Aqueous Chemistry and Thermodynamic Modelling of $CaO-SiO_2-H_2O$ Gels

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Some $CaO-SiO_2-H_2O$ gels of controlled composition have been synthesised by the hydrolysis of mixed alkoxide precursors and by direct reaction between colloidal SiO_2 and $Ca(OH)_2$. The gels were equilibrated with water at 25 °C after different ageing treatments, and the water compositions analysed. A mathematical model describing the free energy of formation of the gel as a function of its composition has been developed which accounts for the experimental data. The model assumes that both SiO_2 (amorphous) and $Ca(OH)_2$ can form limited solid solutions with an intermediate compound and hence only a small number of parameters is required to characterise the entire system.

Portland cements, and concretes based on them, are complex chemical systems which have the potential to react within themselves (*e.g.* during setting and curing), and with their environment. These reactions can be beneficial, leading to increased strength, or deleterious, leading to degradation and loss of strength. The chemical conditions within cement, particularly the pH and chloride-ion concentration in aqueous solution, also control the corrosion of steel reinforcement and influence the behaviour of cement used to contain radioactive waste. In the latter case the high pH established by the cement serves to restrict the aqueous solubility of some radioactive elements (*e.g.* Am) to extremely low levels. In order to understand these processes and be able to predict how the passage of time could influence them, it is necessary to have a quantitative description of chemical equilibrium in cement, particularly in the presence of excess of water.

Within cement the dominant system which will control chemical behaviour is the $CaO-SiO_2-H_2O$ (C–S–H) system which contains hydrated calcium silicates; these are non-stoicheiometric colloidal gels which are almost amorphous. Although these poorly crystalline solids are metastable with respect to crystalline minerals such as tobermorite ($5CaO{\cdot}6SiO_2{\cdot}5.5H_2O$) or jennite ($9CaO{\cdot}6SiO_2{\cdot}11H_2O$), they are nevertheless capable of existing for extremely long times under normal ambient conditions. Their existence has been reported in Victorian cements about 136 years old,[1] in ancient cements about 2 000 years old,[2] and in natural formations estimated to be about 60 million years old.[3]

The general term 'C–S–H gel' covers a class of solids which vary widely in composition and crystallinity. Some are relatively well defined in terms of structure and composition such as the C–S–H(I) and C–S–H(II) gels studied by Taylor and co-workers.[4,5] C–S–H(I) has some structural characteristics of tobermorite and a Ca/Si atom ratio in the range 0.8—1.3:1 whereas C–S–H(II) gel has some similarity to jennite and a greater Ca/Si ratio. The gels which form during the hydration of Portland cement pastes are thought to be similar to C–S–H(II), but of even lower crystallinity.[4] Many studies have indicated that the maximum Ca/Si ratio in the gel is about 1.8:1, at which point the gel is in equilibrium with solid $Ca(OH)_2$ (portlandite). Thus hydrated Portland cements (for which Ca/Si is greater than 1.8:1) normally contain both C–S–H gel and portlandite. However, it is possible to conceive of circumstances in which the overall Ca/Si ratio may be much lower than 0.8:1 (*e.g.* when excess of SiO_2 is deliberately added, or when Ca is removed by reactions with an aqueous environment). Therefore, the behaviour of this system is of interest for Ca/Si ratios covering the range 0—*ca.* 2:1.

There have been numerous previous studies in which solids in the C–S–H system have been equilibrated with water and the chemical composition of the solids and liquid characterised. Most of the early studies were reviewed by Steinour.[6] More recent studies are typified by the work of Greenberg and Chang[7,8] and Fujii and Kondo.[9,10] Greenberg and Chang synthesised C–S–H gels by treating silica gel with calcium oxide in water. Fujii and Kondo synthesised their C–S–H gels by reaction of aqueous solutions of sodium silicate and calcium nitrate. These methods of synthesis are typical of those used in studies of the C–S–H system. Such methods are not ideal in that they do not necessarily give a reaction product having a homogeneous composition and, in the case of the second method, foreign ions (Na^+ and NO_3^-) may be incorporated into the product to an unknown degree. Furthermore, these techniques are not readily extended to multicomponent systems which are necessary for a more realistic description of cements (*e.g.* by including Al in the system). Most of the previous studies (with the exception of those of Greenberg and Chang) have concentrated on average compositions in the solid phases between about 1.0 and 3:1 (as Ca/Si ratio). This is because this range is of most interest for understanding the hydration of cement. However, from the point of view of cement durability and long-term properties in general, low Ca/Si ratios (0—1.0:1) are also important since many processes (leaching, carbonation, *etc.*) tend to remove Ca from the C–S–H system.

The aim of the work described here was to develop a new, and more flexible, route for synthesising C–S–H gels based on sol–gel chemistry and to determine their thermodynamic properties by studying their equilibration with water. The preparative route described here is based on the hydrolysis of mixed alkoxides and offers the advantages of homogeneous mixing on the atomic scale, a ready extension to include other elements (such as Al) and a product free from contamination by other ions. A second aim was to obtain more experimental data in the composition range having Ca/Si ratios between 0 and 1.0:1.

The preparation of the gels and their equilibration with water is described and the results compared with gels synthesised by the earlier methods. The chemistry of C–S–H gel is then quantified in terms of a solid-solution model which expresses the free energy of formation of the gel as a function of its composition (Ca/Si ratio). Both the experiments and the model constitute a first step towards a comprehensive and flexible approach to synthesising the poorly crystalline solids that control the properties of hydrated cement and describing their chemistry in a quantitative way. The next stage of development from this initial study will be to extend the composition range to include aluminium.

Experimental

Synthesis of C–S–H *Xerogels.*—The method used to prepare high-purity, homogeneous C–S–H gels was to hydrolyse an ethanolic solution of calcium ethoxide and tetraethyl orthosilicate $[Si(OC_2H_5)_4]$ to give a gel which was converted into a xerogel[11] by evaporation of excess of alcohol and water. The term xerogel is used in this paper to describe the dried gel which results from this method.

