

# Experimental research on the volatilization and condensation of ammonium bisulfate as SCR byproduct

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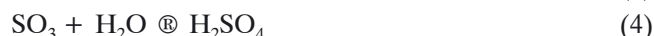
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In this paper, the research progress of ammonium bisulfate (ABS) volatilization in coal-fired power plants the SCR denitrification process was reviewed. Combination with self-made experiments, SEM, flue gas analyzer and TG-DTG curves of ABS and ion chromatography. The volatilization and condensation characteristics of ABS were investigated carefully. Results show that as the temperature increased by 50 °C, the ABS/AS volatilization rate increased by an order of magnitude. The decomposition process of ABS should have a two-step reaction. The reaction in the initial volatilization stage is ABS dehydration turned into (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>7</sub>. The reaction in the rapid volatilization stage is (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>7</sub> decomposed into NH<sub>3</sub>, N<sub>2</sub>, SO<sub>2</sub> and H<sub>2</sub>O. There is an inter-section in the reaction temperature range (especially 300 °C) between the two-step re-action. This research provides an experimental basis for temperature control of ABS to avoid air pre-heater fouling.

**Keywords:** Ammonium bisulfate (ABS), influencing factors, volatilization rate, condensation pattern.

## INTRODUCTION

According to the requirements of the national environmental protection policy, the "ultra-low emission" technical transformation has been fully implemented in coal-fired power plants of China. After the technical transformation, the concentration of nitrogen oxides (NO<sub>x</sub>) emitted is limited at 50 mg/m<sup>3</sup>. The denitrification transformation technology is mainly focused on improving the efficiency of the selective catalytic reduction (SCR) denitrification system. The main technologies include the addition of catalyst bed, the optimization of ammonia injection system and so on<sup>1</sup>. Commercial SCR catalysts contain 0.5 to 4.0 wt% V<sub>2</sub>O<sub>5</sub>, which can oxidize some of the SO<sub>2</sub> (0.75 %~1.5 %) in the flue gas into SO<sub>3</sub><sup>2-3</sup>. For component-determined catalyst, the increase of catalyst makes the concentration of SO<sub>3</sub> in flue gas increase. Ammonia escape is serious when the quantity of ammonia injection increases, boiler load changes and operation at low load. SO<sub>3</sub>, NH<sub>3</sub> and H<sub>2</sub>O in the flue gas react each other as follows<sup>4-7</sup>:



Therefore, two new substances, ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, AS) and ammonium bisulfate (NH<sub>4</sub>HSO<sub>4</sub>, ABS), are formed in the flue gas<sup>8-9</sup>. While increasing the NO<sub>x</sub> removal efficiency in coal-fired power plants, the AS and ABS content in the flue gas will increase significantly. In general, the melting point of AS is 513 °C<sup>10</sup>, at this temperature, AS can decompose into ABS easily. the melting point of ABS is 147 °C and the boiling point is 350 °C. Traditional design temperature range of the cold end and intermediate layer of the air preheater in SCR downstream is around 120–230 °C<sup>11</sup>. In this temperature range, ABS is in liquid-solid phase conversion process. Liquid phase ABS has high viscosi-

ty, strong hygroscopicity and strong corrosivity. A large amount of fly ash in the flue gas is adsorbed by the liquid phase ammonium bisulfate, then bonded to the surface of heat exchange element of the air preheater, finally foul on the metal wall or stuck in the middle of interlayers<sup>12-13</sup>, causing a series of problems in the air preheater, such as corrosion, clogging, decrease of cross-sectional area of flue gas flow, increase of running resistance, reduction of heat transfer efficiency, etc<sup>14-18</sup>. In recent years, Air preheater fouling has often occurred, and these problems will lead to reduced boiler efficiency, stall of induction fan, and negative pressure sloshing in boilers. Which seriously affects the safety and economic operation in coal-fired power plants.

Domestic and foreign scholars have carried out a lot of research on the formation and deposition of ABS in SCR denitrification system and air preheater<sup>4, 19-22</sup>. The formation mechanism and deposition law of ABS were basically clarified, the influence of catalyst on the formation and deposition of ABS in SCR denitrification system was discussed. Commercial V-based catalysts can increase the conversion of SO<sub>2</sub> to SO<sub>3</sub> in the flue gas, thereby enhancing the formation of ABS. The ABS deposited on the catalyst surface will cause catalyst deactivation and reduce the SCR denitration efficiency<sup>23</sup>. Based on earlier research<sup>2, 24-25</sup>, the author further studied the reaction characteristics of fly ash in ABS and the corrosion characteristics of ABS on the metal material of boiler tail<sup>26-27</sup>. At present, coal-fired power plants have made many practical improvements to solve the fouling problem of air preheaters caused by ABS. Such as improving the heat exchange material of the air preheater, increasing the steam pressure and cleaning frequency of the air preheater. Optimize the ammonia injection system of the air preheater, and apply reasonable soot blowing methods for the air preheater such as high-pressure water washing, steam soot blowing, and sonic soot blowing. Although these methods alleviate the problems caused by fouling of the air preheater

to a certain extent but cannot fundamentally solve the deposition and fouling of ABS on the air preheater.

At present, there is no better way to avoid the deposition and corrosion of ABS in the air preheater. Therefore, studying the decomposition and volatilization process of ABS can clarify the reaction temperature, and mechanism of ABS decomposition and volatilization. Starting from temperature control is also one of the research ideas to solve the problem of air preheater fouling. Li Jinghua et al.<sup>28</sup> studied the thermal decomposition characteristics of pure ABS earlier from the perspective of chemical energy storage. In this study, by analyzing the Arrhenius parameters, the kinetic compensation number, and the reaction rate constant ( $k$  value) derived from the isothermal method and the compensation law, ABS was considered to have a decomposition temperature above 345 °C, and the thermal decomposition mechanism was one-dimensional phase boundary reaction. Shi Yajuan et al.<sup>4</sup> believed that the thermal decomposition characteristics of pure ABS and ABS deposited on the catalyst were different significantly. Deamination and SO<sub>2</sub> release tend to occur simultaneously during the decomposition of pure ABS. However, when the ABS is decomposed on the catalyst, the temperature windows of deamination and SO<sub>2</sub> release are inconsistent and the two processes occur step by step. Zhu et al.<sup>22</sup> found that the decomposition of pure ABS starts at 390 °C, and the decomposition rate reaches the maximum at 490 °C. It was found that different catalyst supports have different effects on the ABS decomposition reaction on the catalyst surface. Shu Hang et al.<sup>23</sup> found that NO can reduce the temperature window of ABS decomposition by directly reacting with NH<sub>4</sub><sup>+</sup> in ABS to promote its decomposition behavior on the catalyst surface. The removal of NO and the formation of ABS are mutually inhibiting relationships. Urano<sup>29</sup> and Fan et al.<sup>30</sup> studied the thermal decomposition process of AS. The results show that AS thermal decomposition is divided into three steps. First, AS deamination produces ABS, then ABS loses water to form ammonium pyrosulfate, and finally, ammonium pyrophosphate further decomposes. The decomposition process of ABS is uniform weight loss, and the temperature range is around 308–330 °C.

