Temperature Dependent Gibbs Free Energies of Reaction of Uranyl Containing Materials Based on Density Functional Theory

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ABSTRACT

The thermodynamic properties of uranyl containing materials including dehydrated schoepite, metastudtite, studtite, soddyite, rutherfordine and $\gamma - \text{UO}_3$, determined by means of density functional theory using a new norm-conserving pseudopotential for uranium atom in previous works, were used to obtain the enthalpies and Gibbs free energies of eight reactions involving these materials and its variation with the temperature. The first five reactions represent the formation of the first five considered materials in terms of the corresponding oxides, and the remaining reactions are the transformations of rutherfordine into dehydrated schoepite, studtite into metastudtite and uranium trioxide into triuranium octoxide, respectively. The experimental values of the enthalpies of these reactions, which are only known at the standard state (temperature of 298.15 K and pressure of 1 bar), were reproduced accurately by these calculations, the errors being 2.5, 2.5, 0.2, 0.0, 12.3, -1.1, 0.9 and 4.0 $\text{kJ} \cdot \text{mol}^{-1}$, respectively. These calculations predict that soddyite is stable with respect to the corresponding oxides at all the temperatures considered (280 to 500 K), and that studtite and metastudtite are unstable. However, dehydrated schoepite and rutherfordine are stable for temperatures lower than $462.5 \pm 16.7 \text{ K}$ and $513.7 \pm 35.8 \text{ K}$, respectively, and become unstable for higher temperatures. The relative stability of the uranyl peroxide hydrates, studtite and metastudtite, with respect to $\gamma - \text{UO}_3$, dehydrated schoepite, rutherfordine and soddyite in the presence of water and hydrogen peroxide was also studied by considering the corresponding reactions. The experimental values of the enthalpies of two of these reactions, those relating studtite and metastudtite with $\gamma - \text{UO}_3$ in the presence of water and hydrogen peroxide, which are only known at the standard state, were theoretically very well reproduced (within 0.1 $\text{kJ} \cdot \text{mol}^{-1}$). From the results, we conclude that metastudtite and studtite become stable phases at low temperatures in the presence of water and small amounts of hydrogen peroxide. However, the stability of the studtite phase decreases rapidly when the temperature increases. Finally, the relative stability of these phases in the

presence of very high concentrations of hydrogen peroxide was evaluated. The results show that in this case, occurring under very intense radiation fields causing radiolysis of most of the water present, studtite is by far the most stable phase within the full range of temperature studied.

KEYWORDS

Uranyl containing materials, Thermodynamic properties, Enthalpies of reaction, Free energies of reaction, DFT.

I. INTRODUCTION

The performance of a geologic nuclear waste repository will be influenced by the interaction between the spent nuclear fuel (SNF) and the environment in which it will be placed. The expected weathering of SNF under oxidizing conditions will likely result in the formation of uranyl secondary mineral phases¹⁻³ and, consequently, the formation and stability of uranyl minerals will impact the release of U(VI) and other actinide elements from the waste package, and potentially also from the repository to the environment.^{1,4}

Uranyl secondary phases are usually studied by analyzing natural minerals containing the uranyl ion, $\text{U}^{\text{VI}}\text{O}_2^{2+}$, found as alteration products of uraninite,⁵ which is a natural analogue of the SNF matrix. The general trend of the temporal sequence of alteration products of natural uraninites at different geochemical conditions was first recognized by Frondel,⁶⁻⁷ and it is still widely accepted nowadays.^{1,5,8-10} In this sequence, the uranyl oxide hydrates appear at the first place, then the uranyl silicates and, less frequently, the uranyl phosphates; although the specific alteration products depend on the local conditions. Carbonate and bicarbonate, present in significant concentrations in many natural waters, are exceptionally strong complexing agents for actinide ions¹¹ and, therefore, carbonate complexes of actinide ions play an important role in

migration from a nuclear waste repository or in accidental site contamination. Uranyl carbonates may precipitate where evaporation is significant and the partial pressure of CO_2 is large.³ Studtite and metastudtite are the only known uranyl peroxide phases and are very important alteration products of the spent nuclear fuel due to the production of hydrogen peroxide resulting from the radiolysis of water due to the ionizing radiation of the SNF.¹²⁻²⁰ Therefore, the study of all these types of uranyl minerals, is very important for understanding the long-term performance of a geological repository for nuclear waste.

In order to predict the stability and solubility of uranyl minerals as a function of solution composition and temperature, it is necessary to know the Gibbs free energy, enthalpy and entropy of formation for each phase of interest and their variation with temperature. The release of uranium from geologic nuclear waste repositories under oxidizing conditions, as well as the mobility of uranium in the environment can only be modeled if the thermodynamic properties of the secondary uranyl minerals that form in the repository setting are known. Therefore, these thermodynamic parameters are crucial for predicting repository performance.²¹⁻²³ However, despite the potential importance of these properties, reliable temperature dependent thermodynamic data are completely lacking for most of the uranyl containing materials and the development of a complete thermodynamic database for these minerals is mandatory.

In this work, the thermodynamic properties of uranyl containing materials including dehydrated schoepite ($\text{UO}_2(\text{OH})_2$), metastudtite ($(\text{UO}_2)_2\text{O}_2 \cdot 2\text{H}_2\text{O}$), studtite ($(\text{UO}_2)_2\text{O}_2 \cdot 4\text{H}_2\text{O}$), soddyite ($(\text{UO}_2)_2(\text{SiO}_4) \cdot 2\text{H}_2\text{O}$), rutherfordine (UO_2CO_3) and gamma uranium trioxide ($\gamma\text{-UO}_3$), determined by means of density functional theory using plane waves and pseudopotentials²⁴ in previous works,²⁵⁻³¹ were used in order to obtain the enthalpies and free energies of eight reactions involving these materials:

- (A) $(\text{UO}_2)_2(\text{SiO}_4) \cdot 2\text{H}_2\text{O} (\text{cr}) \rightarrow 2 \text{UO}_3 (\text{cr}) + \text{SiO}_2 (\text{cr}) + 2 \text{H}_2\text{O} (\text{l})$
- (B) $\text{UO}_2(\text{OH})_2 (\text{cr}) \rightarrow \text{UO}_3 (\text{cr}) + \text{H}_2\text{O} (\text{l})$
- (C) $(\text{UO}_2)_2\text{O}_2 \cdot 4\text{H}_2\text{O} (\text{cr}) \rightarrow \text{UO}_3 (\text{cr}) + 4 \text{H}_2\text{O} (\text{l}) + 1/2 \text{O}_2 (\text{g})$
- (D) $(\text{UO}_2)_2\text{O}_2 \cdot 2\text{H}_2\text{O} (\text{cr}) \rightarrow \text{UO}_3 (\text{cr}) + 2 \text{H}_2\text{O} (\text{l}) + 1/2 \text{O}_2 (\text{g})$
- (E) $\text{UO}_2\text{CO}_3 (\text{cr}) \rightarrow \text{UO}_3 (\text{cr}) + \text{CO}_2 (\text{g})$
- (F) $\text{UO}_2\text{CO}_3 (\text{cr}) + \text{H}_2\text{O} (\text{g}) \rightarrow \text{UO}_2(\text{OH})_2(\text{cr}) + \text{CO}_2(\text{g})$
- (G) $(\text{UO}_2)_2\text{O}_2 \cdot 4 \text{H}_2\text{O} (\text{cr}) \rightarrow (\text{UO}_2)_2\text{O}_2 \cdot 2\text{H}_2\text{O} (\text{cr}) + 2 \text{H}_2\text{O} (\text{l})$
- (H) $\text{UO}_3(\text{cr}) \rightarrow 1/3 \text{U}_3\text{O}_8 (\text{cr}) + 1/6 \text{O}_2 (\text{g})$

The first five reactions represent the formation of the considered materials in terms of the corresponding oxides, and reactions (F) to (H) are the transformations of rutherfordine into dehydrated schoepite, studtite into metastudtite and uranium trioxide into triuranium octoxide, respectively. A simple view to reactions (A) to (E) shows that the precise knowledge of the thermodynamic properties of uranium trioxide²⁸ is completely needed for the determination of the thermodynamic properties of formation of uranyl containing materials. The experimental values of the enthalpies of these reactions are known only at the standard state (temperature of 298.15 K and pressure of 1 bar) and the computations reported here have permitted to determine the corresponding enthalpies, free energies and reaction constants in a wide range of temperatures.

