Effects of Magnetic Fields on the Improving Mass Transfer in Flue Gas Desulfurization with a Fluidized Bed

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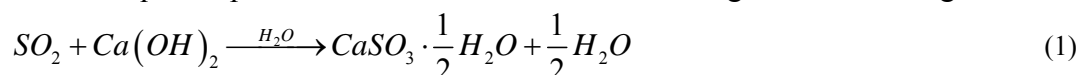(College of Energy and Environment, Southeast University, Nanjing, Jiangsu, P. R. China)

Abstract: Effects of magnetic fields on improving mass transfer in flue gas desulfurization with a fluidized bed are investigated in the paper. In this research, the magnetically fluidized bed (MFB) is used as the reactor in which ferromagnetic particles are fluidized with simulated flue gas under the influence of an external magnetic field. Lime slurry is continuously sprayed into the reactor. As a consequence, the desulfurization reaction and the slurry drying process take place simultaneously in the MFB. In this paper, the effects of ferromagnetic particles and external magnetic fields on the desulphurization are studied and compared with that of quartz particles as the fluidized particles. Experimental results show that the ferromagnetic particles not only act as a platform for lime slurry to drop on like quartz particles, but also act as a catalyst and a SO_2 sorbent. The results also show that the specific area of ferromagnetic particles after reaction is increased with the magnetic intensity, and the external magnetic field promotes the oxidation of S(IV), improving the mass transfer between sulphur and its sorbent. Hence, the efficiency of desulphurization under the effects of external magnetic fields is higher than that in the general fluidized bed.

Keywords: mass transfer, flue gas desulfurization, magnetic field, catalytically oxidation, magnetically fluidized bed

1. Introduction

Pollution of SO_x from flue gas emitted from combustion of fossil fuels has been a worldwide problem due to its influence on the environment. Various technologies for flue gas desulphurization (FGD) has been proposed. They can be roughly classified into three different types (Soud, 1995): wet scrubbers, semi-dry processes (typically represented by spray dry scrubbers) and dry processes. In the worldwide hierarchy of applied FGD systems, spray dry scrubbers are at the second place only behind wet scrubber.

In spray dry scrubbers, a fine spray of lime slurry is brought into contact with the flue gas inside a spray dryer in order to remove SO_2 by chemical absorption. The sprayed droplets simultaneously evaporate, and the absorbed SO_2 reacts in the alkaline aqueous phase with the dissolved lime according to the following reaction

$$SO_2 + Ca(OH)_2 \xrightarrow{\;H_2O\;} CaSO_3 \cdot \frac{1}{2}H_2O + \frac{1}{2}H_2O \tag{1}$$

where the resulting calcium sulfite precipitates as a consequence of its low solubility in water. The dry product, consisting of unreacted hydrated lime and calcium sulfite,

is carried by the flue gas downstream to a particulate collection device (e.g., ESP or fabric filter) and continues to react with SO_2 in the solid cake there.

Spray dry scrubbers are mostly used for relatively small to medium capacity boilers using low to medium sulphur (2.5%) coal, for they hardly exceed 70% SO_2 removal efficiency at 1-2 calcium to sulphur ratios (Ca/S) while wet scrubbers can achieve an efficiency of higher than 90% in this situation. In order to develop new semidry FGD technology with higher efficiency and lower operation cost, two semi-dry FGD processes have been proposed in the literature, i.e., the circulating dry scrubber (CDS) (Neathery, 1996) and the semidry FGD technology with powder-particle spouted bed (Ma et al., 1999). However, it is difficult to realize a SO_2 removal efficiency higher than 90% using the circulating dry scrubber when Ca/S is set at its stoichiometric value (Xu et al., 2000). In addition, the semidry FGD technology with powder-particle spouted bed has only been demonstrated for high SO_2 removal efficiency in a laboratory-scale reactor with relatively low SO_2 inlet concentration (300-500 ppm) (Xu et al., 2000; Ma et al.,2000). Therefore, it remains an urgent problem to develop new semidry FGD methods with high efficiency, low cost and high operation reliability.

