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# Low SO<sub>2</sub> emission from CFB co-firing MSW and bituminous

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Abstract: Influence of co-firing rate on  $SO_2$  emission from co-firing municipal solid waste (MSW) and bituminous containing high amount of sulfur (1.79%) was studied in a 0.15 MWt circulating fluidized bed (CFB). The temperature selected is 1123 K, typical for MSW incineration using CFB. The particle concentration in the dilution zone of the furnace, the alkali metal concentration and sulfate concentration in the recirculating ash and fly ash, and flue gas composition were determined. The results showed that the addition of MSW leads to a significant decrease in  $SO_2$  emission. Concentration of  $SO_2$  in flue gas decreased to 0 with the co-firing rate greater than 51%. This reduction in  $SO_2$  emission is attributed both to the high particle concentration in the dilution zone of the furnace, the high content of alkali metals in the bed material, and to the comparatively high concentration of HCl in flue gas during co-firing of MSW and bituminous.

Keywords: co-firing; municipal solid waste; bituminous; CFB; SO<sub>2</sub>

# Introduction

The MSW production in China was 0.14 billion tons in 2002 (SEPA, 2002), and the disposal has posed a very serious environmental challenge. Incineration is an attractive technology for MSW disposal with hygienic control, volume reduction and energy recovery and is widely used (Lawrence, 1998). Coal, as an auxiliary fuel for MSW incineration, can suppress the PCDD/F formation (Lu, 2003; Gullett, 2000; Raghunathan, 1996; Lindbauer, 1992). Fluidized bed combustion as a well established technique, is especially feasible for MSW incineration with the advantages of burning wide variety of fuel and low emissions. As a result, co-firing MSW and coal in CFB might meet the requirement (Wang, 2002) about MSW incineration of the three "T", which means high furnace "temperatures", strong gas "turbulence" in furnaces and enough gas residence "time" in furnaces under the above two conditions.

During co-firing MSW and coal, presence of HCl in flue gas can effectively promotes the SO2 capture ability of alkali metals. Lawrence (Lawrence, 1999) investigated the interactions of SO<sub>2</sub>, HCl and calcium in a fluidized reactor and the results showed that presence of 2000 ppm HCl greatly improves the SO<sub>2</sub> capture capacity of the sulfated, calcined limestone. Wei (Wei, 1999) studied the interaction between emissions of HCl and SO<sub>2</sub> in a fluidized bed combustor by adding PVC to bituminous, and found that the utilization of calcium in the presence of HCl is improved to higher level, as much as 100% more than when only SO2 exists in flue gas. During co-firing of MSW and bituminous with 0.7 wt % sulfur in a CFB, Desroches-Ducarne et al. (Desroches-Ducarne, 1998) found that increasing MSW addition from 0 to 100 wt% led to a significant reduction in the conversion rate of fuel sulfur to SO<sub>2</sub>. The tests (Dong, 2002) of co-firing MSW with bituminous in a 0.15 MWt CFB showed that increase of MSW addition from 0 to 68 wt% led to a half emission of SO<sub>2</sub>.

There have been numerous reports about the  $SO_2$  reduction under the presence of HCl or the addition of MSW during coal combustion. However, the information about the reason for lower  $SO_2$  emission during co-firing coal and MSW

in CFB is very scarce. As a result, the main objective of this study was to determine the reasons for SO<sub>2</sub> reduction during co-firing MSW and bituminous in CFB. The particle concentration in the dilution zone of the furnace, alkali metal concentration in the recirculating ash and fly ash, the sulfate concentration in the recirculating ash and fly ash were investigated under different co-firing rates. And the influence of HCl on SO<sub>2</sub> emission was also studied through PVC addition as the source of HCl during bituminous combustion in CFB.

### 1 Experimental

# 1.1 MSW and bituminous tested

The bituminous used in the experiments was high sulfur coal(S, 1.79%), and MSW was collected form domestic area of Beijing City. The ultimate and proximate analyses of the bituminous and MSW are given in Table 1. It is interesting that the calcium content in the MSW is much higher than that in the bituminous, which leads to very high Ca/(S+0.5C1) molar ratios with co-firing MSW and bituminous. The sources of high calcium content in the MSW include the calcium in construction material and food waste, such as animal bone, eggshell and seashell. Most bituminous particles are smaller than 6 mm with 50% cut size of about 1 mm, and the MSW is pulverized to 10 mm or smaller.

