

Interim Report

Environmental Management Science Program

Corrosion of Spent Nuclear Fuel: The Long-Term Assessment

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EXECUTIVE SUMMARY

Spent nuclear fuel accounts for over 95% of the total radioactivity in the radioactive wastes in the United States that require disposal, disposition or remediation. Uranium is the dominant actinide element in most of these nuclear wastes. The UO_2 in spent nuclear fuel is not stable under oxidizing conditions and may be altered even under reducing conditions.

Under oxidizing conditions, uranium has a strong tendency to exist as U^{6+} in the uranyl molecule, UO_2^{2+} . The uranyl ion reacts with a wide variety of inorganic and organic anions to form complexes that are often highly soluble. The result is a rather rapid dissolution of UO_2 and the formation of a wide variety of uranyl oxide hydrates, uranyl silicates and uranyl phosphates. The kinetics for this transformation is rapid and essentially instantaneous on geologic time scales. Under reducing conditions UO_2 is stable, but may alter to U^{4+} compounds, such as coffinite, USiO_4 , depending on ground water compositions.

Under both oxidizing and reducing conditions, the formation of new uranium phases may lead to the release or retardation of trace elements, such as the fission product elements and actinides in spent nuclear fuel. Over the long term, and depending on the extent to which the secondary uranium phases can incorporate fission products and actinides, *these alteration phases become the near-field source term.*

Based on experiments and field studies supported by this EMSP program, we have established that natural uraninite and its alteration products are good "natural analogues" for the study of the corrosion of UO_2 in spent nuclear fuel. In this research program we address the following issues:

1. What are the *long-term* corrosion products of natural UO_{2+x} , uraninite, under oxidizing and reducing conditions?
2. What is the paragenesis or the reaction path for the phases that form during alteration? How is the sequence of formation related to the structure of these uranium phases and reacting ground water composition?
3. What is the trace element content in the corrosion products as compared with the original UO_{2+x} ? Do the trace element contents substantiate models developed to predict radionuclide incorporation into the secondary phases?
4. Are the corrosion products accurately predicted from geochemical codes (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 effective barriers to radionuclide release?

6. Experimental results and theoretical models for the corrosion of spent nuclear fuel under oxidizing and reducing conditions have been tested by comparison to results from studies of samples from the Oklo natural fission reactors.

This research program is providing fundamental data on the geochemistry of uranium and related transuranium elements, as well as the fate and transport of long-lived fission products. We provide a basis for testing the models that are now used in performance assessments of nuclear waste repositories. These data and this approach are essential to determining the long-term behavior of spent nuclear fuel in a nuclear waste repository.

RESEARCH OBJECTIVES

The successful disposal of spent nuclear fuel (SNF) is one of the most serious challenges to the successful completion of the nuclear fuel cycle and the future of nuclear power generation (Ewing, 1999a, 1999b). In the United States, 21 percent of the electricity is generated by 107 commercial nuclear power plants (NPP), each of which generates 20 metric tons of spent nuclear fuel annually. In 1996, the total accumulation of spent nuclear fuel was 33,700 metric tons of heavy metal (MTHM) stored at 70 sites around the country (Richardson, 1997). The end-of-life projection for current nuclear power plants (NPP) is approximately 86,000 MTHM. In the proposed nuclear waste repository at Yucca Mountain over 95% of the radioactivity originates from spent nuclear fuel. World-wide in 1998, approximately 130,000 MTHM of SNF have accumulated, most of it located at 236 NPP in 36 countries (Carter and Pigford, 1999). Annual production of SNF is approximately 10,000 MTHM, containing about 100 tons of "reactor grade" plutonium. Any reasonable increase in the proportion of energy production by NPP, i.e., as a substitute for hydrocarbon-based sources of energy, will significantly increase spent nuclear fuel production.

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 24,500 years; ^{237}Np 2 million years; ^{129}I 16 million years; ^{79}Se 1.1 millions 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 and risk 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) as required by the performance objectives set in regulations, i.e. 10 CFR 60. 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 (Ewing and Jercinovic, 1987; Ewing, 1991, 1992, 1993a, 1993b, 1999b). 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 (Fayek et al., 1997a; Janeczek and Ewing, 1991a, 1991b, 1992a, 1992b, 1995; Janeczek et al., 1993, 1996; Murphy, 1993, 1995; Murphy et al., 1995; Percy et al., 1994).

This proposal is based on the study of uraninite and the naturally occurring alteration products of UO_{2+x} under oxidizing and reducing conditions.

The UO_2 in spent nuclear fuel is not stable under oxidizing conditions. In oxic solutions, uranium has a strong tendency to exist as U^{6+} in the uranyl molecule, UO_2^{2+} . Uranyl ions react with a wide variety of inorganic and organic anions to form complexes. Throughout most of the natural range of pH, U^{6+} forms strong complexes with oxygen-bearing ions like CO_3^{2-} , HCO_3^- , SO_4^{2-} , PO_4^{3-} , and AsO_4^{3-} , which are present in most oxidized stream and subsurface waters. In arid environments, the U^{6+} ion can precipitate as a wide variety of uranyl oxide hydrates, uranyl silicates and uranyl phosphates. This is well demonstrated in experimental work, e.g., in long term drip tests on UO_2 (Wronkiewicz et al., 1992, 1996, 1997; Buck et al., 1997; Wronkiewicz and Buck, 1999; Finch et al., 1999) and is confirmed by natural occurrences of UO_2 in

which a wide variety of uranyl phases form as alteration products (Finch and Ewing, 1989, 1991a, 1991b, 1991c, 1992a, 1992b, 1992c, 1993, 1994, 1997; Finch et al., 1998; Percy et al., 1994). The most striking feature of these studies is the very close parallel in the paragenetic sequences (i.e. phase formation sequence) between the very long term (10 year tests) (Wronkiewicz et al., 1996, 1997; Wronkiewicz and Buck, 1999; Finch et al., 1999) and the young (therefore, low-Pb uraninites) of the Nopal I deposit in Mexico (Percy et al., 1994). Thus, both the experiments utilizing drip tests and the study of natural uranium deposits may be used to simulate the reaction progress expected for the UO_2 in spent fuel in the proposed Yucca Mountain repository (Finch and Ewing, 1992c; Wronkiewicz et al., 1996, 1997)

Under oxidizing conditions, the reaction kinetics of the conversion of UO_2 to uranyl phases is rapid (Murphy and Pabalan, 1995), and most of the UO_2 will be dissolved in the presence of oxidizing fluids during the dissolution and replacement reactions. Wronkiewicz et al. (1996) estimated that UO_2 pellets in their experiments (90°C) would have been completely altered in 660 years. They concluded,

"The speed at which the UO_2 reactions occurred suggests that an advanced stage of uranyl alteration phase development can occur almost instantaneously within the constraints of the time-scale expected for repository disposal."

