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Effect of temperature on studtite stability: Thermogravimetry and differential scanning calorimetry investigations

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ABSTRACT

The main objective of this work is the study of the influence of temperature on the stability of the uranyl peroxide tetrahydrate ($UO_2O_2 \cdot 4H_2O$) studtite, which may form on the spent nuclear fuel surface as a secondary solid phase. Preliminary results on the synthesis of studtite in the laboratory at different temperatures have shown that the solid phases formed when mixing hydrogen peroxide and uranyl nitrate depends on temperature. Studtite is obtained at 298 K, meta-studtite ($UO_2O_2 \cdot 2H_2O$) at 373 K, and meta-schoepite ($UO_3 \cdot nH_2O$, with $n < 2$) at 423 K. Because of the temperature effect on the stability of uranyl peroxides, a thermogravimetric (TG) study of studtite has been performed. The main results obtained are that three transformations occur depending on temperature. At 403 K, studtite transforms to meta-studtite, at 504 K, meta-studtite transforms to meta-schoepite, and, finally, at 840 K, meta-schoepite transforms to U_3O_8. By means of the differential scanning calorimetry the molar enthalpies of the transformations occurring at 403 and 504 K have been determined to be -42 ± 10 and -46 ± 2 kJ mol^{-1}, respectively.

1. Introduction

The performance safety assessment of a future spent nuclear fuel (SNF) deep geological repository needs, among many others things, the knowledge of the effect that surface secondary phases formed under different environmental conditions might have on the long-term dissolution behaviour of the wastes. Hence, the coating formed on the SNF surface could become an effective barrier for retarding the corrosion process of SNF and it could retain the radionuclides released from the spent fuel preventing or, at least, retarding their release from the repository.

A large experimental effort has been directed to the understanding of the mechanism of formation of secondary phases under oxic conditions, using both irradiated and unirradiated uranium dioxide. Several studies [1–3] have shown that secondary phase precipitation on unirradiated UO_2 surface follows a paragenetic sequence that includes: hydrated uranyl oxide (schoepite and dehydrated schoepite), U(VI) oxides with alkaline and alkaline-earth elements (becquerilite and compreignacite), U(VI) silicates, (specially uranophane, sodyite, and boltwoodite), and uranyl sulphates, phosphates or carbonates, depending on the groundwater composition. In the case of spent nuclear fuel, the results obtained show a similar paragenetic sequence to the one observed for unirradiated UO_2, since Na-boltwoodite and β-uranophane have been detected on the fuel surface [4] as well as schoepite and dehydrated schoepite [5].

In recent years, an increasing effort has been directed to the study of uranyl peroxides (studtite and meta-studtite, $UO_2O_2 \cdot 4H_2O$ and $UO_2O_2 \cdot 2H_2O$), due to the fact that these peroxides have been found to be formed under several dissolution experimental conditions in the absence of carbonates: UO_2 in presence of hydrogen peroxide [6], α-doped UO_2 [7,8], UO_2 under α [9], β [10], and γ [11] radiation. However, the most relevant study to actual SNF alteration is the experiment performed by McNamara et al. [12], who found these peroxides during the leaching of SNF.

Studtite and meta-studtite are the only peroxide minerals found in nature. Kubatko et al. [13] showed that α radiolysis of water is the only source in nature that provides the quantity of hydrogen peroxide needed for the formation of studtite. Although, the uranyl oxide hydrate is the alteration product that precipitates at the first stage of UO_2 alteration, uranyl peroxides are the thermodynamically stable phases in the presence of hydrogen peroxide. Uranyl peroxides can in this way form by the alteration of SNF due to the H_2O_2 produced by the α radiolysis of water [7,12,14] in free-carbonate solutions.

The temperatures in the repository near field are expected to be above 373 K for thousands of years due to the heat emitted by the wastes [15] although, in the European deep repository concepts of the time interval may be shorter. Hence, temperature is

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Table 1
Bibliographic summary of studtite transformations.

