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Journal of Nuclear Materials 321 (2003) 49–59

journal of nuclear materials

www.elsevier.com/locate/jnucmat

UO_2 dissolution in Boom Clay conditions

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Received 21 March 2002; accepted 25 March 2003

Abstract

The solubility of uranium dioxide (UO_2) was measured in real and synthetic Boom Clay waters with varying concentrations of humic acids and carbonate under reducing conditions at 20 °C. Uranium concentrations in function of time suggest the reduction of U(VI) to U(IV) by the humic acids which is occurring faster in real clay water than in synthetic clay waters. Humic acids induce also a competition to complex U(VI) in carbonate-containing solution, but they are not able to control the uranium concentration at high bicarbonate concentration (0.02 $\mathrm{mol\,dm^{-3}}$). Nevertheless they may play a role at low carbonate concentration. In our experimental conditions, the geochemical calculations indicate that two uranium secondary phases (U_4O_9 and $UO_{2(c)}$) are susceptible to control the uranium concentration in solution. These calculations are in good agreement with results of the X-ray photoelectron spectroscopy. At the end of tests, uranium concentrations reach steady-state values between 3×10^{-8} and 5×10^{-8} $\mathrm{mol\,dm^{-3}}$ in the bicarbonate-rich solutions. Although these concentrations are considered as conservative, they are 10–100 times higher than in natural Boom Clay. The consequence is that spent fuel could slowly dissolve in the interstitial clay water undersaturated with respect to UO_2/UO_{2+x} of the fuel.

1. Introduction

In the past, the Belgian strategy concerning spent nuclear fuel and nuclear waste management was based on reprocessing. Nowadays, the Belgian government considers also the direct disposal of spent nuclear fuel as an alternative.

The spent fuel is planned to be disposed of in a repository constructed at a depth of about 230 m. The Boom Clay represents the candidate geological formation for the direct disposal of nuclear waste in Belgium. This host rock has been selected due to its low hydraulic conductivity, its reducing redox capacity, its slightly alkaline character (pH of 8.2), its high specific surface area, its cationic exchange capacity and its plasticity. Important characteristics of this geological formation are the high carbonate concentration (10^{-2} $\mathrm{mol\,dm^{-3}}$) and high concentration of organic materials [1,2].

The repository for the disposal of spent fuel is based on a multibarrier concept. In such a concept, the barriers for radionuclides released into the environment are the clay host rock, the backfill, the canister overpack and the fuel itself. The innermost barrier is the limited solubility of the UO_2 matrix, which is the main component of the spent fuel.

To assess the performance of the possible final disposal of spent fuel in the Boom Clay formation in Belgium, it is important to know the maximum uranium concentration in the interstitial Boom Clay water in contact with spent fuel. The objective of this work was to measure the uranium solubility of unirradiated UO_2 in interstitial Boom Clay water and to assess the impact of various concentrations of dissolved natural organic matter and carbonate on this solubility at 20 °C. The experimental results are compared with PHREEQC geochemical calculations, to propose possible solubility controlling solid phases. The measured uranium concentration could be representative for the dissolution of

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doi:10.1016/S0022-3115(03)00199-5

spent fuel in reducing conditions, more specifically in the case of a fuel with an alpha activity that has decayed to the level where the fuel dissolution kinetics is chemically controlled.

2. Experimental

Depleted UO_2 powder with a particle diameter ranging between 50 and 100 μm was immersed in PTFE containers with interstitial and synthetic clay waters for various reaction times, at a target SA/V (= UO_2 surface area/leachant volume) of 1000 m^{-1}. The specific surface area of the UO_2 powder was estimated to be 0.044 $m^{-2}\,g^{-1}$ based on BET measurements. Moreover, UO_2 disks were added in some containers to verify the oxidation state of the surface by X-ray photoelectron spectrometry (XPS).

Four types of clay water were used: real interstitial Boom Clay water (‘RIC’, sampled in the underground laboratory), synthetic Boom Clay water without humic acids (‘SCW’), synthetic Boom Clay water with humic acids (‘SCWHA’) and synthetic Boom Clay water with humic acids and low carbonate content (‘SCWHA\C’). To synthesise the SCW, SCWHA and SCWHA\C solutions, commercial salts were dissolved in degassed high performance liquid chromatography (HPLC) water. In order to prepare the SCWHA and SCWHA\C solutions, organic acids extracted from real clay water were used. This extract is a concentrate of dissolved natural organic matter (‘NOM’), consisting mainly of humic acids. The different clay solutions differ essentially in their Na^+, Cl^-, SO_4^{2-}, total HCO_3^- inorganic carbon and organic content. Considering our experimental conditions and the definition of total inorganic carbon (Eq. (1)), total inorganic carbon could be assumed to $[HCO_3^-]$ in a simplified hypothesis, even if this value is slightly overestimated.

$$\mathrm{TIC} = [\mathrm{CO_2}]_{\mathrm{aq}} + [\mathrm{H_2CO_3}] + [\mathrm{HCO_3^-}] + [\mathrm{CO_3^{2-}}] \tag{1}$$

Typical compositions of the blank test solutions are presented in Table 1 where total inorganic carbon is presented as $[HCO_3^-]$. Only the main elements are presented.

The solubility tests were carried out in duplicate, at 20 °C. Tests with carbonate-rich solutions were performed in a glove box with an atmosphere consisting of 99.6% Ar/0.4% CO_2 to stabilise the pH at a value around 8.2 – the pH of the Boom Clay water – without too many fluctuations. Tests with the carbonate-poor solution (SCWHA\C) were placed in a glove box with argon atmosphere and the pH was maintained around 8.2 by adding 0.1 M HCl or 0.1 M NaOH when it was necessary. Small volumes of a Na_2S solution (10 $mg\,l^{-1}$ sulphide in degassed high performance liquid chromatography water) were added to the leaching container at regular time intervals, to keep the measured redox potential lower than −150 m/V vs SHE.

