Heterogeneous Equilibrium of Calcium Silicate Hydrate in Water at 30 °C

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Calcium silicate hydrates (C–S–H), prepared at 20 °C and 50 °C to have various CaO : SiO_2 molar ratios (n), were examined for their compositions with particular attention to the combined water contents and to their solubilities in water at 30 °C. The C–S–H gels may be described as solid solutions of the type $n\mathrm{CaO{\cdot}SiO_2{\cdot}}(n + 0.8)\mathrm{H_2O}$, where $n \gtrsim 0.8$. A thermodynamic treatment was developed which enabled n to be calculated from solubility data; the n values observed were compared with those calculated. The conclusion reached was that non-equilibrium was liable to occur owing to the immature state of C–S–H. Also observed was the unusual property that the response to the varying calcium ion concentrations in the solutions was limited to within the surface layer of the C–S–H particles. The possible phase relations under the state of equilibrium are presented.

KNOWLEDGE of the composition and properties of calcium silicate hydrate, $n\mathrm{CaO{\cdot}SiO_2(aq)}$ (hereafter abbreviated as C–S–H),† and its equilibrium is very important in cement chemistry. When synthesised at room temperature from calcium hydroxide and hydrated silica, or produced by hydration of $3\mathrm{CaO{\cdot}SiO_2}$ or β-$2\mathrm{CaO{\cdot}SiO_2}$, it assumes a colloidal state having an indefinite molar CaO : SiO_2 (C : S) ratio (n) and occurs as a highly disordered phase which exhibits up to five broadened X-ray powder diffraction lines.[1–3] In a CaO–SiO_2–H_2O system containing C–S–H, the solid–liquid phase relation generally varies as follows. The ratio (n) in the solid phase rises abruptly to the order of about 0.85—1.1 : 1 as the calcium ion concentration reaches the level of 2 mmol dm^{-3}. Beyond this point the increase in the ratio becomes much more gradual but continues as the calcium ion concentration is further increased. Finally, the ratios attained in saturated calcium hydroxide solutions have ranged from 1.4 to 2.0 in various investigations.[1,2,4]

The nature of this continuous rise has contributed to a controversy as to the state of the actual chemical combination. Either a solid solution [4,5] or a gradual modification of tobermorite-like structure to a jennite-like one [3,6] has been assumed. To explain the divergence in n values at a constant calcium ion concentration, a special kind of internal absorptive system was suggested for C–S–H, where an expansible layer structure might expand irregularly depending upon the manner in which it had been prepared.[7] The model for the internal structure of C–S–H particles should be evidenced in some way. Because C–S–H is almost amorphous with only short-range order, X-ray methods give only a little information about its structure. Of the various methods that have been used to provide information about the internal structures of C–S–H particles, trimethylsilylation has proved the most effective,[8] by which anion constituents of C–S–H can be qualitatively or quantitatively determined. Since the pioneer study by Lentz [9] the method has been improved,[10,11] especially by Tamás *et al.* Although rapid progress is being made with it at the present time and a number of other measurements have been reported,[8,12] it does not appear that C–S–H has as yet been well characterised.

In the present study, the gross compositions of the various colloidal C–S–H gels were determined as reported previously,[4,13–15] using an improved solvent extraction method for the estimation of combined water. The solubilities of C–S–H were examined at 30 °C, the silica concentration in the high calcium ion concentration zone being especially carefully measured. The data have been discussed as regards to whether they are indicative of 'true' equilibrium or not on the basis of an equation, derived through a thermodynamic approach, to permit the ratio (n) of the C–S–H, postulated as a solid solution, to be calculable from the composition of a co-existing aqueous solution.

EXPERIMENTAL

Preparation of C–S–H *Specimens for Analysis.*—The C–S–H specimens were prepared by double decomposition of sodium silicate and calcium nitrate so as to give a value of n in the range 0.3—2.0, see equation (1).

$$n\mathrm{Na_2O{\cdot}SiO_2(aq)} + n\mathrm{Ca[NO_3]_2} \longrightarrow n\mathrm{CaO{\cdot}SiO_2(aq)} + 2n\mathrm{Na[NO_3]} \quad (1)$$

A freshly prepared sodium silicate solution (*ca.* 10 g as $n\mathrm{Na_2O{\cdot}SiO_2}$) was placed in a polyethylene bottle and diluted with CO_2-free water. An equivalent amount of calcium nitrate solution (1 mol dm^{-3}) was gradually added with continual stirring until the total volume reached *ca.* 500 cm^3. After the resultant mixtures were aged at 20 °C or 50 °C with occasional stirring for about one month, the precipitates produced were separated and washed centrifugally with calcium hydroxide solution (*ca.* 0.01 mol dm^{-3}) to remove sodium and nitrate ions. The precipitate was then placed in a filter press ‡ to squeeze out the excess of water, to form a hard paste having a water content of about 50—60% by weight. During this operation, precautions were exercised to prevent specimens from absorbing CO_2. However, since a small amount of carbonate (less than 2.5 wt.% CO_2 on the ignited sample basis) was present, each

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† Throughout this paper, conventional cement chemistry notation is used, *i.e.* C = CaO, S = SiO_2, and H = H_2O.

‡ The precipitate was placed inside a rubber ring (20 mm inside diameter, 35 mm outside diameter, and 3.5 mm in thickness), held between opposed strata each consisting of one sheet of nylon cloth and several sheets of filter paper (for absorption of water), squeezed with a plunger to a pressure of 50—100 kg cm^{-2}, and then, after replacing the sheets of filter paper with new ones, squeezed again.

specimen was analysed separately for both carbonate and free calcium hydroxide to permit necessary correction. The correction for sodium or nitrate ions was of little significance. Sodium oxide was determined by flame photometry in two cases: 0.05 and 0.023 wt.% for specimens of C : S of 1.75 and 1.24 : 1 respectively, while NO_3^- was less than 0.2 wt.% for both when determined by a conventional method using Devarda's alloy to reduce nitrate ion to ammonia.