Thermal transformation reported	
Synthetic studtite	
$UO_2O_2 \cdot 4H_2O \xrightarrow{373\ K} UO_2O_2 \cdot 2H_2O \xrightarrow{493\ K} UO_x \xrightarrow{758\ K} \alpha - UO_3 \xrightarrow{853\ K} U_3O_8 \quad 3 < x < 3.5$	TG XRD IR, [20]
$UO_2O_2 \cdot 4H_2O \rightarrow UO_2O_2 \cdot 2H_2O \xrightarrow{603\ K} UO_3 \cdot 0.5H_2O \xrightarrow{758\ K} UO_{3_{am}} \rightarrow UO_{2.9} \xrightarrow{793\ K} \gamma - UO_3 \xrightarrow{853\ K} U_3O_8$	TG DTA, [22]
$UO_2O_2 \cdot 4H_2O \xrightarrow{383-423\ K} UO_2O_2 \cdot 2H_2O \xrightarrow{423-573\ K} UO_3 \cdot xH_2O \xrightarrow{723\ K} UO_3 \xrightarrow{853\ K} U_3O_8/UO_2$	TG DTA IR, [21]
$UO_2O_2 \cdot 4H_2O \xrightarrow{403\ K} UO_2O_2 \cdot 2H_2O \xrightarrow{503\ K} UO_3/UO_3 \cdot nH_2O \xrightarrow{840\ K} U_3O_8$	TG XRD DSC, this study
Natural studtite	
$UO_2O_2 \cdot 4H_2O \xrightarrow{333\ K} UO_2O_2 \cdot 2H_2O$	XRD, [23]
$UO_2O_2 \cdot 4H_2O \xrightarrow{418\ K} UO_2O_2 \cdot 2H_2O \xrightarrow{573\ K} UO_x \cdot nH_2O \rightarrow UO_{3_{am}} \rightarrow \alpha - UO_{2.89} \rightarrow UO_{2.67} \quad 3 < x < 3.5,\ 0 < n < 0.5,\ am = amorphous$	XRD TG IR, [24]

TG: thermogravimetry; XRD: X-ray diffraction; IR: infrared spectroscopy; DTA: differential thermal analysis.

undoubtedly a variable that should be taken into account to determine what effect it might have on the formation of the secondary phases. Alonso et al., [16], reported that meta-studtite forms when the precipitate is dried under specially controlled conditions, while studtite is stable when the sample is dried in air at room temperature. Sato [17,18] obtained uranium peroxide hydrates with a different procedure than [16] and obtained, successively, the formation of studtite at temperatures below 323 K, meta-studtite at temperatures above 343 K and a mixture of both of them at 333 K. The studies also concluded that the drying method can clearly influence the temperature of the transition from studtite to meta-studtite, and observed that the transition occurs at 373 K when the solid is dried at ambient pressure or at room temperature if vacuum is used to dry the sample.

Thermal decomposition studies of synthetic uranium peroxides have been performed by using thermogravimetric (TG) analysis, X-ray diffraction (XRD) and infrared spectroscopy (IR) [19–22]. The reaction schemes postulated by the authors are summarized in Table 1. It is important to see that in all cases the thermal decomposition takes place through formation of meta-studtite and the final product is U_3O_8 except in Rocchiccioli et al. [21] who found a mixture of U_3O_8 and UO_2.

Walenta [23], and Cejka et al., [24] studied the thermal decomposition using natural samples from Menzenschwand (Germany) and from Shinkolobwe (Rep. Congo), respectively. The first step of both studies is in good agreement with the results obtained from synthetic studtite above, but for the second step it is not clear what kind of intermediate phase forms before transforming to amorphous UO_3. Indeed, Cejka et al., [24] only proposed the chemical formula of this intermediate phase as $UO_x \cdot nH_2O$ based on the formula proposed in others works [20,22].

Based on the observations of the studies found in the literature and summarized above, it is clear that it is important to investigate studtite synthesis in a temperature range from 298 to 423 K in order to determine the final product generated. In addition, it is also essential to study how the temperature might affect the stability of the phases produced in order to evaluate their behaviour in the repository.

