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

Final Report for the Period
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by

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4. 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 for the current year include the study of sorbents made from $\text{Ca}(\text{OH})_2$, from mixtures of $\text{Ca}(\text{OH})_2$ and SiO_2 , and from portland cement. They also include the study of sorbents made from model compounds.

During this year, sorbents prepared from $\text{Ca}(\text{OH})_2$ and from mixtures of $\text{Ca}(\text{OH})_2$ and fumed SiO_2 were investigated. The results show that very good SiO_2 -modified $\text{Ca}(\text{OH})_2$ sorbents in which the Si-to-Ca reactant ratio is low can be prepared from $\text{Ca}(\text{OH})_2$ and fumed SiO_2 . This is significant because in some cases it could be economically advantageous to use SiO_2 -modified $\text{Ca}(\text{OH})_2$ sorbents in which the Si-to-Ca reactant ratio is low rather than high. Sorbents prepared from $\text{Ca}(\text{OH})_2$ and natural SiO_2 or natural SiO_2 sources were also studied. The results obtained show that very good SiO_2 -modified $\text{Ca}(\text{OH})_2$ sorbents and calcium silicate hydrate sorbents, C-S-H sorbents, can be prepared from $\text{Ca}(\text{OH})_2$ and diatomite, pumice or perlite, minerals that are readily available.

In addition, sorbents prepared from Ca_3SiO_5 and $\beta\text{-Ca}_2\text{SiO}_4$ and from mixtures of these compounds and SiO_2 were studied. This model work was done in

support of the work on the cement-derived sorbents. The results secured demonstrate that very good C-S-H rich sorbents can be prepared from these compounds and from mixtures of them with SiO_2 . They also provide information useful for interpreting the cement sorbent results.

Sorbents prepared from cement and from mixtures of cement and natural SiO_2 or SiO_2 sources were investigated as well. The results secured show that cement and mixtures of it with diatomite, pumice or perlite rapidly yield excellent sorbents with the proper reaction conditions. They further suggest that such sorbents are attractive for practical use.

In sum, the project proceeded as anticipated to the extent a research project can be expected too, and it provided valuable results.

Work To Be Done

In the coming year, work will be done in an effort to find ways to make C-S-H type sorbents that have still better combinations of SO_2 uptake, Ca utilization and projected cost. Work will also be done in an effort to find C-S-H type adsorbents and absorbents for Se in flue gas. The work is designed to yield highly effective sorbents that can be made by means that are fast, cheap and reliable. Work on pure compounds will be done when necessary to provide base-line data.

Collaborations

During the course of the year, collaborative work with other members of the consortium was done. A sample of a cement-derived sorbent and data on it were

given the Professor T. C. Keener of the University of Cincinnati. A visit to his laboratories was made and discussions on his scale-up work on cement-derived sorbents were carried out. In addition, a sample of a cement-derived sorbent and data on it were given to Professor L.-S. Fan of Ohio State University for use in his Se sorbent studies. Also, infrared analysis of samples from the air toxics studies of Professor P. Biswas of the University of Cincinnati was carried out for Professor Biswas.

5. 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 has been, and continues to be, that of finding one or more good induct injection sorbents. Particular emphasis has been given in this work to calcium-based sorbents because calcium is abundant and environmentally acceptable.

The objectives of the current year include study of sorbents made from $\text{Ca}(\text{OH})_2$, from mixtures of $\text{Ca}(\text{OH})_2$ and SiO_2 , and from portland cement. They also include study of sorbents made from model compounds.

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

6. SiO₂-MODIFIED Ca(OH)₂ SORBENTS

INTRODUCTION

Calcium hydroxide has a high capacity for SO₂, contains an environmentally acceptable cation and is relatively inexpensive (~\$ 60/ton in Cleveland in 1994¹). Because of these and other features of it, considerable effort has been devoted earlier to finding ways of preparing practical Ca(OH)₂ sorbents and practical Ca(OH)₂-based sorbents. An effort devoted to a search for such sorbents which was carried out in this study is described in this chapter.

Synthesis of Ca(OH)₂. Calcium hydroxide is generally prepared from CaCO₃ by a two-step synthesis. In the first step, the CaCO₃ is calcined:

If the calcination temperature is below about 1000 °C, the CaO has a relatively low density, while if the calcination temperature is above about 1000 °C, it has a higher density.² In the second step, the CaO is hydrated with water or steam:

The low density CaO hydrates much more rapidly than the high density CaO.³ The mechanism of the hydration of the low density form is not understood. That of the high density form is believed to entail the adsorption of H₂O on the CaO, the formation of CaO·2H₂O, and finally the formation Ca(OH)₂.⁴

Typically about 3-4 moles of water per mole of CaO are used when CaO is hydrated.⁵ The excess water is used to compensate for the loss of H₂O as steam during the hydration (the hydration of CaO is quite exothermic, $\Delta H = 64.8 \text{ KJ/mol}$).

The surface area of the Ca(OH)₂ produced when CaO is hydrated with a low water-to-solids ratio or with steam is in the range of $\sim 13\text{-}22 \text{ m}^2/\text{g}$.⁶ This is insufficient for this Ca(OH)₂ to be useful as an in-duct flue gas sorbent.

Calcium hydroxide produced when the CaO is hydrated with a high water-to-solids ratio is initially colloidal. However, this colloidal Ca(OH)₂ quickly flocculates and agglomerates. This is attributable to the high density of the OH groups on the surface of the particles and to the tendency of such groups to hydrogen bond. The agglomerated Ca(OH)₂ has a surface area that is still relatively low.⁷ Again its surface area is not sufficient for it to be useful as an in-duct flue gas sorbent.

Structure and Morphology of Ca(OH)₂. Calcium hydroxide crystallizes in the brucite structure. It thus has a layer structure, Figure 1.⁸

When prepared by mixing aqueous solutions of CaCl₂ and NaOH, Ca(OH)₂ occurs as hexagonal prisms.⁹ In contrast, Ca(OH)₂ prepared by repeatedly heating and cooling suspensions of the irregular Ca(OH)₂ particles occurs as hexagonal plates.¹⁰

The presence of foreign species during the precipitation of Ca(OH)₂ can affect its morphology. Thus, Ca(OH)₂ prepared by mixing aqueous solutions of CaCl₂ and

(a)

(b)

Figure 1. Structure of $\text{Ca}(\text{OH})_2$. (a) A single layer projected along $\langle 001 \rangle$. (b) Edge view of two layers.

NaOH with ethanol occurs as hexagonal plates.¹¹ The plate morphology of this $\text{Ca}(\text{OH})_2$ is attributable to the adsorption of ethanol molecules on those of its crystal faces which are parallel to its OH planes, Figure 1. Calcium hydroxide formed during the hydration of cement also occurs as hexagonal plates.¹² This can be ascribed to the adsorption of silicic acids on its OH faces.

Modified $\text{Ca}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ -Based Sorbents. A number of different approaches have been tried in the work done in an effort to get useful $\text{Ca}(\text{OH})_2$ or $\text{Ca}(\text{OH})_2$ -based sorbents. Thus, to provide H_2O to aid the SO_2 - $\text{Ca}(\text{OH})_2$ reaction, mixtures of calcium hydroxide and deliquescent salts have been prepared.¹³ To modify its morphology and increase its surface area, $\text{Ca}(\text{OH})_2$ has been treated with lignosulfonate.¹⁴ $\text{Ca}(\text{OH})_2$ has likewise been prepared in the presence of ethanol to accomplish the same objective.¹⁵ It has also been prepared in the presence of kaolinite in an attempt to favorably alter its pore structure.¹⁶ In addition, it has been milled in an attempt to increase its surface area.¹⁷ None of these approaches has been carried beyond the pilot plant stage.

Approach of Work

In this work, products derived by treating $\text{Ca}(\text{OH})_2$ with fumed SiO_2 were investigated. In an extension of this approach, sorbents derived by fully reacting $\text{Ca}(\text{OH})_2$ with SiO_2 or an SiO_2 source were also investigated. The sorbents were analyzed by infrared spectroscopy, X-ray powder diffractometry, scanning electron microscopy, BET surface area measurement, and SO_2 uptake.

EXPERIMENTAL

Chemicals

CaCO_3 and $\text{Ca}(\text{OH})_2$ were purchased from Fisher (Pittsburgh, PA), and fumed silica (99.9% SiO_2 , 350 m^2/g) and anatase (TiO_2) were obtained from Alfa/Johnson Matthey (Ward Hill, MA). Uncalcined diatomite was obtained as a gift from Celite (Lompoc, CA), and pumice (Tamez Mountains, NM) and tripoli were purchased from Ward's Natural Science Establishment (Rochester, NY). Perlite was obtained as a gift from Harborlite (Vicksburg, MI), and rottenstone was obtained as a gift from Keystone Filler and Manufacturing (Muncy, PA).

Sorbent Synthesis

CaO, Shaken Reaction Without Beads. A mixture of CaO (3.00 g) and H_2O (30 mL) in a capped polyethylene bottle (80 mL) was shaken with a shaker (~ 2-3 Hz) at room temperature for 5 min. The resulting slurry was filtered (Whatman #2) and the solid was washed with water (5 mL), vacuum dried (~60 °C, ~60 torr) for 12 h and weighed (3.87 g). IR (Nujol mull, cm^{-1}): 3644 (s, OH). XRD ($d(\text{\AA})$ (I/I_0)): 4.90 (64, CH), 3.11 (38, CH), 2.63 (100, CH), 1.93 (34, CH), 1.80 (32, CH), 1.69 (18, CH).

The sorbent was a moderate density, white powder.

Fumed SiO_2 , Shaken Reactions Without Beads. In a representative reaction (Table I, run 2), a mixture of CaO (produced by calcining CaCO_3 at 960 °C for 6 h, 2.24 g) and H_2O (25 mL) in a capped polyethylene bottle (80 mL) was

shaken with a shaker ($\sim 2\text{-}3\text{ Hz}$) at room temperature for 5 min. Fumed SiO_2 (0.48 g) was added to the mixture and it was shaken ($\sim 2\text{-}3\text{ Hz}$) at room temperature for an additional 6 h. The resulting slurry was filtered (Whatman #2) and the solid was washed with ethanol ($\sim 5\text{ mL}$) and ether ($\sim 10\text{ mL}$), vacuum dried ($\sim 60^\circ\text{C}$, $\sim 60\text{ torr}$) for 9 h and weighed (3.28 g). IR (Nujol mull, cm^{-1}): 3645 (s, OH), 3620 (s br, OH), 1650 (w br, OH), 972 (s br, SiO). XRD ($d(\text{\AA})$ (I/I_0)): 4.90 (63, CH), 3.04 (12, CSH), 3.11 (40, CH), 2.63 (100, CH), 1.93 (33, CH), 1.80 (32, CH), 1.69 (19, CH).

The sorbent was a low density, white powder.

Natural SiO_2 Source, Stirred Reactions Without Beads. In a typical reaction (Table II, run 1), a mixture of $\text{Ca}(\text{OH})_2$ (3.00 g), diatomite (2.16 g) and H_2O (50 mL) was stirred (magnetic stirring bar, $\sim 150\text{ rpm}$) without open access to the atmosphere while being heated (oil bath, 100°C) for 5 h and filtered (Whatman #2). The solid was washed with water ($\sim 5\text{ mL}$), vacuum dried ($\sim 60^\circ\text{C}$, $\sim 60\text{ torr}$) for $\sim 24\text{ h}$, weighed (5.92 g) and crushed. IR (Nujol mull, cm^{-1}): 3418 (s br, OH), 1650 (w br, OH), 969 (s, SiO), 458 (w, SiO). XRD ($d(\text{\AA})$ (I/I_0)): 3.04 (100, CSH), 2.80 (27, CSH), 1.82 (26, CSH).

