OCDO--94012360

NEW, HIGH-CAPACITY, CALCIUM-BASED SORBENTS - CALCIUM SILICATE SORBENTS

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FEB 22 1994
DEPARTMENT OF DEVELOPMENT
OHIO COAL DEV OFFICE

FINAL REPORT

OCRC/92-1.8

This project was funded in part by the
Ohio Coal Development Office, Department
of Development, State of Ohio

September 30, 1993

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1. Executive Summary

Aim. A search is being carried out for new calcium-based SO_2 sorbents for induct injection. More specifically, a search is being carried out for induct injection calcium silicate sorbents that are highly cost effective.

Current Year Objectives. The objectives of the past year were to study the sorption of SO_2 by representative calcium silicates, to study the composition of the $Ca(OH)_2$-fly ash sorbent, and to install a humidity sensor in the sorption system.

Work Accomplished. During this year, a number of experiments on the uptake of SO_2 by calcium silicate sorbents were done. In one set of experiments in which eight calcium silicates were used, it was found that the sorbents ranged from very poor to very good. It was concluded that the Ca:Si ratio of a sorbent does not influence its effectiveness but that its water content, degree of crystallinity and morphology do. The results of another set of experiments in which a gas mixture containing both SO_2 and CO_2 was used showed that the presence of CO_2 in the mixture leads to a clear but only moderate reduction in the SO_2 uptake of a sorbent. The small size of the reduction was attributed to the relative strengths of carbonic and sulfurous acid. In a third set of experiments, it was found that the composition and SO_2 uptake of sorbents made by the hydration of β-Ca_2SiO_4 and Ca_3SiO_5 were greatly dependent on the hydration conditions used. This result demonstrated the need for careful attention to the conditions used in making calcium-based sorbents.

Experiments on the CO_2 uptake by calcium-based sorbents were also done. It was found that at most only moderate amounts of CO_2 were absorbed. This was ascribed to the weakness of carbonic acid.

A series of experiments was done on the $Ca(OH)_2$-fly ash sorbent. It was found that under one set of conditions the sorbent can contain $Ca(OH)_2$, $Ca_3Al_2O_6 \cdot Ca(OH)_2 \cdot 12H_2O$, $Ca_3Al_2(SiO_4)(O_4H_4)_2$, C-S-H, and $2AlO_3 \cdot 2SiO_2 \cdot H_2O$. It was concluded that the best SO_2 sorbent in this mixture was the C-S-H. This appeared to be formed from the aluminosilicate glass spheres in the fly ash. When enough of C-S-H had been formed, it appeared that it enveloped the unreacted fly ash particles.

In addition, experiments were done on cement and modified cement sorbents. These were prepared by milling cement-H_2O or cement-SiO_2-water slurries. It was found that under favorable conditions the sorbent produced consisted mainly of C-S-H and $Ca(OH)_2$. This sorbent exhibited a very high SO_2 uptake and calcium utilization.

Another group of experiments was done on $Ca(OH)_2$ and modified $Ca(OH)_2$ sorbents. These were prepared by milling $Ca(OH)_2$-H_2O and $Ca(OH)_2$-SiO_2-H_2O slurries. It was found that under favorable conditions the $Ca(OH)_2$-SiO_2-H_2O product consisted of $Ca(OH)_2$ and C-S-H. The $Ca(OH)_2$-H_2O product exhibited a good calcium utilization and the $Ca(OH)_2$-SiO_2-H_2O product an excellent one.

Finally a humidity sensor was installed in the sorption system. Tests showed it performed well.

Work To Be Done. In the coming year, work will be done on the $Ca(OH)_2$ and modified $Ca(OH)_2$ sorbents, on the cement and modified cement sorbents and on $Ca(OH)_2$-SiO_2 sorbents. This work is designed to yield highly effective sorbents that can be made by means that are fast, cheap and reliable. Work on pure calcium compounds will be done when necessary to provide baseline information.

Throughout the year contact will be maintained with industrial investigators active in the sorbent field so that the real-world requirements of flue gas desulfurization can be kept constantly in focus.

The project proceeded as anticipated and produced some valuable results. Collaborative work is now being undertaken with Prof. Keener of the University of Cincinnati at the request of OCDO to move the cement sorbent work to the pilot plant scale.

2. Introduction

At present highly effective, cheap, easy-to-prepare SO_2 sorbents for induct injection are lacking. This led to the current multiyear study. The main aim of this study is to find one or more good induct injection sorbents. Particular emphasis has been given in the work already done to calcium-based sorbents because calcium is abundant and environmentally acceptable.

The objectives for the current year were to study the uptake of SO_2 by representative calcium silicates, to study the composition of the $Ca(OH)_2$-fly ash sorbent, and to install a humidity sensor in the bench-scale sorption system being used.

The co-sponsor of the project was Case Western Reserve University. It contributed time of the principal investigator.

3. Uptake of SO_2 and CO_2 by Known Calcium Silicates

As indicated in the Final Report for OCRC/91-1.8, over 30 calcium silicates are known. Some of these occur naturally as a result of geological processes and some are made by high temperature (electric furnace) processes. Others are made by aqueous solution processes in the 100 to 250 °C range, and still others are made by aqueous solution processes in the room temperature to 100 °C range[1].

Some of these calcium silicates occur relatively abundantly naturally and some can be made relatively easily in good purity. It is members of these two subgroups that are of interest in these studies. During the current year, eight members of these two subgroups have been studied. A list of them is given in Table 1. In addition, calcium silicate mixtures synthesized from these silicates also have been studied.

Table I. Calcium Silicates Studied

Name	Formula
calcium silicate hydrate[2]	$CaO\text{-}SiO_2\text{-}H_2O$
β-dicalcium silicate[3]	$\beta\text{-}Ca_2SiO_4$
γ-dicalcium silicate[4]	$\gamma\text{-}Ca_2SiO_4$
α-dicalcium silicate hydrate[5]	$\alpha\text{-}Ca_2(SiO_3OH)OH$
hillebrandite[6]	$Ca_2(SiO_3)(OH)_2$
tobermorite[7]	$Ca_5Si_6O_{16}(OH)_2{\cdot}4H_2O$
wollastonite[8]	$\beta\text{-}CaSiO_3$
xonotlite[9]	$Ca_6Si_6O_{17}(OH)_2$

Experimental Conditions. The SO_2 uptake studies were carried out with the procedure and apparatus described in Final Report OCRC/91-1.8. Briefly , 0.5 g of the sorbent was mixed with 20 g of sea sand and the mixture was placed in the sorption vessel.

A simulated flue gas was passed through the sorbent at a temperature of 60 °C and a flow rate 1 L/min for 1 h. The simulated flue gas used was composed of either 2000 ppm of SO_2, sufficient water to give 60 % relative humidity, and the balance N_2; or alternatively 2000 ppm SO_2, 11 % CO_2, sufficient water to give 60 % relative humidity at 60 °C and the balance N_2. The uptake of SO_2 in mmole of SO_2 per g of sorbent was calculated from the data collected.

The CO_2 uptake studies were carried out with the same apparatus. Here, 0.5 g of the sorbent (undiluted with sea sand) was placed in the sorption vessel. A simulated flue gas was passed through the sorbent at a temperature of 60 °C and a flow rate of ~1 L/min for 1 h. The simulated flue gas was composed of either 10 % CO_2 and the balance N_2, or 10 % CO_2 , sufficient water to give 60 % relative humidity at 60 °C and the balance N_2. In these experiments, the uptake of the CO_2 was evaluated from the infrared spectra of the spent sorbents.

The calcium silicate mixtures that were synthesized were characterized by X-ray powder diffractometry (XRD) and infrared spectroscopy (IR). The percent compositions given are approximate.

Results and Discussion. In one set of SO_2-uptake experiments in which the eight calcium silicates were used and in which the SO_2-H_2O-N_2 simulated flue gas was used, it was found that the sorbents ranged from very poor to very good relative to $Ca(OH)_2$, Table II. On the basis of the data obtained, it is concluded that the Ca to Si ratio of a sorbent does not influence its effectiveness to important extent (compare wollastonite and C-S-H).
In contrast, it is concluded that the amount of water in a sorbent does influence its effectiveness (counting two hydroxyl groups to be equivalent to one water molecule and one oxide ion as mineralogists do). However, it is also apparent that water content is not the only important factor (compare α-dicalcium silicate hydrate and xonotlite). It is further concluded that the morphology and the crystallinity of a sorbent are also important.

Table II. SO_2 Uptake of Calcium Silicates and Calcium Hydroxide from SO_2-H_2O-N_2 Mixture

Name	Formula	Abbrev.	Source	Ca : Si	H_2O (%)	Morphology	Crystallinity	SO_2 Uptake (mmole/g)
calcium hydroxide	$Ca(OH)_2$	CH	Smith Lime	1:0	24	grains	high	2.6
tobermorite	$Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$	$C_5S_6H_6$	synthesis	0.8:1	12	platelets	low	5.9
wollastonite	β-$CaSiO_3$	β-CS	Ward's	1:1	0	fibers	high	0.2
xonotlite	$Ca_6Si_6O_{17}(OH)_2$	C_6S_6H	synthesis	1:1	3	fibers	high	6.3
calcium silicate hydrate	CaO-SiO_2-H_2O	C-S-H	synthesis	1:1	15	foil, fibers	very low	6.0
β-dicalcium silicate	β-Ca_2SiO_4	β-C_2S	CTL	2:1	0	rounded grains	high	0.0
γ-dicalcium silicate	γ-Ca_2SiO_4	γ-C_2S	CTL	2:1	0	rounded grains	high	0.0
α-dicalcium silicate hydrate	α-$Ca_2(SiO_3(OH))OH$	α-C_2SH	synthesis	2:1	10	tablets	high	2.2
hillebrandite	$Ca_2(SiO_3)(OH)_2$	C_2SH	synthesis	2:1	10	fibers	high	3.4

Comparison of the morphology and crystallinity data for C-S-H and wollastonite helps to make this relationship clear. C-S-H is composed of irregular foils and fibers.[10] It is relatively amorphous and has a high surface area. Wollastonite, in contrast, is composed of fibers packed in a tight and orderly manner.[11] It is highly crystalline and has relatively low surface area. The high reactivity of C-S-H appears to arise to mostly from its high surface area and from its amorphous character, while the low reactivity of wollastonite appears to arise to a large extent from its low surface area and its high crystallinity (of course, the high water content of C-S-H contributes significantly to its reactivity).

