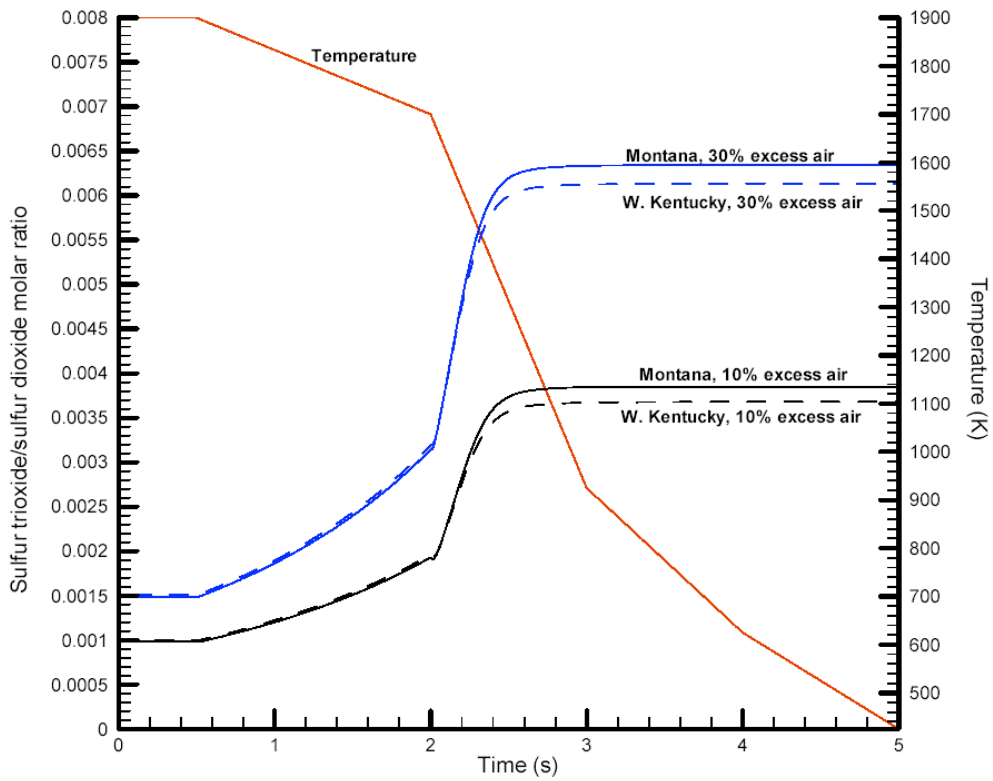


Figure 1
SO₂ Conversion during Coal Combustion [1]