In this paper, a Magnetically Fluidized Bed (MFB) is used as the reactor in a new semi-dry FGD process. The MFB is a fluidized bed of magnetizable particles under the influence of an external magnetic field (Rosensweig, 1978). It has the advantage of combining the constant pressure drop of a fluidized bed with the bubble free operation of a fixed bed (Liu et al., 1991). Early in 1980s, Pirkle has conceptually proposed and experimentally demonstrated the use of countercurrent MFBs in continuous absorptive separation for purification of gases including ethylene, cryogenic-plant gas, natural gas, flue gas etc (Pirkle, 1981). It is the first time that MFBs are used as the reactor in the spray dry FGD process. The use of MFB in the FGD process makes the process more convenient and the contact of flue gas and droplets more sufficient. In addition, due to the adhesion of fine sorbent onto the magnetizable particles, the residence time of the droplets becomes longer in the MFB. Moreover, the ferromagnetic particles and the external magnetic field also exert substantial impact on the desulfurization chemistry and thus promote the desulfurization reaction (Zhang, 2008).

The goal of this paper is to experimentally demonstrate the effects of ferromagnetic particles and external magnetic fields on the desulphurization. Our study substantiates that the ferromagnetic particles not only act as a platform for lime slurry to drop on like quartz particles, but also act as a catalyst and a SO_2 sorbent, and the external magnetic field promotes the oxidation of S(IV), improving the mass transfer between sulphur and its sorbent. Hence, the new semi-dry FGD process with MFB has a high efficiency of desulphurization under the effects of external magnetic fields.

2. Experimental set-up

The structure of the experimental facility is shown in Fig.1. The spray dry absorption experiments were performed in a laboratory scale MFB with an inner diameter of 0.1m and a length of 0.8m. The MFB consists of a stainless-steel column wrapped with glass wool to prevent loss of heat, a pair of Hemholtz coils fixed at the outer circle of the glass wool, and fluidization medium (here ferromagnetic particles are used). The magnetic field generated by the coils is spatially uniform and time-invariant in a certain area with 0.192 m in diameter and 0.204 m in height. The electric current in the coils is adjusted from 0 to 5A and thus the magnetic field intensity increases from 0 to 300 Oe.

An artificial flue gas is produced by mixing SO_2 into a flow of heated ambient air. The inlet concentration of SO_2 varies from 700 to 1050 ppm. A perforated plate at the bottom of the MFB ensures an even distribution of the gas flow between 40, 50 and 60m^3/h. The lime slurry used contained 3 to 8wt% lime. For atomization, a two-fluid nozzle is used. At the outlet of the spray dryer the reaction product is separated from the gas stream by a fabric filter. Actually, the desulfurization reaction occurs not only in the MFB but also in the fabric filter. Hence, in this paper, we also take into account the SO_2 removed in the fabric filter in order to give a relatively precise estimate of the overall SO_2 removal efficiency.

The temperatures of the MFB at different heights are measured by the thermocouples. Inlet and outlet SO_2 concentration are measured by a gas analyzer (MRU SAE-19). SEM/energy dispersive X-ray(EDX) analysis of the deselfurization product collected on the surface of the ferromagnetic particles were performed using FE sirion 200 SEM and PV 9100 EDAX, respectively. X-ray diffraction analyzer (SHIMADZU XD-3A) was used to determine the composition of the product. Table 1 summarizes the specifications of the ferromagnetic particles and lime particles used in the paper.

In this study, SO_2 removal efficiency, denoted by η, is defined as

$$\eta = (1 - \frac{C_{out}}{C_{in}}) \times 100\% \tag{1}$$

where C_{in} and C_{out} are the inlet SO_2 concentration and outlet SO_2 concentration, respectively.

