

531. *Hydrated Calcium Silicates. Part II.* Hydrothermal Reactions: Lime:Silica Ratio 1:1.*

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Calcium silicate hydrate (I), $\text{CaO}, \text{SiO}_2, \text{aq.} - 3\text{CaO}, 2\text{SiO}_2, \text{aq.}$ (*J.*, 1950, 3682), has now been prepared hydrothermally in a crystalline condition; its *X*-ray powder pattern shows many lines which are not disclosed by samples prepared at room temperature and can be assigned indices on the basis of the unit cell already tentatively proposed; but single-crystal photographs will probably be necessary to determine the unit cell with certainty.

At 110°, calcium silicate hydrate (I) appears to be the final product of hydrothermal treatment of mixtures of lime: silica ratio 1:1. At higher temperatures, up to at least 320°, it is obtained only as an intermediate product, more prolonged treatment yielding other species. At 135–180°, the compound $\text{CaO}, \text{SiO}_2, \text{H}_2\text{O}$, described by Flint and his co-workers, is obtained as a final product and is distinct from calcium silicate hydrate (I). At 160–300°, xonotlite is produced. The evidence that xonotlite contains zeolitic water is shown to be inconclusive. At 350° a product was obtained which gave the *X*-ray powder pattern of xonotlite together with certain additional lines, indicating either a new modification of xonotlite or the presence of a second as yet unidentified phase.

IN Part I of this series * it was shown that calcium silicate hydrate (I) could be formed in the $\text{CaO}-\text{SiO}_2-\text{H}_2\text{O}$ system at room temperature, and that its composition varied between approximately $\text{CaO}, \text{SiO}_2, \text{aq.}$, and $3\text{CaO}, 2\text{SiO}_2, \text{aq.}$ Although the *X*-ray powder data gave some indications of the structure, further investigation was not possible because of the very small size of the crystals and partial disorder in their structure.

Foret (*Compt. rend.*, 1936, **203**, 80; 1937, **204**, 977) showed that, on hydrothermal treatment at 100–140°, mixtures of lime: silica ratio 1:1 yielded a product having an *X*-ray pattern similar to that of material prepared at room temperature by Chassevent (*ibid.*, 1934, **199**, 673). As was shown in Part I, the latter material probably consisted of calcium silicate hydrate (I) mixed with calcite. Inspection of Foret's data suggests the same conclusion, only three of the spacings quoted (3.0, 2.8 and 1.85 Å.) being unambiguously attributable to calcium silicate hydrate (I). Nevertheless, the results suggest that this compound can be formed under

* Part I, *J.*, 1950, 3682.

hydrothermal conditions and it appeared possible that a more detailed investigation might enable it to be prepared in a more crystalline condition and in a relatively pure state.

At higher temperatures, up to approximately 350°, all previous investigators have found the hydrothermal treatment of mixtures of lime : silica ratio 1 : 1 to yield xonotlite ($\text{CaO}, \text{SiO}_2, 0.2$ or $0.25\text{H}_2\text{O}$), whereas wollastonite is produced at 400° or above; for references and discussion see Taylor and Bessey (*Mag. Concrete Res.*, 1950, 1, No. 4, 15). Flint, McMurdie, and Wells (*J. Res. Nat. Bur. Stand.*, 1938, 21, 617) obtained at 150° a further compound which they believed to be $\text{CaO}, \text{SiO}_2, \text{H}_2\text{O}$. The X-ray data for this compound (McMurdie and Flint, *ibid.*, 1943, 31, 225) show a certain resemblance to those of calcium silicate hydrate (I), but it is not clear from their data whether a well-crystallised form of the latter compound or a further distinct species had been produced.

The present investigation was carried out (i) to determine whether the crystallisation of calcium silicate hydrate (I) could be improved so as to obtain material suitable for a more detailed X-ray investigation, and (ii) to establish the relation of this compound to those obtained at higher temperatures, and especially with the $\text{CaO}, \text{SiO}_2, \text{H}_2\text{O}$ reported by Flint, McMurdie, and Wells.

EXPERIMENTAL.

