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Effect of NaOH Addition on the Reactivities of Iron Blast Furnace Slag/Hydrated Lime Sorbents for Low-Temperature Flue Gas Desulfurization

Chiung-Fang Liu and Shih-Min Shih*

Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan 106

NaOH was added to iron blast furnace slag (BFS)/hydrated lime (HL) slurries to prepare the sorbents for semidry and dry flue gas desulfurization (FGD) processes. For sorbents prepared without NaOH, both the Ca utilization and the SO_2 capture increased with increasing slurrying temperature and varied with the BFS/HL weight ratio. With NaOH addition, the sorbents contained much less high surface area products of pozzolanic reaction. Their reactivities were insensitive to the slurrying temperature and greatly enhanced when the NaOH/(BFS + HL) ratio was about 10/100. NaOH is deliquescent, and its presence increases the amount of water collected by a sorbent, which is required for the sulfation of a sorbent at low temperatures. The use of NaOH addition at or below the optimal ratio can raise the sorbent reactivity and reduce the cost of sorbent for a semidry or dry FGD process.

Introduction

The spray-drying (semidry) and dry flue gas desulfurization (FGD) processes are effective means of reducing SO_2 emissions from coal-fired power stations.[1,2] These processes have the advantages of easier retrofit and simpler waste treatment; however, the conversion of the sorbent, which is mostly hydrated lime ($Ca(OH)_2$), in these processes is usually low. Thus, increasing the reactivity of sorbent has been an important subject for the application of these FGD processes.

Brodnax and Rochelle[3] recently reported that sorbents prepared from hydrated lime (HL) and iron blast furnace slag (BFS) through a hydration process have greater surface areas and higher reactivities toward SO_2 than HL. BFS is the waste of iron and steel industries. It is mainly composed of SiO_2, Al_2O_3, and CaO and is a pozzolanic material, which can react with HL to form calcium silicate hydrates under the presence of water.[4] Our recent study[5] confirmed that BFS/HL sorbents are indeed highly reactive toward SO_2. We also found that the structural properties and reactivity of this kind of sorbent are affected by the BFS/HL weight ratio, the fineness of slag, and the hydration conditions. The sorbent with a BFS/HL ratio of 30/70 was found to have the highest Ca utilization and SO_2 capture, the values of which increase as the slurrying temperature and time increase and as the particle size of BFS decreases.

Successful use of sorbents prepared from BFS not only reduces the operating cost of the desulfurization process but also helps the utilization of BFS produced from iron and steel industries. Thus, this kind of sorbent deserves more studies.

To further raise the sorbent reactivity, Brodnax and Rochelle used gypsum and $CaCl_2$ as the additives to prepare their sorbents.[3] In our recent work,[6] we used NaOH as the additive. By adding NaOH at an NaOH/(BFS + HL) ratio of 10/100, the sorbent reactivity was found to be greatly enhanced. NaOH has been used to enhance the reactivities of sorbents prepared from fly ash, which is also a pozzolanic material, and HL.[7−10] Petersen and Rochelle[8] pointed out that the addition of NaOH to the slurry of fly ash and HL increases the dissolution of silica from fly ash but decreases that of HL; therefore, there is an optimum NaOH concentration that is related to the source of fly ash, the amount of fly ash, the addition of calcium sulfite, and slurrying temperature. It has been shown that the reaction of a fly ash/$Ca(OH)_2$ sorbent with SO_2 at low temperatures requires the presence of a water layer adsorbed on the sorbent surface.[11] Thus, according to Kind et al.,[10] the role played by NaOH is to increase the water adsorption capacities of sorbents because NaOH is a deliquescent material.

In this work, sorbents were prepared at different BFS/HL/NaOH weight ratios and slurrying temperatures. The sorbents were subjected to reaction with SO_2 with the aim to elucidate the effect of NaOH addition on the sorbent reactivity.

