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

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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 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 biochemical and photochemical 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 2 years of a 3-year project. During this period we (i) synthesized 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 (ICP-AES, XRD, XPS, FTIR, XANES, EXAFS); (iii) determined the dissolution profile of Fe and U from the oxides by HCl and citric acid; (iv) determined the rate and extent of biodegradation of citric acid in the extracts followed by photodegradation to recover U; (v) determined the nature of U association with the rust from pre- and post-rusted U contaminated plain carbon steel coupons; (vi) determined the extent of coupon decontamination following citric acid treatment; and (vii) determined the rate and extent of Fe and U removal from the citric acid extract following decontamination of the coupons. In addition, we collected ^{137}Cs and ^{60}Co contaminated rusts samples and characterized them for total activity and mineral phases.

Synthetically Prepared Iron Oxides Containing Uranium. Ferrihydrite ($\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$), goethite ($\alpha\text{-FeOOH}$), green rust II, lepidocrocite ($\gamma\text{-FeOOH}$), and magnetite (Fe_3O_4), with and without U were synthesized. The iron content of the oxides varied from 48 to 72%. Essentially all of the added U was incorporated in the oxide. The U was associated with magnetite and goethite as uranyl hydroxide, while U in ferrihydrite and lepidocrocite formed an inner sphere complex with Fe. A slight reduction in the ionicity of the Fe-oxyhydroxide bonding on the sample surface was noted as a result of U adsorption. Correlation of the rate and extent of Fe with U dissolution in 6M HCl varied in the following order: ferrihydrite > lepidocrocite > magnetite > goethite. Uranium from goethite and magnetite was completely extracted by citric acid, whereas with ferrihydrite and lepidocrocite it increased with decreasing pH. Biodegradation of citric acid in the extract was completed within 48 hours with U remaining in solution. Photodegradation of the supernates from biodegradation resulted in the precipitation of 87% to 99% of the U from solution.

Characterization of Corroded Steel Coupons Before Treatment. FTIR and XPS analyses were performed on the surfaces 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 (uranyl) nitrate in solution resulted in an accelerated Fe corrosion product.

XPS analysis 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.

Decontamination of U-Contaminated Steel Coupons. The effectiveness of decontamination of U-contaminated coupons which have undergone alternate cycles of U exposure and rusting (ER/ER) by (i) citric acid alone; (ii) oxalic acid-hydrogen peroxide-citric acid; or (iii) citric acid-hydrogen peroxide-citric acid treatment has been determined. Treatment (i) resulted in removal of 63.6% of the U, treatment (ii) resulted in removal of 67±2% of the U, while treatment (iii) removed 72±1% of the U from the coupon surface.

Characterization of Coupons After Decontamination. XPS analysis of the U-contaminated coupons showed three species of carbon on the sample surface: adventitious hydrocarbon (284.6 eV); -CH₂OH (286.1 eV); and -COOH (288.2 eV). In addition, a small U4f peak could be detected. The U4f_{7/2} binding energy of the residual contaminant was 382.2 eV, about 0.5 eV lower than that of U(VI) from a uranyl or oxide standard. This likely represents a complexed U species incompletely removed from the surface by the decontamination process. The Fe2p_{3/2} spectra indicates ferrous species (Fe²⁺) was predominant.

FTIR microspectroscopy conducted at the National Synchrotron Light Source showed that small amounts of residual U contaminant remained in heavily corroded areas. This indicates it is present as a result of occlusion by iron oxides. In areas where a thin yellow deposit was visible, FTIR indicated the presence of a complexed form of U with a mixed 4+/6+ character and strong IR absorption frequencies indicative of carboxylate salts. Additional absorption peaks within the spectra from these areas are being investigated and may indicate complexation with Fe corrosion products that were not removed by rinsing. A U-O stretching frequency indicative of purely U(VI) species (and very similar to published data for uranyl hydroxides) was detected from small amounts of residual U on dark corrosion products rich in magnetite. These areas represent the chemical sites of the most tenacious contaminants, and though lower in overall U retention levels (as compared to the incompletely removed complexed U described above), these are likely the strongest U binding sites.

Treatment of U-Contaminated Citric Acid Solution from Coupon. Biodegradation of the citric acid extract solution from decontamination of U-contaminated low carbon steel coupon resulted in complete removal of citric acid and iron from solution but not U which remained in solution. The supernate was filtered, the pH adjusted to 3.5, and the solution was exposed to light. Soluble U decreased from 29.5 µM (7.2 ppm) to 5.7 µM (1.4 ppm). The precipitate was previously identified as uranium trioxide.

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 oxalic acid and 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

1. Francis, A.J., C.J. Dodge, J.B. Gillow, G.P. Halada, and C.R. Clayton. Mechanisms of Radionuclide-Hydroxycarboxylic Acid Interactions for Decontamination of Metallic Surfaces. Paper presented at the EMSP National Workshop 2000, April 24-28, 2000, Atlanta, GA.
2. Dodge, C.J. Structural Characterization of a Ternary Fe(III)-U(VI)-Citrate Complex. Ph.D. Dissertation, 1999. SUNY-SB, Stony Brook, NY.
3. Halada, G.P., C.R. Clayton, A. Gupta, A.J. Francis, C.J. Dodge and J.B. Gillow. Removal of Contaminant Uranium from Corroded Steel Surfaces Using Citric Acid. Paper presented at the 197th Meeting of the Electrochemical Society, May 15-19, 2000, Toronto, Canada.
4. Halada, G.P., C.R. Clayton, A. Gupta, A.J. Francis, C.J. Dodge and J.B. Gillow. Removal of Contaminant Uranium from Corroded Steel Surfaces Using Citric Acid. Paper presented at the 1999 Tri-Service Conference on Corrosion, organized by the U.S. Army Research Laboratory, Aberdeen Proving Grounds, MD Nov 15-19, 1999, Myrtle Beach, SC (Paper No. 0006).

5. Halada, G.P., C.R. Clayton, A. Gupta, A.J. Francis, C.J. Dodge and J.B. Gillow. A Study of the Interaction of Contaminant Uranium with Atmospheric Corrosion Products on Steel and Subsequent Complexation by Hydroxycarboxylic Acid. Paper presented at the 1999 Joint International Meeting, The Electrochemical Society and the Electrochemical Society of Japan, October 17-22, 1999, Honolulu, Hawaii (Abstract no. 617).
6. Francis, A.J., C.J. Dodge, J.B. Gillow, G.P. Halada, and C.R. Clayton. Decontamination of Uranium Contaminated Metallic Surfaces with Uranium Recovery. Paper presented at the Symposium on First Accomplishments of Environmental Management Science Program, 218th American Chemical Society, Annual Meeting, August 22-26, 1999, New Orleans, LA, (paper NUCL-65).
7. Halada, G.P., C.R. Clayton, A. Gupta, J. Sakal, A.J. Francis, C.J. Dodge and J.B. Gillow. A Spectroscopic Study of the Association of Contaminant Uranium with Mild Steel Corrosion Products. Paper presented at the 218th Annual ACS Meeting, First Accomplishments of the EMSP, New Orleans, 1999.
8. Halada, G.P., C.R. Clayton, M.J. Vasquez, A. Gupta, A.J. Francis, C.J. Dodge and J.B. Gillow. Interaction of Uranium with Corrosion Products Formed on Plain Carbon Steel. Paper presented at the 195th Meeting of the Electrochemical Society, May 2-6, 1999, Seattle, WA (Abstract. No. 108).