

## Rates and mechanisms of uranyl oxyhydroxide mineral dissolution

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The fate and transport of uranium(VI) in waste-weathered sediments is controlled by solid phase precipitation and sorption during initial release, and subsequently by dissolution, desorption and transformation in groundwater aquifers over time. Understanding these processes at a molecular scale and quantification of dissolution rates in simple systems are crucial for improving predictions of uranium migration in complex subsurface systems. Towards that goal, dissolution of two oxyhydroxide U-minerals, compreignacite,  $\text{K}_2(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ , and Na-compreignacite,  $\text{Na}_2(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ , potentially present in uranium contaminated Hanford sediments was investigated in flow-through column experiments.

Pure mineral phases were synthesized from uranyl nitrate and  $\text{K}_2\text{CO}_3$  or  $\text{Na}_2\text{CO}_3$  salts at elevated temperature and pressure. Synthesized solids were characterized by XRD, SEM,  $\text{N}_2$ -BET surface area, digestion and elemental analysis, thermogravimetric analysis, and extended X-ray absorption fine structure (EXAFS). Dissolution rates were measured using  $1 \text{ cm}^3$  flow-through columns filled with a 1:4 U-mineral:quartz mixture and leached upwards ( $0.037 \text{ mL min}^{-1}$ ) with simulated groundwater for 1400 pore volumes (172 h).

Constant U effluent concentrations were reached after 400 PV for compreignacite columns and 800 PV for Na-compreignacite columns. Apparent steady-state dissolution rates normalized to BET surface area were slightly higher for Na-compreignacite than compreignacite ( $2.81 \cdot 10^{-13}$  vs.  $5.78 \cdot 10^{-14} \text{ mol m}^{-2} \text{ s}^{-1}$ ). Solid samples after column reaction were analyzed by EXAFS to identify changes in U speciation during leaching. Linear combination fits of reacted Na-compreignacite with reference spectra suggest that a large fraction of U is no longer bonded in the mineral structure but is either re-adsorbed to quartz or present in an altered surface layer. Uranium speciation in compreignacite columns however remained mostly unaltered (within the detection limits of LC-EXAFS). Reactive transport modeling of U breakthrough and steady-state dissolution is in progress (using CrunchFlow) incorporating mineral dissolution, ion exchange, sorption and complexation reactions.