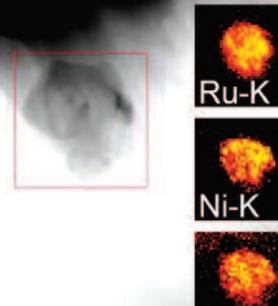


Spent Nuclear Fuel

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The primary waste form resulting from nuclear energy production is spent nuclear fuel (SNF). There are a number of different types of fuel, but they are predominantly uranium based, mainly UO₂ or, in some cases, metallic U. The UO₂ in SNF is a redox-sensitive semiconductor consisting of a fine-grained (5–10 nm), polycrystalline aggregate containing fission-product and transuranium elements in concentrations of 4 to 6 atomic percent. The challenge is to predict the long-term behavior of UO₂ under a range of redox conditions. Experimental results and observations from natural systems, such as the Oklo natural reactors, have been used to assess the long-term performance of SNF.

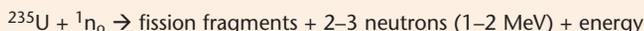
KEYWORDS: UO₂, spent nuclear fuel, actinides, fission products, Oklo

INTRODUCTION

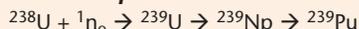
All nuclear fuel cycles are based on achieving criticality—sustained nuclear chain-reactions—with a fissionable nuclide in a reactor. Fissile ²³⁵U has an appreciable fission cross-section for thermal neutrons; hence, nuclear fuel cycles are initially based on uranium. Uranium consists of two isotopes of interest: ²³⁵U (0.72 atomic %), which is fissile, and ²³⁸U (99.27 atomic %), which is fertile. For most light water reactors (LWR), the uranium fuel is enriched to 3 to 5% ²³⁵U as a low-enriched uranium (LEU) fuel. Some reactors, such as research reactors, use highly enriched uranium (HEU) with >20% ²³⁵U. Weapons-grade material (>85% ²³⁵U) from dismantled nuclear weapons can be blended down for use in LWRs. Some reactors, such as the Canadian CANDU reactors, which use deuterium as a moderator, use unenriched, natural uranium in the fuel. A fertile nucleus is a non-fissile nucleus that can be converted into a fissile nucleus through neutron capture, typically followed by β decay. The two principal fertile nuclides, ²³²Th and ²³⁸U, can be “bred” to produce fissionable ²³³U and ²³⁹Pu, respectively, which may also be used in reactor fuels.

In a typical LWR, the fuel is exposed to a thermal neutron flux (~0.03 eV) that causes two principal types of nuclear reactions:

fission



neutron capture and beta decay



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The fission fragments form a bimodal distribution of elements (the fission yield) whose atomic masses are approximately half that of the fissioned uranium. Although many hundreds of fission-product isotopes are formed in the reactor, most have very short half-lives and decay within days to weeks of their formation. Neutron capture reactions, followed by β decay, lead to the formation of transuranium elements (Z > 92), of which Pu is the most abundant. Hence, the Pu concentration in the fuel increases with time, and isotopes, such as ²³⁹Pu, can then be fissioned, providing up to one-third of the energy generated in a nuclear power plant. The energy of the neutron spectrum can be adjusted so that higher-energy (>1 MeV) “fast” neutrons can be used to fission ²³⁸U and the “minor” actinides, such as Np, Cm, and Am. The final composition of the fuel depends on the initial fuel type, chemical composition, the level of enrichment of ²³⁵U, the neutron energy spectrum, and the “burn-up” or the amount of fission. As a rule of thumb, a burn-up of 40 MWd/kg U results in the conversion of 4% of the uranium to approximately 3% fission products and 1% transuranium elements. Typical burn-ups are in the range of 35 to 45 MWd/kg U, but it is likely that higher burn-ups will be attained in the future. Typically, a nuclear reactor will generate ~20 metric tonnes of spent nuclear fuel per year. Worldwide, the approximately 430 nuclear reactors have generated a global inventory of some 270,000 metric tonnes of spent fuel. In the United States, the inventory is ~62,000 metric tonnes of spent fuel, and the projected inventory to the end-of-life for currently operating nuclear power plants in the United States is at least twice this amount.

Chemical processing is used to reclaim the fissile nuclides ²³⁵U and ²³⁹Pu from spent nuclear fuel, and this material is then fabricated into a mixed-oxide fuel, MOX (5 to 10% ²³⁹Pu mixed with uranium), or an inert matrix fuel (IMF), such as ZrO₂, which does not contain fertile nuclides (e.g. ²³⁸U). The use of IMFs is one strategy for “burning” Pu and the minor actinides without creating more transuranium elements.