In summary, studying the decomposition and volatilization behavior of ABS by temperature regulation is another way to solve the ABS deposition problem in air preheaters. But there are several different understandings about the thermal decomposition process and thermal decomposition temperature of ABS. Therefore, determining ABS volatilization process, temperature window

and related influencing factors are the prerequisites for temperature control to prevent the deposition of ABS in air preheater.

In this paper, the effects of different temperatures and fly ash ratios on the volatilization characteristics of ABS were investigated through the self-built ABS volatilization and condensation test bench. Flue gas analyzer, Scanning electron microscope (SEM), Thermogravimetric-Derivative Thermogravimetry (TG-DTG) and Differential Scanning Calorimetry (DSC) were combined to explore the mechanism of ABS volatilization process. The research provides theoretical support for the use of temperature control methods to prevent ABS deposition in air preheaters.

## EXPERIMENTS

### Experimental device and instrument

Pure ABS volatilization and condensation experimental system are shown in Fig. 1. The sample that need to be tested was placed in a constant high temperature zone heated by a fully automatic industrial analyzer. It can be used for online monitoring. The weight of the sample (AS, ABS and ABS samples prepared on demand) was measured and recorded continuously. The mixed gas prepared from high purity N<sub>2</sub> and O<sub>2</sub> was preheated through a heating tube and then passed to the analyzer. Under the purging of N<sub>2</sub> and O<sub>2</sub> atmosphere, the internal and external diffusion during the volatilization of ABS is closer to the actual situation. The gaseous product produced by volatilization of the sample was first cooled by a condenser, and then pumped to the washing bottle for absorption by a vacuum pump placed at the end of the experimental system. The condenser and washing bottle were placed in a constant temperature water bath (30 °C) to maintain a stable condensation absorption temperature. The dynamic balance between intake and vacuum pump exhaust was maintained by adjusting the flow meter. The concentration of SO<sub>4</sub><sup>2-</sup> in the condensation product was detected by ion chromatography. The concentration of NH<sub>4</sub><sup>+</sup> in the condensed product was measured by ammonium ion concentration meter.

### Experimental method

The experimental atmosphere was 79% N<sub>2</sub> and 21% O<sub>2</sub>, and the total flow rate was controlled at 1 L/min. The experimental system was adjusted to a dynamic equilibrium before the analyzer was heated to the desired temperature and kept constant. The high temperature

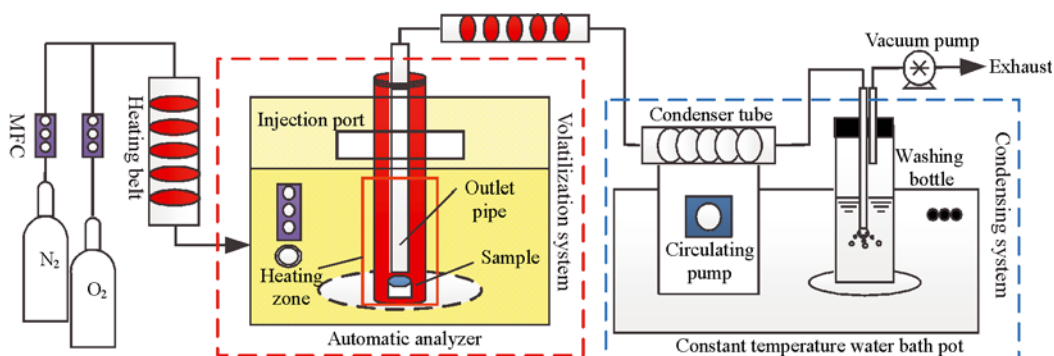


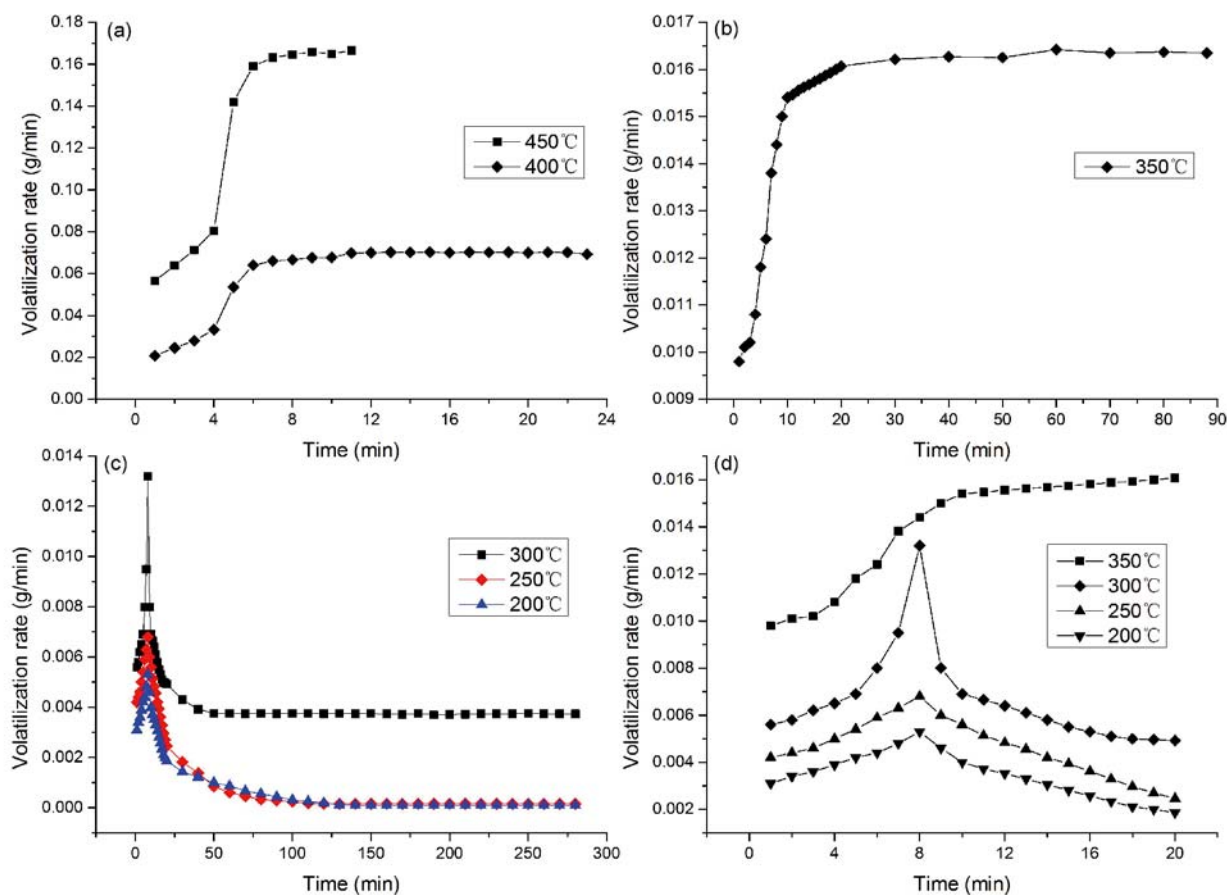
Figure 1. ABS volatilization and condensation experiment system

zone of the analyzer should be controlled at 200–450 °C, and the temperature interval was 50 °C. The sample tray was moved to the high temperature zone of the analyzer for sample volatilization experiments after the sample was placed in the sample tray through injection port. The sample quality was recorded according to the experimental requirements. In the condensing system, 300 ml ultrapure water was used in the washing bottle to absorb the vaporized gaseous product. At the end of the experiment, the condensation products in the condenser were washed with ultrapure water to the volume of 300 ml. Finally, the concentration of the absorbed product was measured.