The redox potential was determined with a Pt–Ag/AgCl combined electrode. The precision of such measurements in pure clay water is in general low, and the measured E_h does not necessarily reflect the redox state of the system. Therefore, the results of the redox measurements are only a rough indication of the oxidising or reducing capacity of the solution.

The pH was measured with a combined glass electrode. The 95% confidence interval is 0.2 pH units.

At regular time intervals, aliquots of a few ml were taken from the leachates to determine the dissolved uranium concentration, and the test containers were replenished to the original volume with fresh solution. In the leachates, the concentrations of uranium were measured after ultrafiltration at 30 000 molecular weight cut-off, whereas the concentrations of bicarbonate and organic matter were determined without any filtration. The uranium concentrations were measured by inductively coupled plasma-mass spectrometry (ICP-MS); the 95% confidence interval 2σ is about 15%. The bicarbonate and organic matter concentrations were measured with a total organic carbon–total inorganic carbon analyser (Rosemount Dohrmann). At the beginning and at the end of the leaching tests, major anionic and cationic species of the solution were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

Table 1
Concentration of the main elements in the blank test solutions

	Na^+ ($mg\,l^{-1}$)	Cl^- ($mg\,l^{-1}$)	SO_4^{2-} ($mg\,l^{-1}$)	$HCO_3^{-\,a}$ ($mg\,l^{-1}$)	NOM ($mg\,l^{-1}$)	U ($mol\,dm^{-3}$)
RIC	420	28	<1	900	167	1×10^{-9}
SCW	347	56	20	900	<10	1×10^{-8}
SCWHA	590	367	20	900	177	1×10^{-9}
SCWHA\C	240	367	20	4	177	4×10^{-8}

The 95% confidence interval 2σ is about: 10% (Na^+), 5% (Cl^-, SO_4^{2-}), 20% (HCO_3^-, NOM), 15% (U).

[a] Measured as Total Inorganic Carbon.

Before the solubility tests were started, the oxidised layer of the UO_2 powder was removed by a 'pre-dissolution' procedure. About 4 g of the UO_2 powder was weighed and transferred into a PTFE container of 200 ml volume. A volume of 40 ml of 'pre-dissolution' solution was added. The containers were kept at 20 °C in the argon or argon/CO_2 purged glove boxes. Every few days, the leachate was replaced by fresh solution. The uranium concentrations in the leachates were measured by ICP-MS. When the dissolution rate was constant, the oxidised layer was considered to be removed, and the solubility tests were started. The completeness of the pre-dissolution was verified by surface analysis on one UO_2 disk during the pre-dissolution.

The pre-dissolution of the tests with carbonate-rich solutions was performed with SCW water (900 $mg\,l^{-1}$ HCO_3^-). By using only one type of pre-dissolution solution, we make sure that we have a comparable UO_2 surface for all bicarbonate-rich solutions at the end of the pre-dissolution step. The pre-dissolution for the bicarbonate-poor solution was performed with a solution, similar to SCW water, but with less bicarbonate, called SCW\C. To decrease the carbonate content, the SCW\C solution was acidified until pH 5, warmed to 50 °C and simultaneously flushed with argon. Finally, to obtain a pH equal to 8.2 as in Boom Clay water, the solution was neutralised with NaOH, which was first treated with $BaCl_2$ to precipitate the traces of carbonate as $BaCO_3$. The resulting carbonate concentration of SCW\C was 10 $mg\,l^{-1}$.

3. Results and discussion

3.1. Pre-dissolution

In the pre-dissolution step, the leachant was replaced 50 times in 207 days for the bicarbonate-rich solutions and 22 times in 126 days for the bicarbonate-poor solution.

The dissolution rate decreases drastically in the first few days (Figs. 1 and 2). The dissolution rate is one order of magnitude lower in the bicarbonate-poor solution; this is due to a combined effect of the lower bicarbonate content and maybe also due to the lower oxygen content in the glove box ($\leqslant$ 1 ppm in the argon box, compared with 3 ppm in the Ar/CO_2 box). By the end of the pre-dissolution step, when most U(VI) is dissolved, the uranium concentrations are very sensitive to fluctuations of the oxygen concentration in the glove box. After 207 days, when the dissolution rate of uranium was fluctuating around 3×10^{-8} $mol\,m^{-2}\,d^{-1}$ in the bicarbonate-rich solutions, the leaching tests were started. For the bicarbonate-poor solution, the pre-dissolution was stopped after 126 days, when the dissolution rate was about 4×10^{-9} $mol\,m^{-2}\,d^{-1}$.

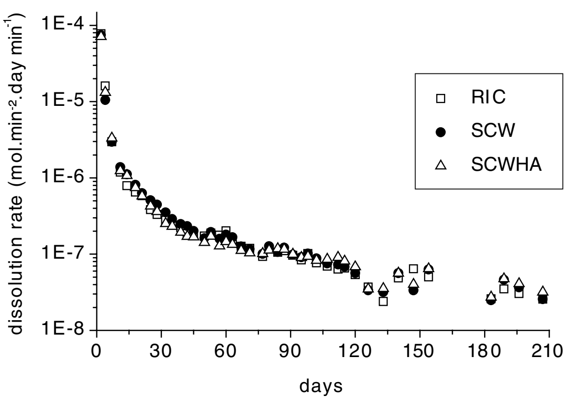

Fig. 1. UO_2 dissolution rate during the pre-dissolution step in the bicarbonate-rich solutions; RIC = real interstitial Boom Clay water; SCW = synthetic Clay water; SCWHA = synthetic Clay water with humic acids.

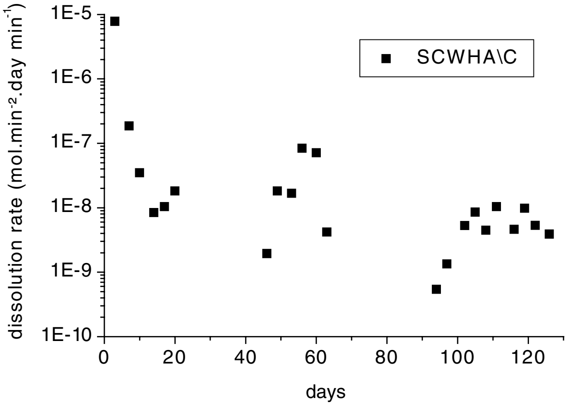

Fig. 2. UO_2 dissolution rate during the pre-dissolution step in the bicarbonate-poor solution; SCWHA\C = synthetic Clay water with humic acids and low carbonate content.

