

Enhancement of the Reactivities of Iron Blast Furnace Slag/Hydrated Lime Sorbents toward SO₂ by NaOH

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Abstract—NaOH was added to iron blast furnace slag (BFS)/hydrated lime (HL) slurries to prepare sorbents for semidry and dry flue gas desulfurization (FGD) processes. The addition of NaOH greatly enhanced the sorbent reactivities toward SO₂ because NaOH is deliquescent and its presence increased the amount of water collected by the sorbent. In the case of sorbents prepared without NaOH addition, both the Ca utilization and the SO₂ capture increased with increasing slurring temperature and varied with the BFS/HL weight ratio; however, in the case of sorbents prepared with NaOH addition, their Ca utilization increased to a level that was nearly independent of the slurring temperature and the BFS/HL weight ratio. NaOH addition can raise the level of sorbent reactivity and reduce the sorbent cost in a semidry or dry FGD process.

Key Words : Iron blast furnace slag, Hydrated lime, SO₂, Flue gas desulfurization, Reaction kinetics

INTRODUCTION

The spray-drying (semidry) and dry flue gas desulfurization (FGD) processes are effective means of reducing SO₂ emissions from coal fired power stations (Miller, 1986; Farber, 1986); however, conversion of the sorbent, which is mostly hydrated lime (HL), in these processes is low. Therefore, increasing the utilization of hydrated lime has become an important subject in the study of these FGD processes.

Recently, Brodnax and Rochelle (2000) reported that sorbents prepared from hydrated lime and iron blast furnace slag (BFS) through a hydration process had greater surface areas and higher reactivities toward SO₂ than hydrated lime. BFS, mainly composed of SiO₂, Al₂O₃, and CaO, is a pozzolanic material (Taylor, 1964). Our recent study (Liu and Shih, 2001) confirmed that BFS/HL sorbents are indeed highly reactive toward SO₂. We also found that the structural properties and reactivity of this kind of sorbent were affected by the BFS/HL weight ratio, the fineness of the slag, and the hydration conditions. A sorbent with a BFS/HL ratio of 30/70 was found to have the highest Ca utilization and SO₂ capture ability, the values of which increased as the slurring temperature and time increased and as the particle size of the BFS decreased.

Successful use of sorbents prepared from BFS not only reduces the operating cost of the desulfuri-

zation process, but also aids the utilization of BFS waste. Thus, this kind of sorbent deserves further study.

In order to further enhance the sorbent reactivity, some additives, such as gypsum and CaCl₂, have been added during the preparation of sorbents (Brodnax and Rochelle, 2000). In the present work, we used NaOH as an additive. NaOH has been used to enhance the reactivities of sorbents prepared from fly ash, which is also a pozzolanic material, and hydrated lime (Jozewicz *et al.*, 1988; Peterson and Rochelle, 1988; Chu and Rochelle, 1989; Kind *et al.*, 1994). Peterson and Rochelle (1988) found that the addition of NaOH to the slurry of fly ash and Ca(OH)₂ increased the dissolution of silica from fly ash but decreased that of Ca(OH)₂, therefore, there is an optimum NaOH concentration which is related to the source of the fly ash, the amount of fly ash, the addition of calcium sulfite, and the slurring temperature. It has been shown that the reaction of a fly ash/Ca(OH)₂ sorbent with SO₂ at low temperatures requires the presence of a water layer adsorbed on the sorbent surface (Liu and Shih, 2002). Thus, according to Kind *et al.* (1994), NaOH increases the water adsorption capacity of sorbents because it is a deliquescent material.

In this work, sorbents were prepared with and without the addition of NaOH under different BFS/HL weight ratios and slurring temperatures.

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The sorbents were subjected to reaction with SO_2 with the aim of elucidating the effect of NaOH addition on sorbent reactivity.

