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Effects of pH, temperature, and aqueous organic material on the dissolution kinetics of meta-autunite minerals, $(Na, Ca)_{2\text{-}1}[(UO_2)(PO_4)]_2{\cdot}3H_2O$

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Abstract

Autunite-group minerals have been frequently identified in contaminated sediments as the long-term controlling phase of U. Under these conditions, the mobility of U in subsurface pore waters is limited by the rate of dissolution of autunite and meta-autunite group minerals, $X^{(n)*}_{3-n}[(UO_2)(PO_4)]_2{\cdot}xH_2O$, where X = Ca or Na. Single-pass flow-through (SPFT) tests were conducted to quantify the dissolution kinetics of natural Ca meta-autunite, $Ca[(UO_2)(PO_4)]_2{\cdot}3H_2O$, and synthetic Na meta-autunite, $Na_2[(UO_2)(PO_4)]_2{\cdot}3H_2O$, as a function of pH (7–10) and temperature (5–70 °C) in the presence and absence of aqueous organic material. The data indicate that release of U and P are non-stoichiometric over the range of experimental conditions investigated. In a 0.1 *M* NH_4OH buffer solution, acquisition of valid dissolution rate data was limited by uramphite solubility, $NH_4[(UO_2)(PO_4)]_2{\cdot}xH_2O$. Dissolution rates obtained in a 0.01 *M* TRIS [tris (hydroxymethyl) aminomethane] buffered solution increased by a factor of ~100× over the pH interval of 7 to 10 ($\eta = 0.90 \pm 0.08$), irrespective of temperature. At constant pH the rate data showed a minor increase with temperature. Data from experiments using a more concentrated 0.05 *M* TRIS buffer exhibited a ~35-fold increase in rates compared to those in a 0.01 *M* TRIS buffer at constant temperature and pH. The difference in release rate between interlayer cation (Na^+ or Ca^{2+}) and U is ~10 000 in neutral solutions; however, the difference diminishes to ~10 at higher pH values. The combination of structural dissolution and ion exchange explain these trends in interlayer cation behavior. Data presented here illustrate the significance of pH and dissolved organic material on the dissolution of autunite minerals.

Keywords: Autunite, dissolution, kinetics, uranium, organic material