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## POTENTIAL INCORPORATION OF TRANSURANICS INTO URANIUM PHASES

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### ABSTRACT

The  $\text{UO}_2$  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  $\text{U}^{6+}$  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  $\text{Ce}^{4+}$  and  $\text{Nd}^{3+}$  (surrogates for  $\text{Pu}^{4+}$  and  $\text{Am}^{3+}$ , 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  $\text{HNO}_3$  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  $\text{UO}_2$  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  $\text{UO}_2$  and spent nuclear fuel under such conditions have shown that the alteration products are primarily uranyl ( $\text{UO}_2^{2+}$ ) phases [1-3]. Spent nuclear fuel typically contains 95 to 99%  $\text{UO}_2$ , 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  $\text{UO}_2$  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  $\text{Ce}^{4+}$  and  $\text{Nd}^{3+}$  may be similar to  $\text{Pu}^{4+}$  and  $\text{Am}^{3+}$ , respectively, because of the similarity of valence charges and their ionic radii ( $\text{Ce}^{4+}$ , 0.94 Å;  $\text{Pu}^{4+}$ , 0.93 Å;

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$\text{Nd}^{3+}$ , 1.04 Å;  $\text{Am}^{3+}$ , 1.07 Å [7]). Thus,  $\text{Ce}^{4+}$  and  $\text{Nd}^{3+}$  may be used as appropriate surrogate elements for  $\text{Pu}^{4+}$  and  $\text{Am}^{3+}$ , respectively. Kim et al. [8] have experimentally examined the potential for actinide substitution in dehydrated schoepite by using  $\text{Ce}^{4+}$  as a surrogate for  $\text{Pu}^{4+}$ . 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  $\text{U}^{4+}$  and  $\text{U}^{6+}$  ions into its structure. The structure of ianthinite will accommodate considerable amounts of  $\text{Pu}^{4+}$ . In corrosion experiments of  $\text{UO}_2$  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  $\text{Pu}^{4+}$  and  $\text{Am}^{3+}$  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  $\text{Ce}^{4+}$  and  $\text{Nd}^{3+}$ . 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  $\text{Ce}^{4+}$  or  $\text{Nd}^{3+}$ . 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  $\text{Cu}^{2+}$  and  $\text{Cu}^+$ , 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 ( $\text{Cu}_2\text{O}$ ) and tenorite ( $\text{CuO}$ ). 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  $\text{Ce}^{4+}$  or  $\text{Nd}^{3+}$ . 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 LaB<sub>6</sub> 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.

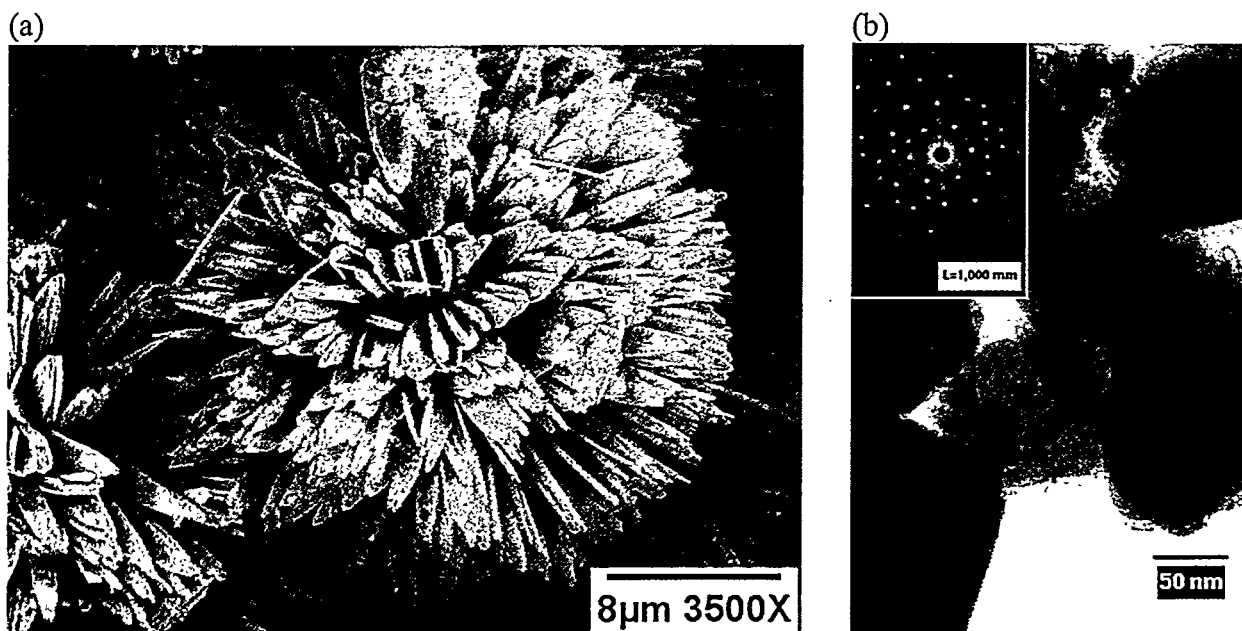


Figure 1. (a) SEM micrographs of ianthinite crystals. (b) AEM bright field image of ianthinite particles. Inset: Selected area electron diffraction pattern from ianthinite.