Once the thermodynamic properties of the reactions of formation of these materials in terms of the oxides were determined, the relative stability the uranyl peroxide hydrates, studtite and metastudtite, with respect to $\gamma - \text{UO}_3$, dehydrated schoepite, rutherfordine and soddyite in the

presence of water and hydrogen peroxide was studied by considering the corresponding reactions:

For these reactions, the unique values known for the enthalpies of reaction are those of the reactions relating studtite (I) and metastudtite (J) with $\gamma - \text{UO}_3$ in the presence of water and hydrogen peroxide at 298.15 K, which were reported by Kubatko *et al.*¹⁵ and Guo *et al.*,¹⁸ respectively.

Finally, the relative stability of these phases in the presence of very high concentrations of hydrogen peroxide and absence of water was studied by evaluating the free energies of the reactions relating metastudtite, uranium trioxide, dehydrated schoepite and soddyite with studtite in the presence of hydrogen peroxide:

These reactions are extraordinarily important since they are expected to occur when these materials are in contact with water exposed to very intense radiation fields causing radiolysis of most of the water present. However, despite of its importance, these reactions have not been studied in detail experimentally and, as far as we know, the corresponding experimental values of the enthalpies and free energies of reaction have not been reported.

These results extend a previous work,³¹ in which the enthalpies and free energies of formation in terms of the elements were successfully determined as a function of temperature, thus confirming that the use of theoretical methods is a safe and accurate method for the determination of the thermodynamic properties of uranyl containing materials. In fact, they open the access to the determination of the temperature dependence of the thermodynamic properties of these materials, this feature being an extraordinarily difficult task from the experimental point of view. These temperature dependent properties are a key parameter for the performance assessment of radioactive waste repositories because the stability of the secondary phases of the spent nuclear fuel under final geological disposal conditions is shown to be highly dependent of the temperature.

II. METHODS

The free-energies and enthalpies of reaction at different temperatures were obtained, using our calculated free energy and entropy of formation functions,³¹ $\Delta_f G(T)^{calc}$ and $\Delta_f S(T)^{calc}$, by means of the expressions:³²

$$\Delta_r G(T) = \sum_i^{products} n_i \Delta_f G^i(T) - \sum_j^{reactants} n_j \Delta_f G^j(T) \quad (1)$$

$$\Delta_r H(T) = \Delta_r G(T) + T \cdot \Delta_r S(T) \quad (2)$$

where,

$$\Delta_r S(T) = \sum_i^{products} n_i \Delta_f S^i(T) - \sum_j^{reactants} n_j \Delta_f S^j(T) \quad (3)$$

In these equations, $\Delta_f G^i(T)$ and $\Delta_f S^i(T)$, are the free energy and entropy of formation at temperature T (and pressure of 1 bar) of compound i entering in the reaction with stoichiometric coefficient n_i . The specific values used of these properties for dehydrated schoepite, metastudtite, studtite, soddyite, rutherfordine and $\gamma - \text{UO}_3$ were determined in a previous work.³¹ For triuranium octoxide, U_3O_8 (cr), the free energy and entropy of formation functions were taken from the experimental work of Hemingway.³³ The corresponding data for SiO_2 (cr), H_2O (l), O_2 (g) and CO_2 (g) were taken from JANAF tables,³² and the data for H_2O_2 (l) were taken from Barin.³⁴ The reaction equilibrium constants were determined in terms of the corresponding free energies of reaction by using the well-known relationship:³² $\Delta_r G(T) = -R T \ln K$.

III. RESULTS

III.1. Formation of soddyite, dehydrated schoepite, studtite, metastudtite and rutherfordine in terms of oxides. Reactions (A) to (E)

The reactions of formation of soddyite, dehydrated schoepite, studtite and metastudtite and rutherfordine in terms of the corresponding oxides are the reactions (A) to (E) given in the Introduction Section. By using the calculated thermodynamic properties these materials and those of $\gamma - \text{UO}_3$,³¹ as well as the experimental ones of quartz, water, oxygen and carbon given in JANAF tables,³² we obtained the enthalpies and free-energies of formation and associated reaction constants shown in Table 1.

For comparison, the experimental values of the standard enthalpies of formation in terms of oxides of these materials and the calculated enthalpies of formation at the temperature of 298.15 K are given in Table 2. The errors in the computed enthalpies of formation are 2.5, 2.5, 0.2, 0.0 and 12.3 kJ · mol⁻¹, respectively.

III.2. Reactions (F) to (H)

The reaction of transformation of rutherfordine into dehydrated schoepite is the reaction (F) given in the Introduction Section. From the calculated thermodynamic properties of rutherfordine and dehydrated schoepite³¹ and the experimental ones of water and carbon dioxide given in JANAF tables,³² we obtained the enthalpies, free-energies and reaction constants given in Table 1. For comparison (see Table 2), the experimental value of the standard enthalpy of this reaction,²¹ $\Delta_r H^0 = 63.0 \text{ kJ} \cdot \text{mol}^{-1}$ differs from the calculated value by 1.7%.

Table 1. Calculated enthalpies ($\Delta_r H$) and free-energies ($\Delta_r G$) of the reactions (A) to (H) and associated reaction constants ($\text{Log } K$) as a function of temperature. The values of ΔH and ΔG are in units of $\text{kJ} \cdot \text{mol}^{-1}$.

Reaction A				Reaction B				Reaction C				Reaction D			
T (K)	$\Delta_f H$	$\Delta_f G$	Log K	T (K)	$\Delta_f H$	$\Delta_f G$	Log K	T (K)	$\Delta_f H$	$\Delta_f G$	Log K	T (K)	$\Delta_f H$	$\Delta_f G$	Log K
280	-119.43	-106.40	19.85	280	-25.48	-15.71	2.93	280	19.31	84.30	-15.73	280	13.39	55.68	-10.39
298.15	-115.30	-100.00	17.52	298.15	-24.89	-13.64	2.39	298.15	22.46	94.97	-16.64	298.15	15.82	62.38	-10.93
300	-114.92	-99.38	17.30	300	-24.83	-13.43	2.34	300	22.74	96.03	-16.72	300	16.04	63.04	-10.98
320	-111.20	-93.11	15.20	320	-24.33	-11.28	1.84	320	25.45	107.13	-17.49	320	18.20	69.94	-11.42
340	-108.16	-87.47	13.44	340	-23.97	-9.25	1.42	340	27.49	117.65	-18.07	340	19.91	76.41	-11.74
360	-105.52	-82.19	11.93	360	-23.63	-7.22	1.05	360	29.32	128.06	-18.58	360	21.41	82.73	-12.00
380	-103.81	-77.80	10.69	380	-23.61	-5.48	0.75	380	29.79	137.21	-18.86	380	22.14	88.31	-12.14
400	-102.38	-73.62	9.61	400	-23.60	-3.73	0.49	400	30.13	146.34	-19.11	400	22.74	93.81	-12.25
420	-101.38	-69.82	8.68	420	-23.70	-2.06	0.26	420	29.99	155.10	-19.29	420	23.04	99.05	-12.32
440	-100.77	-66.35	7.88	440	-23.89	-0.46	0.05	440	29.40	163.53	-19.41	440	23.06	104.08	-12.36
460	-100.54	-63.17	7.17	460	-24.18	1.09	-0.12	460	28.37	171.67	-19.49	460	22.82	108.91	-12.37
480	-100.66	-60.26	6.56	480	-24.56	2.58	-0.28	480	26.91	179.56	-19.54	480	22.33	113.57	-12.36
500	-101.12	-57.57	6.01	500	-25.03	4.02	-0.42	500	25.03	187.23	-19.56	500	21.59	118.09	-12.34