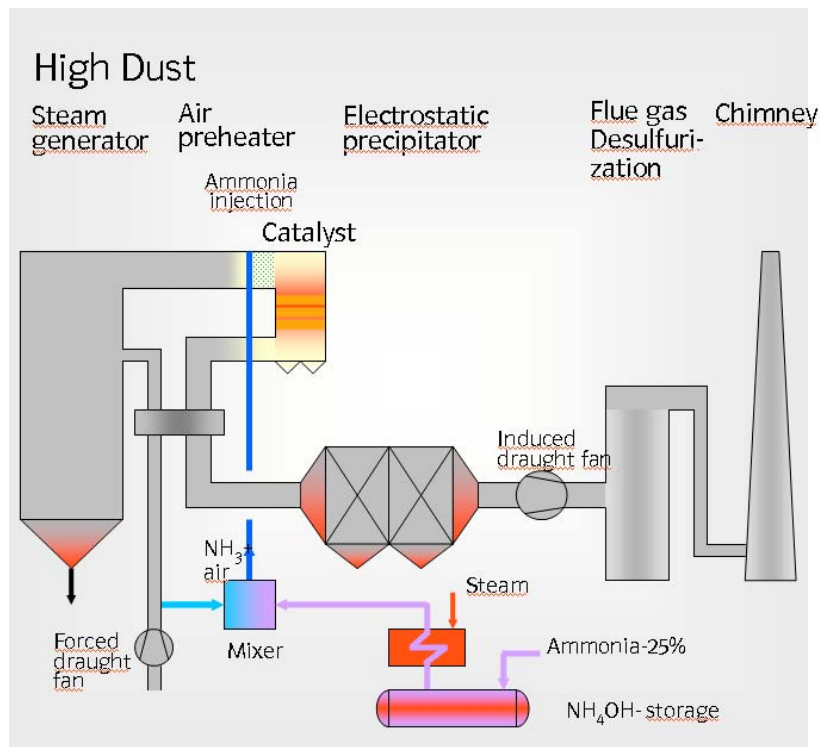


Figure 2
High Dust SCR

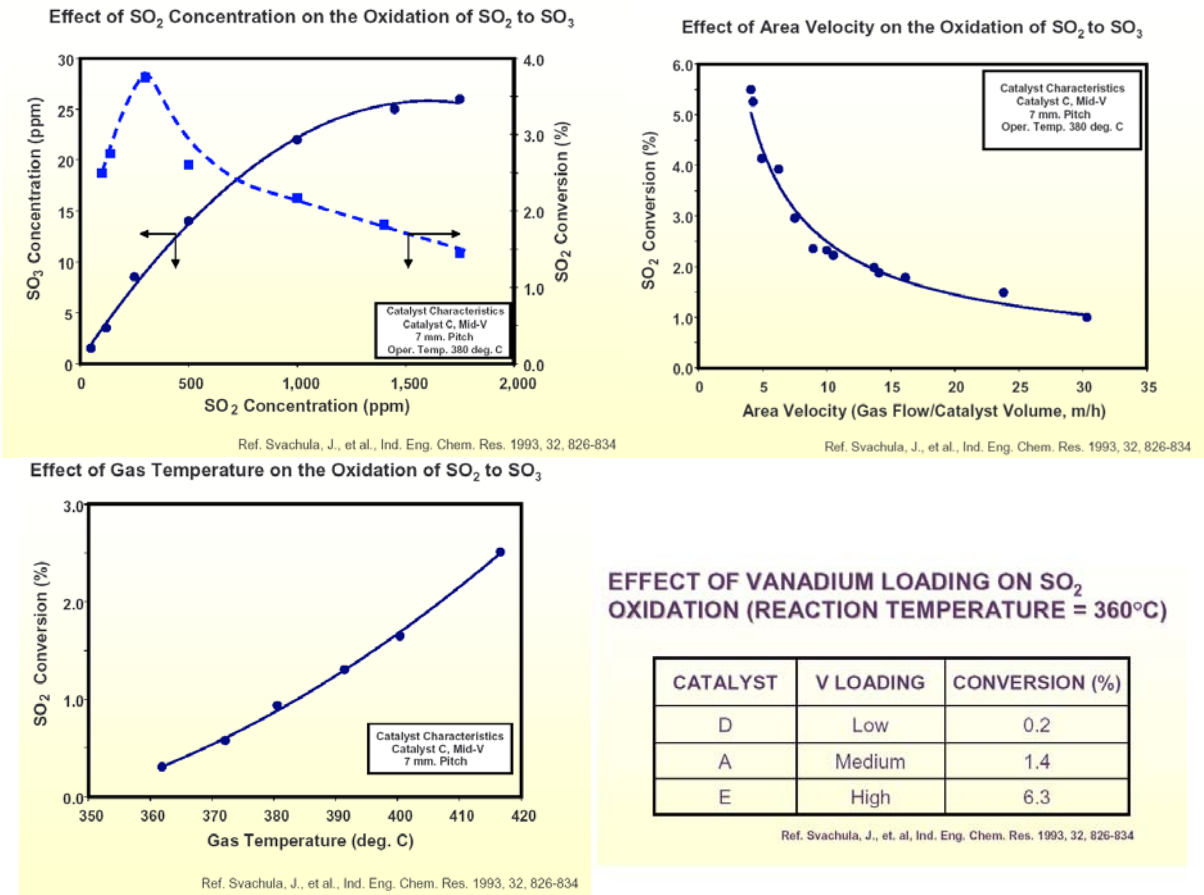


Figure 3
Influences on SO₂-Conversion [3]

