55

STUDIES ON
TOBERMORITE-LIKE
CALCIUM SILICATE HYDRATES

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by
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Technical Paper

STUDIES ON TOBERMORITE-LIKE CALCIUM SILICATE HYDRATES

TO: K. B. Woods, Director
Joint Highway Research Project

FROM: H. L. Michael, Assistant Director
Joint Highway Research Project

October 31, 1963

File: 4-6-9
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The technical paper attached entitled "Studies on Tobermorite-Like Calcium Silicate Hydrates" by Sidney Diamond, W. L. Dolch, and Joe L. White is submitted for approval of presentation and publication. The presentation is proposed to the Annual Meeting of the Highway Research Board in Washington D.C. in January 1964. Publication would be by that organization.

The paper is a part of the investigation known as "Calcium Silicate Hydrates" which was conducted by the Joint Highway Research Project utilizing HPS funds. The material is taken from the Final Report on this project which has been submitted for review and acceptance. In the event that approval for presentation has not been received by the date of presentation, the presentation will include a statement that review of the paper has not been made by the ISHC or the BPR. This is the second paper which has been prepared from this research and which has been submitted for review. A third paper is contemplated and will be submitted upon completion of it.

The paper is presented to the Board for approval of presentation and publication.

Respectfully submitted,

H. L. Michael

H. L. Michael, Secretary

HLM:bc

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Technical Paper

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ABSTRACT

Parallel studies were carried out on certain characteristics of CSH(I) synthesized at room temperature and on CSH(gel) produced by paste or bottle hydration of β -C₂S, C₃S and alite. Instrumental methods employed included x-ray diffraction, DTA, infrared spectroscopy, and electron microscopy. Surface areas of the CSH(I) samples were measured by water vapor adsorption and heats of adsorption were calculated. Both CSH(I) and CSH(gel) were shown to have a negative surface charge in the absence of Ca(OH)₂. A method was devised to measure the cation exchange capacities of these materials, and the exchange capacities measured were the order of 5 -20 meq/100g.

The evidence suggests that CSH(gel) is a single, well-defined phase regardless of starting material or mode of hydration, and that CSH(I) has well-defined properties regardless of variations in composition. The two phases are difficult to distinguish by x-ray methods, but can be differentiated by the intensity of the high-temperature exotherm on DTA, by particle shape as revealed by electron-microscopic observation, and by the appearance of the main Si-O vibration band region in infrared spectroscopy.

INTRODUCTION

The poorly-crystallized calcium silicate hydrates that resemble the well-crystallized mineral tobermorite comprise a group of materials of importance to cement chemists, and are also of theoretical interest. The present work is an attempt to characterize in detail some of the

properties of two of these phases, CSH(I) and CSH(gel). The latter is also known as "tobermorite(G)." The approach employed features the study of a number of relevant properties of a suite of what is hoped are representative materials of each kind, prepared in several different ways. Methods of study include x-ray diffraction, DTA, electron microscopy, infrared spectroscopy, water vapor-adsorption and several others. Somewhat parallel studies were carried out with certain synthetic well-crystallized tobermorites primarily to determine the effects of lattice substitution; these will be reported elsewhere.

Reference to much of the published work in this field is made difficult by the conflicting terminology used in designating the individual phases, and by failure of some workers consistently to distinguish between tobermorite itself and the several poorly-crystallized phases now recognized.

A brief summary of some of the known properties of these materials will be presented before proceeding to the details of the present study. Reviews by Taylor (1) and by Brunauer and Greenberg (2) contain considerable information.

CSH(I) is a poorly-crystallized synthetic calcium silicate hydrate distinct from, but related to, tobermorite. It can be prepared by reaction at room temperature, or as a transient phase under hydrothermal conditions (3). The structure is presumably a layer structure related to that of tobermorite, but details are not known with certainty. X-ray diffraction patterns display peaks at the positions of the strong (hk0) lines of tobermorite; a diffuse basal spacing is sometimes observed in the range from about 10Å to about 14Å, depending on the state of hydration and on the Ca:Si ratio of the particular material (1). CSH(I) specimens showing similar x-ray patterns have been prepared in

which the Ca:Si ratio may vary from 0.8 to about 1.5. The DTA pattern of CSH(I) is characterized by a strong, sharp high-temperature exothermic peak at about 850-900°C (4). Electron microscopy reveals a particle morphology generally described as consisting of crinkled or crumpled foils; the foils are usually only a few unit layers in thickness (5, 6).

CSH(gel) is produced by paste or bottle hydration of C_3S , or by paste or ball-mill hydration of β - C_2S , under room-temperature conditions (2). X-ray diffraction shows only three peaks, corresponding to the positions of the strongest (hk0) lines of tobermorite; basal spacings are not usually observed. The detailed structure is unknown, but it is thought to be related to that of tobermorite. This is a comparatively high-lime phase with Ca:Si ratio as high as 1.5, and possibly as high as 1.7. CSH(gel) is usually considered to be mostly straight, comparatively long fibers, the fibers themselves being composed of rolled up sheets. An adequate DTA pattern for a pure CSH(gel) phase has not previously been published, although partial information is available (2).

Bottle hydration of β - C_2S is said to give rise to a distinct phase called CSH(II) (7), which may also be formed on extended reaction of C_3S in supersaturated lime solution (8), as an initial product in hydrothermal reaction (3) and, reportedly, by reaction of calcium glycerate solution with silica gel (9). CSH(II) is a lime-rich phase with Ca:Si ratio of 1.5-2.0; thus its composition overlaps that of CSH(gel). In contrast to the latter, an x-ray basal spacing of about 10Å is generally recorded (1). It has been suggested that this phase can be identified among calcium silicate hydrates by an x-ray peak at 1.56Å (10). Again, the detailed structure is unknown. The morphology

is fibrous; sometimes cigar-shaped bundles of fibers of distinctive appearance are observed (5, 7). The DTA pattern is marked by an exothermic bulge at intermediate temperatures and by a relatively small high-temperature peak in the 850°C region (4).

