

## C-S-H Solubility Modeling At Different Temperatures

J. A. Gisby<sup>1</sup>, R.H. Davies<sup>1</sup>, A. T. Dinsdale<sup>1</sup>, M. Tyrer<sup>2</sup>, F. P. Glasser<sup>3</sup>,  
J. Hill<sup>4</sup>, P. Livesey<sup>5</sup>, C. Walker<sup>6</sup>

<sup>1</sup>National Physical Laboratory, Teddington, UK; <sup>2</sup>Imperial College London, UK;

<sup>3</sup>University of Aberdeen, UK; <sup>4</sup>AMECNNC, Cheshire, UK;

<sup>5</sup>Castle Cement Ltd, Clitheroe, UK; <sup>6</sup> Natural History Museum, London, UK

### Abstract

Thermodynamic models are recognised as a valuable tool in investigating the long-term stability of cement based materials in a repository environment. Work at the National Physical Laboratory (NPL) on the development and testing of such models for calcium silicate hydrate (C-S-H) gels is described. The ability of the model to predict the thermodynamic and phase behaviour of C-S-H gels in different aqueous environments, from room temperature up to 85 °C, is demonstrated by means of a comparison between calculations performed using the computer program MTDATA (Thermodynamics and Phase Equilibria Software from the NPL) and measured solubility data, such as pH and calcium and silicon concentrations in solution.

### 1. Introduction

The engineered component of a low and intermediate level nuclear waste repository in the United Kingdom will almost certainly consist primarily of ordinary Portland cement (OPC) based materials. OPC provides a chemical barrier by its ability to buffer the pH  $\geq 12$  as it dissolves in a percolating groundwater. A high pH in a repository is desirable because it helps to minimize the solubility of many radionuclides, metal corrosion and microbial activity. In order to assess the likely performance of the chemical barrier, reliable models are required with which to make predictions beyond the spatial and temporal limits imposed by experiment and observation.

The application of thermodynamic modeling to cement chemistry has been advocated by numerous authors over the last two decades [1-4]. Its development has been driven largely by the need for a predictive capability in modeling the near field processes, which govern the performance of proposed nuclear waste storage facilities. Early work [1-3] sought to develop pragmatic models with which to simulate the thermodynamic evolution of cements in the repository environment. In achieving this goal, of critical importance was the development of a robust description of the incongruent dissolution of C-S-H gel because of its major contribution to the longevity of the chemical barrier.

It is expected that a nuclear waste repository would experience elevated temperatures, due both to the heat of hydration of the cement and to radiolytic heating, and that this perturbation may last for thousands of years. Long-term experiments at elevated temperatures have been shown to have a marked effect on the solubility behavior of C-S-H gel [5]. Thus, developing a credible predictive model, which can be used to describe the dissolution of C-S-H gel at room and elevated temperatures, is of critical importance.

### 2. Previous Modeling Studies

The conventional modeling approach takes either one or two pure solid phases with variable solubility products and the model parameters are arbitrarily adjusted until a match

is made with the measured solubility data of the C-S-H system [1-3]. Whilst these models are pragmatic and effective, they are not based on strong thermodynamic theory, nor readily expanded to include elevated temperatures. Despite these observations, the Berner Model [3], and its variants, has been the most widely used owing to its elegant simplicity. A more thermodynamically rigorous description of the C-S-H system uses a solid solution aqueous solution based model [6-8], which can only be applied to Ca/Si ratios > 1.0 in the C-S-H gel and are only reliable at room temperature.

True free energy-based models (of which this paper represents one example) strive for greater flexibility and rely more on thermodynamic realism than earlier methods. They can therefore account for all Ca/Si ratios expected in the C-S-H gel and extend the limits of temperature.

### 3. MTDATA

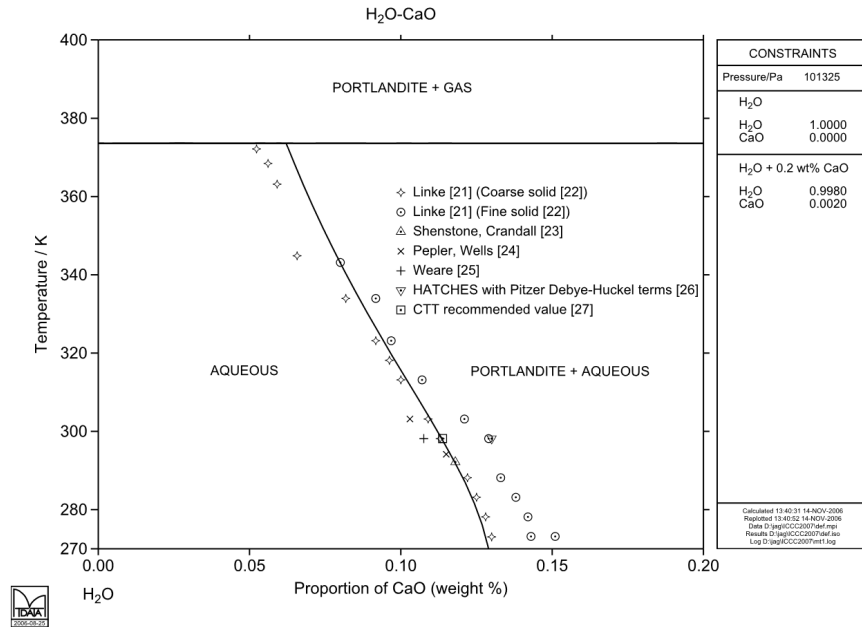
A number of computer programs implementing the principles of the calculation of chemical and phase equilibria, reviewed by Bale and Eriksson [9], have been reported over the years. Many of these have been limited to handling problems involving specific systems, types of materials or stoichiometric compounds, but this is not the case with MTDATA [10], a reliable and general software tool for calculating phase and chemical equilibria involving multiple solution or stoichiometric phases with ease and reliability. It provides true Gibbs energy minimisation through the solution of a non-linear optimisation problem with linear constraints using the NPL Numerical Optimisation Software Library (NOSL), which guarantees mathematically that the Gibbs energy reduces each time it is evaluated.

