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Incorporation of Radionuclides in the Alteration Phases of Spent Nuclear Fuel

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Abstract

Alteration may be expected for spent nuclear fuel exposed to groundwater under oxidizing conditions such as that which exist at the proposed nuclear waste repository at Yucca Mountain, Nevada. The actinide elements released during the corrosion of spent fuel may be incorporated into the structures of secondary U^{6+} phases. The incorporation of transuranics into the crystal structures of the alteration products may significantly decrease their mobility. A series of precipitation tests were conducted at 90°C to determine the potential incorporation of Ce^{4+} and Nd^{3+} (surrogates for Pu^{4+} and Am^{3+}, respectively) into uranyl phase. Dehydrated schoepite ($UO_3 \cdot 0.8\text{-}1.0H_2O$) was produced by hydrolysis of a uranium oxyacetate solution containing either cerium or neodymium. ICP-MS analysis of the leachant, leachate, and solid phase reaction products which were dissolved in a HNO_3 solution indicates that 26 ppm of Ce was incorporated into dehydrated schoepite. ICP-MS results from the Nd-doped tests indicate significant

neodymium incorporation as well, however, the heterogeneous distribution of Nd in the solid phase noted during the AEM/EELS examination implies that neodymium may not incorporate into the structure of dehydrated schoepite.

Introduction

The oxidation and dissolution of spent nuclear fuel from commercial power reactors represents the largest potential source of radionuclide release from high-level nuclear waste forms in a repository because of the large volumes of spent fuel that need to be disposed of and high concentrations of radioactive isotopes [1]. Consequently, the radionuclide release estimate in the event of the breaching of the spent fuel container is a critical parameter that will need to be determined before the performance of a nuclear waste repository containing spent fuel can be assessed.

Commercial spent nuclear fuel is composed of ≥ 95 wt% UO_2. The remaining 5 wt% or less of the commercial spent nuclear fuel is made up of transuranic elements (e.g., Np, Pu, Am, Cm) and fission products (e.g., Sr, Cs, Tc, I, Mo, Se) that have formed during nuclear power operations [2]. Alteration of spent nuclear fuel may be expected under unsaturated moist oxidizing conditions such as those which exist at the proposed nuclear waste repository at Yucca Mountain, Nevada [3]. Experimental studies examining the alteration of UO_2 and spent nuclear fuel under such conditions have shown that the alteration products are primarily uranyl (U^{6+}) phases [2,4]. Recent results of experiments on the oxidative dissolution of spent fuel indicate actinides such as Np, and fission products such as ^{137}Cs and ^{90}Sr, are being incorporated into the alteration products [5,6].

Thus, the oxidized alteration products may play an important role in limiting the release of radionuclides from the spent fuel waste package [2,7].

The radioactivity and toxicity of long-lived actinide elements contained in spent fuel is a cause for concern if they are released into the environment. Under oxidizing conditions the ions of environmental concern may include $U^{4+,6+}$, $Np^{4+,5+}$, $Pu^{3+,4+,5+,6+}$, Am^{3+}, and Cm^{3+}. Transport of these nuclides in solution will be the principal mechanism of release from the spent fuel [8].

The actinides contained in the spent fuel (U, Np, Pu, Am, and Cm) will be released during the oxidation and dissolution of the UO_2 matrix, and their mobility may be influenced by their ability to be incorporated into the structures of U^{6+} alteration phases. The relatively low concentrations of the transuranic elements in spent fuel will preclude the formation of separate, pure phases [7]. The incorporation of relatively small quantities of the actinide elements into the uranyl phases may therefore impact upon their mobility. The objective of this paper is to characterize the incorporation of Pu^{4+} and Am^{3+} into uranium alteration products by synthesizing uranyl phase doped with Ce^{4+} and Nd^{3+} (appropriate surrogate elements for Pu^{4+} and Am^{3+}, respectively). Results from this study may provide a useful tool for estimating a realistic release rate for radionuclides from the repository's near-field environment.

Experimental

It is known that the crystal chemistry of Pu^{4+} and Am^{3+} may be similar to Ce^{4+} and Nd^{3+}, respectively, because of the similarity of their ionic radii ($^{[9]}Pu^{4+}$:0.93 Å, Ce^{4+}:0.94 Å; Am^{3+}:1.07 Å, Nd^{3+}:1.04 Å) and electron configurations. Thus, Ce^{4+} and Nd^{3+} may be used as appropriate surrogate elements for Pu^{4+} and Am^{3+}, respectively in order to facilitate the ease of handling of the samples in this testing program. Elevated temperatures, 90°C, are used in this study to accelerate reactions and simulate the realistic temperature of first potential water contact with a waste form in the proposed Yucca Mountain repository.

