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Effect of Na on the NO_x Formation Characteristic at High Temperature

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ABSTRACT

The effect of alkali metal sodium on the NO_x formation characteristic of zhundong coal under different temperatures, combustion atmospheres and loading amounts were studied on a fixed bed experimental system. The results show that alkali metal sodium could suppress the formation of NO_x during coal combustion. The peak value of volatile nitrogen decreases with the increase in the adding amount of NaCl and increase with the temperature. When the combustion temperature is 1773 K, the alkali metal sodium addition of 1% has the most significant inhibitory effect on the NO_x formation. The NO_x conversion ratio can be reduced by 45.8%.

Keywords: alkali metal sodium, NO_x formation, high temperature, Zhundong Coal

1. INTRODUCTION

Zhundong coal is an excellent power coal due to the excellent ignition and burnout performances and strong combustion stability. However, the content of alkali metal in Zhundong coal is very high. The alkali metal in coal not only cause boiler fouling, but also affect the formation characteristics of nitrogen oxides during coal combustion.

Scholars have conducted research on the influence of alkali metals on NO_x formation characteristics during the combustion of pulverized coal [1-3]. Liu et al. [4] studied the influence of Na additives on the release of fuel nitrogen on the TG/EGA analysis equipment. The results show that the formation of NO in the temperature region above 873 K is strongly inhibited by the Na additives. Na inhibits the heterogeneous oxidation of the stable nitrogen-containing heterocycles in the char, and promotes the heterogeneous reduction of NO. Zhou et al. [5] studied the influence of alkali metals on the NO_x formation during the combustion of char by loading different contents of alkali metal compounds. The results shown that the effect of alkali metals on reducing NO_x formation are not linear with the loading amount of Na additives and temperature. Wei et al. [6] investigated the influence of alkali metal compounds (K_2CO_3 and NaCl) on the combustion characteristics of coal below 1073 K. The results show that NaCl mainly catalyzes the combustion of fixed carbon. Both K_2CO_3 and NaCl can reduce the apparent activation energy of the coal and increase the combustion reaction rate. The research of Wang et al. [7] has reported that Na affects the migration and transformation of nitrogen in the acid washed coal and raw coal. This is because Na promotes the conversion of nitrogen in coal to NH_3, while inhibiting the production of HCN. Wen et al. [8] used quantum chemistry calculations to study the catalytic mechanism of the heterogeneous reduction of NO with char by alkali metals. The calculation results show that alkali metals reduce the activation energy of char for heterogeneous reduction of NO and increase the reaction rate.

Much work has been conducted on the effect of alkali metal on the NO_x formation and combustion characteristics. Studies have shown that alkali metals can inhibit the formation of nitrogen oxides. However, the temperature of related research is generally low （usually below 1373 K）. The effect of alkali metals on the nitrogen formation during coal combustion at higher temperatures is still unclear. Therefore, in this study, the effect of Na on the NO_x formation characteristic is investigate at higher temperature (1773 K) on a fixed bed experimental system. In addition, the effect of Na on the NO_x formation characteristic at different temperature, different combustion atmospheres and different loading amount are studied.

