

Effect of CuO on the efficiency of sulfur capture of Ca-based compounds during coal combustion

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Abstract: The efficiency of sulfur capture of CaO, Ca(OH)₂ and CaCO₃ as well as the effect of CuO on them were studied. Results showed that the efficiency of sulfur capture of Ca(OH)₂ is the highest among these three compounds. When CuO was used with each of CaO, Ca(OH)₂ and CaCO₃ at the same time, the efficiency of all of them would rise, and that of Ca(OH)₂ raise most. The efficiency of sulfur capture of Ca(OH)₂ with CuO is 14.4% higher than that without CuO.

Keywords: CuO; Ca(OH)₂; sulfur capture

Introduction

Coal is an important fuel in China. Large quantities of SO₂ produced during coal combustion have caused the air pollution and further the formation of acid rain in some areas. So reducing the SO₂ emission is very important in China. Many researches have been done to find how to reduce the SO₂ emission during coal combustion. In-bed desulfurization was proved to be one of the efficient ways. Due to their low cost, Ca-based compounds were often used to fix sulfur during coal combustion. But the efficiency of sulfur capture of Ca-based compounds is not high at high temperature. In order to rise the efficiency of sulfur capture of Ca-based compounds, many researches have been done. The results showed that when some material such as Fe₂O₃, V₂O₅ (Yang, 1987), Fe(NO₃)₂ (Desal, 1983), SiO₂ and Fe₂O₃ (Xiao, 1995; Chang, 1998), Ba(NO₃)₂ (Liu, 2001), SrCO₃ (Xiao, 1994), Na (Zhou, 1997; Fu, 1994; Slaughter, 1986), K (Zhou, 1997) etc. was added to coal with Ca-based compounds, the efficiency of sulfur capture of Ca-based compounds will become higher. In this paper, CuO as additive was investigated to show its effect on the efficiency of sulfur capture of Ca-based compounds.

1 Experiment

1.1 Materials and apparatus

1.1.1 Materials

Coal sample: From Dayugou Mine of Gongyi County, containing S of 2.46%; CaO(A.R): Beijing Chemical Factory; CaCO₃(A.R): Beijing Chemical Factory; Ca(OH)₂(A.R): Beijing Chemical Factory.

1.1.2 Apparatus

CS-GD1 photo-electronic SO₂ analyzer from Luoyang Analytic Instrument Factory; D/Max-3B X-ray diffraction analyzer from Rigaku Corporation of Japan; DT-40 Thermal-gravity analyzer from Shimadzu Corporation of Japan.

1.2 Experimental methods

1.2.1 Experimental equipment

The experimental equipment is shown in Fig.1. In the experiment, the temperature controller was started first to make the temperature of the tube furnace reach the set temperature. Before the ceramic boat containing sample was sent into the tube furnace from the left of the tube furnace, the air pump started to work at the airflow of 0.05 L/min. Meanwhile, the SO₂ analyzer began to work to analyze the amount of SO₂ emitted from the tube furnace during the coal combustion, and then the emission ratio and capture ratio of SO₂ were calculated. Duplicated tests were carried out in all of our experiments, and every experiment result reported in this paper was taken the mean of that of duplicated tests.

1.2.2 Effect of CuO on the efficiency of sulfur capture of Ca(OH)₂, CaO and CaCO₃

The coal was fortified with each of sulfur fixative of Ca(OH)₂, CaO and CaCO₃, whose amount were controlled as the

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molecular ratio of Ca to S (in the coal) as 2 respectively. Four series of mixtures were obtained by putting different amounts of CuO into the fortified coal and the raw coal. These mixtures were ground into powder and homogenized. Thus four series of experimental samples were produced as follows. 1 # Coal + different amount of CuO; 2 # Coal + CaO ($\text{Ca/S} = 2$) + different amount of CuO; 3 # Coal + CaCO_3 ($\text{Ca/S} = 2$) + different amount of CuO; 4 # Coal + Ca(OH)_2 ($\text{Ca/S} = 2$) + different amount of CuO.