Methods.—Hydrothermal reactions were carried out in stainless steel pressure vessels in an electric oven at 110—350°. The quantity of water was always such that both liquid and vapour phases were present. At temperatures above 100° the solubilities of both lime and silica are small (Flint, McMurdie, and Wells, *loc. cit.*), and the pressure developed is therefore practically equal to the saturated vapour pressure of steam at the operating temperature. For the same reason, the lime : silica ratio of the solid product is almost that of the starting materials. These were in some cases mixtures of calcium hydroxide and silica gel, and in others calcium silicate hydrate (I) which had been prepared by one of the methods described in Part I. In all cases the lime : silica molar ratio of the starting material was approx. 1 : 1, and the solid and liquid phases were in contact throughout the reaction.

After the hydrothermal treatment, the reaction mixture was filtered. The solid residue was washed with a minimum of water followed by acetone, and dried in a vacuum-desiccator over anhydrous calcium chloride. The solid was investigated optically and by X-ray powder photographs.

Starting Materials.—The calcium silicate hydrate (I) samples were prepared by methods already described (Part I, *loc. cit.*). The silica gel was the sample described in the same paper. A total dry weight of 150—200 mg. was used in each experiment, together with 5 ml. of water.

Hydrothermal Reactions.—The reaction mixtures were placed in silver test-tubes of height 3" and external diameter $\frac{1}{4}$ ". These fitted into stainless steel tubes based on a design by Barrer (*J.*, 1948, 127). The tubes were made from hexagonal bar of width 1" across the flat, and length $5\frac{1}{4}$ ". An axial hole 4" deep and $17/32$ " in diameter was bored into one end. The first $\frac{3}{4}$ " of the hole was tapped with a $\frac{3}{8}$ " Whitworth thread, and a screw cap made to fit from the same material as the tube. An annealed copper washer $\frac{1}{4}$ " thick formed the gasket. Knife-edged ridges of approx. 0.015" in height were turned on the surfaces of the tube and the cap; these bit into the copper washer.

The tubes were heated in an electric oven whose temperature could be regulated to within $\pm 2^\circ$.

While the general trend of the results, as shown in Table I (below), was clear, the rate of the reactions was to some extent irreproducible. Apparently identical samples, which received identical treatment, reacted to different extents; some mixtures failed to crystallise appreciably. These have been excluded from Table I. It was found that badly crystallised samples, possibly on account of their higher pH values, showed a greater tendency to absorb atmospheric carbon dioxide during the isolation of the solid product.

X-Ray Apparatus.—A sealed, filament X-ray tube with copper target was operated at approx. 35 kv. and 15—20 mA. Photographs were taken with a powder camera of 19-cm. diameter, with a nickel-foil filter in contact with the film to remove $K\beta$ and fluorescent radiations. Exposures of about 20 hours were normally required, Ilfex double coated film being used; with the recently available Ilford Industrial G film this was reduced to about 8 hours. In a few cases, in order to observe the longer spacings clearly, single-crystal cameras of 6-cm. diameter were used. Spacings were determined by use of a travelling microscope, and are probably correct to within ± 0.01 Å. at 1.5 Å. or below, rising to ± 0.02 at 3 Å. and ± 0.1 Å. at 6 Å. Intensities were estimated visually.

RESULTS AND DISCUSSION.

The products obtained from each experiment, together with the experimental conditions, are given in Table I. Xonotlite, where present, was identified by its optical properties and X-ray powder data (Taylor and Bessey, *loc. cit.*), as were calcium carbonate and hydroxide. The characterisation of the remaining species is discussed later.

Calcium Silicate Hydrate (I).—Several of the experiments (nos. 88, 82, 47, and 62) yielded X-ray photographs which, apart from the presence of calcium carbonate and/or hydroxide lines in some cases, were identical with that of calcium silicate hydrate (I) prepared at room temperature (Taylor, *loc. cit.*). This compound can therefore be produced under hydrothermal conditions. At 110° it was present even after prolonged treatment, but as explained later it

TABLE I.

Results of hydrothermal experiments.