A weighed quantity of calcium turnings (99.5% Ca) was dissolved in dry ethanol (1 l) under reflux and dry argon. The resulting calcium ethoxide solution was analysed (see below) to determine the calcium content. The calcium ethoxide solution was then mixed with the quantity of tetraethyl orthosilicate ('electronic grade,' >99%) required for the eventual Ca/Si ratio in the gel. Mixing of the solutions ensures a uniform distribution of Ca and Si. The alkoxide mixture was hydrolysed by addition, to the vigorously stirred clear solution, of sufficient water to give a 5% mixture by volume with the ethanol. The added water was freed of other gaseous impurities by argon purging and was far in excess of that required to hydrolyse the ethoxides (*i.e.* two water molecules per Ca and four per Si). The resulting opalescent gel was allowed to stand under argon and the ethanol subsequently removed by low-pressure distillation at ambient temperature in a stream of argon. The dry xerogel product (a fine powder) was handled in all subsequent operations under dry argon since exposure to air resulted in the rapid uptake of carbon dioxide. Six such preparations were carried out with final compositions (Ca/Si) in the range 0.28—1.7:1.

Synthesis of C–S–H *gels by Reaction of* $Ca(OH)_2$ *with* SiO_2 (*Reacted Gels*).—Equilibration experiments using the xerogels showed some deviation from the earlier studies of Greenberg and Chang (see Results section). In order to examine these differences further, some gels were prepared from SiO_2 and $Ca(OH)_2$ in a manner similar to that described by Greenberg and Chang. In the present study, gels of this type were prepared by treating a SiO_2 sol with a suspension of $Ca(OH)_2$ (produced by treating Ca metal with water) at either 25 or 80 °C under argon. The resulting gel–water mixture was not separated. (In fact, it could not be readily separated by filtration through 0.2-μm aperture filters.) The SiO_2 sol was prepared from high-surface-area SiO_2 (Aerosil 380, Degussa, particle size 7 nm) which had been pretreated at 500 °C in argon to remove traces of HCl.

Gels of low Ca/Si ratio (<0.05:1) were prepared by reaction with saturated $Ca(OH)_2$ solution, as opposed to the suspension which was used at higher concentrations of Ca.

Ageing of C–S–H *Gels and their Equilibration with Water.*—Some samples of the xerogels were equilibrated with water as soon as possible after preparation (usually within a day or so). The water used was Analar grade which had been purged with argon. Typically, 10 g of xerogel were equilibrated with water (80 cm^3) for a period of 20 d. Experiments in which pH of the water was monitored as a function of time indicated that pH equilibrium was achieved in a very short time (typically less than 1 h). The ratio of solid to liquid in the equilibrations with the $SiO_2/Ca(OH)_2$ reacted gels is estimated to be approximately 5 g solid in 100 cm^3 liquid. The reacted gels formed from $Ca(OH)_2$ suspension required much longer to equilibrate (typically 2 weeks), whereas those formed from $Ca(OH)_2$ solution equilibrated almost as rapidly as the xerogels.

In the earlier studies by other workers, different thermal treatments were used to try to ensure chemical homogeneity of the solid phases. However, these heat treatments also bring the risk of changing the structure of the gel itself and, perhaps, its chemical properties. For example, Fujii and Kondo[9] report different properties for gels aged at 25 and 50 °C. In order to examine these effects, some samples of gels prepared by both methods (described above) were aged, after initial equilibration, for up to 455 d at 25 °C or 116 d at 80 °C. These experiments were carried out in double-sealed containers to minimise the risk of carbonation during ageing. The inner container was Polythene and the outer container was Pyrex. All free spaces were argon-filled and the outer vessel contained a quantity of soda lime to absorb carbon dioxide. The samples which had been aged at 80 °C were allowed to re-equilibrate (without change of water) for a further 20 d at 25 °C before chemical analysis. Thus the data reported for the heat-treated gels refer to their state at 25, not at 80 °C.

Chemical Analysis of Solid and Liquid Phases.—In the case of the xerogels, analysis was carried out to determine the Ca and Si in the solid phase and Ca, Si, and pH in the liquid phase. Since separation of solids and liquid was difficult for the reacted gels (see above) the Ca/Si ratio of the solid was assumed to be that originally established before reaction and only the pH was measured in the liquid.

The Ca/Si ratio in the xerogels was determined in two ways. The first was by mass balance from the preparation method. Some unreacted silicon ethoxide was lost from the gels during gelation and therefore it was necessary to analyse the contents of the drying trap for silicon in order to account for this. The second method was to dissolve the gel in a minimum quantity of HF and to analyse the solution for Ca and Si as described below. The two methods were in agreement to a relative accuracy of approximately 1%.

The liquid phase was sampled by taking aliquots (5 cm^3) through a poly(tetrafluoroethylene) (ptfe) disposable filter with 0.2-μm apertures (Acrodisc, Gelman Scientific). Colorimetric methods were used to analyse for Ca and Si in the liquid.

For analysis of Si the methods employed were those described by Iler.[12] For SiO_2 concentrations in the range 3×10^{-5}—3×10^{-2} mol l^{-1} the β silicomolybdate method was used and the molybdenum blue method for lower concentrations. The accuracy of both methods, based on gravimetric standards, was estimated to be ±0.3% relative. These methods are sensitive to Si in different states of polymerisation since the molybdate reagent reacts at different rates with species of different molecular weight. In particular it can readily distinguish between low-molecular-weight polysilicic acid ($\lesssim 2$ SiO_2 units) and larger units. No evidence of polymeric species having more than two units was detected. Furthermore, analysis of some filtered aliquots acidified with HF for Ca, Si, and pH gave identical results to those for corresponding unacidified ones. We therefore conclude that these xerogels do not generate appreciable colloidal species and therefore all the silicon analyses are assumed to determine monomeric silicate species.

Calcium in solution was determined by the calcichrome method[13] with calcium concentrations in the range 1×10^{-5}—3×10^{-4} mol l^{-1}. More concentrated solutions had to be diluted to fall within this range. The relative accuracy was estimated to be ±1.5% based on gravimetric standards.

The pH of the liquid was measured using a glass electrode (working range up to pH 14) calibrated against freshly prepared saturated $Ca(OH)_2$ solution at 25 °C (pH 12.45). The accuracy of pH measurement is estimated to be ±0.05 unit.

