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Research on prediction model of formation temperature of ammonium bisulfate in air preheater of coal-fired power plant

Kai Zhang [1], Fangming Xue [2], Zhiqiang Wang [1,*], Xingxing Cheng [1,*]

[1] School of Energy and Power Engineering, Shandong University, Jinan 250061, China
[2] Huadian Electric Power Research Institute Co., Ltd., Hangzhou 310030, China

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ABSTRACT

Ammonium bisulfate (ABS) is a viscous compound produced by the escape NH_3 in the NO reduction process and SO_3 in the flue gas at a certain temperature, which can cause the ash corrosion of the air preheater in coal-fired power plants. Therefore, it is essential to study the formation temperature of ABS to prevent the deposition of ABS in air preheaters. In this paper, the SO_3 reaction kinetic model is used to analyze the SO_3 generation process from coal combustion to the selective catalytic reduction (SCR) exit stage, and the kinetic model of NO reduction is used to analyze the NH_3 escape process. A prediction model for calculating the ABS formation temperature based on the S content in coal and NO reduction parameters of the SCR is proposed, solving the difficulty of measuring SO_3 concentration and NH_3 concentration in the previous calculation equation of ABS formation temperature. And the reliability of the model is verified by the actual data of the power plant. Then the influence of S content in coal, NH_3/NO_x molar ratio, different NO_x concentrations at SCR inlet, and NO removal efficiency on the formation temperature of ABS are analyzed.

1. Introduction

The selective catalytic reduction (SCR) technology is widely used in the treatment of power plant tail gas due to its high efficiency of NO_x removal [1,2]. The escaped NH_3 generated during the NO reduction process and the SO_3 in the flue gas will generate ammonium bisulfate (ABS), which sticks to the air preheater, causing the pressure difference of the air preheater to rise.

Saleem *et al.* [3] and Burke *et al.* [4] conducted a theoretical analysis on the formation temperature of ABS and found that the formation temperature of ABS is related to the concentration of reactants NH_3 and SO_3. Ammonium sulfate (AS) is the preferred product of thermodynamic analysis, and the resulting product is also affected by NH_3/SO_3 molar ratio. Saleem *et al.* and Burke *et al.* predict the formation temperature of ABS is relatively low, between 150–190 °C and 180–215 °C respectively. Matsuda *et al.* [5] first carried out the experimental research on the formation temperature of ABS. And the reactant concentration in this experiment deviated from the actual power plant reactant concentration, and the ABS formation temperature obtained was higher, between 260 °C and 330 °C. Wei *et al.* [6] used acid dew point measurement to measure the formation temperature of ABS. Menasha *et al.* [7] designed an experiment to simulate the formation of ABS with a single-channel air preheater and found that ABS was first appeared in the form of aerosol and then condensed on the wall. The formation temperatures of ABS predicted by Wei *et al.* and Menasha *et al.* are relatively close and are between those predicted by Saleem *et al.* and Matsuda *et al.* Although the formation temperature range of ABS obtained by different researchers is different under different experimental conditions, the formation temperature of ABS is positively correlated with the product of NH_3 and SO_3 concentrations.

According to many previous studies, the formation temperature of ABS is mainly measured by experimental methods, and it is mainly related to the concentration of escaped NH_3 and the concentration of SO_3 in the flue gas. Whether in the experiment or the actual operation of the power plant, it is difficult to accurately measure the concentration of escaped NH_3 and SO_3, which makes it difficult to measure the formation temperature of ABS. To solve the thorny problem, a kinetic model of SO_3 generated is built, which can get the concentration change of SO_3 from the boiler to the SCR outlet according to the sulfur content in coal. Then the kinetic model of NO reduction is built, and the NH_3 escape concentration can be obtained by some available parameters such as NO_x concentration at the inlet of the SCR and NO removal efficiency, *etc.* Finally, the experimental data

* Corresponding authors.
E-mail addresses: jackywzq@sdu.edu.cn (W. Zhiqiang), xcheng@sdu.edu.cn (C. Xingxing).

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of Menasha *et al*, which is the most precise experimental process of ABS formation temperature at home and abroad, is selected as an important basis, and the Clausius-Clapeyron relation is established to fit his experimental data to obtain the basic equation of ABS formation temperature, which is related to the concentration of SO_3 and NH_3. Substituting the SO_3 and NH_3 in the equations with easily available coal sulfur content and parameters of NO reduction, respectively, a model can be obtained that predicts the formation temperature of ABS in flue gas by parameters such as coal sulfur content and parameters of NO reduction. This model cleverly solves the problem of the difficulty of measuring SO_3 and NH_3 to obtain the formation temperature of ABS, and the detailed flow chart is shown in Fig. 1.

2. Model Development

Firstly, based on the kinetic theory of S-SO_2-SO_3 conversion, a model for obtaining the SO_3 concentration in flue gas according to the sulfur content in coal is established. Then, based on the kinetic theory of NO reduction in the process of SCR, a model for calculating the NH_3 escape concentration after SCR denitration is established based on the parameters of the NO reduction process. Finally, the established SO_3 generation model and NH_3 escape model are applied to the equation obtained by Menasha's experiment to explore the ABS formation temperature, and the prediction model of the formation temperature of ABS is obtained.

2.1. SO_2 produced by combustion of S in coal

There are more than 30 chemical elements in coal, and coal combustion is mainly a chemical reaction between combustible elements C, H and S in coal and oxygen in the air, and the flue gas produced mainly includes N_2, CO_2, SO_2, and water vapor. The SO_2 concentration in the flue gas is related to the theoretical air supply, excess air coefficient, and theoretical flue gas volume. Assuming that the air required for fuel combustion and flue gas are ideal gases, the volume of SO_2 produced by the combustion of 1 kg received base fuel is as shown in Eq. (1) and the SO_2 concentration in the flue gas is as shown in Eq. (2) [8].

$$V_{SO_2} = 0.7 \times \frac{S_{ar}}{100} \tag{1}$$

$$C_{SO_2} = \frac{V_{SO_2}}{V_y} \tag{2}$$

where, V_{SO_2} represents the volume of SO_2 produced by the combustion of 1 kg received base fuel, $m^3 \cdot kg^{-1}$; S_{ar} represents the sulfur content in coal, kg; C_{SO_2} represents the SO_2 concentration in the flue gas, $mg \cdot m^{-3}$; V_y represents the actual amount of gas, $m^3 \cdot kg^{-1}$; 0.7 represents 0.7 m^3 SO_3 produced by the complete combustion of 1 kg sulfur.

2.2. Generation model of SO_3

Almost all S contained in coal is converted into SO_2 after combustion [9], and part of SO_2 is converted into SO_3 by homogeneous and heterogeneous reactions. The homogeneous reaction is mainly the gas phase reaction in the furnace flame combustion, and the heterogeneous reaction is mainly the gas–solid catalytic reaction of fly ash and the SCR catalyst in the flue gas. The chemical reactions involved in the model are included in R(1) — R(4) [10].

