Environmental Management Science Program

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

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Research Objectives:

This research program is focused on developing models of the long-term alteration of UO$_2$ in spent nuclear fuel. The models are based on detailed studies of the long-term corrosion products of naturally occurring UO$_{2+x}$ under oxidizing conditions. The natural samples range in age from a few millions of years (Colorado Plateau in the U.S.A.) to approximately 2 billion years (the Oklo natural reactors in Africa). This research program identifies the phases that form, evaluates their stability and the ability of U$^{6+}$-phases to incorporate key radionuclides. We have focused on radionuclides ($^{237}$Np, $^{239}$Pu, $^{99}$Tc, $^{79}$Se and $^{129}$I) that make important contributions to exposure dose during geologic disposal.

Research Progress and Implications:

As of February, 2000, this report summarizes work that has been completed during the first two-and-half years of a three year program. During this time, a post-doctoral fellow, F. Chen, has focused his efforts on the development of a theoretical basis for predicting the Gibbs free energies, enthalpies and entropies of formation of uranium (VI) phases. A second post-doctoral fellow, Donggao Zhao, completed microchemical analysis of the corrosion products of natural uraninites, UO$_{2+x}$. Zhao’s work has demonstrated that the secondary alteration products can incorporate trace elements into their structures and hence provide for effective retardation. A third post-doctoral fellow, Keld Jensen, has begun a detailed study of samples from the Oklo natural reactors to evaluate the transport and retardation of radionuclides. In collaboration with Professor Peter Burns at Notre Dame, we have continued the evaluation of the capabilities of the uranyl phases to incorporate and retard release of important radionuclides: $^{237}$Np, $^{79}$Se, $^{99}$Tc and $^{129}$I.

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 $\Delta G^\circ_f$ and $\Delta H^\circ_f$ are derived by multiple regression using the thermodynamic data of phases for which the crystal structures are known. There is good agreement between the predicted mineral stability relations and field occurrences, thus providing confidence in this method for the estimation of $\Delta G^\circ_f$ and $\Delta H^\circ_f$ of the U(VI) phases.

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. This may affect calculated solubilities. The ideal site-mixing configurational entropies of uranates, uranyl oxide hydrates, silicates, phosphates, carbonates and sulphates have been calculated based on crystallographic data. Considerable residual entropy may be caused by disorder of hydrogen bonds associated with interstitial H$_2$O groups. The effect of residual entropy on the solubility of solid phases can be substantial.

$^{79}$Se is a long-lived (1.1×10$^6$ year) fission product which is chemically and radiologically toxic. Under Eh-pH conditions typical of oxidative alteration of spent nuclear fuel, selenite, SeO$_3^{2-}$ or HSeO$_3^-$, or selenate, SeO$_4^{2-}$, are the dominant aqueous species of selenium. $^{79}$Se 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 (SeO$_3$) may substitute for (SiO$_3$OH) in structures of $\alpha$-uranophane and boltwoodite that are expected to be the dominant alteration products of UO$_2$ in Si-rich groundwater.

$^{99}$Tc is a long-lived radioactive fission product with a half-life of $2.13 \times 10^5$ years and a fission yield of 6.13% in nuclear reactors. $^{99}$Tc is a prominent contributor to dose in safety assessments of nuclear waste repositories. Under Eh-pH conditions corresponding to the oxidative corrosion of spent nuclear fuel, which is constrained by the stability of uranyl phases relative to that of UO$_{2+x}$ phases, TcO$_4^-$ is the predominant species. TcO$_4^-$ is highly soluble and weakly adsorbed in the near-field. The incorporation of Tc$^{7+}$ into the structure of uranyl phases that are expected to occur as alteration products of spent nuclear fuel will destabilize the structure, suggesting that significant substitution of (TcO$_4^-$) will not occur in uranyl phases.

**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 $^{129}$I incorporation into uranyl phases.

**Information Access:**

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