33. *Hydrated Calcium Silicates. Part V.* The Water Content of Calcium Silicate Hydrate* (I).

By H. F. W. TAYLOR.

The water content of calcium silicate hydrate (I), (1—$1{\cdot}5CaO,SiO_2,xH_2O$), has been investigated, principally by dehydration isobars and *X*-ray photographs of samples partly or fully dehydrated under various conditions. Laboratory preparations, made by four different methods, and natural riversideite, have been studied. Three distinct states of hydration exist, having $x = 2{\cdot}5$ approx., 1·0, and 0·5, and *c*- or inter-layer spacings of 14·0, 10·4, and 9·3 Å, respectively. The *a*- and *b*-axes are unaffected during dehydration to the monohydrate, but further dehydration causes them to shrink slightly, and it is probable that one molecule of water is essential to the structure of the layers. The expelled water can be replaced completely if the water content has not been reduced below 1·0, but there is a marked hysteresis effect, and the original *c*-spacing is not fully regained. The water : silica ratio *x*, after any given conditions of dehydration, is independent of the lime : silica ratio of the sample. This seems to rule out the theory that the variable lime content is due to adsorption of calcium hydroxide. The products formed on complete dehydration have been investigated; at 800°, β-wollastonite is formed. A high degree of order is maintained throughout the dehydration process, and a structural resemblance must exist between calcium silicate hydrate (I) and β-wollastonite.

IN Part I (*J.*, 1950, 3682), the preparation at room temperature of calcium silicate hydrate (I) was described, and it was shown to have a variable composition, approximating to 1·0—1·5CaO, SiO_2,xH_2O, and a layer structure showing certain similarities to those of the clay minerals. The present paper deals with the water content *x* of this substance, including the dependence of this quantity on the lime : silica ratio, and on the conditions of temperature and humidity, and with its relation to the spacing between the layers within the crystal.

Previous Investigations.—A few investigations of a limited character are on record. For samples of lime : silica ratio 1 : 1, the water content, after the substance had been brought into equilibrium with an atmosphere of ordinary temperature and humidity ($p_{H_2O} \approxeq 10$ mm. of Hg), is in the region of 2—2·5 (Le Chatelier, *Ann. Mines*, 1887, **11**, 345; Bessey, "Symposium on the Chemistry of Cements," Stockholm, 1938, p. 178; Hedin, "Chemical Processes in the Hardening of Portland Cement," Stockholm, 1945; Brocard, *Ann. Inst. Tech. Batiment*, 1948, No. 1, 1). This is reduced to approximately 1·0 by drying over calcium oxide at room temperature (Keevil and Thorvaldson, *Canadian J. Res.*, 1936, **14**, *B*, 20; Bessey, *op. cit.*), by heating to 100—150° (Cirilli, *Ann. Chim. appl.*, 1938, **28**, 239; Forsen, "Symposium on the Chemistry of Cements," Stockholm, 1938, p. 298; Hedin, *loc. cit.*), or by extraction of loosely held water with liquid ammonia (Thilo, Funk, and Wichmann, *Abhand. Deut. Akad. Wiss. Berlin*, 1950, No. 4, 1). On the basis of such evidence, Roller and Ervin (*J. Amer. Chem. Soc.*, 1940, **62**, 461) and Thilo (*Angew. Chem.*, 1951, 201) considered the composition of calcium silicate hydrate (I) to be CaH_2SiO_4.

Somewhat contradictory results have been obtained for samples of higher lime : silica ratio. Lefol (*Compt. rend.*, 1935, **201**, 669) found the dehydration isotherm, for a sample of composition $1{\cdot}2CaO,SiO_2,xH_2O$, to be a smooth curve, in agreement with that obtained by Bessey (*op. cit.*) for one of composition CaO,SiO_2,xH_2O. On the other hand, Cirilli (*Ric. Sci.*, 1939, **10**, 459) and Hedin (*loc. cit.*) reported values of the water content, after given conditions of dehydration, which were markedly dependent upon the lime : silica ratio.

In none of the heating experiments mentioned above does any attempt appear to have been made to control the humidity of the atmosphere with which the substance was in contact. The results obtained from them are therefore of uncertain significance. No attempts to correlate variations in water content with *X*-ray spacings have been reported.

Considerable help was given in the present investigation by the recent observation

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* Part IV, *J.*, 1952, 2535.

(Taylor, *Min. Mag.*, in the press) that natural riversideite is a close fibrous intergrowth of an apatite mineral, wilkeite, with calcium silicate hydrate (I). The latter, despite the presence of the wilkeite, is in a physical state more amenable to crystallographic investigation than in any of the laboratory preparations so far made. This enabled more detailed results to be obtained than would otherwise have been possible.

