

POTENTIAL INCORPORATION OF TRANSURANICS INTO URANIUM PHASES

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ABSTRACT

The UO_2 in spent nuclear fuel is unstable under moist oxidizing conditions and will be altered to uranyl oxide hydrate phases. The transuranics released during the corrosion of spent fuel may also be incorporated into the structures of secondary U^{6+} phases. The incorporation of radionuclides into alteration products will affect their mobility. A series of precipitation tests were conducted at either 150 or 90°C for seven days to determine the potential incorporation of Ce^{4+} and Nd^{3+} (surrogates for Pu^{4+} and Am^{3+} , respectively) into uranium phases. Ianthinite ($[\text{U}_2^{4+}(\text{UO}_2)_4\text{O}_6(\text{OH})_4(\text{H}_2\text{O})_4](\text{H}_2\text{O})_5$) was produced by dissolving uranium oxyacetate in a solution containing copper acetate monohydrate as a reductant. The leachant used in these tests were doped with either 2.1 ppm cerium or 399 ppm neodymium. Inductively coupled plasma-mass spectrometer (ICP-MS) analysis of the solid phase reaction products which were dissolved in a HNO_3 solution indicates that about 306 ppm Ce ($K_d=146$) was incorporated into ianthinite, while neodymium contents were much higher, being approximately 24,800 ppm ($K_d=62$). Solid phase examinations using an analytical transmission electron microscope/electron energy-loss spectrometer (AEM/EELS) indicate a uniform distribution of Nd, while Ce contents were below detection. Becquerelite ($\text{Ca}[(\text{UO}_2)_6\text{O}_4(\text{OH})_6] \cdot 8\text{H}_2\text{O}$) was produced by dissolving uranium oxyacetate in a solution containing calcium acetate. The leachant in these tests was doped with either 2.1 ppm cerium or 277 ppm neodymium. ICP-MS results indicate that about 33 ppm Ce ($K_d=16$) was incorporated into becquerelite, while neodymium contents were higher, being approximately 1,300 ppm ($K_d=5$). Homogeneous distribution of Nd in the solid phase was noted during AEM/EELS examination, and Ce contents were also below detection.

INTRODUCTION

The UO_2 in spent nuclear fuel is unstable under moist oxidizing conditions such as those which are expected to exist at the proposed nuclear waste repository at Yucca Mountain, Nevada. Laboratory studies examining the alteration of UO_2 and spent nuclear fuel under such conditions have shown that the alteration products are primarily uranyl (UO_2^{2+}) phases [1-3]. Spent nuclear fuel typically contains 95 to 99% UO_2 , up to 1% Pu, and up to 4% other actinides (e.g., Np, Am, Cm) and fission products (e.g., Sr, Cs, Tc, I, Mo, Se) [4]. The radioactivity and toxicity of long-lived actinide elements is a cause for concern if they are released into the environment. The actinides contained in the spent fuel (U, Np, Pu, Am, and Cm) may be released during the oxidation and dissolution of the UO_2 matrix. Migration of these elements may be retarded by their incorporation into the structures of uranium phases. Results of experiments on the corrosion of spent fuel indicate that actinides such as Np, and fission products such as Cs, Sr, and Mo are being incorporated into the alteration products [3,5,6].

The crystal chemistry of Ce^{4+} and Nd^{3+} may be similar to Pu^{4+} and Am^{3+} , respectively, because of the similarity of valence charges and their ionic radii (Ce^{4+} , 0.94 Å; Pu^{4+} , 0.93 Å;