PREPARATION OF SAMPLES

CSH(I)

Seven samples of CSH(I) were prepared by several methods, all of which involved reactions at room temperature. Five of these were made by double decomposition reactions, and two were made by direct synthesis from lime and silica.

Four samples were prepared in the same general manner, in which solutions of sodium silicate and a calcium salt were poured simultaneously into a third container and vigorously stirred, the calcium silicate hydrate precipitating as large white flocs. The sodium silicate used was 0.5 M in each instance; the calcium salt solution used was 0.5 M CaCl_2 in one sample, 0.5 M $\text{Ca}(\text{NO}_3)_2$ in the others. The molar ratios of Ca to Si were 1.0 for the sample prepared with CaCl_2 and one of the samples made with $\text{Ca}(\text{NO}_3)_2$, and 1.5 and 2.0 respectively for the other two samples made with $\text{Ca}(\text{NO}_3)_2$. After precipitation the products were diluted with distilled water, filtered over suction, washed several times, first with water, then with acetone, and finally with ether, and then dried at 110°C.

A fifth sample was prepared by a more elaborate procedure, devised in an effort to promote microscopic homogeneity. Two 10-ml Luer-lock syringes were mounted obliquely to each other with their tips almost touching, so that when the two syringes were simultaneously depressed the two fine streams produced were intimately mixed and the combined

droplets produced would fall into a flask mounted below the syringes. The contents of the flask were stirred continuously. Separate reservoirs were attached to the two syringes so that they could be repeatedly refilled without disturbing the arrangement. Two hundred ml each of solutions of sodium silicate and calcium nitrate were loaded into the respective reservoirs and mixed by simultaneously depressing the syringes, reloading, and repeating the process. The concentrations of the solutions were adjusted to yield a Ca:Si molar ratio of 3.5 to 1, in order to get a high-lime product. After all the solutions had been combined, the precipitated material was filtered and washed exhaustively, this time starting with saturated calcium hydroxide solution. The washing was continued using a water-acetone mixture, acetone, and finally ether, and then the washed sample was dried at 110°C under vacuum.

Two samples were prepared by direct reaction of a concentrated silica sol (Nalco-Ag 10-22, National Aluminate Company) with reagent-grade $\text{Ca}(\text{OH})_2$. The first preparation was made by direct addition of the reagents in 1:1 molar proportion. The resulting suspension was diluted with distilled water and transferred to a polyethylene bottle. This was rotated on a roller mill for two days, then allowed to stand undisturbed for three weeks. The aged precipitate was then filtered, the initially cloudy filtrate being recycled until the effluent solution was clear. The pH of the filtrate was 10.6, suggesting that all the free $\text{Ca}(\text{OH})_2$ had reacted; consequently the sample was washed once with water and dried. A second preparation was made in the same way except that a Ca:Si ratio of 2:1 was used; here the pH of the recycled and clarified filtrate was 12.5, indicating that unreacted $\text{Ca}(\text{OH})_2$ was

present. The product was washed with water until the pH dropped below 12.3 and x-ray examination disclosed the absence of crystalline $\text{Ca}(\text{OH})_2$. After one additional wash the sample was dried and stored.

For discussion purposes these samples are designated CSH(I)-1 through CSH(I)-7, respectively. Chemical analyses were carried out on each of them by standard methods and the conventional compositional formulae determined. These are given in Table 1, along with information on preparatory methods. Considering that the mole ratio of starting mixtures varied from 1:1 to 3.5:1, the fact that the observed Ca:Si ratios of the five samples made by double decomposition were all so close to 1 is somewhat unexpected. In contrast, the CSH(I)-7 sample, prepared by direct synthesis and aged prior to washing and drying, had a Ca:Si ratio of almost 1.6:1. Despite the fact that this ratio is slightly higher than the upper limit normally ascribed to CSH(I), this sample appears to be CSH(I) rather than CSH(II), as will be made clear later.

CSH(gel)

CSH(gel) samples were prepared by hydration of $\beta\text{-C}_2\text{S}$, C_3S and alite. Well-characterized samples of these cement compounds were kindly contributed by D. L. Kantro and L. E. Copeland of the Portland Cement Association, and a second sample of alite of somewhat different composition was donated by A. Klein of the University of California, Berkeley. Paste hydration of the $\beta\text{-C}_2\text{S}$ and C_3S samples was carried out at 23°C using a water:solids ratio of 0.7, and the hydration was allowed to proceed for a period of seven months. Bottle hydration at the same temperature was carried out in polyethylene bottles rotated on a wheel at about 30 rpm; in this case the water:solids ratio was

9.0. Bottle hydration of the β -C₂S and C₃S samples was allowed to proceed for six months, and of the alites for four months. In all experiments freshly-boiled distilled water that had been cooled to below room temperature was used, and the containers were sealed against carbon dioxide penetration.

The designations for the specific samples to be discussed in this paper are given in Table 2. In addition to the samples listed, bottle hydration products for an additional sample of C₃S and of alite were prepared and examined, but the results were essentially identical to those discussed. The bottle hydration of C₃S and of alite specimens yielded a hydration product apparently similar in all significant respects to the other hydration products of the cement minerals, and these products are considered to be CSH(gel) in this report.