After a typical burn-up, the radioactivity of the spent fuel has increased by a factor of a million (10¹⁷ becquerel/metric tonne of fuel). One year after discharge from a reactor, the dose rate measured one meter from the fuel assembly is one million millisieverts per hour (for comparison, the natural background dose is on the order of three millisieverts per year). A person exposed to this level of radioactivity at a distance of one meter would receive a lethal dose in less than

a minute; hence spent fuel must be handled remotely. This dramatic increase in radioactivity is caused by the presence of 3 to 4 atomic percent of fission products (e.g. ^{129}I , ^{131}I , ^{137}Cs , ^{90}Sr), transuranium elements (e.g. ^{239}Pu , ^{237}Np , ^{241}Am), and activation products (e.g. ^{14}C , ^{60}Co , and ^{63}Ni) in the metal spent fuel assemblies. The very penetrating ionizing radiation (β and γ) comes mainly from short-lived fission products, such as ^{137}Cs and ^{90}Sr , with half-lives of about 30 years. These fission products are mainly responsible for the thermal heat from the fuel (1300 watts/tonne of fuel after 40 years). The less penetrating radiation from α -decay events comes mainly from the very long-lived actinides, such as ^{239}Pu and ^{237}Np , with half-lives of 24,100 years and 2.1 million years, respectively. The composition of the spent fuel, when it is initially removed from the reactor, is very complex because it contains hundreds of short-lived radionuclides. With time the total radioactivity drops quickly, so that after 10,000 years, it is 0.01 percent of the activity one month after removal from the reactor (Hedin 1997). After several hundred thousand years, the total radioactivity of the SNF equals the radioactivity of the original uranium ore mined to create the nuclear fuel (FIG. 1). Over the periods of interest for geologic disposal, hundreds of thousands of years, the radionuclides of interest are limited in number (TABLE 1); they include the isotopes of uranium and plutonium, ^{237}Np , and some long-lived fission products, such as ^{99}Tc and ^{129}I . The radionuclides of environmental interest will depend not only on their half-lives and radiotoxicity, but also on their mobility under the geochemical and hydrologic conditions at a specific repository site.

TABLE 1 CONCENTRATION (PPM) OF FISSION-PRODUCT ELEMENTS AND THOSE THAT RESULT FROM NEUTRON CAPTURE AND DECAY REACTIONS (E.G. NP, PU, AM, AND CM) IN A LOW BURN-UP (30 MWD/KG U) SPENT NUCLEAR FUEL (BUCK ET AL. 2004)

Element	ppm	Element	ppm
Xe	5657	La	1269
I	259	Ce	2469
Cs	2605	Pr	1161
Sr	794	Nd	4190
Ba	1750	Sm	815
Se	58	Eu	155
Te	529	Gd	142
Zr	3639		
Mo	3497	Np-237	468
Tc	799	Pu (total)	9459
Ru	2404	Am (total)	484
Rh	484	Cm (total)	39
Pd	1684		
Ag	92		

The radionuclides of greatest environmental impact in a geologic repository will be those that have some combination of high radiotoxicity, geochemical mobility, and a long half-life. Examples are ^{99}Tc (half-life = 200,000 years), ^{129}I (16 million years), ^{79}Se (1 million years), ^{135}Cs (2.3 million years), ^{239}Pu (24,100 years), ^{237}Np (2.1 million years), and ^{235}U (700 million years). Some radionuclides, such as ^{36}Cl (300,000 years) and ^{14}C (5700 years), are activation products. Some radionuclides increase in concentration over time due to radioactive decay, e.g. ^{237}Np by alpha decay from ^{241}Am .

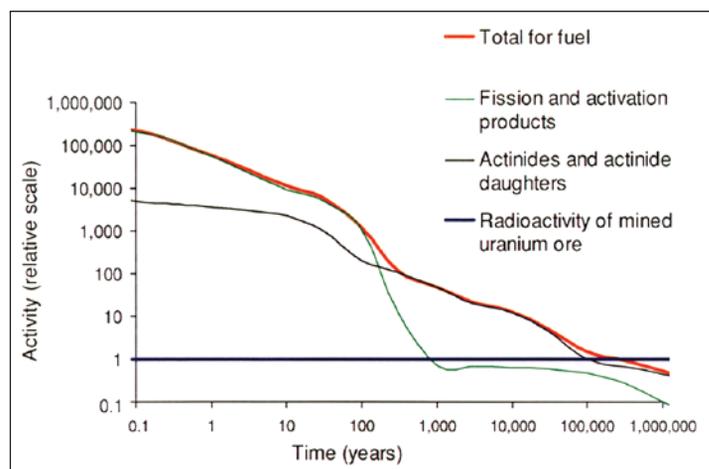


FIGURE 1 Relative radioactivity of spent nuclear fuel with a burn-up of 38 MWD/kg U. The activity is dominated by fission products during the first 100 years, thereafter by actinides (Hedin 1997).

