

Modelling the geochemical degradation of cements in a waste repository

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Introduction.

Cements are a favoured material for immobilising low and medium level radioactive waste, and are also being considered for encapsulating toxic wastes. These cements are often blends, incorporating Ordinary Portland Cement (OPC) with Blast Furnace Slag (BFS) and/or Fly Ash (FA). Cements provide a reactive system chemistry, and for radwastes, greater long term reliance is placed on chemical, rather than physical mechanisms for immobilisation. In order to predict the subsequent migration behaviour of radionuclides in a saturated repository over 10^2 – 10^4 years, it is necessary to use a modelling approach. The 'near field' chemistry will be dominated by cements; it is important to forecast the solid phases present (potential sorption/ lattice incorporation sites), and the co-existing aqueous phase composition (controlling speciation and solubility of nuclides). The pH function is particularly important; most transuranics are relatively insoluble at high pH.

The present paper gives an example calculation, using OPC, and how to model its chemical degradation in water. The maintenance of high pH is emphasised.

Method.

We have been actively developing thermodynamic models to predict the solid phases formed in fully matured cement blends. Cement systems have been simplified to six chemical components: CaO- Al₂O₃- SiO₂- SO₃- MgO- H₂O. Within this framework, the equilibrium phase relations are solved: Fig.1 illustrates the phase relations within the most important sub-system, Ca-Al-Si-H₂O, at 25°C. A computer program has been written on this basis of the six component system, which calculates the hydrate assemblage formed, as a function of percentage blend in cement mixtures (CEMCHAM). After full hydration, some water remains within the cement matrix, in micropores. The composition of this 'pore fluid' can be estimated, by assuming it is in thermodynamic equilibrium with the surrounding solids. A speciation code has been used, with a database specially developed for cements (PHREEQE/AU), to 'dissolve' the cement phases into water. Groundwater interactions have been modelled using this code, by mixing 50% pore fluid/ 50% water in exchange cycles, taking full account of precipitation/ dissolution reactions. PHREEQE is also being used to study cement degradation in seawater.

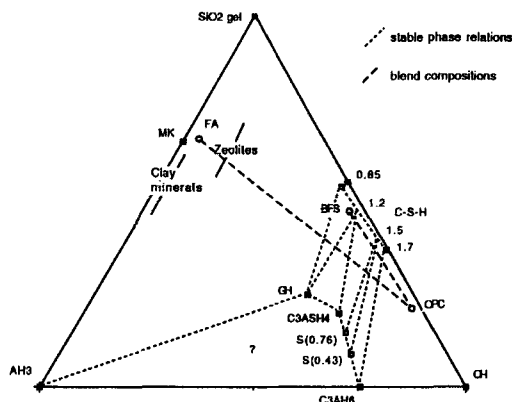


FIG. 1. Phase relations in the water-saturated portion of the C-A-S system at 25°C: CEMCHAM 1, in relation to cement blends (mol%). Approximate composition ranges for zeolites and clays are also shown.

Results and interpretation.

For an OPC, CEMCHAM calculates the hydrate assemblage in moles/kg to be: 10.2 Ca(OH)₂, 0.16 ettringite (AFt), 0.47 hydrotalcite (HT), 9.2 calcium silicate hydrate (CSH), with Ca/Si ratio = 1.8) and 0.85 siliceous hydrogarnet (SiHG, 3CaO·Al₂O₃·0.5SiO₂·5H₂O). Dissolution and pH evolution, in response to equilibrium exchange cycles in pure water are plotted in Fig.2. pH declines with increasing exchanges, with plateaus of nearly constant pH buffered by

different solid assemblages. Fresh OPC has a pH exceeding 13.0, maintained by soluble Na/K hydroxides. These are leached out relatively rapidly, the pH is then buffered at 12.5, principally by $\text{Ca}(\text{OH})_2$. This latter phase dissolves most rapidly, disappearing at cycle 960. From this point the Ca/Si ratio of CSH decreases, and gehlenite hydrate (GH) precipitates soon after; the pH is buffered at 11.4. SiHG is the next phase to disappear, at cycle 2570, followed by AFt at cycle 2970. There follows a long period of ~ constant pH, maintained by CSH + HT + GH, at pH 11.0. CSH finally becomes exhausted after cycle 19900. The next stable assemblage (and consequent pH) is uncertain, after crossing the boundary from 'known' phase relations in Fig.1.

During leaching calculations, choices have to be made, when a solid is phase is predicted to be saturated. In the example, sepiolite (Mg hydroxysilicate) is predicted to be slightly supersaturated from cycle 3000 onward. Fig.2 shows the effect of including this phase in the solid assemblage; it has little effect on pH evolution. Other phases showed strong supersaturation effects, but were disallowed from precipitating, due to their known (prohibitive) crystallisation kinetics at 25°C, eg. talc. Therefore, not only is a high quality thermodynamic database required, but also a knowledge of formation conditions for each phase.

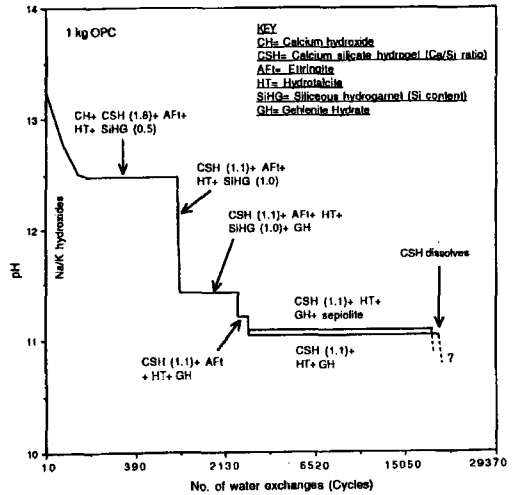


FIG. 2. Predicted pH evolution and phase assemblages in Ordinary Portland Cement leached by pure water at 25°C (PHREEQE).