Reaction E				Reaction F				Reaction G				Reaction H			
T (K)	$\Delta_f H$	$\Delta_f G$	Log K	T (K)	$\Delta_r H$	$\Delta_r G$	Log K	T (K)	$\Delta_r H$	$\Delta_r G$	Log K	T (K)	$\Delta_r H$	$\Delta_r G$	Log K
10	-955.75	-955.44	4990.58	280	63.07	27.01	-5.04	280	-5.93	-28.62	5.34	298.15	32.23	21.67	-3.80
50	-225.90	-220.02	229.85	298.15	61.91	24.36	-4.27	298.15	-6.64	-32.59	5.71	400	20.52	5.47	-0.71
100	-141.46	-125.34	65.47	300	61.79	24.10	-4.20	300	-6.70	-32.99	5.74	500	16.81	-2.97	0.31
200	-100.16	-67.48	17.62	320	60.63	21.34	-3.48	320	-7.25	-37.19	6.07	600	16.99	-7.34	0.64
298.15	-86.78	-37.99	6.65	340	59.55	18.69	-2.87	340	-7.58	-41.24	6.33	700	19.49	-9.19	0.69
300	-86.66	-37.56	6.54	360	58.64	16.25	-2.36	360	-7.91	-45.33	6.58	800	23.75	-9.34	0.61
400	-80.23	-15.00	1.96	380	57.57	13.69	-1.88	380	-7.65	-48.90	6.72	900	29.41	-8.34	0.48
500	-77.06	3.90	-0.41	400	56.64	11.29	-1.47	400	-7.39	-52.53	6.86	-	-	-	-
600	-75.65	20.66	-1.80	420	55.72	8.96	-1.11	420	-6.95	-56.04	6.97	-	-	-	-
700	-75.68	35.64	-2.66	440	54.81	6.68	-0.79	440	-6.34	-59.45	7.06	-	-	-	-
-	-	-	-	460	53.90	4.44	-0.50	460	-5.55	-62.76	7.13	-	-	-	-
-	-	-	-	480	52.98	2.25	-0.25	480	-4.59	-65.99	7.18	-	-	-	-
-	-	-	-	500	52.03	0.11	-0.01	500	-3.44	-69.13	7.22	-	-	-	-

Table 2. Comparison of the experimental and calculated values of the enthalpies of reactions (A) to (H) at 298.15 K in terms of the corresponding oxides.

Reaction	$\Delta_r H^{calc}(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_r H^{exp}(\text{kJ} \cdot \text{mol}^{-1})$	Reference
A	-115.30	-117.8 ± 4.3	Gorman-Lewis <i>et al.</i> ²³
B	-24.89	-27.4 ± 0.2	Guillaumont <i>et al.</i> ²²
C	22.46	22.3 ± 3.9	Kubatko <i>et al.</i> ¹⁵
D	15.82	15.8 ± 1.7	Guo <i>et al.</i> ¹⁸
E	-86.78	-99.1 ± 4.2	Kubatko <i>et al.</i> ³⁵
F	61.91	63.0	Grenthe <i>et al.</i> ²¹
G	-6.64	-7.5 ± 3.6	Guo <i>et al.</i> ¹⁸
H	32.23	36.2 ± 4.2	Cordfunke and Aling ³⁶

Similarly, the reaction of transformation of studtite into metastudtite is the reaction (G) and from the calculated thermodynamic properties of studtite and metastudtite³¹ and the experimental ones of water given in JANAF tables,³² we obtained the enthalpies, free-energies and reaction constants given in Table 1. The experimental value of the standard enthalpy of this reaction (see Table 2) is^{18,15} $\Delta_r H^0 = -7.5 \pm 3.6 \text{ kJ} \cdot \text{mol}^{-1}$, which differs from the calculated value by $0.9 \text{ kJ} \cdot \text{mol}^{-1}$.

Finally, the reaction of transformation of uranium trioxide into triuranium octoxide is the reaction (H) given in the Introduction Section. From the calculated thermodynamic properties of $\gamma - \text{UO}_3$ ³¹ and the experimental properties of U_3O_8 ³³ and oxygen,³² we obtained the enthalpies, free-energies and reaction constants given in Table 1. The experimental value of the standard enthalpy of this reaction is $\Delta_r H^0 = 36.2 \pm 4.2 \text{ kJ} \cdot \text{mol}^{-1}$ ($8.66 \pm 1 \text{ kcal} \cdot \text{mol}^{-1}$).³⁶ The calculated value has an error of only $4.0 \text{ kJ} \cdot \text{mol}^{-1}$ (see Table 1).

III.3. Transformation of uranium trioxide, dehydrated schoepite, rutherfordine and soddyite into studtite and metastudtite in the presence of water and hydrogen peroxide

The reactions of transformation of uranium trioxide into studtite and metastudtite in the presence of water and hydrogen peroxide are the reactions (I) and (J) given in the Introduction Section. We obtained the enthalpies, free-energies and reaction constants given in Table 3 from the calculated thermodynamic properties of $\gamma - \text{UO}_3$, studtite and metastudtite³¹ and the experimental properties of water³² and hydrogen peroxide.³⁴ For comparison, the experimental values of the standard enthalpy of reactions (I) and (J) are¹³ $\Delta_r H^0(\text{I}) = -75.7 \pm 4.1 \text{ kJ} \cdot \text{mol}^{-1}$ and¹⁸ $\Delta_r H^0(\text{J}) = -82.3 \pm 1.7 \text{ kJ} \cdot \text{mol}^{-1}$, respectively, which differ from the calculated values by about $0.1 \text{ kJ} \cdot \text{mol}^{-1}$ (see Table 3).

The reactions of transformation of dehydrated schoepite, rutherfordine and soddyite into studtite and metastudtite in the presence of water and hydrogen peroxide are the reactions (K) to (P) given in the Introduction. We obtained the enthalpies, free-energies and reaction constants given in Table 3 from the calculated thermodynamic properties of these materials³¹ and the experimental properties of water, carbon dioxide and quartz from Chase *et al.*³² and hydrogen peroxide from Barin.³⁴

Table 3. Calculated enthalpies ($\Delta_r H$) and free-energies ($\Delta_r G$) of the reactions (I) to (P) and associated reaction constants (Log K) as a function of temperature. The values of ΔH and ΔG are in units of $\text{kJ} \cdot \text{mol}^{-1}$.