THE "MINERALOGY" OF SPENT NUCLEAR FUEL

Prior to irradiation, the fuel consists mainly of uranium as UO_2 or U metal. The fuel is less radioactive than the original uranium ore because all the decay daughter products have been removed during chemical enrichment to create "yellow cake," U_3O_8 . The U_3O_8 is converted to gaseous uranium hexafluoride so that it can be enriched in ^{235}U , typically by gaseous diffusion or centrifuge separation. The UO_2 is produced by chemical conversion of the enriched UF_6 , and the oxygen concentration is adjusted by interstitial oxygens, with stoichiometric values up to $\text{UO}_{2.25}$. After reactor operation, the stoichiometry of the spent fuel is very close to $\text{UO}_{2.000}$ (Kleykamp 1979).

Most commercial spent fuel assemblies are rods composed of UO_2 compacted into cylindrical pellets 8 to 10 millimeters in diameter and 9 to 15 millimeters thick. The pellets are stacked in tubes of corrosion-resistant cladding materials, typically a zirconium alloy or stainless steel (FIG. 2). Empty spaces, including a narrow annular gap between the fuel pellets and the surrounding cladding, as well as the space at the ends of the fuel rods, are filled with helium gas. During reactor operation, the gap closes as the fuel expands slightly during irradiation. The type of fuel rod assembly used depends on reactor design. Each fuel assembly weighs as much as 500 kg.

The structure and composition of the various types of spent fuel have been investigated from the perspectives of reactor operation and geologic disposal (Johnson and Shoesmith 1988; Oversby 1994). At the end of the fuel's useful life in the reactor, about 95% of the spent nuclear fuel still consists of UO_2 . The remainder consists of fission products, transuranium elements, and activation products (FIG. 3), but these components occur in many different forms (Kleykamp 1985): (1) fission-product gases, such as Xe and Kr, which occur as finely dispersed bubbles in the fuel grains; (2) metallic fission products, such as Mo, Tc, Ru, Rh, and Pd, which occur as immiscible, micron- to nanometer-sized metallic precipitates (e-particles); (3) fission products that occur as oxide precipitates of Rb, Cs, Ba, and Zr; (4) fission products that form solid solutions with the UO_2 fuel, such as Sr, Zr, Nb, and the rare earth elements; (5) transuranium elements that substitute for U in the UO_2 . The distribution of elements is not homogeneous within a single pellet (FIG. 2) because of the steep thermal gradient within the pellet (temperature as high as 1700°C at the center of the pellet and decreasing to 400°C at its rim). Thermal excursions

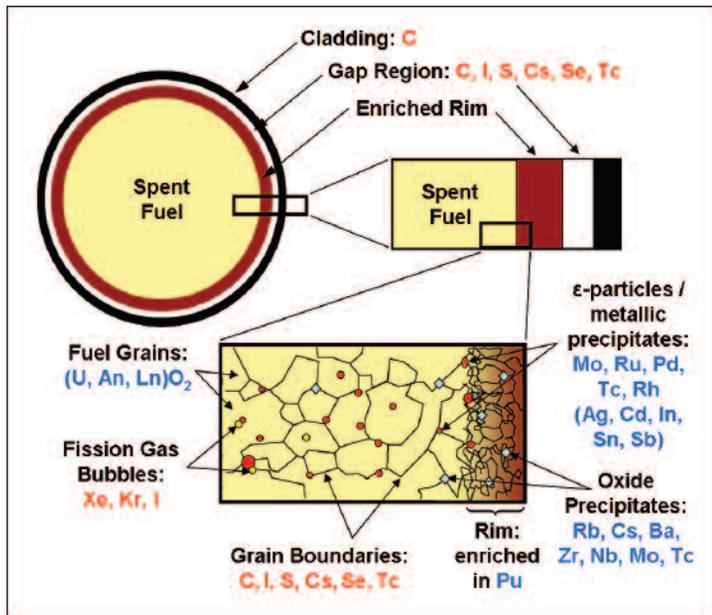


FIGURE 2 Schematic illustration of the microstructure of spent fuel and the distribution of actinides and fission products following burn-up in a reactor. Red labels indicate nearly instantaneous release upon contact with water; blue indicates slower release rates. An = actinides and Ln = lanthanides in solid solution in the UO_2 matrix. Figure adapted from Buck et al. (2004) and Shoesmith (2000)

during reactor operation can cause a coarsening of the grain size and extensive microfracturing. Volatile elements, such as Cs and I, migrate to grain boundaries, fractures, and the “gap” between the edge of the fuel pellet and the surrounding metal cladding. The burn-up is also not uniform across the fuel pellet. Higher burn-ups at the edge of the pellet lead to higher concentrations of ^{239}Pu at the fuel edge, an increase in porosity, and polygonization of the UO_2 grains resulting in a reduction in the size of individual grains (~ 0.15 to $0.3 \mu\text{m}$)—the so-called “rim effect” (FIG. 2). Thus, spent fuel has a complex chemistry in a very mixed phase assemblage that results from its thermal history, the neutronics, and the initial composition of the fuel.

