

**Annual Report**  
(September 15, 2001 to October 15, 2002)

**Environmental Management Science Program  
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**Corrosion of Spent Nuclear Fuel:  
The Long-Term Assessment**

**Rodney C. Ewing**

Nuclear Engineering and Radiological Sciences  
Materials Science & Engineering  
Geological Sciences

University of Michigan  
Cooley Bldg., 2355 Bonisteel Boulevard  
Ann Arbor, Michigan 48109-2104

Phone: (734) 647 8529

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## PROGRESS REPORT (1<sup>ST</sup> Year)

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### Research Objectives

*The successful disposal of spent nuclear fuel (SNF) is one of the most serious challenges to the success of the nuclear fuel cycle and the future of nuclear power generation.* Spent nuclear fuel is essentially  $\text{UO}_2$  with approximately 4-5 atomic percent actinides and fission product elements. A number of these elements have long half-lives ( $^{239}\text{Pu}$ : 24,100 years;  $^{237}\text{Np}$ : 2 million years;  $^{129}\text{I}$ : 16 million years;  $^{79}\text{Se}$ : 1.1 million years;  $^{99}\text{Tc}$ : 200,000 years); hence, *the long-term behavior of the  $\text{UO}_2$  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,  $\text{UO}_{2+x}$ ) 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,  $\text{UO}_{2+x}$ , with its impurities, is a good structural and chemical analogue for the analysis of the long-term behavior of the  $\text{UO}_2$  in spent nuclear fuel.

*This research program is based on the study of uraninite and the naturally occurring alteration products of  $\text{UO}_{2+x}$  under oxidizing and reducing conditions. We address the following issues:*

1. What are the *long-term* corrosion products of natural  $\text{UO}_{2+x}$  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  $\text{UO}_2$ ), 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 October 15, 2002, the second phase of this research program has been in progress for 2 years. During the past year our work has emphasized the following areas:

#### Thermodynamic Parameters for $\text{U}^{6+}$ Phases:

During the first year of the program, we focused on extending our model of Gibbs free energies to include the effects of site-mixing and structural disorder on the residual entropy of uranyl phases. The Gibbs free energies and enthalpies for uranyl phases are generally not well known, as few appropriate experiments have been completed. Because of the contribution of the residual entropy, which cannot be determined by calorimetric measurements, is neglected, the true third-law entropies of the uranyl phases may be quite different from the values derived from thermal data. This affects the calculated solubility constants that are used in geochemical calculations of  $\text{UO}_2$  corrosion. Contributions from configuration entropy come mainly from disordering of hydrogen bonds in the  $\text{U}^{6+}$  oxyhydroxide phases that form as alteration products on spent nuclear fuel. The first paper on this subject has been accepted for publication (Fanrong Chen and R.C.

Ewing, in press, *Science*, China). We have then used the extended, empirical model to calculate the Gibbs free energies for phases used in a geochemical modeling of the groundwater compositions at the Bangombé natural reactor in Gabon (Jensen, Palenik and Ewing, in press, *Radiochimica Acta*). This work demonstrates the limitations of present geochemical models in complex, natural systems.

### **UO<sub>2</sub> Incorporation of Trace Elements:**

We have previously analyzed the ability of uranyl phases to incorporate <sup>79</sup>Se (*Journal of Nuclear Materials* 275, 81-94, 1999) and <sup>99</sup>Tc (*Journal of Nuclear Materials* 278, 225-232, 2000). We are completing a similar analysis for <sup>129</sup>I. In collaboration with Peter Burns, we have completed the crystallo-chemical analysis of the incorporation of iodine into the structures of U<sup>6+</sup>. Unlike the previous studies, however, we are attempting to complete an analysis of the global impact of <sup>129</sup>I production from the nuclear fuel cycle. This will provide the basis for an analysis of the environmental impact of the release of iodine from spent nuclear fuel. This work is part of a larger effort to make a global evaluation of the impact of the nuclear fuel cycle on the environment. This year, Professor Ewing received a Guggenheim Fellowship that will support part of this work.

