

## Fe-Si promoter for sulfur capture during coal briquette combustion \*

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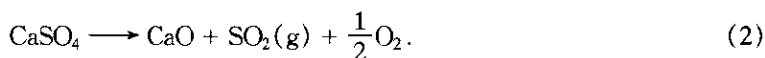
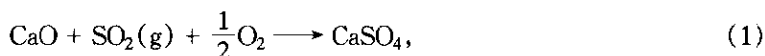
**Abstract**—In this paper, a new Fe-Si promoter for sulfur capture was proposed for coal-briquette combustion at high temperature. Various factors affecting sulfur removal efficiency, such as coal and sorbent particle size, shaping pressure, ratios of Ca: Fe:Si, combustion temperature, *etc.*, were studied. Characterization of the slag left after combustion was carried out by means of *x*-ray diffraction, energy-dispersion *x*-ray analysis and electron spectroscopy for chemical analysis. A new phase  $\text{CaFe}_3(\text{SiO}_4)_2\text{OH}$  was identified, which is thermally stable. This might explain its stabilizing role in sulfur fixation.

**Keywords:** Fe-Si promoter; sulfur capture; coal briquette combustion.

### 1 Introduction

It is well known that coal is the main energy source in China. The proportion of coal will be about 75% at the end of this century. Most equipment of coal burning for industrial use or for household utilization are medium- or small-size boilers. Industrial boilers and household stoves consume nearly two thirds of coal produced (referred to the Year Book of Energy of China, 1991) and hence are the main emitters of  $\text{SO}_2$ . To reduce  $\text{SO}_2$  emission during coal combustion, coal briquetting with calcium-based sorbents as a low-cost  $\text{SO}_2$  abatement measure (Zhuang, 1990) has been demonstrated in various parts of China to curtail  $\text{SO}_2$  emission from industrial boilers and household stoves. Calcium-based sorbents are added into coal briquettes to convert  $\text{SO}_2$  into  $\text{CaSO}_4$  and retain the sulfur in the slag after combustion.

During coal combustion, the following reactions take place (Cao, 1989):



$\text{CaSO}_4$  is not a thermally stable phase at a high combustion temperature. Reid (Reid, 1970) indicated that Equation (1) is the main reaction below  $800^\circ\text{C}$ . Direct calcium addition can only be used for low-temperature combustion appliance, in order to obtain a satisfactory efficiency of sulfur capture. If the combustion temperature exceeds  $800^\circ\text{C}$ , Equation (2) becomes dominant, and  $\text{CaSO}_4$  decomposes. Thus,  $\text{SO}_2$  is released again. Some promoters may be effective for sulfur

\* This work was supported by the National Natural Science Foundation of China(5967602)

capture, such as Na or Cr salts. Our previous experience (Xiao, 1994) showed that the addition of minute amount of Sr salt into the calcium oxide improves the sulfur removal efficiency during high temperature combustion. In this paper, minute amounts of Fe-Si oxides were added into the calcium-based sorbent as a kind of sulfur-capture promoter. A thermally stable compound  $\text{CaFe}_3(\text{SiO}_4)_2\text{OH}$  was identified, which might encapsulate the  $\text{CaSO}_4$  grains. This gives a hint to the mechanism of sulfur fixation during coal briquette combustion.

## 2 Experimental

### 2.1 Material and reagents

High-sulfur Chongqing soft coal was used throughout our study. The analysis for coal sample is given in Table 1. CaO and other promoters are chemically pure reagents.

Table 1 The analysis for Chongqing soft coal (air dried, %)

| Moisture | Volatile matter | Ash   | Sulfur | Carbon | Hydrogen | Oxygen | Nitrogen | Fixed carbon |
|----------|-----------------|-------|--------|--------|----------|--------|----------|--------------|
| 2.00     | 9.61            | 21.38 | 2.05   | 67.49  | 2.77     | 3.12   | 1.19     | 67.01        |

### 2.2 Preparation of the samples and experimental apparatus

Fig. 1 is a schematic drawing of our experimental apparatus. Weigh specific amounts of coal, sulfur capture and promoters, then mix them to form the coal briquettes with a die, dry them up at  $100^\circ\text{C}$  about 1h, put the briquette in a small porcelain boat; push the boat into a tubular heater; turn on the temperature control system,  $\text{SO}_2$  analyzer and the recorder. The boat is heated slowly to  $1200^\circ\text{C}$  and constant temperature is maintained for 1/2 hour. The air flow rate is about 5 L/min.

