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

Final Report for the Period
September 1, 1993 to August 31, 1994

by

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# 1. TABLE OF CONTENTS

## 2. LIST OF FIGURES

## 3. LIST OF TABLES

## 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 $Ca(OH)_2$, from mixtures of $Ca(OH)_2$ and $SiO_2$, and from portland cement. They also include the study of sorbents made from model compounds.

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

In addition, sorbents prepared from $Ca_3SiO_5$ and $\beta$-$Ca_2SiO_4$ 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 $Ca(OH)_2$, from mixtures of $Ca(OH)_2$ 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. $SiO_2$-MODIFIED $Ca(OH)_2$ SORBENTS

### INTRODUCTION

Calcium hydroxide has a high capacity for $SO_2$, contains an environmentally acceptable cation and is relatively inexpensive (~\$ 60/ton in Cleveland in 1994[1]). 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 $CaCO_3$ by a two-step synthesis. In the first step, the $CaCO_3$ is calcined:

$$CaCO_3 \longrightarrow CaO + CO_2 \qquad (1)$$

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:

$$CaO + H_2O \longrightarrow Ca(OH)_2 \qquad (2)$$

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 $H_2O$ on the CaO, the formation of $CaO \cdot 2H_2O$, 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 $H_2O$ as steam during the hydration (the hydration of CaO is quite exothermic, $\Delta H = 64.8$ 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 ~13-22 $m^2/g$.[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 $CaCl_2$ 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 $CaCl_2$ and

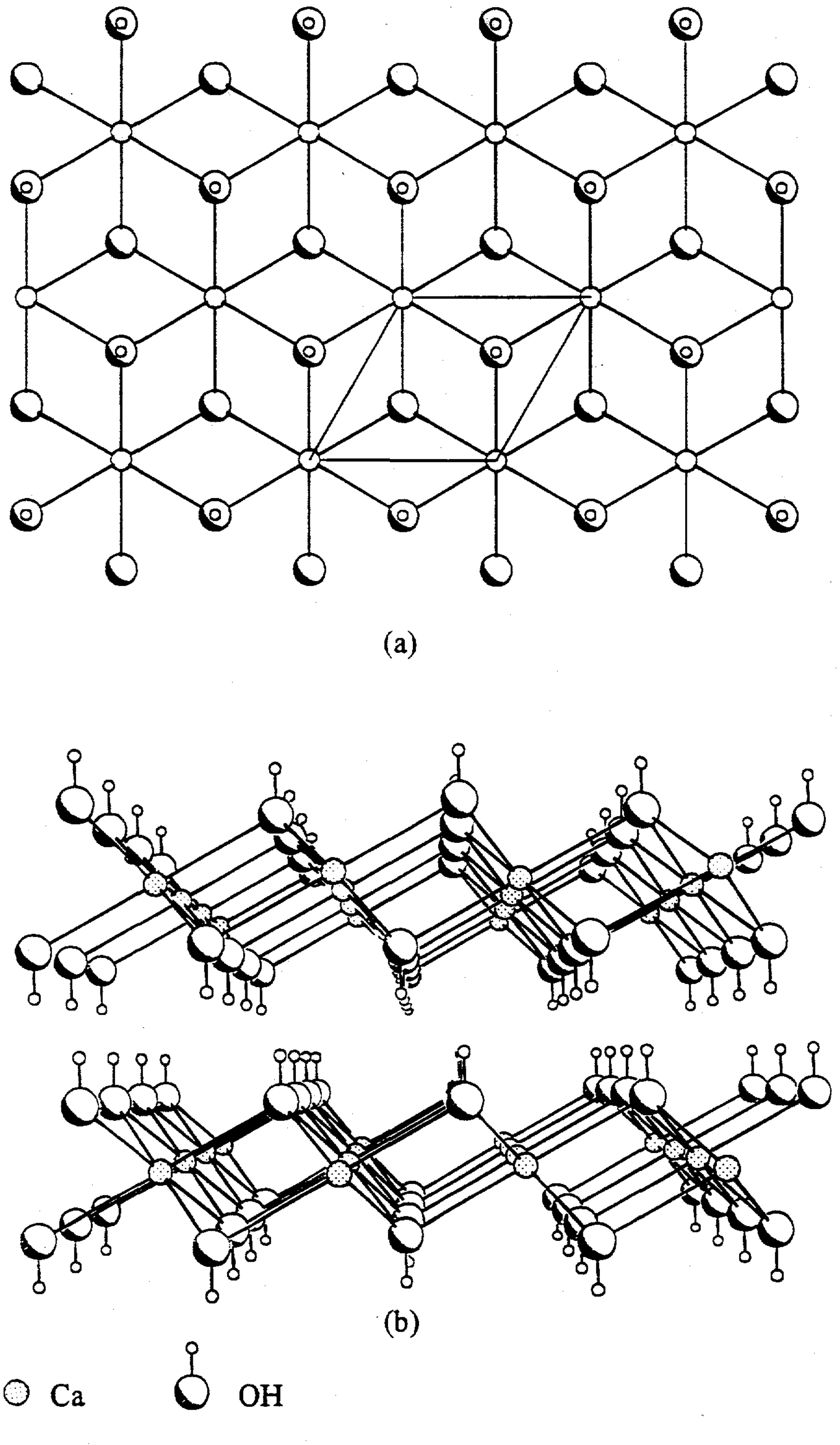


**Figure 1.** Structure of $Ca(OH)_2$. (a) A single layer projected along <001>. (b) Edge view of two layers.

NaOH with ethanol occurs as hexagonal plates.[11] The plate morphology of this $Ca(OH)_2$ 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 ascribed to the adsorption of silicic acids on its OH faces.

**Modified $Ca(OH)_2$ and $Ca(OH)_2$-Based Sorbents.** A number of different approaches have been tried in the work done in an effort to get useful $Ca(OH)_2$ or $Ca(OH)_2$-based sorbents. Thus, to provide $H_2O$ to aid the $SO_2$-$Ca(OH)_2$ reaction, mixtures of calcium hydroxide and deliquescent salts have been prepared.[13] To modify its morphology and increase its surface area, $Ca(OH)_2$ has been treated with lignosulfonate.[14] $Ca(OH)_2$ 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 $Ca(OH)_2$ with fumed $SiO_2$ were investigated. In an extension of this approach, sorbents derived by fully reacting $Ca(OH)_2$ 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 $Ca(OH)_2$ 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(Å) ($I/I_o$)): 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 cap[illegible]ethylene bottle (80 mL) was shaken with a shaker (~ 2-3 Hz) at room temperature for 5 min. Fumed $SiO_2$ ( 0.48 g) was added to the mixture and it was shaken (~ 2-3 Hz) at room temperature for an additional 6 h. The resulting slurry was filtered (Whatman #2) and the solid was washed with ethanol (~ 5 mL) and ether (~10 mL), vacuum dried (~60 °C, ~60 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(Å) ($I/I_o$)): 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 $Ca(OH)_2$ (3.00 g), diatomite (2.16 g) and $H_2O$ (50 mL) was stirred (magnetic stirring bar, ~150 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 (~ 5 mL), vacuum dried (~60 °C, ~60 torr) for ~24 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(Å) ($I/I_o$)): 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 $Ca(OH)_2$ (3.00 g), pumice (2.16 g), $H_2O$ (50 mL) and $ZrO_2$ beads (Mg-stabilized, 1.4-1.6 mm, ~15 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 $H_2O$ (~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) ($I/I_o$)): 3.04 (100, CSH), 2.80 (26, CSH), 1.82 (27, CSH).

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

**Analysis of Fumed $SiO_2$, 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

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

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

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

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 $Ca(OH)_2$ reflections of the mixture. Next the weight fractions of $Ca(OH)_2$ and C-S-H in the sorbents in these mixtures, $f_{CH}$ and $f_{CSH}$, were calculated with the formulas:

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

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

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:

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

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

where $Ca_{CH}$ is the number of moles of Ca in the $Ca(OH)_2$ in the sorbent in a mixture, and $Ca_{tot}$ and $S_{tot}$ 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 ~20 °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 (%) | | ($m^2/g$) | (mmol/g) | (%) |
| 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, $CaO$-$SiO_2$-$H_2O$