MTDATA has a long history of application dating back to the 1970s in fields such as ferrous and non-ferrous metallurgy [11-13], slag and matte chemistry [14-16], nuclear accident simulation [17], molten salt chemistry [18] and cement clinkering [19]. The aim of the work described here has been to develop a rigorous model and associated thermodynamic data for the C-S-H system, at room and elevated temperatures, which are compatible with existing NPL oxide and aqueous species databases.

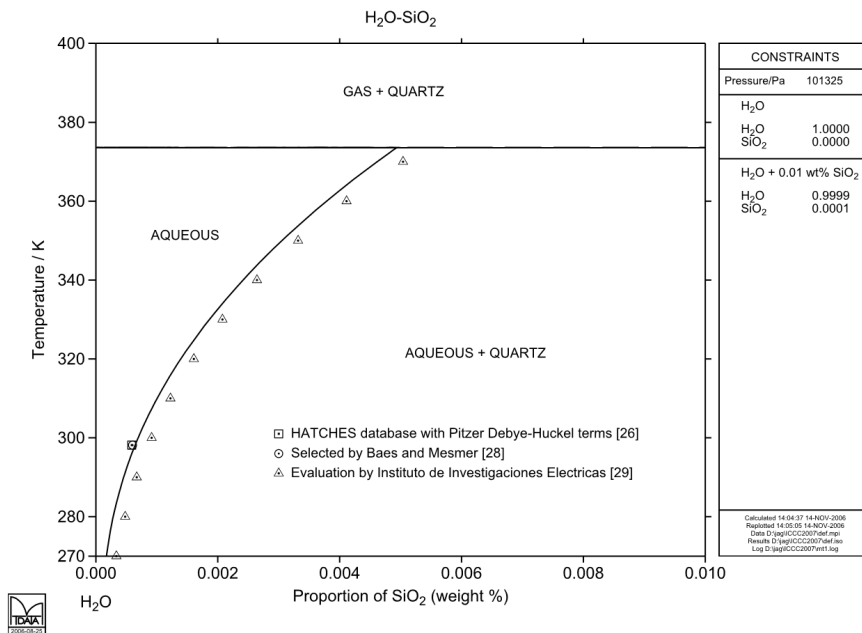
The CALPHAD [10] modeling principle embodied within MTDATA is that a database developer derives parameters to accurately represent the Gibbs energy of each phase that might form in a system as a function of temperature, composition and, if necessary, pressure. This is achieved using data assessment tools within MTDATA, which allow parameters to be optimised to give the best possible agreement between calculated thermodynamic properties (such as heat capacities, activities, enthalpies of mixing), phase equilibria (solubilities) and collated experimental properties. Generally, such data assessment is undertaken for “small” systems (one, two or three components combined) allowing predictions to be made in “large” multicomponent (multi-element) systems, which may contain a great many species. Examples of calculated phase diagrams for the CaO-H<sub>2</sub>O and SiO<sub>2</sub>-H<sub>2</sub>O binary oxide systems, compared with experimental data, are shown in Figures 1 and 2, respectively.

In single point calculations, predictions are made by specifying an overall system composition and temperature. MTDATA then determines the combination of phases and phase compositions that gives the lowest overall Gibbs energy, based upon the Gibbs energy parameters in its databases, and reports that as the equilibrium state. A series of calculations of this type can be completed automatically and the results presented in a range of different ways including binary phase diagrams, ternary isothermal sections, cuts

through multicomponent systems or general x-y plots, where x and y can be overall composition variables (phase amounts or speciation variables such as molalities), temperature, pressure, thermodynamic properties (such as heat capacity or enthalpy), pH, or Eh. All of these properties are calculable from the stored Gibbs energy functions.



**Figure 1.** CaO-H<sub>2</sub>O phase diagram showing the stability field of the aqueous phase in equilibrium with gas and portlandite. Data for Ca(OH)<sub>2</sub> from SGSUB [20] were adjusted slightly to give correct CaO-H<sub>2</sub>O equilibria [21-27].



**Figure 2.** SiO<sub>2</sub>-H<sub>2</sub>O phase diagram showing the stability field of the aqueous phase in equilibrium with gas and quartz, compared with experimental data from [26, 28, 29].

#### 4. Modeling Approach

In the current work, the well established compound energy model [30] has been used to represent the Gibbs energy of the C-S-H system as a function of composition and temperature, extending earlier work on C-S-H and SiO<sub>2</sub> gels [31,32] by fully modeling the temperature dependence of the Gibbs energy of the phase, including Cp(T) of the species (or unaries) at its solution limits, consistent with reference states used throughout the worldwide modeling group SGTE [20]. This ensured compatibility between the C-S-H model and a wealth of data already available for oxide phases, alloys, gaseous species and aqueous solutions, including high ionic strength aqueous solutions, available in other MTDATA databases.

The compound energy model distributes species among a series of sublattices where they may interact either ideally or non-ideally. In the current model, the C-S-H gel was represented using five sublattices, as in [32], with occupancies as follows, where Va indicates a potentially vacant sublattice:

Sublattice	Occupancy	Number and Type of Sites
1	CaO	$\frac{1}{3}$ interlayer site, 2 sites pairing with SiO <sub>2</sub>
2	CaO, H <sub>2</sub> O	1 interlayer site
3	SiO <sub>2</sub>	2 sites pairing with CaO
4	SiO <sub>2</sub> , Va	1 site representing bridging SiO <sub>2</sub> or Vacancy
5	H <sub>2</sub> O	6 sites