Reaction I				Reaction J				Reaction K				Reaction L			
T (K)	$\Delta_r H$	$\Delta_r G$	Log K	T (K)	$\Delta_r H$	$\Delta_r G$	Log K	T (K)	$\Delta_r H$	$\Delta_r G$	Log K	T (K)	$\Delta_r H$	$\Delta_r G$	Log K
298.15	-75.60	-21.84	3.83	298.15	-82.23	-54.43	9.54	298.15	-50.71	-8.21	1.44	298.15	-57.35	-40.80	7.15
300	-75.31	-20.90	3.64	300	-82.01	-53.89	9.38	300	-50.47	-7.47	1.30	300	-57.17	-40.46	7.04
320	-72.58	-11.06	1.81	320	-79.83	-48.25	7.88	320	-48.25	0.22	-0.04	320	-55.50	-36.97	6.03
340	-70.53	-1.79	0.28	340	-78.11	-43.03	6.61	340	-46.56	7.45	-1.14	340	-54.14	-33.78	5.19
360	-68.77	7.25	-1.05	360	-76.68	-38.08	5.53	360	-45.14	14.47	-2.10	360	-53.05	-30.87	4.48
380	-68.17	15.23	-2.09	380	-75.82	-33.66	4.63	380	-44.55	20.71	-2.85	380	-52.20	-28.18	3.87
400	-67.77	23.10	-3.02	400	-75.16	-29.43	3.84	400	-44.17	26.83	-3.50	400	-51.56	-25.70	3.36
420	-67.84	30.59	-3.80	420	-74.79	-25.46	3.17	420	-44.14	32.65	-4.06	420	-51.09	-23.40	2.91
440	-68.34	37.75	-4.48	440	-74.68	-21.70	2.58	440	-44.45	38.20	-4.54	440	-50.79	-21.25	2.52
460	-69.26	44.61	-5.07	460	-74.81	-18.15	2.06	460	-45.08	43.53	-4.94	460	-50.63	-19.24	2.18
480	-70.58	51.22	-5.57	480	-75.16	-14.76	1.61	480	-46.02	48.64	-5.29	480	-50.61	-17.34	1.89
500	-72.31	57.60	-6.02	500	-75.74	-11.53	1.20	500	-47.27	53.58	-5.60	500	-50.71	-15.56	1.63

Reaction M				Reaction N				Reaction O				Reaction P			
T (K)	$\Delta_r H$	$\Delta_r G$	Log K	T (K)	$\Delta_r H$	$\Delta_r G$	Log K	T (K)	$\Delta_r H$	$\Delta_r G$	Log K	T (K)	$\Delta_r H$	$\Delta_r G$	Log K
298.15	11.15	16.11	-2.82	298.15	4.52	-16.48	2.89	298.15	-17.94	28.16	-4.93	298.15	-24.58	-4.43	0.78
300	11.32	16.63	-2.90	300	4.62	-16.35	2.85	300	-17.85	28.79	-5.01	300	-24.55	-4.20	0.73
320	12.38	21.56	-3.52	320	5.13	-15.63	2.55	320	-16.99	35.49	-5.79	320	-24.23	-1.70	0.28
340	13.00	26.15	-4.02	340	5.41	-15.09	2.32	340	-16.45	41.94	-6.44	340	-24.03	0.70	-0.11
360	13.50	30.72	-4.46	360	5.59	-14.62	2.12	360	-16.01	48.35	-7.01	360	-23.92	3.01	-0.44
380	13.02	34.40	-4.73	380	5.37	-14.50	1.99	380	-16.26	54.13	-7.44	380	-23.91	5.23	-0.72
400	12.47	38.12	-4.98	400	5.08	-14.41	1.88	400	-16.58	59.91	-7.82	400	-23.97	7.38	-0.96
420	11.58	41.60	-5.17	420	4.63	-14.44	1.80	420	-17.15	65.50	-8.15	420	-24.10	9.45	-1.18
440	10.36	44.88	-5.33	440	4.02	-14.57	1.73	440	-17.95	70.92	-8.42	440	-24.29	11.47	-1.36
460	8.82	47.97	-5.45	460	3.27	-14.79	1.68	460	-18.99	76.20	-8.65	460	-24.54	13.44	-1.53
480	6.96	50.90	-5.54	480	2.37	-15.09	1.64	480	-20.25	81.35	-8.85	480	-24.83	15.36	-1.67
500	4.75	53.69	-5.61	500	1.32	-15.47	1.61	500	-21.75	86.39	-9.02	500	-25.19	17.25	-1.80

III.4. Transformation of metastudtite, uranium trioxide, dehydrated schoepite, rutherfordine and soddyite into studtite in the presence of high concentrations of hydrogen peroxide

The reactions of transformation of metastudtite, uranium trioxide, dehydrated schoepite, rutherfordine and soddyite into studtite in the presence of hydrogen peroxide and absence of water are the reactions (Q) to (U) given in the Introduction Section. We obtained the enthalpies, free-energies and reaction constants given in Table 4 from the calculated thermodynamic properties of these materials³¹ and the experimental properties of hydrogen, oxygen, quartz³² and hydrogen peroxide.³⁴

IV. DISCUSSION

IV.1. Reactions (A) to (H)

The experimental values of the enthalpies of the reactions (A) to (H), which are known only at the standard state (temperature of 298.15 K and pressure of 1 bar), were reproduced accurately by these calculations (see Table 2). The errors in the computed enthalpies are 2.5, 2.5, 0.2, 0.0, 12.3, -1.1, 0.9 and 4.0 kJ · mol⁻¹, respectively.

The results obtained for the free-energies and associated reaction constants as a function of temperature for the reactions (A) to (H) are displayed in Figure 1. These calculations predict that soddyite (reaction (A) in Figure 1) is stable with respect to the corresponding oxides at all the temperatures considered and that studtite and metastudtite are unstable (reactions (C) and (D) in Figure 1). However, dehydrated schoepite and rutherfordine (reactions (B) and (E) in Figure 1) are stable for temperatures smaller than 445.8 K and 478.0 K, respectively, and become unstable

for higher temperatures. All these trends are illustrated in Figure 2, where the stability order of all these phases with respect to $\gamma - \text{UO}_3$ is shown.

Table 4. Calculated enthalpies ($\Delta_r H$) and free-energies ($\Delta_r G$) of the reactions (Q) to (U) and associated reaction constants ($\text{Log } K$) as a function of temperature. The values of ΔH and ΔG are in units of $\text{kJ} \cdot \text{mol}^{-1}$.

Reaction Q				Reaction R				Reaction S			
T (K)	$\Delta_r H$	$\Delta_r G$	$\text{Log } K$	T (K)	$\Delta_r H$	$\Delta_r G$	$\text{Log } K$	T (K)	$\Delta_r H$	$\Delta_r G$	$\text{Log } K$
298.15	-377.25	-321.36	56.30	298.15	-557.53	-492.61	86.30	298.15	-434.59	-362.16	63.45
300	-377.12	-320.78	55.85	300	-557.18	-491.60	85.59	300	-434.29	-361.24	62.90
320	-375.92	-314.59	51.35	320	-553.78	-481.03	78.52	320	-431.42	-351.56	57.39
340	-374.94	-308.61	47.41	340	-551.06	-471.08	72.37	340	-429.08	-342.39	52.60
360	-374.15	-302.80	43.93	360	-548.93	-461.70	66.99	360	-427.20	-333.67	48.41
380	-373.55	-297.18	40.85	380	-547.32	-452.82	62.24	380	-425.75	-325.36	44.72
400	-373.10	-291.72	38.09	400	-546.17	-444.39	58.03	400	-424.66	-317.42	41.45
420	-372.81	-286.41	35.62	420	-545.43	-436.37	54.27	420	-423.91	-309.81	38.53
440	-372.66	-281.24	33.39	440	-545.08	-428.73	50.89	440	-423.45	-302.49	35.91
460	-372.64	-276.21	31.36	460	-545.07	-421.41	47.85	460	-423.27	-295.44	33.55
480	-372.75	-271.29	29.52	480	-545.40	-414.39	45.09	480	-423.36	-288.64	31.41
500	-372.99	-266.49	27.84	500	-546.07	-407.65	42.59	500	-423.70	-282.05	29.46

Reaction T				Reaction U			
T (K)	$\Delta_r H$	$\Delta_r G$	$\text{Log } K$	T (K)	$\Delta_r H$	$\Delta_r G$	$\text{Log } K$
298.15	-470.78	-454.65	79.65	298.15	-401.83	-325.80	57.07
300	-470.55	-454.06	79.06	300	-401.67	-324.98	56.58
320	-468.82	-448.41	73.19	320	-400.15	-316.29	51.63
340	-467.54	-443.14	68.08	340	-398.97	-307.90	47.30
360	-466.66	-438.23	63.58	360	-398.08	-299.79	43.50
380	-466.13	-433.65	59.61	380	-397.46	-291.94	40.13
400	-465.93	-429.37	56.07	400	-397.08	-284.34	37.13
420	-466.02	-425.36	52.90	420	-396.91	-276.95	34.44
440	-466.38	-421.59	50.05	440	-396.95	-269.77	32.02
460	-467.00	-418.06	47.47	460	-397.18	-262.77	29.84
480	-467.87	-414.72	45.13	480	-397.59	-255.93	27.85
500	-469.01	-411.56	42.99	500	-398.18	-249.24	26.04