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Nd^{3+} , 1.04 Å; Am^{3+} , 1.07 Å [7]). Thus, Ce^{4+} and Nd^{3+} may be used as appropriate surrogate elements for Pu^{4+} and Am^{3+} , respectively. Kim et al. [8] have experimentally examined the potential for actinide substitution in dehydrated schoepite by using Ce^{4+} as a surrogate for Pu^{4+} . Results indicate a Ce concentration of approximately 25 to 10 ppm, with the concentration in the solid progressively decreasing with increasing reaction time and crystal size. Ianthinite is of interest with respect to potential transuranic element retention due to the presence of both U^{4+} and U^{6+} ions into its structure. The structure of ianthinite will accommodate considerable amounts of Pu^{4+} . In corrosion experiments of UO_2 with groundwater, becquerelite is a common alteration product, and it is one of the early phases to form [1,2]. The purpose of this study is to characterize the potential for the incorporation of Pu^{4+} and Am^{3+} into uranium phases by synthesizing ianthinite ($[\text{U}_2^{4+}(\text{UO}_2)_4\text{O}_6(\text{OH})_4(\text{H}_2\text{O})_4](\text{H}_2\text{O})_5$) and becquerelite ($\text{Ca}[(\text{UO}_2)_6\text{O}_4(\text{OH})_6] \cdot 8\text{H}_2\text{O}$) doped with Ce^{4+} and Nd^{3+} . Results from this study may provide useful data for estimating realistic release rates for radionuclides from near-field environments within the repository.

EXPERIMENTAL

Ianthinite was produced in this study by dissolving uranium oxyacetate ($\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and copper acetate monohydrate ($\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$) as a reductant into a solution containing either Ce^{4+} or Nd^{3+} . Solutions were produced by dissolving 0.32 grams of uranium oxyacetate and 0.08 grams of Cu acetate monohydrate into a 15 ml solution containing either 2.1 ppm cerium or 399 ppm neodymium. The pH of the resulting leachant was 3.3. The solution was transferred into Teflon-lined Parr reaction bombs (Model 4749). The bombs were heated at 150°C in Lindberg/Blue M mechanical convection ovens with a temperature uniformity of $\pm 2^\circ\text{C}$. Copper acetate, at 140°C, decomposes to Cu^{2+} and Cu^+ , the latter which plays a role as a reducing agent for uranium [9]. After seven days, the reaction bombs were cooled to room temperature. The precipitates consisted of fine purple crystals of ianthinite, small crystals of cuprite (Cu_2O) and tenorite (CuO). The crystals that formed were rinsed three times with deionized water and then air-dried.

Becquerelite was produced in the present study by dissolving uranium oxyacetate and calcium acetate ($(\text{CH}_3\text{COO})_2\text{Ca} \cdot \text{H}_2\text{O}$) in a solution containing either Ce^{4+} or Nd^{3+} . Solutions were produced by dissolving 0.42 grams of uranium oxyacetate and 0.35 grams of Ca acetate into a 20 ml solution containing either 2.1 ppm cerium or 277 ppm neodymium. The pH of the resulting leachant was 5.1. Test solutions were maintained in Savillex Teflon vessels (Model 561R2) that were heated to $90 \pm 2^\circ\text{C}$ for seven days. After cooling to room temperature, the precipitates consisted of fine platy yellow crystals of becquerelite. The solid phase reaction products that formed were rinsed three times with deionized water and then air-dried.

An analysis of the 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). Duplicate ICP-MS scans demonstrated that the average percent deviations were 0.5 and 6.7 for the Ce and Nd analysis, respectively. An analysis of standard solutions also indicated that the accuracy values for the Ce and Nd analysis were within $\pm 5\%$ or better. A selected portion of the solid phase reaction products were also transferred onto aluminum mounts, coated with carbon, and examined in a JEOL T330A scanning electron microscope (SEM) operated at 15 kV. 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 200 kV with a LaB₆ 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 uranium phases formed in this study.

Crystallographic data were also collected from the inorganic crystal structure database produced jointly by Gmelin-Institut für Anorganische Chemie and Fachinformationszentrum FIZ Karlsruhe, so that electron diffraction patterns could be simulated with a computer utilizing Desktop Microscopist software.

RESULTS AND DISCUSSION

Ianthinite

SEM examination of the solid phase reaction products demonstrated the presence of characteristic crystals of ianthinite (Fig. 1a). The figure 1b shows an AEM image of the ianthinite particles. The computer simulations of ianthinite partially matched with the experimentally obtained CCD electron diffraction pattern from the uranium phase shown in the inset of figure 1b, but extra diffraction patterns appeared suggesting the presence of an additional phase. There are several factors that may contribute to the pattern-matching difficulties. These particles were noted to slowly and progressively change from the purple color of ianthinite to a yellowish color more characteristic of dehydrated schoepite following their removal from the test solutions. The sample that was examined by AEM may therefore have been partially to a schoepite type phase. In addition to oxidation, dehydration in the vacuum chamber during analysis could lead to structural rearrangement [10]. Finally, there is limited information on atomic parameters of ianthinite for the computer simulations.