Table 1 Characteristics of bituminous and MSW

	Bituminous	MSW
Ultimate analysis		
(wt%, as received basis)		
C	62.01	23.10
Н	2.86	2.50
0	5.28	4.80
s	1.79	0.12
N	0.94	1.00
Cl	0.00	0.15
Ca	3.32	3.10
Ca/(S+0.5Cl)	1.49	13.20
Proximate analysis		
(wt%, as received basis)		
Moisture	0.42	11.70
Ash	27.00	57.50
Volatile	13.20	26.60
Fixed carbon	59.38	10.60
LHV (MJ/kg, as received basis)	23.54	6.43

#### 1.2 The CFBC pilot plant

The experimental work was conducted using a 0.15 MWt circulating fluidized bed combustion (CFBC) pilot plant, shown in Fig. 1. It consists of combustion system, control system, flue-gas sampling and analysis system.

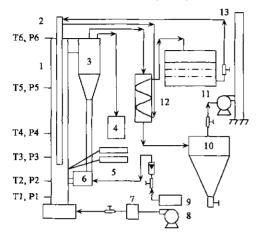


Fig. 1 Test facilities of the pilot scale CFBC plant
1. furnace; 2. water tube; 3. cyclone; 4. gas analyzer; 5. coal and MSW screws; 6. U-valve; 7. primary air meter; 8. forced draft fan; 9. air compressor; 10. bag filter; 11. induced draft fan; 12. economizer; 13. stack; T1—T6. thermocouples; P1—P6. pressure taps

The combustion system is composed of a furnace with inside diameter of 300 mm and height of 6000 mm, a cyclone and a U-valve. The refractory-lined bottom of the furnace is 800 mm in height. The other parts are all made of high temperature alloy covered with heat insulation material on the outside.

Forty kilograms of quartz sand with the size of 0.5—1.0 mm was fed into the furnace as bed material during start-up. MSW and bituminous were separately added into the furnace through two screw feeders from the holes 890 mm above the air distributor, in the range 0—74 kg/h and 6—24 kg/h, respectively, depending on the co-firing rates. The co-firing rate is the heat input with the MSW divided by the total heat input with bituminous and MSW, and it was between 0 and 76% in this work. Thermal input to the furnace with bituminous and MSW was between 0.15 and 0.17 MWt.

The primary air was fed into the furnace through the air distributor in the flow range 250—280 m³/h and the superficial air velocity of the furnace was between 3.6 m/s and 4.0 m/s. Because of the limited height of the furnace, no secondary air was used.

#### 1.3 Method of sampling and analysis

Flue gas composition, including  $H_2\,O$ ,  $SO_2$ , HCl, CO,  $CO_2$ , NO,  $NO_2$ , and  $N_2\,O$ , were continuously analyzed with an on-line infrared type gas analyzer, and these gas analysis data were stored at an interval of 60 s. The gas-sampling nozzle was at the exit of the cyclone, which was maintained at 423—453 K to avoid water condensation. Oxygen concentration in flue gas was kept in 7%-9%, which was analyzed with a Zr-type probe. All gas emissions presented in this paper are normalized to dry gas with an oxygen concentration of 6%, at 273 K and 101.3~kPa.

During experiments, the sample of the recirculating ash was withdrawn through a valve attached to the U-valve and the fly ash was collected with a bag filter.

Main operation parameters of the furnace, including the

temperatures and pressure drops along the height of the furnace and primary air flow rate, together with oxygen data were recorded in a computer at the interval of 15 s.

In the experiments, the highest furnace temperatures were at the location of 820 mm or 1520 mm above the air distributor, and the highest temperature was defined as the furnace temperature and was controlled at 1123 K. During all the experiments reported in this work, the temperature differences between the top and the bottom of the furnace were within 50 K.

The particle concentration in the dilution zone was calculated through the whole pressure drop and the height of the dilution zone. The dilution zone defined in this work was the part of the furnace between 820 mm and 6000 mm above the air distributor.