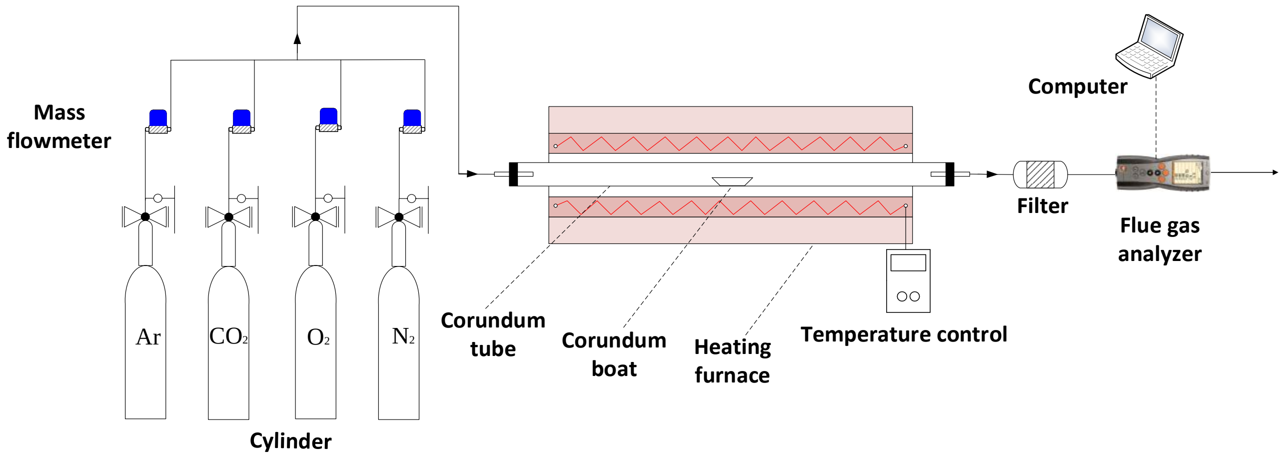

Fig. 1 The experimental system

2. EXPERIMENTAL

2.1 Experimental system

The fixed bed experimental system which composed of high temperature electric heating tube furnace, gas cylinders, pressure reducing valves, mass flow meters and flue gas analyzer is shown in Fig. 1. The tube furnace has an inner diameter of 60 mm and a length of 1200 mm. The combustion temperature was controlled by a temperature control instrument.

Firstly, the reaction gas was sent into the high temperature tube furnace by the gas distribution device. Then when the flow of gas was stable, the coal sample placed in the corundum boat has sent to the tube furnace. The coal samples were combusted in the tube furnace. Then the filtered flue gas produced by combustion was measured by flue gas analyzer. The concentrations of NO, NO_2 and O_2 were analyzed by the gas analyzer (Testo 350) which the estimated uncertainty limits of ±0.8%. In order to investigate the effect of alkali metal sodium on the NO_x formation characteristic at different atmospheres and temperatures, the reaction atmosphere are O_2/N_2, O_2/Ar and O_2/CO_2, and the reaction temperature are 1173, 1373, 1573 and 1773 K. The experimental conditions are shown in Table 1.

Table 1 Experimental conditions

Sample	Additive amount /%	Atmosphere	Temperature/ K
DJJM	-	$N_2/Ar/CO_2$	1173/1373/ 1573/1773
DJJM+ NaCl	1%/5%/10%	$N_2/Ar/CO_2$	1173/1373/ 1573/1773

2.2 Coal preparation

The Jiangjunmiao (JJM) coal with a particle size of 50-100 μm was used in the study. The elemental and proximate characteristics are shown in Table 2. The JJM coal samples were dried at 105 ℃ for 24 h. In order to investigate the effect of loading amount of alkali metal sodium on the NO_x formation characteristic, the coal samples were acid washed with dilute (1 mol·L^{-1}) hydrochloric acid solution. Then the dipping method was used to add Na to acid-eluted coal (DJJM) through NaCl solution. The loading amount of NaCl are 1%, 5% and 10%.

Table 2 The proximate and ultimate analyses of coal

Coal	Proximate analysis（wt%, d）				
	V		A		FC
JJM	36.82		7.43		55.75
	Ultimate analysis（wt%, d）				
Coal	C	H	N	S	O
JJM	74.91	3.76	0.78	0.56	12.56

2.3 Calculation

The conversion rate of fuel N-NO can be obtained by

$$X_{\text{NO-N}} = \frac{\int_{t_0}^{t_0+\Delta t} F \cdot C_{\text{NO}} \cdot 10^{-6} \cdot dt / 22.4}{M_{\text{N}} / 14} \times 100,\quad \% \qquad (1)$$

where C_{NO} is the concentration of NO /μL·L^{-1}, F is the volume flow of flue gas /L·s^{-1}, t_0 is the Initial time, Δt is measure time /s, M_N is nitrogen content in coal sample /g, which can be calculated by

$$M_{\text{N}} = M \cdot N_{\text{d}} \cdot \frac{1}{1+X_{\text{a}}} \qquad (2)$$

where M is the mass of sample / g, N_d is the nitrogen content of the DJJM at a dry basis, X_a is the mass ratio of the alkali metal compound loaded in the coal sample.

