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The Stoichiometry of the Hydration of β-Dicalcium Silicate and Tricalcium Silicate at Room Temperature

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The hydration of β-Ca_2SiO_4 was carried out at room temperature by three methods: (a) in a small steel ball mill, (b) in paste form, and (c) in a polyethylene bottle rotated on a wheel. Ca_3SiO_5 was hydrated by methods (b) and (c). The probable stoichiometry is represented by the equations 2β-$Ca_2SiO_4 + 4H_2O = Ca_3Si_2O_7 \cdot 3H_2O + Ca(OH)_2$; $2Ca_3SiO_5 + 6H_2O = Ca_3Si_2O_7 \cdot 3H_2O + 3Ca(OH)_2$. The same calcium silicate hydrate was produced in all five cases, and it was similar to the natural mineral tobermorite. The $Ca(OH)_2$ was obtained in two forms: the normal crystalline one and as an amorphous phase. The densities of tobermorites of composition $Ca_3Si_2O_7 \cdot 2H_2O$ and $Ca_3Si_2O_7 \cdot 2.80H_2O$ were 2.86 and 2.73 g./cc., respectively. Thus, the apparent density of the water in excess of 2 moles was 1.39 g./cc. The calculated density of $Ca_2Si_2O_7 \cdot 3H_2O$ was 2.71 g./cc. The X-ray diffraction patterns showed only the (110), (200) and (020) spacings of tobermorite. The (001) spacing was calculated from these and from density data. Relationships between surface area, particle dimensions, crystal structure and certain swelling properties of tobermorite are discussed.

Introduction

Tricalcium silicate, Ca_3SiO_5, and β-dicalcium silicate, β-Ca_2SiO_4, are two of the major components of portland cement, together constituting 70–85% of portland cement by weight. The stoichiometry of the hydration of Ca_3SiO_5 at room temperature was reported in two papers, one discussing hydration in a ball mill,[1] the other, hydration in paste form.[2] In the present investigations, the stoichiometry of the hydration of β-Ca_2SiO_4 at room temperature was determined under three conditions: (a) in a small steel ball mill, (b) in paste form and (c) in a polyethylene bottle rotated on a wheel; and the stoichiometry of the hydration of Ca_3SiO_5 was determined under condition (c). Also, further work was done on the hydration of Ca_3SiO_5 under condition (b).

Experimental

1. The preparation of β-Ca_2SiO_4 was described in an earlier paper.[3] The hard, stone-like material obtained in a small kiln was crushed in a Braun pulverizer, then ground in a porcelain jar mill with flint pebbles. The fraction used had a Blaine surface (ASTM Designation C-204-51) of about 4500 cm.^{2}/g. The iron introduced in the pulverizer was removed by a magnetic separator. The analysis of the β-Ca_2SiO_4 was the same as reported before,[3] except that it contained only 0.22% free silica, instead of 0.45%. The Ca_3SiO_5 was identical with that used earlier.[3]

2. The ball-mill hydration of β-Ca_2SiO_4 was carried out in the same manner as that of Ca_3SiO_5.[1] Because β-Ca_2SiO_4 hydrates slowly, it was ball-milled for 46 days. The product was designated D-28.

The paste hydration of β-Ca_2SiO_4, likewise, was conducted in the same way as that of Ca_3SiO_5.[2] The Ca_2SiO_4 paste, C-23, as well as two Ca_3SiO_5 pastes, C-17 and C-18, were hydrated for 17 months.

In the third type of hydration, β-Ca_2SiO_4 or Ca_3SiO_5 was mixed with nine times its weight of distilled water and placed in a 1000-ml. polyethylene bottle. The bottle was stoppered, paraffin-sealed, and rotated at 30 r.p.m. For the Ca_2SiO_4 batch, D-40, the bottle was rotated for 162 days; for three Ca_3SiO_5 batches, D-35, D-42 and D-43, the bottles were rotated for 47, 49 and 49 days, respectively.

All hydration experiments were carried out in a constant-temperature room, kept at 23.5 ± 0.5°.

3. The drying of the batches and the removal of adsorbed water were described in earlier papers.[1,4] Six batches were dried at a vapor pressure of 5 × 10^{-4} mm. Two batches, C-18 and D-43, were dried at the equilibrium pressure of $Mg(ClO_4)_2 \cdot 2H_2O$ and $Mg(ClO_4)_2 \cdot 4H_2O$, which is 8.15 × 10^{-3} mm.[5]

4. Density at 27.2° was determined by measuring the displacement of a saturated calcium hydroxide solution in Welds type pycnometers.

5. X-Ray diffraction patterns were obtained with a Norelco Wide Range Geiger Counter Diffractometer or with

(1) S. Brunauer, L. E. Copeland and R. H. Bragg, J. Phys. Chem., 60, 112 (1956).

(2) S. Brunauer, L. E. Copeland and R. H. Bragg, ibid., 60, 116 (1956).

(3) S. Brunauer, D. L. Kantro and C. H. Weise, ibid., 60, 771 (1956).

(4) S. Brunauer, J. C. Hayes and W. E. Hass, ibid. 58, 279 (1954).

