Journal of Environmental Sciences Vol. 13, No. 1, pp. 75—78, 2001 ISSN 1001—0742 CN11—2629/X

Article ID: 1001-0742(2001)01-0075-04 **CLC number**: X13 **Document code**: A

Role of barium nitrate on the sulfur fixation of calcium oxide

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Abstract: In this paper, the effect of $Ba(NO_3)_2$ on the efficiency of sulfur fixation of calcium oxide during coal combustion was studied. The results showed that addition of barium nitrate to the CaO can enhance the sulfur removal rate of CaO significantly. The *X*-ray diffraction spectrum of residual ash of coal added some sulfur fixative expressed that Ba^{2+} can form a compound of Ba-Al-Si-O which encloses the $CaSO_4$ to prevent it's decomposition, so Ba^{2+} can improve the action of sulfur fixation of CaO. The combustion character of the original coal and original coal added sulfur fixative was researched with thermal-gravity analyzer and the results expressed that adding some sulfur fixative to the coal will make the combustion character of coal change little.

Key words: coal combustion; sulfur fixation; calcium oxide; barium nitrate

Introduction

Coal is an important fuel in China. Large quantities of SO_2 produced in coal combustion have caused the air pollution and further the formation of acid rain in some areas, so reducing the SO_2 emission is very important in China. Generally, calcium compounds are used as sulfur fixative due to their abundance in nature and low cost in practice. The results of some researches (Xiao, 1994) showed that when the combustion temperature is below 800℃, the CaO will react with SO_2 as follows:

$$CaO + SO_2 + 1/2O_2 \rightarrow CaSO_4. \quad (1)$$

When the temperature rise above 800 ℃, another reaction will occur

$$CaSO_4 \rightarrow CaO + SO_2 + 1/2O_2. \quad (2)$$

In fact, the temperature in the coal-fired industrial boiler often reaches 1200℃, so single CaO can not fix SO_2 efficiently. Researches that some people have done showed that some additives such as Na (Bake, 1987), Cr (Fu, 1994) and Si, Fe (Chang, 1998) can delay $CaSO_4$ decomposition and improve the sulfur fixation of CaO. In this paper we try to study the effect of barium nitrate on the efficiency of sulfur fixation of CaO to illustrate the effect of the same group element on the sulfur fixation of CaO.

1 Experimental section

1.1 Materials and apparatus

1.1.1 Materials

Coal sample: Cf 68.59%, Sf 3.03%, Hf 4.48%, Nf 1.17%, Af 34.17%, Vf 13.88%, Qf 28.33MJ, CaO(A.R; Beijing Chemical Factory); $Ba(NO_3)_2$(A.R.; The Third Chemical Factory of Tianjin).

1.1.2 Apparatus

CS-GD1 Photo-Electronic SO_2 Analyzer; Japan DT-40 Thermal Gravity Analyzer; Japan D/Max-3B *X*-ray Diffraction Analyzer.

1.2 Experimental methods

1.2.1 Comparative experiment about efficiency of sulfur fixation by CaO and $Ba(NO_3)_2$

Ten kinds of sulfur fixative were produced under the condition of keeping the total molar number of CaO and $Ba(NO_3)_2$ constant and changing their molar ratio. Every fixative was mixed with fixed weight coal and then the mixture was ground into powder and homogenized. Some mixture was put into a quartz ship which was sent into the furnace when the furnace temperature was raised to 1000℃. Then the furnace temperature was programmed to raise to 1200 ℃ and stationed here for 30 minutes. The SO_2 produced in the process of combustion was measured by CS-GD1 Photo-Electronic Analyzer. At the same time, the SO_2 produced by the same weight coal was also measured at the same condition, according to which efficiency of sulfur fixation was calculated.

1.2.2 The effect of $Ba(NO_3)_2$ on the efficiency of sulfur fixation of CaO

In order to determine the effect of $Ba(NO_3)_2$ on the efficiency of sulfur fixation of CaO, different quantities of $Ba(NO_3)_2$ were added to the same amount of CaO to get a series of fixative. Each of these fixatives was added to the coal with Ca/S molar ratio as 2, and the efficiency of them were determined as the same process as 2.1.

1.2.3 The effect of temperature on the efficiency of sulfur fixation

Three kinds of samples were prepared: (1) Sample 1: original coal; (2) sample 2: original coal + CaO (Ca/S=2); (3) sample 3: original coal + CaO (Ca/S=2) + $Ba(NO_3)_2$ (0.4% of original coal).

At the room temperature, the quartz ships loading these three samples were respectively sent into the tube furnace, then the furnace temperature was raised to 1200 ℃ at certain speed. The quantity of SO_2 produced in every temperature period was recorded.

