

272. Tricalcium Silicate Hydrate.

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The composition is shown to be $3\text{CaO}, \text{SiO}_2, 1\frac{1}{2}\text{H}_2\text{O}$, and the ionic constitution possibly $\text{Ca}_6(\text{Si}_2\text{O}_7)(\text{OH})_6$. Hydrothermal formation from anhydrous tricalcium silicate at $180\text{--}500^\circ$ is confirmed. Optical and electron-microscope studies show that the compound crystallises in long, thin needles or fibres which often have foil-like (possibly tubular) extensions at the ends. From single-crystal electron-diffraction and powder *X*-ray data the unit cell is shown to be geometrically hexagonal or trigonal with $a = 10.00$, $c = 7.48 \text{ \AA}$, with strong pseudo-halving of c , and atomic contents $\text{Ca}_{12}\text{Si}_4\text{O}_{26}\text{H}_{12}$. The *X*-ray density is 2.61 g. cm.^{-3} . Dehydration occurs within the range $420\text{--}550^\circ$; the products at 700° are $\gamma\text{-Ca}_2\text{SiO}_4$ and lime.

TRICALCIUM SILICATE HYDRATE * ($3\text{CaO}, \text{SiO}_2, x\text{H}_2\text{O}$) has usually been obtained by hydrothermal treatment of anhydrous tricalcium silicate,¹⁻⁴ although it can also be made hydrothermally from mixtures of less basic hydrated calcium silicates with calcium hydroxide.⁴ The water content (x) has usually been taken as 2, but values ranging from 1.3 to 2.0 have been reported. Optical data for crystalline aggregates are well established; a typical description⁴ is of broad, fibrous crystals with parallel extinction, positive elongation, low birefringence, and indices α 1.590, γ 1.602, both ± 0.003 . *X*-Ray data^{3, 5, 6} are not in complete agreement, which suggests that some or all of the preparations may have been impure. The specific gravity has been reported² as 2.56 for a preparation with $x = 1.6$. Dehydration is reported to occur between 500° and 900° , the final products being CaO and β - or $\gamma\text{-Ca}_2\text{SiO}_4$.^{3, 4}

Work in progress by us confirms earlier suggestions³ that tricalcium silicate hydrate may occur in steam-cured Portland cement pastes, and a fuller study of its properties seemed desirable. The main aims of the present work were: (i) to study the morphology; (ii) to establish the unit-cell and obtain reliable *X*-ray powder data; (iii) to determine the water content and more exact conditions of thermal dehydration with a view to developing a thermogravimetric technique for its estimation. Further results were obtained concerning the conditions of formation and are now partly reported; experiments relating mainly to the setting of tricalcium silicate pastes will be fully described elsewhere.

* The terms "hydrate" and "hydrated calcium silicate" as used in this paper, do not necessarily imply presence of water molecules. The broad usages are well established in the literature on calcium silicates.

¹ Bessey, Report of the Building Research Board, 1935 (London, 1936; H.M.S.O.), 36.

² *Idem*, Proc. Symp. Chem. Cements, Stockholm, 1938, 178.

³ Keevil and Thorvaldson, *Canad. J. Res.*, 1936, B, 14, 20.

⁴ Flint, McMurdie, and Wells, *Bur. Stand. J. Res.*, 1938, 21, 617.

⁵ McMurdie and Flint, *ibid.*, 1943, 31, 225.

⁶ Heller and Taylor, Crystallographic Data for the Calcium Silicates (London, H.M.S.O., 1956), 65.

EXPERIMENTAL

Preparation.—Tricalcium silicate hydrate was prepared, approximately as described by Flint *et al.*,⁴ by suspending tricalcium silicate (particle size $< 20 \mu$) in water and autoclaving it at various temperatures above 200° . A poorly-crystalline synthetic tobermorite, mixed with calcium oxide to give Ca:Si = 3:1, was also successfully used as starting material. Suspensions were contained in stainless-steel bombs of about 7 ml. capacity, closed with screw stoppers and copper gaskets. The bombs were heated in a thermostatted electric oven for temperatures below 300° , or for higher temperatures in an electric furnace. The products were washed out of the bombs with acetone and recovered by filtration. After a final wash with light petroleum they were dried in a vacuum desiccator and stored in tubes with waxed stoppers.