Expt. no.	Temp. of prepn.	Starting material.*	Time of prepn. (days).	Products.‡
15	350°	P	7 †	Xonotlite + A
88	320	M	$\frac{1}{2}$	CSH(I) + CC
13	300	P	4	Xonotlite
14	300	P	4	Xonotlite
6	240	P	6	Xonotlite
36	200	P	5	CSH(I)
46	200	P	60 †	Xonotlite
11	200	P	30	Xonotlite
12	200	M	30	Xonotlite
82	180	M	2	CSH(I) + CC
91	180	M	42	CSH(I) + B
93	180	M	28	CSH(I) + B + xonotlite
92	180	M	14	Xonotlite
18	160	P	16	CSH(I)
21	160	P	30	Xonotlite + B
23	160	P	36	Xonotlite + B
47	150	M	35	CSH(I) + CH + CC
62	140	M	60	CSH(I) + CH + CC
67	140	Q	27	CSH(I)
80	140	M	75	CSH(I) + B
78	140	Q	75	CSH(I) + B
51	135	M	60	CSH(I) + B
39	110	M	63	CSH(I)
58	110	M	200	CSH(I)

* M = mixture of $\text{Ca}(\text{OH})_2$ and SiO_2 gel; P or Q = calcium silicate hydrate (I) made by double decomposition or from silica gel respectively (Taylor, *loc. cit.*). † Preceded by 28 days at 200° and then 6 days at 300°. ‡ Preceded by 35 days at 150°. § CSH(I) = calcium silicate hydrate (I); CH = calcium hydroxide; CC = calcium carbonate; A, B, see text. || In a well-crystallised form; see text.

was in this case in a better state of crystallisation, giving a more complete X-ray powder diagram. At higher temperatures it was always observed in the products obtained after shorter periods (Expts. 82, 36, and 88, at 180°, 200°, and 320° respectively), whereas more prolonged treatment yielded other species, notably xonotlite. This was so whether a mixture of calcium hydroxide and silica gel, or calcium silicate hydrate (I) made at room temperature, was used as the starting material. At temperatures above about 130°, calcium silicate hydrate (I) is therefore an intermediate product in the formation of other species.

In some cases (Expts. 67, 36, 39, and 58) many additional X-ray lines were observed and the pattern as a whole was much sharper. The data for a typical sample are given in Table II. With one minor exception, these lines always occurred with the same intensities relative both to each other and to the original lines. This was also largely true for preparations of higher lime : silica ratio in which the same pattern was obtained (Heller and Taylor, unpublished work). It therefore appeared probable that the additional lines represented spacings which, on account of imperfect crystallisation, did not occur in the first set of preparations, or in those made at room temperature. This was supported by the results of optical examinations. The preparations showing only the original lines appeared amorphous, but those showing the full pattern consisted of minute irregular crystals which were weakly birefringent and had mean refractive indices of 1.55—1.565. The refractive index appeared to vary slightly with both the temperature of preparation and the degree of crystallinity, the more crystalline preparations and those made at higher temperatures tending to have the higher values. It is possible that the refractive index of the sample may depend on its water content. The largest crystal observed (in sample 36) was $30 \times 10 \times 10 \mu.$, but the crystals were usually very much smaller (about $3 \mu.$), and thus not suitable for more complete optical investigation.

Table II also includes spacings and intensities calculated on the basis of the unit cell already tentatively suggested (Taylor, *loc. cit.*). While many of the observed lines can be accounted for, the agreement is less satisfactory in other cases, and it is possible that the true cell may be larger or less symmetrical than that proposed. More conclusive results than this can scarcely be obtained in the absence of single-crystal photographs. No attempt has been made to index spacings shorter than 2.0 Å., except for the $hk0$ lines, as the possibility of finding a fit increases rapidly with diminishing spacing, so that any comparison beyond this point would be of little significance.

TABLE II.
 X-Ray data for calcium silicate hydrate (I).