R(1): $SO_2 + O + M = SO_3 + M$ (M is a third body substance)

R(2): $SO_2 + OH(+M) = HOSO_2+(M)$

R(3): $HOSO_2 + O_2 = SO_3 + HO_2$

R(4): $SO_2 + 1/2O_2 = SO_3$

2.2.1. Homogeneous formation of SO_3

Some scholars have analyzed the elementary reactions in the process of SO_3 homogeneous reaction under boiler combustion conditions by CHEMIKIN software, and the main reactions involved are R(1) — R(3) [11]. The H_2O and O_2 in the flue gas will increase the amount of OH and O and promote the formation of SO_3. The detailed elementary reactions involved are more complicated and difficult to use and calculate. To simplify the calculation process of homogeneous and heterogeneous reaction of SO_3, the oxidation process of SO_2 is simplified as R(4). The research of Graham *et al.* [12] found that the reaction order of SO_2 in the R(4) is 1, and the reaction order of O_2 is 0.5. Therefore, the reaction rate Eqs. (3) and (4) of SO_3 formation can be obtained based on the kinetics of the chemical reaction and the conversion rate of SO_3 in the process of SO_2 oxidation in the furnace is shown in Eq. (5).

$$R_{f1} = K_1 \times C_{SO_2} \times C_{O_2}^{0.5} \tag{3}$$

$$K_1 = A_1 \times \exp(-E_{a1}/RT) \tag{4}$$

$$\eta = \frac{C_{SO_3}}{C_{SO_2}} \times 100\% \tag{5}$$

where, A_1 represents the pre-exponential factor, $(m^3 \cdot mg^{-1})^{0.5} \cdot s^{-1}$; E_{a1} represents the activation energy, $kJ \cdot mol^{-1}$; R represents the gas constant, 8.3145 $J \cdot mol^{-1} \cdot K^{-1}$; T represents the absolute temperature, K; C_{SO_2} and C_{O_2} represent the mass concentration of SO_2 and O_2, $mg \cdot m^{-3}$; C_{SO_3} represent the mass concentration of SO_3, $mg \cdot m^{-3}$.

Studies [13,14] show that the homogeneous oxidation rate of SO_2 decreases when the temperature is lower than 900 °C . Liu and Fleig *et al.* [15,16] studied the relationship between SO_3 conversion rate and temperature and found that the reaction rate increased with the increase of temperature when the temperature was between 800 and 1100 °C, and decreased when the temperature was higher than 1100 °C. This is because R(2) and R(3) play a major role in the formation of SO_3 at 800 °C — 1100 °C. With the increase of temperature, the OH content produced by the decomposition of H_2O increases, which promotes the positive reaction of R(2), and then promotes the formation of SO_3 in R(3). When the temperature is higher than 1100 °C, the main effect on the formation of SO_3 is R(1). When the temperature is higher, the decomposition of $HOSO_2$ occurs, reducing the SO_3 generated in R(2) and R (3), and the decomposition reaction of SO_3 is accelerated.

2.2.2. Formation of SO_3 catalyzed by fly ash

The flue gas fly ash contains SiO_2, Al_3O_4, Fe_2O_3, and other compounds, which have a certain catalytic effect on the SO_2 contained in the flue gas and Fe_2O_3 has a more obvious catalytic effect on SO_2. Kim *et al.* [17] studied the catalytic reaction mechanism of fly ash and found that the reaction order of SO_2 is 1, and the reaction order of O_2 is 0.5. The reaction rate equation of SO_2 catalytic oxidation is proposed as follows:

$$R_{f2} = K_2 \times C_{SO_2} \times C_{O_2}^{0.5} \tag{6}$$

$$K_2 = A_2 \times \exp(-E_{a2}/RT) \tag{7}$$

Xiao *et al.* [18] studied the fly ash formed at different furnace temperatures and found that the fly ash in the high temperature furnace (above 1500 °C) contains complex iron oxides with more oxygen vacancies, which has a more obvious catalytic effect on SO_2 than Fe_2O_3. The catalytic effect of fly ash containing composite

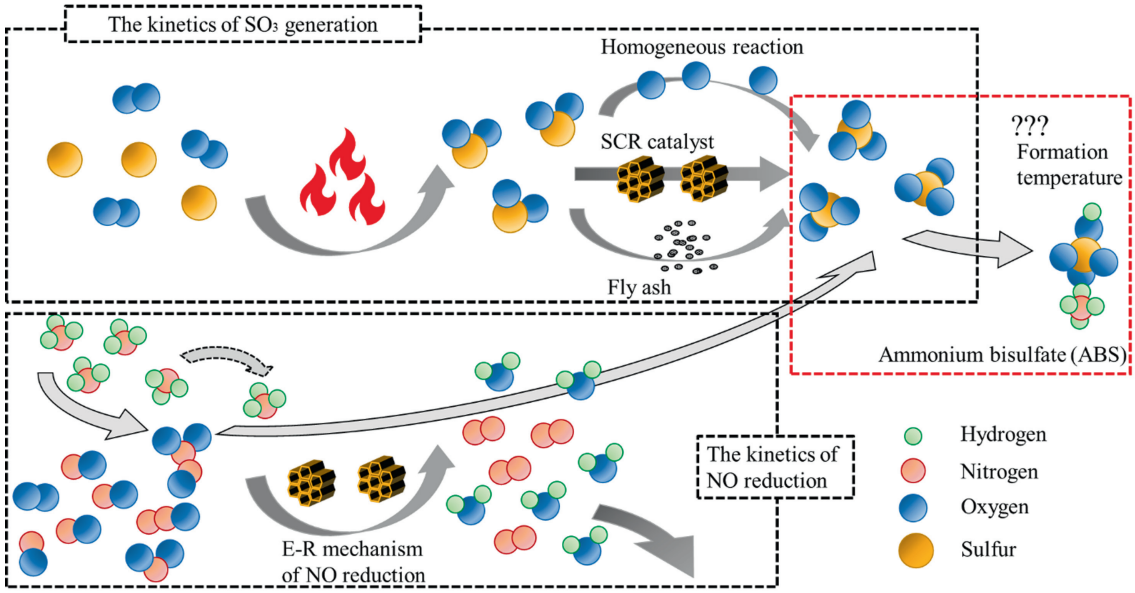

Fig. 1. Flow chart of the ABS formation temperature model.

iron oxide on SO_2 first increases and then decreases with the increase of temperature and the catalytic effect is most obvious at 900 °C, which may be related to the participation of other substances such as CaO contained in fly ash in chemical reactions. Therefore, the reaction rate constant K_2 in Eq. (6) needs to be discussed in different temperature ranges.

