

Fluoride complexation of yttrium under hydrothermal conditions

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As a result of the recent upsurge in demand for new resources of the REE, there is an urgent need to better understand their behavior in hydrothermal systems. Here we report results of a study designed to determine formation constants for yttrium fluoride species by measuring the solubility of YF₃ in fluoride-bearing solutions. The experiments were performed at 150, 200, and 250°C and saturated water pressure, using the method of Migdisov *et al.* [1]. The pH and fluorine concentration were 0.85 to 3.05 and 3e-4 to 1e-1 mol/kg, respectively. Based on these experiments, Y speciation is dominated by mono-fluoride and di-fluoride complexes.

The elements Y and Ho are geochemical twins, with nearly identical ionic radii (900 pm and 901 pm) and the same oxidation state (3+) in nature. Consequently, they do not fractionate strongly in most geological systems. Important exceptions are fluorine-rich hydrothermal systems, in which their fractionation is pronounced. Our results allow us to assess fluoride-induced fractionation as a function of temperature and fluoride concentration and can be used to quantitatively model Y/Ho ratios in hydrothermal systems. This important geochemical indicator can extend our understanding of the transport processes of the economically important and geochemically interesting Rare Earth Elements.

[1] Migdisov, A.A. Williams-Jones, A.E. & Wagner, T. (2009) *Geochim. Cosmochim. Acta* **73**, 7087–7109.

Geochemical modeling of reactive minerals associated with *in situ* recovery of uranium

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Dissolution of uraninite and pyrite in the presence of oxidants and SO₄²⁻ derived from H₂SO₄ are important geochemical processes taking place during *in situ* recovery (ISR) of uranium worldwide. During ISR of uranium using H₂SO₄, pH values of 3 or less are typically achieved depending on the buffering capacity of reactive (intermediate kinetic) minerals. Reactions involve significant dissolution of uraninite and primary silicate minerals. Possible precipitation of secondary minerals (gypsum, alunite, and jurbanite) can also occur under localized acidic conditions. Geochemical modeling using PHREEQC and HYTEC was conducted to quantify dissolution and redox reactions. The pre-extraction geochemistry is built, in agreement with observations, by equilibrating groundwater with primary phases (uraninite, pyrite, K-feldspar, hematite, calcite, kaolinite, Mg-montmorillonite, and Ca-nontronite). Acidification results in early-stage dissolution of Fe (III) minerals, which initiates oxidative and irreversible dissolution of uraninite and pyrite. Surface-controlled dissolution of K-feldspar, kaolinite, and Mg-montmorillonite with intermediate kinetics produces an acidic, mixed solute [Al-Ca-Fe (II)-SO₄] composition, enhancing precipitation of alunite and jurbanite. 2D simulations were then performed to study mixing effects, particularly near the production wells. Flow velocities can be much smaller for longer stream-tubes allowing for slower kinetic reactions to be effective. The amount of buffering by calcite increases along these flow paths characterized by increasing pH- buffering capacity.