Gibbs energies of unaries formed by taking one species from each sublattice in turn, i.e. (CaO)<sub>7/3</sub>(H<sub>2</sub>O)<sub>1</sub>(SiO<sub>2</sub>)<sub>2</sub>(SiO<sub>2</sub>)<sub>1</sub>(H<sub>2</sub>O)<sub>6</sub>, (CaO)<sub>7/3</sub>(CaO)<sub>1</sub>(SiO<sub>2</sub>)<sub>2</sub>(SiO<sub>2</sub>)<sub>1</sub>(H<sub>2</sub>O)<sub>6</sub>, (CaO)<sub>7/3</sub>(CaO)<sub>1</sub>(SiO<sub>2</sub>)<sub>2</sub>(Va)<sub>1</sub>(H<sub>2</sub>O)<sub>6</sub> and (CaO)<sub>7/3</sub>(H<sub>2</sub>O)<sub>1</sub>(SiO<sub>2</sub>)<sub>2</sub>(Va)<sub>1</sub>(H<sub>2</sub>O)<sub>6</sub> were described using a standard function of the form:  $G(T) = A + BT + CT \ln T + DT^2 + ET^3 + F/T$

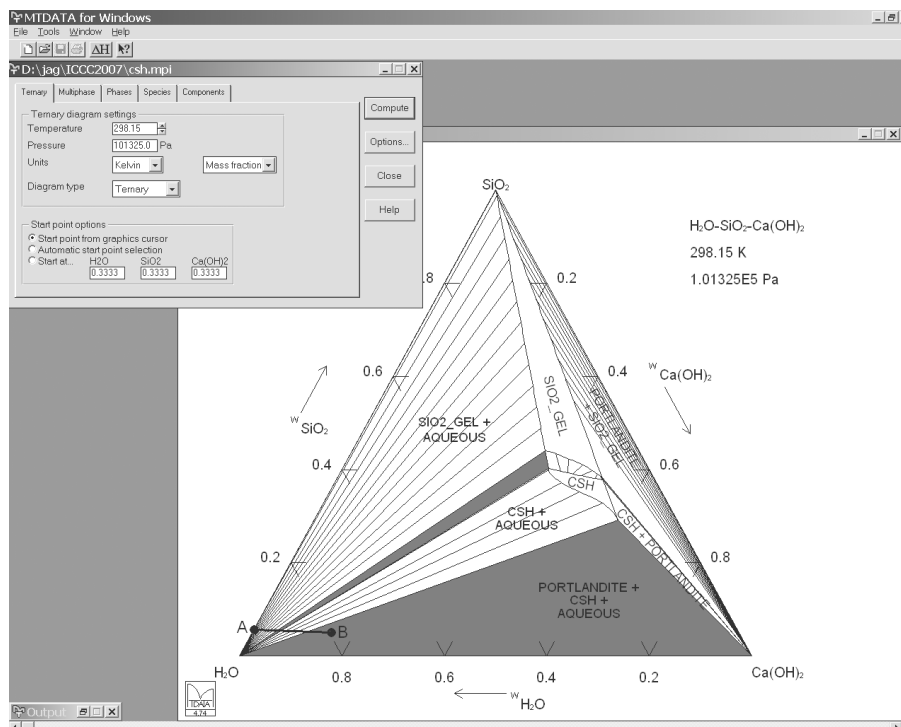
The *C*, *D*, *E*, *F* parameters were obtained from estimates of Cp(T) for each species guided by those for portlandite and notional compounds like plombierite, for which thermodynamic data could be found in the SGTE substance database [20]. Initial values for the entropy-like *B* parameters and enthalpy-like *A* parameters were estimated on a similar basis. The *A* parameters were then adjusted, along with others introduced to represent excess Gibbs energies of interaction between sublattice species, using MTDATA's data assessment tools to reproduce measured compositions of C-S-H gel and aqueous phases in equilibrium from data available in the literature [1, 33-42].

The SiO<sub>2</sub> gel was represented using two sublattices with occupancies as follows:

Sublattice	Occupancy	Number of Sites
1	Ca <sub>7/3</sub> H <sub>14</sub> O <sub>28/3</sub> , Ca <sub>10/3</sub> H <sub>12</sub> O <sub>28/3</sub> , Va	1
2	SiO <sub>2</sub>	3

This model allow the composition of the SiO<sub>2</sub> gel phase to vary within a triangle formed by the unaries (Ca<sub>7/3</sub>H<sub>14</sub>O<sub>28/3</sub>)<sub>1</sub>(SiO<sub>2</sub>)<sub>3</sub>, (Ca<sub>10/3</sub>H<sub>12</sub>O<sub>28/3</sub>)<sub>1</sub>(SiO<sub>2</sub>)<sub>3</sub> and (SiO<sub>2</sub>)<sub>3</sub> as opposed to a line used by Kulik and Kersten [31]. The first two of these unaries lie along the SiO<sub>2</sub> rich side of the composition parallelogram formed by the four C-S-H unaries. Data for the pure SiO<sub>2</sub> unary were based upon those for amorphous SiO<sub>2</sub> in the SGTE substance database. Parameters representing interactions between species on the first sublattice in this phase were derived, as for the C-S-H gel phase, to represent experimental phase equilibrium and experimental solubility data as closely as possible.

Calculations are most flexibly undertaken in MTDATA by specifying start and end compositions at a fixed temperature or start and end temperatures with a fixed composition. The program will perform a series of phase equilibrium calculations for conditions varying between the specified extremes and results can be plotted in terms of phase amounts, aqueous species, element distributions or pH values. Thermodynamic equilibria between C-S-H and SiO<sub>2</sub> gels, portlandite and an aqueous phase could, for example, be calculated by stepping across the H<sub>2</sub>O-SiO<sub>2</sub>-Ca(OH)<sub>2</sub> composition triangle between points A and B, shown in Figure 3, accounting for all expected Ca/Si ratios of C-S-H gels in OPC. These points correspond to overall systems containing 1kg of H<sub>2</sub>O and 1 mole of SiO<sub>2</sub> with 0 (A) and 2.5 (B) moles of CaO.



**Figure 3.** MTDATA calculating a ternary phase diagram of the system Ca(OH)<sub>2</sub>-SiO<sub>2</sub>-H<sub>2</sub>O at room temperature and pressure. Axes of diagram indicate mass fraction of components.