Details, with results of X-ray and optical examination of the products, are given in Table 1. In all cases, products are listed in apparent decreasing order of abundance. In no preparation was tricalcium silicate hydrate the sole product. The most usual impurity was a phase, or

TABLE 1. *Preparations, with results of X-ray and optical examination.*

Specimen No.	Starting material(s) *	Temp.	Time of autoclaving	Phases detected in product: *	
				by X-rays	optically
SD93	C ₃ S	180°	6 hrs.	TSH, CH	TSH, T, CH, C \bar{C}
A100	C ₃ S	250	9 days	α , CH, TSH	α , TSH, C \bar{C}
A124	C ₃ S	275	7 days	α , CH, TSH	TSH, α , C \bar{C}
A66	C ₃ S	375	6 days	TSH, γ	TSH, γ , C \bar{C}
A69	C ₃ S	375	8 days	TSH, γ	TSH, γ , C \bar{C}
A75	C ₃ S	375	17 days	TSH, γ	TSH, γ , C \bar{C}
A77	C ₃ S	375	32 days	TSH, γ	TSH, γ , C \bar{C}
A73	T + CaO	375	24 days	TSH, γ	TSH, γ , CH, C \bar{C}
A79	C ₃ S	430	62 hrs.	TSH, γ	TSH, γ , C \bar{C}
A78	C ₃ S	500	5 days	γ , TSH	CH, α , γ , C \bar{C}

* Abbreviations: C₃S, tricalcium silicate; TSH, tricalcium silicate hydrate; CH, calcium hydroxide; C \bar{C} , calcium carbonate (calcite); T, tobermorite; α , dicalcium silicate α -hydrate [dicalcium silicate hydrate (A)]; γ , gamma-hydrate(s) (see text).

possibly a mixture of closely similar phases, resembling dicalcium silicate γ -hydrate [dicalcium silicate hydrate (C)]. Throughout this paper this will be termed "gamma-hydrate(s)." Table 1 also includes data for a preparation (SD93), kindly supplied by Mr. G. E. Bessey, made by autoclaving a tricalcium silicate-water paste.

Optical Examination.—All products contained clusters of extremely thin fibres or needles, often 100μ long, interspersed with prismatic material. With most preparations the fibres were visible only when immersed in a liquid of very different refractive index. Plate 1 shows material from A79 immersed in liquid paraffin ($n = 1.48$). Fibres from SD93 were of sufficient size for some optical properties to be determined. The results [|| extinction, + elongation, α (or ω) 1.593, γ (or ϵ) 1.597, both ± 0.003] agreed with those of earlier workers.¹⁻⁴

Electron Microscopy and Diffraction.—Specimens, prepared by crushing lightly in water and allowing drops of the suspensions to evaporate on Formvar-coated specimen grids, were examined with a Metropolitan-Vickers EM3 electron microscope. A typical electron micrograph (Plate 2) of material from A77 shows the principal constituent to be long, narrow, lamellar fibres, 500 — 2500 \AA wide, and up to 100μ long. The fibres terminate in extremely thin foils, which appear to be either trough-shaped or tubular in section. Prismatic crystals, which could have been calcite or gamma-hydrate(s), are also visible.

Electron-diffraction patterns from individual fibres showed them to be single crystals. Interpretation of such patterns and a procedure for estimation of the "third row" lattice spacing from the radii of Laue zones have been described.⁷ Plate 3(a) shows a typical diffraction pattern; a few were also recorded of the type shown in Plate 3(b), suggesting a different orientation around the fibre axis. The mean spacing in the fibre direction, which will be called c , was $7.5 \pm 0.1 \text{ \AA}$. As reflections on all the patterns fell on orthogonal nets, c coincides with c^* .

⁷ Gard, *Brit. J. Appl. Phys.*, 1956, **7**, 361; *J. Sci. Instr.*, 1956, **33**, 307.

