



# Formation of ammonia bisulfate in coal-fired power plant equipped with SCR reactors and the effect of reduced load operation

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**Abstract.** Coal fired power plant are still responsible for vast amount of electricity and heat production in Poland in 2019. Increasing number of units is equipped with SCR reactors in order to mitigate NO<sub>x</sub> emission. Older units have been designed to work in a base load operation, however increasing number of intermittent energy sources on the market, forces power plant owners to operate such units in reduced load for significant number of hours in a year. Most of parameters in coal-fired boiler would change in reduced load operation, particularly flue gas parameters. That would affect the formation of ammonia bisulfate (NH<sub>4</sub>HSO<sub>4</sub>) as well as operation of SCR reactors in the boiler. The NH<sub>4</sub>HSO<sub>4</sub> formation is highly undesired as it can plug the catalyst or heating surfaces in the boiler. To investigate this phenomenon, the NH<sub>4</sub>HSO<sub>4</sub> formation was comprehensively studied. Moreover, reduced load operation of boiler in a medium size CHP plant was simulated, using computer modelling tools. Obtained parameters were used to analyse, how different flue gas parameters affect NH<sub>4</sub>HSO<sub>4</sub> formation and what consequences does it have for boiler operation. In particular, effect related with operation of SCR reactors equipped with V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst was deeply studied.

## 1. Introduction

Ammonia bisulfates formation is one of the major problems related to DeNO<sub>x</sub> installations, such as SCR (Selective Catalytic Reduction) or SNCR (Selective Non-Catalytic Reduction), in solid fuels power plants. Ammonia (NH<sub>3</sub>) that can escapes from these installations reacts with sulfur trioxide, forming compounds such as ammonium bisulfates NH<sub>4</sub>HSO<sub>4</sub> and ammonium sulfates (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. The problem is related with the first one in particular - salt which at a temperature below its condensation point, forms sticky substance that covers porous structure of the SCR catalysts, as well as it can contaminate surfaces of the rotary air heater and the electrostatic precipitator [1] [2] [3] [4]. Because it condensates at a certain temperature, region that can be affected by plugging depends on the boiler load. The NH<sub>4</sub>HSO<sub>4</sub> also passes in solid form to the fly ash, which results in increased ammonia content in the combustion by products.

## 2. SO<sub>3</sub> formation

The SO<sub>3</sub> in flue gas exists because of SO<sub>2</sub> to SO<sub>3</sub> conversion. Due to the fact that SO<sub>3</sub> concentration is crucial for ammonia bisulfate formation, it is vital to discuss this mechanism in details. Sulfur in the combustion chamber is delivered together with the fuel. Modern solid fuels boilers use a division of the combustion process into a reduction zone (with oxygen deficiency) and a post-combustion zone (with excess oxygen). During combustion, sulfur contained in coal is oxidized according

to the following reaction:



The largest amount of SO<sub>2</sub> is formed in the first stage of combustion. Then, some part of SO<sub>2</sub> is converted to SO<sub>3</sub>. The main parameters that support this process is temperature, the residence time of the particle, oxygen concentration, as well as the composition and size of the mineral fraction in fuel. The effect of temperature on the degree of conversion begins to be visible above 700°C. However, the influence of temperature on the conversion process is small compared with catalytic influence, discussed in below [5]. Overall conversion in combustion zone is up to 2% [6].

Above the area of the boiler where the combustion process has been completed, sulfur is mainly present in the form of SO<sub>2</sub>. The SO<sub>3</sub> concentration depends on the sulfur content in fuel. Also, elements such as iron, nickel, wolfram, titanium and vanadium show catalytic properties for the conversion of SO<sub>2</sub> to SO<sub>3</sub>. Thus, along with the increase of these elements in the fuel, the potential SO<sub>3</sub> emission will also increase. On the other hand, the presence of alkaline elements may prevent this process by binding both SO<sub>2</sub> and SO<sub>3</sub> in the form of sulfates (e.g. K<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>) at temperature below 1000°C. The highest intensity of catalytic reactions is recorded at a temperature of about 700°C and their impact on the overall level of SO<sub>2</sub> to SO<sub>3</sub> conversion is much greater than other factors. Table 1

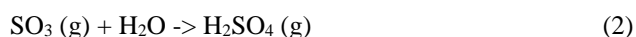
shows the influence of temperature and the above-mentioned catalysts on the SO<sub>2</sub> conversion process. It can be seen, that at temperature of 700°C as much as 95% of the total conversion occurs due to the action of catalysts [7].

