Quantum-mechanical evaluation of Np-incorporation into studtite

LINDSAY C. SHULLER,^{1,*} RODNEY C. EWING,^{1,2} AND UDO BECKER²

¹Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109, U.S.A. ²Geological Sciences, University of Michigan, Ann Arbor, Michigan 48109, U.S.A.

ABSTRACT

Radionuclide incorporation into the alteration products of corroded UO₂ in used nuclear fuel may control the release and mobility of key radionuclides, such as the very long-lived minor actinide, ²³⁷Np $(\tau_{1/2} = 2.1 \text{ Ma})$. Studite, $[UO_2(O_2)(H_2O)_2](H_2O)_2$, may form in the presence of peroxide produced by radiolysis of water in contact with the spent fuel. Experiments have indicated that the studtite structure can incorporate Np; however, due to the low concentrations in the solid, the incorporation mechanism could not be determined. In this study, density functional theory is used to calculate an optimized structure, determine the electronic density of states, and calculate the energetics of the incorporation of Np^{6+} vs. $Np^{5+}+H^+$ into the studtite structure. The definition of the source/sink phase (reference phase) for the cations involved in the incorporation process greatly affects the final incorporation energy. The incorporation energy of Np into studiite based on the 4^+ oxide reference phases (e.g., source/sink = NpO₂/UO₂) results in lower incorporation energies (-0.07 and 0.63 eV for Np⁶⁺ and Np⁵⁺ incorporation, respectively) than the incorporation energy calculated using higher-oxide reference phases (e.g., Np_2O_5/UO_3), where the incorporation energies for Np^{6+} and Np^{5+} into studtite are 0.42 and 1.12 eV, respectively. In addition, Np⁶⁺-incorporation into studite is energetically more favorable than Np⁵⁺incorporation as assessed from the lower incorporation energy. Estimates of the solid-solution behavior from a combination of quantum-mechanical calculations and Monte-Carlo simulations indicate that the Np⁶⁺- and U⁶⁺-studtite solid solution is completely miscible at room temperature with respect to a hypothetical Np⁶⁺-studtite structure. The Np-studtite structure was calculated to be stable with respect to the corresponding oxides, but its formation may be kinetically hindered. Knowledge of the electronic structure provides insight into Np-bonding in the studtite structure. The Np 5f orbitals are within the band gap of studtite, which results in the narrow band gap of Np-incorporated studtite (1.09 eV), as compared with the band gap of studtite alone (2.29 eV).

Keywords: Studtite, Np-incorporation, density functional theory (DFT), quantum-mechanical calculations, electronic structure

INTRODUCTION

Used nuclear fuel (UNF) is composed of 95-99% uranium dioxide (UO₂) and 1–5% fission products (e.g., ¹³⁷Cs, ⁹⁰Sr, ⁹⁹Tc) and transuranium elements, e.g., 239Pu, 237Np, and 241Am (Barner 1985; Bruno and Ewing 2006). The oxidation and corrosion of the UO2 matrix causes the oxidation and release of fission products and transuranium elements. Specific radionuclides, such as 99Tc or ²³⁷Np, are of concern due to their mobility and long half-lives. For example, Np is mobile as an aqueous Np5+-complex, and ²³⁷Np has a half-life of 2.1 Ma. Experimental corrosion studies of synthetic UO₂ and natural uraninite (UO_{2+x}) show a similar U-alteration paragenesis-beginning with uranyl oxyhydroxides, followed by uranyl silicates (Finch and Ewing 1992; Wronkiewicz et al. 1992, 1996). More recent UNF corrosion studies show the precipitation of studtite $[UO_2(O_2)(H_2O)_2(H_2O)_2]$ and meta-studtite [UO₂(O₂)(H₂O)₂] (Hanson et al. 2005; McNamara et al. 2005), which are the only stable uranyl peroxide minerals (Kubatko et al. 2003) and, to the authors' knowledge, the only stable peroxide minerals. Studtite has also been observed as a

The studtite structure was first determined by Walenta (1973) and later refined by Burns and Hughes (2003). Studtite (C2/c) is composed of chains of distorted uranyl hexagonal bipyramids with water in the interlayer (Fig. 1). The six uranyl equatorial bonds include two unique equatorial H₂O and two symmetrically equivalent equatorial peroxide (O_2)^{2–} groups. The peroxide forms the equatorial edges that polymerize the uranyl polyhedra into chains parallel to [001]. U⁶⁺ is also strongly bonded to axial O^{2-} , forming the linear uranyl complex. Chains of the distorted uranyl hexagonal bipyramids are weakly linked by hydrogen bonding. Here, the chemical formula for studtite is written [(UO₂)O₂(H₂O)₂](H₂O)₂, where the UO₂ signifies the uranyl molecule, the O₂ is the equatorial peroxide molecule, the H₂O inside the square bracket is the equatorial water molecule, and the other H₂O is the interlayer water molecule.

While other uranyl peroxide phases have been synthesized

major alteration phase of UNF at the K East Basins of the Hanford site (Abrefah et al. 1998) in Washington, U.S.A. Studtite forms by the incorporation of peroxide (Amme 2002), which oxidizes some of the U⁴⁺ to U⁶⁺. The peroxide is formed due to radiolysis of water at the surface of highly radioactive UNF.

^{*} E-mail: lshuller@umich.edu



FIGURE 1. Studtite projected on the (010) showing chains of uranyl polyhedra bonded by peroxide molecules, where the unique O atoms are labeled in the detailed inset of two adjacent uranyl polyhedra. U atoms = blue; O atoms = red; H atoms = white.

in laboratory experiments focused on uranium(VI)-peroxide chemistry in alkaline conditions (Burns et al. 2005; Kubatko and Burns 2006; Kubatko et al. 2007), studtite and meta-studtite are the only known stable uranyl hydroxyl-peroxide mineral phases to form under repository conditions (Kubatko et al. 2003; Wronkiewicz et al. 1992, 1996). These two minerals may be the first alteration phases to form in both oxidizing and reducing repository environments due to the near-surface oxidizing conditions and presence of hydrogen peroxide created by radiolysis (Amme 2002; Cejka et al. 1996; Debets 1963). Thus, studtite and meta-studtite are potentially important phases for radionuclide incorporation and retention.

The transport of radionuclides, such as Np, may be limited by incorporation into U-alteration phases (Burns et al. 1997). Electron energy loss spectroscopy (EELS) analysis shows about 500 ppm Np incorporated into the uranyl oxyhydroxide phase of dehydrated schoepite $[UO_3(H_2O)_{0.8}]$ (Buck et al. 1997). However, EELS analysis at the Np My energy peak is of limited value for studies of Np5+ because of a plural-scattering event that generates an erroneous peak at this energy (Fortner et al. 2004). Synchrotron X-ray absorption spectroscopy has been used to determine the incorporation limit of Np into uranyl oxyhydroxides and showed that there was a significantly lower concentration of Np incorporated into dehydrated schoepite (200 ppm) than the previous EELS analysis indicated (Fortner et al. 2004). Inductively coupled plasma-mass spectroscopy (ICP-MS) has also been used to study Np-incorporation into meta-schoepite $(UO_3 2H_2O)$, Na-compreignacite { $Na_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$ }, uranophane $[Ca(UO_2)_2(SiO_3OH)_2(H_2O)_5]$, and β -(UO₂)(OH)₂ (Burns et al. 2004). Uranyl structures with interlayer cations, such as uranophane, incorporated more Np (~400 ppm) than structures without interlayer cations, such as meta-schoepite (a few parts per million). Most recently, laser ablation (LA) ICP-MS analysis has shown that Na-substituted meta-schoepite has a greater affinity for Np than meta-schoepite (Klingensmith et al. 2007). Another experiment showed that Np has a greater affinity for studtite than for schoepite (Douglas et al. 2005a, 2005b). The oxidation state of the Np in the studtite is expected to be 5+ (Kaszuba and Runde 1999); however, there is some speculation that Np⁶⁺ could be incorporated (Douglas et al. 2005a). There is also evidence that Np5+ and Np6+ can be reduced by hydrogen peroxide forming Np⁴⁺ (Malkova et al. 1986; Shilov et al. 1998); however, this reduction is observed in highly concentrated acid solutions and is not expected in near-neutral solutions such as those associated with geologic repository environments.