In corrosion experiments of UO_2 with groundwater, dehydrated schoepite ($UO_3 \cdot 0.8\text{-}1.0H_2O$) was one of the first phases to form [2,4]. Dehydrated schoepite was produced in the present study by dissolving uranium oxyacetate ($UO_2(CH_3COO)_2 \cdot 2H_2O$) into a solution containing either Ce^{4+} or Nd^{3+}. Solutions were produced by dissolving 0.42 g uranium oxyacetate into a 20 ml solution containing either 2.1 ppm cerium or 286 ppm neodymium. The pH of the resulting leachant solution was 4.0. The solution was transferred into Savillex Teflon vessels (Model 561R2). The vessels were heated at 90°C in Lindberg/Blue M mechanical convection ovens with a temperature uniformity of ±2°C. Tests were conducted for intervals of 7, 35, and 190 days. After the prescribed test interval, the vessels were cooled to room temperature. The fluid was filtered through a Nalgene 0.45 μm syringe filter to be analyzed by ICP-MS. The solid products that formed were rinsed three times with deionized water and then air-dried.

An analysis of the leachant, leachate, and solid phase reaction products (after dissolution in a nitric acid solution) was performed by a Perkin-Elmer ELAN-5000 inductively coupled plasma (Ar-plasma)-mass spectrometer (ICP-MS). A selected portion of the solid phase reaction products were also transferred onto aluminum mounts and coated with carbon using a Denton DV-515 evaporator. The samples were examined in a JEOL T330A scanning electron microscope (SEM) operated at 15 kV with a tungsten filament. The SEM is equipped with an energy dispersive X-ray spectrometer (EDS). Selected particles of the reaction products were also crushed into thin particles. The resultant electron-transparent thin-sections of the particles were transferred to holey carbon-coated copper grids and examined in a JEOL 2000 FX II analytical transmission electron microscope (AEM) operated at 100 kV with a LaB_6 filament. The AEM is equipped with a Gatan 666 parallel electron energy-loss spectrometer (EELS), which has an energy resolution of about 1.6-1.8 eV. Electron diffraction patterns were taken with a charge-coupled device (CCD) camera which permits very low intensity viewing and, therefore, is ideal for electron beam-sensitive materials such as the uranyl phases formed in this study. In order to simulate the electron diffraction patterns with a computer utilizing a Desktop Microscopist software, crystallographic data were collected from the inorganic crystal structure database produced jointly by Gmelin-Institut für Anorganische Chemie and Fachinformationszentrum FIZ Karlsruhe.

Results and Discussion

Examination of the solid phase reaction products with SEM demonstrated the presence of characteristic boat-shaped crystals of dehydrated schoepite (Fig. 1). In Figure 1a and b, it is important to note that the crystals progressively become coarser over time. With SEM/EDS it was not possible to detect any elements in the dehydrated schoepite other than uranium and oxygen.

The AEM image of the uranyl phase also shows the characteristic morphology of dehydrated schoepite (Fig. 2a). The presence of dehydrated schoepite was confirmed with electron diffraction in the AEM (Fig. 2b). The computer simulations of dehydrated schoepite agreed with the experimentally obtained CCD electron diffraction pattern from the uranyl oxide phase shown in Figure 2b.

EELS was performed on particles that were sufficiently thin. However, the cerium concentration in subsequently formed dehydrated schoepite was below the detection limit of the AEM/EELS technique. ICP-MS results indicate a Ce concentration that decreased from 26, to 20, and finally 11 ppm for crystals produced in 7, 35, and 190 day tests, respectively. This pattern suggests a lowering of the potential for cerium substitution in dehydrated schoepite as the crystals progressively become coarser over time. ICP-MS results indicate an overall composition of 1240 ppm neodymium in the seven-day test, and 920 ppm after 35 days. However, a heterogeneous distribution of Nd was noted during the AEM/EELS examination of these samples (Fig. 3). This evidence suggests that a separate Nd-rich solid phase must have precipitated. Its formation may result from a high concentration of neodymium (286 ppm) in the test matrix.

One of the earliest alteration products to form when UO_2 corrodes in contact with oxygen-rich groundwater is dehydrated schoepite ($UO_3 \cdot 0.8\text{-}1.0H_2O$) [2,4], and its structure consists of sheets of uranyl polyhedra. In this structure, the high-valence cations are restricted to the sheets of polyhedra, and the sheets are connected through hydrogen bonds [7,9]. The incorporation of Ce^{4+} into this structure is likely to occur by substituting for U^{6+} within the polyhedra sheet, assuming that appropriate charge-balancing substitutions occur. One possible substitution is $OH^- \leftrightarrow O^{2-}$. Therefore, the suggested coupled substitution will be $Ce^{4+} + 2OH^- \leftrightarrow U^{6+} + 2O^{2-}$. The Nd^{3+} may not substitute for U^{6+} in the crystal structure of dehydrated schoepite due to the larger disparity of charge and ionic radius ($^{[9]}U^{6+}$:0.80 Å, Nd^{3+}:1.04 Å; Ce^{4+}:0.94 Å).

Conclusions

This paper presents some preliminary results from a study of potential incorporation of transuranics into uranium alteration phases.

1. Ce^{4+} (surrogate for Pu^{4+}) substitutes for U^{6+} in the structure of dehydrated schoepite, together with local charge-balancing substitutions.
2. Concentration of Ce^{4+} decreased from 26 to 11 ppm as crystal grain sizes increased with reaction time.
3. Substitution of Nd^{3+} (surrogate for Am^{3+}) for U^{6+} in the structure of dehydrated schoepite was not detected. A separate Nd^{3+} phase appears to have formed.

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