Table1

Specifications of the lime particle and the ferromagnetic particle

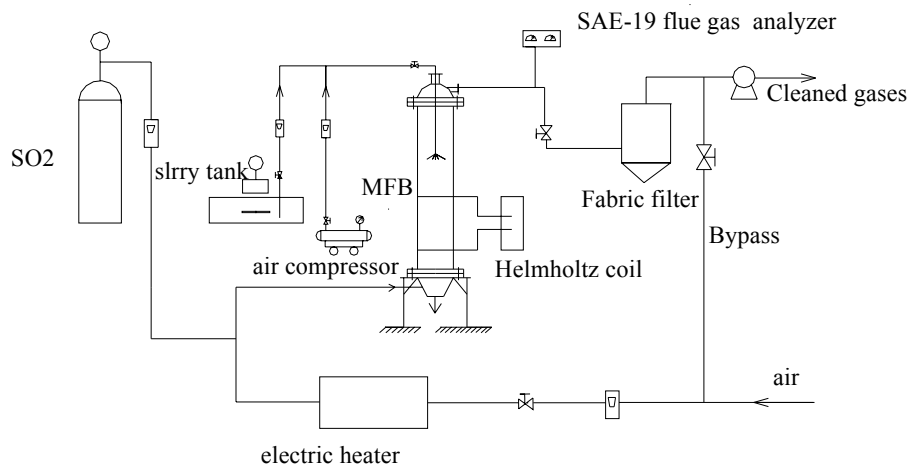| Material	d_p(μm)	ρ_p(kg/m^3)	S_{BET}(m^2/g)
Hydrated lime	10	2240	3.748
Ferromagnetic particles	220-450	5440	0.097

Fig 1. schematic diagram of the experimental apparatus

3. Results and discussion

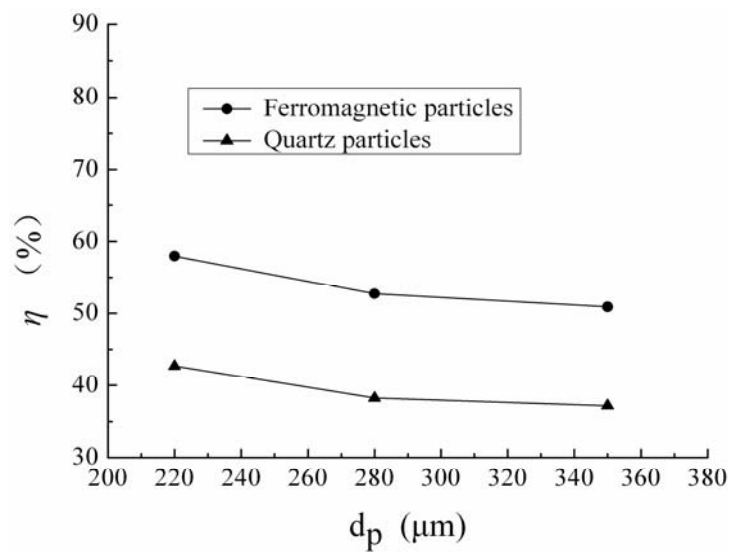## 3.1 The effects of ferromagnetic particles

Fig.2 Comparison of the SO_2 removal efficiency using ferromagnetic particles and quartz particles

As illustrated in Fig.2, the SO_2 removal efficiency of using ferromagnetic particles is about 14% higher than that of quartz particles, and it decreases as the average diameter of the particles increases. This is because when the particles are finer, their specific area is larger and the dispersion of droplets on their surface becomes more uniform, which leads to higher contact efficiency and faster reaction between the sorbent and SO_2.

Under the magnetic field intensity of 0Oe, the MFB of ferromagnetic particles essentially becomes a conventional bubbling bed and the SO_2 removal reaction is identical to that of using quartz particles. The difference in removal efficiency is only due to the difference in reactivity of these two fluidization materials with SO_2. According to the XRD patterns of desulfurization products in Fig 3(a), there is only $CaSO_3$ in the product of the reaction using quartz particles. Yet Fig 3(b) shows that the compositions of the product of the reaction with ferromagnetic particles consists of $CaSO_3$, $CaSO_4$, $FeSO_3$ and $Fe_2(SO_4)_3$. This indicates that while quartz particles only act as a platform for the lime slurry to drop on as they cannot react with sulfur species, the ferromagnetic particles act not only as a platform but also as a catalyst as well as a SO_2 sorbent. Hence, the efficiency of the bed with ferromagnetic particles is higher than that with quartz particles.