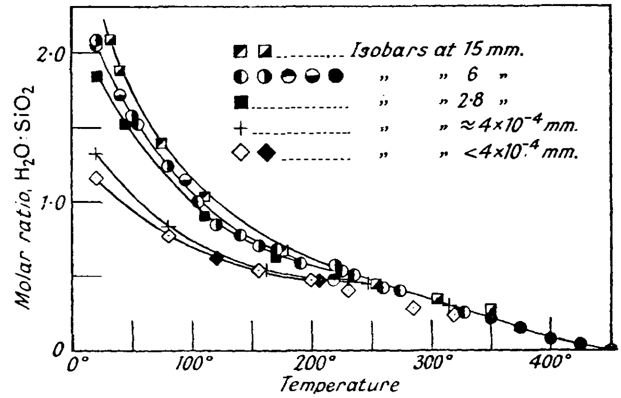
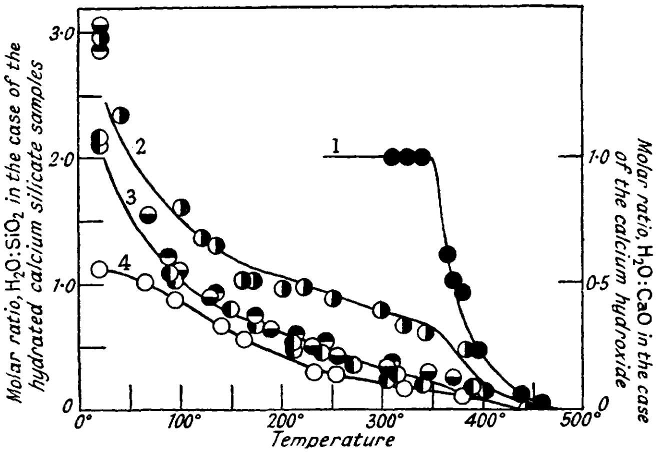


FIG. 1. *Dehydration isobars for calcium silicate hydrate* (I). *Effect of variation in the partial pressure of water vapour* : *Sample* (1), CaO : SiO_2 = 0·99.

Each type of point represents a separate experiment. Full curves are drawn through the points for each isobar separately up to *ca.* 230°; at higher temperatures, only a single curve, for pressure 6 mm., is drawn.

FIG. 2. *Dehydration isobars for several preparations of calcium silicate hydrate* (I), *and for calcium hydroxide. Partial pressure of water vapour* = 6 *mm.*



1. —●— *Calcium hydroxide.*
◑ *Sample* 7. CaO : SiO_2 = 1·95.
2. ——— *Calculated for* 1 *mol. of calcium silicate hydrate* (I) +0·45 *mol. of calcium hydroxide.*
3. ——— *Sample* 1. CaO : SiO_2 = 0·99.
⊖ *Sample* 9. CaO : SiO_2 = 1·37.
◐ *Sample* 2. CaO : SiO_2 = 1·30.
⊖ *Sample* 6. CaO : SiO_2 = 1·24.
4. —○— *Sample* 10. (*Hydrothermal preparation.*)

Results.—(1) *Dehydration isobars for a sample of composition* CaO,SiO_2,xH_2O : *effect of variation in pressure.* A series of isobars, obtained at different partial pressures of water vapour, is shown in Fig. 1. The sample was made at room temperature by reaction between calcium hydroxide solution and silica gel (Part I, *loc. cit.*). The results confirm earlier indications that about 1·0 mol. of water remains after heating to 100° under normal conditions of humidity, or after standing over powerful dehydrating agents at room temperature. They do not, however, give any indication of the existence of a definite hydrate of this composition. On the other hand, the isobars all show a point of inflection, in the neighbourhood of 220°, possibly indicating the existence of a hemihydrate.

(2) *Dehydration isobars for various samples of approximate composition* CaO,SiO_2,xH_2O. In order to test reproducibility, isobars at 6 mm. pressure of water vapour were obtained for five additional samples having lime : silica ratios near 1 : 1. Four of these gave results in close agreement with those already described; each of these had been prepared at room temperature, either by double decomposition of calcium nitrate and sodium silicate (nos. 3, 4, and 5) or by the action of water on Ca_3SiO_5 (no. 8). Reproducible results are thus obtainable for samples made at room temperature, irrespective of the method of preparation. The fifth sample (no. 10), prepared hydrothermally (Part II, *J.*, 1951, 2397), gave a curve (Fig. 2) which was not very different from the others at 100° and above, but showed a much lower water content at room temperature, the curve tending to a distinct limit at a water content of about 1 : 1. In this case, therefore, there is some indication that a monohydrate may exist.

