

# Experimental studies on gas-phase mercury oxidation removal and denitration of coal combustion with $\text{NH}_4\text{Br}$ addition

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**Abstract:** In order to remove gas-phase mercury and  $\text{NO}_x$  from flue gas, experimental studies on flue gas mercury oxidation removal and denitration of Guizhou anthracite combustion with  $\text{NH}_4\text{Br}$  addition were carried out. The influence of  $\text{NH}_4\text{Br}$  addition on the ignition temperature and combustion characteristics was studied using a thermogravimetric analyzer. The effects of the  $\text{NH}_4\text{Br}$  addition amount on gas-phase mercury oxidation and removal were investigated in a bench scale of 6 kW fluidized bed combustor (FBC). Mercury concentrations in flue gas were determined by the Ontario hydro method (OHM) and the mercury mass balance was obtained. Results show that the  $\text{NH}_4\text{Br}$  addition has little influence on the ignition temperature of Guizhou anthracite. With the mercury mass balance of 95.47%, the proportion of particulate mercury  $\text{Hg}^p$ , gaseous mercury  $\text{Hg}^0$  and  $\text{Hg}^{2+}$  are 75.28%, 11.60% and 13.12%, respectively, as raw coal combustion. The high particulate mercury  $\text{Hg}^p$  in flue gas is caused by the high unburned carbon content in fly ash. When the  $\text{NH}_4\text{Br}$  addition amount increases from 0 to 0.3%, the concentration of gaseous  $\text{Hg}^0$  and  $\text{Hg}^{2+}$  in flue gas decreases continuously, leading to the  $\text{Hg}^p$  increase accordingly. The oxidation rate of  $\text{Hg}^0$  is positively correlated to the Br addition amount. It demonstrates that coal combustion with  $\text{NH}_4\text{Br}$  addition can promote  $\text{Hg}^0$  oxidation and removal.  $\text{NO}_x$  concentration in flue gas exhibits a descending trend with the  $\text{NH}_4\text{Br}$  addition and the removal rate reaches 17.31% with the addition amount of 0.3%. Adding  $\text{NH}_4\text{Br}$  to coal also plays a synergistic role in denitration.

**Key words:** coal additives;  $\text{NH}_4\text{Br}$ ; mercury oxidation; mercury removal; synergistic denitration

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Mercury is one of the most harmful trace elements, which can enter the human body through breathing, skin absorption and the digestive tract, causing language obstacles, movement disorders, and renal failure, etc.<sup>[1-2]</sup>. Mercury emissions from coal combustion has become one of the largest anthropogenic emission sources, with emissions accounting for 1/3 of the total amount of mercury emitted into the air.<sup>[3-4]</sup> It has caused a huge negative effect on the environment and human beings. Owing to the widespread concern about mercury pollution, the Chinese government enacted the “Thermal Power Plant Air Pollutant Emission Standards” (GB 13223—2011) in 2012, which was executed on January 1, 2015. According to the standards, the mercury emission concentration in coal-fired power plants has been limited to 0.03 mg/m<sup>3</sup>. Mercury exists in flue gas in three forms: elemental mercury  $\text{Hg}^0$ , oxidized mercury  $\text{Hg}^{2+}$  and particulate mercury  $\text{Hg}^p$ .  $\text{Hg}^{2+}$  can be captured by the wet flue gas desulfurization due to its water solubility, and  $\text{Hg}^p$  can be removed easily by dust removal equipment such as ESP or baghouse. Due to the long-term stability, water insolubility and long-distance transport in the atmosphere, it is difficult to remove the  $\text{Hg}^0$  from the flue gas, and further research is required<sup>[5-7]</sup>.