CORROSION AND ALTERATION OF SNF IN A GEOLOGIC REPOSITORY

From the perspective of geologic disposal, spent nuclear fuel— UO_2 —is a complex, redox-sensitive, semiconducting, polycrystalline ceramic. Although the composition of the system is dominated by uranium, the geochemical mobility of a limited, but chemically very different, array of radionuclides is important (TABLE 1). These radionuclides are

heterogeneously distributed throughout the fuel assembly and occur in a variety of phases, from inert gases to relatively stable oxides. The composition of the fuel changes with time due to radioactive decay, as do the thermal and radiation fields. Most regulatory assessments of the “success” of a geologic repository depend on a calculation of the risk to humans due to the release of radionuclides that travel some kilometers from the repository over periods of hundreds of thousands of years. The science that supports such an analysis requires (1) a detailed knowledge of the fuel after it is removed from the reactor and as it evolves over time; (2) a thorough understanding of the potential release mechanisms as a function of evolving geochemical and hydrologic conditions as the thermal and radiation fields evolve; (3) an understanding of the mobility of the radionuclides in the near- and far-field environment of the geologic repository; and (4) the radiotoxicity of each radionuclide as a function of the expected pathways for exposure to a specified population.

Dissolution and Alteration of Spent Nuclear Fuel

The processes controlling the dissolution of spent nuclear fuel and the release of radionuclides, as well as their mechanisms and rates, have been the focus of extensive research efforts (Johnson and Shoesmith 1988; Oversby 1994, 1999; Shoesmith 2000; Buck et al. 2004; Johnson et al. 2005; Poinsot et al. 2005a, 2005b). As an example, the European Commission coordinated a research program—*Source Term for Performance Assessment of Spent Fuel as a Waste Form*—that involved nine institutions. The goal was to develop a fundamental understanding of the processes of dissolution and alteration of the UO_2 in spent fuel under reducing disposal conditions (Grambow et al. 2000). In the United States, the Science and Technology and International Program of the Office of Civilian Radioactive Waste in the Department of Energy has created a *Source Term Research Program* for the study of the behavior of spent nuclear fuel under oxidizing conditions (Ewing and Peters 2005).

The general approach in developing a “source-term” model for radionuclide release from spent nuclear fuel in a saturated medium involves the combination of many different processes, which can be grouped into two stages:

Instantaneous release at the time of waste package failure This is generally referred to as the Instant Release Fraction (IRF), which is the fraction of the inventory rapidly released when the metal canister is breached. The radionuclides of most interest during this rapid release are mainly the fission gases, such as Xe and Kr, and the volatile elements, such as I, Cs, and Cl, that have migrated to grain boundaries and the gap between the fuel pellet and the metal cladding. The inventory and extent of segregation of fission-product gases and volatile elements depend

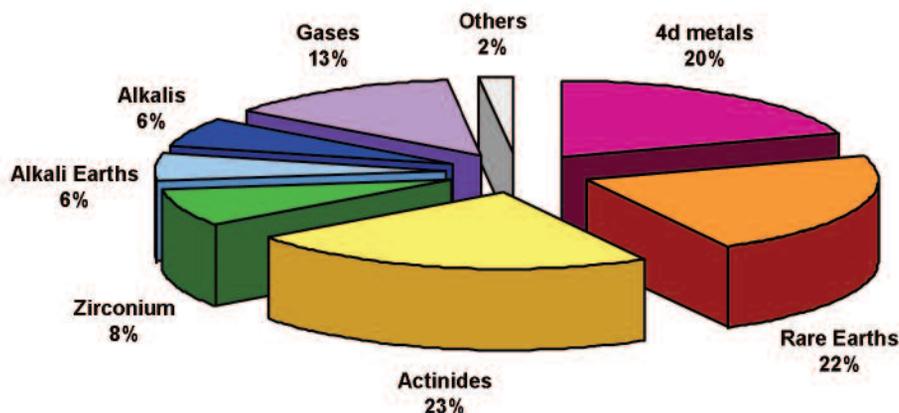


FIGURE 3 Pie diagram showing the relative proportions of the major types of fission products and transuranium elements that are found in spent fuel of moderate burn-up (Buck et al. 2004)

on the burn-up of the fuel and the temperature gradient from the center to the edge of the fuel pellet. The release fraction can vary significantly depending on the type of fuel. As an example, MOX fuel (a mixture of U and Pu) may experience much higher burn-ups along the rim of the pellet, leading to the formation of restructured Pu-rich agglomerates with much higher inventories of fission gases than at the center of the fuel pellet. Even after in-reactor diffusion and segregation of radionuclides, other processes, such as radiation-enhanced diffusion, may affect the fuel over the long periods of geologic disposal. Depending on the type of fuel, IRF estimates are either best estimates, e.g. UO_2 fuel of moderate burn-up, or bounding estimates, e.g. high burn-up UO_2 fuel and MOX fuel.