EXPERIMENTAL PROCEDURE

Preparation of sorbents

The hydrated lime used in this study was reagent grade $\text{Ca}(\text{OH})_2$ (purity > 95%, Hayashi Pure Chemical Industries, Ltd.). The iron blast furnace slag was supplied by the China Hi-Ment Corporation, and its chemical composition was: 42.00% CaO, 33.47% SiO_2 , 13.78% Al_2O_3 , 6.98% MgO, 0.39% Fe_2O_3 , 0.42% SO_3 , 1.67% alkalinity, 0.27% sulfite, and 1.67% ignition loss. The volume mean particle diameters of the HL and BFS used in this study were 6.0 and 5.9 μm , respectively.

HL and BFS, together with deionized water or 0.25N NaOH solution, were placed into a 250 mL polypropylene conical flask with a solid weight of 8 g and a liquid volume/solid weight (L/S) ratio of 10 mL/g. When NaOH solution is used, the L/S ratio is equivalent to 0.1 g NaOH per gram of HL and BFS. The BFS/HL weight ratios tested here are shown in Table 1. The flask was then sealed with a rubber stopper at the mouth and inserted into a thermostat. The slurry was stirred with a magnetic stirrer for 16 h. The slurring temperatures used were 25 and 65°C. After slurring ended, the slurry was placed in a vacuum oven to evaporate the water; the remaining solid was further dried at 105°C for 8 h. The dry cake obtained was crushed into powder and sealed in a bottle before use.

Sulfation test

The sulfation test was performed by reacting a sample of about 30 mg with a gas mixture containing N_2 , H_2O , and 1000 ppm SO_2 in a differential fixed-bed reactor at 60°C and a relative humidity (RH) of 70% for 1 h. The sulfation conditions were selected so as to simulate the typical sulfation conditions in the bag filters of a spray-drying FGD process. CO_2 , O_2 , and NO_x were not used to make the synthetic flue gas because the test was only conducted for screening purposes. The details of the experimental setup and procedure have been described in a previous report (Ho and Shih, 1992).

The utilization of Ca (X) for a reacted sample was defined as the $\text{SO}_3^{2-}/\text{Ca}^{2+}$ molar ratio. The SO_3^{2-} content in a reacted sample was determined by means of iodometric titration, and the Ca^{2+} content by means of EDTA titration (Ho and Shih, 1993).

The SO_2 capture (SC) for a reacted sample was defined as the ratio of the weight of the SO_2 captured

to the initial weight of the sample. SC is related to the utilization of Ca as follows:

$$SC = M_{\text{SO}_2} \cdot M^{-1} \cdot \text{utilization of Ca}, \quad (1)$$

where M_{SO_2} is the molecular weight of SO_2 and M is the initial sorbent weight per mole of Ca. The value of M for a sorbent, as shown in Table 1, was determined from its Ca^{2+} content, which was measured by means of EDTA titration for an unreacted sample.

RESULTS AND DISCUSSION

The 1 h sulfation results for all the sorbents tested are summarized in Table 1 in terms of the Ca utilization and the SO_2 capture. To illustrate the effect of NaOH addition, the results are plotted in Figs. 1 and 2. One can easily see that at the same BFS/HL ratio and slurring temperature, the sorbent with added NaOH was more reactive than that without.

As shown in Fig. 1, in the case of the sorbents prepared without NaOH addition at a slurring temperature of 65°C, both the Ca utilization and the SO_2 capture of the sorbents varied significantly with the BFS/HL weight ratio. The sorbent with a ratio of 35/65 had the highest 1 h Ca utilization, 0.68, and the one with a ratio of 30/70 had the highest SO_2 capture, 0.45 g SO_2/g sorbent. As for the sorbents prepared with NaOH addition, both the Ca utilization and the SO_2 capture of the sorbents were higher for each BFS/HL ratio and became less sensitive to the ratio. Except for the sorbent with a ratio of 0/100, all the sorbents had about the same Ca utilization, the average value of which was 0.82 ± 0.03 . The highest SO_2 capture, 0.58 g SO_2/g sorbent, was achieved by the sorbent with a lower ratio, 10/90. In general, the effect of NaOH addition became greater as the ratio approached 100/0 (BFS) and 0/100 ($\text{Ca}(\text{OH})_2$).