Adding additives to coal to achieve the transformation of  $\text{Hg}^0$  to  $\text{Hg}^{2+}$  during combustion process in the furnace is one of the most promising mercury removal technologies, which has the features of being a simple device, having reliable operation and a low cost. Studies have shown that halogen is a key element for  $\text{Hg}^0$  oxidation. Gao et al.<sup>[8]</sup> carried out coal combustion with 1%, 2% and 3%  $\text{CaBr}_2$  addition in a high-temperature tube furnace, and the results showed that the addition of  $\text{CaBr}_2$  was beneficial in increasing both  $\text{Hg}^p$  content and proportion. The combustion experiment of Liuzhi bituminous coal added with  $\text{NaBr}$  was carried out in a fixed quartz reactor by Ma et al.<sup>[9]</sup>, which aimed to study the impact of  $\text{NaBr}$  on mercury transformation during the coal combustion process. Experimental results indicate that  $\text{NaBr}$  has a positive effect on mercury oxidation, particularly at temperatures from 250 to 400 °C. Pan et al.<sup>[10]</sup> combined numerical simulations and experimental methods to study the effects of adding  $\text{NH}_4\text{Cl}$  to simulated flue gas on Hg and NO emissions. They found that with the increase in

the injected amount of NH<sub>4</sub>Cl, the proportion of gaseous Hg<sup>0</sup> and Hg<sup>2+</sup> decreased, and the Hg<sup>p</sup> proportion increased correspondingly. Within a suitable temperature range, NH<sub>3</sub> was conducive to flue gas denitrification. Cao et al.<sup>[11]</sup> pointed out that spraying HBr into the coal-fired flue gas has better oxidation effect on Hg<sup>0</sup> than HCl, and the presence of Br can promote oxidation of Cl on Hg<sup>0</sup>. Moreover, the corrosion of Br on the equipment is much less than Cl. However, the mercury transformation mechanism by adding Br into coal during combustion is not entirely understood.

Based on previous research, this paper selected NH<sub>4</sub>Br as a mercury removal additive in the coal combustion process. Thermogravimetric analysis was used to study the impact of NH<sub>4</sub>Br addition on Guizhou anthracite ignition temperature and combustion characteristics. Then, the effects of adding different proportions of NH<sub>4</sub>Br to coal on flue gas mercury speciation, oxidation and removal were investigated in a bench scale of 6 kW FBC

experimental facility, which aimed to reveal the mechanism of mercury oxidation, transformation and removal with synergistic denitration.

## 1 Experimental

### 1.1 Coal analysis

The proximate and ultimate analyses of Guizhou anthracite were analyzed and the results are shown in Tab. 1 and Tab. 2, respectively. From Tab. 2, we can see that the mercury content of coal (0.159 mg/kg) is slightly lower than the average mercury content of Chinese coal (0.22 mg/kg<sup>[12]</sup>). According to the classification scheme of chlorine content in coal (MT/5597—1996), this kind of coal belongs to special low-chlorine coal.

**Tab. 1** Proximate analysis of coal on as received basis %

w(M)	w(A)	w(V)	w(FC)
3.74	31.24	6.60	58.42

**Tab. 2** Ultimate analysis of coal on as received basis

w(C)/%	w(H)/%	w(O)/%	w(N)/%	w(S)/%	w(Cl)/%	w(F)/(μg · g <sup>-1</sup> )	w(Hg)/(mg · kg <sup>-1</sup> )	Q <sub>net</sub> /(MJ · kg <sup>-1</sup> )
57.28	2.25	3.47	0.70	1.32	0.006	135	0.159	21.62

According to Ref. [13], chlorine can corrode pipes and carbonize furnace walls as well as shorten the life of equipment when its content in coal exceeds 0.3%. To enhance oxidizability resistance and weaken corrosivity, the Br addition proportion of 0.1%, 0.2% to 0.3% (mass ratio) in the form of NH<sub>4</sub>Br was added to the coal.

### 1.2 Thermogravimetric analysis (TGA) pre-test

To explore the effects of adding NH<sub>4</sub>Br on coal combustion characteristics, raw Guizhou coal (10 mg) and coal added with 10% NH<sub>4</sub>Br were conducted using a thermogravimetric analyzer (TGA92, a French SETARAM Company) under the conditions of air atmosphere and the heating rate of 20 °C/min.