CSH(II)

Several attempts were made to prepare CSH(II) by the synthesis described by Toropov et. al. (9). CaO from freshly calcined CaCO₃ was mixed with silica gel, using a Ca:Si ratio of 2:1. The mixture was ground under several drops of glycerol, as described by these authors, placed in a flask with the specified amount of hot, dried glycerol, and stirred continuously while being heated over a hot plate. Toropov et. al. reported that their mixture began to froth at 180-185°C and continued to froth for several hours until the liquid became clear. No such action occurred with our material despite extended heating, and after several trials the attempted synthesis was abandoned.

X-RAY DIFFRACTION

The dried and powdered samples were examined by x-ray diffraction. A General Electric XRD-5A instrument employing nickel-filtered copper radiation was used. Samples were prepared as randomly oriented powder specimens by a slight modification of the method of McGreery (12).

X-ray diffractometer traces for all seven CSH(I) samples are given in Figure 1. Five of the seven, CSH(I)-3 through CSH(I)-7, are remarkably alike, and are typical CSH(I) patterns. All have the strong main peak at around 3.05A, which characterizes tobermorite-like calcium silicate hydrates, and weak peaks at about 2.78A and 1.81A. Faint peaks are noticeable at 1.66A and 3.25A for most of the samples. No peak occurs at or near 1.56A, which would characterize the phase CSH(II), even for the high-lime sample CSH(I)-7. It is sometimes loosely stated that CSH(I) exhibits the three strongest peaks of tobermorite. Well-crystallized tobermorite has a peak at 2.97A (the (222) reflection) that is always greater in tobermorite than the 2.8A and 1.8A peaks, but there is no evidence for the former peak in the CSH(I) patterns. Furthermore no basal peaks are observed. This suggests that the present material is disordered in the c-axis direction, the peaks available being all reflections from planes of atoms entirely within the unit layer.

One sample, CSH(I)-2, seems to be essentially amorphous to x-rays; however, the broad general diffraction in the 3 A region may indicate some short-range order.

The pattern for CSH(I)-1 is unexplained. Originally, diffraction runs made shortly after preparation of this sample showed a pattern

similar to the other weakly crystalline CSH(I) samples. However, reexamination after storage for approximately a year yielded a changed pattern as shown in the figure. The new peaks (starred in the figure) occur at 3.56Å, 3.27Å, 2.72Å, 2.05Å, and 1.91Å. The pattern resembles that of xonotlite, as given by Heller and Taylor (10), but observation of the infrared spectrum suggests that that compound is probably not present in appreciable amount.

Attempts were made to obtain estimates of the basal spacings of CSH(I) preparations by use of oriented aggregate specimens prepared by sedimentation after ultrasonic dispersion treatments, the sedimentation onto glass slides being carried out in vacuo over ascarite, to prevent carbonation. The results were disappointing. Broad, shallow peaks in the 10-14Å region were observed, but peak positions were indefinite and reproducibility was poor. The difficulty was not due to the existence of a random collection of mixed-layer hydration states in the material, since oven-drying did not improve the patterns. It was apparent that dispersion to primary particles was not attained, and that the particles settling on the glass were themselves aggregates of cemented particles in random crystallographic orientation. In contrast, it was found that well-crystallized synthetic tobermorite dispersed to primary particles spontaneously even without ultrasonic treatment, and deposited films showed excellent orientation.

X-ray diffractometer traces for powder mounts of the CSH(gel) products described in Table 2 are given in Figure 2, in which peaks attributable to the CSH(gel) phase are shaded. It appears that x-ray diffraction is not a particularly fruitful tool for studying the

characteristics of the CSH (gel) phase in hydrating cement mineral systems, since, in general, the calcium silicate hydrate peaks are even broader and less intense than those of the CSH(I) preparations.

The pattern for the paste-hydrated β -C₂S (CSH(gel)P-1) shows that a relatively large amount of unreacted β -C₂S remains and only small peaks for calcium hydroxide are observed. The paste product derived from C₃S (CSH(gel)P-2) has produced much more Ca(OH)₂, and almost all of the C₃S seems to have reacted. These observations are in accord with expectation.

The four remaining patterns are for bottle-hydrated material. All show strongly enhanced Ca(OH)₂ basal peaks. Much of the lime is present in large, well-formed crystals that orient preferentially despite all efforts to prevent this in the powder sample preparation. β -C₂S seems to hydrate slowly even under the bottle hydration conditions, the pattern for CSH(gel)B-1 showing that a good deal of the original compound is unreacted. The C₃S bottle hydration product (CSH(gel)B-2) and one of the alite products (CSH(gel)B-3) have reacted almost completely, but the other alite, which has a relatively high content of MgO, does not seem to have reacted to as great an extent.

Basal peaks for hydrated cement phases are apparently difficult to obtain (2). Figure 3 is a trace of the C₃S bottle hydration product, prepared as an oriented aggregate on a porous tile mount (12). A 14Å basal spacing with a second order peak at 7Å is clearly visible. Efforts to prepare similar mounts for the other materials were not as successful, the reason for the difficulties being unclear.

PARTICLE MORPHOLOGY

Electron microscopic study of some of these materials was carried out by Dr. John Radavich of Micro-Met Laboratories, Incorporated, using an RCA EMU-3 instrument operated at 50 kvp. The sample preparation procedure used represents a departure from the usual techniques, in that dispersion was achieved using a non-aqueous system without ultrasonic vibration. This technique precluded the usual clumping together of particles that occurs on drying an aqueous suspension and clearly revealed the morphology of the individual particles. Avoidance of artifacts due to the violent disruption of ultrasonic treatment is another advantage.