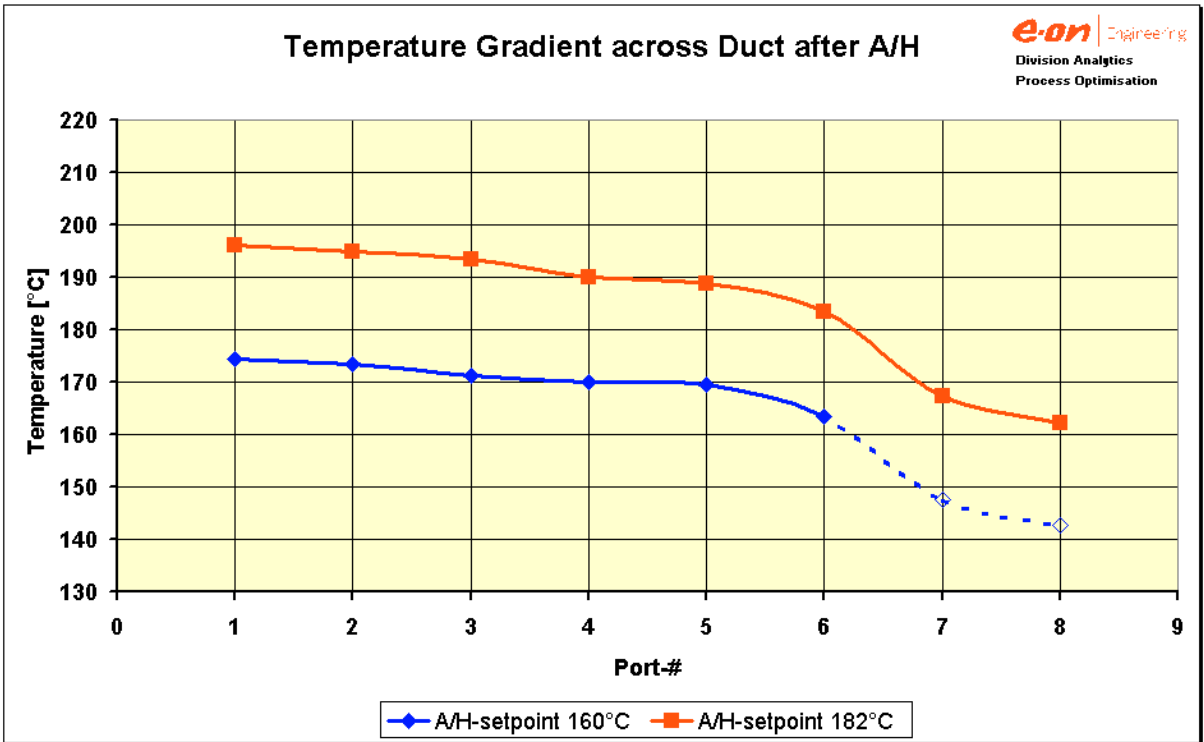


Figure 4
Temperature Gradient across Duct after A/H

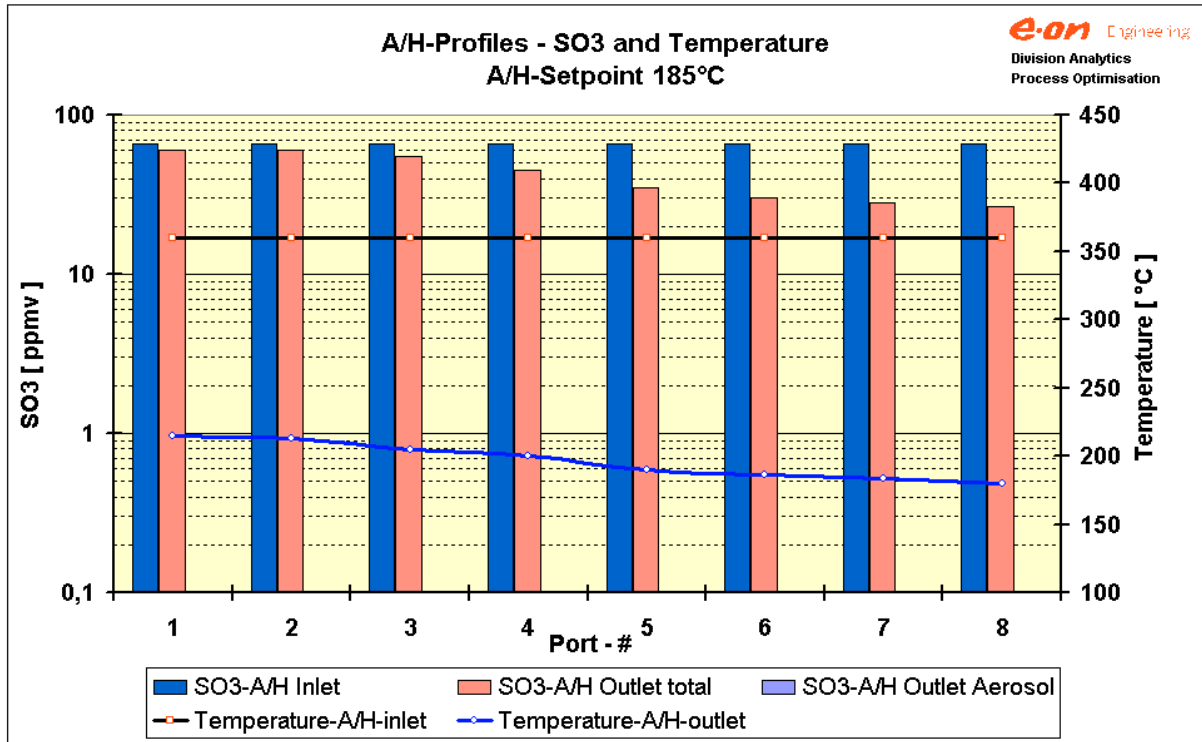


Figure 5