### 1.3 6 kW FBC system

The schematic diagram of a 6 kW coal-fired FBC test facility is shown in Fig. 1. It consists of a circulating fluidized bed combustor, coal feeding, gas and solid sampling for mercury measurement and gas component analyses. Two levels of coal feeding hopper were installed to ensure coal feed continuity. There was an air supply system and furnace temperature control device mounted to the FBC. The average particle size of the coal was 0.5 to 1.6 mm. The coal feeding rate was 1 kg/h and the excessive air ratio was 1.4 with the furnace temperature of 900 °C.

The mercury speciation sampling and analysis were conducted by strictly following the Ontario hydro method (OHM) recommended by US-EPA<sup>[14]</sup>. The temperature of the sampling line was kept at 140 °C by using the elec-

tric heating system to prevent the mercury vapor from condensing. The mercury content in coal, fly ash and bottom ash were determined by the Leeman Labs automatic mercury analyzer Hydra-C. Gaseous Hg<sup>0</sup> and Hg<sup>2+</sup> were determined by the automatic mercury analyzer Hydra AA, which was based on cold vapor atomic absorption spectrometry (CVAAS). The NO<sub>x</sub> concentration in flue gas was determined by German Ecom J2KN multifunctional gas analyzer.

## 2 Results and Discussion

### 2.1 TGA test results

The TGA results of Guizhou raw coal and the coal mixed with 10% NH<sub>4</sub>Br are shown in Fig. 2 and Fig. 3. The weight loss of raw coal in Fig. 2 can be divided into stages of evaporation of moisture, combustion of volatile matter and the residual coke burnout. According to the TG-DTG classification method<sup>[15]</sup>, the ignition temperature  $T_i$  and burnout temperature  $T_b$  of raw coal can be determined to be about 550 and 800 °C, respectively. Compared to Fig. 2, the DTG curve in Fig. 3 has a distinct peak approximately at 200 to 350 °C. In this temperature range, the weight loss is about 1 mg, which corresponds to the amount of 10% NH<sub>4</sub>Br. According to the physical and chemical properties of NH<sub>4</sub>Br, it can be inferred that NH<sub>4</sub>Br decomposition and volatilization occur between 200 and 350 °C. The TG and DTG curves in Figs. 2 and 3 are basically the same when the temperature goes higher than 350 °C, which indicates that NH<sub>4</sub>Br addition has no effect on the raw coal combustion characteristics.