(5) L. E. Copeland and R. H. Bragg, ibid., 58, 1075 (1954).

a Norelco Counting Rate Computer used in conjunction with the diffractometer. Cu $K\alpha$ radiation was used. Intensity measurements were obtained as described earlier.[1] Quantitative analyses were made for $Ca(OH)_2$, unhydrated β-Ca_2SiO_4 and unhydrated Ca_3SiO_5 by means of a method developed by Copeland and Bragg.[6] Mixtures of known compositions of $Mg(OH)_2$ and $Ca(OH)_2$ were prepared, and the relative intensity of the 2.63 Å. $Ca(OH)_2$ line to the 2.37 Å. $Mg(OH)_2$ line was determined as a function of the weight ratio of the mixture. Similarly, known mixtures of $Mg(OH)_2$ and β-Ca_2SiO_4 and $Mg(OH)_2$ and Ca_3SiO_5 were employed to obtain calibration curves; the 2.79 and 2.20 Å. lines of β-Ca_2SiO_4, the 2.20 Å. line of Ca_3SiO_5, and the 2.37 Å. line of $Mg(OH)_2$ were used. The determinations of the unknown quantities of $Ca(OH)_2$, Ca_2SiO_4 and Ca_3SiO_5 were then carried out by adding a known weight of $Mg(OH)_2$ to a known weight of sample, determining the appropriate line intensity ratios, and using the calibration charts.

6. Surface areas were measured by the B.E.T. method,[7] using water vapor and nitrogen as adsorbates. Water vapor adsorption was measured gravimetrically at 25° and nitrogen adsorption volumetrically at −195.8°.

7. Ignition loss and carbon dioxide content were determined, chemical analyses were performed, and the compositions of the substances were calculated according to methods described before.[4]

8. A fraction of the calcium hydroxide was extracted from parts of batches D-42, D-28 and C-18 by a modification of the method of Franke.[8] These extracted portions were designated D-42A, D-28A and C-18A, respectively. They were dried at a vapor pressure of 5×10^{-4} mm.

9. The average numbers of samples used in the different determinations were as follows: chemical analysis 2, X-ray analysis 4, ignition loss 4, carbon dioxide 3, density 4, water surface 4, nitrogen surface 2.

Results and Discussion

Although in all experiments reported here, β-Ca_2SiO_4 or Ca_3SiO_5 was mixed with water, lime saturation was established at an early stage of hydration, and thereafter the reaction progressed in a saturated $Ca(OH)_2$ solution. The probable stoichiometry of the hydration of β-Ca_2SiO_4 at 23.5° at or near completion of the reaction under all three conditions investigated can be represented by the equation

$$2\beta\text{-}Ca_2SiO_4 + 4H_2O = Ca_3Si_2O_7 \cdot 3H_2O + Ca(OH)_2 \quad (1)$$

The probable stoichiometry of the hydration of Ca_3SiO_5 in the polyethylene bottle at 23.5° can be represented by the equation

$$2Ca_3SiO_5 + 6H_2O = Ca_3Si_2O_7 \cdot 3H_2O + 3Ca(OH)_2 \quad (2)$$
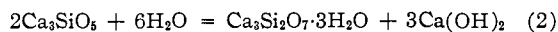
The calcium silicate hydrate produced in both reactions was the high-lime end-member of a series of hydrates designated by Taylor[9] as calcium silicate hydrate (I) or CSH(I). Because of its similarity to the natural mineral tobermorite,[10] in the earlier papers[1,2] it was called tobermorite, and that name will be retained in the present paper. Bogue[11] recommended the designation CSH(B) tobermorite, and in a recent paper Grudemo[12] used the designation CSH(B). Bernal[13] tentatively assigned the

(6) L. E. Copeland and R. H. Bragg, to be published in *Anal. Chem.*

(7) S. Brunauer, P. H. Emmett and E. Teller, This Journal, **60**, 309 (1938).

(8) E. E. Pressler, S. Brunauer and D. L. Kantro, *Anal. Chem.*, **28**, 896 (1956).

(9) H. F. W. Taylor, *J. Chem. Soc.*, 3682 (1950).

(10) G. F. Claringbull and M. H. Hey, *Mineral. Mag.*, **29**, 960 (1952).

(11) R. H. Bogue, *Mag. Concrete Res.*, No. 14, 87 (1953).

(12) A. Grudemo, Handlingar, Nr. 26, Stockholm, 1955.

(13) J. D. Bernal, "Proceedings of the Third International Symposium on the Chemistry of Cement," London, 1952, p. 216.

structural formula $Ca_2[SiO_2(OH)_2]_2[Ca(OH)_2]$ to this compound.

As will be shown, all three types of hydration of β-Ca_2SiO_4 and the "bottle" hydration of Ca_3SiO_5 produce the same calcium silicate hydrate as is produced in the paste hydration of Ca_3SiO_5.[2] Only the ball-mill hydration of Ca_3SiO_5 gives a different calcium silicate hydrate, afwillite.[1]

Extent of Hydration.—Two of the Ca_3SiO_5 batches (C-17 and C-18) and one of the β-Ca_2SiO_4 batches (D-28) were completely hydrated. The X-ray powder diffraction patterns of these materials showed none of the reflections corresponding to the unhydrated substances, and microscopic examination showed absence of unhydrated Ca_3SiO_5 or Ca_2SiO_4.

The quantities of unhydrated Ca_2SiO_4 in C-23 and D-40 and Ca_3SiO_5 in D-35 and D-43 were determined by X-ray analysis, and the results are given in Table I. The values in each column were obtained for different samples of the same batch. The term "batch" refers to the end product of the hydration; it includes, therefore, the unhydrated material when present.