Air Heater Setpoint 185°C

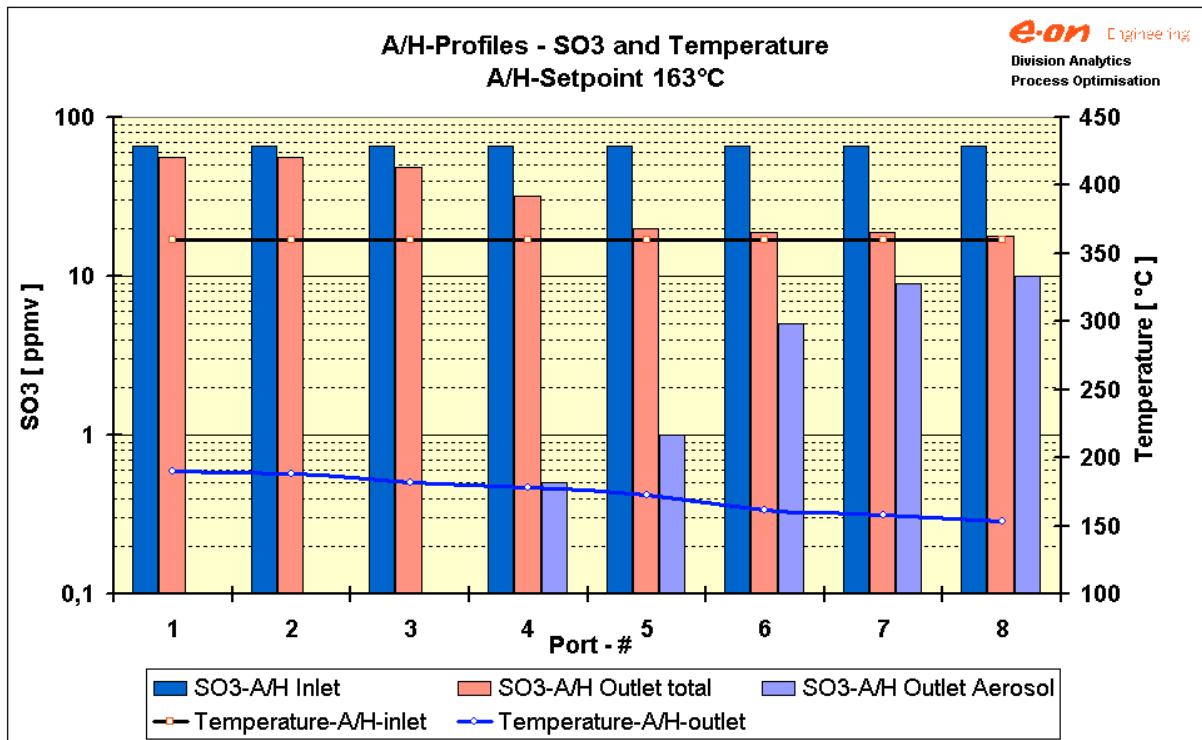


Figure 6
Air Heater Setpoint 163°C

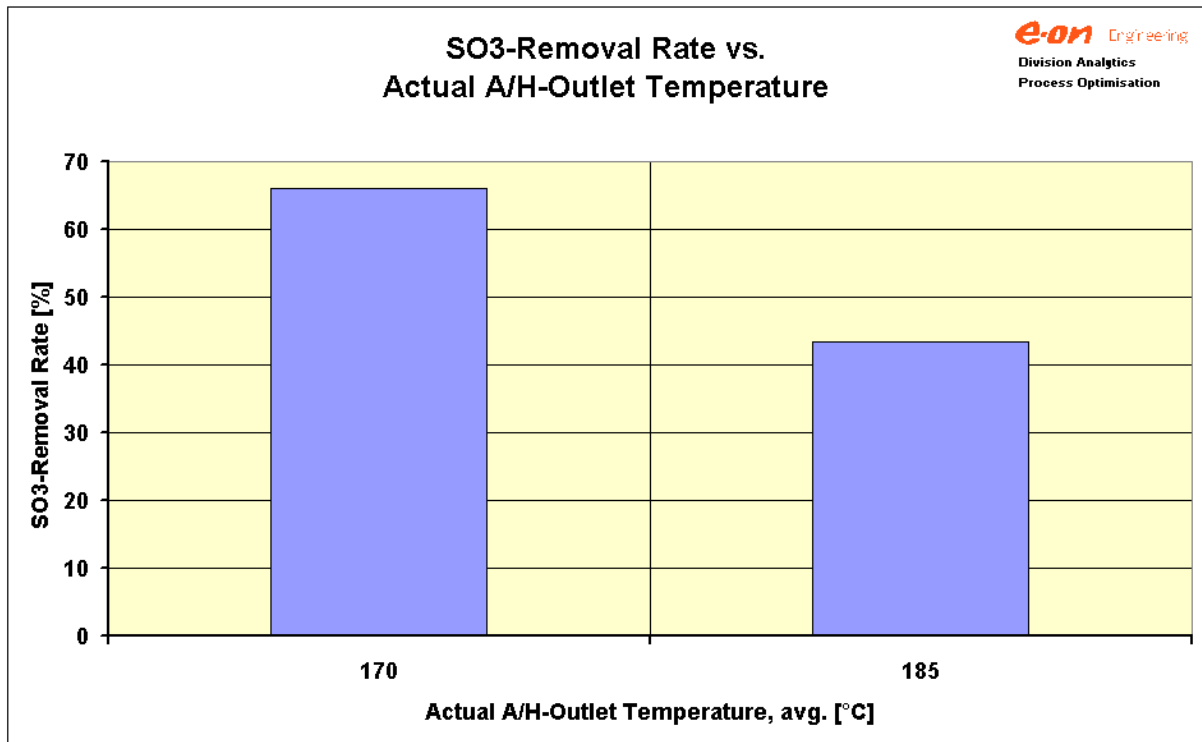


