Studies on Tobermorite-Like Calcium Silicate Hydrates

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Parallel studies were carried out on certain characteristics of CSH(I) synthesized at room temperature and on tobermorite gel produced by paste or bottle hydration of β-C_2S, C_3S, 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 tobermorite gel had negative surface charge in the absence of $Ca(OH)_2$. A method was devised to measure the cation exchange capacities of these materials, which were on the order of 5 to 25 meq/100 gm.

CSH(I) appears to be a distinct and reasonably homogeneous physicochemical entity despite compositional variation, and similarly the tobermorite gel products appear to be members of a distinct phase regardless of the particular cement mineral or mode of hydration used. The two phases exhibited similar surface properties, and the primary particles of both seemed to be intrinsically cemented into microaggregates. The two phases are difficult to differentiate by x-ray methods but may be distinguished from each other by particle morphology, by the intensity of the high-temperature exotherm on DTA, and to some extent, by their infrared spectra.

•THE poorly crystallized calcium silicate hydrates (CSH) 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 tobermorite gel. The latter has also been known as "CSH (gel)" and "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 and water-vapor adsorption. 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. Reviews by Taylor (1) and by Brunauer and Greenberg (2) contain considerable information on the known properties of these materials.

CSH(I) is a poorly crystallized synthetic CSH distinct from, but related to, tobermorite. It can be prepared by reaction at room temperature or under hydrothermal conditions (3). The structure is 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 (hkO) lines of tobermorite; a diffuse basal spacing is sometimes observed in the approximate range of 10 A to 14 A, depending on the state of hydration and 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 approximately 1.5. The DTA pattern of CSH(I) is characterized by a strong, sharp high-temperature exothermic peak at 850 to 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).

Tobermorite 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. X-ray diffraction shows only three peaks, corresponding to the positions of the strongest (hkO) lines of tobermorite; basal spacings have not been observed, except in a single instance (2). 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 normally varying from about 1.4 to 1.7. Tobermorite gel is usually considered to consist of mostly straight, comparatively long fibers, the fibers themselves being composed of rolled sheets. An adequate DTA pattern for a pure tobermorite 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 to 2.0; thus, its composition overlaps that of tobermorite gel. In contrast to the latter, an x-ray basal spacing of about 10 A is generally recorded (1). It has been suggested that this phase can be identified by an x-ray peak at 1.5 A (10). Again, the detailed structure is unknown. The morphology is fibrous, and cigar-shaped bundles of fibers of distinctive appearance are often observed (5, 7). The DTA pattern is marked by an exothermic bulge at about 400 to 450 C, 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 were made by double decomposition reactions, and two 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 CSH precipitating as large white flocs. The sodium silicate used was 0.5 N in each instance; the calcium salt solution used was 0.5 N $CaCl_2$ in one sample, 0.5 N $Ca(NO_3)_2$ in the others. The Ca:Si molar ratios were 1.0 for the sample prepared with $CaCl_2$ and one of the samples made with $Ca(NO_3)_2$, and 1.5 and 2.0, respectively, for the other two samples made with $Ca(NO_3)_2$. 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 dried at 110 C.

A fifth sample was prepared by a more elaborate procedure, devised 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 syringes were simultaneously depressed the two fine streams produced were intimately mixed and the combined droplets produced fell 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 get a high-lime product. After all solutions had been reacted, the precipitated material was filtered and washed exhaustively, this time starting with saturated $Ca(OH)_2$ solution. The washing was continued using a

Sample No.	Starting Materials	Ca:Si Ratio of Reactants	Composition of Final Product
CSH(I)-1	Na_2SiO_3, $CaCl_2$	1:1	$C_{0.97}S_{1.00}H_{2.74}$
CSH(I)-2	Na_2SiO_3, $Ca(NO_3)_2$	1:1	$C_{0.96}S_{1.00}H_{1.59}$
CSH(I)-3	Na_2SiO_3, $Ca(NO_3)_2$	1.5:1	$C_{0.99}S_{1.00}H_{1.62}$
CSH(I)-4	Na_2SiO_3, $Ca(NO_3)_2$	2:1	$C_{1.01}S_{1.00}H_{1.84}$
CSH(I)-5	Na_2SiO_3, $Ca(NO_3)_2$	3.5:1	$C_{1.16}S_{1.00}H_{1.00}$
CSH(I)-6	SiO_2, $Ca(OH)_2$	1:1	$C_{0.91}S_{1.00}H_{1.08}$
CSH(I)-7	SiO_2, $Ca(OH)_2$	2:1	$C_{1.58}S_{1.00}H_{1.80}$

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 Co.) with reagent-grade $Ca(OH)_2$. 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 2 days, then allowed to stand undisturbed for 3 wk. 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 free $Ca(OH)_2$ 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 2.0 was used; here the pH of the recycled and clarified filtrate was 12.5, indicating that unreacted $Ca(OH)_2$ was present. The product was washed with water until the pH dropped below 12.3 and x-ray examination disclosed the absence of crystalline $Ca(OH)_2$. After one additional wash the sample was dried and stored.

The samples are designated CSH(I)-1 through CSH(I)-7. Chemical analyses were carried out by standard methods and the conventional compositional formulas were determined (Table 1). Considering that the molar ratio of starting mixtures varied from 1.0 to 3.5, 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. Although 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).