2.2.3. Formation of SO_3 catalyzed by catalyst during NO reduction

In the SCR process, V_2O_5-WO_3/TiO_2 is the most commonly used catalyst, containing Ti, W, V, and other elements, among which V_2O_5 has the most significant catalytic effect on SO_2. Svachula *et al.* [19] systematically studied the effects of experimental operating conditions, catalyst design parameters, and gas composition (O_2, SO_2, H_2O, NO_x and NH_3 concentration) on the catalytic oxidation of SO_2 to SO_3 on honeycomb commercial catalysts. Combined with the catalytic reaction mechanism of SO_2, a kinetic model of SO_2 catalytic oxidation reaction is proposed [20]:

$$R_{f\_2}=\frac{k_1\cdot C_{SO_2}\cdot C_{SO_3}\cdot(1+b\cdot C_{NO})}{1+k_2\cdot C_{SO_3}+k_3\cdot C_{SO_2}\cdot C_{SO_3}+k_4\cdot C_{SO_3}\cdot C_{H_2O}+k_5\cdot C_{NH_3}\cdot C_{SO_3}+k_6\cdot C_{SO_2}\cdot\frac{C_{SO_3}}{\sqrt{C_{O_2}}}} \tag{8}$$

where, C_{SO_2}, C_{SO_3}, C_{NO}, C_{H_2O}, C_{NH_3}, C_{O_2} respectively represent the molar concentration of SO_2, SO_3, NO, H_2O, NH_3, O_2 in the flue gas, mol·cm^{-3}; k_1, k_2, k_3, k_4, k_5, k_6 and b respectively represent the influence coefficients of different substances.

The kinetic equation can explain the following phenomena in related experimental studies [20]: When the SO_2 concentration is low, the SO_2 reaction order is about 1, but with the increase of SO_2 concentration, the reaction order of SO_2 decreases; When the concentration of O_2 is high, the effect on the catalytic reaction of SO_2 is almost zero; H_2O and NH_3 have a certain promotion effect; NO has a certain promotion effect on the catalytic oxidation of SO_2.

2.3. NH_3 escape model

NH_3 is one of the important reactants of ABS. Based on SCR reaction kinetics, this section combines SCR reactor performance index reactor potential, the generation of escaped NH_3 is explored [21,22]. Relevant studies [23] have shown that the E-R mechanism is suitable for reactions above 200 ℃, and the L-H mechanism is suitable for reactions below 200 °C. The temperature range of NO reduction is generally 300— 400 °C in the SCR, so the E-R mechanism is dominant. Therefore, the reaction kinetics of NO reduction is built based on the E-R mechanism [24,25], such as Eqs. (9)–(11). Combined with the reaction rate of NO reduction and the time of flue gas passes through the SCR catalyst, the NO_x concentration at the outlet of the SCR and its removal efficiency can be obtained as Eq. (12).

$$R_{NO}=K_3\times C_{NO}\times\frac{aC_{NH_3}}{1+aC_{NH_3}} \tag{9}$$

$$K_3=A_3\times\exp(-E_1/RT) \tag{10}$$

$$a=a_0\times\exp(-E_2/RT) \tag{11}$$

$$\eta=\frac{C_{NO_xin}-C_{NO_xout}}{C_{NO_xin}}\times 100\% \tag{12}$$

where, R_{NO} represents the reaction rate of NO, mol·m^{-3}·s^{-1}; C_{NO} and C_{NH_3} represent the molar concentration of NO and NH_3, mol·m^{-3}; a represents the adsorption rate constant of NH_3, s^{-1}; η represents the NO removal efficiency, %; C_{NO_xin} and C_{NO_xout} respectively represent the NO inlet and outlet concentration of the SCR reactor, mg·m^{-3}.

After conducting a large number of experiments and field tests, Song *et al.* proposed the potential P of the SCR reactor to measure the performance of the SCR catalyst under actual flue gas conditions [21]. The relationship between reactor potential and NO removal efficiency, NO_x concentration, NH_3/NO_x molar ratio, and NH_3 escape concentration is as follows Eqs. (13) and (14). The Eq. (15) of NH_3 escape concentration can be obtained by combining Eqs. (9)–(14).

$$P=0.5\times\ln\left[\frac{M_R}{(M_R-\eta)\times(1-\eta)}\right] \tag{13}$$

$$M_R=\frac{\eta}{100}+2.7\times\frac{C_{NH_3}}{C_{NO_xin}} \tag{14}$$

$$C_{NH_3} = \frac{\eta}{(1-\eta)\times \exp(2\times P)-1}\times \frac{C_{NO_x in}}{1.765} \quad (15)$$

where, P represents the potential of the reactor; M_R represents the molar ratio of NH_3/NO_x; η represents the NO removal efficiency; C_{NH_3} represents the concentration of escape NH_3, mg·m^{-3}; $C_{NO_x in}$ represents the NO_x concentration at the SCR inlet, mg·m^{-3}.

2.4. Prediction model of ABS formation temperature

Comparing with several existing experiments about ABS formation temperature, it is found that Menasha *et al*'s experimental process is more precise and the physical model was established to simulate the single-channel air preheater to study the formation temperature of ABS. The advantages of this experiment are outstanding, and the measurement accuracy is extremely high and its innovation of this experiment lies in not only the visual observation and electrode measurement of generation of ABS, but also the design of a control experiment without thermocouple and electrode interference to avoid the influence of thermocouple and electrode, which is not found in other studies about formation temperature of ABS. In addition, the NH_3 and SO_3 concentrations of the typical SCR outlet selected in this experiment are also more in line with the actual process, and the actual operating conditions of the air preheater are simulated as accurately as possible in every detail. The experimental data show that the formation temperature of ABS is related to the concentration of reactants. The higher the concentration product of reactants, the higher the formation temperature of ABS. There is two equilibrium in the reaction process of ABS formation: the first is the chemical reaction equilibrium in which NH_3 reacts with SO_3 (or H_2SO_4) to form gas phase ABS, and the second is the condensation equilibrium in which gas phase ABS condenses into liquid ABS when it is cold, as follows R(5):

$$NH_3(g) + H_2SO_4(g) \underset{\text{balance}}{\overset{\text{Chemical reaction}}{\rightleftharpoons}} NH_4HSO_4(g) \underset{\text{balance}}{\overset{\text{Condensation}}{\rightleftharpoons}} NH_4HSO_4(l)$$

The relationship between temperature and pressure in the process of ABS condensation equilibrium can be expressed by the Clausius–Clapeyron relation. Due to technical reasons, it is difficult to measure the partial pressure of ABS. Because the concentration of the reactant is related to the partial pressure of the reactant, the concentration product of NH_3 and SO_3 is used to represent the partial pressure of ABS. Therefore, the concentration of ABS can be expressed as the relationship between the NH_3 and SO_3 concentration product and the temperature, as shown in Fig. 2.