(3) *Dehydration isobar for natural riversideite.* This is shown in Fig. 3. The isobar, obtained at 6 mm. pressure, shows distinct points of inflection at temperatures in the neighbourhood of 100° and 220°. Owing to the difficulties of obtaining a pure sample, or in making allowance for the impurities present (Taylor, *Min. Mag.*, *loc. cit.*), the values of the water content corresponding to these points of inflection are approximate. The water contents at 100° and 220° are 0·8 and 0·5, respectively. The first of these corresponds very roughly with the water content, below 100°, of the hydrothermal preparation already described, and the second corresponds with the point of inflection at 220° and 0·5 mol. shown in varying degrees by all the artificial samples.

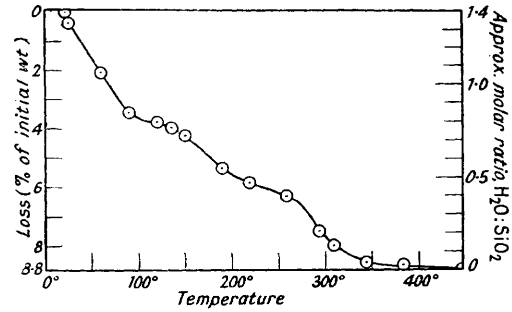


FIG. 3. *Dehydration isobar for natural riversideite. Partial pressure of water vapour = 6 mm.*

(4) *Dehydration isobars for samples of calcium silicate hydrate* (I) *having varying molar ratios of lime to silica.* Fig. 2 includes data for three samples having lime : silica molar ratios (y) within the range 1·0 : 1 and 1·5 : 1. All had been prepared at room temperatures : one had been made by double decomposition, and had $y = 1{\cdot}24$; a second was prepared from calcium hydroxide and silica gel, and had $y = 1{\cdot}30$; the third was obtained from tricalcium silicate and had $y = 1{\cdot}37$. The dehydration isobars of all three are in close agreement with those of the samples having $y = 1{\cdot}0$. For samples prepared at room temperature, therefore, the water content x at any given temperature and pressure is independent, within the limits of error of the present experiments, both of the method of preparation and of the molar lime : silica ratio y.

(5) *Dehydration isobars for calcium hydroxide, and for a mixture of calcium hydroxide with calcium silicate hydrate* (I). Attempts to prepare samples of the hydrate (I) having lime : silica ratios in excess of 1·5 : 1 yield, at least at room temperature, mixtures of this substance with calcium hydroxide (Part I, *loc. cit.*). The dehydration isobar, at 6 mm. pressure, for one such sample is included in Fig. 2. The sample was prepared by double decomposition, and had an overall lime : silica molar ratio of 1·95 : 1. For the purpose of comparison, a dehydration isobar for calcium hydroxide was obtained at the same pressure (Fig. 2). It will be seen that almost all the water in this compound is lost within the range 350—450°. This is in close agreement with the results obtained by Krauss and Jörns at 7 mm. (*Zement*, 1931, **20**, 314, 341). Curve 2 in Fig. 2 was calculated by adding together at each temperature the observed water contents for 1·0 mol. of calcium silicate hydrate (I), of composition $1{\cdot}5CaO,SiO_2,xH_2O$, and 0·45 mol. of calcium hydroxide. The close agree-

ment with the experimental points for the sample of lime : silica ratio 1·95 : 1 shows that the lime in excess of 1·5 mol. in the latter is present in the form of hydroxide.

(6) *Rehydration of calcium silicate hydrate* (I) *on cooling from various temperatures.* Fig. 4 shows the results of attempts to bring about rehydration of a calcium silicate hydrate (I) sample by cooling from various temperatures, 6 mm. pressure of water vapour being maintained throughout. Care was taken to ensure that constant weight was attained at each stage; in several cases this took one month or more, as the re-absorption of water was in general very slow. The proportion of the expelled water, that was regained on reaching equilibrium at 20°, decreased as the temperature to which the material had been heated increased, the samples heated to 95°, 230°, and 330° regaining, respectively, 57, 25, and 14% of the expelled water on cooling to 20°. With the first sample increase of the partial vapour pressure to 15 mm. at 20° brought about complete replacement of the expelled water.