These results imply that alteration may occur simply due to the exposure of spent nuclear fuel to moisture in an unsaturated repository setting. The results are additionally supported by kinetic and thermodynamic models of UO_2 corrosion (e.g., Bruno et al., 1995; 1996) in which the final steps of the corrosion process are the precipitation and subsequent dissolution of the secondary uranium phases.

The UO_2 in spent nuclear fuel will contain between 1 to 2 percent plutonium and up to 4 percent other actinides and fission products, depending on the burn-up of the fuel. The rapid matrix dissolution of the UO_2 will release these radionuclides, and at their low levels of concentration it is not expected that they will form phases in which their compositions predominate. More likely, the fissionogenic actinides and fission products will be incorporated in trace amounts into the structures of the uranyl phases formed during the corrosion of UO_2 . Unfortunately, there are a wide variety of uranyl phases (approximately two hundred mineral names for these phases, see for example Cejka and Urbanec, 1990; Baran, 1992; Fleischer and Mandarino, 1995; Burns, 1999); and they are poorly described, their structures are often not known, and critical parameters such as their thermodynamic stability have not been determined experimentally.

Most importantly, there has been no systematic determination of the capacity of these phases to incorporate and retard the mobility of the released actinides and fission products. The fate of these radionuclides is critical to the performance assessment of a spent fuel repository in an oxidizing or reducing environment. A basic understanding of the compositions, structures and stabilities of these phases is essential to the DOE environmental remediation program.

This scientific program is designed to address the following questions:

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?

7. Most of the work of the previous three years has focused on U^{6+} -phases. However, we propose to expand the studies of UO_2 behavior to include reducing conditions that subsequently become oxidizing, in order to understand redox controls on uranium mobility and the related effect on radionuclide migration. This will be based on studies of samples from the Oklo natural reactors.

RELEVANCE, IMPACT AND TECHNOLOGY TRANSFER

This research program provides the fundamental data and necessary understanding to predict the long-term behavior of spent nuclear fuel during storage and permanent disposal. An integral part of the performance assessment of a repository (such as the recently completed Total System Performance Assessment – Viability Assessment of the Yucca Mountain site) will be the extrapolated or interpolated behavior of the UO_2 in spent nuclear fuel during alteration and corrosion. This research program provides the basis for establishing the extent to which models of alteration and corrosion processes used in the performance assessment of the near-field repository environment are useful or valid (TSPA-VA, 1998). It is essential that the presently large uncertainties inherent in these models be reduced (see for example the discussion by Ahn, 1996a, 1996b). Studies of natural samples of great age and appropriate geochemical environments offer the possibility of reducing uncertainties in these corrosion models.

This research focuses on near-field phenomena, particularly waste form degradation. This is important because the successful understanding of relevant phenomena in the near-field reduces uncertainties in the total system performance assessment (TSPA-VA, 1998) because:

□ *The radionuclides are initially located in the UO_2 of the spent fuel. Initially, the only part of the repository that is radioactive is the waste form (spent fuel or the glass logs). **The successful performance of the waste form or subsequent incorporation of radionuclides into alteration products of the corrosion process results in near-field containment.** This is much preferred to geologic isolation that essentially relies on long travel times, dilution and dispersion, and sorption on mineral and rock surfaces. These geologic processes presume release and movement of radionuclides.*

□ *The chemistry and physics of the corrosion and alteration of a UO_2 , with the subsequent release or retention of radionuclides over some range of conditions, is inherently more simply modeled and extrapolated over time than the use of coupled hydrologic, geochemical and geophysical models of the movement of radionuclides through the far-field of a geologic repository. That is, the extrapolation of the corrosion behavior of the UO_2 over long periods rests on a firmer scientific foundation than the extrapolated behavior of, as an example, hydrologic systems that are site specific and highly dependent on idealized boundary conditions (e.g., climate and recharge).*

□ *Naturally occurring UO_2 and its alteration products, provide fundamental data for the “confirmation” of extrapolated or interpolated behavior of the UO_2 in spent fuel over long periods of time.* This approach holds great potential for the confirmation of performance assessments of near-field behavior. Uraninite provides one of the rare opportunities in which studies of a natural material can provide unambiguous data for the long-term behavior of spent nuclear fuel.

Finally, we note that uranium is the most abundant actinide element in the DOE complex and the dominant element present in spent nuclear fuel. The results of this research program are broadly applicable to DOE's efforts to clean up its numerous sites, such as at Fernald, Ohio, and Paducah, Kentucky, as well as dispose of defense and commercially

generated spent nuclear fuels. This research also provides data that are required to evaluate the long term behavior of fuel held in storage sites, both in pools or in dry casks.

PROJECT PRODUCTIVITY & PUBLICATIONS

During the past three years, we have made significant progress in our studies of the behavior of uranium and the corrosion of UO_2 . Much of this work has already been published and a full list of publications is given at the end of this section.

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 developed an empirical model that provides for the calculation of these much needed parameters (Clark et al., 1998; Chen et al., 1999a). The thermodynamic parameters have been estimated based on a method that sums polyhedral contributions. The molar contributions of the structural components to ΔG_f° and ΔH_f° 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° and ΔH_f° 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° values, activity-activity diagrams in SiO_2 -CaO- UO_3 - H_2O and CO_2 -CaO- UO_3 - H_2O systems at 298.15K and 1 bar were constructed using the predicted ΔG_f° values for the relevant U^{6+} 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° and ΔH_f° of the U^{6+} 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 that 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 H_2O 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 H_2O groups. The effect of residual entropy on the solubility of solid phases can be substantial. These results have been submitted for publication in *Radiochimica Acta*.

