A simple thermodynamical model to describe the control of the dissolution of uranium dioxide in granitic groundwater by secondary phase formation

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Abstract

Uranium dioxide leaching tests conducted at 96°C in a synthetic granitic water under oxidizing or reducing conditions are discussed. Results concerning the total uranium content in the leachates (ICP-MS) and solid surface characterization (SEM, RBS and XPS) are given. The formation of a secondary phase has been clearly shown under oxidizing conditions for high S/V ratio and long duration tests and only suspected under reducing conditions. A simple thermodynamical model based on chemical equilibria has been built to predict the total uranium content in the leachate in function of pH and total aqueous carbonate concentration. Then, the model has been applied in the case of the formation of partially dehydrated schoepite $[UO_2(OH)_2]$ under oxidizing conditions. The results have been compared both with the experimental data and theoretical calculations from PHREEQC. The agreement obtained is relatively good. For reducing conditions, model predictions only agree with experimental data and do not fit PHREEQC calculation results. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

It is now currently accepted that uraninite solubility in aqueous media under oxidizing conditions can be controlled by the growth onto the leached surface of secondary phases such as uranyl hydrates and carbonates [1–5]. Nevertheless, conventional uranium dioxide leaching tests do not systematically lead to a thermodynamical control of the uranium concentration in the leachate. Recently, Cachoir and coworkers have shown that a kinetic control without formation of secondary compounds could also be obtained [6].

In this paper, we present recent experimental data obtained by combining micro-characterization of the leached UO_2 surfaces and analysis of the leachates. After some theoretical calculations conducted using the geocode PHREEQC [7] in order to identify some probable controlling uranium species, we present a simple

thermodynamical model able to correctly describe the uranium dioxide behaviour under oxidizing or reducing conditions. Finally, we discuss about the agreement between experimental data, model predictions and theoretical calculations.

2. Experimental data

Sintered uranium dioxide pellets ($\sim UO_{2.1}$) have been leached in a synthetic granitic groundwater at 96°C according to the conditions shown in Table 1. Two types of leaching devices were used. For low S/V ratio and short duration leaching tests, it corresponds to the three connected reactors device previously described [8]. For high S/V ratio and long duration leaching test, a small volume stainless steel reactor with a PTFE inner jacket was used. In each case, the leachant is submitted to the same conditioning process before to be transferred to the leaching reactor. Oxidizing conditions have been imposed by maintaining a constant O_2 partial pressure in the device (70–80 ppm) and reducing conditions have been obtained using a constant flowing of hydrogen in

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Table 1
Summary of the configurations adopted for UO_2 leaching tests under oxidizing or reducing conditions and experimental uranium concentrations measured [a]

Test	pCO_2 (vol. ppm)	t (d)	S/V (cm^{-1})	pH initial/final	E (mV) Ag/AgCl	C_U (mol l^{-1})
1	400	21	0.003	8.00/7.72	242	0.92×10^{-9}
2 [b]	400	161	0.50	8.0	242	2.77×10^{-4}
3	2000	30	0.006	8.07/7.88	145	1.45×10^{-8}
4	23 400	28	0.003	8.17/8.29	169	6.86×10^{-9}
5 [b]	23 400	169	0.5	7.90/8.14	169	5.00×10^{-5}
6 [b]	23 400	253	0.5	7.90/8.04	169	3.50×10^{-5}
7	400	27	0.006	8.46/8.44	−178	0.57×10^{-8}
8 [c]	400	89	0.5	8.46	−178	3.47×10^{-7}
9	2000	27	0.006	8.43/8.03	−200	9.97×10^{-9}
10	23 400	28	0.006	8.52/8.48	−110	1.14×10^{-7}
11	23 400	239	0.5	8.08/8.38	−146	1.40×10^{-6}

[a] The mean value for pO2 is typically around 7.2×10^{-5} atm in oxidizing conditions and less than 5.0×10^{-5} atm in reducing conditions.
[b] The formation of a secondary phase was clearly observed.
[c] The formation of a secondary phase was suspected.

the vessel (the final pO_2 is always less than 50 ppm). Moreover, the carbonate content in the leaching solution was controlled by maintaining a constant partial pressure of CO_2, using commercial N_2/CO_2 gas mixtures qualified at a CO_2 level about 400, 2000 or 23 400 volumic ppm.

