480. *Hydrated Calcium Silicates. Part IV.*[*] *Hydrothermal Reactions: Lime : Silica Ratios* 2 : 1 *and* 3 : 1.

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Hydrothermal reactions were carried out at 100—200° with mixtures of lime and silica gel in the molar ratio 2 : 1, and also with the compounds β- and γ-Ca_2SiO_4 and Ca_3SiO_5. The starting materials of lime : silica molar ratio 2 : 1 yield calcium silicate hydrate (I) as the initial product at the lower temperatures, more prolonged treatment giving afwillite. At higher temperatures one or more of the dicalcium silicate α-, β-, and γ-hydrates are obtained. These tend to predominate in the product at successively higher temperatures, but the α-hydrate appears to be only a transition product when formed from starting materials of its own composition. Dicalcium silicate β-hydrate resembles natural hillebrandite very closely, but the *X*-ray powder photographs show slight but distinct differences.

Ca_3SiO_5 also yields calcium silicate hydrate (I) or (II) as the initial product up to at least 120°. The final products at 120° are dicalcium silicate α-hydrate and calcium hydroxide; these products were also obtained at the higher temperatures, even after relatively short times of reaction.

STUDIES by earlier investigators on the hydrothermal treatment of mixtures or compounds of the compositions $2CaO,SiO_2$ or $3CaO,SiO_2$ have yielded conflicting results. The products most often obtained from starting materials of the former composition have been the dicalcium silicate α-, β-, and γ-hydrates. The α-, β-, and γ-hydrates appear to predominate

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[*] Part III, *J.*, 1952, 1018.

in the product at successively higher temperatures over the range 150—350°. Tricalcium silicate hydrolyses to dicalcium silicate α-hydrate at about 150° and yields a hydrate $3CaO,SiO_2,2H_2O$ at higher temperatures (for references and fuller discussion see Taylor and Bessey, *Mag. Concrete Res.*, 1950, No. 4, p. 15). Foret (*Compt. rend.*, 1937, **204**, 977), however, obtained from mixtures of lime and quartz a product which was probably calcium silicate hydrate (I) or (II) (Part II, *J.*, 1951, 2397). She was unable to detect any other product, although the temperatures employed varied from 120° to 300° and the molar ratios of lime to silica from 2 : 1 to 4 : 1. No compounds other than dicalcium silicate α-, β-, and γ-hydrates, and tricalcium silicate hydrate, have been identified in the products obtained from the anhydrous calcium silicates.

The apparent contradiction between Foret's results and those of other workers suggested a need for further investigation. The present study was therefore carried out, with the particular aim of establishing whether the di- and the tri-calcium silicate hydrates were in fact the only compounds that could be formed hydrothermally from the anhydrous calcium silicates at 100—200°. A knowledge of this is of importance in connection with the steam curing of Portland cement (Nurse, Proc. Building Res. Congr., London, 1951).

EXPERIMENTAL

Starting Materials.—The calcium hydroxide and silica gel samples have already been described (Parts III and I respectively, *J.*, 1952, 1018; 1950, 3682). The β- and γ-dicalcium silicates and the tricalcium silicate were kindly supplied by Mr. R. W. Nurse of the Building Research Station, Watford, Herts., and had been prepared from pure calcium carbonate and silica. Their optical properties and *X*-ray powder lines were in satisfactory agreement with published data (Bogue, " The Chemistry of Portland Cement," Reinhold Publ. Corp., New York, 1947).

Methods.—In each experiment, the starting materials were treated with liquid water under its own vapour pressure at the temperature of the reaction. The products were examined optically and by *X*-ray powder photographs. Details of the procedures used have already been given (Part II, *loc. cit.*).

The results obtained are given in Tables 1—4. The *X*-ray and optical methods of examination were found complementary. Small amounts of a compound, which in the presence of a more abundant phase could not be detected by its *X*-ray pattern, could often be detected optically. This was particularly true in the case of afwillite and dicalcium silicate α-hydrate, which form relatively large crystals. On the other hand, in some cases, where optical examination showed only ill-defined material, the *X*-ray method gave conclusive results.