The sorbent was a low density, off-white powder.

Natural SiO_2 Source, Stirred Reactions With Beads. In a representative reaction (Table II, run 3), a mixture of $\text{Ca}(\text{OH})_2$ (3.00 g), pumice (2.16 g), H_2O (50 mL) and ZrO_2 beads (Mg-stabilized, 1.4-1.6 mm, $\sim 15\text{ g}$) was stirred (magnetic stirring bar) without open access to the atmosphere while being heated (oil bath,

100 °C) for 10 h. The resulting mixture was filtered (60-mesh bronze screen) and the beads were washed with H₂O (~5 mL). The filtrate and washings were combined and filtered (Whatman #2), and the solid was washed with water (~5 mL), vacuum dried (~60 °C, ~60 torr) for ~24 h, weighed (5.64 g) and crushed. IR (Nujol mull, cm⁻¹): 3414 (s br, OH), 1650 (w br, OH), 971 (s, SiO), 498 (s, SiO). XRD (d(Å) (I/I₀)): 3.04 (100, CSH), 2.80 (26, CSH), 1.82 (27, CSH).

The sorbent was a low density, off-white powder.

Analysis of Fumed SiO₂, Shaken Reaction Sorbents. The relative intensities of the 2.63 Å and 3.52 Å powder pattern reflections of Ca(OH)₂ and anatase in a 1:1 weight-weight mixture of these compounds were obtained. The relative intensities of the same reflections in mixtures containing known weights of the sorbents and anatase also were obtained.

These data were then used to determine analytical values pertaining the sorbents. First, the relative intensity factor for anatase and Ca(OH)₂ in the sorbent-anatase mixtures, f_{rel} , was calculated as

$$f_{\text{rel}} = \frac{I'_{\text{an}}}{I'_{\text{CH}}} \cdot \frac{w'_{\text{CH}}}{w'_{\text{an}}} \quad (3)$$

where I'_{an} and I'_{CH} are the intensities of the 2.63 Å anatase and 3.52 Å Ca(OH)₂ reflections of the 1:1 anatase-Ca(OH)₂ mixture and w'_{CH} and w'_{an} are the weights of anatase and Ca(OH)₂ in it. Then the weights of Ca(OH)₂ in the sorbent-anatase mixtures, w_{CH} , were calculated as

$$w_{CH} = w_{an} \cdot f_{rel} \cdot \frac{I_{CH}}{I_{an}} \quad (4)$$

where w_{an} is the weight of anatase in a mixture and I_{CH} and I_{an} are the intensities of the 2.63 Å anatase and 3.52 Å $\text{Ca}(\text{OH})_2$ reflections of the mixture. Next the weight fractions of $\text{Ca}(\text{OH})_2$ and C-S-H in the sorbents in these mixtures, f_{CH} and f_{CSH} , were calculated with the formulas:

$$f_{CH} = \frac{w_{CH}}{w_{tot}} \quad (5)$$

$$f_{CSH} = 1 - f_{CH} \quad (6)$$

where w_{tot} is the total weight of the sorbent in a mixture. Finally, the Ca-to-Si ratios of the C-S-H in the mixtures, r , were calculated with the formulas:

$$Ca_{CH} = \frac{w_{CH}}{74.09} \quad (7)$$

$$r = [Ca_{tot}(1 - Ca_{CH})]/Si_{tot} \quad (8)$$

where Ca_{CH} is the number of moles of Ca in the $\text{Ca}(\text{OH})_2$ in the sorbent in a mixture, and Ca_{tot} and Si_{tot} are the number of moles of Ca and Si in the sorbent in a mixture.

Because of the difficulties inherent in this type of analytical methodology, the calculated values obtained probably are subject to considerable systematic error (perhaps 30 %).

RESULTS AND DISCUSSION

Fumed SiO_2 - Ca(OH)_2 Studies

Effect of Si-to-Ca Reactant Ratio on Composition and Non Sorption

Properties of Products. In the fumed SiO_2 - Ca(OH)_2 work, studies of the effect of the Si-to-Ca reactant ratio on the composition and non sorption related properties of the fumed SiO_2 - Ca(OH)_2 product were carried out. Results of six runs made in these studies are summarized in Table I. The values of the composition of the products are based, as indicated in the previous section, on diffraction data.

With an Si-to-Ca reactant ratio of 0.2, a 6-hour reaction time, an $\sim 20^\circ\text{C}$ reaction temperature and mild agitation, complete utilization of the SiO_2 was obtained. The product was composed of Ca(OH)_2 and C-S-H, Figures 2 and 3, run 2 and Table I, run 2. The relative rapidity of the reaction is attributable to the very high surface area of the fumed SiO_2 and to the tendency of fumed SiO_2 to adsorb on Ca(OH)_2 .¹⁸ The fact the product was composed of C-S-H is as expected since Ca(OH)_2 and SiO_2 can react to yield C-S-H. Given the conditions under which the reaction was carried out, it appears that the SiO_2 reacted with the surface of the Ca(OH)_2 particles and that this occurred in such a way as to leave them rough. It further appears that the C-S-H produced was deposited on the surfaces of the particles and that this led to their envelopment by C-S-H and their isolation from one another, Figure 4.

With an Si-to-Ca reactant ratio of 0.4-1.0 and the same reaction conditions, again full utilization of the SiO_2 was obtained. The products were composed of

Table I. Synthesis and Properties of Ca(OH)_2 and Fumed SiO_2 - Ca(OH)_2 Products

SiO ₂ Source	Si/Ca mole ratio	Conditions				Composition		CSH Ca/Si mole ratio	BET Area	SO ₂ Uptake	Ca Util
		Time (h)	Temp (°C)	Media	Agit	CH (%)	CSH (%)				
1	0.0	6	~20		shaking	100	0		24	5.2	39
2 fumed SiO ₂	0.2	6	~20		shaking					7.4	61
3 fumed SiO ₂	0.4	6	~20		shaking	22	78	1.8		7.9	74
4 fumed SiO ₂	0.5	6	~20		shaking	15	85	1.6		8.1	77
5 fumed SiO ₂	0.6	6	~20		shaking	10	90	1.4		8.0	84
6 fumed SiO ₂	0.8	6	~20		shaking	4	96	1.2		7.3	85
7 fumed SiO ₂	1.0	6	~20		shaking	0	100	1.0		5.9	86

^a CH, Ca(OH)_2 ; CSH, $\text{CaO-SiO}_2\text{-H}_2\text{O}$

Figure 2. X-ray powder diffraction patterns of fumed SiO_2 - Ca(OH)_2 products.

Figure 3. Infrared spectra of fumed $\text{SiO}_2\text{-Ca(OH)}_2$ products.

Figure 4. Schematic representation of the Ca(OH)_2 -fumed SiO_2 reaction.

C-S-H and some to no Ca(OH)_2 . The proportion of C-S-H was higher the higher Si-to-Ca reactant ratio, and the Ca-to-Si ratio in the C-S-H formed was lower the higher the Si-to-Ca reactant ratio. These results are as expected.¹⁹ The proportion of C-S-H in the products was relatively high when the Si-to-Ca reactant ratio was low. This is attributable to the formation of C-S-H low in Si. In this set of products, it also appears that the Ca(OH)_2 occurred, when it was present, as small, rough particles enveloped in C-S-H and isolated from each other.

Reference Ca(OH)_2 . An investigation of Ca(OH)_2 prepared in such way as to make it acceptable as a reference sorbent was also done. This Ca(OH)_2 had a relatively low surface area, Table I, run 1. This is as expected in view of the way it was prepared.²⁰

Effect of Si-to-Ca Reactant Ratio on SO_2 Sorption Properties of Products. Studies of the effect of the Si-to-Ca reactant ratio on the SO_2 sorption properties of the fumed SiO_2 - Ca(OH)_2 products were also carried out. The results are summarized in Table I. They show that all the products take up SO_2 very well. They

also show that the higher the Si-to-Ca reactant ratio up to a value of ~ 0.5 , the larger the amount of SO_2 that was taken up per gram, and the higher the ratio above ~ 0.5 the smaller the amount that was taken up per gram. This can be ascribed to the combined effects of the ratio on the size of $\text{Ca}(\text{OH})_2$ particles and on the amount of Ca in the C-S-H. The sorption results also show that the Ca utilization of the all the products was high, and that it was higher the higher the Si-to-Ca reactant ratio. The high Ca utilization of the low Si-to-Ca reactant ratio products is attributable to the high proportion of C-S-H in them and the high Ca utilization of the high Si-to-Ca reactant ratio products is as expected.

Natural SiO_2 or SiO_2 -Source Sorbents

Effect of SiO_2 or SiO_2 -Source on Composition and Non Sorption

Properties of Sorbents. In the natural SiO_2 or SiO_2 -source studies, the effect of the source of the SiO_2 or SiO_2 -source reactant on the composition and non sorption related properties of the SiO_2 or SiO_2 -source sorbents was investigated. The results of six runs made in these studies are summarized in Table II. The composition values are estimates and are subject to considerable error.

With diatomite as the SiO_2 source, a 1:1 Si-to-Ca reactant ratio, a 5-hour reaction time, a 100°C reaction temperature and mild agitation, complete reaction was obtained. The only species identified in the product was C-S-H. Its surface area was very high, Figure 5, run 8 and Table II, run 8. The relative rapidity of the reaction is attributable to the porosity and high surface area of the diatomite.²¹ The

Table II. Synthesis and Properties of Natural SiO₂ Source-Ca(OH)₂ Sorbents

SiO ₂ Source	Si/Ca mole ratio	Conditions				Estimated Composition ^a			BET Area (m ² /g)	SO ₂ Uptake (mmol /g)	Ca Util (%)
		Time (h)	Temp (°C)	Media	Agit	CH (%)	CSH (%)	C ₂ SH (%)			
8 diatomite (Celite)	1:1	5	100		stirring		100		245	5.8	85
9 diatomite (Celite)	1:2	5	100		stirring	40	60		170	7.9	76
10 pumice	1:1	10	100	ZrO ₂ ^b	stirring		100		85	6.0	83
11 perlite	1:1	12	100	ZrO ₂ ^b	stirring		100		95	6.1	84
12 rottenstone	1:1	12	100	ZrO ₂ ^b	stirring	60	20	20	22		
13 tripoli	1:1	18	100	ZrO ₂ ^b	stirring	60	20	20	24		

^a CH, Ca(OH)₂; CSH, CaO-SiO₂-H₂O; C₂SH, α-Ca₂(SiO₃OH)(OH). ^b 1.4 -1.6-mm Mg-stabilized ZrO₂ beads

high surface area of the product is ascribed to these same properties since their existence permits the C-S-H to grow relatively unhindered physically.