2. Experimental

2.1. Materials

Uranyl peroxides have been synthesized at room temperature by mixing 10^{-4} M uranyl nitrate and 1 M H_2O_2. A small amount of uraninite in the grain size 100–320 μm was added to promote precipitation.

The same synthesis method was followed at different temperatures in an acid digestion PARR bomb in a SELECTA oven at different temperatures.

2.2. Analysis

Products characterization from the synthesis below, were carried out by a BRUKER AXS D-5005 XRD with a step of 0.05° and a step time of 3 s. Products from the isothermal analysis were characterized with a XRD X-Pert-MPD PHILIPS with a X-ray source KαCu.

Thermogravimetry (TG) was performed with a TG-DSC Mettler Toledo TG-50 model, with a control device TC 15–TA. The temperature range was 298–1123 K, with a heating rate of 5 K min^{-1}.

In order to better characterize the solid phase obtained at each temperature, an isotherm study was done. It consisted of: (1) increasing the temperature of the sample with a heating rate of 5 K min^{-1} until the temperature of transformation was reached; and (2) once the temperature is reached, it was kept constant during 4 h. After that time, the solid phases were characterized by XRD.

Differential scanning calorimetry (DSC) was performed with a TG-DSC Mettler Toledo, DSC-25, model with a control device TC 15–TA. DSC was registered from 298–873 K with a heating rate of 5 K min^{-1}.The reference sample was aluminium, because it has thermal properties that remain constant through the temperature range studied in this work.

3. Results and discussion

3.1. Preliminary results on synthesis of studtite at different temperatures

In order to cover the temperature range expected under repository conditions, the temperatures chosen in this work for the studtite synthesis were in the range 298–423 K. The X-ray diffraction spectra of the solids obtained in these experiments show that different solid phases were formed depending on temperature (Fig. 1). According to the ICDD (international central diffraction data) database the characterization was done as follows: at 298 K the phase formed corresponds to uranyl peroxide tetrahydrated, (studtite $UO_2O_2 \cdot 4H_2O$), (Fig. 1(a)) at 373 K the precipitate obtained is the uranyl peroxide dehydrated, (meta-studtite, $UO_2O_2 \cdot 2H_2O$), (Fig. 1(b)), while at 423 K, there is no evidence of uranyl peroxide formation, but a uranium hydrated oxide is formed (meta-schoepite, $UO_3 \cdot nH_2O$ ($n < 2$)) (Fig. 1(c)).

3.2. Thermogravimetry and differential scanning calorimetry

The thermal decomposition of studtite takes place in several stages as it can be seen in Figs. 2 and 3. The curve representing the variation of weight sample with temperature is shown in Fig. 2 as well as the derivative of this curve (mg min^{-1}) vs. temperature. Fig. 3 shows the fraction of weight loss vs. temperature.

