

Synchrotron Studies of the Transformation of Uranyl Complexes on Metallic Surfaces

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Organic complexation and inorganic reactions with contaminant uranium are of major concern in development and optimization of remediation technologies, in understanding the fate and transport of uranium and mixed wastes, and in predicting bioavailability of uranium. The organic ligands involved in these complexes arise from organic matter in the soil, microorganisms in the environment, and industrial wastes. Characterization of these complexes is essential, both in their initial state and following transformation that occurs through agents of electron transfer. Electron transfer and subsequent changes in the molecular complex will have a major impact on the issues listed above. These reaction pathways can arise from microbiological activity, interaction with remediation agents (including chelators and zero valent iron), and through reactions on actively corroding metallic surfaces. We have studied the nature of these reactions through a combination of electrochemical analysis and synchrotron-based techniques, including IR microspectroscopy and EXAFS. Data generated from these spectroscopic techniques has been used to refine computational molecular models of the initial and transformed complexes.

Earlier studies have shown that exposure of uranyl nitrate to actively corroding carbon steel surfaces results in a variety of uranium and mixed uranium-iron oxyhydroxides.^{1,2} The results were found to be consistent with iron corrosion products co-precipitated with uranium (though synchrotron IR microspectroscopy (SIRMS) indicates that physical occlusion and trapping by thick oxides and oxyhydroxides formed on a metal surface also play a role in retention of contaminants).³ Treatment of these corroded surfaces with organic acids (hydroxycarboxylic acid) leads to transformation and generation of uranium organic ligands which can then be acted upon by bacteria as part of a bioreduction/photoreduction remediation process.

In recent studies, SIRMS has been used to characterize the nature of association of uranium with organic ligands and bacteria. This includes not only the complexes formed during remediation, but also those formed through interaction with components of humic and fulvic acids (prevalent in the environment). Complexes characterized included uranium liganded to catechol, salicylic acid, malic acid and fulvic acid. Synchrotron IR studies of the aromatic compounds showed that the ring stays intact after complexation. In general, the uranium usually binds to the hydroxyl or carboxylate groups. The uranium was found to be associated with both phenol groups in the catechol complex, with a uranyl (UO_2^{2+}) vibration at $\sim 890\text{ cm}^{-1}$, which was obscured by C-H deformations. Two types of carboxylate coordination can be characterized using FTIR: unidentate or bidentate/bridging. The difference in the wavenumbers of the asymmetric ($\sim 1550\text{-}1650\text{ cm}^{-1}$) and symmetric

stretching ($1340\text{-}1440\text{ cm}^{-1}$) of unidentate carboxylate bonding is greater than the bidentate/bridging bonding. IR shows that both the carboxylate (1599 and 1412 cm^{-1}) and phenol group participate in the uranium-salicylate complex, which had a U-O vibration at $\sim 910\text{ cm}^{-1}$. Bidentate (1562 and 1420 cm^{-1}) and unidentate (shoulders: 1614 and 1341 cm^{-1}) coordination between the uranium and carboxylate groups were found in the uranium-malate complex, which also had a U-O vibration at $\sim 910\text{ cm}^{-1}$. Uranium-fulvate samples were then compared to these analogs and it was found that the uranium complexes to the fulvic ligand via the carboxylate group in a unidentate fashion (1644 and 1440 cm^{-1}). The U-O stretching frequency was found to be at $\sim 920\text{ cm}^{-1}$, which was higher than the other U-organic analogs.

The stability of these complexes and nature of the electron transfer reaction was then characterized through exposure of the complexes in solution to a platinum electrode in an electrochemical cell. Changes in the complexes could then be monitored and analyzed by EXAFS analysis and by IR spectroscopy. Preliminary results of these electrochemical redox studies on platinum, iron and stainless steel electrodes were conducted, and the resulting data used to characterize changes in the complexes which would effect attachment, transport, remediation and bioavailability. Molecular modeling software is being used to aid in interpretation of the vibrational spectra from the baseline uranium organic complexes described above as well as from complexes which have undergone transformation through electron transfer mechanisms. Reactions with corrosion products and with bacteria (*Chlostridia sp.*) are investigated by SIRMS and modeling, while X-ray Photoelectron Spectroscopy (XPS) and EXAFS are used to characterize the reduction products on the electrode in the electrochemical cell.

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