In sum, on the basis of the data obtained on the eight calcium silicates, it appears that the uptake capacity of calcium silicates is somewhat influenced by their water content, and highly influenced by their morphology and crystallinity.

The results of another set of SO_2 uptake experiments in which four of the eight silicates were used and in which the SO_2-CO_2-H_2O-N_2 simulated flue gas was used gave, when combined with the previous results, further insight into the behavior of the sorbents. From the data obtained, Table III, it is apparent that the presence of CO_2 in the flue gas leads to only a moderate reduction in the SO_2 uptake value of a sorbent. This result is attributed to the low acidity of carbonic acid relative to that of sulfurous acid.[12]

The uptake data for the eight calcium silicates arranged in order of SO_2 uptake from the SO_2-H_2O-N_2 gas mixture, Table IV, show that tobermorite, C-S-H, and xonotlite are the best of these silicates. This can be ascribed to the high surface area of these silicates and to the water available or potentially available in them.

In another set of SO_2-uptake experiments, four sorbents were made from C_2S and C_3S and their SO_2 uptake was studied. One of these sorbents, S1 was prepared by stirring a 1:10 β-C_2S-H_2O slurry at 100 °C for 3 days. A second, S2 was prepared by milling (shaking, ZrO_2 beads) a 1:10 β-C_2S-H_2O slurry at ~ 25 °C for 3 days. A third, S3, was made by stirring a 1:10 C_3S-H_2O slurry at 100 °C for 3 days. The final one, S4, was made by milling a 1:10 C_3S-H_2O slurry at ~25 °C for 3 days.

Table III. SO_2 Uptake of Calcium Silicates from SO_2-H_2O-N_2 and SO_2-CO_2-H_2O-N_2 Mixtures

Name	Formula	Abbrev.	Source	SO_2 Uptake	
				SO_2-H_2O-N_2 (mmole/g)	SO_2-CO_2-H_2O-N_2 (mmole/g)
calcium hydroxide	$Ca(OH)_2$	CH	Smith Lime	2.6	1.9
calcium silicate hydrate	CaO-SiO_2-H_2O	C-S-H	synthesis	6.0	5.4
α-dicalcium silicate hydrate	α-$Ca_2(SiO_3OH)OH$	α-C_2SH	synthesis	2.2	1.9
tobermorite	$Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$	$C_5S_6H_5$	synthesis	5.9	4.6
xonotlite	$Ca_6Si_6O_{17}(OH)_2$	C_6S_6H	synthesis	6.3	4.3

Table IV. SO_2 Uptake of Calcium Silicates from SO_2-H_2O-N_2 and SO_2-CO_2-H_2O-N_2 Mixtures Arranged by SO_2 Uptake from SO_2-H_2O-N_2 Mixture

Name	Formula	SO_2 Uptake (mmole/g)	
		SO_2-H_2O-N_2 (mmole/g)	SO_2-CO_2-H_2O-N_2 (mmole/g)
α-dicalcium silicate hydrate	*α-$Ca_2(SiO_3OH)(OH)$*	2.2	1.9
calcium hydroxide	$Ca(OH)_2$	2.6	1.9
tobermorite	$Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$	5.9	4.6
calcium silicate hydrate	CaO-SiO_2-H_2O	6.0	5.4
xonotlite	$Ca_6Si_6O_{17}(OH)_2$	6.3	4.3

The results of the studies of these sorbents are summarized in Table V. With $Ca(OH)_2$ taken as reference, S1 and S3 are fair sorbents and S2 and S4 are excellent sorbents. The moderate effectiveness of S1 and S3 is ascribed to the high proportion of α-C_2SH, a moderately effective sorbent, in these two sorbents. The excellent effectiveness of S2 and S3 is attributed to the high proportion of C-S-H, an excellent sorbent, in them.

Experiments on four sorbents made by the hydration of C_3S gave insight into the composition of C_3S-derived sorbents as a function of synthesis time. These sorbents, S5 to S9, were made by milling (shaker, ZrO_2 beads) 1:10 C_3S-H_2O slurries for from 1 to 72 hours.

The results obtained are summarized in Table VI. As is apparent, the ratios of the hydration products of C_3S change considerably with time, with $C_3S_2H_3$ (afwillite)[13] occurring in higher proportions at longer times.

These results emphasize the need to carefully examine the chemistry that occurs when sorbents are subjected to what appear to be similar procedures. Clearly the products of apparently similar procedures can be quite different.

In a set of CO_2-N_2 uptake experiments, C-S-H and α-C_2SH were treated with CO_2-N_2 and CO_2-H_2O-N_2 simulated flue gases. From infrared spectra of the spent sorbents, Figures 1 and 2, it is apparent that neither sorbent reacts significantly with the CO_2-N_2 gas mixture under the conditions used. It is further apparent that the α-C_2SH reacts with the CO_2-H_2O-N_2 gas mixture to only a small extent, and that while the C-S-H reacts more, it still reacts to only a relatively small extent.

Thus, in spite of the fact the CO_2 concentration was fifty times higher in these experiments than was the SO_2 concentration in the SO_2 experiments, it is apparent that SO_2 is much more reactive. The dominance of SO_2 can be ascribed to the higher acidity of sulfurous acid compared to carbonic acid.[14]

Table V. Composition of β-C_2S and C_3S Derived Sorbents

Sorbent	Reactants	Ratio	Conditions			Composition					Completion	SO_2 Uptake
			Time (day)	Temp. (°C)	Agitation	C-S-H (%)	CH (%)	β-C_2S (%)	α-C_2SH (%)	$C_3S_2H_3$ (%)	(%)	(mmole/g)
$Ca(OH)_2$							100					2.6
S1	β-C_2S, H_2O	1:10	3	100	stirring			5	95		95	2.2
S2	β-C_2S, H_2O	1:10	3	~ 25	milling	70	10	20			80	6.4
S3	C_3S, H_2O	1:10	3	100	stirring		30		70		100	2.4
S4	C_3S, H_2O	1:10	3	~ 25	milling	40	40			20	100	6.2

Table VI. Composition of Additional C_3S Derived Sorbents

Sorbent	Reactants	Ratio	Conditions			Composition			Completion
			Time (h)	Temp. (°C)	Agitation	C-S-H (%)	CH (%)	$C_3S_2H_3$ (%)	(%)
S5	C_3S, H_2O	1:10	1	~ 25	milling	30	20		50
S6	C_3S, H_2O	1:10	3	~ 25	milling	45	20	5	70
S7	C_3S, H_2O	1:10	6	~ 25	milling	45	30	15	90
S8	C_3S, H_2O	1:10	12	~ 25	milling	40	40	20	100

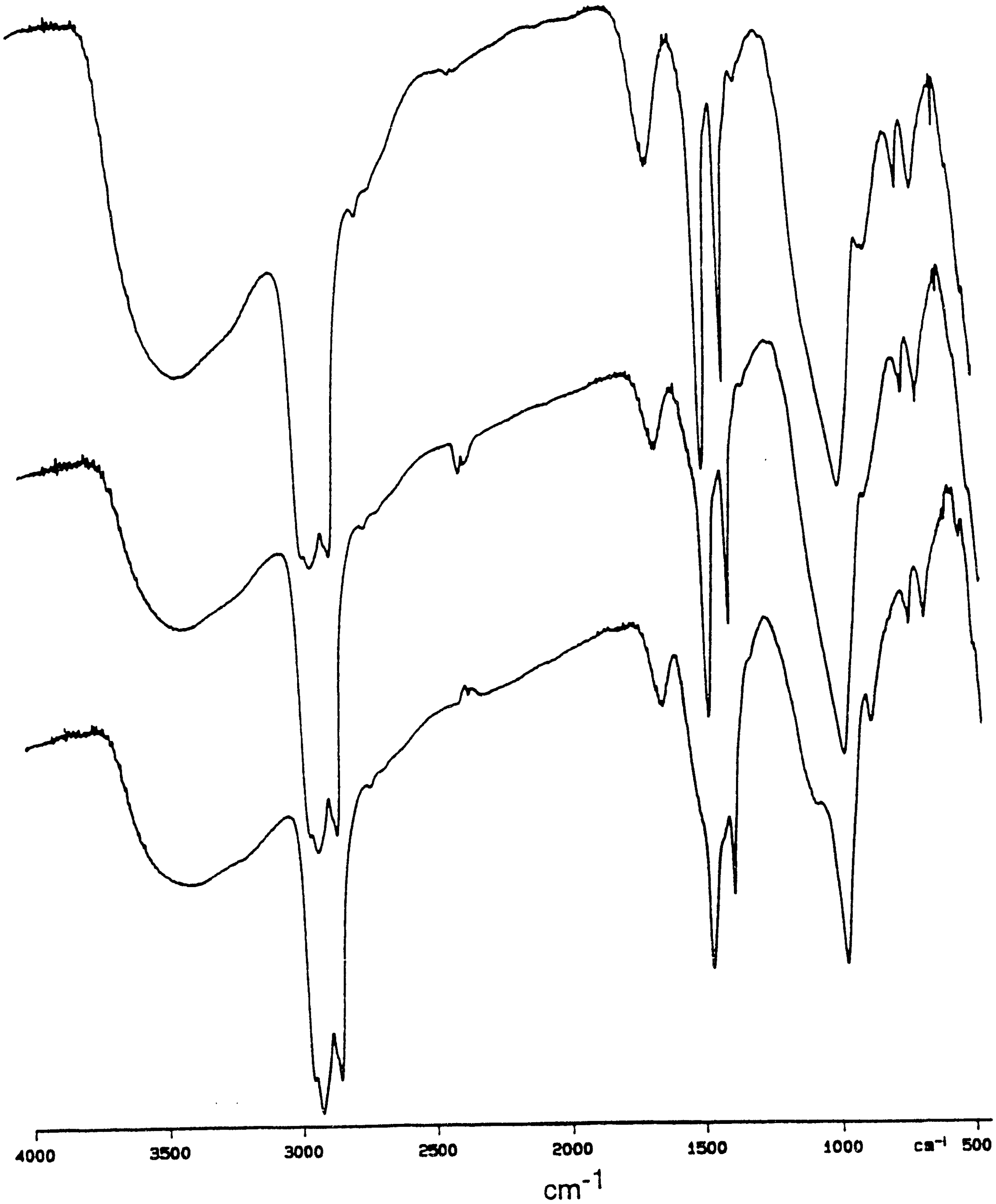

Figure 1. Infrared spectra of C-S-H as made, after exposure to CO_2-N_2 gas mixture, and after exposure to CO_2-H_2O-N_2 gas mixture.