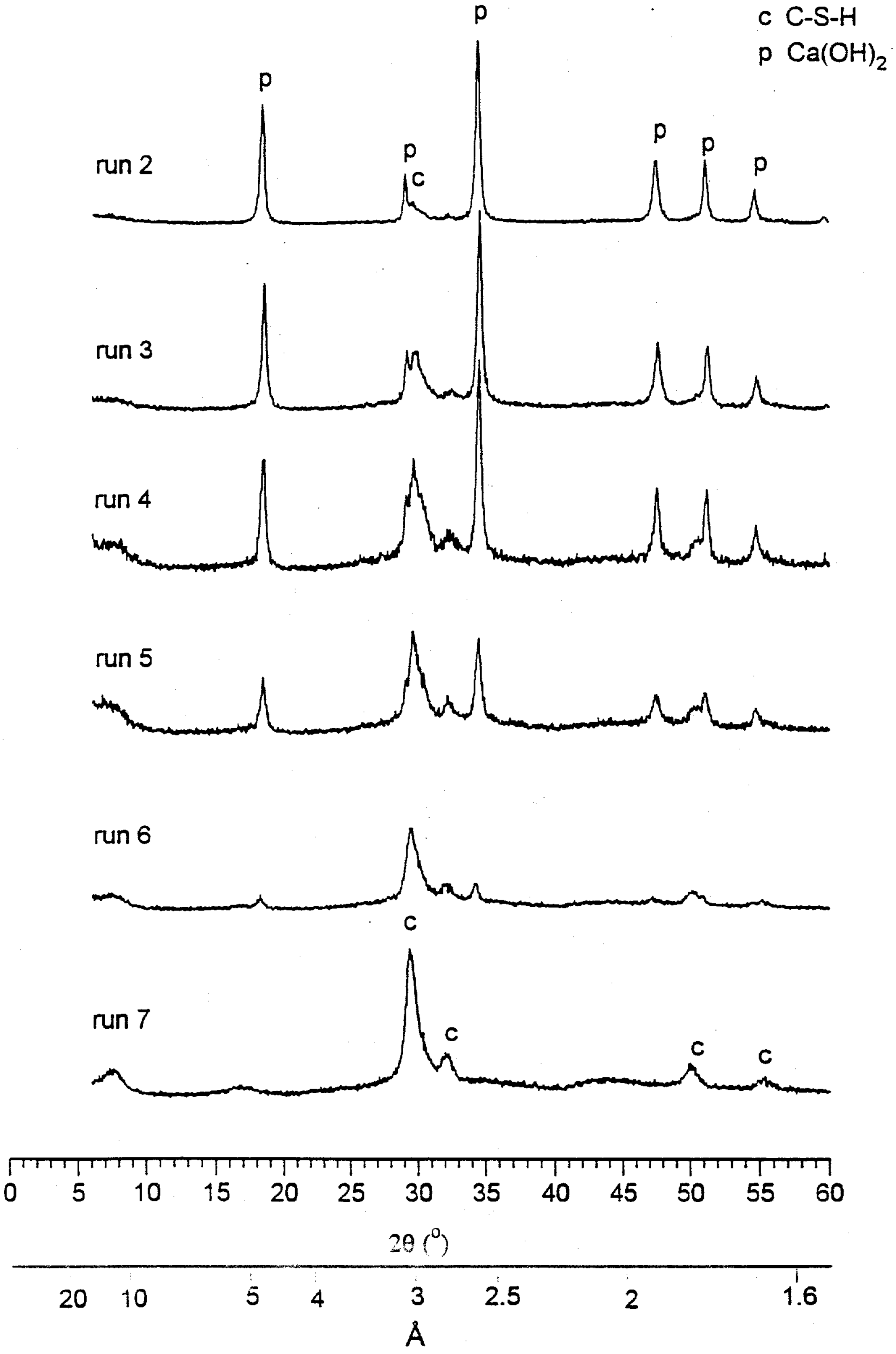


**Figure 2**. X-ray powder diffraction patterns of fumed $SiO_2$-$Ca(OH)_2$ products.

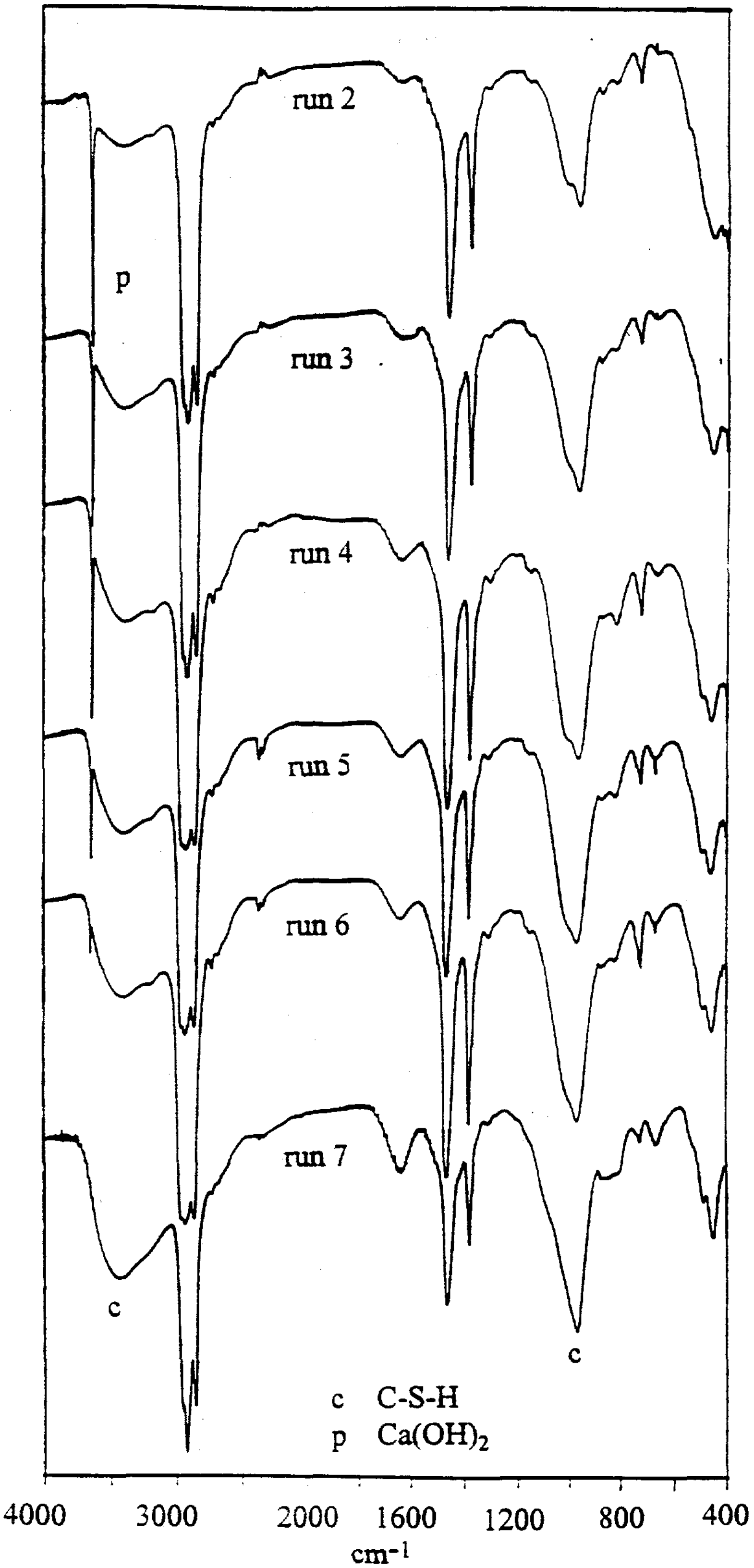


**Figure 3.** Infrared spectra of fumed $SiO_2$-$Ca(OH)_2$ products.

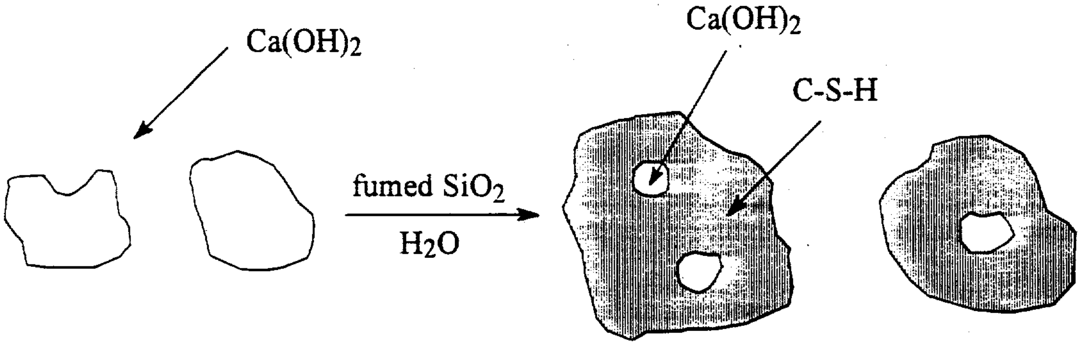


**Figure 4.** Schematic representation of the $Ca(OH)_2$-fumed $SiO_2$ reaction.

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 $Ca(OH)_2$ 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 $SiO_2$ Source-$Ca(OH)_2$ Sorbents

|  | $SiO_2$ Source | Si/Ca mole ratio | Conditions |  |  |  | Estimated Composition[a] |  |  | BET Area | $SO_2$ Uptake | Ca Util |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | Time (h) | Temp (°C) | Media | Agit | CH (%) | CSH (%) | $C_2SH$ (%) | ($m^2/g$) | (mmol /g) | (%) |
| 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, $CaO\text{-}SiO_2\text{-}H_2O$; $C_2SH$, $\alpha\text{-}Ca_2(SiO_3OH)(OH)$. [b] 1.4 -1.6-mm Mg-stabilized $ZrO_2$ 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

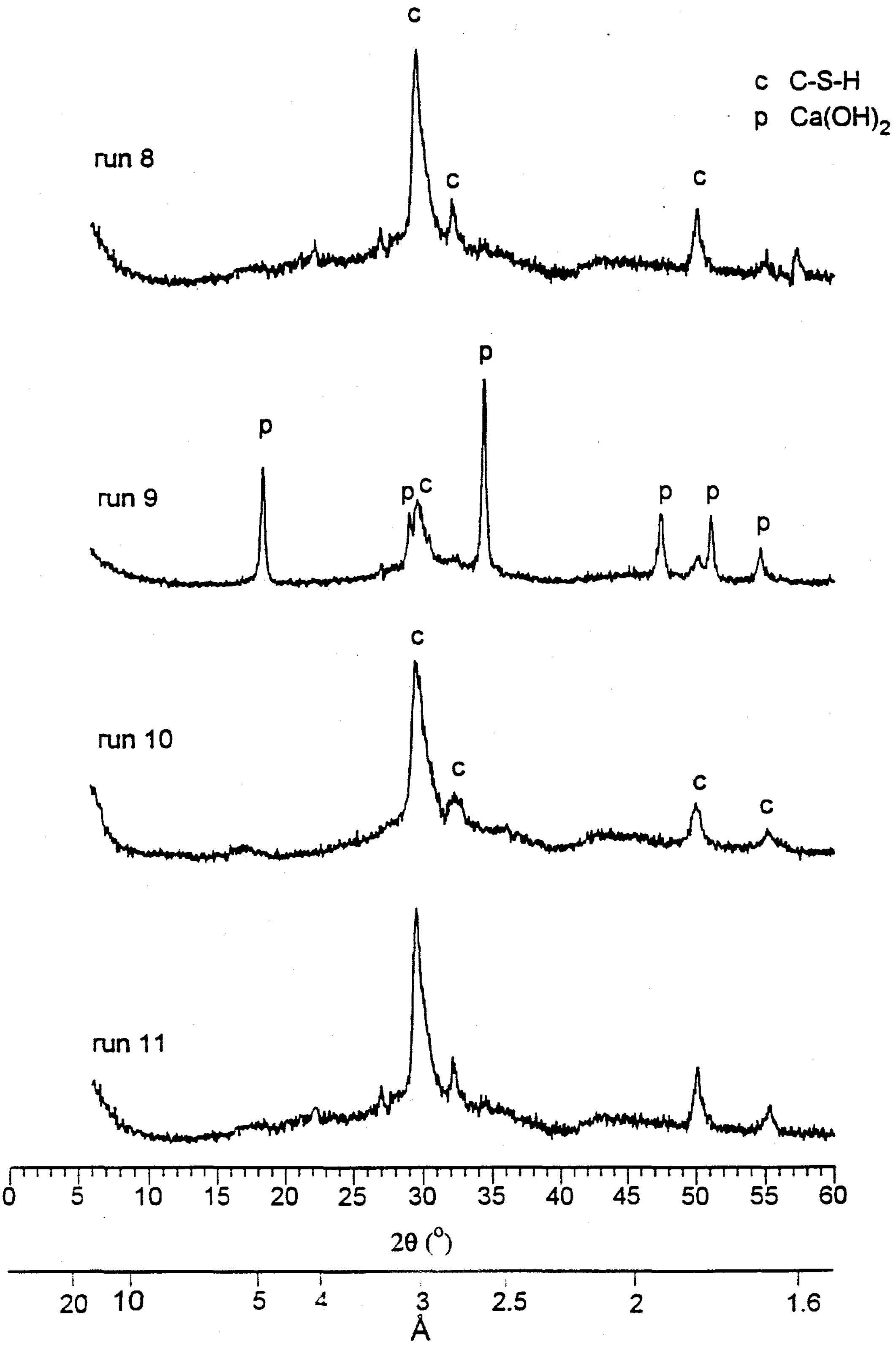


**Figure 5**. X-ray powder patterns of natural SiO$_2$ source-Ca(OH)$_2$ sorbents.

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 $\alpha$-$Ca_2(SiO_3OH)(OH)$ 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 $\alpha$-$Ca_2(SiO_3OH)(OH)$ 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]

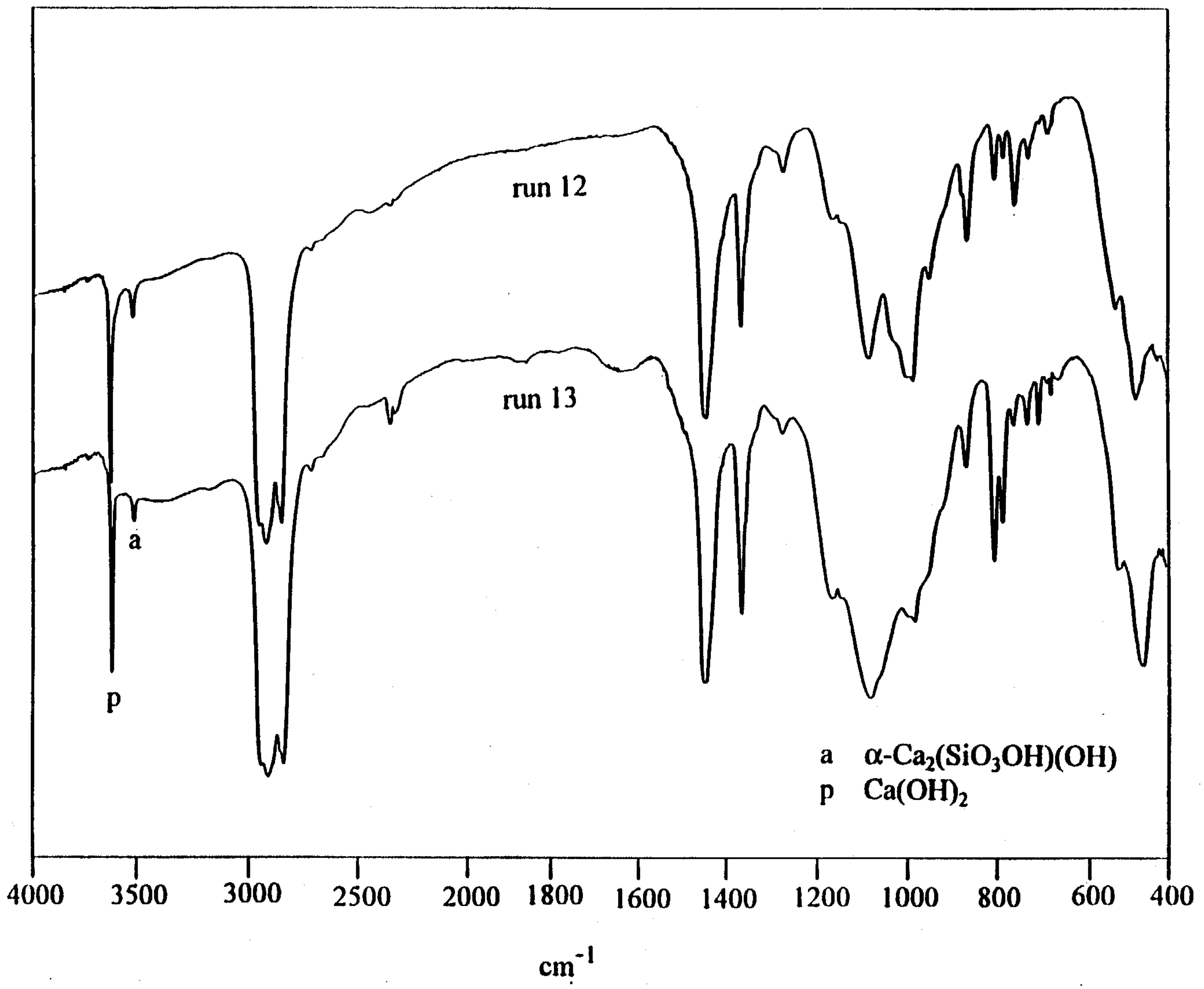


Figure 6. Infrared spectra of natural $SiO_2$ source-$Ca(OH)_2$ sorbents.

## 7. HYDRATED $Ca_3SiO_5$ AND $\beta$-$Ca_2SiO_4$ 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 $Ca(OH)_2$

$$Ca(OH)_2 + SiO_2 + xH_2O \longrightarrow CaO\text{-}SiO_2\text{-}xH_2O \qquad (9)$$

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

$$CaCl_2 + Na_2SiO_3 + xH_2O \longrightarrow CaO\text{-}SiO_2\text{-}xH_2O + 2NaCl \qquad (10)$$

The third involves the reaction of a calcium silicate and water, e.g. $Ca_3SiO_5$ and $H_2O$ or $\beta$-$Ca_2SiO_4$ and $H_2O$

$$Ca_3SiO_5 + xH_2O \longrightarrow 1.7CaO\text{-}SiO_2\text{-}(x\text{-}1.3)H_2O + 1.3Ca(OH)_2 \qquad (11)$$

$$\beta\text{-}Ca_2SiO_4 + xH_2O \longrightarrow 1.7CaO\text{-}SiO_2\text{-}(x\text{-}0.3) + 0.3Ca(OH)_2 \qquad (12)$$

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 $\beta$-$Ca_2SiO_4$.

