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A THERMODYNAMIC MODEL FOR THE CALCIUM SILICATE HYDRATE GEL, MODELLED AS A NON-IDEAL BINARY SOLID SOLUTION

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ABSTRACT

Solubility calculations have been performed on the CaO-SiO_2-H_2O system. A modified version of the program SOLISOL was used to model the C-S-H gel as a non-ideal binary solid solution. To account for the non-ideality a mixing model of Margules type, expressing the Gibbs excess free energy of a solid solution as a function of the composition was used. The model indicates that the calcium rich gel coexists with almost pure $Ca(OH)_2(s)$. A program PAS-SIPHIC has been written to handle the solubility calculations in the region where the C-S-H phase coexists with Portlandite. © *1997 Elsevier Science Ltd*

Introduction

In the Swedish programme for radioactive waste disposal in deep rock repositories, cement or concrete is considered as solidification, backfill or construction material. It applies especially to disposal of low and intermediate level waste where substantial amounts of Portland cements are to be found. Thus, the near field chemistry of the repository will strongly be influenced by the cement. The transport of radionuclides through the cement matrix will be diffusion controlled. As the chemical environment in cement provides a high internal pH ($\sim$13) the transport of many radionuclides, especially the actinides, will be strongly retarded (1). With time the pH will decrease due to interaction with the groundwater. Thus, it is of importance to model the long term behaviour of the cement chemistry.

Well-hydrated ordinary Portland cement (OPC) consists of a heterogeneous cement matrix and an aqueous phase. The main solid phases in well-hydrated OPC are a calcium silicate hydrate (C-S-H) gel and $Ca(OH)_2(s)$. To predict the interactions of well-hydrated Portland cement with groundwater the CaO-SiO_2-H_2O system may serve as a simple model of the cement.

The C-S-H gel is non-crystalline, has a variable composition and dissolves incongruently. Modelling the chemical behaviour of such a phase using common thermodynamic equilibrium programs is difficult, as these often treat the solids as pure phases with fixed stoichiometric compositions.

Several thermodynamic models have been proposed to describe the incongruent behaviour of the C-S-H phase (2–5). In the present work the C-S-H phase is modelled as a non-ideal

binary solid solution. To model the dissolution of the C-S-H gel a modified version of the program SOLISOL (1,6) was used. In the equilibrium calculations SOLISOL makes use of the program PHREEQE (7).

The C-S-H Phase

The C-S-H phase is amorphous and has a variable composition ranging from a calcium to silicon molar ratio in the solid (Ca/Si) of ~1.8 to ~0.8. The calcium silicate hydrogel is said to form a solid solution (3,8). Greenberg and Chang (8) described the C-S-H gel as a binary solid solution with the end-members $Ca(OH)_2(s)$ and $CaH_2SiO_4(s)$. For Ca/Si ratio >1.4-1.8 the gel coexists with $Ca(OH)_2(s)$ (2,3,4,8,9).

Different methods to model the dissolution of the C-S-H gel have been proposed (2,3,4,5). These are often based on solubility data for the $CaO-SiO_2-H_2O$ system. The model for the C-S-H phase proposed by Greenberg and Chang (8) and considering it as an ideal binary solid solution, has been adopted earlier in modelling the dissolution of the gel using the SOLISOL program (1). To improve the solubility calculations, describing the gel as a non-ideal binary solid solution, a model for the excess free energy of Margules type (cf. Eq. (I)) has been added to the program.