Tobermorite Gel

Tobermorite gel samples were prepared by hydration of β-C_2S, C_3S and alite. Paste hydration of the β-C_2S 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 7 mo. Bottle hydration at the same temperature was carried out in polyethylene bottles rotated on a wheel at approximately 30 rpm; the water:solids ratio was 9.0. Bottle hydration of the β-C_2S and C_3S samples was allowed to proceed for 6 mo, and of the alites for 4 mo. In all experiments freshly boiled distilled water cooled below room temperature was used, and the containers were sealed against carbon dioxide penetration.

The designations for the specific samples studied are given in Table 2. In addition to the samples listed, bottle hydration products for an additional sample of C_3S and of alite were prepared and examined, but the results were essentially identical to those discussed.

Gel Designation	Starting Material	Source and Number	Hydration	
			Method	Time (mo)
P-1	β-C_2S	PCA B-91	Paste	7
P-2	C_3S	PCA B-101	Paste	7
B-1	β-C_2S	PCA B-91	Bottle	6
B-2	C_3S	PCA B-101	Bottle	6
B-3	Alite	PCA B-93	Bottle	4
B-4	Alite	Univ. Calif.	Bottle	4

CSH(II)

Several attempts were made to prepare CSH(II) by the synthesis described by Toropov et al. (9). CaO from freshly calcined $CaCO_3$ was mixed with silica gel, using a Ca:Si ratio of 2.0. The mixture was ground under several drops of glycerol, 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. re-

ported that their mixture began to froth at 180 to 185 C and continued for several hours until the liquid became clear. However, no such action occurred 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 McCreery (12).

X-ray diffractometer traces for all seven CSH(I) samples are shown in Figure 1. Five of the seven, CSH(I)-3 through CSH(I)-7 are remarkably alike. All have the strong main peak at around 3.05 A, which characterizes tobermorite-like CSH, and weak peaks at about 2.78 and 1.8 A. No peak occurs at or near 1.56 A, which would characterize the phase CSH(II), even for the high-lime sample CSH(I)-7. It is sometimes loosely
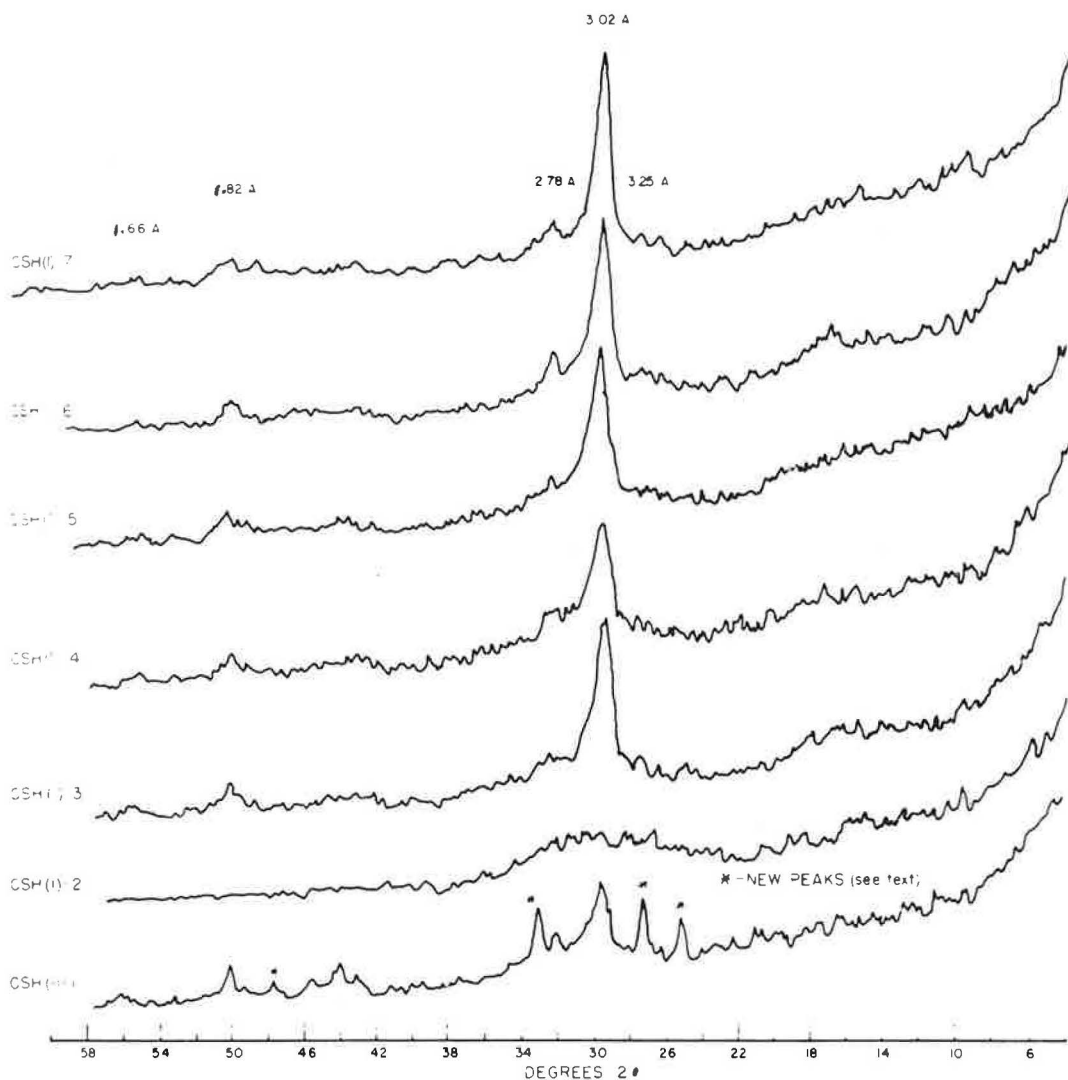