According to the Clausius–Clapeyron relation, the relationship between NH_3 concentration, SO_3 concentration, and the formation temperature of ABS is obtained as Eq. (16). Combined with Eqs. (3), (6), (8), (15), and (16), the prediction model of ABS formation temperature is obtained as Eqs. (17)–(19).

$$[NH_3]\cdot[SO_3] = 7.962\times 10^{12}\times \exp(-190319/RT) \quad (16)$$

$$T_{IFT} = \frac{22.89}{20.804 - \ln\left(C_{NH_3}\cdot C_{SO_3}/10^{12}\right)}\times 1000 - 273.15 \quad (17)$$

$$C_{NH_3} = \frac{\eta}{(1-\eta)\times \exp(2\times P)-1}\times \frac{C_{NO_x in}}{1.765} \quad (18)$$

$$C_{SO_3} = C_{SO_3 f1} + C_{SO_3 f2} + C_{SO_3 f3} \quad (19)$$

where, $[NH_3]\cdot[SO_3]$ represents the concentration product of NH_3 and SO_3, mg^2·m^{-6}; R represents gas constant; T represents ABS formation temperature, K; T_{IFT} represents the ABS formation temperature, ℃; C_{NH_3} represents the escape concentration of NH_3, mg·m^{-3}; C_{SO_3} represents the SO_3 concentration at the inlet of the air preheater, mg·m^{-3}; $C_{SO_3 f1}$, $C_{SO_3 f2}$ and $C_{SO_3 f3}$ represent SO_3 produced by the homogeneous reaction, SO_3 produced by fly ash catalysis, and SO_3 produced by SCR catalyst respectively, mg·m^{-3}.

3. Results and Discussion

The prediction model of ABS formation temperature established in Section 2 is based on the coupling of the SO_3 prediction model and the NH_3 escape model. Subsequently, the SO_3 model and NH_3 escape model are verified by the actual measurement data of the power plant, and then the correctness of the formation temperature prediction model of ABS is indirectly verified. Then, the effects of S content, NH_3/NO_x molar ratio, NO_x concentration at different SCR inlet, and different NO removal efficiency on the formation temperature of ABS are analyzed.

3.1. Model validation

To verify the correctness of the SO_3 prediction model and the NH_3 escape model built in this paper, firstly, the test data of more than 40 units of the power plant are used to analyze, and the results show that the potential of the reactor decreases with the increase of operation time of units, but the degradation trend slows down as shown in Fig. 3, The reactor potential degradation Eq. (20) is obtained by fitting its data. The potential of the reactor increases with the decrease of unit operating load rate, as shown in Fig. 4. Based on the field test data, the relationship between the potential P_0 of the reactor and the operating load rate of the unit is as shown in Eq. (21).

$$\frac{P}{P_0} = \exp\left(-\frac{t}{118000}\right) \quad (20)$$

$$P_0 = -0.534\times L + 3.67 \quad (21)$$

where, t represents the cumulative operating time, h; P_0 represents the reactor potential at a fixed unit operating load rate; L represents unit operating load rate, %.

Under the quality parameters of as-received coal as shown in Table 1, the amount of SO_3 generated by the homogeneous reaction of SO_2, fly ash catalysis, and the catalytic oxidation of V_2O_5 in the SCR catalyst is calculated, and the parameters used in the model calculation are shown in Table 2 and Table 3. The amount of SO_3

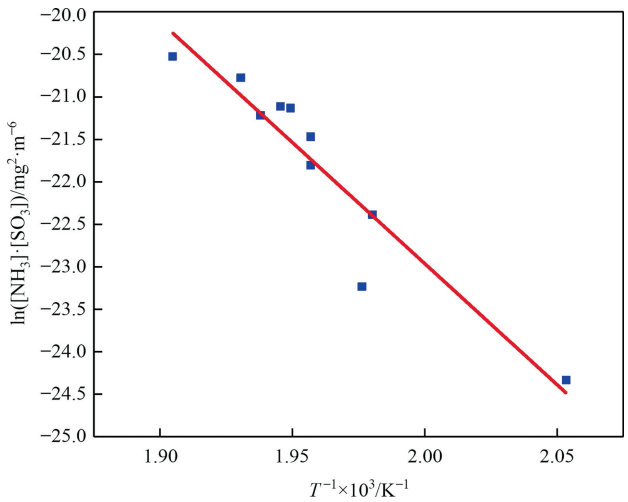

Fig. 2. Experimental data fitting of Menasha *et al.* [7].

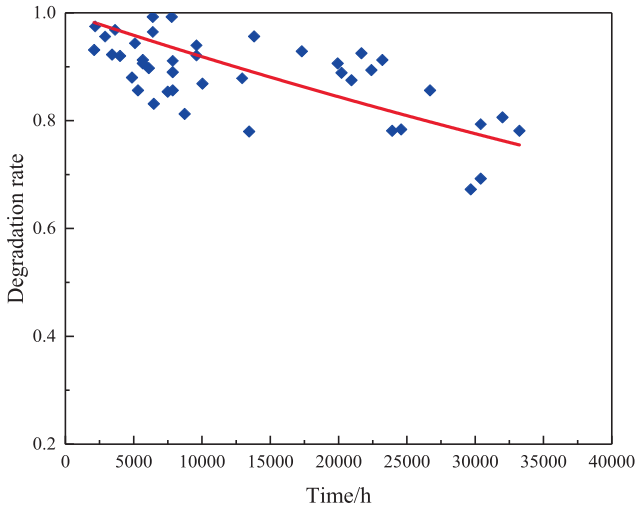

Fig. 3. Derioration trend of reactor potential over time.

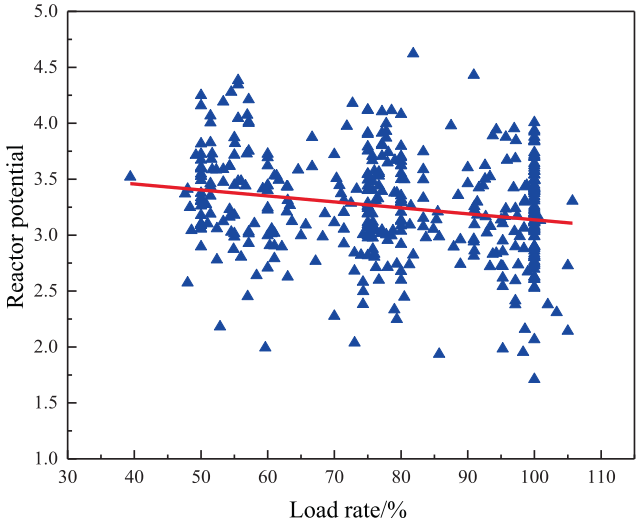

Fig. 4. The relationship between reactor potential and load rate.

generated in the three ways as shown in Fig. 5. Among them, the amount of SO_3 generated by the catalytic oxidation of V_2O_5 is the largest, which is 56.46 mg·m^{-3}; the second is generated by the homogeneous phase, which is 31.9 mg·m^{-3}; the amount of SO_3 generated by fly ash is the least, which is 6.1 mg·m^{-3}, of which the proportion of SO_3 generated by the SCR catalyst accounts for the largest, which is 60%. Therefore, reducing catalytic rate of the SO_2 in the SCR catalyst is the key to reducing the SO_3 in the flue gas.

