Thermochimica Acta, 189 (1991) 1–24
Elsevier Science Publishers B.V., Amsterdam

Characterization of calcium oxide–fly ash sorbents for SO_2 removal *

R.A. Diffenbach, M.J. Hilterman, E.A. Frommell, H.B. Booher and S.W. Hedges

Pittsburgh Energy Technology Center, Pittsburgh, PA 15236 (USA)

(Received 21 December 1990)

Abstract

Sorbents for SO_2 removal from humidified simulated flue gas have been prepared from CaO–fly ash slurries using a pressure hydration technique. The fly ash materials were obtained from the combustion of four bituminous, six sub-bituminous, and two lignite coals. The CaO/fly ash ratio, and the slurry reaction time and temperature were varied in the preparation step. The sorbents were characterized by measuring thermogravimetrically the SO_2 uptake from flue gas, and by X-ray diffraction, surface area, particle size, and optical microscopy studies. The X-ray diffraction results indicated that calcium silicate hydrate, $Ca_2SiO_4 \cdot H_2O$, and calcium aluminum silicate hydroxide, $Ca_3Al_2(SiO_4)(OH)_8$, were the principal Ca-containing species formed during the hydrothermal reaction between CaO and fly ash. There was a good correlation between the surface area of the sorbent and the SO_2 uptake. Particle size measurements and optical microscopy studies indicated that the glass-like spheres in fly ash remained largely intact during the hydrothermal preparation step.

INTRODUCTION

The direct injection of dry sorbents into the flue gas duct-work (duct injection) at a coal-fired boiler offers the possibility of lower capital costs for controlling SO_2 emissions because the process does not require the costly atomizers, slurry preparation systems, or solids dewatering equipment needed for other processes [1–4]. In the injection process, the dry sorbent particles are introduced into the flue gas in the duct between the air preheater and the particulate control device, which may be a fabric filter or an electrostatic precipitator (ESP). As indicated in Fig. 1(top), the flue gas is humidified (humidified duct injection, HDI) by spraying water either upstream or downstream of the sorbent injection port. Another approach is shown in Fig. 1(bottom), where a hydrated lime slurry is injected into the duct; the

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* Reference in this paper to any specific commercial product, process, or service is to facilitate understanding and does not imply endorsement or favoring by the United States Department of Energy.

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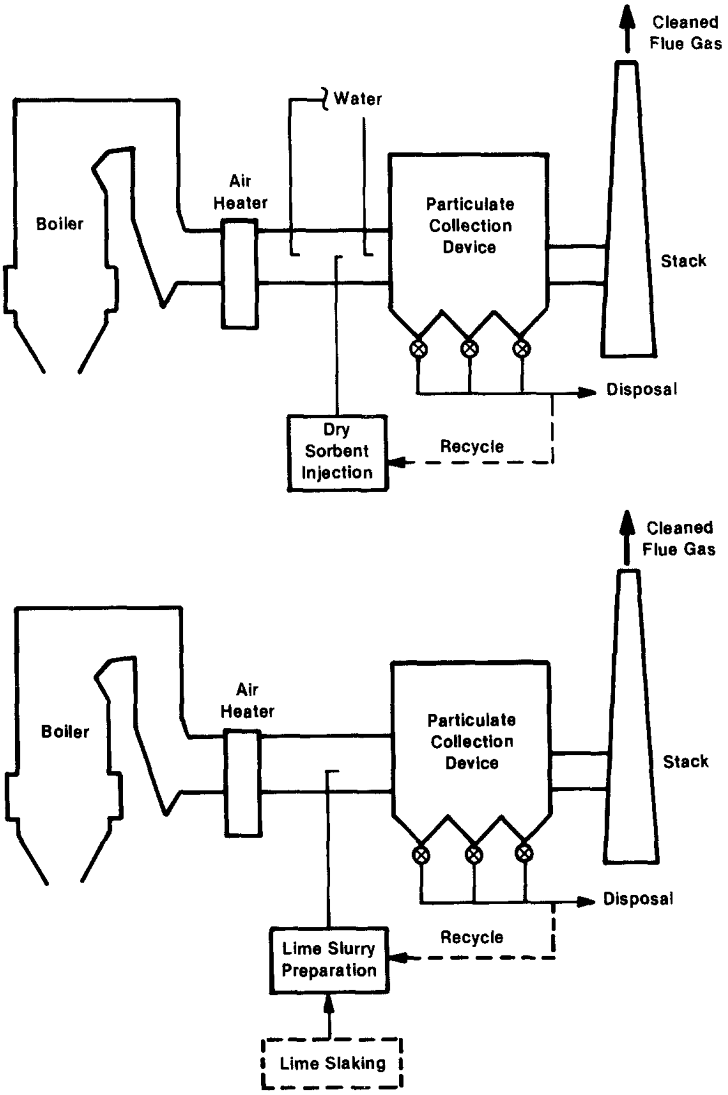

Fig. 1. Top, humidified duct injection using dry sorbent injection. Bottom, humidified duct injection using slurry injection.

evaporation of the water from the slurry provides for humidification of the flue gas. The total SO_2 removal is the sum of the removal in the duct section and the removal in the particulate collection device. Because the residence time in the duct is short (typically 1–3 seconds), recent studies have indicated that most of the SO_2 is removed in the fabric filter. Thus, because of the increased residence time provided by a fabric filter as compared with the short residence time of an ESP, a flue gas clean-up (FGC) installation using duct injection would favor the use of a fabric filter. However, most existing power plants are already equipped with ESPs and may find it economical to continue their use in retrofit situations for SO_2 control. New sorbents with higher reactivity than conventional hydrated lime are needed to increase the normally low SO_2 capture obtained at utility plants with an ESP. By increasing the sorbent reactivity and utilization, the economics of duct injection processes can be improved significantly.

Recently, work has been carried out to produce highly reactive sorbents using fly ash from coal-fired boilers [5]. The earliest of these studies showed that the alkalinity present in the fly ash could be utilized for SO_2 removal [6]. The fly ash was slurried in water and fed into a spray dryer/bag-house system. In a subsequent pilot-plant study, Reed et al. [7] showed that the SO_2 removal was dependent on both the surface area of the fly ash and the alkalinity of the fly ash; up to 30% SO_2 removal was achieved. In more recent studies, the fly ash was not used as a source of alkalinity, but as a source of silica. Jozewicz and Rochelle [8] studied the reaction of fly ash with $Ca(OH)_2$ to produce reactive solids for SO_2 removal. The fly ash was slurried with $Ca(OH)_2$ in water from 25 to 92° C. After water removal, the dry solids were tested for reactivity towards SO_2 in a packed-bed reactor designed to simulate fabric filter conditions. These solids were much more reactive than $Ca(OH)_2$; the high reactivity of these sorbents could be achieved only through long slurrying times (12–16 h) and high fly ash content (up to 20 g fly ash per 1 g $Ca(OH)_2$). Jozewicz claimed that silica was the most reactive component of the fly ash and the rate-limiting step of the reaction of fly ash with $Ca(OH)_2$ was the dissolution of the silica from the fly ash. In order to increase the reaction rate between the fly ash and $Ca(OH)_2$, additives such as NaOH, H_3PO_4, and $NH_4H_2PO_4$ were added to the fly ash–$Ca(OH)_2$ slurries in successful attempts to increase the dissolution of the silica from the fly ash [9,10]. An alternate way to increase the reaction of silica with $Ca(OH)_2$ was to use a more reactive form of silica, such as diatomaceous earths and clays [11]. Although these materials were found to be much more reactive, their high cost compared to that of fly ash precludes their use for this purpose.

Most recently, Jozewicz et al. [12] have found that pressure hydration (rather than atmospheric hydration) is an effective way to reduce sorbent preparation time and to decrease simultaneously the ratio of fly ash to $Ca(OH)_2$. The term "hydration" was used in their study even though hydrated lime [$Ca(OH)_2$], not quicklime (CaO), was reacted with the fly ash. It should not be inferred from our use of the term "hydration" in the present paper that the CaO was converted to $Ca(OH)_2$ only. In addition to $Ca(OH)_2$, more complex calcium compounds such as $Ca_2SiO_4 \cdot H_2O$ and $Ca_3Al_2(SiO_4)(OH)_8$, were also formed.

The purpose of the present study was two-fold:

1. To determine the effect of slurry reaction time and temperature on the performance and properties of sorbents prepared using CaO and fly ash; the techniques used to characterize the sorbents were X-ray diffraction, optical microscopy, surface area, and particle size distribution.