Figure 3 takes the form of a screen shot of how MTDATA would actually appear when calculating an isothermal section showing phase equilibria within the H<sub>2</sub>O-SiO<sub>2</sub>-Ca(OH)<sub>2</sub> composition triangle at 298.15 K. The window to the top left is where the temperature and composition scale (mass or mole fraction) for the diagram is selected. Within the triangle itself white areas indicate single phase fields, tie-lines indicate two phase fields and shaded tie-triangles indicate three phase fields.

Since the data for the C-S-H and SiO<sub>2</sub> phases, for other stoichiometric phases such as quartz and portlandite and for aqueous species (in the MTDATA implementation of the SUPERCRT-98 database) all have Gibbs energies modeled as a function of temperature, as already described, equilibria can be calculated at elevated temperatures just as at room temperature using these data.

Surprisingly few long-term experiments of C-S-H gels maintained at high temperatures have been reported. Work by Glasser *et.al.* [43] has been chosen with which to compare the results of the predictive calculations.

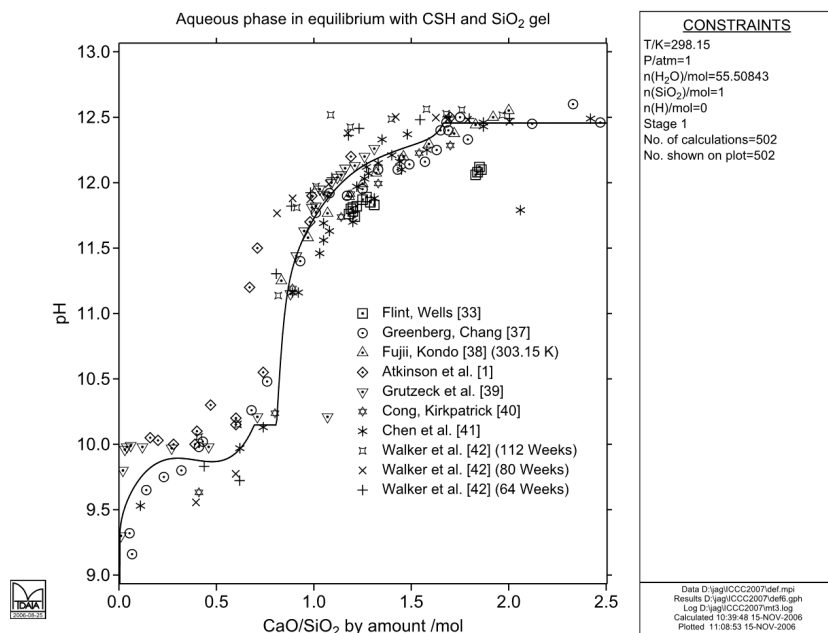
The thermodynamic data derived for the C-S-H and SiO<sub>2</sub> gel phases also allow calculations to be carried out in which leaching by pure water is simulated, using MTDATA's "built-in" process modeling application. A series of calculations was undertaken in which a C-S-H gel with an initial Ca/Si ratio = 2.7 was equilibrated with successive volumes of pure water at room temperature, the equilibrated aqueous phase being replaced each time. Predicted CaO and SiO<sub>2</sub> solubilities and pH values were plotted against the cumulative volume of water for comparison with experimental data published by Harris et al [44].

## 5. Results and Discussion

### 5.1. C-S-H solubility at room temperature

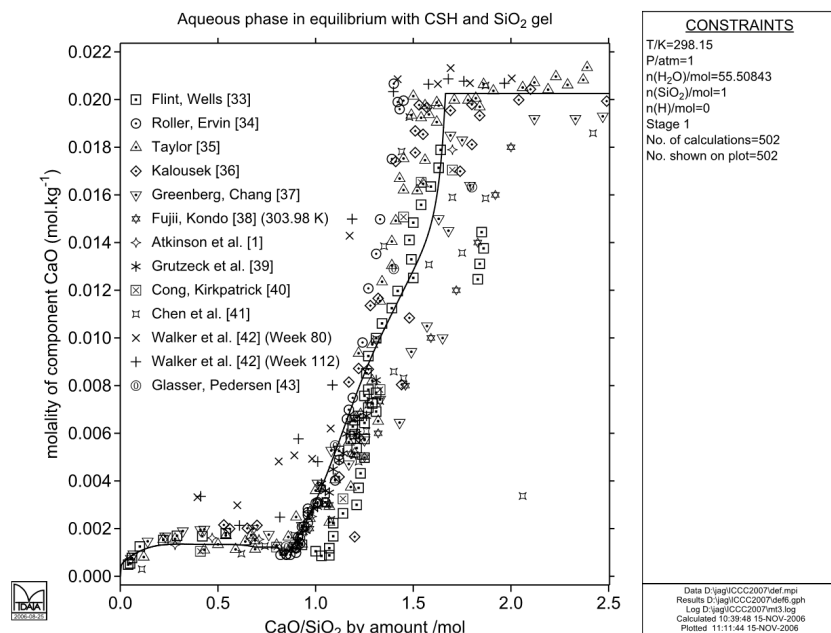
Both the predicted and experimentally derived pH and calcium and silicon concentrations are shown in Figures 4, 5 and 6, respectively, as a function of Ca/Si ratio in the solid phase(s) (including contributions from portlandite and amorphous silica). The experimental data are well matched by the model predictions for all expected Ca/Si ratios in the solid phase(s). The model can therefore be used beyond the compositional limits imposed by other approaches.

The thermodynamic rigour inherent in the modeling approach described here means that not only can the pH and composition of the aqueous solution be predicted, but also a wide range of other thermodynamic properties and phase equilibria involving other phases in the C-S-H system, including the effects of altering temperature. The use of reference states compatible with those adopted in existing MTDATA databases for materials such as complex oxide and sulphide solutions, alloys and high ionic strength aqueous solutions allows the interaction of C-S-H gels with such phases to be predicted. Calculations of this type provide a consistency test of the model framework and parameters derived for the gel phases.