Results

Present Experiments.—The compositions (total Ca, total Si, and pH) of the aqueous phase in equilibrium with xerogels,

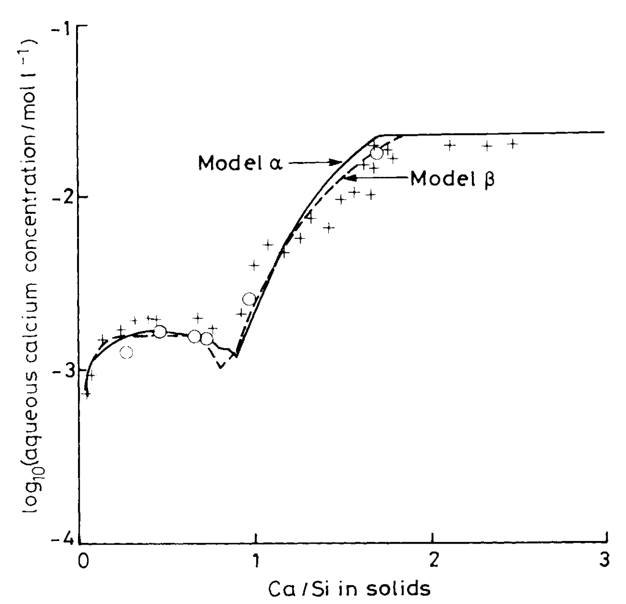

Figure 1. Total calcium in aqueous solution in equilibrium with solids in the CaO–SiO$_2$–H$_2$O system at 25 °C as a function of the Ca/Si atom ratio in the solids. The curves are computed from thermodynamic modelling of the system (see text). ○, Data from xerogels prepared from metal–ethoxide precursors in the present work; +, data from Greenberg and Chang[8]

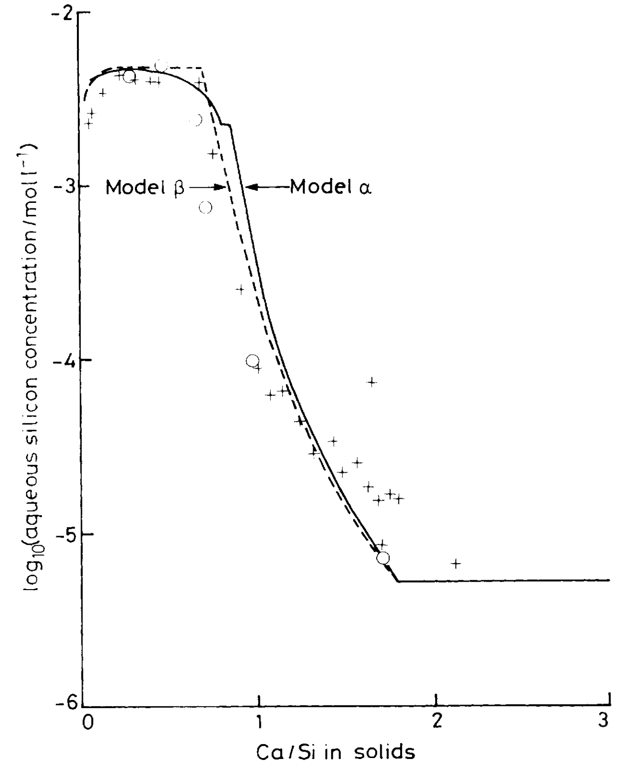

Figure 2. As Figure 1, but showing total silicon in aqueous solution

having a variety of Ca/Si ratios and ageing treatments, are given in Table 1 and Figures 1—3. The tabulated results show a clear effect of ageing treatment in that the longer the ageing time the lower is the pH.

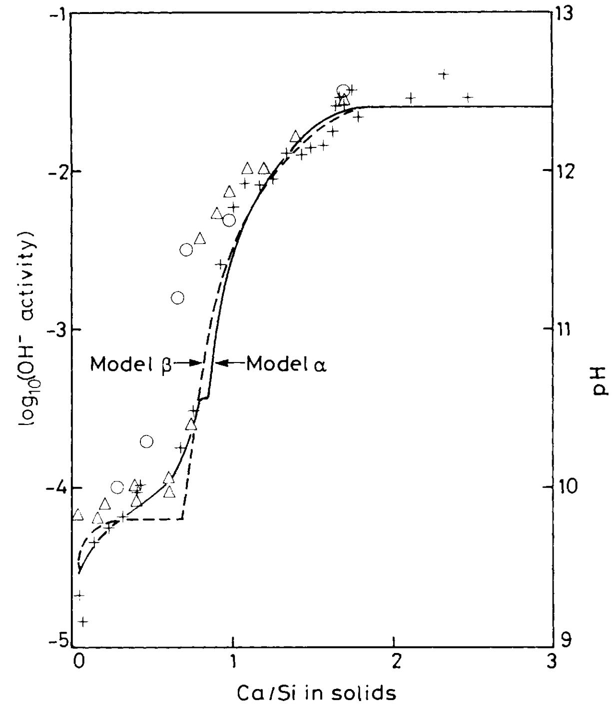

Figure 3. As Figure 1, but showing the pH in aqueous solution. △, Data from solids prepared in the present study using a method similar to that employed by Greenberg and Chang[8]

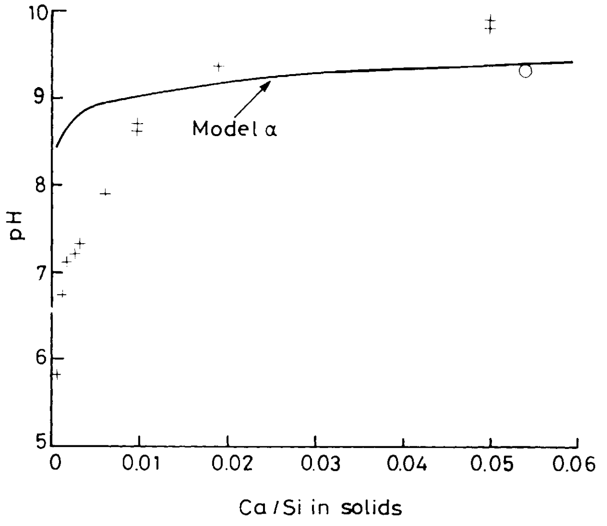

Figure 4. The pH of aqueous solution, in equilibrium with C–S–H gels of low Ca/Si ratio prepared by treating colloidal SiO$_2$ with Ca(OH)$_2$ solution. +, Data from the present experiments; ○, data from Greenberg and Chang[8]

The pH measured for equilibrium with gels produced by reaction of Ca(OH)$_2$ with SiO$_2$ is given in Table 2 and also plotted in Figures 3 and 4 (for Ca/Si ratios $<0.06:1$). Again there is a general tendency for the pH to be slightly lower for specimens which have been aged at 80 °C. The pH established by the reacted gels deviates, in most cases, by not more than 0.2 unit from that established by the xerogels. However, for solids having composition close to Ca/Si = 0.7—0.8:1, the pH is very sensitive to the solid composition and the uncertainties are correspondingly larger.