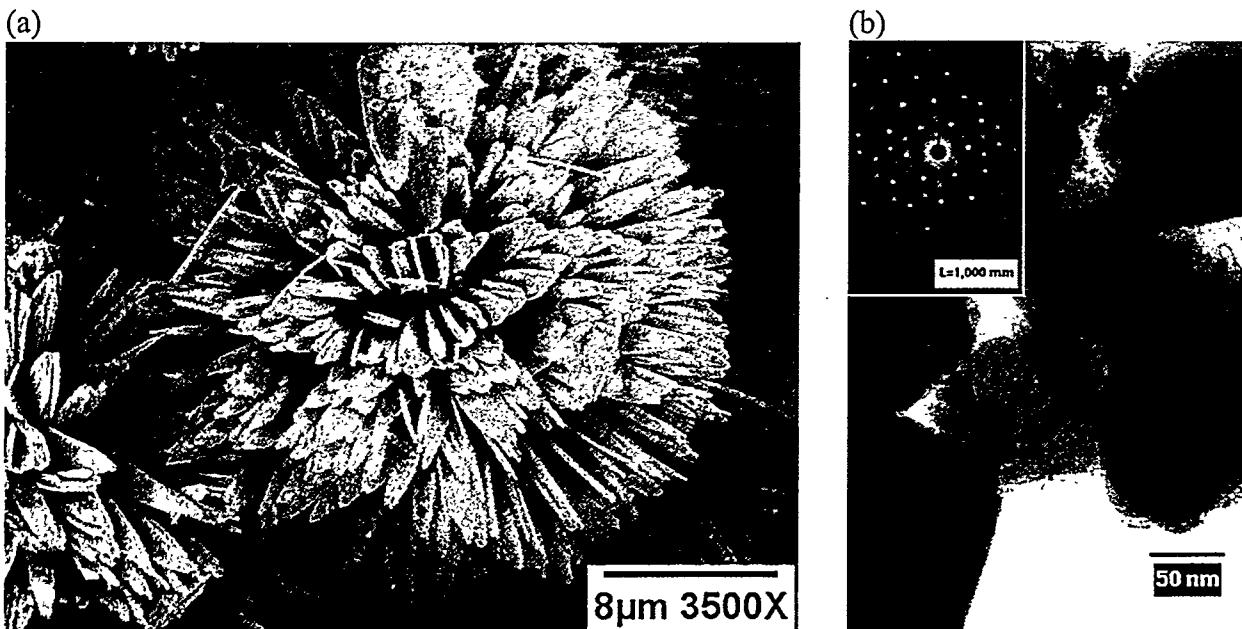


Figure 1. (a) SEM micrographs of ianthinite crystals. (b) AEM bright field image of ianthinite particles. Inset: Selected area electron diffraction pattern from ianthinite.