The leachant corresponds to a thermal granitic water from the south-west part of France, in the Pyrenees chain. This water named 'exalada' is in equilibrium around 60°C with the minerals constituting the host rock formation: quartz, chalcedony, calcite, aragonite, anhydrite, dolomite, gypsum, sepiolite, talc and chrysotile. Its composition is given in Table 2. The deep equilibrium temperature (96°C) was chosen as leaching temperature and water composition was then recalculated by using PHREEQC [7].

The total uranium concentration in the leachate was periodically determined during each test, using inductively coupled plasma mass spectrometry. The pH of the leachate was measured at the end of the test, in the same conditions as during the leaching test ($T = 92$°C and pCO_2 constant). The redox potential (Ag/AgCl electrode) was determined at 75°C. Leached surfaces were

Table 2
Composition of the leachant

Species	Concentration (mmol l^{-1})
Na^+	6.18
Ca^{2+}	0.384
Cl^-	5.86
Al^{3+}	0.0249
Mg^{2+}	0.00123
K^+	0.103
SiO_2	0.993
SO_4^{2-}	0.287

observed and characterized by scanning electron microscopy, X-ray photoelectron spectroscopy and Rutherford backscattering spectrometry. Details concerning the experimental conditions have been given in previous papers [5,6,8].

Table 1 also contains the total aqueous uranium content measured by ICP-MS. In three cases, the formation of a secondary phase is observed (test 2, test 5 and test 6). X-ray microanalysis and microRBS permit us to identify respectively $UO_2(OH)_2$ in the case of test 2, as it is shown in Fig. 1 (SEM image) and Fig. 2 (microRBS investigation). Moreover, the experimental uranium concentration measured after test 11 (1.40×10^{-6} mol l^{-1}) probably indicates a change in the nature of the solubility-controlling specimen.

For tests 5, complementary investigations conducted by SEM coupled with energy dispersive X-ray spectroscopy indicate the presence of K and Si associated with U leading to the assumption of boltwoodite or weeksite formation. A Ca–U phase was also found for test 6 but until now we have not been able to clearly assess its composition. For test 8, red spots appeared on the leached surface and disappeared after a very brief time period (a few hours). This phenomenon probably corresponds to the precipitation of purely stoichiometric UO_2 followed by its oxidation under ambient atmosphere.

X-ray photoelectron spectroscopy was performed both on UO_2 pellets leached under oxidizing and reducing conditions. Figs. 3 and 4 permit to compare the evolution of O 1s and U 4f orbitals. In an oxidative atmosphere, U 4f orbital clearly shows the splitting between U(IV) and U(VI) forms while O 1s orbital exhibits a growing contribution of OH and H_2O signals. On the opposite, under reducing conditions, U 4f orbital remains as U(IV) and O 1s orbital clearly shows an hydratation phenomenon.
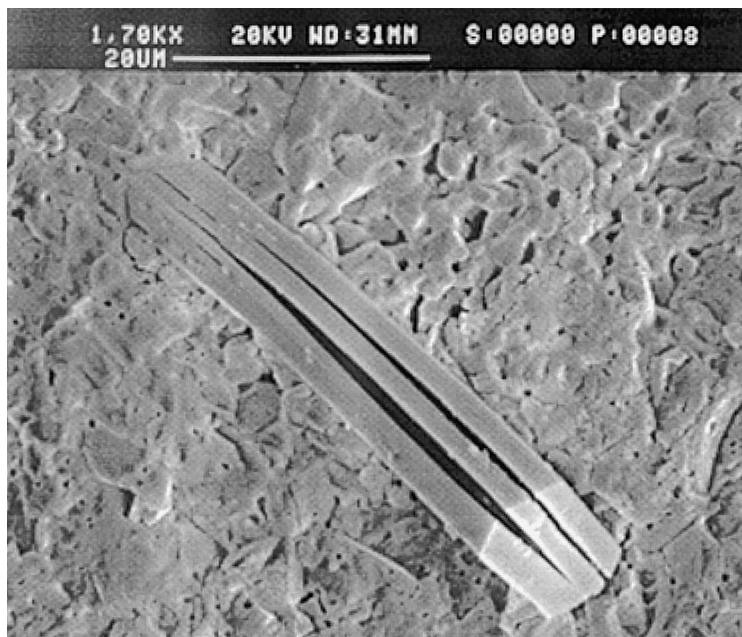
Fig. 1. Schoepite crystal grown on a UO_2 leached surface under oxidizing conditions (data extracted from Cachoir's PhD thesis [9]).