Figure 1. X-ray diffractometer traces for CSH(I) samples.

stated that CSH(I) exhibits the three strongest peaks of tobermorite. Well-crystallized tobermorite has a peak at 2.97 A, the (222) reflection, that is always greater in tobermorite than the 2.8 and 1.8 A peaks, but there is no evidence for the former peak in these 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)-2 displays peaks for vaterite (μ-CaCO$_3$). Originally, diffraction runs made shortly after preparation of this sample showed a pattern similar to the other weakly crystalline CSH(I) samples. However, re-examination after storage for approximately 1 yr produced the pattern shown in Figure 1, indicating that carbonation had taken place on storage.
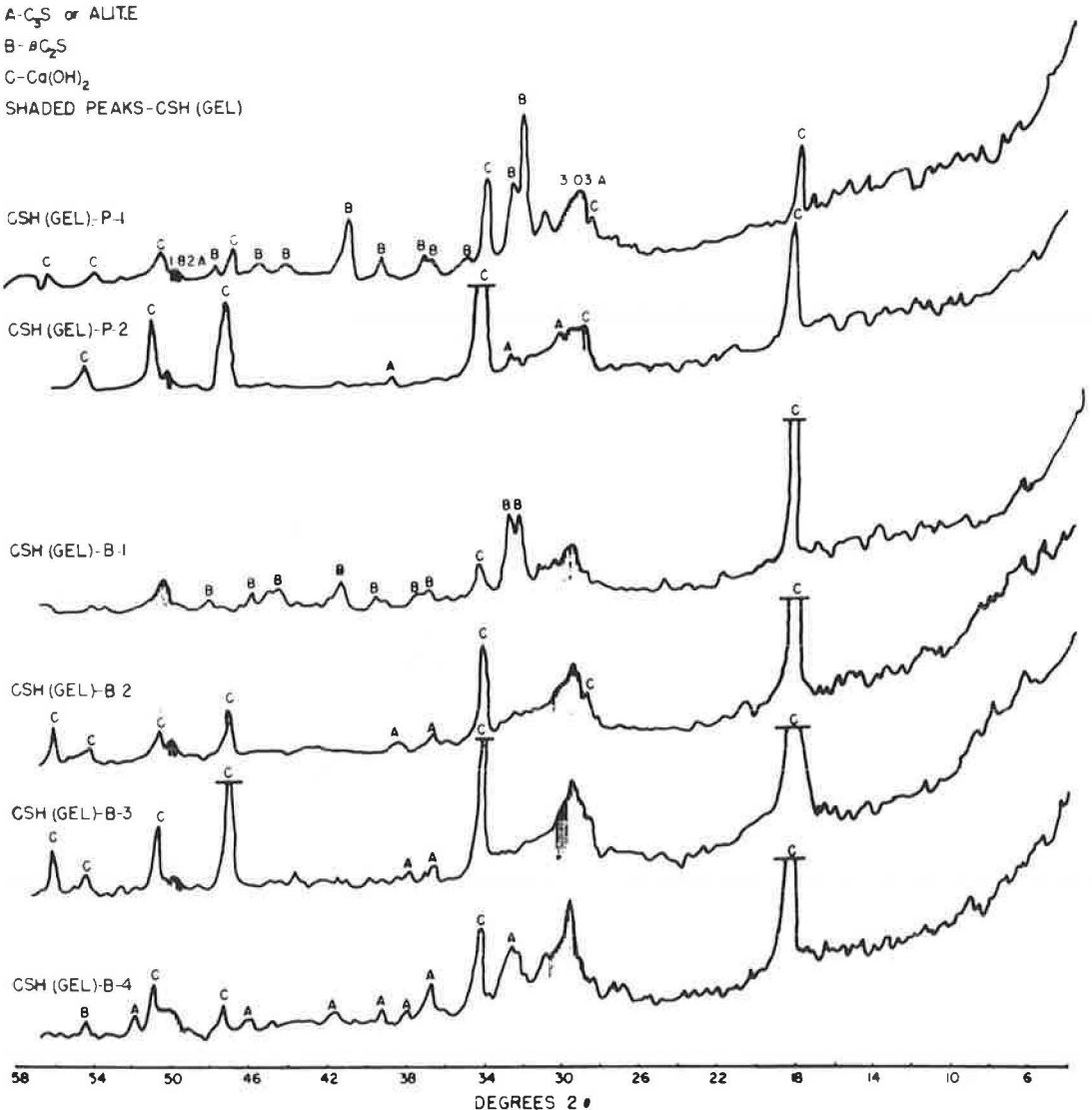

Figure 2. X-ray diffractometer traces for tobermorite gel products.

Attempts were made to obtain estimates of the basal spacings of CSH(I) preparations by use of oriented aggregate specimens. These were 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 to 14 A 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, because 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 tobermorite gel products described in Table 2 are shown in Figure 2, in which peaks attributable to the gel phase are shaded. It appears that x-ray diffraction is not a particularly fruitful tool for studying the characteristics of the gel phase in systems of hydrating cement constituents, because, in general, the CSH peaks are even broader and less intense than those of the CSH(I) preparations.