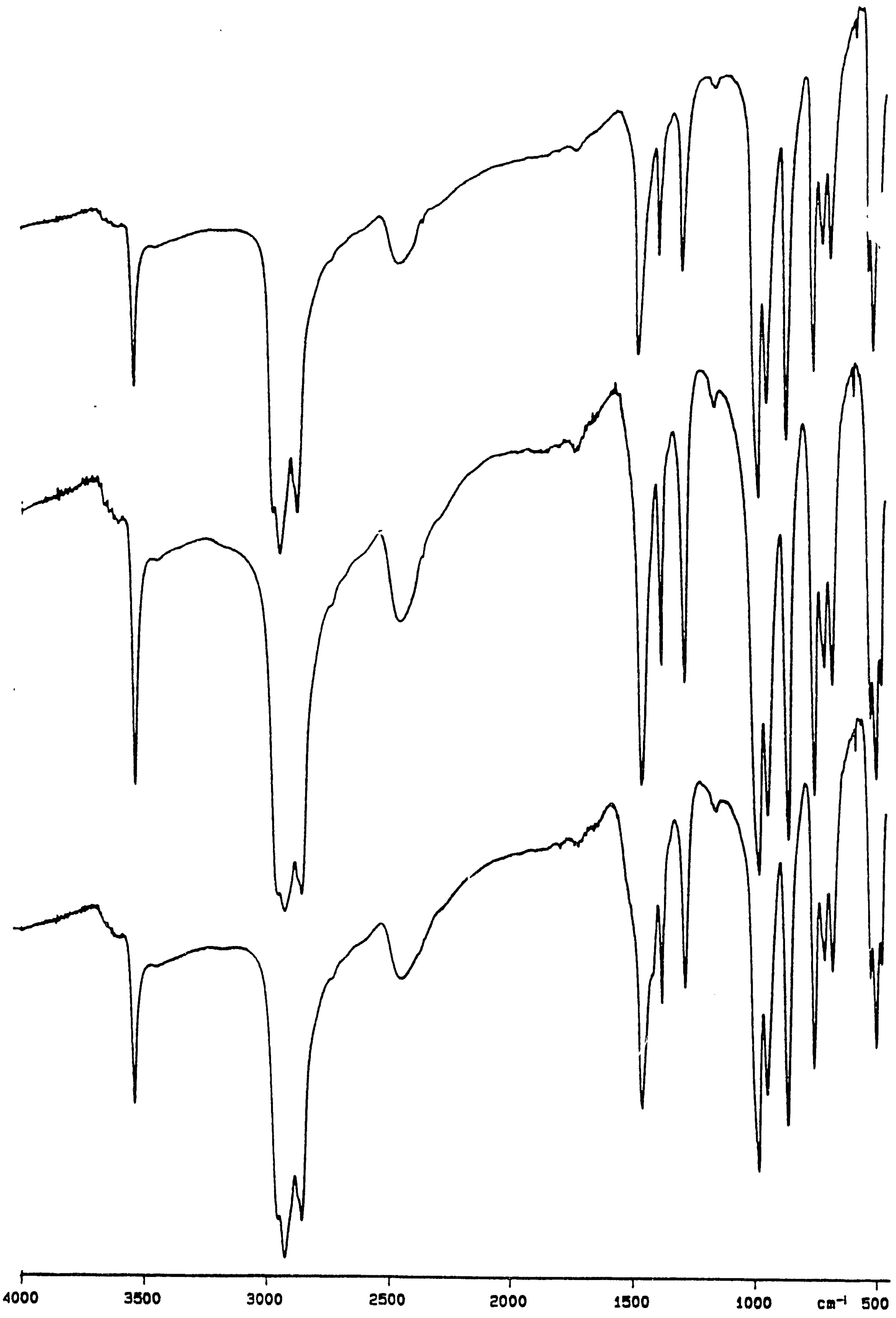

Figure 2. Infrared spectra of α-C_2SH as made, after exposure to CO_2-N_2 gas mixture, and after exposure to CO_2-H_2O-N_2 gas mixture.

4. $Ca(OH)_2$-Fly Ash Sorbent

Considerable attention has been given to a sorbent prepared from $Ca(OH)_2$ and fly ash. This sorbent, the so-called Advacate sorbent,[15] is attractive because it makes use of fly ash. Fly ash is a byproduct of the combustion of coal and is formed from impurities in the coal (e.g., clay and pyrite). Since fly ash is formed very rapidly and since the impurities in the coal are highly variable, fly ash is highly variable on a particle-to-particle level and on a bulk level. The main constituents of a typical bituminous fly ash (the type produced by burning Ohio coal) are an aluminosilicate glass, hematite, ferrite spinel, mullite, quartz, carbon, and alkali sulfates.[16] Physically fly ash is largely composed of spheres. Some of these are made of an aluminosilicate glass.

This variability in the composition of the fly ash causes variability in the reactivity of it towards $Ca(OH)_2$ and makes it very difficult to do studies of the $Ca(OH)_2$-fly ash sorbent that are broadly applicable.

In spite of these difficulties, studies of the composition of the $Ca(OH)_2$-fly ash sorbent, its reactivity, and analytical methods applicable to it are needed. The present study was undertaken to provide some of the required information. As will be seen, the study is incomplete.

Experimental Conditions. Three different types of fly ash were used, a West Virginia coal fly ash (FAS CRG) and two Ohio coal fly ashes (FAS 31 and FAS HC). Three procedures were used in making the sorbent from these fly ashes. In one procedure, Procedure 1, a slurry of unground fly ash, $Ca(OH)_2$ and H_2O (2:1:10 or 3:1:10) was stirred at 70-90 ^{o}C for 9-38 hours. In a second procedure, Procedure 2, a slurry of ground fly ash, $Ca(OH)_2$ and H_2O (3:1:10) was stirred at 90 ^{o}C for 3-6 hours. In the third, Procedure 3, a slurry of unground fly ash, $Ca(OH)_2$ and H_2O (2:1:10 or 3:1:10) was milled (shaking, ZrO_2 beads) at ~ 25-70 ^{o}C for 6-48 hours.

By XRD, it was found that the products of Procedure 1 can contain $Ca(OH)_2$, $Ca_3Al_2O_6 \cdot Ca(OH)_2 \cdot 12H_2O$ (C_4AH_{13}), $Ca_3Al_2(SiO_4)(O_4H_4)_2$ (C_3ASH_4), C-S-H, and

$2\,Al_2O_3 \cdot 2SiO_2 \cdot H_2O$ (A_2S_2H), Table VII. C_4AH_{13} is a known natural aluminosilicate.[17] C_3ASH_4 is katoite, a phase with a composition between that of grossular garnet, $Ca_3Al_2(SiO_4)_3$, and hydrogarnet, $Ca_3Al_2(O_4H_4)_3$.[18] A_2S_2H is hydralsite, a little known layer silicate.[19] All of these components except for $Ca(OH)_2$ are thought to arise from the reaction of the aluminosilicate glass with the $Ca(OH)_2$. Besides these components, the XRD data show that the sorbent contains hematite, ferrite spinel, mullite, quartz. These come from the fly ash. On the basis of the XRD data obtained, it appears that long reaction times favor the formation of C_3ASH_4.

Infrared spectra of the Procedure 1 products prepared from FAS 31 with successively longer and longer reaction times give further data on the composition of the sorbents and how it varies with reaction time. Spectra of the 18-hour product (S9) show a 970 cm^{-1} band, Figure 3. This band is an Si-O band and could arise from the C_3ASH_4 or the C-S-H in the sorbent. Spectra of 38-hour product (S11) show almost none of the 3650 cm^{-1} band seen prominently in S9. This 3650 cm^{-1} band is the OH band of $Ca(OH)_2$, and its near absence indicates that little $Ca(OH)_2$ remained in the 38-hour product.

Scanning electron micrographs (SEM) of FAS 31 and of Procedure 1 products prepared from FAS 31 with successively longer and longer reaction times give insight as to how the reaction proceeds. Micrographs of FAS 31 show the usual spheres, Figure 4. Micrographs of the 9-hour product show that some of the spheres have been covered by a new web-like material, Figure 5. Those of the 18-hour product (S9) show that some of the spheres are heavily covered by the new material, Figure 6. Those of the 38-hour product (S11) show that much of the product is composed of the new material, Figure 7, and that its particles are larger than those in fly ash. High-magnification micrographs of the surface of these particles show clearly the web-like nature of the new material, Figure 8.

To gain further insight into the 38-hour product, some of it was treated with 0.002 N HCl. This treatment dissolved about 50% of the product. Micrographs of the acid-treated

Table VII. Composition of $Ca(OH)_2$-Fly Ash Sorbents

Sorbent	Ash	Proced.	CH:Ash[a]	Conditions			Composition					
				Time (h)	Temp. (°C)	Agitation	$Ca(OH)_2$	C_4AH_{13}[b]	C_3ASH_4[c]	C-S-H	A[d]	A_2S_2
S9	FAS 31	1	2:1	18	85	stirring	+++	+	+			
S10	FAS 31		2:1	24	85	stirring	++	+	++			
S11	FAS 31		2:1	38	85	stirring			+++++			
S12	FAS CR		2:1	24	90	stirring	+++		++			
S13	FAS CR		3:1	10	90	stirring	+	+	+			++
S14	FAS HC		2:1	32	70	stirring	++	++		+		
S15	FAS HC		2:1	32	85	stirring	+++		++			
S16	FAS CRG	2	3:1	3	90	stirring	++	++		+		
S17	FAS CRG		3:1	6	90	stirring			+	++++		
S18	FAS 31	3	2:1	9	70	milling	++			+	++	
S19	FAS 31		2:1	18	70	milling				++	+++	
S20	FAS 31		2:1	18	~25	milling	++++				+	
S21	FAS CR		3:1	18	70	milling		+		++	++	
S22	FAS HC		2:1	6	70	milling	+++			+	+	
S23	FAS HC		2:1	48	~25	milling	++++				+	

[a] CH : Ash: $Ca(OH)_2$: Fly ash. [b] C_4AH_{13}: $Ca_3Al_2O_6 \cdot Ca(OH)_2 \cdot 12H_2O$. [c] C_3ASH_4: katoite, $Ca_3Al_2(SiO_4)(O_4H_4)_2$. [d] A: unidentified amorphous phase (peak 30-31° 2θ). [e] A_2S_2H: hydralsite, $2Al_2O_3 \cdot 2SiO_2 \cdot H_2O$.