The knowledge of the crystal and electronic structure of studtite determined using quantum-mechanical calculations provides the framework for understanding potential incorporation mechanisms. This first-principles study presents a detailed description of the crystal and electronic structure of studtite and Np-substituted studtite and an analysis of the energetics of different Np-substitution mechanisms. The electronic structure of studtite is compared with the electronic structure of Np-modified studtite. Additionally, the incorporation of Np⁶⁺ vs. Np⁵⁺ into studtite is compared, and the charge-balanced incorporation mechanism of Np⁵⁺ into studtite is evaluated.

EXPERIMENTAL METHODS

Quantum-mechanical calculations

The quantum-mechanical program CAmbridge Serial Total Energy Package [CASTEP; Payne et al. (1992); Segall et al. (2002)] was used to optimize the geometry of studtite and Np-substituted studtite and calculate the total energy and electronic structure of both phases. CASTEP is a density functional theory-based code that uses a planewave approach (i.e., the wavefunctions of the valence electrons are composed of a series of sinusoidal functions with different wavelengths) with periodic boundary conditions to approximate solutions to the Schrödinger equation. The total energy of a periodic system is based on the ground state of the valence electrons. Ultra-soft pseudopotentials are used to approximate the influence of the core and inner valence electrons on the outer valence electrons. Outer valence electrons (U 5f36s26p66d17s2, Np 5f46s26p66d17s2, O 2s22p4, and H 1s1) are treated explicitly in the Hamiltonian of the Schrödinger equation. Changing the planewave energy cut-off from 500 to 800 eV changed the final energy of the studtite structure by 0.99 eV and the Np6+-substituted studtite structure by 1.95 eV. Further changing the planewave energy cut-off from 800 to 1000 eV changed the final energy of the studtite structure by only 0.10 eV. A k-point spacing of 0.07 Å-1 was used. No significant changes in energy have been found for increased k-point density; thus, this k-point grid is appropriate for this type of calculation due to the relatively large size of the unit cell. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional (Perdew et al. 1996) was used to approximate electron exchange and correlation. GGA has shown greater structural agreement for UO2 geometry optimizations than LDA (Skomurski et al. 2006). Conventional DFT calculations predict a metallic band structure for UO2, even though UO2 is a weak semi-conductor. Density functional theory approximations beyond GGA, such as the use of a Hubbard U correctional term (Anisimov et al. 1997; Gupta et al. 2007), may be used to more accurately model the strongly correlated 5f electrons for electronic structure calculations. In the current study, GGA is used to optimize the geometry of studtite and Np-substituted studtite and qualitatively compare the corresponding electronic structures. A spin-polarized approach is used for systems that contain Np5+ or Np6+ atoms to allow the unpaired electron spins in the 5f orbitals to adopt the lowest-energy configuration.

Calculation of incorporation energies

Final energies, calculated using CASTEP, are defined as the energy gained by forming a crystal from zero-valent atoms in vacuum. For example, the final energy of studtite is defined by the reaction given by Equation 1

$$\begin{split} & U^0 + 8O^0 + 8H^0 \leftrightarrow [UO_2O_2(H_2O)_2](H_2O)_2 \\ & \Delta E = E\{[UO_2O_2(H_2O)_2](H_2O)_2\} - E\{U^0\} - 8E\{O^0\} - 8E\{H^0\}. \end{split}$$

The energy required for the formation of studite and Np⁶⁺-substituted studite from their respective zero-valent atoms (e.g., Eq. 1), indicates that studite is more thermodynamically stable than Np⁶⁺-substituted studite by about 3.55 eV, where the energies for the zero-valent atoms were calculated for the atoms in a $10 \times 10 \times 10$ Å box. The change in enthalpy describing the energy needed to form the mineral from the atoms in a gas phase is used only to compare studite and Np⁶⁺-substituted studite—not the incorporation energy of Np⁶⁺ into studite.

The energy required for the substitution of Np into a U site in studtite can be derived as the energy of a stoichiometric chemical reaction as shown in Equation 2, where the source for Np is Np₂O₅ and the sink for U is UO₃. The incorporation energy is the difference between the sum of the reactant energies and the sum of the product energies.

$$\begin{aligned} &[UO_2O_2(H_2O)_2](H_2O)_2+\frac{1}{2}Np_2O_5+\frac{1}{4}O_2 \leftrightarrow [(U,Np)O_2O_2(H_2O)_2](H_2O)_2+UO_3\\ &\Delta E = E\{[(U,Np)O_2O_2(H_2O)_2](H_2O)_2\} + E\{UO_3\}\\ &- E\{[UO_2O_2(H_2O)_2](H_2O)_2\} - \frac{1}{2}E\{Np_2O_5\} - \frac{1}{4}E\{O_2\}. \end{aligned}$$

The incorporation energy of Np into the unit cell of studtite, as calculated using Equation 2, depends on the reference phases (i.e., source for Np and sink for U) selected. The incorporation energy is specific to a given incorporation mechanism. For example, Np₂O₅, which is the Np oxide with the highest oxidation state of Np, was selected as the source for Np in the above equation with UO₃ as the uranium sink; however, the incorporation energy is different for different source and sink couples (e.g., ½NpO₂+¼O₂ and UO₂ vs. NpF₆ and UF₆). The different reference phases were chosen to evaluate the effect of changing the cation oxidation state between the reference phases and subject phase. For example, the hexafluorides are used for Np⁶⁺ incorporation so that the incorporation equation can be written without changing the oxidation state of any species. This study focuses on using solid crystalline phases (oxides and fluorides) as sources and sinks for Np and U. The incorporation energies for different Np-incorporation mechanisms are used to determine the trends of favorable incorporation mechanisms.

The substitution of Np⁵⁺ for U⁶⁺ results in a charge imbalance; thus, a charge-balancing mechanism is necessary. For example, one charge-balancing mechanism is the substitution of Np⁵⁺+H⁺ \leftrightarrow U⁶⁺, which is equivalent to the coupled substitution of Np⁵⁺+OH⁻ \leftrightarrow U⁶⁺+O²⁻. The location of the additional H⁺ within the structure is very important to the outcome of the energy calculations. Due to the computational expense of evaluating all of the different substitution mechanisms in a relatively large unit cell, coarse computational parameters (planewave energy cut-off of 500 eV and Γ k-point) were used in the evaluation of different H⁺ positions within the modified studite structure. The positions analyzed include H⁺ bonded to the sxial oxygen, the peroxide oxygen, and the interlayer water. Equation 3 shows the stoichiometric reaction that describes the coupled substitution of Np⁵⁺ and H⁺ into the studite structure.

$$[UO_{2}O_{2}(H_{2}O)_{2}](H_{2}O)_{2}+\frac{1}{2}Np_{2}O_{5}+\frac{1}{2}H_{2}O \leftrightarrow [H(U,Np)O_{2}O_{2}(H_{2}O)_{2}](H_{2}O)_{2}+UO_{3}$$
(3)

The incorporation energy for Np⁵⁺ and H⁺ into studtite is the difference of the sums of the products and reactants of Equation 3. The incorporation energy depends on both the reference phases and the H⁺ position in the modified studtite structure.