(7) *Dehydration and rehydration isotherms for a sample of calcium silicate hydrate* (I). Dehydration isotherms for calcium silicate hydrate (I) might be constructed for any desired temperature from the family of isobars given in Fig. 1. A curve was, however, obtained directly by exposing a single sample to successively lower vapour pressures at room temperature. Subsequently the vapour pressure was raised again, and a rehydration isotherm obtained. The results of two such experiments (see Fig. 5) show, in agreement with those obtained by rehydration of samples heated to 95°, that water in excess of about 1·0 mol. can be replaced by exposure to water vapour at a suitable pressure and temperature. In both cases, however, there is a marked hysteresis effect, and reabsorption of the water is slow. Total periods of 44 and 105 days were occupied in the reabsorption isotherms in experiments I and II respectively, although a considerable proportion of the expelled water was reabsorbed in much shorter times in each case. The dehydration isotherm given in Fig. 5 is of the same general form as that obtained by Bessey (*op. cit.*) for a similar sample. The flat part of the curve occurs at a water content of about 2·0, compared with about 2·5 in Bessey's experiment.

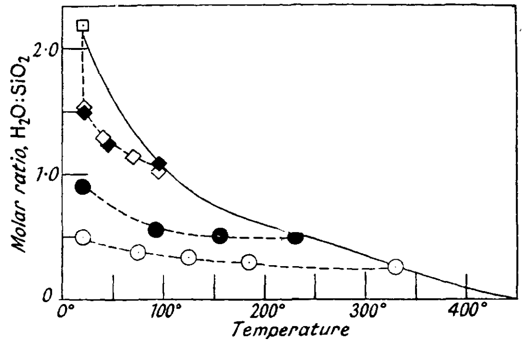


FIG. 4. *Rehydration isobars for calcium silicate hydrate* (I) : *Sample* (1), CaO:SiO$_2$ = 0·99.

Full curve :
Dehydration from H_2O : SiO$_2$ 2·07
○ *Rehydration from* 330°
● *Rehydration from* 230° p_{H_2O} = 6 *mm.*
◇ *Rehydration from* 95°
◆ (*Separate expts.*)
□ *Ditto after standing at* 20° *and* p_{H_2O} = 155 *mm.*

(8) X-*Ray investigation of a fibre of natural riversideite after it had been heated to various temperatures.* As already stated, natural riversideite is a fibrous intergrowth of wilkeite and calcium silicate hydrate (I). A detailed description of this intergrowth, and of the *X*-ray patterns obtained from it, has been given elsewhere (Taylor, *Min. Mag., loc. cit.*). *X*-Ray rotation and zero-layer Weissenberg photographs were taken, about the fibre axis, of a single fibre of riversideite in its natural state and after it had been heated successively to 100°, 250°, 450°, 550°, 700°, 800°, and approximately 1000°. At temperatures up to 450° inclusive, the partial pressure of water vapour was maintained at 6 mm. The photographs all showed reflections corresponding to the presence of a single crystal of wilkeite, with its *c*-axis parallel to the fibre direction, together with preferred orientation patterns of calcium silicate hydrate (I) or its alteration products. The more important features of these preferred orientation patterns, from the standpoint of the present investigation, were as follows :

(*a*) In the unheated material, the calcium silicate hydrate (I) crystals are oriented with the mean position of the *b* or 3·65 Å axis parallel to the fibre direction. Two separate 001 reflections were observed, with spacings of 14·0 ± 0·4 Å (strong) and 10·4 ± 0·4 Å (weak). The indexing of these reflections was established with certainty from oscillation photographs about the fibre axis, and from the Weissenberg photographs.

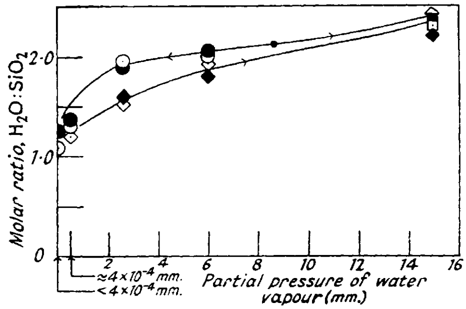
(*b*) The pattern given by the fibre, after it had been heated to 100°, was still essentially that of calcium silicate hydrate (I). The *hk*0 reflections were unchanged in spacings and intensities. However, the 001 spacing of 14 Å had disappeared, whereas that of 10·4 Å had become more intense. Changes in the remaining (*hkl* or 00*l*) reflections were observed; these could be associated with the change in the *c*-axis.

(*c*) After heating to 250°, the pattern given by the fibre was still fundamentally that of calcium silicate hydrate (I). The same *hk*0 reflections were present, but all were slightly reduced in spacing, indicating a decrease in both the *a*- and *b*-axes. The 10·4 Å spacing had been replaced by one of 9·3 ± 0·3 Å. Further changes in the remaining reflections were observed. In a preliminary experiment, a separate fibre was heated to 220°. This showed two 001 reflections, with spacings of 10·4 and 9·3 Å.