With diatomite as the SiO_2 source, a 1:2 Si-to-Ca reactant ratio, and the same conditions as before, complete reaction of the diatomite was again obtained. However, the product contained both C-S-H and unreacted Ca(OH)_2 . The surface area of the product was again very high, Figure 5, run 9 and Table II, run 9. The presence of Ca(OH)_2 in the product is attributable to the low Si-to-Ca ratio.

The use of pumice as the SiO_2 source, a 1:1 Si-to-Ca reactant ratio, a reaction time of 10 hours, a reaction temperature of 100°C and very vigorous agitation gave a product in which the only species identified was C-S-H. As expected, the surface area of the product was high, Figure 5, run 10 and Table II, run 10. The slowness of the reaction is attributable to the relative inertness of pumice. The fate of the cations in the pumice is unknown. Some may have been incorporated with the C-S-H and some may have been carried away in the wash water. The lower surface area of the product is ascribed to the less porous nature of pumice.

The use of perlite as the SiO_2 source, a 1:1 Si-to-Ca reactant ratio, and the same reaction conditions also gave the a product in which the only species was C-S-H. Again the surface area of the product was high, Figure 5, run 11 and Table II, run 11. The slowness of the reaction is attributable to the relative inertness of the perlite, and the lower surface area of the product compared to that of diatomite product is attributable to the non porous nature of perlite.

With rottenstone, a 1:1 Si-to-Ca reactant ratio and the same reaction

Figure 5. X-ray powder patterns of natural SiO_2 source- Ca(OH)_2 sorbents.

conditions, and with tripoli, a 1:1 ratio and similar reaction conditions, complete reaction of reaction of the silicate was not obtained. Here Ca(OH)_2 , C-S-H and $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$ and unreacted silicate were identified in the products. The surface area of the products was low, Figure 6, runs 12 and 13 and Table II, runs 12 and 13. The slowness of the reaction is attributed to the inertness of the silicates. The presence of $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$ in the products is attributed to the combination of the high reaction temperatures and the extended reaction times used.

Effect of SiO_2 or SiO_2 -Source on SO_2 Sorption Properties of the Sorbents. Studies of the effect of the source of the SiO_2 on the SO_2 uptake and Ca utilization of the sorbents were also carried out. The results are summarized in Table II. The uptake and Ca utilization values of the diatomite, pumice and perlite sorbents show that good sorbents can be made from various inexpensive SiO_2 sources.

CONCLUSIONS

The results from the studies with the fumed SiO_2 and Ca(OH)_2 show that the minimum Si-to-Ca reactant ratio required for a good SiO_2 -modified sorbent is low. This is attributable to the envelopment of the Ca(OH)_2 particles of the sorbent in a porous, reactive coating of C-S-H. The results from the studies with natural SiO_2 and natural SiO_2 sources show that good sorbents rich in C-S-H can be made from diatomite, pumice and perlite. This and the outcome of the fumed SiO_2 - Ca(OH)_2 studies indicate that it should be possible to prepare good SiO_2 -modified sorbents with a low Si-to-Ca reactant ratio that are practical and inexpensive. This is important because in some areas Ca(OH)_2 is more available than in reactive SiO_2 .²²

Figure 6. Infrared spectra of natural SiO_2 source- $\text{Ca}(\text{OH})_2$ sorbents.

7. HYDRATED Ca_3SiO_5 AND $\beta\text{-Ca}_2\text{SiO}_4$ SORBENTS

INTRODUCTION

It is apparent from the work described above on pure silicates that the silicate phase C-S-H has the potential to be a useful SO_2 sorbent. However, while the several ways of synthesizing C-S-H have been described, ways of preparing it inexpensively in a form which is suitable for use as an SO_2 sorbent have not.

The known ways of preparing C-S-H can be grouped into three approaches.²³

One of them involves the reaction of SiO_2 and Ca(OH)_2

A second involves the reaction of a calcium salt and a soluble silicate, e.g. CaCl_2 and Na_2SiO_3

The third involves the reaction of a calcium silicate and water, e.g. Ca_3SiO_5 and H_2O or $\beta\text{-Ca}_2\text{SiO}_4$ and H_2O

The most attractive of these three approaches for making C-S-H for sorbent use is the third because much of ordinary (type I) portland cement is made up of two

hydrolyzable calcium silicates. These two silicates are alite and belite. Alite is a phase with a composition similar to that of Ca_3SiO_5 and belite is a phase with composition similar to that of $\beta\text{-Ca}_2\text{SiO}_4$.

However, while the use of cement for the production of a sorbent rich in C-S-H is attractive, there are difficulties. With the low water-to-solids ratio usually used in the hydrolysis of cement (i.e., when it is used in the formation of concrete), the product is a high density, low permeability, unreactive material. Further, the rate at which this material is formed is slow, essentially complete reaction taking months to decades.

This chapter describes fundamental work done in an effort to find ways of rapidly preparing high surface area sorbents from cement that are rich in C-S-H.

Ca_3SiO_5 and $\beta\text{-Ca}_2\text{SiO}_4$

Ca_3SiO_5 and $\beta\text{-Ca}_2\text{SiO}_4$ as Models for Cement and Belite. Besides alite and belite, type I portland cement contains significant amounts of other components. Typically it contains 50-70 % alite ($\sim\text{Ca}_3\text{SiO}_5$), 15-30 % belite ($\sim\text{Ca}_2\text{SiO}_4$), 5-10 % aluminate phase ($\sim\text{Ca}_3\text{Al}_2\text{O}_6$), 5-15 % ferrite phase ($\sim\text{Ca}_2\text{AlFeO}_5$), and 3-4 % gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).^{24a}

Stabilized monoclinic Ca_3SiO_5 serves as fairly good and relative simple model for cement itself and for its alite component, and has been frequently been used for this purpose. (Pure monoclinic Ca_3SiO_5 is not suitable for use as a model because it is

not stable at room temperature.) Generally the stabilizing ions used in stabilized monoclinic Ca_3SiO_5 are Mg^{2+} and Al^{3+} or Mg^{2+} and Fe^{3+} .²⁵

Likewise, stabilized $\beta\text{-Ca}_2\text{SiO}_4$ serves as a fairly good and relatively simple model for the belite phase in cement and has been used for this purpose. (As with Ca_3SiO_5 , the pure compound again cannot be used as a model because it is not stable at room temperature.) Generally the stabilizing ions used in stabilized $\beta\text{-Ca}_2\text{SiO}_4$ are B^{3+} or Al^{3+} , Mg^{2+} and Fe^{3+} .²⁶

Hydration of Ca_3SiO_5 . The hydration of stabilized Ca_3SiO_5 has been reviewed by Taylor and others.^{24b, 27, 28} At room temperature and a low water-to-solids ratio, the product is mainly, as already indicated, C-S-H and $\text{Ca}(\text{OH})_2$. The C-S-H has a calcium-to-silicon ratio of ~ 1.7 and its silicate ions are mainly $\text{Si}_2\text{O}_7^{6-}$ ions.^{29, 30}

At room temperature and a low water-to-solids ratio, the rate of heat evolution curve for Ca_3SiO_5 shows two maxima. With this curve as a basis, the hydration process is generally divided into five stages, Figure 7. During the first of these two stages, it has been shown that a discontinuous layer is formed on the Ca_3SiO_5 .^{31, 32}

The mechanisms underlying the various stages of the hydration Ca_3SiO_5 have still not been fully identified. In the first two stages, it has been suggested that hydroxylation of the surface of the Ca_3SiO_5 , congruent dissolution of this hydroxylated surface, and precipitation of metastable C-S-H on it occur.³³ Alternatively, it has been suggested that incongruent dissolution of the surface of the Ca_3SiO_5 and the formation of metastable C-S-H on this surface occur.^{34, 35} In either case, it is postulated that

Figure 7. Calorimetric curve for hydration of Ca_3SiO_5 at a 1:2 water-to-solids ratio during (a) early part of hydration reaction and (b) intermediate part of hydration reaction.

the built up of the layer of metastable C-S-H accounts for the slowing of the rate of heat evolution in the latter part of stage I. An observed decrease in the length of steps I and II with an increase in temperature is attributed to an increase in the rate of diffusion through the layer of ions which are required by and produced by the hydration.³⁶ In stages III and IV, it has been suggested the metastable C-S-H layer is converted to a stable C-S-H and that this results in disruption of the layer, or alternatively that osmotic pressure disrupts the layer and that this leads to conversion of the metastable C-S-H to stable C-S-H.^{37, 38} In either case, it is thought that a layer of stable C-S-H is formed on the surface of the Ca_3SiO_5 , and that this layer accounts for the slowing of the rate in stage IV. Finally in stage V, it is thought that a diffusion-controlled built-up of C-S-H on the Ca_3SiO_5 occurs, Figure 8.

Figure 8. Schematic representation of Ca_3SiO_5 hydration mechanism.

Full hydration of Ca_3SiO_5 is very slow, Table III. This is consistent with the mechanism postulated for stage V.

Kantrol *et al*³⁹ have shown that the hydration of Ca_3SiO_5 at room temperature and a 9:1 water-to-solids ratio is accelerated by ball milling. However, under these conditions the product is not a mixture of C-S-H and Ca(OH)_2 but rather is a mixture of $\text{Ca}_3(\text{SiO}_3\text{OH})_2 \cdot 2\text{H}_2\text{O}$ (afwillite) and Ca(OH)_2 . It has been suggested that a dispersion of the orthosilicate ions into the solution caused by the milling leads to the formation of the afwillite.⁴⁰ Others have shown that the hydration of Ca_3SiO_5 at room temperature and a 1:1 to 2:1 water-to-solids ratio is accelerated by reactive SiO_2 . In this case, the composition of the product is changed with the product becoming richer in C-S-H.⁴¹ It has been suggested that the reaction is accelerated because the SiO_2 provides nucleation sites for C-S-H and because it reacts with the Ca(OH)_2 formed in the hydration. Also of interest is the fact that C-S-H grows epitaxially on the surface of the calcium germanate hydrate $1.6\text{CaO} \cdot \text{GeO}_2 \cdot n\text{H}_2\text{O}$.⁴² This indicates that Ca_3SiO_5

Table III. Hydration of Ca_3SiO_5 and $\beta\text{-Ca}_2\text{SiO}_4$ Under Ordinary Conditions.^a

Reactants	Wt. Ratio	Conditions				Completion (%)
		Time (d)	Temp. (°C)	Media	Agit	
1 $\text{Ca}_3\text{SiO}_5, \text{H}_2\text{O}$	~2:1	28	~20	none	none	70
2 $\text{Ca}_2\text{SiO}_4, \text{H}_2\text{O}$	~2:1	28	~20	none	none	30

^aReference 3b

may also provide nucleation sites for the precipitation of C-S-H.