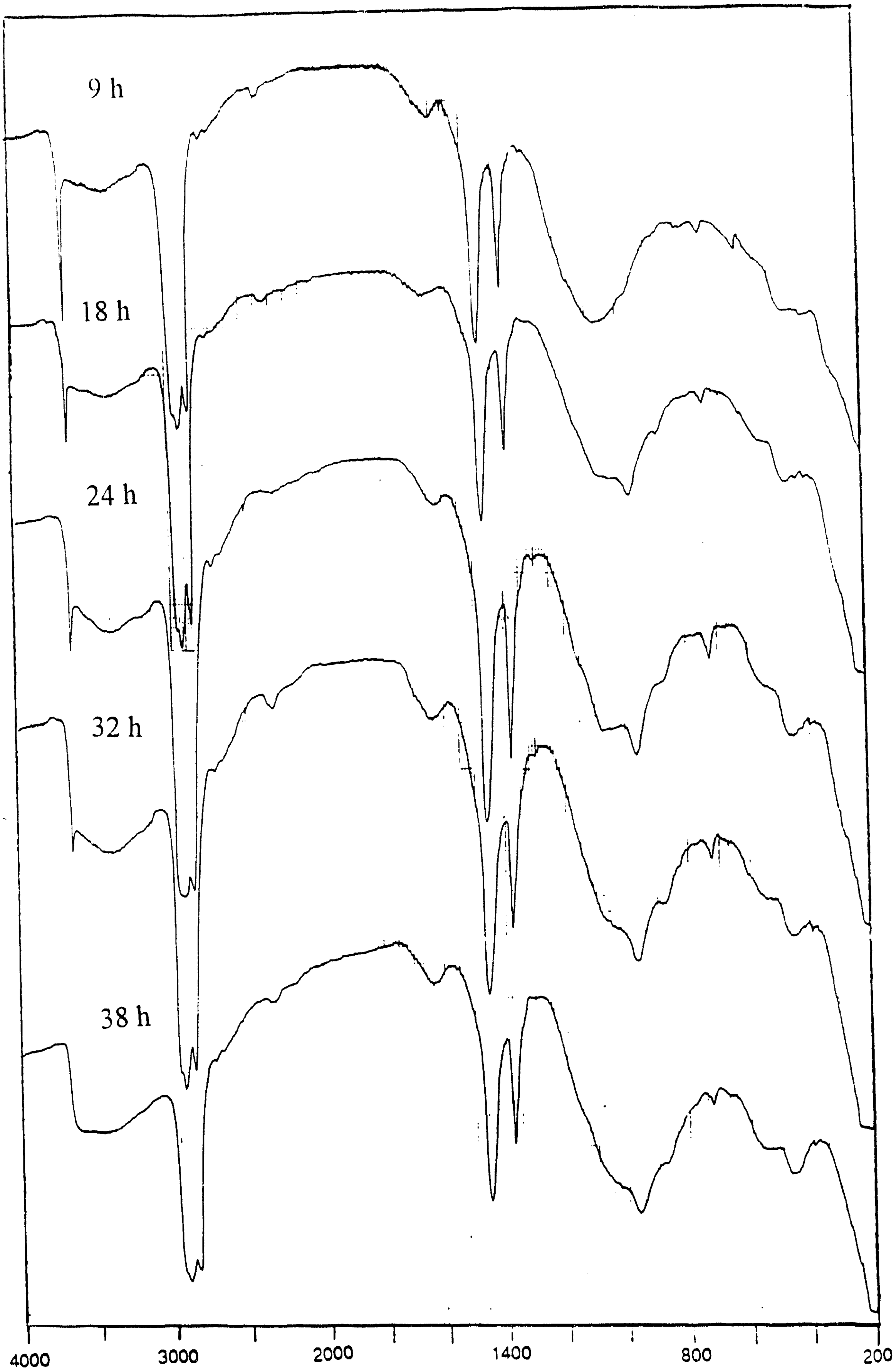

Figure 3. Infrared spectra of Procedure 1 products prepared form FAS 31.

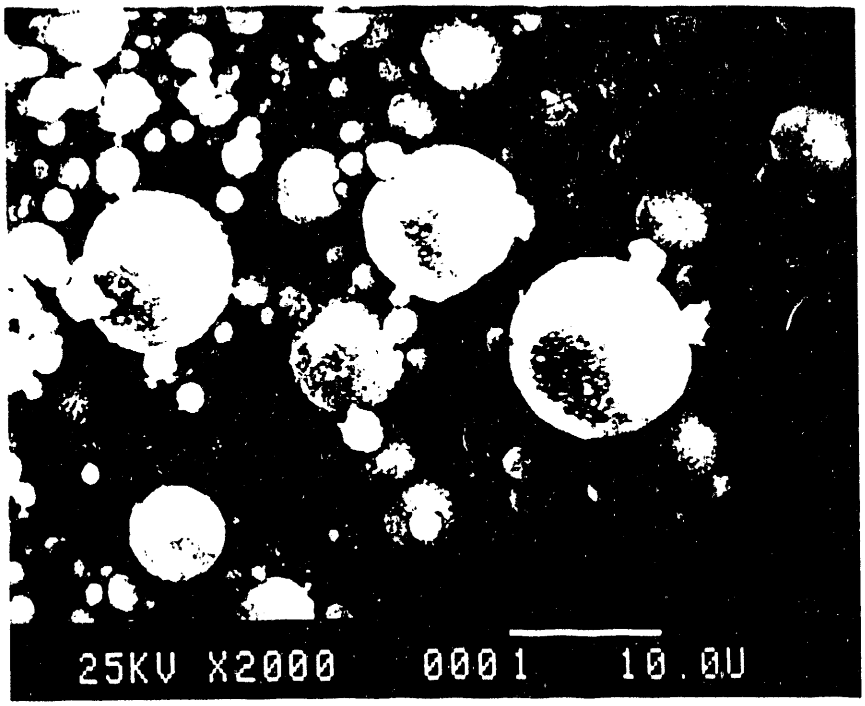

Figure 4. Fly ash FAS 31.

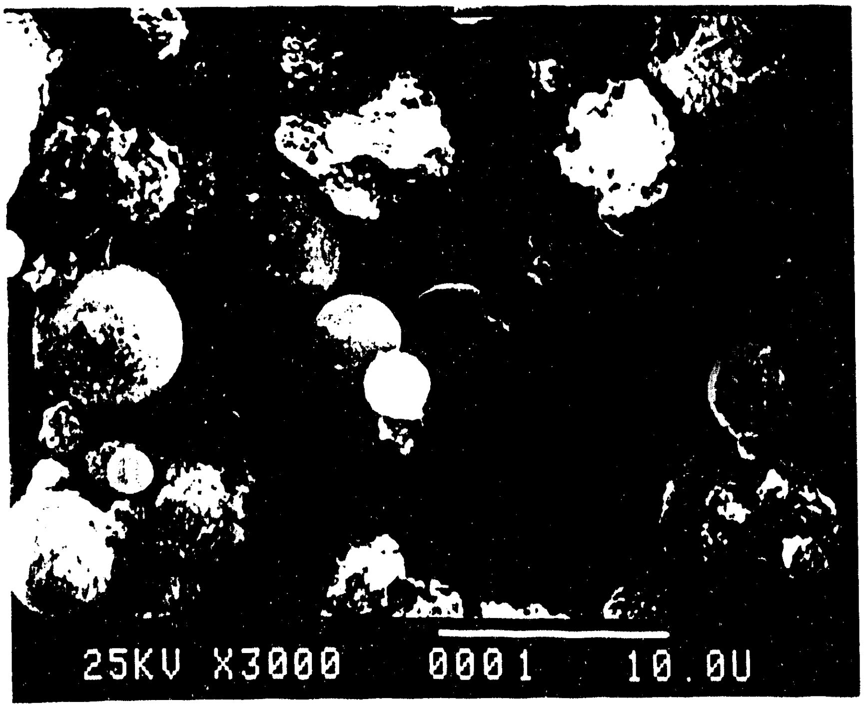

Figure 5. Web-like material coating sphere of 9-hour product.

Figure 6. Web-like material heavily coating sphere of 18-hour product (S9).

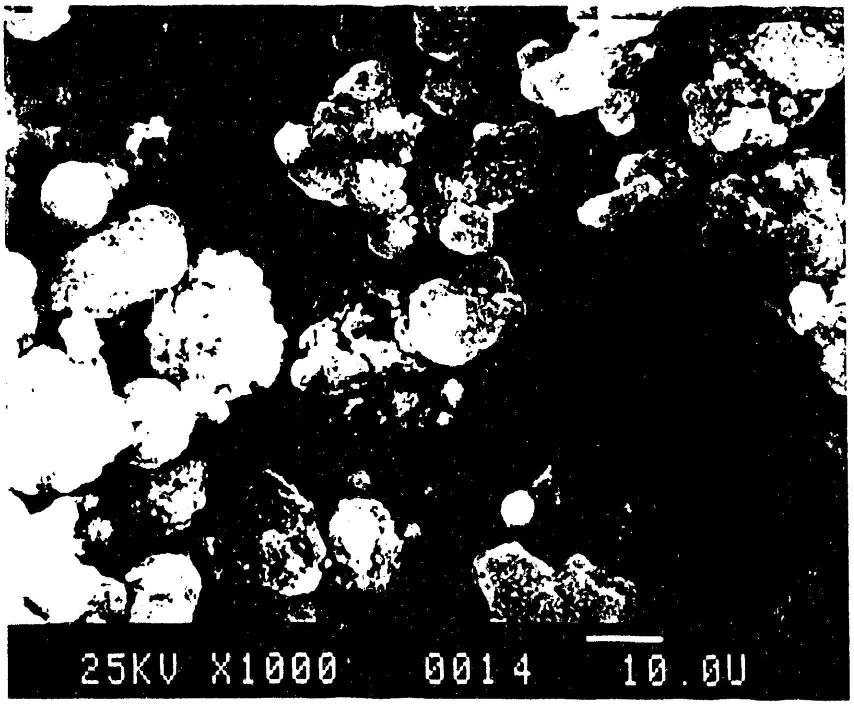

Figure 7. Particles of web-like material in 38-hour product (S11).