All the electron micrographs presented in this work were taken at a direct magnification of 4400 x.

Samples CSH(I)-5, 6, and 7 were examined by the electron microscope and typical fields for these CSH(I) preparations are illustrated in Figure 4. CSH(I)-5 (Figure 4A) occurs primarily as extremely thin foils or "snowflakes." A few fields show a greater proportion of thicker, irregularly-shaped aggregates, the margins of which are toothed as if they were composed of fibrous particles joined together, but no individual fibrous particles can be observed. The product gives a distinct strong polycrystalline electron diffraction diagram consisting of three perfectly smooth rings corresponding to the three main CSH(I) peaks noted on x-ray diffraction. CSH(I)-6 occurs in particles having more definite outlines. The individual particles appear to be aggregates of twisted platy material. A few large aggregates occur, such as that shown in Figure 4B; this is identical in appearance to Figure 1 of Kalousek and Prebus (6). CSH(I)-7 (Figure 4C) is similar to CSH(I)-6 except that a larger proportion of the material is in a fine foil-like condition, and the coarser particles seem

to be more definitely platy. The absence of elongated or fibrous particles confirms the assignment of this material as CSH(I) despite its high lime content.

Electron micrographs of paste and of bottle-hydrated C_3S are given in Figure 5. Figure 5A represents a typical field for CSH(gel)P-2, the paste product. Some of the particles can be described as fibers, with the rest more or less equant in appearance; the latter may actually be bundles of fibers, but this is not evident. In addition there are a number of thin sheet-like particles that show no tendency toward rolling up into tubes or fibers. Figure 5B, for CSH(gel)B-2, the bottle product of the C_3S , is different in that the particles seem to be completely fibrous, with a few bundles of undisturbed fibers clearly visible.

Figures 5C and 5D show the product designated CSH(gel)B-1, resulting from the bottle hydration of β - C_2S . According to Copeland and Schulz (7), Brunauer and Greenberg (2), and others, such a preparation commonly yields CSH(II) with a distinctive cigar-shaped fiber bundle morphology and a slightly different x-ray diffraction pattern than CSH(gel). Neither of these criteria is met by the present sample; both morphological and x-ray evidence suggests that CSH(gel), not CSH(II) has formed.

DIFFERENTIAL THERMAL ANALYSIS

Unfortunately, the comparison of DTA results for CSH(I) and CSH(gel) preparations in the present paper is complicated by the fact that two different differential thermal units were used. The CSH(I) products were examined with a self-recording apparatus capable of maintaining a linear rate of temperature increase; $10^{\circ}C$ was used. Through necessity, the CSH(gel) materials were examined with a modified commercial

portable DTA unit (Eberbach Corporation, Ann Arbor, Michigan) which requires manual recording of the temperature differentials, and which does not maintain a linear heating rate. The modification involved replacement of the transite insulating unit supplied with the equipment by a tight-fitting sleeve of commercial heating pipe insulation. As a result of this improved insulation, temperatures in excess of 1000°C could readily be obtained and the heating rate in the high-temperature region was speeded up enough so that the DTA record in this area was useful. The measured heating rate was 58°C per minute from room temperature to about 600°C ; above this temperature it decreased to 5°C per minute at 1000°C . Several check runs showed that although peak temperatures were not exactly comparable to those secured on more standard laboratory instruments, the deviations were not overly large, and that peak shapes were in general preserved.

DTA results for three of the CSH(I) samples are shown in Figure 6. The major feature is the sharp, strong exothermic reaction marking the transformation to wollastonite at 825°C for the first two specimens and 860°C for the last. All specimens show a strong low-temperature dehydration endotherm, a distinct endothermic dip at about 790°C just prior to the exotherm, and a faint endothermic deflection at about 665°C . In securing these patterns it was observed that considerable shrinkage occurred at the temperature of the strong exotherm, yielding a soft and somewhat friable product which gave an x-ray pattern for wollastonite. A similar strong exothermic response was shown by aluminum-substituted tobermorite (13) but in the latter case the product was hard and well-cemented.

DTA results for some of the CSH(gel) samples are shown in Figure 7, the patterns having been secured with the portable instrument. The patterns shown are all much alike. They display a strong low-temperature endotherm due to release of adsorbed water, a strong endotherm at about 570°C due to the dehydration of lime formed in the hydration reaction, and a small but sharp high-temperature exotherm at about 860°C . In the bottle hydration products there is a small endothermic break in the 750°C zone which may be characteristic of the calcium silicate hydrate or may be the result of a trace of carbonation; it is difficult to decide which. DTA results for bottle hydration products of the two alite samples (not shown) closely resemble that of the corresponding C_3S sample. In fact, the basic similarity of the patterns for all the CSH(gel) products (except for the effects of the varying amounts of lime generated) is noteworthy: this similarity offers support for the concept of CSH(gel) as a distinct and fairly uniform phase, irrespective of the starting mineral or the particular mode of hydration used in its preparation. The distinction between CSH(gel) and CSH(I) on the basis of the difference in intensity of the high-temperature exotherm also seems to be consistent and reliable.