PLATE 1. *Photomicrograph of fibres of tricalcium silicate hydrate, immersed in liquid paraffin.*
(The ruled line represents 10 μ .)

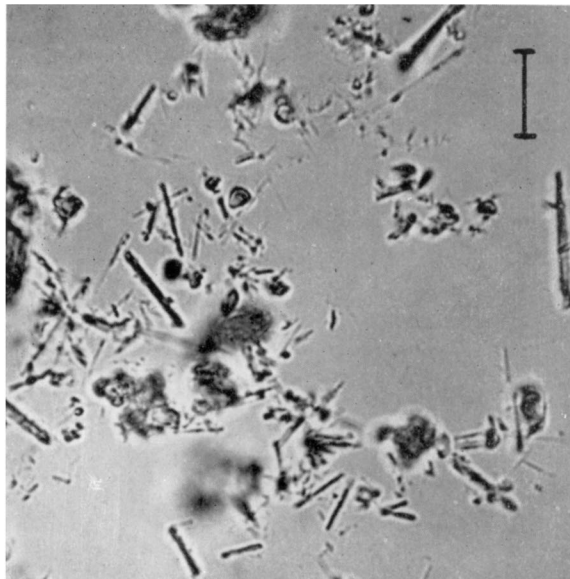
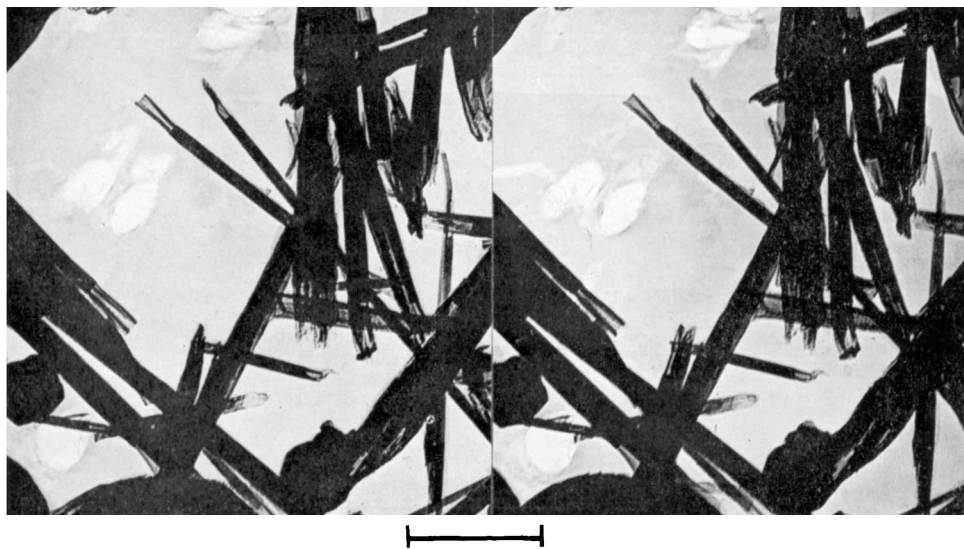


PLATE 2. *Electron micrograph of tricalcium silicate hydrate; stereo-pair showing acicular crystals with foil-like projections.* (The ruled line represents 1 μ .)



[To face p. 1352.]

PLATE 3. Electron-diffraction patterns from single crystals of tricalcium silicate hydrate lying on (a) $(11\bar{2}0)$, and (b) $(10\bar{1}0)$. Arrows show the fibre direction c . In both patterns, odd layers normal to c are weak and slightly streaky, and the rows of spots parallel to c in the first-order Laue zone (marked 1) lie halfway between the corresponding rows in the zero-order zone (marked 0). (The rule line represents 1 \AA^{-1} .)