Experimental Section

Preparation of Sorbents. Reagent grade $Ca(OH)_2$ (purity >95%, Hayashi Pure Chemical Industries, LTD) and NaOH (purity >96%, Nacalai Tesque, Inc.) were used. The iron BFS was supplied by the China Hi-Ment corporation; the high fineness slag was used, and its chemical composition was given as 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% sulfide, and 1.67% ignition loss. The volume mean particle diameters of HL and BFS were 6.0 and 5.9 μm, respectively.

The HL and BFS, together with deioned water or an NaOH solution, were placed in a 250 mL polypropylene conical flask at a solid weight of 8 g and a liquid volume/solid weight (L/S) ratio of 10 mL/g. For the case of using NaOH solutions (0.01−1.00 N), the L/S ratio is equivalent to an NaOH/(BFS + HL) weight ratio of 10/100 for using a 0.25 N NaOH solution. The BFS/HL weight ratios tested were varied from 0/100 to 100/0. The flask

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* To whom correspondence should be addressed. Tel.: 886-2-23633974. Fax: 886-2-236230404. E-mail: smshih@ccms.ntu.edu.tw.

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Table 1. Preparation Conditions, M's (g sorbent/mol Ca), Ca Utilizations (X), Corrected Ca Utilizations (X′), and SO_2 Captures (SC, g SO_2/g Sorbent) of Sorbents[a]

BFS/HL wt ratio	slurrying temp (°C)	NaOH/(BFS + HL) = 0/100			NaOH/(BFS + HL) = 2/100				NaOH/(BFS + HL) = 10/100				NaOH/(BFS + HL) = 40/100			
		M	X	SC	M	X	X′	SC	M	X	X′	SC	M	X	X′	SC
0/100	65	76	0.24	0.20	76	0.43	0.41	0.36	85	0.70	0.61	0.53	107	0.82	0.44	0.49
10/90	65	83	0.42	0.32	84	0.61	0.59	0.46	90	0.82	0.72	0.58	115	0.85	0.46	0.47
30/70	65	94	0.68	0.46	99	0.73	0.71	0.47	106	0.79	0.68	0.48	132	0.94	0.50	0.46
50/50	65	110	0.64	0.37	114	0.66	0.64	0.37	120	0.79	0.67	0.42	150	1.05	0.56	0.45
70/30	65	123	0.56	0.29	126	0.59	0.56	0.30	135	0.84	0.70	0.40	172	0.90	0.34	0.33
90/10	65	137	0.38	0.18	142	0.42	0.39	0.19	150	0.86	0.70	0.37	193	0.84	0.19	0.28
100/0	65	143	0.10	0.04	151	0.36	0.32	0.15	164	0.82	0.64	0.32	211	0.84	0.14	0.25
0/100	25	75	0.22	0.19	78	0.42	0.40	0.34	85	0.67	0.58	0.50	106	0.80	0.42	0.48
10/90	25	84	0.27	0.21	85	0.59	0.57	0.44	92	0.80	0.70	0.56	115	0.83	0.44	0.46
30/70	25	97	0.40	0.26	98	0.70	0.68	0.46	102	0.81	0.70	0.51	133	0.88	0.44	0.42
50/50	25	110	0.42	0.24	113	0.68	0.66	0.39	122	0.79	0.67	0.41	149	1.01	0.52	0.43
70/30	25	123	0.45	0.23	128	0.57	0.54	0.29	136	0.81	0.67	0.38	171	0.91	0.35	0.34
90/10	25	136	0.27	0.13	143	0.45	0.42	0.20	153	0.79	0.60	0.33	194	0.85	0.20	0.28
100/0	25	143	0.08	0.04	149	0.33	0.29	0.14	157	0.83	0.65	0.33	212	0.82	0.12	0.25
					NaOH/(BFS +HL) = 0.4/100				NaOH/(BFS +HL) = 6/100							
0/100	25				76	0.25	0.25	0.21	81	0.56	0.50	0.44				

[a] Slurrying conditions: L/S = 10 mL/g and 16 h. Sulfation conditions: 60 °C, 70% RH, 1000 ppm SO_2, and 1 h.