### **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 fissiogenic Zr (including <sup>90</sup>Sr → <sup>90</sup>Zr), Ce, Nd, and Th (daughter of <sup>238</sup>U(n,γ,2β)<sup>239</sup>Pu(n,γ)<sup>240</sup>Pu and <sup>235</sup>U(n,γ)<sup>236</sup>U) are well-retained in uraninite and retarded by the U-Zr-silicate during migration. Fissiogenic LREE may also have been incorporated into rare monazite. Fissiogenic Ru, including <sup>99</sup>Ru, a daughter of <sup>99</sup>Tc, 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).

We have also completed a study of the U<sup>6+</sup> phases that form in the weathering zone of the Bangombé U-deposit in Oklo. The purpose of this study was to compare the observed mineralogy with the predicted mineralogy using geochemical codes. One of the main limitations of the geochemical modeling effort is the lack of appropriate thermodynamic data for U<sup>6+</sup> phases. We have tested our model values (Chen and Ewing, 1999) as part of the geochemical modeling effort (Jensen, Palenik and Ewing, in press).

We are also collaborating with Peter Stille and Francois Gauthier-Lafaye at CNRS in Strasbourg in a study of REE migration in groundwaters close to the Bangombé reactor zone. This manuscript is in press with *Chemical Geology*.

### **Application of HAADF-STEM/HRTEM to the study of trace metals:**

In our studies of trace metals (1 to 10 ppm) in natural samples, we have found that it is very difficult to find the trace metal-bearing phases for study by HRTEM. Thus, we have spent considerable effort in developing high-angle annular dark field scanning TEM (HAADF-STEM) and STEM-EDX mapping techniques for the study of the Oklo samples. The most recent success has been in identifying the uranium-bearing phases in atmospheric particulates (Utsunomiya et al., in press, *Environmental Science & Technology*).

### **Future Research 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 naturally occurring uraninite or spent nuclear fuel.

### **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. Part of this work is done in collaboration with Mostafa Fayek at Oak Ridge National Laboratory.

#### **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  $U^{6+}/U^{4+}$  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 ( $U^{6+}:U^{4+}$  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.

#### **Corrosion and Alteration of $UO_2$ :**

A new graduate student, Frannie Skomurski, has initiated a study of the interactions of molecular water with the surfaces of single crystals of  $UO_2$ . We plan to use proposed facilities in the Department of Geological Sciences, that include variable temperature AFM, XPS, UPS, high-resolution SEM and LEED capabilities, to complete these studies. Although this work is in its earliest stages, it will provide information that is relevant to the storage of spent fuel in reactor pools and the behavior of spent fuel in a geologic repository. As part of this effort, Satoshi Utsunomiya will use HAADF-STEM to study the nano-scale alteration products of the uraninite in the reactor cores.

#### **Colloid Formation and Radionuclide Transport During the Corrosion of Spent Nuclear Fuel:**

During the past year, we have devoted considerable attention to the role of colloids in the corrosion of  $UO_2$ . Our efforts have focused mainly on developing techniques to study the sorbed, heavy atoms (e.g., U and other actinides) on colloidal particles. Preliminary work was done on samples from the Nevada Test Site in collaboration with Dr. Annie Kersting at LLNL. The preliminary studies have demonstrated the efficacy of using high angle annular dark field (HAADF) STEM to image sorbed heavy metals on colloidal sized particles. We (K. Traexler and R. Ewing) have also completed an extensive literature survey entitled, "Effect of Colloids on Radionuclide Transport in a Geologic Repository for Spent Nuclear Fuel". This work was supported by the Office of Nuclear Material and Spent Fuel and will be the basis for the Ph.D. research program of Kathy Traexler.

#### **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 journal publications (\*students):**

- 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, vol. 113, no. 1, pages 32-62.
- R.C. Ewing (2001) Nuclear waste form glasses: The evaluation of very long-term behavior. Materials Technology, vol. 16(1), 30-36.
- R.C. Ewing (2001) The design and evaluation of nuclear waste forms: Clues from mineralogy. Canadian Mineralogist, vol. 39, 697-715. **Received the Hawley Medal of the Mineralogical Association of Canada as the best paper for 2001.**
- R.C. Ewing (2001) Nuclear waste form glasses: The evaluation of very long-term behavior. Materials Technology, vol. 16(1), 30-36.