Obsd. (sample 58).		Calc.*		Obsd. (sample 58).	
Spacing, A.	Intensity.	Spacing, A.	Indices.	Spacing, A.	Intensity.
11.0	s †	11.0	001	1.56	vvw
5.5	ms †	5.5	002	1.55	mw †
3.49	vvw	3.50	011	1.52	vw
3.29	vvw	—	?	1.50	w
3.07	vs †	3.07	110	1.432	mw
2.97	vs	2.95	111	1.406	mw †
2.81	vs †	2.81	200	1.398	vvw
2.52	w	2.49	202	1.369	vvw
2.48	w	2.46	104	1.312	vvw
2.41	vw	2.35	113	1.295	vvw
2.28	ms †	2.23	203	1.281	vvw
2.22	vw	2.20	005, 014	1.259	vvw
2.14	ms	2.17	211	1.245	w †
2.07	ms	2.06	212	1.214	vw
2.00	ms	2.04	105, 114	1.188	vw †
1.88	vw	—	—	1.163	vw
1.83	vs †	1.83	020	1.138	mw
1.80	w	—	—	1.112	w †
1.76	vw	—	—	1.073	mw †
1.73	vw	—	—	1.058	vvw
1.67	vs †	1.67	310	1.043	vvw
1.62	w	—	—	1.024	vw
1.60	vw	—	—		

* Spacings calculated on the basis of an orthorhombic cell having $a = 5.62$ A., $b = 3.66$ A., $c = 11.0$ A. The spacing or spacings nearest to the observed value are given.

† Lines shown also by the imperfectly crystallised samples. The spacings given here for these lines differ slightly from those recorded previously; this is the result of more accurate measurement and does not represent any real difference.

‡ This line varied in intensity for different samples, being sometimes completely absent.

Xonotlite.—The present results show that xonotlite is formed, either from calcium silicate hydrate (I) or from lime-silica mixtures, over the range 160–350°. Between 200° and 300° it appears to be the sole final product, but outside this range it may be mixed with other species. This is compatible with the previous investigations.

The X-ray results were in close agreement with those recorded by earlier workers (Taylor and Bessey, *loc. cit.*). Whenever xonotlite was obtained, whether pure or mixed with another species, no variations could be detected in either the spacings or the relative intensities of any of its lines. A sample of the natural mineral also gave a photograph indistinguishable from those of the synthetic samples. We are thus unable to confirm the view expressed by Clark and Bunn (*J. Soc. Chem. Ind.*, 1940, **59**, 155) and by Reinhard, Brandenberger, and Oesterheld (*Helv. Chim. Acta*, 1942, **25**, 336) that the xonotlite pattern shows significant differences between natural and synthetic samples.

There has been no general agreement regarding the water content of xonotlite. Most of the early workers used the formula $5\text{CaO}\cdot 5\text{SiO}_2\cdot \text{H}_2\text{O}$ but Nagai (*Z. anorg. Chem.*, 1932, **206**, 177; **207**, 321) and Jander and Franke (*ibid.*, 1941, **247**, 161) considered it to be $4\text{CaO}\cdot 4\text{SiO}_2\cdot \text{H}_2\text{O}$. More recently it has been suggested that the water content is variable (Reinhard, Brandenberger, and Oesterheld, *loc. cit.*), and Alcock, Clark, and Thurston (*J. Soc. Chem. Ind.*, 1944, **63**, 292) describe the compound as zeolitic. The former workers based their view on changes in the X-ray spacings, which, as stated above, we have been unable to confirm. We have also failed to note a shortening of the xonotlite spacings, as described by Reinhard *et al.*, on heating to 280° for 3 days a preparation made at 160°. Apart from this the view seems to have been suggested by the observation of Foret (*loc. cit.*) that the water contents of synthetic samples dried at 100° decrease as the temperature of preparation is raised. The present results suggest, however, that the products obtained by Foret at 140° or slightly higher temperatures may have contained calcium silicate hydrate (I), which almost certainly has a higher water content than has xonotlite. Owing to imperfect crystallisation, this compound may be present to an appreciable extent without being apparent in the X-ray pattern. Thus, while the available evidence does not rule out the possibility of a variable water content, there seems to be no valid reason for postulating this. Most of the previous determination of the water content are in any case of uncertain value owing to the use of inadequately defined conditions of drying. An investigation under isobaric conditions is in progress.