Identification of Calcium Silicate Hydrate (I).—This was most satisfactorily characterised by its *X*-ray powder lines, which were compared with those of a pure specimen (sample 58, Part II, *loc. cit.*). As in the case of previous samples of this compound prepared hydrothermally from mixtures of lime : silica ratios 1 : 1 or 3 : 2, variations in the relative intensities of certain lines were observed. The most marked effect was seen in the case of the 2·28-Å line, which was completely absent in sample 66. The 2·07-Å line also varied in its intensity relative to those of neighbouring lines. It appears probable from other work now in progress that these variations, which do not affect any of the *hk*0 lines, may be due to differences in the states of hydration and consequently of the basal spacing.

TABLE 1. *Products obtained when starting materials were mixtures of calcium hydroxide and silica in the molar ratio* 2 : 1.

No.	Temp.	Time (days)	Products
38	110°	63	CSH(I) + AFW
59	110	200	AFW + weak CH
52	130	52	CSH(I) ‖ + AFW
55	130	55	CSH(I) ‖ + AFW
66	140	120	CSH(I) ‖ + AFW
43	150°	37	CSH(I) ‖ + AFW
84	180	2	CSH(I) * + CH + SiO_2
96	180	30	β + little CSH(I) *
27	200	23	γ + little α and β

For notes, see after Table 4.

TABLE 2. *Products obtained when starting material was* β-Ca_2SiO_4.

No.	Temp.	Time (days)	Products
49	130°	52	Unchanged + CSH(I) * + CH
68	140	1	Unchanged
69	140	4	Unchanged
70	140	5	Unchanged
71	140	5	Unchanged + CSH(I) *
63	140	5	α
76	140	8†	Unchanged + α
72	140	9	Unchanged + CSH(I) *
77	140	12	α + little CSH(I) * and CH
61	140	60	β + little AFW
75	140	151	AFW + CH + CSH(I) ‖ and a little α and β
79	140	166	β
40	160	30	β + little γ
87	180	1/3	Unchanged
85	180	2	γ
97	180	14	β + little γ
33	200	4	γ + little β
32	200	16	γ + little β

For notes, see after Table 4.

TABLE 3. *Products obtained when starting material was* γ-Ca_2SiO_4.

No.	Temp.	Time (days)	Products
41	150°	30	Unchanged + little γ
20	160	13	CSH(I) ‖ + AFW + C
86	180	7	Unchanged + little γ
99	180	30	γ + C + D
35	200	37	γ + little α + D

For notes, see after Table 4.

TABLE 4. *Products obtained when starting material was* Ca_3SiO_5.

No.	Temp.	Time (days)	Products
117	104°	1	Unchanged + CH
118	104	4	Unchanged + CH
119	104	7	Unchanged + CH + CSH(I) *
125	110	2 ‡	Unchanged + CH + CSH(I) *
126	110	3 ‡	Unchanged + CH + CSH(I) *
127	110	6 ‡	Unchanged + CH + CSH(I) * + α
129	115	3 §	CH + CSH(I) * + α
103	120	2	CSH(I) * + CH
105	120	7	CH + α
107	120	14	CH + α
109	140	1	CH + α
113	165	19	CH + α
116	180	1/25	Unchanged + little CH
114	180	5/24	CH + α
104	180	1	CH + α
102	180	2	CH + α
106	180	13	CH + α
108	200	1	CH + α
110	200	6	CH + α
112	200	7	CH + α

CH = calcium hydroxide; CSH(I) = calcium silicate hydrate (I).

* Only two *X*-ray powder lines visible, see text; AFW = afwillite; α, β, γ = dicalcium silicate α-, β-, and γ-hydrates respectively.

† Seeded with a few crystals of dicalcium silicate α-hydrate; C, D = extra *X*-ray powder lines, see text.

‡ Preceded by 5 days at 95°.

§ Preceded by 5 days at 95° and 7 days at 110°.

‖ In a well-crystallised form, see text.

Under the microscope, the calcium silicate hydrate (I) obtained in these experiments appeared as an ill-defined material, in some cases just visibly crystalline, having a mean refractive index near to 1·56. Distinction from calcium hydroxide ($\omega = 1{\cdot}57$, $\varepsilon = 1{\cdot}54$) was often difficult or impossible, since the calcium hydroxide was usually also in a very finely dvided condition.