ABS, AS volatilization rate is defined as the amount of change in ABS and AS mass per unit time expressed as  $\Delta v = \Delta m / \Delta t$ . Where  $v$  represents the volatilization rate;  $\Delta t$  represents the time interval between two consecutive weighings of the sample.  $\Delta m$  represents the mass change of the sample within the time interval  $\Delta t$ . The rate of volatilization of a certain  $\Delta t$  is indicated at the end of the time interval in Fig. 2.

**Table 1.** The equipment parameters

project	specifications	accuracy	measurement
fully automatic industrial analyzer	MAC-2000	$\pm 1$ °C	room temperature~1000 °C
ion chromatography	IC6000	$\pm 0.2\%$	0.1~1000 ppm
thermogravimetric analyzer	TGA4000	$\pm 0.1$ °C	room temperature~1200 °C
Scanning electron microscope	Hitachi S-4800	$\pm 2\%$	0.1 nm~100 $\mu$ m
ammonium ion concentration meter	Bante931	$\pm 2\%$	0.1~18000 ppm



**Figure 2.** ABS volatilization rate curve at different temperatures

## ABS Characterization

1) The surface morphology of ABS samples was measured by SEM.

2) The analytically pure ABS sample was dried in a vacuum drying oven at 50 °C for 1 h before repeatedly ground. Thermogravimetric analysis was performed on thermogravimetric analyzer. The nitrogen atmosphere is at a flow rate of 20 ml/min. The sample was heated at a temperature range of 50–800 °C, the rise rate was 10 °C/min. Finally, a TG curve, a differential curve DTG and a DSC curve reflecting the relationship between the percentage of weight loss of ABS and temperature were obtained.

## Equipment used in the experiment

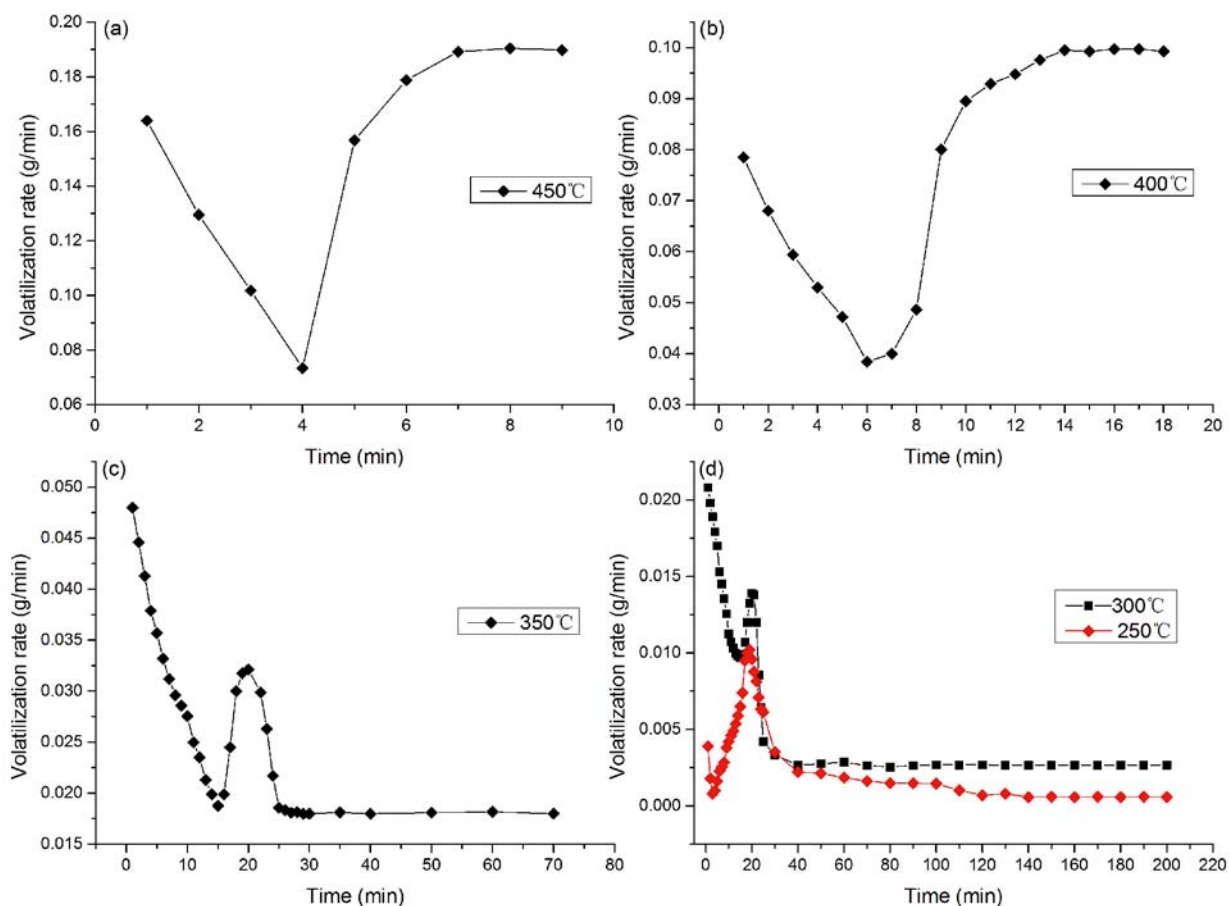
The equipment used in the experiment is shown in Table 1.

## RESULTS

Volatilization of ABS and AS at different temperatures

Firstly, 1.4 g pure ABS and AS samples were prepared separately. The volatilization experiment of ABS and AS





**Figure 3.** AS volatilization rate curve at different temperatures

was conducted at 200–450 °C to detect the volatilization rate. Results are shown in Fig. 2 and Fig. 3.