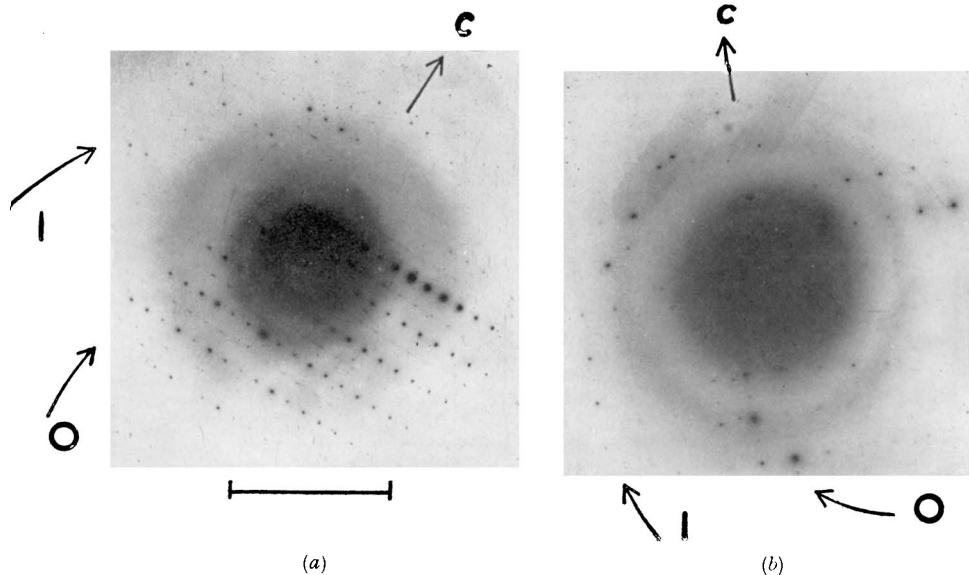
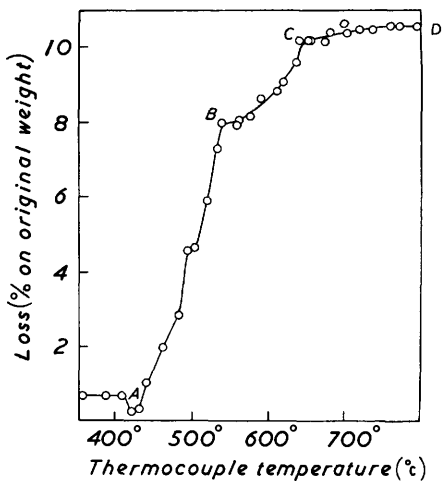


FIGURE. Dehydration isobar for specimen A79, obtained at $p(\text{H}_2\text{O}) = 6 \text{ mm.}$: AB , dehydration of tricalcium silicate hydrate; BC , decomposition of calcite; CD , dehydration of gamma-hydrates.



Relative positions of spots on adjacent Laue zones indicated a *C*-centred reciprocal lattice. From the type of pattern shown in Plate 3(*a*) the spacing normal to *c* in the plane of the supporting film was found to be 17.2 Å, and the spacing parallel to the beam, estimated from the radii of Laue zones, was about 10.5 Å. Corresponding values for the pattern shown in Plate 3(*b*) were 10.0 and about 16.5 Å, respectively. These results confirm that the patterns correspond to different orientations around *c*, and indicate a *C*-centred orthorhombic unit cell with $a = 17.2$, $b = 10.0$, $c = 7.5$ Å. This is, at least geometrically, equivalent to a hexagonal or trigonal unit cell with $a = 10.0$, $c = 7.5$ Å. Since no systematic absences were observed, the unit cell is not rhombohedral. The frequency with which fibres gave patterns of the type shown in Plate 3(*a*) suggests that the principal cleavage is (11 $\bar{2}$ 0). Reflections with *l* odd were systematically weak, and were slightly streaked in the plane normal to *c**. In all the patterns, 0004 was stronger than other *hkl* reflections.

An unsuccessful attempt was made to identify the thin foils projecting from the ends of the crystals. Long exposures were used, with an intermediate aperture that selected an area 0.5 μ in diameter. To ensure accurate focusing of any diffraction pattern, a device was fitted that permitted a reproducible advance to the objective lens current from the setting at which the normal image was in true focus. In spite of this, no diffraction patterns could be obtained.