TABLE 1

Source of fly ash samples

Utility/Station	Coal type [a]	%S	%Ash
1. Duquesne/Elrama	B	2.1	16
2. TVA/Widows Creek 1	B	0.8	14
3. TVA/Widows Creek 7	B	3.4	12
4. Utah P&L/Hunter 1	B	0.5	12–15
5. Arizona Electric/Apache	S	0.6	15–20
6. Colorado Ute/Craig 1	S	0.4	8
7. Colorado Ute/Craig 3	S	0.4	8
8. Public Service-New Mexico/San Juan	S	0.8	22
9. Northern States Power/High Bridge	S	0.3	5
10. Northern States Power/Sherco 3	S	0.6	9
11. Wisconsin P&L/Columbia	L	1.3	12
12. Cooperative Power Assoc./Coal Creek	L	1.3	19

[a] B, bituminous; S, sub-bituminous; L, lignite.

2. To investigate the use of fly ash derived from the combustion of bituminous, sub-bituminous, and lignite coals for making reactive sorbents.

EXPERIMENTAL

Materials

The sorbents were prepared using Baker reagent grade (Lot 1410-1) CaO. The Longview hydrated lime (LL) was obtained from Southern Industries Corporation, Saginaw, Ala. The chemical and physical properties of these materials are provided in ref. 13. The origin and composition of the fly ash samples are shown in Tables 1 and 2, respectively. The high CaO content of the Craig 3 and Sherco 3 fly ash samples is due to the presence of calcium sulfite/sulfate and unreacted hydrated lime, resulting from injection of hydrated lime in the clean-up process. The fly ash was used as-received.

The sorbents were prepared in a 2000 ml Parr stirred reactor. The CaO/fly ash ratio was 12/12, 12/24, or 12/36 (g/g). A number of runs were also made with CaO only (12 g) or with fly ash only (24 g). The materials were loaded into the reactor with 400 ml H_2O at room temperature. The reactor temperature was then increased with stirring to 135, 165, or 200 °C. The times required to reach these temperatures were about 30, 38, and 45 min, respectively. After the desired temperature was reached, this temperature was maintained for a given period of time (0.5, 1, or 2 h). The reactor and its contents were then cooled rapidly, without stirring, to 35–45 °C; the reactor was then disassembled and the contents were filtered. The filter cake was dried in a vacuum oven at 100 °C for 2 h.

TABLE 2

Chemical composition of fly ash samples (%)

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	SO_3	LOI [a]	Total
Elrama	1.7	45.6	19.6	12.4	0.5	1.9	0.4	0.1	16.2	98.4
Widows Creek 1	2.7	53.3	20.5	9.2	0.9	2.5	0.1	0.1	8.3	90.5
Widows Creek 7	3.3	47.7	17.5	20.9	0.7	2.6	0.6	1.0	0.3	94.6
Hunter 1	7.0	56.2	20.8	4.0	2.4	1.2	2.8	3.9	1.1	99.4
Apache	7.6	39.2	20.2	3.6	1.4	0.7	0.7	1.8	24.7	99.9
Craig 1	8.2	56.3	20.8	5.2	2.3	1.3	0.4	1.6	0.4	96.5
Craig 3 [b]	22.6	32.8	16.5	3.3	3.1	1.6	0.9	11.8	4.9	97.5
San Juan	6.2	57.8	23.3	4.0	1.2	1.2	0.8	0.6	0.6	94.5
High Bridge	26.4	35.3	17.0	5.9	5.0	0.3	1.6	1.7	0.1	93.3
Sherco 3 [b]	26.1	27.4	14.9	2.7	3.1	0.5	2.6	15.6	2.3	95.2
Columbia	19.1	42.2	20.2	7.3	2.7	0.7	0.2	1.9	0.1	94.4
Coal Creek	19.9	43.7	14.5	75.0	3.1	1.6	0.8	2.5	0.4	94.0

[a] Weight loss on ignition in air at 800 °C for 4 h.

[b] Except for Craig 3 and Sherco 3, the utility cleanup process consisted of an ESP (where the fly ash was collected) followed by a wet scrubber. Craig 3 and Sherco 3 cleanup processes involved injection of hydrated lime in a spray dryer followed by particulate collection in a bag house.

Apparatus and procedures

The weight increase resulting from exposure of the sorbent to the humidified simulated flue gas (hereafter referred to simply as flue gas) was determined using a modified Perkin–Elmer TGS-2 unit, as described in ref. 13.

It was assumed that the $Ca(OH)_2$ in the sorbent reacted with the SO_2 in the presence of H_2O to form $CaSO_3 \cdot 0.5H_2O$ according to

$$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 \cdot 0.5H_2O + 0.5H_2O \qquad (1)$$

A weight increase of 74.3% would be found if the calcium was fully utilized, i.e. if reaction (1) went to completion. Similarly, if $Ca_2SiO_4 \cdot H_2O$ reacted with SO_2 to form the hemihydrate

$$Ca_2SiO_4 \cdot H_2O + 2SO_2 \rightarrow 2CaSO_3 \cdot 0.5H_2O + SiO_2 \qquad (2)$$

a weight increase of 67.4% would result. Likewise, the reaction of $Ca_3Al_2(SiO_4)(OH)_8$ according to

$$\begin{aligned} Ca_3Al_2(SiO_4)(OH)_8 + 0.5H_2O + 3SO_2 \rightarrow\ & 3CaSO_3 \cdot 0.5H_2O \\ & + 2Al(OH)_3 + SiO_2 \qquad (3) \end{aligned}$$

would result in a weight increase of 53.8%.

The sorption curve for a typical sorbent is shown in Fig. 2. Although the sorbent weight had stabilized after exposure to the humidified N_2 for a few minutes, an exposure of 15 minutes was used to ensure equilibration of the sample. After exposure to the humidified flue gas, there was a rapid weight increase during the first 10 minutes, followed by a rather abrupt decrease in the rate of SO_2 pick-up. A similar weight–time profile was found for all the

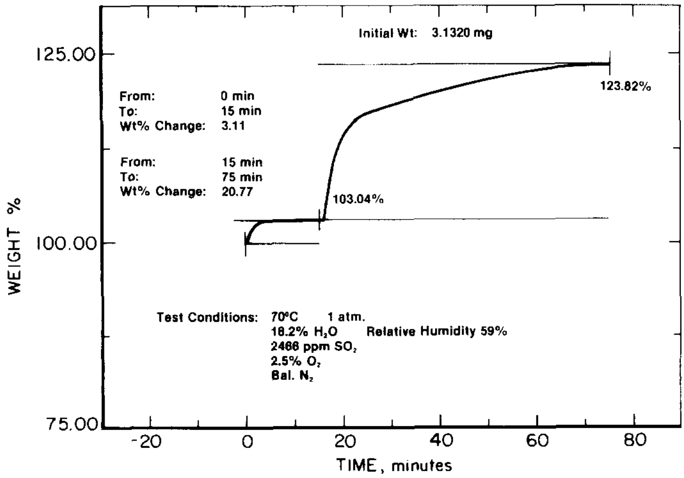

Fig. 2. Weight percent increase in humidified N_2 and flue gas.

TABLE 3

Fly ash characterization

	X-ray diffraction [a]			Surface area [e]
	Quartz [b]	Mullite [c]	Illite [d]	
Elrama	1047	228	–	9.0
Widows Creek 1	1050	160	–	3.4 (2.2)
Widows Creek 7	428	60	7	2.0 (0.6)
Hunter	796	106	18	1.0
Apache	791	210	–	19.3 (0.5)
Craig 1	1327	–	9	1.4
Craig 3	371	77	10	4.2
San Juan	917	347	–	5.4
High Bridge	551	–	–	1.0
Sherco 3	245	–	–	6.0.3
Coal Creek	395	–	–	0.6.4
Columbia	727	127		0.8

[a] Intensities of the maximum peaks for each species.

[b] SiO_2.

[c] $Al_6Si_2O_{13}(OH)_8$.

[d] $(K, Ca)AlO_2SiO_2$.

[e] Surface area (values in parentheses after ignitioin in air at 800 °C for 4 h).

sorbents used in this study. The weight increase was measured after exposure to the flue gas for 60 minutes. Carbon dioxide was excluded from the flue gas to ensure that the weight increase was due only to pick-up of SO_2.

The surface areas were obtained using the BET equation from the adsorption of N_2 in a Micromeritics 2500 unit. A Micromeritics Sedigraph 5000 was used for the particle size distributions; the dispersing liquid (mineral oil plus surfactant) had a viscosity of 4.113 cP and a density of 0.811 g ml^{-1}.