TABLE I

Quantitative X-Ray Analysis of Unhydrated β-Ca_2SiO_4 and Ca_3SiO_5

C-23 Paste hydrated Ca_2SiO_4 % Ca_2SiO_4		D-40 Bottle hydrated Ca_2SiO_4 % Ca_2SiO_4		D-35 Bottle hydrated Ca_3SiO_5 % Ca_3SiO_5	D-43 Bottle hydrated Ca_3SiO_5 % Ca_3SiO_5
2.20 Å.	2.79 Å.	2.20 Å.	2.79 Å.	2.20 Å.	2.20 Å.
26.8	30.4	27.4	29.3	4.2	2.2
27.0	27.8	26.8	29.1	3.1	2.9
25.9	26.0	26.8	27.7	3.2	2.8
28.9	27.1	25.5	27.5	..	2.0
27.1	27.8	26.6	28.4		
Av. 27.5		27.5		3.5	2.5

Hydration on the rotating wheel is considerably faster than in paste form. The same extent of hydration, 69.3%, was achieved for Ca_2SiO_4 on the wheel in 162 days (D-40) as in paste form in 17 months (C-23). Hydration in the ball-mill is still faster; complete hydration of Ca_2SiO_4 was obtained in 46 days (D-28).

It has been long known that the hydration of Ca_3SiO_5 in paste form is much faster than that of β-Ca_2SiO_4. The same is true of the two other types of hydration. Two of the batches of "bottle" hydrated Ca_3SiO_5, D-42 and D-43, were 96.9% hydrated in 49 days, and a third one, D-35, was 96.3% hydrated in 47 days; whereas the Ca_2SiO_4 batch, D-40, under the same conditions was only 69.3% hydrated in 162 days. In the ball-mill, Ca_3SiO_5 can be completely hydrated in 6 days[1] or less, whereas Ca_2SiO_4 under the same conditions is only about one-third hydrated.

Calcium Hydroxide.—1. The quantity of calcium hydroxide was determined in each batch by X-ray analysis, and the results are shown in Table II. In the last three columns the per cent. of $Ca(OH)_2$ is given for the materials from which a part of the $Ca(OH)_2$ had been extracted.

2. The data in the first eight columns will be considered first. The averages of the experimental

Table II
Quantitative X-Ray Analysis of Calcium Hydroxide, %

1 D-28 Ca₂SiO₄ ball-mill completely hydrated	2 C-23 Ca₂SiO₄ paste 69.3% hydrated	3 D-40 Ca₂SiO₄ bottle 69.3% hydrated	4 C-17 Ca₃SiO₅ paste completely hydrated	5 C-18 Ca₃SiO₅ paste completely hydrated	6 D-35 Ca₃SiO₅ bottle 96.3% hydrated	7 D-42 Ca₃SiO₅ bottle 96.9% hydrated	8 D-43 Ca₃SiO₅ bottle 96.9% hydrated	9 D-28A Ca₂SiO₄ ball-mill (extracted)	10 C-18A Ca₃SiO₅ paste (extracted)	11 D-42A Ca₃SiO₅ bottle (extracted)
10.1	6.9	4.9	35.3	32.9	38.5	35.7	34.2	8.6	19.0	20.7
9.2	7.1	5.1	33.2	33.3	36.0	36.0	33.5	9.0	21.2	20.7
8.8	6.0	4.8	34.8	32.0	36.0	36.0	32.3	9.5	19.5	20.9
8.0	6.6	4.0	37.2	31.6	37.0	36.4	..	9.0	19.5	..
10.9	..	..	..	32.8	37.3	..	..	9.4	20.7	..
9.0	..	..	..	..	..	..	..	..	..	..
9.2	..	..	..	..	..	..	..	..	..	..
9.3	6.6	4.7	35.1	32.5	37.0	36.0	33.2	9.1	20.0	20.8
(17.0)	(13.1)	(12.3)	(39.7)	(38.6)	(37.5)	(41.1)	(36.9)	(9.0)	(22.0)	(21.0)

results are given in the row before the last one. The values given in parentheses in the last row are theoretical values based (a) on chemical analyses of the hydration products, and (b) on the assumption that the stoichiometry of the hydration reactions is represented by eq. 1 and 2. It will be noted that in every instance the experimental value is smaller than the theoretical.

A similar result was reported before[2] for the paste hydration of Ca_3SiO_5. The $Ca(OH)_2$ determined by X-ray analysis was about 15% less than the theoretical value, just as for Ca_3SiO_5 paste C-18, column 5. Since X-ray analysis determines the quantity of crystalline $Ca(OH)_2$, the missing $Ca(OH)_2$ was ascribed to adsorption on the tobermorite surface. The present experiments have led to a revision of this view.

There seem to be three possible ways to explain the discrepancy. The missing $Ca(OH)_2$ is (a) adsorbed on the surface of the calcium silicate hydrate, or (b) it is amorphous or very poorly crystallized, or (c) it is a part of the calcium silicate hydrate phase.

If alternative (c) is correct, the stoichiometry represented by eq. 1 and 2 is wrong. The molar CaO/SiO_2 ratio in the calcium silicate hydrate in that case is not 1.5, but it is a variable quantity, ranging from 1.52 to 1.79, as Table III, column 3, shows.

