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Corrosion of Spent Nuclear Fuel: The Long-Term Assessment

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Research Objectives

This research program is a broadly based effort to understand the long-term behavior of spent nuclear fuel (SNF) and its alteration products in a geologic repository.

We have established by experiments and field studies that natural uraninite, UO_{2+x} , and its alteration products are excellent "natural analogues" for the study of the corrosion of UO_2 in SNF. This on-going research program has addressed the following major 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?
3. What is the radionuclide 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 or Geochemist's Workbench) that are used in performance assessments? Can these codes be tested by studies of natural analogue sites (e.g., Oklo, Cigar Lake or Pena Blanca).**

Research Progress & Implications

Thermodynamic Prediction of Observed U^{6+} Phases. Analyses have shown that Blind Prediction Modelling (BPM) fails to predict the reported U^{6+} mineralogy in the weathering horizon of the 2 Ga old supergene-weathered Oklo-Okélobondo and Bangombé U-deposits and their natural fission chain reactors (Salah 2000; Jensen et al., 2002). The major problems appeared to be: 1) the lack of thermodynamic data on key uranyl phases and 2) that important species, such as SO_4^{2-} and PO_4^{3-} were not always included in the modelling. We have developed an empirical model that provides for the calculation of this much-needed thermodynamic data (Clark et al., 1998; Chen et al., 1999a). Using a method that sums the polyhedral contributions for the structural components, the thermodynamic parameters for key uranyl phases have been calculated. Based on this updated data, Eh-pH diagrams predict that coffinite and $U(HPO_4)_2 \cdot 2H_2O$ are stable U^{4+} phases under reducing conditions, and uranopilite, torbernite and bassetite will become stable as conditions become oxidizing. These phases are in accord with mineralogical observations. Previous BPM often omitted P and S and hence failed to predict the uranyl minerals observed at Bangombé. These new modelling results stress the importance of SO_4^{2-} and PO_4^{3-} resulting from dissolution of accessory apatite, monazite and sulphides in the retardation of U owing to the formation of uranyl sulphates and phosphates. This is a very specific example of the use of a natural analogue site to test conceptual models used in a performance assessment. These results have been published in *Radiochimica Acta* 90, 761-769 (2002).

In Situ Isotopic Analysis & High-Resolution Transmission Electron Microscopy (HRTEM) of UO_2 :

One of the challenges in using natural uranium deposits, such as the Cigar Lake Deposit in Canada or the Oklo natural reactors in Gabon, as analogues for the long-term behavior of spent nuclear fuel has been the need to understand their complicated history of repeated alteration and criticality events (in the case of Oklo). In collaboration with Mostafa Fayek (now at Oak Ridge National Laboratory) we have used highly accurate *in situ* isotopic analyses by secondary ionization mass spectrometry (SIMS) to make measurements of the complexly intergrown uranium minerals and their alteration products. The first study was of the uranium minerals at the Cigar Lake Deposit of the Athabasca Basin in Canada. By a combination of SIMS and HRTEM, we were able to demonstrate that the nanoscale formation of alteration products, such as coffinite ($USiO_4$) and calciouranoite ($CaU_2O_7 \cdot 5H_2O$), has a profound and misleading effect on the results of conventional fluorination analyses. Using our nanoscale techniques, we were able to clearly identify 3 stages of alteration in the Cigar Lake uraninites (Fayek et al, 2002). We have extended this approach to studies of the Oklo-Okélobondo natural fission reactors in Gabon (Fayek et al., 2002). In this case, we were able to determine the timing of separate criticality events and subsequent alteration events. Most importantly, we have been able to determine by isotopic analysis that the reactor zones nearest the surface have reacted more extensively with groundwaters of meteoric origin. We have now combined the high-resolution SIMS analysis with advanced microscopy techniques, such as high-angle annular dark-field imaging scanning transmission electron microscopy (HAADF-STEM) to put together a detailed description of the alteration processes of uraninite in the reactor cores at Oklo and Bangombé (Fayek et al. submitted). This work will be continued as part of the Ph.D. research of Chris Palenik. Chris will spend the summer at Oak Ridge National Laboratory collecting additional data on uraninites from natural analogue localities.

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, making ^{99}Tc a prominent contributor to dose in safety assessments of nuclear waste repositories. Under Eh-pH conditions corresponding to the oxidative corrosion of SNF, which is constrained by the stability of uranyl phases relative to that of the UO_{2+x} phase, TcO_4^- is the predominant species of technetium with $\log [TcO_4^-]/[TcO(OH)_2^0] > 2.15$ over the range of pH = 4 – 10. The low solubility of $TcO_2 \cdot H_2O$ and high adsorption of Tc^{4+} by geological materials (e.g. clays), results in a groundwater concentration of Tc^{4+} of less than 10^{-8} M (Chen et al., 1999c). This implies that the incorporation of Tc^{4+} into alteration uranyl phases is not an important retardation mechanism. In contrast, TcO_4^- is highly soluble and weakly adsorbed in the near-field. Thus, the incorporation of Tc^{7+} into the structure of oxidized uranyl phases that might be expected to occur as an alteration product of SNF will actually result in under-bonding at the U^{6+} site,

destabilize the structure. This suggests 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 UO_2 in SNF. Uraninite, schoepite, calciouranoite, uranophane, fourmarierite, a Fe-rich uranyl phase, and coffinite were identified. The primary uraninite and alteration phases generally have low trace element contents, with the exception of coffinite from Caribou Mine, Colorado. The trace element content of uraninite (Zr, Ti, Th and REEs) were in general, lower than the values measured in secondary uranyl phases, suggesting that trace elements are preferentially incorporated into the structures of the secondary uranyl phases. A compositional profile of a concentric structure in schoepite shows that alteration results in a loss of U, Pb and Zr and the incorporation of Si, Ti, Ca and P. 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* (Zhao and Ewing, 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 $^{238}\text{U}(\alpha, \gamma)^{234}\text{Th} \rightarrow ^{234}\text{Pa}(\beta, \gamma)^{234}\text{U}$ and $^{235}\text{U}(\alpha, \gamma)^{235}\text{Np} \rightarrow ^{235}\text{Pu}(\alpha, \gamma)^{239}\text{Pu}$) 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 ($\pm$ Pb, Co, and Ni), such as ruthenarsenite and ruarsite. This work was published in the *Bulletin of the Geological Society of America* (Jensen and Ewing, 2001).

Information Access

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