

Project ID: **64946**

Project Title: **Mechanisms of Radionuclide-Hydroxycarboxylic Acid Interactions for Decontamination of Metallic Surfaces**

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*Progress Report*

## **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 1 year of a 3-year project. During this period we (i) investigated the association of uranium with various synthetic metal oxides commonly formed as corrosion product, and (ii) collected rust samples from contaminated corroded metallic surfaces at BNL and analyzed for total iron and radionuclides.

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

The iron content of the oxides varied from  $8.65 \pm 0.16$  mmol/g (48% Fe) in lepidocrocite to  $13.0 \pm 0.6$  mmol/g (72% Fe) in magnetite. Essentially all of the added uranium was incorporated in the oxide (25% by weight). The identification of the oxides with and without uranium was confirmed by comparing the X-ray diffraction patterns with the JCPDS library: two-line ferrihydrite (29-712), goethite (29-713), lepidocrocite (8-98), and magnetite (19-629). In general, the spectral intensities of the samples with uranium added are less intense indicating the effect of sample dilution due to added uranium, but not on mineral formation. Addition of uranium to the oxide during its formation resulted in some additional spectral peaks for magnetite, goethite, and lepidocrocite: presence of uranyl hydroxide for goethite, while lepidocrocite and magnetite showed peaks attributable to the presence of uranium oxide or oxy-hydroxide. EXAFS analysis at the  $\text{U L}_{\text{III}}$  edge showed the uranium near-neighbor environment is different for each oxide. Analysis of more distant shells showed U-U interaction at  $3.8 \text{ \AA}$  for magnetite and goethite, while U-Fe pairings were observed at  $3.4 \text{ \AA}$  for ferrihydrite and lepidocrocite. The form of uranium associated with goethite has been identified as uranyl hydroxide. The association of uranium with the other oxides is being determined.

X-ray photoelectron spectroscopy analysis of the oxides containing uranium show little change in the bulk material compared to the oxide without added uranium, though slight reduction in the ionicity of the Fe-oxyhydroxide bonding on the sample surface as a result of uranium adsorption is noted. FTIR spectra indicate uranium adsorbs at hydroxide rich sites, resulting in a reduction in the intensity of the Fe-hydroxide signal. Adsorbed uranium 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 for decontamination. HCl dissolution of the oxides showed complete dissolution of the uranium within the first hour of exposure. Correlation of the rate and extent of Fe with U dissolution varied in the following order (low to high correlation): goethite < magnetite < lepidocrocite < ferrihydrite. Citric acid extraction efficiency of uranium from the oxides varied with the mineral form of the oxide. Extraction of uranium from ferrihydrite and lepidocrocite increased with decreasing pH; uranium in goethite and magnetite was completely extracted in all treatments. In general, the extraction efficiency was independent of citric acid concentration, and was pH dependent for ferrihydrite and lepidocrocite. Complete Fe dissolution for lepidocrocite and magnetite occurred at pH 3.5 but not at pH 2.2, indicating the role of citric acid in the selective dissolution of these minerals. Iron dissolution was minimal in goethite and ferrihydrite at all pH and citric acid concentrations tested.

Corroded Steel Coupons. FTIR and XPS analyses were performed from the surfaces of low carbon steel coupons which were dipped in a dilute uranyl nitrate solution 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 following the dipping experiment. 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, as indicated by FTIR. XPS analysis showed that the adsorbed uranium resided at the outer surface of a heavily corroded sample and remained in a hexavalent state, though no longer as uranyl nitrate, as no nitrogen signal was detected. The uranium-oxygen infrared stretching frequency was slightly shifted, indicating weaker bonding, where exposure to the acidic (uranyl) nitrate in solution resulted in an accelerated Fe corrosion product.

Characterization of Contaminated Rust Samples. Rust samples collected from contaminated steels were analyzed for total activity, iron content, and mineral phases. The samples contained  $^{137}\text{Cs}$  ( $1.5 \times 10^{-6}$  to  $2.4 \times 10^{-5}$   $\mu\text{Ci/g}$ ) and/or  $^{60}\text{Co}$  ( $5.4 \times 10^{-8}$  to  $3.4 \times 10^{-7}$   $\mu\text{Ci/g}$ ). 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 and copper pipes (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**

1. Interaction of Uranium with Corrosion Products Formed on Plain Carbon Steel. G.P.Halada, C.R. Clayton, M.J. Vasquez, A. Gupta, A.J. Francis, C.J. Dodge and J.B. Gillow, Paper presented at the 195<sup>th</sup> Meeting of the Electrochemical Society, May 2-6, 1999, Seattle, WA (Abstract no. 108).
2. A Spectroscopic Study of the Association of Contaminant Uranium with Mild Steel Corrosion Products. G.P.Halada, C.R. Clayton, A. Gupta, A.J. Francis, C.J. Dodge and J.B. Gillow, Paper presented at the Symposium on First Accomplishments of Environmental Management Science Program, 218<sup>th</sup> American Chemical Society, Annual Meeting, August 22-26, 1999, New Orleans, LA, (paper NUCL-61).
3. Decontamination of Uranium Contaminated Metallic Surfaces with Uranium Recovery. A.J. Francis, C.J. Dodge, J.B. Gillow, G.P. Halada, and C.R. Clayton. Paper presented at the Symposium on First Accomplishments of Environmental Management Science Program, 218<sup>th</sup> American Chemical Society, Annual Meeting, August 22-26, 1999, New Orleans, LA, (paper NUCL-65).