Figure 7
SO3-Removal Rate vs. A/H-Outlet Temperature

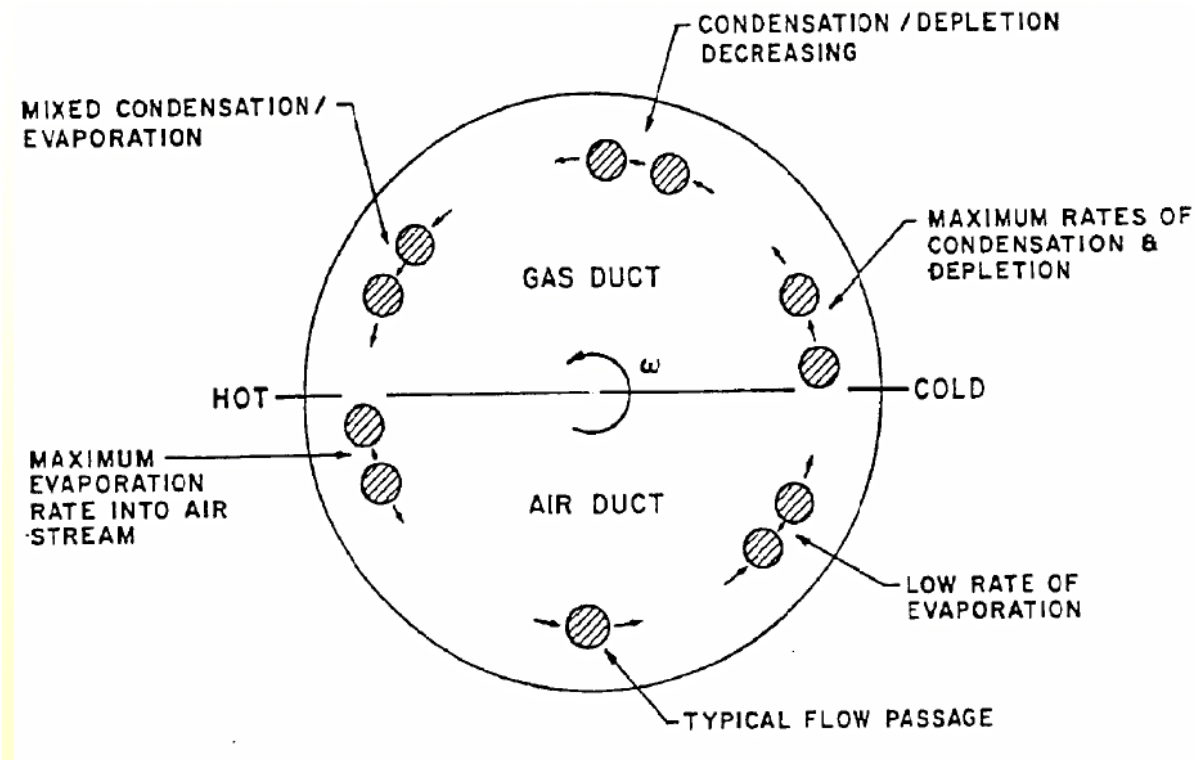


Figure 8
A/H-Acid Deposition and Evaporation [3]