X-Ray Powder Investigation.—X-Ray powder data were obtained by using a Philips 11.46 cm. diameter camera with filtered copper radiation. As indicated in Table 1, all specimens gave patterns containing lines due to other phases. The patterns were compared with each other and with those of all likely impurities, and also with those of the heated specimens described later. The lines of the tricalcium silicate hydrate were thus distinguished and are listed in Table 2. Relative intensities were estimated visually. The unit-cell parameters derived

TABLE 2. X-Ray powder data for tricalcium silicate hydrate, indexed on a hexagonal unit cell with $a = 10.00$, $c = 7.48$ Å.

Spacings (Å), obs.*	Indices	Spacings (Å), calc.	Spacings (Å), obs.*	Indices	Spacings (Å), calc.	Spacings (Å), obs.*	Indices	Spacings (Å), calc.	
8.6 vs	10.0	8.66	2.44 mw	{ 21.2	2.46			10.4	1.827
5.01 ms	11.0	5.00		{ 31.0	2.40	1.753 ms	{ 32.2	1.756	
4.24 w	20.0	4.33	2.28 mw	30.2	2.28		{ 11.4	1.752	
3.78 m	0002	3.74	2.16 mw	40.0	2.16		50.0	1.732	
	10.2	3.43	2.08 s	22.2	2.08		20.4	1.717	
3.28 s	21.0	3.27		31.2	2.02	1.682 ms	41.2	1.686	
3.03 s	11.2	3.00	1.986 m	32.0	1.988	1.666 vw	33.0	1.667	
2.89 s	30.0	2.89	1.897 m	41.0	1.890	1.636 vvw	42.0	1.640	
2.82 m	20.2	2.83		{ 40.2	1.874				
2.49 w	22.2	2.50	1.870 s	{ 0004	1.870				

* Also: 1.557 vvw, 1.497 w, 1.438 w, 1.357 w, 1.247 w, 1.229 w, 1.208 w, 1.176 mw, 1.144 mw, 1.02 m, 0.981 mw.

from the electron-diffraction data were refined by correlation with the X-ray powder pattern. This could be indexed completely on a hexagonal or trigonal unit cell with $a = 10.00$, $c = 7.48$ Å, both ± 0.03 Å. The exact value of *c* followed from the assumption that the strong reflection at 1.870 Å is 0004. Reflections having odd values of *l* were ignored as they were weak in the electron-diffraction patterns, although they may contribute to the intensities of some lines in the X-ray pattern. Table 2 gives observed and calculated values for all spacings greater than 1.63 Å, and having *l* even; below this the choice of indices was not unique. Since reflections 10.2, 31.2, 10.4, 50.0, and 20.4 are present in the electron-diffraction pattern, though absent from the X-ray powder pattern, there are no systematic absences. Agreement between observed and calculated *d*-spacings is good, and supports the view that all the spacings listed in Table 2 are those of tricalcium silicate hydrate.

Densities.—Samples were compressed into pellets by mean of a screw-press and immersed in bromoform-benzene. The pellet was freed from trapped air by outgassing under reduced pressure, and the density of the liquid progressively raised by pumping off benzene. When the pellet could be suspended without movement, the density of the liquid was measured with a pycnometer. Densities obtained, probably reliable to ± 0.01 g. cm.⁻³, were: SD93, 2.49; A79, 2.64; A77, 2.68; A66, 2.69; A75, 2.72 g. cm.⁻³.

Dehydration Isobars.—These were determined by using a helical silica spring balance enclosed in a vertical column. The lower part of this column, which contained the specimen in

a platinum boat, was of silica and passed through an electric tube-furnace. Temperatures were measured with a thermocouple within the silica tube, and as the specimen lost weight the upper end of the silica spring was lowered so that the platinum boat was always just clear of the thermocouple. A continuous, downward flow of carbon dioxide-free air at 6 mm. partial pressure of water vapour was maintained through the column, the lower end of which was fitted with a series of guard tubes to exclude carbon dioxide. Where practicable, spring extensions were recorded at 4-hourly intervals and the temperature was raised by 5–10° when the loss between successive weighings fell to within experimental error. A complete run took about 14 days. Dehydration was usually complete by about 750°.

