E310

Investigation on SO₂ Emission during the Co-combustion of MSW and Coal

Yanhua LIU, Defu CHE, Tongmo XU

School of Energy & Power Engineering, Xi'an Jiaotong University, Xi'an 710049, China

E-mail: yhliu@mail.xjtu.edu.cn

ABSTRACT To understand the effect of chlorides in municipal solid waste (MSW) on SO₂ emission during co-combustion, a simulation study was carried out using a thermogravimetric analyzer. Sodium chloride, as a representative, is added to the coal from Tongchuan of China to simulate the blends of MSW and high sulfur coal. The simulated blends were burned in the combustion chamber of the thermogravimetric analyzer at different heating rates (10, 20 and 30 degrees centigrade per minute respectively) from room temperature to 1000 degrees centigrade and the flue gases were monitored using a MSI compact gas analysis instrument (Germany made) at exhaust opening. It has been found that NaCl in MSW is effective in reducing SO₂ emission during co-combustion. The capability of NaCl to reduce SO₂ emission is limited by the minerals in coal and the addition of calcium compounds to coal is necessary. NaCl reduces SO₂ emission by improving the porosity and the activity of the minerals or the limestone added. It is feasible to recover energy and relieve the impact of emissions on the environment and the corrosion of the heating parts of a boiler by the co-combustion of MSW and coal.

Keywords: sodium chloride, sulfur dioxide, co-combustion

1. INTRODUCTION

The dominating methods to dispose municipal solid waste (MSW) in China have been landfilling and open piling at dumping sites. Along with the dramatic development of economy, more and more MSW has been produced and has already brought about new problems, such as the excessive occupation of land, the pollution on environment and the loss of the energy in MSW. Energy production by MSW is becoming an interesting selection instead of landfilling or piling. Quite a few of MSW fired power plants have been built in China today. However, the efficiency of MSW fired power generation is low since the steam condition is limited to avoid the high temperature corrosion of the boiler tube caused by hydrochloric acid gas in flue gas.

The co-combustion is an attractive way to recover the energy since the emissions during the co-combustion are less than those in the case of MSW combustion or coal combustion separately [1-8]. Matsukata and co-workers indicated that the HCl retention by CaCO₃ or Ca(OH)₂ added into the combustors was possible during the co-combustion of MSW and coal [1]. Then the corrosion of the heating parts of a boiler can be relieved. It is believed that the sulfur compounds in coal is effective in inhibiting the formation of organic compounds [2-6]. The impact of emissions on the environment can be relieved. In addition, there are lots of alkali chlorides in MSW [1]. They still influence the emissions from coal during co-combustion.

The effects of the chlorides in MSW on SO₂ emission from coal have been investigated in this paper. The simulated blends of coal and MSW, made from NaCl and a coal from Tongchuan of China, have been used. The reason

that only NaCl has been chosen instead of all chlorides is just for the best simplification of influencing factors. Furthermore, calcium based absorbents have a capacity of decreasing SO₂ and HCl level in flue gas and the addition of calcium based absorbents to fuel is a familiar way to diminish the emissions from combustion, then the effects of sodium chloride on the absorbcency of calcium carbonate have also been investigated by adding sodium chloride along with calcium carbonate to coal.

2. EXPERIMENTAL

2.1 Procedure and Product Analysis

The experiments were carried out on a thermogravimetric analyzer (made in China). The thermogravimetric analyzer consists of a reactor, a weight detector (TG), a differential weight analyzer (DTG), a differential thermal analyzer (DTA) and gas analyzer. A small quantity of powdery sample, 20mg in each experiment, was placed into the reactor and then heated in a flowing air from room temperature to 1000°C at a constant heating rate of 10°C/min, 20°C/min or 30°C/min. Compressed air was passed through the reactor at a flow rate of 60 cm³/min. The TG, DTG and DTA data versus time were recorded with a recording instrument. The concentrations of SO₂, NO and CO in the flue gas were detected by an on-line gas analyzer (made in Germany) at the gas exit and expressed in volumetric fraction. The errors of the SO₂, NO and CO measurements determined by repeated runs are within ± 5%.