Thermodynamic Model

To model the incongruent behaviour of the gel, describing it as non-ideal binary solid solution, the mixing model proposed by Guggenheim (10,11) has been used. The model expresses excess Gibbs free energy with a power series of the mole fractions (X_i) of the end-members. For a binary non-ideal solid solution the expression becomes

$$G_{excess} = X_1 X_2 [A_0 + A_1(X_1 - X_2) + A_2(X_1 - X_2)^2 + A_3(X_1 - X_2)^3 + \ldots] \qquad (I)$$

The parameters A_0, A_1, ... are not dependent on composition but on temperature and pressure. If the series is terminated after two terms we get

$$G_{excess} = X_1 X_2 [A_0 + A_1(X_1 - X_2)] \qquad (II)$$

The Gibbs excess free energy is also given by

$$G_{excess} = RT \sum_i X_i \ln \gamma_i \qquad (III)$$

where γ_i is the activity coefficient of end-member i. R and T are the molar gas constant and the temperature in Kelvin, respectively. If the standard states for the end-members in the solid solution are the pure end-members at the temperature and pressure of interest, G_{excess} must obey the following boundary conditions (12):

$$G_{excess} = 0 \text{ when } X_1 = 0$$

$$G_{excess} = 0 \text{ when } X_2 = 0$$

To obtain the activity coefficient of end-member i as a function of the composition of the solid solution the following expression given by Prausnitz (12) can be used
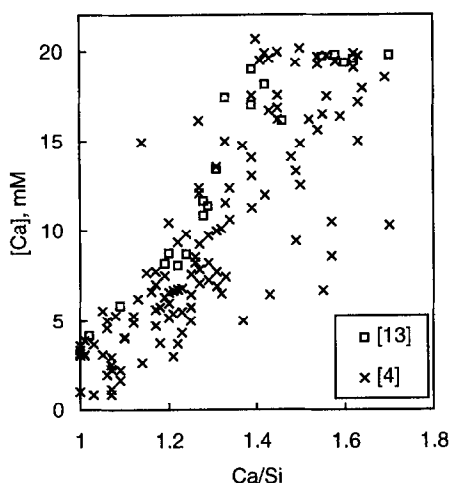
FIG. 1.

Experimental calcium concentration in the aqueous phase as a function of the Ca/Si molar ratio in the C-S-H phase. Experimental data compilation from (4) (Kalousek's data are given by the squares).

$$RT \ln \gamma_i = \left(\frac{\partial n_T G_{\text{excess}}}{\partial n_i} \right)_{T, P, n_j} \qquad \text{(IV)}$$

where n_i is the number of moles of end-member i and n_T is the total number of moles. The derevative is taken at constant temperature, pressure and number of moles of all other end-members except i. Using G_{excess} as given by Eq. (II) in Eq. (IV), the relationship between the activity coefficient for end-member 1 $(Ca(OH)_2(s))$ and the composition in the binary mixture becomes

$$RT \ln \gamma_1 = X_2^2 [A_0 + A_1 (3X_1 - X_2)] \qquad \text{(V)}$$

Using the relation $a_1 = X_1 \cdot \gamma_1$ Eq. (IV) can be written as

$$a_1 = X_1 \exp \left[\frac{X_2^2}{RT} [A_0 + A_1 (3X_1 - X_2)] \right] \qquad \text{(VI)}$$

where a_1 is the activity of the end-member $Ca(OH)_2(s)$.

Application of the Thermodynamic Model

Numerous experimental data on the $CaO\text{-}SiO_2\text{-}H_2O$ system are available in the literature and some of these data have been compiled by Berner (4). These data were used to construct Figure 1 showing the aqueous solution concentrations of calcium in equilibrium with the C-S-H phase for various Ca/Si molar ratios of the solid. The data points represent experiments performed at 17-30°C. As can be seen in the figure there is a great spread in the data points. States of crystallisation and analytical problems may have influenced the results. Thus, a series of experiments performed under similar conditions appears to be the best kind

<div align="center">TABLE 1</div>

<div align="center">Solubility Products for the End-Members Used in the Calculations (25°C)</div>