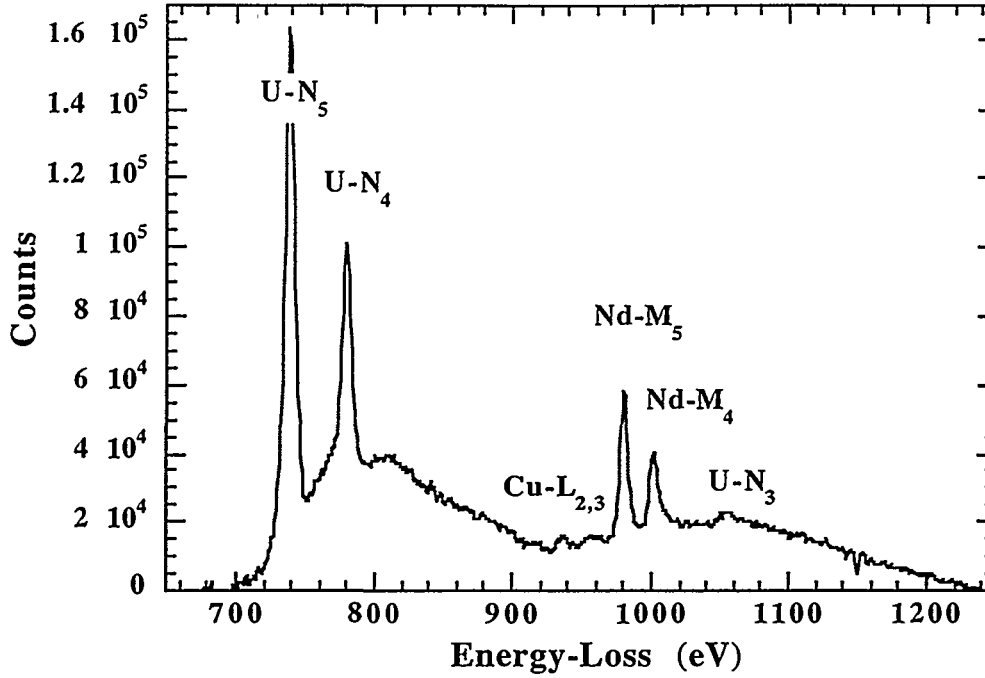
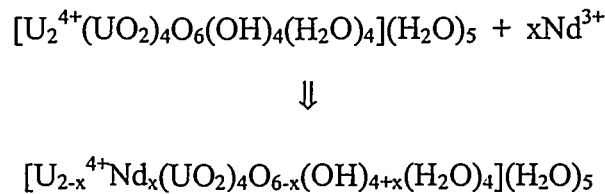


Figure 2. Electron energy-loss spectrum of Nd-bearing ianthinite.  $M_{4,5}$  edges of Nd are clearly visible.

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.

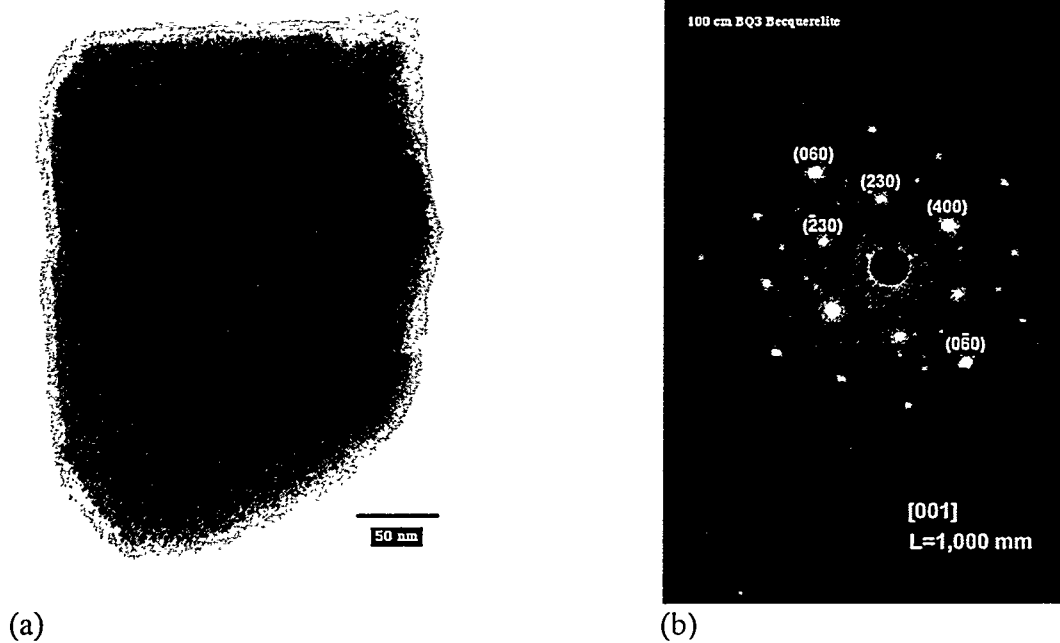


Figure 4. (a) AEM bright field image of becquerelite particle. (b) Selected area electron diffraction pattern from becquerelite.