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 slurrying temperatures used were 25 and 65 °C. After the solutions were slurried, the slurry was dried in an oven at 105 °C and ambient pressure for 12 h. The dry cake obtained was crushed into powder and sealed in a bottle before use.

Sorbents containing NaOH were also prepared by adding NaOH to unslurried mixtures of BFS and HL and to the dry BFS/HL sorbents, which had been prepared without NaOH using the above procedure. In these two cases, NaOH solution was added to the particle bed until the voids between particles were just filled up. The wet cake was then dried by the above drying procedure.

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 under the conditions of 60 °C and 70% relative humidity (RH) for 1 h. The sulfation conditions were selected 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 added to make the synthetic flue gas because the test was only for screening purposes. The sample was dispersed into the quartz wool inserted in the sample pan; the pan was perforated at the bottom to facilitate the passage of the gas. The experimental setup and procedure were similar to that described in a previous report.[12]

The utilization of Ca (X) for a reacted sample was determined from the SO_3^{2-}/Ca^{2+} molar ratio. The SO_3^{2-} content in a sample was determined by iodometric titration, and the Ca^{2+} content was determined by ethylenediaminetetraacetic acid (EDTA) titration.[13]

The SO_2 capture (SC) for a reacted sample was defined as the ratio of the weight of SO_2 captured to the initial weight of the sample. SC is related with the utilization of Ca by

$$SC = M_{SO_2} \cdot M^{-1} \cdot \text{utilization of Ca} \qquad (1)$$

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 EDTA titration for the unreacted sample.

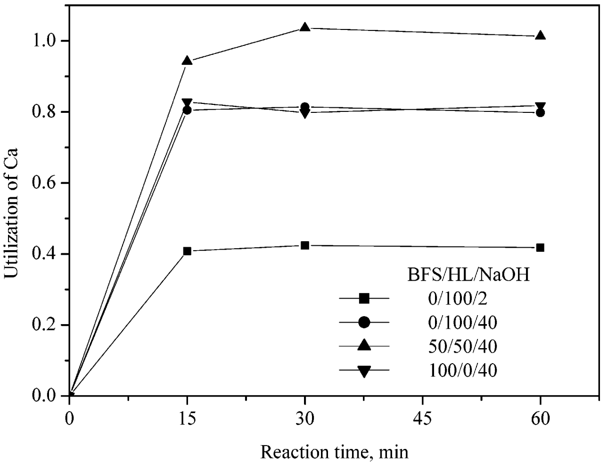

Figure 1. Utilization of Ca vs reaction time for the sulfation of BFS/HL/NaOH sorbents. Slurrying conditions: 25 °C, L/S = 10 mL/g, and 16 h. Sulfation conditions: 60 °C, 70% RH, 1000 ppm SO_2, and 1 h.

At least two repeated runs were performed for each reaction condition, and the average of the results was taken. The absolute experimental error in Ca utilization was about 0.03.

Results and Discussion

As can be seen from Figure 1, the reactions of BFS/HL/NaOH sorbents reach the ultimate extents early before 1 h reaction time. Thus, the 1 h sulfation results represent the ultimate values of sorbent reactivities. The 1 h sulfation results for the sorbents tested are summarized in Table 1 in terms of the Ca utilization (X) and the SO_2 capture (SC). One can easily see that at the same BFS/HL ratio and slurrying temperature, the sorbent prepared with NaOH is more reactive than that without.