Hydration of $\beta\text{-Ca}_2\text{SiO}_4$. Studies of the hydration of $\beta\text{-Ca}_2\text{SiO}_4$ at a low water-to-solids ratio and room temperature indicate that the mechanism of hydration of $\beta\text{-Ca}_2\text{SiO}_4$ is similar to that of Ca_3SiO_5 (although at least one report suggests that no passivating layer is formed in the early stages⁴³). The effect of impurity ions on the hydration of $\beta\text{-Ca}_2\text{SiO}_4$ is not yet clear.⁴⁴

As with Ca_3SiO_5 , full hydration of $\beta\text{-Ca}_2\text{SiO}_4$ is very slow, Table III. This is consistent with the mechanism postulated for the last stage of the hydration. The slower rate of hydration of $\beta\text{-Ca}_2\text{SiO}_4$ compared to that of Ca_3SiO_5 has been attributed to the lack of an oxygen unconnected to a silicon in $\beta\text{-Ca}_2\text{SiO}_4$ and the presence of such an oxygen in Ca_3SiO_5 .⁴⁵ Support for this is found in the fact that $\text{Ca}_3\text{Si}_2\text{O}_7$ and CaSiO_3 , which also lack such oxygens, are very resistant to hydration. It has also been attributed to the distorted 7- or 8-coordination of the calcium in $\beta\text{-Ca}_2\text{SiO}_4$.⁴⁶ Supporting this hypothesis is the resistance of $\gamma\text{-Ca}_2\text{SiO}_4$ to hydration

since the coordination of the calcium in this compound is approximately regular octahedral.

High-surface-area β - Ca_2SiO_4 prepared by the dehydration of the hillebrandite has been shown to hydrate more rapidly than ordinary β - Ca_2SiO_4 . This is as expected on the basis of the hydration mechanism postulated for β - Ca_2SiO_4 .

Objective of Ca_3SiO_5 and Ca_2SiO_4 Studies

The objective of the Ca_3SiO_5 and β - Ca_2SiO_4 studies was to find conditions that would yield products rich in C-S-H and reactive to SO_2 , and thus to be better able to choose conditions yielding good sorbents from portland cement.

EXPERIMENTAL

Chemicals

Monoclinic Ca_3SiO_5 (stabilized with Al_2O_3 and MgO) and β - Ca_2SiO_4 (stabilized with B_2O_3) were obtained from Construction Technology Laboratories, CTL (Skokie, IL). They were ground to pass 270 mesh before use. Fumed SiO_2 (99.9% SiO_2) was obtained from Alfa/Johnson Matthey. Quartz (99.5% SiO_2 , $< 10\mu$) was obtained as a gift from U.S. Silica (Berkley Springs, WV), and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was obtained from Aldrich Chemical (Milwaukee, WI).

Sorbent Syntheses

Stirred Reactions Without Beads. In a typical reaction (Table IV, run 1), a slurry of Ca_3SiO_5 (3.00 g), and water (30 mL) was stirred (magnetic stirring bar, ~150

rpm) without open access to air while being heated (oil bath, 100 °C) for 72 h, and then filtered (Whatman #2). The solid was vacuum dried (~60 °C, ~60 torr) for ~12 h, weighed (3.39 g) and crushed. IR (Nujol mull, cm^{-1}) 3644 (s, OH), 3538 (s, OH), 2466(m br, OH) 1720 (w br, OH), 1282 (s, OH), 1152 (w br), 982 (s, SiO), 946 (s), 767 (m), 754 (s), 710 (m), 520 (m), 498 (s, SiO), 472 (m). XRD ($d(\text{\AA})$ (I/I_0)) 5.32 (11, C_2SH), 4.90 (100, CH), 4.22 (29, C_2SH), 3.91 (16, C_2SH), 3.54 (24, C_2SH), 3.30 (29, C_2SH), 3.27 (100, C_2SH), 3.11 (20, CH), 2.88 (29, C_2SH), 2.82(27, C_2SH), 2.71 (18, C_2SH), 2.69 (15, C_2SH), 2.66 (30, C_2SH), 2.63 (95, CH), 2.61 (34, C_2SH), 2.57 (18, C_2SH), 2.53 (27, C_2SH), 2.42 (55, C_2SH), 2.34 (12, C_2SH), 2.32 (12, C_2SH), 2.30 (14, C_2SH), 2.29 (15, C_2SH), 2.24 (15, C_2SH), 2.16 (11, C_2SH), 2.11 (11, C_2SH), 2.08 (15, C_2SH), 2.06 (22, C_2SH), 2.03 (11, C_2SH), 1.96 (15, C_2SH), 1.93 (69, CH), 1.80 (39, CH), 1.79 (35, C_2SH), 1.69 (28, CH).

Shaken Reactions With Beads. In a typical reaction (Table IV, run 3), a mixture of Ca_3SiO_5 (3.00 g), water (30 mL) and ZrO_2 beads (2 mm, ~30 g) in a capped Teflon bottle (125 mL) was shaken (2-3 Hz) while being heated (heating tape, ~60 °C) for 6 h. The resulting mixture was filtered (60 mesh bronze screen) and the beads were washed with water (~10 mL). The washings and filtrate were combined and filtered (Whatman #2), and the solid was vacuum dried (100 °C, 60 torr) for ~12 h, weighed (5.13 g) and crushed. IR (Nujol mull, cm^{-1}) 3644 (s, OH), 3346 (s br, OH), 1654 (w br, OH), 962 (s br, SiO), 910 (s br), 814 (w), 472 (s br, SiO). XRD ($d(\text{\AA})$ (I/I_0)) 6.52 (46, $\text{C}_3\text{S}_2\text{H}_3$), 4.90 (100, CH), 4.14 (13, $\text{C}_3\text{S}_2\text{H}_3$), 3.88 (13, $\text{C}_3\text{S}_2\text{H}_3$),

3.27 (36, C₃S₂H₃), 3.17 (64, C₃S₂H₃), 3.11 (7, CH), 2.83 (100, C₃S₂H₃), 2.73 (84, C₃S₂H₃), 2.63 (34, CH), 2.35 (26, C₃S₂H₃), 2.31 (20, C₃S₂H₃), 2.15 (45, C₃S₂H₃), 1.98 (22, C₃S₂H₃), 1.95 (52, C₃S₂H₃), 1.93 (26, CH), 1.80 (12, CH), 1.77 (39, C₃S₂H₃), 1.69 (9, CH).

Stirred Reactions With Beads. In a typical reaction (Table IV, run 4), a mixture of Ca₃SiO₅ (3.00 g), water (30 mL) and ZrO₂ beads (0.6-0.8, ~150 g) was stirred (mechanical paddle stirrer, ~500 rpm) without open access to air while being heated (oil bath, 100 °C) for 3h. The resulting mixture was filtered (60 mesh bronze screen) and the beads were washed with water (~10 mL). The filtrate and washings were combined and filtered (Whatman #2), and the solid was vacuum dried (~60 °C, ~60 torr) for ~12h, weighed (4.96 g) and crushed. IR (Nujol mull, cm⁻¹) 3644 (s, OH), 3418 (s br, OH), 1648 (w br, OH), 972 (s br, SiO), 452 (m br, SiO). XRD (d(Å) (I/I₀)) 4.90 (90, CH), 3.11 (30, CH), 3.04 (100, CSH), 2.80 (56, CSH), 2.63 (100, CH), 1.93 (38, CH), 1.82 (38, CSH), 1.80 (28, CH), 1.69 (18, CH).

RESULTS AND DISCUSSION

Rapid Hydration of Ca₃SiO₅ and β-Ca₂SiO₄

Rapid Hydration of Ca₃SiO₅. Various approaches were explored in an effort to find ways to hydrate Ca₃SiO₅ rapidly at a high water-to-solids ratio to products rich in C-S-H. One was based on the use of compounds in the hydration mixture known to accelerate the hydration of Ca₃SiO₅ (and the hydration of portland cement) at a low water-to-solids ratios. The compounds used were CaCl₂, CaSO₄·2H₂O, and Ca(OH)₂.

The use of these compounds did not lead to a significant acceleration of the hydration reaction and their use was not followed further.

Other approaches were based on the use of various combinations of high-shear agitation, elevated temperatures, and the addition of SiO_2 . The results of eight runs based on the use of these approaches are summarized in Table IV. The values listed for the estimated composition of the products made are estimates based on careful inspection of the X-ray and infrared data. They should not be taken as values derived from quantitative composition determinations.

The use of a three-day reaction time and a 100°C reaction temperature gave a complete reaction, Table IV, run 1. However, the product was $\text{Ca}(\text{OH})_2$ and $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$, a poor sorbent and thus an undesired product constituent, Figure 9. This silicate is probably the stable silicate product of the hydration of Ca_3SiO_5 at $\sim 100^\circ\text{C}$. Thus, while C-S-H could have been formed, if so, it was subsequently consumed because of the length of the reaction time. This suggests that if the hydration of Ca_3SiO_5 is to be carried out at $\sim 100^\circ\text{C}$, it must be done quickly.

The use of a 12-hour reaction time, an $\sim 20^\circ\text{C}$ reaction temperature and high-shear agitation also gave a complete reaction, run 2. The observed acceleration of the reaction is attributed to the continuous removal of the the passivating coating assumed to be continuously formed on the Ca_3SiO_5 during the reaction. Again however, the product was not the desired one, in this case being composed of C-S-H,

Table IV. Synthesis and Properties of Hydrated Ca_3SiO_5 Sorbents

Reactants ^a	Wt. Ratio	Conditions			Estimated Composition ^b					SO ₂ Uptake	
		Time (h)	Temp (°C)	Media	Agit	CSH	CH	C ₃ S ₂ H ₃	C ₂ SH	C ₃ S	(mmol/g)
1 Ca ₃ SiO ₅ , H ₂ O	1:10	72	100		stirring	40			60		2.4
2 Ca ₃ SiO ₅ , H ₂ O	1:10	12	~20	ZrO ₂ ^c	shaking	40	20	40			5.9
3 Ca ₃ SiO ₅ , H ₂ O	1:10	6	60	ZrO ₂ ^c	shaking	40	20	40			
4 Ca ₃ SiO ₅ , H ₂ O	1:10	3	100	ZrO ₂ ^d	stirring	60	40				
5 Ca ₃ SiO ₅ , CaSO ₄ ·2H ₂ O, H ₂ O	1:0.05:10	6	60	ZrO ₂ ^c	shaking	60	40				5.3
6 Ca ₃ SiO ₅ , SiO ₂ ^e , H ₂ O	1:0.26:13 ^f	72	100		stirring	40	20		40		
7 Ca ₃ SiO ₅ , SiO ₂ ^g , H ₂ O	1:0.26:13 ^f	72	100		stirring	100					
8 Ca ₃ SiO ₅ , SiO ₂ ^g , H ₂ O	1:0.26:13 ^f	72	~20	ZrO ₂ ^c	shaking	100					6.8

^a Ca_3SiO_5 < 270 mesh. ^b CSH, CaO-SiO₂-H₂O; CH, Ca(OH)₂; C₃S₂H₃, Ca₃(SiO₃OH)₂·2H₂O, afwillite; C₂SH, α-Ca₂(SiO₃OH)(OH). ^c 2-mm diameter ZrO₂ (Mg-stabilized) beads. ^d 0.6-0.8 mm diameter ZrO₂ (Mg-stabilized) beads. ^e Quartz (< 10μ). ^f Ca:Si, 1.5:1. ^g Fumed SiO₂ (350 m²/g).

Figure 9. X-ray powder diffraction patterns of products of runs 1 and 4, Table IV.

$\text{Ca}(\text{OH})_2$, and $\text{Ca}_3(\text{SiO}_3\text{OH})_2 \cdot 2\text{H}_2\text{O}$, another poor sorbent and thus an another unwanted product constituent. Whether $\text{Ca}_3(\text{SiO}_3\text{OH})_2 \cdot 2\text{H}_2\text{O}$ is the stable silicate under these conditions is not clear, and it is thus difficult to account for its formation. Perhaps the Ca_3SiO_5 reacted to give a high SiO_4^{4-} ion concentration under these low-temperature conditions and this led to the precipitation of the $\text{Ca}_3(\text{SiO}_3\text{OH})_2 \cdot 2\text{H}_2\text{O}$.