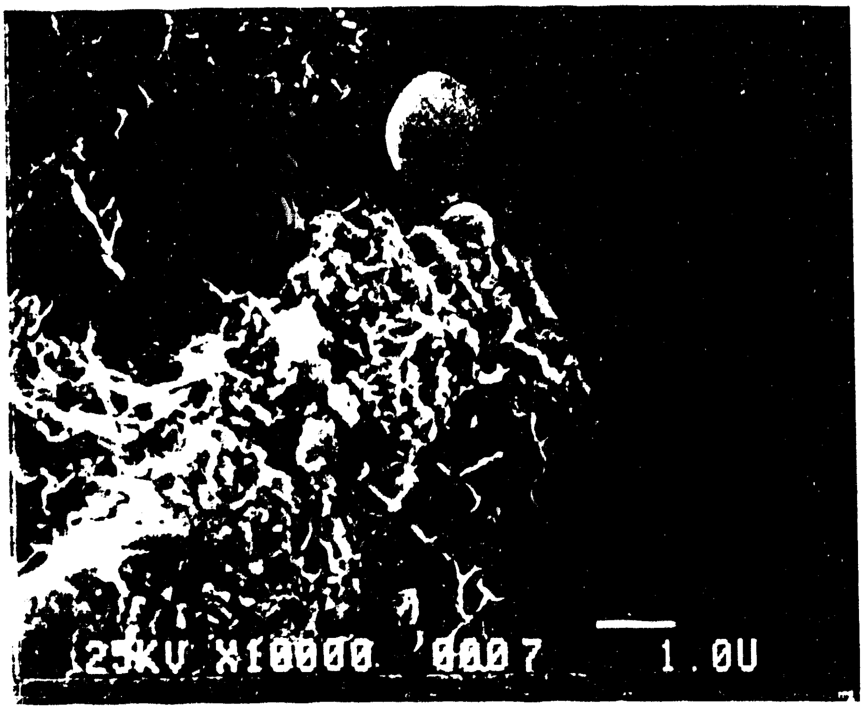

Figure 8. Surface of web-like particle in 38-hour product (S11).

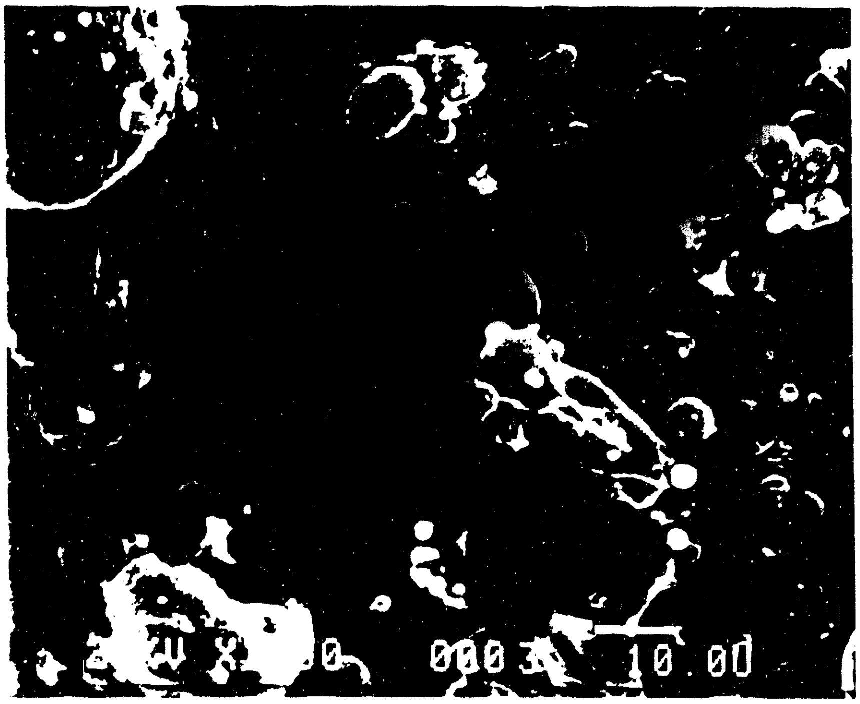

Figure 9. Residue from HCl-treatment of 38-hour particle (S11).

product show that it is composed largely of spheres like those in the original fly ash, Figure 9. It is assumed that the particles in 38-hour product had these spheres embedded in them and that the acid dissolved the new material and left the spheres behind.

On the basis of the data gathered, it appears that the aluminosilicate glass in the fly ash reacts with the $Ca(OH)_2$ under the conditions used to give C-S-H or a related material on the surface of the glass spheres. When enough C-S-H has been formed, both the reactive and the unreactive components of the fly ash become enveloped by it, Figure 10.

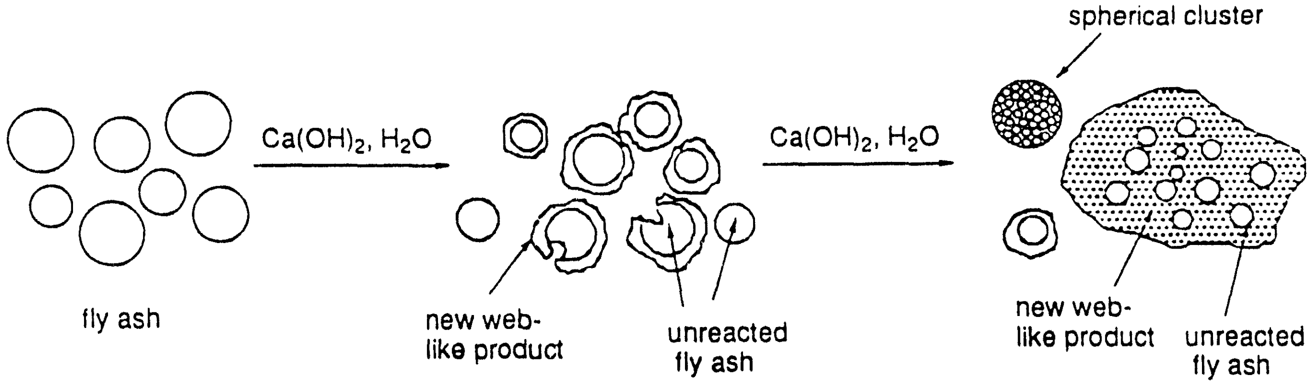

Figure 10. Formation of $Ca(OH)_2$-fly ash sorbent under favorable conditions.

To obtain data on which types of particles take up SO_2, some of the 38-hour product was placed (without being diluted with sea sand) in the sorption system and was treated with an SO_2-N_2-H_2O gas mixture (2000 ppm , 60 % relative humidity at 60 °C). Micrographs of the product show that it contains particles similar in general appearance to those in the 38-hour product itself, Figure 11. Energy dispersive spectroscopy (EDS) of the particles similar to the web-like particles of the 38-hour product shows that the Ca:S ratio in them ranges from 1:0.6 to 1:1. This result provides direct evidence that C-S-H is the component of the sorbent that takes up the SO_2.

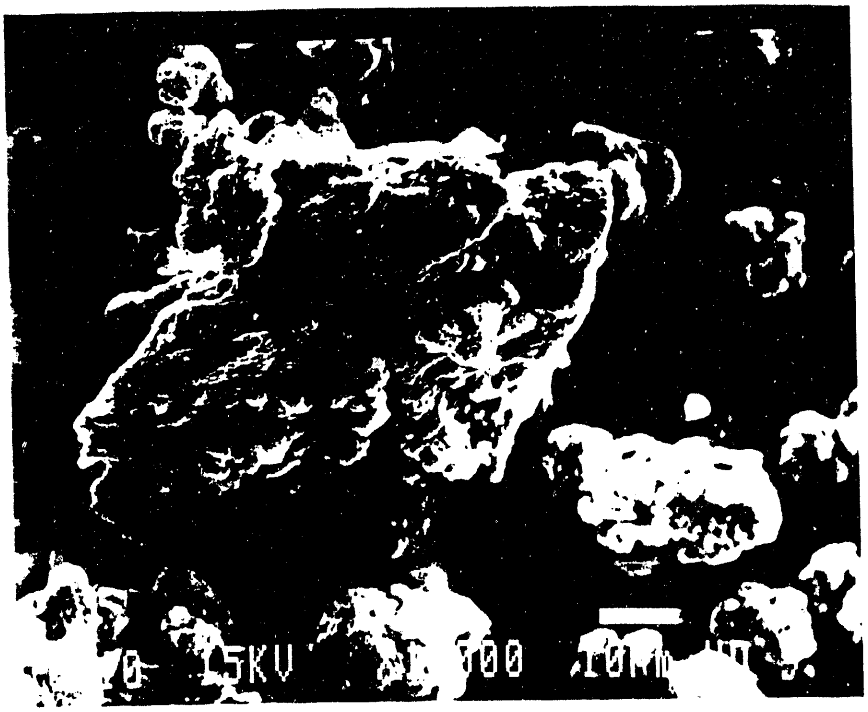

Figure 11. Product from SO_2-treatment of 38-hour product (S11). Ca:S ratio 1 : 0.8.