The optical microscopy studies were carried out with three microscopes. The initial investigation and characterization were performed using a Zeiss SR Stereo Microscope (150 ×) with polarized-light capability and an American Optical Stereo Star Zoom Microscope (60 ×). The photomicrographs were taken with a Leitz Orthoplan Research Polarized Light Microscope (1600 ×) using both simple and cross-polarized light.

The characterization of the fly ash samples is given in Table 3.

RESULTS AND DISCUSSION

As indicated in Table 2, the fly ash samples contained up to 26.4% CaO. Consequently, a significant amount (up to 44%) of the CaO in the sorbents was contributed by the fly ash itself. This study made no attempt to determine if the CaO from the fly ash was more or less effective than the

TABLE 4

Thermogravimetric results and chemical and physical analysis of sorbents

Sorbent [a]	%Ca	%Wt. increase $(+SO_2)$	Surface area $(m^2\ g^{-1})$	%Wt. decrease [c] $(-H_2O)$	$\frac{Ca(OH)_2}{CaSi + CaAlSi}$ [d]	$\frac{CaSi}{CaAlSi}$ [e]
Fly ash–Elrama						
12–12–135–1	27.5	20		9.6	4.9 (1282/261)	1.4 (150/111)
12–12–135–2	25.3	21		9.6		
12–24–135–1		10		6.6	37.8 (1020/27)	0 (0/27)
12–24–135–2	19.8	17		5.4	2.3 (647/285)	1.5 (172/113)
12–36–135–2	17.1	18		4.2	5.8 (374/65)	0 (0/65)
12–12–165–2	26.3	4		6.1	0.5 (569/1131)	1.1 (587/549)
12–12–200–1	19.7	3		7.8		
12–12–200–2	18.7	2		8.4		
12–24–200–1	20.2	4		6.0	0.3 (203/672)	1.8 (429/243)
12–36–200–1	16.9	12		3.5	0.9 (321/354)	2.4 (250/104)
0–12–200–1		1				
0–24–200–1	4.7	1	15			
Fly ash–Widows Creek 1						
12–12–135–2	30.2	19	24	10.1	25 (1431/58)	0 (0/58)
12–24–135–0.5		7		8.1		
12–24–135–1.0		14		7.2		
12–24–135–1.0		12		7.3	(1183/0)	(0/0)
12–24–135–2	21.9	20	15	7.1, 6.4	23 (1004/44)	0 (0/44)
12–36–135–2	17.4	13	10	5.6	18 (676/37)	0 (0/37)
12–12–165–2		3		9.1		
12–24–165–2		5		3.7		
12–36–165–2		6		3.1, 2.5		
12–12–200–1		2		7.3		
12–24–200–1	20.6	4		3.4	0.03 (33/1069)	0.9 (498/587)
					0 (0/1086)	0.9 (506/582)
12–24–200–2	20.1	5	8	3.8	0.06 (63/1016)	1.0 (501/515)
0–24–200–1		<1				
Fly ash–Widows Creek 7						
12–12–135–2	30.4	25	30	10.0	5.0 (1075/213)	0.3 (50/163)
					4.8 (1153/242)	0.3 (62/180)
12–24–135–0.5	16.9	8		8.0	(928/0)	(0/0)
12–24–135–1	21.7	14		6.7	16 (773/47)	0 (0/47)
12–24–135–2	22.1	21	33	5.6	3.3 (499/152)	0 (0/152)
12–12–165–2	30.9	3		7.1	0.5 (586/830)	1.1 (443/387)
12–24–165–2		21		3.1		
12–24–200–1	24.0	19	24	3.9	0.8 (182/213)	1.1 (113/100)
12–24–200–2	23.9	16		3.7	0.3 (97/306)	1.3 (172/134)
Fly ash–Hunter 1						
12–12–135–2	28.2	23				
12–24–135–2	21.6	19		6.4	12 (694/57)	0 (0/57)
12–36–135–2	16.9	16		5.2		
12–24–200–1		23				
12–24–200–1	19.6	23		4.8	(348/0)	(0/0)
0–24–135–2	<1					
0–24–200–1	<1					

TABLE 4 (continued)

Sorbent [a]	%Ca	%Wt. increase [b] (+SO_2)	Surface area ($m^2 g^{-1}$)	%Wt. decrease [c] (−H_2O)	$\frac{Ca(OH)_2}{CaSi+CaAlSi}$ [d]	$\frac{CaSi}{CaAlSi}$ [e]
Fly ash–Apache						
12–24–135–1	23.2	8		8.1		
12–24–135–2	23.4	18		5.5	32 (1111/35)	0 (0/35)
12–24–135–2	22.9	20				
12–12–200–1	31.4	3		5.3	0.1 (48/701)	0.2 (121/580)
12–12–200–1		1		5.3		
12–12–200–1		3		5.2		
12–24–200–1	24.2	4		5.3	0 (0/1101)	0.8 (489/612)
Fly ash–Craig 1						
12–12–135–2	31.9	15		9.9		
12–24–135–2	23.2	15	11	6.8	14 (769/54)	0 (0/54)
12–24–200–1	24.4	18		5.4	16 (476/29)	9.3 (454/49)
12–36–200–1	19.4	11	52	3.7		
0–24–200–1	<1					
Fly ash–Craig 3						
12–12–135–2	37.1	15		10.9		
12–24–135–2	28.1	18		8.6	9.6 (1024/107)	0 (0/107)
12–24–200–1	29.2	8	8	5.4	0.9 (430/488)	0.3 (116/372)
12–36–200–1	25.7	17		3.5		
0–24–135–2		9		1.6	0 (0/114)	0 (0/114)
0–24–200–1		8				
Fly ash–San Juan						
12–12–135–2	32.1	16		11.3		
12–24–135–2	21.2	26	27	6.7	5.9 (822/139)	0.7 (56/83)
12–36–135–2	18.4	20		4.1, 3.5	0.7 (428/593)	1.9 (390/203)
12–24–165–2	21.9	4		4.9		
12–24–200–1	22.0	3	4	4.0	0.3 (278/917)	1.1 (485/432)
12–36–200–1	17.3	9		3.4		
Fly ash–High Bridge						
12–24–135–2	31.4	12		7.9	4.5 (714/158)	0.7 (63/95)
12–36–135–2	27.1	12		6.1		
12–24–200–1	30.8	4		7.3	0.9 (469/536)	2.1 (365/171)
12–36–200–1	27.4	12	18			
0–24–135–2		<1				
0–24–200–1		<1				
Fly ash–Sherco 3						
12–12–135–2	37.6	21		11.5		
12–24–135–2	31.5	11		7.5	7.8 (882/114)	0 (0/114)
12–36–135–1	27.7	27		6.2		
12–36–135–3	27.3	28		6.2	1.8 (545/300)	0.3 (76/234)
12–12–200–1	38.1	6		9.2		
12–24–200–1	30.7	20		6.7		
12–24–200–1	31.3	24		6.5	0.8 (374/455)	0.2 (87/368)
0–24–135–2	16.0	8		1.0		
0–24–200–1	15.2	<1				

TABLE 4 (continued)

Sorbent [a]	%Ca	%Wt. increase [b] $(+SO_2)$	Surface area $(m^2\ g^{-1})$	%Wt. decrease [c] $(-H_2O)$	$\frac{Ca(OH)_2}{CaSi + CaAlSi}$ [d]	$\frac{CaSi}{CaAlSi}$ [e]
Fly ash–Columbia						
12–12–135–1	35.2	15		12.1		
12–12–135–2	35.3	15				
12–24–135–2	29.3	13		7.9	7.9 (801/101)	0 (0/101)
12–36–135–2	25.1	19		5.8		
12–24–200–1	29.4	3		6.7	0.1 (119/835)	0.9 (389/446)
0–24–135–2		4				
Fly ash–Coal Creek						
12–12–135–2	35.6	15		10.4	10.3 (1092/106)	0 (0/106)
12–24–135–2	29.1	18	24	7.8	5.4 (803/148)	0.4 (44/104)
12–36–135–2	23.7	15	22	6.2		
12–24–200–1	28.6	31	26	4.1	0.1 (54/571)	1.3 (321/250)
12–36–200–1	24.0	18		4.1, 4.2		
0–24–135–2		<1				
0–24–200–1		<1				
0–24–200–1		<1				
Longview Lime	48.2	19	17	21.4	–	–

[a] (g calcium oxide)–(g fly ash)–(temperature, °C)–(time, h).

[b] %Weight increase per gram of sorbent after exposure to humidified flue gas for 1 h.