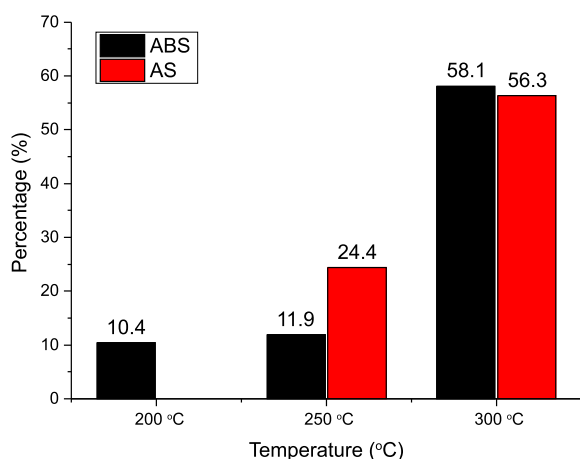
As can be seen from Fig. 2, the volatilization of ABS at 350–450 °C has a law that the volatilization rate first rises and then reaches the maximum volatilization rate, and finally remains stable. The higher the temperature, the shorter the time required for the volatilization rate to rise to maximum. The volatilization of ABS at 200–300 °C has a law that the volatilization rate first rises to a maximum value and then the volatilization rate decreases to a minimum value, and finally remains stable. When the temperature is 450 °C, 400 °C, 350 °C, ABS can be completely volatilized in 11 min, 23 min, 88 min. This finding proves that the decomposition temperature of ABS starts from around 200 °C. Compared with references 22 and 28, the initial decomposition temperature of ABS is reduced by about 150 °C to 200 °C. The average volatilization rate of ABS is 0.127 g/min, 0.058 g/min, 0.016 g/min. When the temperature is 300 °C, 250 °C, 200 °C, ABS cannot be completely volatilized within 280 min, the average volatilization rate of ABS is  $0.397 \times 10^{-2}$  g/min,  $0.644 \times 10^{-3}$  g/min,  $0.549 \times 10^{-4}$  g/min. As the temperature increases (at 50 °C intervals), the ABS volatilization rate shows an order of magnitude increase. It can be considered that the phase transition process of ABS from solid phase to liquid phase and the volatilization process of ABS occur in the rising stage of ABS volatilization rate. At high temperatures (above 300 °C), ABS volatilization may involve two processes, ABS volatilization and ABS decomposition, so in the high

temperature section, the ABS volatilization rate can be kept constant after rising to the highest point. At low temperature (below 300 °C), the decomposition reaction of ABS may not be complete. The ABS volatilization after ABS phase change and the first decomposition reaction of ABS lead to the ABS volatilization rate rising first to the maximum volatilization rate. Since the product after the first decomposition of ABS is no longer decomposed, only the ABS volatilization exists finally. Therefore, the volatilization rate of ABS begins to decrease, and after decreasing to a certain value, the volatilization rate of ABS keep constant. The volatilization of ABS at 300 °C may have the volatilization characteristics of both the high temperature section and the low temperature section.

As can be seen from Fig. 3, the volatilization rate of AS is slightly higher than the ABS volatilization rate at the same temperature. When the temperature is 450 °C, 400 °C, 350 °C, AS can be completely volatilized in 9 min, 18 min, 70 min, and the average volatilization rate of AS is 0.156 g/min, 0.078 g/min, 0.02 g/min. When the temperature is 300 °C, 250 °C, AS cannot be completely volatilized within 200 min, and the average volatilization rate of AS is  $0.394 \times 10^{-2}$  g/min,  $0.171 \times 10^{-2}$  g/min. It has been shown in the literature that the first step in the decomposition of AS at high temperature is deamination to form  $\text{ABS}^{30,31}$ , just as  $(\text{NH}_4)_2\text{SO}_4 \rightarrow \text{NH}_4\text{HSO}_4 + \text{NH}_3$ . This reaction is a good explanation for the tendency of the initial volatilization rate to decrease during AS volatilization. Then the ABS generated by the decomposition

of the AS continues to volatilize, and its volatilization process is consistent with that shown in Fig. 2.

The amount ratio of ABS and AS volatilization in the experiment for 200 min to the total volatilization at the corresponding temperature is shown in Fig. 4. It can be seen that the higher the volatilization temperature, the larger the amount of AS volatilization. Compared with the higher volatilization of ABS at 300 °C, the difference in the amount of ABS between 200 °C and 250 °C is not large. It can be considered that the decomposition reaction of ABS at 200 °C and 250 °C should be consistent. The reason why the ABS volatilization amount at 250 °C is slightly higher than the amount at 200 °C is that the higher the temperature, the more volatilization of the gas phase ABS.



**Figure 4.** Percentage of ABS/AS volatilization at different temperatures

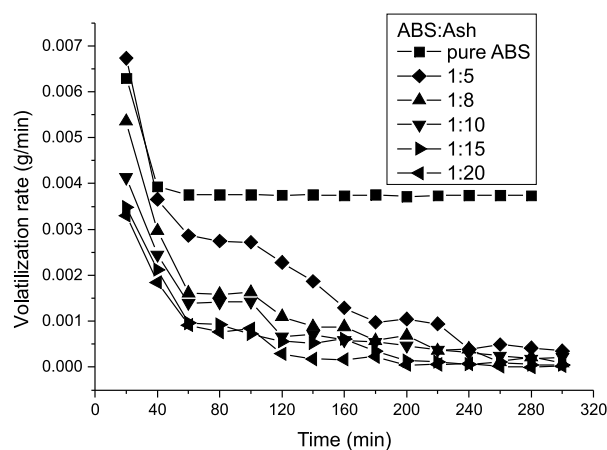
#### ABS volatilization at different ash content

The sample is prepared by mixing pure ABS and fly ash in a ratio without fly ash, 1:5, 1:8, 1:10, 1:15, 1:20 and the total mass of each sample was kept at 4.5 g. The volatilization experiment was carried out at 300 °C. The results are shown in Fig. 5. The experimental data have been deducted from the background value of the volatilization of the pure ash sample.

It can be seen from Fig. 5 that as the doping amount of fly ash increases, the volatilization rate of ABS sample decreases. This indicates that the volatile component of the ABS sample should be mainly ABS. Therefore, the higher ABS content in the sample, the faster volatilization rate. When the ratio of ABS to fly ash is 1:5, the volatilization rate in the first 20 min is slightly higher than that in pure ABS, probably because some substances in the fly ash promote the volatilization of ABS. When the ratio of ABS to fly ash is lower, that is, the amount of ash added is larger, ABS will be hindered by fly ash when volatilized, and thus the rate of ABS volatilization decreases.

#### Condensation after ABS volatilization

The condensing system consists of a condenser tube and a washing bottle, and the cooling temperatures of both components were controlled at 30 °C. It should be noted



**Figure 5.** Volatilization rate curve of ABS samples doped with different amounts of fly ash

that the sample volatilization degree of each experiment is not consistent. Therefore, the data corresponding to each temperature is not comparable. However, the condensation tendency under various temperature conditions and the migration of condensed products after volatilization can be qualitatively judged. The content of  $\text{SO}_4^{2-}$  in the condenser tube and the washing bottle were obtained by ion chromatography. According to the peak area of the  $\text{SO}_4^{2-}$  in each solution measured by ion chromatography, the  $\text{SO}_4^{2-}$  concentration in each solution was obtained. The results are shown in Table 2. The concentration of  $\text{NH}_4^+$  in each solution was measured by the ammonium ion concentration meter. The results are shown in Table 3.

From Table 2, The ratios of  $\text{SO}_4^{2-}$  concentrations in the condenser and the washing bottle at 200 °C, 250 °C, 300 °C, 350 °C, 400 °C and 450 °C are 2.55:1, 2.5:1, 1.96:1, 19.2:1, 23.57:1, 23.78:1, respectively. It is indicated that  $\text{SO}_4^{2-}$ , which was directly volatilized or condensed after decomposition by ABS, mostly transferred to the condenser tube, and a small part transferred to the washing bottle. And as the temperature increases, the proportion of  $\text{SO}_4^{2-}$  in the condenser increases. The  $\text{SO}_4^{2-}$  content in the condenser is related to the amount of  $\text{H}_2\text{O}$  that can be condensed at this location. When the temperature is lower than 300 °C, the concentration of  $\text{SO}_4^{2-}$  is low, indicating that only a small amount of substances (such as  $\text{SO}_2$ ,  $\text{H}_2\text{O}$ ) capable of generating  $\text{SO}_4^{2-}$  are generated in this temperature range. When the temperature rises to 350 °C and 400 °C, this ratio has a significantly increase to the beginning, in particular, the concentration of  $\text{SO}_4^{2-}$  in the condenser has an increase of 2–3 orders of magnitude. When continues to rise the temperature above 400 °C, the ratio does not change much, it indicates that a large amount of substances capable of producing  $\text{SO}_4^{2-}$  appear in the decomposition products of ABS at the temperature range of 300–400 °C.