Identification of Afwillite.—This provides little difficulty either optically or by *X*-ray methods. A powder photograph of a sample of the natural mineral was taken for comparison, and showed about 40 lines, in good agreement with previously recorded data (Clark and Bunn, *J. Soc. Chem. Ind.*, 1940, **59**, 155; McMurdie and Flint, *J. Res. Nat. Bur. Stand.*, 1943, **31**, 225). Identical patterns were obtained from the synthetic samples provided that a sufficient proportion of afwillite was present. Optically, synthetic afwillite can be recognised easily, even in small proportion, since it forms relatively large crystals of prismatic habit. The largest crystals obtained (in experiment 75) were about 0·7 × 0·2 × 0·2 mm. Their optical properties, determined in white light, were :

Biaxial positive, $2V = 55° \pm 10°$, $n_\alpha = 1{\cdot}614$, $n_\beta = 1{\cdot}617$, $n_\gamma = 1{\cdot}630$.

Absolute values of these indices are correct to $\pm 0{\cdot}005$, and values of $n_\beta - n_\alpha$ and $n_\gamma - n_\beta$ to $\pm 0{\cdot}002$. The prism axis of the crystals coincides with the β-direction to within a few degrees. The commonest orientation on the slide was with the obtuse bisectrix about 20° from the vertical; such crystals showed approximately parallel extinction, negative elongation, and a high birefringence. More rarely crystals lay with either one optic axis, or else the acute bisectrix, near the vertical; in the latter case the crystal showed positive elongation and a low birefringence. These results are in close agreement with those of the natural mineral (Parry and Wright, *Min. Mag.*, 1925, **20**, 277).

Identification of Dicalcium Silicate α-Hydrate.—This compound was easily recognised under the microscope, as it formed thin rectangular plates of characteristic appearance, with optical properties in agreement with those found by Vigfussen, Bates, and Thorvaldson (*Canad. J. Res.*, 1934, **11**, 520). Sample 63 was substantially free from other species and gave an *X*-ray pattern showing about sixty lines, in good agreement with those recorded by the above investigators, including McMurdie and Flint (*loc. cit.*), although additional weak lines were present. The powder photograph of this sample was used as a standard for the characterisation of dicalcium silicate α-hydrate in other samples.

TABLE 5. X-*Ray powder data for natural hillebrandite and for synthetic dicalcium silicate* β-*hydrate* (*sample* 79). *Spacings in* Å.

Hillebrandite	Sample 79	Hillebrandite	Sample 79	Hillebrandite	Sample 79	Hillebrandite	Sample 79
—	12 vvw ?	2·45 w	2·44 w	1·64 w	1·62 w/d †	1·360 vvw	1·35 vvw/d
8·2 mw	8·1 w	2·37 s	2·36 s	1·62 mw		1·350 vvw	—
6·7 vw	—	2·26 ms	2·23 vs †	1·61 mw		1·335 vvw	1·33 vvw
5·8 w	5·7 w	2·23 ms		1·57 mw	1·56 vw †	1·325 w	1·32 vw
4·76 vs	4·74 vs	2·10 vvw	—	1·56 vvw	—	1·300 vvw	—
4·06 mw	4·03 mw	2·06 ms	2·05 ms	1·54 w	1·53 w	1·280 vvw	—
3·52 mw	3·51 ms	1·96 ms	1·95 ms †	1·530 vw	—	1·220 vvw	—
3·33 vs	3·32 ms	1·93 m	1·93 ms	1·525 vw	1·52 vw	1·205 vvw	—
3·02 s	3·00 s	1·87 ms	1·85 ms/d †	1·505 vvw	—	1·190 w	—
2·92 vvs	2·90 vvs	1·85 m		1·500 vvw	—	1·180 w	1·17 mw/d
2·82 s	2·80 w †	1·81 s	1·80 vs	1·470 w	1·46 mw	1·175 w	—
2·76 s	2·75 s	1·75 m	1·75 m	1·450 vw	1·44 vw	1·120 vw.	1·11 vw/d
2·70 w *	2·67 mw/d †	1·72 mw	1·71 mw	1·430 vw	1·42 vw	1·115 vvw	—
2·67 w		1·69 vvw	1·68 vvw	1·415 vw	1·41 vw	1·095 vw	1·09 vw
2·63 mw	2·62 mw	1·67 vvw	1·66 vvw	1·365 vvw	—		

* This line varied in intensity for different samples taken from the same lump of mineral and was probably not wholly due to hillebrandite.