[c] %Weight decrease of sorbent between 300 and 460 °C in N_2.

[d] Ratio of the intensity of the peak of $Ca(OH)_2$ divided by the sum of the intensities of the 3.272 Å peak and the 2.746 Å peak of $Ca_2SiO_4 \cdot H_2O$ and $Ca_3Al_2(SiO_4)_2(OH)_8$, respectively.

[e] The intensity of the 3.272 Å peak of $Ca_2SiO_4 \cdot H_2O$ divided by the intensity of the 2.746 Å peak of $Ca_3Al_2(SiO_4)_2(OH)_8$.

CaSi = $Ca_2SiO_4 \cdot H_2O$ = calcium silicate hydrate.

CaAlSi = $Ca_3Al_2(SiO_4)_2(OH)_8$ = calcium aluminum silicate hydroxide.

CaO reactant in forming species during the slurrying step that would react with SO_2.

The thermogravimetric results and chemical analyses of all the sorbents is shown in Table 4. To simplify a comparison of sorbent reactivities, Table 5 shows only the reactivities for those sorbents prepared using the conditions specified.

With 10 of the fly ash samples, it was possible, by the appropriate choice of slurrying conditions, to prepare sorbents that were at least as reactive as LL on a per gram of sorbent basis (R_1). The average reactivity (R_1) of sorbents prepared at 135 °C for 2 h was about 50% higher than the average reactivity of sorbents prepared at 200 °C for 1 h. It should be noted, however, that four of the latter sorbents were more reactive than those prepared at 135 °C. A comparison of reactivities on a per gram of Ca basis (R_2) indicated that with all 12 fly ash samples, sorbents could be prepared

TABLE 5

Summary of sorbent reactivity [a]

	12–24–135–2 [b]		12–24–200–1 [c]	
	R_1	R_2	R_1	R_2
Elrama	17	36	4	20
Widows Creek 1	20	91	4	19
Widows Creek 7	21	95	19	79
Hunter 1	19	88	23	117
Apache	18	77	4	16
Craig 1	15	65	18	74
Craig 3	18	64	8	27
San Juan	26	123	3	14
High Bridge	12	38	4	13
Sherco 3	11	35	24	77
Columbia	13	44	3	10
Coal Creek	18	62	31	108
Average	17	72	12	48
Longview Lime	19	39	19	39

[a] The reactivities, R_1 and R_2, are defined as the percent weight increase of the sorbent per gram of sorbent (R_1) or per gram of Ca (R_2) after exposure to flue gas for 1 h.

[b] 12 g CaO/24 g fly ash at 135°C for 2 h.

[c] 12 g CaO/24 g fly ash at 200°C for 1 h.

that are at least as reactive as LL. It is evident that the slurry step resulted in much more effective utilization of the calcium in the sorbent.

The sorbent reactivity, R_1, showed no dependence on the source of fly ash (bituminous, sub-bituminous or lignite coal); in the case of R_2, however, R_2 (bit) > R_2 (sub-bit) > R_2 (lignite). This order of reactivity was due, at least in part, to the fact that a substantial part of the calcium in the sorbent was contributed by the fly ash itself. It was assumed that the calcium in the fly ash would not be as effective as free CaO in forming reactive species during the slurry step.

The effect of the CaO/fly-ash ratio was also investigated. Table 6 shows the reactivities R_1 and R_2 for sorbents when the CaO/fly-ash ratio was 12/12, 12/24, or 12/36 (g CaO per 1 g fly ash). Though there were no definite trends in the case of R_1, decreasing the CaO/fly-ash ratio from 12/12 to 12/24 resulted in more effective utilization of the sorbent with the 6 fly ash samples studied. A further decrease of CaO/fly ash from 12/24 to 12/36 resulted in an additional increase of R_2 in four of the sample groups. The increase in Ca utilization was probably related to the amount of SiO_2 and Al_2O_3 that was available to react with the CaO. If the nominal Al_2O_3 and SiO_2 content of the fly ash is 20% and 50%, respectively, then the calculated $CaO/(Al_2O_3 + SiO_2)$ molar ratio is shown in Table 7. The Cao content of the fly ash itself was not included in this calculation.

TABLE 6

Effect of CaO/fly-ash ratio on sorbent reactivity

Fly ash	Sorbent	R_1	R_2
Elrama	12-12-135-2	21	83
	12-24-135-2	17	86
	12-36-135-2	18	105
	12-12-200-1	3	
	12-24-200-1	4	20
	12-36-200-1	12	71
Widows Creek 1	12-12-135-2	19	63
	12-24-135-2	20	91
	12-36-135-2	13	75
Hunter 1	12-12-135-2	23	82
	12-24-135-2	19	88
	12-36-135-2	16	95
San Juan	12-12-135-2	16	50
	12-24-135-2	26	123
	12-36-135-2	20	109
Columbia	12-12-135-2	15	42
	12-24-135-2	13	44
	12-36-135-2	19	76

The X-ray diffraction studies indicated that the principal Ca-containing species formed during the slurrying step was $Ca_3Al_2(SiO_4)(OH)_8$, with a $CaO/(SiO_2 + Al_2O_3)$ ratio of 1.0. It can be seen from Table 7 that excess CaO was present at the 12/12 level; at the 12/36 level, however, it was likely that excess fly ash was used, assuming that all of the SiO_2 and Al_2O_3 were available to react with the CaO. The reactivity data tend to support this hypothesis. In the four sample groups that showed an increase in R_2 with decreasing CaO/fly-ash ratio, the $(SiO_2 + Al_2O_3)$ content was 65% compared with 77% for the other two sample groups.

A summary of the X-ray diffraction results is shown in Table 8. It is evident that a large decrease in the $Ca(OH)_2/(CaSi + CaAlSi)$ ratio occurred when the temperature of the slurrying step was increased from 135 to 200 °C. There was no significant difference in the reactivities of fly ash derived from bituminous, sub-bituminous, or lignite coals. Except when using Elrama fly ash, sorbents prepared at 135 °C for 2 h contained mostly

TABLE 7

Calculated molar ratio

CaO/fly ash (g/g)	$CaO/(SiO_2 + Al_2O_3)$ (molar)
12/12	1.75
12/24	0.88
12/36	0.58

TABLE 8

Summary of X-ray diffraction results [a]

Fly ash	12-24-135-2		12-24-200-1	
	$\frac{Ca(OH)_2}{CaSi + CaSiAl}$	$\frac{CaSi}{CaAlSi}$	$\frac{Ca(OH)_2}{CaSi + CaSiAl}$	$\frac{CaSi}{CaAlSi}$
Elrama	2.3	1.5	0.3	1.8
Widows Creek 1	2.3	< 0.1	0.03	0.9
Widows Creek 7	3.3	< 0.1	0.8	1.1
Hunter 1	12	< 0.1	4.8	< 0.1
Apache	32	< 0.1	0.1	0.2
Craig 1	14	< 0.1	9.3	< 0.1
Craig 3	9.6	< 0.1	0.9	0.3
San Juan	5.9	0.7	0.3	1.1
High Bridge	4.5	0.7	0.9	2.1
Sherco 3	7.8	< 0.1	0.8	0.2
Columbia	7.9	< 0.1	0.1	0.9
Coal Creek	5.4	0.4	0.1	1.3
Average	11	0.3	1.7	0.9

[a] See footnotes of Table 4 for key.

CaAlSi, while CaSi was either absent or present in small amounts. Increasing the reaction temperature to 200 °C resulted in an increase in the CaSi/CaAlSi ratio. The relative concentrations of CaSi and CaAlSi can be explained using two different mechanisms:

Mechanism A

$$\begin{array}{ll} \text{Fly ash} + CaO \xrightarrow{k_1} CaSi & \\ & k_2 > k_1 \\ \text{Fly ash} + CaO \xrightarrow{k_2} CaAlSi & \end{array}$$

The assumption that $k_2 > k_1$ is justified on the basis of data showing that in fly ash the Al and Si are usually found together in compounds such as illite and mullite (Table 3) whereas a large portion of the Si occurs as unreactive quartz or more likely amorphous SiO_2.

Mechanism B

$$\text{Fly ash} + CaO \rightarrow CaSi + CaAlSi$$

$$CaAlSi \xrightarrow{200\,^{\circ}C} CaSi + Al_2O_3$$

As mechanism B indicates, the increase in the CaSi/CaAlSi ratio found at 200 °C may be due to decomposition of CaAlSi to CaSi.

