

Dissolution of uranyl-hydroxy-hydrate minerals

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Batch-dissolution experiments on single crystals of becquerelite, $\text{Ca}(\text{H}_2\text{O})_8[(\text{UO}_2)_6\text{O}_4(\text{OH})_6]$ and curite, $\text{Pb}_3(\text{H}_2\text{O})_3[(\text{UO}_2)_4\text{O}_4(\text{OH})_3]$, have been done in solutions of different pH and composition. Dissolution features on the basal surfaces of the minerals were examined with Atomic-Force-Microscopy, Scanning Electron Microscopy and optical microscopy. Hillocks are the dominant dissolution feature in neutral to alkaline solutions. Etch-pits form only in acidic solutions, indicating that their formation is promoted by a higher activity of protons in solution.

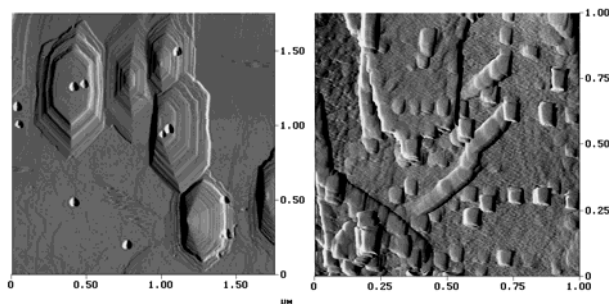


Figure 1: Etch pits (left) and hillocks (right) on the basal surface of becquerelite

Etch pits formed in solutions without any additional cations do not display the symmetry elements of the bulk structure, suggesting incongruent dissolution of becquerelite and curite. Etch pits formed in electrolyte solutions display different symmetries and orientations, depending on the type of cation in solution. The degree of dissolution on the basal surface and its edges also varies with the type of cation in solution. These observations suggest that the cations in solution are adsorbed on the mineral surface, controlling the stability of the edges and the growth of the etch pits perpendicular to the basal surface.

Reference

Schindler, M., Mutter, A., Hawthorne, F.C. & Putnis, A. (2004), *Can. Mineral.* 42, in press.

Crystal chemistry of radionuclides in spent nuclear fuel and its alteration products

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Contained within the x-ray absorption edge spectrum are detailed information about the absorbing element including distances to near neighbors, types and numbers of neighboring atoms, and details of the radial distribution function [Stern, 1988]. We report on our application of this technique using synchrotron radiation to study key radionuclides (Np, Pu, and Tc) in alteration phases and exsolved particles that may effect long-term release behavior from corroded commercial spent nuclear fuel (CSNF) in a geologic repository. The XAS specimens included a sample of reacted fuel from an Argonne unsaturated corrosion test reacted for nearly 8 years [Finn, et al., 2003].

A fundamental difficulty in detecting and measuring the x-ray absorption spectra of small quantities of Np, Mo, or Tc in a uranium matrix is that the fluorescence signal is not well separated in energy from the uranium L- β lines. Measuring useful spectroscopic information requires that the background from the matrix uranium be substantially decreased, which we achieved using a bent-Laue analyzer with a bandwidth of about 75 eV [Zong *et al.* 1999]. Upon comparison with published spectra it seems reasonable to assign to the Pu and Np to a +4 oxidation state, while Mo and Tc were found to exist largely as metals together within a separate phase.

Acknowledgements

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