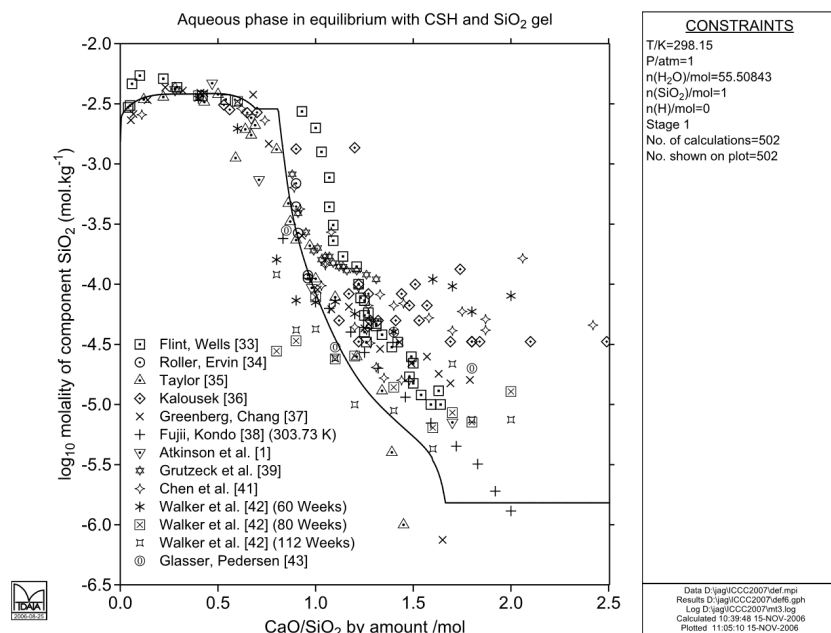


**Figure 4.** Calculated pH in solution as a function of CaO/SiO<sub>2</sub> ratio in the solid phase(s) (solid line) compared to relevant experimental data.

It should be noted that C-S-H gels are generally considered to be metastable because they continue to react very slowly, eventually forming other CaO-SiO<sub>2</sub> phases. MTDATA predicts this true equilibrium state but metastable equilibria can be studied by “classifying as absent” long term decomposition products, or removing them from consideration in the calculations.



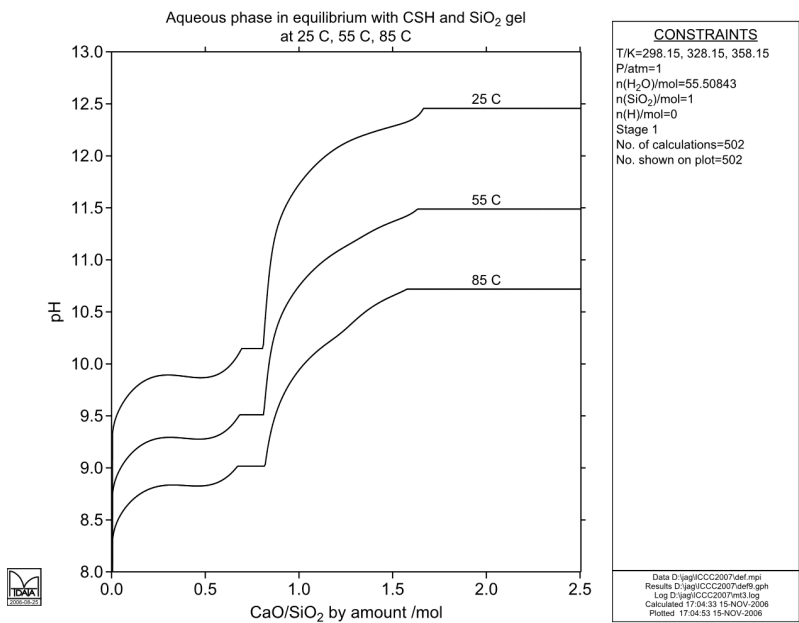
**Figure 5.** Calculated CaO in solution as a function of CaO/SiO<sub>2</sub> in the solid phase(s) (solid line) compared to relevant experimental data.



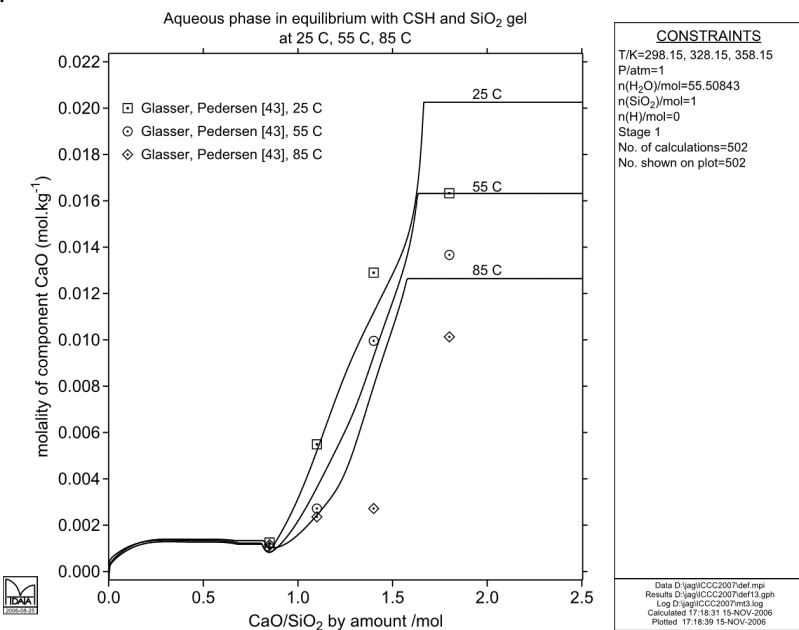
**Figure 6.** Calculated SiO<sub>2</sub> concentration in solution as a function of CaO/SiO<sub>2</sub> in the solid phase(s) (solid line) compared to relevant experimental data.

It has been observed by several authors that the experimental data divide into two populations, depending on whether the solid C-S-H phase has been prepared directly from ions in solution (i.e. by direct reaction or double decomposition) or from the hydration and subsequent leaching of tricalcium silicate (the latter route forming the least soluble solid).