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 $\beta$-$Ca_2SiO_4$

**$Ca_3SiO_5$ and $\beta$-$Ca_2SiO_4$ 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 ($\sim Ca_3SiO_5$), 15-30 % belite ($\sim Ca_2SiO_4$), 5-10 % aluminate phase ($\sim Ca_3Al_2O_6$), 5-15 % ferrite phase ($\sim Ca_2AlFeO_5$), and 3-4 % gypsum ($CaSO_4 \cdot 2H_2O$).[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 $\beta$-$Ca_2SiO_4$ 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 $\beta$-$Ca_2SiO_4$ 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 $Ca(OH)_2$. The C-S-H has a calcium-to-silicon ratio of ~1.7 and its silicate ions are mainly $Si_2O_7^{6-}$ 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 in 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 hydroxlated 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

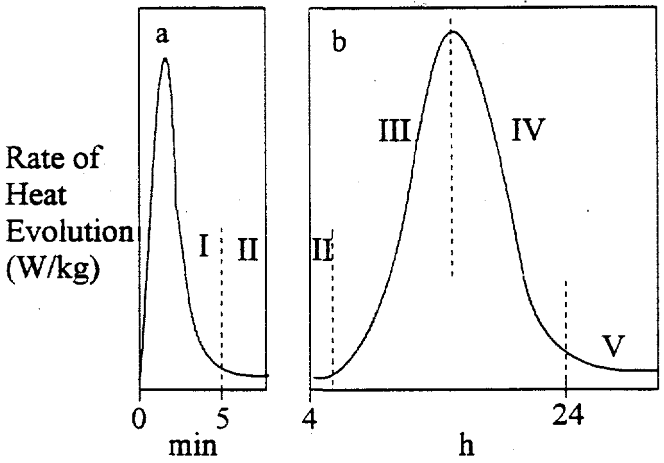


**Figure 7**. Calorimetric curve for hydration of $Ca_3SiO_5$ at a 1:2 water-to-solids ratio during (a) early part of hydration reaction and (b) intermediate part of hydration reaction.

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 metasable 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.

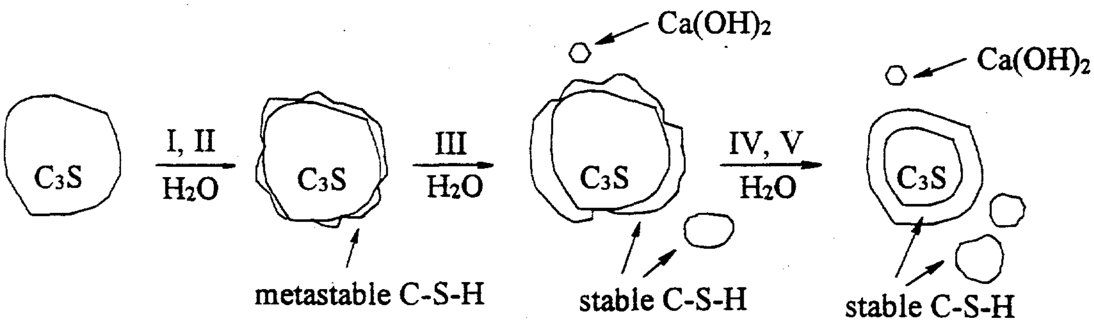


**Figure 8.** Schematic representation of $Ca_3SiO_5$ hydration mechanism.

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 $Ca_3(SiO_3OH)_2\cdot 2H_2O$ (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 $1.6CaO\cdot GeO_2\cdot nH_2O$.[42] This indicates that $Ca_3SiO_5$

**Table III.** Hydration of $Ca_3SiO_5$ and $\beta$-$Ca_2SiO_4$ Under Ordinary Conditions.[a]

| | Reactants | Wt. Ratio | Conditions | | | | Completion |
|---|---|---|---|---|---|---|---|
| | | | Time (d) | Temp. (°C) | Media | Agit | (%) |
| 1 | $Ca_3SiO_5$, $H_2O$ | ~2:1 | 28 | ~20 | none | none | 70 |
| 2 | $Ca_2SiO_4$, $H_2O$ | ~2:1 | 28 | ~20 | none | none | 30 |

[a] Reference 3b

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

**Hydration of $\beta$-$Ca_2SiO_4$.** Studies of the hydration of $\beta$-$Ca_2SiO_4$ at a low water-to-solids ratio and room temperature indicate that the mechanism of hydration of $\beta$-$Ca_2SiO_4$ is similar to that of $Ca_3SiO_5$ (although at least one report suggests that no passivating layer is formed in the early stages[43]). The effect of impurity ions on the hydration of $\beta$-$Ca_2SiO_4$ is not yet clear.[44]

As with $Ca_3SiO_5$, full hydration of $\beta$-$Ca_2SiO_4$ 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 $\beta$-$Ca_2SiO_4$ compared to that of $Ca_3SiO_5$ has been attributed to the lack of an oxygen unconnected to a silicon in $\beta$-$Ca_2SiO_4$ and the presence of such an oxygen in $Ca_3SiO_5$.[45] Support for this is found in the fact that $Ca_3Si_2O_7$ 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 $\beta$-$Ca_2SiO_4$.[46] Supporting this hypothesis is the resistance of $\gamma$-$Ca_2SiO_4$ 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 $CaSO_4 \cdot 2H_2O$ 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(Å) $(I/I_o)$) 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(Å) $(I/I_o)$) 6.52 (46, $C_3S_2H_3$), 4.90 (100, CH), 4.14 (13, $C_3S_2H_3$), 3.88 (13, $C_3S_2H_3$), 3.27 (36, $C_3S_2H_3$), 3.17 (64, $C_3S_2H_3$), 3.11 (7, CH), 2.83 (100, $C_3S_2H_3$), 2.73 (84, $C_3S_2H_3$), 2.63 (34, CH), 2.35 (26, $C_3S_2H_3$), 2.31 (20, $C_3S_2H_3$), 2.15 (45, $C_3S_2H_3$), 1.98 (22, $C_3S_2H_3$), 1.95 (52, $C_3S_2H_3$), 1.93 (26, CH), 1.80 (12, CH), 1.77 (39, $C_3S_2H_3$), 1.69 (9, CH).

**Stirred Reactions With Beads.** In a typical reaction (Table IV, run 4), a mixture of $Ca_3SiO_5$ (3.00 g), water (30 mL) and $ZrO_2$ 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) ($I/I_o$)) 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 $Ca_3SiO_5$ and $\beta$-$Ca_2SiO_4$

**Rapid Hydration of $Ca_3SiO_5$.** Various approaches were explored in an effort to find ways to hydrate $Ca_3SiO_5$ 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 $Ca_3SiO_5$ (and the hydration of portland cement) at a low water-to-solids ratios. The compounds used were $CaCl_2$, $CaSO_4{\cdot}2H_2O$, 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 $Ca(OH)_2$ and $\alpha$-$Ca_2(SiO_3OH)(OH)$, a poor sorbent and thus an undesired product consituent, Figure 9. This silicate is probably the stable silicate product of the hydration of $Ca_3SiO_5$ at ~100 °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 ~100 °C, it must be done quickly.

The use of a 12-hour reaction time, an ~20 °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 | $C_3S_2H_3$ | $C_2SH$ | $C_3S$ | (mmol/g) |
| 1 $Ca_3SiO_5$, $H_2O$ | 1:10 | 72 | 100 |  | stirring |  | 40 |  | 60 |  | 2.4 |
| 2 $Ca_3SiO_5$, $H_2O$ | 1:10 | 12 | ~20 | $ZrO_2$[c] | shaking | 40 | 20 | 40 |  |  | 5.9 |
| 3 $Ca_3SiO_5$, $H_2O$ | 1:10 | 6 | 60 | $ZrO_2$[c] | shaking | 40 | 20 | 40 |  |  |  |
| 4 $Ca_3SiO_5$, $H_2O$ | 1:10 | 3 | 100 | $ZrO_2$[d] | stirring | 60 | 40 |  |  |  |  |
| 5 $Ca_3SiO_5$, $CaSO_4{\cdot}2H_2O$, $H_2O$ | 1:0.05:10 | 6 | 60 | $ZrO_2$[c] | shaking | 60 | 40 |  |  |  | 5.3 |
| 6 $Ca_3SiO_5$, $SiO_2$[e], $H_2O$ | 1:0.26:13[f] | 72 | 100 |  | stirring | 40 | 20 |  | 40 |  |  |
| 7 $Ca_3SiO_5$, $SiO_2$[g], $H_2O$ | 1:0.26:13[f] | 72 | 100 |  | stirring | 100 |  |  |  |  |  |
| 8 $Ca_3SiO_5$, $SiO_2$[g], $H_2O$ | 1:0.26:13[f] | 72 | ~20 | $ZrO_2$[c] | shaking | 100 |  |  |  |  | 6.8 |

[a] $Ca_3SiO_5$ < 270 mesh. [b] CSH, $CaO\text{-}SiO_2\text{-}H_2O$; CH, $Ca(OH)_2$; $C_3S_2H_3$, $Ca_3(SiO_3OH)_2{\cdot}2H_2O$, afwillite; $C_2SH$, $\alpha\text{-}Ca_2(SiO_3OH)(OH)$. [c] 2-mm diameter $ZrO_2$ (Mg-stabilized) beads. [d] 0.6-0.8 mm diameter $ZrO_2$ (Mg-stabilized) beads. [e] Quartz (< 10μ). [f] Ca:Si, 1.5:1. [g] Fumed $SiO_2$ (350 $m^2/g$).

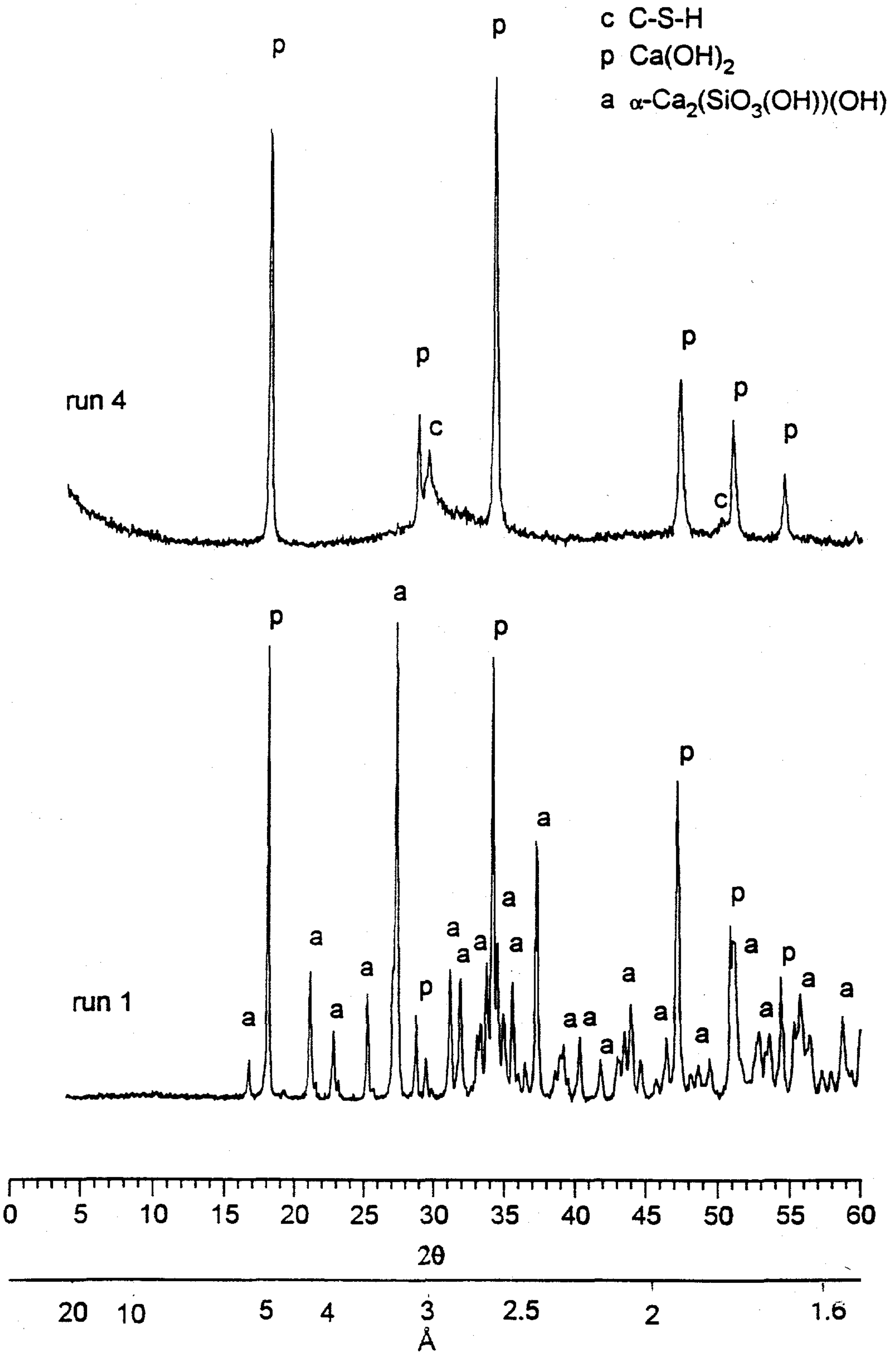


Figure 9. X-ray powder diffraction patterns of products of runs1 and 4, Table IV.