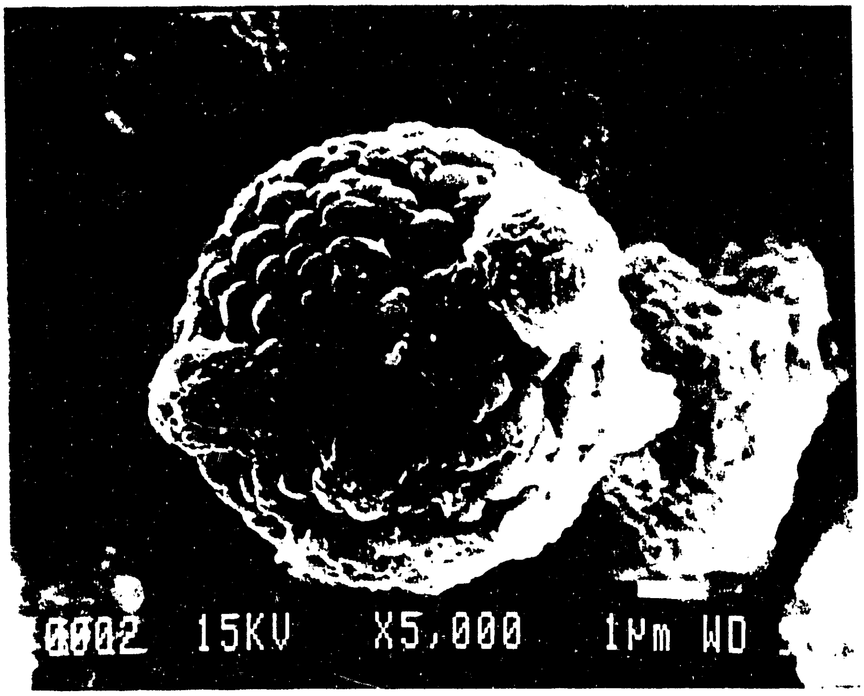

Figure 12. Spherical cluster in product of SO_2-treatment of 38-hour product (S11). Ca : S ratio 15 : 1.

Micrographs of the products often show "spherical clusters". These have a high Ca content (~ 50 %), and when treated with SO_2-N_2-H_2O do not take up S. Figure 12. Their identity is not known.

Procedure 2 appears to lead to C-S-H more efficiently. Probably this occurs because the glass particles in the ground fly ash have a higher surface area, are strained, and have microcracks. Micrographs of a 6-hour product made from FAS CRG (S17) show that it contains a large amount of C-S-H.

Procedure 3 appears to be intermediate in efficiency between the other two procedures. This is as expected in view of the conditions used in it.

While directly applicable data are not available , it seems likely that C_3ASH_4 contributes little to the SO_2 uptake capacity of the products of Procedures 1 and 2. (Tests of the uptake capacity of its isostructural relative, hydrogarnet, show that it is a very poor sorbent (0.3 mmole/g compared with 2.6 mmole/g for $Ca(OH)_2$)).

The aluminum in the glass of the fly ash has both negative and positive aspects. It furnishes the aluminum required for the formation of C_3ASH_4, but it probably makes the glass more soluble in the $Ca(OH)_2$ solution.

Clearly this picture of the $Ca(OH)_2$-fly ash sorbent is incomplete, and it may be incorrect in some details. However, it is believed it is broadly correct . More work on the sorbent is in progress.

5. Cement and Modified Cement Sorbents

On the basis of the data gathered, it is apparent that cheap, readily available sources of calcium silicates are of interest as SO_2 sorbents or as precursors to them. Two such sources are Type I (ordinary) portland cement and hydrated Type I portland cement.

The first of these, Type I portland cement, is a complex mixture. Its main constituents are Ca_3SiO_5, β-Ca_2SiO_4, Ca_2AlFeO_5 and $Ca_3Al_2O_6$. They comprise, respectively, 50-70%, 15-30%, 5-15% and 5-10% of it.[20] Because Ca_3SiO_5 and β-Ca_2SiO_4 are its two most abundant constituents, and because these compounds are poor sorbents, cement itself has little potential as a sorbent.

The second of these calcium silicate sources, hydrated Type I portland cement, is also a complex mixture. As commonly made, its main constituents are C-S-H and $Ca(OH)_2$. These comprise about 60 and 25 volume percent of it.[21] They are, in contrast to the main constituents of cement, excellent and good sorbents, respectively. Thus, hydrated cement has potential as a sorbent.

However, full hydration of cement under the commonly used conditions is a slow, taking a month to a decade.[22] Further, the product is massive and thus physically unsuitable for use as a sorbent. The current work was undertaken to find ways to make hydrated cement rich in C-S-H and $Ca(OH)_2$ that are rapid and give it in a suitable physical form, and to test such hydrated cement as a sorbent.

Experimental Conditions. Six sorbents were studied. One, S24, was made by periodically shaking a 1:10 cement-H_2O slurry at ~25 °C for 30 days. Two others, S25 and S26, were made by stirring 1:10 and 1:0.2:10 cement-H_2O and cement-SiO_2-H_2O slurries at 100 °C for 3 days. Another, S27, was prepared by milling (shaker, ZrO_2 beads) a 1:10 cement-H_2O slurry at 60 °C for 9 hours. A fifth, S28, was prepared by milling a 1:10 cement H_2O slurry at ~ 25 °C for 3 days. The last one, S29, was prepared by milling a 1:0.2:10 cement-SiO_2-H_2O slurry at ~ 25 °C for 3 days.

The approximate composition of the sorbents was determined by XRD and IR. Their SO_2 uptake and hence Ca utilization was determined with the procedures and apparatus described for the determination of the SO_2 uptake of the fly ash sorbents.

Results and Discussion. The percentages of C-S-H and $Ca(OH)_2$ in S24 are high enough so that it could be an acceptable sorbent, Table VIII. However, micrographs of it show that the $Ca(OH)_2$ is present in it as large, well formed crystals, Figure 13. It is concluded that these crystals are unreactive and that this leads to the low SO_2 uptake of this sorbent.

Table VIII. Cement and Modified Cement Sorbents

Sorbent	Reactants	Ratio	Conditions			Composition				SO_2 Uptake	Ca Utilization
			Time (day)	Temp. (°C)	Agitation	C-S-H (%)	$Ca(OH)_2$ (%)	α-C_2SH[a] (%)	AFm[b] (%)	(mmole/g)	(%)
S24	cem, H_2O	1:10	30	~25	periodic shaking	40	20			3.9	35
S25	cem, H_2O	1:10	3	100	stirring	10	40	50		4.2	38
S26	cem, SiO_2,H_2O	1:0.2:10	3	100	stirring	70	10	20		5.6	60
S27	cem, H_2O	1:10	0.4	60	milling	45	25		10	5.9	64
S28	cem, H_2O	1:10	3	~25	milling	50	30		10	6.5	67
S29	cem, SiO_2,H_2O	1:0.2:10	3	~25	milling	70	10		10	6.6	76

[a] α-C_2SH: α-$Ca_2(SiO_3OH)(OH)$. [b] AFm: $Ca_3(Al, Fe)_2O_6 \cdot CaX \cdot 12H_2O$, $X=SO_4$ and $(OH)_2$.

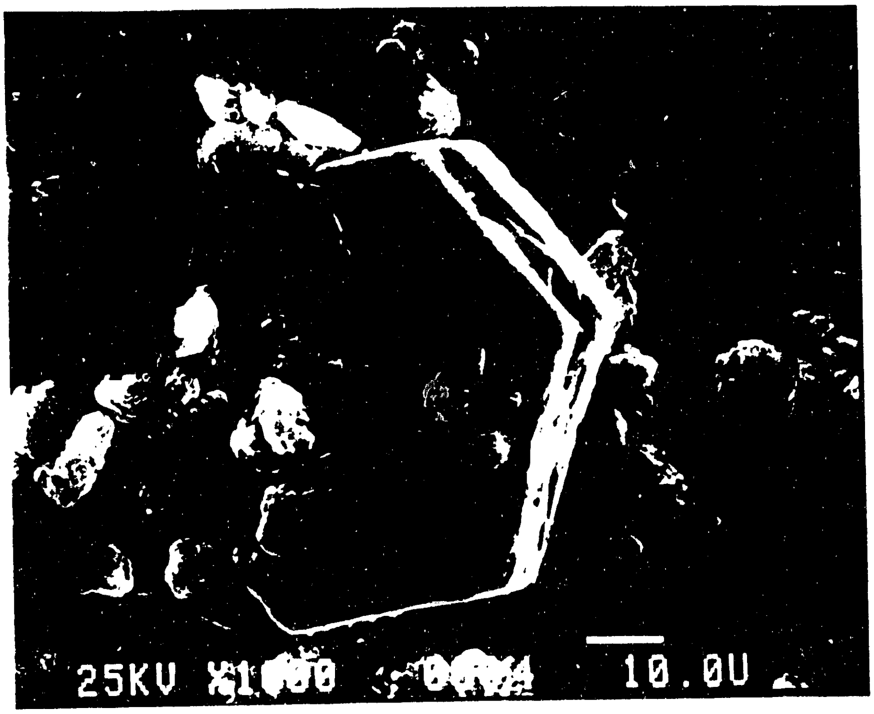

Figure 13. Crystals of $Ca(OH)_2$ in S24.

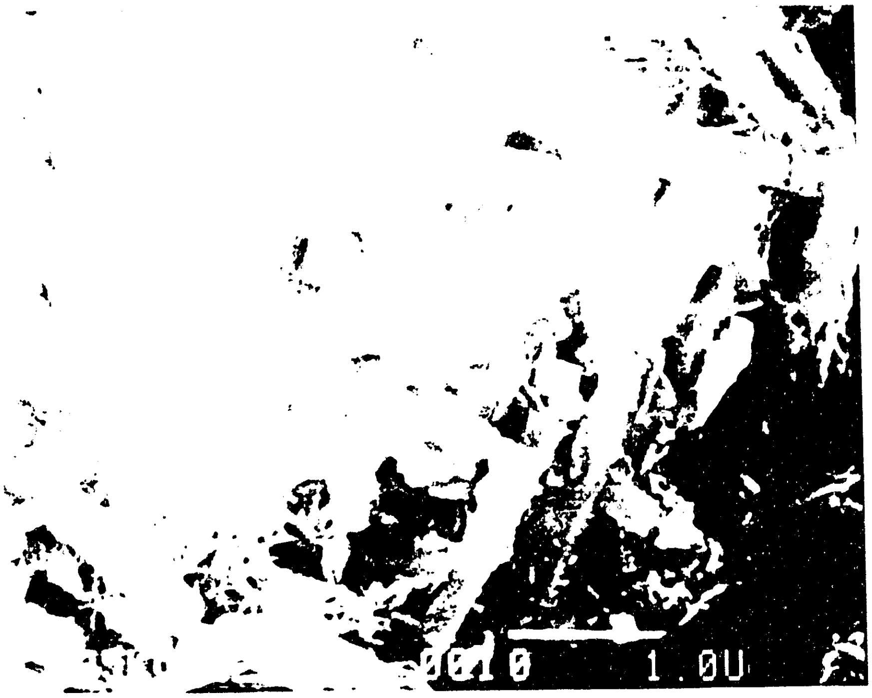

Figure 14. Crystals of α-C_2SH in S25.