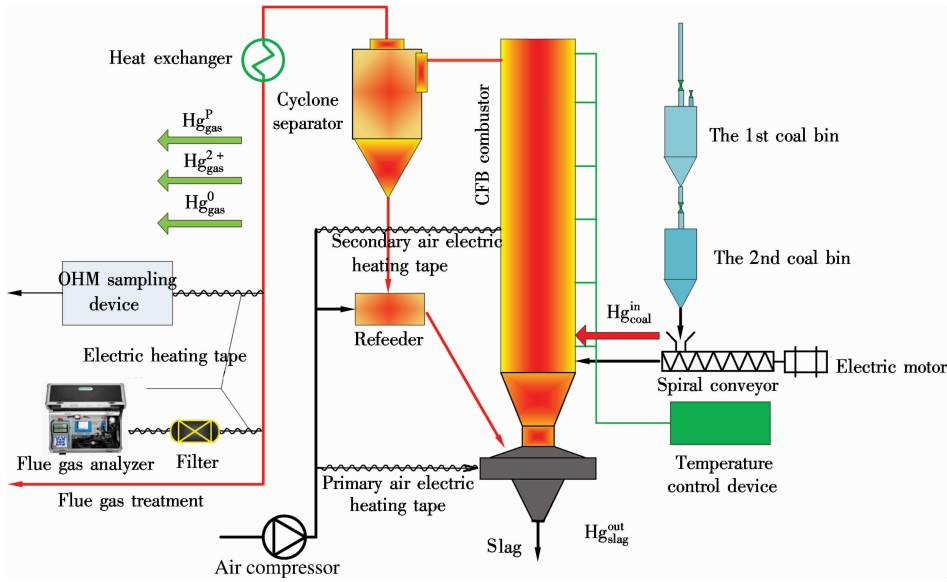


Fig. 1 Schematic diagram of 6 kW coal-fired FBC test facility

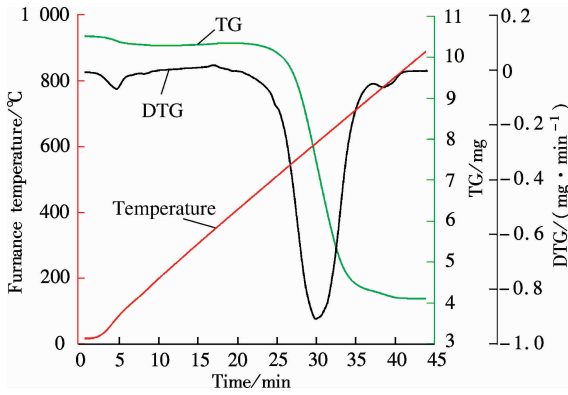


Fig. 2 The TGA of raw coal

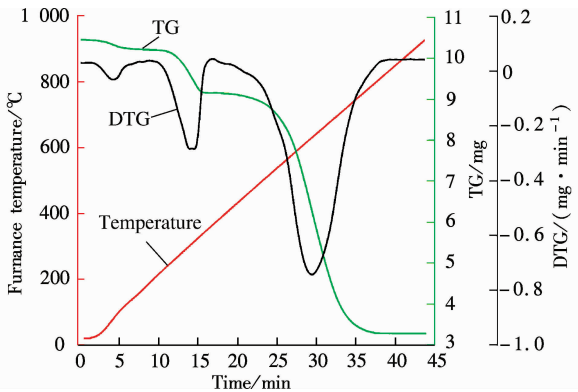


Fig. 3 The TGA of coal added with 10%  $\text{NH}_4\text{Br}$

## 2.2 Mercury mass balance of the raw coal

Measuring mercury mass balance, which is an effective way to verify the data accuracy of the sampling, is usually defined as the ratio of output to input of mercury mass flow per unit time,

$$R = \frac{(C_{\text{Hg}^0, \text{gas}} + C_{\text{Hg}^{2+}, \text{gas}} + C_{\text{Hg}^p, \text{gas}})Q_{\text{gas}}m_{\text{coal}} + C_{\text{Hg}, \text{slag}}m_{\text{slag}}}{C_{\text{Hg}, \text{coal}}m_{\text{coal}}} \times 100\%$$

(1)

where  $C_{\text{Hg}^0, \text{gas}}$ ,  $C_{\text{Hg}^{2+}, \text{gas}}$ ,  $C_{\text{Hg}^p, \text{gas}}$  represent the concentrations of  $\text{Hg}^0$ ,  $\text{Hg}^{2+}$  and  $\text{Hg}^p$  in flue gas, respectively,  $\mu\text{g}/\text{m}^3$ ;  $Q_{\text{gas}}$  is the flue gas volume flow per unit coal mass,  $\text{m}^3/\text{kg}$ ;  $m_{\text{coal}}$  is the coal feed rate,  $\text{kg}/\text{h}$ ;  $C_{\text{Hg}, \text{slag}}$  is the mercury content in slag,  $\mu\text{g}/\text{kg}$ ;  $m_{\text{slag}}$  is the slag mass flow rate,  $\text{kg}/\text{h}$ ;  $C_{\text{Hg}, \text{coal}}$  is the mercury content in coal,  $\mu\text{g}/\text{kg}$ .

Due to the unavoidable error factors in sampling, analysis and experimental running, the mercury mass balance rate between 70% and 130% is conventionally acceptable<sup>[16]</sup>. Fig. 4 shows the mercury mass balance of 95.47% for raw coal combustion. The mercury speciation distribution in flue gas of raw coal combustion is shown in Fig. 5. Gaseous  $\text{Hg}^0$  and  $\text{Hg}^{2+}$  concentrations are 2.276 and 2.572  $\mu\text{g}/\text{m}^3$ , respectively with the corresponding proportions of 11.60% and 13.12%. However, the  $\text{Hg}^p$  concentration in fly ash is 14.766  $\mu\text{g}/\text{m}^3$ , which accounts for 75.28% of the total mercury. Carpi et al.<sup>[17–18]</sup> indicated that  $\text{Hg}^0$  and  $\text{Hg}^{2+}$  occupied approximately 20% to 50% and 50% to 80% of the flue gas of the coal-fired power plant, respectively, of which the