$Ca(OH)_2$, and $Ca_3(SiO_3OH)_2{\cdot}2H_2O$, another poor sorbent and thus an another unwanted product consituent. Whether $Ca_3(SiO_3OH)_2{\cdot}2H_2O$ 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 $SO_4^{4-}$ ion concentration under these low-temperature conditions and this led to the precipitation of the $Ca_3(SiO_3OH)_2{\cdot}2H_2O$.

With the use of a shorter reaction time, a 60 °C reaction temperature and high-shear agitation, the product was again C-S-H, $Ca(OH)_2$, and $Ca_3(SiO_3OH)_2{\cdot}2H_2O$, run 3. Probably the $SiO_4^{4-}$ ion concentration again became high and led to the precipitation of $Ca_3(SiO_3OH)_2{\cdot}2H_2O$. 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 $Ca(OH)_2$, 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 $Ca_3(SiO_3OH)_2{\cdot}2H_2O$ and $\alpha$-$Ca_2(SiO_3OH)(OH)$ 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

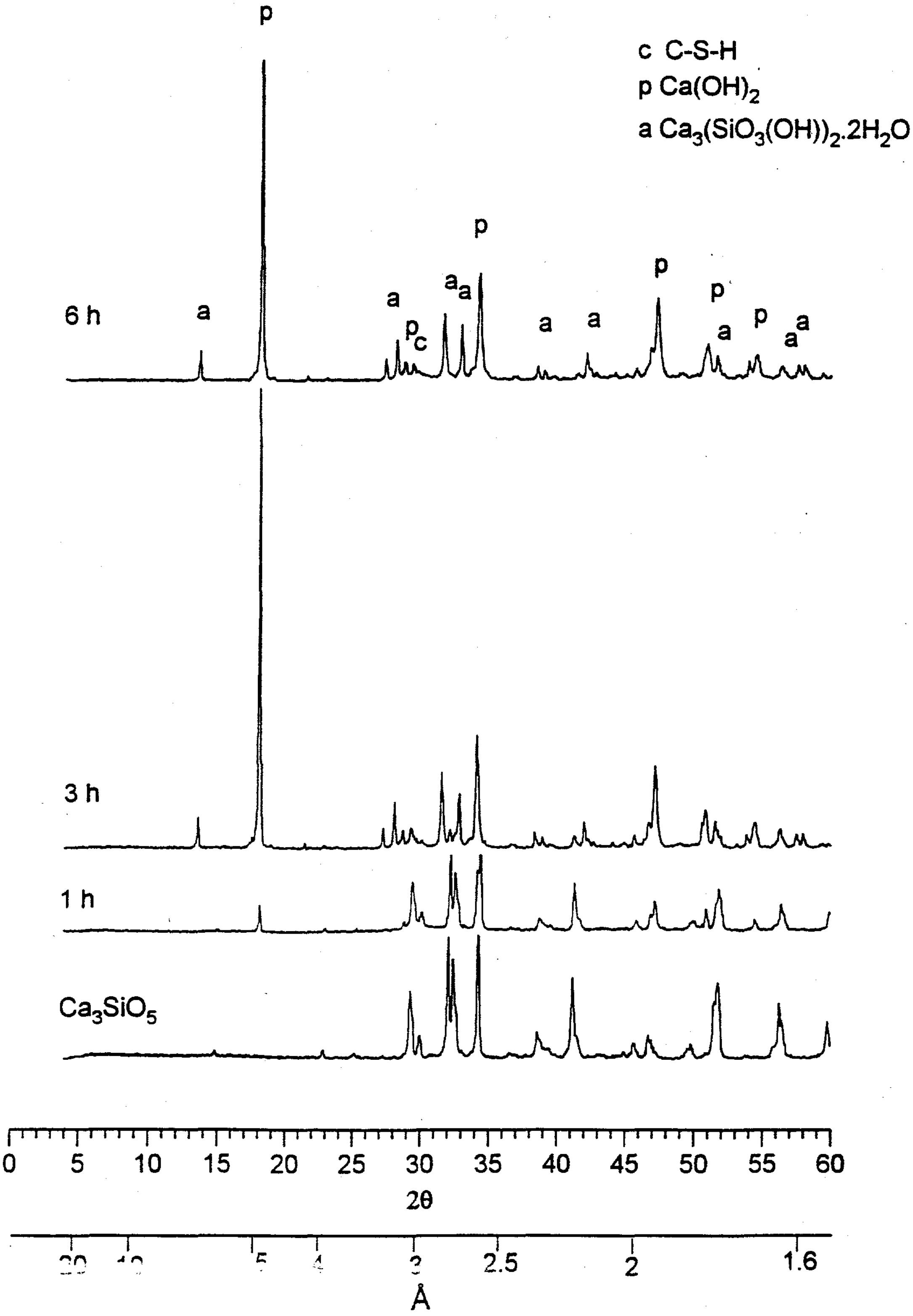


**Figure 10**. X-ray powder diffraction patterns of intermediate and final products of run 3, Table IV.

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 $\alpha$-$Ca_2(SiO_3OH)(OH)$ as a product.

Conditions the same as those of run 3 except for the addition of a small amount of $CaSO_4 \cdot 2H_2O$ to the reaction mixture led to a product composed of C-S-H and $Ca(OH)_2$, run 5. Perhaps the formation of $Ca_3(SiO_3(OH))_2 \cdot 2H_2O$ was inhibited by the deposition of $SO_4^{2-}$ ions in $SiO_4^{4-}$ sites on the surface of the $Ca_3(SiO_3(OH))_2 \cdot 2H_2O$ nuclei.

The use of conditions like those employed in run 1 except for the addition of 10 $\mu$ quartz to the reaction mixture led to a product composed of C-S-H, $Ca(OH)_2$ and $\alpha$-$Ca_2(SiO_3OH)(OH)$, run 6. Probably the finely divided silica reacted with the $Ca(OH)_2$ 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 $Ca(OH)_2$ 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 ~20 °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 $Ca_3(SiO_3OH)_2 \cdot 2H_2O$, Figure 11. This suggests that $Ca_3(SiO_3OH)_2 \cdot 2H_2O$ is not the stable silicate product when $SiO_2$ is present.

**Rapid Hydration of $\beta$-$Ca_2SiO_4$.** Various approaches also were explored in an effort to find ways to rapidly hydrate $\beta$-$Ca_2SiO_4$ 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 $\alpha$-$Ca_2(SiO_3OH)(OH)$ 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 $\beta$-$Ca_2SiO_4$ 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 ~20 °C reaction temperature and high-shear agitation gave a product containing C-S-H, $Ca(OH)_2$ and some unreacted $\beta$-$Ca_2SiO_4$, run 2. This shows that the hydration of $\beta$-$Ca_2SiO_4$ under these water-to-

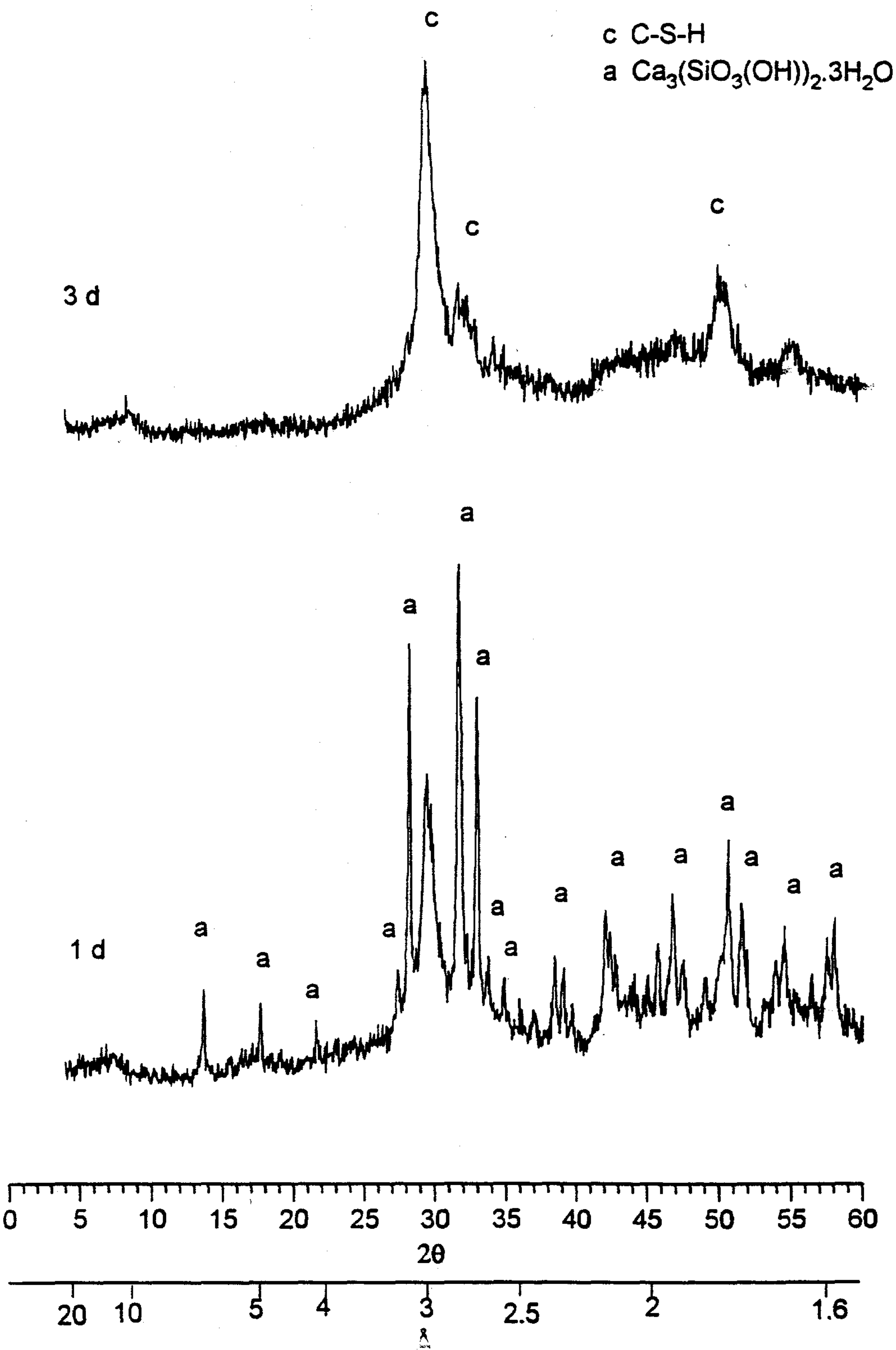


Figure 11. X-ray powder diffraction patterns of intermediate and final products of run 8, Table IV.

**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 | $C_3S_2H_3$ | $C_2SH$ | β$C_2S$ | (mmol/g) |
| 1 $Ca_2SiO_4$, $H_2O$ | 1:10 | 72 | 100 | | stirring | | | | 100 | | 2.2 |
| 2 $Ca_2SiO_4$, $H_2O$ | 1:10 | 72 | ~20 | $ZrO_2$[c] | shaking | 50 | 20 | | | 30 | 6.4 |
| 3 $Ca_2SiO_4$, $H_2O$ | 1:10 | 24 | 80 | $ZrO_2$[c] | shaking | 30 | 20 | | 50 | | |
| 4 $Ca_2SiO_4$, $SiO_2$[d], $H_2O$ | 1:0.35:14[e] | 72 | 100 | | stirring | 100 | | | | | |
| 5 $Ca_2SiO_4$, $SiO_2$[d], $H_2O$ | 1:0.35:14[e] | 72 | ~20 | $ZrO_2$[c] | shaking | 100 | | | | | 6.6 |

[a] β-$Ca_2SiO_4$ < 270 mesh. [b] CSH, $CaO$-$SiO_2$-$H_2O$; CH, $Ca(OH)_2$; $C_3S_2H_3$, $Ca_3(SiO_3OH)_2 \cdot 2H_2O$, afwillite; $C_2SH$, $Ca_2(SiO_3OH)(OH)$; β-$C_2S$, β-$Ca_2SiO_4$. [c] 2-mm diameter $ZrO_2$ (Mg-stabilized) beads [d] Fumed $SiO_2$ (350 $m^2/g$). [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 $\beta$-$Ca_2SiO_4$ surface.

With a one-day reaction time, an 80 °C reaction temperature, and high-shear agitation, the product obtained was C-S-H, $Ca(OH)_2$ and $\alpha$-$Ca_2(SiO_3OH)(OH)$, run 3. Probably as in the case of run 1, the presence of $\alpha$-$Ca_2(SiO_3OH)(OH)$ 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 $\beta$-$Ca_2SiO_4$ when a short reaction time was used, and $\alpha$-$Ca_2(SiO_3OH)(OH)$ 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 $\alpha$-$Ca_2(SiO_3OH)(OH)$ 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

$\alpha$-$Ca_2(SiO_3OH)(OH)$ and $Ca_3(SiO_3OH)_2 \cdot 2H_2O$ 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 $\beta$-$Ca_2SiO_4$ to C-S-H and $Ca(OH)_2$ is slowed by the formation of a passivating coating on the reactant, that it is hindered by the stability of $\alpha$-$Ca_2(SiO_3OH)(OH)$ at high temperatures, and that it is hindered by the ability of $Ca_3(SiO_3OH)_2 \cdot 2H_2O$ form at low temperatures. It further appears that the hydration of $Ca_3SiO_5$ and $\beta$-$Ca_2SiO_4$ 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 $\alpha$-$Ca_2(SiO_3OH)(OH)$ at high temperature.