(*d*) Heating to 450° or 550° produced no further significant changes in the pattern. At 700°, however, a different preferred orientation pattern was observed. This resembled that of the dehydrated calcium silicate hydrate (I), in having a layer line spacing of about 3·60 Å, and a strong reflection on the first layer at 2·97 Å, but differed from it in other respects, other strong spacings occurring at 10·1 and 3·36 Å, both on the zero layer. The formation of this product was confirmed with another fibre of riversideite.

FIG. 5. *Dehydration and rehydration isotherms, at room temperature, for calcium silicate hydrate* (I): *Sample* (1), CaO : SiO_2 = 0·99.

Experiment:	*I*	*II*	
	●	○	*Dehydration isotherms; initial* H_2O : SiO_2 = 2·07.
	◆	◇	*Rehydration isotherms; initial* H_2O : SiO_2 = 1·15 *approx.*
	■	⊡	*Rehydration isotherms; initial* H_2O : SiO_2 = 2·07.
	•		*Initial* H_2O : SiO_2 *ratio of the sample.*



(*e*) At 800° or 1000°, the pattern was identical with that of β-wollastonite ($CaSiO_3$). This substance also has one axis of length 7·27 (2 × 3·635) Å (Warren and Biscoe, *Z. Krist.*, 1931, **80**, 391) and the photographs showed that it was oriented with this axis parallel to the fibre direction. The wilkeite reflections remained unchanged, even after the fibre had been heated to 1000°, and it is reasonable to conclude that this substance does not interact significantly with calcium silicate hydrate (I) or its dehydration products up to this temperature.

(9) X-*Ray powder investigation of an artificially prepared calcium silicate hydrate* (I), *after heating to various temperatures. X*-Ray powder photographs were taken of a laboratory preparation of calcium silicate hydrate (I) (sample 5; lime : silica molar ratio 0·95) after it had been heated to 120°, 240°, 450°, and 1000°. Except at the last temperature, the partial pressure of water vapour was kept at 6 mm. Heating to the first three temperatures left the *X*-ray pattern essentially unaltered, except for a change in the 001 spacing. This was initially 12·3 Å, falling to 10·4 Å at 120° and 9·3 Å at 240° or 450°. All the *hk*0 lines were also slightly decreased in spacing at the last two temperatures, but the change was very small relative to that in the 001 spacing, being in the region of 1—2%. The sample heated to 1000° gave the pattern of β-wollastonite. The sample heated to 120° was rehydrated by standing over water in a vacuum desiccator for 60 days at room temperature. The 001 spacing became diffuse, with a maximum at about 11 Å. This seems to indicate partial but not complete reversal of the lattice shrinkage.

The results of the dehydration experiments thus confirm those given by the natural riversideite, but are necessarily less detailed. They are also consistent with data of Thilo, Funk, and Wichmann (*loc. cit.*) who, however, did not observe the low-angle reflections.

(10) *Differential thermal analysis curve of calcium silicate hydrate* (I). This was kindly determined by Mr. D. B. Honeyborne (Building Research Station), using the sample mentioned in the previous section. The curve (Fig. 6) shows an endothermic peak at about 100° and a marked exothermic one at about 800°.

DISCUSSION

The Hydration States of Calcium Silicate Hydrate (I).—It is well established that the interpretation of dehydration curves is not straightforward in the case of ill-crystallised substances, unless additional data are available. In the present case, the *X*-ray data, taken in conjunction with the isobars, enable a reasonably certain picture of the hydration states to be obtained. Owing to the sharpness of the effects, the data obtained from the natural riversideite were particularly valuable in this respect.

The riversideite results show that calcium silicate hydrate (I) can exist in a number of definite states of hydration. Of these, the most highly hydrated state so far observed corresponds to the 001 spacing of 14 Å, but its exact water content is not certain. The isobars of the samples prepared at room temperature rise to values of 2·0 or more without tending to a limit. On the other hand, the *X*-ray photographs suggest that the 14-Å hydrate is the predominating one in natural riversideite, which has a water content of about 1·4. As will be shown later, the calcium silicate hydrate (I) in riversideite is a mixture of the 14-Å hydrate with one having a water content of 1·0. The water content of the 14-Å hydrate is therefore unlikely to be much above 2·0. It may be 2·5, as supposed by Le Chatelier (*loc. cit.*).