Table III
Some Properties of Hydrated Calcium Silicates

1 Material	2 Missing Ca(OH)₂, %	3 Apparent molar CaO/SiO₂ ratio in hydrate	4 Specific surface area of tobermorite (m.²/g.)	5 Molar H₂O/SiO₂ ratio in tobermorite	6 Density of tobermorite (g./cc.)
D-28, Ca₂SiO₄ ball-mill	7.7	1.71	274	1.04	2.82
D-40, Ca₂SiO₄ bottle	7.6	1.79	303	1.03	2.84
C-23, Ca₂SiO₄ paste	6.5	1.75	299	1.00	2.89
D-35, Ca₃SiO₅ bottle	0.5	1.52	376	1.03	2.86
D-42, Ca₃SiO₅ bottle	5.0	1.70	349	1.10	2.87
C-17, Ca₃SiO₅ paste	4.6	1.67	293	1.06	2.87
C-18, Ca₃SiO₅ paste	6.1	1.73	237	1.40	2.77
D-43, Ca₃SiO₅ bottle	3.3	1.67	293	1.40	2.70

3. If alternative (a) is correct, the amount of missing $Ca(OH)_2$ should increase with increasing surface area of the calcium silicate hydrate. A comparison of columns 2 and 4, Table III, shows that this is not the case. Actually, D-35 had the smallest amount of missing $Ca(OH)_2$ and the largest specific surface area. The quantity of missing $Ca(OH)_2$ in D-35 was about equal to the experimental error.

If the calcium silicate hydrate in D-35 had little or no $Ca(OH)_2$ adsorbed on its surface, this had to be true also of the other batches. The calcium silicate hydrates in all batches were in contact with saturated solutions of $Ca(OH)_2$ at 23.5° for long times. The solvent and the solute compete for adsorption on the surface of the calcium silicate hydrate, and under the experimental conditions, apparently, water has the greater affinity for the surface.

Experiments reported in the literature indicate that the adsorption of $Ca(OH)_2$ on the surface of tobermorite must be small. Bessey,[14] Taylor[9] and Greenberg[15] found that the CaO/SiO_2 ratio in tobermorite at or near lime saturation was 1.5, within their experimental error. Although Greenberg alone measured surface areas, it is probable that the three investigators obtained tobermorites of different specific surface areas, comparable in extent to those reported in this paper. Had the adsorption of $Ca(OH)_2$ been appreciable, the apparent CaO/SiO_2 ratios in their tobermorites would have been variable and all greater than 1.5.

4. Further experiments were performed to decide between alternatives (b) and (c). About half of the theoretical $Ca(OH)_2$ (last row of Table II) was extracted from parts of batches D-28, C-18 and D-42, and the amount of $Ca(OH)_2$ remaining was determined by X-ray analysis. The results are shown in the last three columns of Table II, with averages in the row above the last one.

Since the amount of $Ca(OH)_2$ removed was accurately determined, the $Ca(OH)_2$ remaining as such could be calculated on the bases of alternatives (b) and (c). In the calculations allowance was made for a slight extraction of lime from the calcium silicate hydrate.[8]

If it is assumed that alternative (b) is correct, and that the removal of half of the $Ca(OH)_2$ results in the removal of all amorphous $Ca(OH)_2$, the calculated values of the remaining $Ca(OH)_2$ are

(14) G. E. Bessey, "Proceedings of the Symposium on the Chemistry of Cements," Stockholm, 1938, p. 178.

(15) S. A. Greenberg, J. Phys. Chem., 58, 362 (1954).

those shown in parentheses in the last row of Table II. If alternative (c) is assumed, the calculated values are much smaller: 1.1, 15.4 and 13.2% for D-28A, C-18A and D-42A, respectively. It follows from the experimental results that alternative (b) is correct.

The removal of about half of the $Ca(OH)_2$ from D-28 and D-42 resulted in complete removal of the amorphous $Ca(OH)_2$. Under the same conditions, 70% of the amorphous $Ca(OH)_2$ was removed from C-18. In all three cases, the Franke solvent reacted more rapidly with the amorphous $Ca(OH)_2$ than with crystalline $Ca(OH)_2$. On the other hand, the Franke solvent reacts 50 times as rapidly with $Ca(OH)_2$ as with the lime in the calcium silicate hydrate.[8]

5. Heller and Taylor[16] found some evidence of amorphous or imperfectly crystallized $Ca(OH)_2$ in the products of the reaction between $Ca(OH)_2$ and silica gel at temperatures of 110° and higher. Grudemo, in a private communication, suggested that dissolved silica may have entered the lattice of some of the $Ca(OH)_2$, disturbing or destroying the lattice. Thus, the amorphous $Ca(OH)_2$ may be regarded as impure $Ca(OH)_2$ or as a very lime-rich calcium silicate hydrate. This is possible; but some evidence was obtained showing that if the lattice disturbance of $Ca(OH)_2$ is caused by dissolved silica, a fraction of 1% of silica is responsible for the effect.

