

REDUCING URANIUM WASTE

Waste uranium from power generation, the mining of raw feedstock, and past military-related activities is a growing environmental concern. Coping with this problem will only be possible with a new understanding of how uranium ions in the environment interact with soils and water, and how that affects their transport and fate. Researchers using the MR-CAT 10-ID-B beamline at the APS have turned to titration and x-ray absorption fine structure spectroscopy (EXAFS) analysis to help them determine what factors lead to the immobilization of uranium ions by reduction with sub-soil ferrous [iron(II)] ions. Fe(II) is produced by underground soil bacteria; it is found in clays, green rusts, and magnetite, and is adsorbed on minerals and bacteria. Their results hold promise for understanding how to protect the environment from uranium contamination and for designing methods to remediate water-rock systems.

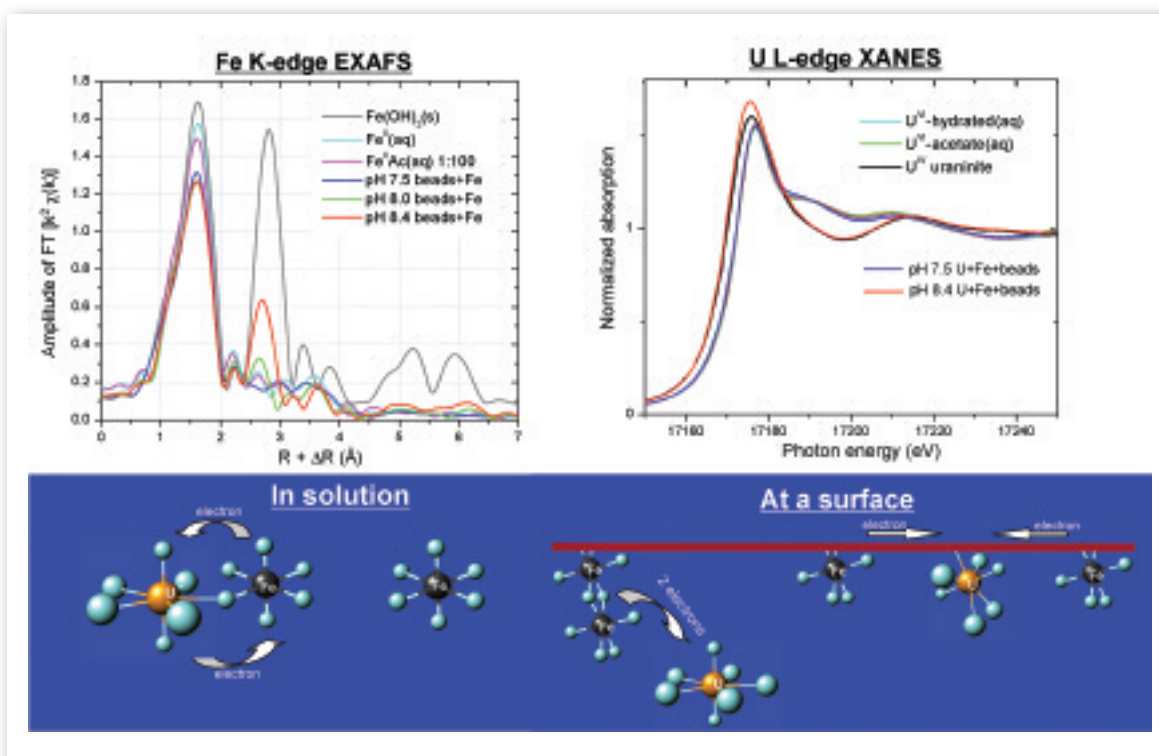


Fig. 1. X-ray absorption near edge structure and EXAFS reveal the differences in behavior of uranium ions in solution or on coated microspheres.

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Uranium in its common "VI" oxidation state, U(VI), can be reduced to a lower oxidation state U(IV) by Fe(II) ions. In the reduced state the uranium ions are not soluble in water and so can become immobilized below ground rather than leaching into water and being dispersed. The researchers have investigated how Fe(II) and U(VI) ions are absorbed onto the surface of microspheres of polystyrene. These microspheres, coated with acidic carboxyl groups, mimic the properties of soil particles and so can act as a model of the behavior of the iron and uranium ions below the surface.

The team used standard acid-base titrations (a method of quantitative/chemical analysis used to determine the concentration of a known reactant) to track the behavior of uranium ions when mixed with Fe(II) ions and the coated microspheres. They coupled these studies with Fe K-edge and U L-edge extended x-ray absorption fine structure (EXAFS) spectroscopy that allowed them to work out the bonding arrangements and the overall atomic environment of iron and uranium ions adsorbed on to the surface (Fig. 1). They found that iron ions mixed by themselves with the microspheres at mildly alkaline values of pH representative of groundwater systems; they had two distinct ways of adsorbing to the surface: either as single Fe(II) ions (pH 7.5) or as aggregates of Fe(II) species on the surface (pH 8.4). Uranium ions mixed alone with the microspheres stuck to the surface as isolated U(VI) ions at the same values of pH.

When the iron, uranium, and microspheres were all mixed together at pH 7.5, the Fe and U ions were co-adsorbed on the surface in the same manner as they are by themselves. After four months, the U(VI) was not reduced by either the adsorbed iron or any free-floating iron in the solution. This was in sharp contrast to the reaction at slightly more alkaline pH 8.4, where Fe(II) atoms aggregated and the U(VI) was completely and rapidly reduced to U(IV) in the form of nanoparticles. The U(IV) nanoparticles could be stored for at least four months in this immobile state provided they were not exposed to air. Air exposure rapidly reoxidized them to the U(VI) state.

These findings could explain why uranium ions appear to be more easily reduced by Fe(II) on a surface rather than free-flowing Fe(II) in solution: it is the ability of the U(VI) atom to rapidly receive two electrons for its reduction to U(IV).

The researchers suggest that a mechanism involving a two-electron transfer to the uranium ion would not occur readily in solution without the support of a surface. They propose that successful reduction from U(VI) to U(IV) requires a quick second electron transfer to a "dead-end" U(V)-Fe(III) intermediate, which returns to separate U(VI) and Fe(II) ions unless another electron is supplied in time.

Moreover, because the reduction takes place in two steps, they require the metal ions to stay close, which is less likely to happen in solution than on the microsphere surface. The presence of the iron oligomers at the higher pH also means there is a ready local supply of electrons for the second stage of reduction. — *David Bradley*

See: Maxim I. Boyanov^{1,2*}, Edward J. O'Loughlin¹, Eric E. Roden³, Jeremy B. Fein², and Kenneth M. Kemner¹, "Adsorption of Fe(II) and U(VI) to carboxyl-functionalized microspheres: The influence of speciation on uranyl reduction studied by titration and XAFS," *Geochim. Cosmochim. Acta* **71**, 1898 (2007). DOI: 10.1016/j.gca.2007.01.025

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10-ID-B • MR-CAT • Materials science, environmental science, chemistry • Microfluorescence (hard x-ray), x-ray absorption fine structure (XAFS), diffraction anomalous fine structure, micro-XAFS • 3.3-cm undulator A • Accepting general users