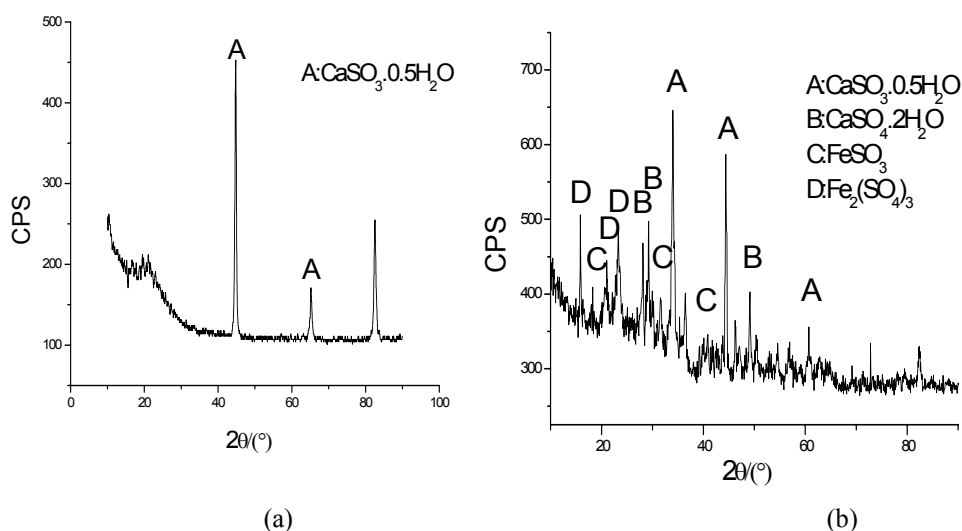(a)   (b)

Fig.3 XRD patterns of desulfurization products with(a) quartz particles (b) ferromagnetic particles

3.2 The effects of external magnetic field

Fig4 shows a plot of the SO_2 removal efficiency as a function of applied field intensity with ferromagnetic particles of different diameters. The plot of η-H curve indicates that there is an almost linearly increasing branch when the applied field intensity increases from 90Oe to 260Oe, and that the increment of removal efficiency is nearly 30% when the magnetic field from 90Oe to 400Oe. There are two reasons underlying this phenomenon. First, the specific area of ferromagnetic particles after reaction is increased with the magnetic intensity. Second, the external magnetic field promotes the oxidation of S(IV), and improve the mass transfer between sulphur and its sorbent. Hence, the efficiency of desulphurization is increased.
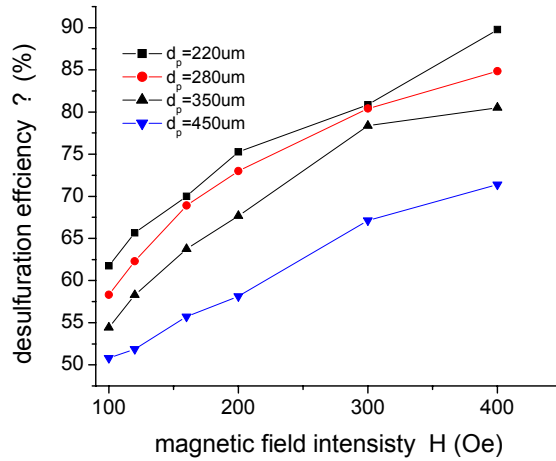
Fig 4 Effect of applied field intensity on desulphurization efficiency

Table 2

Specific area of ferromagnetic particles

	0Oe	100Oe	200Oe
Before desulphurization	$0.097m^2/g$		
After desulphurization	$0.19m^2/g$	$0.213m^2/g$	$0.534m^2/g$

The fact that the specific area of ferromagnetic particles after reaction is increased with the magnetic intensity is shown in Table 2. From this table, it can be seen that specific area of ferromagnetic particles after the reaction is increased. Furthermore, it is also increased with the magnetic intensity. This is because of the high gas-solid contacting efficiency in the magnetically stabilized regime [18]. It implies that the contacting of SO_2 and $Ca(OH)_2$ is sufficient and the evaporation of the droplets is relatively slow in this situation, and the time of the desulfurization reaction in the liquid phase is lengthened. Hence the specific area of ferromagnetic particles becomes larger after reaction.

