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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 Objective

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 May 1998, this report summarizes work that has been completed during the first seven months of a 3 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. This is quite important, as these uranyl phases are the important alteration products that form during the corrosion of UO_2. The thermodynamic data base for these uranyl phase is extremely limited and often contradictory. Most previous efforts have been based on methods that sum, in stoichiometric proportions, the contributions of simpler constituent components to the ΔG^0_f of uranyl phases. Our approach for estimating the $\Delta G^0_{f,298}$ and $\Delta H^0_{f,298}$ of uranium (VI) phases is based on the observation that each type of coordination polyhedron has a set of well defined thermodynamic properties. In our analysis, the ΔG^0_f and ΔH^0_f of U(VI) minerals are considered to be the sum of oxide polyhedral contributions that were determined by multiple linear regression.

There is good agreement between the estimated and measured thermodynamic values for the minerals used in this model (Tables 1 and 2). Additionally, their natural occurrences confirm the potential of this approach as a tool in understanding and predicting the paragenesis and stability of U(VI) phases that form as a result of the alteration of uraninite and the UO_2 in spent nuclear fuel.

This approach offers the following advantages: (1) the structural component-summation technique provides improved accuracy relative to the oxide-summation technique if the coordination of the cation is considered; (2) the ΔG^0_f and ΔH^0_f may be estimated even though data for representative minerals in similar structural classes are not available because each type of cation polyhedron is considered to possess a set of well defined properties; (3) small errors in individual data of the reference phases can be reduced by multiple regression if the data base is large enough.

Although such an approach should not replace accurate experimental determinations, this method can be used in the absence of experimental data to infer the stabilities of U(VI) phases in various systems. Additionally, the estimated thermodynamic data can be used to suggest important pathways for long-term U(VI) phase transformations, and this can serve as a guide for future experimental work. Finally, results obtained by this method can be immediately improved as more accurately determined structures and thermodynamic data for U(VI) minerals become available.

Table 1. Comparison of measured and predicted $\Delta G^0_{f,298}$ values for phases used in the model and the associated errors.

U(VI) phases	Measured (kJ∑mol^{-1})	Predicted (kJ∑mol^{-1})	Absolute residuals (kJ∑mol^{-1})	Relative residuals %
$[(UO_2)_8O_2(OH)_{12}]\cdot 10H_2O$	-13092.0±6.8	-13122.9	30.9	0.24
β-$UO_2(OH)_2$	-1398.7±1.8	-1399.3	-0.6	0.04
$UO_3\cdot 0.9H_2O$	-1374.6±2.5	-1375.6	1.0	0.07
$Na_2U_2O_7$	-3011.5±4.0	-3013.0	1.5	0.05
$Na_4UO_2(CO_3)_3$	-3737.8±2.3	-3739.8	2.0	0.05
UO_2CO_3	-1563.0±1.8	-1562.3	-0.67	0.04
$BaUO_4$	-1883.8±3.4	-1886.6	2.8	0.15
BaU_2O_7	-3052.1±6.7	-3048.8	-3.3	0.11
$UO_2(NO_3)_2\cdot 6H_2O$	-2584.2±1.6	-2583.8	-0.4	0.01
$UO_2(NO_3)_2\cdot 3H_2O$	-1864.7±2.0	-1862.9	-1.8	0.09
$UO_2(NO_3)_2\cdot 2H_2O$	-1620.5±2.0	-1622.6	2.1	0.13
$UO_2SO_4\cdot 3.5H_2O$	-2535.6±1.8	-2537.1	1.5	0.06
$UO_2SO_4\cdot 3H_2O$	-2416.6±1.8	-2416.9	0.3	0.01
$UO_2SO_4\cdot 2.5H_2O$	-2298.5±1.8	-2296.8	-1.7	0.08
$(UO_2)_2\ SiO_4\cdot 2H_2O$	-3655.7±7.6*	-3651.8	-3.9	0.11
$Na(UO_2)(SiO_3OH)\cdot 1.5H_2O$	-2844.8±3.9*	-2838.8	-6.0	0.21
$Na_2\ (UO_2)_2(\ Si_5O_{13})\ \cdot 3H_2O$	-7993.9±9.6*	-8000.5	6.6	0.08
$Ba(UO_2)_6O_4(\ OH)_6\cdot 4H_2O$	-9387.0±17.1*	-9370.0	-17.0	0.18
Average				0.095

*calculated based on the solubility data provided by Nguyen et al. (1992), Casas et al. (1997b) and Vochten and Haverbeke (1990); measured $\Delta G^0_{f,298}$ values for other phases are from Grenthe et al. (1992).

Table 2. Comparison of measured and predicted $\Delta H^0_{f,298}$ values for phases used in the model and the associated errors

Uranyl phases	Measured (kJ∑mol^{-1})	Predicted (kJ∑mol^{-1})	Absolute residuals (kJ∑mol^{-1})	Relative residuals(%)
β-$UO_2(OH)_2$	-1533.8±1.3	-1531.2	-2.6	0.17
γ-$UO_2(OH)_2$	-1531.4±1.3	-1531.2	-0.2	0.01
$UO_3\sum 0.9H_2O$	-1506.3±1.3	-1509.3	3.0	0.20
β-Na_2UO_4	-1884.6±3.6	-1885.5	0.9	0.05
Na_4UO_5	-2456.6±1.7	-2458.7	2.09	0.09
$Na_2U_2O_7$	-3203.8±4.0	-3197.7	-6.12	0.19
Li_2UO_4	-1968.2±1.3	-1973.1	4.87	0.25
Li_4UO_5	-2639.4±1.7	-2633.9	-5.5	0.21
$UO_2(NO_3)_2\cdot 6H_2O$	-3167.5±1.5	-3167.9	0.4	0.01
$UO_2(NO_3)_2\cdot 3H_2O$	-2280.4±1.7	-2277.7	-2.7	0.12
$UO_2(NO_3)_2\cdot 2H_2O$	-1978.7±2.0	-1981.0	2.3	0.12
$UO_2SO_4\cdot 3.5H_2O$	-2901.6±0.8	-2901.7	0.1	0.005
$UO_2SO_4\cdot 3H_2O$	-2751.5±4.6	-2753.4	1.9	0.07
$UO_2SO_4\cdot 2.5H_2O$	-2607.0±0.9	-2605.0	-2.0	0.08
Average				0.11

Note: measured $\Delta H^0_{f,298}$ values are from Grenthe et al. (1992).

Planned Activities

During the next year, our program will focus on four 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 oxiding conditions. **4.** Comparison to theoretical calculations of phase stability to actual natural occurrences of these uranyl phases.