The much slower, long-term release that results from the alteration and dissolution of the fuel matrix, usually UO_2 . The important processes include (1) oxidation of the U(IV) to U(VI) and the formation of higher oxide structures on the fuel surface and at grain boundaries; (2) bulk dissolution of the UO_2 and release of radionuclides (e.g. Pu and Np) that substitute for U; (3) dissolution of segregated oxides and immiscible metallic alloys (epsilon particles) in the fuel grains; (4) the formation of secondary alteration products, such as coffinite (USiO_4) under reducing conditions or U(VI) phases, like becquerelite or uranophane under oxidizing conditions (see Burns and Klingensmith 2006). All these processes occur in a changing thermal and radiation field. One of the important effects is radiolysis, in which radiation breaks water into reactive species, such as H_2O_2 , H_2 , H_3O^+ , etc. Lastly, the chemical reactions depend on groundwater composition and flow rate. Thus, the release of radionuclides from the SNF can only be understood in the context of coupled near-field processes, which include interactions among the corrosion products of the waste package, percolating groundwater, and the surrounding rock.

As an example, the corrosion of the metal waste package will generate hydrogen that may suppress the oxidizing effects of radiolysis.

Of the two stages described above, the second is of most interest to mineralogists and geochemists, and draws on early work on the dissolution of uraninite (Grandstaff 1976; Parks and Pohl 1988). The main processes affecting and controlling the dissolution of UO_2 in spent fuel are schematically illustrated in FIGURE 4. The dissolution and alteration of spent nuclear fuel can be most simply described as a sequence of four processes:

- 1 Radiolysis of water by the alpha, beta, and gamma radiation that reaches the interface between the fuel surface and aqueous solutions. Under ambient reducing conditions, radiolysis can create oxidizing conditions at the surface of the fuel. Under oxidizing conditions, radiolysis is much less important. In the near term, some hundreds of years, the strongest radiation field is from the beta and gamma radiation. In the longer term, the main source of radiation causing radiolysis is the alpha decay of the actinides, which is the most important source of ionizing radiation after 1000 years.
- 2 Oxidants produced during radiolysis, or already present under oxidizing conditions, have a strong tendency to oxidize the surface of the nominal UO_2 to a UO_{2+x} surface oxide. The oxidizing species are taken up by the fuel surface, and additional oxygen atoms enter the UO_2 structure as interstitial oxygens; the fuel reaches a composition of UO_{2+x} , with x ranging between 0.3 and 0.4. This results in a surface that contains some U(VI).
- 3 The oxidized U(VI) at the fuel surface is then dissolved by complexing ligands present in groundwater. The initial groundwater composition may be modified by concentration during evaporation or reaction with backfill and