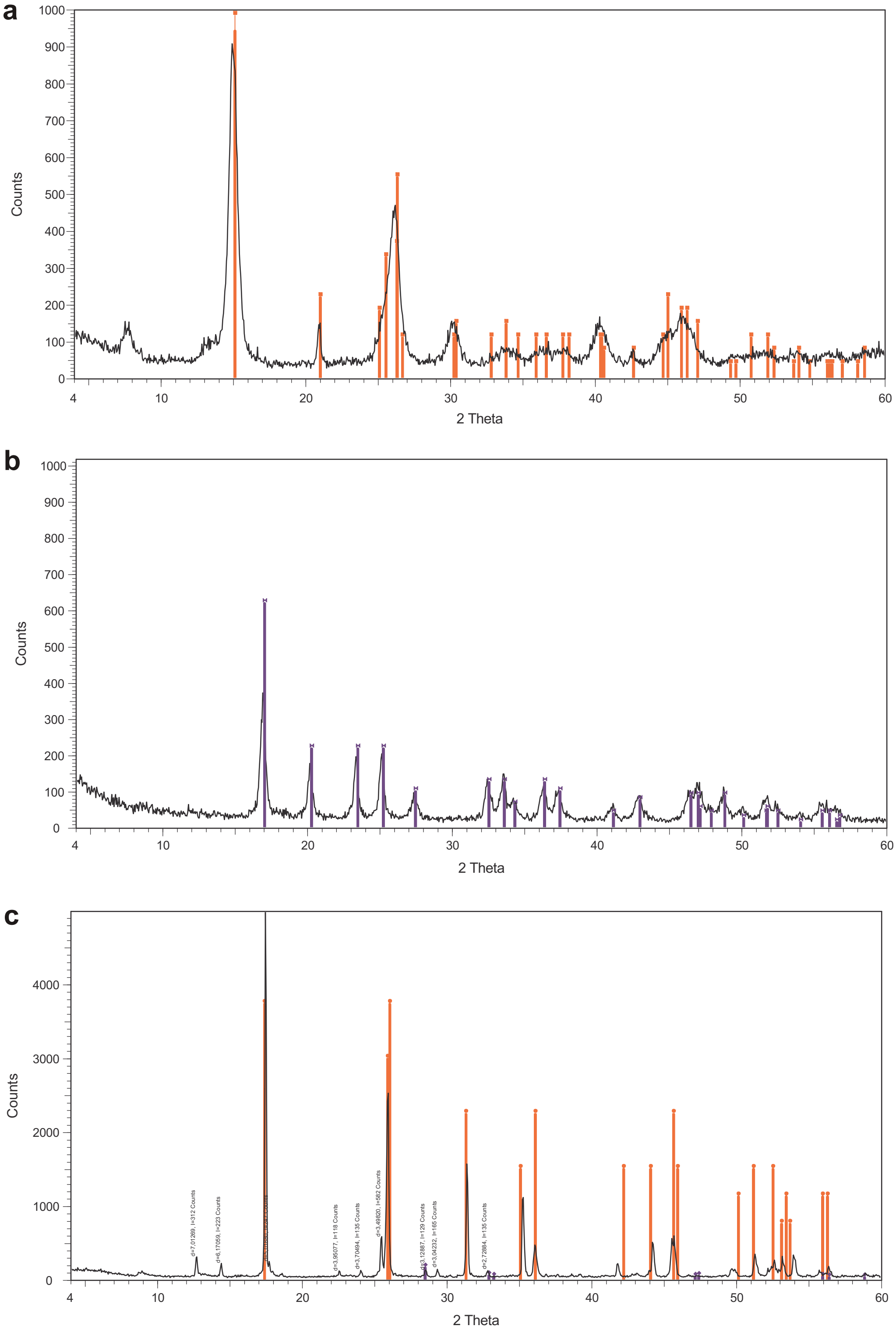

Fig. 1. XRD of the solids precipitated after mixing 10^{-4} M U(VI) and 1 M H_2O_2 30 vol% at different temperatures. The analysis conditions were a step of 0.05° each 3 s. The data are validated with ICDD (international central diffraction data) database, pdf_2 (powder diffraction file) release 2001: (a) 298 K (studtite $UO_2O_2 \cdot 4H_2O$), (b) 373 K (meta-studtite $UO_2O_2 \cdot 2H_2O$), and (c) 423 K (meta-schoepite $UO_3 \cdot 0.8H_2O$).

The isotherm studies were carried out at four temperatures, in order to characterize the final product in each step of the TG curve. These temperatures were chosen according with the TG curve stages (313, 403, 503, and 840 K). Table 2 provides the results of the characterization obtained at each temperature. The theoretical percentage weight loss for each stage was calculated and compared with the values obtained at the experimental TG curve and in the isotherm studies. This comparison is shown in Table 3. As it can be seen, the weight loss percentage obtained in the experiments is higher than the theoretical estimations. At 313 K, the isotherm study did not show any transformation of the initial product, studtite, but a weight loss of 9.6%, which is attributed to