The pattern for the paste-hydrated β-C_2S, gel-P-1, shows that a relatively large amount of unreacted β-C_2S remains and only small peaks for $Ca(OH)_2$ are observed. The paste product derived from C_3S, gel-P-2, has produced much more $Ca(OH)_2$, and almost all C_3S seems to have reacted. These observations are in accord with expectation.

The four remaining patterns 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 efforts to prevent this in the powder sample preparation. β-C_2S seems to hydrate slowly even under the bottle-hydration conditions, the pattern for gel-B-1 showing that a good deal of the original compound is unreacted. The C_3S bottle-hydration product, gel-B-2, and one of the alite products, 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.

Hydrated cement phases do not usually yield basal peaks (2); however, basal reflections were secured in at least one preparation. Figure 3 is a trace of the C_3S bottle-hydration product, prepared as an oriented aggregate on a porous tile mount (12). A 14 A basal spacing with a second order peak at 7 A is clearly visible. Efforts to prepare similar mounts for the other materials were not as successful.
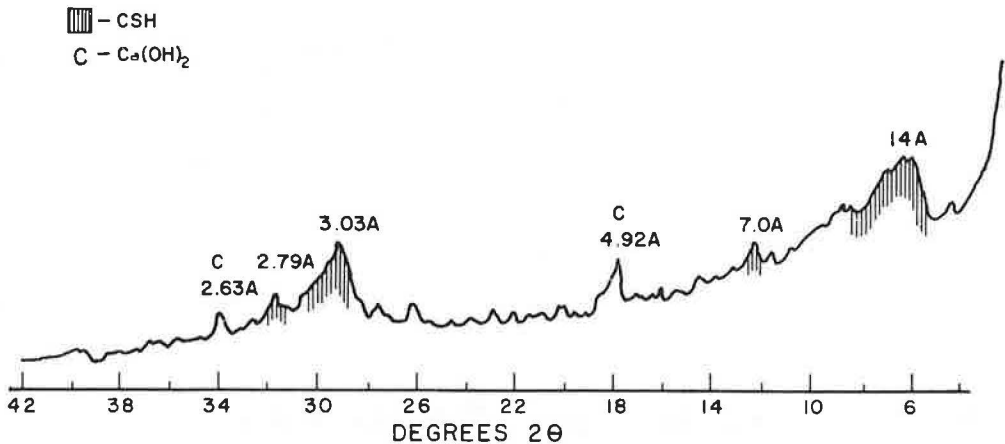

Figure 3.   X-ray diffractometer trace for moist gel B-2 sample prepared as an oriented film.

PARTICLE MORPHOLOGY

Electron microscopic study of some of these materials was carried out 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 nonaqueous system without ultrasonic vibration. This technique precluded the usual clumping together of particles that occurs on drying an aqueous suspension and revealed the morphology of the individual particles. All the electron micrographs were taken at a direct magnification of 4400 x.

Samples CSH(I)-5, 6, and 7 were examined by the electron microscope. Sample CSH(I)-5 (Fig. 4a) occurred primarily as extremely thin foils or "snowflakes." A few fields showed a greater proportion of thicker, irregularly shaped aggregates. The product gave 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 occurred in particles having more definite outlines. The individual particles appeared to be aggregates of twisted plate-like material. A few large aggregates were found, such as that shown in Figure 4b; this is identical in appearance to Figure 1 of Kalousek and Prebus (6). CSH(I)-7 was similar to CSH(I)-6, except that a larger proportion of the material was in fine foil-like condition, and the coarser particles seemed to be more definitely plate-like.

Electron micrographs of paste-hydrated C_3S revealed that most of the particles were fibrous, with the remainder being more or less equant in appearance; the latter may actually be bundles of fibers, but this was not evident. In addition, there were a number of thin sheet-like particles visible that showed no tendency toward rolling up into tubes or fibers. Figure 5a, a representative view of the bottle product of the C_3S, reveals that the particles in this product seem to be completely fibrous. A few bundles of undisturbed fibers are clearly visible.

Figure 5b shows the product designated 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 $\overline{C}SH(II)$ with a distinctive cigar-shaped fiber bundle morphology and a slightly different x-ray diffraction pattern than tobermorite gel. However, in the present case it appears that tobermorite gel rather than CSH(II) has been formed.

