

Assessment of the relevance of Coffinite formation within the near-field environment of spent nuclear fuel geological disposals

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ABSTRACT

Experiments were performed in anoxic gloves box in an attempt to synthesise Coffinite both in representative near-field conditions, and in conditions which were expected to favour its precipitation according to thermodynamic calculations. The experimental results did not confirm the predictions. However, a new mineral was observed instead of Coffinite. In addition, accurate characterization of various natural samples demonstrate the permanent presence of U(VI) within Coffinite contradictory to its theoretical composition. Our observations raise the question on the validity and applicability of available –actually estimated- thermodynamic data of Coffinite. Based on kinetic hindrance of Coffinite formation, coffinitization of spent nuclear fuel in geological disposal is not anticipated to be a dominant short term process.

INTRODUCTION

Most of the reference sites for geological disposal of nuclear waste are characterised by strongly reducing conditions ($E_h < -150$ mV/ENH) in which uranium is mainly at the +4 oxidation state. Spent nuclear fuel alteration in these conditions may proceed by local oxidising conditions at the fuel / water interface under the influence of alpha irradiation. However, due to the strong redox buffer capacity of the near-field materials (especially the canister, the corrosion products and hydrogen generation), most of the near-field environment will remain reducing. In these conditions, uranium may reprecipitate in U(IV) secondary phases. Due to the relative high concentration of silica in such system, Coffinite $USiO_4 \cdot n(H_2O)$ may be a relevant phase to consider as it has been suggested from the natural observations of the natural reactors (Oklo) and uranium ores (Cigar Lake for example).

The aim of this work was to determine the relative stabilities of the UO_2 and $USiO_4 \cdot n(H_2O)$ solids phases. For this, we wanted to study the aqueous precipitation and leaching of Coffinite. We also simulated the near-field repository conditions to observe the nature of the newly secondary phases formed.

EXPERIMENTAL

Attempts of synthesizing Coffinite

Quite few authors published protocols for synthesizing Coffinite, but to our knowledge only one paper from Fuchs showed the XRD pattern of the solid phase produced by this its preparation [1]. We have repeated its preparation procedure: a 1 mmol equimolar mixture of UCl_4 and Na_2SiO_3 was buffered by NaHCO_3 in an anoxic glove box, where a 0.5 M NaOH solution was added until the formation of a green precipitate. The slurry was poured in a stainless steel reactor, and heated for 1 day at 250°C or 4 days at 200°C .

We also reproduced other published preparation procedures [2-3] despite in those publications Coffinite had not been confirmed by XRD analysis. First, an $\text{U}_3\text{O}_8\text{-SiO}_2$ gel was introduced in a platinum capsule. It was welded, and placed in a second gold capsule containing water and a redox buffer (Ni/NiO or Fe/FeO) for producing hydrogen that diffused through the platinum and reduced U(VI) to U(IV), at 350°C - 600°C and 1500 bars-15 kbars.

In an alternative synthesis trial, a pellet and powder of UO_2 were in contact with a silica rich solution buffered in a 0.5 mol.L^{-1} NaHCO_3 aqueous solution. The mixture was poured in a stainless steel reactor, and heated for 1 month at 200°C .

In a third series of synthesis, we used an electrochemical method: a $2.10^{-3} \text{ mol.L}^{-1}$ uranyl nitrate solution was reduced in a first cellule, and transferred in a second cellule containing a solution of equimolar dissolved silica. In each cellule, a negative currency was maintained with a classical three electrode device.

For each experiment, the solid newly precipitated was collected with a filter and analysed by XRD.

Characterization and leaching study of a natural Coffinite sample

We got three natural samples of “Coffinite” from various Institutes. Surprisingly, we detected Coffinite by XRD analysis in only one sample, the sample from CREGU (Nancy, France). In order to eliminate possible U(VI) products of surface alteration, we performed a leaching study of this sample in an anoxic gloves box ($\text{P}(\text{O}_2) < 1\text{ppm}$), before eventually determining its solubility constant. The natural Coffinite sample was ground in a very fine powder. Ten tubes were prepared as described in the Table I. A 0.1 mol.L^{-1} NaHCO_3 solution was prepared at pH 8 under $\text{CO}_2(\text{g})$ and $\text{H}_2(\text{g})$ bubbling before it was introduced into the gloves box. Each tube contained 10 mL of solution.. The tubes were shaken continuously, and aliquots of solution were sampled at different times. After centrifugation, the concentration of uranium was measured by fluorescence analyser UA-3 Scintrex. At the end of the experiments, the solid was filtrated for its characterization.