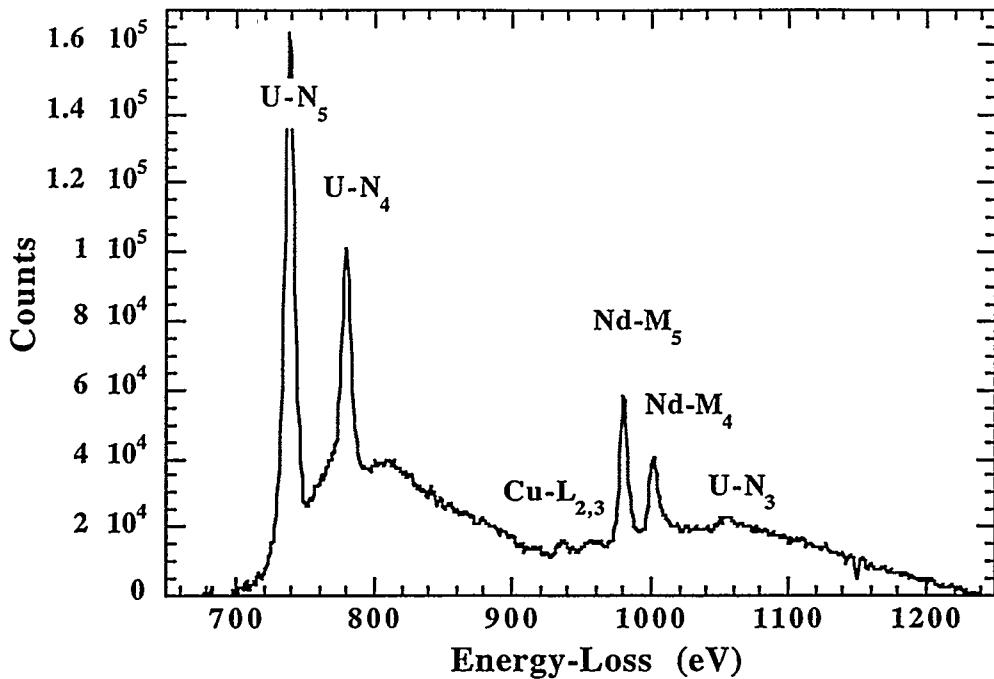
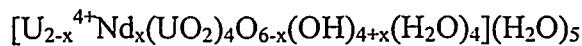
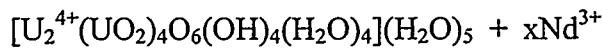


Figure 2. Electron energy-loss spectrum of Nd-bearing ianthinite. $M_{4,5}$ edges of Nd are clearly visible.

EELS analysis was performed on particles that were sufficiently thin for microanalysis. The cerium concentration in ianthinite was below the limit of detection for the AEM/EELS technique. The ICP-MS results from dissolved solids indicate that about 306 ppm Ce was present in the ianthinite, while neodymium contents were much higher, being approximately 24,800 ppm. Neodymium was also detected during the AEM/EELS examination of these samples (Fig. 2). The peak ratio of Nd/O was homogeneous (0.015 to 0.020) throughout the samples suggesting that Nd was uniformly distributed in the structure of ianthinite.

The structure of ianthinite ($[U_2^{4+}(UO_2)_4O_6(OH)_4(H_2O)_4](H_2O)_5$) consists of sheets of uranyl and uranus polyhedra connected through hydrogen bonds to interlayer H_2O groups [11]. The incorporation of Ce^{4+} into this structure is likely to occur by direct substitution for U^{4+} within the polyhedra sheet due to the similarity of valence charges and their ionic radii (Ce^{4+} , 0.94 Å; U^{4+} , 0.97 Å [7]). However, the incorporation of Nd^{3+} needs an appropriate charge-balancing substitution (Nd^{3+} , 1.04 Å; U^{4+} , 0.97 Å [7]). One possible substitution mechanism involves $OH^- \leftrightarrow O^{2-}$ [12], with the suggested charge-coupled substitution being $Nd^{3+} + OH^- \leftrightarrow U^{4+} + O^{2-}$. Therefore, structural formula of the Nd-bearing ianthinite is as follows:



where x is 0.04 in this study

Becquerelite

Examination of the solid phase reaction products with SEM indicates the presence of characteristic platy crystals of becquerelite (Fig. 3). With SEM/EDS it was not possible to detect any elements in the becquerelite other than uranium, calcium, and oxygen. The AEM image of the uranyl phase also shows the characteristic platy morphology of becquerelite (Fig. 4a). The presence of becquerelite was confirmed by electron diffraction analysis (Fig. 4b). The computer simulations of becquerelite agreed with the experimentally obtained CCD electron diffraction pattern from the uranyl phase shown in Figure 4b.



Figure 3. SEM micrographs of becquerelite crystals.