As for $\text{Ca}(\text{OH})_2$, the addition of NaOH at a NaOH/ $\text{Ca}(\text{OH})_2$ ratio of 1/10 raised the level of Ca utilization greatly to 0.70 and SO_2 capture to 0.53 g SO_2/g sorbent, about three times greater than the values obtained before NaOH was added; these values were also greater than the maximum values for the BFS/HL sorbents prepared without NaOH addition at 65°C. Thus, from the viewpoint of increasing the utilization of hydrated lime, the above results reveal that NaOH works better than BFS.

In the case of BFS, the Ca utilization increased from 0.10 to 0.82 and the SO_2 capture increased from 0.04 to 0.32 g SO_2/g sorbent due to the addition of NaOH; the increase in Ca utilization achieved by means of NaOH addition in the case of BFS was the greatest among the sorbents, and the increase in SO_2 capture was second only to that obtained with

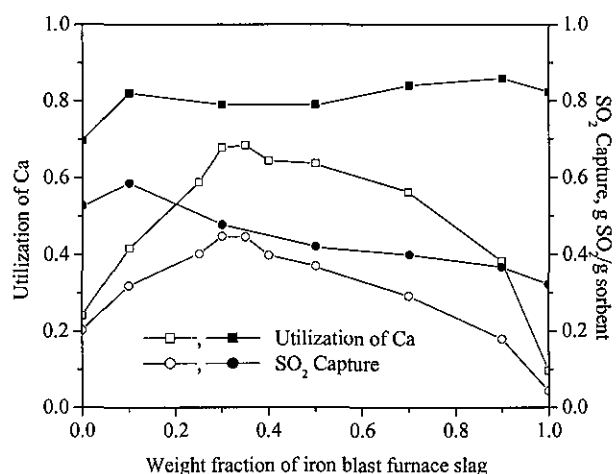


Fig. 1 Utilization of Ca and SO₂ capture versus weight fraction of blast furnace slag for BFS/HL sorbents; slurring conditions: 65°C, *L/S* = 10 mL/g, and 16 h; sulfation conditions: 60°C, 70% RH, and 1000 ppm SO₂ for 1 h. (Solid symbols indicate NaOH addition, while hollow ones indicate no NaOH addition.)

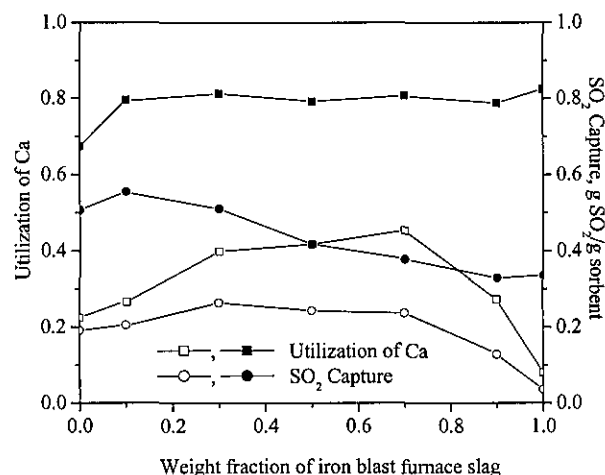


Fig. 2 Utilization of Ca and SO₂ capture versus weight fraction of blast furnace slag for BFS/HL sorbents; slurring conditions: 25°C, *L/S* = 10 mL/g, and 16 h; sulfation conditions: 60°C, 70% RH, and 1000 ppm SO₂ for 1 h. (Solid symbols indicate NaOH addition, while hollow ones indicate no NaOH addition.)

Table 1. Preparation conditions, Ca contents, Ca utilizations, and SO₂ captures of sorbents. Slurring conditions: *L/S* = 10 mL/g and 16 h. Sulfation conditions: 60°C, 70% RH, 1000 ppm SO₂, and 1 h.