3.2. Solubility tests

After the pre-dissolution step, the test containers were filled with 180 ml of the respective solutions (RIC, SCW, SCWHA and SCWHA\C). In order to measure the uranium concentrations in solution, samples were taken every three or four days during the first 15 days of experiment, and then every 15 days. The solubility tests lasted for 249 days for the bicarbonate-poor solution and 370 days for the bicarbonate-rich solutions.

3.2.1. pH and E_h measurements

For the bicarbonate-rich solutions, the mean pH value of the leachates was 8.3–8.4 whereas for the bicarbonate-poor solutions, the pH of the leachates was between 8.2 and 9 with an average value of 8.5. This pH range is in good agreement with the pH of the in situ Boom Clay water (8.2) in all the solutions.

The addition of sodium sulphide to the leachates stabilised the redox potential at values lower than −150 m/V vs SHE; the presumed threshold for oxidative dissolution of UO_2 as discussed in [3]. Nevertheless to maintain the measured E_h lower than −150 m/V vs SHE, sodium sulphide was added three times to the bicarbonate-rich solutions (at the start of the solubility test and after 25 and 84 days), whereas two adjustments (at the start of the solubility and after 117 days) were necessary in the bicarbonate-poor solutions. In the bicarbonate-rich leachates, the average E_h value is around −160/−170 m/V vs SHE whereas it is around −190/−200 m/V vs SHE in the bicarbonate-poor leachates. The bicarbonate-poor solution required less adjustment, and the value of the redox potential was more reducing than in the bicarbonate-rich solutions, because of the smaller quantity of oxygen in the argon glove box (normally $\leqslant 1$ ppm) than in the 99.6% Ar/0.4% CO_2 glove (∼3 ppm), and hence the slower oxidation of sulphide. The different behaviour confirms the importance of the oxygen concentration in the glove box atmosphere.

3.2.2. Solution analysis (anionic and cationic major species)

At the end of the leaching tests, the sodium concentrations in the bicarbonate-rich solutions had increased with about 40 $mg\,l^{-1}$, which corresponds to the three additions of Na_2S solution. At the same time, no increase of sulphate concentration was observed in the leachates. If the sulphide species were oxidised during the leaching, the sulphate concentration would have increased with 90 $mg\,l^{-1}$ maximum. Because this is not the case, we can assume that either the sulphide species remain preserved, or they are oxidised into another form than sulphate species such as thiosulphates. Although the thiosulphates were not analysed, their presence seems not realistic taking into account the E_h–pH diagrams of sulphur [4]. Also, no variation of the cationic content was noticed, which means that no sulphur phases were precipitated from solution.

Table 2
Uranium concentration and pH in solubility tests after 249 and 370 days of leaching

Solution	Leaching duration (days)	pH	[U] ($mol\,dm^{-3}$)
RIC	370	8.2	$2.9–3.6 \times 10^{-8}$
SCW	370	8.2	$3.7–4.4 \times 10^{-8}$
SCWHA	370	8.1	$5.3 \times 10^{-8}–9.7 \times 10^{-8}$[a]
SCWHA\C	249	8.2	1.5×10^{-6}

[a] The highest value (9.7×10^{-8} $mol\,l^{-1}$) at 349 days is not considered.

3.2.3. Uranium concentration

At the end of the leaching tests, the uranium concentrations are between 3×10^{-8} and 1.5×10^{-6} $mol\,dm^{-3}$ in the following order: RIC ≈ SCW ≈ SCWHA ≪ SCWHA\C. The uranium concentrations are given in Table 2. The evolution of the uranium concentrations with time is shown in Fig. 3(a) and (b).

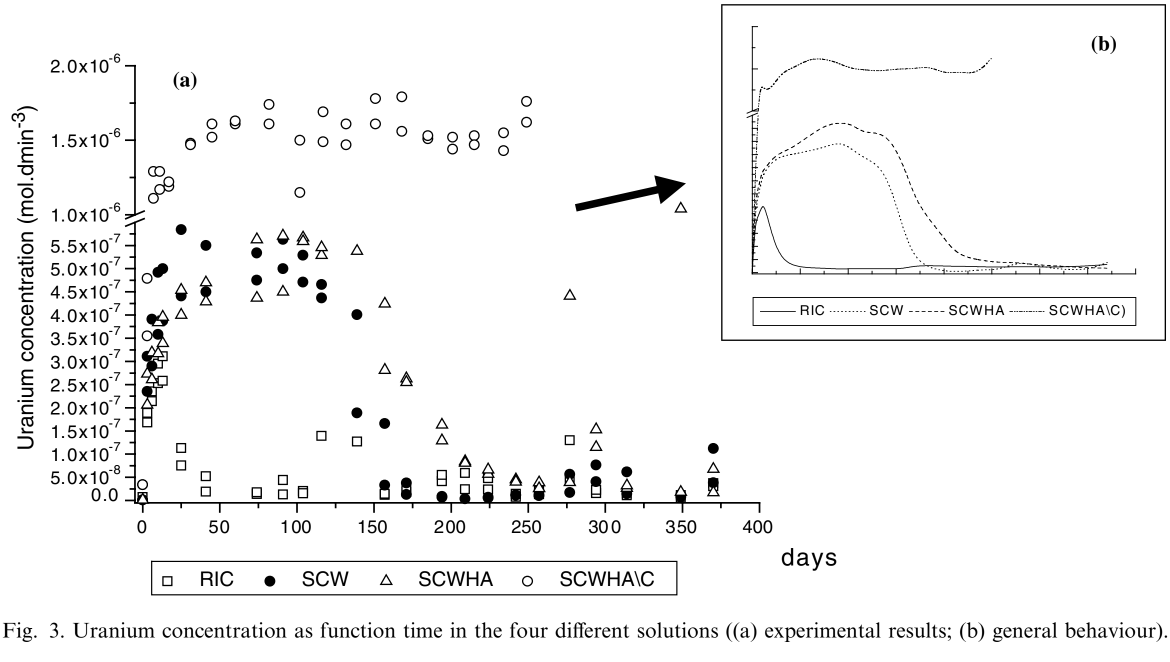

Fig. 3. Uranium concentration as function time in the four different solutions ((a) experimental results; (b) general behaviour).