(a)   (b)
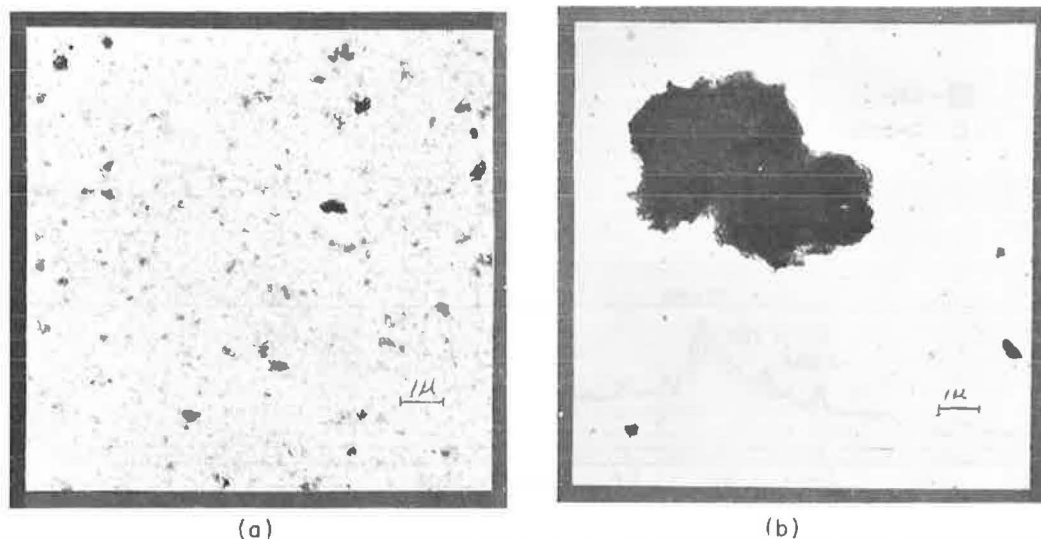
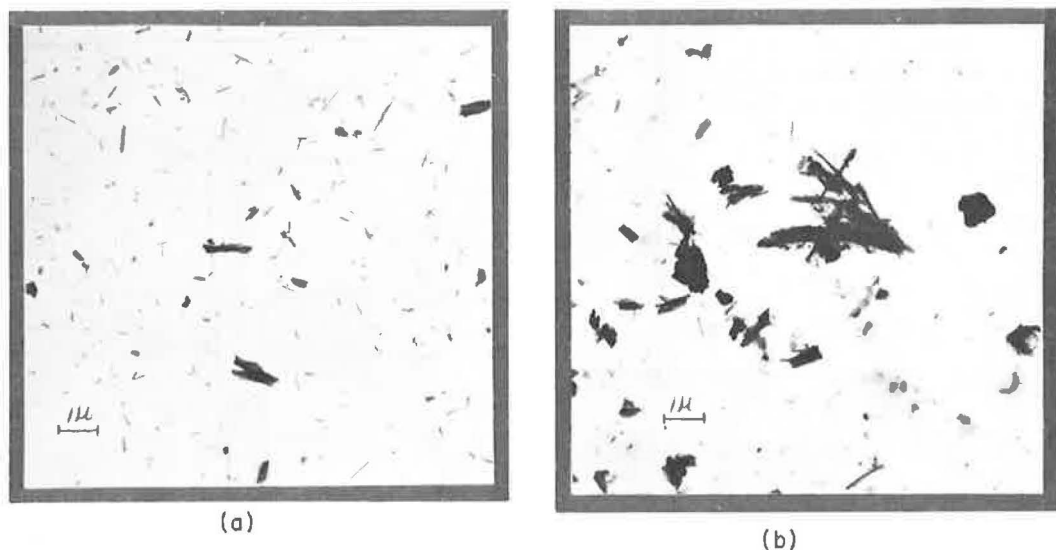Figure 4.   Electron micrographs: (a) CSH(I)-5, and (b) large aggregate in CSH(I)-6.

Figure 5.   Electron micrograph: (a) gel B-2, from bottle hydration of C_3S, and (b) gel B-1, from bottle hydration of β-C_2S.

DIFFERENTIAL THERMAL ANALYSIS

Unfortunately, the comparison of DTA results for CSH(I) and tobermorite gel preparations 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 C was used. Through necessity, the gel materials were examined with a modified commercial portable DTA unit (Eberbach Corp., Ann Arbor, Mich.) 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 be readily 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 constant at 58 C/min from room temperature to about 600 C; above this temperature, it decreased to 5 C/min 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; 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 before 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 tobermorite 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 dehydroxylation 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
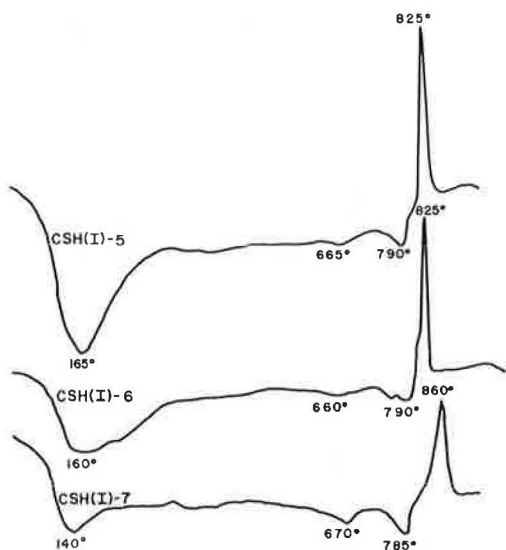
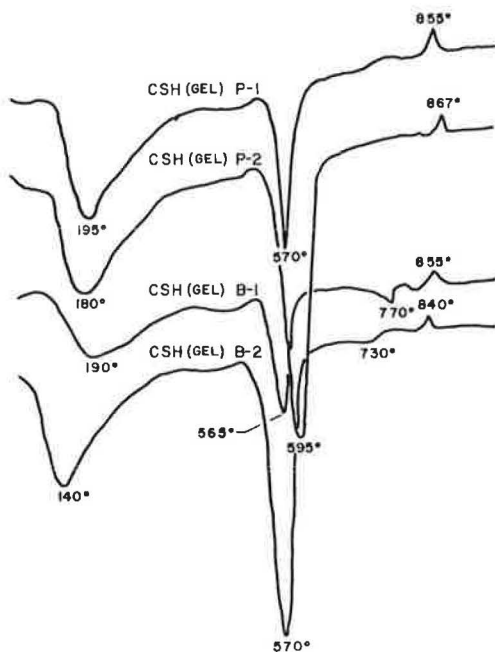Figure 6. DTA of CSH(I) samples, heating rate 10 C/min.