**Table 1.** Effect of temperature and catalysis on SO<sub>2</sub> to SO<sub>3</sub> conversion rate, based on [7]

Temperature	Conversion rate [%]		Catalytic effect on conversion [%]
	Temp. effect	Total conversion	
400°C	0.041	0.042	1
500°C	0.062	0.077	19
700°C	0.098	1.784	95
900°C	0.361	1.308	72
1000°C	0.773	1.791	57

As noted above, vanadium oxide (V<sub>2</sub>O<sub>5</sub>) being part of the SCR catalyst has catalytic properties when converting SO<sub>2</sub> to SO<sub>3</sub>. In modern catalysts, the conversion rate on SCR installations is roughly 1-2%. According to Lu et al. [6], conversion increases in the presence of ammonia in flue gas as well as in the presence of V<sub>2</sub>O<sub>5</sub>, WO<sub>3</sub> and TiO<sub>2</sub>. These compounds constitutes a catalyst, that is most often applied in SCR reactors. Also, if the ratio NH<sub>3</sub>/NO is higher than 0.6, the conversion raises. The effect of oxygen concentration, NO concentration as well as Al<sub>2</sub>O<sub>3</sub> is relatively small on the other hand. Also the conversion rate drops when the amount of SiO<sub>2</sub> and BaO increases [6]. Taking this into account, it is important to ensure that SCR installation operates at its optimal conditions. Operational parameters (such as NO<sub>x</sub> concentration, temperature and flue gas flow before installation) should be observed. The essence of the exhaust gas temperature before the SCR installation is particularly important - when it is too low, there is an increased slip of ammonia, when it is too high - increased amount of sulfur trioxide can be formed [8].

In the zone of the rotary air heater, the sulfur trioxide SO<sub>3</sub> reacts with the steam to form sulfuric acid (VI) according to the equation:



This reaction takes place in temperature range between 204°C and 426°C. At temperatures below 204°C, sulfuric acid is also in the form of an aerosol [8]. Sulfuric (VI) acid is dangerous at temperatures below its condensation point, bringing risk of corrosion occurrence. The temperature of this point increases proportionally to the partial pressure of water vapor and SO<sub>3</sub> in exhaust gases. A typical temperature range in which H<sub>2</sub>SO<sub>4</sub> condensates is in the range of 95-160°C. The increased SO<sub>3</sub> content can therefore lead to sulfuric acid condensation at the cold end

of the air heater. The relationship between the sulfuric acid condensation temperature and SO<sub>3</sub> concentration in the flue gas after the rotating air preheater, is presented in the Table 2 [9] [10].

**Table 2.** The relationship between the sulfuric acid condensation temperature and SO<sub>3</sub> concentration

Acid dew point	SO <sub>3</sub> concentration
155°C	60 ppm
146°C	30 ppm
124°C	5 ppm (desired value)

Although there is a high probability that the flue gas will cool below the acid dew point temperature, the first signs of corrosion caused by sulfuric acid condensation should be expected only at temperatures below 70-80°C [10]. Above this temperature, condensing sulfuric acid will rather bind sticking ash particles together which, however, does not lead to the corrosion of particular surfaces. Another problem for rotating air preheater is further discussed occurrence of liquid ammonium bisulfate [5].