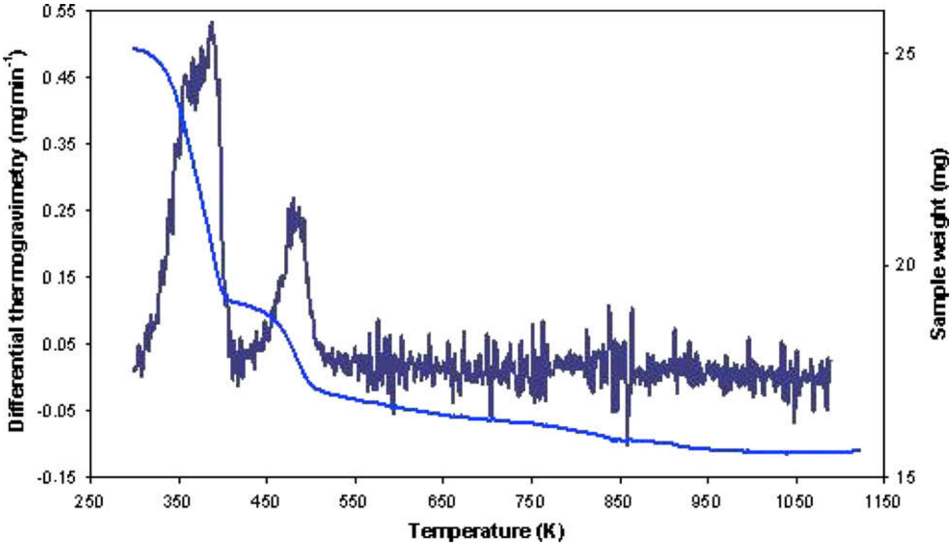

Fig. 2. Studtite thermogravimetric curve and TG derivative with time.

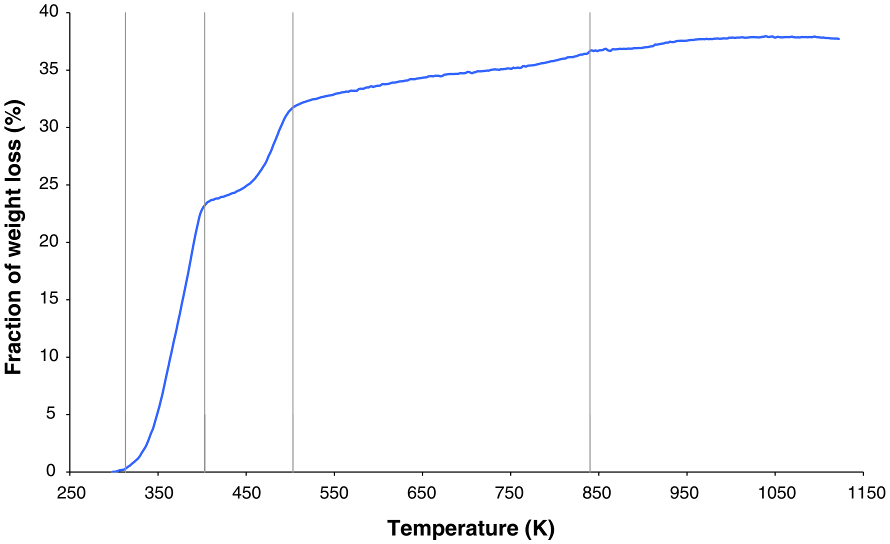

Fig. 3. Studtite TG curve showing temperature values for the isotherm study.

Table 2
Isothermal studies characterization results. Experiments were done with an initial sample of studtite freshly precipitated; heating rate 10 K min^{-1} and temperature maintained constant for 240 min.

Temperature (K)	Mass sample (mg)	XRD result
313 ± 1	22.10	$UO_2O_2 \cdot 4H_2O$
403 ± 1	25.81	$UO_2O_2 \cdot 2H_2O$
503 ± 1	25.16	$UO_3/UO_3 \cdot nH_2O$
840 ± 1	28.82	U_3O_8

the loss of humidity of the sample. This value would be a minimum value for the hydration water in studtite. Table 3 shows an estimation of the percentage attributed to humidity at each stage, calculated considering the theoretical and experimental percentages of weight loss. The average weight lost fraction due to initial studtite humidity is 12.1 ± 2.0%.