3. Theoretical calculations

Using the geocode PHREEQC [7], it is possible to calculate the saturation indexes for a series of uranium compounds provided that corresponding thermodynamical data are available, as it was shown by Gallien [10]. Table 3 contains the thermodynamical data base used for the calculations (extracted from Ref. [11–15]). Table 4 contains the values of the saturation indexes for several possible secondary uranium compounds, corre-

Fig. 2. MicroRBS spectrum of a schoepite crystal showing the splitting of U and O signals compared with virgin UO_2 (data extracted from Cachoir's PhD thesis [9]).

sponding to the aqueous medium composition used in leaching tests 1, 2, 7 and 8. It shows that the most probable secondary uranium phases are by decreasing order of probability:

- uranophane, Na-weeksite, β-$UO_2(OH)_2$, Na-boltwoodite, soddyite and schoepite, for oxidizing conditions,
- U_4O_9, U_3O_8, uranophane, UO_2, coffinite, β-$UO_2(OH)_2$ and Na-boltwoodite for reducing conditions.

The presence of U(VI) compounds is probably due to the character – slightly reducing – of our experimental medium with a redox potential around −200 mV relative to the Ag/AgCl electrode and the presence of a residual pressure of oxygen.

Table 5 gives some calculated concentrations of aqueous uranium species corresponding to experimental tests 2, 5, 6, 8 and 11.

