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STUDIES OF ACTINIDES REDUCTION ON IRON SURFACE BY MEANS OF RESONANT INELASTIC X-RAY SCATTERING

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Abstract

The interaction of actinides with corroded iron surfaces was studied using resonant inelastic x-ray scattering (RIXS) spectroscopy at actinide 5d edges. RIXS profiles, corresponding to the f-f excitations are found to be very sensitive to the chemical states of actinides in different systems. Our results clearly indicate that U(VI) (as soluble uranyl ion) was reduced to U(IV) in the form of relatively insoluble uranium species, indicating that the iron presence significantly affects the mobility of actinides, creating reducing conditions. Also Np(V) and Pu (VI) in the ground water solution were getting reduced by the iron surface to Np(IV) and Pu (IV) respectively. Studying the reduction of actinides compounds will have an important process controlling the environmental behaviour. Using RIXS we have shown that actinides, formed by radiolysis of water in the disposal canister, are likely to be reduced on the inset corrosion products and prevent release from the canister.

The deep geological repository concept involves the encapsulation of used nuclear fuel in long-term engineered canisters which are then placed and sealed in a naturally occurring geological formation at a depth of 500 to 1 000 meters below ground surface. A special issue in constructing the underground repository is questions about safety of the canister in the long-term conditions. A way to predict possible risks during long storage period is to study the reactions and interface phenomena of the spent nuclear waste after it has been placed in geological environment. The canister consists of the outer copper shell, as a corrosion resistant barrier and the inner iron shell, in order to add strength to the canister. The essential part in a safety assessment involves a complete understanding of interactions of materials and environment inside the canister.

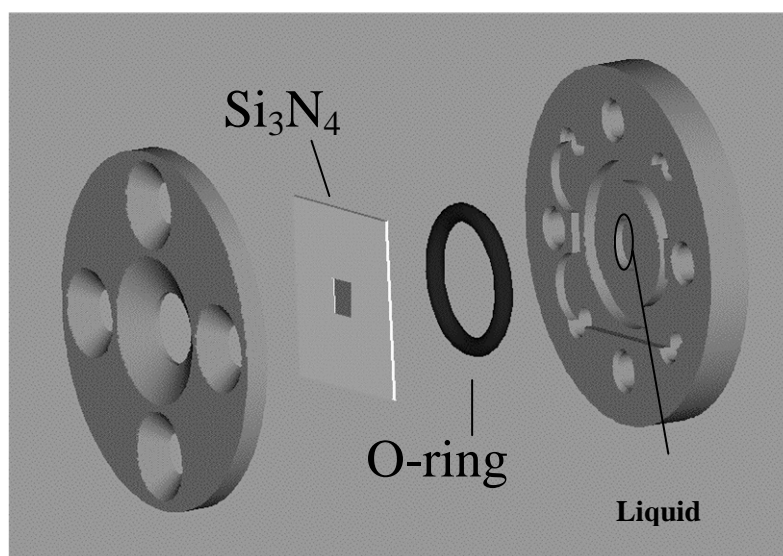
Scientific understanding of processes that control chemical changes of radioactive species from spent fuel can be achieved by studying interactions of actinide ions (U, Np, Pu) with corroded iron surfaces. We made a study of model systems with different actinides in contact with water and iron. The liquid reaction cell was used in some experiments for the in-situ monitoring of the reaction between iron and uranium. The systems were studied with the help of resonant inelastic x-ray scattering (RIXS) spectroscopy, which enables us to determine the oxidation states of actinides in different species. The important advantage of the RIXS spectroscopy in this case in comparison with other spectroscopic techniques, in particular x-ray absorption is the ability to distinguish contributions from species in very small concentrations. Their signal can be clearly separated from that of dominating species as a result of difference in oxidation state and the corresponding 5f multiplet. By going to the actinide 5d edges, the energy resolution of the RIXS experiment can be significantly improved for the same slit settings of the spectrometer.

Our results indicate that actinide ions with high valences in ground water solutions became reduced by the iron surfaces. This fact became significantly important, since the reduction of actinides inside the canister can prevent their release due to the much lower solubility of reduced Np (IV), U(IV) or Pu (IV) than those species with valency V (Np, Pu) and VI (U, Pu).

The Fe samples with U were made by exposing iron strip (99.9994%) to the anoxic allard groundwater solution of uranyl nitride for 17 days. The neptunium containing samples were also prepared by Fe foil exposure to the neptunyl solutions in groundwater. The starting concentration was 2×10^{-6} M for uranium and 4×10^{-7} M for neptunium. The species in solution were calculated to be $\text{UO}_2(\text{CO}_3)_3^{4-}$ (70%) and $\text{UO}_2(\text{CO}_3)_2^{2-}$ (25%) for U and $\text{NpO}_2\text{CO}_3^-$ (75%) and NpO_2^+ (25%) for Np. The U samples were prepared in an inert gas glove box while the Np samples were prepared in pressure vessels with a 50 bar H_2 overpressure.