### 3. SO<sub>3</sub> concentration in flue gas

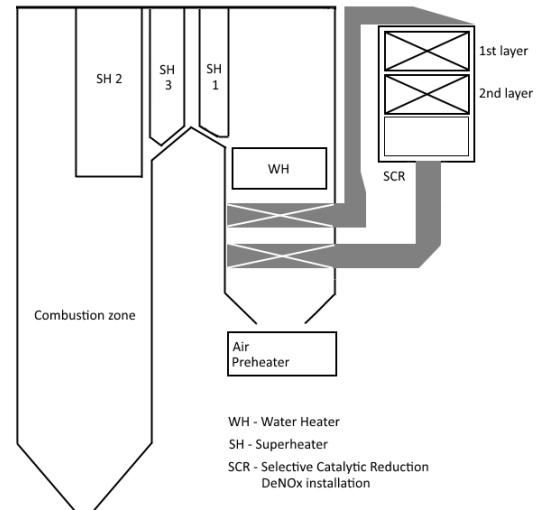
Considering the pulverized coal boiler, it can be estimated that the level of sulfur dioxide emissions is, for the nominal load operation, in the range from about 1200 mg / Nm<sup>3</sup> (458 ppm) to about 2500 mg / Nm<sup>3</sup> (955 ppm), depending on the sulfur content in the fuel (from 0.7% to 1.1%). Assuming the SO<sub>2</sub> to SO<sub>3</sub> conversion (before SCR) equals to 2%, the corresponding range of SO<sub>3</sub> concentration in the furnace chamber is from about 9.2 ppm to 19.1 ppm. Part of SO<sub>3</sub> reacts with alkaline elements in fly ash to form compounds that settle on the boiler heating surfaces (e.g. K<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>). The associated SO<sub>3</sub> reduction will therefore be directly proportional to the alkali content in fly ash. Part of SO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> is also adsorbed on the fly ash particles. After the flue gas passes through successive layers of the SCR installation, the SO<sub>3</sub> concentration increases accordingly: about 5 ppm in the first catalyst layer, about 6 ppm in the second catalyst layer and about 6.5 ppm in the third catalyst layer [8]. The above values may increase when the SCR installation is turned off and the exhaust gas is not bypassed (increase by approx. 30%). The reason for this is the main component of SCR catalysts - vanadium oxide - which also acts as a catalyst for the conversion of SO<sub>2</sub> to SO<sub>3</sub>. Besides that, the increased flue gas temperature and reduced flue gas flow can also influence conversion [8].

Occurrence of ammonia bisulfate in the boiler is important from power plant operation point of view, because it can easily deposit on heating surfaces as well as on SCR catalysts. Moreover, it aggregates fly ash particles carried by flue gas. Plugged heating surfaces would affect heat transfer while plugged catalyst surface would have lower activity. Temperature of ABS condensation has been subjected to numerous studies. There is no consistency for

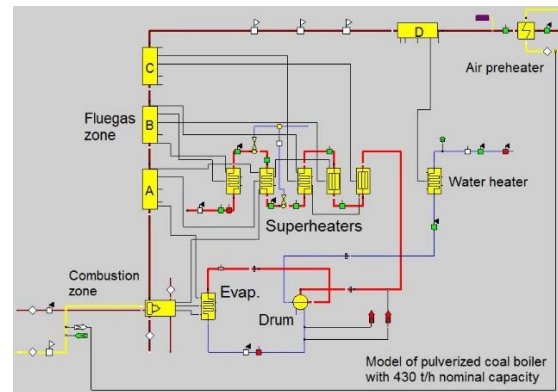
the results though. According to Shi et al. [11] temperature of ABS condensation is in the range of 190°C - 240°C, but other authors indicate, that risk of ABS formation may occur at any temperature. Ammonia bisulfate can be removed when flue gas temperature is higher than 400°C, but this can bring about issues related with catalyst sintering on the other hand. Temperature of ABS condensation is also related to the pores structure of the catalyst. For smaller pores, temperature may increase due to the capillary forces [12] [13]. It can be concluded, that the lower the temperature of SCR operation is, the higher the risk of ammonia bisulfate condensation will be. It is also important to notice, that SCR catalysts producers indicate that proper temperature for the installation should be between 300°C and 400°C.