Table I. Mass and m/V ratios of natural sample of Coffinite used for each test

Batch N°	1	2	3	4	5	6	7	8	9	10
mass (mg)	10.9	10.4	9.6	10.4	9.1	10.1	9.4	12.4	81.7	5
m/V (g/L)	1	1	1	1	0.9	1	0.9	1.2	8.2	0.5

Observation of the nature of phases precipitated out an aqueous solution simulating repository conditions

Batch experiments were conducted in glass bottles flushed with gas mixtures 99.7 % H₂ + 0.3% CO₂. The conditions used are described in Table II.

Table II. Conditions used for the experiments simulating repository conditions

Batch N°	11
Solution	10 mM NaCl, 2 mM NaHCO ₃ , 20 mL, [U] = 0.42 mM [SiO ₂] = 1 mM
Catalyst	2 cm ² Pt foil
Flushing gas	H ₂ + 0.3% CO ₂
Temperature	60°C
Reaction time	15 days

RESULTS

Attempts synthesizing of Coffinite

All the attempts to synthesize Coffinite led to UO₂ + SiO₂ mixtures, contrary to Coffinite USiO₄.nH₂O as expected from thermodynamical calculations (figure 1).

This inconsistency can be attributed to several reasons: the Coffinite's formation is kinetically hindered, or the solubility constant used for Coffinite is incorrect.

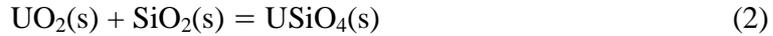
Furthermore, the boundary of the stability fields between UO₂ and Coffinite is actually not well defined because of the incapacity to obtain pure Coffinite for measuring thermodynamic data. For selecting a solubility constant value of Coffinite, Grenthe *et al.* [4] accepted Langmuir's hypothesis [5] which assumed that Uraninite and Coffinite are in equilibrium at Grants Mineral Belt:



Note that UO₂(cr) was written in Reference [4]. We wrote UO₂(s) instead because it is well known that experimental solubilities of U(IV) are several orders of magnitude higher than calculated from the Gibbs Energy of formation for UO₂(cr). This was typically discussed in many papers [4, 6-9].

The concentration of dissolved silica in the region of Grants Mineral Belt is between 10^{-3.5} and 10^{-2.7} mol.L⁻¹. Langmuir assumed an average silica concentration of 10⁻³ mol.L⁻¹ for the Uraninite-Coffinite equilibrium. The procedure of using Equation 1 together with dissolved silica concentrations to determine thermodynamic data of Coffinite is only valid if UO₂ and Coffinite control mutually the dissolved silica concentrations. However, reaction rates of these minerals are

slow and $\text{H}_4\text{SiO}_4(\text{aq})$ concentration are most likely controlled by aluminium silicates or by $\text{SiO}_2(\text{s})$ –where (s) is either for Quartz or Chalcedony. Hence Equation (1) can also be written



which means that for estimating the Coffinite stability, the $\text{H}_4\text{SiO}_4(\text{aq})$ concentration at the $\text{UO}_2(\text{cr}) / \text{USiO}_4(\text{s})$ phase equilibrium was assumed to be at the same position as the solubility of $\text{SiO}_2(\text{s})$. This frontier is between the Quartz and Chalcedony lines for many deep ground-waters. Unless Gibbs Energy of Reaction 2 is fortuitously zero -for given Temperature and Pressure- the three solids cannot be simultaneously stable. Since we always obtained $[\text{UO}_2(\text{s}) + \text{SiO}_2(\text{s})]$, it cannot be excluded that

$$\Delta_r G(2) > 0 \text{kJ.mol}^{-1} \quad (3)$$

in experimental conditions we used.