Sorbent S25 contains a high percentage of α-C_2SH, Table VIII. Micrographs of it show this clearly, Figure 14. Because α-C_2SH is a poor sorbent, the low Ca utilization of this sorbent is as expected.

In contrast to S25, sorbent S26 contains a high percentage of C-S-H. It is thus not surprising that this sorbent exhibits a high Ca utilization.

Sorbents S27, S28 and S29 all have moderate to high C-S-H contents and moderate to low $Ca(OH)_2$ contents. Micrographs of S28 show that it does not contain large $Ca(OH)_2$ crystals, Figure 15. It is believed that S27 and S29 also do not contain large $Ca(OH)_2$ crystals. In view of the small size of the $Ca(OH)_2$ crystals in these sorbents and the high C-S-H content in them, their high Ca utilization is as expected.

In general, it is concluded that hydration of cement at room temperature with mild agitation leads to slow hydration of the cement because of the formation of a protective coating of reaction products on its particles. It is also concluded that these conditions allow the formation of large, unreactive $Ca(OH)_2$ crystals. Thus, these conditions are not desirable.

It is further concluded that hydration of cement at 100 °C with stirring leads to the formation of a considerable amount of α-C_2SH, a poor sorbent. Thus, these conditions are also not desirable.

On the other hand, it is clear that hydration of cement with milling at 20-60 °C leads reasonably rapidly to conversion of much of it to C-S-H and $Ca(OH)_2$, with the $Ca(OH)_2$ in the form of small particles. Accordingly, these conditions are desirable.

The addition of SiO_2 to the cement-H_2O slurry causes the conversion of much of the $Ca(OH)_2$ formed by the hydration of cement to C-S-H. This is highly desirable because C-S-H has a higher Ca utilization than $Ca(OH)_2$. Thus, the process giving the best sorbent is the one in which a cement-SiO_2-H_2O slurry is milled at a moderate temperature.

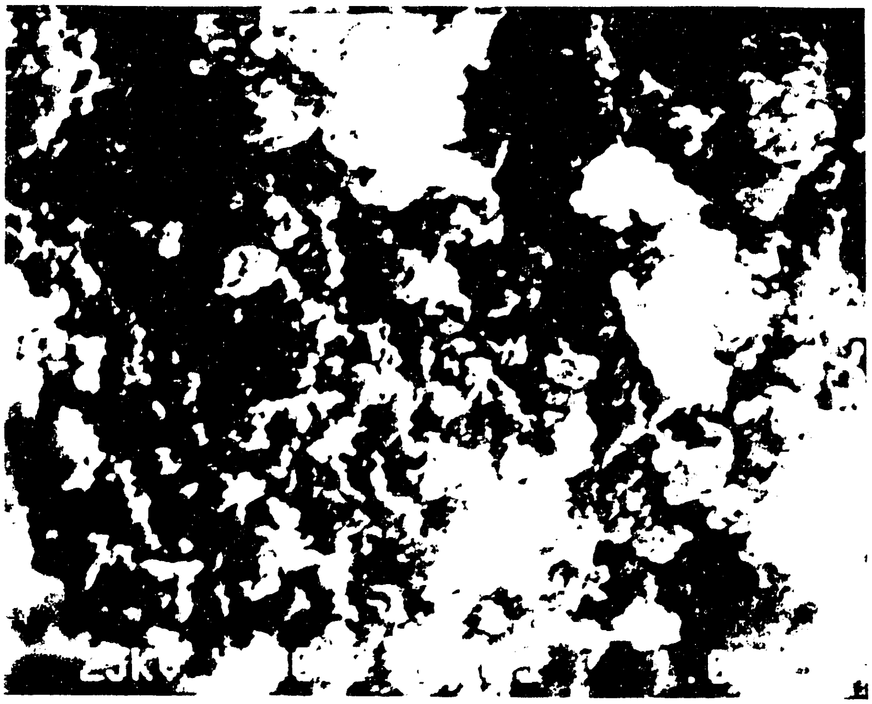

Figure 15. Particles in S28.

6. $Ca(OH)_2$ and Modified $Ca(OH)_2$ Sorbents

$Ca(OH)_2$ is of considerable importance as a sorbent. However, while it is cheap and readily available, it does not take up SO_2 efficiently from flue gas when it is dry.[23] The current work was undertaken to study this problem and to try to find ways to overcome it.

Experimental Conditions. Five sorbents were studied. One, S30, was a commercial $Ca(OH)_2$ prepared by the hydration of CaO with water (Smith Lime Co.). A second, S31, was prepared by milling (shaker, ZrO_2 beads) a 1:10 S30-H_2O slurry for 1 day. A third, S32, was prepared by milling 1:0.2:10 S30-SiO_2-H_2O slurry for 1 day. Another, S33, was made by adding aqueous solutions of $CaCl_2$ and NaOH to ethanol. The final two, S34 and S35, were prepared by milling 1:10 S33-H_2O and 1:0.2:10 S33-SiO_2-H_2O slurries for 1 day.

The SO_2 uptake of these sorbents was determined with the procedure and apparatus described for the determination of the SO_2 uptake of the fly ash sorbents.

Results and Discussion. By SEM it was found that S30 contained small irregular particles. S31 contained irregular particles that were smaller than those of S30, and S32 contained irregular particles that were larger than those of S30. It was further found that S33 contained small well-formed crystals, S34 contained crystals that were similar to those of S33, and S35 contained irregular particles that were larger than the crystals of S33. Table IX and Figures 16-19.

The number of defects in these crystals or particles was estimated on the basis of the vigor of the agitation procedure used. Table IX. The surface layer of S32 was found to be rich in silicon by X-ray photoelectron spectroscopy.

It was concluded that the SO_2 uptake by S30 and S31 and by S33 and S34 was governed partly by the size of the crystals or particles in them. This is consistent with the usual correlation between reaction rate and particle size in solid-solution reactions. It also was concluded that the uptake of SO_2 by S30, S31 and S32 was controlled partly by the number of defects in their crystallites. This is in accordance with the high reactivity generally found at defect sites. In addition, it was concluded that C-S-H was a component of S32 and that it was present as a material enveloping well-separated, highly defective, small crystallites of $Ca(OH)_2$. It was further concluded that C-S-H was also a component of S35 and that it was present in this sorbent as an irregular coating on well-separated, but relatively perfect, relatively large crystals of $Ca(OH)_2$. The presence of well-separated, highly defective, small $Ca(OH)_2$ crystallites embedded in a porous, reactive bed of C-S-H in S30 and the presence of well-separated, but relatively perfect, relatively large crystals of $Ca(OH)_2$ coated with C-S-H in S35 is consistent with the substantially higher SO_2 uptake of S32 relative to S35.

In summary, the results of this work show that milled $Ca(OH)_2$ and silica-modified milled $Ca(OH)_2$ are excellent sorbents and are of practical interest.

Table IX. $Ca(OH)_2$ and Modified $Ca(OH)_2$ Sorbents.

Sorbent	Precursors	Ratio	Conditions			Particles			C-S-H	SO_2 uptake	Ca Utilization
			Time (day)	Temp. (^oC)	Agitation	Size (μ)	Defect	Isolation	(%)	(mmole/g)	(%)
S30	CaO, H_2O					1 - 20	few	low	0	2.6	19
S31	S30,H_2O	1:10	1	~ 25	milling	0.5-10	many	low	0	5.8	43
S32	S30, SiO_2, H_2O	1:0.2:10	1	~ 25	milling	2-20	many	high	20	7.5	60
S33	$CaCl_2$,NaOH	1:1				0.3 - 1	few	low	0	4.0	30
S34	S33, H_2O	1:10	1	~ 25	milling	0.3 - 1	few	low	0	4.3	32
S35	S33, SiO_2, H_2O	1:0.2:10	1	~ 25	milling	1-5	few	high	30	5.3	44

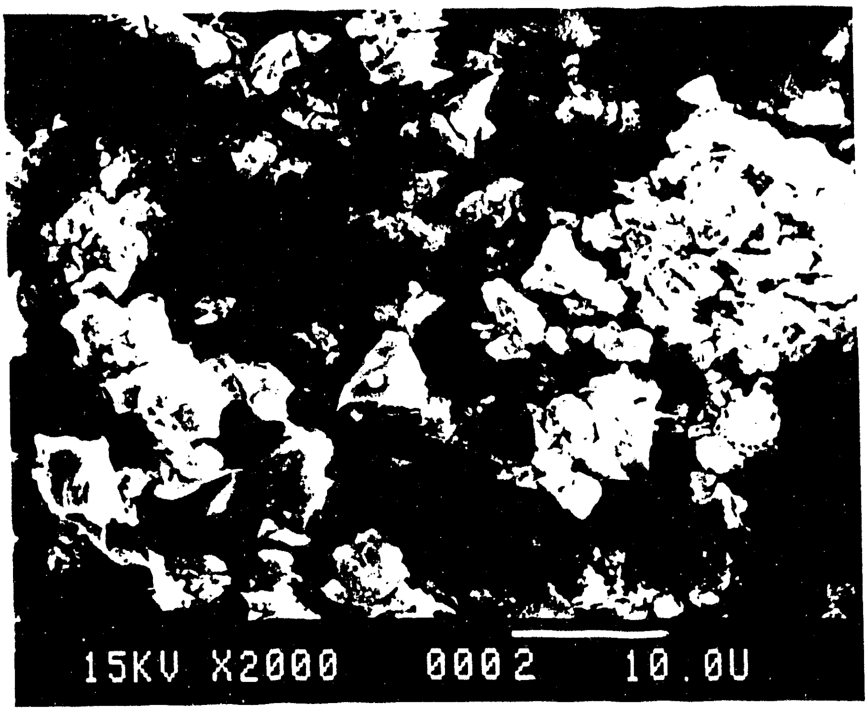

Figure 16. Particles of $Ca(OH)_2$ in S30.