The effect of ageing in lowering the pH established by both types of gel may reflect a real change in gel structure and chemistry, or it may reflect contamination of the gel (*e.g.* by

Table 1. Aqueous solution equilibration data for hydrated calcium silicate xerogel

(*a*) Equilibrium in water at 25 °C

	7 d					183 d	360 d	455 d
Ca/Si in solid	$\frac{[\mathrm{Ca}]_T}{\mathrm{mol\ l^{-1}}}$	$\frac{[\mathrm{Si}]_T}{\mathrm{mol\ l^{-1}}}$	p(Ca)*	p(Si)	pH	pH	pH	pH
1.70	1.79×10^{-2}	7.10×10^{-6}	1.75	5.15	12.50	12.35	12.30	12.20
0.98	2.51×10^{-3}	9.33×10^{-5}	2.60	4.03	11.70	—	11.70	—
0.71	1.55×10^{-3}	7.38×10^{-4}	2.81	3.13	11.50	11.27	11.20	—
0.67	1.56×10^{-3}	2.42×10^{-3}	2.81	2.62	11.20	10.98	10.95	10.45
0.47	1.61×10^{-3}	4.69×10^{-3}	2.79	2.33	10.30	10.27	10.30	10.20
0.28	1.32×10^{-3}	4.15×10^{-3}	2.88	2.38	10.00	10.00	10.00	9.92

(*b*) Equilibrated at 25 °C after hydrothermal treatment at 80 °C

	50 d					116 d
Ca/Si in solid	$\frac{[\mathrm{Ca}]_T}{\mathrm{mol\ l^{-1}}}$	$\frac{10^3[\mathrm{Si}]_T}{\mathrm{mol\ l^{-1}}}$	p(Ca)	p(SiO_2)	pH	pH
1.70	1.46×10^{-2}	—	1.84	—	12.20	11.58
0.98						11.50
0.71						10.42
0.67	1.53×10^{-3}	3.09	2.82	2.51	10.55	10.00
0.47	1.66×10^{-3}	4.32	2.78	2.36	10.17	9.85
0.28	1.27×10^{-3}	4.72	2.89	2.32	9.92	9.58

* The notation p is equivalent to $-\log_{10}([X])$ for Ca and Si and has its conventional meaning for pH.

Table 2. Aqueous solution pH at 25 °C in equilibrium with hydrated calcium silicate formed by reaction between SiO_2 and $Ca(OH)_2$ (reacted gels)

Ca/Si in solid	19 d pH	109 d pH	87 d at 80 °C Equilibrated at 25 °C pH
0.05			9.82
0.16	10.05	10.05	9.80
0.20		10.03	9.90
0.39		10.00	9.91
0.40	10.10	10.10	10.00
0.60_0	10.20	10.20	10.05
0.60_2		10.15	9.95
0.74	10.55	10.55	10.40
0.80			11.55
0.90			11.72
0.99	11.95	11.90	11.85
1.10			12.00
1.19	12.25	12.20	12.00
1.40			12.20
1.70			12.45

CO_2) during the ageing treatments. In view of the precautions taken to exclude contamination this latter explanation is unlikely, but cannot be ruled out at present.

Comparison with Earlier Studies.—As noted in the Introduction, the sum total of data existing for this system is very great. Therefore, in order to make the comparison of the present results with previous data manageable we have chosen to select only the data of Greenberg and Chang[8] since they were the only investigators to measure Ca, Si, and pH in the liquid phase as a function of Ca/Si in the solids (as was also done in the present work).

The present results for $[\mathrm{Ca}]_T$* (measured on xerogels) are in good agreement with those of Greenberg and Chang (measured for reacted gels) as demonstrated in Figure 1. The deviation between the two sets of data is typically less than 25% relative. The $[\mathrm{Si}]_T$ results are also in reasonable agreement (Figure 2), but the deviation is somewhat greater. In particular, the present results are about a factor of two lower for compositions close to Ca/Si = 0.7:1 in the solids. This deviation is even more evident in pH results (Figure 3) where the pH measured on xerogels with Ca/Si = 0.67 and 0.71:1 is greater than that measured by Greenberg and Chang by about one unit. Greenberg and Chang treated $Ca(OH)_2$ with SiO_2 at 50 °C for 50 d in their experiments and therefore the difference in aqueous chemistry could be due to the different ageing temperatures. This is supported by the observations in the present study in which all ageing treatments tended to lower the pH of all the gels. The present results on reacted gels might be expected to be closer to those of Greenberg and Chang since they were prepared using very similar methods. The data in Figure 3 show that the agreement between the present experiments for reacted gels and those of Greenberg and Chang is indeed quite good. The only data point which shows considerable deviation is one of the present experiments at Ca/Si = 0.8:1. However, a second experiment at the same nominal composition gave a pH lower by one unit and in good agreement with that of Greenberg and Chang. We conclude that some of the observed deviation close to this critical composition is probably due to the sensitivity of the liquid composition to small changes in the solid composition close to Ca/Si = 0.8:1 in the solid.

The overall conclusion from the comparison between the earlier study of Greenberg and Chang and the present one is that the general characteristics of the system are reasonably consistent between the three studies, but there are some differences in detail; in particular, the somewhat higher pH established by xerogels with composition close to Ca/Si = 0.8:1. This difference was investigated in more detail using the modelling approach which is described in the Discussion section. The model was used as a check on the self-consistency of the analysis of the aqueous phase by recognising that the three measured parameters, $[\mathrm{Ca}]_T$, $[\mathrm{Si}]_T$, and pH, are not

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* Square brackets are used to denote concentration in aqueous solution (in mol l^{-1}) and subscript 'T' denotes total concentration irrespective of ionic speciation.