Hydrated silica, one of the pure components in the $CaO-SiO_2-H_2O$ system, was also tested for its combined water. The specimens were prepared, some by a method resorting to neutralisation of a sodium silicate solution with nitric acid, and others by a method involving hydrolysis of purified silicon tetrachloride introduced dropwise into water kept constantly at 50 °C, then the silica gel formed was centrifugally washed and then squeezed as described above.

Measurement of the Solubility of C–S–H *in Water.*—The C–S–H gels for this experiment were classified under three types (L, M, and H) all of which were prepared by the same procedure, except that the compaction by filter press was omitted in order to make the precipitate ready for dispersion in calcium hydroxide solution. For the type L, the precipitates from the double decomposition reactions with $n = 1:1$, $2:3$, and $1:3$ in equation (1) were not subjected to ageing in their mother solutions but were immediately washed with CO_2-free water and then with calcium hydroxide solution (4×10^{-3} mol dm^{-3}). By this procedure, three different specimens having corrected C : S molar ratios of 1.15, 0.77, and 0.41 : 1 were prepared, designated as L_a, L_b, and L_c respectively. On the other hand, types M and H were formed with $n = 2:1$ [equation (1)] and the resultant mixtures were left to age for about one month at 20 °C for type M and at 50 °C for type H. The resultant precipitates were washed by the same procedure, except that the concentration of the calcium hydroxide solution was 0.01 mol dm^{-3}. Their corrected C : S molar ratios were 1.24 : 1 (type M) and 1.75 : 1 (type H).

The experiment on the solubility at 30 °C was carried out by using these C–S–H gels; that is, several 10 g portions of each gel (*ca.* 0.2—0.5 g as anhydrous solid) were added to calcium hydroxide solutions (*ca.* 500 cm^3) of various concentrations and left to stand at 30 °C for 1—6 months. During this period, the mixture was stirred once or twice weekly. At the end of the period, both the liquid phase taken out through a 100-cm^3 pipette provided with a special filter * and the co-existing solid phase were analysed.

Analysis and Equipment.—The aqueous solutions were analysed by titrating with a standard solution of ethylenediaminetetra-acetate (edta) for the calcium concentration, spectrophotometrically for the orthosilicic acid,[16] and by titrating with 0.1 mol dm^{-3} HCl solution in the presence of bromothymol blue to determine hydroxide ion. The solid phase was analysed in the usual manner by dissolving in perchloric acid, evaporating to dryness, and igniting the solid residue after filtration. The silica filtrate was analysed for calcium as described. The combined water content of a given pasty specimen was estimated as the difference between the total water and the free water determinable by extraction with ethyl methyl ketone.[17] Free calcium hydroxide was determined by a solvent extraction method using an *o*-cresol–ethyl alcohol solution and a small amount of $CaCl_2 \cdot 2H_2O$.[18] Carbonate was estimated by the titration method of Konishi [19] in which carbon dioxide evolved from the sample by mixing with sulphuric acid is absorbed in alkaline solution (Na[OH] + $BaCl_2$), the residual hydroxide being titrated with standard hydrochloric acid.

The *X*-ray diffractometer used nickel-filtered Cu-K_α radiation at 40 kV and 40 mA. The electron micrographs of the ultrasonicated samples were taken in the usual manner with a transmission electron microscope (JEOL JEM-T8).

RESULTS

Non-stoicheiometry of C–S–H.—In the experiment, special attention was paid to the effect of the change of C : S ratio of C–S–H upon the combined water content. The relation obtained was as represented in Figure 1 after correction was made for free calcium hydroxide and carbonate contents.

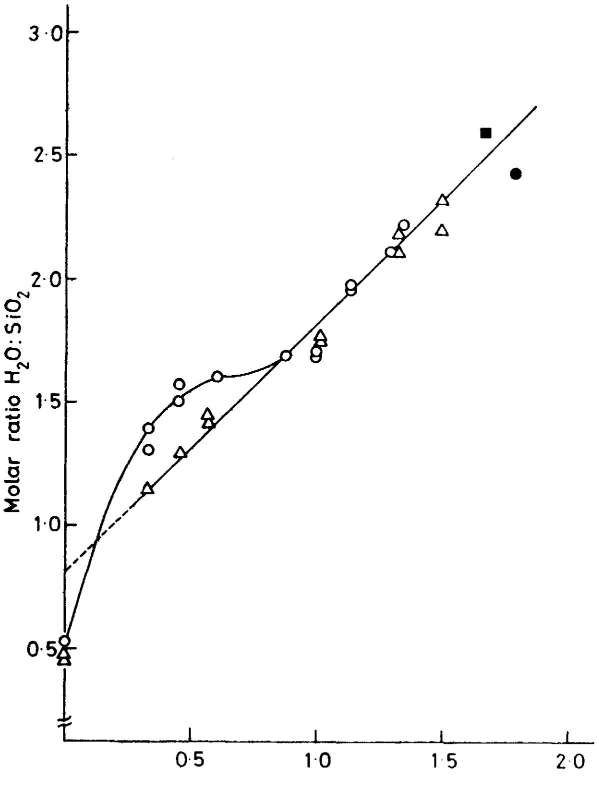

FIGURE 1 Correlation of molar $H_2O : SiO_2$ ratio with $CaO : SiO_2$ (n) of the calcium silicate hydrate (C–S–H): prepared by the method of equation (1) and aged at 20 °C (○) and 50 °C (△); prepared by complete hydration at 20 °C of β-C_2S (●) and C_3S (■)