Calculations of the thermodynamic properties of the (U⁶⁺,Np⁶⁺)-studite solid solution

The thermodynamic mixing properties for the (U6+,Np6+)-studtite solid solution are estimated from a series of quantum-mechanical calculations in which the uranium end-member is pure studtite and the neptunium end-member is a theoretical Np-studtite structure with Np6+ replacing all U6+ atoms. Due to the limited number of cations in the unit cell (4, limited by the computational expense of these calculations), the minimum amount of Np incorporated into the model structure is 25% of the actinyl sites. Note, the concentrations of Np in experimental studies are on the order of a few hundreds of parts per million (Burns et al. 2004; Douglas et al. 2005a, 2005b; Klingensmith et al. 2007). However, quantum-mechanical calculations using lower concentrations of Np are more computationally expensive in terms of both time and memory because lower concentrations require larger unit cells. The computational time increases with number of electrons in a system cubed and is, thus, already prohibitive for a $2 \times 1 \times 1$ supercell (which would be equivalent to a substitution of 12.5% Np into the actinyl sites). To scale up the system, i.e., exploring millions of different configurations at different temperatures and compositions in a unit cell with several thousand cations, it is necessary to describe the total energy as a function of the relative positions of only the cations. The energy of the system is fit with a 2-parameter $(m_1 \text{ and } m_2)$ Margules function (Eq. 4), where E_0 describes the energy of the system as a function of the concentration, x, and accounts for the asymmetry of the system (Ferriss et al. 2009). Deviations from the Margules curve are accounted for with an exchange parameter J, which describes the energy associated with the A-B cation exchange (Eq. 5). Both the Margules parameters and exchange parameters are fit to the enthalpy of mixing from the quantum-mechanical calculations (Eq. 6) and used in a Monte-Carlo simulation (Becker et al. 2000; Bosenick et al. 2001; Becker and Pollok 2002).

$$E_0 = \mathbf{x}(1 - \mathbf{x})[m_1\mathbf{x} + m_2(1 - \mathbf{x})]$$
(4)
$$E_0 = E_1^{i_1} = \frac{1}{2}(E_1^{i_1} + E_2^{i_2})$$
(5)

 $E_{\rm m} = E_0 + \sum n_{\rm A-B}^{\rm a} \sum (A_{\rm A-A} - B_{\rm B-B})^{\rm a}$ (6)

The Monte-Carlo simulation is designed to accept a new configuration with a probability of 1 if the change in energy between the new configuration and the previous configuration is negative. Otherwise, if the exchange increases the energy (ΔE) of the system, the new configuration is accepted with a probability according to a Boltzmann distribution, i.e., the swap is accepted if the Boltzmann factor [exp($-\Delta E/RT$)] at a given temperature *T* is greater than a random number between 0 and 1 (Reich and Becker 2006). The Monte-Carlo simulations allow for calculations using larger supercells (such as an $8 \times 8 \times 8$ supercell containing 2048 exchangeable cation sites). Subsequent Bogoliubov thermodynamic integration was used to calculate the temperature-dependent free energy and entropy of mixing (Yeomans 1992; Ferriss et al. 2008).

RESULTS AND DISCUSSION

Refined crystal structure

Quantum-mechanical calculations involve the positions of all of the atoms in a structure. The crystal structure of studtite has been determined using X-ray diffraction techniques, but the positions of the hydrogen atoms in studtite cannot be determined using traditional X-ray diffraction methods. Therefore, the hydrogen positions available in crystallographic databases are estimated from the O-H bond lengths (0.98 Å) combined with some consideration of bond valence constraints (Burns and Hughes 2003). No neutron-diffraction refinements are available for the determination of the H positions; thus, in this study, energy-optimized hydrogen positions were determined using quantum-mechanical optimizations of the structure. Table 1 shows the experimental studtite unit-cell parameters (Burns and Hughes 2003) vs. the optimized unit-cell parameters. The optimized unit-cell parameters are within ~1% of the experimentally determined unit-cell parameters, with the exception of the b parameter, which is within $\sim 2\%$. The quantum-mechanically optimized studtite unit-cell volume is in close agreement (0.03%)with other density-functional theory calculations (Ostanin and Zeller 2007), which use slightly different computational parameters (e.g., k-point mesh, planewave energy cut-off). The quantum-mechanical optimization results in the alignment of the H atoms of the equatorial water parallel to the (010) plane. Figure 2 shows the orientation of the water molecules pre- and post-optimization, where the alignment of the H⁺ atoms is apparent along with a change in the dihedral angle between the planes parallel to the U-O_{equatorial} bonds (from 12.3 to 1.2°). The quantum-mechanical calculations are static ground-state (0 K) calculations; therefore, the dynamic behavior of the water mol-

TABLE 1. Comparison of measured unit-cell parameters and optimized unit-cell parameters of the conventional unit cell of studtite, (Np⁶₂₅U⁶₇₅)-studtite, and (Np⁶₂₅U⁶₇₅)-studtite

_		1 (] 0.25 0.757	, ,	0.25 0.757	
	Experimental	Computational	Difference (%)	(Np _{0.25} ⁶⁺ U _{0.75})	(Np ⁵⁺ _{0.25} U ⁶⁺ _{0.75})
_				-studtite	-studtite
а	14.07	13.96	-0.78	13.97	13.93
b	6.72	6.88	2.38	6.88	6.98
С	8.43	8.53	1.19	8.53	8.49
α	90.00	90.00	0.00	90.01	90.01
β	123.36	122.55	-0.66	122.40	121.92
γ	90.00	90.00	0.00	90.04	89.65
V	665.7(3)	689.88	3.63	692.54	700.73

Note: The difference column highlights the comparison of the computed studtite parameters with those published by Burns and Hughes (2003).

ecules at room temperature is not captured. Table 2 shows the quantum-mechanically optimized atomic positions for studtite, which have not been previously reported. The total energy difference between the initial structure, using the estimated H positions proposed by Burns and Hughes (2003), and the optimized structure is -129.8 kJ/mol formula unit, where the formula unit is $[(UO_2)(O_2)(H_2O)_2](H_2O)_2$. The significant decrease in total energy of the optimized primitive cell with respect to the initial primitive cell is evidence that the optimized H positions are energetically favored. Additionally, the enthalpy of formation of studtite from UO_3 +H₂O₂+3H₂O yields $\Delta E = -74.2$ kJ/mol, which is in close agreement with the measured enthalpy of formation [-75.7 kJ/mol, Kubatko et al. (2003)].

The Np⁶⁺-substituted structure is isostructural with studite and was constructed by substituting Np⁶⁺ for U⁶⁺ in one of the four actinyl polyhedra (25 atom% Np). The (Np⁶⁺_{0.25}U⁶⁺_{0.75})-studite is optimized using *P*1 symmetry to avoid symmetry restrictions in the relaxation process. The optimized unit-cell volume is 692.54 Å³ (optimized studtite volume = 689.88 Å³). The optimized unit-cell parameters of (Np⁶⁺_{0.25}U⁶⁺_{0.75})-substituted studtite are listed in Table 1. A CIF file for the optimized atomic positions



FIGURE 2. The pre- (**a**) and post- (**b**) optimized uranyl polyhedra show the alignment of the H⁺ parallel to the (010) plane and the change in the dihedral angle between the planes parallel to the Uⁱ-Oⁱ_{equatorial} bonds (traced with dotted lines). Calculations are performed with ground-state (0 K) static conditions; therefore, vibrations of the water molecules at room temperature are not observed. U atoms = blue; O atoms = red; H atoms = white.

 TABLE 2.
 Optimized unit-cell parameters and fractional coordinates of atoms in studtite

	Studtite [(UO ₂)O ₂ (H ₂ O) ₂](H ₂ O) ₂				
Element	Atom no.	х	У	Z	
U	1	0.000	0.000	0.000	
O _{uranyl}	2	-0.004	-0.247	0.072	
Operoxide	3	0.062	0.121	0.305	
O _{equatorial water}	4	0.205	0.004	0.181	
Ointerlayer water	5	-0.159	-0.523	0.052	
H _{equatorial water}	6	0.256	0.005	0.132	
H _{equatorial water}	7	0.254	0.018	0.320	
H _{interlayer water}	8	-0.119	-0.648	0.104	
H _{interlayer water}	9	-0.102	-0.423	0.076	
<i>Note:</i> $a(\text{\AA}) = 13.96$; $b(\text{\AA}) = 6.88$; $c(\text{\AA}) = 8.53$; $\beta(^{\circ}) = 122.55$; $V(\text{\AA}^{3}) = 689.88$; space					

Note: a (A) = 13.96; b (A) = 6.88; c (A) = 8.53; β (°) = 122.55; V (A³) = 689.88; space group = C2/c.

of $(Np_{0.25}^{+}U_{0.75}^{+})$ -studtite is located in the supplemental material.¹ This shows that the unit-cell parameters are not more than 0.01 Å different from those of pure U-studtite.