For the purposes of this model, parameters have been derived to reproduce the lower SiO<sub>2</sub> solubility curve, thought to be appropriate to the most stable gel structure, although reproducing either curve is relatively straightforward.



**Figure 7.** Predicted pH in solution plotted against the CaO/SiO<sub>2</sub> ratio in the solid phase(s) at different temperatures.



**Figure 8.** Predicted and experimental CaO concentrations in solution plotted against the CaO/SiO<sub>2</sub> ratio in the solid phase(s) at different temperatures.

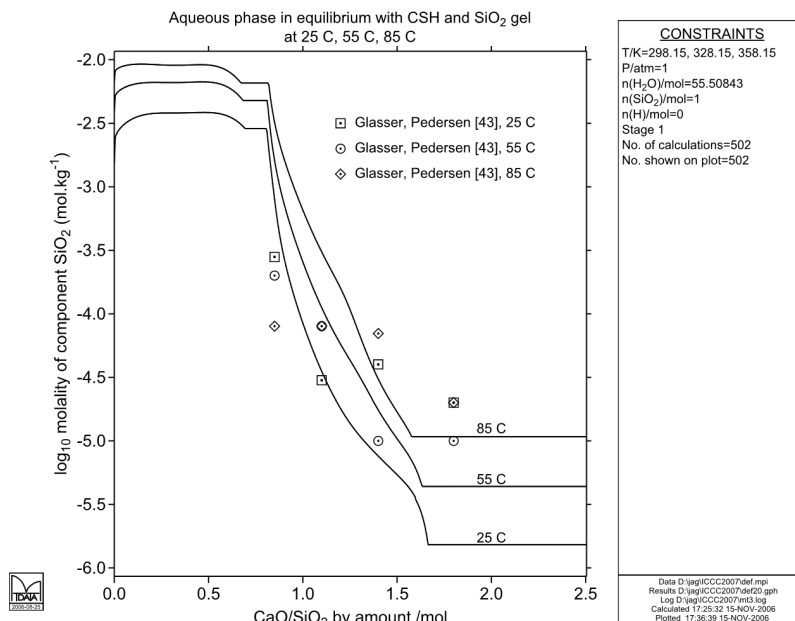
### 5.2. C-S-H solubility at higher temperatures

The predicted solubility of C-S-H gels at elevated temperature and pH are shown in Figures 7 - 9 with experimental data [43] superimposed in Figures 8 and 9. It should be noted that the model predictions were not fitted to the experimental data shown. The order and shape of each curve in Figures 8 and 9 is similar for both predicted and observed results, reflecting a decreasing solubility of C-S-H gel with increasing temperature. The



general magnitude of the changes in solubility with temperature are predicted well, although the match between absolute solubility values at high CaO/SiO<sub>2</sub> ratios, appears poor. When Figure 5 is taken into account, however, it is clear that the room temperature solubility results of [43] for CaO/SiO<sub>2</sub> greater than 1.5 are not representative of the bulk of the experimental solubility data available.

As more high temperature experimental data become available there is every reason to believe that the current calculated results will provide a better match.



**Figure 9.** Predicted and experimental SiO<sub>2</sub> concentrations in solution plotted against the CaO/SiO<sub>2</sub> ratio in the solid phase(s) at different temperatures.

### 5.3. Leaching simulation

The pH and CaO and SiO<sub>2</sub> concentrations in aqueous solution, as predicted using MTDATA and experimentally measured [44], during the leaching of a portlandite/C-S-H gel mixture are shown in Figures 10 and 11. The experimental data are well matched by the predicted model. The thermodynamic properties of the C-S-H gel used for this leaching simulation were derived from the previous calculations to predict the solubility data shown in Figures 4 - 6. These results provide further evidence for the validity of the model and the assumption that the dissolution of the solid phase(s) in the C-S-H system can be predicted by means of phase equilibrium calculations.

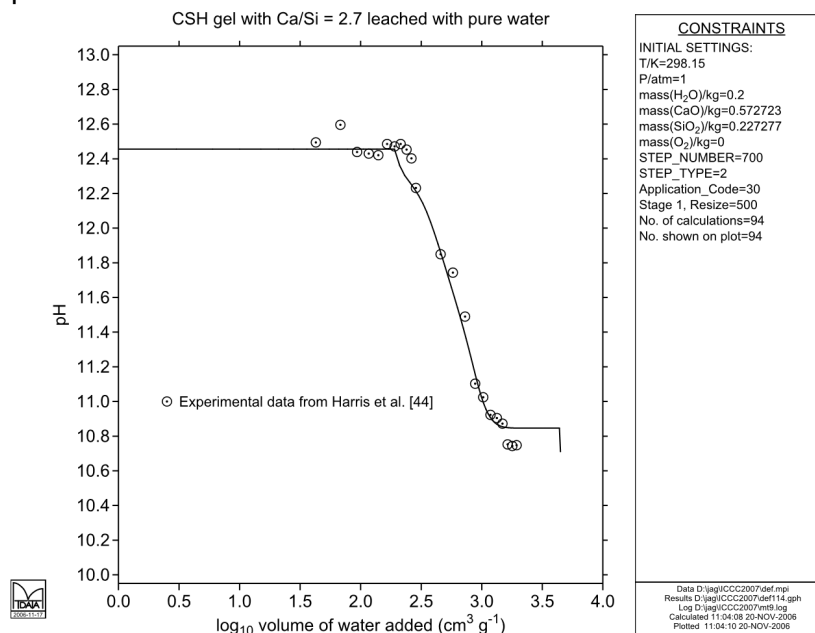
## 6. Conclusions

This work describes the use of a sub-lattice model as a basis for modeling the incongruent dissolution of C-S-H gel at different temperatures. The model correctly predicts the pH and calcium and silicon concentrations as a function of the Ca/Si ratio of the solid phase(s) at room temperature and as a function of volume of water added in simple leaching calculations and describes the general trends in the available solubility data at higher temperatures.