X-Ray Lines "A".—The preparation obtained at 350° showed in its *X-ray* pattern, besides xonotlite, a number of additional lines which are listed in Table III. They do not coincide with the spacings of either α -(pseudo-) or β -(monoclinic) wollastonite (A.S.T.M. index, and Ehrenberg, *Z. physikal. Chem.*, 1931, B, 14, 425, respectively; confirmed by us). Two explanations appear possible: a second species together with xonotlite, or a slightly modified crystalline form of xonotlite, may have been produced. Optical examination showed that most of the sample consisted of very fine needles, having the usual optical properties of xonotlite. A few crystals of higher refractive index could be detected but it is doubtful if they were present in sufficient quantity to account for the extra lines "A." Thus it is not possible to choose between the alternative interpretations on the basis of the available evidence.

X-Ray Lines "B".—Experiments 21 and 23 at 160° gave the *X-ray* pattern characteristic of xonotlite together with a number of extra lines. These are listed in Table IV. Other preparations (51, 78, 80, and 91) showed the lines of calcium silicate hydrate (I) with the same extra lines, whilst preparation 93 showed these together with both xonotlite and calcium silicate hydrate (I). The extra lines were in all cases of the same intensities relative to each other but not to those of the xonotlite or calcium silicate hydrate (I). These facts, and particularly the occurrence of the lines "B" in conjunction with those of either or both of two other species, strongly suggested the presence of a further compound. This was confirmed optically. The above preparations all contained thin needles of mean refractive index 1.60 and negative elongation, in addition to crystals of xonotlite and/or calcium silicate hydrate (I) in accordance with the *X-ray* data.

TABLE III.
X-Ray data; lines "A."

Spacing, A.	Intensity.	Spacing, A.	Intensity.	Spacing, A.	Intensity.
6.25	v.w.	3.49	m.	2.09	v.v.w.
4.71	m.	3.14	v.s.	1.92	v.v.w.
3.85	m.	3.00	v.v.w.	1.80	m.
3.76	v.w.	2.43	w.		

TABLE IV.
X-Ray powder data; lines "B".

This investigation; lines "B".		McMurdie and Flint; CaO, SiO ₂ , H ₂ O.		This investigation; lines "B".		McMurdie and Flint; CaO, SiO ₂ , H ₂ O.	
Spacing, A.	Intensity.	Spacing, A.	Intensity.	Spacing, A.	Intensity.	Spacing, A.	Intensity.
6.04	m.w.	6.13	v.w.	2.10	v.v.w.	2.116	v.w.
4.51	v.v.w.	4.52	w.	2.01	m.w.	2.013	w.
4.23	v.v.s.	4.24	w.	1.925	v.w.	—	—
3.75	m.	3.80	v.w.	1.893	s.	1.893	s.
3.56	m.	3.58	w.	1.867	v.v.w.	1.868	v.w.
3.21	s.	3.21	m.	1.805	v.v.w.	1.808	v.w.
3.03	v.v.s.	3.01	v.s.	1.773	m.w.	1.772	m.
2.78	m.s.	2.78	m.	1.631	v.v.w.	1.632	v.w.
2.50	s.	2.50	m.	1.605	m.w.	1.601	m.
2.24	s.	2.23	s.				

Both the optical and the *X-ray* data (Table IV) for this species are in close agreement with those recorded by Flint and his co-workers (*loc. cit.*) for the compound CaO, SiO₂, H₂O. There are some discrepancies for the relative intensities, notably in the case of the 4.23-A. line, but the agreement is sufficiently close to establish that the compounds are identical. Our attempts to obtain the pure compound, unlike those by Flint, McMurdie, and Wells, were unsuccessful. The present results show, however, that this compound is quite distinct from calcium silicate hydrate (I) and that it is not a well-crystallised form of it.

We thank Professor J. D. Bernal, F.R.S., and Dr. J. W. Jeffery for their interest and advice, Mr. R. W. Nurse, of the Building Research Station, Watford, Herts., for many helpful discussions, and Mr. L. J. Stevens and Mr. A. F. Fry for making the pressure tubes. The work was carried out as part of an extra-mural contract for the Building Research Board and we thank the Director of Building Research for permission to publish this paper.

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[Received, May 19th, 1951.]