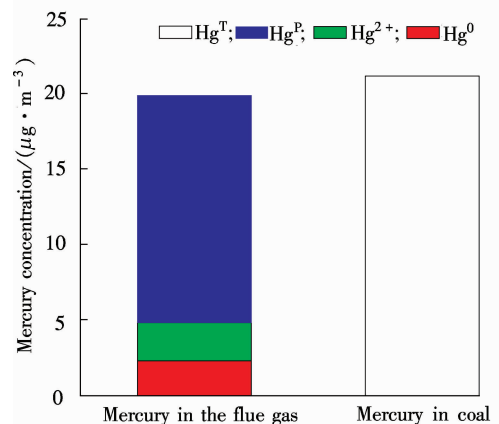


Fig. 4 Mercury mass balance of raw coal

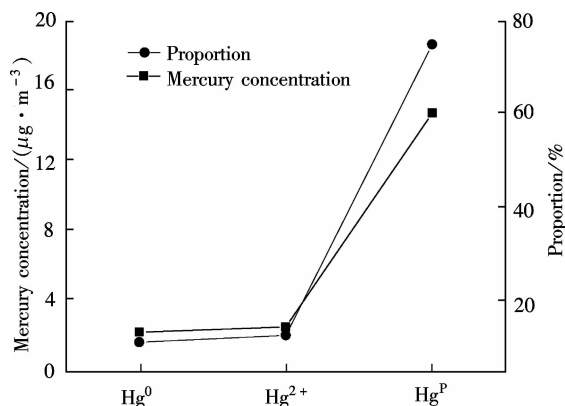
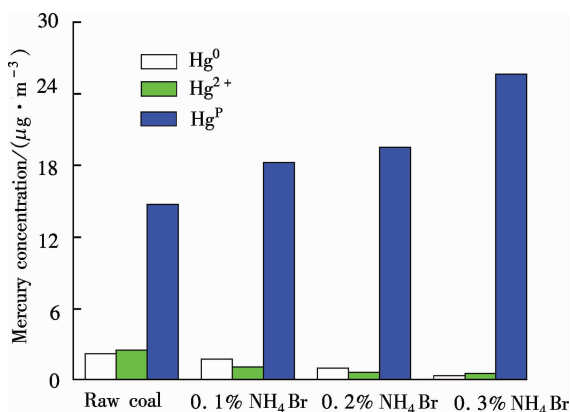


Fig. 5 Mercury speciation in flue gas of raw coal

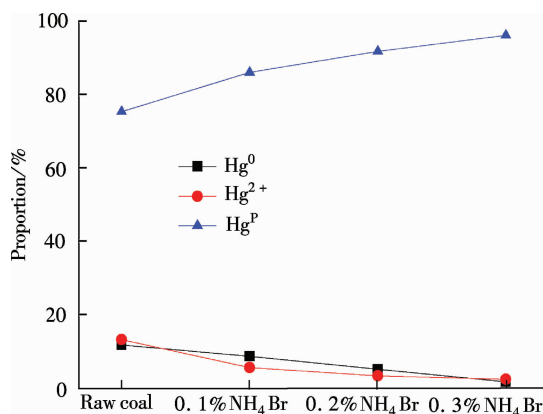
$\text{Hg}^{2+}$  content was significantly higher than that of  $\text{Hg}^0$ . In this experiment,  $\text{Hg}^0$  and  $\text{Hg}^{2+}$  take 46.94% and 53.06% of the sum of gaseous  $\text{Hg}^0$  and  $\text{Hg}^{2+}$ , which is consistent with their results. The  $\text{Hg}^p$  content is much higher than that in the pulverized coal furnace, because the fly ash in FBC has a higher unburned carbon content (about 15% to 20%).