It should be noted that the Ca utilization defined in this work is not the "true" utilization of Ca; instead, it is an "apparent" one. SO_2 can be captured not only by the reactive compounds of Ca but also by those of other metals, such as Na and Mg, in a sorbent. Thus, the Ca

Table 2. Sulfation Results for BFS/HL/NaOH Sorbents Prepared by Different Methods[a]

BFS/HL/NaOH wt ratio	NaOH added without slurrying process		slurrying with NaOH solution		NaOH added after slurrying process	
	X	SC	X	SC	X	SC
100/0/2	0.13	0.06	0.36	0.14		
100/0/10	0.29	0.12	0.83	0.33	0.85	0.34
100/0/40			0.82	0.25		
50/50/2	0.43	0.25	0.68	0.39	0.65	0.36
50/50/10	0.61	0.31	0.79	0.41	0.82	0.42
50/50/40			1.01	0.43	1.08	0.46
30/70/2	0.46	0.30	0.70	0.46	0.77	0.49
30/70/10	0.62	0.38	0.81	0.51	0.79	0.47
30/70/40			0.88	0.42	0.92	0.44
0/100/2	0.45	0.37	0.42	0.34		
0/100/10	0.65	0.50	0.67	0.50		
0/100/40	0.76	0.47	0.80	0.48		

[a] Slurrying conditions: 25 °C, L/S = 10/1 mL/g, and 16 h. Sulfation conditions: 60 °C, 70% RH, 1000 ppm SO_2, and 1 h.

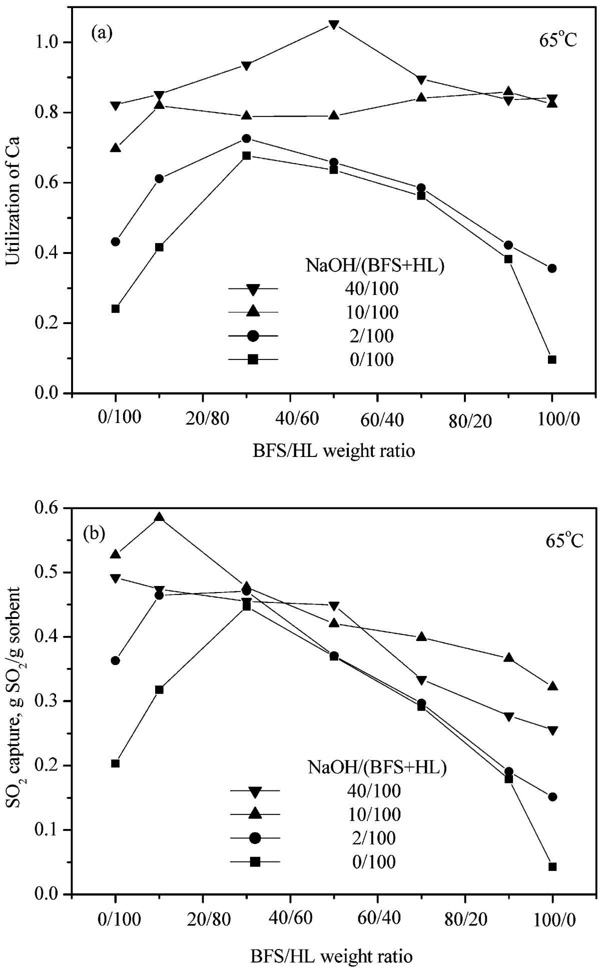

Figure 2. (a) Utilization of Ca and (b) SO_2 capture vs BFS/HL weight ratio for BFS/HL/NaOH sorbents. Slurrying conditions: 65 °C, L/S = 10 mL/g, and 16 h. Sulfation conditions: 60 °C, 70% RH, and 1000 ppm SO_2 for 1 h.

utilization is the total moles of SO_2 captured by all of the reactive species per mole of Ca. According to this definition, the value of Ca utilization may exceed unity.

Comparison of Different Methods of NaOH Addition. To confirm that the best method for preparing the NaOH-containing sorbents is to slurry BFS and HL together with NaOH solution, the reactivities of sorbents prepared by the three different procedures described in the Experimental Section were measured, and the results are compared in Table 2.

As seen from Table 2, all of the sorbents are more reactive than the raw $Ca(OH)_2$ (X = 0.19) and BFS (X = 0.03). At the same BFS/HL/NaOH ratio, except for the ratio of 0/100/10, the reactivity of the sorbent prepared without the slurrying process is the lowest, and that of the sorbent prepared by adding NaOH to the dry slurried BFS/HL sample is close to that of the sorbent prepared by slurrying with NaOH solution.

