2.3.P03

EXAFS study of Ni uptake by hardened cement paste

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Cement has been used worldwide for the stabilization of hazardous and nuclear wastes in order to prevent or lower the mobility of contaminants associated with the waste matrices. A mechanistic understanding of the processes governing the binding of heavy metals, radionuclides and anionic species in cement systems is essential for long-term predictions of the environmental impact of cement-stabilized waste forms. Ni is among the most important contaminants in these wastes, and therefore, Ni uptake by hardened cement paste (HCP) has been studied with the aim of improving our understanding of the immobilization process at the molecular level. For the present study, HCP doped with 5000 ppm Ni was prepared at a water/cement ratio of 0.4 using a sulfate-resisting Portland cement and hydrated over a time period of 3, 30 and 150 days, respectively.

Ni K-edge EXAFS measurements were carried out for both reference samples and powder HCP material. The Ni-doped cement k^3-weighted spectra reveal similarities with those of β-Ni(OH)$_2$ and a synthetic Ni-Al layered double hydroxide (Ni-Al LDH). A characteristic beat pattern at ~8Å^{-1}, used to identify Ni-Al LDH phases [1], was also observed. Data analysis performed with FEFF 8.2 revealed similar interatomic distances (R_{Ni-O} = 2.03-2.04 Å; R_{Ni-Ni} = 3.08-3.10 Å) and coordination numbers for all samples. The R_{Ni-Ni} distance determined for these HCP samples could not be attributed to any pure Ni phase. This finding rather suggests that a mixture of Ni-Al LDH and β-Ni(OH)$_2$ was formed during hydration. To test whether this hypothesis is consistent with the observed fit results, linear least-square fitting (LSF) of the experimental EXAFS spectra of the HCP samples with linear combinations of the reference spectra was undertaken. Best fit results were obtained using a linear combination of pure Ni phases of Ni-Al LDH (R_{Ni-Ni} = 3.06 Å) and β-Ni(OH)$_2$ (R_{Ni-Ni} = 3.12 Å). The weight percentage of Ni-Al LDH in the Ni-doped HCP samples was found to slightly increase with time, whereas β-Ni(OH)$_2$ decreases accordingly. This finding supports the hypothesis that Ni-Al LDH is an important phase in cement matrices as previously suggested from Ni sorption experiments on HCP [2].

References
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2.3.P04

Porosity development in replacement reactions: NaCl-KCl-H$_2$O as a model example

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NaCl and KCl are the major solute constituents of fluids in a wide range of geological environments and form the main constituents of evaporite deposits. Analyses of fluid inclusions have provided information about the chemical compositions of NaCl-KCl rich fluids present during such geological processes as metamorphism, ore deposition, hydrothermal alteration, all of which involve mineral replacement processes.

Whenever a mineral is not in equilibrium with its surrounding fluids, replacement reactions are likely to take place. It has previously been shown that in such replacement reactions involving dissolution-recrystallisation, there is an associated development of porosity, often seen as the development of a cloudy or turbid or sometimes a friable texture. Such a porosity development further enhances the replacement process by providing pathways for the transport of fluids through the mineral, to and from the replacement interface. The development of porosity depends on two main parameters: molar volume differences and solubility differences [1]. This was further discussed by Putnis and Mezger [2] using the solid solution-aqueous solution KCl-KBr-H$_2$O system as a model example. It has been shown that when a mineral is replaced by another mineral, a volume deficit or porosity need not only be dependent on molar volume differences between the parent and the new replacing phase, but solubility differences between the end members play a major role in determining the extent of the porosity produced. In the NaCl-KCl-H$_2$O system KCl has a higher molar volume than NaCl but below 30°C NaCl is more soluble than KCl and KCl replaces NaCl with a crystallographically continuous porous phase. An explanation is presented for the experimentally observed development of porosity in NaCl-KCl-H$_2$O replacement reactions in terms of temperature dependent solubilities and molar volume changes. The development of porosity as a result of replacement reactions in other mineral systems is also discussed.

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