### 2.3 Analysis and characterization

A pulsed-fluorescence  $\text{SO}_2$  analyzer (thermoelectron corporation, model 40) was used for  $\text{SO}_2$  analysis. Crystalline phase analysis was done by using X-ray power diffraction analyzer (XRD, model Y-2). Energy-dispersive X-ray analyzer (model EDAX-9100) and electron spectroscopy for chemical analyzer (ESCA, mold ES-300) were employed for the chemical characterization of samples.

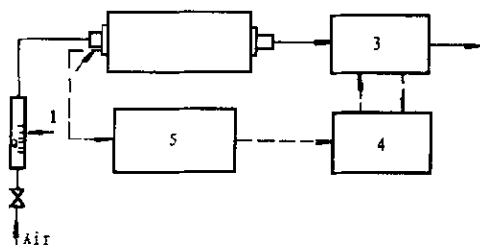


Fig. 1 Experimental apparatus

1. rotameter; 2. furnace; 3.  $\text{SO}_2$  analyzer; 4. recorder; 5. thermometer; 6. Le Chatelier thermocouple

## 3 Results and discussion

### 3.1 Bench-scale simulation of sulfur fixation at high temperatures

In order to simulate the real conditions of coal combustion, some samples were made with the

addition of the following reagents:  $\text{CaSO}_4$ ,  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{S}$ ,  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{FeS}$  and  $\text{SiO}_2 \cdot \text{H}_2\text{O}$ , as the sources of  $\text{Ca}$ ,  $\text{Fe}$ ,  $\text{Si}$ ,  $\text{S}$ , respectively.

Samples were heated slowly to  $1200^\circ\text{C}$  and maintained at that temperature for half an hour under various atmospheres: (1) ambient air; (b) compressed air from cylinder; (c) high-purity  $\text{N}_2$  from steel cylinder; (d) a blended gas from high-purity  $\text{N}_2$  and 1.15%  $\text{CO}$ . The flow rate was kept at 0.15L/min.

The slags and ashes after combustion were characterized by ESCA and XRD. Fig.2 gives the ESCA result of one typical slag of simulated samples. It showed that there were no other species of sulfur besides  $\text{SO}_4^{2-}$ . Fig 3 is the XRD diffraction patterns of two typical slag samples: (a) a simulated sample; (b) a coal briquette with  $\text{Ca-Fe-Si}$  additives. A new phase  $\text{CaFe}_3(\text{SiO}_4)_2\text{OH}$  was formed. Combined with our division's previous work (Lin, 1994), no other sulfates were detected except  $\text{CaSO}_4$  while  $\text{Ca-Fe-Si}$  oxides were the additives. Both ESCA and XRD studies support the fact that there was no new sulfur-containing phase. It can be postulated that a layer of  $\text{CaFe}_3(\text{SiO}_4)_2\text{OH}$  might be formed and the efficiency of sulfur capture was improved, since thermal decomposition of  $\text{CaSO}_4$  was prevented by the layer of  $\text{CaFe}_3(\text{SiO}_4)_2\text{OH}$ .