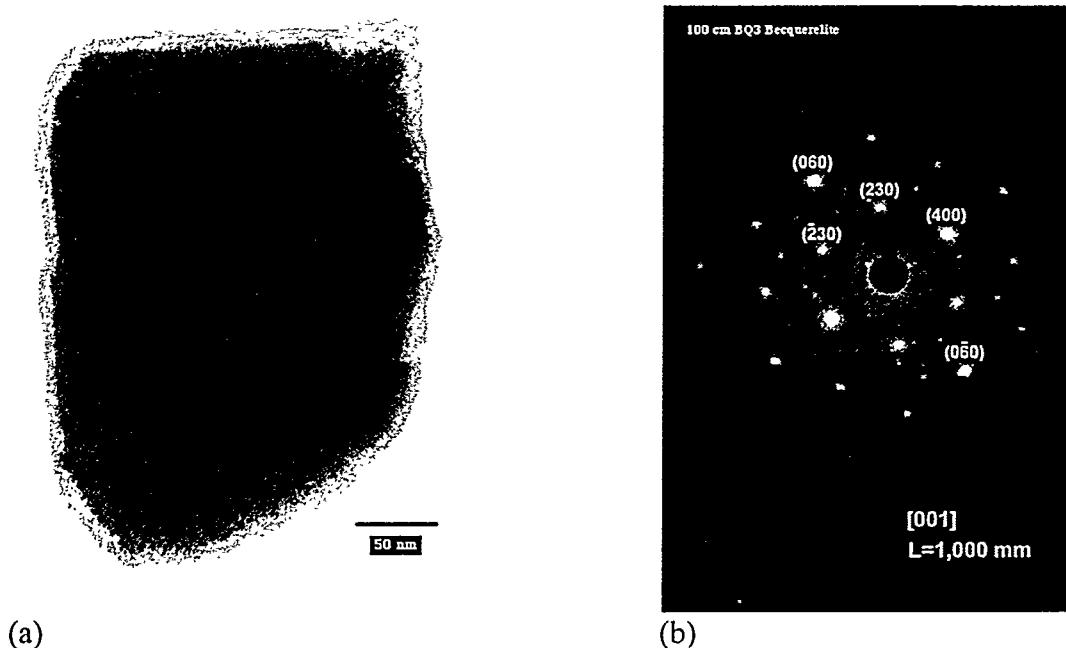


Figure 4. (a) AEM bright field image of becquerelite particle. (b) Selected area electron diffraction pattern from becquerelite.

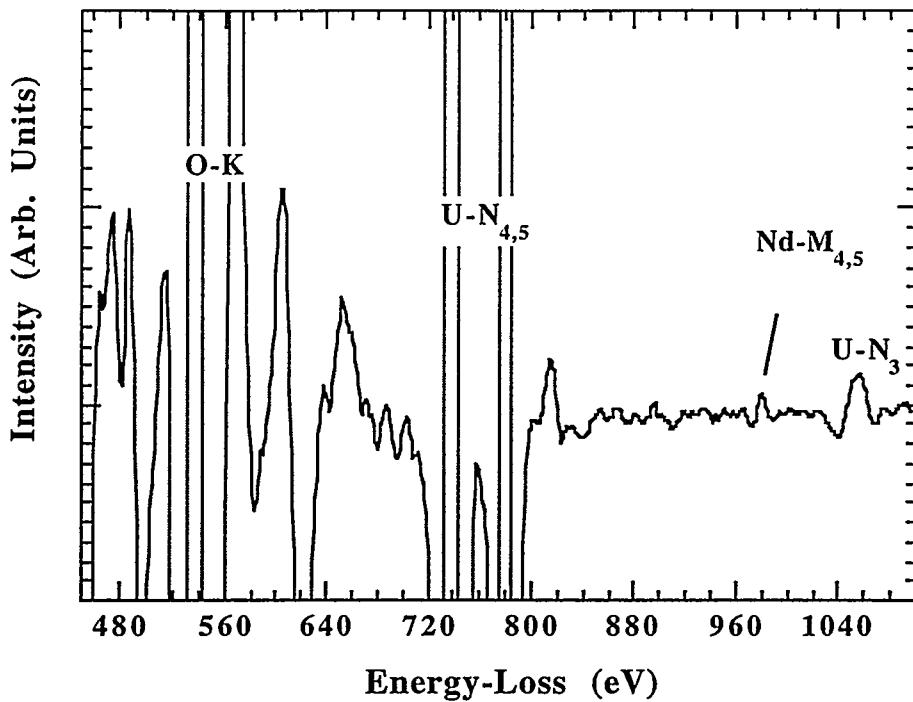


Figure 5. Electron energy-loss spectrum of Nd-bearing becquerelite. The vertical scale intensity has been increased 50x for easier viewing of the Nd peak located at 980 eV.