- C. Ewing (2002) Plutonium: The nuclear fuel cycle & the environment. Facets, 1(2), 11-14.
- Mostafa Fayek, T. Mark Harrison, Rodney C. Ewing, Marty Grove and Chris D. Coath (2002) O and Pb isotopic analyses of uranium minerals by ion microprobe and U-Pb ages from the Cigar Lake deposit. Chemical Geology, 185, 205-225.
- R.C. Ewing and L.M. Wang (2002) Phosphates as Nuclear Waste Forms. Reviews in Mineralogy & Geochemistry, vol. 48, 673-699.
- K.A. Jensen, C.S. Palenik\*, and R.C. Ewing (in press) U<sup>6+</sup>-phases in the weathering zone of the Bangombe U-deposit: Observed and predicted mineralogy. Radiochimica Acta.
- Fanrong Chen and R.C. Ewing (in press) Structure-configurational entropy and its effect on the thermodynamic stability of uranyl phases: With special application for the geological disposal of nuclear waste. Science (China).
- M. Douglas\*, S.B. Clark, Satoshi Utsunomiya and R.C. Ewing (in press) Trace metal incorporation into uranophane [Ca(UO<sub>2</sub>)(SiO<sub>3</sub>OH)<sub>2</sub>5H<sub>2</sub>O]. Journal of Nuclear Technology.
- S. Utsunomiya, K.A. Jensen, G.J. Keeler and R.C. Ewing (in press) Uraninite and fullerene in atmospheric particulates. Environmental Sciences & Technology.

### Conference Proceedings:

- R.C. Ewing, Fanrong Chen and S. B. Clark (2002) An empirical method for calculating thermodynamic parameters for U(VI) phases, applications to performance assessment calculations. Proceedings of a workshop on "The Use of Thermodynamic Databases in Performance Assessment", Nuclear Energy Agency (OECD), 93-102.
- R.C. Ewing (2002) Materials research in nuclear waste management: Reflections on twenty-five MRS symposia. (invited) Eds. B.P. McGrail and G.A. Cragnolino, Scientific Basis for Nuclear Waste Management XXV, Proceedings of the Materials Research Society, 3-14.
- Mostafa Fayek, K.A. Jensen, R.C. Ewing and L.R. Riciputi (2002) In situ isotopic analysis of uraninite microtextures from the Oklo and Okélobondo natural fission reactors. Eds. B.P. McGrail and G.A. Cragnolino, Scientific Basis for Nuclear Waste Management XXV, Proceedings of the Materials Research Society, 849-856.
- C.S. Palenik\* and R.C. Ewing (2002) Microanalysis of radiation damage across a zoned zircon crystal. Eds. B.P. McGrail and G.A. Cragnolino, Scientific Basis for Nuclear Waste Management XXV, Proceedings of the Materials Research Society, 521-527. **Received best paper award for the symposium.**

### Invited presentations:

- "Weapons Plutonium: A Mineralogical Solution": 1349<sup>th</sup> meeting of The Geological Society of Washington, January 23, 2002.
- "Weapons Plutonium: A Mineralogical Solution": Department of Geology Colloquium, George Washington University, Washington, D.C., January 24, 2002.
- "Nuclear Waste: How Big Is the Problem?": Henry Ford Community College, Dearborn, MI, February 4, 2002.
- "Nuclear Waste: How Big Is the Problem?": Learning in Retirement Lecture Series, Ann Arbor, MI, February 18, 2002.
- "Radiation Effects in Minerals & Ceramics": Inaugural lecture on the occasion of being appointed an adjunct Professor at the Aarhus Universitet, February 28, 2002.
- "Radiation-Induced Nano-phase Formation: What Can We Learn from Nature?": NSF-sponsored workshop on Nanogeoscience, Lawrence Berkeley National Laboratory, June 14, 2002.
- "Fate of Plutonium in the Environment: Immobilization & Disposal": invited talk at the CIMTEC-2000, International Congress on Ceramics, Firenze, Italy, July 15, 2002.
- "Impact of the Nuclear Fuel Cycle on the Environment: Waste, Weather & Weapons (2)": invited talk at the 12<sup>th</sup> V.M. Goldschmidt Conference, Davos, Switzerland, August 23, 2002.
- "Immobilization and Disposal of Pu: Radiation Effects in Minerals & Ceramics": invited presentation, International Mineralogical Association, Edinburgh, Scotland, September 6, 2002.
- "The Metamict State: Radiation Effects in Minerals & Ceramics": invited talk at the annual meeting of the Deutschen Mineralogischen Gesellschaft, Hamburg, Germany, September 10, 2002.
- "The Metamict State: Poems & Plutonium": Presidential Address to the Mineralogical Society of America, Annual meeting of the Geological Society of America, Denver, October 29<sup>th</sup>, 2002.