It can be seen from Fig. 6 that the value predicted of SO_3 and the mean value measured at the SCR inlet of the power plant are 38 mg·m^{-3} and 36.36 mg·m^{-3}, respectively, with a relative error of 4.32%. the value predicted of SO_3 and the mean value measured at the exit of SCR are 94.46 mg·m^{-3} and 83.34 mg·m^{-3}, respectively, with a relative error of 11.77%. The predicted value of NH_3 escape is 2.15 mg·m^{-3}, the actual measured average value is 2.39 mg·m^{-3}, and the relative error is 10.04%. The predicted value of SO_3 is consistent with the actual value at the SCR inlet, the deviation of SO_3 concentration is slightly larger at the SCR outlet, and the predicted value of SO_3 concentration is in good agreement with the actual value as a whole. Similarly, the prediction model of NH_3 escape is more accurate, as shown in Fig. 7. The model has high accuracy and good universality and the prediction errors of SO_3 and NH_3 are within the acceptable range The ABS prediction model is a coupling of the SO_3 generation model and the NH_3 escape model, which indirectly proves the accuracy of the ABS prediction model.

3.2. The effect of S in coal on the formation temperature of ABS

Fig. 8 shows the effect of different sulfur content in coal on the formation temperature of ABS. As the S content in coal increases, the SO_3 content in the flue gas increases almost linearly, while the escaped NH_3 volume hardly changes, and the formation temperature of ABS increases, but the growth rate slows down. When the concentration of NH_3 in flue gas is 3.9 mg·m^{-3} and the content of S in the coal changes from 0.1% to 3%, the formation temperature of ABS increases from 209 °C to 243.6 °C, which increases by 34.6 °C. Especially when the S content is within 1%, the formation temperature of ABS increases rapidly with the increase of S content.

With the increase of sulfur content in coal, the concentration product of SO_3 and NH_3 increases, which makes the formation temperature of ABS increase. To reduce the ABS formation temperature, the power plant burns low-sulfur coal as much as possible so that ABS is deposited as much as possible on the cold end of the air preheater instead of the middle section, so that the air preheater can use soot blowing and hot air circulation to reduce the deposited ABS. When the S content in the coal exceeds 2%, the temperature of ABS formation changes little with the increase of the content of S in the coal.

3.3. Effect of NH_3/NO_x molar ratio on the temperature of ABS formation

To study the influence of NH_3/NO_x single factor on ABS formation temperature, NO reduction efficiency is fixed at 90%. Fig. 9 shows the effect of different NH_3/NO_x molar ratios on the formation temperature of ABS. It can be seen from Fig. 9 that with the increase of NH_3/NO_x molar ratio from 0.7 to 1.2, the concentration of escaped NH_3 increased from 3.18 mg·m^{-3} to 4.79 mg·m^{-3}, with an increase of 50.6%. While the concentration of SO_3 gradually decreased from 85.29 mg·m^{-3} to 64.06 mg·m^{-3}, with a decrease of 24.9%; and the formation temperature of ABS changed little, only increased by 1.4 °C. The concentration of NH_3 in the flue gas increases but SO_3 decreases and the concentration product of NH_3 and SO_3 has little change, so the formation temperature of ABS has little change.

The increase of NH_3/NO_x molar ratio will seriously increase the concentration of escape NH_3. The main reason is that the ideal ratio of NH_3 to NO reaction is 1:1. When NH_3/NO_x is excessively increased, the amount of NH_3 that is not involved in the reaction in the flue gas is increased severely, resulting in serious NH_3 escaping. On the contrary, the SO_3 concentration in the flue gas decreases, because the escape NH_3 increased with the increase of NH_3/NO_x during NO reduction, which inhibits the conversion of SO_2 to SO_3, thereby reducing the concentration of SO_3, which is consistent with the results of Svachula *et al* [19]. In the actual process, adding ammonia injection grids and baffles in the SCR flue to reduce the unevenness of the local NH_3/NO_x molar ratio can reduce the escape of NH_3, thereby reducing the formation temperature of ABS.

3.4. The effect of different NO_x inlet concentrations on the formation temperature of ABS

It can be seen from Fig. 10 that with the increase of the NO_x concentration at the SCR inlet the ABS formation temperature gradually increases, which is consistent with the research results of Si *et al* [26]. The main reason is that when the rate of NH_3/NO_x is fixed at 0.908, the concentration of escape NH_3 increases with the increase of NO_x concentration at the SCR inlet, thereby reducing the SO_3 concentration. Generally speaking, the formation tempera-

Table 1
Elemental analysis of coal samples (%)

C_{ar}	H_{ar}	O_{ar}	N_{ar}	S_{ar}	A_{ar}	M_{ar}
52.23	3.32	2.41	1.04	1.66	32	7

Table 2
Kinetic parameters for reaction mentioned: part I

Reaction	Temperature/ C°	Activation energy/ kJ·mol^{-1}		Pre-exp factor/ m^3·mg$^{-0.5}$·s^{-1}	
SO_3 homogeneous reaction	800–1100	E_{a1}	15.2	A_1	5.433×10^{-5}
	>1100		−56		1.078×10^{-7}
SO_3 formation catalyzed by fly ash	600–900	E_{a2}	22.33	A_2	2.599×10^{-5}
	>900		−11.71		6.707×10^{-7}
NO reduction reaction [24,25]	-	E_1	60	A_3	1×10^6
		E_2	−243	a_0	2.68×10^{-17}

Table 3
Kinetic parameters for reaction mentioned: part II

Reaction	Influence coefficient		Unit
SCR catalytic SO_3 formation reaction [19]	k_1	$(7.97 \pm 1.44) \times 10^9$	cm^3·mol^{-1}·s
	k_2	$(5.36 \pm 2.09) \times 10^8$	cm^3·mol^{-1}
	k_3	$(2.06 \pm 0.33) \times 10^{18}$	cm^6·mol^{-2}
	k_4	$(9.39 \pm 4.14) \times 10^{15}$	cm^6·mol^{-2}
	k_5	$(4.28 \pm 1.14) \times 10^{19}$	cm^6·mol^{-2}
	k_6	$(1.14 \pm 0.81) \times 10^{14}$	cm$^{4.5}$·mol^{-1}
	b	$(1.71 \pm 0.51) \times 10^7$	cm^3·mol^{-1}

ture of ABS increases with the increase of the concentration product of NH_3 and SO_3. With the increase of the NO_x concentration at the SCR inlet, the NO removal efficiency decreases, resulting in an increase of the amount of escaped NH_3; The reason for the decrease of SO_3 concentration may be that excessive NH_3 occupies more V^{+5} vacancies, which inhibits the oxidation process of SO_2 on V_2O_5.