In the first 15 days the uranium concentrations in the bicarbonate-rich solutions increase until around 5×10^{-7} mol dm^{-3} although the redox potential is lower than −150 m/V vs SHE. Afterwards, the uranium concentrations decrease with more than one order of magnitude.

After 15 days, a difference in uranium concentration appears between real and synthetic clay waters. Whereas a decrease in uranium concentration is observed in RIC after 13–25 days, this decrease occurs only after about 100 days in the synthetic waters (SCW and SCWHA). In the SCWHA solution, the decrease presents a delay (about 50 days) in comparison to the decrease in the SCW solution. This delay stayed constant until the equilibrium was reached.

Until 100 days, there was no difference between the tests with bicarbonate (SCW) and tests with bicarbonate and humic acids (SCWHA). Because SCW was used for the pre-dissolution of both the SCW and SCWHA, we can consider that the efficiency of the pre-dissolution was the same in both solutions and so, we can assume that humic acids and carbonate species are in competition for the uranium complexation.

Minimum uranium concentrations are reached after about 50 days in RIC, after about 200 days in SCW and after about 250 days in SCWHA. These uranium concentrations showed some variations, probably due to small oxygen contaminations. The fluctuations are more important in synthetic clay waters (SCW and SCWHA) than in real clay water (RIC) in the last 100 days. Nevertheless, the uranium concentrations stay in a relatively narrow range of 3×10^{-8}–9.7×10^{-8} mol dm^{-3} for RIC, SCW and SCWHA. In RIC and SCW, they are close to 4×10^{-8} mol dm^{-3}, whereas in SCWHA they are not lower than 5×10^{-8} mol dm^{-3} (Table 2).

The delay in the decrease of the uranium concentration in the synthetic clay waters SCW and SCWHA, compared with RIC, can be explained by the nature of the redox active species in the respective solutions. In the real clay water (RIC), Fe(II) species are probably involved in the redox control. No ferrous ions are present in the synthetic solutions SCWHA and SCW. Even if the humic acids (HA), used for the preparation of SCWHA, initially contained ferrous ions, these were oxidised to ferric ions during the extraction from the Boom Clay. In RIC, the addition of sulphide could cause the precipitation of an iron-sulphide phase. The presence of such phase was confirmed by the surface analyses of UO_2 fragments (see further). In that case, the redox potential could be controlled by an equilibrium between the iron sulphide and a not specified iron sulphide oxidation product, whereas in the synthetic solutions, the redox couple is probably HS^- and a not specified sulphide oxidation product. Because HS^- is a much slower reductant than Fe(II), the uranium concentration decreases faster in RIC than in SCW and SCWHA. During the first 15 days, the uranium concentrations present the same increase in RIC and in the synthetic solutions, probably because the establishment of redox equilibrium is slow.

Apart from the absence of Fe(II), the presence of oxygen in the commercial salts, used to prepare the synthetic solutions, could contribute to the delayed decrease of the uranium concentration in the solutions. These salts are not added to the RIC, which is sampled in the HADES underground laboratory without exposure to the atmosphere.

Because no potential source of sorption is present in our experiments, we assume that the decrease of the uranium concentration is caused by the reduction of U(VI) to U(IV). The similar final uranium concentrations in RIC, SCW and SCWHA, suggest that the complexation of uranium by humic acids is not important for the total uranium concentration at high bicarbonate concentration. Recently, this assumption was confirmed by Delécaut [5], who demonstrated that uranium carbonates clearly dominate the complexation of uranium(VI) in conditions representative for Boom Clay, and that the organic matter predominantly immobilises uranium(VI), either by reduction or complexation, rather than to mobilise it by complexation in solution. So, although there is a competition between humic acids and carbonate, the U(VI)-carbonate complexes probably dominate in the bicarbonate-rich solutions. The reduction of the complexed U(VI) to U(IV) is fast in the real clay water, but in the synthetic clay water, the humic acids retard the reduction. This is probably due to the fact that the humic acids used to prepare the synthetic water were in contact with oxygen during their extraction from real clay water, and consequently, their reducing capacity is lowered. We can expect that the corresponding U(VI)-HA complexes are more difficult to reduce than the U(VI)-carbonate complexes. Because the U(VI)-HA complexes are a minority, the reduction is only delayed, and the final uranium concentrations are similar as in the other bicarbonate-rich solutions.

In the bicarbonate-poor solution, the uranium concentration is much higher than in the bicarbonate-rich solutions. From 30 until 250 days, the uranium concentration remained stable and around 1.5×10^{-6} mol dm^{-3}. The high initial concentrations are probably due to the fact that the oxidised surface layer was certainly not totally removed, although the dissolution rate of uranium oxide, in bicarbonate-poor water, was very low after 126 days of pre-dissolution (10^{-9} mol U m^{-2} d^{-1}). We assume that this is due to the low concentration of carbonate during the pre-dissolution step. The SCW\C solution used for the pre-dissolution indeed had a low carbonate content and no humic acids. Between 30 and 250 days, no reduction of U(VI) to U(IV) occurs. Probably, when carbonate is absent, or present in small quantities, the humic acids in solution contribute significantly to the complexation of the uranium (VI) in spite of its low affinity for humic acids [5,6]. The possible oxidation of the humic acids during their extraction can explain why these U(VI)-HA complexes are more difficult to reduce than the U(VI)-carbonate complexes (or complexes with more reducing humic acids) in the other solutions. Assuming that the fraction of U(VI)-HA complexes is important in the bicarbonate-poor solution, this could explain why the reduction of U(VI) to U(IV) was completely blocked.