The liquid reaction cell was utilized for in-situ studies of uranium reduction on Fe from the groundwater solution. The schematics of the cell are shown on Figure 1. The liquid cell consists of the 20mm x 20mm frame, which is holding the 10mm x 10mm Si_3N_4 window and O-ring in order to prevent the leaking processes. The height of the liquid cell is 4 mm, which is enough to put one drop of liquid. On the backside of the 100nm thick Si_3N_4 window, the 100Å Fe film was deposited in order to study the chemical reactions between this film and uranium ions in solution. The initial concentration of the UO_2^{2+} (VI) in solution was 2 ppm.

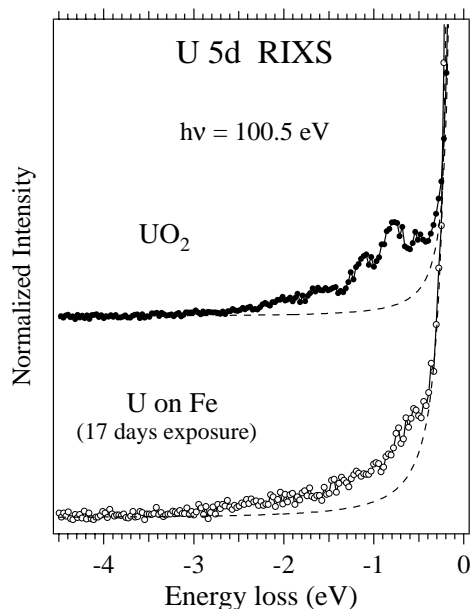
Figure 1. Schematic drawing of liquid cell



The experiments were made at beamline 7.0 of the Advance Light Source, Lawrence Berkeley Laboratory, USA. This undulator beamline includes a spherical grating monochromator, which gives resolution of 50 meV at ~110 eV. RIXS spectra were recorded, using grazing incident grating spectrometer [1-2] with 160 meV resolution for U and Np and 110 meV for Pu samples. The instrument is based on three gratings, mounted at fixed angles of incidence and a large two-dimensional multichannel detector. The incident angle of the photon beam was 20° from the surface for solid samples and 35° for the liquid cell.

Figure 2 shows U 5d RIXS spectra of the iron films exposed to the U(VI) solution in ground water for 17 days. Scattering data were recorded at excitation energy of 100.5 eV, which corresponds to the pre-threshold structure in the U 5d XA spectrum. For simplicity, we plotted RIXS spectra in the energy-loss scale. U 5d scattering spectra for the reference UO₂ sample are also displayed in Figure 2. All the spectra have the elastic peak at 0 eV and inelastic scattering structures at -1.0 –2.0 eV on the energy-loss scale. These structures correspond to the f-f excitations and could be very well reproduced by theoretical calculations, using atomic multiplet theory [3]. Note that the RIXS cross-section for f-f transitions is enhanced at all the energies throughout the pre-threshold structure in the 5d XA spectrum. Such f-f transitions are absent in the UO₃ spectrum [4] (see Figure 3), which could be used as a good “fingerprint” in the study of oxidation states of uranium. Therefore, a reduction of the uranium valency from VI to IV on the iron surface should manifest itself in an appearance of the f-f excitations in the resonant spectra. Our data clearly indicate the presence of the f-f excitations in the RIXS spectra for uranium on the iron film, thus allowing us to conclude that U(VI) is reduced by iron to U(IV). We are also able to derive the amount of reduced uranium by comparison the area under the profile of f-f excitations for UO₂ and studied iron films. The spectra were normalised to the characteristic core-to-core U 6p→ 5d fluorescence lines, which allowed us to deduce the total amount of reduced U (IV) after 17 days of exposure (73%).

Figure 2. U 5d RIXS spectra representing f-f excitations in single crystal UO_2 and U on Fe after 17 days exposure to the U(VI) solution in groundwater. Recorded data are shown by solid lines with markers and broken lines represent a fit to the elastic peak.



Similar results were obtained for Np and Pu samples. Figure 4 shows the Np 5d and Pu 5d RIXS spectra of Np and Pu species formed on the iron strips together with spectra of NpO_2 and PuO_2 . The RIXS spectra of Np and Pu on Fe reveal f-f excitation patterns similar to those of NpO_2 and PuO_2 respectively, thus indicating the existence of Pu(IV), Np(IV) on the iron strips and that reduction of Np(V), Pu (VI) had been taken place.

Figure 3. U5d RIXS scattering spectra of poly-crystalline UO_2 , UO_3 . The energy of the incident photons was set to 100 eV.