Therefore, the rational use of technologies such as low-nitrogen combustion in power plants not only reduces the concentration of NO_x emissions but also helps reduce the formation temperature of ABS, thereby reducing the condensation of ABS in the middle temperature section of the air preheater.

3.5. The effect of NO removal efficiency on ABS formation temperature

To study the effect of NO removal efficiency on the formation temperature of ABS, the molar ratio of NH_3/NO_x is fixed as 1. The influence of different NO removal efficiency on the formation temperature of ABS can be seen in Fig. 11. With the increase of no removal efficiency, the formation temperature of ABS increases gradually, and the growth rate increases, while the SO_3 concentration in the flue gas hardly changes, but the concentration of NH_3 escape increases gradually. Especially when the NO removal efficiency exceeds 90%, if the NO removal efficiency continues to increase, the concentration of NH_3 escape will increase rapidly, and the formation temperature of ABS will increase rapidly, which causes ABS to be produced at a higher temperature, causing more serious clogging and corrosion problems to the SCR catalyst and air preheater.

The interaction between NH_3/NO_x molar ratio and NO removal efficiency can be seen in Fig. 12. With the increase of NH_3/NO_x molar ratio, the NO removal efficiency increases rapidly at first, but when the NH_3/NO_x molar ratio exceeds 0.9, the NO removal efficiency increases very little with the increase of NH_3/NO_x molar ratio, but the concentration of escape NH_3 increases very fast. The synergistic effect between NH_3/NO_x molar ratio and no removal efficiency on ABS formation temperature is shown in Fig. 13. When NH_3/NO_x molar ratio exceeds 0.9, if the NH_3/NO_x molar ratio continues to increase, the ABS formation temperature will increase rapidly. The comprehensive effect between NH_3/NO_x molar ratio and NO removal efficiency on the formation temperature of ABS is shown in Fig. 13. When NH_3/NO_x molar ratio exceeds 0.9, if the NH_3/NO_x molar ratio continues to increase, the formation temperature of ABS will increase rapidly. Therefore, to reduce the formation temperature of ABS, it is necessary to rationally balance the relationship between the NH_3/NO_x molar ratio and the NO removal efficiency, and try to control the NH_3/NO_x molar ratio at about 0.9, which can ensure the higher NO removal efficiency at 85%–90%, and control the lower concentration of escaped NH_3.

4. Conclusions

In this study, a prediction model of ABS formation temperature in air preheater of the coal-fired power plant was established by

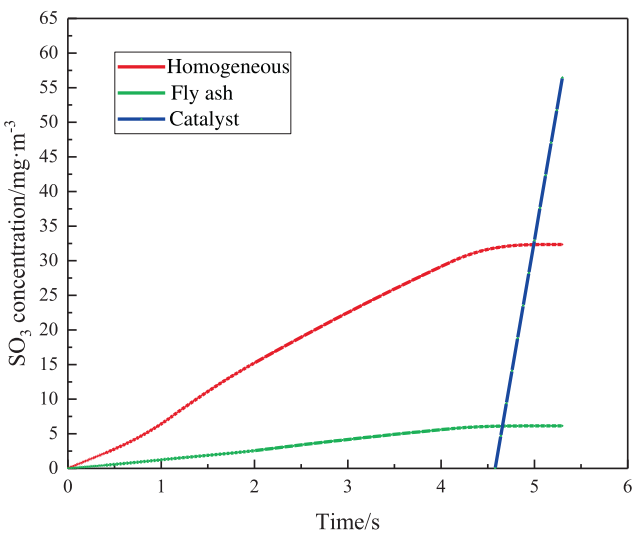

Fig. 5. The production of different forms of SO_3 in flue gas.

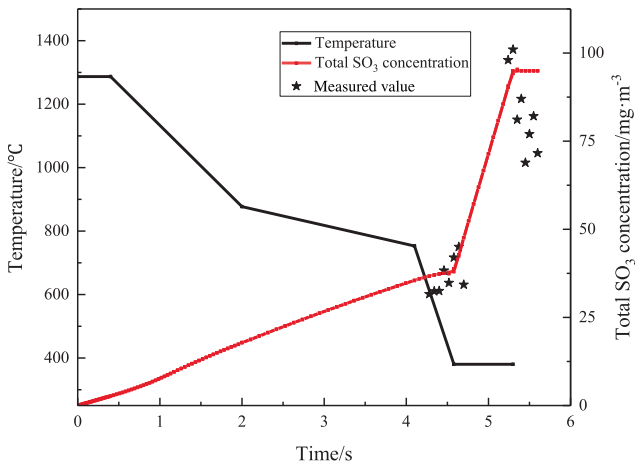

Fig. 6. Trend of total SO_3 generation.

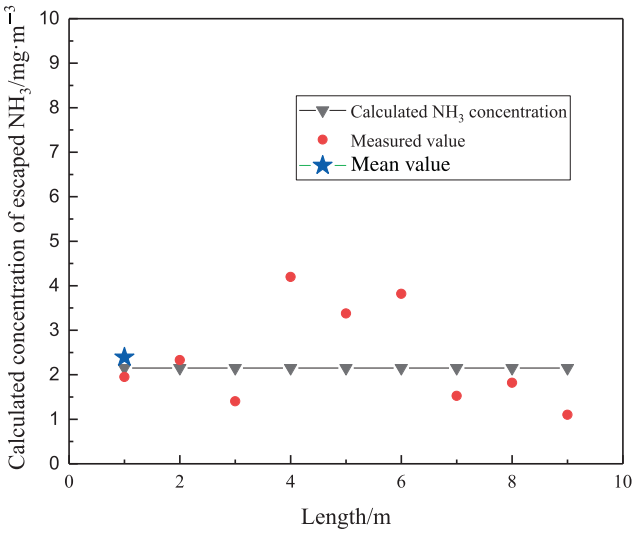

Fig. 7. The trend of concentration of escape NH_3.