#### 4. Modelling of coal-fired boiler operation

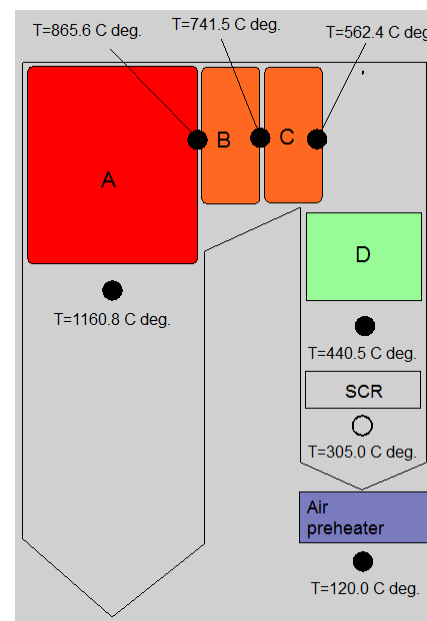
Modelling of the coal-fired boiler was made using Epsilon Professional, the software for thermodynamic simulation of power units [14]. By utilizing this tool, it is possible to design and simulate single devices as well as technological systems for power or heat production. In coal-fired boiler, temperature of flue gas is not measured in every single region of the boiler. Besides that, in the first pass of the boiler, temperatures are too high to install traditional measurement sensors, which leaves room for acoustic temperature measurement systems only. The latter are usually used in combination with SNCR technologies, in order to seek for desired temperature window in real time. However, if the boiler is not equipped with proper flue gas temperature measurements, the only way to find out desired value of temperature, is to simulate the boiler operation. Because, from the SCR operation point of view, it is crucial to understand the temperature distribution, an pulverized coal-fired units with nominal capacity of 430 t/h was simulated. The schematic view of the boiler is shown on Fig. 1 while the corresponding thermodynamic model layout is shown on Fig. 2. What can be notice from Fig. 1, is that simulated boiler has only one stage of steam superheating, and the SCR installation is installed downstream the water heater. What can also be noticed from Fig. 1, is that SCR reactor has two catalytic layers and the third one is left empty. That is often the case for new installations, where the third layer is added after the overall activity of the installation drops under the required limit.



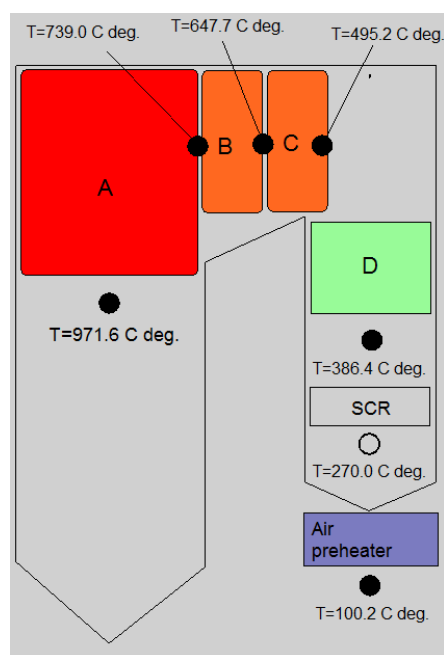
**Fig. 1.** Schematic view on the pulverized coal boiler with 430 t/h nominal capacity, equipped with DeNOx SCR installation.



**Fig. 2.** Layout of the coal-fired boiler model in Epsilon Professional software.



**Fig. 3.** Flue gas temperature distribution in 100% boiler load.



**Fig. 4.** Flue gas temperature distribution in 60% boiler load.

## 5. Model outcomes and discussion

Based on the model outcomes, flue gas temperature distribution along the boiler was determined for nominal (100%) and minimal (60%) load. Results are shown on Fig. 3 and Fig. 4. Rectangles marked with capital letter (A-D), represent areas of the boiler, from where heat is conveyed (through the radiation and convection mechanism) to superheaters and other heat exchangers installed in the boiler. Temperatures indicated by black dots, are calculated as an average value for the cross section between regions A-D. In order to simulate exact temperature in every single place of the boiler, more advance simulation techniques, like Computational Fluid Dynamics (CFD), must be applied. Because the region D represent heat absorbed the water heater, that means temperature calculated downstream this region is also the temperature at the inlet of SCR installation. The temperature downstream the SCR installation shown on Fig. 3 and Fig. 4 (transparent dot), is adopted from power plant measurement system, as the model does not include calculations for temperature drop at the SCR installation.

## 6. Conclusion

In this paper, mechanism of ammonia bisulfate formation was comprehensively described. Also, the mechanism of the  $\text{SO}_2$  to  $\text{SO}_3$  conversion in coal-fired boiler was discussed. In order to investigated temperature of SCR installation operation, the thermodynamic model of an 430 t/h capacity coal-fired boiler was simulated in nominal and minimal load operation. The ammonia bisulfate is dangerous for boiler operation, because it contaminates active surface of the SCR catalyst as well as the cold end of rotating air preheaters. To avoid, or at least reduce issues related with ammonia bisulfate, it is crucial to maintain

proper flue gas temperature as well as prevent excessive ammonia slip and  $\text{SO}_3$  formation.

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