Solubility of UO_2 : Experimental data obtained through collaboration with Spanish colleagues were obtained from uranium dioxide solubility studies as a function of pH and under nominally reducing conditions in a $0.008 \text{ mol dm}^{-3}$ perchlorate medium and in a 1 mol dm^{-3} chloride solution. The solubility of extensively characterized uraninite samples from Cigar Lake, Canada, Jachymov, Czech Republic, and Oklo, Gabon, were determined in a solution matching the composition of a groundwater associated with granitic or tuffaceous terrain. The redox potential of the test solution was monitored throughout the experimental period. The results obtained were modeled using aqueous formation constants compiled by the NEA, using stability constants corrected to appropriate ionic strengths. The solubility curves have been adjusted by calculating the value of K_{s4} ($\text{UO}_{2(s)} + 2\text{H}_2\text{O} \leftrightarrow \text{U}(\text{OH})_{4(\text{aq})}$) that gave the best fit with the experimental data. For a low temperature synthetic UO_2 a value of $\log K_{s4}$ of -7.3 was determined, while for uraninites the best fit was obtained with a value of $\log K_{s4}$ of -8.5 . Differences in solubility between natural and synthetic samples are attributed to the presence of carbonate in the experiments performed with uraninites, while differences in solubility observed among the natural samples can be correlated to radiation effects at the atomic scale. These results have been published in *Geochimica et Cosmochimica Acta*, vol. 62, 2223-2231 (1998).

UO_2 Incorporation of ^{79}Se : ^{79}Se is a long-lived (1.1×10^6 year) fission product that 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. 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, ^{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_3OH) in structures of α -uranophane and boltwoodite that are expected to be the dominant alteration products of UO_2 in Si-rich groundwater. The substitutions $(\text{SeO}_3) \leftrightarrow (\text{SiO}_3\text{OH})$ in sklodowskite, $\text{Mg}[(\text{UO}_2)(\text{SiO}_3\text{OH})_2(\text{H}_2\text{O})_6]$, and $(\text{SeO}_3) \leftrightarrow (\text{PO}_4)$ in phurcalite, $\text{Ca}_2[(\text{UO}_2)_3(\text{PO}_4)_2]_2(\text{H}_2\text{O})_7$, may occur with the eliminated apical anion being substituted for by an H_2O group, but experimental investigation is required. The close similarity between the sheets in the structures of rutherfordine, $[(\text{UO}_2)(\text{CO}_3)]$, and $[(\text{UO}_2)(\text{SeO}_3)]$ implies that the substitution $(\text{SeO}_3) \leftrightarrow (\text{CO}_3)$ can occur in rutherfordine, and possibly other uranyl carbonates. However, the substitutions: $(\text{SeO}_3) \leftrightarrow (\text{SiO}_4)$ in soddyite and $(\text{SeO}_3) \leftrightarrow (\text{PO}_4)$ in phosphuranylite may disrupt their structural connectivity and are, therefore, unlikely. These results have been published in the *Journal of Nuclear Materials* 275, 81-94 (1999)

UO_2 Incorporation of ^{99}Tc : ^{99}Tc is a long-lived radioactive fission product with a half-life of 2.13×10^5 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 of technetium with $\log [\text{TcO}_4^-]/[\text{TcO}(\text{OH})_2^0] > 2.15$ in the range of $\text{pH} = 4 - 10$. Because of the low solubility of $\text{TcO}_2 \cdot \text{H}_2\text{O}$ and high adsorption of Tc^{4+} by geological materials, such as clays, the concentration of Tc^{4+} in groundwater is expected to be less than 10^{-8} M, and the incorporation of Tc^{4+} into alteration uranyl phases is not considered to be an important retardation mechanism. In contrast, 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 result in under-bonding at the U^{6+} site and will destabilize the structure, suggesting that significant substitution of (TcO_4^-) will not occur in uranyl phases. These results have been published in the *Journal of Nuclear Materials* 278, 225-232 (2000).

Uraninite, UO_{2+x} , Incorporation of Trace Elements: Uraninite and associated alteration products from the Colorado Plateau were studied in detail by optical microscopy, electron microprobe analysis (EMPA), scanning electron microscopy (SEM) and backscattered electron (BSE) imaging in order to determine the behavior and fate of trace elements, such as Pb, Ca, Si, Th, Zr, and REE, during corrosion under oxidizing conditions. The long-term alteration products and processes of uraninite provide insight into the corrosion of the UO_2 in spent nuclear fuel. Uraninite, schoepite, calciouranoite, uranophane, fourmarierite, a Fe-rich uranyl phase, and coffinite were identified. The primary uraninites and alteration phases generally have low trace element contents, except for coffinite from Caribou Mine, Colorado that has Y_2O_3 as high as 0.88 wt.%. The highest Zr, Ti, Th and REE values of the uraninite are ThO_2 0.17, Y_2O_3 0.28, La_2O_3 0.03, Ce_2O_3 0.10, Pr_2O_3 0.02, Nd_2O_3 0.14, Sm_2O_3 0.12, Eu_2O_3 0.04, Gd_2O_3 0.08, ZrO_2 0.93, and TiO_2 0.54 wt.%, which are in general lower than the corresponding components in secondary uranyl phases (the highest values are ThO_2 0.21, Y_2O_3 0.88, La_2O_3 0.05, Ce_2O_3 0.15, Pr_2O_3 0.05, Nd_2O_3 0.18, Sm_2O_3 0.14, Eu_2O_3 0.11, Gd_2O_3 0.08, ZrO_2 2.11, and TiO_2 2.74 wt.%), suggesting that trace elements preferentially enter the structures of these secondary uranyl phases. A compositional profile of a concentric structure in schoepite shows that, with increasing alteration, UO_2 , PbO and ZrO_2 decrease, and SiO_2 , TiO_2 , CaO and P_2O_5 increase. Alteration causes loss of U, Pb and Zr and incorporation of Si, Ti, Ca and P into uranyl phases. Concentric structures are usually composed of both uraninite and uranyl phases, while micro-fractures are common in the secondary phases. This work has been published in *Radiochimica Acta* 88, 739-749 (2000).