On the basis of this, it is concluded that $Ca_3SiO_5$ and $\beta$-$Ca_2SiO_4$ could be very rapidly hydrated to C-S-H and $Ca(OH)_2$ 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 $\beta$-$Ca_2SiO_4$ 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 tons[49] (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 $CaSO_4 \cdot 2H_2O$ 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 (~ $Ca_3SiO_5$), 15-30 % belite (~ $Ca_2SiO_4$), 5-10 % aluminate phase (~ $Ca_3Al_2O_6$), 5-15 % ferrite phase (~ $Ca_2AlFeO_5$), and 3-4 % gypsum ($CaSO_4 \cdot 2H_2O$).[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]

$$Ca_3SiO_5 + x\,H_2O \longrightarrow 1.7CaO\text{-}1.0SiO_2\text{-}(x - 1.3)H_2O + 1.3\ Ca(OH)_2 \qquad (13)$$

$$(C_3S + H \longrightarrow 1.7C\text{-}1.0S\text{-}(x - 1.3)H + 1.3\ CH)$$

(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]

$$\beta\text{-}Ca_2SiO_4 + x\,H_2O \longrightarrow 1.7CaO\text{-}1.0SiO_2\text{-}(x - 0.3)H_2O + 0.3\ Ca(OH)_2 \qquad (14)$$

($\beta$-$C_2S$ + H $\longrightarrow$ 1.7C-1.0S-(x - 0.3)H + 0.3 CH)

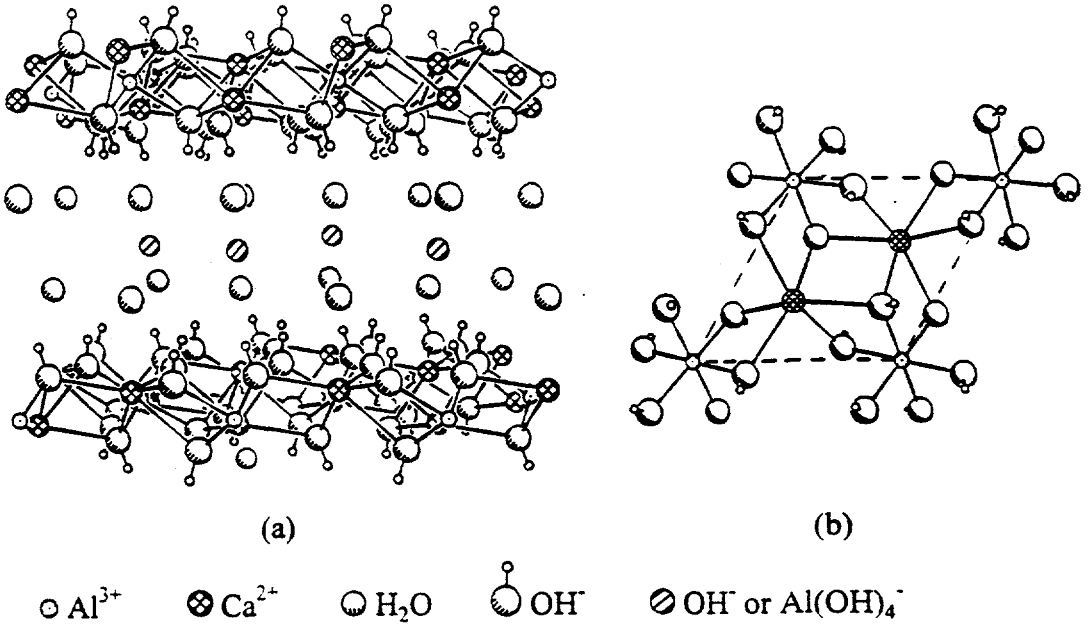
The C-S-H formed by the hydration of the alite and belite in cement apparently has a structure which is similar to but less ordered than the structure of the C-S-H formed by the hydration of $Ca_3SiO_5$ and $\beta$-$Ca_2SiO_4$. It does not contain appreciable amounts of $Al^{3+}$ and $Fe^{3+}$, but it 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 $Ca_3Al_2O_6$. 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 $Ca_3Al_2O_6$. For clarity, it is helpful to consider the hydration of $Ca_3Al_2O_6$ and mixtures of it with $CaSO_4 \cdot 2H_2O$ and $Ca(OH)_2$ before considering the hydration of the aluminate phase itself.

**Hydration of $Ca_3Al_2O_6$.** The hydration of $Ca_3Al_2O_6$ is much more rapid than that of $Ca_3SiO_5$. Within 30 minutes it gives a mixture of $[Ca_2Al(OH)_6](OH) \cdot 6H_2O$ and $[Ca_2Al(OH)_6][Al(OH)_4] \cdot 3H_2O$, Figure 12:

$$2\ Ca_3Al_2O_6 + 27\ H_2O \longrightarrow$$



(a) (b)

**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.

$$[Ca_2Al(OH)_6](OH){\cdot}6H_2O + [Ca_2Al(OH)_6][Al(OH)_4]{\cdot}3H_2O \qquad (15)$$

$$(2\ C_3A + 27\ H \longrightarrow C_4AH_{19} + C_2AH_8)$$

These compounds then interact to give $Ca_3Al_2(O_4H_4)_3$, hydrogarnet, Figure 13, within 24 to 48 hours:[27]

$$2[Ca_2Al(OH)_6](OH){\cdot}6H_2O + [Ca_2Al(OH)_6][Al(OH)_4]{\cdot}3H_2O \longrightarrow 2Ca_3Al_2(O_4H_4)_3 \quad (16)$$

$$(C_4AH_{19} + C_2AH_8 \longrightarrow 2\ C_3AH_6)$$

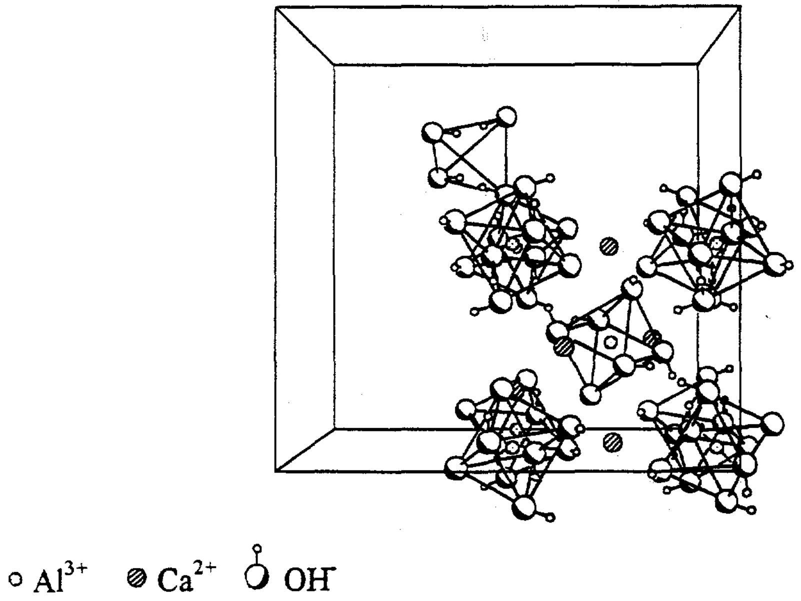


**Figure 13**. Portion of unit cell of $Ca_3Al_2(O_4H_4)_3$, hydrogarnet, showing $Al(OH)_6$ and $(OH)_4$ units in structure.

**Hydration of $Ca_3Al_2O_6$-$CaSO_4$ and $Ca_3Al_2O_6$-$Ca(OH)_2$ Mixtures.** The hydration of a 1:3 mixture of $Ca_3Al_2O_6$ and $CaSO_4 \cdot 2H_2O$ is rapid. In about 10-12 minutes it gives $[Ca_3Al(OH)_6 \cdot 12H_2O]_2(SO_4)_3 \cdot 2H_2O$, trisulfoaluminate hydrate, or the $Al^{3+}$ and $SO_4^{2-}$ end-member of the ettringite family,[27] Figure 14:

$$Ca_3Al_2O_6 + 3\ CaSO_4 \cdot 2H_2O + 26\ H_2O \longrightarrow [Ca_3Al(OH)_6 \cdot 12H_2O]_2(SO_4)_3 \cdot 2H_2O \quad (16)$$

$$(C_3A + 3\ C\bar{S}H_2 + 26\ H \longrightarrow C_6A\bar{S}_3H_{32})$$

The hydration of a mixture richer in $Ca_3Al_2O_6$ gives trisulfoaluminate hydrate as an intermediate and then this reacts with more $Ca_3Al_2O_6$ to give $[Ca_2Al(OH)_6]_2(SO_4) \cdot 6H_2O$, monosulfoaluminate hydrate,[27] Figure 15:

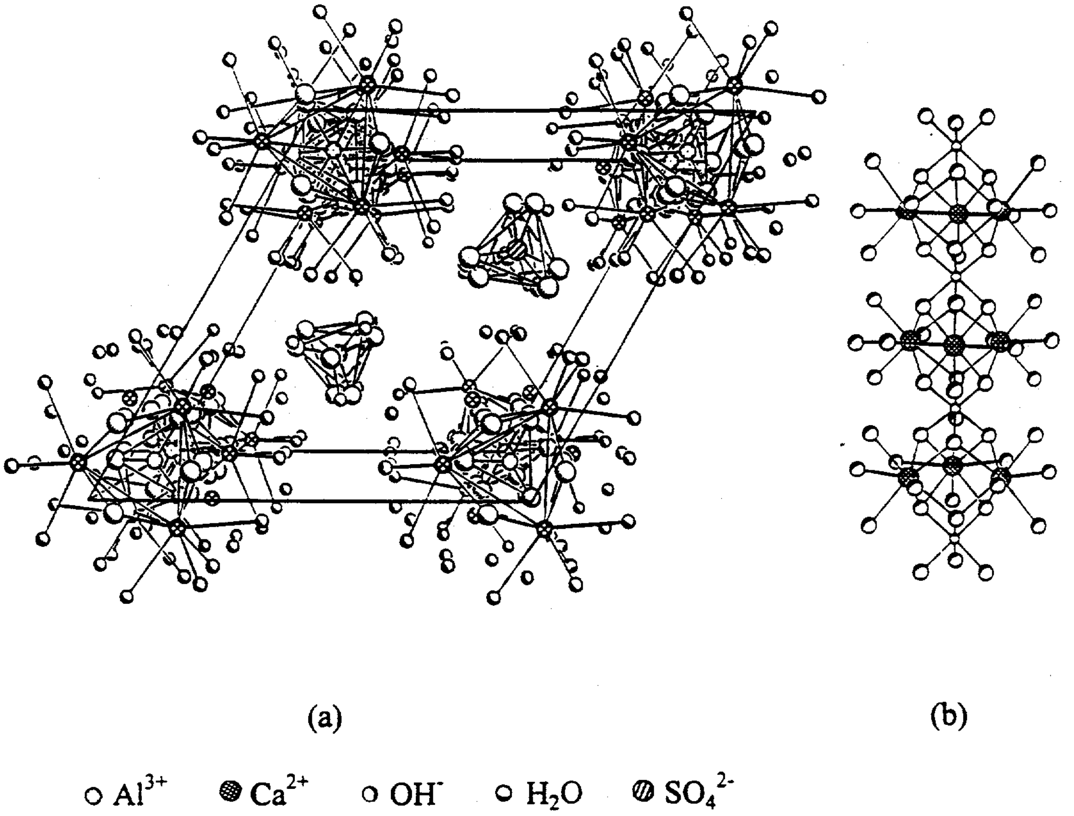


**Figure 14.** (a) Structure of $[Ca_3Al(OH)_6 \cdot 12H_2O]_2(SO_4) \cdot 2H_2O$, trisulfoaluminate hydrate, projected on the <001> showing columns and channels. (b) Structure of $[Ca_3Al(OH)_6 \cdot 12H_2O]^{3+}$ columns.