It can be seen from Table 3 that as the temperature changes, the change of  $\text{NH}_4^+$  concentration in the condenser is similar to the change of  $\text{SO}_4^{2-}$  concentration, which indicates that a large amount of  $\text{NH}_4^+$  containing substances appear in the decomposition products of ABS

**Table 2.**  $\text{SO}_4^{2-}$  concentration in condensed products after ABS volatilization at different temperatures (unit: ppm)

Project	200 °C	250 °C	300 °C	350 °C	400 °C	450 °C
Condenser	0.729	1.115	2.98	230.5	1081.76	1112.09
washing bottle	0.286	0.442	1.517	12.64	45.89	46.76

**Table 3.**  $\text{NH}_4^+$  concentration in condensed products after ABS volatilization at different temperatures (unit: ppm)

project	200 °C	250 °C	300 °C	350 °C	400 °C	450 °C
Condenser	0.335	0.471	1.3	21	64	65
washing bottle	9	11	15	10	11	13

in the temperature range of 300–400 °C. The ratios of  $\text{NH}_4^+$  concentrations in the condenser to the washing bottle at 250 °C, 300 °C, 350 °C, 400 °C and 450 °C are 1:23.35, 1:11.54, 2.1:1, 5.82:1, 5:1, respectively, it indicates that when the concentration of  $\text{NH}_4^+$  in the condenser is low, that is, when the temperature is lower than 300 °C, the substance containing  $\text{NH}_4^+$  is collected by the washing bottle because the condensation tube contains little  $\text{H}_2\text{O}$ . When the temperature is higher than 300 °C, the substance containing  $\text{NH}_4^+$  is mainly collected by the condenser. It can be seen that 300 °C is an important node temperature for the change of ABS condensation product.

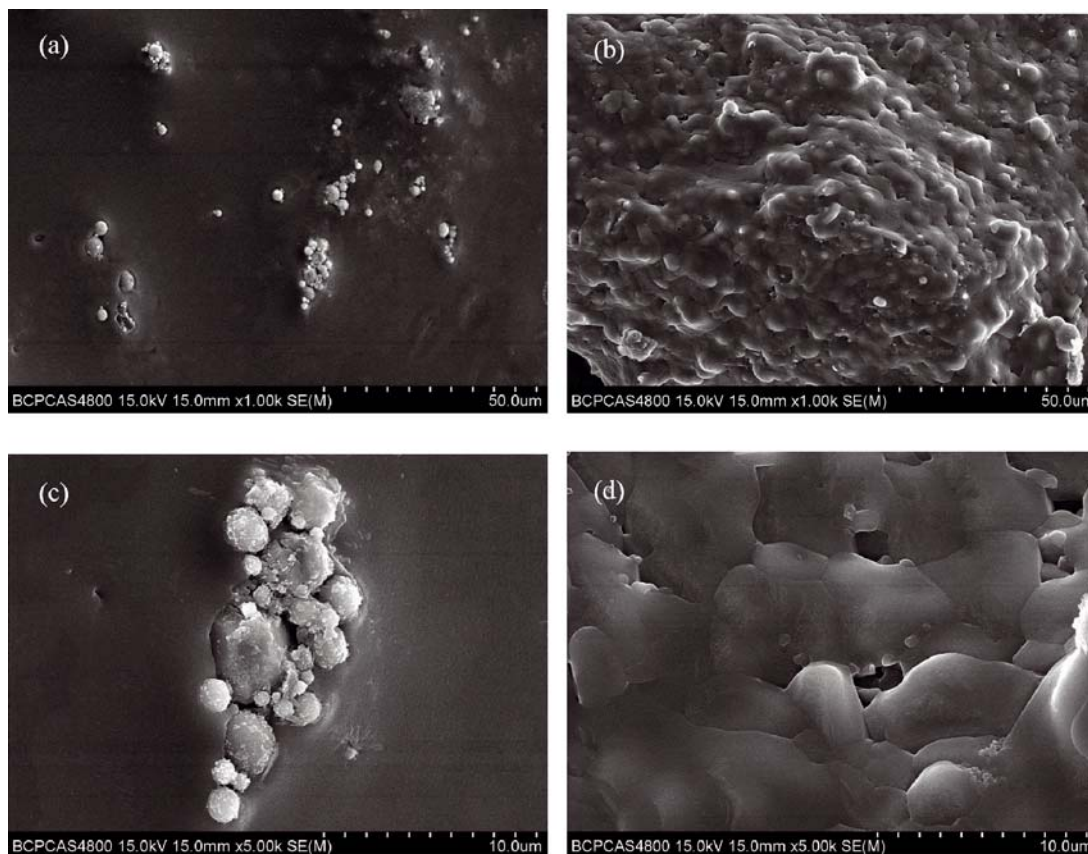
The ratios of  $\text{SO}_4^{2-}$  to  $\text{NH}_4^+$  in the condenser at 200 °C, 250 °C, 300 °C, 350 °C, 400 °C and 450 °C are 2.17:1, 2.44:1, 2.29:1, 10.95:1, 23.5:1, 23.6:1, respectively. The ratio of  $\text{SO}_4^{2-}$  to  $\text{NH}_4^+$  is slightly greater than 2:1 at lower temperatures of 250 °C to 300 °C, and the concentration of  $\text{SO}_4^{2-}$  is much greater than  $\text{NH}_4^+$  at higher temperatures; The ratios of  $\text{SO}_4^{2-}$  to  $\text{NH}_4^+$  in the washing bottle at 200 °C, 250 °C, 300 °C, 350 °C, 400 °C and 450 °C are 1:31.47, 1:24.89, 1:9.89, 1.26:1, 4.17:1, 3.59:1, respectively, which indicates that at lower temperatures, the concentration of  $\text{SO}_4^{2-}$  in the washing bottle is less than  $\text{NH}_4^+$ , and the  $\text{SO}_4^{2-}$  in the washing bottle is gradually higher than  $\text{NH}_4^+$  when the temperature is raised. Therefore, when the temperature is lower than 250 °C (include 250 °C), the product deposited in the condenser and wash bottle may be a small amount

of ABS and most of ABS is deposited in the condenser. When the temperature is higher than 300 °C, the condensation product in the condenser may be  $\text{H}_2\text{SO}_4$  and a small amount of AS, ABS. The substances condensed in the washing bottle are AS and  $\text{H}_2\text{SO}_4$ . The product deposited in the condenser at a temperature of 300 °C may be a small amount of ABS and  $\text{H}_2\text{SO}_4$ . The substance condensed in the washing bottle is a small amount of ammonia water and ABS.

