

Incorporation of REE into Secondary Phase Studtite.

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ABSTRACT

The formation of uranyl peroxide phases was identified as a corrosion product of spent fuel by Hanson et al [1]. The subsequent analysis of this phase showed that metastudtite retained ^{241}Am , ^{237}Np and ^{239}Pu [2]. In this study, the retention of radionuclide Pu^{4+} and An^{3+} , released from the spent fuel matrix into studtite structure, has been evaluated by the precipitation of studtite from uranyl dissolution with variable concentrations of REE (Th, Nd, Sm and Eu). Three different precipitation conditions parameters were studied: media of synthesis, time of synthesis and REE concentration. Synthesized phases were characterized by XRD and the cell parameter was calculated. The REE incorporation was determined by ICP-MS analysis. The results showed that studtite could incorporate 63% of Th in solution during its precipitation. Changes in the “a” cell parameter were identified. The results suggest that studtite coprecipitated with REE could play a role as a limiting for the REE mobility.

INTRODUCTION

The spent fuel (SF) is composed 95% of UO_2 and 5% of actinides (e.g., ^{239}Pu , ^{237}Np , ^{241}Am) and fission product (e.g., ^{137}Cs , ^{90}Sr , ^{99}Tc). The UO_2 is extremely insoluble under reducing conditions [3]. Alpha radiation field associated to SF is able to decompose water in radiolytic products. Those species generate oxidizing conditions in the near field of SF. UO_2 is not stable under this locally oxidizing environment [4] and peroxides coming from the irradiated water oxidize the U(IV) to the more soluble U(VI) oxidation state. Then, hexavalent uranium U(VI) could react with ligands in groundwater and precipitates as secondary phase[5, 1]. The precipitated secondary phases could be capable to retain several radionuclides as Burns et al in 1997 [6] theorized. In this way, Cs, Ba, Np and Pu were identified by radiochemical analysis of secondary phases [7, 2].

Studtite was characterized as corrosion product of SF by Hanson et al. Its structure was described by Walenta 1976 [8] and refined by Burns and Hughes (Figure 1) [9]. Possible incorporation of Np in the transformation of metaschoepite to studtite has been studied by Douglas et al [10].

EXPERIMENTAL

Materials - Synthesis of studtite

Solid-phase synthesis was carried out using the following reagents: uranyl nitrate hexahydrated 99%, Ln and Th dissolution of 1000 $\mu\text{g/l}$ in nitric acid (1-5%wt) and H_2O_2 (30%).

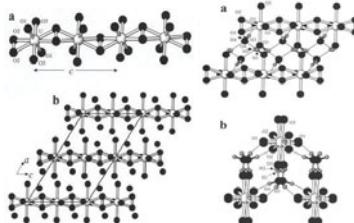


Figure 1. Structure of studtite.[9]

Two sets of precipitation experiments were performed in order to test geological repository conditions: some of them in demineralized water and other in Grimsel Groundwater.

The uranyl nitrate dissolution (0.1M) was prepared by mixing uranyl nitrate hexahydrated 99% Merk with ultrapure water or Grimsel groundwater from Switzerland in order to reproduce the synthesis media. A REE dissolution has been added before precipitation occurs, mixing with uranyl nitrate dissolution. Solid secondary phases have been obtained by addition of excess of H_2O_2 to each solution. Precipitation parameters were evaluated: different synthesis time, water composition and trace element concentration. Experimental conditions used in the synthesis are compiled in Table I.

Table I. Description of experimental conditions of synthesis

Experiment	Media	Element	% mol Trace/ mol U	synthesis time (h)
SD-t	Demineralized	Th	0.2 %	3, 24, 72, 168
SD-c	Demineralized	Th	0.2%, 2%, 20%	72
SD-tc	Demineralized	Th	2%, 4%	3, 24
SD -Ln	Demineralized	Nd, Eu, Sm	2%	72
SG-t	Grimsel	Th	0.2 %	3, 24, 72, 168
SG-Ln	Grimsel	Nd, Eu, Sm	2%	72

Experimental Techniques

To determine the Th and Ln's content, synthesized phases were redissolved. An aliquot of solution was analyzed by ICP-MS using a Perkin Elmer ELAN6000.