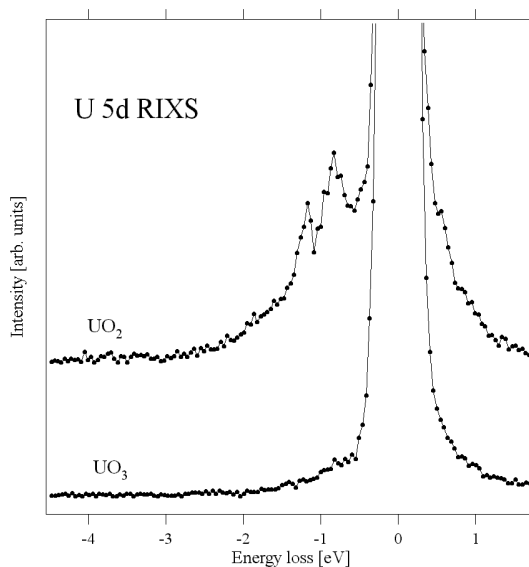
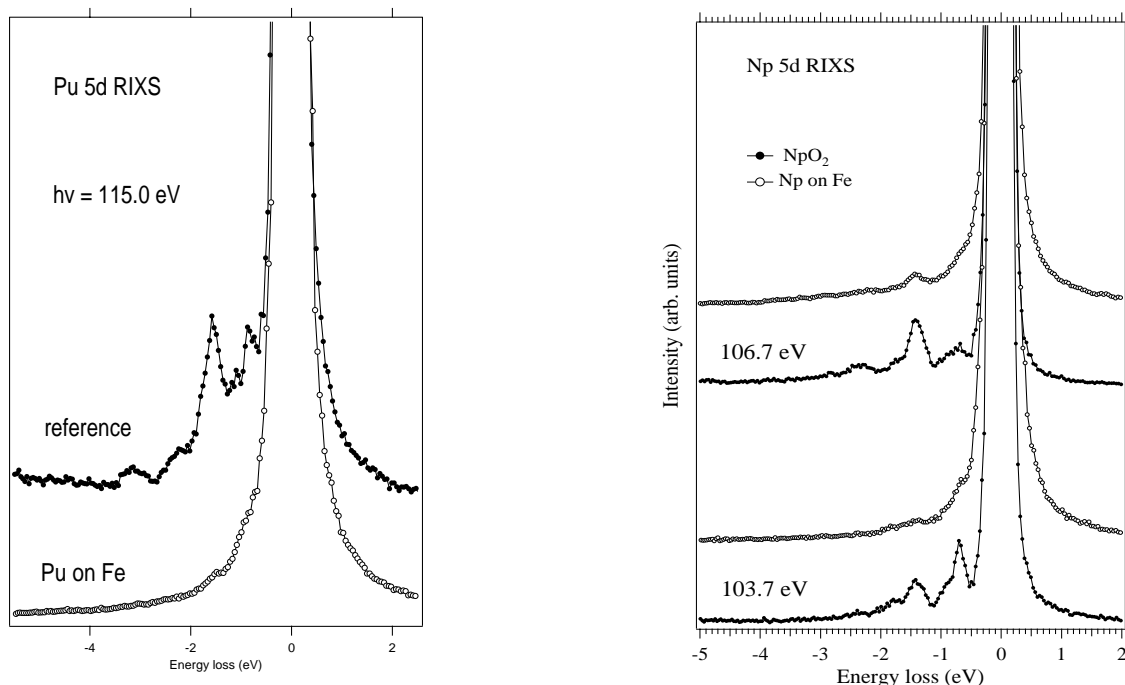
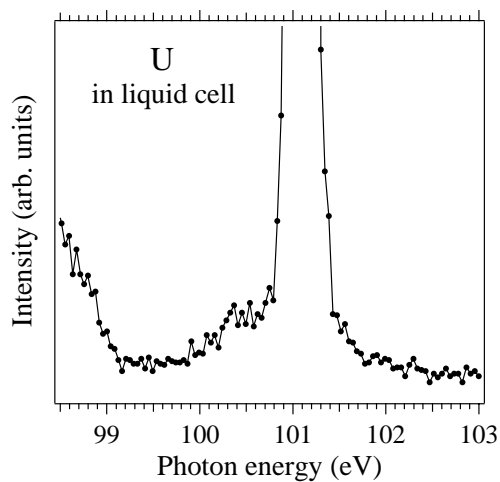


Figure 4. Comparison of RIXS spectra of NpO_2 , PuO_2 (reference) and Np , Pu formed on the Fe strip (respectively), recorded at the excitation energies, close to that of the pre-threshold structure in the Np 5d and Pu 5d XA spectra.



We also monitored a reaction between U(VI) ions and iron using the liquid cell (Figure 1) for the in-situ studies. We used a silicon nitride window for these measurements and therefore the silicon contribution can be observed below 99 eV (Figure 5). After three days of exposure of Fe film to the solution, the f-f transitions can be observed in RIXS spectrum, thus indicating that U(IV) was formed on the thin iron film in the cell.

Fig 5. U 5d RIXS spectra of uranium in the liquid reaction cell



The results of our studies unambiguously indicate that RIXS profiles, corresponding to the f-f excitations are very sensitive to the oxidation states of actinides in different systems, which allowed us to suggest that soluble actinides species (U, Pu, Np) in the disposal canister can be reduced by iron to lower solubility form and prevent release from the canister.

Acknowledgements

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