End-member	Reaction	Log K_S	Reference
$Ca(OH)_2(s)$	$Ca(OH)_2(s) + 2H^+ = Ca^{2+} + 2H_2O$	22.81	(14)
	$Ca(OH)_2(s) + 2H^+ = Ca^{2+} + 2H_2O$	22.70	(15)
$CaH_2SiO_4(s)$	$CaH_2SiO_4(s) = Ca^{2+} + H_2SiO_4^{2-}$	−7.07	(8)

of data to be used for determination of A_0 and A_1. It should be noted that the results then could be expected to give agreement only with cement samples similar to those used to determine the parameters. Among the data compiled by Berner, Kalousek's (13) data were chosen to be used in calculations to determine A_0 and A_1. These data were selected as their internal spread was small. Also, these experiments were performed at 25°C, the temperature at which the equilibrium constant for the end-member $CaH_2SiO_4(s)$ was determined.

Determination of A_0 and A_1

The saturation state of the solution regarding end-member i is given by the saturation index, SI_i

$$SI_i = \log \frac{IAP_i}{K_{S,i}} \tag{VII}$$

where IAP_i is the *ion activity product* of end-member i and $K_{S,i}$ is the solubility product of the pure end-member i. The activity of end-member i in a solid solution in equilibrium with an aqueous phase can be expressed by

$$a_i^{\text{solid solution}} = \frac{IAP_i}{K_{S,i}} \tag{VIII}$$

A detailed derivation of Eq. (VIII) is given in (1). Combining Equations (VII) and (VIII) the activity of the end-member $Ca(OH)_2(s)$ can be calculated according to

$$a_{Ca(OH)2} = 10^{SI_{Ca(OH)2}} \tag{IX}$$

Speciation calculations were performed with the program PHREEQE on Kalousek's data to obtain $SI_{Ca(OH)2(s)}$ values for various Ca/Si ratios. As no pH-values were reported for Kalousek's data, PHREEQE was allowed to use pH adjustments for the charge imbalances.

Two databases were available for the calculations; HATCHES5.0 (14) and CHEMVAL6 (15). Of those the CHEMVAL6 gave Si solubilities which were at least 2 orders of magnitude higher than observed. Hence, HATCHES5.0 was used in the calculations.

Further, the two databases give different values of the solubility product for $Ca(OH)_2(s)$, log K_S = 22.81 (HATCHES5.0) and log K_S = 22.70 (CHEMVAL6), (cf. Table 1). This difference together with other uncertainties in thermodynamic data will affect the saturation index of $Ca(OH)_2(s)$. To investigate the effect of the two different values of the solubility produvts HATCHES5.0 was extended with the CHEMVAL6 thermodynamic data on $Ca(OH)_2(s)$.
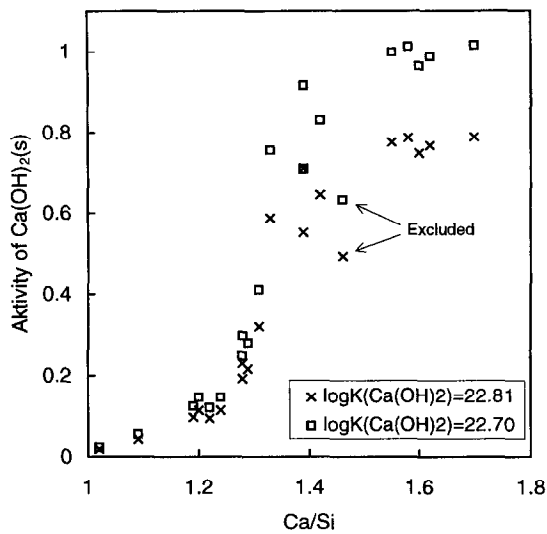
FIG. 2.

Calculated activity of the end-member $Ca(OH)_2(s)$ as a function of composition according to Eq. (IX). Two different values on the solubility product for $Ca(OH)_2(s)$ were used, cf. Tab. 1.

Speciation calculations were performed for each solubility product. The obtained activity values (cf. Eq. (IX)) are given as a function of the Ca/Si molar ratio in Figure 2. The crosses represent the speciation calculations with $logK_S = 22.81$. Calculations with $logK_S = 22.70$ are plotted as squares. Somewhere in the Ca/Si interval 1.4-1.5 the activity becomes approximately constant, cf. Fig. 2.