Figure 7. DTA of tobermorite gel products, heating rate from 58 to 5 C/min.

the 750 C zone which may be characteristic of the CSH or may be the result of a trace of carbonation. 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 gel products (except for the effects of the varying amounts of lime generated) is noteworthy; this similarity offers support for the concept of tobermorite 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 tobermorite 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 poorly crystallized CSH 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 KBr. Because one of the most useful results of infrared examination is an indication of the state of water in the system, and because KBr in powder form is hygroscopic, tending to adsorb and retain traces of water vapor even on evacuation and oven drying, 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 CSH 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 because 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 gel samples were examined using a Perkin-Elmer 221 instrument. The former produces a chart linear in wave number, the latter one linear in wavelength; resolution and other features of the instruments are comparable. The 5 x scale expansion feature was used for all patterns.
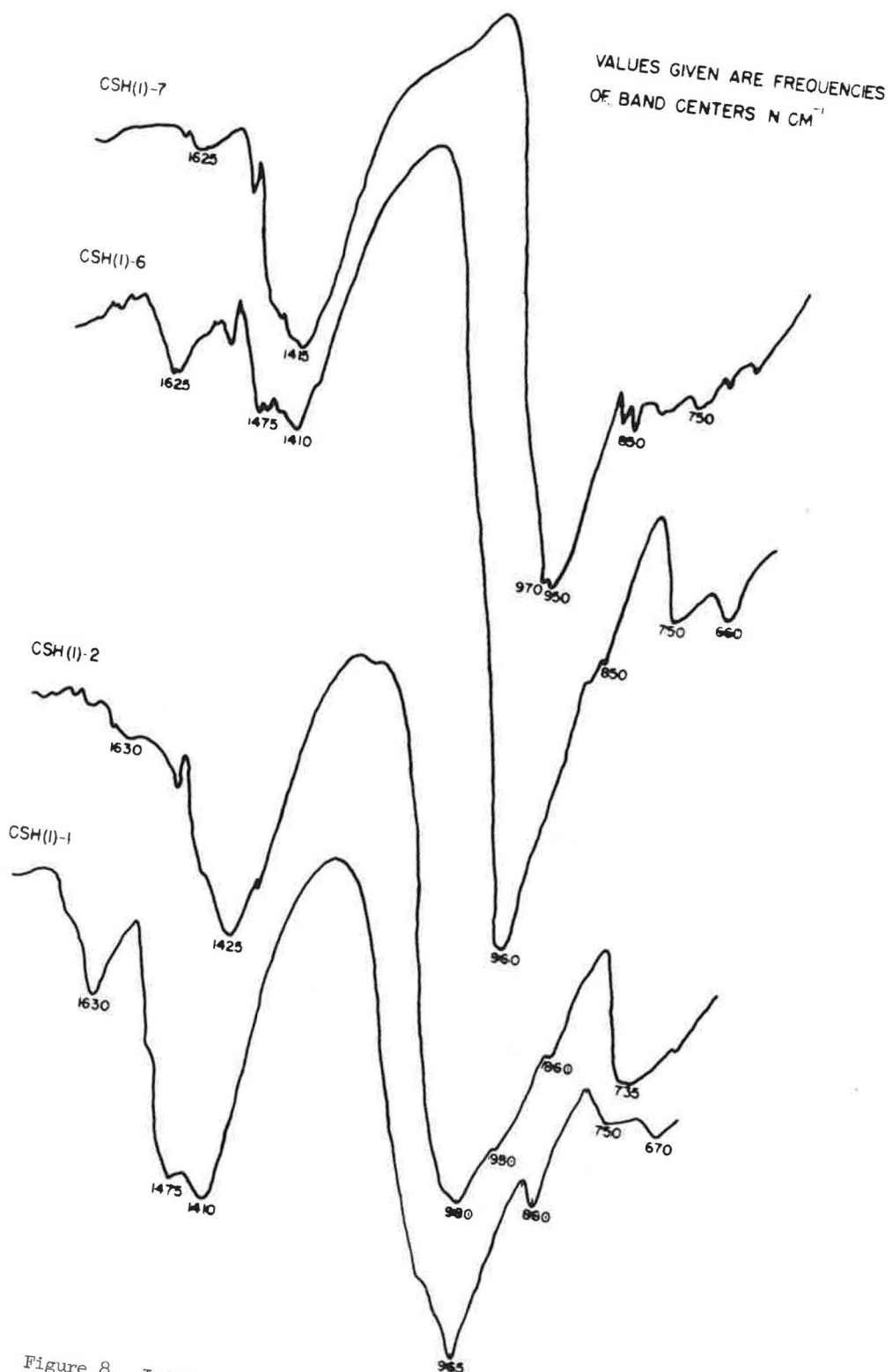
Figure 8. Infrared absorption spectra for CSH(I) samples.

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 hydrogen 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 to 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.