Considering the variability of dissolved silica concentrations between $10^{-3.5}$ and $10^{-2.7} \text{mol.L}^{-1}$ in a similar way as the variability in other natural water systems not containing uranium(IV) minerals and considering that the measured U concentrations agree with solubility control by $\text{UO}_2(\text{s})$, we may conclude that Coffinite is not controlling dissolved silica concentrations, hence, the waters are in equilibrium with Uraninite, but not with Coffinite. The coexistence of natural Uraninite with a probably non-equilibrium natural Coffinite indicates that the establishment of equilibrium may not even be achieved in geological time frames.

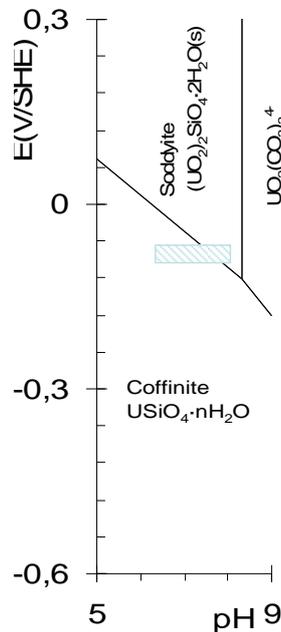


Figure 1. Predominance diagrams of uranium according Fuch's experimental conditions [1]: $[\text{U}] = 0.1 \text{mol.L}^{-1}$, $[\text{SiO}_2] = 0.1 \text{mol.L}^{-1}$, $[\text{HCO}_3^-] = 0.5 \text{mol.L}^{-1}$, $[\text{Na}^+] = 0.7 \text{mol.L}^{-1}$. The hatched area delimitates the experimental conditions we used. The Solubility constants are those selected by Grenthe *et al* [Grenthe 92].

Characterization and leaching study of a natural Coffinite sample

Coffinite, Marcasite-Pyrite (FeS_2), Galena (PbS) and Quartz were detected by XRD analysis. Marcasite and Pyrite (FeS_2) surrounded with Coffinite and Quartz was observed by SEM and EDS (Figure 2). No other Uranium phase - especially no Uraninite- was detected by XRD analysis.

This mineral contained also impurities (Pb, Y, Zr...), and was notably oxidised: 50 % of U(VI) content was estimated by XPS analysis.

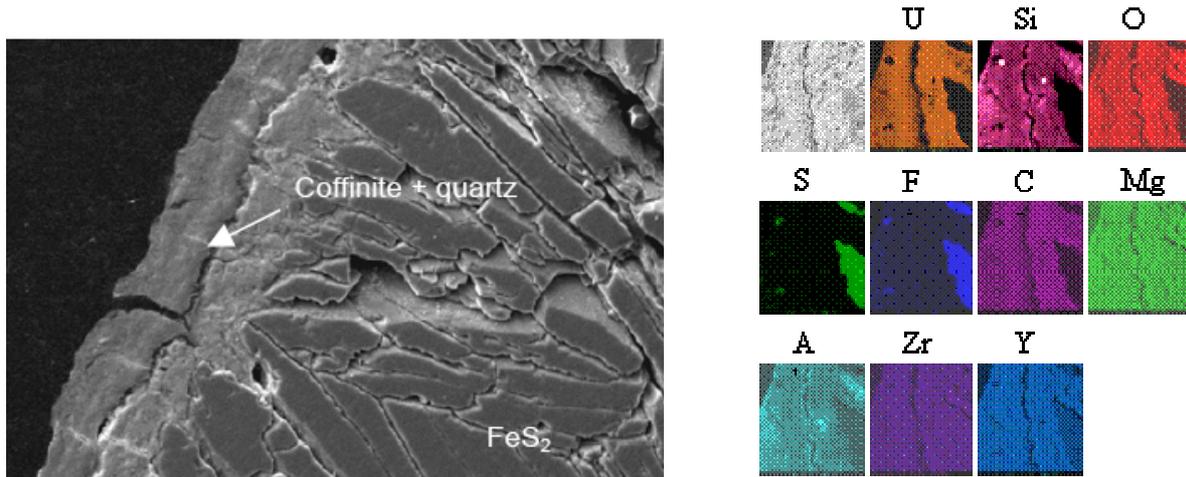


Figure 2. SEM observation of a natural sample of Coffinite from Chardon ore (Vendée/France) with EDS mapping on the right