Although the latter two methods produced sorbents having about equal reactivity, the method of slurrying with NaOH solution requires only one drying process and thus consumes less energy; therefore, it is considered to be the best among the three methods. The present study focuses on sorbents prepared by this method.

Effect of BFS/HL/NaOH Ratio on Sorbent Reactivity. As shown in Figure 2, for the sorbents prepared without NaOH at a slurrying temperature of 65 °C, both the Ca utilization and the SO_2 capture vary significantly with the BFS/HL ratio. The one with a ratio of 30/70 has the highest Ca utilization, 0.68, and SO_2 capture, 0.45 g SO_2/g sorbent.

For the sorbents prepared with NaOH, the Ca utilization, as shown in Figure 2a, is seen to increase with increasing NaOH content for each BFS/HL ratio; however, the Ca utilization becomes less sensitive to the NaOH content as the NaOH content increases. The sorbent prepared with a BFS/HL/NaOH ratio of 50/50/40 has the overall highest Ca utilization of 1.05. It is interesting to note that at the NaOH/(BFS + HL) ratio of 10/100, the Ca utilizations for the sorbents with BFS/HL ratios from 10/90 to 100/0 are about the same, the average value of which is 0.82 ± 0.03.

Although the Ca utilization increases with increasing NaOH content in a sorbent, there is an optimal NaOH content for enhancing the SO_2 capture. From Figure 2b, the SO_2 capture is seen to reach a maximum or very close to it at an NaOH/(BFS + HL) ratio of 10/100 for each BFS/HL ratio. The overall highest SO_2 capture for the sorbents, 0.59 g SO_2/g sorbent, is given by the sorbent with a BFS/HL/NaOH ratio of 10/90/10.

In general, Figure 2 reveals that the effect of NaOH addition becomes greater as the BFS/HL ratio approaches 100/0 (BFS) and 0/100 ($Ca(OH)_2$). As shown in Figure 2, the addition of NaOH at an NaOH/$Ca(OH)_2$ ratio of 10/100 greatly raises the Ca utilization of $Ca(OH)_2$ to 0.70 and the SO_2 capture to 0.53 g SO_2/g sorbent, about three times those before adding NaOH; these values are also greater than the maximum values for the BFS/HL sorbents prepared without NaOH at 65 °C. Thus, from the viewpoint of increasing the utilization of HL, NaOH works better than BFS.

For BFS, Figure 2 indicates that its Ca utilization increases from 0.10 to 0.82 and its SO_2 capture from 0.04 to 0.32 g SO_2/g sorbent due to the addition of NaOH at an NaOH/BFS ratio of 10/100; the increase in Ca utilization is the greatest among the sorbents, and the increase in SO_2 capture is second to that for $Ca(OH)_2$. Furthermore, one can note that NaOH was added to BFS only at a NaOH/BFS ratio of 10/100, but the resulting SO_2 capture is higher than those for $Ca(OH)_2$ and some other sorbents prepared without NaOH. Thus, from the viewpoint of activating BFS to a reactive SO_2 sorbent, NaOH is a better reagent than $Ca(OH)_2$.

Effect of Slurrying Temperature on Sorbent Reactivity. The effect of NaOH is more pronounced for sorbents prepared at a lower slurrying temperature. As seen from Table 1, the sorbents prepared without NaOH at 25 °C are less reactive than those prepared at 65 °C, except for the sorbents with 0/100 and 100/0 ratios, the reactivities of which are about the same at both temperatures. However, with the addition of NaOH, the reactivities of sorbents prepared at 25 and 65 °C are almost the same for each BFS/HL/NaOH ratio. Therefore, the addition of NaOH resulted in a greater enhancement of sorbent reactivity for the sorbents prepared at 25 °C with ratios other than 0/100 and 100/0.