With the use of a shorter reaction time, a 60°C reaction temperature and high-shear agitation, the product was again C-S-H, $\text{Ca}(\text{OH})_2$, and $\text{Ca}_3(\text{SiO}_3\text{OH})_2 \cdot 2\text{H}_2\text{O}$, run 3. Probably the SiO_4^{4-} ion concentration again became high and led to the precipitation of $\text{Ca}_3(\text{SiO}_3\text{OH})_2 \cdot 2\text{H}_2\text{O}$. The X-ray powder patterns of products formed under the same conditions except for the use of shorter reaction times are consistent with this proposal, Figure 10.

Interestingly, the use of a still shorter reaction time, a 100°C reaction temperature and high-shear agitation gave a product composed of C-S-H and $\text{Ca}(\text{OH})_2$, run 4 and Figure 9. At this elevated temperature, it may be that the concentration of the SiO_4^{4-} ions was low because of silicate ion condensation reactions. If so, this low concentration could have favored the formation of C-S-H since C-S-H can accommodate oligomeric silicate ions, and it would have disfavored the immediate formation of $\text{Ca}_3(\text{SiO}_3\text{OH})_2 \cdot 2\text{H}_2\text{O}$ and $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$ since these silicates contain SiO_4^{4-} ions. Consistent with this, it has been suggested that the chain lengths of the silicate ions in C-S-H formed from Ca_3SiO_5 increase with

Figure 10. X-ray powder diffraction patterns of intermediate and final products of run 3, Table IV.

temperature.⁴⁷ Probably the average chain length of the silicate ions of the C-S-H of run 4 was relatively long. It could be that a similar run with a 6-hour instead of 3-hour reaction time would have given $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$ as a product.

Conditions the same as those of run 3 except for the addition of a small amount of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ to the reaction mixture led to a product composed of C-S-H and $\text{Ca}(\text{OH})_2$, run 5. Perhaps the formation of $\text{Ca}_3(\text{SiO}_3(\text{OH}))_2 \cdot 2\text{H}_2\text{O}$ was inhibited by the deposition of SO_4^{2-} ions in SiO_4^{4-} sites on the surface of the $\text{Ca}_3(\text{SiO}_3(\text{OH}))_2 \cdot 2\text{H}_2\text{O}$ nuclei.

The use of conditions like those employed in run 1 except for the addition of 10 μ quartz to the reaction mixture led to a product composed of C-S-H, $\text{Ca}(\text{OH})_2$ and $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$, run 6. Probably the finely divided silica reacted with the $\text{Ca}(\text{OH})_2$ formed by the hydration of Ca_3SiO_5 and gave C-S-H. It may be that it also provided nucleation sites for the precipitation of the C-S-H.

In contrast, the use of conditions the same as those of run 6 except for the substitution of fumed SiO_2 for the powdered quartz led to a product composed of only C-S-H, run 7. Again probably the silica reacted with the $\text{Ca}(\text{OH})_2$ and gave C-S-H, and again it may have provided nucleation sites for C-S-H precipitation. Since fumed SiO_2 is more reactive than powdered quartz, it is not surprising that more C-S-H is formed in run 7 than in run 6.

Finally, a three-day reaction time, a reaction temperature of $\sim 20^\circ\text{C}$, high-shear agitation, and the addition of fumed SiO_2 led to a product composed of only C-S-H, run 8. Similar runs with a shorter reaction times gave products containing $\text{Ca}_3(\text{SiO}_3\text{OH})_2 \cdot 2\text{H}_2\text{O}$, Figure 11. This suggests that $\text{Ca}_3(\text{SiO}_3\text{OH})_2 \cdot 2\text{H}_2\text{O}$ is not the stable silicate product when SiO_2 is present.

Rapid Hydration of $\beta\text{-Ca}_2\text{SiO}_4$. Various approaches also were explored in an effort to find ways to rapidly hydrate $\beta\text{-Ca}_2\text{SiO}_4$ at a high water-to-solids ratio to products rich in C-S-H. These approaches were, as before, based on the use of various combinations of high-shear agitation, elevated temperatures and the addition of SiO_2 to the hydration mixture. The results of five runs utilizing these approaches are summarized in Table V.

The use of a three-day reaction time and a 100°C reaction temperature gave a complete reaction, Table V, run 1. The product, however, consisted entirely $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$ and thus had an undesired composition. This silicate probably is the stable hydration product at a high water-to-solids ratio not only for Ca_3SiO_5 at 100°C but also for $\beta\text{-Ca}_2\text{SiO}_4$ at this temperature. Its apparent stability and the three-day reaction time likely account for its presence in the product.

The use of a three-day reaction time, an $\sim 20^\circ\text{C}$ reaction temperature and high-shear agitation gave a product containing C-S-H, $\text{Ca}(\text{OH})_2$ and some unreacted $\beta\text{-Ca}_2\text{SiO}_4$, run 2. This shows that the hydration of $\beta\text{-Ca}_2\text{SiO}_4$ under these water-to-

Figure 11. X-ray powder diffraction patterns of intermediate and final products of run 8, Table IV.

Table V. Synthesis and Properties of Hydrated β - Ca_2SiO_4 Sorbents

Reactants ^a	Wt. Ratio	Conditions			Estimated Composition ^b					SO ₂ Uptake	
		Time (h)	Temp (°C)	Media	Agit	CSH	CH	C ₃ S ₂ H ₃	C ₂ SH	βC ₂ S	(mmol/g)
1 Ca ₂ SiO ₄ , H ₂ O	1:10	72	100		stirring				100		2.2
2 Ca ₂ SiO ₄ , H ₂ O	1:10	72	~20	ZrO ₂ ^c	shaking	50	20			30	6.4
3 Ca ₂ SiO ₄ , H ₂ O	1:10	24	80	ZrO ₂ ^c	shaking	30	20		50		
4 Ca ₂ SiO ₄ , SiO ₂ ^d , H ₂ O	1:0.35:14 ^e	72	100		stirring	100					
5 Ca ₂ SiO ₄ , SiO ₂ ^d , H ₂ O	1:0.35:14 ^e	72	~20	ZrO ₂ ^c	shaking	100					6.6

^a β - Ca_2SiO_4 < 270 mesh. ^b CSH, $\text{CaO-SiO}_2\text{-H}_2\text{O}$; CH, Ca(OH)_2 ; C₃S₂H₃, $\text{Ca}_3(\text{SiO}_3\text{OH})_2\cdot 2\text{H}_2\text{O}$, afwillite; C₂SH, $\text{Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$; β -C₂S, β - Ca_2SiO_4 . ^c 2-mm diameter ZrO₂ (Mg-stabilized) beads ^d Fumed SiO₂ (350 m²/g). ^e Ca/Si, 1:1.

solids, temperature, and agitation conditions is, as expected, slower than the hydration of Ca_3SiO_5 under the same conditions (compare Table III, run 2). It seems likely that this can be attributed to a greater difficulty of hydroxylating the $\beta\text{-Ca}_2\text{SiO}_4$ surface.

With a one-day reaction time, an 80 °C reaction temperature, and high-shear agitation, the product obtained was C-S-H, $\text{Ca}(\text{OH})_2$ and $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$, run 3. Probably as in the case of run 1, the presence of $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$ in the product reflects the apparent stability of this silicate at elevated temperatures. This conclusion is supported by the fact that a run with a 100 °C reaction temperature and moderate shear agitation gave a product that consisted of C-S-H, CH and $\beta\text{-Ca}_2\text{SiO}_4$ when a short reaction time was used, and $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$ when a three-day reaction time was used.

The use of conditions like those used in run 1 except for the addition of fumed SiO_2 led to a product made up of only C-S-H, run 4. This suggests that $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$ is not the stable product in the presence of active SiO_2 .

With conditions like those used in run 2 except for the addition of fumed SiO_2 , the product was again C-S-H only, run 5. This shows that active SiO_2 accelerates the reaction. Perhaps this is attributable to the provision of nucleation sites for C-S-H by the SiO_2 .

SO_2 Uptake of Hydrated Ca_3SiO_5 Products

The SO_2 uptake values of the products of Table IV runs 1, 2, 5 and 8 and Table V runs 1, 2, and 5 are as expected. Thus, those products that contain

$\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$ and $\text{Ca}_3(\text{SiO}_3\text{OH})_2 \cdot 2\text{H}_2\text{O}$ are not as good as the products that contain only C-S-H (taking the amount calcium in the products into account).

CONCLUSIONS

It appears that the hydration of Ca_3SiO_5 and $\beta\text{-Ca}_2\text{SiO}_4$ to C-S-H and $\text{Ca}(\text{OH})_2$ is slowed by the formation of a passivating coating on the reactant, that it is hindered by the stability of $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$ at high temperatures, and that it is hindered by the ability of $\text{Ca}_3(\text{SiO}_3\text{OH})_2 \cdot 2\text{H}_2\text{O}$ form at low temperatures. It further appears that the hydration of Ca_3SiO_5 and $\beta\text{-Ca}_2\text{SiO}_4$ to C-S-H only is promoted by the presence active SiO_2 , hindered by the formation of a passivating coating on the C-S-H, and hindered by the stability of $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$ at high temperature.

On the basis of this, it is concluded that Ca_3SiO_5 and $\beta\text{-Ca}_2\text{SiO}_4$ could be very rapidly hydrated to C-S-H and $\text{Ca}(\text{OH})_2$ by the use of very high shear conditions (such as those provided by commercial high-shear mills) and high temperatures. It is further concluded that Ca_3SiO_5 and $\beta\text{-Ca}_2\text{SiO}_4$ could be hydrated very rapidly to C-S-H alone by the use of same types of conditions plus the addition of active SiO_2 to the reaction mixture.

8. HYDRATED PORTLAND CEMENT SORBENTS

INTRODUCTION

As already mentioned, portland cement is of interest in this study because it has the potential to yield good SO_2 sorbents. This section deals with experimental work done to uncover this potential.

Portland cement is an exceedingly important material for modern society. It is produced cheaply and on a very large scale worldwide. In Cleveland in 1994 the price of cement was about \$ 65 per ton in bulk quantities.⁴⁸ World production of cement in 1990 was about 1.3 billion tons⁴⁹ (about 0.3 ton for each person in the world).

Cement is produced in a two-step process. In the first step a mixture of certain common rocks is allowed to react at elevated temperature. Typically the rocks are a limestone and a clay or a shale and the reaction temperature is about 1450 °C. The product of this step, clinker, is then ground with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ to obtain cement.⁵⁰

Cement is classified into types based on its composition. Ordinary (type I) cement typically contains, as already stated, 50-70 % alite ($\sim \text{Ca}_3\text{SiO}_5$), 15-30 % belite ($\sim \text{Ca}_2\text{SiO}_4$), 5-10 % aluminate phase ($\sim \text{Ca}_3\text{Al}_2\text{O}_6$), 5-15 % ferrite phase ($\sim \text{Ca}_2\text{AlFeO}_5$), and 3-4 % gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).^{24a}

An enormous literature on the preparation and properties of cement exists. Much of it has been summarized in several recent books and reviews.^{24, 51}

Hydration of the Major Components of Cement

All the main components in portland cement except gypsum are anhydrous. When brought into contact with water most of the anhydrous components are attacked and form hydrated compounds or phases. Because of the complexity of cement, it is useful to discuss the hydration of its major components separately.