Because of the incomplete pre-dissolution, the tests in the bicarbonate-poor solution were not conclusive. However, because the total uranium concentration was not influenced by the addition of humic acids to the synthetic bicarbonate-rich clay water, we can still conclude that complexation of U(VI) by carbonate is more important than complexation by humic acids in Boom Clay water [5]. We cannot yet drawn any conclusion for the U(IV) complexation

Due to the presence of simultaneous humic acids and the high bicarbonate concentration (10^{-2} mol dm^{-3}) in Boom Clay, only few similar experiments can be found in the literature, allowing comparison with our results.

In the TRANCOM project [7] using an oversaturation method, the solubility of a freshly prepared amorphous U(IV) solid phase is about 10^{-4} mol dm^{-3} in Boom Clay interstitial water. This value agrees with the solubility of $UO_{2(am)}$ based on NEA database [8] but it is higher than those determined in our solubility tests (3–5×10^{-8} mol dm^{-3}). The difference of four orders of magnitude in solubility value could be due to a combined effect of (1) the presence of colloids due to the non-filtration of solutions [9], (2) the presence of U(VI) traces (oxidation of U(IV) to U(VI) by the few O_2 ppm in the glove box in absence of reductants) and (3) the different degree of crystallinity of the solid phase (even if the latter argument is debatable [10–12]).

For the solubility of $UO_{2(am)}$, Rai et al. [12] observed uranium concentrations of 10^{-8}–10^{-9} mol dm^{-3} in solution until less than 0.1 M carbonate and in presence of reductants such as Fe powder and $Na_2S_2O_4$. The value determined by Rai is slightly lower than the uranium concentration in our experiments (3–5×10^{-8} mol dm^{-3}). This is may be due to the presence of some U(VI) traces in our tests caused by the difficulties to maintain U in the tetravalent state for a long time. On the other hand, our experiments were performed with a crystalline solid phase, so we do not expect $UO_{2(am)}$ to control solubility.

In reducing conditions obtained by a constant H_2 bubbling using a Pd catalyst and addition of sulfide/ferrous species to a synthetic Boom Clay water, Guilbert et al. [13] determined a uranium concentration of 3.3×10^{-6} mol dm^{-3} after 33 days of leaching of UO_2 pellets. Due to the traces of oxygen in the atmosphere at the beginning of the test, causing an oxidation of the uranium dioxide, this value is one order of magnitude higher than those measured in our solubility tests in SCW and SCWHA before the uranium concentration decreased between 4×10^{-7} and 6×10^{-7} mol dm^{-3}.

Ollila [14] measured a uranium concentration of about 10^{-9} mol dm^{-3} in synthetic groundwaters (saline and fresh modified Allard waters where various amounts of redox species (a.o. sulphide) were added and O_2 concentration less than 0.1 ppm) in contact with UO_2 pellets and UO_2 powders. The higher oxygen concentration in our argon/CO_2 glove box (about 3 ppm), combined with the higher carbonate concentrations in our solutions, stabilising U(VI) even at redox potentials lower than −150 m/V vs SHE, explains the higher uranium concentration in our leaching tests.

The uranium concentrations determined in our reducing conditions are 10–100 high than the concentrations measured in natural Boom Clay water (10^{-9}–10^{-10} mol dm^{-3}) [7]. However, the redox potential (around −160/−170 m/V vs SHE) was always higher than expected in the undistrubed Boom Clay formation (−250/−400 m/V vs SHE), so the measured uranium concentrations are conservative values. Moreover, no clay has been added in the tests performed so far. If the dissolved uranium species sorb onto the clay, this may cause a further decrease of the equilibrium concentrations. Existing data suggest however that the clay impact is small. Indeed, in experiments with UO_2 fuel in the presence of clay, uranium concentrations of the order of magnitude of 10^{-8} mol dm^{-3} were measured [15], which is similar to the concentrations determined in reducing Boom Clay water in our tests.

3.2.4. Modelling

To propose possible solubility controlling solid phases, the experimental results are compared with the results of geochemical modelling. The calculations have been performed with the PHREEQC code, release 1.6 [16] and the thermodynamic date of the uranium solid phases presented in Table 3 which are extracted from the thermodynamic database Wateq4f [17] and completed with data from Bruno and Puigdomenech [18]. The effect of the complex formation of uranium with humic acids is not taken into account in the geochemical calculations for the SCWHA solution. Although data on humic-uranium complexation are available [Delécaut unpublished data], none of these data were determined or interpreted in a rigorous thermodynamic way and they are not suited for use in geochemical calculations.

The input data of the geochemical calculations are based on experimental measurements: pH, E_h, anionic and cationic concentrations of the solution. For the bicarbonate-rich experiments, the HCO_3^- species has been chosen as experimental input data because it is the main carbonate species in our experimental conditions. The [HCO_3^-] concentrations have been determined by a Gran titration [19] and they are presented in Table 4. These

Table 3
Thermodynamic data used in the geochemical calculations [17,18]

Phase or species	Reaction	Log *K*
Uraninite(c)	$UO_{2(c)} + 4H^+ \rightarrow U^{4+} + 2H_2O$	−4.80
$UO_{2(fuel)}$	$UO_{2(fuel)} + 4H^+ \rightarrow U^{4+} + 2H_2O$	−1.60
$U_3O_{8(c)}$	$U_3O_{8(c)} + 16H^+ + 4e^- \rightarrow 3U^{4+} + 8H_2O$	20.53
$U_4O_{9(c)}$	$U_4O_{9(c)} + 18H^+ + 2e^- \rightarrow 4U^{4+} + 9H_2O$	−3.38
$UO_{2(am)}$	$UO_{2(am)} + 4H^+ \rightarrow U^{4+} + 2H_2O$	0.10
$U(OH)_{4(am)}$	$U^{4+} + 4H_2O \rightarrow U(OH)_{4(am)} + 4H^+$	0.50
Coffinite	$USiO_4 + 4H^+ \rightarrow U^{4+} + H_4SiO_4$	−7.67
$U(OH)_{4(aq)}$	$UO_{2(am)} + 4H^+ \rightarrow U^{4+} + 2H_2O$	−8.50