The effects that the external magnetic field promotes the oxidation of S(IV) can be seen from Fig.5. Fig5(a) and (b) show the XRD patterns of the desulphurization products at the applied field intensity of 0Oe and 400Oe respectively. These XRD patterns indicate that the percentage of $CaSO_3$ in the product of the SO_2 removal reaction decreases and the percentage of $CaSO_4$ increases as the intensity of the applied magnetic field increases. Specifically, when H=0Oe, the diffraction intensity of $CaSO_3$ reaches the highest value which indicates it is the dominant composition in the reaction product. However, as the intensity of the magnetic field increases to 400 Oe, $CaSO_3$ only takes up a small proportion in the desulphurization product. In this case, the diffraction intensity of $CaSO_4$ becomes the highest among all the compositions, which indicates that $CaSO_4$ has become the main composition of the product. It means that external magnetic field can promote the oxidation of H_2SO_3 and $CaSO_3$. i.e., the external magnetic field can promote the oxidation of S(IV).
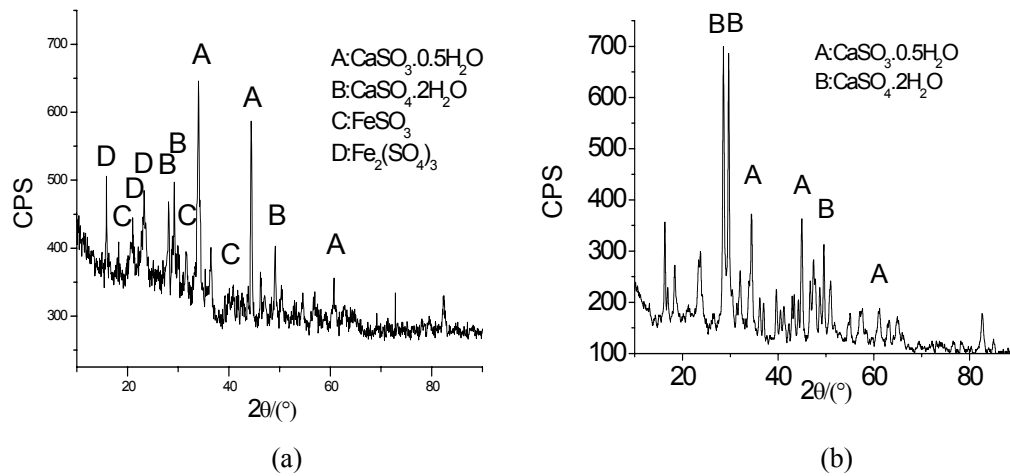
Fig.5 XRD patterns of desulfurization products at different applied field intensities

When H_2SO_3 is oxidated to H_2SO_4, the ionizing constant is promoted from 6.01 $\times 10^{-8}$ (T=298K) to 1.2×10^{-2} (T=298K) , and the density of ionization SO_x^{2-} is increased. On the other hand, when $CaSO_3 \cdot 0.5H_2O$ is oxided to $CaSO_4 \cdot 2H_2O$, the crystal $CaSO_3 \cdot 0.5H_2O$ on the surface of lime particles is reduced, and soluble area of lime particles is increased, hence the solubility of $Ca(OH)_2$ is enhanced.