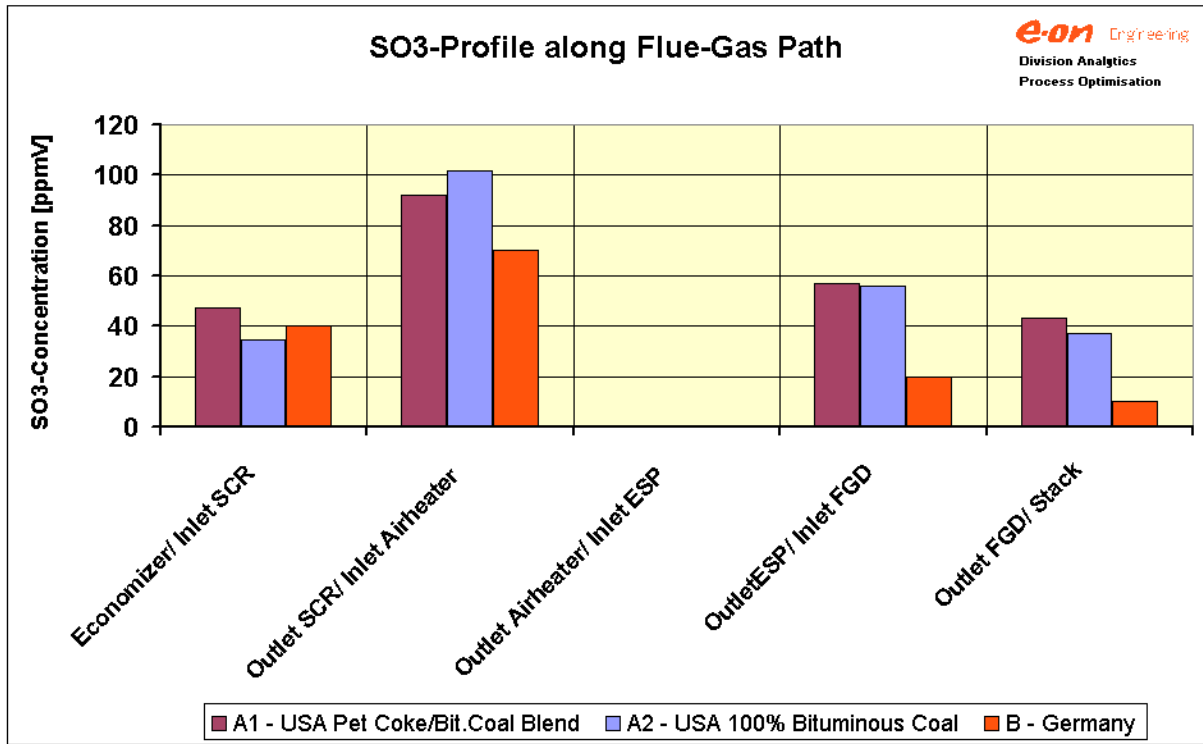


Figure 9
SO₃-Profile along Flue Gas Path

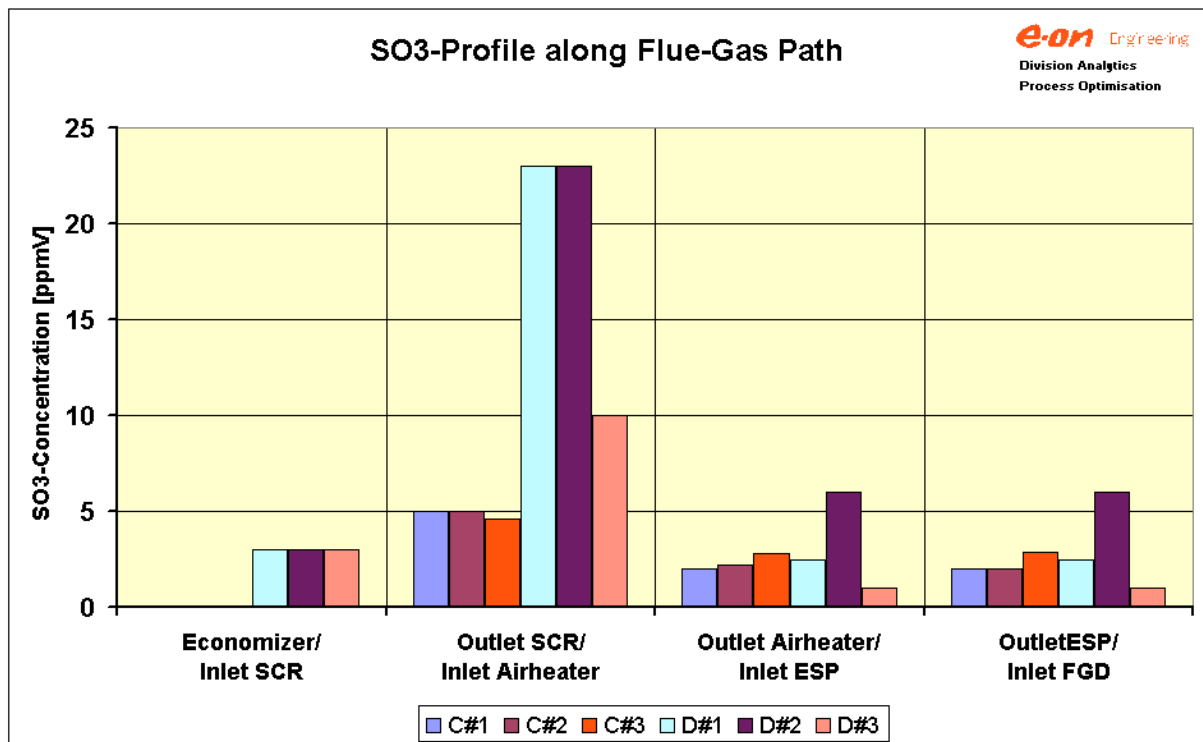


Figure 10
SO₃-Profile along Flue Gas Path - A/H and ESP