Table 4
Mean $[HCO_3^-]$ concentrations obtained by the Gran titration

	$[HCO_3^-]_{aq}$ ($mol\,dm^{-3}$)	$[HCO_3^-]_{aq}$ ($mg\,l^{-1}$)
RIC	8×10^{-3}	488
SCW	6×10^{-3}	366
SCWHA	7.3×10^{-3}	445

concentrations are lower than those presented in Table 1, although the latter values are slightly overestimed because they refer to the total inorganic carbon. Indeed, considering that the Gran titration was performed in a 99.6% Ar/0.4% CO_2 glove box, the equilibrium controlling the carbonate concentration (Eq. (2)) was perturbed when concentrated acid (HCl) was added. This resulted in an underestimation of the bicarbonate concentration.

$$\begin{aligned} &CO_{2(g)} \leftrightarrow CO_{2(aq)} \\ &CO_{2(aq)} + H_2O \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2H^+ \end{aligned} \tag{2}$$

In the bicarbonate-rich tests, $UO_2(CO_3)_3^{4-}$ is calculated to be the dominant species in solution. The calculations predict that two uranium phases could control the UO_2 solubility in our experimental conditions: $U_4O_{9(c)}$ and $UO_{2(c)}$. Such prediction is in good agreement with literature data [20].

However, in these calculations, the measured E_h values were taken as input data. As mentioned in Section 2, the measured E_h does not necessarily reflect the redox state of the system. Consequently, the results of the modelling can only be considered as indicative and must be compared with the other experimental results like the XPS results. Therefore no solubility values are given.

3.2.5. XPS analysis

The spectrometer used was a Physical Electronics ESCA model 1600 with a non-monochromated Al X-ray source ($K_\alpha = 1486.6$ eV) operated at 400 W, installed at the Vrije Universiteit Brussel (VUB, Belgium). The system is PC controlled and the data were acquired during 2 h per sample and analysed with the PHI MULTIPACK package [21]. Low resolution survey spectra were recorded for the 0–1400 eV region to determine the elements present in the sample and to check for surface contamination. High resolution spectra were recorded for the U4f (376–430 eV), O1s (520–545 eV), C1s (280–300 eV) and valence band (0–30 eV) regions, to determine the chemical state and chemical environment of the elements.

The calibration of the spectra was performed by the reposition of the C1s peak at 285 eV stemming from the hydrocarbons of the slight contamination present on the sample surfaces.

Four UO_2 samples were analysed: one sample after the pre-dissolution step and three leached samples at the end the leaching tests (SCW, SCWHA and RIC after 370 days). The UO_2 sample after pre-dissolution will be called our UO_2 reference in the following paragraphs. This sample was compared with a non-oxidised UO_2 sample [21]. The analyses were performed in several campaigns. Table 5 summarises the results obtained for the four specific regions of the four samples. The data of the non-oxidised UO_2 [21] are given as reference data to compare with our samples.

Based on literature spectra [22–26] and on the comparison with the non-oxidised UO_2 [21], the XPS analyses reveal that our UO_2 reference (after the pre-dissolution step) is still slightly oxidised and could correspond to UO_{2+x} with x close to 0.25 or slightly greater than 0.25. The UO_2 samples, leached in the different clay waters (RIC, SCW, SCWHA), are less oxidised than our UO_2 reference. The energy of the U4f orbitals are indeed present at lower binding energy (380.2 eV instead of 380.5 eV) and the peaks are less wide than our UO_2 reference (2 eV instead of 2.6 eV) (Fig. 4). The samples leached in RIC and SCWHA are less oxidised than the sample leached in SCW. Their uranium oxidation state are close to U(IV) due to the values of the U4f peaks close to the UO_2 in [21]. Moreover, the samples leached in RIC and SCWHA, are also more hydrated than the sample leached in SCW, due to the presence of humic acids which can sorb onto the sample surface. This is shown by the presence of the hydroxide-water peaks at

Table 5
X-ray photoelectron spectroscopy results (binding energies are given in eV)

Sample	Uranium	U4f				
	Satellite 1	U4f$_{7/2}$	FWHM[a]	U4f$_{5/2}$	FWHM[a]	Satellite 2
UO$_2$ [21]	386.5	380.0	2.2	390.8	2.2	397.5
UO$_2$ reference	387.5	380.5	2.6	391.3	2.6	398.1
RIC-3	386.9	380.2	2.0	391.0	2.0	398.0
SCW-3	387.2	380.4	2.2	391.2	2.2	398.1
SCWHA-3	387.0	380.2	2.0	391.0	2.0	398.0
	Oxygen	O1s				
	Oxide	Hydroxide-water		Carbonate		FWHM[a]
UO$_2$ [21]	530.4					1.5
UO$_2$ reference	530.7					1.6
RIC-3	530.4	531.8				2.4
SCW-3	530.5	531.7		533		1.8
SCWHA-3	530.2	531.4		533		2.4
	Carbon	C1s				
		Carbonate				FWHM[a]
UO$_2$ [21]		–				1.4
UO$_2$ reference		289.7 (traces)				1.8
RIC-3		289.9 (traces)				2.0
SCW-3		289.8				1.9
SCWHA-3		289.0				2.0
	Valence bands					
	U5f	(U–O2p)				U5f/(U–O2p)
UO$_2$ [21]	1.3	5.0				2.1
UO$_2$ reference	2.2	5.8				2.1
RIC-3	1.4	5.3				2.0
SCW-3	1.6	5.5				2.2
SCWHA-3	1.4	5.2				2.1

The uncertainty of the binding energy is 0.1 eV.
[a] FWHM: full width half-maximum.