4. Description of the model

Basic chemical equilibria involved during the reaction between uranium dioxide and water under oxidizing conditions or under reducing conditions are defined hereafter. We have arbitrarily restricted our description to the cases of the formation of $UO_2(OH)_2$ and UO_2 as controlling species for uranium dioxide solubility in granitic water. The same approach can be developed for any secondary phase provided that thermodynamical data are available.
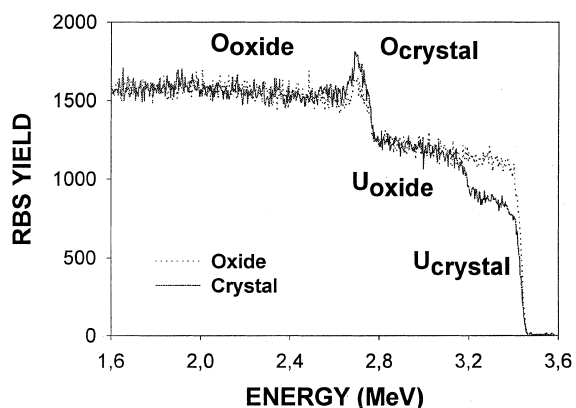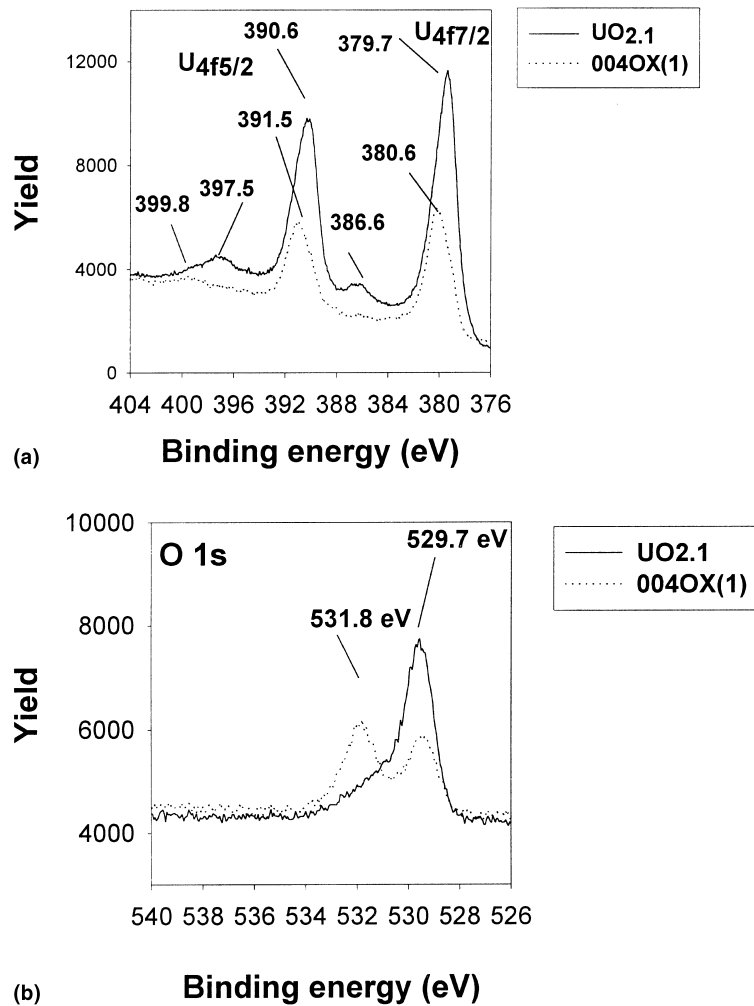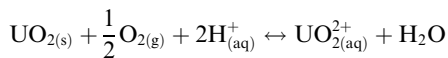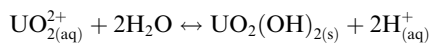
Fig. 3. U 4f and O 1s orbital evolution for oxidative leaching of UO_2 (data extracted from Cachoir's PhD thesis [9]).
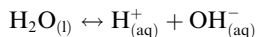
4.1. Case of oxidizing conditions

(I) *Oxidation–dissolution of uranium dioxide*:

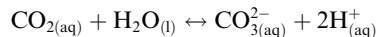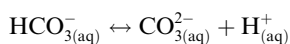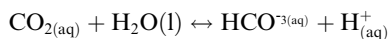$$UO_{2(s)} + \frac{1}{2}O_{2(g)} + 2H^+_{(aq)} \leftrightarrow UO^{2+}_{2(aq)} + H_2O$$

(II) *Formation of crystallized uranium(VI) hydroxide*:

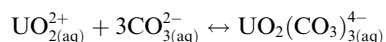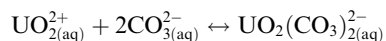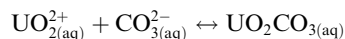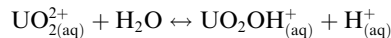$$UO^{2+}_{2(aq)} + 2H_2O \leftrightarrow UO_2(OH)_{2(s)} + 2H^+_{(aq)}$$

(III) *Water dissociation*:

$$H_2O_{(l)} \leftrightarrow H^+_{(aq)} + OH^-_{(aq)}$$

(IV) *Dissolution of carbon dioxide*:

$$CO_{2(aq)} + H_2O(l) \leftrightarrow HCO^{-3(aq)} + H^+_{(aq)}$$

$$HCO^-_{3(aq)} \leftrightarrow CO^{2-}_{3(aq)} + H^+_{(aq)}$$

$$CO_{2(aq)} + H_2O_{(l)} \leftrightarrow CO^{2-}_{3(aq)} + 2H^+_{(aq)}$$

(V) *Hydrolysis and complexation of U(VI) ionic species*:

$$UO^{2+}_{2(aq)} + H_2O \leftrightarrow UO_2OH^+_{(aq)} + H^+_{(aq)}$$

$$UO^{2+}_{2(aq)} + 2H_2O \leftrightarrow UO_2(OH)_{2(aq)} + 2H^+_{(aq)}$$

$$3UO^{2+}_{2(aq)} + 5H_2O \leftrightarrow (UO_2)_3(OH)^+_{5(aq)} + 5H^+_{(aq)}$$

$$UO^{2+}_{2(aq)} + CO^{2-}_{3(aq)} \leftrightarrow UO_2CO_{3(aq)}$$

$$UO^{2+}_{2(aq)} + 2CO^{2-}_{3(aq)} \leftrightarrow UO_2(CO_3)^{2-}_{2(aq)}$$

$$UO^{2+}_{2(aq)} + 3CO^{2-}_{3(aq)} \leftrightarrow UO_2(CO_3)^{4-}_{3(aq)}$$
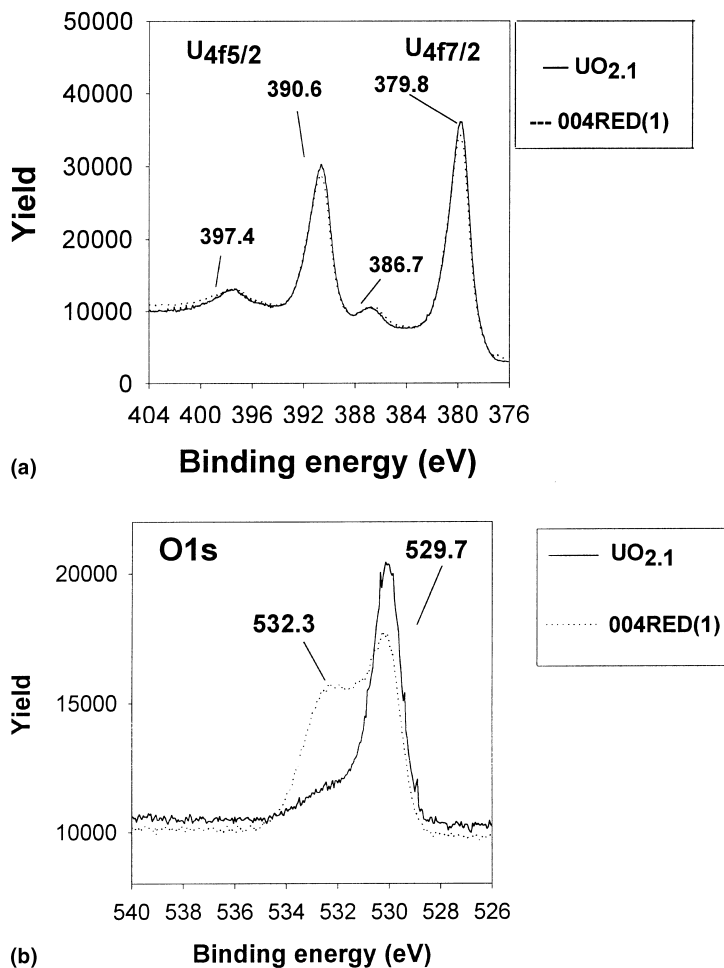
(a)

(b)

Fig. 4. U 4f and O 1s orbital evolution for reductive leaching of UO_2 (data extracted from Cachoir's PhD thesis [9]).
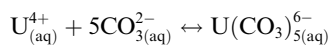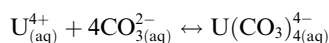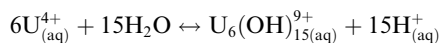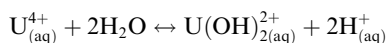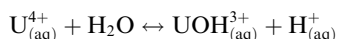
4.2. Case of reducing conditions