Alite

The hydration of the alite phase of cement under the low water-to-solids ratio (0.5:1) normally used is relatively slow, essentially complete hydration requiring about one year. It gives C-S-H and Ca(OH)_2 .⁵²

(To make this section more informative, equations in cement chemist's notation are given in parenthesis in addition to the equations in ordinary chemist's notation.)

Belite

The hydration of the belite phase of cement under the same conditions is still slower, essentially complete hydration requiring more than four years. It also gives a mixture of C-S-H and Ca(OH)_2 , but the proportion of C-S-H in this mixture is greater.⁵³

The C-S-H formed by the hydration of the alite and belite in cement apparently has a structure which is similar to but less ordered than the structure of the C-S-H formed by the hydration of Ca_3SiO_5 and $\beta\text{-Ca}_2\text{SiO}_4$. It does not contain appreciable amounts of Al^{3+} and Fe^{3+} , but it is intimately mixed with the iron-aluminum phase AFm (see below). Its admixture with AFm probably is a cause of its low degree of order.^{24c} Taylor has suggested that cement C-S-H be called cement gel to recognize its unique features.^{24c}

Aluminate Phase

As already indicated, the composition of the aluminate phase of cement is similar to that of $\text{Ca}_3\text{Al}_2\text{O}_6$. In this phase typically ~3 % of the Ca^{2+} is replaced interstitially and isomorphously with 2 Na^+ , ~11 % of the Al^{3+} is replaced isomorphously by Fe^{3+} , and ~9 % of the Al^{3+} is replaced isomorphously by Si^{4+} .^{24d} Not surprisingly, the hydration of the aluminate phase of cement is similar to that of $\text{Ca}_3\text{Al}_2\text{O}_6$. For clarity, it is helpful to consider the hydration of $\text{Ca}_3\text{Al}_2\text{O}_6$ and mixtures of it with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}(\text{OH})_2$ before considering the hydration of the aluminate phase itself.

Hydration of $\text{Ca}_3\text{Al}_2\text{O}_6$. The hydration of $\text{Ca}_3\text{Al}_2\text{O}_6$ is much more rapid than that of Ca_3SiO_5 . Within 30 minutes it gives a mixture of $[\text{Ca}_2\text{Al}(\text{OH})_6](\text{OH}) \cdot 6\text{H}_2\text{O}$ and $[\text{Ca}_2\text{Al}(\text{OH})_6][\text{Al}(\text{OH})_4] \cdot 3\text{H}_2\text{O}$, Figure 12:

Figure 12. (a) Schematic structure of $[Ca_2Al(OH)_6](OH) \cdot 6H_2O$ and $[Ca_2Al(OH)_6][Al(OH)_4] \cdot 3H_2O$ showing $[Ca_2Al(OH)_6]^+$ layers and OH^- or $Al(OH)_4^-$ ions between layers. (b) Structure of $[Ca_2Al(OH)_6]^+$ layers.

These compounds then interact to give $Ca_3Al_2(O_4H_4)_3$, hydrogarnet, Figure 13,

within 24 to 48 hours.²⁷

Figure 13. Portion of unit cell of $\text{Ca}_3\text{Al}_2(\text{O}_4\text{H}_4)_3$, hydrogarnet, showing $\text{Al}(\text{OH})_6$ and $(\text{OH})_4$ units in structure.

Hydration of $\text{Ca}_3\text{Al}_2\text{O}_6$ - CaSO_4 and $\text{Ca}_3\text{Al}_2\text{O}_6$ - $\text{Ca}(\text{OH})_2$ Mixtures. The hydration of a 1:3 mixture of $\text{Ca}_3\text{Al}_2\text{O}_6$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is rapid. In about 10-12 minutes it gives $[\text{Ca}_3\text{Al}(\text{OH})_6 \cdot 12\text{H}_2\text{O}]_2(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$, trisulfoaluminate hydrate, or the Al^{3+} and SO_4^{2-} end-member of the ettringite family,²⁷ Figure 14:

The hydration of a mixture richer in $\text{Ca}_3\text{Al}_2\text{O}_6$ gives trisulfoaluminate hydrate as an intermediate and then this reacts with more $\text{Ca}_3\text{Al}_2\text{O}_6$ to give

$[\text{Ca}_2\text{Al}(\text{OH})_6]_2(\text{SO}_4) \cdot 6\text{H}_2\text{O}$, monosulfoaluminate hydrate,²⁷ Figure 15:

Figure 14. (a) Structure of $[\text{Ca}_3\text{Al}(\text{OH})_6 \cdot 12\text{H}_2\text{O}]_2(\text{SO}_4) \cdot 2\text{H}_2\text{O}$, trisulfoaluminate hydrate, projected on the $\langle 001 \rangle$ showing columns and channels. (b) Structure of $[\text{Ca}_3\text{Al}(\text{OH})_6 \cdot 12\text{H}_2\text{O}]^{3+}$ columns.

Figure 15. Structure of $[\text{Ca}_2\text{Al}(\text{OH})_6]\text{SO}_4 \cdot 6\text{H}_2\text{O}$, monosulfoaluminate hydrate, showing layers of $[\text{Ca}_2\text{Al}(\text{OH})_6]^+$ and H_2O and SO_4^{2-} ions between layers.

Thus a 1:1 ratio of $\text{Ca}_3\text{Al}_2\text{O}_6$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ultimately gives monosulfoaluminate hydrate.²⁷

The SO_4^{2-} ions in this phase can be exchanged for other ions such as OH^- .

Not surprisingly in view of this, the hydration of a 1:1 mixture of $\text{Ca}_3\text{Al}_2\text{O}_6$ and $\text{Ca}(\text{OH})_2$ gives the hydroxy analogue of monosulfoaluminate hydrate,

Hydration of Aluminate Phase in Cement. The hydration of the aluminate phase in cement involves not only this phase and water but also the ferrite phase, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and CO_2 (from the atmosphere). The main product of the hydration is $[\text{Ca}_2(\text{Al}, \text{Fe})(\text{OH})_6]_2(\text{SO}_4, \text{CO}_3, 2\text{OH}) \cdot 6\text{H}_2\text{O}$, or AFm. This phase has a structure like that of monosulfoaluminate hydrate with Fe^{3+} isomorphously replacing Al^{3+} , and CO_3^{2-} and OH^- isomorphously replacing SO_4^{2-} , Figure 16. As is to be expected, the anions of this phase can undergo ion exchange.^{24e}

Figure 16. Schematic structure of $[\text{Ca}_2(\text{Al}, \text{Fe})(\text{OH})_6]_2(\text{SO}_4, \text{CO}_3, 2\text{OH}) \cdot 6\text{H}_2\text{O}$ or AFm.

The hydration of the mixture of the aluminate phase, ferrite phase, and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in cement together with CO_3^{2-} also can lead to $[\text{Ca}_3(\text{Al}, \text{Fe})(\text{OH})_6 \cdot 12\text{H}_2\text{O}]_2(\text{SO}_4, \text{CO}_3, 2\text{OH})_3 \cdot 2\text{H}_2\text{O}$ or AFt. This has a structure similar to trisulfoaluminate hydrate with Fe^{3+} ion isomorphously replacing Al^{3+} and CO_3^{2-} and OH^- isomorphously replacing SO_4^{2-} ,⁵⁹ Figure 17.

In cement this phase loses its water at about 130 °C and becomes amorphous. It is postulated that this dehydrated synthetic AFt still has a column-like structure but with open channels. Interestingly, this dehydrated synthetic AFt shows a high Ca utilization with SO_2 and NO_x .⁵⁴

Figure 17. Schematic structure of $[\text{Ca}_3(\text{Al}, \text{Fe})(\text{OH})_6 \cdot 12\text{H}_2\text{O}]_2(\text{SO}_4, \text{CO}_3, 2\text{OH})_3 \cdot 2\text{H}_2\text{O}$ or AFt.

Ferrite Phase

The ferrite phase in cement is actually a solid solution with a composition between $\text{Ca}_2\text{Fe}_2\text{O}_5$ and $\text{Ca}_6\text{Al}_4\text{Fe}_2\text{O}_{15}$. The formula often used to represent this phase, $\text{Ca}_2\text{AlFeO}_5$, corresponds to an average composition.^{24f} Again it is helpful to consider the hydration of the pure phase and mixtures of it with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ before considering the hydration of it in cement.

Hydration of $\text{Ca}_2\text{AlFeO}_5$. Although its rate is slower, the hydration of $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$ is similar to the hydration of the aluminate phase. First

$[\text{Ca}_2(\text{Al, Fe})(\text{OH})_6](\text{OH}) \cdot 6\text{H}_2\text{O}$ and $[\text{Ca}_2(\text{Al, Fe})(\text{OH})_6][(\text{Al, Fe})(\text{OH})_4] \cdot 3\text{H}_2\text{O}$ are formed and then $\text{Ca}_3(\text{Al, Fe})_2(\text{O}_4\text{H}_4)_3$ is formed.⁵⁵ Possible simplified equations are

and

The structures of $[\text{Ca}_2(\text{Al, Fe})(\text{OH})_6](\text{OH}) \cdot 6\text{H}_2\text{O}$ and $[\text{Ca}_2(\text{Al, Fe})(\text{OH})_6][(\text{Al, Fe})(\text{OH})_4] \cdot 3\text{H}_2\text{O}$ are like those of $[\text{Ca}_2\text{Al}(\text{OH})_6](\text{OH}) \cdot 6\text{H}_2\text{O}$ and $[\text{Ca}_2\text{Al}(\text{OH})_6][\text{Al}(\text{OH})_4] \cdot 3\text{H}_2\text{O}$ and the structure of $\text{Ca}_3(\text{Al, Fe})_2(\text{O}_4\text{H}_4)_3$ is like that of $\text{Ca}_3\text{Al}_2(\text{O}_4\text{H}_4)_3$.

Hydration of $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$ - $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ Mixtures. The hydration of 1:1 mixture $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$ and $\text{Ca}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ is similar to that of a 1:1 mixture of $\text{Ca}_3\text{Al}_2\text{O}_6$ and $\text{Ca}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$. First it gives AFt and then it gives AFm, both apparently are mixed with some $(\text{Al, Fe})(\text{OH})_3$ gel which may contain Ca.⁵⁶ Possible simplified equations for this are

and

Probably the (Al, Fe)(OH)₃ gel forms because of the amount of Fe that can be accommodated in AFt is less than that in the anhydrous ferrite and the amount of Fe that can be accommodated in AFm is less than that in AFt. When the ferrite is hydrated under above conditions except for the additional presence of Ca(OH)₂, it has been reported the AFt has a greater ability to accommodate iron in its structure.⁵⁷ A possible simplified equation for this modified hydration is

Hydration of Ferrite Phase in Cement. The hydration of the ferrite phase in cement is not yet understood. Probably this phase together with CaSO₄·2H₂O and Ca(OH)₂ in the hydrating mixture react to give AFm. The iron from this phase is accommodated largely in the AFm. Apparently no (Al, Fe)(OH)₃ gel is formed during the hydration.⁵⁸

Components in Hydrated Cement

In sum, the hydration of cement gives a product containing ~60 % C-S-H, ~20 % Ca(OH)_2 and ~20 % of a mixture of AFm and AFt. The C-S-H is amorphous, the Ca(OH)_2 is crystalline and the AFm and AFt can be either crystalline or amorphous.