EELS analysis was performed on becquerelite particles that were sufficiently thin for microanalysis. The cerium concentration in becquerelite was also below the limit of detection for the AEM/EELS technique. A uniform distribution of Nd was noted during the AEM/EELS examination of these samples (Fig. 5). The ICP-MS results from dissolved solids indicate that about 33 ppm Ce was present in the becquerelite, while neodymium contents were much higher, being approximately 1,300 ppm.

The structure of becquerelite ($\text{Ca}[(\text{UO}_2)_6\text{O}_4(\text{OH})_6] \cdot 8\text{H}_2\text{O}$) consists of sheets of uranyl polyhedra connected through hydrogen bonds to interlayer Ca^{2+} and water molecules [13]. The incorporation of Nd^{3+} into this structure is likely to occur by substituting for Ca^{2+} in the interlayer, assuming that appropriate charge-balancing substitutions can occur (Nd^{3+} , 1.04 Å; Ca^{2+} , 0.99 Å [7]). One possible substitution mechanism involves $\text{O}^{2-} \leftrightarrow \text{OH}^-$. Therefore, the suggested charge-coupled substitution will be $\text{Nd}^{3+} + \text{O}^{2-} \leftrightarrow \text{Ca}^{2+} + \text{OH}^-$. This is a reverse of the charge-balancing mechanism proposed to occur during the substitution of Nd^{3+} in the structure of ianthinite. The incorporation of Ce^{4+} into this structure is likely to occur by substitution for U^{6+} within the polyhedra sheet (Ce^{4+} , 0.94 Å; U^{6+} , 0.80 Å [7]), together with local charge-balancing substitutions ($\text{Ce}^{4+} + 2\text{OH}^- \leftrightarrow \text{U}^{6+} + 2\text{O}^{2-}$).

Distribution coefficients

Table I shows the distribution coefficients, K_d values, of Ce and Nd in ianthinite and becquerelite tests from this study, and in dehydrated schoepite from the previous work [8]. The K_d value of Ce was higher than that of Nd in ianthinite test, suggesting that substitution of Ce^{4+} for U^{4+} was favored over the substitution of Nd^{3+} for U^{4+} . In the tests with becquerelite, a lower K_d value was obtained for Nd relative to Ce, implying that substitution of Ce^{4+} for U^{6+} is favored

over that of Nd^{3+} for Ca^{2+} . This occurs even though Nd^{3+} and Ca^{2+} have smaller disparity of charge and ionic radius. It is thought to be probably due to the interlayer structure of becquerelite. This has to be further studied in the future. Additional tests with Nd concentrations approximating those of Ce (2.1 ppm) are being conducted to assess differences in atomic substitution between the two lanthanide elements from solutions with similar ionic strengths.

Table I. K_d values of Ce and Nd in uranium alteration phases. All test at seven days.

Uranium alteration phase	Ce in leachant (ppm)	Ce in solid (ppm)	K_d	Nd in leachant (ppm)	Nd in solid (ppm)	K_d
Ianthinite	2.1	306	146	399	24,800	62
Becquerelite	2.1	33	16	277	1,300	5
Dehydrated schoepite [8]	2.1	25	12	286	-	-

CONCLUSIONS

This paper presents results from a study of potential incorporation of transuramics into uranium phases. Results of this study suggest that:

1. Ce^{4+} (surrogate for Pu^{4+}) directly substitutes for U^{4+} in the structure of ianthinite in the amount of about 306 ppm (2.1 ppm in leachant, $K_d=146$).
2. Nd^{3+} (surrogate for Am^{3+}) substitutes for U^{4+} in the structure of ianthinite, together with local charge-balancing substitutions in the amount of approximately 24,800 ppm (399 ppm in leachant, $K_d=62$).
3. Ce^{4+} (surrogate for Pu^{4+}) substitutes for U^{6+} in the structure of becquerelite in the amount of about 33 ppm (2.1 ppm in leachant, $K_d=16$), assuming that local charge-balancing substitutions occur.
4. It is thought that Nd^{3+} (surrogate for Am^{3+}) substitutes for Ca^{2+} in the interlayer sites of becquerelite in the amount of approximately 1,300 ppm (277 ppm in leachant, $K_d=5$), assuming that local charge-balancing substitutions occur.

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