For both sets of the calculated activities shown in Fig. 2 values for the parameters A_0 and A_1 in the Guggenheim equation (cf. Eq. (VI)) were determined. This was done by a least square fit. Values from the region where the gel coexists with $Ca(OH)_2(s)$ were omitted from the fitting procedure. Also excluded from the calculations were the points at the Ca/Si ratio 1.46 (marked in the figure with arrows) as they dramatically differ from the trend. The results are given in Table 2.

The confidence intervals listed in Table 2 are one standard deviation wide and originate from the curve fit, i.e. not experimental or model errors. The standard deviations are calculated according to,

$$\sigma_i = \sqrt{C_{ii}\chi^2}$$

TABLE 2

Fitted values for the parameters
A_0 and A_1

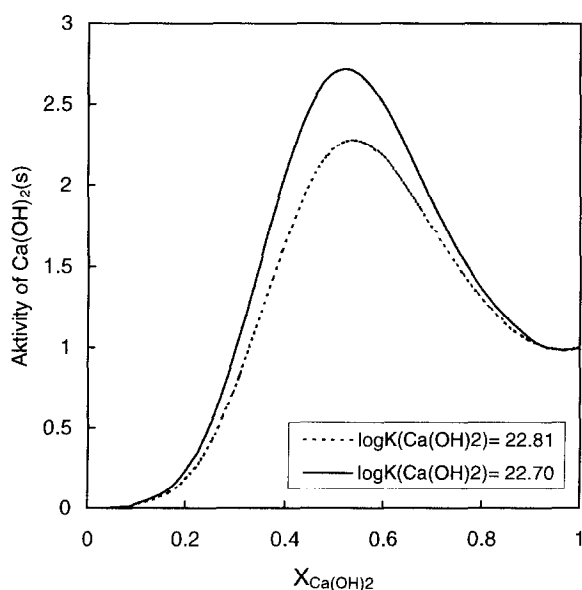| Log K_S	A_0, kJ/mole	A_1, kJ/mole
22.81	2.14 ± 0.3	12.69 ± 2
22.70	3.26 ± 0.3	13.44 ± 2

FIG. 3.

Calculated activity of end-member $Ca(OH)_2(s)$ as a function of composition using Eq. (VI). A_0 and A_1 from Table 2.

where C_{ii} is the diagonal element in the covariance matrix defined as $C = (J^{T*}J)^{-1}$, where J is the Jacobian. χ^2 is the normalised sum of squares according to

$$\chi^2(p_1, p_2, \ldots) = \frac{1}{n - p} \sum_i w_i[y_i - f(x_i; p_1, p_2, \ldots)]^2$$

where n are the number of data points, p the number of fitted parameters, w_i the weight of point i, y_i experimental value and f the calculated value using the obtained parameters. In the calculations presented here all data point where assigned the weight of one.

The obtained values on A_0 and A_1 were used together with Eq. (VI) to calculate the activity of the end-member $Ca(OH)_2(s)$ as a function of its molefraction. The resulting curves can be seen in Figure 3. Since each curve has a maximum and a minimum a phase separation has to occur at certain molefractions. It can then be concluded that the system will contain two solid solutions and an aqueous phase where one of the solid solutions contains almost only $Ca(OH)_2(s)$.

From Figure 3 it can be seen that in the Ca-rich solid solution the activity of the end-member $Ca(OH)_2(s)$ can not be as low as 0.8, cf. Fig. 2. This suggest that only the calculations based on the log $K_S = 22.70$ will give acceptable activities (cf. Fig. 2).