### 2.3 Effects of additives on flue gas mercury oxidation and removal

Mercury species in flue gas varying with the addition amount of  $\text{NH}_4\text{Br}$  is shown in Fig. 6. It illustrates that the



(a)



(b)

Fig. 6 Mercury species in flue gas varied with the added amount of  $\text{NH}_4\text{Br}$ . (a) Concentration; (b) Proportion

$\text{Hg}^0$  concentrations are 2.276, 1.808, 1.069 and 0.424  $\mu\text{g}/\text{m}^3$ , respectively, showing a decreasing trend with the  $\text{NH}_4\text{Br}$  addition amount increasing from 0.0% to 0.3%. The corresponding proportions are 11.60%, 8.51%, 5.02% and 1.59%, respectively.  $\text{Hg}^{2+}$  concentrations are 2.572, 1.162, 0.682 and 0.604  $\mu\text{g}/\text{m}^3$ , which also shows a reducing tendency with the proportions of 13.11%, 5.47%, 3.21% and 2.27% in total flue gas mercury. However, the  $\text{Hg}^p$  concentrations are 14.766, 18.273, 19.524 and 25.629  $\mu\text{g}/\text{m}^3$ , sharing a portion of 75.28%, 86.02%, 91.77% and 96.14%. It exhibits a considerable increasing tendency. Therefore, with the increase in the content of  $\text{NH}_4\text{Br}$  loaded in coal, both  $\text{Hg}^0$  and  $\text{Hg}^{2+}$  concentrations decrease, while  $\text{Hg}^p$  concentrations increase accordingly.

Fig. 7 shows that the  $\text{Hg}^0$  oxidation rate increases apparently with the increasing added amount of Br. The formula of  $\text{Hg}^0$  oxidation rate  $X_{t, \text{Hg}(0)} = (C_{\text{Hg}(0)} - C_{\text{Hg}(0)}^{\text{NH}_4\text{Br}}) / C_{\text{Hg}(0)}$ , where  $C_{\text{Hg}(0)}$  represents the  $\text{Hg}^0$  concentration for raw coal combustion tests,  $\mu\text{g}/\text{m}^3$ ;  $C_{\text{Hg}(0)}^{\text{NH}_4\text{Br}}$  represents  $\text{Hg}^0$  concentration in flue gas under the conditions of adding  $\text{NH}_4\text{Br}$  in raw coal,  $\mu\text{g}/\text{m}^3$ . It indicates that the oxidation rate of  $\text{Hg}^0$  is positively correlated to the added amount of  $\text{NH}_4\text{Br}$ , which promotes both  $\text{Hg}^0$  oxidation and removal. The decrease in the  $\text{Hg}^0$  concentration in flue gas with the increase of  $\text{NH}_4\text{Br}$  can be explained by two aspects. On the one hand, Br can directly oxidize elemental mercury. On the other hand, Br can promote the reaction between  $\text{Hg}^0$  and Cl. The possible reaction mechanisms are shown as follows<sup>[19]</sup>:

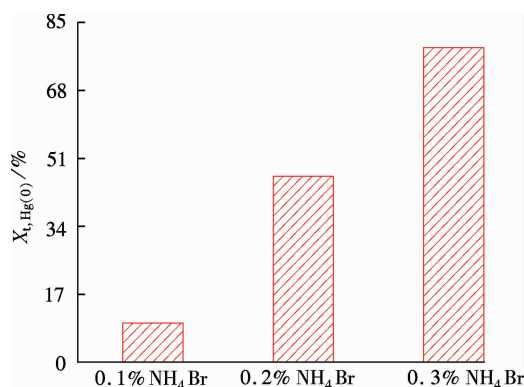
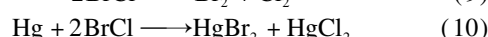
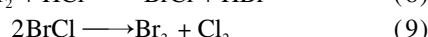
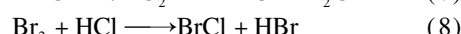
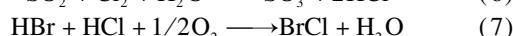
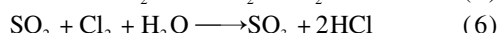
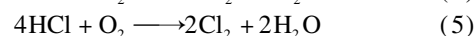
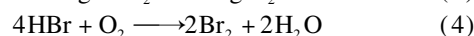
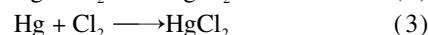