Figure 3 shows the X-ray diffraction data in more detail. As the $Ca(OH)_2/(CaSi + CaAlSi)$ ratio decreased, there was a gradual increase in R_2, reaching a maximum when the ratio was about 5. A further decrease in the ratio resulted in a rapid decrease in R_1. All of the sorbents accounting for this rapid decrease were prepared at 165 and 200 °C, indicating the

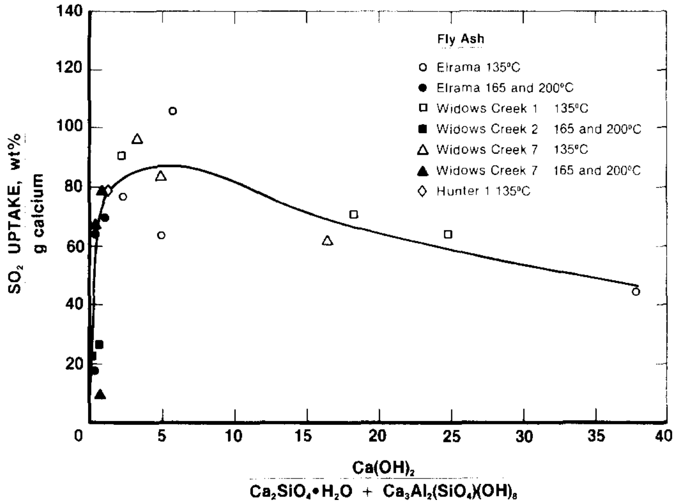

Fig. 3. Reactivity (R_2) of various sorbents as a function of the $Ca(OH)_2/(CaSi+CaAlSi)$ ratio.

deleterious effect of higher slurrying temperatures on the reactivities of sorbents prepared from these three fly ash samples. It should be noted, however, that a slurry temperature of 200 °C actually resulted in an increase in sorbent reactivity for a number of other fly ash samples.

A thermogravimetric study was carried out to determine the weight change for the sorbents when heated from 50 to 800 °C in N_2 (heating rate, 10 °C min^{-1}). The thermograms for LL and a typical sorbent are shown in Fig. 4. A sharp weight loss occurred between 380 and 540 °C, which corresponds to the temperature range found for the dehydration of $Ca(OH)_2$

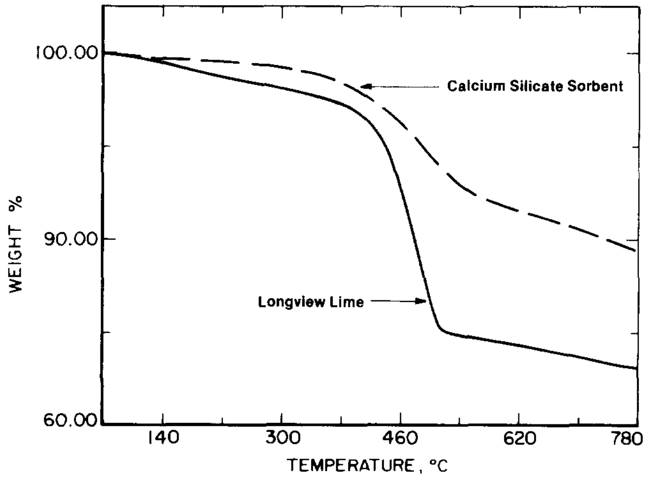

Fig. 4. Decomposition curves for selected sorbents between 50 and 800 °C in N_2.

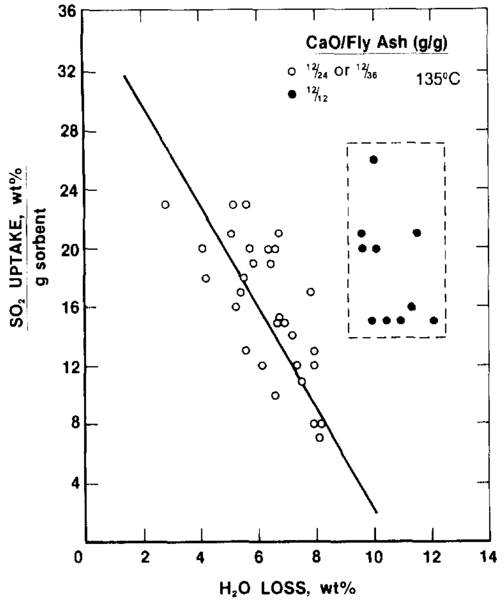

Fig. 5. Reactivity (R_1) of calcium silicate sorbents as a function of H_2O weight loss (380–540 ° C).

to CaO and H_2O. The weight loss over this temperature range (Table 4) was assumed to be a relative measure of the $Ca(OH)_2$ in the sorbents. Figure 5 shows R_1 for the sorbents (135 ° C only) as a function of the weight decrease due to loss of H_2O. A reasonable correlation was obtained for those sorbents prepared using a 12/24 or 12/36 CaO/fly-ash ratio. This indicates that as the $Ca(OH)_2$ content of the sorbent decreased (and was presumably converted to a more reactive species) there was a corresponding increase in the reactivity toward SO_2. Thus, at least for sorbents prepared at 135 ° C, the

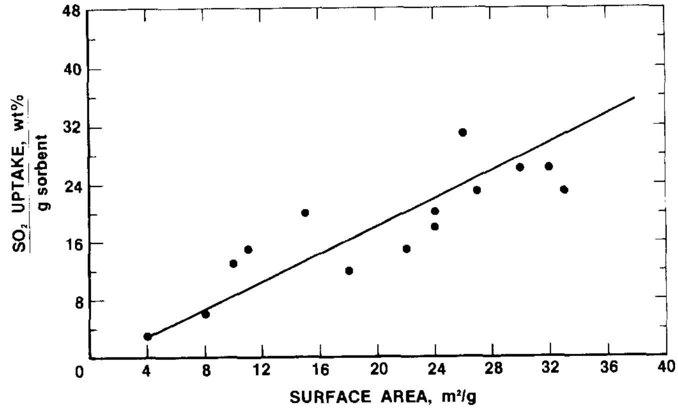

Fig. 6. Reactivity (R_1) as a function of sorbent surface area.

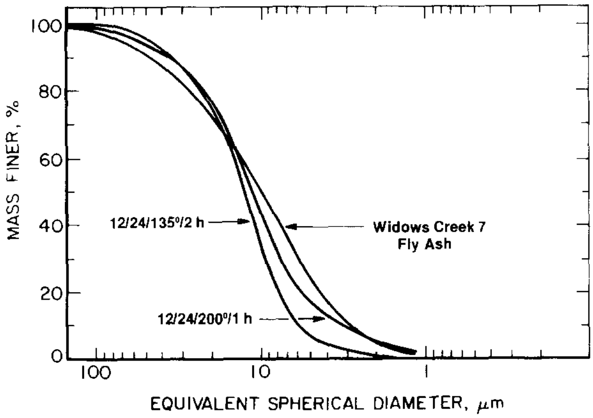

Fig. 7. Particle size distributions.

most important factor in determining sorbent reactivity was the degree of conversion of $Ca(OH)_2$. The deviation of the points for sorbents prepared using a 12/12 CaO/fly-ash ratio was puzzling. A possible explanation was that the low CaO/fly-ash ratio resulted in only a small fraction of the $Ca(OH)_2$ being converted to CaSi or CaAlSi. The presence of the fly ash, however, may result in the unreacted $Ca(OH)_2$ being more highly dispersed and thus more accessible to reaction with SO_2 than is LL or pure $Ca(OH)_2$. The absence of any correlation between R_1 and the H_2O weight-loss for sorbents prepared at 165 and 200 °C suggests that the extent of reaction of $Ca(OH)_2$ with fly ash is not the dominant factor in determining reactivity, as it is at 135 °C.

The sorbent reactivity, R_1, was found to increase with the surface area of the sorbent (N_2), as shown in Fig. 6. This result was not unexpected in view of the results of previous investigators who found that in low-temperature

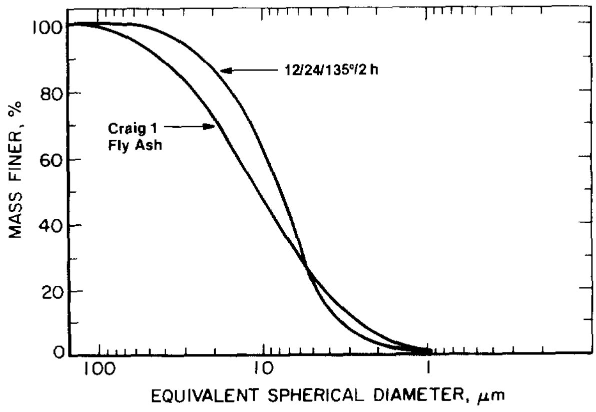

Fig. 8. Particle size distributions.