The unit-cell parameters of $[(Np^{5+}H^+)_{0.25}U_{0.75}^{6+}]$ -structure diverge by not more than 0.1 Å from studite. The substituted Np⁵⁺ is slightly displaced from the original U⁶⁺ position due to the coupled substitution of an H⁺ ion for charge-balance. Different locations for the H⁺ were considered (i.e., bonded to the axial oxygen, to the peroxide oxygen, and to the interlayer water molecule). The most thermodynamically stable position occurs for H⁺ is bonded to the axial O²⁻, which is energetically more favorable than the other positions by 0.8–1.3 eV. The unit-cell volume for $[(Np^{5+}H^+)_{0.25}U_{0.75}^{6+}]$ -structure is 700.73 Å³, which is 1.6% larger than studtite and 1.2% larger than $[(Np^{6+})_{0.25}U_{0.75}^{6+}]$ -structure are listed in Table 1. The quantum-mechanically optimized atomic positions for $[(Np^{5+}H^+)_{0.25}U_{0.75}^{6+}]$ -structure are available as a CIF file¹.

Electronic structure of studtite

The electronic-structure analysis of studtite can be described using the partial density of states (PDOS) and orbital projections. The DOS of the valence electrons for studtite are shown for electron binding energies from -30 to +10 eV in Figure 3. The inner valence band (from about -24 to -10 eV) has electron density contributions from the axial O 2s, peroxide O 2s, equatorial water O 2s, and U 6p orbitals. Each peak in this inner valence band (interval A) is labeled in Figure 3.

The outer valence band of the studite electronic structure (from about -10 to 0 eV; interval B; Fig. 3) is divided into 4 intervals (interval B₁-B₄ in inset of Fig. 3). The lowest interval has contributions from the interlayer water O 2p, equatorial water O 2p, and the peroxide O 2p. The bonding orbitals within the water molecules, as well as hydrogen bonding between the interlayer water molecules and the uranyl polyhedra layers via the peroxide O 2p orbitals, are shown in the electron density orbital projection in this energy range (Fig. 4). The next interval, -6 to -4 eV, has some contribution from all of the unique oxygen 2p orbitals. The U 6d is strongly correlated with both the equatorial water O 2p and peroxide O 2p orbitals.

The interval from -4 to -1 eV has 4 major peaks and shows the strongest correlation between the U 6d and 5f orbitals and the peroxide O 2p, axial O 2p, and equatorial water O 2p orbitals. The -3.5 eV peak is comprised of the interlayer water O 2p, equatorial water O 2p, and the peroxide O 2p orbitals. The -2.5 eV peak is comprised primarily of the axial O 2p orbital. The -2 eV peak is comprised primarily of both the water O 2p orbitals, with smaller contributions from the axial and peroxide O 2p orbitals. Finally, the -1 eV peak is comprised primarily of the peroxide O 2p and the equatorial water O 2p peak, with smaller contributions from the axial O 2p and interlayer water O 2p orbitals. The top of the valence band and just past the Fermi level, from -0.5 to 0.5 eV,

¹ Deposit item AM-10-040, CIFs. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the *American Mineralogist* Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.



FIGURE 3. Partial density of states spectra of studtite over the entire

calculated energy range, where interval A designates the inner valence

band, interval B the outer valence band and interval C the conduction

band. The peaks in interval A of the full studtite PDOS are labeled

according to the contributing molecular orbitals. The peak character of

the outer valence band and conduction band are detailed in the inset,

which is divided into intervals B1, B2, B3, B4, and C. These intervals are

discussed in detail in the text. $a = H_{wat}$ 1s; $b = O_{wat}$ 2p; $c = O_{per}$ 2p; d =

 $O_{ax} 2p; e = U 6d; f = U 5f.$



FIGURE 4. Electron density orbital projection between -8 and -6 eV showing O-H bonding in water molecules as well as hydrogen bonding between the water molecules and uranyl polyhedra.

has contributions solely from the peroxide O 2p orbital. Thus, the highest occupied molecular orbital (HOMO) is composed of electron density contributions from the peroxide O 2p orbital, which may play a role in processes, such as actinide incorporation into the uranyl structure and possible oxidation reactions in the environment. The peroxide O 2p electron density contribution at the HOMO level of the studtite electronic structure is unique to studtite, as studtite is the only thermodynamically stable uranyl peroxide mineral (Kubatko et al. 2003).

As compared with the valence band, the lower conduction band (no higher empty conduction bands are considered in these calculations because they change neither the geometry nor the energetics of the system significantly) is much simpler. The unoccupied U 5f orbitals are the major contribution to the density of states in this region with an admixture of peroxide O 2p and minimal contribution from the axial O 2p orbitals (Fig. 3).

The significant peaks, in particular the peroxide contribution to electron density in the HOMO and the U 5f contribution to the electron density in the LUMO, are comparable to the studtite electronic structure calculation by Ostanin and Zeller (2007). The calculated band gap is 2.29 eV, which compares to the band gap calculated by Ostanin and Zeller (2.3 eV). This lowest-energy HOMO-LUMO transition occurs at the F k-point (0, 0.5, 0) in the studtite *P*1 Brillouin zone.

Electronic structure of (Np_{0.25}U_{0.75})-studtite

The $(Np_{0.25}^{6+}U_{0.75}^{6+})$ -studiite electronic structure is also described using the density of states and electron density projections, along with the band structure. The DOS for the $(Np_{0.25}^{6+}U_{0.75}^{6+})$ -studiite is similar to that of studiite (Fig. 5); however, there are additional unique types of atom/position combinations that must be considered. In studiite, four different oxygen types are unique: peroxide, axial (or uranyl), equatorial (U-bonded) water, and interlayer water; while in $(Np_{0.25}^{6+}U_{0.75}^{6+})$ -studiite, seven different oxygen types are unique: Np-bonded peroxide, U-bonded peroxide, neptunyl, uranyl, Np-bonded equatorial water, U-bonded equatorial water, and interlayer water. The increase in the number of unique O types is due to the change in the bonding environment for an O bonded to a U atom vs. an Np atom, which is primarily due to Np⁶⁺ having an extra unpaired 5f electron, while all of the U electrons are paired.



FIGURE 5. Comparison of the total DOS for studitic (solid curve) and $(Np_{0.25}^{6+}U_{0.75}^{6+})$ -studitic (dotted curve). Peak A has electron density contribution from the Np 5f orbital of the $(Np_{0.25}^{6+}U_{0.75}^{6+})$ -studitic and is located within energy region of the studitic band gap. The tail on the highest energy peak (B) is due to the split Np 5f peaks from the $(Np_{0.25}^{6+}U_{0.75}^{6+})$ -studitie.

From the PDOS, two main differences are observed between studtite and $(Np_{0.25}^{6+}U_{0.75}^{6+})$ -studtite (labeled in Fig. 5). Note that the difference in peak intensity between the spectra is not major, because the intensity is based on the number of electrons explicitly included in the calculation. The (Np_{0.25}U_{0.75})-studtite unit cell has one more valence electron than the studtite unit cell from the substitution of Np (Z = 93) for U (Z = 92), which increases the number of valence electrons explicitly included in the calculation from 280 to 281 total valence electrons in the unit cell. One major difference between the PDOS of studtite and $(Np_{0.25}^{6+}U_{0.75}^{6+})$ studtite is the width of the band gap. While the smallest width of the band gap for $(Np_{0.25}^{6+}U_{0.75}^{6+})$ -studtite is at the same point within Brillouin zone as for studtite (F k-point), the magnitude is smaller (1.09 eV) (Fig. 6). The electron contributions that occupy the energy states within the studtite band gap are from unoccupied Np 5f orbitals. Another major difference between studtite and $(Np_{0.25}^{6+}U_{0.75}^{6+})$ -studtite is the presence of a tail on the highest energy peak in the $(Np_{0.25}^{6+}U_{0.75}^{6+})$ -studtite PDOS due to the extra empty bands used in the $(Np_{0.25}^{6+}U_{0.75}^{6+})$ -studtite calculation for the spin optimization of the unpaired Np 5f electron (Fig. 5).

The subtle differences of the electronic structure caused by the incorporation of Np into the studtite structure are better understood through the comparison of the electron density contribution from Np, Np-neighboring U, and U-neighboring U, as well as the Np-bonded peroxide O and U-bonded peroxide O in the $(Np_{0.25}^{6+}U_{0.75}^{6+})$ -studtite structure (Figs. 7 and 8, respectively). The different contribution to the DOS in this region are best explained by considering the energy states between -10 and 5 eV, as the regions closest to the HOMO and LUMO levels are involved in electron transfer.