2.2 Sample Preparation

The parent coal used in this study is a pulverized coal for power plants from Tongchuan mine of China. The proximate analysis and elemental analysis data are shown in Table 1, the size distribution in Table 2, and the ash analysis in Table 3 respectively. NaCl, which is dry and ground into the fines less than 40 μ m in advance is one of agents used. It is mixed directly with the coal powder at room temperature. The dose rates of NaCl are 1.6 % and 3.2% by weight respectively, covering the content of NaCl in MSW in China. Another agent added to some coal samples is CaCO₃,

Table1. Proximate and elemental analysis of the coal (wt%, as received basis)

Proximate		Ultimate	
Moisture	2.50	Carbon	48.37
Ash	37.73	Hydrogen	2.86
Volatile	14.30	Nitrogen	0.86
Fixed carbon	45.47	Oxygen	4.64
		Sulfur	3.04
		Sulfates	0.55
		Pyrites	1.67
		Organic sulfur	0.82

Table2 Size distribution of the studied coal

Mesh size (μ m)	Distribution (wt%)
<50	31.6
50~57	37.7
58~70	10.4
71~90	12.4
91~110	4.3
111~180	2.8
181~280	0.4
>280	0.4

Table 3 Ash analysis of the studied coal

Components	Content (wt%)
SiO ₂	48.92
Al ₂ O ₃	32.36
Fe ₂ O ₃	6.7
CaO	3.47
MgO	0.55
K ₂ O	0.16
Na ₂ O	2.80
SO ₃	2.83
TiO ₂	1.18

Table 4 Scheme

	CaCO ₃ (Ca/S)	NaCl (wt%)	Heating Rates (°C/min)
1	0	0.0	10
2	1	1.6	20
3	2	3.2	30

whose selected dose rate is to guarantee that the molar ratio of Ca to S is 1 or 2. Table 4 shows the scheme.

3. EXPERIMENTAL RESULTS

3.1 Emission of CO, O₂, SO₂ and NO from the Parent Coal

CO, O₂, SO₂ and NO concentrations, expressed in volume fractions, in the flue gas of the parent coal at 10°C/min are shown in Figure 1.

Fig. 1 SO₂, NO, CO and O₂ emissions of the parent coal at 10°C/min. ●:SO₂; ○:NO; □:CO; ×:O₂.

CO is a dominant product in the flue gas, which shows a peak at 540°C. Around this peak coal char is burnt severely. CO mainly comes from the combustion of char according to the following reaction:

The mark 'C' in the reaction equation denotes the carbon in char. The reaction means the zone of CO₂ formation is nearly the same as that of CO.

O₂ in the flue gas is high enough that the combustion is finished in rich air condition. Beyond the zone in which a great deal of CO is formed, the concentration of O₂ in flue gas is almost unchanged. This result indicates that the consumption of O₂ is mainly due to the oxidation of char, accompanying the formation of CO and CO₂. The oxidation of coal sulfur or nitrogen has a weak effect on the concentration of O₂ in the flue gas.

The peak on NO curve does not appear until the temperature is elevated over 600°C, indicating that it is relatively difficult for coal nitrogen to be released. Both the instantaneous volumetric fraction of NO in flue gas and the total yield of NO for the coal sample are very low because of the low content of the nitrogen in the studied coal.

SO₂ emission shows a different behavior from that of NO. It can be formed at a lower temperature level. Almost its total yield has been obtained as the temperature is elevated to about 650°C at 10°C/min, indicating that coal sulfur is easily released. The possible explanation is the weak thermal stability of pyrite [9] and the high content of the sulfur in the coal.