SO_2-removal processes, increasing the sorbent surface area resulted in more effective sorbents. Higher slurrying temperatures usually resulted in lower surface area and reactivity. The higher temperature probably accelerated the

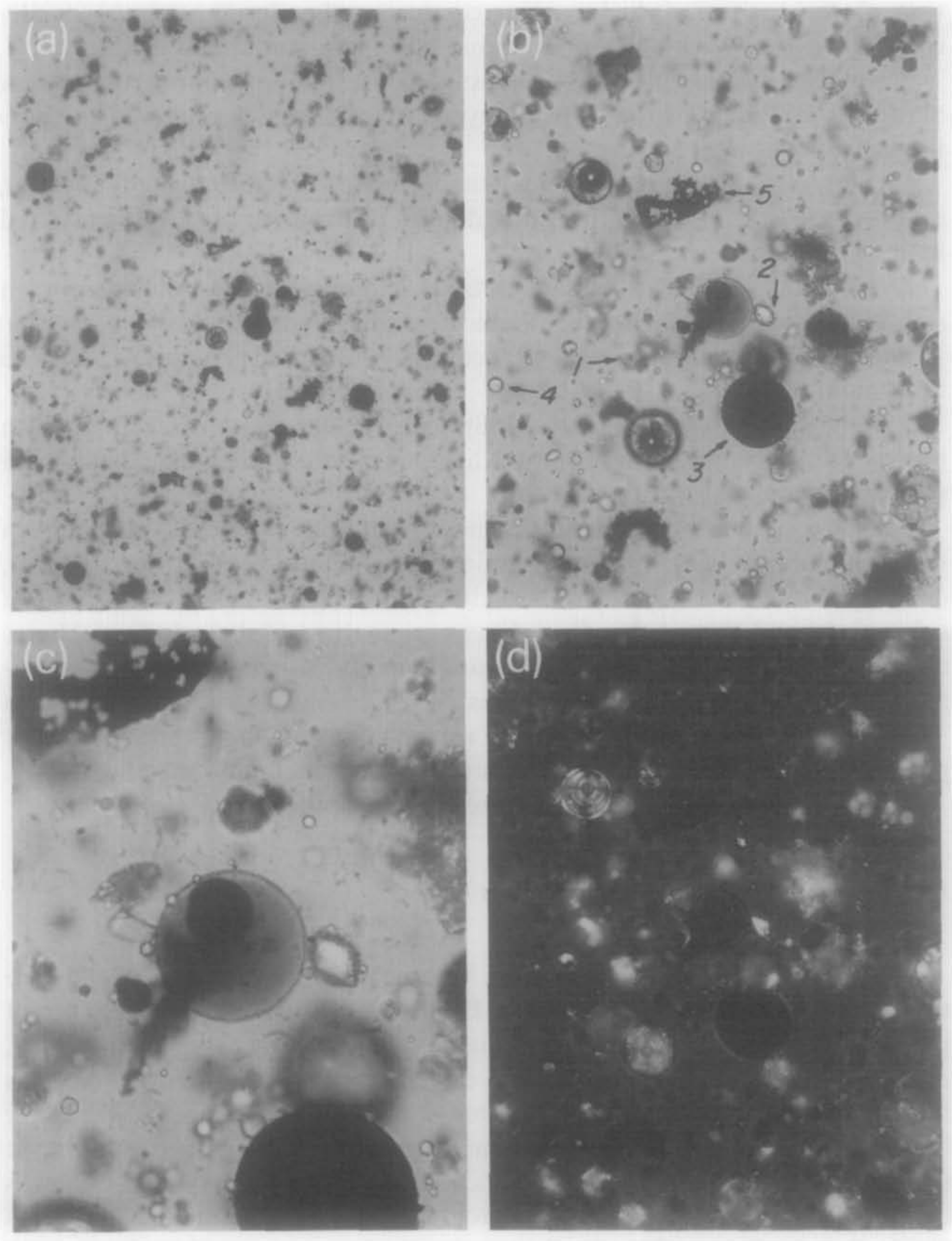

Fig. 9. Photomicrographs of Widows Creek 7 fly ash. Original magnifications: a, 100×; b, 250×; c, 630×; and d, 250×.

crystallization of amorphous Ca-containing species into lower surface-area crystalline compounds.

Figures 7 and 8 indicate little difference in the particle size distributions of the precursor fly ash samples and the sorbents prepared from them, regardless of slurrying conditions. It is likely, however, that some agglomeration of the sorbent particles occurred during the drying step, especially considering the "stickiness" of alumina- and silica-containing solids.

Seven fly ash samples were investigated using optical microscopy. A broad classification of the different types of particulates observed in these fly ash samples is as follows:

1. Refractory—equant particles (shape having nearly equal diameters), rounded edges, colorless in transmitted light, transparent in simple polarized light.
2. Mineral—equant irregular particles, non-crystalline, transparent in simple transmitted polarized light, colorless, sharp edges.

These refractory and mineral particulates constituted less than 1% of the total sample.

3. Magnetic spheres—round or elliptical, various sizes, black to reddish brown color, opaque in transmitted light, respond to magnetic field, high specific gravity, test positive for iron.
4. Glassy spheres—various sizes, smooth to rough exterior, transparent in simple polarized light, isotropic, hollow (contain spheres within spheres), occur in various colors (colorless, light yellow, light to dark red), reddish spheres respond to magnetic field. Chemical analysis of the colorless spheres indicated the presence of oxides of aluminum and silicon, with iron responsible for the red in the colored spheres.
5. Carbonaceous—both equant and spherical morphologies present, highly porous (sponge-like), black, opaque in transmitted light, low specific gravity.

A more detailed description of these samples follows.

Elrama, Widows Creek 1, and Widows Creek 7

The photomicrographs of Widows Creek 7, shown in Figs. 9a–9d, are typical of these three fly ash samples. Examples of the five different types of particulates are shown by the arrows in Fig. 9b: 1, refractory; 2, mineral; 3, magnetic sphere; 4, glassy sphere; 5, carbonaceous. The photomicrographs in Figs. 9a–9c were taken using simple polarized light, while the dark background in Fig. 9d resulted from the use of cross polarized light. It should be noted that Figs. 9b and 9d are identical except for the differences in the type of light used. Photomicrographs of the Elrama and Widows Creek 1 fly ash samples revealed a significant amount of carbonaceous material, an observation consistent with the large weight loss found during ignition of these samples (Table 2).

Apache

This sample was unique in that few of the particulates had the spherical shape that was typical of the previous samples. There was a large amount of carbonaceous material, indicating a relatively low temperature in the combustion zone or a short residence time. The presence of many carbonaceous particulates is consistent with the observation that this sample contained mostly irregularly shaped particles, in contrast to the predominance of spherical particles observed in the earlier samples. The spheres are probably formed by the encapsulation of flue gas by the high-surface-tension molten ash, which was driven to form these minimum surface area particles. A short residence time or low combustion temperature would mitigate the possibility of formation of these spherical particles.

Hunter

The occurrence of fractural isotropic, recondensed particles was characteristic of this fly ash.

Columbia

The cenospheres (hollow spheres) were observed to contain recrystallized deposits, mineral inclusions, bubble-like inclusions, irregular surface deposits, and crystalline surface deposits. Triangular surface crystals were found to occur on both clear and opaque cenospheres (Figs. 10a and 10b).

Coal Creek

This material is characterised by a high percentage of cenospheres, suggesting a high temperature in the combustion zone. The cenospheres were often found to contain internal deposits (Fig. 10c) and bubble inclusions (Fig. 10d). Carbonaceous particles constituted less than 1% of the sample.

The photomicrographs of the sorbent prepared from Widows Creek 1 fly ash are shown in Figs. 11a–11d and 12a–12d. These photomicrographs are representative of the sorbents prepared from all of the fly ash samples, with the exception that photomicrographs of sorbents prepared from fly ash containing large amounts of carbonaceous particles also exhibited similarly large amounts of these particles.

