Annual Report
(September 15, 2000 to June 15, 2001)

Environmental Management Science Program

**Corrosion of Spent Nuclear Fuel:
The Long-Term Assessment**

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Research Objectives

The successful disposal of spent nuclear fuel (SNF) is one of the most serious challenges to the completion of the nuclear fuel cycle and the future of nuclear power generation. Spent nuclear fuel is essentially UO_2 with approximately 4-5 atomic percent actinides and fission product elements. A number of these elements have long half-lives (^{239}Pu : 24,100 years; ^{237}Np : 2 million years; ^{129}I : 16 million years; ^{79}Se : 1.1 million years; ^{99}Tc 200,000 years); hence, *the long-term behavior of the UO_2 is an essential concern in the evaluation of the safety of a repository for spent nuclear fuel. One of the unique and scientifically most difficult aspects of the successful disposal of spent nuclear fuel is the extrapolation of short-term laboratory data (hours to years) to the long time periods (10^3 to 10^5 years).* The direct verification of these extrapolations or interpolations is not possible, but *methods must be developed to demonstrate compliance with government regulations and to satisfy the public that there is a reasonable basis for accepting the long-term extrapolations of spent fuel behavior.* In recent years "natural analogues" for both the repository environment (e.g., the Oklo natural reactors) and nuclear waste form behavior (e.g., corrosion and alteration of uraninite, UO_{2+x}) have been cited as a fundamental means of achieving confirmation of long-term extrapolations. In particular, considerable effort has already been made to establish that uraninite, UO_{2+x} , with its impurities, is a good structural and chemical analogue for the analysis of the long-term behavior of the UO_2 in spent nuclear fuel.

This proposal is based on the study of uraninite and the naturally occurring alteration products of UO_{2+x} under oxidizing and reducing conditions. This scientific program will address the following issues:

1. What are the *long-term* corrosion products of natural UO_{2+x} under reducing and oxidizing conditions?
2. What is the paragenesis or the reaction path of the phases that form during alteration? How is the paragenetic sequence of formation related to the structures and compositions of the phases?
3. What is the trace element content in the corrosion products (as compared with the original UO_2), and does the trace element content substantiate models developed to predict radionuclide incorporation?
4. Are the corrosion products the phases that are predicted from reaction path models (e.g., EQ3/6) that are used in performance assessments?
5. How persistent over time are the metastable phase assemblages that form? Will these phases serve as barriers to radionuclide release?
6. Based on the structures of these phases (mostly sheet structures) can the thermodynamic stabilities of these phases be estimated, or at least bounded, in such a way as to provide for a convincing and substantive performance assessment?

Research Progress and Implications

As of May 15, 2001, the second phase of this research program has been in progress for 8 months. During this time we have continued our research program in the following areas:

Thermodynamic Parameters for U^{6+} Phases: The Gibbs free energies and enthalpies for uranyl phases are generally not well known, as few appropriate experiments have been completed. We have continued to develop an empirical model that provides for the calculation of these much needed parameters. The first model was published in the *American Mineralogist*, vol. 84, 650-654 (1999). We presently investigate the effects of site-mixing and structural disorder on the residual entropy of uranyl phases. Because of the contribution of neglected residual entropy, which cannot be determined by calorimetric measurements, the true third-law entropies of the uranyl phases may be quite different from the values derived from thermal data, and this may affect calculated solubilities that are often used in geochemical calculations of UO_2 corrosion.

UO₂ Incorporation of ¹²⁹I: We have previously analyzed the ability of uranyl phases to incorporate ⁷⁹Se (*Journal of Nuclear Materials* 275, 81-94, 1999) and ⁹⁹Tc (*Journal of Nuclear Materials* 278, 225-232, 2000). We are completing a similar analysis for ¹²⁹I. Unlike the previous studies, however, we are attempting to complete an analysis of the global impact of ¹²⁹I production from the nuclear fuel cycle.

Retardation of Radionuclides in the Oklo Natural Reactors: We have continued our studies of the natural fission reactors in Gabon in order to determine the source term, extent of uraninite alteration, and the means of retardation of nuclear reaction products during their 2 billion years long geological history. A detailed study of the recently excavated Okélobondo reactor zone has been completed. Inferred from mineral chemistry, the fissionogenic Zr (including ⁹⁰Sr → ⁹⁰Zr), Ce, Nd, and Th (daughter of ²³⁸U(n,γ,2β) ²³⁹Pu(n,γ) ²⁴⁰Pu and ²³⁵U(n,γ) ²³⁶U) are well-retained in uraninite and retarded by the U-Zr-silicate during migration. Fissionogenic LREE may also have been incorporated into rare monazite. Fissionogenic Ru, including ⁹⁹Ru, a daughter of ⁹⁹Tc, was mainly retained in ruthenium sulfur-arsenides (± Pb, Co, and Ni), such as ruthenarsenite and ruarsite. A major paper has been published in the *Geological Society of America – Bulletin* 113, 32-62 (2001).

Planned Activities

The next year's effort will focus on the description of the mineralogy, paragenesis and trace element chemistry of radionuclide-bearing phases at the Oklo reactors. Based on our work and the published literature we will be testing geochemical codes that are commonly used to predict the release and transport of radionuclides from buried uraninite or spent nuclear fuel.