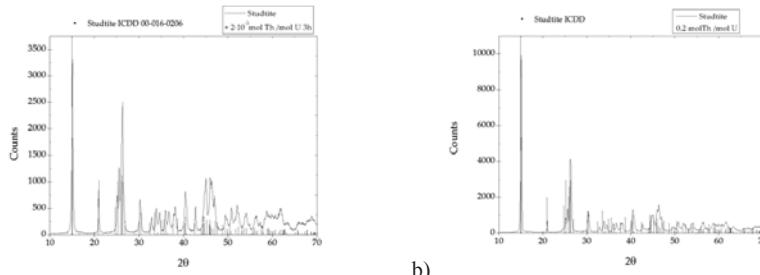
All of the precipitated phases were characterized by X-ray Powder diffraction with a Philips XRD-X' Pert – MDP The International Centre for Diffraction Data Powder Diffraction File (ICDD-PDF) database of reference patterns was used to identify phases present in samples [11]. Also, examination with Microscopy electron diffraction was performed with a Hitachi – SV 6600.

The cell parameter was determined by CELREF v.3 software [12] applying the results of XRD.

RESULTS AND DISCUSSION

Precipitation was achieved in all synthesis conditions: formation of yellow powder of uranyl minerals were observed in all of the cases.

All samples precipitated characterized by XRD were identified as studtite; using the database (ICDD-98-016-7992) [11] (Figure 2). The diffraction patterns did not show significant differences between the samples precipitated in both media; neither was observed differences in the compounds with Th and Ln's. Formation of pure Th or Ln phases was not detected. The sample, precipitated in media 0.2 mol Th/mol U (Figure 2b), showed a better crystallinity level than the other samples tested.



a) b)

Figure 2. Diffractograms of synthetized stutdite with trace element.(lefty-axis) and ICDD reference pattern (right y-axis). (a) Stutdite precipitated in ultrapure water with 0.002 Th/U rate mole., (b) Stutdite precipitated in ultrapure water with 0.2 Th/U rate mole. Synthesis time: 72h.

Figure 3a shows the SEM image of stutdite structure precipitated in Grimsel groundwater with Eu. Figure 3b shows stutdite precipitated with Th (mole ratio Th/U of 0.2). The comparative analysis of samples did not show any important differences. The morphology was similar in all samples. A completely different structure to the other samples precipitated has been observed in the samples precipitated from a solution with 0.2 mol Th/mol U (Figure 2b). A fibrous crystal formation characteristic of the stutdite was detected [8, 9].

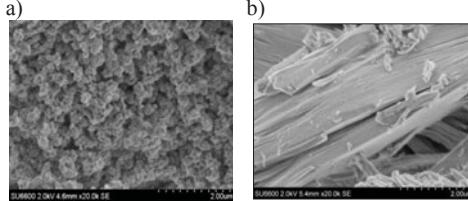


Figure 3. a) Micrography of precipitated stutdite in Grimsel groundwater with Eu, b) Stutdite precipitated with Th 20%.

Table II shows the results of stutdite powder analyzed by ICP-MS. First column corresponds to the ratio of mol of trace element (Tr) incorporated to stutdite by mol of precipitated stutdite. Assay SD-t showed Th incorporation was improved with time. The amount of precipitated stutdite increases when the reaction time also increases, also raising the capability of Th incorporation into the uranyl phase, confirmed by the SG-t results. Looking at SD-c experiment, Th moles incorporated to stutdite increased with Th percentage in the solution. Th is retained into stutdite in the precipitation, so the presence of higher Th% in solution contributes to a higher Th included in stutdite during precipitation process. In order to evaluate the parameter that will determine the Th incorporation, a SD-tc test has been set to compare to the SD-t and SD-c studies. Results showed that Th moles in stutdite increased with the concentration of media, despite of the reaction time increasing. SD-Ln assay did not show important differences among elements. Ln retained into solid sample was two orders of magnitude lower than Th, these results demonstrate that the oxidation state would determine the incorporation in stutdite.

The second column represents the efficiency (η) of incorporation. This parameter has been calculated as the ratio between the mol of Tr incorporated to stutdite and initial Tr mol in the solution. The results showed that coprecipitation efficiency increased with time of synthesis. Distribution coefficient (λ) (column 3) is described by the equation:

$$\ln \frac{[T]}{[T]_0} = \lambda \ln \frac{[U]}{[U]_0} \quad <1>$$

where [T] and [U] are the concentration of Tr and U in solution, respectively, after studtite precipitation. [T]₀ and [U]₀ represent the initial concentration before studtite precipitation .