The value of using both simple polarized light (spl) and cross polarized light (cpl) is shown in Figs. 11b and 12b (spl) and Figs. 11d and 12d (cpl). When using cpl, the Ca-containing material was in sharp contrast to the black background. Chemical analysis of white material scraped off the larger spheres verified that it was in fact a material rich in Ca. This white material was well dispersed in sorbents prepared at 135 °C for 2 h, whereas for those

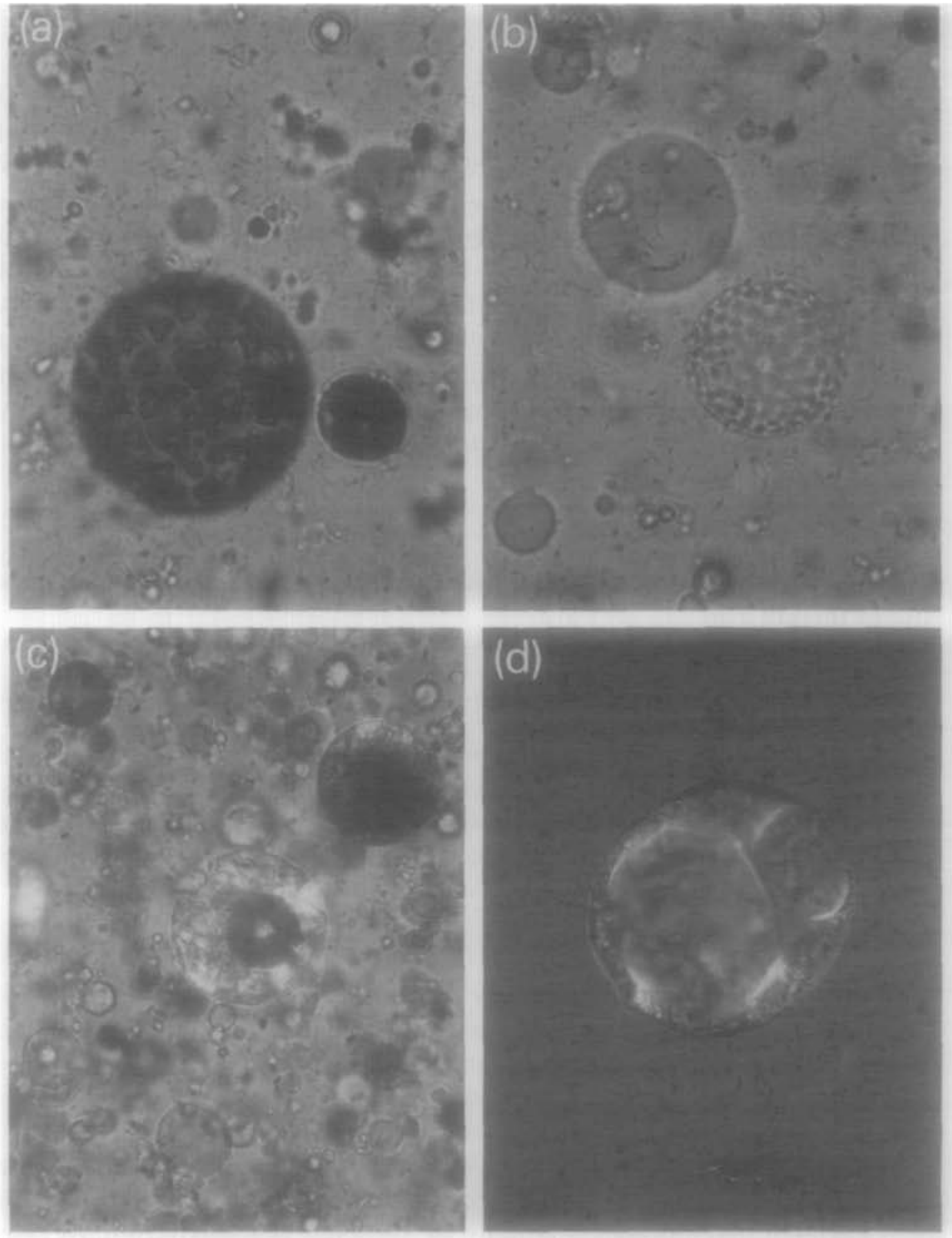

Fig. 10. (a, b) Photomicrographs of Columbia fly ash. Original magnifications: a, 1000 × ; and b, 1000 × . (c, d) Photomicrographs of Coal Creek fly ash. Original magnifications: c, 630 × ; and d, 630 × .

sorbents prepared at 200 °C for 1 h, the major portion of the white material was found to be on the surface of partially reacted spheres. An example of such a sphere is shown in Fig. 13. The more dispersed nature of the

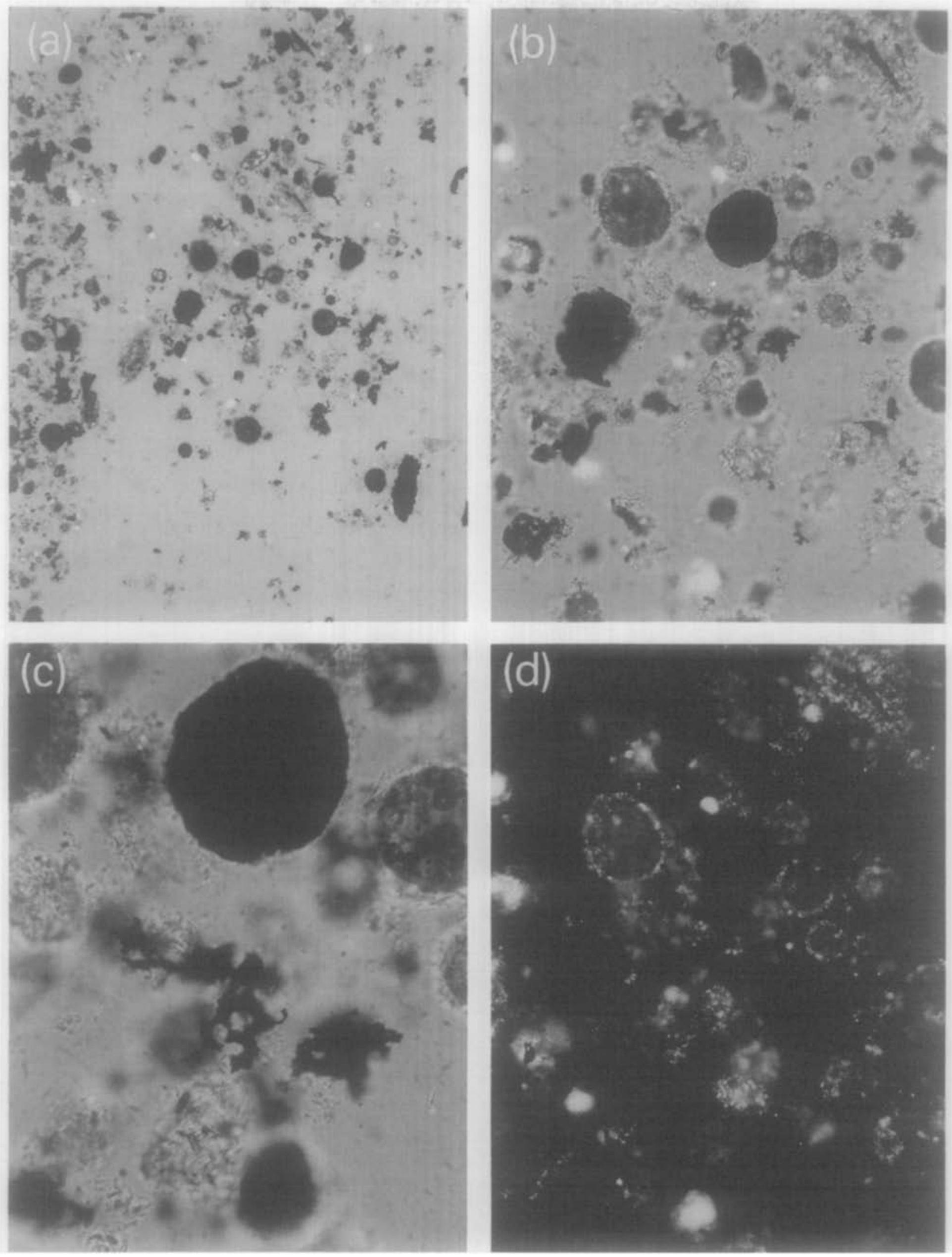

Fig. 11. Photomicrographs of sorbent prepared at 200 °C using Widows Creek 1 fly ash. Original magnifications: a, 100×; b, 250×; c, 630×; and d, 250×.

Ca-containing species in sorbents prepared at 135 °C for 2 h is consistent with the higher surface areas found for these sorbents. The presence of largely intact spheres, or spheres only partially reacted, is also consistent with the observation that there was little or no difference in the particle size distributions of the fly ash and the corresponding sorbents.