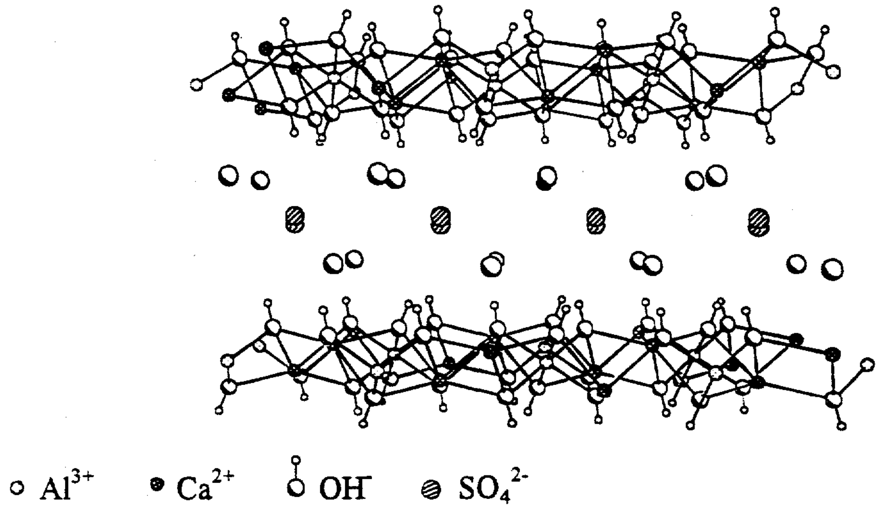


**Figure 15.** Structure of $[Ca_2Al(OH)_6]SO_4 \cdot 6H_2O$, monosulfoaluminate hydrate, showing layers of $[Ca_2Al(OH)_6]^+$ and $H_2O$ and $SO_4^{2-}$ ions between layers.

$$2Ca_3Al_2O_6 + [Ca_3Al(OH)_6\cdot 12H_2O]_2(SO_4)_3\cdot 2H_2O + 4H_2O \longrightarrow 3[Ca_2Al(OH)_6]_2(SO_4)\cdot 6H_2O \quad (17)$$

$$(2C_3A + C_6A\bar{S}_3H_{32} + 4H \longrightarrow 3C_4A\bar{S}H_{12})$$

Thus a 1:1 ratio of $Ca_3Al_2O_6$ and $CaSO_4\cdot 2H_2O$ ultimately gives monosulfoaluminate hydrate:[27]

$$Ca_3Al_2O_6 + CaSO_4\cdot 2H_2O + 10H_2O \longrightarrow [Ca_2Al(OH)_6]_2(SO_4)\cdot 6H_2O \quad (18)$$

$$(C_3A + C\bar{S}H_2 + 10H \longrightarrow C_4A\bar{S}H_{12})$$

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 $Ca_3Al_2O_6$ and $Ca(OH)_2$ gives the hydoxy analogue of monosulfoaluminate hydrate, $[Ca_2Al(OH)_6](OH)\cdot 3H_2O$:[27]

$$Ca_3Al_2O_6 + Ca(OH)_2 + 12H_2O \longrightarrow 2[Ca_2Al(OH)_6](OH)\cdot 3H_2O \quad (19)$$

$$(C_3A + CH + 12H \longrightarrow C_4AH_{13})$$

**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,$CaSO_4\cdot 2H_2O$, and $CO_2$ (from the atmosphere). The main product of the hydration is $[Ca_2(Al, Fe)(OH)_6]_2(SO_4, CO_3, 2OH)\cdot 6H_2O$, 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]

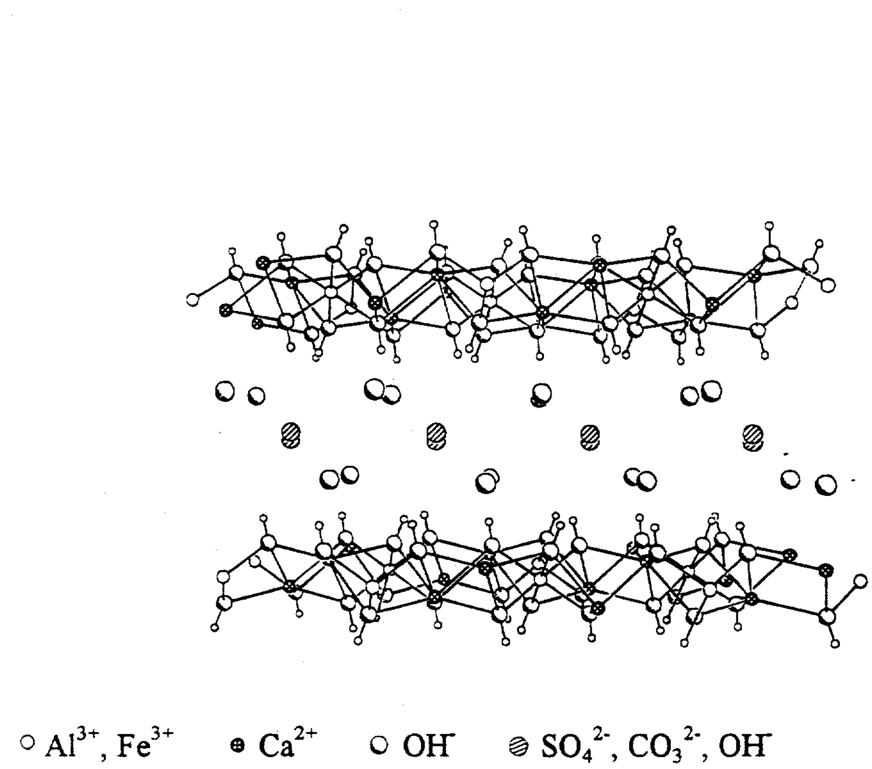


**Figure 16.** Schematic structure of $[Ca_2(Al, Fe)(OH)_6]_2(SO_4, CO_3, 2OH)\cdot 6H_2O$ orAFm.

The hydration of the mixture of the aluminate phase, ferrite phase, and $CaSO_4\cdot 2H_2O$ in cement together with $CO_3^{2-}$ also can lead to $[Ca_3(Al,Fe)(OH)_6\cdot 12H_2O]_2(SO_4, CO_3, 2OH)_3\cdot 2H_2O$ 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]

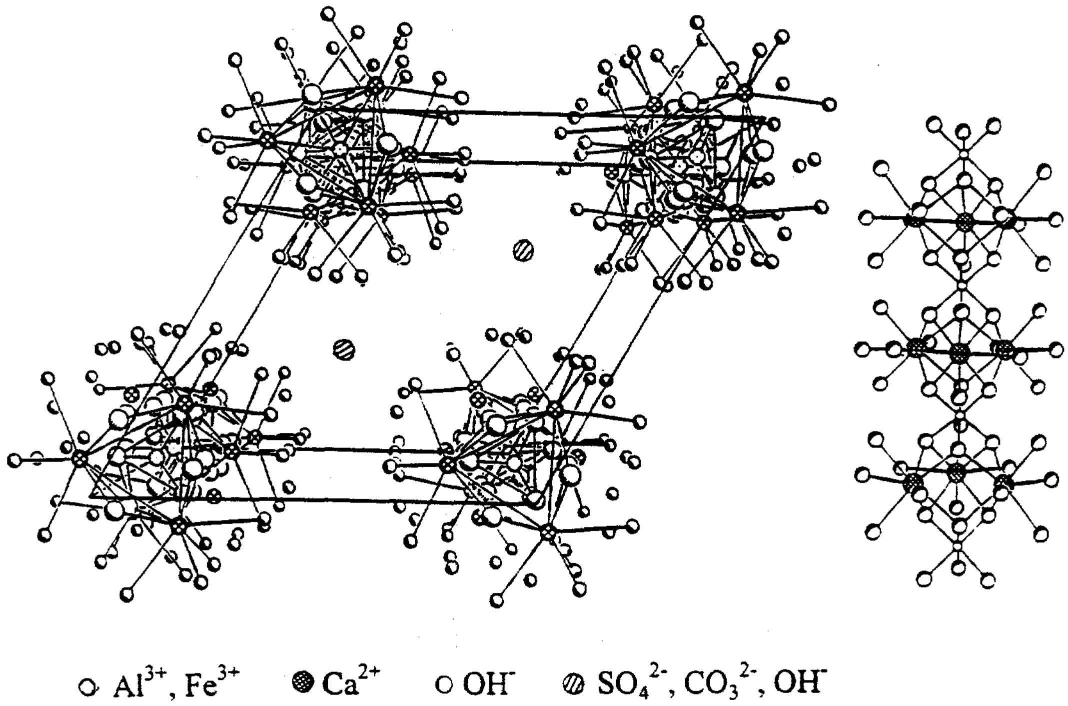


**Figure 17.** Schematic structure of $[Ca_3(Al,Fe)(OH)_6 \cdot 12H_2O]_2(SO_4, CO_3, 2OH)_3 \cdot 2H_2O$ or AFt.

### Ferrite Phase

The ferrite phase in cement is actually a solid solution with a composition between $Ca_2Fe_2O_5$ and $Ca_6Al_4Fe_2O_{15}$. The formula often used to represent this phase, $Ca_2AlFeO_5$, corresponds to an average composition.[24f] Again it is helpful to consider the hydration of the pure phase and mixtures of it with $CaSO_4 \cdot 2H_2O$ before considering the hydration of it in cement.

**Hydration of $Ca_2AlFeO_5$.** Although its rate is slower, the hydration of $Ca_4Al_2Fe_2O_{10}$ is similar to the hydration of the aluminate phase. First

$[Ca_2(Al, Fe)(OH)_6](OH)\cdot 6H_2O$ and $[Ca_2(Al, Fe)(OH)_6][(Al, Fe)(OH)_4]\cdot 3H_2O$ are formed and then $Ca_3(Al, Fe)_2(O_4H_4)_3$ is formed.[55] Possible simplified equations are

$$4Ca_2AlFeO_5 + 38H_2O \longrightarrow 4[Ca_2(Al_{0.5}Fe_{0.5})(OH)_6](OH)\cdot 6H_2O +$$

$$2[Ca_2\,(Al_{0.5}Fe_{0.5})(OH)_6][(Al_{0.5}Fe_{0.5})(OH)_4]\cdot 3H_2O + (Al_{0.5}Fe_{0.5})(OH)_3 \qquad (20)$$

$$(2C_4AF + 38H \longrightarrow C_4(A_{0.5}F_{0.5})H_{19} + 2C_2(A_{0.5}F_{0.5})H_8 + (A_{0.5}F_{0.5})H_3)$$

and

$$2[Ca_2(Al_{0.5}Fe_{0.5})(OH)_6](OH)\cdot 6H_2O + [Ca_2\,(Al_{0.5}Fe_{0.5})(OH)_6][(Al_{0.5}Fe_{0.5})(OH)_4]\cdot 3H_2O$$

$$\longrightarrow 2Ca_3(Al_{0.5}Fe_{0.5})_2(O_4H_4)_3 \qquad (21)$$

$$(C_4(A_{0.5}F_{0.5})H_{19} + C_2(A_{0.5}F_{0.5})H_8 \longrightarrow 2C_3(A_{0.5}F_{0.5})H_6)$$

The structures of $[Ca_2(Al, Fe)(OH)_6](OH)\cdot 6H_2O$ and $[Ca_2(Al, Fe)(OH)_6][(Al, Fe)(OH)_4]\cdot 3H_2O$ are like those of $[Ca_2Al(OH)_6](OH)\cdot 6H_2O$ and $[Ca_2Al(OH)_6][Al(OH)_4]\cdot 3H_2O$ and the structure of $Ca_3(Al, Fe)_2(O_4H_4)_3$ is like that of $Ca_3Al_2(O_4H_4)_3$.

**Hydration of $Ca_4Al_2Fe_2O_{10}$-$CaSO_4\cdot 2H_2O$ Mixtures.** The hydration of 1:1 mixture $Ca_4Al_2Fe_2O_{10}$ and $Ca(SO_4)_2\cdot 2H_2O$ is similar to that of a 1:1 mixture of $Ca_3Al_2O_6$ and $Ca(SO_4)_2\cdot 2H_2O$. First it gives AFt and then it gives AFm, both apparently are mixed with some $(Al, Fe)(OH)_3$ gel which may contain Ca.[56] Possible simplified equations for this are

$$3(CaAlFeO_5)_2 + 12CaSO_4\cdot 2H_2O + 106H_2O \longrightarrow$$

$$4[Ca_3(Al_{0.5}Fe_{0.5})(OH)_6\cdot 12H_2O]_2(SO_4)_3\cdot 2H_2O + 4(Al_{0.5}Fe_{0.5})(OH)_3 \qquad (22)$$

$$(3C_4AF + 12C\bar{S}H_2 + 106H \longrightarrow 4C_6(A_{0.5}F_{0.5})\,\bar{S}_3{\cdot}H_{31} + 2(A_{0.5}F_{0.5})H_3)$$

and

$$3(CaAlFeO_5)_2 + 2[Ca_3(Al_{0.5}Fe_{0.5})(OH)_6{\cdot}12H_2O]_2(SO_4)_3{\cdot}2H_2O \longrightarrow$$

$$6[Ca_2(Al_{0.5}Fe_{0.5})(OH)_6]_2(SO_4){\cdot}6H_2O + 4(Al_{0.5}Fe_{0.5})(OH)_3 \qquad (23)$$

$$(3C_4AF + 2C_6(A_{0.5}F_{0.5})\,\bar{S}_3{\cdot}H_{31} + 16H \longrightarrow 6C_4(A_{0.5}F_{0.5})\,\bar{S}H_{12} + 2(A_{0.5}F_{0.5})H_3)$$

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

$$2Ca_2AlFeO_5 + 2Ca(OH)_2 + 6CaSO_4{\cdot}2H_2O + 50H_2O \longrightarrow$$

$$[Ca_3Al_{0.5}Fe_{0.5}(OH)_6{\cdot}12H_2O]_2(SO_4)_3{\cdot}2H_2O \qquad (24)$$

$$(C_4AF + 2CH + 6C\bar{S}H_2 + 50H \longrightarrow 2C_6(A_{0.5}F_{0.5})\,\bar{S}_3H_{32})$$

**Hydration of Ferrite Phase in Cement.** The hydration of the ferrite phase in cement is not yet understood. Probably this phase together with $CaSO_4{\cdot}2H_2O$ 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 $\beta$-$Ca_2SiO_4$ 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). $Ca_3Al_2O_6$ was purchased from CTL and $CaSO_3 \cdot 0.5H_2O$ was purchased from Pfaltz and Bauer (Waterbury, CT) and $CaSO_4 \cdot 2H_2O$ 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 (~60 °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(Å) ($I/I_o$)): 7.92 (9, AFm), 4.90 (100, CH), 3.11 (10, CH), 3.04 (25, CSH), 2.79-2.73 (31, $\beta$-$C_2S$), 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 (~60 °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(Å) ($I/I_o$)): 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 VI, run 6), a mixture of portland cement (type I, 5.00 g), water (50 mL) and $ZrO_2$ 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(Å) ($I/I_o$)): 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(Å) ($I/I_o$)): 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-$SiO_2$ Source Mixtures