1.2.4 The determination of residual constituent

After thoroughly combustion, the residual ash of sample 3 was collected and analyzed with *X*-ray diffraction spectrum to determine its constituent.

1.2.5 The effect of sulfur fixative on the coal combustion character

The combustion character of sample 1 (only original coal) and sample 3 (original coal with sulfur fixative) described above(1.2.3) was analyzed with DT-40 analyzer to determine whether there are significant difference between these two samples.

2 Results and discussion

2.1 The efficiency of sulfur fixation under different Ba/Ca molar ratio

Table 1 Effect of different Ba/Ca molar ratio on the efficiency of sulfur fixation

Number	Ba/Ca (molar ratio)	Efficiency of sulfur capture, %	Number	Ba/Ca (molar ratio)	Efficiency of sulfur capture, %
1	∞	94.9	6	1:2	78.7
2	10:1	92.3	7	1:4	75.1
3	5:1	93.6	8	1:5	69.2
4	4:1	89.9	9	1:10	67.6
5	1:1	85.1	10	0	18.9

The efficiency of sulfur fixation under different Ba/Ca molar ratio is listed in Table 1. From Table 1 we can see that the higher of the Ba/Ca molar ratio, the higher of the efficiency of sulfur fixation. This showed that the Ba is more efficient than Ca in sulfur fixation at the same molecule. The reason turning out this result is that both Ba^{2+} and Ca^{2+} can react with S in the process of coal combustion to form $BaSO_4$ and $CaSO_4$ respectively, but $BaSO_4$ beginning to decompose at 1580℃ (Shanghai Chemical Reagent Purchasing and Supplying Office of Chinese Medical Incorporation, Reagent Handbook, 1984) is more stable than $CaSO_4$ beginning to decompose at 800℃. From Table 1 we also can see that even adding low ratio of Ba^{2+} to CaO, the efficiency of sulfur fixation of CaO can increase very high. For the coal added CaO and few quantity of $Ba(NO_3)_2$, even if all of the adding Ba^{2+} react with S to form stable $BaSO_4$, the efficiency of sulfur fixation can not rise so high according to the theoretical calculation. Thus, it suggested that the adding Ba^{2+} not only can react with S directly, but also will improve the sulfur fixation of CaO.

2.2 Effect of the adding amount of $Ba(NO_3)_2$ on the efficiency of sulfur fixation

When the amount of CaO is fixed at Ca/S molar ratio as 2, the efficiency of sulfur fixation of

CaO will rise with the amount of Ba^{2+} added to it. Originally, the efficiency of sulfur fixation rises very quickly with the adding Ba^{2+}, then slowly. When the adding amount of $Ba(NO_3)_2$ reaches 0.4% of coal, the efficiency of sulfur fixation is stable at about 80% (Fig. 1).

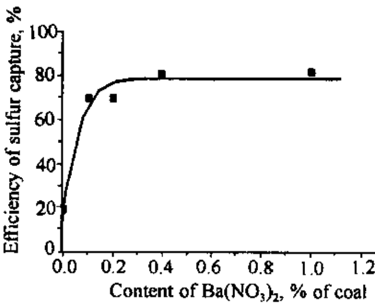

Fig. 1 The relationship between content of $Ba(NO_3)_2$ and the efficiency of sulfur capture

2.3 The effect of temperature on the efficiency of sulfur fixation

The result is shown in Fig. 2. The curves of cumulative SO_2 emission of sample 1 (original coal), sample 2 (original coal + CaO(Ca/S = 2)), and sample 3 (original coal + CaO (Ca/S = 2) + $Ba(NO_3)_2$(0.4%)) are significantly different. The sample 2 has a low cumulative ratio of SO_2 emission at lower temperature compared with sample 1, but it has almost the same cumulative ratio of SO_2 emission as sample 1 when the temperature reaches 1200 ℃. This means that CaO has high efficiency of sulfur fixation at low temperature, but the efficiency decreases with the temperature rising. Due to the temperature of practical boiler often reaches 1200 ℃, so CaO has low efficiency of sulfur fixation in practice. Sample 3 has a low cumulative ratio of SO_2 emission not only at low temperature, but also at high temperature. This expresses that adding Ba^{2+} can improve the efficiency of sulfur fixation notably in all temperature period.