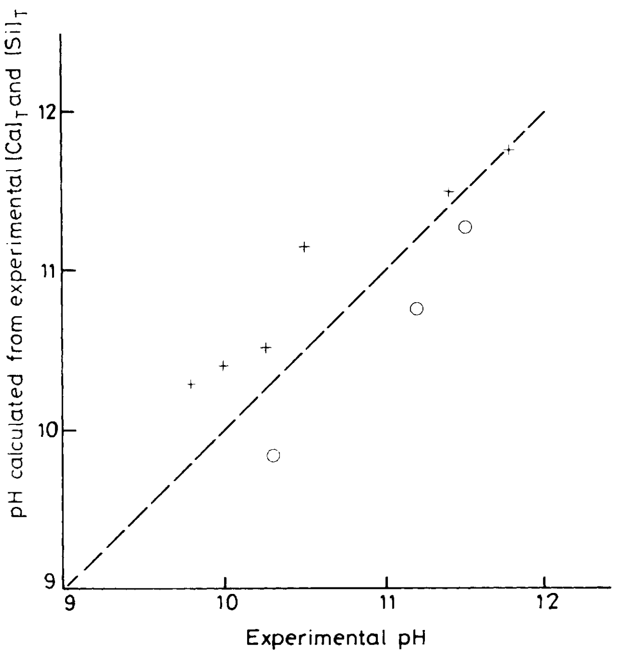

Figure 5. Comparison between experimentally measured pH and that predicted from the measured Ca and Si in aqueous solution and thermodynamic data for the aqueous species. Symbols as in Figure 1

independent. Thus if an aqueous system contains only calcium and silicon species in solution, knowledge of $[Ca]_T$, and $[Si]_T$ is sufficient to fix the pH. The thermodynamic model of the aqueous phase was used to calculate the pH which would be expected for the experimentally measured values of $[Ca]_T$ and $[Si]_T$ using data for equilibrium with both the xerogels from the present study and the reacted gels from the earlier study of Greenberg and Chang. The expected pH calculated using the model is shown compared with the measured pH in Figure 5. The broken line indicates equality and therefore complete self-consistency. It is clear from Figure 5 that there is a systematic bias in both studies of approximately equal magnitude, but in opposite directions. On this basis it cannot be argued that one set of experimental data is preferred to the other. Both appear to suffer from some deficiency in analytical technique which may be associated with any one (or all) of the three variables. We therefore conclude that the discrepancies between the two studies have their origin in experimental methods and analysis rather than in different chemical properties of the gels themselves.

Discussion

Chemistry and Structure of C–S–H *Gels.*—The suitability of a thermodynamic description of these solids has recently been discussed by Jennings.[14] Whilst it is universally acknowledged that the gels are metastable with respect to crystalline compounds, the observed longevity of the gels indicates that under ambient conditions the time constant for the transformation is extremely long (perhaps up to millions of years). Nevertheless, there is some evidence that the free energy of the gels is not well defined and is influenced by the way in which they are prepared. Jennings[14] surveyed a large number of data sets in which $[Ca]_T$ and $[Si]_T$ had been reported. When $[Si]_T$ was plotted against $[Ca]_T$ Jennings observed that the data sets divided into two groups which he designated A and B. For a given $[Ca]_T$ in aqueous solution, the gels in group B are in equilibrium with a higher $[Si]_T$ than those of group A, *i.e.* group B gels are less stable than group A. The gels in group B were all prepared by reaction of unhydrated $3CaO{\cdot}SiO_2$ with water. The more stable gels forming group A [which Jennings argues are closely related to C–S–H(I)] were synthesised by methods such as those used by Greenberg and Chang and Fujii and Kondo. [Jennings appears to have omitted to label the data of Fujii and Kondo which are plotted as open squares in Figure 1(*a*) of his paper.] The data for xerogels in the present study fall into group A and are therefore similar to what are believed to be the most stable gels in this system. Therefore the thermodynamic approach to describing the chemistry of C–S–H gels is further justified by the observation that their aqueous chemistry is not as ill defined as may have been anticipated and that the gels which have been studied here are probably the most stable variety.

The atomic structure of C–S–H gels has recently been discussed by Taylor[15] in terms of the crystalline analogues, tobermorite and jennite. According to Taylor, the crystalline structures are best regarded in terms of layers. The layers themselves are composed of rumpled chains of corner-sharing $[SiO_4]^{4-}$ tetrahedra. Some non-bridging oxygens are terminated by protons (OH groups) but most are compensated by Ca^{2+} ions. In tobermorite the Si-containing layer has the ideal formula $[Ca_4(Si_3O_9H)_2]^{2-}$ and in jennite, $[Ca_8(Si_3O_9H)_2(OH)_8]^{2-}$. These Si-containing layers are linked together by Ca^{2+} ions and interstitial water molecules. The C–S–H gels are known to have some structural characteristics which are similar to these crystalline compounds. However, in amorphous, or poorly crystalline, materials the basic structures offer considerable scope for compositional variations by incorporating a variety of defects. For example, Taylor[15] has proposed that defects in the silicate chains can allow the tobermorite type structure to have a Ca/Si ratio between 0.833 and 1.25 : 1 and the jennite type between 1.5 and 2.25 : 1. On the silica-rich side of the 'parent' composition the silicate chains could polymerise into sheets and networks by the elimination of interstitial $Ca(OH)_2$ and the formation of Si–O–Si bridges. These structural changes which give continuously varying compositions can be represented formally in a thermodynamic model as solid solutions even through they are not solid solutions in the sense of two species mixing on a given set of crystalline lattice sites.

Modelling the Solid and Aqueous Phases.—The experimental data in Figures 1—3 (and the consensus of other studies) indicate that the phase diagram can be split into three subsidiary regions (*e.g.* ref. 8). (*i*) A region where, in the solids, Ca/Si $\gtrsim$ 1.8 : 1. In this region the composition of the aqueous phase is independent of the composition of the solids which implies two solid phases co-existing in equilibrium. These are $Ca(OH)_2$ and C–S–H gel with Ca/Si $\simeq$ 1.8 : 1. (*ii*) A region with 0.8 $\lesssim$ Ca/Si $\lesssim$ 1.8 in which the aqueous composition changes dramatically with Ca/Si in the solids. This implies a single solid phase (*i.e.* C–S–H gel) of variable composition which can be regarded as a solid solution. (*iii*) A region with Ca/Si $\lesssim$ 0.8 in which the aqueous composition is relatively insensitive to Ca/Si in the solids. This has usually been regarded as indicating the coexistence of two solid phases (*e.g.* hydrated amorphous SiO_2 and a C–S–H gel with Ca/Si $\approx$ 0.8). However, the pH data of Greenberg and Chang do not show a well defined plateau in this region and therefore it is necessary to consider the possibility of solid solutions in this region.