In an attempt to remove possible superficial U(VI) corrosion products, we leached the sample with a 0.1 M NaHCO_3 aqueous solution renewed for 800 hours. The concentration of lixiviated uranium never decreased below 10^{-7} M, a concentration much higher than the expected solubility of Coffinite, when assuming it is more stable –hence less soluble- than $\text{UO}_2(\text{s})$ in these conditions ($10^{-9.5}$ mol.L⁻¹ according to Grenthe *at al.*). All tests with $m/V = 1$ g.L⁻¹ led to a complete dissolution of the solid after 800 hours leaching. With $m/V = 8$ g.L⁻¹, the remaining solid was analysed by MEB XPS and XRD (Figure 3).

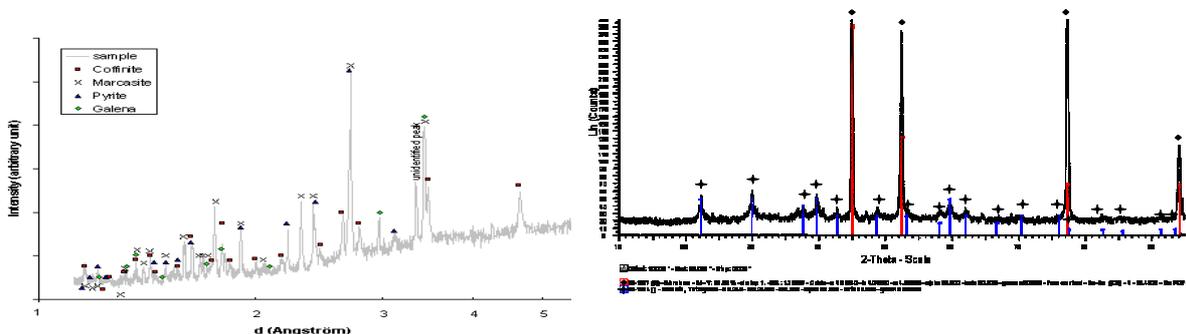


Figure 3. XRD analysis of natural sample of Coffinite, after 800 leaching with NaHCO_3 0.1 mol.L⁻¹ on the left, and of initial Coffinite isolated by hand on the right (the four highest peaks intensity are attributed to the aluminium sample holder).

The solid still contained Coffinite, Marcasite and galena. The absence of iron sulphate attests the non oxidative conditions during the leaching, moreover Pyrite was still detected after leaching, and the evolution of the XPS signals showed an increase of reduced sulphur species. Nevertheless, XPS analysis also showed the presence of 27% of uranium(VI) even after leaching and dissolution of most of the solid sample: this suggests U(VI) might have been in the Coffinite sample. We could not obtain the XRD pattern of pure Coffinite. However, we show it (Fig.3) since, to our knowledge, not any such spectrum is available in literature –only the list of the main rays is published. However, we also isolated by hand Coffinite in a part of the initial sample (Fig.3).

Observation of the phases precipitated out an aqueous solution simulating repository conditions

A new black phase progressively precipitated on the Pt foil first under the form of isolated precipitates after one day then covering the whole foil after 4 days. Its XRD pattern did not match any published U-Si phase. The diffraction data observed are listed in Table II and crystal lattice parameters derived by XRD deconvolution techniques indicate a monoclinic mineral:

$$\begin{array}{ll} a = 15.10 \text{ \AA} & \alpha = 90.0^\circ \\ b = 6.68 \text{ \AA} & \beta = 94.3^\circ \\ c = 10.13 \text{ \AA} & \gamma = 90.0^\circ \end{array}$$

Its U(IV) content was measured to be ~90-92% both by kinetic phosphorescence analysis (KPA) and an anion exchanger method. An extensive mineralogical characterisation of this new phase has been undertaken (ATD, TEM, SEM, WDS...) and will allow in a near-future to propose an accurate composition and structure.