Trace-Element Incorporation in Alteration Phases: Although the present results are encouraging, the electron microprobe results are limited by the fact that we cannot determine directly the U⁶⁺/U⁴⁺ ratio and cannot determine directly the (OH) or molecular water content of the samples. This information is essential if we are to correctly identify the alteration phases and complete a structural evaluation of their ability to incorporate radionuclides. During this study, we will: 1.) Determine the oxidation state of uranium (U⁶⁺:U⁴⁺ ratio) directly using electron energy loss spectroscopy (EELS); 2.) Determine the amount and type of water in the U-phases by infrared analysis. Based on the structural formulas derived from procedures in steps 1 and 2, we will be able to evaluate the structural incorporation of trace elements into the uranyl phases; 3.) We are investigating solid-solution relations and solubility limits of key phases.

Geochemical Models of UO₂ Corrosion and Alteration: A combination of natural analogue studies (long-term corrosion), laboratory corrosion tests (short-term corrosion and column experiments), super-saturation precipitation experiments of uranyl phases, as well as computer simulation are proposed to describe and understand the important corrosion processes of UO₂.

Oklo Natural Reactors – An Analogue for Spent Fuel Corrosion: We will investigate the migration behavior of radionuclides around the Okélobondo natural fission reactor. The Okélobondo natural fission reactor (RZOKE) was the last reactor to be excavated in the Francevillian uranium deposits where mining has now been terminated. The only detailed geological and mineralogical analysis of this reactor zone has been completed by Jensen and Ewing (2001). Based on mineralogy and mineral chemistry, there is evidence for migration and retardation of both actinides (U, Pu) and fission products (Ru, Tc, Sr, Zr, lanthanides) during criticality in RZOKE and regional heating 1000 – 750 Ma ago. However, isotopic analysis is required to support the detailed mineralogical analysis and to quantify the amount of released isotopes. The extent of alteration that has occurred during these events and the total inventories of radionuclides in the reactor zones and the near-field environment will be quantified.

Information Access

Up-to-date information on the research activities of the group can be found at the following website:
<http://relw.engin.umich.edu>.

Recent publications:

- F. Chen, P.C. Burns and R.C. Ewing (2000) Near-field behavior of ^{99}Tc during the oxidative alteration of spent nuclear fuel. Journal of Nuclear Materials 278, 225-232.
- M. Fayek, Peter Burns, Young-Xiang Guo and R.C. Ewing (2000) Micro-structures associated with uraninite alteration. Journal of Nuclear Materials 277, 204-210.
- D. Zhao and R.C. Ewing (2000) Alteration products of uraninite from the Colorado Plateau. Radiochimica Acta 88, 739-749 (2000).
- K.A. Jensen., J. Janeczek, R.C. Ewing, P. Stille, F. Gauthier-Lafaye and S. Salah(2000) Crandallites and coffinite: retardation of nuclear reaction products at the Bangombé natural fission reactor, Scientific Basis for Nuclear Waste Management XXII. J. Shoesmith and R.W. Smith, Eds., Materials Research Society Symposium Proceedings, vol. 608, 525-532.
- K.A. Jensen and R.C. Ewing (2000) Microtexture and chemistry of “unaltered” uraninite in the Oklo, Okelobondo and Bangombe natural Fission Reactors. *Nuclear Science and Technology*, EUR 19116, 61-91.
- K.A. Jensen and R.C. Ewing (2001) The Okélobondo natural fission reactor, southeast Gabon: Geology, mineralogy and retardation of nuclear reaction products. Geological Society of America Bulletin 113, 32-62.
- R.C. Ewing (2001) Crystalline ceramics: Waste forms for the disposal of actinides. (invited) Proceedings of the BRNS-DAE National Symposium on Nuclear and Radiochemistry, University of Pune, Pune, India, pp. 74-86.
- R.C. Ewing (2001) Ageing studies of nuclear waste forms: The evaluation of long-term behaviour. (invited) Proceedings of Ageing Studies & Lifetime Extension of Materials (Kluwer Academic /Plenum Publishers, New York) 15-22.
- R.C. Ewing (2001) Nuclear waste form glasses: The evaluation of very long-term behavior. (invited) Materials Technology 16, 30-36.
- R.C. Ewing (in press) The design of nuclear waste forms: Clues from mineralogy. (invited) Canadian Mineralogist.

Invited presentations:

- “Source Term Partitioning and the Development of Waste Forms”: Gordon Conference on Nuclear Waste and Energy, Colby-Sawyer College, New London, NH, July 16-21, 2000.
- “Probabilistic Performance Assessment vs. Geologic Common Sense”: invited lecture at the Pardee Symposium of the annual meeting of the Geological Society of America, Reno, Nevada, November 14, 2000.
- “Crystalline Ceramics for Radioactive Waste Management”: Chemistry Colloquium, Indira Gandhi Centre for Atomic Research, Kalpakkam, India, February 1, 2001.
- “Important Performance Properties of Nuclear Waste Forms”: Radiochemistry Colloquium, Bhabha Atomic Research Centre, Mumbai, India, February 5, 2001.
- “Crystalline Ceramics: Waste Forms for the Disposal of Actinides”: invited talk, 5th Nuclear and Radiochemistry Symposium, University of Pune, Pune, India, February 9, 2001.
- “An Empirical Method for Calculating the Thermodynamic Properties of U(VI) Phases”: OECD/NEA Thermodynamic Data Base Workshop on the Use of Thermodynamic Databases in Performance Assessment, Barcelona, Spain, May 29, 2001.
- “Energy & the Environment : The Nuclear Fuel Cycle“: invited presentation at the Universitat Politècnica de Catalunya, Barcelona, Spain, May 31, 2001.