It is seen that in the zone of higher C : S molar ratios, the $H_2O : SiO_2$ ratio increases with the increasing C : S ratio in a substantially straight line relationship with an inclination of about 45°; this line intersects the vertical axis where $H_2O : SiO_2 \simeq 0.8 : 1$, no matter whether the specimens had been prepared at 20 °C or 50 °C. The C–S–H specimens prepared by the hydration of $3CaO \cdot SiO_2$ and β-$2CaO \cdot SiO_2$ have compositions expressed as $1.68CaO \cdot SiO_2 \cdot 2.58H_2O$ [17] and $1.80CaO \cdot SiO_2 \cdot 2.41H_2O$,[20] respectively. When these particular compositions are plotted on the same graph, they assume positions close to the same line. From these results, the C–S–H composition may be approximately represented by the formula $nCaO \cdot SiO_2 \cdot (n + 0.8)H_2O$ (where,

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* A polyethylene tube (7 mm in diameter) was packed densely with a bed of vinyl chloride fibres to a height of about 50 mm, and each end was covered with a sheet of nylon cloth.

$0.8 < n < 1.8$), which suggests the formation of a solid-solution series consisting of two components; $Ca[OH]_2$ and ' $SiO_2{\cdot}0.8H_2O$ '.

It is noted that the applicable range of the formula extends as far as $n \simeq 0.3$ in the case of specimens prepared at 50 °C, whereas in the case of specimens at 20 °C the co-ordinates deviate by leaping from the straight line below $n \simeq 0.8$. This deviation may possibly reflect the structure as being in an immature state.

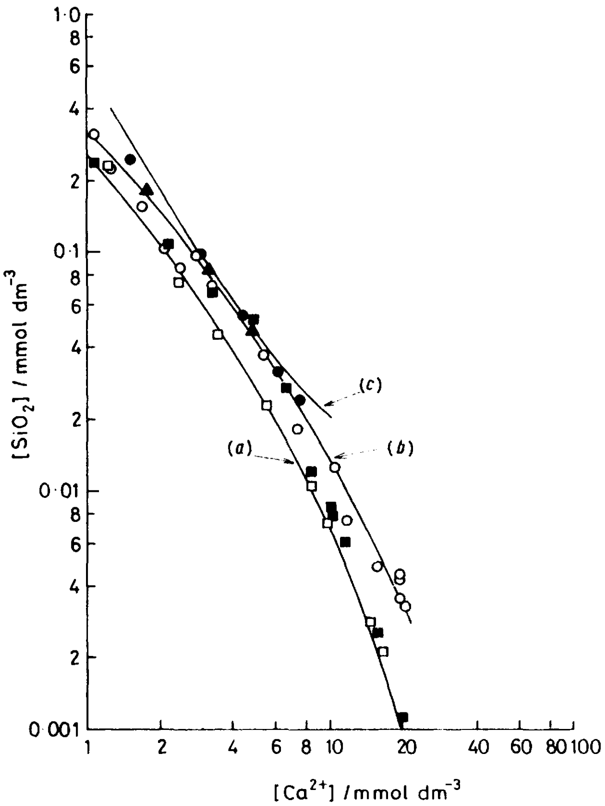

FIGURE 2 Variation in concentration of silica with that of calcium ion at 30 °C. Curve (*a*) represents the minimum relation between them (*i.e.* the minimum value of one at any given value of the other), while curve (*b*) is for specimens L_a (○), L_b (●), L_c (▲). The initial molar C : S ratios were 1.15, 0.77, and 0.41 : 1 for L_a, L_b, and L_c, and 1.24 and 1.75 : 1 for M (□) and H (■) respectively. Curve (*c*) is from ref. 22

X-Ray patterns of the specimens having $n = 0.9$ (prepared at 20 °C), 1.24 (20 °C), 1.49 (50 °C), and 1.75 (50 °C) were obtained. The four lines characteristic of C–S–H at 3.06, 2.80, 1.83, and 1.67 Å were found for all of them. The specimens with $n = 1.49$ and 1.75 however gave weaker lines than those of $n = 0.9$ and 1.24 (except the line at 1.83 Å) and assumed fibrous or needle-like habit. The particles of $n = 0.9$ and 1.24 were in the shape of crumpled foils or plates. The specimen with $n = 0.34$ had an amorphous structure consisting of thin plate-like particles 0.05—0.1 μm in diameter, in contrast to an extremely small globule-like appearance of hydrous silica particles (0.02—0.03 μm).

The combined water content of the specimens of hydrous silica prepared from sodium silicate and from $SiCl_4$ invariably fell within the range of 0.22 ± 0.04 in terms of $H_2O : SiO_2$ molar ratio, whether after vacuum drying at 40 °C or after solvent extraction with ethanol. These values do not contradict those reported.[21] The values obtained by solvent extraction using a mild solvent, ethyl methyl ketone, capable of providing selective solution of free water with least dissolving action on bound water molecules, fell within the range 0.44—0.53 (approximating to 0.5). This fact suggests that the hydrous silica has a composition of $SiO_2{\cdot}0.5H_2O$ or $SiO_{1.5}(OH)$ and has a structure with an average of one OH group bound to one corner of each SiO_2 tetrahedron.

Solubility of C–S–H *in Water at* 30 °C.—Of the results for the solubility of C–S–H at 30 °C, the relation between calcium and silica concentrations in the liquid phase, is represented in Figure 2, and the dependency of the C : S molar ratio in the solid phase upon the calcium concentration in the liquid phase in Figure 3. The final compositions of the solid and liquid phases varied depending on the initial C : S molar ratio in C–S–H and the calcium ion concentration in the liquid phase; *viz.* the initial C–S–H absorbed Ca^{2+} ion from the liquid phase of high calcium ion concentration, and conversely released Ca^{2+} ion into the liquid phase of low calcium ion concentration, so as to reach the state of an apparent equilibrium. Roller and Ervin [22] found five days' contact sufficed for the system to reach the steady state, but in this work the contact was continued for 1—6 months, even though no further significant difference in analytical composition of liquid phase was observed.