#### 2 Results and discussion

# 2.1 SO, emission from CFB combustion

Effects of co-firing rates on both SO<sub>2</sub> emission and desulfurization efficiency are shown in Fig. 2 and Fig. 3, respectively. As can be seen in Fig. 2, when the co-firing rate is 0, i.e. without MSW addition and bituminous was the only fuel of the furnace, the SO<sub>2</sub> concentration in the flue gas is very high, 1745 mg/m<sup>3</sup>. But when the co-firing rate is increased to 31.5%, the SO<sub>2</sub> emission decreases to only 265 mg/m<sup>3</sup>, and further increase in the co-firing rate to 51% or higher leads to the SO<sub>2</sub> reduction to 0. It can be seen from Table 1 that the sulfur content in the MSW is much lower than that in the bituminous, which indicates that the sulfur content in the blend will decrease with the increase of cofiring rates, and that SO<sub>2</sub> emission will also decrease. However, there must be other reasons for SO, reduction during co-firing MSW and bituminous, because there is a mark increase in desulfurization efficiency with more MSW addition, shown in Fig. 3. The desulfurization efficiency becomes greater than 90% when the co-firing rates are greater than 31.5%, and it even gets to 100 % with the cofiring rates higher than 51%. And the other reasons that lead to both low SO2 emission and high desulfurization efficiency during co-firing MSW and bituminous are discussed in detail as follows.

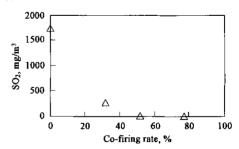


Fig. 2 Effect of co-firing rate on SO<sub>2</sub> emission

# 2.2 Particle concentration in the dilution zone of the furnace

There is a sharp rise in particle concentration in the dilution zone of the furnace with the increase of the co-firing rates, in Fig. 4, which results from the high ash content in MSW, as listed in Table 1. Particle concentration in the dilution zone of the furnace is one of the important parameters influencing emissions from CFBC and the rise in particle

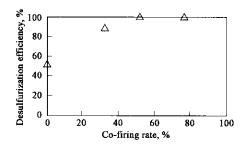


Fig. 3 Effect co-firing rate on desulfurization efficiency

concentration benefits the reaction between the particle and the flue gas in three main aspects. With the increase of the particle concentration, there are more particles that have chances to contact and react with flue gas, and the fine particle concentration also increases, which provides much more surface area for solid-gas reaction. In addition, the turbulence of the flue gas in the furnace is strengthened under the condition of the higher particle concentration, which to certain extent also promotes the solid-gas reaction.

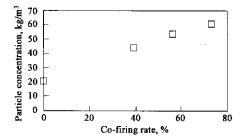


Fig. 4 Effect of co-firing rate on particle concentration in the dilution zone of the furnace

#### 2.3 Alkali metals in recirculating ash and in fly ash

It is reported that high alkali metal content in biomass has shown the capability comparable to or even better than limestone for sulfur capture during co-firing high sulfur fuels and biomass (Nordin, 1995). In the experiments reported in this work, alkali metal content, including calcium and sodium, in recirculating ash and in fly ash was analyzed and shown in Fig. 4. The calcium and sodium contents in recirculating ash are about 6 wt% and 1.5 wt%, The recirculating ash is composed of the particles that escape from the furnace and are captured by the cyclone and then return to the furnace through a U-valve. There is much higher alkali metal content in the fly ash, which is composed of the fine particles that escape from the cyclone and are captured by the bag filter. Although the sodium content is also 1.5 wt %, almost the same as that in recirculating ash, the calcium content in fly ash is much higher than that in recirculating ash and increase significantly with the rise of co-firing rates. As can be seen from Fig.4, the particle concentration in the dilution zone of the furnace increases significantly with greater co-firing rates, which implies that the concentration of fine particles in the dilution zone is also higher. So, the increase in fine particle concentration and the alkali metal concentration increase in fine particles, i.e. fly ash, as in Fig.5, lead to a rise of alkali metal concentration in the dilution of the furnace, which enhances the SO<sub>2</sub> retention. In addition, the increase in particle surface area resulted from the higher fine particle concentration further promotes SO2 capture by alkali metals.