Retardation of Radionuclides in the Oklo Natural Reactors: The natural fission reactors in Gabon have been studied in detail by optical microscopy, BSE, and EMPA to determine the source term, extent of uraninite alteration, and the means of retardation of nuclear reaction products during their 2 Ga year long geological history. A detailed study of the recently excavated Okélobondo reactor zone was conducted. This reactor zone consists of a ~ 55 cm thick reactor core overlain by a typically less than 60 cm thick hydrothermal alteration halo, *argile de pile*. The reactor core mainly consists of uraninite (≤ 90 vol.%), galena, illite, and minor chlorite. The *argile de pile* consists mainly of chlorite cut by fine illite veinlets. The uraninite has been subjected to minor degree of coffinitization ($\text{UO}_2 \rightarrow \text{USiO}_4 \cdot n\text{H}_2\text{O}$). Several accessory

phases occur in the reactor zone of which U-Zr-silicate, monazite, sulfides, and sulfur-arsenides are particularly important with respect to retardation of fissionogenic elements. The “unaltered” uraninite is relatively pure and consists of 87.01 ± 0.72 to 91.24 ± 0.91 wt.% UO_2 and 5.66 ± 0.61 to 7.22 ± 0.53 wt.% PbO . The major impurities are SiO_2 ($\leq 0.78 \pm 0.11$ wt.%), CaO ($\leq 1.84 \pm 0.09$ wt.%), and FeO ($\leq 0.55 \pm 0.04$ wt.%). The concentration of fissionogenic trace elements is low: $\text{ZrO}_2 \leq 0.09 \pm 0.04$ wt.%, $\text{ThO}_2 \leq 0.20 \pm 0.11$ wt.%, $\text{Ce}_2\text{O}_3 \leq 0.09 \pm 0.02$ wt.%, and $\text{Nd}_2\text{O}_3 \leq 0.10 \pm 0.06$ wt.%, but showed a distinct variation with location in the reactor zone. The concentration of the fissionogenic trace elements was higher ($\text{ZrO}_2 \leq 24.29$ wt.%, $\text{ThO}_2 \leq 0.31$ wt.%, $\text{Ce}_2\text{O}_3 \leq 0.75$ wt.%, and $\text{Nd}_2\text{O}_3 \leq 0.50$ wt.%) in U-Zr-silicate observed in fracture veinlets and mineral coatings in the reactor zone. Inferred from mineral chemistry, the fissionogenic Zr (including $^{90}\text{Sr} \rightarrow ^{90}\text{Zr}$), Ce, Nd, and Th (daughter of $^{238}\text{U}(\alpha, \gamma, 2\beta)$, $^{239}\text{Pu}(\alpha, \gamma)$, ^{240}Pu and $^{235}\text{U}(\alpha, \gamma)$, ^{236}U) 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 ^{99}Ru a daughter of ^{99}Tc , was mainly retained in ruthenium sulfur-arsenides ($\pm \text{Pb}$, Co , and Ni), such as ruthenarsenite and ruarsite. This work has been published in the *Geological Society of America – Bulletin* 113, 32-62 (2001).

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PERSONNEL SUPPORTED

This research program has provided support for:

- R.C. Ewing** (Professor and P.I.): 1.5 months during the summer
- Dr. Donggao Zhao** (Ph.D. from the University of Michigan): Post-doctoral fellow for 1.5 years. Now employed at the Electron Microscopy Center at the University of South Carolina.
- Dr. Keld Jensen** (Ph.D. from Aarhus University, Denmark): Ph.D. candidate and Post-doctoral fellow for 1.5 years. Now employed at the National Institute of Occupational Health, Copenhagen, Denmark.
- Dr. Satoshi Utsunomiya** (Ph.D. from the University of Tokyo): Post-Doctoral Fellow at University of Michigan
- Mr. Christopher Palenik** (B.S. in Chemistry from the University of Chicago): Ph.D. candidate at University of Michigan.

We are presently interviewing potential graduate students to work on this program.

INTERACTIONS & TRANSITIONS

During the past three years, my research group at the University of Michigan has had an active program of research on uranium-bearing phases, the corrosion products of uraninite, and the UO_2 in spent nuclear fuel. The work has benefited from numerous collaborations, many of them international. As an example, Professor Ewing was a participant in the European Union project to study radionuclide migration around the Oklo reactors in Gabon. The EU program supported collaborations with scientists in Denmark, Poland, France, Spain and Japan. As a result of this collaboration, Professor Ewing now has an extensive research collection of Oklo samples that provide the basis for future work. Through a NATO program there is an active collaboration with Russian colleagues at the Khlopin Radium Institute in St. Petersburg in studies of minerals suitable for use as actinide waste forms. We are continuing our collaboration with Dr. F. Chen at the Guangzhou Institute of Geochemistry of the Chinese Academy of Sciences.

Within the United States, Professor Ewing serves on many committees associated with DOE projects. He served as a member of the Committee for the "Peer Review of the Total System Performance Assessment – Viability Assessment of the Yucca Mountain Repository", as a member of the National Research Council's committee on "Alternative High-Level Waste Treatments at the INEEL Site", and on the NSF

committee for “Opportunities in Mineral and Rock Physics and Chemistry.” He was a member of the program committee for the Materials Research Society symposium, “Scientific Basis for Nuclear Waste Management” held in Sydney, Australia, in August of 2000. All of these activities have provided opportunities to present the results of this EMSP-supported program.

During the year 2000, Professor Ewing has been invited to participate in meetings of the *Nuclear Waste Technology Review Board* (invited guest), *Advisory Committee on Nuclear Waste of the Nuclear Regulatory Commission* (invited expert) and has been appointed to serve on the *Board of Radioactive Waste Management of the National Research Council* (member). Each of these committee and board assignments provide an important opportunity to utilize the results of our, and other, EMSP programs.

The impact of this work is further enhanced by numerous **invited presentations** by Professor Ewing:

- “Design of Advanced Waste Forms for Actinide Immobilization”: Actinides '97, Baden-Baden, Germany, September 25, 1997.
- “Radiation Effects in Materials Utilized in Nuclear Waste Management”: Annual meeting of the Geological Society of America, Symposium on “Environmental Mineralogy: Science & Politics”, Salt Lake City, Utah, October 22, 1997.
- “Nuclear Waste Disposal: Materials Science Issues”: Nuclear Engineering and Radiological Sciences, Weekly Colloquium, The University of Michigan, Ann Arbor, MI, January 23, 1998.
- “The Mineralogy of Spent Nuclear Fuel”: Scott Turner Lecture Series, Department of Geological Sciences, The University of Michigan, Ann Arbor, MI, March 27, 1998.
- “Invited Comments”: XVI Mendeleev Congress on General and Applied Chemistry, Vol. 3, St. Petersburg, Russia, May 29, 1998.
- “Host Materials for High Level Nuclear Waste Isolation”: World Ceramics Congress & Forum on New Materials, Florence, Italy, June 19, 1998.
- “Natural Glasses and the Verification of the Long-Term Durability of Nuclear Waste Glasses”: 18th International Congress on Glass, San Francisco, California, July 10, 1998.
- “The Design of Nuclear Waste Forms: Clues From Mineralogy” (invited plenary lecture): 17th General Meeting of the International Mineralogical Association, Toronto, Canada, August, 14, 1998.
- “Nuclear Waste Forms for Actinides”: National Academy of Sciences colloquium “Geology, Mineralogy and Human Welfare”, Beckman Center, Irvine, CA, November 9, 1998.
- “Performance Assessments: The Design, Selection and Importance of Nuclear Waste Forms”: Chemistry Division Colloquium, Argonne National Laboratory, IL, April 5, 1999.
- “Radiation Effects in ABO_4 Orthophosphates and Orthosilicates”: HLW and Pu Immobilization Workshop, CEA, Saclay, France, April 22, 1999.
- “The Yucca Mountain Repository: What Has Changed?”: American Geophysical Union, Spring meeting, Boston, Massachusetts, June 1, 1999.
- “Ageing Studies of Nuclear Waste Forms: The Evaluation of Long-Term Behaviour”: Plenary lecture for International Conference on Ageing Studies & Lifetime Extension of Materials, St. Catherine’s College, Oxford, United Kingdom, July 12, 1999.
- “Radiation Effects in Zircon”: Invited seminar at the Université Henri Poincaré, Nancy, France, September 10, 1999.
- “Natural Systems: Applications to Nuclear Waste Management”: Invited presentation at workshop sponsored by the Russian Academy of Sciences and the U.S. Department of Energy, Moscow, Russia, October 20, 1999.
- “Mineralogy: Applications to Nuclear Waste Disposal”: Plenary presentation at the Twentieth Annual New Mexico Mineral Symposium, New Mexico Institute of Mining and Technology, Socorro, New Mexico, November 13, 1999.
- “Immobilization of Plutonium: Recent Developments in Materials Science”: Nuclear Security Decisionmakers’ Forum, Albuquerque, New Mexico, March 30, 2000.
- “Natural Glasses and the Verification of the Long-Term Durability of Nuclear Waste Glasses: Reducing Uncertainty”: Invited presentation at the International Workshop on Glass in its Disposal Environment, Bruges, Belgium, April 13, 2000.
- “Radiation Effects in Nuclear Waste Materials”: Annual meeting of the American Ceramic Society in the symposium, “Waste Management Science and Technology in the Ceramic and Nuclear Industries”, St. Louis, Missouri, May 2, 2000.

- “Radiation Effects in Nuclear Waste Materials”: invited seminar at Argonne-West, Idaho Falls, Idaho, May 11, 2000.
- “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.
- “Radiation Effects in Minerals”: Department of Earth & Planetary Sciences Colloquium, Washington University, St. Louis, MO, November 2, 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.
- “Radiation Effects in Nuclear Waste Forms”: Materials Science & Engineering Colloquium, University of Michigan, Ann Arbor, MI, December 1, 2000.
- “Radiation Effects in Nuclear Waste Forms”: Department of Chemical Engineering & Materials Science Colloquium, University of California at Davis, January 23, 2001.
- “Crystalline Ceramics for Radioactive Waste Management”: Chemistry Colloquium, Indira Gandhi Centre for Atomic Research, Kalpakkam, India, February 1, 2001.
- “Radiation Effects in Nuclear Waste Forms”: Indira Gandhi Centre Colloquium, Indira Gandhi Centre for Atomic Research, Kalpakkam, India, February 2, 2001.
- “Radiation Effects in 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.

COLLABORATIVE INTERACTIONS

Because of our long involvement in this field, particularly with international scientists, we will continue our long-term collaborations with colleagues working on various aspects of uranium chemistry. .

The main collaborations are listed below:

Dr. Peter Burns	Notre Dame University structural studies and refinements of uranium minerals
Dr. Jordi Bruno	QuantiSci, Barcelona, Spain leaching studies of uranium minerals; solution chemistry of actinides
Dr. Fanrong Chen	Guangzhou Institute of Geochemistry Chinese Academy of Sciences, Wushan, P.R. China geochemical modeling of uranium-phase dissolution
Professor Sue Clark	Department of Chemistry Washington State University structure-based models of solubility
Dr. Mostafa Fayek	Center of Isotope Geochemistry Oak Ridge National Laboratory & University of Tennessee isotopic studies of uranium deposits
Professor Frank Hawthorne	Department of Geological Sciences University of Manitoba crystal structure refinements of uranium minerals
Professor Janusz Janeczek	Faculty of Earth Sciences University of Silesia

mineralogy and geochemistry of the Oklo reactors

FUTURE WORK

Previous work by Ewing and colleagues has shown that the behavior of uraninite, naturally occurring UO_{2+x} , can be used to evaluate the long-term behavior of the UO_2 in spent nuclear fuel under oxidizing and reducing conditions (Janeczek et al., 1997, Finch and Ewing, 1992c; Finch et al. 1992; Janeczek and Ewing, 1995, 1996a; Janeczek et al. 1996). Despite some important differences between uraninite and the UO_2 in spent fuel (e.g., the thermal and radiation histories are substantially different, and the much older uraninite contains substantial quantities of Pb that is not present in the UO_2 of spent fuel), much has been learned about the alteration of SNF. However, **the quantitative determination of the release rates of nuclear reaction products and our understanding of their retardation by sorption and/or incorporation into secondary phases during SNF alteration is still in its earliest stages.**

A complete program of research on the secondary, uranium phases requires the refinement of critical structure-types, an analysis and classification of the topologies of the structures, a theoretical analysis of the crystal chemistry of actinide and fission products in these host-phases, confirmation of the theoretical predictions based on experimental synthesis with actual radionuclides, and chemical analyses of naturally occurring alteration products of uraninite to confirm (or validate) long-term behavior. **Our work continues to focus on naturally occurring uranium phases that form by the corrosion of uraninite under oxidizing and reducing conditions.** The present research program includes the following studies:

Trace-Element Incorporation in Alteration Phases:

During the first three years of this research program, we have investigated the behavior of uranium minerals in reducing (Zhao and Ewing, 1999) and oxidizing (Zhao and Ewing, 2000) environments. These investigations have required that we assemble a research collection of appropriate materials, mainly younger uranium phases for which the Pb-content is low. We have developed analytical techniques for the electron microprobe analysis of 24 elements, with special emphasis on Th and the rare earth elements (Zhao and Ewing, 2000). Although the trace element contents of these samples are extremely low, often below the limits of detection, present results confirm that trace elements are incorporated into the secondary alteration phases and that, in general, the trace element contents are increased in the alteration phases. This provides a potential mechanism for the retardation of radionuclides during the alteration of spent nuclear fuel.