† Principal cases in which the synthetic material differed from the natural mineral, apart from the generally shorter spacings of corresponding lines.

Identification of Dicalcium Silicate β-Hydrate.—Comparison of the *X*-ray powder photograph of sample 79 with those of other samples showed that it did not contain lines due to any likely product other than dicalcium silicate β-hydrate. The results thus obtained (Table 5) are in satisfactory agreement with those recorded previously for this compound (McMurdie and Flint, *loc. cit.*; see also Taylor and Bessey, *loc. cit.*), and the photograph was used as a standard for its detection in other samples. Optical investigation gave little more than confirmatory evidence, since the crystals were always extremely small. In favourable cases it was possible to recognise needles of mean refractive index 1·60, with parallel extinction and positive elongation.

For comparison, powder photographs of natural hillebrandite were taken and the resulting data are included in Table 5. They are in tolerable agreement with the results of Clark and Bunn (*loc. cit.*) and McMurdie and Flint (*loc. cit.*).

Identification of Dicalcium Silicate γ-Hydrate.—This compound was most readily identified by its *X*-ray pattern. Sample 85, which appeared to be substantially pure, gave a pattern showing twelve lines, in agreement with those found by Keevil and Thorvaldson (*Canad. J. Res.*, 1936, **14**, A, 20) and by McMurdie and Flint (*loc. cit.*). The strong spacing of approx. 1·90 Å recorded by these investigators was found to be a close doublet and as such proved particularly useful for the characterisation of the compound in other samples. The crystals were even smaller than in the case of the β-hydrate; the mean refractive index lay in the region 1·62—1·64, in agreement with the earlier investigations (Keevil and Thorvaldson, *loc. cit.*).

X-*Ray Lines* C *and* D.—In three experiments starting with γ-Ca_2SiO_4 (Table 3) two sets of *X*-ray powder lines were observed which could not be attributed to any known compound. Their spacings (in Å) and relative intensities were as follows: Extra lines " C ": 4·2 vs, 2·59 w, 2·26 m, 2·24 m. Extra lines " D ": 3·63 m, 2·85 s, 2·35 vvw, 1·95 m, 1·68 w, 1·52 vvw, 1·50 vvw, 1·48 vvw. All three products were largely composed of indefinitely crystalline material and, except for the detection of afwillite in sample 20, optical investigation was inconclusive. The significance of these lines is therefore obscure.

DISCUSSION

The results show that the products of hydrothermal treatment of starting materials containing lime and silica in the molar ratios 2 : 1 and 3 : 1 are more complex than the previous investigators have concluded. In the former case, at 100—200°, not only the three dicalcium silicate hydrates, but also afwillite and calcium silicate hydrate (I) may be obtained. In the latter case, in addition to dicalcium silicate α-hydrate and tricalcium silicate hydrate, calcium silicate hydrate (I) may again be one of the products.

Formation of Calcium Silicate Hydrate (I).—This product was obtained from all four of the starting materials. It was the main product in, for example, preparations 52 and 55, made from mixtures of lime : silica ratio 2 : 1; 49 and 71, made from β-Ca_2SiO_4; 20, made from γ-Ca_2SiO_4; and 103, made from Ca_3SiO_5. The temperatures of the experiments in which it was formed ranged from 104° to 180°; at the lower temperatures it was nearly always found in the products, but as the temperature was increased, it occurred less frequently. It was not obtained from Ca_3SiO_5 at temperatures above 120°. For any given combination of temperature and starting material, the proportion of calcium silicate hydrate (I) relative to other products tended to decrease with the time of the hydrothermal treatment. This is shown, for example, in the experiments with Ca_3SiO_5 at 120° (103, 105, 107; Table 4) and with the mixtures at 180° (84, 96, Table 1).