Fig. 7  $\text{Hg}^0$  oxidation rate varied with the added amount of  $\text{NH}_4\text{Br}$

Combining the TGA analytical results, the HBr generated by  $\text{NH}_4\text{Br}$  decomposition in the combustion process can increase active Br content in the flue gas, which then promotes the reactions (2) to (10) and strengthens  $\text{Hg}^0$  oxidation according to the chemical reaction kinetics. Unburned carbon in fly ash plays an important role in directly adsorbing gaseous mercury in flue gas, and  $\text{Hg}^{2+}$  can be easily adsorbed to form  $\text{Hg}^p$  than  $\text{Hg}^0$ . The presence of Br can promote the generation of active sites on the fly ash surface, which enhances chemisorption. Therefore, the proportion of  $\text{Hg}^p$  increases with  $\text{NH}_4\text{Br}$  addition. In this paper, the  $\text{Hg}^0$  oxidation rate increases while the  $\text{Hg}^{2+}$  content decreases, because the presence of Br makes  $\text{Hg}^{2+}$  adsorption capacity for fly ash stronger than its oxidation on  $\text{Hg}^0$ .

## 2.4 Effect of additives on $\text{NO}_x$ emission

$\text{NO}_x$  in flue gas varying with the additional amount of  $\text{NH}_4\text{Br}$  is plotted in Fig. 8. It was reported that when the temperature was higher than  $800^\circ\text{C}$ ,  $\text{NH}_3$  decomposed from  $\text{NH}_4\text{Br}$  can react with  $\text{NO}_x$  and reduce it to  $\text{N}_2$  [20],

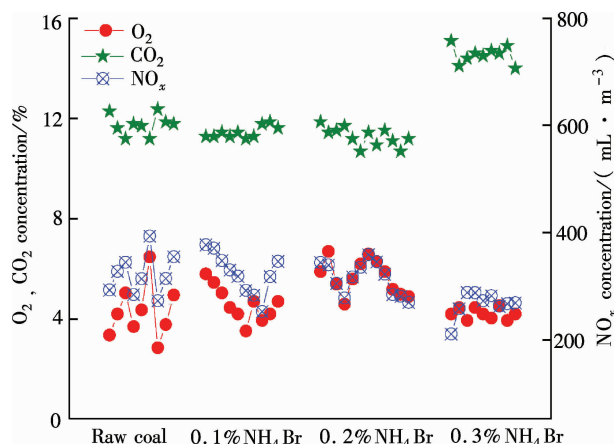
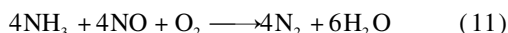


Fig. 8  $\text{NO}_x$  variation with the added amount of  $\text{NH}_4\text{Br}$

With the added amount of  $\text{NH}_4\text{Br}$  increasing from 0.1%, 0.2%, to 0.3%, the corresponding  $\text{NH}_3$  concentrations are 33.5, 75.2 and  $101.0 \text{ mL}/\text{m}^3$ , respectively, which are the equivalent amounts of  $\text{NH}_3$  injected into the furnace. Fig. 8 shows that when the amount of  $\text{NH}_4\text{Br}$  increases, the  $\text{NO}_x$  in flue gas presents a tendency to decrease on the whole. Hence, the  $\text{NO}_x$  removal rate tends to increase. With the added amount of 0.3%, the  $\text{NO}_x$  removal rate reaches the maximum of 17.31%. This is because the increase of  $\text{NH}_3$  concentration in the flue gas promotes the reductive reaction of  $\text{NO}_x$ .