It is well known that studtite and metastudtite are very important alteration products of spent nuclear fuel.^{37-41,12-20} Studtite has been found as an alteration product of spent fuel in cooling basins at the Hanford, Washington site,³⁷⁻⁴⁰ and on Chernobyl “lava” that formed during the nuclear accident that occurred in 1986.⁴¹ The formation of metastudtite on uranium dioxide samples as a direct effect α -radiolysis of water was observed by Sattonay *et al.*¹². Studtite and metastudtite could be identified by Hanson *et al.*¹⁴ as the only secondary phases found in a two-year corrosion experiment of spent nuclear fuel in deionized water. Since studtite and metastudtite are unstable with respect to the corresponding oxides, their observation as alteration products of the SNF should come from the stabilization of these phases in contact with water exposed to intense radiation fields associated to the SNF causing the radiolysis of water. The study of the stability of these phases under the presence of hydrogen peroxide, the most important product of the radiolysis of water, is studied in detail in the next sections.

As showed by Guo *et al.*,¹⁸ the dehydration transformation of studtite to metastudtite is exothermic at 298.15 K. Our results show that studtite dehydrates spontaneously into metastudtite in the full range of temperatures considered, 280-500 K, since the free-energy of reaction is negative at all the temperatures (see reaction (G) in Figure 1). Therefore, at these temperatures, studtite is a metastable phase, which dehydrates irreversibly into metastudtite.⁴²

Figure 1. Calculated free-energies of the reactions (A) to (H) and associated reaction constants as a function of temperature.

Figure 2. Relative stabilities of studtite, metastudtite, soddyite, dehydrated schoepite, and rutherfordine with respect to $\gamma - \text{UO}_3$ as a function of temperature in the absence of hydrogen peroxide.

The transformation of the uranyl carbonate rutherfordine into dehydrated schoepite does not occur spontaneously because the free energy of reaction is positive at all the temperatures considered (see reaction (F) in Figure 1). Uranyl carbonates may precipitate where evaporation is significant and the partial pressure of CO_2 is large, rutherfordine becoming the stable uranium phase with respect to schoepite.³ Rutherfordine would be expected to replace schoepite in environments where the $p\text{CO}_2$ pressure is higher, possibly in a repository environment or in saturated soils. Replacement of schoepite by rutherfordine has been observed at the Shinkolobwe U-deposit.^{1,3}

The free energies of the transformation of gamma uranium trioxide into triuranium octoxide are shown in Figure 1 (reaction H). As it may be appreciated, the free energy of reaction becomes negative at a temperature of 457.2 K. Therefore, at this temperature UO_3 begins to decompose to U_3O_8 . As it can be seen in this Figure the free-energy function of the reaction (H)

shows a minimum at 759.2 K. Therefore, at this temperature, the conversion rate of uranium trioxide into triuranium octoxide reaches a maximum.

In order to improve our results by reproducing the experimental data at the standard state, the calculated temperature dependent free energies and enthalpies were shifted in such a way that the calculated enthalpies of reaction at 298.15 K become equal to experimentally known standard state enthalpies ($\Delta_r H^0$). This was carried out by adding the shifting parameter h to the calculated $\Delta_r G(T)$ and $\Delta_r H(T)$ functions:

$$\Delta_r G'(T) = \Delta_r G(T) + h \quad (4)$$

$$\Delta_r H'(T) = \Delta_r G'(T) + T \cdot \Delta_r S(T) = \Delta_r H(T) + h \quad (5)$$

where,

$$h = \Delta_r H^0 - \Delta_r H(T) \quad (6)$$

In this way,

$$\Delta_r H'(298.15K) = \Delta_r H^0 \quad (7)$$

The resulting values of the enthalpies, free-energies and reaction constants are given in Tables S.1 to S.8 of the Supporting Information. The free-energies and associated reaction constants as a function of temperature for reactions (A) to (H) are displayed in Figure S.1 of the Supporting Information. As it can be seen in this Figure, the shifting procedure does not change drastically our results. Nevertheless, it should improve them to some extent and allow to obtain an error range in the temperatures at which dehydrated schoepite and rutherfordine become unstable with respect to the corresponding oxides. From the shifted functions, the temperatures at which $\Delta_r G'(T) = 0$ are now calculated to be at 479.1 K and 549.4 K, respectively. Considering the shifted and unshifted results, we obtain the final estimates for the temperature of destabilization of 462.5 ± 16.7 K and 513.7 ± 35.8 K for dehydrated schoepite and rutherfordine, respectively.

Similarly, when the shifting procedure is applied to the reaction (H), the temperature at which gamma uranium trioxide begins to decompose to triuranium octoxide becomes 518.1 K and, taking into account the shifted and unshifted results, we obtain the final estimate of this decomposition temperature of 487.6 ± 30.5 K.

IV.2. Stability of studtite and metastudtite in the presence of water and hydrogen peroxide: Reactions (I) to (P)

The results obtained for the free-energies and associated reaction constants as a function of temperature for reactions (I) to (P), presented in Table 3, are displayed in Figure 3. Since the unique experimental values of the standard enthalpies of these reactions known are those of the reactions (I) and (J), the shifting procedure could be only applied to these cases. In these two cases the modifications introduced by the procedure are very small since the enthalpies of reaction at the standard state are very satisfactorily reproduced theoretically (within $0.1 \text{ kJ} \cdot \text{mol}^{-1}$). For the transformation of dehydrated schoepite into studtite in the presence of water and hydrogen peroxide (reaction (K)), Kubatko *et al.*¹⁵ obtained an experimental value of the standard enthalpy of reaction of $\Delta_r H^0(\text{K}) = -58.2 \pm 4.3 \text{ kJ/mol}$, which may be compared with the computed value of $-50.71 \text{ kJ} \cdot \text{mol}^{-1}$. However, this value is for $\text{UO}_2 \cdot 0.80 \text{ H}_2\text{O}$ instead of $\text{UO}_2 \cdot \text{H}_2\text{O}$ and, therefore, this value serves as a reference, but we cannot compare these enthalpies in a rigorous way. The resulting values of the shifted enthalpies and free-energies and the associated reaction constants are given in Tables S.9 and S.10 of the Supporting Information and are displayed in Figure S.2.

Figure 3. Calculated free-energies of the reactions (I) to (P) and associated reaction constants as a function of temperature.

Figure 3 (reaction J) shows that gamma uranium trioxide in the presence of water and hydrogen peroxide is much less stable than metastudtite, since the free energy of reaction (J) is negative everywhere within the temperature range considered. However, as it can be seen in Figure 3 (reaction I), while the reaction of uranium trioxide with water and hydrogen peroxide to produce studtite is exothermic at all the temperatures considered ($\Delta_r H < 0$, see Table 3), the free energy is not negative in the full range of temperatures. Thus, studtite is more stable than uranium trioxide in the presence of water and hydrogen peroxide only for temperatures smaller than 70.7 °C (343.8 K) due to the variation of entropy with temperature.

Similar results are found for dehydrated schoepite. Dehydrated schoepite is also less stable than metastudtite in the presence of hydrogen peroxide and water from 280 to 500 K, as shown in Figure 3 (reaction L). However, as it can be seen in Figure 3 (reaction K), while the reaction of dehydrated schoepite with water and hydrogen peroxide to produce studtite is exothermic at all the temperatures considered ($\Delta_r H < 0$, see Table 3), the free energy is only negative very near 298 K. Therefore, the calculations predict that dehydrated schoepite become more stable than studtite in the presence of water and hydrogen peroxide from the temperature of 46.2 °C (319.4 K).