The main differences in the valence and conduction band are associated with the electron density contribution from the U and Np 5f orbitals. The differences in peak intensity are attributed to the number of total U and Np valence electrons. $(Np_{0.25}^{6+}U_{0.75}^{6+})$ -studite contains 3 U and 1 Np, which means that 42 U electrons and 15 Np valence electrons are calculated



FIGURE 6. Band structure showing the band gap of studitie ($E_{gap} = 2.29 \text{ eV}$) and ($Np_{0.25}^{+}U_{0.75}^{+}$)-studitie ($E_{gap} = 1.09 \text{ eV}$), where the letters (k-points) on the x-axis signify a point within the Brillouin zone, Γ (0, 0, 0); F (0, 0.5, 0); Q (0, 0.5, 0.5); Z (0, 0, 0.5).



FIGURE 7. PDOS of $(Np_{0.25}^{4}U_{0.75}^{4})$ -studtite highlighting the 5f orbital contribution from the Np in the peroxide chain, Np-neighboring U in the peroxide chain, and U-neighboring U in the peroxide chain, where the arrow points to the unoccupied Np 5f orbital that is in the studtite band gap.

explicitly. Therefore, an energy state with equal contributions from Np and U orbitals will appear to have a greater contribution from the U (both Np-neighboring and U-neighboring) by a ratio of 14:5. In the conduction band (0.5 and 2.0 eV), as well as in the top of the valence band (~ -0.5 eV), the major contributor to the electron density is the Np 5f orbital, which is the most significant difference between the Np⁶⁺ and U⁶⁺ electron density in the (Np⁶⁺₂₅U⁶⁺₂₅)-studtite bonding environment. Between 2 and



FIGURE 8. PDOS of $(Np_{0.25}^{6}U_{0.75}^{6})$ -studite highlighting the 2s and 2p orbital contribution from the Np-bonded and U-bonded peroxide oxygen, where the arrow points to the Np-bonded peroxide 2p contribution that is in the studite band gap.

4 eV, the U-neighboring U and Np-neighboring U 5f orbital has most of the density contribution, as evidenced from the single strong PDOS peak. In the same range, additional Np f-orbital peaks are observed due to the inclusion of more empty energy bands in the calculation. The extra empty bands were included to allow for the spin optimization due to the unpaired 5f electron of the Np⁶⁺ in the modified studtite structure.

The density contributions from the U-bonded O and the Npbonded O are similar at lower energy states, but show different behaviors in the conduction band. Between 0.5 and 2 eV, only the peroxide O linking the Np- and U-polyhedra contribute to the electron density, while the peroxide O linking two U-polyhedra do not (Fig. 8). This is the same energy state mentioned in the previous section, where the Np 5f orbital contributes to the partial density of states, while the U 5f orbital does not. The peroxide could be important for the control of the oxidation state of incorporated species. For example, the amount of Np incorporated into studtite has been experimentally determined; however, the oxidation state of the Np (5+ vs. 6+) was not determined (Douglas et al. 2005a). The oxidation of Np from 5+ to 6+ during incorporation into the studtite structure may be facilitated by the peroxide. The smaller band gap of $(Np_{0.25}^{6+}U_{0.75}^{6+})$ -studtite as compared with studtite, as evidenced from the Np-studtite DOS, indicates that less energy is needed to excite an electron from the valence band to the conduction band for Np-doped studtite, as compared with studtite. Thus, $(Np_{0.25}^{6+}U_{0.75}^{6+})$ -studtite may be more sensitive to redox conditions during bulk dissolution.

Thermodynamics of Np-incorporation into studtite

The incorporation energy for the substitution of one Np⁶⁺ for one U⁶⁺ or one Np⁵⁺ and H⁺ for one U⁶⁺ in studtite is the difference between the sum of the final enthalpies of the products minus the sum of the final enthalpies of the reactants from a stoichiometric reaction describing the incorporation mechanism (e.g., Eq. 2). The source for Np and sink for U are strategically chosen, as shown by the comparison using binary-oxide reference phases and hexafluoride reference phases (e.g., Table 3, Eqs. 1 and 5, respectively). The oxide reference phase sources for Np are NpO2 and Np₂O₅, while the sinks for U are UO₂ and UO₃, where Np is in the 4+ and 5+ oxidation state and U is in the 4+ and 6+ oxidation state. Incorporation reactions are balanced using appropriate amounts of O2 and, in the case of Np5+ incorporation, H2O. The difference between Np-incorporation energies for the cases in which the U sink is UO_3 and the Np source is either NpO₂ or Np_2O_5 (i.e., the difference between reactions 3 and 1 in Table 3) is equal to the enthalpy of formation of Np2O5 via the following reaction: NpO₂+O₂ $\rightarrow \frac{1}{2}$ Np₂O₅ (-0.49 eV). The formation of ¹/₂Np₂O₅ is favorable with respect to NpO₂ and ¹/₂O₂, which is supported by the synthesis of Np₂O₅ at low temperature from aqueous NpO₂⁺ on calcite crystals in O₂-saturated solutions (Forbes et al. 2007), as well as the formation of Np₂O₅ on NpO₂ films reacted with atomic oxygen (Seibert et al. 2009). In addition, the experimentally measured enthalpy of formation of Np₂O₅ is -2162.7 kJ/mol (-22.4 eV), which is significantly lower in energy than that of NpO₂ (-1074.0 kJ/mol; -11.1 eV) (Guillaumont et al. 2003). The measured enthalpy of formation of 1/2Np2O5 from NpO₂ and ¹/₂O₂ is -7.4 kJ/mol (Robie and Hemingway 1995), which is very different from the calculated results (-47.4 kJ/mol). The consideration of a few possible sources of error brings the values into better agreement. First, the enthalpy of formation of O₂ is 0; however, computationally, some enthalpy contributes to the formation equation described above because the energy of O_2 in a box is that of $O^0 + O^0 \rightarrow O_2$. Thus, a PdV term for the O₂ (2.2 kJ/mol) can be added to the experimental value. In addition, Np₂O₅ was calculated with an antiferromagnetic spin configuration, which was 10.6 kJ/mol more energetically favorable than the ferromagnetic spin configuration. Magnetic susceptibility data for polycrystalline Np2O5 indicate a transition from antiferromagnetic to ferromagnetic coupling of the Np moments at ~22 K and a subsequent transition from ferromagnetic to paramagnetic above 50 K. Thus, the Np₂O₅ spin configuration would have been paramagnetic for the experimental enthalpy measurement. Finally, the Np₂O₅ used for enthalpy measurements may not have had high crystallinity (Lemire et al. 2001), which could account for other differences between the computational and experimental enthalpy of formation.

Similarly, the difference between incorporation energies for the cases in which the Np source is Np₂O₅ and the U sink is either UO₂ or UO₃ is equal to the enthalpy of formation of the following reaction: UO₂ + $\frac{1}{2}O_2 \rightarrow$ UO₃. The measured enthalpy of formation of UO₃ from UO₂ and $\frac{1}{2}O_2$ is -138.9 kJ/mol (Robie and Hemingway 1995), which is in relatively good agreement with the calculated results (-179.9 kJ/mol).