Although the present results are encouraging, the electron microprobe results are limited by the fact that we cannot determine directly the $\text{U}^{6+}/\text{U}^{4+}$ 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:

Determine the oxidation state of uranium ($\text{U}^{6+}:\text{U}^{4+}$ ratio) directly using electron energy loss spectroscopy (EELS). We are presently in the process of installing a new field emission gun transmission electron microscope that will have EELS capability. EELS can also be used to determine the oxidation states of Fe and rare earth elements, such as Ce. Redox state is an important parameter for the formation of uranium minerals. Whether uranium exists as U^{4+} or U^{6+} depends on the redox state of the environment. Our studies of uraninite from the Colorado Plateau reveal two types of uraninite. One has a high U^{6+} content from 0.587 to 0.808 apfu, close to or similar to altered secondary uraninite with a stoichiometry of U_3O_8 . The other has a low U^{6+} content from 0.212 to 0.489 apfu, close to that of primary uraninite from the Cigar Lake deposit in Canada. The U^{6+} content is an indication of the redox state. Uranium minerals with different $\text{U}^{6+}/(\text{U}^{4+} + \text{U}^{6+})$ ratios will have different capabilities to incorporate impurity elements, such as radionuclides released from corroding SNF.

Determine the amount and type of water in the U-phases by infrared analysis. We now have in our research collection, suitable material that can serve as standards for this type of 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. Where necessary, we will also complete detailed high resolution transmission electron microscopy to confirm that these phases are homogeneous at the atomic-scale (that is that the trace elements are not incorporated as inclusions) and single crystal x-ray diffraction refinements to confirm the structural parameters of these phases.

We are investigating solid-solution relations and solubility limits of key phases. The discovery of Zr-rich uranium phases (Zhao and Ewing, 1999; Jensen and Ewing, 1999; 2000) suggests the possibility of extensive solid solution among uraninite and Zr-phases. A Zr- and Si-rich uranium phase identified by Zhao and Ewing (1999) contains as high as 8.3 wt % ZrO₂ and 4.9 wt % SiO₂. In the three component system UO₂ - SiO₂ - ZrO₂, coffinite and zircon both belong to tetragonal system, while UO₂ is cubic. Investigation of substitution mechanism of elements in each phase will allow us to develop models of the ability of these phases to incorporate impurities, including fission products and actinides.

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 address the following questions:

Natural alteration of uraninite: We are completing studies of U-phases formed under oxidizing conditions from a variety of sites, such as the Nopal I deposit in Peña Blanca district, Chihuahua, Mexico (Goddel, 1981, George-Aniel et al., 1991; Percy et al., 1994). Localities that have oxidizing conditions are chosen because they have a geochemical and climatic environment similar to that of Yucca Mountain. We will use optical microscopy, electron microscopy and the electron microprobe to analyze the formation sequence, paragenesis and composition (including trace element contents) of the uraninite and its alteration products. Moreover, the composition of groundwater passing through the ore and from the host rocks close to the ore body will also be analyzed (either by direct determination or use of values from the literature). We will determine the alteration conditions and reaction paths based on these studies.

Laboratory simulation of the alteration of uranium ore: These alteration experiments will use the uranium ore and a leaching fluid with a groundwater composition typical of those found in tuffaceous or granitic rock types. Simple column tests will be designed. The uraninite ore will be ground to standard size and subjected to oxidative alteration at three temperatures (25°C, 60°C and 90°C) under oxidizing conditions. We will change the drip rate to see how kinetics effect the formation of phases with increasing reaction progress. Phases formed at different levels in the test column will be characterized using electron microscopy (particularly cross-sectional microscopy of ultra-thin microtomed sections) and electron microprobe analysis. We are especially interested in determining the fate of trace elements in uraninite (Th and rare earth elements) by careful analysis of the solids formed by measurement of solution compositions. The result will be used to calculate distribution coefficients of the trace elements between the secondary phases and solution. The experimental results will be compared to the output of computer simulations and the observations made of natural occurrences to determine the differences between long-term and short-term alteration, and where differences occur, we will investigate the causes of these differences.

Geochemical simulations: Theoretically, many geological processes can be described using thermodynamic models. However, phases with faster crystallization kinetics will form in the early stage of alteration and in laboratory experiments. Thermodynamic models using the solubility data obtained in this research will be developed to simulate both the long-term (natural) and the short-term (laboratory) alteration. A comparison of thermodynamic model output with observations made of natural alteration and the results from alteration experiments made at different drip rates will provide insight into the influence of crystallization kinetics on reaction path and trace element release. The kinetic parameters and equations obtained from the precipitation experiments will be used to validate the corrosion model.

Oklo Natural Reactors – An Analogue for Spent Fuel Corrosion:

Natural fission reactors were discovered first in the 2 Ga old Oklo uranium deposit in SE-Gabon by *Commissariat a l'Energie Atomique* (CEA) in 1972. Since then a total of sixteen natural fission reactors have been discovered in the Oklo-Okélobondo uranium deposit (Gauthier-Lafaye et al., 1989, 1996). A single

natural fission reactor has also been identified in the Bangombé uranium deposit, 25 km southeast of Oklo-Okélobondo. The natural fission reactors in Gabon are unique in that: **1)** They are the only place on Earth where self-sustained fission reactions have occurred naturally. **2)** The uranium ore-bodies and the reactors are of great age (~ 2 billion years) and have not been subjected to post-criticality metamorphism and thus are well preserved. **3)** The natural fission reactors occur along a depth profile ranging from 12 m depth (at Bangombé) to 330 m (Okélobondo). This range in depth allows the evaluation of the stability of uraninite as function of oxidizing to reducing alteration conditions (Pourcelot and Gauthier-Lafaye, 1998; Jensen and Ewing, 1999).