3.2 Effects of NaCl on SO₂ Emission

The instantaneous SO₂ concentrations in the flue gas from the coals with and without doping NaCl at 20°C/min are given in Fig. 2, and those at the heating rates of 10°C/min and at 30°C/min are shown in Fig.3. From the data in Fig.2 the following analysis statements can be conducted.

Fig. 2 Effects of NaCl on SO₂ emission at 20 °C/min: ●: Parent coal; ○: doped with NaCl of 1.6%; +: doped with NaCl of 3.2%.

- NaCl added to coal is effective in reducing SO₂ concentration in the flue gas in the range of between 383 °C and 677°C. The magnitude reduced depends on the fraction of NaCl added in the coal. In the experiment, SO₂ concentration in the flue gas decreases with increasing fraction of NaCl in the coal. The area beneath each SO₂ curve figure out the total amount of SO₂ emitted from a sample. It can be seen that the total amount of SO₂ from the coal doped with NaCl is less than that from the parent coal in the range of between 383 °C and 677°C. As expected, the total amount of SO₂ released decreases as the doping rate increases. Addition of NaCl at the doping rate of 3.2% diminishes SO₂ emission by 29.5%, while a slight reduction of SO₂, by 1.65%, is obtained at the doping rate of 1.6%. Similar behaviors of NaCl are found at the heating rate of 10°C/min (Fig.3,a). Despite wide different from the behavior at 10°C/min (Fig.3), SO₂ emission at the heating rate of 30°C/min is still decreased by the addition of NaCl to the coal. SO₂ emission decreases so considerably at the doping rate of 1.6% that it approaches to the emission at the doping ratio of 3.2%.
- In Fig.2, an obvious SO₂ reduction by NaCl in the range of between 383°C and 677°C is observed and there is hardly SO₂ in the flue gas when the temperature is close to 700°C. But the reappearance of SO₂ in the flue gas occurs when the temperature is elevated over 700°C, even a small peak around 830°C, called second peak (SP) in this paper, is formed. The peak value reaches 15 ppm at 20°C/min. A similar SP is observed in the case of 10°C/min (Fig.3, a). Although there is no obvious SP observed at 30°C/min (Fig.3, b), the concentration SO₂ in the flue gas is really increased as the temperature is up to 800°C,

which exhibits the same function of NaCl. The SP phenomenon on SO₂ curves indicates that the part of SO₂ captured by NaCl will go back into the flue gas when the temperature is relatively high. The reason for the appearance of the SP, the authors believe, is that the capability for NaCl to capture SO₂ depends on the minerals in coal. If the calcium compounds in coal is lack the SP will appear. Detailed discussions are given in section 4. The presence of SP also indicates that the reduction in SO₂ emission caused by single NaCl is unreliable. Adding assistant absorbents such as CaCO₃ together with NaCl to coal is necessary for a more stable SO₂ reduction.

- During the coal combustion process, the temperature at which SO₂ starts forming is around 400°C. It appears in Fig.2 and Fig.3, that the dosage of NaCl and the heating rate do not change this starting temperature.

Fig. 3 Effects of NaCl on SO₂ emission: (a) 10°C/min; (b) 30°C/min. ●: Parent coal; ○: doped with NaCl of 1.6%; +: doped with NaCl of 3.2%.

3.3 Effects of NaCl on the Capacity of CaCO₃ Absorbing SO₂

Calcite and dolomite are common minerals in coal and influence SO₂ emission during combustion. In order to assess the role of the minerals, CaCO₃ has been employed as an assistant additive in the present study. Fig.4 shows the SO₂ emission curves of parent coal, the coal doped with CaCO₃ and the coal doped with both NaCl and CaCO₃ as the heating rate is 10°C/min. It is clear that due to the presence of CaCO₃, SO₂ concentration in the flue gas

decreases. The total amount of SO_2 emission from the coal is reduced by 38 % when the ratio of Ca/S is 2 (Fig.4, b), and it is reduced by 19% when the ratio of Ca/S is 1 (Fig.4, a), which indicate that the reduction in SO_2 emission caused by CaCO_3 is proportional to the fraction of CaCO_3 added to coal.