Grudemo[12] presented electron micrographs of hydrated Ca_3SiO_5, in some of which he identified a constituent as amorphous $Ca(OH)_2$ or a very lime-rich calcium silicate hydrate. Selected area electron diffraction showed that the strongest line of this substance was at 2.8 to 3.0 Å. (private communication). Tobermorite has a broad X-ray diffraction line at about 2.8 Å., which masks the amorphous $Ca(OH)_2$ line. However, a comparison of this line obtained from D-28 and D-28A showed that removal of the amorphous $Ca(OH)_2$ had changed both the shape and intensity of the line. In D-28, the 2.8 Å. line had a sharper peak than in D-28A, and the intensity of the line relative to the 3.05 Å. tobermorite line was greater in D-28 than in D-28A. Thus, it seems that the amorphous $Ca(OH)_2$ produced in the present experiments had an X-ray line at about 2.8 Å.

6. The specific surface area of $Ca(OH)_2$ produced in the paste hydration of Ca_3SiO_5 was determined by two methods: water vapor adsorption and X-ray line broadening measurements. In the adsorption experiments, the surface area was measured before and after complete extraction of the $Ca(OH)_2$, and it was assumed that the extraction did not change the specific surface area of tobermorite. The molecular area of adsorbed water was taken to be 11.4 Å.[2], for reasons to be given later. The method used in the line broadening experiments was described in an earlier paper.[17] The height of the average hexagonal prism was determined from the broadening of the 4.91 Å. line (001) of $Ca(OH)_2$, as before, but the side of the

hexagon was evaluated from two lines: the 3.11 Å. line (100) and the 1.81 Å. line (110).

For the $Ca(OH)_2$ in C-17, water vapor adsorption gave a specific surface area of 8.6 m.^{2}/g., and line broadening gave 7.0 m.^{2}/g. Adsorption measures the surface area of all $Ca(OH)_2$, crystalline and amorphous, whereas the line broadening gives a measure of the surface area of crystalline $Ca(OH)_2$ only. In C-17, amorphous $Ca(OH)_2$ was about 12% of the total $Ca(OH)_2$ (Table II).

High accuracy cannot be expected from either type of experiment. In the adsorption experiments, the surface area of $Ca(OH)_2$ is obtained as a relatively small difference between two large values. (The surface area of $Ca(OH)_2$ is less than 2% of the surface area of the hydration products.) In the line broadening experiments, the 3.11 and 1.81 Å. lines of $Ca(OH)_2$ are overlapped by the very broad 3.05 and 1.82 Å. lines of tobermorite, and correction must be made for this.

The specific surface areas of $Ca(OH)_2$ in bottle hydrated Ca_3SiO_5, D-42, and in ball-mill hydrated Ca_2SiO_4, D-28, were estimated by X-ray line broadening. The former was negligible, but the latter had an apparent value of 53.4 m.^{2}/g. Line broadening is caused by imperfections and by crystal size. Six weeks of grinding in a ball mill is likely to produce not only small crystals but imperfect ones as well. If half of the broadening was caused by imperfections, the specific surface area of $Ca(OH)_2$ in D-28 was 26.7 m.^{2}/g.

Water of Hydration.—1. That one molecule of Ca_3SiO_5 reacts with exactly three molecules of water and one molecule of β-Ca_2SiO_4 with two molecules of water could not be demonstrated in the present investigations. The reason for this is that a reliable method is lacking to distinguish quantitatively between adsorbed water and chemically bound water in tobermorite. As Table III, column 4, shows, tobermorite has a very large specific surface area. To estimate the water of hydration, the adsorbed water must be removed from the surface, but this cannot be accomplished without removing some of the water of hydration.

2. Six batches were dried to equilibrium at a water vapor pressure of 5×10^{-4} mm. The molar H_2O/SiO_2 ratio in the tobermorite was close to 1.0, but it was not exactly that, as Table III, column 5, shows. The values ranged from 1.00 to 1.10. The amount of water in excess of 1.00 mole did not depend on the surface area of the tobermorite, nor on the source of the tobermorite (Ca_3SiO_5 or β-Ca_2SiO_4), nor on the type of hydration (paste, ball mill or bottle). Apparently, the colloidal particles form aggregates of various sizes, and it is possible that some of the particles deep inside the largest aggregates did not equilibrate fully. Perhaps months or years of drying would have been needed to bring about complete equilibration.

3. C-18 and D-43 were dried to equilibrium at a vapor pressure of 8×10^{-3} mm., and the molar H_2O/SiO_2 ratio was 1.40. A part of this water was probably adsorbed water. If it is assumed that the water of hydration in excess of a molar H_2O/SiO_2 ratio of 1.00 has no influence on the surface area,

(16) L. Heller and H. F. W. Taylor, *J. Chem. Soc.*, 2535 (1952).

(17) S. Brunauer, D. L. Kantro and C. H. Weise, *Can. J. Chem.*, **34**, 729 (1956).

but water adsorbed prior to the surface area determination causes an apparent diminution of the surface area, molecule for molecule, the quantity of adsorbed water can be estimated. C-17 and C-18 were parts of the same paste hydrated Ca_3SiO_5, dried to different water contents. If C-18 contained no adsorbed water, its surface area would have been the same as that of C-17, but actually a lower apparent value was obtained (Table III, column 4). The difference indicates 0.13 mole of adsorbed water per mole of SiO_2. Similar calculations for bottle hydrated Ca_3SiO_5 batches D-42 and D-43 lead to the same result. Thus, the molar ratio of chemically bound water to SiO_2 in the tobermorites of C-18 and D-43 was 1.27.