Solubility Calculations of the $CaO-SiO_2-H_2O$ System

The solubility of the $CaO-SiO_2-H_2O$ system has been modelled. The programs PASSIPHIC (Pure phAses and Solid Solutions In PHreeqe equIlibrium Calculations) (17) and SOLISOL were used in the calculations. The program package PASSIPHIC handles complex phases in

solubility calculations with an aqueous phase. The complex phase may constitute solid solutions and pure solid phases. In solubility calculations with solid solutions PASSIPHIC makes use of the SOLISOL program. It is worth mentioning that SOLISOL is also a stand-alone program. The program PHREEQE is used in all equilibrium calculations.

The original SOLISOL program treated ideal solid solutions only. The ability to use non-ideal binary solid solutions has been added to the program using the mixing model proposed by Guggenheim as described above. The primary task for SOLISOL (1) is to calculate a saturation index for each end-member in the solid solution and make it available to PHREEQE.

The log K_S = 22.70 for the end-member $Ca(OH)_2(s)$ was used together with the data base HATCHES 5.0. The data base was also extended with data for the second end-member $CaH_2SiO_4(s)$, derived from Greenberg and Chang (8), cf. Tab. 1. According to our model the phase separation occur at the Ca/Si ratio 1.43, where the activity of end-member $Ca(OH)_2(s)$ equals unity. In the calculations the aqueous phase was pure water and the temperature 25°C.

Model solid in the region 1 < Ca/Si ≤ 1.43

The model solid for the $CaO-SiO_2-H_2O$ system in this region was the C—S-H gel modelled as a non-ideal solid solution composed of the end-members $Ca(OH)_2(s)$ and $CaH_2SiO_4(s)$.

Model solids in the region 1.43 < Ca/Si ≤ 1.7

This region lies in the phase separation region. Two solid solutions were assumed. The first solid solution, the C-S-H gel, constituted the end-members $Ca(OH)_2(s)$ and $CaH_2SiO_4(s)$ and the second solid solution was approximated with pure $Ca(OH)_2(s)$.

Results and Discussion

The result from the solubility calculations performed on the $CaO-SiO_2-H_2O$ system using the thermodynamic model described in this paper can be seen in Fig. 4. The modelled activity of end-member $Ca(OH)_2(s)$ as a function of the Ca/Si ratio in the C-S-H gel is shown in Fig. 4a together with the activity obtained from the speciation calculations. In Figure 4b the calculated calcium concentration in the aqueous phase is plotted as a function of the Ca/Si mole ratio of the C-S-H gel. Also shown in Fig. 4b are the experimental data compiled by Berner (4), giving Kalousek's data separately. The results predicted by the thermodynamic model provide a good approximation to the experimental data by Kalousek (13).

Limitation of the model

The C-S-H phase is modelled as a solid solution constituting the end-members $Ca(OH)_2(s)$ and $CaH_2SiO_4(s)$. Both end-members contain calcium and this will cause the end-member $Ca(OH)_2(s)$ to be assigned a non-zero activity even if $X_{Ca(OH)2}$ = 0. Hence, the model is valid only when the calcium concentration in the aqueous solution is much greater than the silica concentration.
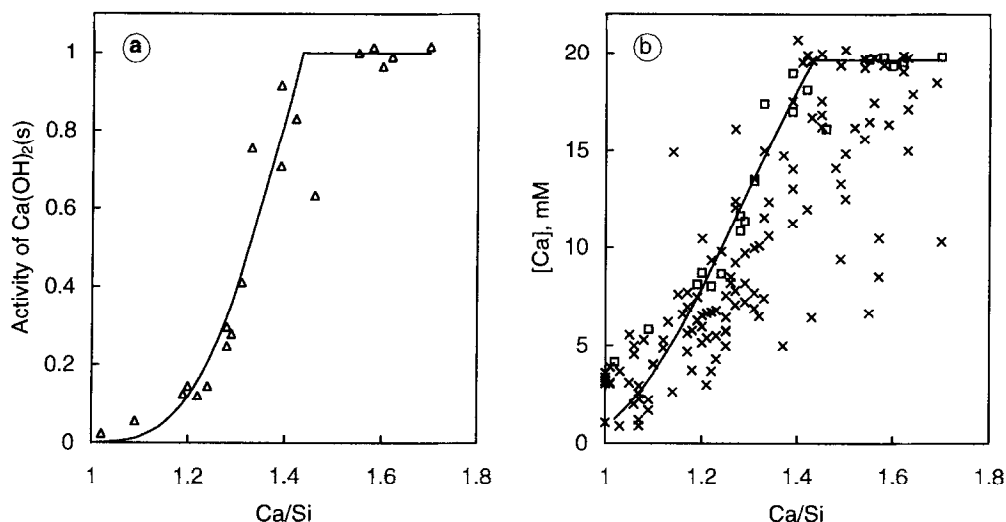
FIG. 4.
a) Calculated activity of end-member $Ca(OH)_2(s)$ as a function of the Ca/Si ratio of the C-S-H gel. Speciation calculation is shown as triangles and the model results indicated as solid line. b) Figure 1 with model results indicated as solid line.