This behaviour is similar to that observed in the case of mixtures of lower lime : silica ratio (Parts II and III, *locc. cit.*), and admits of the same explanation: calcium silicate hydrate (I) is formed as the first product of the hydrothermal treatment of all these materials, at any rate up to a limiting temperature in each case, and subsequently changes into other phases, depending on the temperature and composition. This explains Foret's observations (*loc. cit.*), since the starting materials (lime and quartz) are not very reactive, and the times of her experiments (6—8 days) were relatively short. Her results suggest that calcium silicate hydrate (I) can be produced from lime and quartz at all temperatures up to 300°.

Characterisation, Degree of Crystallisation and Composition of Calcium Silicate Hydrate (I).—In some cases (75, 20, etc.), where calcium silicate hydrate (I) was formed, it gave the full *X*-ray pattern characteristic of the well-crystallised material (Part II, *loc. cit.*). In other cases, only the *hk*0 lines were visible, but these were perfectly sufficient to distinguish the compound from calcium silicate hydrate (II) or any other known hydrated calcium silicate. In a few cases (49, 84, etc.), only the two strongest spacings of 3·07 and 1·83 Å were observed. These coincide with strong spacings of calcium silicate hydrate (II) (Part I, *loc. cit.*). It does not appear likely that this compound was formed in any of the experiments with lime : silica ratio 2 : 1, since the characteristic lines of calcium silicate hydrate (II), which distinguish it from calcium silicate hydrate (I), were not observed, although the reverse was often true (*e.g.*, in products 38, 75, and 20). In the products obtained from Ca_3SiO_5, the conclusions are less certain. The 3·07 and 1·83-Å lines were given by several products made below 120°, showing that either calcium silicate hydrate (I) or (II) had been produced. Attempts to obtain this in a better crystallised form, by increase in time or temperature, to enable a distinction to be made, were unsuccessful, because transition to dicalcium silicate α-hydrate occurred. At 20°, calcium silicate hydrate (II) is the initial product of the hydrolysis of Ca_3SiO_5 (Part I, *loc. cit.*) and it might therefore be expected as the product in the present case. However, it is unstable in the presence of aqueous calcium hydroxide less concentrated than 0·02M, giving calcium silicate hydrate (I) and calcium hydroxide. The solubility of the latter at 100° and above is far below 0·02M (Flint, McMurdie, and Wells, *J. Res. Nat. Bur. Stand.*, 1938, **21**, 617) and this may cause calcium silicate hydrate (I), rather than (II), to be the product under hydrothermal conditions.

The maximum lime : silica molar ratio of calcium silicate hydrate (I), determined on material formed at room temperature, is 3 : 2 (Part I, *loc. cit.*). It might therefore be expected that when this material is obtained from starting materials of lime : silica ratio 2 : 1 an equivalent amount of calcium hydroxide would be formed. In fact, the *X*-ray patterns of many such samples (66, 72, 20, etc.) did not contain the lines of calcium hydroxide. Two explanations seem possible. Calcium silicate hydrate (I), when formed under hydrothermal conditions, may have a maximum lime : silica ratio greater than 3 : 2. Alternatively, the calcium hydroxide may have been present in so imperfectly crystalline a state that it could not be detected in the powder photograph. For reasons already given, optical investigation gave inconclusive results in this case. The fact that sample 59, in which afwillite was formed from a 2 : 1 mixture, gave an *X*-ray powder photograph in which the calcium hydroxide lines were only very weakly visible, tends to support the second hypothesis, since afwillite has the definite composition $Ca_3(HSiO_4)_2,2H_2O$. The matter cannot however be considered as settled on the present evidence.