BFS/HL Weight Ratio	Slurring Temp. (°C)	NaOH Concentration (N)	<i>M</i> (g sorbent/mol Ca)	<i>X</i>	<i>SC</i> (g SO ₂ /g sorbent)
0/100	—	0	74	0.20	0.17
0/100	65	0	76	0.24	0.20
10/90	65	0	83	0.42	0.32
25/75	65	0	94	0.59	0.40
30/70	65	0	97	0.68	0.45
35/65	65	0	98	0.68	0.44
40/60	65	0	104	0.64	0.40
50/50	65	0	110	0.64	0.37
70/30	65	0	123	0.56	0.29
90/10	65	0	137	0.38	0.18
100/0	65	0	143	0.10	0.04
0/100	65	0.25	85	0.70	0.53
10/90	65	0.25	90	0.82	0.58
30/70	65	0.25	106	0.79	0.48
50/50	65	0.25	120	0.79	0.42
70/30	65	0.25	135	0.84	0.40
90/10	65	0.25	150	0.86	0.37
100/0	65	0.25	164	0.82	0.32
0/100	25	0	75	0.22	0.19
10/90	25	0	84	0.27	0.21
30/70	25	0	97	0.40	0.26
50/50	25	0	110	0.42	0.24
70/30	25	0	123	0.45	0.23
90/10	25	0	136	0.27	0.13
100/0	25	0	143	0.08	0.04
0/100	25	0.25	85	0.67	0.50
10/90	25	0.25	92	0.80	0.56
30/70	25	0.25	102	0.81	0.51
50/50	25	0.25	122	0.79	0.41
70/30	25	0.25	136	0.81	0.38
90/10	25	0.25	153	0.79	0.33
100/0	25	0.25	157	0.83	0.34

$\text{Ca}(\text{OH})_2$. Furthermore, it should be noted that NaOH was added to BFS only at a NaOH/BFS weight ratio of 1/10, yet the resulting SO_2 capture was higher than those for $\text{Ca}(\text{OH})_2$ and some other sorbents prepared without NaOH addition. Thus, from the viewpoint of activating BFS as a reactive SO_2 sorbent, the above results indicate that NaOH is a better reagent than $\text{Ca}(\text{OH})_2$.

The effect of NaOH addition was more pronounced in the case of sorbents prepared at lower slurring temperatures. As seen from Figs. 1 and 2, the sorbents prepared without NaOH addition at 25°C were less reactive than those prepared at 65°C , except for the sorbents with 0/100 and 100/0 ratios, the reactivities of which were about the same at both temperatures. The maximum Ca utilization (0.45 for the sorbent with a ratio of 70/30) and the maximum SO_2 capture (0.26 g SO_2/g sorbent for the sorbent with a ratio of 30/70) of the sorbents prepared at 25°C were much lower than the maximum values for those prepared at 65°C . However, with the addition of NaOH, the reactivities of sorbents prepared at 25°C and 65°C were almost the same. For the sorbents prepared with NaOH addition at 25°C , the average Ca utilization was found to be 0.80 ± 0.02 for those sorbents with ratios other than 0/100, and it was found that the one with a ratio of 10/90 had the highest SO_2 capture of 0.56 g SO_2/g sorbent. Therefore, the addition of NaOH resulted in greater enhancement of the sorbent reactivity for the sorbents prepared at 25°C with ratios other than 0/100 and 100/0.

The enhancement effect of NaOH addition is thought to result from the deliquescence property of NaOH. It was observed that the powders of sorbents that did not contain NaOH were dry and loose before and after the sulfation test, while the powder particles of sorbents containing NaOH tended to stick together and had a wet appearance. Our recent study on the structural and chemical properties of sorbents revealed that sorbents prepared with NaOH addition had very much smaller specific surface area, pore volume, and amount of hydration products than those prepared without NaOH addition (Liu and Shih, 2002).