The main conclusion is that thermal decomposition takes place in different stages: (i) at 403 K studtite transforms to meta-studtite losing two molecules of water. (ii) Structural water and oxygen begin to be liberated at 453 K, giving a maximum weight loss at 503 K, and the transformation of meta-studtite to UO_3 and $UO_3 \cdot n$-H_2O with $n < 2$, the later product could be referred as meta-shoepite, with $n = 0.8$ since the estimations of the (%) weight loss point to this product, however, it is not possible to distinguish between UO_3 and $UO_3 \cdot 0.8H_2O$ because of the amorphous condition of the sample. (iii) The last stage of the curve is not evident, it starts at 833 K, a maximum is observed at 840 K, and the transformation gives the final product U_3O_8.

The different processes are summarized in Table 1 and are compared to literature data. Previous works that aimed to establish the thermal behaviour of studtite show some discrepancies, there are differences in either the temperatures of the transformations and the solid phases formed. As it is shown from the results of this work, there are three different transformations in the *T* range studied. The first one consists on the transformation of studtite to meta-studtite at 403 K, at similar temperatures than in previous works. The second transformation consists on the meta-studtite to a mixture of crystalline and amorphous hydrated and dehydrated phases $UO_3 \cdot 0.8H_2O$ and UO_3. In this step is where more

Table 3
Theoretical and experimental fraction of weight loss (wt%) for isotherm and TG studies.

Stage	Theoretical	Experimental weight loss			
				Humidity	
		Isoth.	TG	Isoth.	TG
$UO_2O_2 \cdot 4H_2O \rightarrow UO_2O_2 \cdot 2H_2O$	9.6	23.8 ± 2	23.1 ± 2	14.2 ± 2	13.4 ± 2
$UO_2O_2 \cdot 4H_2O \rightarrow UO_3 \cdot 0.8H_2O$	19.6	31.8 ± 2	31.7 ± 2	12.2 ± 2	12.1 ± 2
$UO_2O_2 \cdot 4H_2O \rightarrow U_3O_8$	24.9	33.7 ± 2	36.7 ± 2	8.7 ± 2	11.1 ± 2

contradictory results had been obtained in previous works. The third stage consists of the transformation of this mixture of phases to the final product, U_3O_8, the results are concordant in previous works, but in this work, although, the transformation seems to be coincident, it has not been possible to clearly distinguish the weight changes at the curve, as in some literature data.

The temperatures for the maxima of weight loss have been obtained by the representation of the variation of weight sample with temperature. As it can be seen in Fig. 2 there is a maximum at 387 K corresponding to the studtite–meta-studtite transformation. The deconvolution of this peak by a Gaussian multi-peak method shows two different peaks at 352 and 383 K. The derivative curve shows another maximum at 479 K corresponding to the transformation of meta-studtite to the UO_3 and $UO_3 \cdot 0.8H_2O$ mixture. It seems to be another maximum at 838 K that would correspond to the transformation of UO_3 and $UO_3 \cdot 0.8H_2O$ to the final product U_3O_8.

Once the transformations temperatures are defined the next objective is the determination of each transformation enthalpies. In this sense, DSC is a useful method to determine the heat differences during the progress of a reaction or a transformation. Enthalpies are calculated from the representation of heat flow in (W mol $^{-1}$) vs. time (s). The areas for each peak are calculated by the Gaussian method and the enthalpy values are calculated in J mol^{-1}. The DSC curve at a heating rate of 5 K min^{-1} is shown in Fig. 4.