As it may be appreciated in Figure 3 (reactions M and N), while the uranyl carbonate rutherfordine is less stable than metastudtite in the presence of water and hydrogen peroxide in the full range of temperature considered, rutherfordine is more stable than studtite at all temperatures. The reaction M of rutherfordine with water and hydrogen peroxide to produce studtite is endothermic up to 500 K (see Table 3).

The uranyl silicate soddyite (see reaction (O) in Figure 3) is also more stable than studtite under the presence of water and hydrogen peroxide, although the corresponding reaction O is

exothermic everywhere (see Table 3). As it can be seen in Figure 3 (reaction P), soddyite appears to be less stable than metastudtite in the presence of hydrogen and water peroxide up to 60.9 °C (334.1 K), but the opposite is true for higher temperatures.

All these features are shown in Figure 4, where the stability order of studtite, soddyite, dehydrated schoepite, rutherfordine and $\gamma - \text{UO}_3$ with respect to metastudtite (which is the most stable phase in the presence of water and hydrogen peroxide at ambient temperature) is shown.

Figure 4. Relative stabilities of studtite, soddyite, dehydrated schoepite, rutherfordine gamma uranium trioxide with respect to metastudtite as a function of temperature in the presence of water and hydrogen peroxide.

IV.3. Stability of secondary phases under the presence of high concentrations of hydrogen peroxide: Reactions (Q) to (U)

The relative stability of the secondary phases in the presence of very high concentrations of hydrogen peroxide and absence of water was investigated by evaluating the free energies of the reactions (Q) to (U). These reactions are very important since they are expected to occur when these materials are in contact with water exposed to very intense radiation fields causing

radiolysis of most of the water present. The results obtained for the free-energies and associated reaction constants as a function of temperature for reactions (Q) to (U), presented in Table 4, are displayed in Figure 5. Since the experimental values of the standard enthalpies of these reactions are unknown, the shifting procedure was not applied in these cases.

As it may be appreciated in the Figure 5 (reactions Q to U), in the presence of high concentrations of hydrogen peroxide, studtite is by far the most stable phase within the full range of temperature studied since the free energy of all the reactions of transformation is negative everywhere. Thus, all these materials will transform spontaneously into studtite in the presence of high concentration of hydrogen peroxide. The relative stability of all materials considered with respect to studtite is displayed in Figure 6, where it is shown that the metastudtite and soddyite are the second most stable phases for temperatures smaller and higher than 60.9 °C (334.1 K), respectively. The free energies of reaction of conversion of these phases into studtite range from $-321 \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K to $-249 \text{ kJ} \cdot \text{mol}^{-1}$ at 500 K. After studtite, metastudtite and soddyite, the most stable materials in the presence of high concentrations of hydrogen peroxide among those considered in this study are dehydrated schoepite, rutherfordine and gamma uranium trioxide, although as observed in Figure 6, the stability order of the last two materials changes at the temperature of 205.1 °C (478.2 K).

The conversion of dehydrated schoepite and soddyite into studtite in the presence of aqueous solutions containing high concentrations of hydrogen peroxide was studied experimentally by Forbes *et al.*¹⁶. These authors observed that, at ambient temperature, both phases readily convert into studtite following the corresponding reaction stoichiometry. The results of our calculations for the conversion of dehydrated schoepite and soddyite into studtite agree completely with this experimental study since these phases in the presence high concentrations of hydrogen peroxide

are much less stable than studtite. This study shows that the same will occur not only at ambient temperature but also at temperatures as high as 500 K. From our results, metastudtite and rutherfordine are predicted to transform also to studtite. Since the studtite stability under these conditions is so high, it is likely that the same will happen with most of the other secondary phases of SNF.²⁵ In fact, becquerelite phase in the presence of high concentrations of hydrogen peroxide also transforms into studtite within eight hours.⁴³

Figure 5. Calculated free-energies of the reactions (Q) to (U) and associated reaction constants as a function of temperature.

Figure 6. Relative stabilities of metastudtite, soddyite, dehydrated schoepite, rutherfordine gamma uranium trioxide with respect to studtite as a function of temperature in the presence of high concentrations of hydrogen peroxide.

Note that while studtite and metastudtite have been observed to decompose in air at temperatures of about 330 K and 513 K, respectively,^{44-45,18} these temperatures may be much higher in the presence of large concentrations of hydrogen peroxide. As shown in a previous experimental study of the dehydration of studtite,²⁹ the lifetime of this metastable phase is also very large in the presence of water, this phase being observed at least up to 90°C (363 K).

Present results also allow to understand why studtite and metastudtite were identified by Hanson *et al.*¹⁴ as the only secondary phases left in a two-year corrosion experiment of spent nuclear fuel in deionized water. These two phases are the most stable ones in the presence of high concentrations of hydrogen peroxide at ambient temperature. This will occur not only in deionized water but also in water containing silicate ions since studtite is much more stable than soddyite, and probably more stable than most other uranyl silicate phases under these conditions.

However, at larger temperatures soddyite becomes more stable than metastudtite and the relative stability of studtite with respect to the other secondary phases decreases. If the concentration of hydrogen peroxide decreases with time, as expected from the diminution of the intensity of radiation fields over time in a radioactive waste disposal,⁴⁶ the stability of the two hydrated peroxide phases, studtite and metastudtite, will decrease and the formation of other secondary phases will occur.

Concluding, this study indicates that under the presence of high concentrations of hydrogen peroxide, studtite is the most stable phase among those studied in this work and, therefore, it must be considered as a one of the most fundamental phases resulting from alteration of spent nuclear fuel. Clearly, a full evaluation and understanding of the number and relative amount of the secondary phases of spent nuclear fuel present at the conditions of a final geological disposal over time requires the realization of complete thermodynamic calculations employing thermochemical data for a significant number of materials, including the most important secondary phases, amorphous phases and aqueous species, at a wide range of temperature and pressure conditions.

V. CONCLUSIONS

In this work, the thermodynamic properties of uranyl containing materials including dehydrated schoepite, metastudtite, studtite, soddyite, rutherfordine and $\gamma - \text{UO}_3$, determined in previous works by means of density functional theory using plane waves and pseudopotentials, were used in order to obtain the enthalpies and free energies of eight reactions involving these materials and its variation with the temperature. The first five reactions represent the formation of the considered materials in terms of the corresponding oxides and the other ones are the

transformations of rutherfordine into dehydrated schoepite, studtite into metastudtite and uranium trioxide into triuranium octoxide, respectively.

The experimental values of the enthalpies of these reactions, which are known only at the standard state (temperature of 298.15 K and pressure of 1 bar), were reproduced accurately by these calculations, the errors being 2.5, 2.5, 0.2, 0.0, 12.3, -1.1, 0.9 and 4.0 kJ · mol⁻¹, respectively. Furthermore, using these computations we have been able to determine the corresponding enthalpies, free energies and reaction constants in a wide range of temperatures. These calculations predict that soddyite is stable with respect to the corresponding oxides at all the temperatures considered and that studtite and metastudtite are unstable. However, dehydrated schoepite and rutherfordine are stable for temperatures smaller than 462.5 ± 16.7 K and 513.7 ± 35.8 K, respectively, and become unstable for higher temperatures.

In order to improve our results by reproducing the experimental data at the standard state, the calculated temperature dependent free energies and enthalpies were shifted in such a way that the calculated enthalpies of reaction at 298.15 K become equal to experimentally known standard state enthalpies. This also allowed to obtain an error for the estimates of the temperatures at which dehydrated schoepite and rutherfordine become unstable with respect to the corresponding oxides and gamma uranium trioxide begins to decompose to triuranium octoxide.