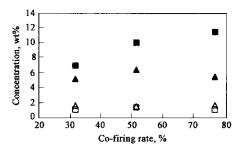


Fig. 5 Effect of co-firing rate on alkali metal concentration in recirculating ash and in fly ash (Solid squares and triangles represent calcium content in fly ash and recirculating ash, respectively; blank squares and triangles represent sodium content in fly ash and recirculating ash, respectively)

# 2.4 The sulfate concentration in the recirculating ash and fly ash

The sulfate concentrations in recirculating ash and in fly ash were analyzed and the results, shown in Fig. 6, are in good agreement with the above discussion. As can be seen in Fig. 6, the sulfate in the fly ash increases from 1.0 wt% to 1.8 wt% with the rise of the co-firing rates from 31.5% to 51%, but further increase in the co-firing rates from 51% to 76% leads to a reduction in the sulfate concentration in fly ash. As discussed in the sections 2.2 and 2.3, the alkali metal concentration, the particle surface area and the flue gas turbulence all increase with higher co-firing rates, which means that the capability for SO<sub>2</sub> reduction is strengthened. So, the sulfur captured by the alkali metal increases and the sulfate concentration in the fly ash increases with higher cofiring rate in the range 0-51%. But attention should be paid to the fact that, the sulfur content in the MSW is much lower than that in bituminous and the sulfur content in the blend of MSW and bituminous decreases with the increase of co-firing rate, which implies that the sulfur captured by the alkali metals decreases with the increase of co-firing rate after the desulfurization efficiency gets 100% at co-firing 51%. In addition, the volume of fly ash increases with greater cofiring rate because of higher ash content in the MSW. As a result, the decrease in the amount of sulfur captured by the alkali metals and the increase in the volume of fly ash lead to the reduction of sulfate concentration in the fly ash with higher co-firing rates in the co-firing rate range of 51% 76%, as in Fig. 6. It is also clear that the sulfate concentration in the recirculating ash decreases with higher co-firing rate, which also might be caused by the decreased sulfur addition and the increased ash addition with the higher co-firing rates.

### 2.5 Effect of HCl on SO<sub>2</sub> emission

The presence of HCl leading to lower SO<sub>2</sub> emission was observed in this work, which can be due to the aggregates and voids formed on the surface of the limestone, providing the diffusion path for SO<sub>2</sub> toward the interior of a limestone particle (Matsukata, 1996). In the experiments, PVC was added as the source of HCl during bituminous combustion and the results are shown in Fig. 7. Without PVC addition, SO<sub>2</sub> concentration in the flue gas remained steady at bout 1150 mg/m<sup>3</sup>, and HCl concentration stayed at quite low level. From the time 17:26, 0.1 kg PVC per 2 kg bituminous was added to the furnace, and there is a sharp increase in HCl emission and a sharp decrease in SO<sub>2</sub> emission. After 10

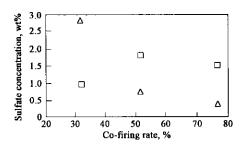


Fig. 6 The effect of co-firing rate on sulfate concentration in fly ash and in recirculating ash (Blank squares and triangles represent sodium content in fly ash and recirculating ash, respectively)

minutes, the HCl increases to as high as 596 mg/m³, and gas sampling was stopped in case of the over-range. Then less PVC, 0.02 kg per 2 kg bituminous was added to the furnace. After 30 minutes, gas sampling started again, and the HCl was in the range of 510—580 mg/m³, SO<sub>2</sub> in 810 mg/m³—880 mg/m³. After remaining the stable test for 30 min, PVC addition was stopped and bituminous was the only fuel of the furnace, and then SO<sub>2</sub> and HCl quickly returned to their original level as before PVC addition. During the whole process, NO emission remained quite steady, about 300 mg/m³.

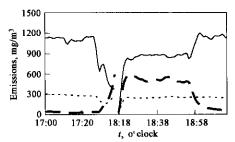


Fig. 7  $SO_2$ , HCl and NO emissions with PVC addition to the bituminous (The fine solid line represents  $SO_2$  and fine dash line NO, the bold dash line HCl)