λ results showed that trace ions was removed from the dissolution and incorporated to the solid while the studtite precipitated.

Table II. ICP-MS results obtained from the analyzed samples after dissolved studtite precipitated with Trace (Tr) element leached.

Essay	Sample	mol trace element/ mol studtite precipitated	η	λ
SD-t	SDTh-3	$2.43 \cdot 10^{-04}$	0.09	0.1784
	SDTh-24	$9.27 \cdot 10^{-04}$	0.34	0.0692
	SDTh-72	$1.19 \cdot 10^{-03}$	0.15	0.4378
	SDTh-168	$1.62 \cdot 10^{-03}$	0.47	0.0686
SD-c	SDTh	$3.16 \cdot 10^{-03}$	0.13	0.0235
	SDTh-10	$1.82 \cdot 10^{-01}$	0.63	0.2879
SD-tc	SD2Th-24	$7.93 \cdot 10^{-03}$	0.32	0.2702
	SD2Th-72	$6.86 \cdot 10^{-03}$	0.27	0.1058
	SD4Th-24	$8.21 \cdot 10^{-03}$	0.18	0.1156
	SD4Th-72	$2.06 \cdot 10^{-02}$	0.38	0.3315
SG-t	SGTh-3	$1.32 \cdot 10^{-03}$	0.36	0.0518
	SGTh-24	$8.34 \cdot 10^{-04}$	0.25	0.0833
	SGTh-72	$1.20 \cdot 10^{-03}$	0.37	0.0723
	SGTh-168	$1.90 \cdot 10^{-03}$	0.48	0.0933
SD-Ln	SDNd	$9.29 \cdot 10^{-05}$	0.0046	0.0106
	SDEu	$9.10 \cdot 10^{-05}$	0.0041	0.0014
	SDSm	$4.19 \cdot 10^{-05}$	0.0013	0.0049
SG-Ln	SGNd	$1.28 \cdot 10^{-04}$	0.0028	0.0012
	SGEu	$7.85 \cdot 10^{-05}$	0.0020	0.0007
	SGSm	$5.05 \cdot 10^{-05}$	0.0016	0.0006

The cell parameter a, b, c and β angle were calculated from the XRD results. In Figure 4 and 5 the value of parameter (a, b, c and β) as a function of mol trace/mol studtite can be observed .

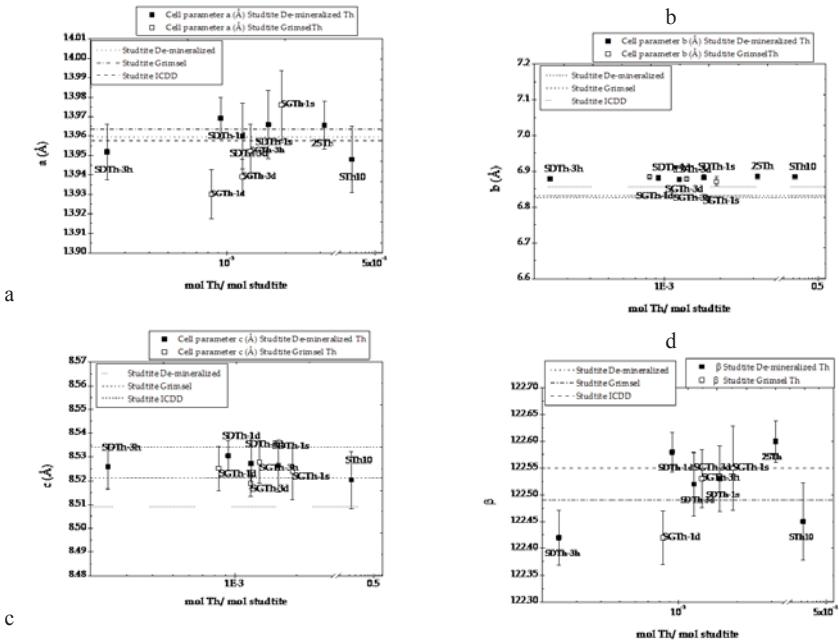


Figure 4. Cell parameter of studtite precipitated with Th. (a) Cell parameter a . (b) cell parameter b . (c) cell parameter c . (c) β angle