Each sample was put into ceramic boat and sent into the tube furnace when the temperature of tube furnace reached 1040°C , where the boat was stayed continuously for 30 min to make the coal burn thoroughly. The SO_2 produced during coal combustion was measured with CS-GD1 photo-electronic analyzer and the efficiency of sulfur capture of these fixatives was calculated.

1.2.3 The effect of temperature on the efficiency of sulfur capture of Ca(OH)_2 -CuO fixative

The sample containing coal and Ca(OH)_2 -CuO fixative ($\text{Ca/S} = 2$, $\text{CuO} = 0.3\%$ coal) produced as in section 1.2.2 was put into ceramic boat which was sent into the tube furnace when the temperature of the tube furnace reached 880°C , 960°C , 1040°C , 1120°C and 1200°C respectively, where the boat was stayed continuously for 30 min. The SO_2 produced in the process was measured with CS-GD1 photo-electronic analyzer, and the efficiency of sulfur capture of Ca(OH)_2 -CuO fixative at different temperature was calculated.

The same sample as above was put into ceramic boat and sent into tube furnace at room temperature, then the temperature of the tube furnace was raised to 880°C , 960°C , 1040°C , 1120°C and 1200°C at the speed of 40°C/min respectively. The ceramic boat was stayed continuously in the tube furnace for 20 min after the temperature of the tube furnace reached the set temperature. The SO_2 produced in the process was measured and the efficiency of sulfur capture of Ca(OH)_2 -CuO fixative was calculated.

1.2.4 The determination of residual constituent

Residual ash 1: The sample containing coal and Ca(OH)_2 -CuO fixative ($\text{Ca/S} = 2$, $\text{CuO} = 0.3\%$ coal) produced as in the section 1.2.2 was put into ceramic boat which was sent into tube furnace at 1040°C , and stayed continuously there for 30 min. After thorough combustion, the residual ash was collected and analyzed with X-ray diffraction analyzer to determine its constituent.

Residual ash 2: The same sample as above was put into ceramic boat which was sent into tube furnace at room temperature, and stayed there continuously for 20 min after the temperature of the tube furnace was raised to 1200°C at the speed of 40°C/min . The residual ash was collected and its constituent was analyzed.

Residual ash 3: The same sample as above was put into ceramic boat which was sent into the tube furnace at 1200°C and stayed there for 30 min. The residual ash was collected to analyze its constituent.

1.2.5 The effect of sulfur fixative on the coal combustion character

The combustion character of coal (sample 1) and coal with sulfur fixative (sample 2) were analyzed with DT-40 thermal-gravity analyzer to determine whether the fixative has significant effect on the coal combustion. The sample was heated in the air condition and the rising rate of temperature of the analyzer was controlled as 8.0°C/min . Meanwhile, the reference sample of Al_2O_3 was heated at the same condition. The gravity changes of sample and temperature difference (ΔT) between the sample and the reference sample with the increase of temperature were recorded.

2 Results and discussion

2.1 The effect of CuO on the efficiency of sulfur capture of Ca-based compounds

The results are labeled in Table 1. From Table 1 we can see that: (1) CuO has no capacity to fix sulfur during coal

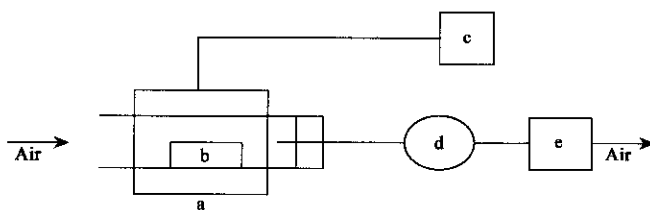


Fig.1 The schematic diagram of experimental equipment

a: tube furnace; b: ceramic boat; c: temperature controller; d: SO_2 analyzer; e: air pump

combustion, by contraries it can improve SO₂ emission. What result in these will be explained in section 2.3. (2) Among these three sulfur fixatives, the capacity of sulfur capture of Ca(OH)₂ is the strongest and that of CaCO₃ is the weakest. (3) CuO can improve the efficiency of sulfur capture of CaCO₃, CaO and Ca(OH)₂ and the improvement to that of Ca(OH)₂ is the most. The efficiency of sulfur capture of Ca(OH)₂-CuO fixative can reach 83.3%, which is 14.4% higher than that of Ca(OH)₂ only. So we chose Ca(OH)₂-CuO as fixative to do next experiments.