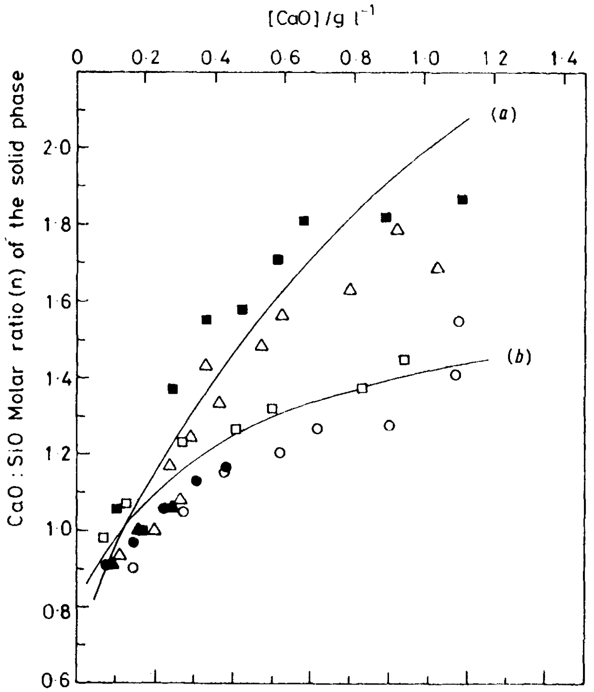

FIGURE 3 Molar ratio C : S of solids as a function of the concentration of calcium ion in water at 30 °C. Data are for L_a (○), L_b (●), L_c (▲), M (□), and H (■); and from ref. 4 (△). Curve (*a*) represents the relation most approximating the ' true ' equilibrium, and curve (*b*) is for the specimens of L type; the two curves are obtained by use of equation (12), and the data from curves (*a*) and (*b*) in Figure 2 respectively

As has been previously discussed,[1] however, the data on equilibria between the solid and liquid phases depend on the original C–S–H specimens. It is noted from Figure 3 that in the system using the low-calcium type specimen L_a the C : S molar ratio in the solid phase was generally low so that it barely rose to the level of 1.5 even in a saturated calcium hydroxide solution, whereas in the system using the high-calcium (type H) specimen, the ratio reached the level of 1.87 as the maximum. In conjunction with this, it is seen from Figure 2 that, near the saturated calcium hydroxide concentration, the silica concentration was lower in the system using the specimen H. This suggests that the system of the specimen H assumed a state more approximating the equilibrium in such a zone of high calcium ion concentration than the type L specimens. In contrast, in the zone of medium to low calcium ion concentration, the specimen M exhibited the lowest silica concentration and it is closer to the state of equilibrium than the specimen H.

Of the results shown in Figure 2, the data obtained for the specimen L are fairly close to those of Roller and Ervin [22] in the zone of medium calcium ion concentration. In view of the enhanced solubility, however, the steady state attained for this specimen will hardly represent a thermodynamic equilibrium. At the time of preparation the specimens M and H were subjected to ageing for about one month in their mother solution, while L had no ageing, which may have caused it to be in a metastable or an immature state.

DISCUSSION

The C–S–H gels have been prepared from various starting materials, such as tricalcium silicate, a mixture of calcium hydroxide–silica gel, and calcium nitrate–sodium silicate. These different preparations, when formed at room temperature with $n = 0.9$—1.5 in early work by Taylor,[2] gave almost the same X-ray pattern for the product. In the present work, the composition of C–S–H gel was formulated as $n\mathrm{CaO{\cdot}SiO_2{\cdot}}(n + 0.8)\mathrm{H_2O}$, where n varies within the range $0.8 < n < 1.8$. These results may imply the formation of a solid-solution series with regard to C–S–H gel, and if the solid solution is postulated it is possible to estimate the value of n from the solubility data using an equation (12) derived thermodynamically as follows.

Derivation of the Formula indicating a Phase Relation in Heterogeneous Equilibrium.—We assume C–S–H to be a two-component solid solution consisting of $\mathrm{Ca[OH]_2}$ and an imaginary component ' $\mathrm{SiO_2{\cdot}0.8H_2O}$ ' with mol fractions X_1 and X_2 and chemical potentials $\mu_1(\mathrm{s})$ and $\mu_2(\mathrm{s})$ respectively; the Gibbs–Duhem equation for

$$X_1\mathrm{d}\mu_1(\mathrm{s}) + X_2\mathrm{d}\mu_2(\mathrm{s}) = 0 \qquad (2)$$

$$n = X_1/X_2 = -\mathrm{d}\mu_2(\mathrm{s})/\mathrm{d}\mu_1(\mathrm{s}) \qquad (3)$$

C–S–H under constant temperature and pressure can be written in equations (2) or (3).

When this solid dissolves in water to establish a heterogeneous equilibrium, the silica component will mostly dissociate to give such monomeric anions as $\mathrm{H_3SiO_4^-}$ and $\mathrm{H_2SiO_4^{2-}}$ of very low concentration in the resultant alkaline solution.[9,23] Hence $\mu_1(\mathrm{s}) = \mu_1(\mathrm{l})$ and $\mu_2(\mathrm{s}) + 1.2\mu_{\mathrm{H_2O}}(\mathrm{l}) = \mu_2(\mathrm{l})$ may be always satisfied, where $\mu_1(\mathrm{l})$, $\mu_2(\mathrm{l})$, and $\mu_{\mathrm{H_2O}}(\mathrm{l})$ are the chemical potentials of each of the $\mathrm{Ca[OH]_2}$, $\mathrm{H_4SiO_4}$, and $\mathrm{H_2O}$ components respectively in the liquid phase and orthosilicic acid is formed by a dissolution reaction nominally described as ' $\mathrm{SiO_2{\cdot}0.8H_2O}$ ' + $1.2\mathrm{H_2O} = \mathrm{H_4SiO_4}$.