The relative stability the uranyl peroxide hydrates, studtite and metastudtite, with respect to $\gamma - \text{UO}_3$, dehydrated schoepite, rutherfordine and soddyite in the presence of water and hydrogen peroxide was also studied by considering the corresponding reactions. The experimental values of the enthalpies of two of these reactions, those relating studtite and metastudtite with $\gamma - \text{UO}_3$ in the presence of hydrogen peroxide, were very well reproduced theoretically at the standard state (within 0.1 kJ · mol⁻¹). Metastudtite and studtite are shown to

be very stable phases in the presence water and hydrogen peroxide at low temperatures in accordance with previous experimental studies. However, the stability of studtite phase decreases rapidly when the temperature increases.

From the study of the stability of studtite and metastudtite in the presence of water and hydrogen peroxide, we can conclude that: a) gamma uranium trioxide in the presence of water and hydrogen peroxide is much less stable than metastudtite. Studtite is more stable than uranium trioxide in the presence of water and hydrogen peroxide only for temperatures smaller than 70.7 °C (343.8 K); b) dehydrated schoepite is also less stable than metastudtite in the presence of hydrogen peroxide from 280 to 500 K. The calculations predict that dehydrated schoepite becomes more stable than studtite from 46.2 °C (319.4 K); c) the uranyl carbonate rutherfordine is less stable than metastudtite in the full range of temperature considered (300-500 K), but rutherfordine is more stable than studtite at all these temperatures; and d) the uranyl silicate soddyite is also more stable than studtite. However, it appears to be less stable than metastudtite in the presence of water and hydrogen peroxide only up to 60.9 °C (334.1 K).

Finally, the relative stability of the secondary phases in the presence of very high concentrations of hydrogen peroxide and absence of water was investigated. This situation is very important since it is very likely to occur when these materials are in contact with water exposed to very intense radiation fields causing radiolysis of most of the water present. In this case, studtite is by far the most stable phase within the full range of temperature studied being more stable than metastudtite, the second most stable secondary phase at ambient temperature, by about $-321 \text{ kJ} \cdot \text{mol}^{-1}$. Soddyite become more stable than metastudtite at about 335 K. These results agree with the experimental results of Forbes *et al.*,¹⁶ which showed that dehydrated schoepite and soddyite readily transforms into soddyite in the presence of high concentrations of

hydrogen peroxide and justify the results of Hanson *et al.*,¹⁴ which found studtite and metastudtite to be the only secondary phases left in a two-year corrosion experiment of spent nuclear fuel in deionized water. Since the stability of studtite under these conditions is very high, it is expected that most secondary phases will transform into studtite in the presence of very high concentrations of hydrogen peroxide, and that this phase will be the unique secondary phase found at the surface of the SNF during the time in which the radiation fields associated to the SNF are sufficiently intense to cause the radiolysis of most of the water reaching this surface.

SUPPORTING INFORMATION

Supplementary data associated with this article are included in a separate file. Tables S.1 to S.10 report the shifted values of the enthalpies and free-energies of reactions (A) to (J) and the associated reaction constants (see text). The shifted values of the free-energies of reactions (A) to (H) and (I) to (J) and the associated reaction constants are displayed in Figures S.1 and S.2, respectively.

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REFERENCES

- (1) Finch, R. J.; Ewing, R. C. The Corrosion of Uraninite under Oxidizing Conditions. *J. Nucl. Mater.* **1992**, *190*, 133–156.
- (2) Finch, R. J.; Murakami, T. Systematics and Paragenesis of Uranium Minerals. *Rev. Mineral. Geochem.* **1999**, *38*, 91–180.
- (3) Grenthe, I.; Drozdzyński, J.; Fujino, T.; Buck, E. C.; Albrecht-Schmitt, T. E.; Wolf, S.F. Uranium; in *The Chemistry of Actinide and Transactinide Elements*; Chapter V, Vol. I; Morss L. R., Edelstein N. M., Fuger J., Eds.; Springer Science and Business Media: Berlin, 2006; pp. 253–638.

- (4) Burns, P. C.; Ewing, R. C.; Miller, M. L. Incorporation Mechanisms of Actinide Elements in to the Structures of U^{6+} Phases Formed During the Oxidation of Spent Nuclear Fuel. *J. Nucl. Mater.* **1997**, *245*, 1–9.
- (5) Plasil J. Oxidation-Hydration Weathering of Uraninite: The Current State-of Knowledge. *J. Geosci.* **2014**, *59*, 99–114.
- (6) Frondel, C. Mineral Composition of Gummite. *Am. Mineral.* **1956**, *41*, 539–568
- (7) Frondel, C. Systematic Mineralogy of Uranium and Thorium. *U.S. Geol. Surv. Bull.* **1958**, *1064*.
- (8) Percy, E. C.; Prikryl, J. D.; Murphy, W. M.; Leslie, B. W. Alteration of Uraninite from the Nopal I Deposit, Peña Blanca District, Chihuahua, Mexico, Compared to Degradation of Spent Nuclear Fuel in the Proposed US High-Level Nuclear Waste Repository at Yucca Mountain, Nevada. *Appl. Geochem.* **1994**, *9*, 713–732.
- (9) Wronkiewicz, D. J.; Bates, J. K.; Gerding, T. J.; Veleckis, E.; Tani, B. S. Uranium Release and Secondary Phase Formation During Unsaturated Testing of UO_2 at 90°C. *J. Nucl. Mater.* **1992**, *190*, 107–127.
- (10) Wronkiewicz, D. J.; Bates, J. K.; Wolf, S. F.; Buck, E. C. Ten-Year Results from Unsaturated Drip Tests with UO_2 at 90°C: Implications for the Corrosion of Spent Nuclear Fuel. *J. Nucl. Mater.* **1996**, *238*, 78–95.
- (11) Clark, D. L.; Hobart, D. E.; Neu, M. P. Actinide Carbonate Complexes and Their Importance in Actinide Environmental Chemistry. *Chem. Rev.* **1995**, *95*, 25–48.

- (12) Sattonnay, G.; Ardois, C.; Corbel, C.; Lucchini, J. F.; Barthe, M.-F.; Garrido, F.; Gosset, D. Alpha-Radiolysis Effects on UO₂ Alteration in Water. *J. Nucl. Mater.* **2001**, 288, 11–19.
- (13) McNamara, B.; Buck, E. C.; Hanson, B. Observation of Studtite and Metastudtite on Spent Fuel. *Mater. Res. Soc. Symp.* **2002**, 757, 401–406.
- (14) Hanson, B. D.; McNamara, B.; Buck, E. C.; Friese, J. I.; Jenson, E.; Krupka, K.; Arey, B. W. Corrosion of Commercial Spent Nuclear Fuel. 1. Formation of Studtite and Metastudtite. *Radiochim. Acta* **2005**, 93, 159–168.
- (15) Kubatko, K.-A.; Helean, K. B.; Navrotsky, A.; Burns, P. C. Stability of Peroxide-Containing Uranyl Minerals. *Science* **2003**, 302, 1191–1193.
- (16) Forbes, T. Z.; Horan, P.; Devine, T.; McInnis, D.; Burns, P. C. Alteration of Dehydrated Schoepite and Soddyite to Studtite, [(UO₂)O₂(H₂O)₂](H₂O)₂. *Am. Miner.* **2011**, 96, 202–206.
- (17) Armstrong, C. R.; Nyman, M.; Shvareva, T. Y.; Sigmon, G. E.; Burns, P. C.; Navrotsky, A. Uranyl Peroxide Enhanced Nuclear Fuel Corrosion in Seawater. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, 109, 1874–1877.
- (18) Guo, X.; Ushakova S. V.; Labs, S.; Curtius, H.; Bosbach, D.; Navrotsky, A. Energetics of Metastudtite and Implications for Nuclear Waste Alteration. *Proc. Natl. Acad. Sci. U.S.A.* **2014**, 111, 17737–17742.
- (19) Weck, P. F.; Kim, E.; Buck, E. C. On the Mechanical Stability of Uranyl Peroxide Hydrates: Implications for Nuclear Fuel Degradation. *RSC Adv.* **2015**, 5, 79090–79097.
- (20) Weck, P. F.; Kim, E. Uncloaking the Thermodynamics of the Studtite to Metastudtite Shear-Induced Transformation. *J. Phys. Chem. C* **2016**, 120, 16553–16560.