Table 1 The effect of CuO on the efficiency of sulfur capture of Ca-based compounds

CuO		0.0	0.1	0.3	0.5	0.7	0.9	1.0
Efficiency of sulfur capture, %	A	23.3	17.8	17.8	10.0	18.9	20.0	13.3
	B	53.3	53.3	55.6	61.1	63.3	56.7	56.3
	C	40.0	48.9	52.2	47.8	42.3	48.9	50.0
	D	68.9	75.6	83.3	78.9	80.0	75.6	74.5

Notes: A. Coal; B. Coal + CaO(Ca/S = 2); C. Coal + CaCO₃(Ca/S = 2); D. Coal + Ca(OH)₂(Ca/S = 2)

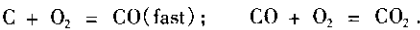
2.2 The effect of temperature on the efficiency of sulfur capture of Ca(OH)₂-CuO fixative

The results are labeled in Table 2. From Table 2 we can see that sample combustion under designed temperature or from room temperature to design temperature played an important role on the efficiency of sulfur capture of Ca(OH)₂-CuO fixative, especially under high temperature. When temperature is 880℃, 960℃ and 1040℃, the efficiency of sulfur capture following way 1 that ceramic boat was directly sent into the tube furnace at the designed temperature is similar to that following way 2 that ceramic boat was sent into the tube furnace at room temperature and then the temperature was raised to the designed point. But at the temperature of 1120℃, and 1200℃, the efficiency of sulfur capture following way 2 or way 1 is markedly different. Especially at the temperature of 1200℃, the efficiency of way 2 reach 84.4%, which is much higher than that following way 1 that reaches only 17.8%. These will be explained in next section.

Table 2 The effect of temperature on the efficiency of sulfur capture of Ca(OH)₂-CuO fixative

Temperature		880℃	960℃	1040℃	1120℃	1200℃
Efficiency of sulfur capture, %	Way 1	90.0	85.6	83.3	71.1	17.8
	Way 2	88.9	88.9	86.7	84.4	84.4

sulfur existing in coal are fixed in the residual ash in the form of CaSO₄ during coal combustion; CuO did not form any new compound containing S, but turned into Cu₂O in Figs. 2 and 4, CaCu₂O₃ in Fig.3. These results showed that the role of CuO in the fixative is not to fix sulfur directly, but to improve the capacity of sulfur capture of Ca(OH)₂. According to the research done by Chang(Chang, 1986), the quantity of CO emission would become less when CuO was added to the coal before it combustion. During the coal combustion, C will react with O₂ as follows:



And S contained in the coal will be oxidized to SO₂, and SO₂ can react with Ca(OH)₂.

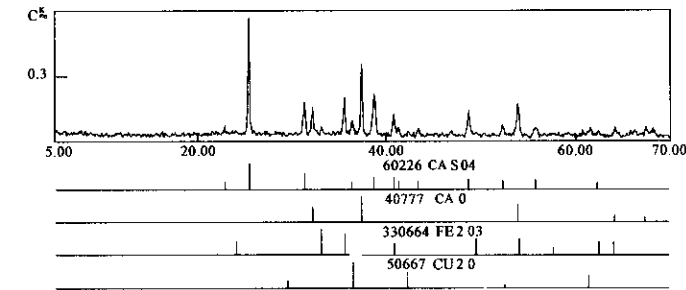


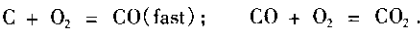
Fig.2 The X-ray spectrum of residual ash 1

2.3 The probable mechanism of sulfur capture of Ca(OH)₂-CuO fixative

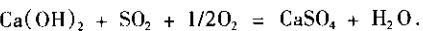
The X-ray diffraction spectrum of residual ash 1, residual ash 2 and residual ash 3 are shown in Figs.2, 3 and 4, respectively.