INFRARED SPECTROSCOPY

Infrared spectra of the poorly-crystallized calcium silicate hydrates have been published by several workers including Kalousek and Roy (14), Hunt (15, 16), Lehmann and Dutz (17, 18), and Midgley (19). All have used the KBr pellet technique, involving preparation of a transparent pellet by pressure exerted on a mixture of the sample with a large excess of powdered potassium bromide. Since one of the most useful results of infrared examination is an indication of the state of

water in the system, and since KBr in powder form is hygroscopic, tending to adsorb and retain traces of water vapor even on evacuation, it was thought desirable to avoid this technique. A simple procedure was evolved in which the sample was mulled briefly with spectral-grade CCl_4 and the resulting suspension pipetted onto the plane surface of a polished KBr plate that had been dried and kept at about 60°C in an oven. The CCl_4 evaporated in a minute or so leaving a deposit of calcium silicate hydrate sample on the KBr disc. This provided a useful and reproducible spectrum. Some skill was found to be required to avoid the deposition of too much or too little sample, but since an incorrectly-prepared specimen could be washed off in CCl_4 and a new one prepared in a few minutes, satisfactory results were readily obtained.

CSH(I) spectra were run on a Perkin-Elmer 421 dual-grating spectrophotometer, but the CSH(gel) samples were examined using a Perkin-Elmer 221 instrument. The former produces a chart that is linear in wave number, the latter in wave length; resolution and other features of the instruments are comparable. The 5x scale expansion feature was used for all patterns shown in this report.

Portions of the spectra of four of the CSH(I) samples are shown in Figure 8. The "hydroxyl region" is not shown, but in each case the hydroxyl stretching vibration band consisted of a broad, shallow trough centered at about 3400 cm^{-1} , a position characteristic of vibration of bonded OH groups; in no case was a band observed in the "free" OH stretching vibration region at about 3700 cm^{-1} . This suggests that free (non hydrogen-bonded) hydroxyl groups are not present in these materials. Also, the strengths of the hydroxyl stretching bands in these patterns were only about 10-15 percent of the strengths of the main Si-O lattice vibration band. Previously published results, in

which the KBr pellet technique was employed, generally showed much stronger hydroxyl bands relative to their Si-O bands.

The remaining spectral details of the present samples shown in Figure 8 are allocated as follows: the band at approximately 1630 cm^{-1} is the bending vibration of water, in this case water present in the CSH(I); the large band between 1400 and 1500 cm^{-1} (split in some of the materials) is probably due to the asymmetrical stretching mode of the carbonate ion (15); presumably the carbonate was present as a result of carbon dioxide reaction with the surface of the CSH(I) material. Hunt has shown that a very small percentage of CO_3 in $\text{Ca}(\text{OH})_2$ can produce a disproportionately large effect on the infrared spectrum, and this has been confirmed in trials in our laboratory. The major band at about 970 cm^{-1} is the main Si-O lattice vibration effect previously mentioned. The small band at about 860 cm^{-1} may be the out-of-plane bending vibration of the carbonate group, although this is usually recorded at about 890 cm^{-1} (20).

Infrared spectra for CSH(I)-3, -4, and -5, not shown, are similar to that shown for CSH(I)-6, which may thus be considered typical of the group as a whole.

Certain specific details of the individual patterns should be pointed out. First, CSH(I)-1, which provided an unusual x-ray pattern with peaks reminiscent of xonotlite, produces an infrared spectrum that is similar to those of the other members of the group. A published infrared spectrum for xonotlite (14) has a strong band at about 1200 cm^{-1} ; no trace of this is observed in the present spectrum. A second point is that the infrared spectrum for CSH(I)-2, the x-ray-amorphous member of the group, is similar to those of the other samples. A third note-

worthy point is the weakness of the water bending mode at about 1625 cm^{-1} in some samples; it is almost absent in CSH(I)-2 and CSH(I)-7 despite the high structural water content of these samples. A fourth observation is that the exact position of maximum absorption for the Si-O lattice vibration band varies somewhat from sample to sample, from perhaps 950 cm^{-1} (portion of a split peak in CSH(I)-7) to as high as 980 cm^{-1} for CSH(I)-2. Lehmann and Dutz (17) suggested that similar differences in the spectra of the hydration products of the cement minerals may indicate variation in the degree of polymerization of the silica tetrahedra making up part of the framework of the mineral, increasing degree of polymerization being marked by higher wave numbers (shorter wave length). A systematic study of this point may be of considerable importance in clearing up details of the structure of the CSH(I) phase. A final feature of interest is the pronounced minimum in absorption in the region of about $1150 - 1200\text{ cm}^{-1}$. As will be seen later, this feature is even more pronounced with CSH(gel) spectra, and discussion of it is postponed until they are considered.

Spectra for five of the products of the hydrated cement minerals are shown in Figure 9. As previously stated, these spectra were secured using an instrument the presentation of which is linear in wave length rather than wave number; in consequence peaks at lower wave numbers are broader and more diffuse than they would be on the instrument used for the CSH(I) spectra.

The most obvious feature of the CSH(gel) spectra is the very strong minimum in absorption at about 1200 cm^{-1} , stronger and more pronounced than the corresponding effect with the CSH(I) materials.

The prominence of the effect is not due to the particular instrumentation employed, since the 421 instrument gave an identical effect. The effect is not apparent in previously-published spectra of CSH(gel) products in which the KBr pellet procedure had been employed. This minimum is thought to be attributable to the "Christiansen filter effect," which is known to occur with powdered solids suspended in a fluid (in this case air), and has been demonstrated in infrared spectroscopy on various classes of material (21, 22). Briefly, the Christiansen filter effect is due to the rapidly changing index of refraction of the particulate solid with wave length, in the region of a strong absorption band. At a wave length slightly shorter than that of the absorption band the index of refraction of the solid may match that of the fluid, and at this point scattering by multiple reflection and refraction at the many powder-fluid interfaces is at a minimum; consequently a pronounced minimum in absorption is observed.