### ANALYSIS OF ABS VOLATILIZATION PROCESS

The morphological characteristics of the ABS samples before and after volatilization at 300 °C for 280 minutes were compared and the results are shown in Fig. 7.

It can be seen from Fig. 6 that after the experiment at 300 °C, a significant melting change occurred on the surface of the ABS sample. Part of the fine particle packing structure and smooth external on the surface of the ABS sample showed a condensed sheet-like stacked form resulted by melting after the experiment. It indicates that ABS had a phase change of the solid phase to the liquid phase in the experiment. Combined with the volatilization rate curve and condensation product analysis of ABS at 300 °C, ABS has a gas phase volatilization and a decomposition reaction at this temperature. At this time, the sample contains ABS and products decomposed by ABS.



**Figure 6.** Scanning electron micrograph of the sample before and after ABS volatilization (a,c: ABS Before volatilization; b, d: ABS after volatilization at 300 °C for 280 min)



The TG and DTG curves of ABS are shown in Fig. 7. The DSC curve of ABS under the same conditions is shown in Fig. 8.

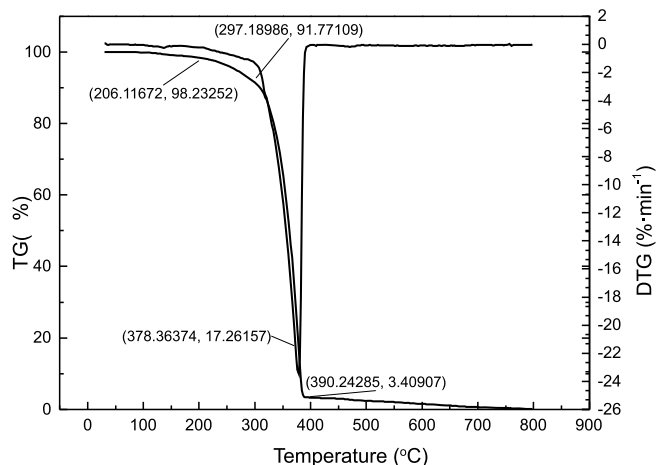


Figure 7. TG and DTG curves of ABS

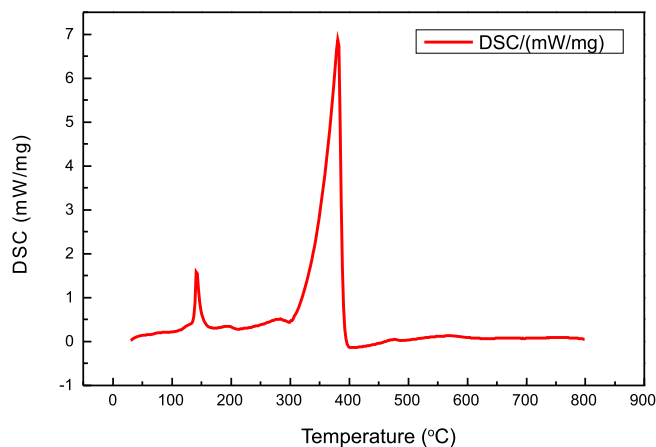


Figure 8. DSC curve of ABS

It can be seen from Fig. 7 and Fig. 8 that at about 140 °C, there is a distinct endothermic peak, but ABS weight loss is not obvious. At this time, ABS mainly undergoes a phase change from solid to liquid. The weight loss of ABS may be caused by slight volatilization of the sample. Combined with the DTG and DSC curves, the ABS decomposition process can be divided into two steps. In the first step, the volatilization rate at 206.12–297.19 °C is initially slower but enhances with increasing temperature. The weight loss percentage of the whole temperature range is 6.46%, and the average weight loss rate is  $6.7 \times 10^{-5}$  g/min. In the second step, ABS has a rapid decomposition at 297.19–390.24 °C. The weight loss percentage of the whole temperature range is 88.36%, and the average weight loss rate is  $1.03 \times 10^{-2}$  g/min. ABS has a maximum volatilization rate at 378.36 °C.

Since ABS is first liquefied at a higher temperature and then decomposed, when ABS is in the first stage and the second stage of decomposition, the products in the first stage of ABS and ABS are in a liquid state. Therefore, the decomposed gaseous product needs to overcome the liquid film resistance to precipitate from the gas-liquid interface. The physical diffusion coefficient of ABS decomposition products increases with increasing temperature. Therefore, the decomposition rate gradually increases as the temperature increases. At the same time,

when the temperature is at the junction of the temperature at the end of the first stage and the beginning of the second stage, the decomposition rate of ABS is accelerated, possibly because the decomposition reactions of the first stage and the second stage occur simultaneously. This also explains the change in the volatilization rate curve of ABS in Fig. 2. Incomplete weight loss after the second stage is caused by slight volatilization of ABS and other impurities contained in ABS.

The tubular resistance furnace is used for ABS high temperature volatilization place, the downstream pipeline is connected with flue gas analyzer, and 1L/min N<sub>2</sub> is used as carrier gas to detect the decomposition products of ABS at 400 °C and 450 °C. The result is shown in Fig. 9. Due to the lower temperature of the desiccant and gas line upstream of the flue gas analyzer, part of ABS decomposition products condensed and deposited in the upstream pipeline, so the data shown in Fig. 9 has a large error. The results in Fig. 9 are only used in this paper to clarify the qualitative analysis of the components of the ABS decomposition products.

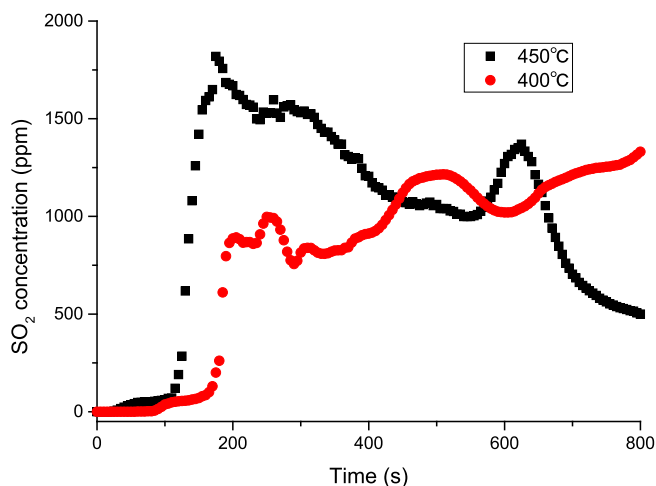


Figure 9. Concentration curve of SO<sub>2</sub> from ABS decomposition

It can be seen from Fig. 9 that ABS can be decomposed to produce SO<sub>2</sub> at 400 °C and 450 °C. ABS volatilization completely within 14 minutes. The change of the SO<sub>2</sub> concentration curve is basically the same as that in Figure 2, and the reason is shown in the analysis results of Figure 2. In combination with the ABS volatilization rate curve (Fig. 2) and the thermogravimetric results (Fig. 7, Fig. 8), we can speculate on the volatilization and decomposition process of ABS that ABS undergoes solid-liquid phase transition at around 140 °C. During the decomposition of ABS, the first step of ABS dehydration is to form (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>7</sub> at 206.12–297.19 °C. When the dehydration reaction of ABS occurs, the dehydration rate increases as the temperature increases. When the temperature rises around 300 °C, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>7</sub> begins to decompose, but the decomposition rate is low. The decomposition product (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>7</sub> of ABS decomposes at 297.19–390.24 °C. The decomposition rate of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>7</sub> increases with increasing temperature. The higher temperature, the shorter time it takes for (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>7</sub> to completely decompose. Volatilization of gas phase ABS occurs throughout the volatilization process. The two-step reaction of ABS decomposition can occur simultaneously at around 297 °C. The detailed

