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In situ study of uraninite dissolution and neoformation of solid phases at the UO₂(111)-water interface using synchrotron radiation-based techniques

Scientific Background and Aims of the experiment

Operation of pressurized-water nuclear reactors, and disposal of spent fuel in cooling pools or in nuclear waste repositories can result in contact between water and UO₂ (uraninite) fuel. Uraninite dissolution can then lead to the release of toxic U and hazardous radionuclides in the environment. An quantitative estimate of RN release then requires that the mechanisms of UO₂(cr) dissolution be correctly understood. This entails an accurate description of UO₂(cr) alteration and possible neoformation of secondary phases in solutions of complex composition corresponding to pool in presence of radiolysis, or to geological porewaters.

Several solution chemistry studies have quantified the amount of uranium released upon UO₂(cr) dissolution as a function of physico-chemical parameters such as pH, overspace atmosphere, and carbonate concentration [1-3]. To relate the measured rates to molecular reactions at the oxide-water interface, leached UO₂(cr) surfaces were analyzed *ex situ* using standard spectroscopic and diffractometric methods [3-5]. These observations hinted at the possible formation of studtite (UO₂)O₂·4(H₂O) in presence of H₂O₂ (a product of water radiolysis by radioactivity). *Ex situ* analysis is however prone to artifacts, if only because UO₂(cr) is extremely susceptible to oxidation. To mitigate these possible transformations, we developed a double envelope cell for *in situ* study of a radioactive surface by Grazing-Incidence X-Ray Diffraction (GI-XRD), Grazing Incidence X-ray Absorption Fine Structure (GI-XAFS) spectroscopy, and high-resolution X-ray reflectivity. In this setup, the sample is kept in a reacting cell which can be filled with the reacting solution, or emptied after a given time. Because of regulation requirements, a double envelope is confining the sample and the reactants. The cell was used in this study to monitor the surface evolution of an (111) surface of monocrystalline uraninite in a 0.5 M H₂O₂ solution by GI-XRD.

During the scheduled beamtime, several goals were to be met.

- (1) After preparation in our laboratory at Saclay and transport to Grenoble, the cell had to be installed on the goniometer of the CRG-IF beamline without any geometrical hindrance.
- (2) The cell had to be filled with the reacting solution at a given time. After the reaction, the solution had to be drained away.
- (3) Diffraction patterns were to be collected at a significant pace, and with a correct signal-to-noise ratio.

Results

All of the goals were met without any significant problem. The energy of the X-ray beam was set at 27 keV in order to probe the uraninite surface under several mm of solution with a significant signal-to-noise ratio. After careful alignment, a preliminary diffraction scan was collected at a fixed incidence angle of the X-ray beam (2° with respect to the sample plane). The cell was then filled with 0.5 M H₂O₂, and 2θ-scans were collected with a point detector. Comparison of these scans revealed the gradual buildup of a solid phase at the interface, identified by its diffraction pattern as studtite ((UO₂)O₂·4(H₂O)) (figure 1a). Interestingly, initially the amplitude of the (hk0) peaks increased first, whereas that of the (hkl) (l ≠ 0) remained weak. In contrast, after ~6 h of reaction, the amplitude of the (hk0) peaks no longer increased, whereas that of the (hkl) (l ≠ 0) steadily increased. This amplitude behaviour could be qualitatively interpreted as resulting from a reorientation of the studtite.

After ~11 h of reaction, the cell content was drained away, and diffraction patterns of the surface were still collected. Figure 1b reveals the formation of a new solid phase, corresponding to the hydroxide schoepite

$((\text{UO}_2)_8\text{O}_2(\text{OH})_{12} \bullet 12(\text{H}_2\text{O}))$. This clearly demonstrates the necessity of performing reliable characterization of secondary phases directly *in situ*, and not on samples potentially affected by drying operations. Additional analysis of the diffraction patterns is currently performed, in order to determine quantitatively the change in size of the diffracting domains, or the nature and amplitude of the observed anisotropy in crystal orientation.