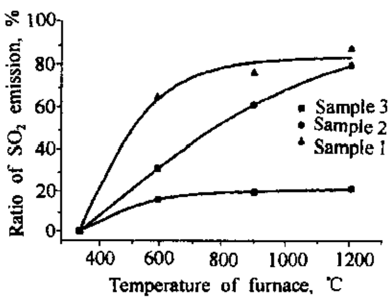

Fig. 2 The relationship between temperature and ratio of SO_2 emission sample 1: original coal; sample 2: original coal + CaO (Ca/S = 2); sample 3: original coal + CaO (Ca/S = 2) + 0.4% $Ba(NO_3)_2$

2.4 The probable mechanism of sulfur fixation of CaO with $Ba(NO_3)_2$

The *X*-ray diffraction spectrum of residual ash of sample 3 is shown in Fig. 3. According to Fig. 3, sulfur is fixed in the residual ash as $CaSO_4$ and Ba exits in the residual ash as Ba-Al-Si-O compound, whose molar formula is not determined by *X*-ray diffraction spectrum yet. Thus it is turned out that the improving action of Ba^{2+} to the sulfur fixation of CaO is not to form $BaSO_4$ directly, but to form a complicated compound which do not contain sulfur. The probable mechanism of sulfur fixation of CaO with $Ba(NO_3)_2$ is that the SO_2 produced during coal combustion will react with CaO to form $CaSO_4$ that is enclosed by compound of Ba-Al-Si-O produced at the same time. The compound of Ba-Al-Si-O has high melting point, so it can form a stable and dense layer in the surface of $CaSO_4$. This layer can prevent the emission of SO_2 produced in the decomposition of $CaSO_4$ at high temperature and cause the partial pressure of SO_2 around

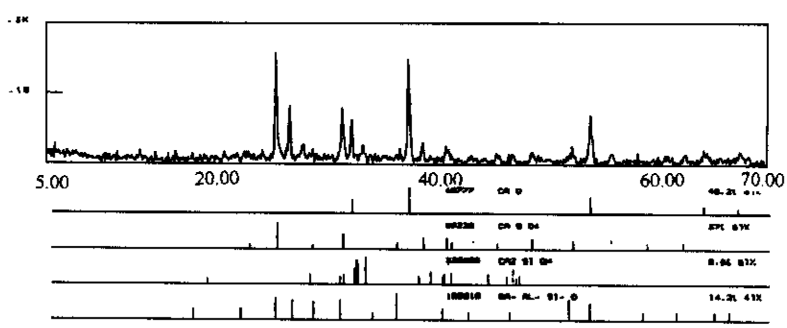

Fig. 3 *X*-ray diffraction spectrum of residual ash of sample 3

$CaSO_4$ rising high, which can prevent the decomposition of $CaSO_4$ according to Equation (2).

2.5 The effect of sulfur fixative on the coal comtustion character

The thermo-gravity characters of sample 1 and sample 3 are shown in Fig. 4 and Fig. 5 respectively. We can see that no matter adding the sulfur fixative or not, the burning point and heat discharge of the coal have no significant difference. So we can say that this kind of sulfur fixative has little effect on the coal combustion character.

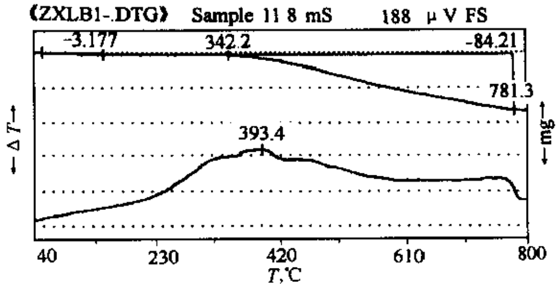

Fig. 4 The TDG curve of sample 1

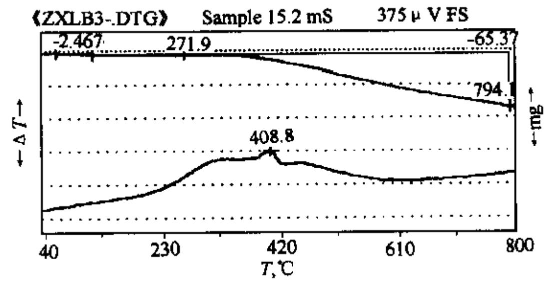

Fig. 5 The TDG curve of sample 3

3 Conclusion

$Ba(NO_3)_2$ has stronger capability of sulfur fixation. The more $Ba(NO_3)_2$ is added to the coal, the higher efficiency of sulfur fixation is seen.

$Ba(NO_3)_2$ as additives can improve the action of sulfur fixation of CaO.

The probable mechanism of the improving action of $Ba(NO_3)_2$ to sulfur fixation of CaO is that Ba^{2+} will form a stable compound of Ba-Al-Si-O which encloses the $CaSO_4$ and prevents its decomposition.

The effect of the sulfur fixative on the combustion characters of coal is little.

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(Received for review December 21, 1999. Accepted March 4, 2000)