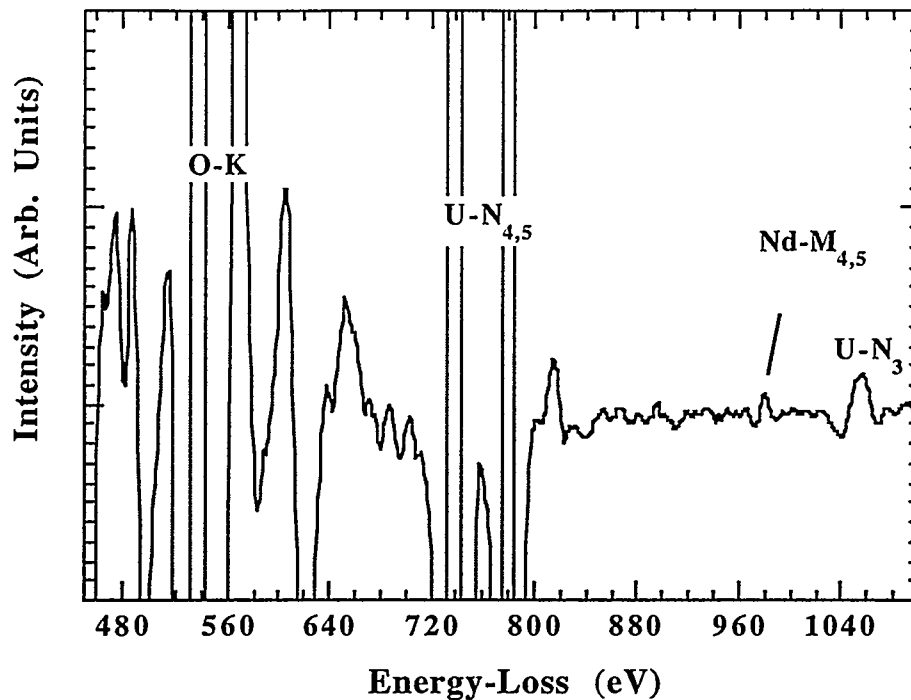


Figure 5. Electron energy-loss spectrum of Nd-bearing becquerelite. The vertical scale intensity has been increased 50x for easier viewing of the Nd peak located at 980 eV.

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  $\text{Ca}^{2+}$  and water molecules [13]. The incorporation of  $\text{Nd}^{3+}$  into this structure is likely to occur by substituting for  $\text{Ca}^{2+}$  in the interlayer, assuming that appropriate charge-balancing substitutions can occur ( $\text{Nd}^{3+}$ , 1.04 Å;  $\text{Ca}^{2+}$ , 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  $\text{Nd}^{3+}$  in the structure of ianthinite. The incorporation of  $\text{Ce}^{4+}$  into this structure is likely to occur by substitution for  $\text{U}^{6+}$  within the polyhedra sheet ( $\text{Ce}^{4+}$ , 0.94 Å;  $\text{U}^{6+}$ , 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  $\text{Ce}^{4+}$  for  $\text{U}^{4+}$  was favored over the substitution of  $\text{Nd}^{3+}$  for  $\text{U}^{4+}$ . In the tests with becquerelite, a lower  $K_d$  value was obtained for Nd relative to Ce, implying that substitution of  $\text{Ce}^{4+}$  for  $\text{U}^{6+}$  is favored



over that of  $\text{Nd}^{3+}$  for  $\text{Ca}^{2+}$ . This occurs even though  $\text{Nd}^{3+}$  and  $\text{Ca}^{2+}$  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 transuranics into uranium phases. Results of this study suggest that:

1.  $\text{Ce}^{4+}$  (surrogate for  $\text{Pu}^{4+}$ ) directly substitutes for  $\text{U}^{4+}$  in the structure of ianthinite in the amount of about 306 ppm (2.1 ppm in leachant,  $K_d=146$ ).
2.  $\text{Nd}^{3+}$  (surrogate for  $\text{Am}^{3+}$ ) substitutes for  $\text{U}^{4+}$  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.  $\text{Ce}^{4+}$  (surrogate for  $\text{Pu}^{4+}$ ) substitutes for  $\text{U}^{6+}$  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  $\text{Nd}^{3+}$  (surrogate for  $\text{Am}^{3+}$ ) substitutes for  $\text{Ca}^{2+}$  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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