Fig. 4 Effects of NaCl on the capacity of CaCO_3 absorbing SO_2 at $10^{\circ}\text{C}/\text{min}$: (a) Ca/S=1 (b) Ca/S=2

It is remarkable in Fig.4 that more reduction in SO_2 emission can be achieved as long as NaCl is added together with CaCO_3 to the coal. When the ratio of Ca/S is 1 and the doping rate of NaCl is 1.6%, a reduction of 40% in SO_2 emission is achieved (Fig.4, a). The effectiveness is almost the same as the double amount of CaCO_3 is added (the ratio of Ca/S is 2). It means that little addition of NaCl may decrease the amount of CaCO_3 added to the coal. It is must mentioned that, more effective reduction in SO_2 emission, which is 58%, has been achieved (Fig.4, b) when the ratio of Ca/S is 2 and the doping rate of NaCl is 3.2%.

Fig. 5 shows the SO_2 concentration curves when heating rates are $20^{\circ}\text{C}/\text{min}$ and $30^{\circ}\text{C}/\text{min}$, and the ratio Ca/S is 2. Similar results to those above can be obtained. When the heating rate is $20^{\circ}\text{C}/\text{min}$ (Fig.5, a), SO_2 emission is reduced by 64% when NaCl and CaCO_3 is added together, greater than that in the case when only CaCO_3 is added, in which only 40% reduction is obtained. While the heating rate is $30^{\circ}\text{C}/\text{min}$, the reduction of SO_2 by NaCl and CaCO_3 is 63% and it is 49% as CaCO_3 alone is added to the coal.

NaCl is able to enhance the absorbency of CaCO_3 , it is unimportant that CaCO_3 is added or has existed as the mineral in coal. The discussion will be presented in the next section.

It must be mentioned that in Fig.4 and Fig.5 no SP

appears in the simultaneous presence of NaCl and CaCO_3 in the coal, which indicates that the addition of CaCO_3 is helpful to the capture of SO_2 .

In Fig. 4, the initial temperature for SO_2 to be generated increases slightly when the coal is doped with CaCO_3 or CaCO_3 and NaCl. As mentioned before (See Fig.2 and Fig.3), the presence of NaCl does not affect the initial temperature. Therefore, the increase may result from the presence of CaCO_3 .

Fig. 5 Effects of NaCl on the capacity of CaCO_3 absorbing SO_2 when Ca/S=2: (a) $20^{\circ}\text{C}/\text{min}$, (b) $30^{\circ}\text{C}/\text{min}$. ●: Parent coal; ○: doped with CaCO_3 only; +: doped with CaCO_3 and NaCl of 1.6%.

4. Discussions

Most coals contain sulfur, which exists in organic or inorganic forms, i.e. organic sulfur, pyrites and sulfates. Sulfates are generally stable, while organic sulfur and pyrites are active and can be oxidized to produce SO_x (SO_2 and SO_3). The most part of SO_x generated during coal combustion is SO_2 .

The reaction between organic sulfur and oxygen can be divided into two stages according to temperature. When temperature is low the sulfur in C—S, S—H will be decomposed and then reacts with oxygen to form SO_2 ; When the temperature is high polycyclic thiophenes will be decomposed and then react with oxygen to form SO_2 .

The reactions between pyrites and oxygen proceed easily even at the temperature under 400°C . The products are sulfates, oxides SO_2 , and so on.