**Table 4.** ABS decomposition process and corresponding changes

Temperature (°C)	Weight loss percentage of TG (%)	chemical reaction	Theoretical weight loss percentage
206.2–297.2	6.56%	$2\text{NH}_4\text{HSO}_4 \rightarrow (\text{NH}_4)_2\text{S}_2\text{O}_7 + \text{H}_2\text{O}$	7.83%
297.2–390.2	88.36%	$3(\text{NH}_4)_2\text{S}_2\text{O}_7 \rightarrow 2\text{NH}_3 + 2\text{N}_2 + 6\text{SO}_2 + 9\text{H}_2\text{O}$	92.17%
390.2–560.5	3.41%	else	—

decomposition process of ABS is shown in Table 4. By comparing the thermogravimetric experiment and the theoretical calculation of the weight loss percentage, it can be confirmed that the presumed ABS decomposition reaction is correct. The weight loss percentage at 200 °C and 250 °C in Fig. 4 is slightly higher than the thermogravimetric and theoretical data, probably due to the volatilization of the gas phase ABS.

According to Table 2 and Table 4, when the temperature is lower than 300 °C, ABS undergoes dehydration reaction and slight volatilization. Most of the water and volatile ABS are deposited in the condenser. When the temperature is higher than 300 °C, ABS has completed the dehydration reaction, after which the reactant was  $(\text{NH}_4)_2\text{S}_2\text{O}_7$ . Most of the  $\text{SO}_2$  and water generated by  $(\text{NH}_4)_2\text{S}_2\text{O}_7$  decomposition are collected by the condenser. Part of  $\text{SO}_2$  and  $\text{NH}_3$  are collected by washing bottles. The presence of  $\text{O}_2$  in the atmosphere causes the condensation product to be  $\text{H}_2\text{SO}_4$ . When the temperature is 300 °C, the volatilization, dehydration and decomposition of  $(\text{NH}_4)_2\text{S}_2\text{O}_7$  occur simultaneously. The results are relatively consistent with the conclusions of references 29 and 30 and provide an accurate temperature range for the ABS decomposition reaction.

## CONCLUSIONS

(1) With the increase of temperature, the volatilization rate of ABS and AS increase. At the same temperature, the volatilization rate of AS is higher than that of ABS. Increasing the temperature at intervals of 50 °C, the ABS volatilization rate shows an increasing trend on the order of magnitude. When the ABS volatilization temperature is lower than 300 °C, the product recondenses after volatilization is mainly ABS. And the ABS volatilization temperature is higher than 300 °C, the product recondensed after volatilization are mainly AS, ABS,  $\text{H}_2\text{SO}_4$  and ammonia.

(2) At about 140 °C, ABS is converted from the solid phase to the liquid phase. The ABS volatilization and decomposition processes can be concluded as follow: 206.12–297.19 °C is the initial volatilization stage, 297.19–390.24 °C is the rapid volatilization stage. The volatilization rate reaches a maximum at 378.36 °C. The initial phase of ABS reaction is  $\text{NH}_4\text{HSO}_4 \rightarrow (\text{NH}_4)_2\text{S}_2\text{O}_7 + \text{H}_2\text{O}$ ; The rapid phase of ABS reaction probably is  $3(\text{NH}_4)_2\text{S}_2\text{O}_7 \rightarrow 2\text{NH}_3 + 2\text{N}_2 + 6\text{SO}_2 + 9\text{H}_2\text{O}$ . There is an intersection in the reaction temperature range between the initial volatilization phase and the rapid volatilization phase.

(3) To solve the problem of ABS deposition in the air preheater, the accurate determination of the volatilization temperature of ABS is the decisive condition for temperature regulation. In the future, we should focus on the actual working conditions of flue gas in coal-fired power plants. Under the condition of mixed deposition of ABS and fly ash, the volatilization and decomposition process of sediment should get much deeper studied.

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## DATA AVAILABILITY STATEMENT

All data generated or analyzed during this study are included in this published article (and its supplementary information files).

## LITERATURE CITED

- Wang, L.L., Yang, M., Wu, S.S., Huang, C.Y., Zhang, Q.W., Zhu, L., Yao, Y., He, J.L., Kong, F.H. & He, J. (2016). Difficulties and countermeasures of SCR denitrification system operation in ultra low emission situation. *THERMAL POWER GENERATION*. 45(12), 19–24. DOI: 10.19666/j.rlfid.201912286.
- Ma, S.C., Deng, Y., Wu, W.L., Zhang, L.N., Ma, J.X. & Zhang, X.N. (2016). Experimental research on characteristic of ABS formation in the process of SCR. *J. Chinese Soc. Power Engin.* 36(2), 143–150. DOI: 10.3969/j.issn.1674-7607.2016.02.010.
- Mark, A., Nan-Yu, T. & J.A., D. (2003). Density functional theory studies of mechanistic aspects of the SCR reaction on vanadium oxide catalysts. *J. Catal.* 213(2), 115–125. DOI: 10.1016/S0021-9517(02)00031-3.
- Ya, J.S., H, S., Yu, H.Z., Hong, M.F., Ya, P.Z. & Lin, J.Y. (2016). Formation and decomposition of  $\text{NH}_4\text{HSO}_4$  during selective catalytic reduction of NO with  $\text{NH}_3$  over  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  catalysts. *Fuel Proces. Technol.* 150, 141–147. DOI: 10.1016/j.fuproc.2016.05.016.
- Srivastava, R.K., Hall, R.E., Khan, S., Culligan, K. & Bruce, W.L. (2005). Nitrogen oxides emission control options for coal-fire delectric utility boiler. *J. Air & Waste Manag. Assoc.* 55, 1367–1388. DOI: 10.1080/10473289.2005.10464736.
- Wang, Y.C. & Tang, G.H. (2016). Prediction of sulfuric acid dew point temperature on heat transfer fin surface. *Appl. Thermal Engin.* 98, 492–501. DOI: 10.1016/j.applthermaleng.2015.12.078.
- Zhu, Y.Q., Zhou, W.H., Xia, C. & Hou, Q.C. (2022). Application and Development of Selective Catalytic Reduction Technology for Marine Low-Speed Diesel Engine: Trade-Off among High Sulfur Fuel, High Thermal Efficiency, and Low Pollution Emission. *Atmosphere*. 13, 1–21. DOI: 10.3390/atmos13050731.
- Zhou, C.Y., Zhang, L.N., Deng, Y. & Ma, S.C. (2016). Research progress on ammonium bisulfate formation and control in the process of selective catalytic reduction. *Environ. Progress & Sustainable Energy*. DOI: 10.1002/ep.12409.
- Muzio, L., Bogseth, S., Himes, R., Chien, Y.C. & Rankin, D.D. (2017). Ammonium bisulfate formation and reduced load SCR operation. *Fuel*. 206, 180–189. DOI: 10.1016/j.fuel.2017.05.081.
- Liu, K.W. & Chen, T.L. (2002). Studies on the thermal decomposition of ammonium sulfate. *Chem. Res. Applic.* 14(6), 737–738. DOI: 10.3969/j.issn.1004-1656.2002.06.038.
- Wang, L.M., Bu, Y.F., Li, D.C., Tang, C.L. & Che, D.F. (2019). Single and multi-objective optimizations of rotary regenerative air preheater for coal-fired power plant considering



the ammonium bisulfate deposition. *Internat. J. Thermal Sci.* 136, 52–59. DOI: 10.1016/j.ijthermalsci.2018.10.005.