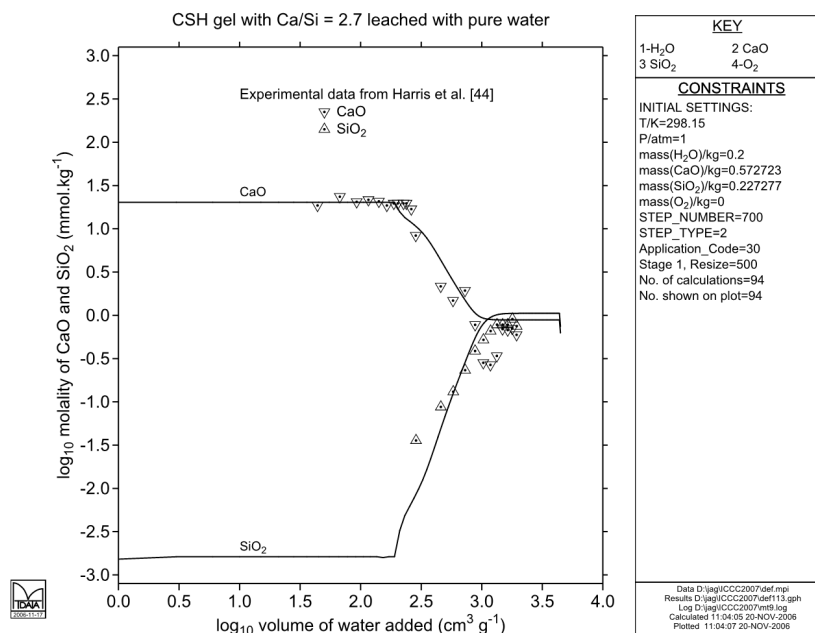
Rather than imposing constraints, the sub-lattice model imparts a degree of flexibility that can be used to include other previously unaddressed variables. Ongoing work includes

mixing of  $\text{Al}_2\text{O}_3$  and alkali metal hydroxides in the C-S-H sublattice, collating available Pitzer virial coefficients for calculations at high ionic strength, and the solubility behaviour of other cement hydrate phases under a range of physicochemical conditions.

Ultimately, the harmonisation of data for cementitious phases with those for pollutant species and radionuclides will increase the range of systems, which may be addressed. This may lead to coupling of MTDATA to other codes; for example groundwater transport, in order to assess the likely behaviour of cemented wastefoms and structures for environmental protection.



**Figure 10.** Predicted pH of the aqueous phase plotted against the volume of pure water added at 25 °C in a leaching simulation for a simple mixture of portlandite/C-S-H gel with an initial Ca/Si ratio = 2.7.



**Figure 11.** Predicted CaO and SiO<sub>2</sub> concentrations in the aqueous phase plotted against the volume of pure water added at 25 °C in a leaching simulation for a simple portlandite/C-S-H gel mixture with an initial Ca/Si ratio = 2.7.

## 7. Literature Cited

- [1] A. Atkinson, J.A. Hearne and C.F. Knights, Aqueous and Thermodynamic Modeling of CaO-SiO<sub>2</sub>-H<sub>2</sub>O Gels. UK Atomic Energy Authority, Report AERER12548, 1987.
- [2] F.P. Glasser, D.E. MacPhee and E.E. Lachowski. Solubility Modeling of Cements: Implications for Radioactive Waste Immobilization. *Mat. Res. Soc. Symp. Proc.* 84 (1987) 331-341.
- [3] U.R. Berner, Modeling the Incongruent Dissolution of Hydrated Cement Minerals. *Radiochimica Acta* 44/45 (1988) 387-393.
- [4] E.J. Reardon, An Ion Interaction Model for the Determination of Chemical Equilibria in Cement/Water Systems. *Cem. Concr. Res.* 20 (1990) 175-192.
- [5] F.P. Glasser, J. Pedersen, K. Goldthorpe, and M. Atkins, Solubility reactions of cement components with NaCl solutions : I. Ca(OH)<sub>2</sub> and C-S-H. *Adv. Cem. Res.* 17(2) (2005) 57-64.
- [6] M. Kersten, Aqueous Solubility Diagrams for Cementitious Waste Stabilization Systems. 1. The CSH Solid-Solution System. *Environ. Sci. Tech.* 30 (1996) 2286-2293.
- [7] S. Börjesson, A. Emrén and C. Ekberg, A thermodynamic model for the calcium silicate hydrate gel, modelled as a non-ideal binary solid solution. *Cem. Concr. Res.* 27 (1997) 1649-1657.
- [8] M. Mazibur Rahman, S. Nagasaki and S. Tanaka, A model for dissolution of CaO-SiO<sub>2</sub>-H<sub>2</sub>O gel at Ca/Si > 1. *Cem. Concr. Res.* 29 (1999) 1091-1097.
- [9] C W Bale, G Eriksson, *Canad. Metal. Quart.*, 29 (1990) 105-132.
- [10] R.H. Davies, A.T. Dinsdale, J.A. Gisby, J.A.J. Robinson, S.M. Martin, MTDATA - Thermodynamics and Phase Equilibrium Software from the National Physical Laboratory, *CALPHAD*, 26(2) (2002) 229-271.
- [11] C. Hunt, J. Nottay, A. Brewin, A.T. Dinsdale, NPL Report MATC(A) 83, (2002).
- [12] J. Wang, S. van der Zwaag, 2001, Composition Design of a Novel P Containing TRIP Steel, *Z. Metallkd.*, 92 (2001) 1299-1311.
- [13] D C Putman, R C Thomson, Modeling Microstructural Evolution of Austempered Ductile Iron, *International Journal of Cast Metals Research*, 16(1), (2003), 191-196.
- [14] P. Taskinen, A.T. Dinsdale, J.A. Gisby, *Industrial Slag Chemistry - A Case Study of Computational Thermodynamics*, Metal Separation Technologies III, Copper Mountain (2004).
- [15] J.A. Gisby, A.T. Dinsdale, I. Barton-Jones, A. Gibbon, P.A. Taskinen, J.R. Taylor, Phase Equilibria in Oxide and Sulphide Systems, in *Sulfide Smelting 2002*, Eds. R.L. Stephens, H.Y. Sohn, TMS Meeting, Seattle (2002).
- [16] T.I. Barry, A.T. Dinsdale, J.A. Gisby, Predictive Thermochemistry and Phase Equilibria of Slags, *JOM*, 45(4) (1993) 32-38.
- [17] R.G.J. Ball, M.A. Mignanelli, T.I. Barry, J.A. Gisby, The calculation of phase equilibria of oxide core-concrete systems, *J. Nucl. Mater.*, 201, (1993), 238-249.
- [18] T.I. Barry, A.T. Dinsdale, *Thermodynamics of Metal-Gas-Liquid Reactions*, *Mat. Sci. Tech.* 3 (1987) 501-511.
- [19] T.I. Barry, F.P. Glasser, Calculation of Portland cement clinkering reactions, *Adv. Cem. Res.* 12(1) (2000) 19-28.
- [20] SGTE substance database, *Thermodynamic Properties of Inorganic Materials*, Landolt-Börnstein Group IV (Physical Chemistry), Volume 19, Pub. Springer Berlin / Heidelberg.
- [21] W.F. Linke, *Solubilities of Inorganic and Metal-Organic Compounds (A-Ir) Vol I*, 4th Ed. (1958), Ed. F W Linke, D van Nostrand Company Inc., Princeton.
- [22] H. Bassett, Jr., *J. Chem. Soc. (Lond)*, (1934), 1270-1275