From these three spectrums we can see that

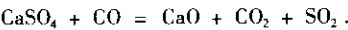
sulfur existing in coal are fixed in the residual ash in the form of CaSO₄ during coal combustion; CuO did not form any new compound containing S, but turned into Cu₂O in Figs. 2 and 4, CaCu₂O₃ in Fig.3. These results showed that the role of CuO in the fixative is not to fix sulfur directly, but to improve the capacity of sulfur capture of Ca(OH)₂. According to the research done by Chang(Chang, 1986), the quantity of CO emission would become less when CuO was added to the coal before it combustion. During the coal combustion, C will react with O₂ as follows:



And S contained in the coal will be oxidized to SO₂, and SO₂ can react with Ca(OH)₂.



When temperature rise above 800℃, CaSO₄ will react with CO as follows(Yang, 1987):



So CO will improve the decomposition of CaSO₄ and cause the drop of the efficiency of sulfur capture of Ca-based compounds. Because CuO added to the coal led to the less emission of CO during coal combustion, the CO density around CaSO₄ become lower, which led to the

decomposition of CaSO_4 slowly. So we suggest that the probable mechanism of sulfur capture of $\text{Ca}(\text{OH})_2\text{-CuO}$ fixative is that CuO added to the coal can quicken the oxidization of CO and make the reaction rate of decomposition of CaSO_4 slow. This is the same reason why CuO can improve the SO_2 emission when no other sulfur fixatives exit in the coal—the quicker oxidization of CO can lead to the high combustion temperature which result in the faster and more SO_2 emission during coal combustion. According to the results of section 2.2, the efficiency following way 2 is much higher than that following way 1 especially at high temperature. The reasons caused these may be that when coal was directly sent into tube furnace at high temperature, coal would burn rapidly to produce a large quantity of CO, which led to the speedy decomposition of CaSO_4 . The higher of the temperature, the larger quantity of CO produced, and the lower efficiency of sulfur capture. When coal was sent into tube furnace at room temperature and then the temperature was raised to the designed point, the coal burn slowly and the quantity of CO emitted was little, which led to the slow decomposition of CaSO_4 and the higher efficiency of sulfur capture. Meanwhile, element Cu existing in form of Cu^{2+} in residual ash 2 and in form of Cu^+ in residual ash 1 and residual ash 3 can also prove that there is more CO produced during coal combustion in way 1 than in way 2. So the efficiency of sulfur capture of $\text{Ca}(\text{OH})_2\text{-CuO}$ fixative is lower following way 1 than that following way 2.