Figure 4 shows the cell parameters of the samples synthesized with Th. The cell parameter “a” (Figure 4a) was modified by the Th incorporation into studtite. An increase of this cell parameter for incorporation of $8 \cdot 10^{-4} - 10^{-3}$ mol Th/mol studtite was observed. However, it decreased with higher concentrations of retained Th. The “b” parameter kept constant for all samples independent on Th concentration incorporated. “c” parameter was slightly modified by the incorporation of Th, discovering that an increasing in Th composition could be related to “c” parameter reduction. The discrepancies in “c” could be associated to experimental errors in the “c” determination. The incorporation of Th modified the studtite “ β ” angle too. It keep nearly constant for $8 \cdot 10^{-4} - 10^{-3}$ mol Th/mol studtite, but this value decreases for higher Th incorporation. The synthesis media slightly modified the cell parameters.

As a summary, these results indicated that the incorporation of Th would not modify the uranyl chain (Figure 1), coming about Th did not replace U (VI) atoms in the studite structure. The incorporation would take place in the interlayer of uranyl chains connected by hydrogen bonds (Figure 1) [9]. The drop of cell parameters observed when the incorporation of $\text{Th} > 10^{-2}$ mol Th/mol studite could be explained by the retention of Th outside the crystal lattice (e.g. dislocations [13]).

Studying Ln^{3+} incorporation as analogue of Ac^{3+} (see Figure 5), the variations observed in the cell parameters showed that an increase of Ln concentration is associated to a reduction of

“a” cell parameter (Figure 5a). The 1 “b” cell parameter was not modified by the incorporation of trace element in this structure as Th incorporation showed.

Summarizing, these results indicate that incorporation of trace element occurs in the interlayer between the uranyl chains, as the Th results firstly showed.

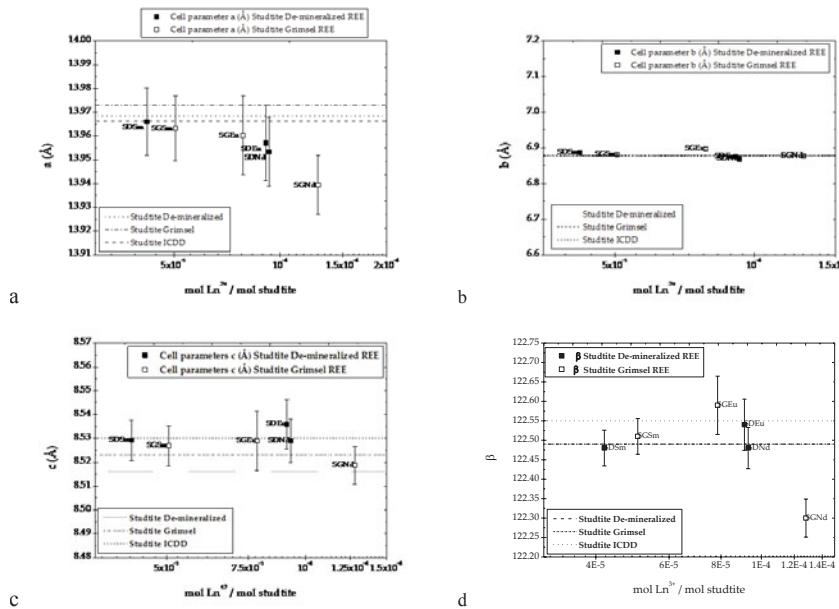


Figure 5. Cell parameter of studtite precipitated with Ln. (a) Cell parameter “a”. (b) cell parameter “b”. (c) cell parameter “c”. (d) “ β ” angle

CONCLUSIONS

The different synthesis conditions studied in this work allow us to conclude that the method of synthesis developed in this work it is as an adequate process to obtain the studtite pure and unique phase. Moreover, during the process, phases of trace elements have not been identified. The precipitation synthesis media did not alter the incorporation of radionuclide into the studtite structure. Besides, the time and composition in the media of synthesis improve the incorporation of radionuclides into the studtite structure. Solid phase characterization has confirmed that the incorporation of Th⁴⁺ into the studtite is more favourable than that for the Ln³⁺. On the other hand, the incorporation of trace element into studtite did not modify the cell. The REE tested in this work did not replace the U⁶⁺ into the structure they could be retained between uranyl chains.

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