Migration behavior of radionuclides around the Okélobondo natural fission reactor – Implications for the performance of a spent nuclear fuel repository:

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 (in press). 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 phases observed to be most important with respect to retardation of the nuclear reaction products in RZOKE are U-Zr-silicate, monazite, and Ru-sulfur-arsenides in addition to uraninite itself. The presence of phases that contain fissiogenic trace elements suggests that during the alteration of SNF radionuclides can be incorporated into the secondary, alteration phases. This may have occurred either during or as a post-criticality event. 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 have not been quantified. Previous analyses have been concentrated on *in situ* analysis or the migration nuclear reaction products in bulk-rock specimens (e.g., Curtis et al., 1989; Loss et al., 1989; Brookins, 1990; Menet et al., 1992; Hidaka et al., 1994a, 1994b, 1999; Hidaka and Holliger, 1998; Hidaka and Gauthier-Lafaye, submitted). These analyses are usually incomplete due to the lack of correlation between mineralogy and geochemistry or insufficient sample coverage. However, a compilation of migration data collected from various studies were summarized by Janeczek (1999) and showed that most radionuclides have been detected within 6.5 m from the reactor core. However, Ru and Tc have been detected at distances up to 10 –12 m; whereas, most of the Xe, Kr, I, Cs, Rb, and Sr are lost from reactor-environment (Fig. 1).

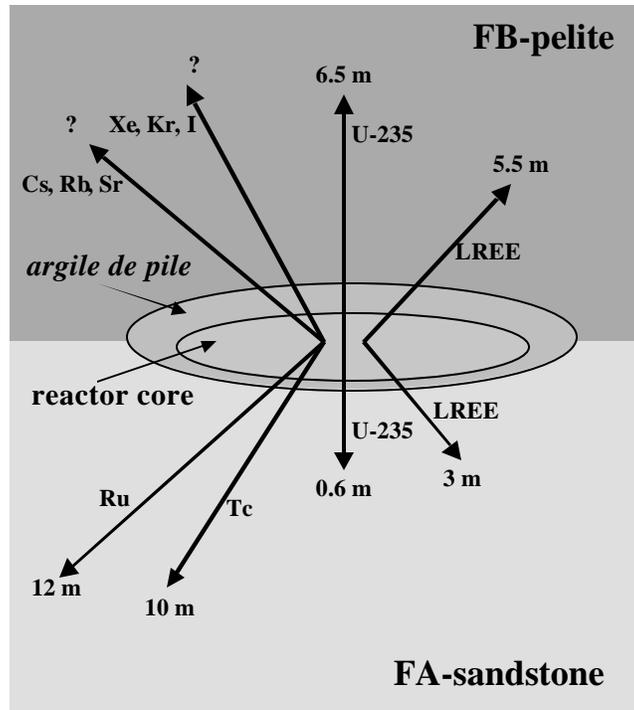


Figure 1: Compilation of migration data from studies of the natural fission reactors in Gabon. Modified from Janeczek (1999).

Based on an outstanding sample collection from RZOKÉ and its near-field environment, we propose to complete a detailed geochemical and isotopic analysis of the Okélobondo natural fission reactor zone. By a combination of detailed mineralogical, chemical and isotopic analysis, we anticipate being able to quantify the amounts of fissionogenic nuclides that have been released from the natural SNF during criticality and subsequent alteration. Combination of mineralogical observations and geochemical data, also enables an analysis of the prevailing pH-Eh-conditions during corrosion of the uraninite and subsequent radionuclide migration. The results will improve our understanding of the SNF stability and radionuclide behavior in the geosphere under low-temperature hydrothermal alteration conditions. Based on the temperatures (200 –300°C) at the reactor boundaries, normally reached during criticality, these results are applicable to understanding the release of radionuclides during the alteration of unconfined SNF in a nuclear waste repository at overall reducing conditions. Whole-rock geochemistry will be obtained by XRF analysis and ICP-AES or INAA. Whole-rock isotope analysis will be completed by ICP-MS. *In situ* isotope analysis may be conducted by SIMS through collaboration with Dr. Mostafa Fayek at ORNL/University of Tennessee. Additional mineralogical analysis will be completed using EMPA, TEM/HRTEM with EELS to analyze fine-grained accessory phases and the nanoscale homogeneity and alteration of uraninite.

Low-temperature diffusion and recrystallization behavior in natural uraninite - Implications for the long-term mechanical behavior of spent nuclear fuel: Previously, most of the studies of SNF behavior have been concentrated on the mechanical properties, fracturing, as well as the formation of the ϵ -phase (aggregates of Mo, Ru, Tc, Pd, and Rh) and gas-bubbles during irradiation of the fuel (Solomon, 1973; d’Annucci et al., 1977; Matzke, 1987; Guenther et al., 1989; Thomas and Guenther, 1989; Ray et al., 1992; Matzke and Spino, 1997; Nogita and Une, 1997). Even-though some fission products substitute for U in the uraninite structure or form particles and gas-bubbles during irradiation of the fuel rods, incompatible fission products will also occur in interstitial sites in the UO_{2+x} lattice. All of these parameters are of importance for evaluating the release rate and corrosion behavior of the SNF, should it be subjected to long-term geological alteration. Experimental results have shown that the accumulation of α -decay damage can result in a significant long-term macroscopic volume expansion of up to 2.5 vol.% of the uraninite and SNF (Evron et al., 1994). Evron et al. concluded that the volume expansion can lead to cracking and disintegration of the SNF.

In fact, petrographic analysis of uraninite from the 2 billion year old natural fission reactors frequently show “cracked” uraninite grains. However, diffusion/recrystallization-related mechanisms may also induce cracking. This is particularly evident in uraninite from natural fission reactor zone 13, which is located 10 – 30 meters from a 755 ± 83 Ma dolerite dyke intrusion. These uraninite grains show clear evidence of mechanical brecciation due to accumulation of Pb and formation of galena during the dolerite dike intrusion (Fig. 2).

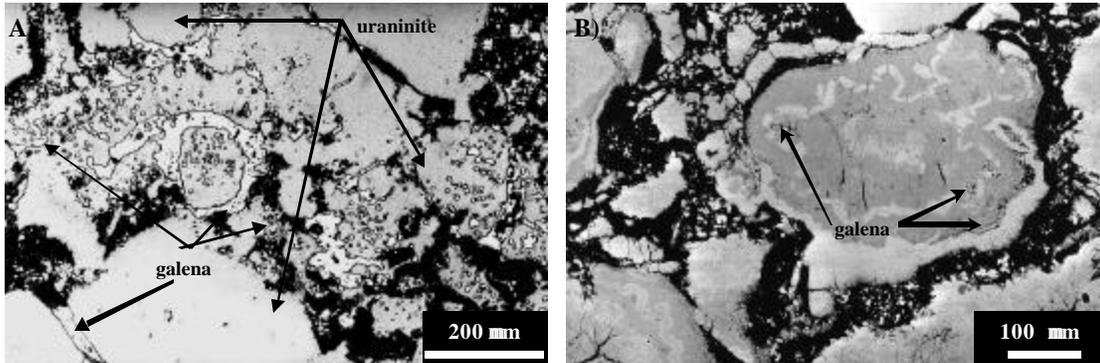
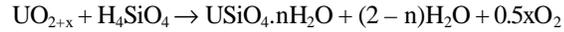


Figure 2: A) Example of uraninite brecciation due to lead accumulation and formation of galena in RZ13 in the Oklo-Okélobondo uranium deposit (reflected light micrograph). B) Development of diffusion bands in uraninite from RZ13. The bright regions have higher concentration of UO_2 (+1-2 wt.%) and PbO (+1 wt.%) lower concentrations of ZrO_2 (- 0.2 wt.%), CaO (- 0.5 wt.%) (Backscattered electron image).