SO_2 Uptake by NaOH and Corrected Ca Utilization. Because NaOH is alkaline, it is able to react with SO_2. The actual SO_2 uptake by the NaOH contained in a sorbent was not measured in this work. However, the 1 h conversion of NaOH alone at the reaction conditions of this study was measured, and the value was 0.94 ± 0.02, which is close to unity. Thus, the maximum possible contribution of NaOH to sorbent reactivity can be estimated by assuming that the NaOH contained in a sorbent would be completely converted to Na_2SO_3.

For the NaOH/(BFS + HL) ratio of 10/100, the maximum contribution to SO_2 capture is 0.07 g SO_2/g sorbent and that to Ca utilization is from 0.09 to 0.18 as the BFS/HL ratio increases from 0/100 to 100/0. These values are much smaller than the corresponding values of SC and X shown in Table 1. Therefore, the contributions of NaOH at an NaOH/(BFS + HL) ratio of 10/100 or less are small. However, for the NaOH/(BFS + HL) ratio of 40/100, the corresponding contributions, 0.23 g SO_2/g sorbent and 0.38 to 0.70, are significant.

Because the reactive solid species in a sorbent are mainly compounds of Ca and Na, the utilization of the Ca-containing species can be estimated by the corrected Ca utilization, X′, which is obtained by subtracting the maximum contribution of NaOH from the Ca utilization (X) measured. The values of X′ are given in Table 1. One can see that for each BFS/HL ratio, X′ reaches a maximum or very close to it at an NaOH/(BFS + HL) ratio of 10/100 when the ratio increases from 0/100 to 40/100 and that for some BFS/HL ratios, the X′ value at the NaOH/(BFS + HL) ratio of 40/100 is smaller than the X value at the ratio of 0/100. One also can note that for the sorbents prepared with BFS/HL ratios of 30/70 and 50/50 at 65 °C, their X′ values are only slightly affected by varying the NaOH/(BFS + HL) ratio from 0/100 to 10/100, whereas for the BFS, the change of its X′ value is pronounced and is the largest among the sorbents prepared at 25 or 65 °C.

Effect of NaOH Addition on Sorbent Properties. It was observed that the powders of sorbents not containing NaOH are dry and loose before and after the sulfation test, but the particles of sorbents containing NaOH tend to stick together and have a wet appearance due to the deliquescence of NaOH. Apparently, these two kinds of sorbents are different in structural and chemical properties.

The specific surface areas of some sorbents (BFS/HL = 100/0 and 30/70) prepared without and with NaOH (NaOH/(BFS + HL) = 10/100) were measured and are compared in Table 2. One can see that the sorbent specific surface area was greatly reduced by the addition of NaOH. Also, the effect of slurrying temperature on the specific surface area is seen to be insignificant when NaOH is present, indicating that the sorbent structural properties may be insensitive to the slurrying temperature. This may be the reason that the sorbents prepared with the same BFS/HL/NaOH ratio at different slurrying temperatures had about the same Ca utilization and SO_2 capture.

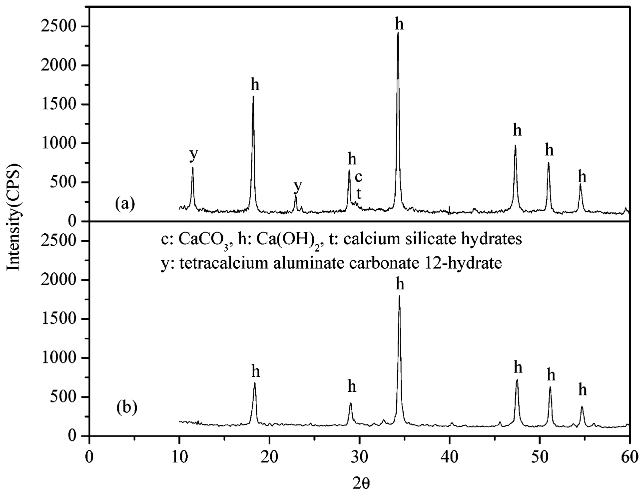

Figure 3. XRD patterns of (a) BFS/HL (30/70) sorbent and (b) BFS/HL/NaOH (30/70/10) sorbent. Slurrying conditions: 65 °C, L/S = 10 mL/g, and 16 h.

