Modelling of cement-groundwater interactions

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Cement is likely to be used extensively in the geological disposal of radioactive wastes since its high-pH pore fluids will minimise the corrosion of metal canisters and the solubility of certain radio-nuclide-bearing solids. High pH is a function of the solubility and mass of pH-controlling solids within the cement, groundwater-cement reactions, and the rate of flow of groundwater through the system. The principal cement phase believed to be controlling pH in the long-term is calcium silicate hydrate (CSH) gel.

CSH gel does not have a fixed chemical composition and has a variable Ca/Si ratio up to ~3. At solid Ca/Si ratios > 1, CSH gel dissolves incongruently in water with aqueous Ca concentrations being much higher than those of Si. The extent of incongruent dissolution behaviour increases with the Ca/Si ratio of the solid. Despite the non-stoichiometric dissolution behaviour, there is good evidence that thermodynamic equilibrium holds. Kersten (1996) has suggested a model which treats CSH gel as a solid-solution with a silicate end-member of general composition CaH_4SiO_5 ('CS'), and a calcium end-member represented by portlandite, $Ca(OH)_2$ ('CH'). Both these end-members are assumed to be congruently soluble. Applying solid-solution theory developed by Lippmann (1980) and Glynn and co-workers (e.g. Glynn, 1991) allows definition of the total solubility product constant ($\Sigma\Pi_{eq}$) and the total solubility product variable ($\Sigma\Pi$) for the solid-solution:

$$\Sigma\Pi_{eq} = K_{CS}X_{CS}\gamma_{CS} + K_{CH}X_{CH}X_{CH}\gamma_{CH}$$
$$\Sigma\Pi = [Ca(OH)^+][(H_3SiO_4^-] + [OH^-])$$

where K, X, and γ are the equilibrium constant, mole fraction, and solid phase activity coefficient respectively, of the subscripted end-member. Square brackets refer to activities of aqueous species.

TABLE 1. Equilibrium constants for portlandite (CH) and Ca-silicate (CS) end-members of a CSH gel solid-solution input to PHREEQC for calculation of coexisting fluid composition (in moles/litre)

| Gel X_{CH}	log K CH	log K CS	pH	$[CaOH^+]$	$[H_3SiO_4^-]$	$[OH^-]$
0.67	−4.01	−8.97	12.45	3.4E−3	3.2E−7	0.310
0.60	−4.05	−8.90	12.44	3.2E−3	3.9E−7	0.027
0.55	−4.11	−8.83	12.42	3.0E−3	5.0E−7	0.026
0.50	−4.19	−8.74	12.39	2.7E−3	6.9E−7	0.025
0.45	−4.30	−8.64	12.35	2.2E−3	1.0E−6	0.022
0.40	−4.45	−8.53	12.29	1.8E−3	1.7E−6	0.020
0.35	−4.65	−8.41	12.22	1.4E−3	2.9E−6	0.017
0.30	−4.89	−8.29	12.13	9.5E−4	5.4E−6	0.014
0.25	−5.19	−8.18	12.03	6.1E−4	1.1E−5	0.011
0.20	−5.56	−8.07	11.89	3.5E−4	2.4E−5	0.008
0.15	−6.02	−7.98	11.73	1.8E−4	5.9E−5	0.005
0.10	−6.58	−7.90	11.53	7.8E−5	1.6E−4	0.003
0.05	−7.33	−7.84	11.24	2.7E−5	5.4E−4	0.002
0.00		−7.80	11.04	1.6E−5	1.0E−3	0.001
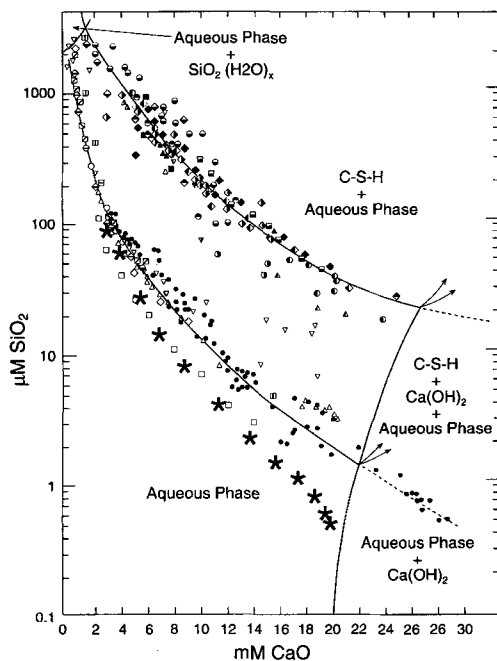
FIG. 1. Comparison of fluid phase compositions calculated for a CSH gel solid-solution model (starred data points) with those determined in laboratory CSH gel-water equilibration experiments (Jennings, 1986).

The computer code 'MBSSAS' (Glynn, 1991) was used to investigate solid-solution behaviour in the CSH gel-H_2O system. MBSSAS uses a Guggenheim sub-regular solid-solution model to calculate free energies of mixing of the two components within the solid-solution. For input to MBSSAS, a miscibility gap between $X_{CH} = 0.67$ and $X_{CH} = 0.95$ was chosen. Equilibrium constants of the two pure end-members K_{CS} and K_{CH}, were log -7.8 and log -4.0, respectively. Compositions of the aqueous phase coexisting with a CSH gel solid solution have been calculated using values of $\Sigma\Pi_{eq}$ derived from the MBSSAS calculations using PHREEQC (Parkhurst, 1995). Since PHREEQC cannot explicitly deal with solid-solutions as input data, solid solution behaviour was treated as two discrete phases, calcium silicate and portlandite. Equilibrium constants for these two phases were calculated to satisfy the solid-solution relationships and are presented in Table 1.

Calculated fluid compositional data have been compared with solubility data for CSH gels compiled by Jennings (1986) [Fig. 1]. It may be seen from Fig. 1 that there is a reasonable fit of the model data to those from laboratory studies of the CSH gel system. This provides confidence in the use of the model to simulate cement-groundwater interactions in the long-term. However, the divergence in the modelled and experimental data suggests that boundary conditions for the modelling (gel miscibility gap, solubility constants for the two end-members) could be re-evaluated to attempt to provide a better fit to the experimental data.

References

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