The strong absorption band here is the Si-O lattice vibration feature; this occurs at about 940 cm^{-1} , except for the paste hydration product of $\beta\text{-C}_2\text{S}$, for which the position is apparently 970 cm^{-1} . The theoretical absorption band cited by Lehmann and Dutz (17) for completely unpolymerized silica tetrahedra (i.e. an orthosilicate) is 935 cm^{-1} ; the closeness of the observed positions to this figure seems to imply that, in agreement with the views of Brunauer and Greenberg (2), CSH(gel) tends to be largely an orthosilicate.

The band itself is somewhat broader and less marked than the corresponding CSH(I) feature. Secondary maxima, the origin of which is at present obscure, are observed at about 900 cm^{-1} and at about 820 cm^{-1} in most of the samples. Small bands occur at $1600\text{-}1630\text{ cm}^{-1}$

(presumably due to the water bending vibration) and near 1400 cm^{-1} (probably indicating some carbonation has taken place). If these bands are interpreted correctly, one would suppose from the appearance of the patterns that these samples retained somewhat more water and had somewhat less carbonate than the CSH(I) samples discussed previously. Also the wave number of the band attributable to the carbonate ion is distinctly lower in the present spectra, suggesting that the carbonate ions are held more tightly in the CSH(gel) samples than in CSH(I).

In Figure 9 a number of small features can be observed in the $2000\text{-}4000\text{ cm}^{-1}$ region. A comparatively weak and broad band is observable at $3340\text{-}3400\text{ cm}^{-1}$, which is the OH stretching vibration for bonded OH groups. Patterns for both paste-and bottle-hydrated samples derived from $\beta\text{-C}_2\text{S}$ show a sharp, complex absorption feature at 3780 ; and all of the samples show additional small, sharp features at around 2900 cm^{-1} and between 2300 and 2400 cm^{-1} , the causes of which are uncertain.

In general the spectra are all similar to each other, and sufficiently different from the CSH(I) materials (by virtue of the stronger absorption minimum and the broader Si-O band) that one can readily distinguish them from that phase.

WATER VAPOR ADSORPTION AND SURFACE AREA

Water vapor adsorption isotherms at 21°C were secured in order to characterize the CSH(I) samples. In view of the many water vapor surface area measurements of CSH(gel) products by other workers, and in view of the experimental difficulties involved in correcting for the presence of lime and residual unhydrated material, sorption measurements for the CSH(gel) materials were not attempted.

The procedure involved outgassing over P_2O_5 at room temperature for 4 days, then equilibration over concentrated sulfuric acid solutions of successively lower concentration. The concentration of each solution was determined by titration after equilibration, and the partial pressure of water vapor was determined from this. For each sample at least five points were secured in duplicate in the BET range, and a more extended set of determinations was made with one. The surface areas were computed using an assigned area of $11.4 \text{ \AA}^2$ per water molecule (2), and an estimate of the heat of adsorption of the uniform portion of the first layer (" E_1 ") was calculated according to the BET procedure (23).

The quantitative results for these determinations are given in Table 3. The approximate range in surface area for the CSH(I) materials was 150 to $350 \text{ m}^2/\text{g}$; these limits are consistent with the range of $135\text{-}380 \text{ m}^2/\text{g}$ cited recently by Brunauer (24). The first four samples, prepared by rapid precipitation without any particular opportunity for aging were significantly higher in surface area than the others. There does not seem to be a relationship between high surface area and poor crystallinity, however, since the x-ray-amorphous sample CSH(I)-2, with by far the poorest degree of crystallinity, occupies the median position with respect to surface area.

The measured E_1 values range from about 12,500 to over 13,500 cal/mole, that is to say the difference between E_1 and the bulk heat of condensation of water vapor is generally of the order of 2500 to 3000 cal/mole. It is noteworthy that the x-ray-amorphous sample CSH(I)-2 has an unusually low E_1 , which is only about 1200 cal/mole higher than the heat of condensation of water.

A reduced water vapor adsorption isotherm for six of the seven CSH(I) materials is given in Figure 10; as noted in the legend, data points for two pairs of samples which proved to be adjacent to each other were given a single symbol to avoid crowding the figure. The relative concordance of all the data plotted in this way (which removes the effect of the differing surface areas of the individual samples) suggests that the samples for which points are plotted have surfaces that are qualitatively the same, at least with respect to the sorption of water vapor. The isotherm is clearly a standard BET type II, and no particular restriction on the number of layers that can be adsorbed seems to occur.

The data for the x-ray-amorphous sample (not plotted) fall far below the line for the other samples. This is not surprising in view of the low E_1 value calculated for this material, and the two facts suggest that the surface of the amorphous sample has a relatively weak attraction for water vapor compared to the surfaces of the better-crystallized CSH(I) samples.

SURFACE CHARGE

Attempts were made to measure zeta potentials of these CSH(I) and CSH(gel) samples by means of the standard flat-cell microelectrophoresis apparatus (25). These attempts were unsuccessful, however, owing to an inability to achieve a satisfactory degree of dispersion. Even after continued ultrasonic treatment for long periods the particles occurring in water suspension were aggregates that settled to the bottom of the microelectrophoresis cell so rapidly that measurement of horizontal particle velocity under influence of the applied electric

current was not possible. However, since the direction of travel of the particles could readily be determined the sign of the net surface charge could be obtained.

It was determined that CSH(I) particles dispersed in distilled water were charged negatively; but the same materials dispersed in saturated calcium hydroxide solutions were charged positively.