The details of the thermodynamic modelling in these regions are presented in the Appendix. The overall approach was to consider C–S–H gels as solid solutions based on a 'parent' solid phase having a Ca/Si ratio of about 0.8 : 1. For Ca/Si $\gtrsim$ 0.8 : 1 this compound (*i.e.* C–S–H gel with Ca/Si = 0.8 : 1) is assumed to form a solid solution with $Ca(OH)_2$ subject to the constraint that $Ca(OH)_2$ itself becomes a stable solid phase when Ca/Si $\gtrsim$ 1.8 : 1. For Ca/Si $\lesssim$ 0.8 : 1 the C–S–H– gel (with Ca/Si = 0.8 : 1) is assumed to form a solid solution with amorphous hydrated

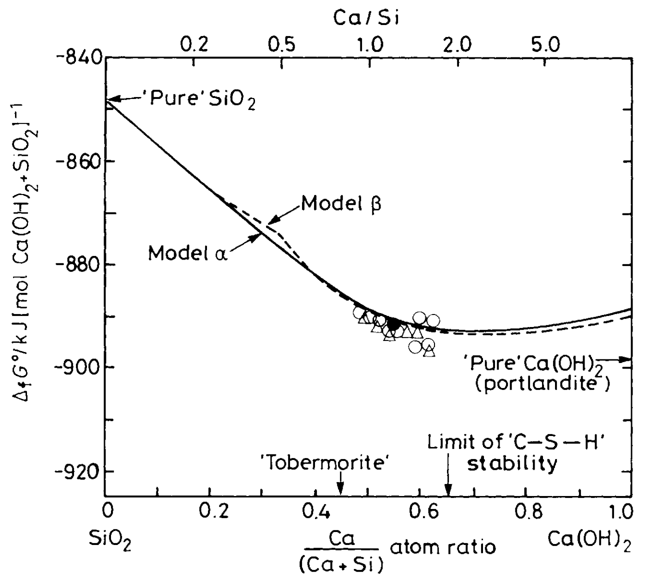

Figure 6. The standard free energy of formation of poorly crystalline C–S–H solids as a function of composition deduced from the thermodynamic models. Model α is based on solid solutions with a compound with Ca/Si = 0.833:1 and model β with Ca/Si = 0.5:1. The points are free energies deduced by Glasser *et al.*[16] All the free energies have been normalised to 1 mol of Ca plus Si in total and 1 mol of H_2O per mol Ca

SiO_2. These solid solutions are feasible from the structural point of view (see above).

The solid-solution parameters and the composition and free energy of formation of the 'parent' C–S–H gel were adjusted to obtain best fits to the experimental data as described in the Appendix. It was found that the scatter in the experimental data is sufficiently large that no unique thermodynamic model can be deduced. This is illustrated by the two different models, α and β, which are shown as curves superimposed on the experimental results, but have different input data and lead to different phase diagrams. This is particularly so in the region Ca/Si $\lesssim$ 0.8 where model β predicts the stable phases to be two solids (in fact two solid solutions; one with Ca/Si $\approx$ 0.1:1 and the other with $\approx$0.7:1), whereas model α predicts a single solid phase (a solid solution of varying composition). From the work of Taylor we would tend to favour model α since it is based on the structurally related tobermorite composition. At very low Ca/Si ratios the model tends to overestimate the experimentally measured pH. This may indicate the existence of a further phenomenon not included in the model such as adsorption of Ca^{2+} ions onto solid surfaces in addition to their incorporation into the amorphous solid structure.

Relationship to Other Modelling Studies.—Greenberg and Chang[8] interpreted their results in a similar manner to that described here, but with some differences in detail. They considered the solid phase for Ca/Si $\gtrsim$ 1:1 to be a solid solution of $Ca(OH)_2$ in $CaO{\cdot}SiO_2{\cdot}H_2O$ (*i.e.* $n = m = 1$ in the formula nCaO·SiO$_2$·mH_2O). The solid solution was described by allowing the activity of $Ca(OH)_2$ to vary with Ca/Si ratio. They also considered a solid solution of SiO_2 and $CaO{\cdot}SiO_2{\cdot}H_2O$ for Ca/Si < 1:1. It was concluded that a strongly non-ideal solution would be required to explain the results.

Glasser *et al.*[16] reinterpreted the experimental results of Greenberg and Chang and Fujii and Kondo for Ca/Si > 1:1 in terms of a single solid C–S–H phase whose solubility product depends on composition. This results in a free energy of formation which depends on composition (Figure 6).

These alternatives are both consistent with the present thermodynamic model. They are merely different ways of expressing the fact that in a solid solution the thermodynamic parameters vary with composition. The advantages of the method used in the present model are, however, as follows. (*i*) The whole range of solid solution is described by just two parameters having a firm theoretical basis. (*ii*) The thermodynamic description is in a suitable form for use in a computer code which is capable of generating phase diagrams for complex systems. This allows the model to be extended to include other elements (*e.g.* Al) or be applied readily to systems with other phases present. This latter feature is particularly valuable for interpreting reactions occurring between cement and complex chemical environments.

Conclusions

A method of preparing homogeneous gels (xerogels) in the $CaO–SiO_2–H_2O$ system has been developed based on hydrolysis of mixed alkoxide precursors. When these xerogels are equilibrated with water an aqueous phase is established which is very similar to that of non-homogeneous gels produced by treating SiO_2 with $Ca(OH)_2$. There are some small but significant differences in experimental results between the present study and the earlier investigation of Greenberg and Chang at compositions close to Ca/Si = 0.8:1 in the solids (which is where the aqueous composition is very sensitive to the solid composition). The differences appear to be related to differences in experimental technique and not to differences in the properties of the C–S–H gels. The solubility of C–S–H gels appears to change slightly with ageing both at room temperature and at 80 °C. This may reflect a real change in free energy of the gel, or some contamination during the ageing process.

The aqueous solubility of C–S–H gels can be described reasonably well by assuming solid solutions between amorphous SiO_2 and $Ca(OH)_2$ with an intermediate compound having a composition close to that of the mineral tobermorite (Ca/Si = 0.833:1). The free energies of formation of all the solid phases in the system are then described in terms of a few parameters. The solid-solution model based on tobermorite is also consistent with current concepts of the atomic structure of C–S–H gels. Nevertheless, this model is not unique and the experimental data can be described equally well by an alternative model based on solid solutions with an intermediate compound with Ca/Si = 0.5:1.

The thermodynamic model has considerable power for predicting the behaviour of cement (or concretes) and changes in cement chemistry as a result of chemical reactions either with the external environment, or with internal additives.

Appendix

Thermodynamic Modelling of the $CaO–SiO_2–H_2O$ *System.*—Modelling of the composition of the liquid and solid phases based on thermodynamic data was accomplished using the computer code SOLGASMIX.[17] This code finds the equilibrium state of a system by minimising its total free energy within the overall constraints of constant composition, charge neutrality, and, in the present case, constant total pressure. It requires, as input, thermodynamic parameters for the key species in both the liquid and solid phases.