An exothermic reaction is observed from starts at 303 to 392 K. The heat flow peak is deconvoluted by Gaussian multi-peak method in three peaks (Fig. 5). The molar enthalpies, $\Delta H°$, for these transitions are −92 ± 14, −40 ± 20, and −42 ± 10 kJ mol^{-1}, respectively. The first peak of this deconvolution could be attributed to the humidity retained at the studtite ($UO_2O_2 \cdot 4H_2O$), as could be seen from the estimations of the (%) weight loss. The last peak is attributed to the transformation of $UO_2O_2 \cdot 4H_2O$ to $UO_2O_2 \cdot 2H_2O$, with the loss of two structural water molecules. However, the second peak of this series has not been attributed, yet. One possibility is that the studtite–meta-studtite transformation proceeds via another uranyl peroxide $UO_2O_2 \cdot xH_2O$, where $x = 2$–4; however, more experimental work would be necessary to demonstrate its existence. The second stage is an exothermic reaction which occurs between 422 and 508 K with a maximum peak at 478 K. The enthalpy for this transition is −46.26 ± 1.74 kJ mol^{-1}. Table 4 summarizes the enthalpies values for each transition.

DSC profiles show exothermic peaks characteristics of dehydration processes. The peaks and enthalpies observed in DSC curves are attributed to the thermal transformations found at the TG/DTG curves. Table 5 summarizes the maximum temperatures found in both DTG and DSC. The first exothermic stage at the DSC curve shows clearly two exothermic peaks at 348 and 367 K, which can be observed at the DTG curve at 352 and 383 K. This peak at 348 K in DSC and 352 K in DTG would be referred to a previous dehydration before the transformation of studtite to meta-studtite.

Temperature is shown to be an important parameter to be considered in the studtite stability. At the temperatures expected in the repository, the formation of studtite or meta-studtite shall depend critically on temperature, as it is shown in our preliminary results on the uranyl peroxides synthesis at different temperatures. Studtite stability is affected by temperature in the range of temperatures predicted for the repository [15,25–27], because the studtite–meta-studtite transformation has been demonstrated to occur at relatively low temperatures (384 K from the TG, and 367 K from the DSC data). Actually, in the McNamara and co-work-

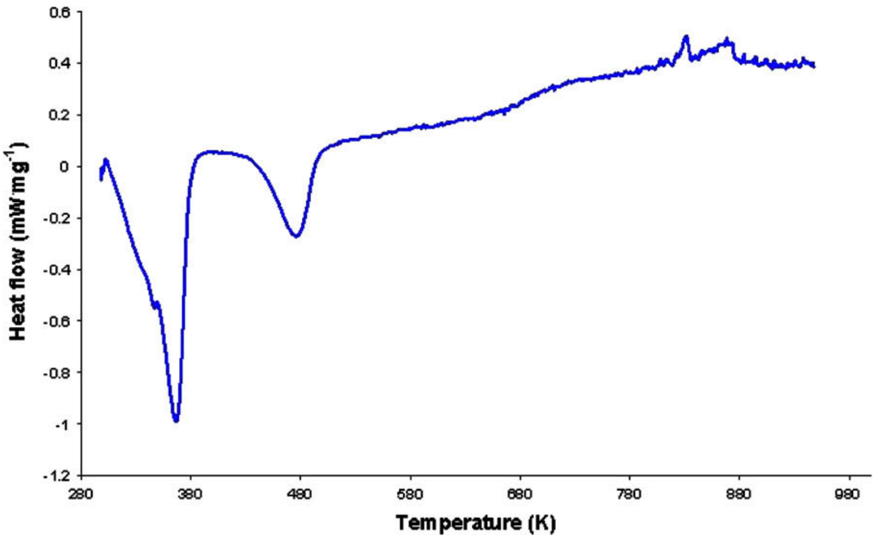

Fig. 4. DSC results.