The increasing ionizations SO_x^{2-} and Ca^{2+} improves the mass transfer between sulphur and its sorbent, and thus increases the efficiency of desulphurization. This is indicated by the SO_2 absorbing process in a single drop of slurry illustrated in Fig.6. In Fig.6, $C_{SO_x^{2-}iH}$ and $C_{SO_x^{2-}i}$, represent the mole density of ionizations SO_3^{2-} and SO_4^{2-} with and without the effects of magnetic fields respectively, and $C_{Ca,lH}$ and $C_{Ca,l}$, represent the mole density of ionizations Ca^{2+} with and without the effects of magnetic fields respectively. The SO_2 absorbing process in a single drop of slurry is as follows. SO_2 in gas phase diffuses to the interface between gas and liquid through the gas film, and dissolves and ionizes to ionizations SO_3^{2-} and SO_4^{2-},.These ionizations then diffuse in the liquid film. Meanwhile, $Ca(OH)_2$ dissolves and ionizes to ionizations Ca^{2+}, and diffuses in the liquid film. When these positive and negative ionizations meet, they can react at once, and the density of ionizations drops to zero. Therefore, the pervasion of ionizations in the liquid film becomes the main factor which controls SO_2 absorbing process.
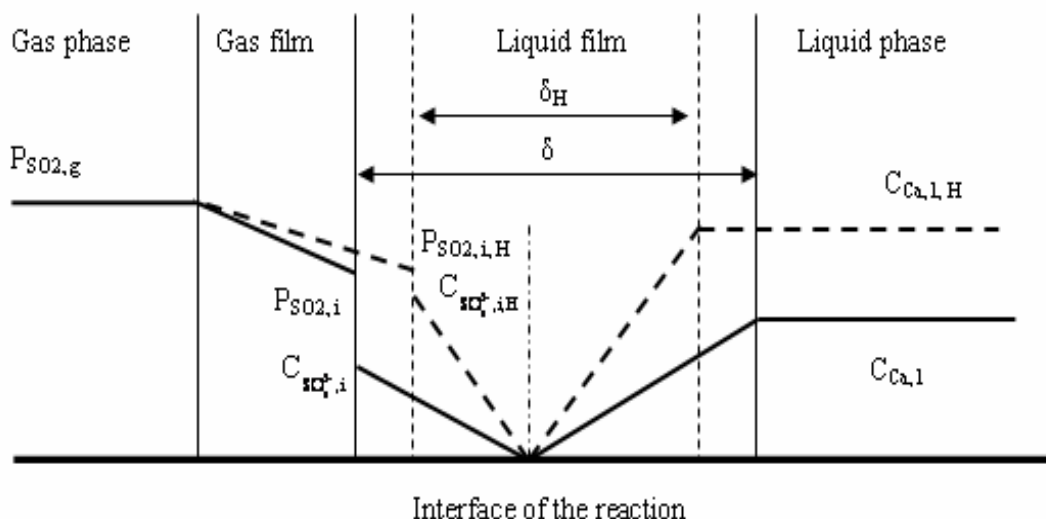
Figure 6   Effects of magnetic fields on the improving mass transfer in desulphurization

The solid line in Fig.6 illustrates the situation without the effects of magnetic fields. In this situation, the liquid film is thicker, and both the density of ionizations SO_3^{2-} and SO_4^{2-} in the interface between gas and liquid, and that of ionizations Ca^{2+} in liquid phase are low. Contrarily, the dashed line in Fig.6 shows the case under the effects of magnetic field. It can be seen from Fig.6 that now the liquid film is thinner, and both the density of ionizations SO_3^{2-} and SO_4^{2-}, and that of ionizations Ca^{2+} on the same region are higher. Hence, the density grade of ionizations in the liquid film is enhanced, the mass transfer is improved, and the desulphurization efficiency is increased.

4. Conclusions

In this paper, the effects of magnetic fields on the improving mass transfer in flue gas desulfurization with a fluidized bed are investigated experimentally. Following conclusions are obtained according to the experimental results.
(1) The ferromagnetic particles not only act as a platform for lime slurry to drop on like quartz particles, but also act as the catalyst as well as the SO_2 sorbent.
(2) The specific area of ferromagnetic particles after reaction is increased with the magnetic intensity, and external magnetic field reinforces the oxidation of S(IV), improving the mass transfer between sulphur and its sorbent.
(3) The efficiency of desulphurization with the effects of external magnetic fields is higher than that in the general fluidized bed.

Acknowledgements

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