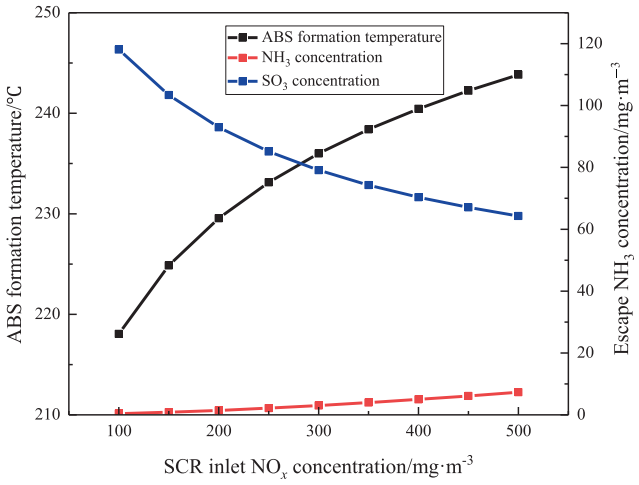

Fig. 10. The influence of different NO_x inlet concentrations on ABS formation temperature and escaped NH_3.

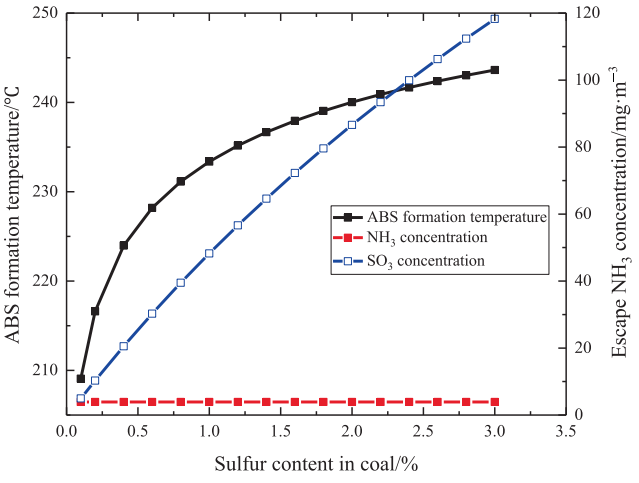

Fig. 8. Relationship between S content in coal and ABS generation temperature.

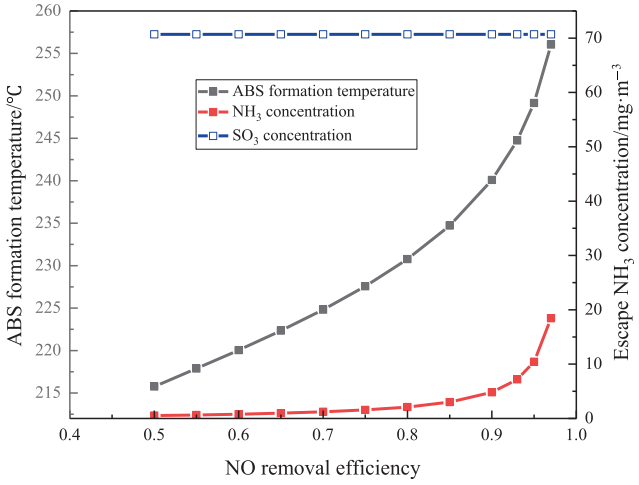

Fig. 11. The effect of NO removal efficiency on ABS formation temperature.

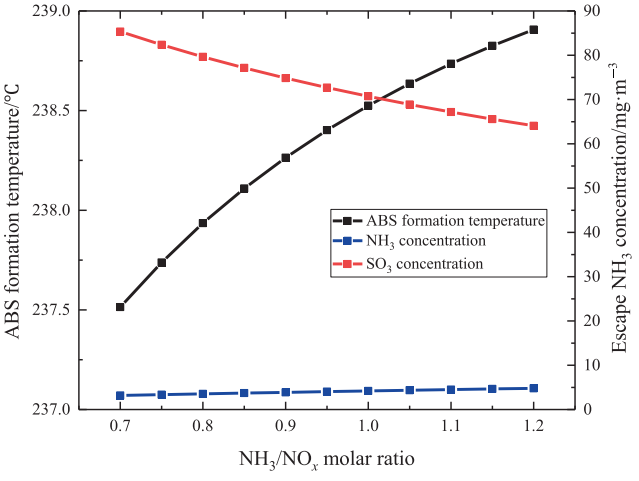

Fig. 9. The influence of NH_3/NO_x molar ratio on ABS formation temperature and escaped NH_3.

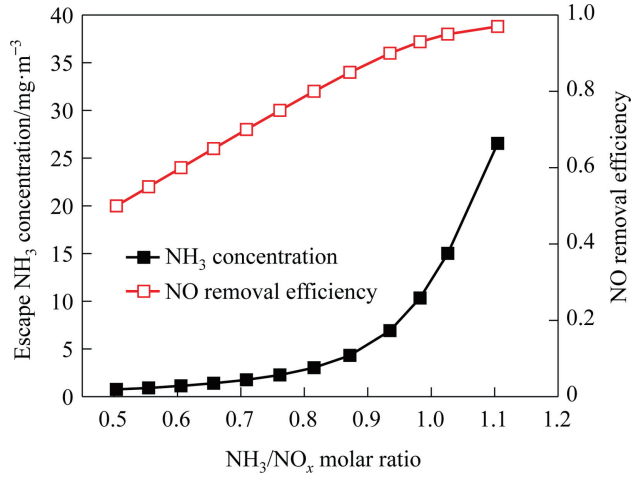

Fig. 12. The relationship between NH_3/NO_x molar ratio, NO removal efficiency, and the concentration of escaped NH_3.