H	K	L	D-obs (Å) measured	estimated intensity	2θ observed	2θ calculated	Δ
1	0	1	8.100	*	10.903	10.903	0.000
0	0	2	5.045	*	17.548	17.549	-0.001
3	0	0	5.025	*	17.662	17.661	0.000
-3	0	1	4.640	*	19.130	19.131	-0.001
2	2	0	3.050	*****	29.258	29.246	0.012
3	2	0	2.780	*****	32.173	32.184	-0.011
-1	2	2	2.760	****	32.429	32.428	0.001
4	1	2	2.670	***	33.532	33.530	0.002
-6	0	1	2.480	**	36.205	36.205	0.000
-2	0	4	2.450		36.650	36.646	0.004
0	2	3	2.370	*	37.930	37.930	0.000
1	1	4	2.310		38.989	38.990	-0.001
5	2	0	2.235		40.312	40.310	0.002
3	0	4	2.190	*	41.188	41.188	0.000
3	1	4	2.080	*	43.455	43.454	0.001
0	0	5	2.020	*	44.833	44.836	-0.003
1	1	5	1.900		47.826	47.828	-0.001
1	3	4	1.650	*	55.654	55.652	0.002

Table II: The XRD patterns of the black phase precipitated on Pt foil. Higher star numbers (0-6) means higher intensity. The measured XRD data are matched by the logiciel PERUM.

The precipitate (Figure 4)) formed on the Pt foil was analysed by SEM-EDS. The distribution determined in this phase is: 40 at% Uranium, 35 at % Silicon and 25 at % Sodium.

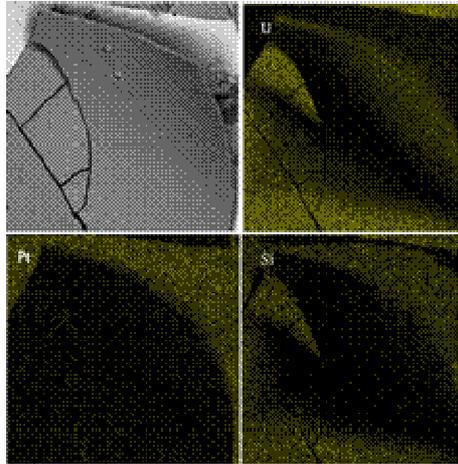


Figure 4. SEM image – EDS mapping of the U-Si phase precipitated on Pt foil.

The result of Kinetic Phosphorescence Analysis (KPA) shows 92.5% of U(IV) in total uranium in the black phase. A similar result, 90%, was achieved by the method of anion exchange separation of U(IV) and U(VI) in the dissolved precipitates. It can be concluded that the dominant part of uranium in the black phase is U(IV). The precipitate on Pt foil is not stable in air. Six months later, a sample of this phase was analysed by XRD, not any XRD peaks has then be observed. It means that the phase became amorphous upon oxidation.

CONCLUSIONS

Coffinite was synthesized and clearly identified by XRD in only one publication. We only obtained $\text{UO}_2 + \text{SiO}_2$ in all our attempts to synthesize it: no USiO_4 was detected by XRD. However, we obtained a new solid phase containing U(IV) and Si in simulated conditions of a deep repository and this new phase is still under investigation. From natural observations, the solubility of natural Coffinite is expected to be less than that of UO_2 in reducing groundwaters, but experimental confirmations are still needed. We did not succeed to measure Coffinite solubility in short time laboratory experiments, and to our knowledge no such measurements have ever been published. Based on this set of results, coffinitization of spent nuclear fuel in geological disposal is not anticipated to be a dominant short term process, but this still needs to be experimentally confirmed. These conclusions are quite surprising since (i) Coffinite is proposed for interpreting many published studies and (ii) the stabilities of ThSiO_4 compounds have been experimentally confirmed although Th is considered as a chemical analogue of U(IV). In fact, thermodynamic data deduced from the natural co-existence of Uraninite and Coffinite are probably erroneous since natural Coffinite appears to be not in thermodynamic equilibrium with groundwaters even when geological time frames are considered. The strong kinetic hindrance of Coffinite formation observed experimentally and in nature leads us to conclude that long-term coffinitisation of spent fuel, if existing, is probably a very slow process which hardly will increase the spent fuel dissolution rates under reducing non-radiolytic conditions.

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