**Rapid Hydration of Cement.** In parallel with the work done on the hydration of $Ca_3SiO_5$ and β-$Ca_2SiO_4$, 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 $Ca(OH)_2$. 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 | $SO_2$ Uptake | Ca Util |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Time (h) | Temp (°C) | Media[b] | Agit | CSH (%) | CH (%) | AFm[c] (%) | $C_2SH$ (%) | cem (%) | ($m^2/g$) | (mmol/g) | (%) |
| 1 | cem, $H_2O$ | 1 : 10 | 720 | ~20 | | | 45 | 20 | 25[d] | | 10 | | 3.9 | 35 |
| 2 | cem, $H_2O$ | 1 : 10 | 360 | ~20 | | | 35 | 10 | 25[e, f] | | 30 | | | |
| 3 | cem, $H_2O$ | 1 : 10 | 72 | 100 | | stirring | | 20 | 20[d] | 50 | 10 | | 4.2 | 38 |
| 4 | cem, $H_2O$ | 1 : 10 | 24 | 100 | | stirring | 15 | 15 | 20[d] | 30 | 20 | | | |
| 5 | cem, $H_2O$ | 1 : 10 | 72 | ~20 | $ZrO_2$ | shaking | 45 | 20 | 25[d] | | 10 | 64 | 6.5 | 67 |
| 6 | cem, $H_2O$ | 1 : 10 | 24 | ~20 | $ZrO_2$ | shaking | 30 | 15 | 25[d] | | 30 | | | |
| 7 | cem, $H_2O$ | 1 : 10 | 24 | ~20 | $ZrO_2$ | stirring | 45 | 20 | 25[d] | | 10 | 62 | | |
| 8 | cem, $H_2O$ | 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 Aeea | $SO_2$ Uptake | Ca Util |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Time (h) | Temp (ºC) | Media[b] | Agit | CSH (%) | CH (%) | AFmc[c] (%) | $C_2SH$ (%) | cem (%) | ($m^2$/g) | (mmol/g) | (%) |
| 9 | cem, $H_2O$ | 1 : 10 | 5 | 80 | $ZrO_2$ | stirring | 45 | 20 | 25[d] | | 10 | 63 | 6.4 | 63 |
| 10 | cem, $H_2O$ | 1 : 10 | 3 | 100 | $ZrO_2$ | stirring | 45 | 20 | 25[d] | | 10 | 85 | 6.4 | 63 |

[a] CSH, $CaO\text{-}SiO_2\text{-}H_2O$; CH, $Ca(OH)_2$; AFm, $[Ca_2(Al,Fe)(OH)_6]_2(SO_4,CO_3,2OH)\cdot 6H_2O$ or a related amorphous phase; $C_2SH$, $\alpha\text{-}Ca_2(SiO_3OH)(OH)$; cem, mainly unreacted belite. [b] 2-mm diameter Mg-stabilized $ZrO_2$ beads. [c] amount inferred from cement composition and literature data. [d] relatively amorphous. [e] probably $[Ca_2Al(OH)_6](OH)\cdot 3H_2O$, $C_4AH_{13}$. [f] relatively ordered.

The use of a 30-day reaction time, an ~20 °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 $[Ca_2(Al, Fe)(OH)_6]_2(SO_4, CO_3, 2OH)\cdot 6H_2O$ 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 ~ 60 µ. 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

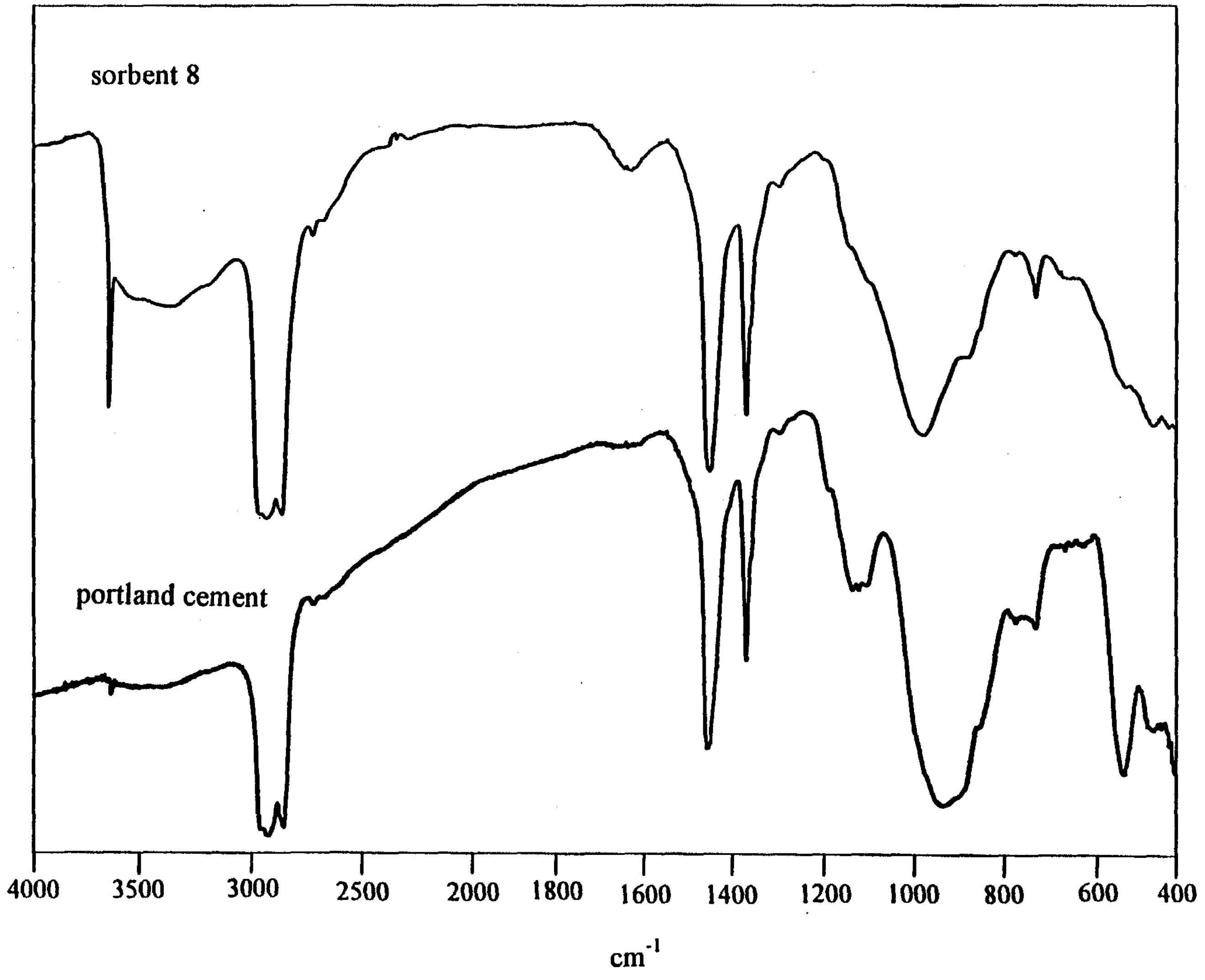


Figure 18. Infrared spectra of sorbent 8, Table VI and portland cement.

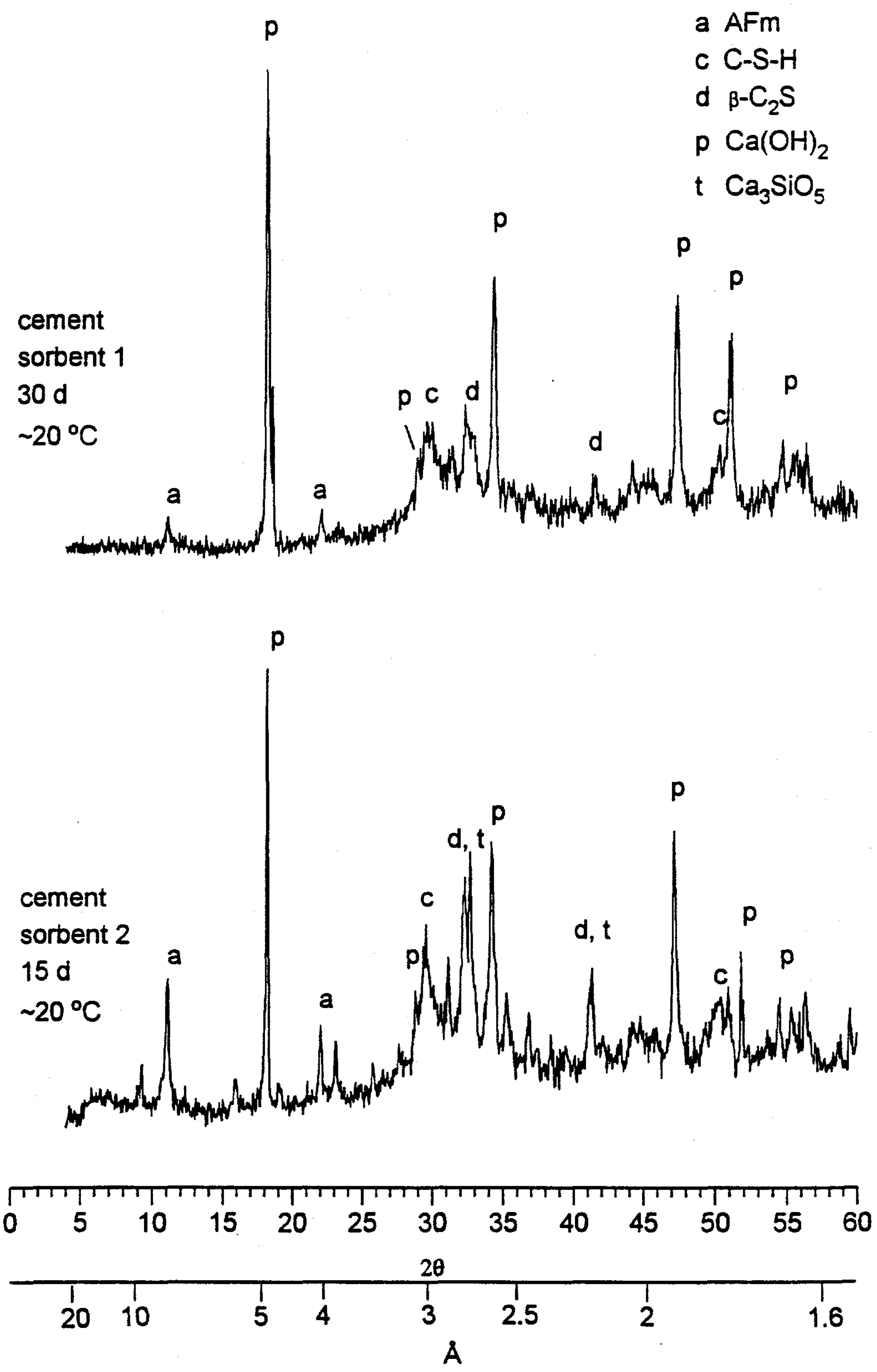


**Figure 19**. X-ray powder diffraction patterns of cement sorbents 1 and 2 , Table VI.

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 $[Ca_2Al(OH)_6](OH)\cdot 3H_2O$. 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 $\alpha$-$Ca_2(SiO_3OH)(OH)$. 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 $\alpha$-$Ca_2(SiO_3OH)(OH)$ 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 $\alpha$-$Ca_2(SiO_3OH)(OH)$, run 4. This result emphasizes the relative stability of $\alpha$-$Ca_2(SiO_3OH)(OH)$ 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 ~20 °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 $[Ca_2Al(OH)_6](OH)\cdot 6H_2O$.