In Figure 8, 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 material) 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). The band for sample CSH(I)-1, which displayed vaterite x-ray diffraction peaks, was not appreciably stronger than those for the other samples. Hunt (15) has shown that a very small percentage of carbonate can produce a disproportionately large effect on the infrared spectrum, and this has been confirmed in laboratory trials. 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 the other CSH(I) samples, 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, the infrared spectrum for CSH(I)-2, the x-ray-amorphous member of the group, is similar to those of the other samples. A second 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 third 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 wavelength). 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 to 1200 cm^{-1}. This feature is even more pronounced with tobermorite gel spectra.

Spectra for five of the products of the hydrated cement minerals are shown in Figure 9. Because these spectra were secured using an instrument the presentation of which is linear in wavelength rather than wave number, 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 tobermorite 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 because the 421 instrument gave an identical effect. The effect is not apparent in previously published spectra of 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 a wide variation in the index of refraction of certain particulate solids with wavelength in the region of a strong absorption band. At a wavelength 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.
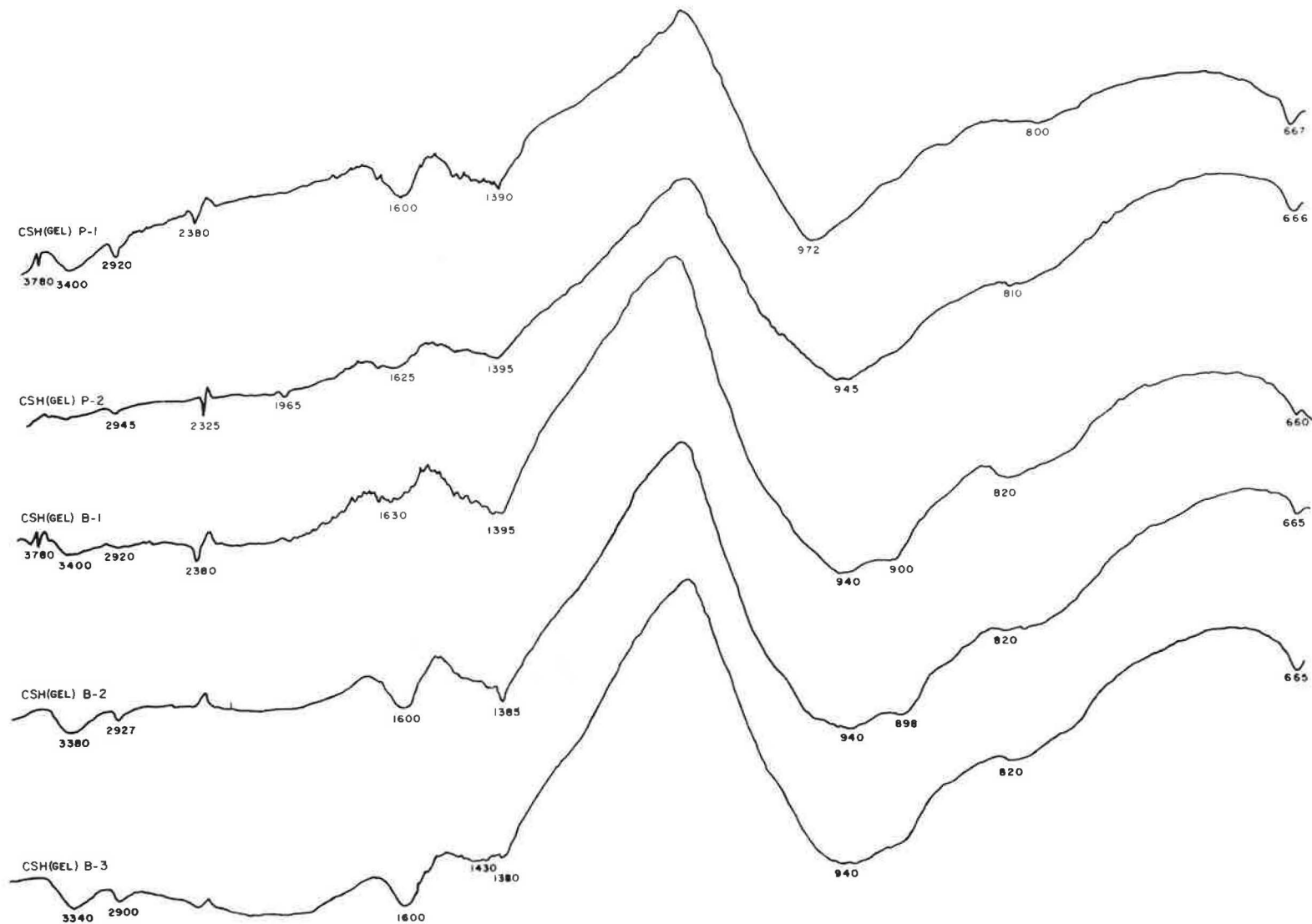
Figure 9. Infrared absorption spectra for tobermorite gel products.

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 β-C_2S 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), the tobermorite gel tends to be largely an orthosilicate.