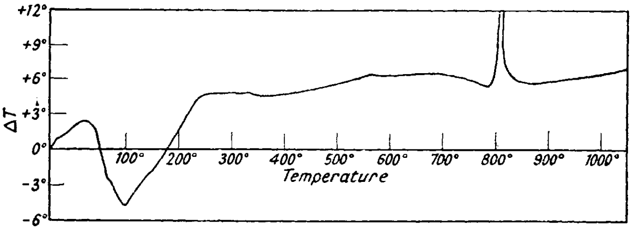


Fig. 6. *Differential thermal analysis curve for calcium silicate hydrate* (I): *Sample* (1), CaO : SiO$_2$ = 0·99.

The second state of hydration corresponds to an 001 spacing of 10·4 Å. No point of inflection corresponding to this hydrate is visible in the isobars of the samples prepared at room temperature, but those of the hydrothermal preparation, and of natural riversideite, show points of inflection at water contents of 1·1 and 0·8, respectively. In view of the uncertainties involved, especially in the case of the riversideite, it is reasonable to conclude that this hydrate has a water content of 1·0.

A third state of hydration corresponds to an 001 spacing of 9·3 Å and a water content of 0·5 mol. The point of inflection corresponding to this hydrate is shown, to varying degrees, in the isobars of all the samples studied. Further dehydration yields an anhydrous residue.

The water contents, 001 spacings, and temperatures of formation of the three hydrates can thus be summarised in the following table :

Water content, mols.	*ca.* 2·5	1·0	0·5
001 Spacing, Å	14·0 ± 0·4	10·4 ± 0·4	9·3 ± 0·3
Approx. temp. of formation at ordinary humidities	<20°	100°	250°

Formation of Mixed Hydrates.—On account of its layer structure, calcium silicate hydrate (I) readily forms mixed hydrates. These are of two extreme types. In natural riversideite, both the 14·0 Å and the 10·4 Å state are present; separate 001 spacings, probably corresponding to both *c*-axes, can be distinguished in the *X*-ray photographs. This must indicate that each crystal contains both hydrates, in blocks stacked in a direction parallel to the *c*-axis, and each containing a sufficient number of unit cells to produce sharp diffraction effects.

The samples prepared at room temperature, on the other hand, give a single 001 spacing at an intermediate value of about 12 Å. The 001 reflection is usually broad, and few if any *hkl* reflections can be detected (Part I, *loc. cit.*). This appears to indicate that layers of both hydrates are present, as in natural riversideite, but that they are mixed together in a more or less random manner.

The differences between the dehydration isobars of riversideite and those of the artificial preparations lend support to these conclusions. In the former, a distinct point of inflection is observed at about 100°, corresponding to the formation of the monohydrate. This can be accounted for if the higher hydrate, which is present at lower temperatures, is in the form of relatively large crystals, which would undergo dehydration at a sharply defined temperature. The absence of this point of inflection in the laboratory samples, on the other hand, may well be explained if the crystals of the higher hydrate are small and variable in size, in the order of a few unit cells. Such crystals would be expected to dehydrate over a wider range of temperature, thereby giving rise to a smooth isobar.

Constitutional Water.—Dehydration from the highest observed state of hydration to the monohydrate reduces the *c*-spacing, but does not affect the *hk*0 reflections. This suggests that water in excess of one molecule is not essential to the structure of the layers, but is present in the form of molecules held loosely between them. This behaviour is closely analogous to that of montmorillonite and other clay minerals (Brindley, " X-Ray Identification and Crystal Structure of Clay Minerals," Min. Soc., London, 1951).

Reduction in the molar water content below 1·0 is usually accompanied by a decrease in the *a* and *b* axes, and a certain tendency to broadening of the *hk*0 lines. It is therefore probable, as Roller and Ervin (*loc. cit.*) and Thilo (*loc. cit.*) have suggested, that this quantity of water is essential to the structure. This may indicate that the compound is built from Ca^{2+} ions and $(H_2SiO_4)^{2-}$ groups. However, the existence of other possibilities, such as $Ca(SiO_3H)(OH)$, implying the existence of metasilicate chains or rings, cannot be overlooked. The fact that the remaining water is lost in two equal stages, at temperatures in the neighbourhood of 170° and 300° respectively, indeed provides some support for this hypothesis.

The Products of Complete Dehydration of Calcium Silicate Hydrate (I).—The results described in sections 8 and 9 indicate that the conversion of calcium silicate hydrate (I) into β-wollastonite does not occur through the intermediate formation of any amorphous phase. The β-wollastonite, formed at 800° or above, is oriented, and all the products that were obtained at lower temperatures contained oriented, crystalline material. A high degree of order thus appears to be maintained throughout the dehydration process.