Based on observations from the natural fission reactors, there are strong indications from natural uraninite that thermally-induced recrystallization and diffusion can cause inhomogenization and disintegration of the SNF during long-term storage. The responsible diffusion/segregation mechanisms require clarification in order to define the threshold value for the long-term mechanical inhomogenization of the SNF. We will study uraninite from natural fission reactor zones 10, 13, and the Okélobondo natural fission reactor in order to elucidate the role and mechanisms of the diffusion processes in detail. We will: 1) determine the extent of compositional zoning in uraninite and 2) complete a detailed nanotextural/nanochemical analysis of the uraninite. The extensive solid state characterization will be followed by experimental heating experiments of unzoned uraninite from the natural fission reactors to analyze the annealing and diffusion behavior of the impurities observed in the uraninite. The initial analysis will require detailed backscattered electron microscopy and electron microprobe analyses. The phase homogeneity, crystallinity, and d-spacings will be analyzed by X-ray diffraction analysis and transmission electron microscopy in order to locate the atomic scale position of the chemical impurities observed in the uraninite. The main focus of the heating experiments will be the low-temperature annealing and diffusion effects in uraninite, that is the annealing and diffusion behavior below $400^\circ C$. “Real-time” observations may be made in a TEM equipped with a heating stage. The samples from the furnace experiments will be subsequently analyzed in detail by XRD, SEM/BSE, EMPA, and TEM/HRTEM. The annealing results will be discussed in relation to results from other natural and synthetic uraninite specimens. These results will provide an understanding of the long-term stability of the spent fuel, as well as an evaluation of the risk of segregation of incompatible elements and particles that can increase the potential for incongruent SNF dissolution.

Conditions and kinetics of coffinitization: Under reducing conditions, uraninite is altered either through dissolution (Bruno et al., 1988; Casas et al., 1998), recrystallization, or coffinitization ($UO_2 \rightarrow USiO_4 \cdot nH_2O$) (Janeczek and Ewing, 1992b, 1995). This is frequently observed in uranium ore deposits (Speer, 1982). Similar to oxidative corrosion, these alteration mechanisms can result in significant release of radionuclides to the geosphere. For example, analysis of natural specimens from the Bangombé natural fission reactor has shown a loss of up to 46 mole% U and incompatible elements during coffinitization of uraninite (Jensen et al., in press). Compatible elements, such as Th, Zr, and the lanthanides were preferentially retained.

Coffinitization is the replacement of uraninite with a uranium silicate and is assumed to occur through dissolution of UO_{2+x} followed by reprecipitation of the uranium as $\text{USiO}_4 \cdot n\text{H}_2\text{O}$.



However, the reaction becomes much more complicated when the complete crystal chemistry of the uraninite ($\text{U}^{4+}_{1-x-y-z-u-v}\text{U}^{6+}_x\text{R}^{4+}_y\text{R}^{3+}_z\text{R}^{2+}_u\text{O}_{2+x-z/4-u/2-4v}$) and the reactivity of inclusions therein are considered. Currently the natural formation conditions of coffinite are poorly understood. Moreover, the behavior of coffinite during oxidation and rates of dissolution are completely unknown. If coffinitization of SNF occurs, it will be the stability and behavior of coffinite that determines the initial release rate of radionuclides to the geosphere.

In spite of the ease with which coffinite forms at low temperatures in nature, low-temperature synthesis of coffinite has not been successful. However, coffinite, has been produced in the laboratory by hydrothermal synthesis at approximately 200°C from gels in basic alkaline solutions (Fuchs and Hoekstra, 1959). Based on the data of Fuchs and Hoekstra for the formation of coffinite at pH=8.3, it is evident that the formation kinetics of coffinite are relatively rapid at higher temperatures; whereas, the longer time-constraints at temperatures below, say 200°C, are unknown. The upper limit for coffinite stability was determined to be ~ 500°C in air (Fuechs and Hoekstra, 1959). An obvious paradox arises when these data are compared with the maximum stability temperature (130°C) for coffinite determined by a purely thermodynamic approach (Xu and Wang, 1999).

As consequence of the poorly defined coffinite formation conditions, a series of experiments combined with studies of natural specimens will be completed to resolve the “coffinite-problem” and its relation to SNF alteration. We will determine the conditions under which “low-temperature” coffinitization occurs through a compilation of natural occurrences, followed by controlled isothermal batch reactor studies. The initial reactor experiments will address the conditions and kinetics of coffinite formation from synthetic UO_{2-x} , various concentrations of H_4SiO_4 , and at various buffered pH-Eh-conditions. Subsequent analyses will be conducted to analyze the oxidation behavior (furnace experiments) and dissolution rates (stirred continuous-flow reactors) of coffinite as function of pH and Eh. The coffinite alteration experiments will be followed by coffinitization experiments with well-characterized uraninite from the natural fission reactors in Gabon to analyze the release-rates of U and impurity elements during coffinitization. These experiments will be conducted in continuous-flow reactors and will subsequently be expanded to the analysis of coffinitization in more complex water compositions with various degrees of alkalinity and H_2CO_3 , H_3PO_4 , and H_2SO_4 contents. The analysis will contribute significantly to predicting the performance of the coffinite as a potential secondary SNF waste form.

The results will be obtained through a detailed solid-state characterization of the starting materials and reaction products (minerals and reactor fluids). The solid state characterization will involve XRD analysis, cross-sectional TEM with EELS, and EMPA when applicable. The analysis of the reactor fluids will be performed by AAS and/or ICP-AES. All analysis can be completed in the Department of Geological Sciences at the University of Michigan.

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The principal investigator's name (this proposal) is indicated in **bold type** in the list of cited references.

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