180. *Hydrated Calcium Silicates. Part III.* Hydrothermal Reactions of Mixtures of Lime : Silica Molar Ratio 3 : 2.*

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Hydrothermal treatment of mixtures of lime and silica gel in the molar ratio 3 : 2 yields calcium silicate hydrate (I) as the sole product at temperatures below 140°. This product gives an *X*-ray pattern almost the same as that of similarly prepared material of lime : silica ratio 1 : 1. At higher temperatures, at least up to 180°, calcium silicate hydrate (I) appears to be the initial product. More prolonged treatment yields at 140—160° afwillite, and at 180—200° principally xonotlite and hillebrandite.

Part II * of this series dealt with reactions of mixtures of lime and silica gel of molar ratio 1 : 1. Similar reactions of mixtures of lime : silica ratio 3 : 2 are now described. The investigation was carried out to study the products obtained below 200°, the maximum temperature commonly employed for the steam curing of Portland cement, and in particular to establish whether calcium silicate hydrate (I) could be formed under hydrothermal conditions from preparations of this composition.

Previous Work.—Three investigations on this range of composition have been reported. Nagai (*Z. anorg. Chem.*, 1932, **206**, 177; **207**, 321) found that hydrothermal treatment for 6 days at 153° of a mixture of lime and quartz yielded a compound which he identified optically as afwillite. Similar experiments at 180° and 200° gave xonotlite mixed with a phase described as needles of composition $3CaO,2SiO_2,H_2O$. The analyses were corrected for the presence of unchanged calcium hydroxide, determined by extraction with glycerol, and of quartz which was regarded as the residue insoluble in aqueous sodium carbonate. Büssem ("Symposium on the Chemistry of Cements," Stockholm, 1938, 141) took *X*-ray photographs of two of Nagai's preparations and affirmed that the products which Nagai had described as afwillite were actually dicalcium silicate α-hydrate.† He claimed that these two compounds were almost indistinguishable by optical methods.

Flint, McMurdie, and Wells (*J. Res. Nat. Bur. Stand.*, 1938, **21**, 617) obtained CaO,SiO_2,H_2O at 150—200° and xonotlite at temperatures up to 400°. They inferred the presence of another phase from the overall composition but failed to observe it experimentally.

Jander and Franke (*Z. anorg. Chem.*, 1941, **247**, 161) carried out experiments at 300° and 350°. They found that the products of short-term hydrothermal treatment at 300° were a mixture of xonotlite and hillebrandite, while longer periods of heating gave in addition a compound described as $3CaO,2SiO_2,H_2O$. Taylor and Bessey (*Mag. Concrete Res.*, 1950, **4**, 15) suggested that this may have been foshagite. At 350° only the $3CaO,2SiO_2,H_2O$ was produced.

The earlier investigators thus agree in finding xonotlite as one of the products at 180° or above. Otherwise there is little agreement, especially regarding the lower-temperature products. In no case was the formation of calcium silicate hydrate (I) observed.

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* Part II, *J.*, 1951, 2397.

† The nomenclature used for the dicalcium silicate hydrates is that of Bessey (*op. cit.*, p. 178).

Experimental.—The experimental methods, and the samples of calcium hydroxide and silica gel used as starting materials, were identical with those described in Part II (*loc. cit.*). The calcium hydroxide contained, as the only significant impurities, CO_2, 0·65; Na_2O, 0·11%.

For the purpose of comparison, *X*-ray powder photographs were taken of natural xonotlite, afwillite, and hillebrandite. The results were in satisfactory agreement with those recorded in the literature (see Taylor and Bessey, *loc. cit.*).

The conditions of each experiment, and the products as identified by optical and *X*-ray methods, are given in Table 1.

TABLE 1. *Products of hydrothermal reactions.*

Exp. No.	Temp.	Duration (days)	Products *
90	110°	42	CSH(I) ‖
56	130	56	CSH(I) ‖
57	130	60	CSH(I) ‖
65	140	90	CSH(I) ‖ + AFW
73	140	120	CSH(I) ‖ + AFW
74	140	54	CSH(I) ‖ + AFW
48	150	40	CSH(I) ‖
19	160	5	CSH(I) + little CC
22	160	15	CSH(I) + AFW
83	180	2	CSH(I) + CC + SiO_2 gel + CH
94	180	14	XON + β + α
95	180	30	β + possible γ
25	200	20	β + XON + α
26	200	22	β + XON + α

* CSH(I) = Calcium silicate hydrate (I); ||, in a well crystallised form, see text; AFW = afwillite; CC = calcium carbonate; CH = calcium hydroxide; XON = xonotlite; α, β, γ = dicalcium silicate α-, β-, and γ-hydrates, respectively.

DISCUSSION

Calcium Silicate Hydrate (I).—At temperatures up to about 130° (Expts. 90, 56, and 57) this was the sole product detectable by *X*-ray or optical methods. At higher temperatures, it was formed alone only after short periods of treatment (Expts. 19 and 83). More prolonged treatment yielded additional or alternative products. Calcium silicate hydrate (I) thus appears, as in the case of mixtures of lime : silica ratio 1 : 1, to be a transition product at the higher temperatures.