Since the liquid phase will be a very dilute solution with a molality not exceeding 0.1 mol kg^{-1}, $\mu_{\mathrm{H_2O}}(\mathrm{l})$ may be regarded as a constant and both $\mu_1(\mathrm{l})$ and $\mu_2(\mathrm{l})$ as functions of only the molalities m_1 and m_2 of these components. Thus, equations (4) and (5) can be obtained.

$$\mathrm{d}\mu_2(\mathrm{s})/\mathrm{d}\mu_1(\mathrm{s}) = \mathrm{d}\mu_2(\mathrm{l})/\mathrm{d}\mu_1(\mathrm{l}) \qquad (4)$$

$$\left.\begin{aligned}\mathrm{d}\mu_1(\mathrm{l}) &= \mathrm{d}\mu_1 = (\partial\mu_1/\partial m_1)\mathrm{d}m_1 + (\partial\mu_1/\partial m_2)\mathrm{d}m_2\\ \mathrm{d}\mu_2(\mathrm{l}) &= \mathrm{d}\mu_2 = (\partial\mu_2/\partial m_1)\mathrm{d}m_1 + (\partial\mu_2/\partial m_2)\mathrm{d}m_2\end{aligned}\right\} \qquad (5)$$

Hence we have the ratio of the two total differentials in the form of equation (6). Let $(\partial\mu_1/\partial m_1)$, $(\partial\mu_1/\partial m_2)$, *etc.*

$$\mathrm{d}\mu_2/\mathrm{d}\mu_1 = [G_{21} + G_{22}(\mathrm{d}m_2/\mathrm{d}m_1)]/[G_{11} + G_{12}(\mathrm{d}m_2/\mathrm{d}m_1)] \qquad (6)$$

be abbreviated as G_{11}, G_{12}, *etc.*, and $G_{12} = G_{21}$ will generally hold from the standpoint of differentiation.

The chemical potential, μ_1, of calcium hydroxide in the aqueous solution can be expressed as in equations (7) and (8), wherein μ_1^0 denotes a constant and γ and m the

$$\mu_1 = \mu_1^0 + RT\ln\gamma_1(m_{\mathrm{Ca^{2+}}})(m_{\mathrm{OH^-}})^2 \qquad (7)$$

$$\gamma_1 = (\gamma_{\mathrm{Ca^{2+}}})(\gamma_{\mathrm{OH^-}})^2 \qquad (8)$$

activity coefficient and molality of the ion indicated as a subscript. Differentiation of μ_1 with respect to m_1 and m_2 yields equations (9) and (10). Based on consideration

$$G_{11} = \frac{\partial\mu_1}{\partial m_1} = RT\left(\frac{\partial\ln\gamma_1}{\partial m_1} + \frac{1}{m_1} + \frac{2}{m_{\mathrm{OH^-}}}\frac{\partial m_{\mathrm{OH^-}}}{\partial m_1}\right) \qquad (9)$$

$$G_{12} = G_{21} = \frac{\partial\mu_1}{\partial m_2} = RT\left(\frac{\partial\ln\gamma_1}{\partial m_2} + \frac{2}{m_{\mathrm{OH^-}}}\frac{\partial m_{\mathrm{OH^-}}}{\partial m_2}\right) \qquad (10)$$

of the equilibrium condition for the dissociation of silicic acid, we obtained the derivative of μ_2 with respect to m_2 in the form shown in equation (11) (see Appendix 1).

$$G_{22} = \partial\mu_2/\partial m_2 \approx RT/m_2 \qquad (11)$$

The equations (9), (10), and (11) can be substituted in equation (6). Since a review of the numerical values involved indicates $G_{11} \gg G_{12}\,(\mathrm{d}m_2/\mathrm{d}m_1)$ in practice, rearrangement of equation (6) gives equation (12).

$$\frac{\mathrm{d}\mu_2}{\mathrm{d}\mu_1} = \frac{m_1(\partial\ln\gamma_1/\partial m_2) + 2(m_1/m_{\mathrm{OH^-}})(\partial m_{\mathrm{OH^-}}/\partial m_2) + (\mathrm{d}\ln m_2/\mathrm{d}\ln m_1)}{1 + m_1(\partial\ln\gamma_1/\partial m_1) + 2(m_1/m_{\mathrm{OH^-}})(\partial m_{\mathrm{OH^-}}/\partial m_1)} \qquad (12)$$

In this equation, the derivatives $(\partial\ln\gamma_1/\partial m_1)$, $(\partial\ln\gamma_1/\partial m_2)$, $(\partial m_{\mathrm{OH^-}}/\partial m_1)$, and $(\partial m_{\mathrm{OH^-}}/\partial m_2)$ can be evaluated from the experimentally found m_1 and m_2 values by use of the following equations (13)—(20). The derivations of these equations are briefly shown in Appendix 2.

I is ionic strength and K_{w} and K_2 denote the dissociation constant of water and that for the equilibrium $\mathrm{H_3SiO_4^-} \rightleftharpoons \mathrm{H^+} + \mathrm{H_2SiO_4^{2-}}$, respectively.