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

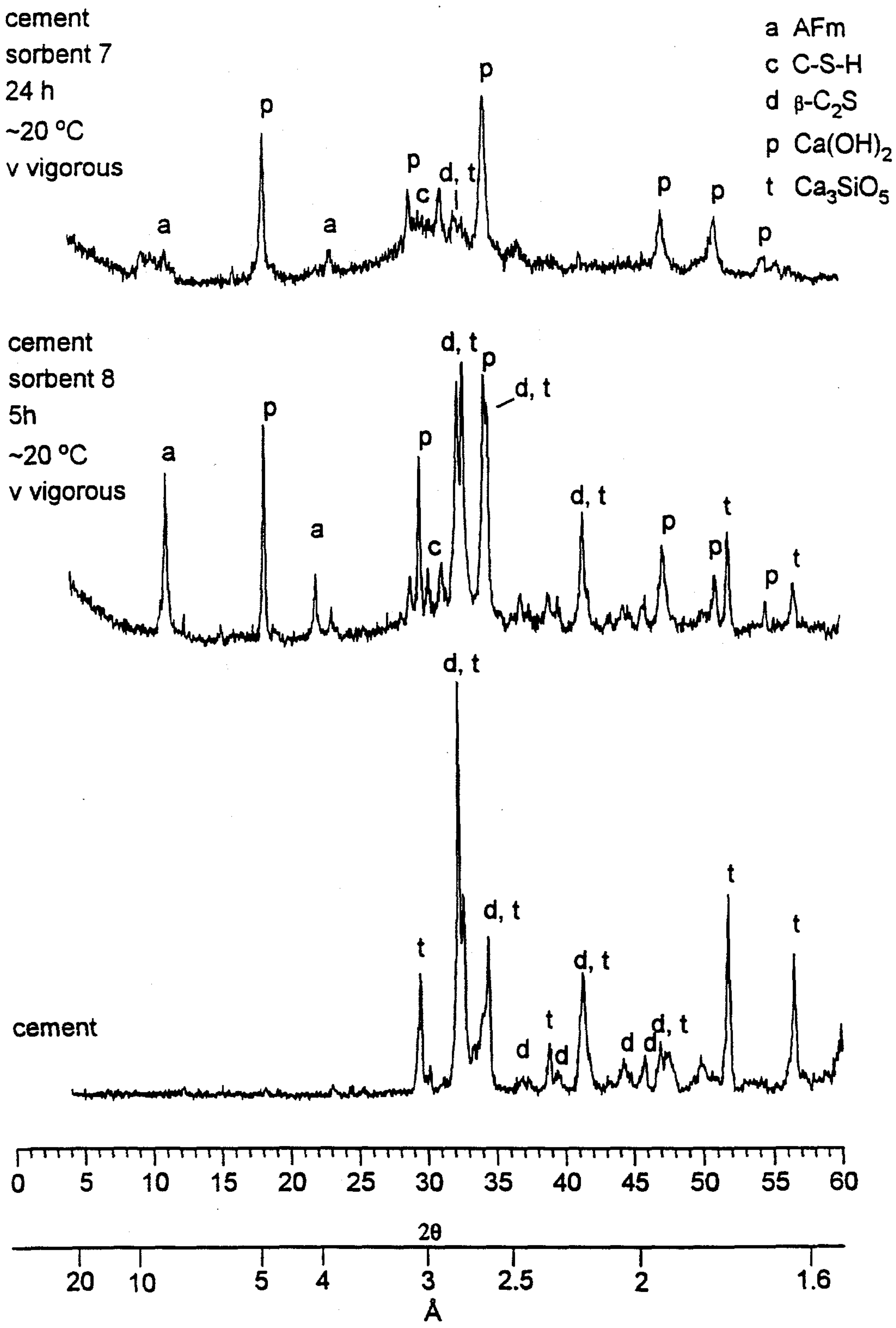


**Figure 20**. X-ray powder diffraction patterns of cement and cement sorbents 7 and 8, Table VI.

amorphous and had a substantial surface area, Figure 21 and Table VI, run 9. The lack of $\alpha$-$Ca_2(SiO_3OH)(OH)$ in this product is significant and shows that if the hydration time is sufficiently short, this silicate is not favored at elevated tempertaures.

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-$SiO_2$ Source Mixtures.** In an extension of the work on the hydration of cement, similar work was carried out on the hydration of cement-$SiO_2$ 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-$SiO_2$ 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 $SiO_2$. The absence of $Ca(OH)_2$ in the product is attributable to the presence of sufficient $SiO_2$ in

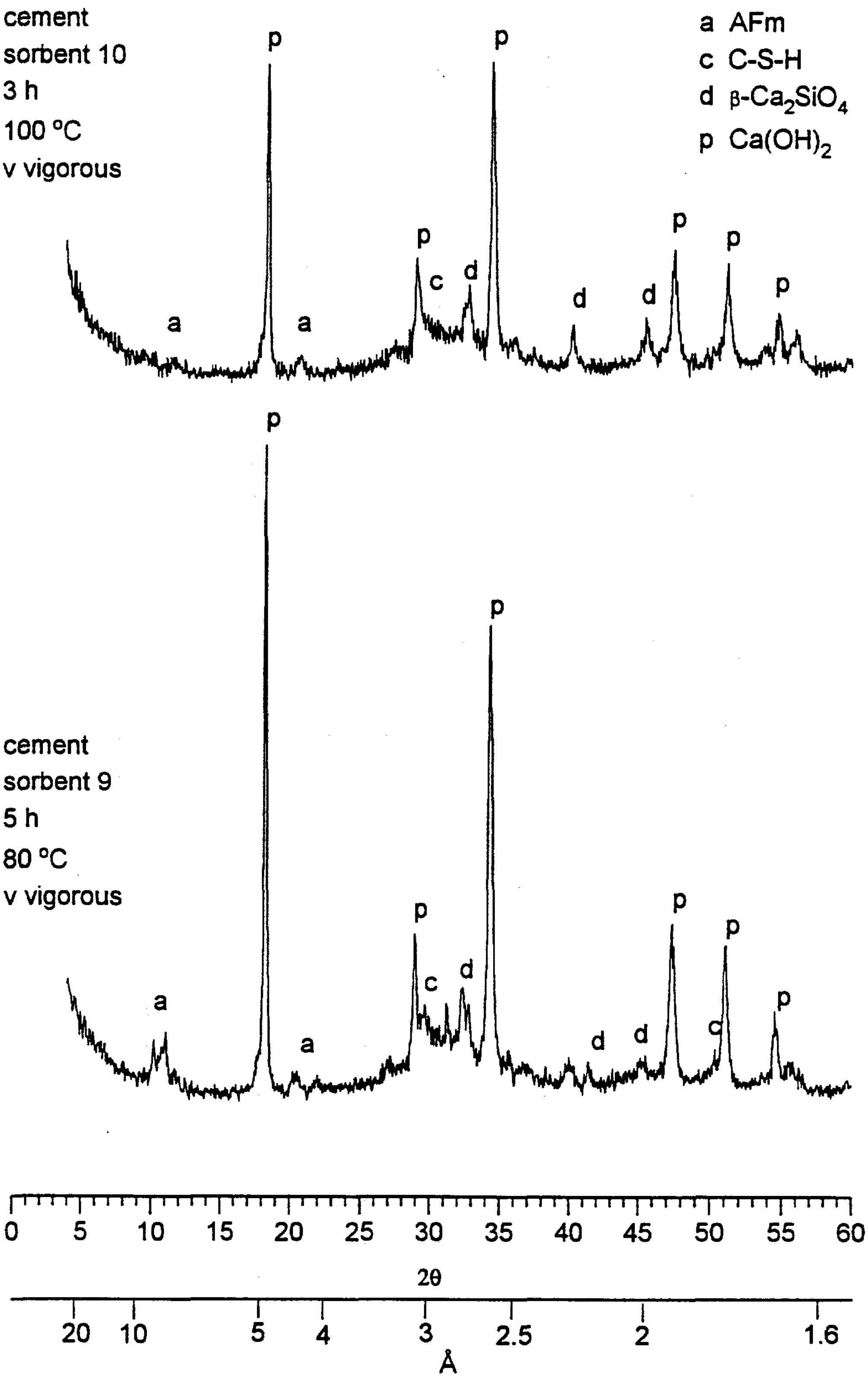


**Figure 21.** X-ray powder diffraction patterns of cement sorbents 9 and 10, Table VI.

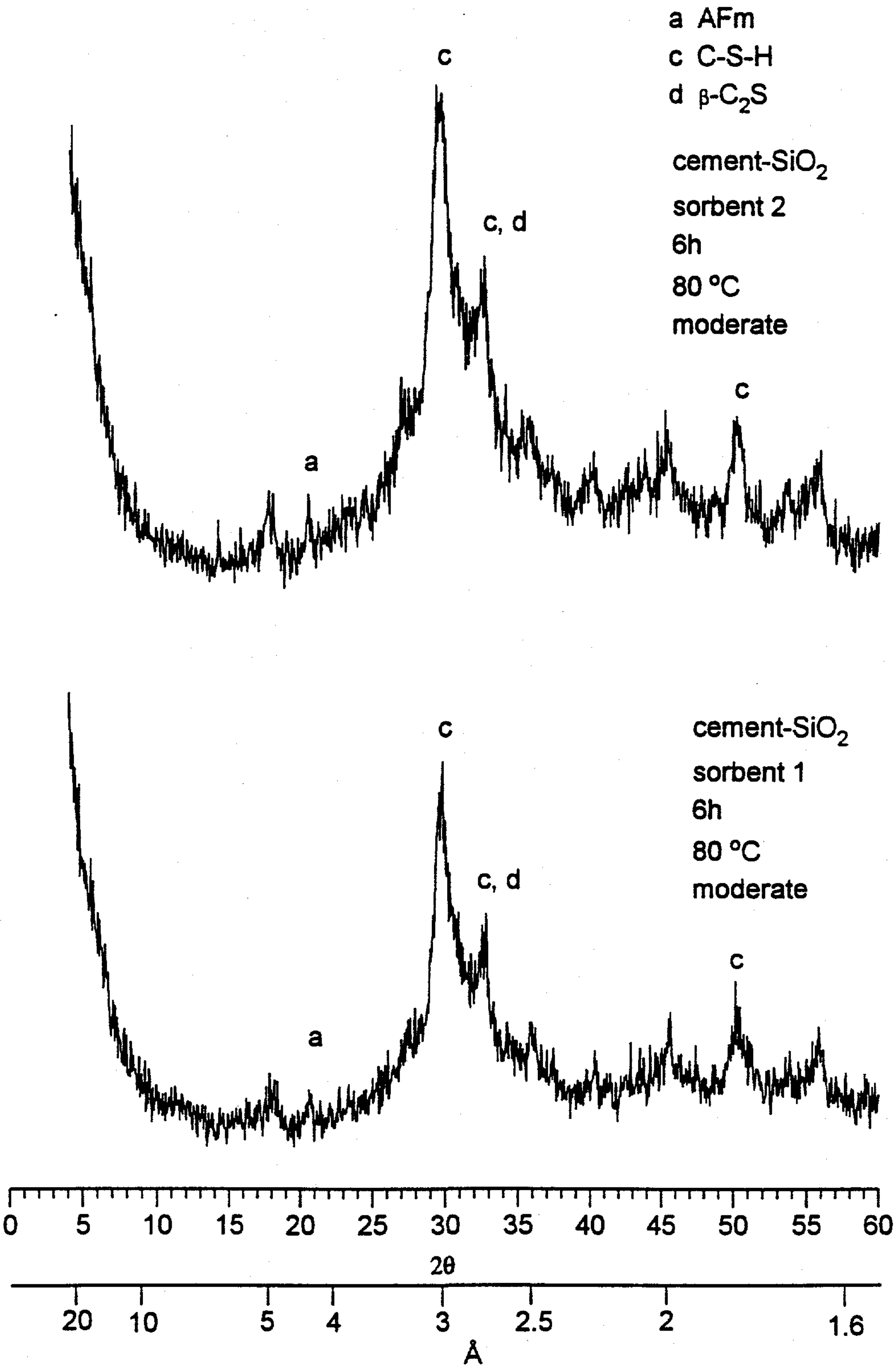


**Figure 22**. X-ray powder diffraction patterns of cement-$SiO_2$ sorbents 1 and 2, Table VII.

**Table VII.** Synthesis and Properties of Hydrated Cement-$SiO_2$ Sorbents

|  | Reactants | Wt. Ratio | Conditions |  |  |  | Estimated Composition[a] |  |  |  | BET Area | $SO_2$ Uptake | Ca Util |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | Time ( h ) | Temp (°C) | Media | Agit | CSH | CH | AFm[b,c] | cem | ($m^2/g$) | (mmol/g) | (%) |
| 1 | cem, $SiO_2^{d}$, $H_2O$ | 1 : 0.3 : 13 | 6 | 80 | $ZrO_2^{e}$ | stirring | 70 |  | $15^{f}$ | 15 | 102 | 7.4 | 86 |
| 2 | cem, diatomite, $H_2O$ | 1 : 0.3 : 13 | 6 | 80 | $ZrO_2^{g}$ | stirring | 70 |  | $15^{f}$ | 15 | 211 | 6.4 | 79 |
| 3 | cem, diatomite, $H_2O$ | 1 : 0.3 : 13 | 6 | 100 | $ZrO_2^{e}$ | stirring | 70 |  | $15^{f}$ | 15 | 215 | 6.3 | 77 |
| 4 | cem, pumice, $H_2O$ | 1 : 0.3 : 13 | 8 | 80 | $ZrO_2^{g}$ | stirring | 70 |  | $15^{f}$ | 15 | 154 | 6.5 | 73 |
| 5 | cem, perlite, $H_2O$ | 1 : 0.3 : 13 | 7 | 80 | $ZrO_2^{g}$ | stirrin | 55 | 15 | $15^{f}$ | 15 | 174 | 6.1 | 71 |

[a] CSH, $CaO\text{-}SiO_2\text{-}H_2O$; CH, $Ca(OH)_2$; AFm, $[Ca_2(Al,Fe)(OH)_6]_2(SO_4,CO_3,OH)\cdot 6H_2O$ 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 $SiO_2$ fume. [e] 2-mm diameter Mg-stabilized $ZrO_2$ beads. [f] relatively amorphous. [g] 0.6-0.8 mm diameter Mg-stabilized $ZrO_2$ 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 $Ca(OH)_2$ in the product is attributable to the low reactivity of perlite.

### $SO_2$ Uptake of Sorbents

**Hydrated Cement Sorbents.** The $SO_2$ 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 $Ca(OH)_2$ crystals and hence the unavailability of its $Ca(OH)_2$. The low value of sorbent 3 is consistent with the presence of considerable $\alpha$-$Ca_2(SiO_3OH)(OH)$ in it. For Sorbents 5, 9 and 10, the high values fit with the composition and high surface areas of these sorbents.

**Hydrated Cement-$SiO_2$ Source Sorbents.** The $SO_2$ uptake and Ca utilization values of the hydrated cement-$SiO_2$ 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, $Ca(OH)_2$ 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-$SiO_2$ 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. CEMENT CHEMIST'S NOTATION

| Symbol | Equivalent |
|---|---|
| A | $Al_2O_3$ |
| C | CaO |
| $\overline{C}$ | $CO_2$ |
| F | $Fe_2O_3$ |
| S | $SiO_2$ |
| $\overline{S}$ | $SO_3$ |

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