The adsorbed water in C-18 and D-43 corresponds to a surface coverage of 19 and 16%, respectively. If, in the pressure range below 8×10^{-3} mm., the amount adsorbed varies linearly with pressure, the surface coverage at 5×10^{-4} mm. pressure is about 1%. This corresponds to less than 0.01 mole of adsorbed water per mole of SiO_2. The H_2O/SiO_2 ratios in Table III, column 5, were not corrected for adsorbed water.

4. The molecular formula of the tobermorites in C-18 and D-43, corrected for adsorbed water, is $Ca_3Si_2O_7 \cdot 2.54H_2O$. It is clear that drying at a vapor pressure greater than 8×10^{-3} mm. would have led to a higher water content. On the basis of arguments advanced in an earlier paper,[2] as well as on the basis of the present results, it seems reasonable to suppose that in a saturated $Ca(OH)_2$ solution tobermorite contains 3 molecules of combined water.

Taylor[18] determined the variation with temperature of the molar H_2O/SiO_2 ratio of a tobermorite having a molar CaO/SiO_2 ratio of 1.5. He obtained a sharp break at about 150° and an H_2O/SiO_2 ratio of about 1.0, indicating a difference between the bindings of two of the water molecules and the third one. The present experiments also show that two of the water molecules are very firmly held.

Tobermorite.—1. It was shown before that the CaO/SiO_2 ratio in tobermorites obtained by complete (or nearly complete) hydration of Ca_3SiO_5 and β-Ca_2SiO_4 was 1.5. Taylor[9] also obtained tobermorite in the hydration of Ca_3SiO_5; however, in an experiment conducted under rather special conditions he obtained a calcium silicate hydrate that differed slightly in X-ray pattern from tobermorite. He designated this hydrate C_2SH-(II). The apparent CaO/SiO_2 ratio was about 1.9, and the hydrate exhibited certain morphological differences from tobermorite.[12]

Recently, van Bemst[19] conducted investigations on the hydration of calcium silicates, and he reported that the calcium silicate hydrate formed in the paste hydration of Ca_3SiO_5 at 25° and lower temperatures (as well as in certain other experiments) was C_2SH(II), with CaO/SiO_2 ratios between 1.7 and 2.0. Recent experiments in this laboratory revealed the presence of tobermorites having CaO/SiO_2 ratios greater than 1.5 in hydrated β-Ca_2SiO_4 and in hydrated portland cements high

(18) H. F. W. Taylor, J. Chem. Soc., 163 (1953).
(19) A. van Bemst, Bull. soc. chim. Belg., 64, 333 (1955).

in β-Ca_2SiO_4. These high-lime tobermorites appear to be intermediate products in the hydration of β-Ca_2SiO_4 and possibly also of Ca_3SiO_5.

2. The densities of the tobermorites in the eight batches of hydrated β-$CaSiO_4$ and Ca_3SiO_5 are shown in Table III, column 6. The measured densities of the hydration products were corrected for $Ca(OH)_2$, as well as for the slight amounts of impurities, by assuming additivity of the densities. The density of amorphous $Ca(OH)_2$ was taken to be the same as that of crystalline $Ca(OH)_2$, 2.241 g./cc. This appeared to be true within the rather large experimental error, since no trend in density was evident with the per cent. of amorphous $Ca(OH)_2$ in the batch. On the other hand, there was a trend with water content.

The density of tobermorite, having the composition $Ca_3Si_2O_7 \cdot 2H_2O$, can be calculated by assuming that the density change is directly proportional to the water content in excess of 2 moles. Using the first six values of Table III, column 6, and the method of least squares, one obtains

$$d(Ca_3Si_2O_7 \cdot 2H_2O) = 2.86 \pm 0.2 \text{ g./cc.}$$

The tobermorite in C-18 and D-43 had a water content of 2.80 moles. Using their average density, one can calculate the average density of the water in excess of 2 moles. Dividing the weight increase by the volume increase, one obtains

$$d(H_2O) = 1.39 \text{ g./cc.}$$

It was pointed out before that C-18 and D-43 contained 0.26 mole of adsorbed water. Stamm[20] reported a value of 1.3 g./cc. for the density of water adsorbed on wood, when the surface coverage was a fraction of a monolayer. If the same density is assumed for the adsorbed water in C-18 and D-43, the density of the water of hydration in tobermorite, in excess of 2 moles, is 1.42 g./cc. However, the assumption is questionable.

The density of tobermorite of composition $Ca_3Si_2O_7 \cdot 3H_2O$ was calculated by assuming that the third mole of water had an average density of 1.39 g./cc. Thus, one obtains

$$d(Ca_3Si_2O_7 \cdot 3H_2O) = 2.71 \pm 0.02 \text{ g./cc.}$$

This value replaces the value of 2.44 g./cc. reported in an earlier paper.[2] The earlier value was obtained by an experimental technique that was later found not reliable.

C-18 and D-43 exhibited slow swelling in the saturated $Ca(OH)_2$ solution used in the density experiments. Their initial densities were 2.56 and 2.54 g./cc., respectively. For several days the density decreased very slowly, finally attaining a constant apparent value of 2.46 g./cc. for both.

The first six density values in Table III, column 6, showed no appreciable change with time. Apparently, tobermorite dried to a water content close to 1 mole per mole of SiO_2 loses its swelling properties. To investigate this point further, the density of paste hydrated Ca_3SiO_5 was determined using six different solid to liquid ratios (duplicate samples at each ratio). The range of ratios was twenty-fold. Within experimental error, the density was uninfluenced by the solid to liquid ratio. Five of the twelve samples showed a very slight

(20) A. J. Stamm, Ind. Eng. Chem., 30, 1280 (1938).

apparent decrease in density with time, three showed a very slight apparent increase, and four remained unchanged.