The term $(-\mathrm{d}\mu_2/\mathrm{d}\mu_1)$ equals the value of n indicating the C : S molar ratio of the solid C–S–H from equation

$$\partial\ln\gamma_1/\partial m_1 = -(3\delta - 4.14)[5 - (\partial m_{\mathrm{OH^-}}/\partial m_1)] \quad (13)$$

$$\partial\ln\gamma_1/\partial m_2 = (3\delta - 4.14)[1 + (\partial m_{\mathrm{OH^-}}/\partial m_2)] \quad (14)$$

$$\partial m_{\mathrm{OH^-}}/\partial m_1 = \frac{2 - 5m_2\beta\delta(1+\beta)^{-2}}{1 + \beta m_2(m_{\mathrm{OH^-}})^{-1}(1 - m_{\mathrm{OH^-}}\delta)(1+\beta)^{-2}} \quad (15)$$

$$\partial m_{\mathrm{OH^-}}/\partial m_2 = \frac{m_2\beta\delta(1+\beta)^{-2} - (1+2\beta)(1+\beta)^{-1}}{1 + \beta m_2(m_{\mathrm{OH^-}})^{-1}(1 - m_{\mathrm{OH^-}}\delta)(1+\beta)^{-2}} \quad (16)$$

where

$$\alpha = 2.326I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) + 0.691I \quad (17)$$

$$\beta = m_{\mathrm{OH^-}}K_{\mathrm{w}}^{-1}K_2\exp\alpha \quad (18)$$

$$\delta = 1.163/I^{\frac{1}{2}}(1 + I^{\frac{1}{2}})^2 + 0.691 \quad (19)$$

$$I = 5m_1 - m_{\mathrm{OH^-}} - m_2 \quad (20)$$

(3), therefore n can be calculated from the m_1 and m_2 actually found in the liquid phase.

The Nature of C–S–H *in Equilibrium*.—The data shown in Figure 3 indicate a divergence in n values at a constant calcium ion concentration, which is contrary to the solubility behaviour of a pure substance. In order to find out why this lack of reproducibility occurs, we examined whether true equilibrium was attained in different experiments. That is, by applying equation (12), an n value was estimated for C–S–H, which ought to be in equilibrium with the aqueous solution at any given molality of m_1 and m_2, with which those observed were compared.

In using the equation, the term $\mathrm{d}\ln m_2/\mathrm{d}\ln m_1$ can be found from the gradient of the smooth curve drawn through the experimental points in Figure 2, where curve (*b*) is for the specimen L and curve (*a*) represents the minimum relation between m_1 and m_2.* The values of $m_{\mathrm{OH^-}}$ were measured experimentally, and also found by use of equation (33) (see Appendix) as a function of m_1 and m_2. Two series of computations for $m_{\mathrm{OH^-}}$ were made using the values of m_1 and m_2 from curves (*a*) and (*b*) in Figure 2. The resultant values, as indicated in Figure 4, are in good agreement with those measured. The numerical values of $m_{\mathrm{OH^-}}$ obtained with regard to curve (*a*) are listed in the Table. The average charge of silicate ion, Z(charge/silicon atom), in aqueous solution was obtained from $(2m_1 - m_{\mathrm{OH^-}})/m_2$, where the calculated values of $m_{\mathrm{OH^-}}$ were used. From the inset in Figure 4, the negative charge Z is found to increase sharply from 1.2 to 1.8 with increasing m_1 from 1.0 to 8.0 mmol kg^{-1}, then flatten below a level of 2. This result does not conflict with the postulation that the monomers, $H_3SiO_4^-$ and $H_2SiO_4^{2-}$, are predominant of the silicate ions in a dilute calcium hydroxide solution.

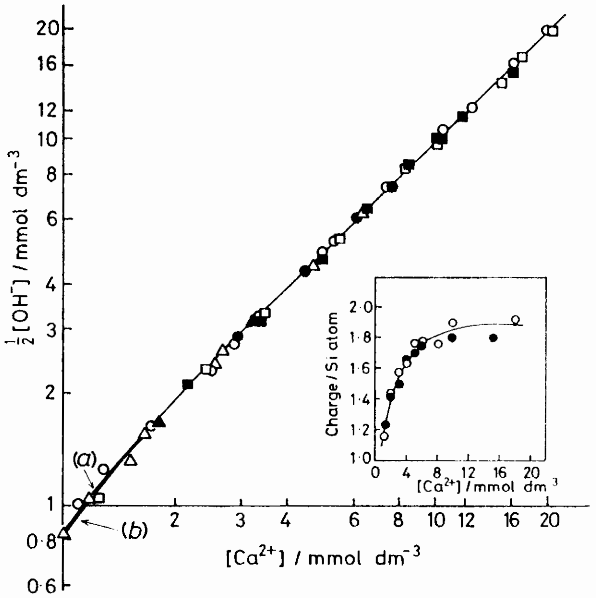

FIGURE 4 Variation in concentration of hydroxide ion with that of calcium ion at 30 °C. Data are for L_a (○), L_b (●), L_c (▲), M (□), and H (■); and from ref. 22 (△). Curves (*a*) and (*b*) were calculated by use of equation (33) and data from curves (*a*) and (*b*) in Figure 2, which fit the observed plots. Inset [data from curve (*a*) (●), curve (*b*) (○)] shows the dependence of average charges of silicate ion (Z) on the concentration of calcium ion

Calculation of molar CaO : SiO_2 ratio (n) in C–S–H by use of equation (12) and data given by curve (*a*) in Figure 2

m_1/ mmol kg^{-1}	m_2/ mmol kg^{-1}	$m_{\mathrm{OH^-}}$/ mmol kg^{-1}	I/ mmol kg^{-1}	$(\partial m_{\mathrm{OH^-}}/\partial m_1)$	$(\partial m_{\mathrm{OH^-}}/\partial m_2)$	$(\mathrm{d}\ln m_1/\mathrm{d}\ln m_2)$	$(\mathrm{d}\mu_2/\mathrm{d}\mu_1)$
1	0.260	1.67	3.07	1.944	−1.197	−1.16	−0.82
2	0.112	3.84	6.05	1.985	−1.41	−1.27	−0.97
3	0.063	5.90	9.03	1.994	−1.53	−1.35	−1.07
4	0.040	7.94	12.0	1.997	−1.61	−1.54	−1.18
5	0.027	9.95	15.0	1.999	−1.67	−1.63	−1.25
6	0.020	11.97	18.0	2.00	−1.72	−1.73	−1.32
8	0.011 5	15.98	24.0	2.00	−1.78	−2.00	−1.46
10	0.007	19.99	30.0	2.00	−1.82	−2.25	−1.59
12	0.004 5	24.0	36.0	2.00	−1.85	−2.52	−1.72
14	0.003 2	28.0	42.0	2.00	−1.87	−2.76	−1.83
16	0.001 95	32.0	48.0	2.00	−1.89	−2.95	−1.92
18	0.001 33	36.0	54.0	2.00	−1.90	−3.14	−2.00
20	0.000 9	40.0	60.0	2.00	−1.91	−3.31	−2.08