The *X*-ray patterns of both natural and artificial samples heated to 450° or 550° show that the essential framework of calcium silicate hydrate (I) can exist, though probably in a partly disordered form, after all the water has been driven out. At 700° a rearrangement takes place, giving a hitherto unrecognised phase, and at 800° a further change to β-wollastonite occurs. The *X*-ray patterns of all these compounds show certain marked resemblances, notably in the existence of an axis of approximately 7·3 or 3·65 Å, the orientation of which is unchanged throughout the dehydration process. Close structural resemblances between all of them evidently exist.

The Relation Between Water Content and Molar Lime : Silica Ratio.—The results given in Fig. 2 show that the water content of calcium silicate hydrate (I), expressed as the ratio $H_2O : SiO_2$, is independent of the lime : silica molar ratio for any given conditions of temperature and humidity. This appears to rule out the hypothesis put forward by Le Chatelier (*loc. cit.*), and accepted by many later investigators, that the varying lime : silica ratio can be explained by the adsorption of varying amounts of calcium hydroxide on the surface of a hydrated monocalcium silicate. If this were the case, the adsorbed lime would almost certainly be in the form of hydroxide, and this would cause the water content of the sample to vary with the lime : silica ratio. The adsorbed calcium hydroxide would, furthermore, be expected to decompose in the region of 400°; the isobars show conclusively that this does not occur. The results show that the variation in lime : silica ratio can be described as addition to, or removal from, the structure of the elements of calcium oxide.

This appears to denote the existence of some form of solid solution. More precise understanding of the nature of this must await further information concerning the structure.

Interpretation of the Differential Thermal Analysis Curve.—Comparison of the thermal analysis curve (Fig. 6) with the dehydration isobars of the same sample (Fig. 1) shows that the endothermic peak at about 100° in the former can be attributed to the loss of the interlamellar water. The only other significant feature on the curve is the pronounced exothermic peak at about 800°. This can be attributed to the recrystallisation of the anhydrous residue into wollastonite. This conclusion is in accordance with the results of Thilo, Funk, and Wichmann (*loc. cit.*), who observed that this change took place at 750° and that it was strongly exothermic.

Determination of Calcium Hydroxide in the Presence of Calcium Silicate Hydrate (I).—On account of its importance in relation to the chemistry of Portland cement, numerous methods have been suggested for the quantitative determination of uncombined calcium hydroxide in the presence of hydrated calcium silicates. The majority consisted in the extraction of the uncombined calcium hydroxide with ethylene glycol or similar solvents. It was, however, shown by Bessey (*op. cit.*, p. 285) that such methods were unsatisfactory when applied to hydrated materials. This has been confirmed by the present author (unpublished work).

The close agreement between the observed and the calculated curves in Fig. 2, for the sample of lime : silica molar ratio 1·95, suggests that analysis of the dehydration isobars would provide a more satisfactory method of analysis. This was to some extent envisaged by Bessey (*op. cit.*), who attempted to determine the amount of uncombined calcium hydroxide from the loss in weight between 350° and 550°. The dehydration isobar method can only safely be applied at present in cases where hydrated calcium silicates other than calcium silicate hydrate (I) are known to be absent. The determination of the dehydration isobars of calcium silicate hydrate (II) (Part I, *loc. cit.*), and other related substances, is being undertaken.

EXPERIMENTAL

Determination of Dehydration Isobars.—100—400 Mg. of the substance were placed in a glass weighing tube, which, with its stopper, was placed in a stainless-steel boat. This was inserted into a horizontally mounted glass tube 2·5 cm. in diameter, of which one end was stoppered, and the other sealed off and placed within an electric furnace. This could be operated up to 520°, the temperature being measured by means of a chromel–alumel thermocouple. The tube carried two side arms. One of these led to a flask containing a saturated solution, or in some cases a mixture of two solid phases, and immersed in a thermostat at 21°; this maintained a constant partial pressure of water vapour in the apparatus. The other, bearing a tap, enabled the apparatus to be evacuated to a nominal pressure of about 10 mm. as read on a miniature McLeod (Edwards's " Vacustat ") gauge, in order to accelerate the attainment of equilibrium.

In operation, the furnace was raised to successively higher temperatures, commencing at room temperature. The tube and its contents were cooled over phosphoric oxide after each period of heating, and weighed, according to a standardised procedure. The times needed to reach equilibrium at each successive temperature varied between a few hours and 2—3 days, depending chiefly on the temperature and the increment in the temperature. In all doubtful cases, a series of weighings was made at the same temperature, and the loss in weight plotted against the time, in order to establish whether equilibrium was being attained. A complete run on a single sample, ending at the maximum temperature of 520°, usually occupied 7—14 days.