- [23] Shenstone, Crandall, J. Chem. Soc. (Lond), 43 (1883) 550.
- [24] R.B. Pepler, L.A. Wells, 1954, J. Res. Nat. Bur. Stand., 52 (1954) 75-92.
- [25] J.H. Weare, Reviews in Mineralogy 17, Eds. I.S.E. Carmichael, H.P. Eugster, Chapter 5, (1987), 143-176
- [26] MTDATA implementation of HATCHES: A Referenced Thermodynamic Database for Chemical Equilibrium Studies, K.A. Bond, T.G. Heath, C.J. Tweed, Nirex Report NSS/R379, December 1997.
- [27] CODATA Thermodynamic Tables, 1987, Eds. D. Garvin, V.B. Parker, H.J. White, Hemisphere Publishing Corp., New York,
- [28] C.F. Baes, R.E. Mesmer, The Hydrolysis of Cations, Wiley-Interscience, New York (1976).
- [29] M.P. Verma, Proceedings World Geothermal Congress, Kyushu - Tohoku, Japan, May 28 -June 10 (2000).
- [30] T.I. Barry, A.T. Dinsdale, J.A. Gisby, B Hallstedt, M Hillert, B Jansson, S Jonsson, B. Sundman, J.R. Taylor, The compound energy model for ionic solutions with applications to solid oxides, J. Phase Equilibria, 13(5) (1992) 459-475.
- [31] D.A. Kulik and M. Kersten, Aqueous Solubility Diagrams for Cementitious Waste Stabilization Systems: II, End-Member Stoichiometries of Ideal Calcium Silicate Hydrate Solid Solutions. J. Am. Cer. Soc. 84(12) (2001) 3017-26.
- [32] J.J. Thomas, H.M. Jennings, Free-Energy-Based Model of Chemical Equilibria in the CaO-SiO<sub>2</sub>-H<sub>2</sub>O System, J. Am. Ceram. Soc., 83(3), (1998), 606-612.
- [33] E.P. Flint, L.S. Wells, Study of the system CaO-SiO<sub>2</sub>-H<sub>2</sub>O at 30°C and of the reaction of water on anhydrous calcium silicates, J. Res. Natl. Bur. Stan. 12 (1934) 751-783.
- [34] P.S. Roller, G. Ervin, Jr., The system calcium-silica-water at 30°. The association of silicate ion in dilute alkaline solution, J. Am. Chem. Soc. 62 (3) (1940) 461-471.
- [35] H.F.W. Taylor, Hydrated calcium silicates. Part I. Compound formation at ordinary temperature, J. Chem. Soc. 726 (1950) 3682-3690.
- [36] G. Kalousek, 1952. Application of differential thermal analysis in a study of the system lime-silica-water. In: Third international symposium on the chemistry of cement, London, 296-311.
- [37] S.A. Greenberg, T.N. Chang, Investigation of the colloidal hydrated calcium silicates. II. Solubility relationships in the calcium-silica-water system at 25°C, J. Phys. Chem. 69 (1965) 182-188.
- [38] K. Fujii, W. Kondo, Heterogeneous equilibrium of calcium silicate hydrate in water at 30°C, J. Chem. Soc./ Dalt. Trans. 2 (1981) 645-651.
- [39] M. Grutzeck, A. Benesi, B. Fanning, Silicon-29 magic angle spinning nuclear magnetic resonance study of calcium silicate hydrates, J. Am. Ceram. Soc. 72 (1989) 665-668.
- [40] X. Cong and R.J. Kirkpatrick, <sup>29</sup>Si MAS NMR study of the structure of calcium silicate hydrate, Adv. Cem. Bas. Mat. 3 (1996) 144-156.
- [41] J.J. Chen, J.J. Thomas, H.F.W. Taylor, H.M. Jennings, Solubility and structure of calcium silicate hydrate, Cem. Concr. Res. 34 (2004) 1499-1519.
- [42] C.S. Walker, D. Savage, M. Tyrer, and K.V. Ragnarsdottir, Non-ideal solid solution aqueous solution modeling of synthetic calcium silicate hydrate, Cem. Concr. Res. (accepted 2006).
- [43] F.P. Glasser, J. Pedersen, K. Goldthorpe, M. Atkins, Adv. Cem. Res., 17(2), (2005), 57-64.
- [44] Harris, A.W., Manning, M.C., Tearle, W.M. and Tweed, C.J., Testing of models of the dissolution of cements - leaching of synthetic CSH gels. Cement and Concrete Research, 32 (2002) 731-746.