531.8 eV and the large width of the O1s peak (2.4 eV instead of 1.6 eV) (Fig. 5). The presence of carbonate is also suspected for the samples leached in SCWHA and SCW due to the band around 533 eV (Fig. 5). This is confirmed by a not well defined peak around 289 eV (Fig. 6). Based on the spectra, we propose that the chemical composition would be close to U$_4$O$_9$ for the sample leached in SCW, whereas it would be between UO$_2$ and U$_4$O$_9$ (with some hydroxyl or water traces) for the samples leached in RIC and SCWHA. The structure of the valence bands (not shown) and the value of the ratio of the intensity of the peaks U5f/(U–O2p) indicate that a more oxidised composition can be excluded (Table 5). In fact, in the valence bands the intensity of the U5f peak decreases as the O/U ratio increases whereas at the same time, the intensity of the U–O2p peak increases [27]. If the sample is oxidised, the ratio is around 1, and it is around 2 when the sample is reduced. These results are in good agreement with the geochemical modelling of the experiments which predict UO$_2$ and U$_4$O$_9$ as potential controlling solid phase of the UO$_2$ solubility in our experimental conditions.

Moreover on the samples leached in SCW and SCWHA, we suspect the presence of NaHCO$_3$, which is the major compound of these synthetic clay waters. This explains also the presence of the carbonate in the O1s and C1 regions. Indeed in such solutions (SCW and SCWHA), it is possible to find on the surface some particles or grains, precipitated during the leaching tests due to the slightly non-equilibrated composition. This kind of precipitation is less likely in the RIC water, which is the real interstitial water, in good equilibrium with the geological medium.

On the survey spectra (not shown), the main difference concerns the presence of sulphur on the leached sample in RIC. Other elements such as Na, Ca, Cl and Fe coming from the solution, are present on the three leached sample surfaces. These elements are due to the evaporation of water from the surface of the sample when the sample is removed from the leaching container.

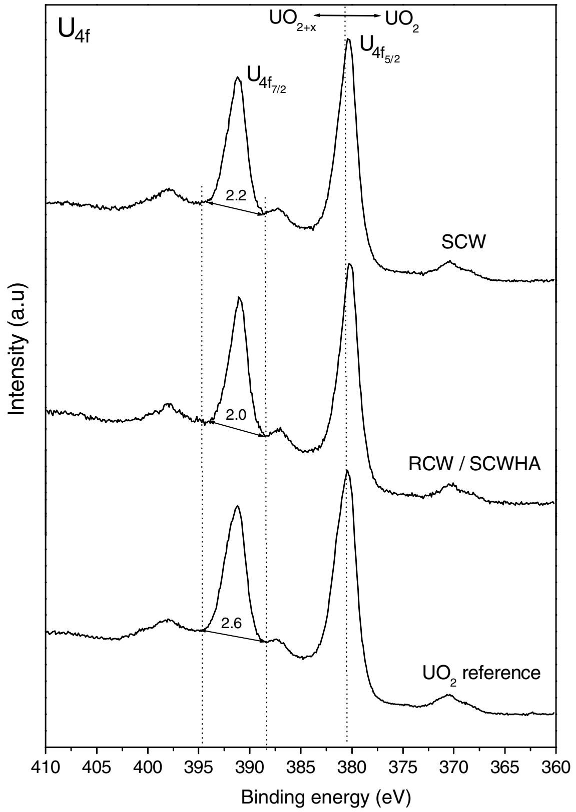

Fig. 4. U4f region for the UO_2 reference and the samples leached in RCW, SCW and SCWHA waters.

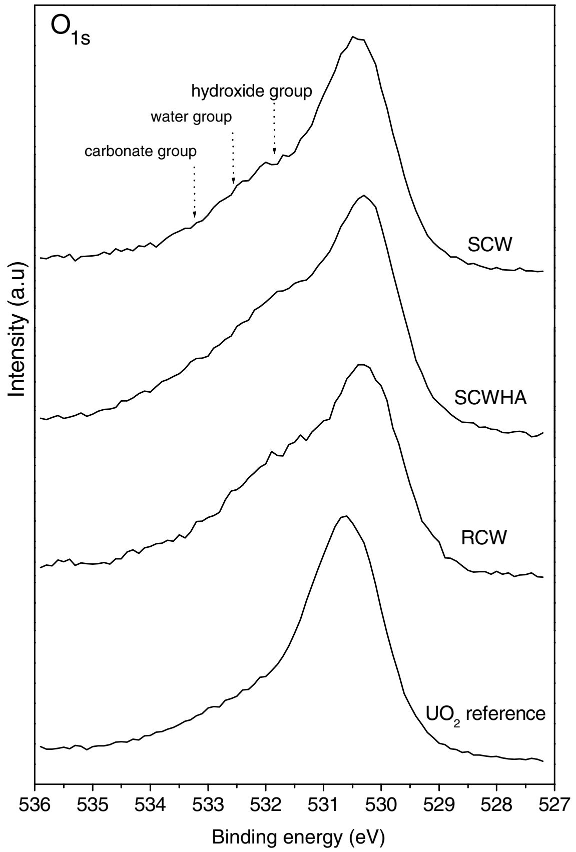

Fig. 5. O1s region for the UO_2 reference and the samples leached in RCW, SCW and SCWHA waters.

Nevertheless, the presence of iron on the leached sample in SCW is surprising, because the solution does not contain humic acids, which is the most likely source of Fe in our system. Because of this, complementary analyses were performed on this sample and on the sample leached in RIC after cleaning the surface by an Ar beam (2.5×2.5 mm^2, 1 min at 4 kV).