The standard free energies of formation for the aqueous species which were used in the modelling are listed in Table A1. There is some uncertainty in the literature concerning the values for the dissociation constants of silicic acid, H_4SiO_4.

Table A1. Thermodynamic data used in the calculations of solution equilibria

Species[a]	$\Delta_f G^\circ_{298.15\,K}$/ J mol^{-1}	Ref.	Comment	
H^+	0			
$H_2O(l)$	−237 160	*b*	NBS values[20]	−237 178
$H_2O(g)$	−228 603	*b*		−228 589
OH^-	−157 293	20		
Ca^{2+}	−552 806	*b*		−553 543
$Ca(OH)^+$	−717 972	*b*		−718 393
$Ca(OH)_2$[c]	−867 392	*b*		−868 138
$Ca(OH)_2(c)$	−897 498	*b*		−898 556
SiO_4^{4-}	−1 002 986		Derived from the solubility of silica (quartz) in water as H_4SiO_4[21,22] together with the dissociation constants[18,19] (see Table A2)	
$HSiO_4^{3-}$	−1 100 591			
$H_2SiO_4^{2-}$	−1 183 926			
$H_3SiO_4^-$	−1 252 992			
H_4SiO_4	−1 307 788[d]			
SiO_2[e]	−848 530		Derived from solubility in aqueous solution[23] compared with that of α-quartz[21,22,f]	

[a] In aqueous solution unless indicated to be crystalline (c) or gaseous (g). [b] D. Garvin, V. B. Parker, and H. J. White, 'Codata Thermodynamic Tables. Selection of Some Compounds of Calcium and Related Mixtures,' National Bureau of Standards, Washington, 1986. [c] Undissociated. [d] The NBS value (see footnote *b*) of $\Delta_f G^\circ_{298.15\,K} = -1\,316\,705$ J mol^{-1} is acknowledged to be wrong. (D. Garvin, personal communication, 1984.) [e] Amorphous, in contact with water. [f] The NBS value[20] for $\Delta_f G^\circ_{298.15\,K}$ [SiO_2(α-quartz)] $= -856\,674$ J mol^{-1}. The solubility of α-quartz in water at 25 °C is taken as 6 p.p.m. (w/w).[21,22] The solubility of amorphous silica in water at 25 °C is taken as 138 p.p.m. (w/w) (2.3×10^{-3} mol l^{-1}).[23]

Table A2. Dissociation constants for $H_xSiO_4^{(4-x)-}$ species in aqueous solution; $H_xSiO_4^{(4-x)-} \rightleftharpoons H_{x-1}SiO_4^{[4-(x-1)]-} + H^+$; $-\log_{10}K_x = pK_x$ where K_x = equilibrium constant

	pK_x	
x	Cobble[18]	Stumm and Morgan[19]
4	9.6	9.46
3	12.1	12.56
2	14.6 *	15.66 *
1	17.1 *	18.76 *

In Table A1 the values of $\Delta_f G^\circ_{298.15\,K}$ for $H_3SiO_4^-$, $H_2SiO_4^{2-}$, $HSiO_4^{3-}$, and SiO_4^{4-} use the p*K* values 9.6, 12.1, 14.6, and 17.1.
* Estimated.

Two sets of constants were tried (Table A2) based on the first and second dissociation constants given by either Cobble[18] or Stumm and Morgan.[19] (The higher dissociation constants were estimated by assuming a constant increment for each successive value of pK.) Subsequent use of the model revealed that the results were relatively insensitive to which set was used. In all the results quoted here the set based on Cobble was used. It was also found necessary to make a significant adjustment to the value of the free energy of formation of undissociated silicic acid, H_4SiO_4, tabulated in ref. 20 since this value led to an overestimate of the measured solubility of α-quartz in dilute acid[21,22] by about a factor of twenty. The value given in Table A1 accurately reproduces the measured solubility.

Departures from ideal solubility in the aqueous phase were taken into account by the use of an activity coefficient, γ, for each aqueous species calculated using the Davies equation[19] (A1), where z is the net number of electronic charges on the species and I is the ionic strength of the solution.

$$\log_{10}\gamma = 0.5\,z^2\left(\frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - 0.3\,I\right) \qquad \text{(A1)}$$

The solid phases which form the end members of this system are amorphous silica (in whatever hydrated state is in equilibrium with water) and crystalline $Ca(OH)_2$ (portlandite). The standard free energies of formation which were used for these phases are also given in A1. The free energy of formation of amorphous SiO_2 has been adjusted with respect to that given in ref. 20 in order to account for the relative observed solubilities of amorphous SiO_2 and α-quartz.[21–23] The resulting database was then found to give acceptable agreement with experimental data for the solubility of amorphous SiO_2 as a function of pH and the solubility of portlandite. For example the pH and $[Ca]_T$ for portlandite in water at 25 °C were calculated to be 12.41 and 0.0225 respectively, whereas the corresponding measured values are 12.45 and 0.0203.

Several different models for the C–S–H gels (*i.e.* the solids of intermediate composition) were examined in an attempt to fit the solid–water equilibrium data. Following previous workers,[8,10], these models were based on the assumption that either of the end members can form a continuous series of solid solutions with a third solid of intermediate composition (but not with each other). We denote this intermediate compound as X and assume it to have the general formula nCaO·SiO$_2$·mH$_2$O. Greenberg and Chang[8] assumed X to be CaO·SiO$_2$·H$_2$O ($n = 1$, $m = 1$) whereas Fujii and Kondo[10] assumed X to be 5CaO·6SiO$_2$·5.5H$_2$O ($n = 0.833$, $m = 0.917$). This latter composition is that of one form of tobermorite and is justified as an intermediate compound because *X*-ray diffraction studies suggest it has some structural characteristics in common with C–S–H gels.[4,5] Although we assume that continuous solid solutions are possible it does not necessarily follow that every composition in the solid solution range can exist as a stable single phase in the phase diagram. We show later how the model can lead to limits on the extent of solid solubility in the stable phases.