Relatively little work has been done on the hydration of cement at a high (10:1) water-to-solids ratios. However, it appears that the same types of reactions take place. The products obtained are not massive but rather are powders.

Approach of Work

The approach used in this work on the hydration of cement is similar to that used in the work on the hydration of the cement models $\beta\text{-Ca}_2\text{SiO}_4$ and Ca_3SiO_5 , that is, hydration of cement under various conditions and then analysis of the products by infrared spectroscopy, powder X-ray diffractometry, BET surface area measurement and SO_2 uptake measurement.

EXPERIMENTAL

Chemicals

Type I portland cement (SiO_2 20.73 %, Al_2O_3 5.22 %, Fe_2O_3 3.30 %, CaO 63.71 %, MgO 1.33 %, SO_3 2.63 %, Na_2O 0.15 %, K_2O 0.83 %, TiO_2 0.27 %, P_2O_5 0.15 %, Mn_2O_3 0.13 %, SrO 0.15 %, LOI 1.78 %) was obtained through a retail store from Medusa Cement (Cleveland, OH). Byproduct silica fume (Microsilica EMS 960) was obtained as a gift from Elkem Materials (Pittsburgh, PA) and uncalcined

diatomite was obtained as a gift from Celite (Lompoc, CA). Pumice (Tamez Mountains, NM) was purchased from Ward's Natural Science Establishment and perlite was obtained as a gift from Harborlite (Vicksburg, MI). $\text{Ca}_3\text{Al}_2\text{O}_6$ was purchased from CTL and $\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$ was purchased from Pfaltz and Bauer (Waterbury, CT) and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was purchased from Aldrich Chemical.

Sorbent Syntheses

Unagitated Reactions. In a typical reaction (Table VI, run 2), a mixture of cement (type I, 10.0 g) and water (100 mL) in a capped polyethylene bottle (250 mL) was shaken by hand for several minutes, and then held without agitation at room temperature for 30 days. (During this time the color of the slurry changed from greenish-gray to off-white). The resulting mixture was filtered (Whatman #2), and the solid was dried ($\sim 60^\circ\text{C}$, ~ 60 torr) and weighed (10.1 g). IR (Nujol mull) (cm^{-1}): 3644 (s br, OH), 1650 (w br, OH), 974 (s br, SiO). XRD ($d(\text{\AA})$ (I/I_0)): 7.92 (9, AFm), 4.90 (100, CH), 3.11 (10, CH), 3.04 (25, CSH), 2.79-2.73 (31, $\beta\text{-C}_2\text{S}$), 2.63 (60, CH), 1.93 (55, CH), 1.80 (50, CH), 1.69 (15, CH).

Stirred Reactions Without Beads. In a typical reaction (Table VI, run 4), a mixture of cement (type I, 10.0 g) and water (100 mL) was stirred (magnetic stirring bar, ~ 150 rpm) while being heated (oil bath, 100°C) without access to the atmosphere for 72 h, and then filtered (Whatman #2). (During this time the color of the slurry changed from greenish-gray to off-white). The solid was vacuum dried ($\sim 60^\circ\text{C}$, ~ 60 torr) for ~ 24 h, weighed (10.2 g) and crushed. IR (Nujol mull, cm^{-1}):

3644 (s, OH), 3538 (s, OH), 2466 (m br, OH) 1720 (w br, OH), 1282 (s, OH), 1152 (w br), 982 (s, SiO), 946 (s), 767 (m), 754 (s), 710 (m), 520 (m), 498 (s, SiO), 472 (m). XRD ($d(\text{\AA})$ (I/I_0)): 5.32 (11, C₂SH), 4.90 (100, CH), 4.22 (29, C₂SH), 3.91 (16, C₂SH), 3.54 (24, C₂SH), 3.30 (29, C₂SH), 3.27 (100, C₂SH), 3.11 (20, CH), 2.88 (29, C₂SH), 2.82 (27, C₂SH), 2.71 (18, C₂SH), 2.69 (15, C₂SH), 2.66 (30, C₂SH), 2.63 (95, CH), 2.61 (34, C₂SH), 2.57 (18, C₂SH), 2.53 (27, C₂SH), 2.42 (55, C₂SH), 2.34 (12, C₂SH), 2.32 (12, C₂SH), 2.30 (14, C₂SH), 2.29 (15, C₂SH), 2.24 (15, C₂SH), 2.16 (11, C₂SH), 2.11 (11, C₂SH), 2.08 (15, C₂SH), 2.06 (22, C₂SH), 2.03 (11, C₂SH), 1.96 (15, C₂SH), 1.93 (69, CH), 1.80 (39, CH), 1.79 (35, C₂SH), 1.69 (28, CH).

Shaken Reactions with Beads. In a typical reaction (Table VI, run 6), a mixture of portland cement (type I, 5.00 g), water (50 mL) and ZrO₂ beads (Mg-stabilized, 2 mm, ~50 g) in a capped polyethylene bottle (125 mL) was shaken with a shaker (~2-3 Hz) at room temperature for 3 days. (During this time the color of the cement-water slurry changed from greenish-gray to off-white). The resulting mixture was filtered (60 mesh bronze screen), and the beads were washed with water (~10 mL). The washings and filtrate were combined and refiltered (Whatman #2), and the solid was vacuum dried (~60 °C, 60 torr) for ~24 h, weighed (5.79 g) and crushed. IR (Nujol mull) (cm⁻¹): 3644 (s br, OH), 1650 (w br, OH), 974 (s br, SiO). XRD ($d(\text{\AA})$ (I/I_0)): 7.92 (10, AFm), 4.90 (96, CH), 3.11 (45, CH), 3.04 (25, CSH), 2.63 (100, CH), 1.93 (55, CH), 1.80 (55, CH), 1.69 (21, CH).

Stirred Reactions With Beads. In a typical reaction (Table VI, run 9), a mixture of cement (10.0 g), water (100 mL) and ZrO_2 beads (Mg-stabilized, 0.6-0.8 mm, ~600 g) was stirred (mechanical paddle stirrer, ~500 rpm) while being heated (oil bath, 100 °C) for 3 h. The resulting mixture was filtered (60 mesh bronze screen) and the beads were washed with water (~10 mL). The filtrate and washings were combined and filtered (Whatman #2), and the solid was vacuum dried (~60 °C, ~60 torr) for ~24 h, weighed (10.8 g) and crushed. IR (Nujol mull, cm^{-1}): 3644 (s, OH), 3418 (s br, OH), 1648 (w br, OH), 972 (s br, SiO), 452 (m br, SiO). XRD ($d(\text{\AA})$ (I/I_0)): 4.90 (90, CH), 3.11 (30, CH), 3.04 (15, CSH), 2.63 (100, CH), 1.93 (36, CH), 1.82 (10, CSH), 1.80 (28, CH), 1.69 (18, CH).

RESULTS AND DISCUSSION

Rapid Hydration of Cement and Cement-SiO₂ Source Mixtures

Rapid Hydration of Cement. In parallel with the work done on the hydration of Ca_3SiO_5 and $\beta\text{-Ca}_2\text{SiO}_4$, various approaches were explored in an effort to find ways to hydrate cement rapidly at high water-to-solids ratios to products rich in C-S-H, AFm and, in some case, also $\text{Ca}(\text{OH})_2$. These approaches were based on the use of a number of different combinations of reaction time, reaction temperature and degree of agitation. The results of ten runs based on these approaches are summarized in Table VI. The values given for the composition of the products made are subject to considerable error and should not be taken as precise.

Table VI. Synthesis and Properties of Hydrated Cement Sorbents

Reactants	Wt. Ratio	Conditions			Estimated Composition ^a					BET Area (m ² /g)	SO ₂ Uptake (mmol/g)	Ca Util (%)
		Time (h)	Temp (°C)	Media ^b	Agit	CSH (%)	CH (%)	AFm ^c (%)	C ₂ SH (%)	cem (%)		
1 cem, H ₂ O	1 : 10	720	~20			45	20	25 ^d		10	3.9	35
2 cem, H ₂ O	1 : 10	360	~20			35	10	25 ^{e, f}		30		
3 cem, H ₂ O	1 : 10	72	100		stirring		20	20 ^d	50	10	4.2	38
4 cem, H ₂ O	1 : 10	24	100		stirring	15	15	20 ^d	30	20		
5 cem, H ₂ O	1 : 10	72	~20	ZrO ₂	shaking	45	20	25 ^d		10	64	67
6 cem, H ₂ O	1 : 10	24	~20	ZrO ₂	shaking	30	15	25 ^d		30		
7 cem, H ₂ O	1 : 10	24	~20	ZrO ₂	stirring	45	20	25 ^d		10	62	
8 cem, H ₂ O	1 : 10	5	~20	ZrO ₂	stirring	30	15	25 ^{e, f}		30	26	

Table VI. Synthesis and Properties of Hydrated Cement Sorbents (Con't)

Reactants	Wt. Ratio	Conditions				Estimated Composition ^a					BET Acea	SO ₂ Uptake	Ca Util
		Time (h)	Temp (°C)	Media ^b	Agit	CSH	CH	AFmc ^c	C ₂ SH	cem			
						(%)	(%)	(%)	(%)	(%)			
9 cem, H ₂ O	1 : 10	5	80	ZrO ₂	stirring	45	20	25 ^d		10	63	6.4	63
10 cem, H ₂ O	1 : 10	3	100	ZrO ₂	stirring	45	20	25 ^d		10	85	6.4	63

^a CSH, CaO-SiO₂-H₂O; CH, Ca(OH)₂; AFm, [Ca₂(Al,Fe)(OH)₆]₂(SO₄,CO₃,2OH)·6H₂O or a related amorphous phase; C₂SH, α-Ca₂(SiO₃OH)(OH); cem, mainly unreacted belite. ^b 2-mm diameter Mg-stabilized ZrO₂ beads. ^c amount inferred from cement composition and literature data. ^d relatively amorphous. ^e probably [Ca₂Al(OH)₆](OH)·3H₂O, C₄AH₁₃. ^f relatively ordered.

The use of a 30-day reaction time, an $\sim 20^\circ\text{C}$ reaction temperature and very little agitation gave a relatively complete reaction with the hydrated components of the product being mainly C-S-H, Ca(OH)_2 and AFm. (AFm is used to mean $[\text{Ca}_2(\text{Al, Fe})(\text{OH})_6]_2(\text{SO}_4, \text{CO}_3, 2\text{OH}) \cdot 6\text{H}_2\text{O}$ or a related amorphous phase here and below.) The 7.92 and 3.99 Å AFm lines and the 3.04 and 1.82 Å C-S-H lines of the product were weak and its 4.90, 3.11, 1.93, 1.80, and 1.69 Å Ca(OH)_2 lines were split. The 3650 cm^{-1} Ca(OH)_2 hydroxy band, the 3450 cm^{-1} C-S-H hydroxy band, and the 970 cm^{-1} C-S-H Si-O band were all distinct, Figure 18. The habit of the Ca(OH)_2 crystals as shown by electron micrographs was tabular with typical face dimensions being $\sim 60\text{ }\mu$. Not surprisingly, the main component in the unreacted cement was belite, Figure 19 and Table VI, run 1. In view of known cement chemistry, the composition of the hydrated components of the product is as expected. The weakness of the AFm lines indicates that the AFm was relatively amorphous. Probably the AFm was intermixed intimately with C-S-H and effects arising from this intermixing led to the relatively amorphous nature of the AFm. The splitting of the Ca(OH)_2 lines indicates that the Ca(OH)_2 had a defective structure (e.g., extra ions between its layers or layer stacking faults). The relatively large size of the Ca(OH)_2 crystals is attributable to the long reaction time and the absence of vigorous agitation during the reaction. In general, the results from this run are consistent with those from similar runs described in the literature.⁵⁹

With the same reaction conditions except for the use of a 15-day reaction

Figure 18. Infrared spectra of sorbent 8, Table VI and portland cement.