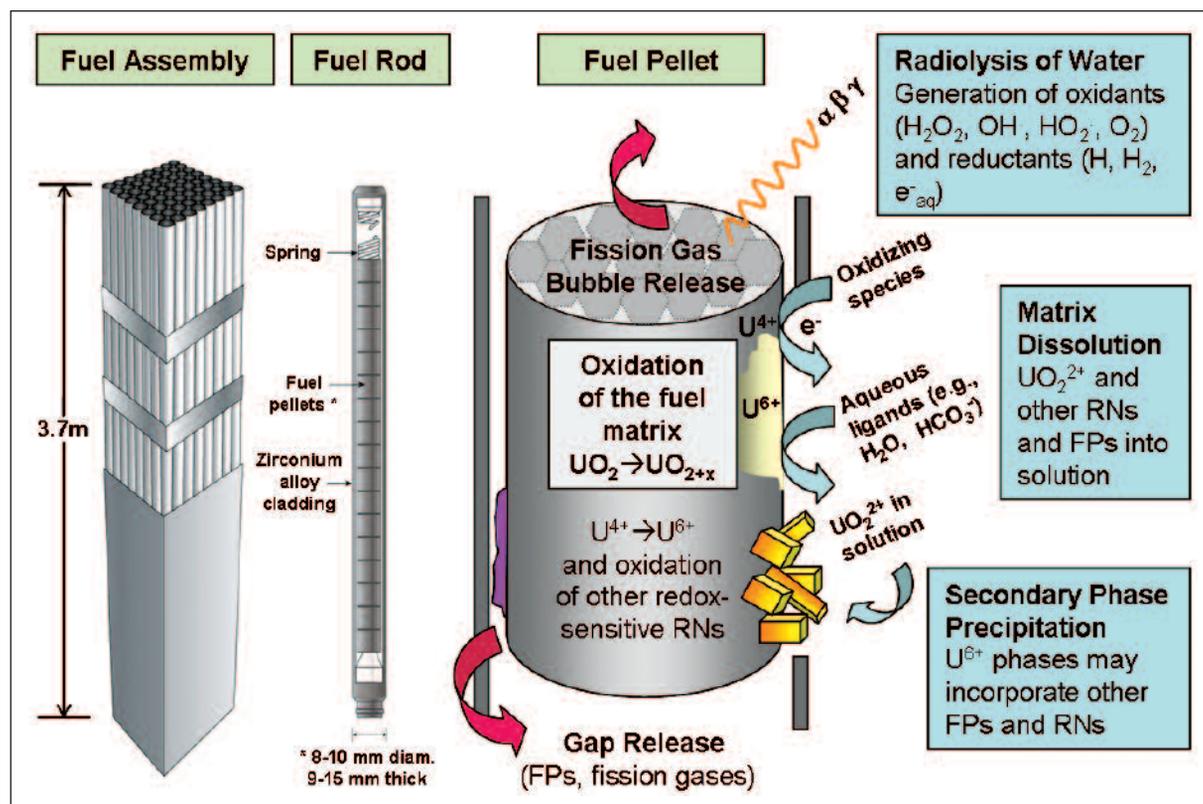


FIGURE 4 Depiction of the fundamental processes governing the alteration of spent nuclear fuel upon breaching of the fuel rod, assuming the presence of water (after Poinssot et al. 2005). The fuel

assembly is representative of one used in a typical light water reactor (adapted from <http://www.ocrwm.doe.gov>). FPs: fission products; RNs: radionuclides.

the metal waste package. Uranium (VI) has a strong tendency to form complexes in solution with oxygen-containing ligands, particularly the carbonates. The main oxygen-containing ligands in groundwaters contemplated in present geologic disposal conditions are bicarbonate (HCO_3^-) and hydroxide (OH^-).

- 4 The dissolution of U(VI) continues, resulting in the precipitation of secondary U(VI) phases under oxidizing conditions.

During the corrosion of spent nuclear fuel, there are many coupled processes. As an example, reducing species, such as hydrogen, are also produced during water radiolysis. These reducing species have a counterbalancing effect on the oxidation of the UO_2 surface. In addition, corrosion, in the absence of oxygen, of an iron canister can produce large amounts of hydrogen. There is evidence that hydrogen overpressure switches off the radiolytic processes that we have described, in which case no dissolution occurs (Carbol et al. 2005).

In Europe, the geologic disposal concepts under development are based on saturated flow below the water table under reducing conditions. The only source of oxidants would be by the radiolysis of water. Reducing conditions favor the stability of the UO_2 in the spent fuel matrix (Fig. 5). This disposal concept relies on the canister and the clay backfill to minimize contact with water. In the United States, the proposed geologic repository is in an oxidizing environment in the unsaturated zone. Thus, at Yucca Mountain, the principal barrier is not the stability of the spent nuclear fuel, but rather the limited amount of water that may come into contact with the waste package. In this case, the role of the waste package in preventing the access of water is critical to the safety assessment.

This basic difference between the various spent fuel repository concepts is graphically shown in an Eh–pH diagram for the uranium system (Fig. 5), where the “stability field” of the different repository concepts is superimposed on the stability diagram of $\text{UO}_2(\text{solid})$ in average groundwater compositions that are common to Fennoscandian granites and Yucca Mountain volcanic tuff. Very clearly, the stability of UO_2 depends on the redox conditions of the repository.

NATURE’S SPENT NUCLEAR FUEL

One of the challenges in assessing the stability of UO_2 in spent fuel and the mobility of fission products and transuranium elements released during its corrosion has been the need to make long-term predictions of their behavior. One approach has been to use natural systems, so-called “natural analogues,” to study long-term behavior in a variety of geologic settings (Bruno et al. 2002). Uraninite, UO_{2+x} , and UO_2 in spent fuel share identical structures, and their compositions are essentially the same (Janeczek et al. 1996). Under oxidizing conditions, the paragenesis of the U(VI) alteration products are also very similar (Finch and Ewing 1992; Wronkiewicz and Buck 1999). Thus, the study of natural uranium systems has provided insights into the processes and alteration products controlling the long-term behavior of spent fuel.

One exceptionally interesting uranium deposit of particular relevance to nuclear waste management is in Gabon, where at least 15 natural fission reactors have been discovered at Oklo (Gauthier-Lafaye et al. 1996, 1997; Janeczek 1999). These reactors were discovered from the depleted concentrations of ^{235}U that resulted from its consumption during the nuclear reactions (Neuilly et al. 1972). This is the only area where there is evidence of sustained nuclear reactions occurring in a natural uranium deposit. The natural reactors