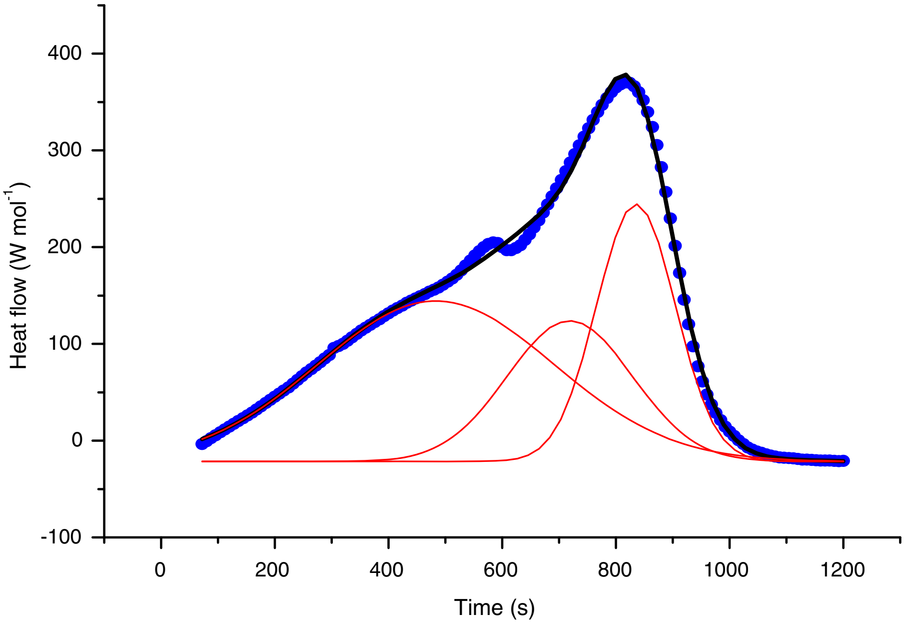

Fig. 5. First peak deconvolution by the Gauss multi-peak method. Experimental data are represented in circles, and multi Gaussian peaks as lines.

Table 4
Thermodynamical data gained from DSC experiments.

Reaction	ΔH (kJ mol^{-1})
$UO_2O_2 \cdot 4H_2O \leftrightarrow UO_2O_2 \cdot 2H_2O + 2H_2O$	−42 ± 10.0
$UO_2O_2 \cdot 2H_2O \leftrightarrow UO_3 \cdot 0.8H_2O + H_2O_2 + 2.2H_2O$	−46.26 ± 1.7

Table 5
Peak maximum temperature found for DTG and DSC experiments.

Peak	$T_{DTG,Max}$ (K)	$T_{DSC,Max}$ (K)
1	352 ± 1	348 ± 1
	373 ± 1	367 ± 1
2	479 ± 1	478 ± 1
3	838 ± 1	–

ers experiments [12], not only studtite was found on the surface of the fuel, but a mixture of studtite and meta-studtite. Again, these authors also point that temperature is a critical parameter that affects the composition of the uranyl peroxides formed as a secondary solid phase.

4. Conclusions

This study provides information of the thermal behaviour of studtite and gives the first thermodynamic values associated to its transitions. Preliminary studies on synthesis of studtite at different temperature have shown that studtite obtained in a range value from $298 < T < 373$ K, meta-studtite $373 \leqslant T < 423$ K and meta-schoepite $T = 423$ K.

The transformation behaviour of studtite was analyzed by combining thermogravimetry and differential scanning calorimetry, obtaining a good agreement between the transformation temperatures and heats of transformation.

$$UO_2O_2 \cdot 4H_2O \overset{403\ \text{K}}{\xrightarrow{-42\ \text{kj mol}^{-1}}} UO_2O_2 \cdot 2H_2O \overset{503\ \text{K}}{\xrightarrow{-46.26\ \text{kj mol}^{-1}}} UO_3/UO_3 \cdot nH_2O \xrightarrow{840\ \text{K}} U_3O_8.$$

This work reports the first thermodynamic values of the transitions of uranium peroxides improving the knowledge about thermal effect on studtite.

This work also suggest that the transformation of studtite into meta-studtite must be subject of further study to demonstrate if this transformation takes place in one or more stages involving phases with different number of water molecules in their structure.

Acknowledgments

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