Owing to the virtual impossibility of preparing samples of calcium silicate hydrate (I) free from calcite, and the ready reaction of the substance towards atmospheric carbon dioxide, certain precautions were necessary in order to avoid errors in the assumed composition, arising from uncertainty in the amount of the dioxide present. The most satisfactory procedure was to continue the isobar to 450° or above, at which temperatures all the water is driven off. The residue was transferred to a platinum crucible and ignited; the loss in weight gave the amount of carbon dioxide present in the sample actually used for determining the isobar. In cases where the isobar was terminated at a lower temperature, this method was inapplicable, and the carbon dioxide content and ignition loss were determined on separate portions.

The solutions and mixtures used for maintaining constant partial pressures of water vapour were as follows: saturated $(NH_4)_2SO_4$, $p_{H_2O} = 15$ mm., saturated $CaCl_2,6H_2O$, $p_{H_2O} = 6$ mm., and saturated $LiCl,H_2O$, $p_{H_2O} = 2{\cdot}8$ mm. (data from O'Brien, *J. Sci. Instr.*, 1948, **25**, 73), and $Mg(ClO_4)_2,2H_2O + Mg(ClO_4)_2,4H_2O$, $p_{H_2O} \approx 4 \times 10^{-4}$ mm., and $Mg(ClO_4)_2 + Mg(ClO_4)_2,2H_2O$, $p_{H_2O} < 4 \times 10^{-4}$ mm. (data of Powers and Brownyard, *J. Amer. Concrete Inst.*, 1947, **43**, 249). Phosphoric oxide was also used, and appeared to maintain a vapour pressure similar to that of anhydrous magnesium perchlorate; but the attainment of equilibrium was found to be very slow, probably as a result of the formation of a surface film on the oxide, and its use was therefore abandoned.

The thermostat was operated at as little as possible above room temperature, in order to avoid the danger of water condensing on those parts of the apparatus which were at room temperature, when saturated ammonium sulphate was being used, and thereby introducing doubt regarding the vapour pressure within the apparatus.

The procedure described above was used also in the rehydration experiments (Fig. 4). The times taken for reaching apparent equilibrium at each temperature were, as already mentioned, very much greater than in the dehydration experiments. It is therefore unlikely that any serious error can have been introduced into any of the present results by changes in weight occurring between removal of the substance from the furnace and weighing.

Determination of Isotherms.—The isotherms shown in Fig. 5 were obtained by measurement of the changes in weight of samples contained in porcelain crucibles placed in vacuum-desiccators at room temperature. The same reagents were used for maintaining given partial pressures of water vapour as in the isobaric experiments.

Differential Thermal Analysis.—The result given in Fig. 6 was determined for a heating rate of 10°/min. The reference material was fused kaolinite and the mass of sample used was 0·21 g.

X-*Ray Apparatus.*—The Unicam 6-cm. diameter single-crystal camera and a 5·73-cm. diameter Weissenberg camera were used with a sealed *X*-ray tube giving copper radiation. A nickel-foil filter was placed in contact with the film. The single-crystal camera was also used for the powder work.

Materials.—The calcium silicate hydrate (I) samples were prepared by methods already described in Parts I and II (*locc. cit.*). Analytical data, expressed as percentage composition and molar lime : silica ratio, are as follows :

	CaO, %	SiO_2, %	H_2O, %	$CaCO_3$, %	CaO/SiO_2
(*a*) Samples prepared from $Ca(OH)_2$ and SiO_2 gel.					
(1)	35·7	38·5	24·0	1·7	0·99
(2)	42·0	34·7	22·1	1·2	1·30
(*b*) Samples prepared by double decomposition.					
(3)	19·2	21·3	58·6	0·8	0·91
(4)	32·3	36·8	27·2	3·6	0·94
(5)	33·3	37·6	25·5	3·6	0·95
(6)	37·1	32·2	27·3	3·4	1·24
(7)	42·4	23·3	20·1	14·5	1·95
(*c*) Samples prepared from Ca_3SiO_5.					
(8)	30·2	36·3	22·1	11·4	0·89
(9)	35·7	27·9	25·6	10·9	1·37
(*d*) Sample prepared hydrothermally.*					
(10)	37·2	42·6	14·1	6·1	0·94
(*e*) Natural riversideite.†					
(11)	17·7	21·5	8·8	—	0·9

* This was sample 67 of Part II (*loc. cit.*).

† This is a very approximate result obtained (Taylor, *Min. Mag.*, *loc. cit.*) by correcting the actual analysis for the presence of wilkeite, diopside, idocrase, and calcite.

The analysis of the calcium hydroxide sample was given in Part II (*loc. cit.*).

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