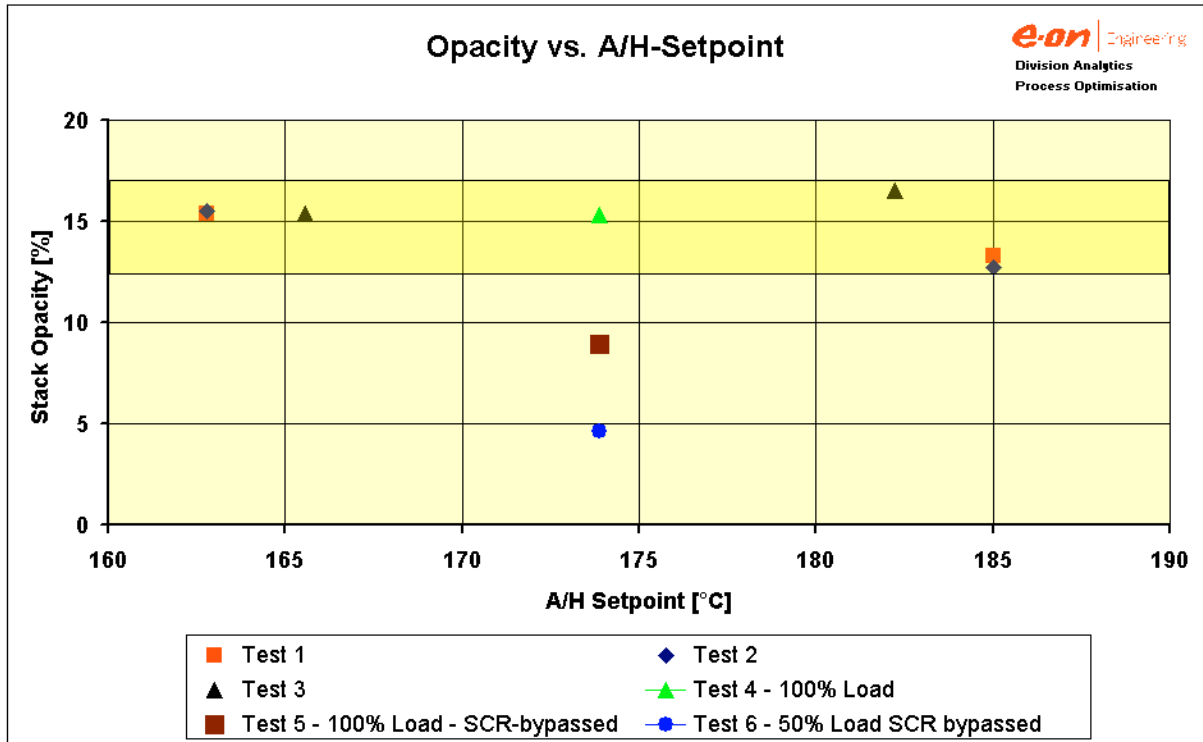


Figure 11
A/H-Setpoint vs. Opacity

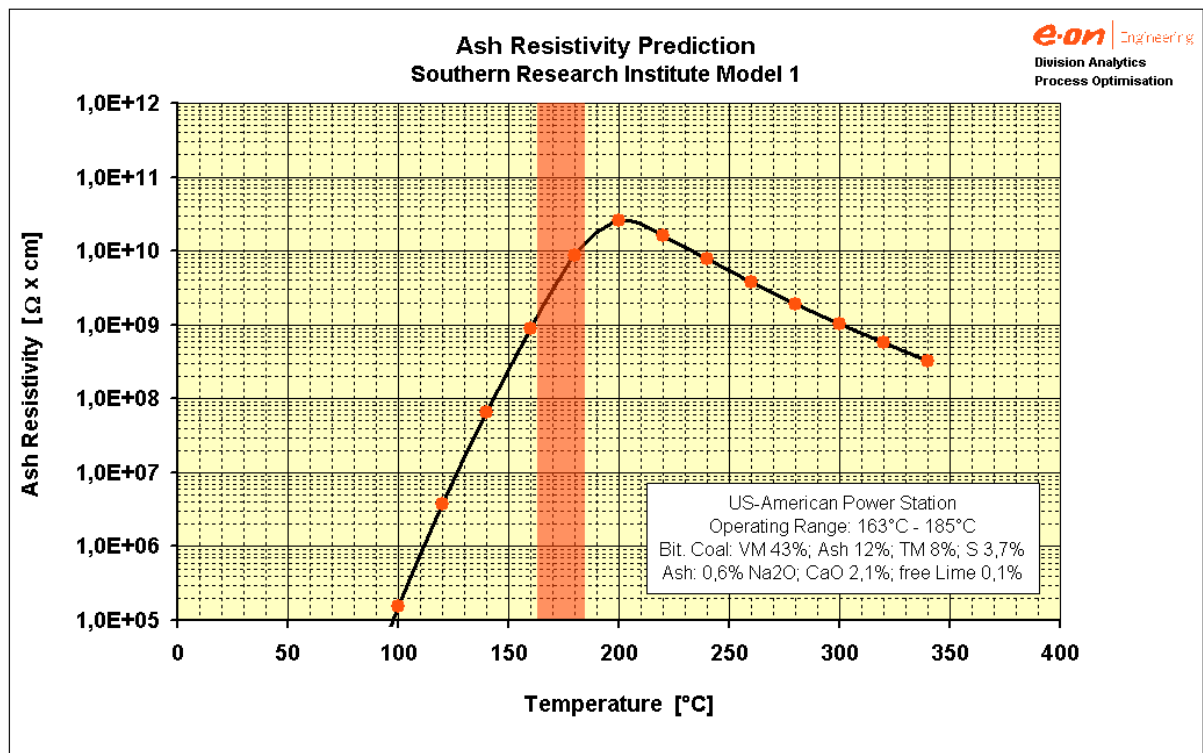


Figure 12
Ash Resistivity and Flue Gas Temperature Operating Range