The poorly crystallised material obtained in Expts. 19 and 83 yielded *X*-ray patterns identical with those of samples having a lime : silica ratio 1 : 1 and showing a similar degree of crystallisation. The better crystallised material obtained in Expts. 90, 56, etc., gave photographs almost identical with those of the correspondingly crystallised samples of lime : silica ratio 1 : 1. A few minor differences were observed in the *X*-ray patterns of these samples; lines showing variations in spacing or intensity are given in Table 2. In all other respects the *X*-ray patterns were the same as that of sample 58, described in the previous paper.

Only in the case of sample 83 could unchanged calcium hydroxide be detected in the products. The invariability of the *X*-ray pattern of calcium silicate hydrate (I) with lime : silica ratio, has already been demonstrated as regards the limited number of spacings shown by the room-temperature preparations (Part I, *J.*, 1950, 3682). The present results show that this extends at least approximately to the fuller patterns given by the more crystalline materials. The explanation of this effect is still not clear.

TABLE 2. *Variations in the* X*-ray powder patterns of calcium silicate hydrate* (I) || *samples.*

Line	Intensity in different samples :					
(Å)	58	56	57	65	74	48
2·48	w	w	absent	w	absent	w
2·28	ms	ms	mw/d	vvw	absent	absent
2·22	vw	vw	absent	vvw	absent	ms
2·07	ms	ms	mw	mw	mw	m
1·88	vw	vw	vw	w	vw	split into doublet

The significance of this table lies in the comparison of the relative intensities of the lines from sample to sample; *e.g.*, the 2·28 and 2·07 Å lines are of the same intensity in samples 58, 56, and 57, but not in samples 65, 74, and 48.

Afwillite.—This was identified optically and by *X*-ray methods. Samples 65, 73, 74, and 22 gave *X*-ray powder patterns identical with those of the natural mineral mixed with calcium silicate hydrate (I). Moreover, a single crystal was selected from sample 22, and oscillation photographs taken about two crystallographic axes; the axial lengths so determined agreed closely with those found by Megaw for natural afwillite. The photographs could be indexed satisfactorily on the basis of Megaw's unit cell ($a = 16{\cdot}27$, $b = 5{\cdot}63$, $c = 13{\cdot}23$ Å, $\beta = 134° 48'$; private communication).

The present results indicate that afwillite is probably the final product of the hydrothermal reactions at 140—160°. However, the presence of a considerable amount of calcium silicate hydrate (I) in samples which had reacted for as long as four months suggests that the reaction would require very prolonged treatment for its completion.

Nagai's original characterisation of the product which he obtained at 153° as afwillite is in agreement with our results. We cannot confirm Büssem's observation that afwillite is optically very difficult to distinguish from dicalcium silicate α-hydrate. Although the principal refractive indices of the two compounds are very similar, afwillite forms characteristic needles of considerable thickness, unlike any other hydrated calcium silicate, whereas dicalcium silicate α-hydrate, in our experience, occurs as thin plates.

We are unable to correlate our results with those of Flint, McMurdie, and Wells, who failed to find either calcium silicate hydrate (I) or afwillite in any of their products, but recorded the formation of a compound CaO,SiO_2,H_2O, which we have shown to differ from calcium silicate hydrate (I) (Part II, *loc. cit.*). We could not obtain this compound from any mixtures having lime : silica ratios greater than 1 : 1.

Xonotlite and Hillebrandite.—The results of the experiments at 180° and 200° were difficult to interpret but indicated xonotlite and hillebrandite (dicalcium silicate β-hydrate) as the main products. Comparison of the *X*-ray powder photographs with those of the natural minerals showed in sample 94 all the lines of xonotlite together with the strongest lines of hillebrandite. Samples 25 and 26 gave patterns very similar to natural hillebrandite together with the strongest lines of xonotlite. Sample 95 showed hillebrandite and also the strongest line of dicalcium silicate γ-hydrate. In three of the samples a few crystals of dicalcium silicate α-hydrate could also be detected optically and by single crystal *X*-ray photographs. The structure of this compound was investigated and will be discussed elsewhere.

Optical investigation showed all three samples to consist principally of very small acicular crystals (under 10μ long) of positive elongation and refractive index near to 1·59. These data are compatible with either xonotlite or hillebrandite. Further optical data which would have distinguished between them could not be obtained owing to the small size of the crystals. It was thus not possible to confirm the conclusion derived from the *X*-ray data that the relative proportions of the two compounds were not the same in the four samples. The reason for the anomaly is not clear: if xonotlite and hillebrandite are the only products they must be formed in equimolar amounts. A possible explanation is that preferential crystallisation of either compound can occur, the other remaining in a badly crystallised state giving rise to a weak *X*-ray pattern.

These results can be correlated with those of Jander and Franke, who obtained a mixture of xonotlite and hillebrandite at 300°. Nagai, and Flint, McMurdie, and Wells also obtained xonotlite at 180—200° and 250°, respectively, together with other products. The most probable interpretation of the present and earlier results at temperatures of 180° and above is that the main products are xonotlite and a hydrated dicalcium silicate which is usually the β-, but may under certain conditions be the α- or the γ-hydrate.

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 Dr. F. A. Bannister, of the British Museum (Natural History), for the mineral specimens. 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, November* 12*th*, 1951.]