12. Zhao, H., Zhang, J.K. & Zhang, K. (2018). Investigation of the deposition characteristics of ammonium bisulfate and fly ash blend using an on-line digital image technique: Effect of deposition surface temperature. *Fuel Proc. Technol.* 179, 359–368. DOI: 10.1016/j.fuproc.2018.07.030.

13. Luo, M., Zhao, L.L. & Li, S.Y. (2016). Numerical simulation of ash deposition with adhesion of  $\text{NH}_4\text{HSO}_4$  in an air preheater. *Chin. Soc. Power Eng.* 36, 883–888. DOI: 10.3969/j.issn.1674-7607.2016.11.005.

14. Chen, H., Pan, P.Y., Wang, Y.G. & Zhao, Q.X. (2016). Field study on the corrosion and ash deposition of low-temperature heating surface in a large-scale coal-fired power plant. *Fuel*. 208, 149–159. DOI: 10.1016/j.fuel.2017.06.120.

15. Wei, W., Sun, F.Z. & Ma, L. (2018). Effect of fine ash particles on formation mechanism of fouling covering heat exchangers in coal-fired power plants. *Appl. Thermal Engin.* 142, 269–277. DOI: 10.1016/j.applthermaleng.2018.06.086.

16. Chen, H., Pan, P.Y., Shao, H.S., Wang, Y.G. & Zhao, Q.X. (2017). Corrosion and viscous ash deposition of a rotary air preheater in a coal-fired power plant. *Appl. Thermal Engin.* 113, 373–385. DOI: 10.1016/j.applthermaleng.2016.10.160.

17. Bu, Y.F., Wang, L.M., Chen, X., Wei, X.Y., Deng, L. & Che, D.F. (2018). Numerical analysis of ABS deposition and corrosion on a rotary air preheater. *Appl. Thermal Engin.* 131, 669–677. DOI: 10.1016/j.applthermaleng.2017.11.082.

18. Cheng, M., Chen, Z., Liao, Q., Zhang, J., Ding, Y. & Zhu, X. (2019). Experimental research on the ash deposition characteristics of 3-D finned tube bundle. *Appl. Thermal Engin.* 153, 556–564. DOI: 10.1016/j.applthermaleng.2019.03.051.

19. Burke, J.M. & Johnson, K.L. (1982). Ammonium sulfate and bisulfate formation in air preheaters. *British Med. J.* 329(7463), 446.

20. Pan, L., Liu, Q.Y. & Zhenyu Liu. (2012). Behaviors of  $\text{NH}_4\text{HSO}_4$  in SCR of NO by  $\text{NH}_3$  over different cokes. *Chem. Engin. J.* (181–182), 169–173. DOI: 10.1016/j.cej.2011.11.051.

21. Menasha, J., Dunn-Rankin, D., Muzio, L. & Stallings, J. (2011). Ammonium bisulfate formation temperature in a bench-scale single-channel air preheater. *Fuel*. 90, 2445–2453. DOI: 10.1016/j.fuel.2011.03.006.

22. Zhu, Z.P., Niu, H.X., Liu, Z.Y. & Liu, S. (2000). Decomposition and Reactivity of  $\text{NH}_4\text{HSO}_4$  on  $\text{V}_2\text{O}_5/\text{AC}$  Catalysts Used

for NO Reduction with Ammonia. *J. Catal.* 195(2), 268–278. DOI: 10.1006/jcat.2000.2961.

23. Shu, H., Zhang, Y.H., Fan, H.M., Zhang, Y.P. & Yang, L. (2015). FT-IR study of formation and decomposition of ammonium bisulfates on surface of SCR catalyst for nitrogen removal. *CIESC Journal*. 66(11), 4460–4468. DOI: 10.11949/j.jssn.0438-1157.20150450.

24. Ma, S., Jin, X., Sun, Y. & Cui, J. (2010). The formation mechanism of ammonium bisulfate in SCR flue gas denitrification process and control thereof. *THERMAL POWER GENERATION*. 39(8), 12–17. DOI: 10.3969/j.issn.10022336.4.2010.08.012.

25. Ma, S., Guo, M., Song, H., Chen, G., Yang, J., Zang, B. & Li, D. (2014). Formation mechanism and influencing factors of ammonium bisulfate during the selective catalytic reduction process. *THERMAL POWER GENERATION*. 43(2), 75–78, 86. DOI: 10.3969/j.issn.1002-3364.2014.02.075.

26. Ma, S., Deng, Y., Wu, W. & Zhang, L. (2016). Reaction characteristic of by-product ammonium bisulfate from SCR denitrification and fly ash in air preheater. *Chinese J. Environ. Engin.* 10(11), 6563–6570. DOI: 10.12030/j.cjee.201507027.

27. Ma, S., Deng, Y., Wu, W., Tan, Y., Zhang, L., Chai, F., Sun, P. & Zhang, X. (2016). Corrosion Characteristics of Downstream Metal Material of Boiler System in Solution of By-product Ammonium Bisulfate from SCR Dinitrification. *J. Chinese Society for Corrosion and Protection*. 36(4), 335–342. DOI: 10.11902/1005.4537.2015.155.

28. Li, J. & Zhang, G. (1992). Investigation of the Kinetics and Mechanism of Decomposition of Ammonium Hydrogen Sulfate. *ACTA PHYSICO-CHIMICA SINICA*. 8(1), 123–127. DOI: 10.3866/PKU.WHXB19920122.

29. Raisaku, K. & Kohei, U. (1970). Mechanism, kinetics, and equilibrium of thermal decomposition of ammonium sulfate. *Ind. Eng. Chem. Process Des Develop.* 9(4), 489–494.

30. Fan, Y. & Cao, F. (2011). Thermal Decomposition Kinetics of Ammonium Sulfate. *J. Chem. Engin. Chin. Univ.* 25(2), 341–346. DOI: 10.3969/j.issn.1003-9015.2011.02.028.

31. Tang, H., Li, H., Yang, H., Lin, Z., Zhuang, K., Lu, Q. & Li, W. (2018). Research progress on the formation and decomposition mechanism of ammonium-sulfate salts in  $\text{NH}_3$ -SCR technology. *Chem. Ind. Engin. Progress*. 37(3), 822–831. DOI: 10.16085/j.issn.1000-6613.2017-0797.