The hexafluoride reference phase used for Np⁶⁺ is NpF₆, while the corresponding sink for U⁶⁺ is UF₆, which is commonly used to manufacture nuclear fuel. Both UF₆ and NpF₆ are orthorhombic (*Pnma*), with slightly varying unit-cell pa-

 TABLE 3.
 Incorporation equations and energies for Np⁶⁺ in studtite with various reference phases

_						
Reactants		\leftrightarrow	Products	<i>E</i> (eV)		
1	studtite+1/2Np2O5+1/4O2	\leftrightarrow	(studtite-U ⁶⁺ +Np ⁶⁺)+UO ₃	0.42		
2	studtite+½Np₂O₅	\leftrightarrow	(studtite-U ⁶⁺ +Np ⁶⁺)+UO ₂ +1/4O ₂	2.28		
3	studtite+NpO ₂ +1/2O ₂	\leftrightarrow	(studtite–U ⁶⁺ +Np ⁶⁺)+UO ₃	-0.07		
4	studtite+NpO ₂	\leftrightarrow	(studtite-U ⁶⁺ +Np ⁶⁺)+UO ₂	1.79		
5	studtite+NpF ₆	\leftrightarrow	(studtite–U ⁶⁺ +Np ⁶⁺)+UF ₆	-0.10		

rameters, thus the chemistry and bonding environment for both phases are similar; therefore, the energy difference between the two is primarily due to the additional 5f electron of Np. The hexafluoride phases, however, are molecular crystals, and quantum-mechanical density functional theory calculations do not capture the van der Waals bonding in molecular crystals very accurately. The optimized unit-cell parameters of the bulk hexafluoride structures are ~10% greater than the experimentally determined unit-cell parameters.

The relative stability of the cation reference phases (i.e., source for Np and sink for U) affects the final incorporation energy significantly. The lowest incorporation energy is observed for the balanced equation in which the actinide source phase is the least stable with respect to other possible reference phases. For example, the incorporation energy calculated with NpO₂ is lower than the incorporation energy calculated with Np2O₅ because NpO₂ (and O₂) is less stable with respect to Np2O₅; thus, it is easier to incorporate the Np from NpO₂ into studtite. Similarly, the incorporation energy calculated with UO₃ is lower than the incorporation energy calculated with UO₃ is lower than the incorporation energy calculated with UO₃ is lower than the incorporation energy calculated with UO₃ is lower than the incorporation energy calculated with UO₃ is lower than the incorporation energy calculated with UO₃ is lower than the incorporation energy calculated with UO₃ is lower than the incorporation energy calculated with UO₃ is lower than the incorporation energy calculated with UO₃ is lower than the incorporation energy calculated with UO₃ is lower than the incorporation energy calculated with UO₃ is lower than the incorporation energy calculated with UO₃ as a sink for U is favored.

The incorporation energy of Np⁶⁺ into the studite structure, based on the hexafluoride reference phases, is -0.10 eV (-9.65 kJ/ mol; Table 3, Eq. 5), while the incorporation energy of Np⁶⁺ into the studite structure based on the binary oxide reference phases is -0.07 eV (-6.75 kJ/mol; Table 3, Eq. 1). The more negative incorporation energy associated with the hexafluoride reference phases is in part due to the instability of NpF₆ in comparison to UF₆. The standard enthalpy of formation for NpF₆ (-1970 kJ/mol) is less negative than that of UF₆ (-2317 kJ/mol), indicating that more energy is necessary for the formation of NpF₆ (Lemire et al. 2001). The instability of NpF₆ as compared to UF₆ drives the incorporation equation, resulting in a more negative incorporation energy for Np in studite using the hexafluoride reference phases; however, the presence of such hexafluoride reference phases in a geologic repository is unlikely.

Most of the incorporation energies for the binary oxide and hexafluoride reference phases are outside the range of the other common substitution processes where charge and ionic radius are comparable. For example, the exchange energetics for Cs/K exchange in muscovite ranges from -5.3 to 15.4 kJ/mol, depending on the mechanism for cation exchange (Rosso et al. 2001). However, the NpO₂/UO₃ reference phase case results in a reasonably negative incorporation energy (-0.07 eV; -6.89 kJ/mol).

The same reference phases were used to determine the energy needed to incorporate Np⁵⁺ into studitie (Table 4). The chargebalancing mechanism was the coupled substitution of Np⁵⁺ and OH⁻ for U⁶⁺ and O²⁻. The substitution of OH⁻ for O²⁻ is achieved by adding an H⁺ atom bonded to an O²⁻ within the studite structure. As previously detailed, the thermodynamically favorable position for the additional H⁺ atom is bonded to the axial O²⁻. The same energy trends between the different reference phase cases are observed for Np⁵⁺ incorporation as for Np⁶⁺ incorporation. The incorporation energy of Np⁵⁺ into the studite structure, based on the hexafluoride reference phases, is 0.60 eV (57.43 kJ/ mol; Table 4, Eq. 5), and the incorporation energy of Np⁵⁺ into the studite structure based on the binary oxide reference phases

 TABLE 4.
 Incorporation equations and energies for Np⁵⁺ in studtite with various reference phases

_			•	
Reactants		\rightarrow	Products	E(eV)
1	studtite+1/2Np2O5+1/2H2O	\rightarrow	(studtite-U ⁶⁺ +Np ⁵⁺ +H ⁺)+UO ₃	1.12
2	studtite+ ½Np ₂ O ₅ +½H ₂ O	\rightarrow	(studtite-U ⁶⁺ +Np ⁵⁺ +H ⁺)+UO ₂ +1/ ₂ O ₂	2.98
3	studtite+NpO ₂ +1/4O ₂ +1/2H ₂ O	\rightarrow	(studtite–U ⁶⁺ +Np ⁵⁺ +H ⁺)+UO ₃	0.63
4	studtite+NpO ₂ +½H ₂ O	\rightarrow	(studtite-U ⁶⁺ +Np ⁵⁺ +H ⁺)+UO ₂ +1/4O ₂	2.49
5	studtite+NpF ₆ +1/ ₂ H ₂ O	\rightarrow	$(studtite - U^{6+} + Np^{5+} + H^{+}) + UF_{6} + \frac{1}{4}O_{2}$	0.60

(i.e., NpO₂ and UO₃) is 0.63 eV (60.79 kJ/mol; Table 4, Eq. 1). The difference between incorporation energy for the Np⁵⁺ and Np⁶⁺ cases is 0.70 eV (67.54 kJ/mol). Thus, Np⁶⁺ incorporation is favored over Np⁵⁺ in studtite.

Thermodynamic properties of the (U,Np)-studtite solid solution

Thermodynamic properties of the (U,Np)-studtite solid solution are calculated to estimate incorporation limits as a function of incorporation temperature. Enthalpies of mixing are based on the relative energy of different cation compositions and configurations with the U and Np-studtite phases as reference points. Different enthalpies of mixing for the same composition are due to different structural arrangements of the cations. For example, the relative enthalpies of mixing for 50:50 compositions range from -0.18 kJ/(mol exchangeable cation) to 0.68 kJ/(mol exchangeable cation), where the negative enthalpies of mixing correspond to configurations in which the exchanged cations are in the same actinyl chain along the [001] zone axis. The positive enthalpies of mixing correspond to configurations in which the cation exchange occurs along the [110] and [111] zone axes. The interaction parameters and Margules parameters are fit to all configurations and compositions from the quantummechanical calculations. The Margules parameters for this system are $m_1 = 2.75$ kJ/(mol exchangeable cation) and $m_2 = -0.65$ kJ/(mol exchangeable cation). The interaction parameters are J_1 = 0.0486 kJ/(mol U-Np interaction), J_2 = 0.0004 kJ/(mol U-Np interaction), and $J_3 = -0.0253 \text{ kJ/(mol U-Np interaction)}$, where J_1 describes nearest-neighbor interactions along the [001], J_2 along the [110], and J_3 along the [111]. Positive J values indicate that homocationic interactions are favored, while negative J values indicate that heterocationic interactions are favored. Thus, the (Np⁶⁺,U⁶⁺)-studtite solid solution favors the same cations along the [001] and different cations along the [111]. The Margules and interaction parameters are on the same order of magnitude as the (Hf,Zr)SiO₄ series, which is a complete solid solution (Ferriss et al. 2009). The absolute value of the enthalpy of mixing for any composition or configuration of this solid solution is similar to the enthalpies of mixing for the complete (Hf,Zr) SiO₄ solid solution, but small relative to other incomplete solid solutions, such as (U,Zr)SiO₄ solid solution (Ferriss et al. 2009). The contribution of the excess enthalpy of mixing to the free energy of mixing is small as compared with the contribution of -temperature (-T) times the configurational entropy for all temperatures calculated (333–3000 K); thus, the free energy of mixing is negative for all compositions of the solid solution (Fig. 9), indicating complete solid solution.