For the sample leached in SCW, the iron can be considered as a pollution coming from the analysis preparation of the sample in the glove box. During the first analysis of the sample leached in RIC, iron and sulphur were present on the entire surface, probably associated with each other. The position of the iron and sulphur peaks corresponds to an iron-sulphide phase. After this first XPS analysis, the sample was stored during 300 days in the Ar/CO_2 glove box before a second analysis was performed, revealing a separate phase. We envisage that during the storage duration, the iron–sulphur layer got concentrated into a spot. The spot is green–grey and can be easily observed by the eye. After the Ar cleaning, iron is still present. The analysis of the spot shows the presence of iron and sulphur without uranium. To verify this result, the spot was also observed by SEM and analysed by energy dispersive X-ray spectrometry (EDS). The analysis indicates a stochiometry close to FeS. This phase corresponds to a metastable iron–sulphur phase important as precursor to pyrite formation in sediments and hydrothermal systems [28,29]. Therefore the presence of this phase in our system is plausible. The precipitation of FeS phase or pyrite on the leached sample in RIC supports the assumption of a probable redox control by such iron phases.

4. Conclusion

The uranium solubility was measured with unirradiated UO_2 as the solid phase at 20 °C in reducing conditions, in real Boom Clay water (RIC) and in synthetic Boom Clay water with humic acids (SCWHA), without humic acids (SCW), and with humic acids but low bicarbonate content (SCWHA\C).

The $CO_{2(g)}$ content of the atmosphere was controlled using an Ar/CO_2 glove box, and reducing conditions were achieved by addition of sulphide to the clay waters. The addition of sulphide caused a decrease with time of

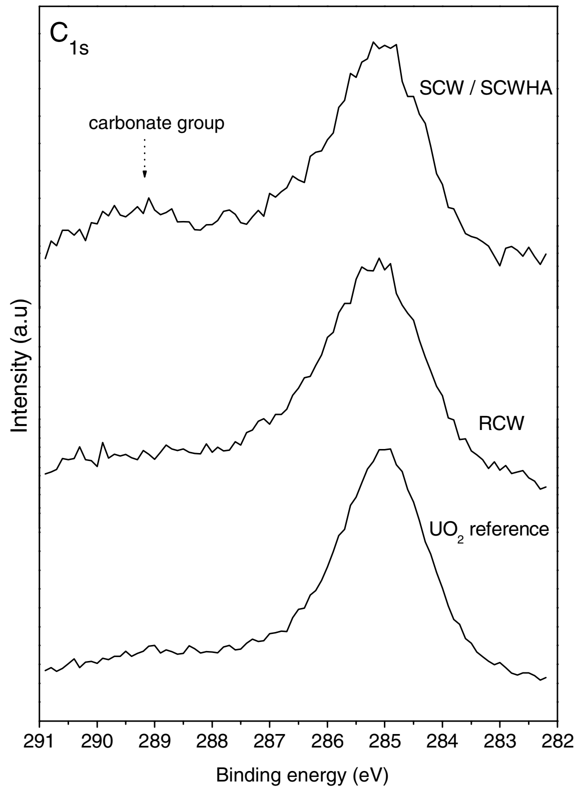

Fig. 6. C1s region for the UO_2 reference and the samples leached in RCW, SCW and SCWHA waters.

the uranium to minimum values between 3×10^{-8} and 5×10^{-8} mol dm^{-3} in the bicarbonate-rich solutions. This decrease is probably caused by the reduction of U(VI) into U(IV). There are indications that in the real clay water (RIC), the faster reduction is due to the redox control by an iron sulphide phase (presence of Fe and HS^-), whereas the redox control may be caused by sulphide in the synthetic clay solutions. The minimum uranium concentrations are reached after 70 days in real clay water (RIC), after 200 days in synthetic clay water without humic acids (SCW) and after 250 days in synthetic clay water with humic acids (SCWHA). The humic acids delay the reduction of U(VI) to U(IV) in synthetic clay water when they are oxidised, but not in real clay water, when they remain well preserved. At the end of the tests, the uranium concentrations are between 3×10^{-8} and 1.5×10^{-6} mol dm^{-3}, in the following order: $\mathrm{RIC} \approx \mathrm{SCW} \approx \mathrm{SCWHA} \ll \mathrm{SCWHA\backslash C}$. The addition of humic acids to the bicarbonate-containing solution probably induces a competition to complex U(VI) in solution, but this did not influence the total uranium concentration. Therefore it is unlikely that humic acids determine the uranium concentration at high bicarbonate concentration. However, because of an incomplete pre-dissolution of the UO_2 in the bicarbonate-poor medium (SCWHA\C), we could not distinguish the effect of HA on the uranium solubility in this solution. Hence, we cannot exclude that HA may play a role at low carbonate concentration.

Geochemical modelling suggests two potential uranium phases, U_4O_9 and $UO_{2(c)}$, as solubility controlling solids in RIC and SCW. The outcome of the modelling depends, however, on the redox potential of the system, which is not well known. Nevertheless, the presence of U_4O_9 and UO_2 was confirmed by XPS analyses.

For the SCWHA and RIC solutions, the XPS analyses indicate a surface composition solution between U_4O_9 and UO_2 with a hydration layer due to the presence of humic acids. Nevertheless, this result was not confirmed by the geochemical calculations because of inaccurate data for uranium complexation by humic acids.

The redox potential was always higher than expected under *in situ* conditions in the Boom Clay. Moreover, no clay has been added, so the measured uranium concentrations are not lowered by sorption and can be considered as conservative. The uranium concentrations measured under reducing conditions are 10–100 times higher than the concentrations measured in natural Boom Clay water (10^{-10}–10^{-9} mol dm^{-3}) [7]. This means that a concentration gradient of uranium will exist at the interface between the near-field and the far-field. The consequence is that spent fuel could slowly dissolve in the interstitial water undersaturated with respect to UO_2/UO_{2+x} of the fuel.

Acknowledgements

This work was supported by the Belgian Agency for Radioactive Waste and Enriched Fissile Materials (NIRAS/ONDRAF) and the European Commission (EC).

The authors gratefully acknowledge Regina Vercauter, Ben Gielen and Louis Van Ravestyn for the technical assistance and Ann Dierckx, Pierre De Cannière, Lian Wang and Grégory Delécaut for the scientific discussion.

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