Figure 19. X-ray powder diffraction patterns of cement sorbents
 1 and 2, Table VI.

time, the reaction was incomplete. The AFm powder pattern lines of the product were stronger and the Ca(OH)_2 lines were unsplit, Figure 19 and Table VI, run 2. The less amorphous nature of the AFm is attributable to a reduced intermixing of it with C-S-H. Based on the position and sharpness of 7.92 Å AFm line, it appears this AFm may be $[\text{Ca}_2\text{Al(OH)}_6](\text{OH}) \cdot 3\text{H}_2\text{O}$. The reason of the Ca(OH)_2 from this run was less defective than that from run 1 is not known.

The use of a 3-day reaction time, a 100 °C reaction temperature and vigorous agitation gave a relatively complete reaction. In addition to C-S-H, Ca(OH)_2 and AFm, the main hydration components in the product also included $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$. The AFm was relatively amorphous. The habit of this silicate as shown by electron microscopy was rod-like with typical axial dimensions being ~3 μ, run 3. In view of the results obtained from the studies on the hydration of Ca_3SiO_5 at 100 °C, Table IV, run 1, and the apparent stability of $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$ at 100 °C, the presence of this calcium silicate in the product of this run is not surprising.

When a shorter reaction time, 1 day, was used, the product contained less, but still considerable $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$, run 4. This result emphasizes the relative stability of $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$ at 100 °C.

With a 3-day reaction time, an ~20 °C reaction temperature and very vigorous agitation, a relatively complete reaction was obtained. As with runs 1 and 2, the hydrated components of the product were mainly C-S-H, Ca(OH)_2 and AFm. The

AFm was relatively amorphous, and the product had an appreciable surface area, run 5. The relative completeness of the reaction in spite of the shortness of the reaction time is attributable to the continuous removal of the passivating film formed on the cement particles by the high-shear agitation used. The substantial surface area of the product is not surprising because C-S-H and AFm can have high surface areas.⁶⁰

When a shorter reaction time, 1 day, was used, the reaction was less complete, run 6. This is unsurprising given the slowness of the hydration of cement.

The use of a 1-day reaction time, an $\sim 20^\circ\text{C}$ reaction temperature and very vigorous agitation (this time provided by stirred beads) gave a relatively complete reaction with the hydrated components of the product being mainly C-S-H, Ca(OH)_2 and AFm. The AFm in this product, like that in the product of run 1, was relatively amorphous, and the surface area of the product was appreciable, Figure 20, and Table VI, run 7. The greater completeness of the reaction compared to that of run 6 is attributable to the more efficient agitation used.

With the same reaction conditions except for the use of a 5-hour reaction time, the reaction was relatively incomplete, and the product had a low surface area and the AFm was less amorphous, Figure 20 and Table VI, run 8. Again the the AFm may be $[\text{Ca}_2\text{Al(OH)}_6](\text{OH})\cdot 6\text{H}_2\text{O}$.

The use of the same conditions except for an 80°C reaction temperature gave a relatively complete reaction with the hydrated components of the product being mainly C-S-H, Ca(OH)_2 and AFm. The AFm in the product was relatively

Figure 20. X-ray powder diffraction patterns of cement and cement sorbents 7 and 8, Table VI.

amorphous and had a substantial surface area, Figure 21 and Table VI, run 9. The lack of $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$ in this product is significant and shows that if the hydration time is sufficiently short, this silicate is not favored at elevated temperatures.

Finally, the use of the same reaction conditions except for a 3-hour reaction time and a 100°C reaction temperature gave a like product, Figure 21 and Table VI, run 10. This result is noteworthy because it shows that cement can be hydrated rapidly to a desirable mixture if sufficiently vigorous agitation and an elevated temperature are used.

Rapid Hydration of Cement-SiO₂ Source Mixtures. In an extension of the work on the hydration of cement, similar work was carried out on the hydration of cement-SiO₂ source mixtures.

The use of a 6-hour reaction time, an 80°C reaction temperature and very vigorous agitation with a 1:0.3 cement-SiO₂ fume mixture gave a relatively complete reaction with the hydrated components of the product being mainly C-S-H and AFm. The AFm in the product was very amorphous, and, in contrast to the cement products, the surface area of the product was quite high. As with the cement products, the unreacted cement in this product was mainly belite, Figure 22 and Table VII, run 1. The slow rate of the reaction compared to the rates of similar cement reactions, e.g., Table VI, run 9, can be ascribed to the relative inertness of SiO₂. The absence of $\text{Ca}(\text{OH})_2$ in the product is attributable to the presence of sufficient SiO₂ in

cement
sorbent 10
3 h
100 °C
v vigorous

a AFm
c C-S-H
d β - Ca_2SiO_4
p $\text{Ca}(\text{OH})_2$

cement
sorbent 9
5 h
80 °C
v vigorous

Figure 21. X-ray powder diffraction patterns of cement sorbents 9 and 10, Table VI.

Figure 22. X-ray powder diffraction patterns of cement-SiO₂ sorbents 1 and 2, Table VII.

Table VII. Synthesis and Properties of Hydrated Cement-SiO₂ Sorbents

	Reactants	Wt. Ratio	Conditions				Estimated Composition ^a				BET Area (m ² /g)	SO ₂ Uptake (mmol/g)	Ca Util (%)
			Time (h)	Temp (°C)	Media	Agit	CSH	CH	AFm ^{b,c}	cem			
1	cem, SiO ₂ ^d , H ₂ O	1 : 0.3 : 13	6	80	ZrO ₂ ^e	stirring	70		15 ^f	15	102	7.4	86
2	cem, diatomite, H ₂ O	1 : 0.3 : 13	6	80	ZrO ₂ ^g	stirring	70		15 ^f	15	211	6.4	79
3	cem, diatomite, H ₂ O	1 : 0.3 : 13	6	100	ZrO ₂ ^e	stirring	70		15 ^f	15	215	6.3	77
4	cem, pumice, H ₂ O	1 : 0.3 : 13	8	80	ZrO ₂ ^g	stirring	70		15 ^f	15	154	6.5	73
5	cem, perlite, H ₂ O	1 : 0.3 : 13	7	80	ZrO ₂ ^g	stirrin	55	15	15 ^f	15	174	6.1	71

^a CSH, CaO-SiO₂-H₂O; CH, Ca(OH)₂; AFm, [Ca₂(Al,Fe)(OH)₆]₂(SO₄,CO₃,OH)·6H₂O or a related amorphous phase; cem, mainly unreacted belite. ^b existence inferred mainly from cement composition and literature data. ^c amount inferred from cement composition and literature data. ^d Byproduct SiO₂ fume. ^e 2-mm diameter Mg-stabilized ZrO₂ beads. ^f relatively amorphous. ^g 0.6-0.8 mm diameter Mg-stabilized ZrO₂ beads.

the reaction mixture to convert the Ca(OH)_2 formed by the hydration of the cement to C-S-H. The high surface area of the product is consistent with the fact it was composed largely C-S-H and highly amorphous AFm. The presence of AFm in the product was inferred on the basis of the composition of cement and literature data indicating that only a small amount of the Si in C-S-H that is high in Ca^{2+} , such as that found in hydrated cement product, can be replaced by Fe and Al.^{24g}

Under the same reaction conditions, a cement-diatomite mixture gave a relatively complete reaction with the main hydrated components of the product being the same. This product had a very high surface area, Figure 22 and Table VII, run 2. Perhaps its very high surface area is attributable to the filigree structure of the diatom skeletons in diatomite since this could allow the C-S-H to grow with fewer restrictions than usual.

When the same reaction conditions were used except for a 100 °C reaction temperature, the product was very similar, run 3. Here the use of a higher temperature did not appear to significantly shorten the required reaction time.

The use of reaction conditions like those used in runs 1 and 2 with a cement-pumice mixture gave a product like that of run 3 except that it had a somewhat lower surface area, run 4. No evidence for byproducts arising from the metal ions in the pumice was observed.

When similar reaction conditions were used with a cement-perlite mixture, a product having as its main hydration components C-S-H, Ca(OH)_2 and AFm was

obtained (again no evidence for byproducts was observed). The surface area of this product was quite high, run 5. The presence of $\text{Ca}(\text{OH})_2$ in the product is attributable to the low reactivity of perlite.

SO₂ Uptake of Sorbents

Hydrated Cement Sorbents. The SO₂ uptake and utilization values of the hydrated cement products are generally as expected, Table VI. The low value of Sorbent 1 is consistent with the large size of its $\text{Ca}(\text{OH})_2$ crystals and hence the unavailability of its $\text{Ca}(\text{OH})_2$. The low value of sorbent 3 is consistent with the presence of considerable $\alpha\text{-Ca}_2(\text{SiO}_3\text{OH})(\text{OH})$ in it. For Sorbents 5, 9 and 10, the high values fit with the composition and high surface areas of these sorbents.

Hydrated Cement-SiO₂ Source Sorbents. The SO₂ uptake and Ca utilization values of the hydrated cement-SiO₂ source products are also generally as expected, Table VII. Their high values fit with their compositions and their high surface areas.

CONCLUSIONS

The results from the cement hydration work show that excellent sorbents composed mainly of C-S-H, $\text{Ca}(\text{OH})_2$ and AFm can be made from cement. They further show that sorbents of this type can be made with short reaction times. Thus such sorbents are attractive for practical use.

The results from the cement-SiO₂ source hydration studies show that very good sorbents composed mainly of C-S-H and AFm can be made from cement and

readily available and cheap SiO_2 sources. In addition, they show that sorbents of this type can be made with moderate reaction times. Thus sorbents of this type also are attractive for practical use.

9. COLLABORATIONS

During the year, collaborative work with other members of the consortium was done. A visit was made to the laboratory of Professor T. C. Keener and discussion on the scale-up work on cement-derived sorbents being done at Cincinnati were carried out. In conjunction with this, a sample of a cement-derived sorbent and data on it were given to Professor Keener. In addition a sample of a cement-derived sorbent and data on it were given to Professor L.-S. Fan of Ohio State University for use in his Se sorbent studies. Also infrared analysis of samples from the air toxics studies of Professor P. Biswas of the University of Cincinnati was carried out for Professor Biswas.

**10. APPENDIX I.
NOTATION**

CEMENT CHEMIST'S

Symbol

Equivalent

A

Al_2O_3

C

CaO

$\overline{\text{C}}$

CO_2

F

Fe_2O_3

S

SiO_2

$\overline{\text{S}}$

SO_3

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