Products obtained at 100—110°.—It is probable that, even at the lowest temperatures studied, calcium silicate hydrate (I), although more persistent than at higher temperatures, is not a stable product. In experiment 38 it was formed together with afwillite after 63 days at 110°, but after 200 days (experiment 59) the same starting material gave only afwillite. Bessey (quoted by Taylor and Bessey, *loc. cit.*) similarly obtained afwillite from a 2 : 1 mixture of lime and silica at 98°. It therefore appears that the calcium silicate hydrate (I) changes into afwillite on long treatment even at 100°. With tricalcium silicate as starting material, 7 days' treatment at 104° (experiment 119) gave calcium silicate hydrate (I) and calcium hydroxide. However, Flint, McMurdie, and Wells (*loc. cit.*) in an experiment at 100° of 14 days' duration observed the formation of dicalcium silicate α-hydrate, which was also obtained by the present authors at 110° and above (experiments 127, etc.). The final products obtained from Ca_3SiO_5 at 100—110° are therefore probably dicalcium silicate α-hydrate and calcium hydroxide.

At lime : silica ratios of 1 : 1 or 3 : 2, calcium silicate hydrate (I) appears to be stable at 110° under hydrothermal conditions (Parts II and III, *locc. cit.*).

Formation of Afwillite.—The results, together with those reported in Part III (*loc. cit.*), show that afwillite is produced only under mildly hydrothermal conditions, the highest temperature at which it was obtained being 160°. Partly, perhaps, for this reason its formation tends to be very slow. Most of the earlier workers in this field concentrated on experiments at higher temperatures and of relatively short duration. This probably explains why, apart from the one experiment by Bessey already mentioned, no conclusive synthesis of this compound has previously been recorded.

Formation of the Dicalcium Silicate Hydrates.—After sufficiently prolonged treatment at temperatures of 140° or above, the mixtures or compounds of lime : silica ratio 2 : 1 gave principally the dicalcium silicate α-, β-, or γ-hydrates. The present results on the whole support the view that the α-, β-, and γ-hydrates predominate at successively higher temperatures. However, at 140° the α-hydrate was only the main product in experiments of short duration (63, 76, and 77; 5, 8, and 12 days respectively), longer treatment giving other products. It therefore appears to be no more than a transition product when formed from starting materials of its own lime : silica ratio, even at the lowest temperature at which it can readily be obtained. At 180° and 200° mixtures of two or all three of the hydrates are commonly obtained (experiments 27, 97, 33, 32, and 35). These results show that, at any rate below 200°, it is extremely difficult to attain equilibrium. This almost certainly accounts for the wide variations in the ranges of temperature and other conditions reported by the earlier workers as giving one or the other hydrate.

It is noteworthy that the hydrolysis of Ca_3SiO_5 at temperatures between 100° and 200° always yields the α- and never the β- or γ-hydrate. It appears probable that in the presence of excess of calcium hydroxide the α-hydrate is the stable form over this range of temperature.

Tricalcium silicate hydrate was not obtained in any of the present experiments. It is probable that the temperatures employed were inadequate for its formation, since Flint, McMurdie, and Wells (*loc. cit.*) only obtained it as the main product from Ca_3SiO_5 at 250° and above.

The Relation of Dicalcium Silicate β-*Hydrate to Natural Hillebrandite.*—While several of the earlier workers claimed to have synthesised hillebrandite, others (Flint, McMurdie, and Wells, *loc. cit.*; Vigfussen, Bates, and Thorvaldson, *loc. cit.*) considered that dicalcium silicate β-hydrate was not identical with the natural mineral. This view was, however, based on incorrect *X*-ray powder data for the natural mineral and, on the basis of a comparison of more recent data for both natural and artificial samples, Taylor and Bessey (*loc. cit.*) pointed out that the natural and the artificial material were closely similar, if not identical.

In the present investigation comparison of an *X*-ray powder photograph of the natural mineral with that of sample 79, which was regarded as pure dicalcium silicate β-hydrate, showed a close resemblance extending even to the shortest spacings observed, but also some distinct differences. These include a general slight diminution of the spacings (Table 5). It is probable that, while the natural and artificial products are essentially similar, the structure of the former is very slightly modified by some kind of solid solution. To avoid confusion, it may be considered desirable to restrict the names hillebrandite and dicalcium silicate β-hydrate to the natural and the artificial substance respectively.

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 for the samples of β- and γ-Ca_2SiO_4, Ca_3SiO_5, and natural hillebrandite; and Dr. F. A. Bannister, of the British Museum (Natural History), for the natural afwillite. 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, March* 26*th*, 1952.]