Although the incorporation energy of Np⁶⁺ into studtite is positive for the oxide reference phases, the thermodynamically stable limit of Np⁶⁺-incorporation into studtite based on the full



FIGURE 9. Enthalpy of mixing [kJ/(mol exchangeable cation)], configurational entropy of mixing [kJ/(K mol exchangeable cation)], and Gibbs free energy of mixing [kJ/(mol exchangeable cation)] vs. concentration of Np for (Np⁶⁺,U⁶⁺)-studtite solid solution. The quantum-mechanical and Monte-Carlo results are overlaid for the enthalpy of mixing. The configurational entropy of mixing is close to the point entropy, which indicates that the system does not order.

solid-solution analysis indicates that Np⁶⁺ is completely miscible in studtite, assuming that there is a fully substituted studtite (Np⁶⁺-studtite) that is isostructural with the U⁶⁺-studtite. Both studtite and Np⁶⁺-studtite are stable with respect to their oxide components (Table 5). The components used for this analysis include crystalline hydrogen peroxide (Abrahams et al. 1951), cubic ice, O₂ molecule in a $10 \times 10 \times 10$ Å box, UO₃ (Loopstra et al. 1977), and Np₂O₅ (Forbes et al. 2007). The negative formation energy for Np⁶⁺-studtite indicates the possibility for mineral formation; however, there are potential kinetic hindrances for the formation of Np⁶⁺-studtite. The formation of Np⁶⁺-studtite

TABLE 5. Enthalpy of formation from the oxide components for studtite, Np⁶⁺-studtite, UO₃, and NpO₃, where the formation of NpO₃ from NpO₂ is compared with the formation from Np₂O₅

non npozio compared marine remation nepzos				
Reactants	\leftrightarrow	Products	$\Delta H_{\rm f} (\rm eV)$	
UO ₃ +H ₂ O ₂ +3H ₂ O	\leftrightarrow	studtite	-0.77	
$\frac{1}{2}Np_{2}O_{5}+H_{2}O_{2}+3H_{2}O+\frac{1}{4}O_{2}$	\leftrightarrow	Np ⁶⁺ -studtite	-0.35	
$UO_2 + \frac{1}{2}O_2$	\leftrightarrow	UO ₃	-1.86	
NpO ₂ +½O ₂	\leftrightarrow	NpO ₃	-0.19	
¹ / ₂ Np ₂ O ₅ + ¹ / ₄ O ₂	\leftrightarrow	NpO ₃	0.30	
NpO ₂ +¼O ₂	\leftrightarrow	1/2Np2O5	-0.49	
	<			

Notes: The formation of Np₂O₃ from NpO₂ is also listed for comparison. Hydrogen peroxide and water were calculated in their solid crystalline state. NpO₃ was constructed using the *Fddd* UO₃ structure. Gaseous O₂ is necessary to oxidize the Np⁵⁺ in the formation of Np⁶⁺-studtite.

requires the oxidation of Np either in solution or in the solid state. The oxidation of aqueous Np⁵⁺, which is the dominate oxidation state in solution, to Np⁶⁺ requires highly oxidizing conditions (Silva and Nitsche 1995; Kaszuba and Runde 1999; Choppin 2007).

The formation energies of Np₂O₅ and NpO₃ were compared to understand possible kinetic hindrances in the solid state. While Np₂O₅ is the oxide with the highest Np oxidation state (Forbes et al. 2007; Seibert et al. 2009), the formation energy of NpO₃ with the UO₃ (Fddd) structure was calculated for comparison. From the Np⁴⁺-oxide (NpO₂) and oxygen, the formation of NpO₃ is energetically favored, while from the Np⁵⁺-oxide (Np₂O₅) and oxygen, the formation of NpO₃ is not energetically favorable. The formation Np₂O₅ from NpO₂ and oxygen is more thermodynamically favorable than the formation of NpO₃ from the same reactants (Table 5). Thus, an energy barrier exists to oxidizing NpO_2 to NpO_3 via Np_2O_5 . This energy barrier may be the reason that Np⁶⁺-studtite has not been synthesized. Thus, the complete miscibility of Np6+ in studtite is wholly based on the assumption of the formation of an Np6+-studtite end-member, which is probably kinetically hindered.

ACKNOWLEDGMENTS

The authors acknowledge support from the Office of Basic Energy Sciences (Grant DE FG02 06ER15783). L.C.S. also thanks the Department of Energy for the Office of Civilian and Radioactive Waste Management Graduate Fellowship. R.C.E. was supported as part of the Materials Science of Actinides, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001089. Computational resources were provided by the NSF-NIRT grant (EAR-0403732).

REFERENCES CITED

- Abrahams, S.C., Collin, R.L., and Lipscomb, W.N. (1951) The crystal structure of hydrogen peroxide. Acta Crystallographia, 4, 15–19.
- Abrefah, J., Marschmann, S., and Jenson, E.D. (1998) Examination of the surface coatings removed from K-East Basin fuel elements. Pacific Northwest National Laboratory Report 14856. Pacific Northwest National Laboratory, Richland, Washington.
- Amme, M. (2002) Contrary effects of the water radiolysis product H₂O₂ upon the dissolution of nuclear fuel in natural ground water and deionized water. Radiochimica Acta, 90, 399–406.
- Anisimov, V.I., Aryasetiawan, F., and Lichtenstein, A.I. (1997) First-principles calculations of the electronic structure and spectra of strongly correlated systems: The LDA+U method. Journal of Physics-Condensed Matter, 9, 767–808.
- Barner, J.O. (1985) Characterization of LWR spent fuel MCC—Approved testing material—ATM-101. Pacific Northwest National Laboratory Report 5109. Pacific Northwest National Laboratory, Richland, Washington.
- Becker, U. and Pollok, K. (2002) Molecular simulations of interfacial and thermodynamic mixing properties of grossular-andradite garnets. Physics and Chemistry of Minerals, 29, 52–64.
- Becker, U., Fernandez-Gonzalez, A., Prieto, M., Harrison, R., and Putnis, A. (2000) Direct calculation of thermodynamic properties of the barite/celestite solid solution from molecular principles. Physical Chemical Mineralogy, 27, 291–300.

Bosenick, A., Dove, M.T., Myers, E.R., Palin, E.J., Sainz-Diaz, C.I., Guiton, B.S., Warren, M.C., Craig, M.S., and Redfern, S.A.T. (2001) Computational methods for the study of energies of cation distribution: applications to cation-ordering phase transitions and solid solutions. Mineralogy Magazine, 65, 193–219.

Bruno, J. and Ewing, R.C. (2006) Spent nuclear fuel. Elements, 2, 343-349.