The solubility data for the L type specimen were treated first. In the steady state, the solid showed enhanced solubility on the whole and its n value rarely exceeded 1.5 even after prolonged contact with the

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* For a very dilute solution of C–S–H in water, the concentration data (mol dm^{-3} of solution) can approximately be used in terms of molality (mol kg^{-1} of water).

nearly saturated calcium hydroxide solution. This suggests that the solid remains in its original immature state attained at the time of preparation, as aforementioned. The *n* values were estimated in accordance with equation (12) using the data of curve (*b*) in Figure 2. Curve (*b*) of Figure 3 is consequently obtained, which fairly well follows the experimental plot (although displaced slightly above it).

It is noteworthy in Figure 2 that above 8 mmol kg^{-1} with respect to m_1 almost the same solubilities are found for both M and H specimens, despite the different compositions of the equilibrated solid phases as shown in Figure 3. This unusual behaviour may be explained by postulating that the response of the C–S–H to the varying calcium ion concentrations in the liquid phases in which they were placed is limited to only the surface layer of the C–S–H particles. In other words, the different kinds of M and H particles are modified to have the same surface layer product, but most of the respective inner-core portions remain unchanged during equilibration.* This apparent equilibration may be illustrated schematically by line 3 in Figure 5 which indicates the change in chemical potentials, μ(s) and μ(l), with regard to the component Ca[OH]$_2$ through a boundary product between solid and liquid phases.

If this model is acceptable, curve (*b*) in Figure 3 might indicate the *n* values for the exposed surface products of the equilibrated solid particles from L type specimens, and further it is possible to estimate those for the surface products in the state most approximating the thermodynamic equilibrium under the assumption that the postulated surface products form a continuous series of solid solutions. For this estimation, curve (*a*) in Figure 2 will be useful since it reflects the state required, and so the *n* values were calculated in a similar manner using equation (12). The results are given in the Table and by curve (*a*) of Figure 3.

From Figure 5, the postulated surface product, when equilibrated in dilute calcium hydroxide solution, should have a lower *n* value than the average for the whole solid particle as interpreted by line 1, whereas in a concentrated calcium hydroxide solution it should have a higher *n* value (line 3, Figure 5). In compliance with this requirement, the resultant curve (*a*) in Figure 3 falls below the plot found with the specimens of H type in the zone of a lower calcium ion concentration, and above the plot in the zone of a higher concentration ($m_1 >$ *ca.* 13 mmol kg^{-1}). The *n* value for curve (*a*) in Figure (3) at $m_1 = 13$ mmol kg^{-1} is *ca.* 1.75, and is equal to the initial *n* value of the specimen of H type. This situation fairly well corresponds to the state of line 2 in Figure 5. A similar tendency is found with regard to the plot from the specimens of M type having an initial *n* value of 1.24.

From these results, the authors believe that the formation of the surface products or ' a surface layer equilibration ' is a useful postulate for understanding the solubility behaviour of C–S–H, and that curve (*a*) in Figure 3 derived from the solubility data represents the possible phase relation between C–S–H and water most approximating the thermodynamic equilibrium. Among the published results, those obtained by Greenberg and Chang[4] approximately fit the curve (*a*) of Figure 3, except for the zone of high calcium ion concentration. The C–S–H specimens they used were obtained by stirring hydrated silica and calcium hydroxide in a suspended state at 50 °C for a long time and were subjected to tests for equilibrium at 25 °C. It has been reported that C–S–H having a value of *n* of 1.5—2.0 can be formed in a substantially saturated calcium hydroxide solution.[1] Recently, when the hydration product of tricalcium silicate was tested by means of scanning-electron microscopy (s.e.m.) and electron-microprobe analysis[25-27] or by the combination of s.e.m. and energy-dispersive spectrometry,[28] the *n* values were found to range from 1.9 to 2.0 at some, if not all, sites. These values closely approximate the *n* value of *ca.* 2.1 calculated for the zone of calcium ion concentration near saturation.

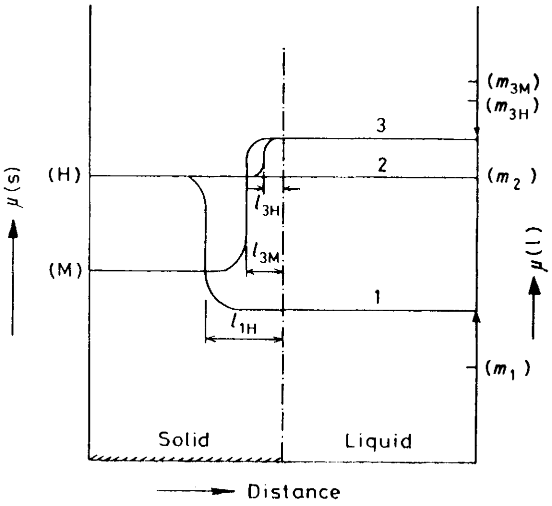

FIGURE 5 Schematic diagram for the apparent equilibration of C–S–H in calcium hydroxide solution through the formation of a surface product, as interpreted by the chemical potential (μ) of a component, Ca[OH]$_2$, *vs.* distance. Line 1: from C–S–H particles (H type) the component Ca[OH]$_2$, with an initial μ(s) of (H) on the ordinate, is partially released to form the surface product with a thickness of l_{1H} and a potential level of 1, when they contact a dilute calcium hydroxide solution of molality m_1, whose equivalent μ(l) is indicated by (m_1). Line 2: no substantial change occurs for the same particles when they contact a calcium hydroxide solution of molality m_2. Line 3: for C–S–H particles (H and M types), adsorption of calcium (with slight release of silica) occurs to form the surface product with the same potential level of 3, when they contact concentrated calcium hydroxide solutions of molalities m_{3H} and m_{3M} respectively