Conclusion

Implementation of the Guggenheim mixing model for non-ideal binary solid solutions in the program SOLISOL and the use of the PASSIPHIC program makes it possible to reproduce the solubility data of the $CaO-SiO_2-H_2O$ system satisfactorily. Presently, the PASSIPHIC program is used to simulate cement leaching experiments performed earlier (18). In this simulation work other cement phases, beside those discussed here, are included in the model, i.e. Ettringite and Hydrogarnet.

Acknowledgement

References

1. S. Börjesson, Licentiate thesis, Department of Nuclear Chemistry, Chalmers University of Technology, S-412 96 Göteborg, Sweden, 1994.
2. A. Atkinson, J.A. Hearne, and C.F. Knights, DOE Report RW/87.048, U.K. Atomic Energy Authority Report AEAR-R12548, 1987.
3. F.P. Glasser, D.E. Macphee, and E.E. Lachowski, Mat. Res. Soc. Symp. Proc. 84, 1987.
4. U. Berner, Waste Management 12, 2/3, 201 (1992).
5. E.J. Reardon, Waste Management 12, 2/3, 189 (1992).

6. K.S. Börjesson and A.T. Emrén, Computers & Geosciences, 19, 1065-1070 (1993).
7. D.L. Parkhurst, D.C. Thorstenson, and L.N. Plummer, USGS/WRI p. 80-96, 1980,. Version current, August 3, 1984. Changes: a/Yamaguchi, Y., NEA DB December 17, 1984 and b/Fridemo, L., Dept. of Nuclear Chemistry, CTH, July 5, 1985.
8. S.A. Greenberg and T.N. Chang, J. Phys. Chem. 69 (1965).
9. M. Atkins and F.P. Glasser, Waste Management 12, 2/3, 201 (1992).
10. S.K. Saxena, Springer-Verlag, Berlin, 1973.
11. P.D. Glynn, Computers & Geosciences, 17, 907-966 (1991).
12. J.M. Prausnitz, Prentice-Hall, Inc., Engelwood Cliffs, New Jersey, 1969.
13. G.L. Kalousek, Proc. 3rd Int. Symp. on Chemistry of Cements, p. 296, London 1952.
14. K.A. Bond, A.D. Moreton, and T.G. Heath, Hatches 5.0—The Harwell/NIREX Database, Harwell Laboratory, Oxfordshire OX11, ORA, UK, 1992.
15. CHEMVAL6, Thermodynamic Database Version 6, Provided by Dr. S. Duerden, HMIP P3/008A, 2 Marsham Street, London SW1P 3EB, England, 1995.
16. K. Fujii, and W. Kondo, J. Chem. Soc. Dalton, 2 (1981).
17. S. Börjesson. In preparation, 1997.
18. I. Engkvist, Y. Albinsson, and W. Johansson Engkvist, SKB Technical Report, SKB TR 96-09, 1996.