The CSH(gel) samples initially dispersed in water were positively charged, but in view of the calcium hydroxide that is present as a companion product of the hydration reactions, this result was not unexpected. When the CSH(gel) products were washed repeatedly in distilled water to remove the accompanying calcium hydroxide, the positive charge was visibly decreased as the pH of the suspension was reduced, and at a pH of about 10 the sign of the surface charge became negative. Thus the basic observations of Stein (26) on tobermorite are apparently applicable to CSH(I) and CSH(gel) as well.

It was noted that the sign reversal did not appear to influence the state of aggregation of the particles; the colloidal aggregates remained well-cemented regardless of the charge.

CATION EXCHANGE CAPACITY MEASUREMENTS

The idea that tobermorite and perhaps the poorly-crystallized tobermorite-like calcium silicate hydrates might have distinctive cation-exchange properties is not new; speculations to this effect were given by McConnell (27) and by Roy (28) some years ago. Nevertheless, to the knowledge of the writers no laboratory confirmation of such properties has been reported. One difficulty is that, due to the small but not negligible solubility of CSH(I) and CSH(gel) in

water, the methods normally employed for cation exchange determinations are untrustworthy. The difficulty is that after treating the sample with solutions containing a large excess of a measuring cation to insure replacement of the original cations on the exchange sites, it is necessary to remove all of the measuring cations introduced in excess of those actually exchanged. This is usually accomplished by repeated washing treatments. Repeated washing of CSH(I) and CSH(gel) with water leads to breakdown and eventual dissolution of the sample. This breakdown and dissolution liberates calcium ions, which exchange with some of the measuring cations adsorbed on the exchange sites, thus invalidating the determination.

After a good deal of experimentation a method was devised to eliminate this difficulty. Potassium ions were used as the measuring cations, and absolute ethanol as the solvent and washing medium. The potassium was added as a 1 N solution of potassium acetate in ethanol. After overnight equilibration and repeated treatments with fresh solution to insure complete exchange, the excess potassium acetate was removed by repeated washing in ethanol. After five such washing treatments, the potassium remaining ("exchanged potassium") was in turn replaced by either sodium or ammonium ions derived from repeated additions of solutions of the corresponding acetate in ethanol. The washings containing the released potassium were combined, diluted, and the potassium content determined by flame photometry. Details of the method can be found in the unpublished thesis of the senior author (29).

It was discovered that the polyethylene centrifuge tubes used for the saturation and washing treatments adsorbed and retained a

small quantity of potassium against washing, and a blank correction for this effect was required. Furthermore, it was found that use of the ammonium acetate to replace exchanged potassium in some cases resulted in the formation of a gel, which made the necessary washing treatments mechanically difficult to carry out. Use of the sodium salt met no such handicap, but unfortunately sodium acetate is far less soluble in ethanol than is the ammonium salt.

A check of the method with unfractionated "Volclay" brand Wyoming bentonite yielded a value of 85 meq/100g, in good agreement with more conventional determinations.

Cation exchange capacities for five of the seven CSH(I) samples were determined. Values obtained, using sodium acetate as the replacing salt, ranged from 4 meq/100g for CSH(I)-5 to as much as 24 meq/100g for CSH(I)-6. The exchange capacities do not appear to be related to either the surface area or any other measured characteristic of the samples. Similar determinations were carried out on some of the CSH(gel) materials with ammonium acetate used as the replacing salt. These values were of the same order of magnitude, the bottle-hydrated C_3S product yielding the low value of 7 meq/100g and the paste product of the same material yielding the high value of about 20 meq/100g. The bottle-hydrated alites both gave values somewhat higher than the corresponding bottle hydrated C_3S product, both hydrated alite samples giving 18 meq/100g. Separate measurements were made on calcium hydroxide and on the cement minerals C_3S , alite, and β - C_2S . Of these, a zero exchange capacity was recorded for the lime, and small exchange capacities of about 3 meq/100g were recorded for each of the others. Thus the observed exchange capacities of the

CSH(gel) samples relate primarily to the CSH(gel) per se, and not to the accessory constituents present.

DISCUSSION AND CONCLUSIONS

As a result of parallel studies on CSH(I) samples and on the hydration products of cement minerals, it can be concluded that the CSH(I) phase and the CSH(gel) phase are distinctive entities with only limited ranges of variation in properties. In particular, the CSH(gel) materials produced by paste and by bottle hydration of β -C₂S, C₃S, and alite are all remarkably similar to each other. These phases are distinct from tobermorite not only because of their poor crystallinity but in a number of other ways.

One of the notable differences between the CSH(gel) and CSH(I) materials and tobermorite is that the particles of the former two materials are inherently cemented to form aggregates that resist dispersion. This cementation seems to be unaffected by the zeta potential of the material; at least changes in surface charge from strongly positive to strongly negative do not result in any noticeable tendency for the aggregated particles to disperse. This feature is as pronounced with CSH(I) as it is with CSH(gel). A corollary to this observation is the discovery, reported elsewhere (30), that when CSH(I) is produced by reaction of calcium hydroxide on clay minerals cementation is as effective and permanent as when CSH(gel) is produced under similar circumstances. These results point to the importance of the chemical factor in cementation.

The present results confirm and to some extent supplement earlier results relative to x-ray diffraction, DTA, morphology, and infrared behavior of these materials. One of the chief benefits

derived from the work is that all these results are now available for the same well-defined group of samples.

The observed cation-exchange properties of these materials are not explainable in terms of isomorphous substitution, since most of the samples are pure calcium silicate hydrates. The other commonly-accepted source of cation-exchange sites in silicate minerals are so-called "broken-bond" sites arising at the edges of the particles. However, in view of the lack of knowledge of the detailed structure of these calcium silicate hydrates, speculation as to the location of the exchange sites seems to be premature.