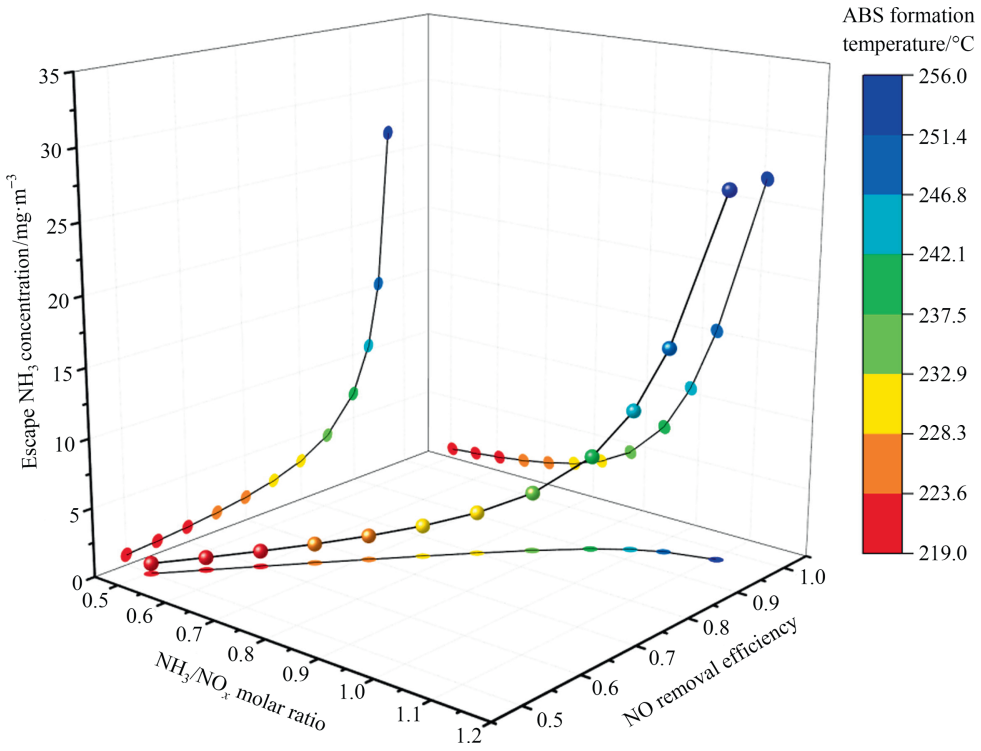

Fig. 13. The comprehensive effect between NH_3/NO_x molar ratio and NO removal efficiency on the formation temperature of ABS.

combining the reaction kinetics of SO_3 and kinetics of NO reduction. The amount of SO_3 generated from the combustion of S in coal to the inlet of the air preheater was calculated by the reaction kinetics of SO_3, and the concentration of escaped NH_3 was calculated by the reaction kinetics of NO reduction, and finally, the model of predicting the ABS formation temperature was obtained. Considering the whole process, the prediction model of ABS formation temperature obtained by using S content in coal and parameters of NO reduction overcomes the difficulty of calculating the formation temperature of ABS by measuring the SO_3 concentration and NH_3 concentration in the past, and the prediction results of the model are in good agreement with the actual data, which has good applicability.

The following conclusions can be noted:

(1) The prediction model of SO_3 concentration shows that in the process of coal combustion to the SCR outlet, the SO_3 generated by the catalysis of V_2O_5 accounted for 60%, by the homogeneously generated SO_3 accounted for 33.8%, and the fly ash catalyzed SO_3 accounted for 6.2%. Reducing the catalytic oxidation of SO_2 on the SCR catalyst is the key to reducing the concentration of SO_3, which is beneficial to lower the formation temperature of ABS, thereby slowing down the deposition of ABS on the air preheater.

(2) The formation temperature of ABS is directly related to the S content in coal. The increase of the sulfur content in coal leads to the increase of SO_3 concentration in the flue gas, which makes the formation temperature of ABS increase rapidly. To reduce the influence of ABS from the source, low sulfur coal should be burned as far as possible or desulfurization treatment should be carried out before combustion.

(3) Although the change of the NH_3/NO_x molar ratio has little effect on the ABS formation temperature when the NH_3/NO_x deviates from the design value seriously, it will cause serious NH_3 escape. Therefore, in practical, adding ammonia injection grid and guide plate in SCR Flue can reduce the non-uniformity of local NH_3/NO_x molar ratio, which can not only improve the NO removal efficiency but also effectively reduce NH_3 escape, thus reducing the formation temperature of ABS. When the NH_3/NO_x molar ratio is fixed, the formation temperature of ABS increases with the increase of the emission concentration of NO_x at the SCR inlet. Therefore, the use of low-nitrogen combustion technology not only reduces NO_x emissions concentration, but also reduces the formation temperature of ABS.

(4) Although the improvement of NO removal efficiency has little effect on the SO_3 concentration, it has a greater impact on the concentration of NH_3 escape. As the NO removal efficiency exceeds 90%, continuing to increase the NH_3/NO_x molar ratio will not significantly improve the NO removal efficiency, but will increase the NH_3 concentration rapidly, resulting in the rapid increase of ABS formation temperature. Therefore, to control the formation temperature of ABS, adjusting the NH_3/NO_x molar ratio at about 0.9 can not only ensure the NO removal efficiency at 85%–90% but also control the concentration of NH_3 escape at a low level.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Nomenclature

A	the adsorption rate constant of NH_3, s^{-1}
A_1	the pre-exponential factor, $(m^3 \cdot mg^{-1})^{0.5} \cdot s^{-1}$
A_2	the pre-exponential factor, $(m^3 \cdot mg^{-1})^{0.5} \cdot s^{-1}$
b	simplify the factor

C_{H_2O}	the molar concentration of H_2O, mol·cm^{-3}
C_{NO}	the molar concentration of NO, mol·cm^{-3}
C_{NH_3}	the molar concentration of NH_3, mol·cm^{-3}
$C_{NO_x in}$	the NO_x concentration at the SCR inlet, mg·m^{-3}
$C_{NO_x out}$	the NO_x concentration at the SCR outlet, mg·m^{-3}
C_{O_2}	the mass concentration of O_2, mg·m^{-3}
C_{SO_2}	SO_2 concentration in the flue gas, mg·m^{-3}
C_{SO_3}	SO_3 concentration in the flue gas, mg·m^{-3}
$C_{SO_3 f\_1}$	the amount of SO_3 produced in the homogeneous phase, mg·m^{-3}
$C_{SO_3 f\_2}$	the amount of SO_3 produced by fly ash catalysis, mg·m^{-3}
$C_{SO_3 f\_3}$	the amount of SO_3 produced by SCR catalysis, mg·m^{-3}
E_{a1}	the activation energy, kJ·mol^{-1}
E_{a2}	the activation energy, kJ·mol^{-1}
K_1	the homogeneous reaction rate constant
K_2	fly ash catalytic reaction rate constant
K_3	the reaction rate constant of NO reduction
k_i	the influence coefficients of different substances, i = 1, . . ., 6
L	unit operating load rate, %
M_R	the molar ratio of NH_3/NO_x
$[NH_3]$	escape NH_3 concentration, mg·m^{-3}
P	the potential of the reactor
P_0	initial reactor potential
R	the gas constant, J·mol^{-1}·K^{-1}
R_{f_1}	homogeneous SO_3 formation rate, mol·L^{-1}·s^{-1}
R_{f_2}	fly ash catalytic SO_3 generation rate, mol·L^{-1}·s^{-1}
R_{f_3}	De-NO_x catalytic SO_3 generation rate, mol·L^{-1}·s^{-1}
R_{NO}	the reaction rate of NO, mol·m^{-3}·s^{-1}
S	sulphur content in coal,%
S_{ar}	the sulfur content in coal, kg
$[SO_3]$	SO_3 concentration, mg·m^{-3}
T	the absolute temperature, K
T_{IFT}	the ABS formation temperature, ℃
V_{SO_2}	the volume of SO_2, m^3·kg^{-1}
V_y	the actual amount of gas, m^3·kg^{-1}
η	NO removal efficiency,%

Subscript

ar	as-received basis
in	the NO at the SCR inlet
out	the NO at the SCR outlet

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