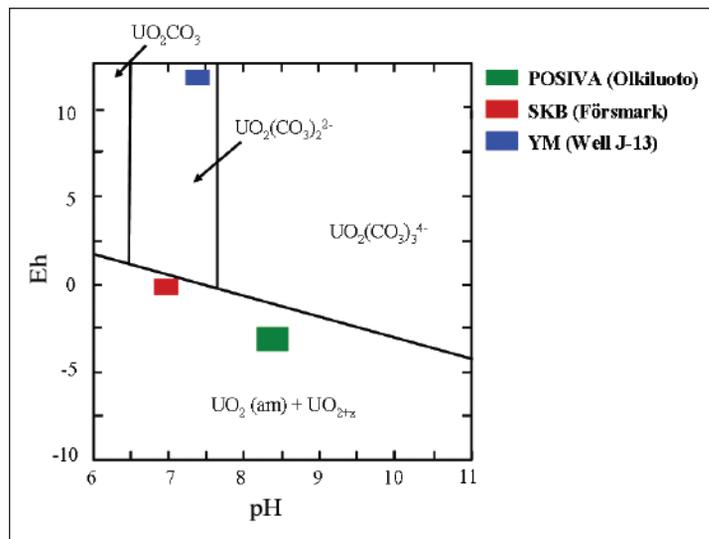


FIGURE 5 Eh–pH diagram of the uranium system. $[\text{CO}_3^{2-}]_{\text{tot}} = 10^{-3}$ M and $[\text{U}] = 10^{-8}$ M. All thermodynamic data are from the uranium NEA-TDB compilation (Grenthe et al. 1992; Guillaumont et al. 2003). The colored boxes indicate the redox and conditions for three potential repository sites: Olkiluoto, Finland; Forsmark, Sweden; Yucca Mountain, Nevada, USA (YM).

operated two billion years ago, when the concentration of ^{235}U in natural uranium ore was approximately 3.5%, typical of the concentration in the nuclear fuel of a light water reactor. Water, and in some cases carbon, served as a moderator. The fortuitous absence of neutron absorbers, such as vanadium, and the presence of neutron reflectors, such as quartz, in the surrounding sandstone enabled the nuclear reactions. The temperatures of these reactors, a few meters in dimension, were between 400 and 500°C, but at the centers of the reactors, temperatures may have reached 1000°C. Thus, small hydrothermal systems were created around each reactor zone, in which quartz was replaced by clay, the *argile de pile* (Jensen and Ewing 2001). The reactors turned themselves on and off as the moderator, water, entered the pores of the rock and then was driven from the core by the heat released during fission. Once the reactor zone cooled, water returned to the reactor, and the nuclear reactions began again. Collectively, these reactors fissioned more than ten tons of ^{235}U over several hundred thousand years. A full account of this unique phenomenon can be found in Naudet (1991).

From the perspective of the geologic disposal of spent fuel, these natural reactors have provided an exceptional opportunity to understand the conditions under which spent fuel may be preserved for billions of years and also to understand the mobility and fate of fission-product and actinide elements. As an example, ^{239}Pu was “captured” and incorporated into apatite (now evident by the enrichment of ^{235}U , the daughter decay product of ^{239}Pu , in apatite). In fact, the European Community supported a multi-year study, the Oklo Natural Analogue Project, under the leadership of the Commissariat de l’Energie Atomique (CEA) of France, to investigate aspects of these natural nuclear reactors that are relevant to the geologic disposal of spent nuclear fuel (Gauthier-Lafaye et al. 2000). One of the interesting similarities between spent nuclear fuel and uraninite from Oklo is that both contain micrometer- to nanometer-sized metal alloy inclusions (e.g. Mo, Ru, Pd, Tc, and Rh)—the epsilon phase (Fig. 6). The release of these small particles during the corrosion of the fuel enhances the mobility of ^{99}Tc . These small particles have been found incorporated in the clays surrounding the nuclear reactors (Utsunomiya