- (21) Grenthe, I.; Fuger, J.; Konings, R. J. M.; Lemire, R. J.; Muller, A. B.; Nguyen-Trung, C.; Wanner, H. *Chemical Thermodynamics of Uranium*; Nuclear Energy Agency Organisation for Economic Co-Operation and Development, OECD: Issy-les-Moulineaux, France, 2004.
- (22) Guillaumont, N. Y. R.; Fanghänel, T.; Neck, V.; Fuger, J.; Palmer, D. A.; Grenthe, I.; Rand, M. H. *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium, and Technetium*; Mompean, F. J., Illemassene, M., Domenech-Orti, C., Ben Said, K., Eds.; OECD Nuclear Energy Agency, Data Bank: Issy-les-Moulineaux, France, 2003.
- (23) Gorman-Lewis, D.; Mazeina, L.; Fein, J. B.; Szymanowski, J. E. S.; Burns, P. C.; Navrotsky, A. Thermodynamic Properties of Soddyite from Solubility and Calorimetry Measurements. *J. Chem. Thermodyn.* **2007**, *39*, 568–575.
- (24) Payne, M. C.; Teter, M. P.; Ailan, D. C.; Arias, A.; Joannopoulos, J. D. Iterative Minimization Techniques for *Ab Initio* Total-Energy Calculations: Molecular Dynamics and Conjugate Gradients. *Rev. Mod. Phys.* **1992**, *64*, 1045–1097.
- (25) Colmenero, F. *Characterization of Secondary Phases of Spent Nuclear Fuel under Final Geological Disposal Conditions*. Ph. D. Thesis, Universidad Autónoma de Madrid, Madrid, 2017, 443 pp.
- (26) Bonales, L. J.; Colmenero, F.; Cobos, J.; Timón, V. Spectroscopic Raman Characterization of Rutherfordine: a Combined DFT and Experimental Study. *Phys. Chem. Chem. Phys.* **2016**, *18*, 16575–16584.

- (27) Colmenero, F.; Bonales, L. J.; Cobos, J.; Timón, V. Thermodynamic and Mechanical Properties of Rutherfordine Mineral Based on Density Functional Theory. *J. Phys. Chem. C* **2017**, *121*, 5994–6001.
- (28) Colmenero, F.; Bonales, L. J.; Cobos, J.; Timón, V. Density Functional Theory Study of the Thermodynamic and Raman Vibrational Properties of γ – UO_3 Polymorph. *J. Phys. Chem. C* **2017**, *121*, 14507–14516.
- (29) Colmenero, F.; Bonales, L. J.; Cobos, J.; Timón, V. Study of the Thermal Stability of Studtite by *In Situ* Raman Spectroscopy and DFT Calculations. *Spectrochim. Acta. A* **2017**, *174*, 245–253.
- (30) Colmenero, F.; Bonales, L. J.; Cobos, J.; Timón, V. Structural, Mechanical and Vibrational Study of Uranyl Silicate Mineral Soddyite by DFT Calculations. *J. Solid. State Chem.* **2017**, *253*, 249–257.
- (31) Colmenero, F.; Fernández, A. M.; Cobos, J.; Timón, V. Thermodynamic Properties of Uranyl Containing Materials Based on Density Functional Theory. *J. Phys. Chem. C*, submitted.
- (32) Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. JANAF Thermochemical Tables. Third Edition. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1, 1–1856.
- (33) Hemingway, B. S. *Thermodynamic Properties of Selected Uranium Compounds and Aqueous Species at 298.15 K and 1 Bar and at Higher Temperatures - Preliminary Models for the Origin of Coffinite Deposits*; USGS Open-File Report 82–619: 1982.

(34) Barin, I. *Thermochemical Data of Pure Substances; Third edition*; VCH: Weinheim, 1995.

(35) Kubatko, K.-A.; Helean, K. B.; Navrotsky, A.; Burns, P. C. Thermodynamics of Uranyl Minerals: Enthalpies of Formation of Rutherfordine, UO_2CO_3 , Andersonite, $\text{Na}_2\text{CaUO}_2(\text{CO}_3)_3(\text{H}_2\text{O})_5$, and Grimselite, $\text{K}_3\text{NaUO}_2(\text{CO}_3)\cdot 3\text{H}_2\text{O}$. *Am. Mineral.* **2005**, *90*, 1284–1290.

(36) Cordfunke, E. H. P.; Aling, P. System $\text{UO}_3 + \text{U}_3\text{O}_8$: Dissociation Pressure of $\gamma - \text{UO}_3$. *Trans. Faraday Soc.* **1965**, *61*, 50-53.

(37) Abrefah, J.; Marschmann, S.; Jenson, E. D. *Examination of the Surface Coatings Removed from K-East Basin Fuel Elements*; Report of the U.S. Department of Energy, Pacific Northwest National laboratory PNNL-11806; US-DOE: Richland, Washington, 1998.

(38) Schmidt, A. J.; Delegard, C. H. *Assessment of K Basin Sludge Volume Expansion Resulting from Uranium Corrosion During Storage*; Report of the U.S. Department of Energy, Pacific Northwest National laboratory PNNL-13786; US-DOE: Richland, Washington, 2002.

(39) Delegard, C. H.; Schmidt, A. J. *Uranium Metal Reaction Behavior in Water, Sludge, and Grout*; Report of the U.S. Department of Energy, Pacific Northwest National laboratory PNNL-17815; US-DOE: Richland, Washington, 2008.

(40) Delegard, C. H.; Schmidt, A. J.; Chenault, J. W. *Mechanical Properties of K Basin Sludge Constituents and Their Surrogates*; Report of the U.S. Department of Energy, Pacific Northwest National laboratory PNNL-14947; US-DOE: Richland, Washington, 2004.

- (41) Burakov, B. E.; Strykanova, E. E.; Anderson, E. B. Secondary Uranium Minerals on the Surface of Chernobyl “lava.”. *Mat. Res. Soc. Symp. Proc.* **1997**, *465*, 1309–1311.
- (42) Walenta K. Studtite and its Composition. *Am. Miner.* **1974**, *59*, 166–171.
- (43) Kubatko, K.-A.; Unruh, D.; Burns, P. C. Affects of Hydrogen Peroxide on the Stability of Becquerelite. *Mater. Res. Soc. Symp. Proc.* **2006**, *893*, 423.
- (44) Bauer, J. D.; Labs, S.; Winkler, B.; Curtius, H.; Bosbach, D. Temperature Dependent X-Ray Diffraction Study of the Transformation of Studtite, $\text{UO}_4 \cdot 4 \text{H}_2\text{O}$ to Metastudtite $\text{UO}_4 \cdot 2 \text{H}_2\text{O}$; MS12-T2, 22th Annual Meeting of the German Crystallographic Society (DGK); Berlin, 2014.
- (45) Rey, A.; Casas, I.; Giménez, J.; Quiñones, J.; de Pablo, J. Effect of Temperature on Studtite Stability: Thermogravimetry and Differential Scanning Calorimetry Investigations. *J. Nucl. Mater.* **2009**, *385*, 467–473.
- (46) Shoesmith, D. W. Used Fuel and Uranium Dioxide Dissolution Studies - A Review; NWMO Technical Report 2007-03. University of Western Ontario, Canada, 2014.

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Thermodynamic stability order of studtite, metastudtite, soddyite, dehydrated schoepite, rutherfordine and $\gamma - \text{UO}_3$ as a function of temperature: (A) in absence of hydrogen peroxide; (B) in the presence of high concentrations of hydrogen peroxide.