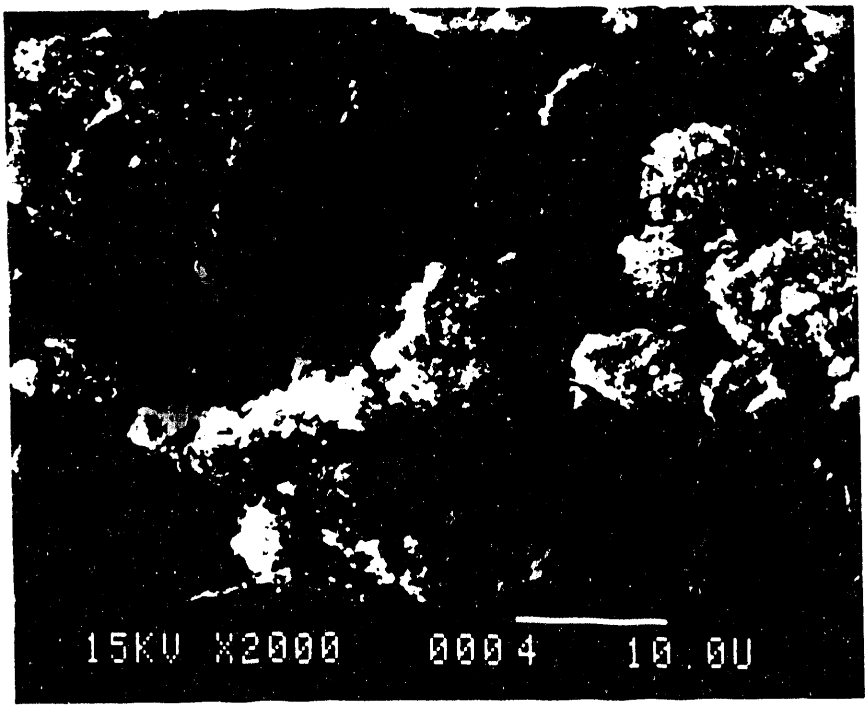

Figure 17. Particles in S32.

Figure 18. Crystals of $Ca(OH)_2$ in S33.

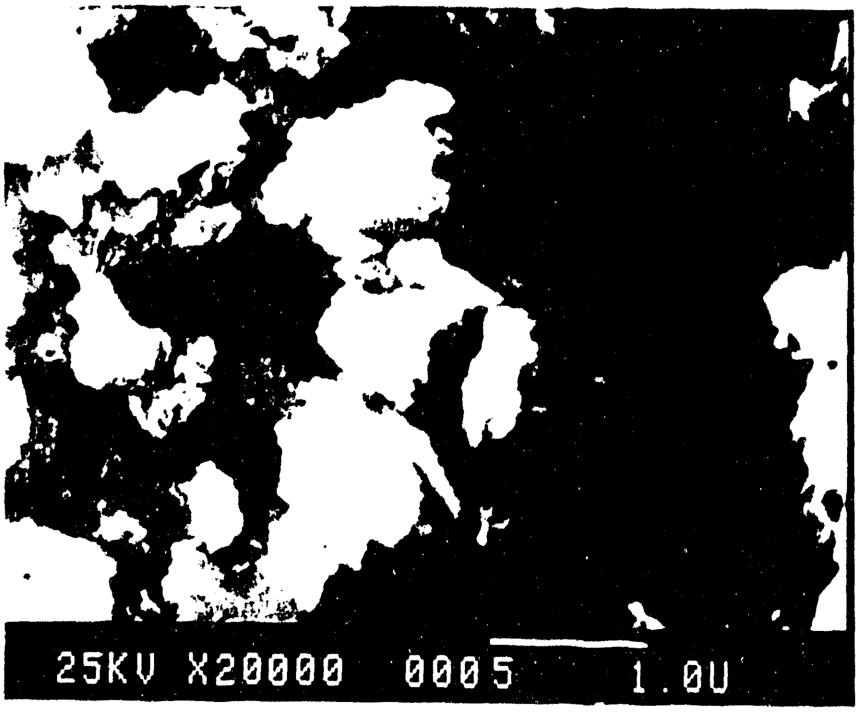

Figure 19. Particles in S35.

7. Installation of Humidity Sensor

In the original configuration of the bench-scale sand-bed sorber, there was no relative humidity sensing device. The humidity was determined from the flow rate of the gas and injection rate of the water. While this arrangement was satisfactory, it seemed desirable to add a humidity sensing device to the sorber.

Accordingly, a wet-bulb dry-bulb humidity sensor was added. It was positioned just before the sand-bed reactor.

In one run with this sensor in the sorber, the flow rate of the gas was 1 L/min, the injection rate of the water was 6.5 mL/h, the wet bulb reading was 51.0 ± 0.5 °C and the dry bulb reading was 60 °C. The relative humidity calculated from the injection rate of the water was 60% while that calculated from the sensor was 62 %. It was concluded that both the injection method and the sensor method for the determining the humidity of the gas in the sorption system were satisfactory.

The time required for the sensor to come to equilibrium was about 3 min. The sensor thus responded reasonably rapidly.

8. Marketing

The sorbents made are designed to have potential for induct injection. In the coming year effort will be devoted to outlining possible markets for the spent sorbents and to determining the costs of the sorbents relative to other known sorbents.

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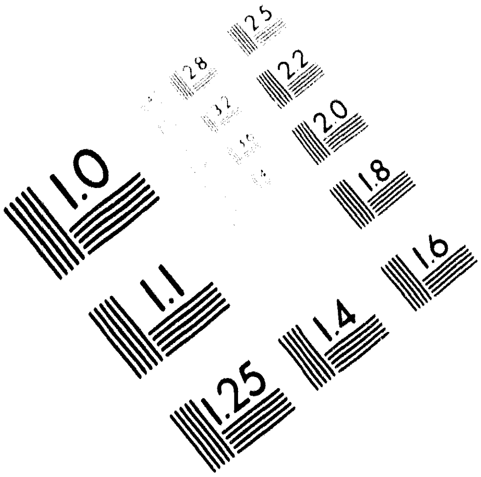

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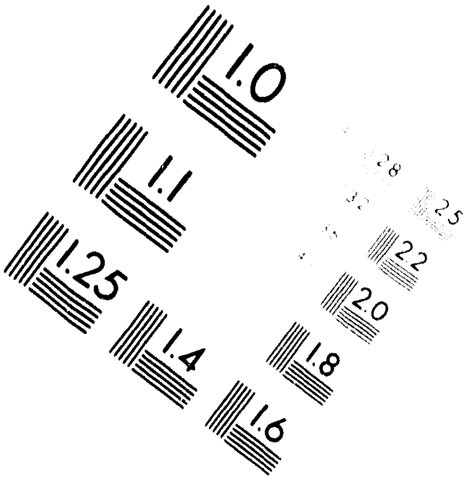

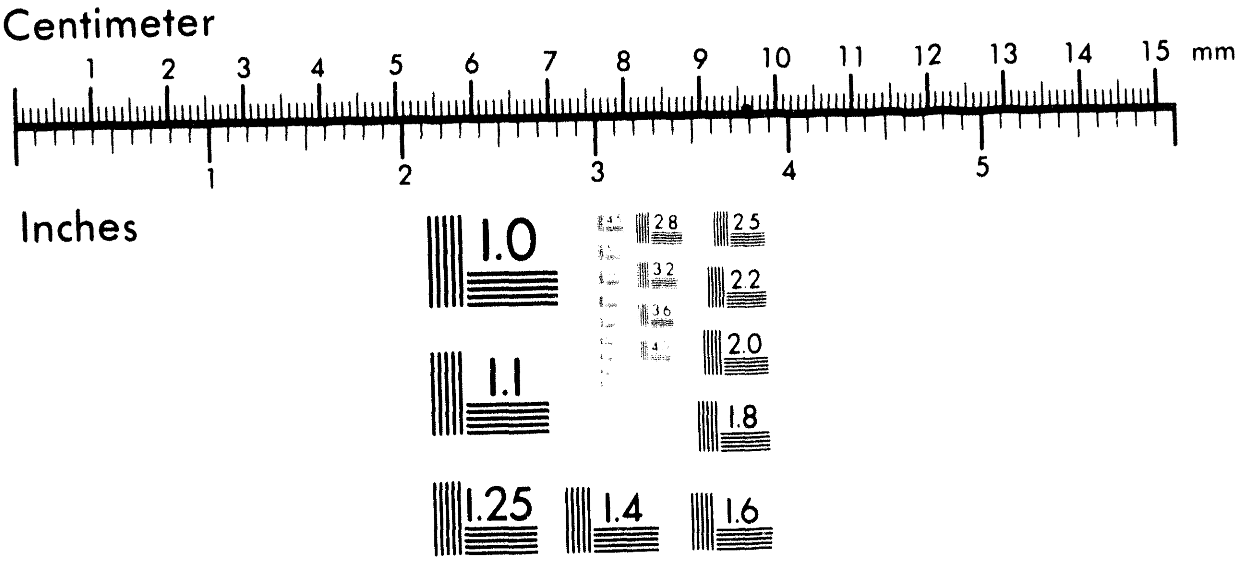

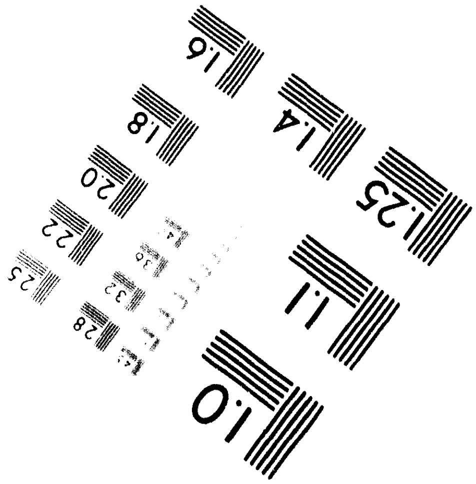

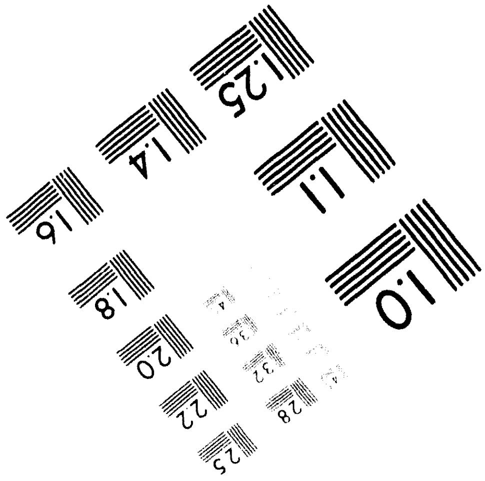

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