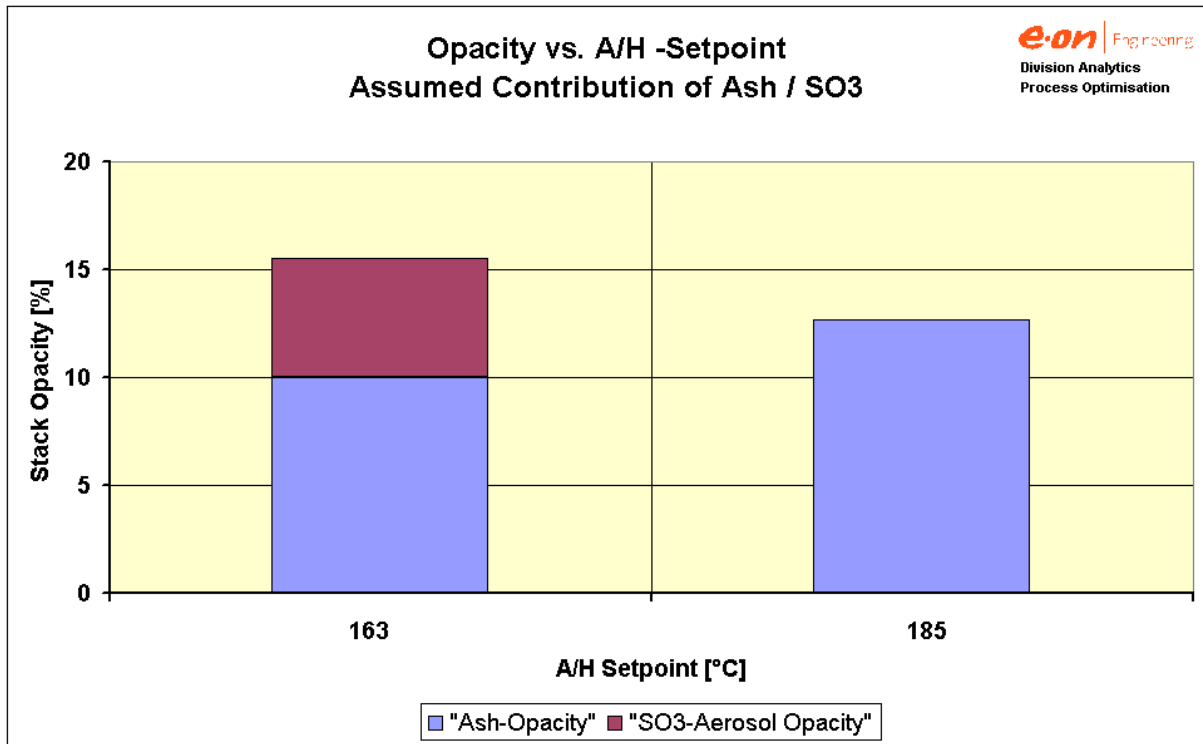


Figure 13
Assumed Individual Contribution of Fly Ash and SO₃-Aerosol to Opacity

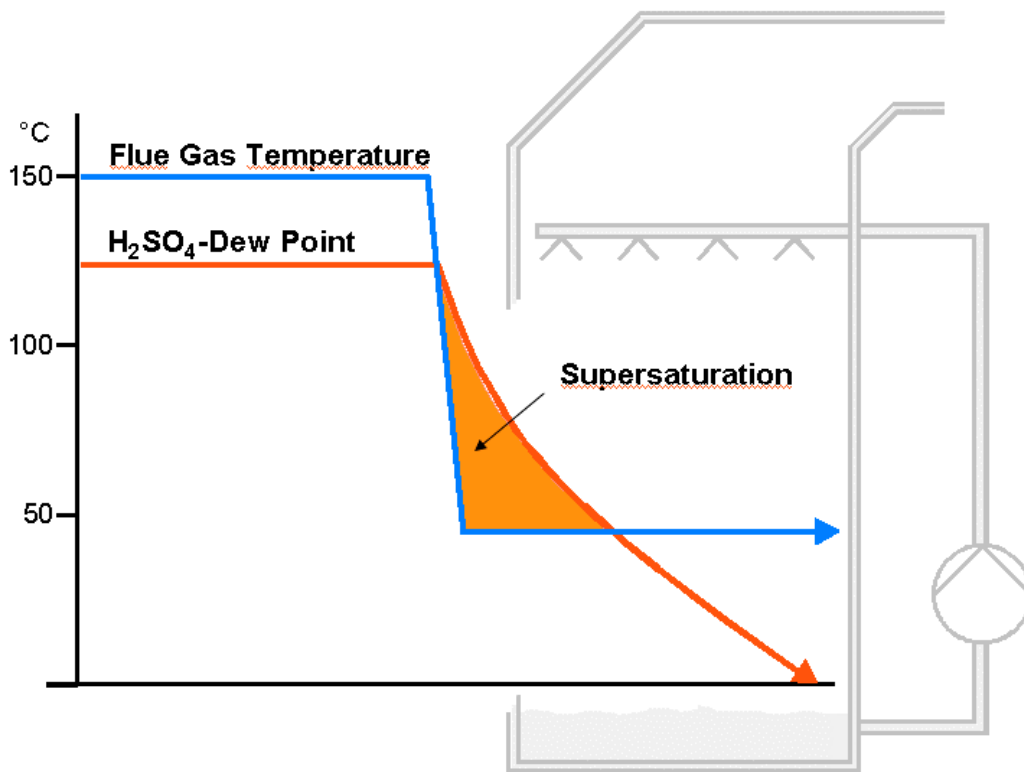


Figure 14
Supersaturation in the FGD-System