Each end member is assumed to form a continuous solid solution with the intermediate compound, X. The free energy of each solid solution is then described by the normal expression for ideal mixing with two additional terms to describe non-ideal solid solubility. The first is a lattice stability term, characterised by the parameter L. This is an adjustment to the free energy of formation of one of the end members to account for the possibility that in a solid solution the end member may not be in its most stable structural configuration (*i.e.* the structure of the solid solution does not evolve smoothly into the most stable configuration for that end member). The second is a regular solution term, characterised by the parameter A, which accounts for interactions between the two end members in the solid solution.[24] The resulting expression for the free energy of formation of the solid solution between amorphous SiO_2 (denoted by S) and the compound X (*i.e.* $0 < \mathrm{Ca/Si} < n$) is (A2). In this expression x_S denotes the mole fraction of the SiO_2 end member and X has the formula nCaO·SiO$_2$·mH$_2$O. Thus the Ca/Si ratio in the solid solution is $n(1 - x_S)$. Similarly for C–S–H gels with Ca/Si $> n$ we have a solid solution between X and $Ca(OH)_2$ (portlandite, denoted by P). The corresponding free energy expression is (A3) where x_P is the mole fraction of portlandite and the Ca/Si ratio is $n/1 - x_P$).

$$\Delta_f G^\circ \text{ (per mol Si)} = x_S \Delta_f G_S{}^\circ + x_X \Delta_f G_X{}^\circ + RT(x_S \ln x_S + x_X \ln x_X) + L_{SX} x_S + A_{SX} x_S x_X \qquad \text{(A2)}$$

Table A3. Thermodynamic parameters used in the expressions for the free energy of formation of solid solutions [equations (A2) and (A3)]

	Model α (tobermorite)	Model β
n	0.833	0.500
m	0.917	1.500
$\Delta_f G_X^{\circ}$ (J per mol X)	−1 643 708	−1 548 329
L_{SX} (J per mol Si)	0	0
A_{SX} (J per mol Si)	2 000	−1 000
L_{PX} (J per mol Ca)	9 000	7 000
A_{PX} (J per mol Ca)	−29 000	−79 000

$X = n\text{CaO}\cdot\text{SiO}_2\cdot m\text{H}_2\text{O}$.

$$\Delta_f G^{\circ} \text{ (per mol Ca)} = x_P \Delta_f G_P^{\circ} + x_{X/n} \Delta_f G_{X/n}^{\circ} + RT(x_P \ln x_P + x_{X/n} \ln x_{X/n}) + L_{PX} x_P + A_{PX} x_P x_{X/n} \quad \text{(A3)}$$

The model was first tried by assuming (following Fujii and Kondo) the intermediate compound to be of tobermorite composition, *i.e.* $X = 0.833\text{CaO}\cdot\text{SiO}_2\cdot0.917\text{H}_2\text{O}$. The parameters L_{SX}, A_{SX}, L_{PX}, A_{PX}, and $\Delta_f G_X^{\circ}$ were varied in order to obtain the best fit between the model and the data points. This is shown by the curves labelled 'model α' in Figures 1—4, with parameter values given in Table A3. The fit to the data for $[\text{Ca}]_T$ is seen to be very good, but the model slightly overestimates $[\text{Si}]_T$ and underestimates pH in the range $0.6 < \text{Ca/Si} < 1.0:1$. This is the same range in which deviations are evident between different data sets and, indeed, model α provides a good fit to the pH data of Greenberg and Chang (Figure 3). The fit to the present data could not be improved merely by optimising the values of the thermodynamic parameters.

It is apparent from Figures 1—3 that the rapid change of pH and $[\text{Si}]_T$ with composition occurs at lower Ca/Si ratio in the present experiments than predicted by model α. Consequently, attempts were made to obtain a better fit by choosing intermediate compounds, X, of lower Ca/Si ratio. The compositions which were tried were $0.667\text{CaO}\cdot\text{SiO}_2\cdot1.33\text{H}_2\text{O}$, $0.667\text{CaO}\cdot\text{SiO}_2\cdot0.833\text{H}_2\text{O}$ (gyrolite), and $0.5\text{CaO}\cdot\text{SiO}_2\cdot1.5\text{H}_2\text{O}$. In no case could a much improved fit be achieved. For example, the curves labelled 'model β' are the best which could be obtained with $X = 0.5\text{CaO}\cdot\text{SiO}_2\cdot1.5\text{H}_2\text{O}$ (using parameters listed in Table A3). The fit to the experimental data is slightly better than that obtained with model α in some regions, but slightly worse in others. This example demonstrates that the choice of a solid-solution model, within the constraints imposed by equations (A2) and (A3), is not unique and that there are likely to be other similar models which would be just as good a fit to the data as either models α or β described here.

Although the fits of models α and β to the data are both equally good, they do have significantly different implications for the SiO_2–Ca(OH)_2 phase diagram. In particular, according to model β, there is a two-phase region for Ca/Si between about 0.1 and 0.7:1, whereas model α predicts a single solid-solution phase in the same composition range. Since the experimental data cannot distinguish between the models, the existence of a two-phase region in this composition range is uncertain. The same comments apply to a much narrower two-phase region predicted by model α near the tobermorite composition (Ca/Si = 0.833:1).

The free energy of formation of the C–S–H gel, according to the two models, as a function of composition across the whole range is shown in Figure 6. The free energies which are plotted are normalised so that the sum of the number of moles of SiO_2 and Ca(OH)_2 is unity and that Ca(OH)_2 is the only source of 'bound water,' *i.e.* the ratio $\text{CaO/H}_2\text{O} = 1:1$. This latter normalisation is achieved by subtracting the free energy of formation of the number of moles of water (Table A1) which are required to bring the $\text{CaO/H}_2\text{O}$ ratio in the gel to unity. This adjustment is justified since the aqueous solution composition does not depend on knowing the number of water molecules bound in the gel.

The data points plotted in Figure 6 are taken from Glasser *et al.*[16] who derived free energies of the gel *via* the solubility product of the aqueous species (Ca^{2+}, $\text{H}_2\text{SiO}_4^{2-}$, and OH^-) using the experimental data of Greenberg and Chang[8] and Fujii and Kondo.[10] The values tabulated by Glasser *et al.* have been normalised here in the same way as in models α and β so that they are all directly comparable. Although the free energies are all in reasonable agreement in the common composition range, the scatter of results given by Glasser *et al.* is rather large (≈ 6 kJ mol^{-1}, which is equivalent to a factor of ten expressed as a solubility product).

The increase in free energy of the portlandite solid solution [embodied in the positive lattice stability term, L_{PX}, in equation (A3) and Table A3] leads to a two-phase region at high calcium contents, as observed experimentally. The two phases are 'pure' portlandite and C–S–H gel with $\text{Ca/Si} \approx 1.7:1$. Thus the free-energy curves (Figure 6) for gels having $\text{Ca/Si} > 1.7:1$ are not accessible in the experiments because these gels are not stable with respect to the end members of the two-phase regions.

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