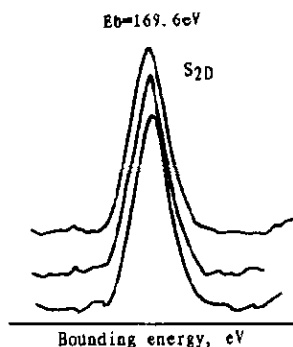


Fig.2 The ESCA pattern of sulfur species in slag samples burnt in air

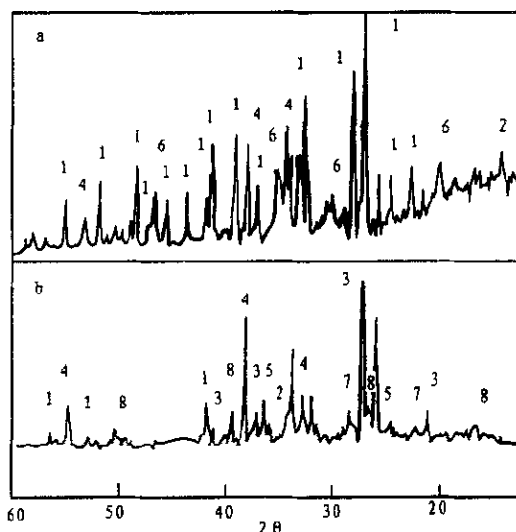


Fig.3 The XRD diffraction patterns of two typical slag samples (a) a simulated sample; (b) a coal briquette with  $\text{Ca-Fe-Si}$  additives

1.  $\text{CaSO}_4$  2.  $\text{CaFe}_3(\text{SiO}_4)_2\text{OH}$  3.  $\text{SiO}_2$  4.  $\text{CaO}$   
5.  $\text{Fe}_2\text{O}_3$  6.  $\text{Ca}(\text{OH})_2$  7. Feldspar 8.  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$

### 3.2 The effect of temperature on efficiency of sulfur fixation

Coal briquettes with the additives, pressed under  $200 \text{ kg/cm}^2$  pressure, was broken into pieces, divided into six portions and heated to  $1170^\circ\text{C}$ ,  $1180^\circ\text{C}$ ,  $1190^\circ\text{C}$ ,  $1200^\circ\text{C}$ ,  $1210^\circ\text{C}$ ,  $1220^\circ\text{C}$ , respectively. Temperature was then maintained for 15 minutes. Fig. 4 shows the evolution of sulfur dioxide during coal briquettes' combustion. It is obvious that  $\text{SO}_2$  would not be emitted unless the temperature was maintained for a long enough time. Fig. 5 shows that when the temperature exceeded  $1200^\circ\text{C}$ , the sulfur removal efficiency dropped rapidly. Below  $1200^\circ\text{C}$ , a better efficiency was obtained. There are two possible explanations of such results. One is that a

new sulfur-containing phase was formed during combustion. When temperature was higher than 1200℃, the new phase decomposed. The efficiency of sulfur capture dropped, and SO<sub>2</sub> was emitted again. Another possibility was the formation of thermally stable sulfur-free compound, which covered the surface of the CaSO<sub>4</sub> grains. In a certain range of temperature, it was stable and inhibited CaSO<sub>4</sub> decomposition effectively. According to the XRD patterns, the second situation was more potable. It seemed that diffusion rate of sulfur dioxide through the protective layer became higher at higher temperatures.

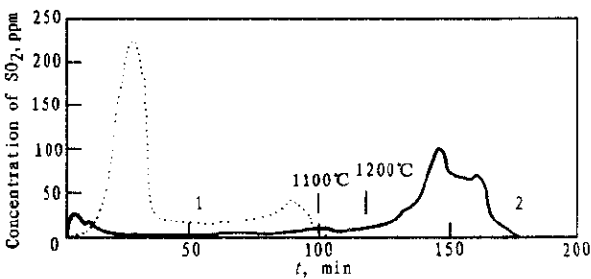


Fig.4 The curves of SO<sub>2</sub> emission during coal briquette combustion  
1. Chongqing soft coal was slowly heated to 1100℃; 2. Chongqing soft coal with CaO sorbent and Fe-Si promoter was slowly heated to 1200℃ and maintained for an hour

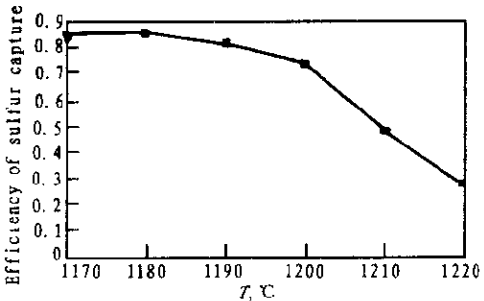


Fig. 5 The effect of temperature on efficiency of sulfur fixation (Constant temperature is maintained for 1/4 hour)

3.3 Effect of shaping pressure on efficiency of sulfur capture

Five briquette samples were made separately under different pressures. The effect of shaping pressure on efficiency of sulfur capture is shown in Fig.6. There was only a slight effect of pressure on sulfur fixation efficiency. When the sample was given a higher pressure, they were more chances for the formation of CaFe<sub>3</sub>(SiO<sub>4</sub>)<sub>2</sub>OH, which could effectively delay CaSO<sub>4</sub> decomposition.