As seen in Figure 3, the X-ray diffraction patterns for the sorbents (BFS/HL = 30/70) prepared without and with NaOH (NaOH/(BFS + HL) = 10/100), the peaks of the products of pozzolanic reaction, calcium silicate hydrates and tetracalcium aluminate carbonate 12-hydrate, are not distinguishable for the sorbent containing NaOH. This result indicates that the sorbents prepared with NaOH contained much less of these products. This finding explains the results of surface area measurement because calcium silicate hydrates are high surface area foil-like materials.[4,11−14]

SEM observations[5,6] showed that the raw BFS particles have smooth surfaces, but the surfaces of the particles are very rough after hydration with water or NaOH solution, indicating that the dissolution of BFS had occurred during the hydration process. The SEM observations also showed that the particles of BFS/HL sorbents not containing NaOH are mainly composed of foil-like substances, and highly porous, but few foil-like substances can be observed, and the particles are less porous for sorbents containing NaOH.

The above findings indicate that the pozzolanic reaction between BFS and HL during the hydration process had been inhibited by NaOH. The reason is thought to be that the NaOH solution (0.25 N) is a strong base and the dissolution of HL and the CaO contained in BFS was limited due to the common ion effect.[8]

However, the dissolution of the silica contained in BFS was enhanced in the NaOH solution.[8] The dissolution of silica from a BFS particle would cause the particle to become porous or even disintegrate into smaller particles, as evidenced by the SEM observations[6] and the moderate increase in the specific surface area for the BFS that had been slurried with NaOH solution (Table 3). In this case, the CaO contained in the interior of the BFS particle would also become accessible to SO_2. This may be the reason that the sorbents containing NaOH were highly reactive even though they contained few high surface area materials. Furthermore, that the sorbents prepared without slur-

Table 3. Specific Surface Areas of BFS/HL/NaOH Sorbents

BFS/HL/NaOH wt ratio	slurrying temp (°C)	slurrying time (h)	L/S (mL/g)	S_{g0} (m^2/g)
raw BFS				1.5
100/0/0	65	16	10/1	17.1
30/70/0	25	16	10/1	22.3
30/70/0	65	16	10/1	28.9
100/0/10	25	16	10/1	2.6
100/0/10	65	16	10/1	3.7
30/70/10	25	16	10/1	4.4
30/70/10	65	16	10/1	4.4

rying process were less reactive (Table 2) may be due to the lack of enough time for silica to dissolve from BFS particles.

Discussion on the Enhancement Effect of NaOH Addition. The enhancement effect of NaOH addition on the sorbent reactivity is thought to be result mainly from the deliquescence property of NaOH.

The amounts of water adsorbed on the sorbents with BFS/HL/NaOH ratios of 30/70/0, 30/70/10, and 30/70/40 were measured to be 153, 316, and 569 g H_2O/kg sorbent, respectively, at 60 °C and 70% RH. The value was 248 g H_2O/kg sorbent for the sorbent with 30/70/10 ratio, which was prepared by adding NaOH to the sorbent with a 30/70/0 ratio. These results indicate that more water was collected when NaOH was present.