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* It is noted that an analogous solubility behaviour was observed in the system of hydroxyapatite–water, where the release of ions from the particles and the simultaneous formation of the surface complex, $Ca_2(HPO_4)(OH)_2$, account for the apparent solubility of hydroxyapatite.[24] Thus a contributing factor to the solubility is likely to be the presence of a surface complex with definite composition, while in the C–S–H–H_2O system the surface product is non-stoicheiometric, which would make the solubility behaviour of the C–S–H more complicated.

APPENDIX

1. In dilute alkaline solution (pH > 10), most of the silicic acid dissociates into such monomeric ions as $H_3SiO_4^-$ and $H_2SiO_4^{2-}$,[9,23] for which the successive dissociation constants K_1 and K_2 [equations (21) and (22)] are estimated

$$K_1 = (\gamma_{S1} m_{S1} K_w)/(\gamma_{OH^-} m_{OH^-} m_{S0}) \qquad (21)$$

$$K_2 = (\gamma_{S2} m_{S2} K_w)/(\gamma_{S1} \gamma_{OH^-} m_{S1} m_{OH^-}) \qquad (22)$$

to be $10^{-9.8}$ and $10^{-11.8}$ at 25 °C.[23] The balances in mass and electric charge in the aqueous solution of C–S–H are represented by (23) and (24) where subscripts S0, S1, and S2

$$m_2 = m_{S0} + m_{S1} + m_{S2} \qquad (23)$$

$$2m_1 = m_{OH^-} + m_{S1} + 2m_{S2} \qquad (24)$$

denote H_4SiO_4, $H_3SiO_4^-$, and $H_2SiO_4^{2-}$ respectively. Thus, when m_1 and m_2 are defined as independent variables the other molalities m_{OH^-}, m_{S0}, m_{S1}, and m_{S2} and the activity coefficients become the functions of the two variables since they are related by the four equations.

The equilibrium condition for the dissociation of silicic acid

$$\mu_2 = \mu_{S0} = \mu_{H^+} + \mu_{S1} = 2\mu_{H^+} + \mu_{S2} \qquad (25)$$

$$\mu_2 = \mu_{S0}^0 + RT \ln m_{S0} \qquad (26)$$

requires equation (25) to hold, giving equation (26). The differentiation of μ_2 with respect to m_2 gives equation (27).

$$\frac{\partial \mu_2}{\partial m_2} = \left(\frac{\partial \mu_2}{\partial m_{S0}}\right) \Big/ \left(\frac{\partial m_2}{\partial m_{S0}}\right) = \left(\frac{RT}{m_{S0}}\right) \Big/ \left(\frac{\partial m_2}{\partial m_{S0}}\right) \qquad (27)$$

By eliminating m_{S1} and m_{S2} from equations (21), (22), and (23), we obtain equation (28). Replacing the terms in the

$$m_2 = [1 + (m_{OH^-} \gamma_{OH^-} K_1/\gamma_{S1} K_w) + (m_{OH^-})^2 (\gamma_{OH^-})^2 (K_1 K_2/\gamma_{S2} K_w^2)] m_{S0} \qquad (28)$$

square bracket temporarily by F and differentiating this equation gives equation (29).

$$\partial m_2/\partial m_{S0} = F + m_{S0}(\partial F/\partial m_{S0}) \qquad (29)$$

Since data analysis shows $F \gg m_{S0}(\partial F/\partial m_{S0})$, the right-hand side of this equation can be approximated to F. Therefore, equation (27) reduces to equation (11).

2. For the activity coefficient of an ion with charge Z in a solution with an ionic strength $I < 0.1$ mol dm^{-3}, an extended Debye-Hückel relation is written in the form [29] of equation (30) and thus $\ln\gamma_1$ [$= \ln(\gamma_{Ca^{2+}})(\gamma_{OH^-})^2$] becomes equation (31), where the ionic strength I is given by equation (32). Since m_{S0} is much smaller than $(m_{S1} + m_{S2})$, we can make the approximation (23′). Thus, from equations (23′) and (24), equation (32) reduces to give equation (32′).

$$-\log_{10}\gamma = 0.505 Z^2 I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0.3I \qquad (30)$$

$$-\ln\gamma_1 = 6.978 I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 2.07I \qquad (31)$$

$$I = \tfrac{1}{2}(4m_{Ca^{2+}} + m_{OH^-} + m_{S1} + 4m_S)_2 \qquad (32)$$

$$m_2 \approx m_{S1} + m_{S2} \qquad (23')$$

$$I = 5m_1 - m_{OH^-} - m_2 \qquad (32')$$

Partial differentiation of $\ln\gamma_1$ with respect to m_1 and m_2 by making use of equations (31) and (32′) yields equations (13) and (14).

The relation between m_1, m_2, and m_{OH^-} can be shown as equation (33), which is derived from equations (22), (23′), (24), and (30).

$$2m_1 = m_{OH^-} + m_2[(1 + 2m_{OH^-} K_w^{-1} K_2 \exp\alpha)/(1 + m_{OH^-} K_w^{-1} K_2 \exp\alpha)] \qquad (33)$$

Then, the partial differential coefficients $(\partial m_{OH^-}/\partial m_1)$ and $(\partial m_{OH^-}/\partial m_2)$ can be obtained by carrying out the implicit differentiation with respect to equation (33) in the forms of equations (15) and (16).

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