When the oxygen is enriched and the temperature is over 500°C, the following reactions will proceed:

It has been known that not all of the total sulfur in coal is emitted as gas species after coal combustion is completed, no matter how the coal is burnt. Part of the sulfur will be retained as solid compounds in ash due to neutralization of alkali components of the parent coal. In the studied coal most of the calcium is present as calcite or dolomite [10]. They are rapidly decomposed to produce lime when the temperature is over 600-700°C [11]:

The porous CaO and MgO produced from these reactions will be converted subsequently into CaSO₄ and MgSO₄ to result in sulfur retention:

While the temperatures are low enough, the calcination reaction is thermodynamically disfavored and the limestone reacts with SO₂ by a direct mechanism:

According to Matsukata [1], Delmon and van Houte in 1978 reported that a slight amount of CaCl₂ (2 wt%) added to CaCO₃ promoted SO₂ absorption in the temperature range of 573-908K. By TEM they observed that the morphology on CaCO₃ crystals was dramatically altered to form large aggregates and voids by the addition of CaCl₂. NaCl, the authors believe, has the same effect as CaCl₂. NaCl can improve the pore distribution of the minerals in the coal, and then enhance the sulfur retention capacity of the minerals in coal. In other words, NaCl present in coal promotes the reactions between SO₂ and the minerals (R7-9).

In practice, HCl is definitely generated in the facilities for the co-combustion of MSW and high sulfur coal due to the presence of organic chlorides in the MSW. With scanning electron microscopy (SEM), Matsukata et al

[1] found that large voids were formed on the surface of limestone in the presence of HCl. So the SO₂ absorption by the limestone will be accelerated.

The other reason for NaCl to decrease SO₂ emission is that NaCl can absorb moisture around it easily and keep the pore moisture staying in coal body for longer time, which is helpful to the absorption of SO₂.

Firstly, the Fe₂(SO₄)₃ in reaction R2 or R4 will be decomposed rapidly when temperature is over 650 °C and to be accelerated by moisture:

The SO₃ generated is easily absorbed by minerals in coal while Fe₂O₃ has catalysis on the absorption reactions of SO₂ with mineral substances in coal. The more Fe₂O₃ is generated, the more SO₂ is absorbed [12].

Secondly, the moisture kept in coal temporarily is able to improve the reactivity of alkali substances in coal or added, then the reactions R6 through R9 is accelerated.

It must be mentioned that the capacity of NaCl capturing SO₂ is limited by limestone in coal. When the coal has less limestone in it some of SO₂ captured in physisorption would return to the flue gas at elevated temperatures. This is why there is a second peak on SO₂ emission curves of the coals added with NaCl only (Fig. 2 and Fig. 3).

Adding limestone is a better way to capture SO₂. As the effect on the minerals in coal, NaCl can identically improve the behavior of the limestone added and enhance the efficiency of SO₂ capture. No SP appears again when enough limestone is added in the coal is an evidence (Fig. 4 and Fig. 5).

In summary, NaCl can enhance the reactions between SO₂ and the mineral substances in coal or the limestone added. As a result the emission of SO₂ from the coal decreases.

5. CONCLUSIONS

- (1) NaCl added to coal or in MSW is effective in reducing SO₂ emission during co-combustion. The efficiency depends on the fraction of NaCl in the blends of MSW and coal. SO₂ emission decreases with increasing fraction of NaCl. NaCl reduces SO₂ emission by improving the porosity and the activity of minerals in coal body.
- (2) The capability of NaCl to reduce SO₂ emission is limited by the minerals in coal. There is a second peak on the SO₂ curve as the amount of minerals is small. The addition of calcium compounds to coal is necessary. When enough limestone is added to the coal, no second peak appears again and more SO₂ is captured. NaCl can improve the porosity and the activity of the limestone added.
- (3) It is feasible to develop the co-combustion technology of MSW and coal. Besides the recovery of the energy in MSW, the alkali in MSW can neutralize SO₂. With the addition of calcium compounds HCl from MSW can be reduced, then the corrosion of boilers is

relieved. The impact of the emissions on the environment is also relieved.

Acknowledgement

The financial supports from The Special Funds for Major State Basic Research Projects of China (G1999022210) and Special Research Fund for Doctoral Degree Awarded Disciplines of Chinese Universities are gratefully acknowledged.

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