Perspectives

The results demonstrate that our cell can be reliably used for *in situ* study of radioactive samples. We plan now to extend our investigation of the uraninite surface reactivity in solution conditions to interim storage in cooling pools, or to final disposal in deep geological repositories.

References

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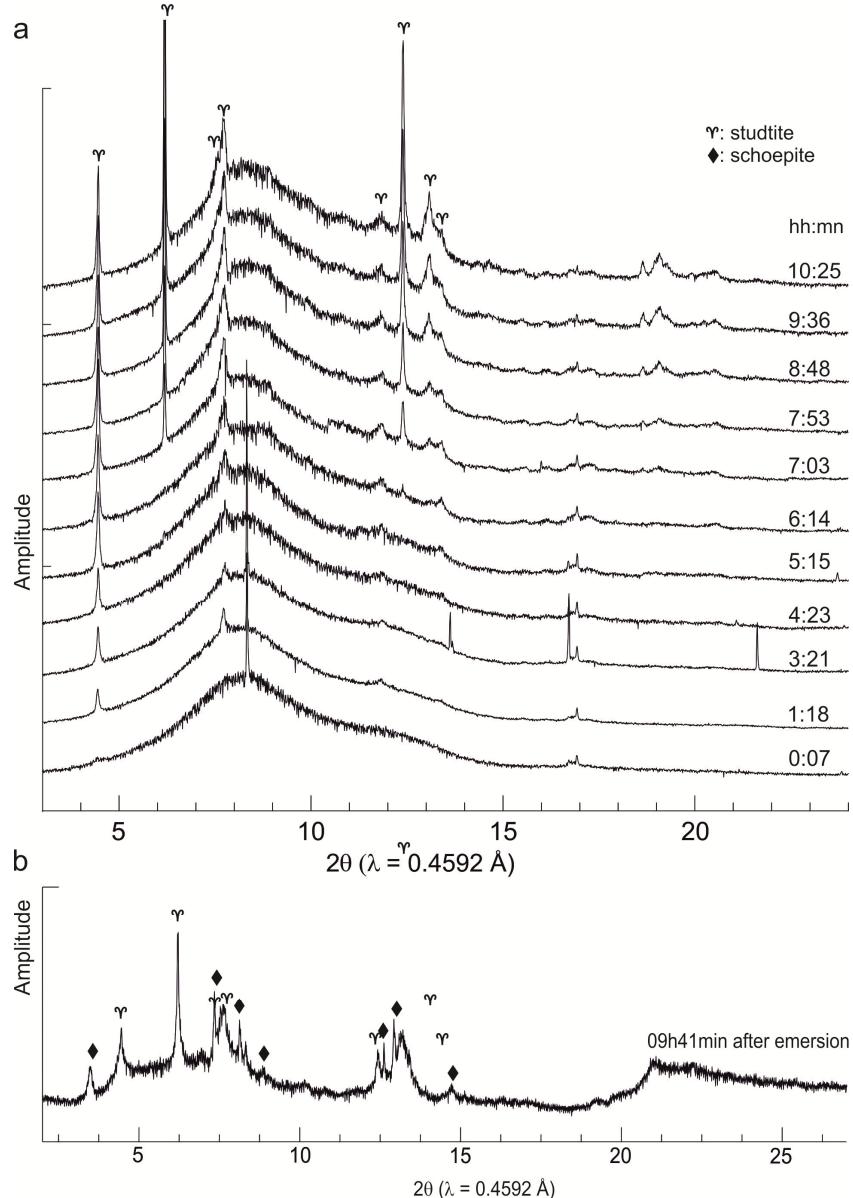


Figure 1. (a) Evolution of GI-XRD data collected at the uraninite- H_2O_2 solution as a function of reaction time. Listed times correspond to the start of acquisition. Each scan lasts ~ 40 min. note the large diffusion band due to water. (b) Example of a diffractogram collected after removal of the surface solution, showing the contribution of studtite and schoepite.