This experiment implies that the presence of HCl in the flue gas strengthens the SO<sub>2</sub> retention. But SO<sub>2</sub> concentration is still quite high, as high as 870 mg/m<sup>3</sup> even with the presence of 570 mg/m<sup>3</sup> HCl. During co-firing MSW and bituminous in the CFB, HCl concentration is in the range of  $180-300 \text{ mg/m}^3$  with co-firing rate 31.5%-76%, shown in Fig. 8. However, the SO<sub>2</sub> concentration is below 265 mg/ m<sup>3</sup>. Under the conditions of both co-firing MSW with bituminous and combustion of bituminous with PVC addition, the HCl concentration in the flue gas is comparatively high, but there are great differences in SO2 level between the two combustion conditions: SO2 emission from co-firing MSW and bituminous is much lower than that from bituminous combustion with PVC addition. And attention should be paid to the fact that the particle concentration in the dilution zone of the furnace is quite different for these two combustion conditions. The particle concentration in the dilution zone of the furnace is only 9-17 mg/m<sup>3</sup> for bituminous with PVC addition, but 46-62 kg/m3 for co-firing MSW and bituminous. In addition, the alkali metals in the fly ash of the co-firing runs were also high. So, the high particle concentration and high alkali metal concentration in the fine

particles are the main reasons for low SO<sub>2</sub> emission from cofiring MSW and bituminous.

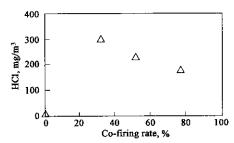


Fig. 8 HCl concentration in flue gas

# 3 Conclusions

Through co-firing sulfur containing bituminous and MSW at different co-firing rates in a pilot scale CFB, the following conclusions are obtained:

Addition of MSW to bituminous coal combustion leads to a significant reduction in  $SO_2$  emission and an increase in desulfurization efficiency.

Both the particle concentration in the dilution zone of the furnace and the alkali metal contents in the fly ash and recirculating ash are comparatively high with greater co-firing rates, which present strong ability for SO<sub>2</sub> capture, leading to the increase of the sulfate concentration in the fly ash.

The presence of HCl during co-firing bituminous and MSW further enhances SO<sub>2</sub> retention.

#### References:

Desroches-Ducarne E, Marty E, Martin G et al., 1998. Co-combustion of coal and municipal solid waste in a circulating fluidized bed [J]. Fuel, 77: 1311--1315.

Dong C Q, Jin B S, Zhong Z et al., 2002. Tests on co-firing municipal solid waste and coal in a circulating fluidized bed [J]. Energy Conversion and Management, 43: 2189—2199.

Gullett B K, Dunn J E, Raghunathan K, 2000. Effect of cofiring coal on formation of polychlorinated dibenzo-p-dioxins and dibenzofurans during waste combustion[J]. Environ Sci Technol, 34: 282—290.

Lawrence A R, 1998. Energy from municipal solid waste: a comparison with coal combustion technology[J]. Prog Energy Combust Sci, 24: 545—564.

Lawrence A D, Bu J, Gokulakrishnan P, 1999. The interactions between SO<sub>2</sub>, NOx, HCl and Ca in a bench-scale fluidized combustors [J]. Journal of the Institute of Energy, 72: 34—40.

Lindbauer R, Wurst F, Prey T, 1992. Combustion dioxin suppression in municipal solid waste incineration with sulfur addictives [J]. Chemosphere, 25: 1409—1414.

Lu Q G, Na Y J, Bao S L et al., 2003. Experimental study on CFBC co-firing of municipal solid waste and coal[J]. Journal of Engineering Thermophysics, 24: 347—350.

Matsukata M, Takeda K, Miyatani T et al., 1996. Simultaneous chlorination and sulphation of calcined limestone [J]. Chemical Engineering Science, 51: 2529—2534.

Nordin A, 1995. Optimization of sulfur retention in ash when cocombustion high sulfur fuels and biomass fuels in a small pilot scale fluidized[J]. Fuel, 74: 615—622.

Raghunathan K, Gullett B K, 1996. Role of sulfur in reducing PCDD and PCDF formation[J]. Environ Sci Technol, 30: 1827—1834.

State Environmental Protection Administration of China(SEPA), 2002. Report on the State of the Environment in China (annually)(EB). http://www.zhb.gov.cn.

Wang J, Ma H C, Hu S R, 2002. Basel convention (BC) on the control of transboundary movements of hazardous wastes and their disposal adopted by the conference of the plenipotentiaries on 22 March 1989 (M). Beijing: Chemical Industry Press. 348.

Wei X, Liu K, Pan WP et al., 1999. Interaction between emissions of SO<sub>2</sub> and HCl in fluidized bed combustors[J]. Fuel, 78: 1425-1436.

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