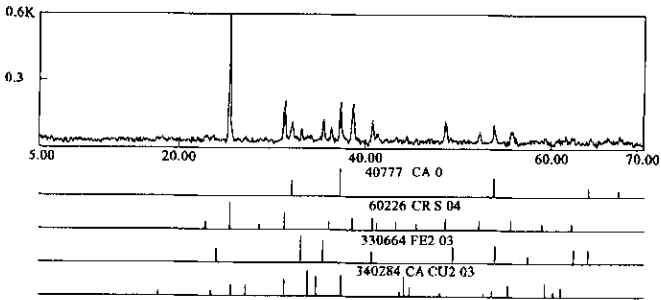


Fig.3 The X-ray spectrum of residual ash 2

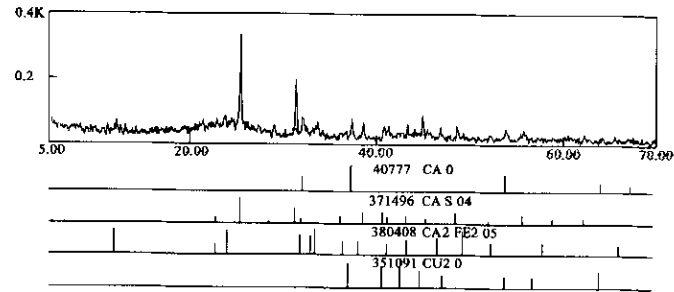


Fig.4 The X-ray spectrum of residual ash 3

2.4 The effect of sulfur fixative on the coal combustion character

The thermo-gravity curves of coal and coal with $\text{Ca}(\text{OH})_2\text{-CuO}$ fixative are shown in Figs. 5 and 6 respectively. From these two figures we can see that the gravity loss ratio of sample 1 and sample 2 were 90.68% and 74.63% respectively. Based on the fact that in the sample 2 11.38% $\text{Ca}(\text{OH})_2$ ($\text{Ca:S} = 2$) and 0.3% CuO were added to the coal, the practical gravity loss ratio of the coal in the

sample 2 was calculated as 83.3%. And considering that 2.46% of S in the coal was captured in the sample 2, the difference of gravity loss ratio between sample 1 and sample 2 was not significant. On the other hand, the volatile matter,

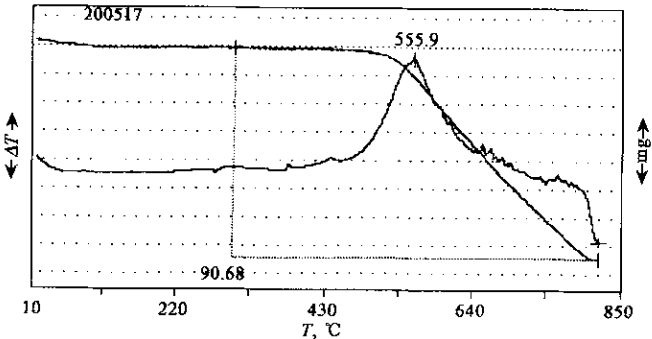


Fig.5 The thermo-gravity curves of coal

which cause the violent combustion of coal, existing in sample 2 is comparatively less because of the addition of $\text{Ca}(\text{OH})_2$ and CuO , so the temperature of maximum peak of heat emission of coal mixed with $\text{Ca}(\text{OH})_2$ - CuO fixative (sample 2) was 8.7 higher than that of coal without $\text{Ca}(\text{OH})_2$ - CuO fixative (sample 1), but the little delay of the temperature of violent combustion of coal has no marked effects on the coal combustion in high temperature.

3 Conclusions

CuO has no capacity of sulfur capture, by contraries it can quicken the SO_2 emission.

Among CaO , CaCO_3 and $\text{Ca}(\text{OH})_2$, the capacity of sulfur capture of $\text{Ca}(\text{OH})_2$ is the strongest and the capacity of sulfur capture of CaCO_3 is the weakest. CuO can improve the efficiency of sulfur capture of them, especially to that of $\text{Ca}(\text{OH})_2$.

The probable mechanism of the improvement of CuO to the sulfur capture of Ca-based compounds is that CuO can quicken the oxidization of CO to prevent the decomposition of CaSO_4 .

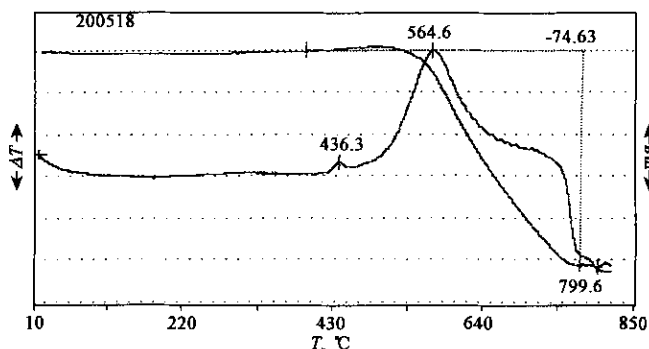


Fig. 6 The thermo-gravity curves of coal with fixative

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