## 3 Conclusions

The influence of adding  $\text{NH}_4\text{Br}$  into coal on the ignition temperature and combustion characteristics of

Guizhou anthracite was studied in a thermogravimetric analyzer. The effects of different adding proportions of  $\text{NH}_4\text{Br}$  to coal on flue gas mercury oxidation and removal were investigated in a bench scale of 6 kW FBC experimental facility. The OHM method was used to determine the mercury speciation in flue gas and calculate the mercury mass balance rate. The mechanism of the impacts on flue gas mercury speciation and  $\text{NO}_x$  emission by adding  $\text{NH}_4\text{Br}$  into the coal was analyzed and discussed. The main conclusions are listed as follows:

1) The TGA results indicate that when the Guizhou anthracite ignition temperature is about  $550^\circ\text{C}$  and the burn-out temperature is about  $800^\circ\text{C}$ , the  $\text{NH}_4\text{Br}$  addition has no effect on the coal combustion characteristics.

2) Based on the mercury mass balance of 95.47% conducted in the 6 kW FBC furnace, it is demonstrated that particulate mercury  $\text{Hg}^p$ , gaseous mercury  $\text{Hg}^0$  and  $\text{Hg}^{2+}$  account for 75.28%, 11.60%, 13.12%, respectively, for the raw coal combustion. The high  $\text{Hg}^p$  proportion is caused by the high carbon content in fly ash.

3) With the added amount of  $\text{NH}_4\text{Br}$  loaded into coal increasing from 0.1% to 0.3%, the concentrations of gaseous  $\text{Hg}^0$  and  $\text{Hg}^{2+}$  in flue gas decrease and  $\text{Hg}^p$  increases accordingly. The oxidation rate of  $\text{Hg}^0$  is positively correlated to the amount of  $\text{NH}_4\text{Br}$  added to coal. The presence of Br makes fly ash adsorption for  $\text{Hg}^{2+}$  stronger than its oxidation on  $\text{Hg}^0$ .

4)  $\text{NO}_x$  emission decreases with the increasing amount of  $\text{NH}_4\text{Br}$  added to coal, which indicates that  $\text{NH}_4\text{Br}$  plays a synergistic role of denitration.

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## 煤中添加 $\text{NH}_4\text{Br}$ 对气相汞氧化脱除及脱硝的实验研究

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**摘要:**为脱除烟气中的气相汞和  $\text{NO}_x$ , 进行了贵州无烟煤中添加  $\text{NH}_4\text{Br}$  对烟气汞氧化脱除协同脱硝的实验研究. 在热重分析仪上研究添加  $\text{NH}_4\text{Br}$  对着火温度和燃烧特性的影响. 在 6 kW 流化床燃烧(FBC)试验装置上研究了在煤中不同  $\text{NH}_4\text{Br}$  添加量对气相汞氧化脱除的影响. 采用安大略法(OHM)对烟气中汞形态浓度进行了测定并得出汞质量平衡. 结果表明, 添加  $\text{NH}_4\text{Br}$  对贵州无烟煤的着火温度没有影响. 原煤燃烧汞质量平衡率为 95.47%, 颗粒汞  $\text{Hg}^p$ 、气态  $\text{Hg}^0$  和  $\text{Hg}^{2+}$  比例分别为 75.28%, 11.60%, 13.12%. 由于飞灰中含有较高的未燃尽碳, 烟气中  $\text{Hg}^p$  浓度较高. 随着  $\text{NH}_4\text{Br}$  添加量从 0 增加至 0.3%, 烟气中气态  $\text{Hg}^0$  和  $\text{Hg}^{2+}$  减少,  $\text{Hg}^p$  相应增加.  $\text{Hg}^0$  的氧化率与煤中 Br 的添加量成正相关. 这表明煤燃烧中添加  $\text{NH}_4\text{Br}$  可促进  $\text{Hg}^0$  的氧化和脱除. 烟气中  $\text{NO}_x$  随着  $\text{NH}_4\text{Br}$  的添加呈减小趋势, 其脱除率在 0.3% 添加量时达最大(17.31%). 添加  $\text{NH}_4\text{Br}$  同时具有协同脱硝的作用.

**关键词:**煤添加剂; 溴化铵; 汞氧化; 汞脱除; 协同脱硝

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