It has been shown that the low temperature reaction of SO_2 with Ca-containing sorbents requires the presence of a water layer on the surfaces of sorbent particles, and the reaction extent, i.e., the Ca utilization, increases with an increasing amount of water adsorbed.[11,15] 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 RH of the gas mixture, is very small, e.g., only about 2.3 monolayers thick at 70% RH for $Ca(OH)_2$.[15] In this case, a large sorbent surface area is required to adsorb an appreciable amount of water in order to have a high sorbent reactivity. The variation of Ca utilization with the BFS/HL ratio and slurrying temperature for the sorbents not containing NaOH should reflect a variation of the sorbent specific surface area with the ratio and temperature; this inference has been proved experimentally.[5]

In the presence of a deliquescent material, such as NaOH, a greater quantity of water can be collected by the sorbent, and the reaction will, therefore, be greatly enhanced. In this case, the sorbent reactivity would be controlled predominantly by the type and the amount of the deliquescent material because these factors determine the amount of water available in a sorbent. This may explain the fact that the sorbents prepared by slurrying with NaOH solution and by adding NaOH after slurrying had about equal reactivity at the same BFS/HL/NaOH ratio (Table 2).

However, NaOH will dissolve into the water that it collects to form NaOH solution. NaOH solution, being a strong base, can absorb SO_2 and transform it into SO_3^{2-}, and, in the meantime, inhibit the dissolution of $Ca(OH)_2$, the CaO contained in BFS, and other Ca-containing species. Thus, the dissolution of Ca-containing species takes place only after most NaOH has been consumed. The large amount of solution left at this stage is beneficial to the dissolution of Ca-containing species and thereby can raise the SO_2 uptake of the sorbent. However, if the concentration of SO_3^{2-} in the solution is already very high, which might be the case for sorbents with a NaOH/(BFS + HL) ratio of 40/100, the precipitation of $CaSO_3{\cdot}0.5H_2O$ and hence the covering of the reacting surface by $CaSO_3{\cdot}0.5H_2O$ will take place before the dissolution of Ca-containing species can reach a higher extent;[15] therefore, the ultimate utilization of Ca-containing species and the total amount of SO_2 captured will be reduced (Table 1). This may explain the fact that there was an optimal fraction of NaOH (NaOH/(BFS + HL) = 10/100) for enhancing the utilization of Ca-containing species and the SO_2 capture of sorbent.

Practical Implication. The results of this study show that the addition of NaOH at an NaOH/(BFS + HL) ratio of 10/100 enhanced the Ca utilization of sorbent to a level that was nearly independent of the slurrying temperature and the BFS/HL ratio used to prepare a sorbent. This finding indicates that the use of NaOH addition at or below this optimal ratio has advantages in practical applications. The amount of $Ca(OH)_2$ required can be cut down, and the energy consumed in the hydration process can be saved without decreasing the sorbent reactivity. Therefore, the cost of sorbent and hence the operating cost in a semidry or dry FGD process can be reduced.

Conclusion

For BFS/HL sorbents prepared without NaOH, the Ca utilization and SO_2 capture increased with increasing slurrying temperature and varied with the BFS/HL ratio. For sorbents prepared with NaOH, the sorbents contained much less high surface area products of pozzolanic reaction due to the inhibition effect of NaOH in the hydration process. Their reactivities were insensitive to the slurrying temperature and were greatly enhanced when the NaOH/(BFS + HL) ratio was about 10/100. At this optimal ratio, the Ca utilizations of sorbents were raised to a level that was nearly independent of the BFS/HL ratio. The enhancement effect of NaOH addition at or below the optimal ratio mainly resulted from the fact that NaOH is deliquescent and its presence increases the amount of water collected by a sorbent, which is required for the sulfation of a sorbent at low temperatures. The use of NaOH addition at or below the optimal ratio can raise the sorbent reactivity and reduce the sorbent cost in a semidry or dry FGD process.

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Nomenclature

BFS = iron blast furnace slag
FGD = flue gas desulfurization
HL = hydrated lime
L = liquid volume (mL)
M = initial weight of solid per mol of Ca (g/mol Ca)
M_{SO_2} = molecular weight of SO_2 (g/mol)
S = weight of iron blast furnace slag and hydrated lime (g)
SC = SO_2 capture (g SO_2/g sorbent)
S_{g0} = initial specific surface area (m^2/g)
X = utilization of Ca
X′ = corrected utilization of Ca

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