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

In Figure 9, a number of small features can be observed in the 2000 to 4000 cm^{-1} region. A comparatively weak and broad band is observable at 3340 to 3400 cm^{-1}, which is the OH stretching vibration for hydrogen-bonded OH groups. Patterns for both paste- and bottle-hydrated samples derived from β-C_2S show a sharp, complex absorption feature at 3780 cm^{-1}; and all 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 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 tobermorite 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 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 sq A/water molecule (2), and an estimate of the heat of adsorption of the uniform portion of the first layer, $\overline{E_1}$, 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 sq m/gm; these limits are consistent with the range of 135 to 380 sq m/gm cited recently by Brunauer (24). This range is similar to that usually found for tobermorite gels. The first four samples, prepared by rapid precipitation without any particular opportunity for aging, were significantly higher in surface area than the others. However, there does not seem to be a relationship between high surface area and poor crystallinity: CSH(I)-2, the x-ray-amorphous sample, has by far the poorest degree of crystallinity, yet it 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 2,000 to 3,000 cal/mole. It is noteworthy that the x-ray-amorphous samples have an unusually low E_1, which is only about 1,200 cal/mole higher than the heat of condensation of water.

A reduced water-vapor adsorption isotherm for six of the seven materials is given in Figure 10. The relative concordance of all data plotted in this way (which removes

TABLE 3

SURFACE AREAS AND HEATS OF
ADSORPTION OF WATER VAPOR[a]

Sample No.	Surface Area (sq m/gm)	E_1 (cal/mole)
CSH(I)-1	355	12,700
CSH(I)-2	245	11,700
CSH(I)-3	280	12,800
CSH(I)-4	300	12,500
CSH(I)-5	165	13,100
CSH(I)-6	175	13,700
CSH(I)-7	155	12,700

[a]For CSH(I) preparations at 21 C.

Figure 10. Reduced water vapor adsorption isotherm for CSH(I) samples.

the effect of the differing surface areas of the individual samples) suggests that the samples for which points are plotted have surfaces qualitatively similar 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 both CSH(I) and tobermorite 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 horizontal particle velocity could not be measured under influence of the applied electric current. However, because the direction of travel of the particles could readily be determined, the sign of the net surface charge could be obtained.

The CSH(I) particles dispersed in distilled water were charged negatively, but the same materials dispersed in saturated calcium hydroxide solutions were charged positively. The tobermorite gel samples initially dispersed in water were positively charged, but in view of the calcium hydroxide present as a companion product of the hydration reactions, this result was not unexpected. When the 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 also to CSH(I) and tobermorite gel. 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 CSH might have distinctive cation-exchange properties is not new; speculations to this effect were given by McConnell (27) and by Roy (28). However, no laboratory confirmation of
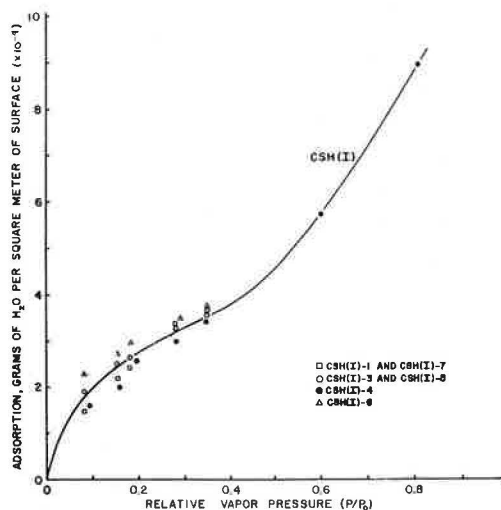
such properties can be found. One difficulty is that, due to the small but not negligible solubility of these phases in water, the methods normally employed for cation exchange determinations are untrustworthy. The difficulty is that after treating the sample with solutions containing a large excess of a measuring cation to insure replacement of the original cations on the exchange sites, all excess measuring cation must be removed. This is usually accomplished by repeated washing. However, repeated washing of CSH(I) and tobermorite gel with water leads to breakdown and eventual dissolution of the sample. This 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 obviate this difficulty (29). Potassium ions were used as the measuring cations with 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.

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, use of ammonium acetate to replace exchanged potassium in some cases resulted in the formation of a gel, which made the necessary washing treatments mechanically difficult. 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/100 gm, 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 to 24 meq/100 gm. 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 tobermorite 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/100 gm and the paste product of the same material yielding the high value of about 20 meq/100 gm. The bottle-hydrated alites both gave values somewhat higher than the corresponding bottle-hydrated C_3S product, both hydrated alite samples giving 18 meq/100 gm. 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 exchange capacities of about 3 meq/100 gm were recorded for each of the others. Thus, the observed exchange capacities of the gel samples relate primarily to the tobermorite 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, the CSH(I) phase and the tobermorite gel phase appear to be distinctive entities with only limited ranges of variation in properties despite the wide compositional range of the former. The gel materials produced by paste and by bottle hydration of β-C_2S, C_3S, and alite were all remarkably similar to each other. These phases are distinct from well-crystallized tobermorite not only in their poor crystallinity but also in a number of other ways.

One of the notable differences found between the tobermorite gel, 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 par-

ticles to disperse. This feature is as pronounced with CSH(I) as it is with tobermorite gel. A corollary to this observation is the discovery (30) that when CSH(I) is produced by reaction of calcium hydroxide on clay minerals, cementation is as effective and permanent as when tobermorite 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 is that all these results are available for the same well-defined group of samples.

The observed cation-exchange properties of these materials are not easily explainable in terms of isomorphous substitution, because most of the samples are pure CSH. The other commonly accepted source of cation-exchange sites in silicate minerals is 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 CSH, 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 tobermorite 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, whereas tobermorite 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 plate-like, or crinkled foil appearance, whereas tobermorite gel is essentially fibrous. Infrared spectra are of some utility in identification of the phases, the patterns for the 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 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.

ACKNOWLEDGMENTS

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