3. RESULTS AND DISCUSSION

3.1 Effect of loading amount

Fig.2 shows the NO releasing during the combustion of the de-ashed coal samples (DJJM) and the coal samples with different loading amounts of NaCl at 1573 K. The release trends are consistent. A peak of NO releasing is appeared soon after the coal sample burning. Then NO releases slowly. Subsequently, a small NO release peak is appeared. The two peaks are named volatile nitrogen releasing peak and char nitrogen releasing peak, respectively. Compared with DJJM, the burnout time loaded with NaCl is significantly shorter. This is because the adding of Na reduces the reaction activation energy of the nitrogen-containing functional groups in the coal, accelerating the burnout of pulverized coal. The burnout time is shortened with the increase in the loading amount of NaCl. When the loading amount of NaCl is increased from 1% to 10%, the burn out time is shortened from 296 to 240 s, which is about 18.9% shorter.

Table 3 shows the peak values of volatile nitrogen and conversion rates of N-NO for the de-ashed coal and the coal with different loading amounts of NaCl at 1573 K. With the increase of adding amount of NaCl, the peak value of volatile nitrogen decreases from 109 to 65 $\mu L \cdot L^{-1}$ (a decrease of 40.37%). NaCl may inhibit the conversion of fuel nitrogen to volatile nitrogen. Literature [4] has shown that alkali metal sodium can inhibit the release of precursor HCN during combustion and promote the formation of N_2 from the interaction of NO and HCN.

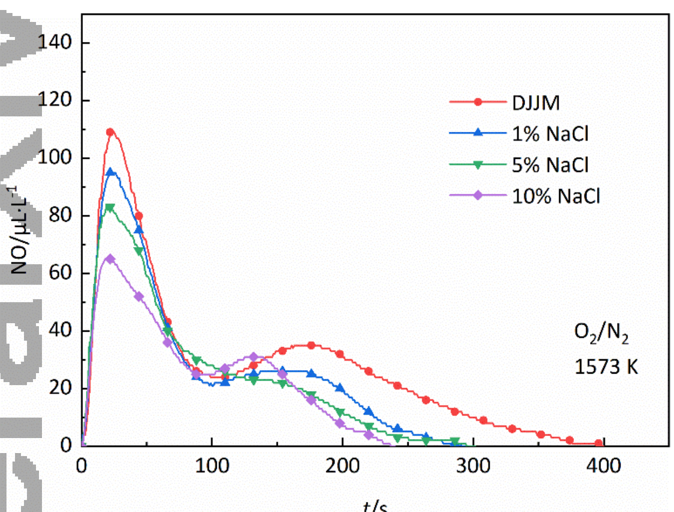

Fig. 2 The effect of the loading amount on the NO releasing

The loading of NaCl also reduces the conversion rate of fuel N-NO during pulverized coal combustion. The sodium additive has an inhibitory effect on the formation of NO during combustion. The addition of Na is beneficial to promote the heterogeneous reduction of NO on the char surface. The reduction reaction is as follows:

$$C + 2NO \rightarrow N_2 + CO_2 \quad (3)$$

$$C(O) + NO \rightarrow \frac{1}{2} N_2 + CO_2 \quad (4)$$

$$C + 2NO \rightarrow N_2O + CO \quad (5)$$

$$C + 2NO \rightarrow N_2 + CO_2 \quad (6)$$

where C(O) is a surface complex formed by oxygen on the char surface.