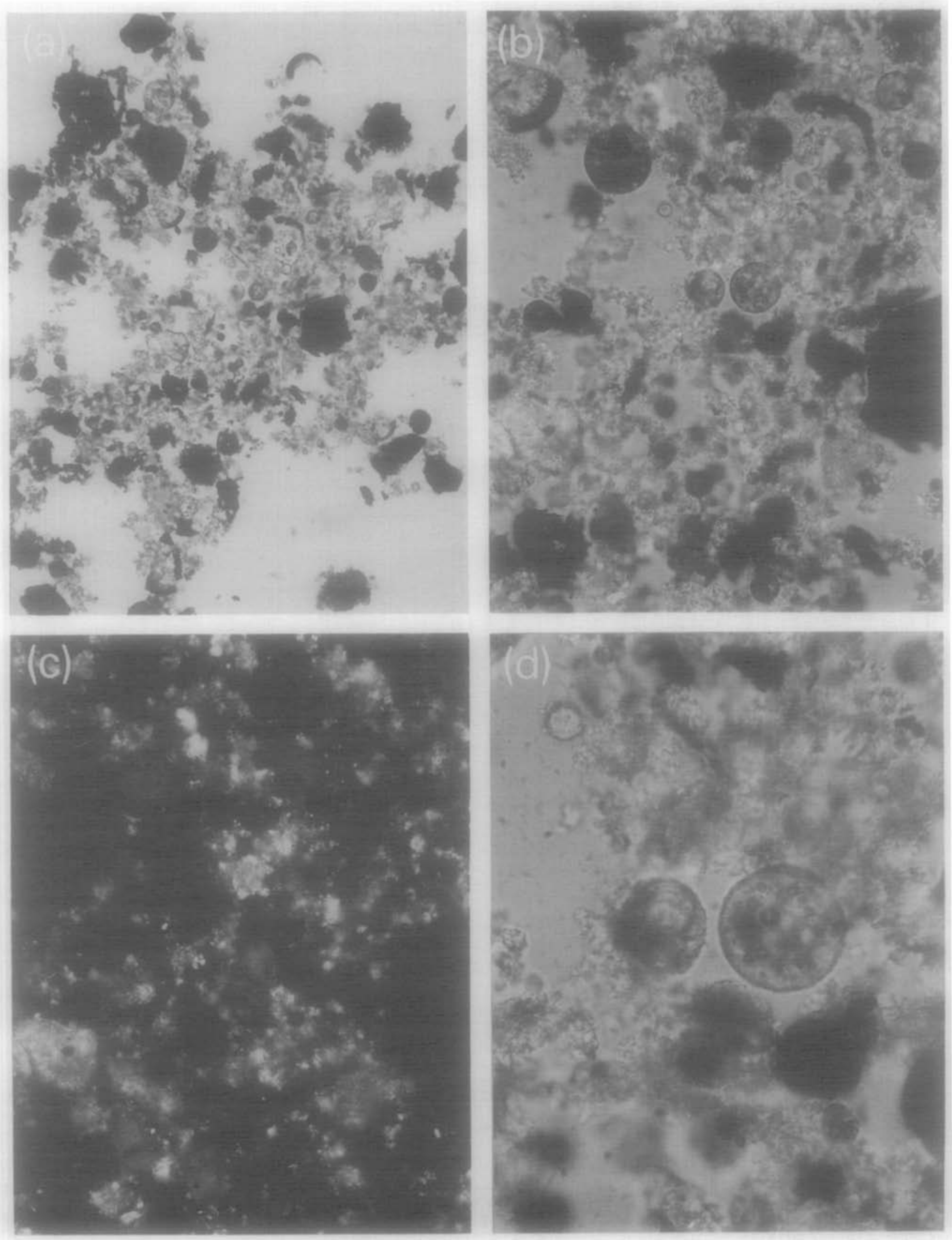

Fig. 12. Photomicrographs of sorbent prepared at 135 °C using Widows Creek 1 fly ash. Original magnifications: Original magnifications: a, 100 ×; b, 250 ×; c, 630 ×; and d, 250 ×.

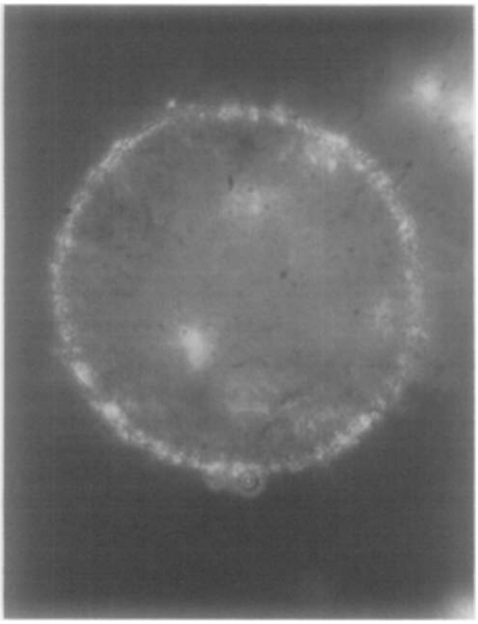

Fig. 13. Photomicrograph of sorbent prepared at 200 ° C using Widows Creek 1 fly ash. Original magnification: 1000×.

CONCLUSIONS

1. Sorbents prepared from the pressure hydration of calcium oxide–fly ash slurries were up to 33% more reactive than commercial hydrated lime on a per gram of sorbent basis. On a per gram of CaO basis (CaO from reactant CaO), these sorbents were over four times as reactive as hydrated lime.
2. The three principal Ca-containing compounds formed during the reaction of CaO and fly ash were $Ca(OH)_2$, $Ca_2SiO_4 \cdot H_2O$, and $Ca_3Al_2(SiO_4)(OH)_8$.
3. There was not a monotonic increase in sorbent reactivity with the time of hydration at a given temperature of hydration. The lower surface areas (and reactivity) of sorbents prepared at higher temperatures (200 ° C) and long reaction times (2 h) indicate that high surface area species crystallize into solids of lower reactivity with SO_2.
4. No significant differences were found in the reactivity of sorbents prepared from the fly ash obtained from the combustion of bituminous, sub-bituminous, and lignite coals.
5. The abundance of fly ash in the U.S. [14–19] and its low level of utilization (less than 20%) indicate an ample supply of fly ash for preparing these sorbents. These sorbents could result in a significant decrease in SO_2 emissions using duct injection.

REFERENCES

1 J. Makansi, Power, 130 (1986) 27.
2 R. Remirez, Chem. Eng., 93 (1986) 17.
3 M.R. Stouffer, H. Yoon, and F.P. Burke, Ind. Eng. Chem. Res., 28 (1989) 20.
4 J.A. Withum and H. Yoon, Environ. Sci. Technol., 23 (1989) 821.
5 T. Petersen and H.T. Karlsson, Chem. Eng. Technol., 11 (1988) 298.
6 T.B. Hurst and G.T. Bielawski, Dry Scrubber Demonstration Plant, EPA 600/9-81-019b, 1981.
7 G.T. Reed, W.T. Davis, and R.E. Pudelek, Environ. Sci. Technol., 18 (1984) 548.
8 W. Jozewicz and G.J. Rochelle, Environ. Progress, 5 (1986) 219.
9 W. Jozewicz and J.C.S. Chang, presented at the AIChE Spring National Meeting, Houston, TX, 1987.
10 P. Chu and G.T. Rochelle, Air Pollut. Control Assoc. J., 39 (1989) 175.
11 W. Jozewicz, C. Jorgensen, J.C.S. Chang, C.B. Sedman, and T.G. Brna, Air Pollut. Control Assoc. J., 38 (1988) 796.
12 W. Jozewicz, J.C.S. Chang, C.G. Sedman, and T.G. Brna, Air Pollut. Control Assoc. J., 38 (1988) 1027.
13 R.A. Diffenbach, S.W. Hedges, and S. Friedman, Thermochim. Acta, 127 (1988) 57.
14 S. Diamond, Cem. Concr. Res., 14 (1984) 455.
15 M.R. Schure, P.A. Soltys, D.F.S. Natusch, and T. Mauney, Envir. Sci. Technol., 19 (1985) 82.
16 S. Diamond, Cem. Concr. Res., 16 (1986) 569.
17 A. Hazrati and J.T. Schrodt, Surf. and Interface Anal., 13 (1988) 142.
18 K. Tazaki, W.S. Fyfe, K.C. Sahu, and M. Powell, Fuel, 68 (1989) 727.
19 W. Jozewicz, J.C.S. Chang, T.G. Brna, and C.B. Sedman, Envir. Sci. Technol., 21 (1987) 664.