3. The six tobermorites dried to a water content of approximately one mole per mole of SiO_2 showed only three X-ray powder diffraction lines: at 3.05, 2.79 and 1.82 Å. Heller and Taylor[21] found that these spacings have indices of (110), (200) and (020), respectively, and they reported the same spacings at 3.07, 2.81 and 1.83 Å. Taylor[18] pointed out that drying results in a slight shrinkage of the ($hk0$) spacings. All three lines obtained in the present experiments were very broad, indicating small and imperfect crystals.

The unit cell of tobermorite is orthorhombic,[21] with $a = 5.59$ and $b = 3.64$ Å., when the composition is $Ca_3Si_2O_7 \cdot 2H_2O$. None of the samples in the present experiments showed the (001) line, probably because of the thinness and the rolling of the tobermorite sheets (see later). The c spacing was obtained from density measurements, with the assumption that the pseudocell of tobermorite, dried at a vapor pressure of 5×10^{-4} mm., contained one molecule of $Ca_3Si_2O_7 \cdot 2H_2O$.

The density of 2.86 ± 0.02 g./cc. corresponds to a c spacing of 9.3 ± 0.1 Å. By X-ray diffraction, Taylor[18] obtained the value of 9.3 ± 0.3 Å. for tobermorite of composition $Ca_2Si_2O_6 \cdot H_2O$. Apparently, therefore, the extra mole of $Ca(OH)_2$ that is present in the first six tobermorites of Table III does not influence appreciably either the (00l) or the ($hk0$) spacings.

The tobermorite of composition $Ca_3Si_2O_7 \cdot 3H_2O$ had a density of 2.71 ± 0.02 g./cc. Again assuming that a unit cell contains one molecule, one obtains a c spacing of 10.3 ± 0.1 Å. By X-ray diffraction, Taylor obtained a c spacing of 10.4 ± 0.4 Å. for tobermorite of composition $Ca_2Si_2O_6 \cdot 2H_2O$. In this case also, the extra mole of $Ca(OH)_2$ seems to make no appreciable difference in the spacings.

A comparison of the c spacings of $Ca_2Si_2O_6 \cdot 2H_2O$ obtained by Taylor and of $Ca_3Si_2O_7 \cdot 2H_2O$ obtained in the present experiments shows that the addition of one mole of CaO reduces the spacing from 10.4 to 9.3 Å. A qualitatively similar result was obtained by Grudemo.[12] Apparently, the contraction produced by one mole of CaO is approximately equal to the expansion produced by one mole of water; consequently, $Ca(OH)_2$ has no effect on the c spacing.

4. Tobermorite is a layer crystal,[13] like the clay minerals. A partial determination of the crystal structure of tobermorite was published recently by Megaw and Kelsey.[22] Electron micrographs show[12] that tobermorites of low CaO/SiO_2 ratios crystallize in large and very thin sheets. The dimensions of the sheets are of the order of several thousand ångström units; the thickness is only a few unit cells. In saturated or supersaturated $Ca(OH)_2$ solutions one obtains a fibrous or needle-like growth of crystals, "probably caused by a degeneration of the sheets into lath-like structures and by twisting or rolling of the crystal sheets."[12]

Since the thickness of a crystallite is small compared to the two dimensions of the layer, practically all of the surface area resides in the two sides of the layer. Knowing a and b, the dimensions of the unit cell within the layer, and assuming, as before, that a unit cell contains one molecule of $Ca_3Si_2O_7 \cdot 2H_2O$, the specific surface area of tobermorite of this composition can be calculated for any given thickness of the average crystallite. If the thickness is one unit cell (9.3 Å.), the specific surface area is 755 m.^{2}/g.

If the thickness is two unit cells, the specific surface area is 377 m.^{2}/g. The largest specific surface area measured by water vapor adsorption was that of the tobermorite in D-35, and it was 376 m.^{2}/g. (Table III, column 4). Naturally, the almost exact agreement is fortuitous. If the length and breadth of the average crystallite are 100 times as great as its thickness, neglecting the edge areas makes the calculated specific surface area 2% less than the true area. On the other hand, aggregation of the crystallites (possibly, bonding at the contact areas) reduces the surface accessible to water molecules for adsorption. The adsorption on the edge areas and the lack of adsorption at the contacts, apparently, compensate for each other in the tobermorite of D-35.

If the thickness is three unit cells, the calculated specific surface area (again, neglecting the edge areas) is 252 m.^{2}/g. The smallest surface area measured for a tobermorite having a molar H_2O/SiO_2 ratio of approximately 1.0, was that of the tobermorite in D-28, and it was 274 m.^{2}/g. The indication is in this case that most of the crystallites were three unit cells thick. The four other tobermorites are intermediate in surface areas between those of D-35 and D-28. Apparently, a very small percentage of the crystallites, if any, is more than three unit cells thick.

The low apparent specific surface areas of the tobermorites in C-18 and D-43 were discussed before.