The results point to a number of differences in the properties of CSH(I) and CSH(gel) that may be useful for identification. X-ray diffraction is felt to be inadequate for the purpose, but the DTA pattern seems to be diagnostic; CSH(I) always produces a strong, sharp, high-temperature exothermic response, while CSH(gel) always produces a much less intense exotherm at about the same position. The morphologies of the two phases are distinct, CSH(I) having a "snowflake", thin platy, or "crinkled foil" appearance, while CSH(gel) is essentially fibrous. Infrared spectra are of some utility in identification of the phases, the patterns for CSH(gel), of whatever origin, being broader and more diffuse than those for CSH(I). For samples prepared in the manner employed in the present work, the sharpness and intensity of the absorption minimum is uniformly more pronounced for the CSH(gel) materials; this may be of diagnostic utility.

Finally, attention is drawn to the failure to produce CSH(II) by the method described by Toropov, et. al. Independent confirmation

of this synthesis is apparently still lacking, despite the fact that the paper describing it is almost ten years old at the time of this writing.

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This work is part of a larger study the results of which were presented as a Ph. D. thesis submitted to the faculty of Purdue University by the senior author (29). In addition to the present work, studies on well-crystallized tobermorite phases and on lime-clay mineral reaction products were carried out; these will be published elsewhere.

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Table 1. Designation, Origin, and Composition of CSH(I) Products

Designation	Starting Materials	Ca:Si Ratio of Reactants	Composition of Final Washed Product
CSH(I) -1	Na_2SiO_3 and CaCl_2	1:1	$\text{C}_{0.97}\text{S}_{1.00}\text{H}_{2.74}$
CSH(I) -2	Na_2SiO_3 and $\text{Ca}(\text{NO}_3)_2$	1:1	$\text{C}_{0.96}\text{S}_{1.00}\text{H}_{1.59}$
CSH(I) -3	Na_2SiO_3 and $\text{Ca}(\text{NO}_3)_2$	1.5:1	$\text{C}_{0.99}\text{S}_{1.00}\text{H}_{1.62}$
CSH(I) -4	Na_2SiO_3 and $\text{Ca}(\text{NO}_3)_2$	2:1	$\text{C}_{1.01}\text{S}_{1.00}\text{H}_{1.64}$
CSH(I) -5	Na_2SiO_3 and $\text{Ca}(\text{NO}_3)_2$	3.5:1	$\text{C}_{1.16}\text{S}_{1.00}\text{H}_{1.00}$
CSH(I) -6	SiO_2 and $\text{Ca}(\text{OH})_2$	1:1	$\text{C}_{0.91}\text{S}_{1.00}\text{H}_{1.08}$
CSH(I) -7	SiO_2 and	2:1	$\text{C}_{1.58}\text{S}_{1.00}\text{H}_{1.80}$

Table 2. Designation and Preparation of CSH(gel) Products

Designation	Starting Material	Source and Number	Method of Hydration	Time of Hydration
CSH(gel)P-1	β -C ₂ S	PCA B-91	Paste	7 months
CSH(gel)P-2	C ₃ S	PCA B-101	Paste	7 months
CSH(gel)B-1	β -C ₂ S	PCA B-91	Bottle	6 months
CSH(gel)B-2	C ₃ S	PCA B-101	Bottle	6 months
CSH(gel)B-3	Alite	PCA B-93	Bottle	4 months
CSH(gel)B-4	Alite	U. Calif.	Bottle	4 months

Table 3. Surface Areas and Heats of Adsorption of Water Vapor for CSH(I) Preparations at 21°C.

Sample No.	Surface Area (m^2/g)	" E_1 " (cal/mole)
CSH(I) -1	355	12,700
CSH(I) -2	245	11,700
CSH(I) -3	278	12,800
CSH(I) -4	300	12,500
CSH(I) -5	167	13,100
CSH(I) -6	175	13,700
CSH(I) -7	157	12,700

Figure 1. X-ray Diffractometer Traces for CSH(I) Samples Synthesized at Room Temperature.

A C_3S or ALITEB βC_2S C $Ca(OH)_2$

SHADED PEAKS CSH (GEL)

Figure 2. X-ray Diffractometer Traces for Paste and Bottle Hydration Products of βC_2S , C_3S and Alite.

- CSH
 C - $\text{Ca}(\text{OH})_2$

Figure 3. X-ray Diffractometer Trace for Moist CSH(gel) B - 2 Prepared as an Oriented Aggregate on a Porous Tile Mount.

Figure 4. Electron Micrographs of CSH(I) Preparations.

(A) CSH(I) - 5. (B) CSH(I) - 7.

Figure 4 . Electron Micrographs of CSH(I) - 6.

(A)

(B)

Figure 5 . Electron Micrographs of Paste and Bottle Hydration Products of C_3S . (A) Paste Product, CSH(gel) P - 2. (B) Bottle Product, CSH(gel) B - 2.

Figure 5. Electron Micrographs of Bottle-Hydrated β -C₂S,
CSH(gel) B - 1.

Figure 6. DTA of CSH(I) Preparations. Heating Rate 10°C Per Minute.

Figure 7. Differential Thermal Analysis of CSH(gel) Products. Heating Rate Varies from 53°C to 5°C per Minute.

Figure 8. Infrared Absorption Spectra for CSH(I) Preparations.

Figure 9 . Infrared Absorption Spectra for CSH(gel) Products.

Figure 10. Reduced Water Vapor Adsorption Isotherm for CSH(1)

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