Isobars were obtained for specimens SD93, A79, A77, A66, and A75. A typical one, for A79, is given in the Figure. The impurities in this specimen were calcite and gamma-hydrate(s) (Table 1). Separate experiments showed that, under the conditions used, calcite decomposed within the range 550–650° and gamma-hydrate(s) at 650–750°. The portion *AB* of the curve in the Figure at 420–550° therefore corresponds to dehydration of the tricalcium silicate hydrate, while *BC* and *CD* correspond to decomposition of the calcite and the gamma-hydrate(s) respectively. The small drop in the curve near *A* was possibly caused by dehydration of a trace of calcium hydroxide and subsequent absorption of carbon dioxide which, despite all precautions, entered the apparatus.

X-Ray Examination of Heated Material.—Specimens were heated to constant weight at various temperatures under the conditions used for determination of dehydration isobars, and subsequent *X-ray* powder photographs gave the results in Table 3. "A" denotes an unidentified phase or mixture of phases giving the following pattern (spacings in Å): 4·9 w,

Specimen	Temp.	Phases detected	Specimen	Temp.	Phases detected
A75	Unheated	TSH, γ	SD93	550°	"A"
"	450°	TSH, γ	"	600	"A"
"	600	γ	"	700	γ -Ca ₂ SiO ₄ , CaO
SD93	Unheated	TSH, CH	A66	Unheated	TSH, CH
"	500°	"A"	"	960°	β -Ca ₂ SiO ₄ , γ -Ca ₂ SiO ₄ , CaO
"	525	"A"			

4·3 w, 3·77 m, 3·32 vw, 3·01 s, 2·87 w, 2·73 vs, 2·66 w, 2·60 w, 2·51 mw, 2·46 vw, 2·39 vw, 2·27 vw, 2·18 mw, 2·03 w, 1·90 s, 1·80 mw, 1·75 w, 1·69 mw, 1·66 w, 1·54 w, 1·50 vw, 1·46 w. Most of the lines were broad. With the specimen of A75 heated at 600°, γ -Ca₂SiO₄, or "A", or both, could also have been present, as the strong lines of both coincide with ones of gamma-hydrate(s). With the specimen of SD93 heated at 700°, the 2·18 Å line of γ -Ca₂SiO₄ was abnormally strong.

DISCUSSION

Conditions of Formation, and Characterisation of Tricalcium Silicate Hydrate as a Distinct Compound.—The hydrothermal synthesis of tricalcium silicate hydrate reported by earlier workers has been confirmed, and the difficulty of obtaining a pure specimen demonstrated. Products made below about 300° contained also calcium hydroxide together with tobermorite or dicalcium silicate α -hydrate, while at higher temperatures gamma-hydrate(s) were the main impurity. The proportion of these relative to tricalcium silicate hydrate appears to increase sharply with temperature above about 430°. Earlier workers seem to have had the same difficulty in trying to make pure material. Keevil and Thorvaldson's *X-ray* data³ closely resemble those of specimen A66, which contained gamma-hydrate(s). McMurdie and Flint's data⁵ for a product made⁴ at 250° indicate that it was substantially free from gamma-hydrate(s). Experiment A100 (Table 1) was an attempt to repeat this preparation, but it gave a product contaminated mainly by dicalcium silicate α -hydrate and calcium hydroxide.

The status of tricalcium silicate hydrate as a distinct compound is confirmed. Kalousek, Logiudice, and Dodson⁸ noted similarities between the *X-ray* powder patterns of tricalcium silicate hydrate, hillebrandite (2CaO, SiO₂, H₂O), and foshagite⁹ (4CaO, 3SiO₂, H₂O), and suggested that the three substances might belong to a structurally

⁸ Kalousek, Logiudice, and Dodson, *J. Amer. Ceramic Soc.*, 1954, **37**, 7.

⁹ Gard and Taylor, *Amer. Min.*, 1958, **43**, 3.

related series of variable composition. Comparison of the unit cells of tricalcium silicate hydrate, foshagite,⁹ and hillebrandite¹⁰ does not support this view.

