

Aqueous-solid solution model of strontium uptake in C-S-H phases

D.A. KULIK, J. TITS AND E. WIELAND

Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland
(dmitrii.kulik@psi.ch)

Cement wasteforms are composed mainly of calcium silicate hydrate (C-S-H) phases which can incorporate divalent cations such as Sr (including the fission product ^{90}Sr relevant in nuclear waste disposal). In this context, our C-S-H Aq-SS model was extended with Sr, Na, and K end members. We used our Sr uptake data in pure water and in artificial cement water (ACW); Nagra-PSI chemical thermodynamic database; and the GEMS code (<http://es.web.psi.ch/Software/GEMS-PSI>) in forward chemical modeling and inverse dual-thermodynamic calculations (DTC).

DTC can retrieve unknown stoichiometry and standard molar Gibbs energy G° of an ideal solid solution end member from several experimental bulk compositions of co-existing aqueous solution and solid solution phases. Using DTC with 13 end member candidates, the following "optimal" stoichiometries were found: $\text{Sr}(\text{OH})_2\text{SiO}_2\text{H}_2\text{O}$ (SrSH); $[(\text{NaOH})_{2.5}\text{SiO}_2\text{H}_2\text{O}]_{0.2}$ (NaSH); $[(\text{KOH})_{2.5}\text{SiO}_2\text{H}_2\text{O}]_{0.2}$ (KSH), with the associated mean G°_{298} values and 2σ uncertainty intervals.

Two extended C-S-H quinary ideal solid solutions were used in forward modeling of our Sr uptake data (ca. 90 experiments at ambient T,P). Two modeled cement degradation scenarios show that Sr is retained much stronger in the "carbonation" than in the "dilution" (CO_2 -free leaching) process.

The Aq-SS approach requires somewhat different $G^\circ_{298}(\text{SrSH})$ value for modeling Sr uptake in C-S-H (Ca:Si $\sim 1.1 \pm 0.1$) prepared in water than that prepared in the alkaline ACW. The difference (ca. 3.4 kJ mol^{-1}) could be explained by a weaker silicon tetrahedra polymerization in C-S-H during synthesis with alkali cations. Preliminary studies also indicate that the Ca-Na-K-Sr ion-exchange model on "tobermorite" sorbent may be more precise in predicting Sr uptake by C-S-H in ACW than the ideal solid solution model.

References

- Kulik D.A. and Kersten M. (2001), *J. Am. Ceram. Soc.* **84**, 3017-3026.
Kulik D.A. (2006), *Chem. Geol.* **225**, 189-212.
Tits J. et al. (2006), *J. Coll. Interf. Sci.* **300**, 78-87.

Binding of metal ions by natural organic matter (NOM) – Investigated by lanthanide ion probe spectroscopy (LIPS)

M.U. KUMKE, SASCHA EIDNER, BETTINA MARMODÉE AND STEFFANIE KUKÉ

Institute of Chemistry, University of Potsdam, Karl-Liebknecht-Str. 24-25, 14476 Potsdam-Golm, Germany
(Kumke@chem.uni-potsdam.de)

The binding to natural organic matter (NOM) determines transport, bioavailability, and toxicity of metal ions in water and soil environments. The understanding of the underlying interaction mechanisms between NOM and metal ions is therefore indispensable for the development of reliable models for the prediction of mobility and fate of metal ions in the environment. Because of their outstanding spectroscopic properties lanthanide ions (Ln^{3+}) are excellent probes for the direct investigation of metal binding to NOM. Especially, the spectral sensitivity to changes in the close coordination sphere of the Ln^{3+} ion as well as the dependence of the luminescence decay time on the type of ligand coordinated can yield valuable information on the stoichiometry and symmetry of metals bound to NOM.

In our experiments Eu^{3+} and Tb^{3+} ions were used as luminescence probes to investigate the binding of metal ions to humic acids (HA) and fulvic acids (FA), which represent a major part of NOM. The Ln^{3+} luminescence was excited either directly or via sensitization by radiationless energy transfer from HA or FA ligands. The intra- and intermolecular energy transfer processes were investigated in detail using H_2O and D_2O as solvents.

Because of the high complexity of NOM simpler organic model ligands such as aromatic and aliphatic hydroxy carboxylic acids were investigated as well. In ultra-low temperature measurements at 4 K the non-degenerated $^5\text{D}_0$ - $^7\text{F}_0$ transition of Eu^{3+} and the Stark splitting of the $^7\text{F}_1$ and $^7\text{F}_2$ levels were used to evaluate the stoichiometry and the symmetry of the complexes formed. Furthermore, time-resolved luminescence spectra of $\text{Ln}^{3+}\text{-L}$ (L = NOM or model ligand) measured in H_2O and D_2O were analyzed and the number of coordinated water molecules was determined.