

Project ID: **59849**

Project Title: **Radionuclide Immobilization in the Phases Formed by Corrosion of Spent Nuclear Fuel: The Long-Term Assessment**

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Environmental Management Science Program

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Research Objectives:

This research program is designed to identify the long-term corrosion products of naturally occurring UO_{2+x} under oxidizing conditions as an analogue for corrosion of UO_2 in spent nuclear fuel. This work will identify the phases that form, the reaction path during their formation, their stability, and their ability to incorporate key radionuclides.

Research Progress and Implications:

As of June 1, 1999, this report summarizes work that has been completed during the second year of a three year research program. During this period, a post-doctoral fellow, F. Chen, has focused his efforts on the development of a theoretical basis for predicting the Gibbs free energies and enthalpies of formation of uranium (VI) phases. A second post-doctoral fellow, Donggao Zhao, joined the research program in 1999, and he has focused his efforts on the microchemical analysis of the corrosion products of natural uraninites, UO_{2+x} . The two approaches complement one another, as the analytical work on natural uraninites can be used to confirm the theoretical calculations of uranyl phase stability. Conversely, the analytical results can be used to guide the theoretical analysis. In collaboration with Professor Peter Burns at Notre Dame, we have continued our efforts to evaluate the capabilities of the uranyl phases to incorporate and retard release of important radionuclides: ^{237}Np , ^{79}Se , ^{99}Tc and ^{129}I . Research results and highlights are summarized in the following paragraphs.

The Gibbs free energies and enthalpies for uranyl phases have been estimated based on a method that sums polyhedral contributions. The molar contributions of the structural components to ΔG_f^0 and ΔH_f^0 are derived by multiple regression using the thermodynamic data of phases for which the crystal structures are known. In comparison with experimentally determined values, the average residuals associated with the predicted ΔG_f^0 and ΔH_f^0 for the uranyl phases used in the model are 0.08 and 0.10%, respectively, well below the limits of uncertainty for the experimentally determined values. In order to analyze the reliability of the predicted ΔG_f^0 values, activity-activity diagrams in SiO_2 - $\text{CaO-UO}_3\text{-H}_2\text{O}$ and $\text{CO}_2\text{-CaO-UO}_3\text{-H}_2\text{O}$ systems at 298.15K and 1 bar were constructed using the predicted $\Delta G_{f,298.15}^0$ values for the relevant U(VI) phases. There is good agreement between the predicted mineral stability relations and field occurrences, thus providing confidence in this method for the estimation of ΔG_f^0 and ΔH_f^0 of the U(VI) phases. These results were recently published in the *American Mineralogist*, vol. 84, 650-654 (1999).

With the incorporation of radionuclides into uranyl phases, site-mixing and structural disorder may occur, both of these phenomena can affect the residual entropy of the uranyl phase. The entropies of uranyl phases used in geochemical calculations are usually based on calorimetric measurements. However, because of the contribution of neglected residual entropy, which cannot be determined by calorimetric measurements, the true third-law entropies for many phases may be quite different from the entropy values

derived from thermal data, and this may affect calculated solubilities which are often used in geochemical calculations. Most uranyl phases are based on sheet or chain structures and usually contain several molecular water groups; thus, site-mixing, vacancies, as well as disorder in the orientation of hydrogen bonds and the polar H₂O molecules may occur. The ideal site-mixing configurational entropies of uranates, uranyl oxide hydrates, silicates, phosphates, carbonates and sulphates were calculated based on crystallographic data. The calculated results indicate that the residual contributions that arise from substitutions and vacancies to the third law entropies of uranyl phases may be as high as tens of percent of their calorimetric entropies. An examination of the crystal chemistry of molecular water in uranyl phases suggests that considerable residual entropy may be caused by disorder of hydrogen bonds associated with interstitial H₂O groups. The effect of residual entropy on the solubility of solid phases can be substantial. These results have been submitted for publication in *Applied Geochemistry*.

⁷⁹Se is a long-lived (1.1×10⁶ year) fission product which is chemically and radiologically toxic. Under Eh-pH conditions typical of oxidative alteration of spent nuclear fuel, selenite, SeO₃²⁻ or HSeO₃⁻, or selenate, SeO₄²⁻, are the dominant aqueous species of selenium. Because of the high solubility of metal-selenites and metal-selenates and the low adsorption of selenite and selenate aqueous species by geological materials under alkaline conditions, selenium may be highly mobile. However, ⁷⁹Se released from altered fuel may become immobilized by incorporation into secondary uranyl phases as low concentration impurities, and this may significantly reduce the mobility of selenium. Analysis and comparison of the known structures of uranyl phases indicate that (SeO₃) may substitute for (SiO₃OH) in structures of α-uranophane and boltwoodite that are expected to be the dominant alteration products of UO₂ in Si-rich groundwater. The substitutions (SeO₃) ↔ (SiO₃OH) in sklodowskite, Mg[(UO₂)(SiO₃OH)]₂(H₂O)₆, and (SeO₃) ↔ (PO₄) in phurcalite, Ca₂[(UO₂)₃(PO₄)₂O₂](H₂O)₇, may occur with the eliminated apical anion being substituted for by an H₂O group, but experimental investigation is required. The close similarity between the sheets in the structures of rutherfordine, [(UO₂)(CO₃)], and [(UO₂)(SeO₃)] implies that the substitution (SeO₃) ↔ (CO₃) can occur in rutherfordine, and possibly other uranyl carbonates. However, the substitutions: (SeO₃) ↔ (SiO₄) in soddyite and (SeO₃) ↔ (PO₄) in phosphuranylite may disrupt their structural connectivity and are, therefore, unlikely. These results have been accepted for publication in the *Journal of Nuclear Materials*. A similar study of ⁹⁹Tc incorporation into uranyl phases has been submitted to the *Journal of Nuclear Materials* and is presently being reviewed.

Finally, we have established an extensive collection of uranium minerals and phases (approximately 700) that are the basis for the detailed electron microprobe studies by Donggao Zhao. Analytical protocols for trace element analysis have been completed and the first results of the uranyl phase analyses will be presented the “Seventh International Conference on the Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere”, September 26-October 1, 1999, at Lake, Tahoe, CA.

Planned Activities:

During the next year, our program will continue to focus on five areas: **1.** Detailed analysis of natural samples to identify the principal phases and their proportions as a function of geochemical conditions and reaction progress. **2.** Analysis of uranyl phases for their trace element content, that is a determination of the fate of impurity elements that are released during matrix dissolution of the UO_2 . **3.** An evaluation of the long-term stability of uranyl phases under oxidizing conditions. **4.** Comparison to theoretical calculations of phase stability to actual natural occurrences of these uranyl phases. **5.** An evaluation of radionuclide incorporation into uranyl phases, particularly ^{99}Tc and ^{129}I .