Water Content and Density.—Attempts to determine the water content directly from the dehydration isobar gave inconclusive results because of uncertainties about the composition and proportions of the admixed tobermorite or gamma-hydrate(s). The water content was therefore estimated indirectly from the unit-cell volume and the density (D). The latter must lie between that of SD93 (2.49) and that of A79 (2.64), because the principal impurities in SD93 (tobermorite and calcium hydroxide) have densities below 2.49 while the gamma-hydrate(s) in A79 have densities near 2.83. Taken in conjunction with the unit-cell volume this indicates the unit-cell content $4[3\text{CaO}, \text{SiO}_2, x\text{H}_2\text{O}]$ where x lies between 0.8 and 1.7. Closer estimates of D and x were obtained as follows. The density can be calculated for any postulated water content either from the X-ray data ($D = 1.66M/V$) or from the mean refractive index by using the Lorentz-Lorenz relation. The latter method gives results usually reliable to within $\pm 2\%$ for calcium silicates if the empirical atomic refractions $\text{Ca} = 3.25$, $\text{O} = 3.65$, and $\text{Si} = \text{H} = 0$ are used.¹¹ The two methods give results that vary in opposite senses with x . The values of density and water content consistent with both methods are $D = 2.60$, $x = 1.42$. In view of the uncertainties involved in the calculation from refractive index, the formula $3\text{CaO}, \text{SiO}_2, 1\frac{1}{2}\text{H}_2\text{O}$ is suggested. The corresponding X-ray density is 2.61 g. cm.⁻³.

The previously accepted formula $3\text{CaO}, \text{SiO}_2, 2\text{H}_2\text{O}$ seems to have been based mainly on a water content of 13.56% found by Flint *et al.*⁴ for a specimen made at 275°. However, the specimen made at 250°, for which the X-ray data were afterwards reported, contained only 11.53% of water, giving $x = 1.63$. They also report a loss of 10.1% over the range 215—700° for an unspecified preparation; this indicates $x = 1.42$. Bessey^{1,2} found about 1.6 mol. of water firmly bound and a density of 2.56, which agrees substantially with the present result.

Dehydration.—The isobar (Figure) and X-ray evidence show that water is lost at 420—550°. From the loss over this range the proportion of tricalcium silicate hydrate in A79 can be estimated as about 75%. Dehydration seems to occur in two approximately equal stages; the intermediate arrest, although slight, appears genuine, as it was found with all the specimens studied; its significance is not known. The X-ray pattern of "A," given by specimens heated at 500—600°, resembles that of $\gamma\text{-Ca}_2\text{SiO}_4$ ⁶ but shows significant differences. As lime was not detected below 700°, it may have been formed initially in a poorly-crystallised condition; it is also possible that some of the expelled lime could have been incorporated in the $\gamma\text{-Ca}_2\text{SiO}_4$, thereby affecting its powder pattern. Even with the specimen heated at 700°, the $\gamma\text{-Ca}_2\text{SiO}_4$ pattern was slightly anomalous. It thus appears that dehydration gives $\gamma\text{-Ca}_2\text{SiO}_4$ and lime, but crystallisation of these develops gradually with rise of temperature.

Constitution.—The fact that tricalcium silicate hydrate can be formed at temperatures as high as 500°, together with the relatively high temperature of dehydration, suggests that the water may be present as hydroxyl not attached to silicon, though this cannot be considered certain. This hypothesis supports the ionic formula $\text{Ca}_6(\text{Si}_2\text{O}_7)(\text{OH})_6$ proposed by Bessey.¹ The weakness of reflections with l odd suggests, by analogy with other calcium silicates, that the calcium-oxygen pattern may repeat at intervals of $c/2$, and the streaking of these reflections similarly suggests disorder in the positions of the Si_2O_7 groups.

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¹⁰ Heller, *Min. Mag.*, 1953, **30**, 150.

¹¹ Howison and Taylor, *Mag. Concrete Res.*, 1957, **9**, 13.