- Buck, E.C., Finch, R.J., Finn, P.A., and Bates, J.K. (1997) Retention of neptunium in uranyl alteration phases formed during spent fuel corrosion. In I.G. McKinley and C. McCombie, Eds., 21st International Symposium on the Scientific Basis for Nuclear Waste Management, p. 87–94. Materials Research Society, Davos, Switzerland.
- Burns, P.C. and Hughes, K.A. (2003) Studite, [(UO₂)(O₂)(H₂O)₂](H₂O)₂: The first structure of a peroxide mineral. American Mineralogist, 88, 1165–1168.
- Burns, P.C., Ewing, R.C., and Hawthorne, F.C. (1997) The crystal chemistry of hexavalent uranium: Polyhedron geometries, bond-valence parameters, and polymerization of polyhedra. Canadian Mineralogist, 35, 1551–1570.
- Burns, P.C., Deely, K.M., and Skanthakumar, S. (2004) Neptunium incorporation into uranyl compounds that form as alteration products of spent nuclear fuel: Implications for geologic repository performance. Radiochimica Acta, 92, 151–159.
- Burns, P.C., Kubatko, K.A., Sigmon, G., Fryer, B.J., Gagnon, J.E., Antonio, M.R., and Soderholm, L. (2005) Actinyl peroxide nanospheres. Angewandte Chemie International Edition, 44, 2135–2139.
- Cejka, J., Sejkora, J., and Deliens, M. (1996) New data on studtite, UO₄·4H₂O, from Shinkolobwe, Shaba, Zaire. Neues Jahrbuch für Mineralogie-Monatshefte, 125–134.
- Choppin, G.R. (2007) Actinide speciation in the environment. Journal of Radioanalytical and Nuclear Chemistry, 273, 695–703.
- Debets, P.C. (1963) X-ray diffraction data on hydrated uranium peroxide. Journal of Inorganic and Nuclear Chemistry, 25, 727–730.
- Douglas, M., Clark, S.B., Friese, J.I., Arey, B.W., Buck, E.C., and Hanson, B.D. (2005a) Neptunium(V) partitioning to uranium(VI) oxide and peroxide solids. Environmental Science and Technology, 39, 4117–4124.
- Douglas, M., Clark, S.B., Friese, J.I., Arey, B.W., Buck, E.C., Hanson, B.D., Utsunomiya, S., and Ewing, R.C. (2005b) Microscale characterization of uranium(VI) silicate solids and associated neptunium(V). Radiochimica Acta 93. 265–272.
- Ferriss, E.D.A., Essene, E.J., and Becker, U. (2008) Computational study of the effect of pressure on the Ti-in-zircon geothermometer. European Journal of Mineralogy, 20, 745–755.
- (2009) Simulation of thermodynamic mixing properties of actinide-containing zircon solid solutions. American Mineralogist, 95, 229–241.
- Finch, R.J. and Ewing, R.C. (1992) The corrosion of uraninite under oxidizing conditions. Journal of Nuclear Materials, 190, 133–156.
- Forbes, T.Z., Burns, P.C., Skanthakumar, S., and Soderholm, L. (2007) Synthesis, structure, and magnetism of Np₂O₅. Journal of the American Chemical Society, 129, 2760–2761.
- Fortner, J.A., Finch, R.J., Kropf, A.J., and Cunnane, J.C. (2004) Re-evaluating neptunium in uranyl phases derived from corroded spent fuel. Nuclear Technology, 148, 174–180.
- Guillaumont, R., Fanghanel, T., Fuger, J., Grenthe, I., Neck, V., Palmer, D.A., and Rand, M.H. (2003) Update on Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium, and Technetium. Elsevier, Amsterdam.
- Gupta, F., Brillant, G., and Pasturel, A. (2007) Correlation effects and energetics of point defects in uranium dioxide: a first principle investigation. Philosophical Magazine, 87, 2561–2569.
- Hanson, B., McNamara, B., Buck, E., Friese, J., Jenson, E., Krupka, K., and Arey, B. (2005) Corrosion of commercial spent nuclear fuel. 1. Formation of studite and metastudite. Radiochimica Acta, 93, 159–168.
- Kaszuba, J.P. and Runde, W.H. (1999) The aqueous geochemistry of neptunium: Dynamic control of soluble concentrations with applications to nuclear waste disposal. Environmental Science and Technology, 33, 4427–4433.
- Klingensmith, A.L., Deely, K.M., Kinman, W.S., Kelly, V., and Burns, P.C. (2007) Neptunium incorporation in sodium-substituted metaschoepite. American Mineralogist, 92, 662–669.
- Kubatko, K.A. and Burns, P.C. (2006) Expanding the crystal chemistry of actinyl peroxides: Open sheets of uranyl polyhedra in Na₅[(UO₂)₃(O₂)₄(OH)₃](H₂O)₁₃. Inorganic Chemistry, 45, 6096–6098.
- Kubatko, K.A.H., Helean, K.B., Navrotsky, A., and Burns, P.C. (2003) Stability of peroxide-containing uranyl minerals. Science, 302, 1191–1193.
- Kubatko, K.A., Forbes, T.Z., Klingensmith, A.L., and Burns, P.C. (2007) Ex-

panding the crystal chemistry of uranyl peroxides: Synthesis and structures of Di- and triperoxodioxouranium(VI) complexes. Inorganic Chemistry, 46, 3657–3662.

- Lemire, R.J., Fuger, J., Nitsche, H., Potter, P.E., Rand, M.H., Rydberg, J., Spahiu, K., Sullivan, J.C., Ullman, W.J., Vitorge, P., and Wanner, H. (2001) Chemical Thermodynamics of Neptunium and Plutonium, 4, 872 p. Chemical Thermodynamics, Elsevier, Amsterdam.
- Loopstra, B.O., Taylor, J.C., and Waugh, A.B. (1977) Neutron powder profile studies of the gamma uranium trioxide phases. Journal of Solid State Chemistry, 20, 9–19.
- Malkova, N.N., Matyukha, V.A., Afanaseva, T.V., and Krot, N.N. (1986) Reduction of Np(V) by hydrogen-peroxide in the presence of oxalic-acid. Soviet Radiochemistry, 28, 294–300.
- McNamara, B., Hanson, B., Buck, E., and Soderquist, C. (2005) Corrosion of commercial spent nuclear fuel. 2. Radiochemical analyses of metastudtite and leachates. Radiochimica Acta, 93, 169–175.
- Ostanin, S. and Zeller, P. (2007) Ab initio study of uranyl peroxides: Electronic factors behind the phase stability. Physical Review B, 75, 073101.
- Payne, M.C., Teter, M.P., Allan, D.C., Arias, T.A., and Joannopoulos, J.D. (1992) Iterative minimization techniques for abinitio total-energy calculations— Molecular-dynamics and conjugate gradients. Reviews of Modern Physics, 64, 1045–1097.
- Perdew, J.P., Burke, K., and Ernzerhof, M. (1996) Generalized gradient approximation made simple. Physical Review Letters, 77, 3865–3868.
- Reich, M. and Becker, U. (2006) First-principles claculations of the thermodynamic mixing properties of arsenic incorporation into pyrite and marcasite. Chemical Geology, 225, 278–290.
- Robie, R.A. and Hemingway, B.S. (1995) Thermodynamic properties of minerals and related substances at 298.15 K and 1 Bar (105 Pascals) pressure and at higher temperatures. U.S. Geological Survey Bulletin No. 2131, Washington, D.C.
- Rosso, K.M., Rustad, J.R., and Bylaska, E.J. (2001) The Cs/K exchange in muscovite interlayers: An ab initio treatment. Clays and Clay Minerals, 49, 500–513.
- Segall, M.D., Lindan, P.J.D., Probert, M.J., Pickard, C.J., Hasnip, P.J., Clark, S.J., and Payne, M.C. (2002) First-principles simulation: ideas, illustrations and the CASTEP code. Journal of Physics-Condensed Matter, 14, 2717–2744.
- Seibert, A., Gouder, T., and Huber, F. (2009) Reaction of neptunium with molecular and atomic oxygen: Formation and stability of surface oxides. Journal of Nuclear Materials, 389, 470–478.
- Shilov, V.P., Gogolev, A.V., and Pikaev, A.E. (1998) The formation of neptunium peroxo complexes upon reduction of neptunium(VI) by hydrogen peroxide in concentrated solutions of alkalis. Mendeleev Communications, 6, 220–222.
- Silva, R.J. and Nitsche, H. (1995) Actinide environmental chemistry. Radiochimica Acta, 70–71, 377–396.
- Skomurski, F.N., Ewing, R.C., Rohl, A.L., Gale, J.D., and Becker, U. (2006) Quantum mechanical vs. empirical potential modeling of uranium dioxide (UO₂) surfaces: (111), (110), and (100). American Mineralogist, 91, 1761–1772.
- Walenta, K. (1973) Studite and its composition. American Mineralogist, 59, 166–171.
- Wronkiewicz, D.J., Bates, J.K., Gerding, T.J., Veleckis, E., and Tani, B.S. (1992) Uranium release and secondary phase formation during unsaturated testing of UO₂ at 90 °C. Journal of Nuclear Materials, 190, 107–127.
- Wronkiewicz, D.J., Bates, J.K., Wolf, S.F., and Buck, E.C. (1996) Ten-year results from unsaturated drip tests with UO₂ at 90 °C: Implications for the corrosion of spent nuclear fuel. Journal of Nuclear Materials, 238, 78–95.
- Yeomans, J.M. (1992) Statistical Mechanics of Phase Transitions, 164 p. Oxford Science Publications, Clarendon Press, Oxford.

MANUSCRIPT RECEIVED JANUARY 6, 2010 MANUSCRIPT ACCEPTED APRIL 27, 2010 MANUSCRIPT HANDLED BY HONGWU XU