Mechanisms of Radionuclide-Hydroxycarboxylic Acid Interactions for Decontamination of Metallic Surfaces

Project ID: 64946

Dr. A. J. Francis, Brookhaven National Laboratory

Research Objective

This project addresses key fundamental issues involved in the use of simple and safe methods for the removal of radioactive contamination from equipment and facilities using hydroxycarboxylic acids. The objectives of this research are to (i) determine the nature of the association of radionuclides with the metal surfaces commonly found at sites targeted for decontamination and decommissioning, such as plain carbon steel and stainless steel; (ii) selectively remove the low levels of radionuclides such as U, Pu, Co, Cs, and Sr from contaminated metallic surfaces using hydroxycarboxylic acids (citric acid and its analogs) by elucidating the coordination, complexation, dissolution and removal mechanisms; and (iii) recover radionuclides in a concentrated form by photochemical and biochemical degradation of the extract containing radionuclide-organic complexes thereby resulting in significant reduction in secondary waste generation. The basic information derived from this study should also be applicable to decontamination of other metallic surfaces as well as porous materials such as cement.

Research Progress and Implications

This report summarizes work after 17 months of a 3-year project. During this period we (i) synthesized the iron oxides ferrihydrite, goethite, green rust II, lepidocrocite, and magnetite containing U; (ii) determined the chemical composition and the nature of association of U with the oxides (total metal, XRD, XPS, FTIR, XANES, EXAFS); (iii) determined the dissolution profile of Fe and U from the oxides by i) HCl, and ii) citric acid; (iv) determined the rate and extent of biodegradation of citric acid in the extracts to remove citric acid; followed by photodegradation of the extracts to recover U; and (v) initiated studies with pre-, and post-rusted U contaminated plain carbon steel coupons to determine the nature of U association with the rust and the extent of decontamination with citric acid treatment. In addition, we collected $^{137}$Cs and $^{60}$Co contaminated rusts samples and characterized them for total activity and mineral phases.

Characterization of Iron Oxides Containing Uranium. Ferrihydrite ($\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$), goethite ($\alpha$-$\text{FeOOH}$), lepidocrocite ($\gamma$-$\text{FeOOH}$), magnetite ($\text{Fe}_3\text{O}_4$), and green rust II with and without U, were analyzed for metal content; XRD for mineral form; XPS and FTIR to determine structural changes in the oxides as a result of U incorporation; and EXAFS to determine nearest neighbor association of U. These samples represent compounds typical of corrosion products formed on low carbon steel under atmospheric conditions.

The iron content of the oxides varied from 48 to 72%. Essentially all of the added U was incorporated in the oxide. The identification of the oxides with and without U was confirmed by comparing the X-ray diffraction patterns with the JCPDS library. Uranium containing samples showed additional spectral peaks indicating the presence of uranyl hydroxide with goethite, and uranium oxide or oxy-hydroxide with lepidocrocite and magnetite. EXAFS analysis at the U $L_{\text{III}}$ edge showed the uranium near-neighbor environment is different for each oxide. A U-U interaction was observed at 3.8Å for magnetite and goethite, while U-Fe pairings were observed at 3.4Å for ferrihydrite and lepidocrocite.

X-ray photoelectron spectroscopy analysis of the oxides containing U showed little change in the bulk material compared to the oxide without U, though slight reduction in the ionicity of the Fe-
oxyhydroxide bonding on the sample surface as a result of U adsorption is noted. FTIR spectra indicate adsorbed U appears to form a uranyl-hydroxo complex.

**Decorporation of Uranium From the Oxides by Citric Acid.** We determined the exchangeable form of Fe and U; the chemical association of U with the oxide by HCl dissolution; and the decorporation of U from the oxide by citric acid. HCl dissolution of the oxides showed complete dissolution of the U within the first hour of exposure. Correlation of the rate and extent of Fe with U dissolution varied in the following order: ferrihydrite > lepidocrocite > magnetite > goethite. Citric acid extraction efficiency of U from the oxides varied with the mineral form of the oxide. Uranium from goethite and magnetite was completely extracted by citric acid, whereas with ferrihydrite and lepidocrocite it increased with decreasing pH. Complete dissolution of Fe from lepidocrocite and magnetite occurred at pH 3.5 but not at pH 2.2, indicating selectivity in the dissolution of these minerals by citric acid.

**Corroded Steel Coupons.** FTIR and XPS analyses were performed from the surface of low carbon steel coupons which were either dipped in a dilute uranyl nitrate solution or contaminated through atomization of a uranyl nitrate solution onto the coupon surface following various times of accelerated corrosion in a high humidity chamber developed for this program. All exposed samples showed a heterogeneous distribution of uranyl groups on the surface. Samples which were allowed to corrode further at 90% relative humidity for three days to one week following uranyl exposure showed some occlusion of the contaminant uranium by a loosely bound amorphous hydrated corrosion product. Surface areas covered by a thinner iron oxy-hydroxide corrosion layer showed stronger uranyl adsorption. The uranium-oxygen infrared stretching frequency was slightly shifted, indicating weaker bonding, whereas exposure to the acidic (uranil) nitrate in solution resulted in an accelerated Fe corrosion product.

XPS data indicates that the uranium exists in a mixed U(VI)/U(IV) state following exposure to a lightly corroded or non-corroded surface and primarily as U(VI) when incorporated onto a heavily corroded steel surface. The samples were subsequently cleaned in a 0.1 M citric acid solution, and both the surfaces and the solution were analyzed. Citric acid was found to effectively chelate and remove uranium from all surfaces. Both FTIR and XPS analysis showed removal of most uranyl contamination by citric acid treatment. In addition, coupons exposed to citric acid were found to retain a thin layer of iron carboxylate which may act as a protective layer, thereby retarding additional atmospheric corrosion.

Secondary ion mass spectroscopy (SIMS) studies have been initiated on the contaminated and the rinsed surfaces. Data is currently being compared to the XPS and FTIR results.

**Characterization of Contaminated Rust Samples.** Rust samples collected from contaminated steels were analyzed for total activity, iron content, and mineral phases. The samples contained $^{137}$Cs ($1.5 \times 10^{-6}$ to $2.4 \times 10^{-5} \mu$Ci/g) and/or $^{60}$Co ($5.4 \times 10^{-8}$ to $3.4 \times 10^{-7} \mu$Ci/g). The iron content ranged from 54 to 80% in the samples. X-ray diffraction analysis showed the presence of magnetite, goethite, and/or lepidocrocite as predominant phases.

**Planned Activities**

- Characterization of radionuclides (U, Co, Cs and Sr) associated with plain carbon steel, stainless steel and copper pipes; elucidate the mechanisms of selective complexation and dissolution of the radionuclides by citric acid from contaminated steels (FY 2000).
- Decontamination of contaminated metallic surfaces obtained from DOE sites and treatment of waste stream by biodegradation followed by photodegradation with radionuclide recovery resulting in waste volume reduction and waste minimization (FY 2001).

**Information Access**