3.4 Effect of additives

The effect of additives on the efficiency of sulfur capture is shown in Table 2. Addition of SiO<sub>2</sub> as a promoter (Sample 4) favors sulfur capture. Addition of Fe<sub>2</sub>O<sub>3</sub> alone (Sample 3) had no obvious effect on sulfur removal. Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> have a synergistic effect on sulfur removal.

| Table 2 The effect of additives on sulfur capture |                     |         |   |                              |
|---|---------------------|---------|---|------------------------------|
| Sample No.  | Coal                | Sorbent | Promoter  | Efficiency of sulfur capture |
| 1   | Chongqing soft coal | —       | —   | 0.232                        |
| 2   |                     | CaO     | —   | 0.495                        |
| 3   |                     | CaO     | Fe <sub>2</sub> O <sub>3</sub>                    | 0.483                        |
| 4   |                     | CaO     | SiO <sub>2</sub>                                  | 0.576                        |
| 5   |                     | CaO     | Fe <sub>2</sub> O <sub>3</sub> + SiO <sub>2</sub> | 0.650                        |

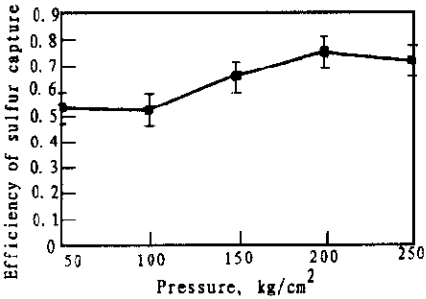


Fig.6 The effect of shaping pressure on efficiency of sulfur fixation

$\text{SiO}_2$  favors for the formation of thermally stable silicates. Addition of  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_2$  not only speeded up the formation of silicate surrounding  $\text{CaSO}_4$  particles, but also improved the sulfur affinity of the matrix (Fincham, 1954). Thus a higher efficiency of sulfur capture was obtained at high temperatures.

### 3.5 Effect of Si/Fe ratio

Fig. 7 shows the effect of Si/Fe ratio on sulfur removal. It could be seen that the more the content of  $\text{SiO}_2$ , the better the efficiency of sulfur capture.

About 23% of sulfur was retained in the slag for the coal sample with no additive (referred to Table 2). This can be explained by the fact that natural iron and silicon oxides contents in coal perhaps made some contributions to sulfur capture.

### 3.6 Effect of particle size

Several briquette samples were made of pulverized coal of various particle sizes, CaO of 60—120 mesh and other additives. The effect of particle size on sulfur removal efficiency is shown in Fig. 8. There seemed to be an optimum particle size for sulfur fixation.

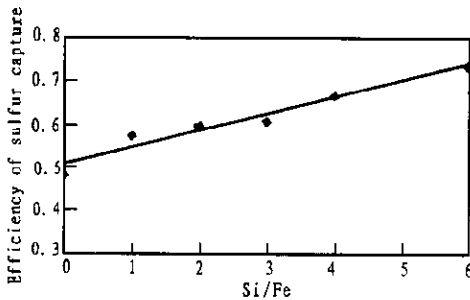


Fig. 7 The effect to Si/Fe ratio

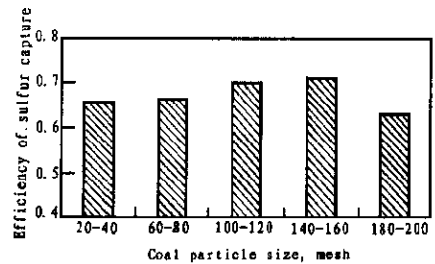


Fig. 8 The effect of coal particle size

## 5 Conclusion

A thermally stable compound  $\text{CaFe}_3(\text{SiO}_4)_2\text{OH}$  was identified, which could have delayed the decomposition of  $\text{CaSO}_4$ . Shaping pressure, reaction temperature, Si/Fe ratio particle size are important factors for sulfur capture.  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_2$  have a synergistic effect on sulfur removal.

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