## Personnel

**R.C. Ewing** devotes one month per year to this research program. His main focus has been on the application of geochemical modeling to the Oklo natural reactors.

**Satoshi Utsunomiya** is a post-doctoral fellow who is supported, in part, on this EMSP program. Satoshi is responsible for developing advanced techniques in electron microscopy (HAADF-STEM) for the study of nano-scale phases in the Oklo samples.

**Keld Alstrup Jensen** completed his Ph.D. with support from this EMSP program. He now works at the National Institute for Occupational Health in Denmark. He returns to the University of Michigan each summer for one month as a research scientist to work on the geochemical modeling of the Oklo reactors.

**Christopher Palenik** is a Ph.D. candidate in the Department of Geological Sciences. This is his fourth year in the program, and he has now completed all of the written and oral examinations for Ph.D. candidacy and his course work. He will be working full time on the TEM and EMPA analysis of uranium minerals and geochemical modeling of the Oklo natural reactors. Chris was originally supported by this EMSP program, but he has been awarded a two year fellowship by the Office of Civilian Radioactive Waste Management.

**Kathy Traexler** is a Ph.D. candidate in the Department of Nuclear Engineering and Radiological Sciences. She is in her fourth year of graduate study and has completed all written and oral examinations for Ph.D. candidacy, as well as required course work (she was awarded an M.S. degree this past year). She is now working full time on the issue of colloid formation during the corrosion of spent nuclear fuel and the transport of radionuclides by colloids.

**Frannie Skomurski** is a Ph.D. candidate in her second year in the Department of Geological Sciences. She will be developing surface science techniques to investigate the behavior of molecular water on the surfaces of  $\text{UO}_2$ .

## Relevance, Impact and Technology Transfer

This research program provides a fundamental underpinning for DOE's efforts to dispose of and model the long term behavior of spent nuclear fuel. The DOE supported research program has received recognition for the quality of work. Professor Ewing received a Guggenheim Fellowship (2002) to further support his analysis of the impact of the nuclear fuel cycle on the environment. One of Professor Ewing's papers, "The design and evaluation of nuclear waste forms: Clues from mineralogy", received the Hawley Medal of the Mineralogical Association of Canada as the best paper for 2001. A paper by C. Palenik and R. Ewing, "Microanalysis of radiation damage across a zoned zircon crystal", received the Best Paper Award from the symposium *Scientific Basis for Nuclear Waste Management* in 2001.

The biggest impact of our work has been in validating the geochemical models used to predict the behavior of spent nuclear fuel in geologic repositories. We have combined our empirical model of thermodynamic parameters with actual field scale tests at the Oklo natural reactors. We have demonstrated some of the limitations of the geochemical models, e.g. failure to identify minor phases, and we have identified some of the major data gaps. I know that we have inspired other colleagues (Peter Burns and Alex Navrotsky) to complete calorimetric measurements of some of the important U(VI) phases. Another colleague, Frank Hawthorne at the University of Manitoba, has consulted us in his development of a structural model to describe the behavior of uranium in solution.

We have also made important progress in the application of HAADF/STEM to the study of heavy metal sorption on colloids. This work will provide critical information for the models used to describe radionuclide transport at the Yucca Mountain repository.