5. The surface areas of the tobermorites investigated were measured by both nitrogen and water vapor adsorption. In all cases except one, nitrogen adsorption gave a smaller surface area than water adsorption. The exception was D-28, β-Ca_2SiO_4 hydrated in the ball-mill. The surface areas in this case were equal, if the molecular area of nitrogen was taken to be 16.2 Å.^{2} and that of water as 11.4 Å.^{2}.

The variability of the molecular area of physically adsorbed water was discussed in an earlier paper.[23] It is interesting to note that 11.4 Å.^{2} is the average between the molecular area of water adsorbed on $Ca(OH)_2$, 10.3 Å.^{2},[17] and that adsorbed on hydrous silica (silanol), 12.5 Å.^{2}.[23] Because of this and of the results obtained for D-28, the value of 11.4 Å.^{2} was adopted as the molecular area of water for all eight tobermorites. Using this value, the surface area measured by nitrogen adsorption ranged from 21% of the water area (C-23) to 56% (D-35) for the tobermorites obtained by paste hydration and bottle hydration.

It has been long known that increase in relative

(21) L. Heller and H. F. W. Taylor, J. Chem. Soc., 2397 (1951).

(22) H. D. Megaw and C. H. Kelsey, Nature, 177, 390 (1956).

(23) S. Brunauer, D. L. Kantro and C. H. Weise, Can. J. Chem., 34, 1483 (1956).

humidity produces swelling in hydrated calcium silicates and portland cements. Bernal[18] suggested that swelling may be caused by entry of water between the layers of tobermorite, thus increasing the c spacing. Kalousek[24] determined the surface areas of various concrete specimens by nitrogen and water vapor adsorption, and he noted that the former was always smaller than the latter. He attributed the difference between the two to the ability of water and the inability of nitrogen to penetrate between the layers of the calcium silicate hydrate. The same explanation was used by the present investigators to account for the difference between the water and nitrogen surface areas of tobermorite.[2]

The investigations reported in this paper indicate that this explanation is not valid. The density experiments showed that tobermorite dried to an H_2O/SiO_2 ratio of approximately 1.0 does not swell in a saturated $Ca(OH)_2$ solution. Prior to surface area determinations, tobermorite is dried to this water content. The maximum relative humidity used in the surface area determinations was 33%; it seems, therefore, very unlikely that water vapor entered between the layers in the adsorption experiments. Yet, there was a fivefold discrepancy between the nitrogen and water surface areas of C-23. It seems that the rolling of the sheets of tobermorite or aggregation of the crystallites or both together produce surfaces in-

accessible to nitrogen molecules, though accessible to water molecules.

The above evidence does not show that Bernal's hypothesis as to the swelling of tobermorite is incorrect. The tobermorites in C-18 and D-43, having an H_2O/SiO_2 ratio of 1.4, exhibited a slow swelling in a saturated $Ca(OH)_2$ solution. It is possible that water can enter between the layers of a less thoroughly dried tobermorite more rapidly and at relative humidities below 100%.

6. The average index of refraction of the tobermorite in hydrated β-Ca_2SiO_4 was 1.56 ± 0.01. The same value was found earlier for tobermorite in paste-hydrated Ca_3SiO_5.[2] Heller and Taylor[16] obtained the same value for tobermorite prepared by the hydrothermal reaction of $Ca(OH)_2$ and silica gel. A sample of the natural mineral tobermorite, investigated by McConnell,[25] had an average index of refraction of 1.57.

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(24) G. L. Kalousek, *J. Am. Concrete Inst.*, **26**, 233 (1954).

(25) J. D. C. McConnell, *Mineral. Mag.*, **30**, 293 (1954).

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Nickel, Copper and Some of their Alloys as Catalysts for the Hydrogenation of Carbon Dioxide[1]

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The activity of nickel, copper and some of their alloys as catalysts for the hydrogenation of carbon dioxide has been determined. X-Ray diffraction and magnetic measurements indicate that, although these catalysts were prepared by the reduction of oxides obtained from precipitated metal carbonates, they were essentially homogeneous, equilibrium solids. Alloying 11% or less of copper with nickel caused sharp parallel drops in both the magnetic susceptibility and in the power of the catalysts to hydrogenate carbon dioxide to methane rather than carbon monoxide. Alloys containing more than 50% copper behaved essentially like pure copper in that carbon monoxide but no methane was produced.

Introduction

Nickel and copper are completely miscible in the solid state and show an essentially linear lattice parameter relationship in their alloys, therefore any significant deviations of catalytic activity from such a relationship offer evidence of the importance of non-geometric factors such as the electronic factor. Since nickel is a strong methanation catalyst and copper a much weaker hydrogenation catalyst, yet active in the water gas shift, a study of the nickel–copper system employing the hydrogenation of carbon dioxide appeared to offer interesting possibilities. The catalysts used were prepared as in

an earlier investigation[3] involving the hydrogenation of ethylene in which no simple relation was found between the activity of the catalysts and their metallic composition. Even though these catalysts were formed by reduction of oxides obtained from precipitated metal carbonates, X-ray measurements in the present work as in the earlier work[3] yielded lattice constants characteristic of equilibrium alloys formed by melting the components together. Recently, Hall and Alexander[4] have made careful X-ray diffraction measurements on nickel–copper catalysts, prepared according to Best and Russell,[3] both before and after reduction of the metal oxides. These measurements also confirm that normal alloying occurs between nickel and copper and is very complete. These authors[4]

(3) R. J. Best and W. W. Russell, This Journal, **76**, 838 (1954).

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