Table 3 Peak value of volatile nitrogen and conversion rate of N-NO at 1573 K

Sample	Peak value of volatile nitrogen /$\mu L \cdot L^{-1}$	$X_{NO\text{-}N}$/%
DJJM	109	10.61
DJJM+1%NaCl	95	8.24
DJJM+5%NaCl	83	8.67
DJJM+10%NaCl	65	8.74

It should be noted that the conversion rate of N-NO increases when the loading amount of NaCl increases from 1% to 10%. This is because NO in the flue gas is unable to contact with the activated carbon ions due to the blocking of the pores by excess NaCl. Hence, the heterogeneous reduction reaction between char and NO weakens, resulting in the increase of N-NO conversion rate.

3.2 Effect of temperature

Figs. 3 and 4 show the peak values of volatile nitrogen and conversion rates of N-NO at different temperatures. The combustion reaction becomes intense as the combustion temperature increases. Hence, the amount of N released in the form of volatile matter increases with the temperature, resulting in the increase in the peak value of volatile nitrogen. The increment of the peak value becomes smaller as the adding amount of NaCl increases. The peak value of volatile nitrogen for DJJM increases from 40 to 210 $\mu L \cdot L^{-1}$ when the temperature increases from 1173 to 1773 K, whereas the peak value increases from 28 to 133 $\mu L \cdot L^{-1}$ for the coal added with 10% NaCl. The increment of the peak value of volatile nitrogen released from coal samples loaded with NaCl is significantly lower than that of DJJM.

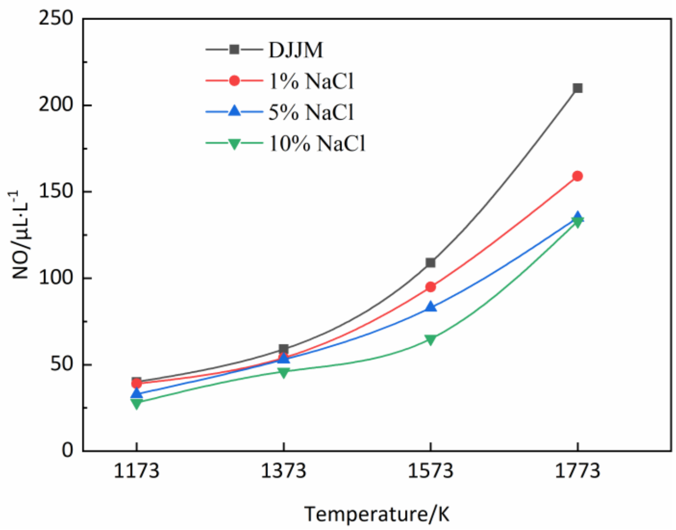

Fig. 3 Peak value of volatile nitrogen at different temperatures

As shown in Fig. 4, the adding of NaCl can reduce the conversion rate of N-NO at different temperatures. The conversion rate of N-NO of coal sample loaded with 1% NaCl is up to 45.8% when the temperature is 1773 K. The reason may be that the alkali metal compound consumes the active oxide groups OH and H at high temperature (above 1700 K), inhibiting the formation of NO.