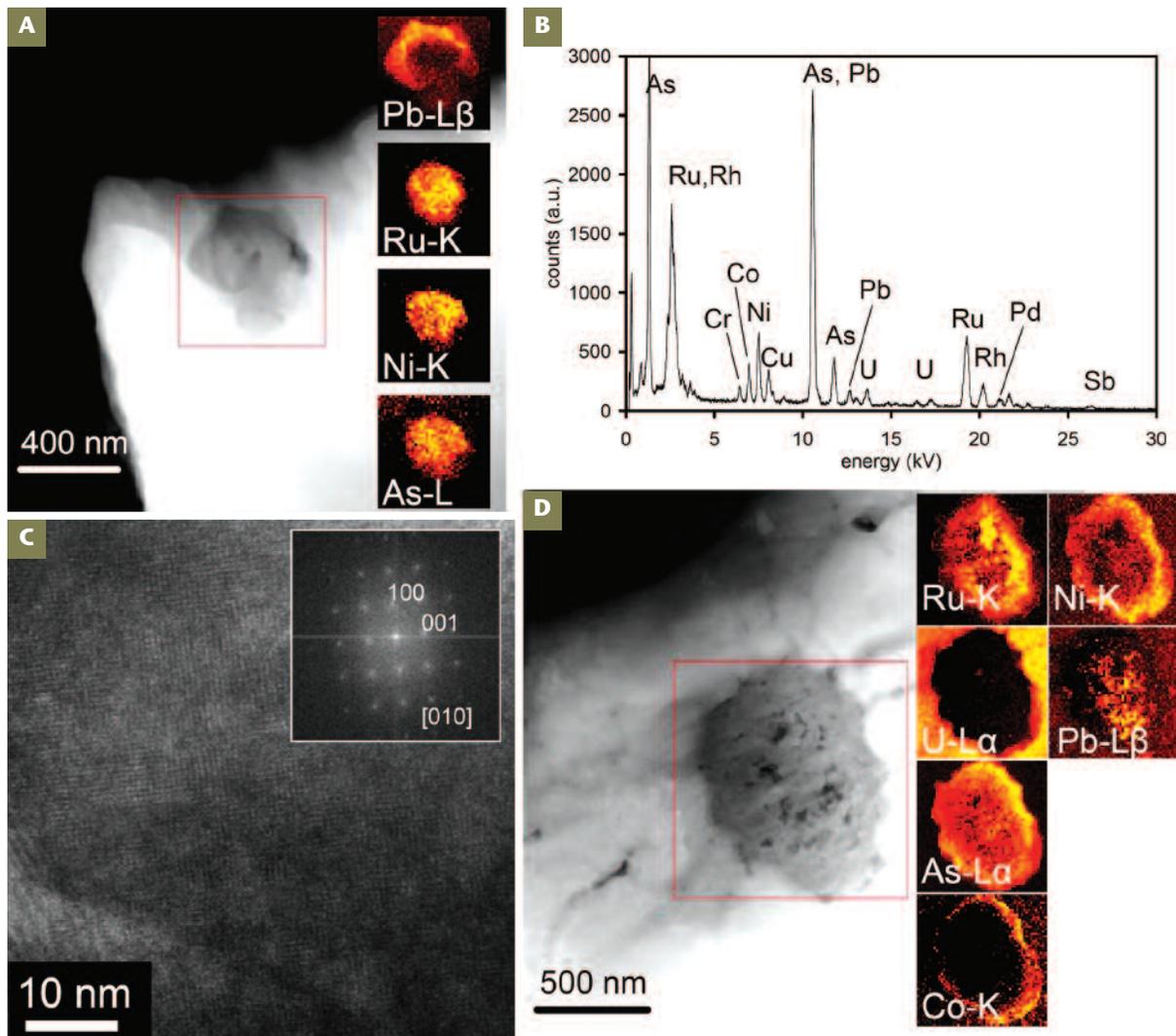


FIGURE 6 (A) Electron microscopy image (HAADF-STEM) of a Ru particle found in uraninite from the Oklo natural reactor, along with associated elemental maps of the region outlined by a square. (B) EDS profile and (C) HRTEM image of the Ru particle. (D) HAADF STEM image of the other Ru phase showing complex chemical zoning (Utsunomiya and Ewing 2006).

and Ewing 2006). Although much remains to be done with the Oklo reactors, the main patterns regarding the relative mobility of the various radionuclides at Oklo have been summarized by Janeczek (1999). Plutonium appears to have been mostly incorporated into apatite or sorbed onto the surfaces of chlorite. Rare earths are incorporated into apatite, coffinite, and REE uranyl phosphates. Cs and Sr have been mostly lost from the reactor cores. Further, the mineralogy of the secondary alteration phases is related to the groundwater composition responsible for the alteration of the primary minerals (Jensen et al. 2002). Many of the dissolution, alteration, and retardation processes relevant to the behavior of UO_2 in spent fuel have been identified and successfully modeled at Oklo, thus providing additional confidence in our understanding of the long-term behavior of spent fuel (Bruno et al. 2002).

FUTURE RESEARCH

There is already a long history of effort devoted to understanding and modeling the long-term behavior of UO_2 in spent nuclear fuel and in uranium ore deposits. Much of this work was initiated in the 1950s, when uranium resources were exploited for the first generation of nuclear power reactors. However, the past decade has seen a “renaissance” in research on the geochemistry of uranium (Burns and Finch 1999); the structure of secondary U(VI) phases (Burns 2005); the thermodynamic stability of these phases (Chen et al. 1999; Kubatko et al. 2003), and the processes by which they dissolve (Schindler et al. 2005, 2006), precipitate (Schindler and Hawthorne 2004), and incorporate actinides and fission products (Burns and Klingensmith 2006)—to name a few. These studies by mineralogists and geochemists find direct application in the safe disposal of spent nuclear fuel. However, important areas of research remain:

- What is the effect of radiolysis at the interface between water and UO_2 ?
- What are the mechanisms and limits to the incorporation of radionuclides, such as Np and Pu, into uranium alteration phases?
- What is the effect of alpha decay on the crystalline structure of secondary U(VI) phases?

- What is the relation between the thermodynamic stability and structure of U(VI) phases?
- What is the relation between the burn-up of the fuel and its detailed “mineralogy”?

All of these questions can be repeated as we look beyond uranium to the crystal-chemistry and geochemistry of the transuranium elements, such as plutonium and neptunium. The journey has just begun.

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ACKNOWLEDGMENTS

We thank David Sassani, Christophe Poinssot, and Ron Fleming for reviews of an early version of this manuscript. Frannie Skomurski reviewed the final version of this paper and created a number of the figures. We thank Allan Hedin for allowing us to reproduce FIGURE 1 and Edgar Buck for FIGURES 2 and 3. ■