It has been shown that the reaction of SO_2 with Ca-containing sorbents requires the presence of a water layer on the surfaces of sorbent particles, and that the extent of reaction, *i.e.*, Ca utilization, increases with an increasing amount of adsorbed water (Ho *et al.*, 2002; Liu *et al.*, 2002). Therefore, the sulfation results of the present sorbents can be explained by considering the ability of a sorbent to collect water. Without the presence of any deliquescent material in a sorbent, the thickness of the water layer, which is a function of the relative humidity (RH) of the gas mixture, is very small, *e.g.*, only about 2.3

monolayers thick at 70% RH for $\text{Ca}(\text{OH})_2$ (Ho *et al.*, 2002). In this case, a large sorbent surface area is required to adsorb an appreciable amount of water in order to have high sorbent reactivity. The variation of Ca utilization with the BFS/HL ratio and slurring temperature for sorbents that do not contain NaOH should reflect variation of the sorbent specific surface area with the ratio and temperature, and this inference has been proved experimentally (Liu and Shih, 2001). However, in the presence of deliquescent material, such as NaOH, a great quantity of water can be collected by the sorbent, and the reaction will, therefore, be greatly enhanced. In this case, the sorbent reactivity is controlled mainly by the type and amount of the deliquescent material because these factors determine the amount of water available in a sorbent. This may be the reason why sorbents containing NaOH prepared at different slurring temperatures have about the same reactivity.

When a sorbent containing NaOH is reacted, SO_2 will react not only with $\text{Ca}(\text{OH})_2$ and calcium silicate, but also with NaOH. If the NaOH contained in the present sorbents could be converted completely to Na_2SO_3 , its contribution to SO_2 capture would be 0.07 g SO_2/g sorbent, and its contribution to Ca utilization would range from 0.10 to 0.18 as the weight ratio increased from 0/100 to 100/0. These contributions would be much smaller than the results shown in Figs. 1 and 2.

The results of this study show that the addition of NaOH enhanced the Ca utilization of sorbents to levels that were nearly independent of the slurring temperature and the BFS/HL weight ratio used to prepare the sorbents. This finding indicates that NaOH addition has advantages in practical applications. The amount of required $\text{Ca}(\text{OH})_2$ can be cut down, and the energy consumed in the hydration process can be reduced without sacrificing sorbent reactivity. Therefore, the cost of the sorbent and, hence, the operating cost of the semidry or dry FGD process can be reduced.

CONCLUSION

In the case of BFS/HL sorbents prepared without NaOH addition, the Ca utilization and SO_2 capture of the sorbents increased with increasing slurring temperature and varied with the BFS/HL weight ratio. In the case of sorbents prepared with NaOH addition, their reactivities were greatly enhanced, and their Ca utilization increased to a level that was nearly independent of the slurring temperature and the BFS/HL weight ratio. The effect of NaOH addition resulted from the fact that NaOH is deliquescent, and that its presence increased the amount of water collected by the sorbents. NaOH addition can raise the level of

sorbent reactivity and reduce the sorbent cost in a semidry or dry FGD process.

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NOMENCLATURE

<i>L</i>	liquid volume, mL
<i>M</i>	initial weight of solid per mol of Ca, g/mol Ca
<i>M</i> _{SO₂}	molecular weight of SO ₂ , g/mol
<i>S</i>	weight of iron blast furnace slag and hydrated lime, g
<i>SC</i>	SO ₂ capture, g SO ₂ /g sorbent
<i>X</i>	the utilization of Ca

Acronyms

BFS	iron blast furnace slag
FGD	flue gas desulfurization
HL	hydrated lime

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氫氧化鈉對爐石／氫氧化鈣吸收劑與二氧化硫之反應性之促進作用研究

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摘 要

本研究於爐石／氫氧化鈣泥漿中添加氫氧化鈉以製備煙道氣除硫吸收劑。由於氫氧化鈉的潮解性質，使較多的水分能吸附在吸收劑表面，提高了吸收劑與二氧化硫的反應性。未添加氫氧化鈉的爐石／氫氧化鈣吸收劑與二氧化硫反應的鈣利用率與二氧化硫捕捉率隨漿化溫度的增加而增加，且隨爐石／氫氧化鈣重量配比而改變；添加氫氧化鈉後，吸收劑之鈣利用率幾乎相同，不受漿化溫度與重量配比影響。添加氫氧化鈉可以提昇吸收劑之反應性，並且可降低半乾式或乾式煙道氣除硫程序的成本。