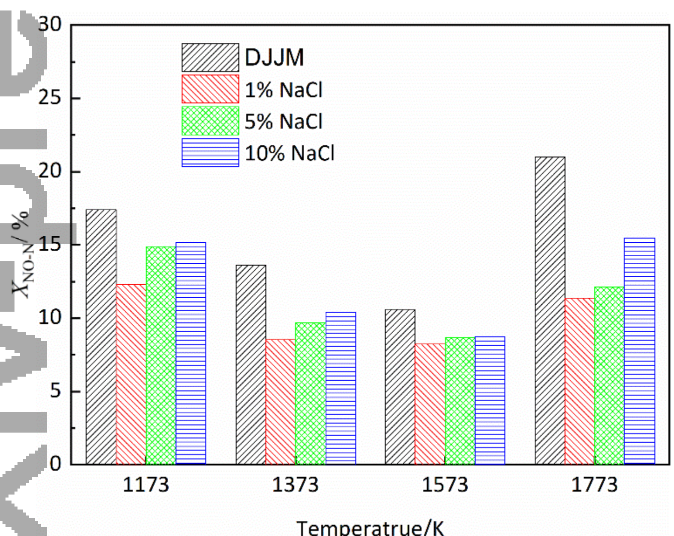

Fig. 4 The conversion rate of N-NO at different temperatures

3.3 *Effect of atmosphere*

Fig. 5 shows the effect of alkali metal sodium additive on NO releasing under different atmospheres at 1573 K when the loading amount of NaCl is 5%. Under O_2/N_2 and O_2/Ar atmospheres, the NO releasing curves of the coal sample loaded with NaCl are almost consistent with that of the DJJM. The loading of NaCl reduces the peak value of volatile nitrogen and the burnout time. In the O_2/CO_2 atmosphere, the total amount of NO is lower than that of in O_2/N_2 and O_2/Ar atmospheres due to the high concentration of CO. CO not only catalyzes the reduction reaction between char and NO, but also directly reacts with NO on the surface of unburned char to convert NO to N_2. A reducing atmosphere is formed on the particle surface in O_2/CO_2 atmosphere, thereby promoting the eutectic of surface minerals and alkali metal compounds. NO in the flue gas cannot contact with the activated char ions due to the blocking of the pores on the char surface by the eutectic. Therefore, the heterogeneous reduction reaction between the char and NO weakens, resulting in the increase in the peak value of char nitrogen.

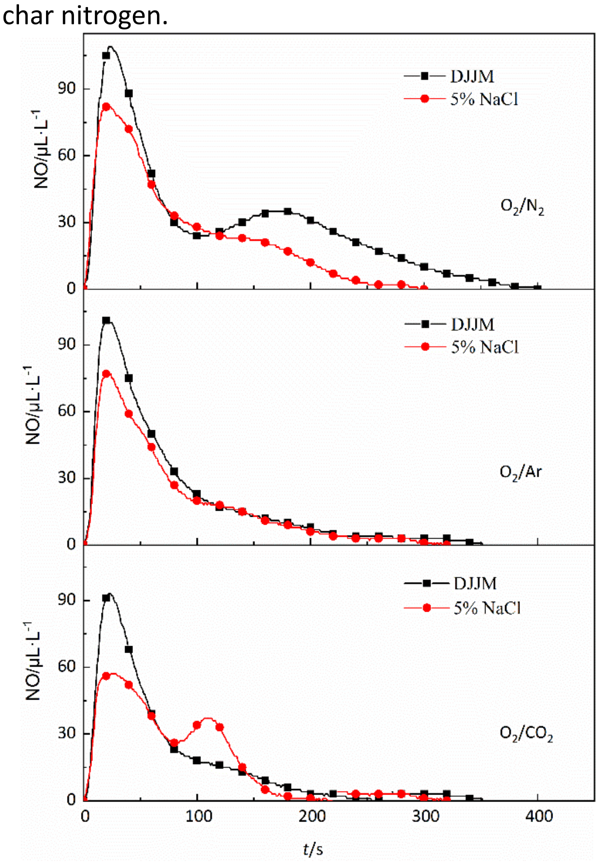

Fig. 5 Effects of combustion atmosphere on NO releasing

4. *CONCLUSIONS*

The effect of alkali metal sodium on the NO_x formation characteristic of pulverized coal combustion is investigated in the study. The addition of NaCl can inhibit the formation of NO in pulverized coal combustion. The peak value of volatile nitrogen decreases with the increase in the adding amount of NaCl and increase with the temperature. In addition, in O_2/CO_2 atmosphere, the conversion rate of N-NO of coal sample loaded with 1% NaCl is up to 45.8% when the temperature is 1773 K.

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