In the following part, only U(IV) aqueous uranium species will be considered for our model, the contribution of U(VI) species will be neglected. Nevertheless, PHREEQC calculations will take into account the redox potential and then consider U(VI) contribution together with U(IV).
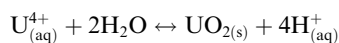
(VI) *Dissolution of uranium dioxide*:

$$UO_{2(s)} + 2H_2O \leftrightarrow U^{4+}_{(aq)} + 4OH^-_{(aq)}$$
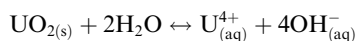
(VII) *Hydrolysis and complexation of U(IV) ionic species*:

$$U^{4+}_{(aq)} + H_2O \leftrightarrow UOH^{3+}_{(aq)} + H^+_{(aq)}$$

$$U^{4+}_{(aq)} + 2H_2O \leftrightarrow U(OH)^{2+}_{2(aq)} + 2H^+_{(aq)}$$

$$U^{4+}_{(aq)} + 4H_2O \leftrightarrow U(OH)_{4(aq)} + 4H^+_{(aq)}$$

$$6U^{4+}_{(aq)} + 15H_2O \leftrightarrow U_6(OH)^{9+}_{15(aq)} + 15H^+_{(aq)}$$

$$U^{4+}_{(aq)} + 4CO^{2-}_{3(aq)} \leftrightarrow U(CO_3)^{4-}_{4(aq)}$$

$$U^{4+}_{(aq)} + 5CO^{2-}_{3(aq)} \leftrightarrow U(CO_3)^{6-}_{5(aq)}$$

(VIII) *Formation of hydrated U(IV) species*:

$$U^{4+}_{(aq)} + 4H_2O \leftrightarrow U(OH)_{4(am)} + 4H^+_{(aq)}$$

$$U^{4+}_{(aq)} + 4H_2O \leftrightarrow UO_2 . 2H_2O_{(S)} + 4H^+_{(aq)}$$

$$U^{4+}_{(aq)} + 2H_2O \leftrightarrow UO_{2(s)} + 4H^+_{(aq)}$$
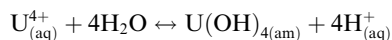
The subscripts (aq), (g) and (s) represent respectively aqueous, gaseous or solid species and the exponents O or R represent oxidizing and reducing conditions. In our case, the most probable aqueous species of U(VI) are those resulting from the hydrolysis and complexation of $UO^{2+}_{2\ (aq)}$ by the main ligands present in the liquid

Table 3
333Available thermodynamical data used for PHREEQE calculations and in the model [11–15]

Species	ΔfG_m^o (kJ mol^{-1})	ΔfH_m^o (kJ mol^{-1})	S_m^o
$H^+_{(aq)}$	0	0	0
$OH^-_{(aq)}$	−157.3 ± 0.1	−230.01 ± 0.04	−10.9 ± 0.2
H_2O	−237.14 ± 0.04	−285.83 ± 0.04	69.95 ± 0.03
$CO_{2(g)}$	−394.37 ± 0.13	−393.5 ± 0.13	213.79 ± 0.01
$O_{2(g)}$	0	0	0
$CO_{2(aq)}$	−385.97 ± 0.27	−413.26 ± 0.20	119.36 ± 0.60
$CO_3^{2-}{}_{(aq)}$	−527.9 ± 0.4	−675.2 ± 0.25	−50.0 ± 1.0
$HCO_3^-{}_{(aq)}$	−586.8 ± 0.3	−689.9 ± 0.2	98.4 ± 0.5
$UO_2^{2+}{}_{(aq)}$	−952.6 ± 1.7	−1019.0 ± 1.5	−98.2 ± 3.0
$UO_2(OH)_{2(s)}$	−1398.7 ± 1.8	−1533.8 ± 1.3	138.0 ± 4.0
$UO_2OH^+_{(aq)}$	−1160.0 ± 2.5	−1261.7 ± 15.1	17.0 ± 50.0
$UO_2(OH)_{2(aq)}$	−1368.0		
$(UO_2)_3(OH)_5^+{}_{(aq)}$	−3954.6 ± 5.3	−4389.1 ± 10.4	83.00 ± 30.0
$UO_2CO_{3(aq)}$	−1535.7 ± 1.8	−1689.2 ± 2.5	53.9 ± 7.5
$UO_2(CO_3)_2^{2-}{}_{(aq)}$	−2105.0 ± 2.0	−2350.9 ± 4.3	188.2 ± 14.1
$UO_2(CO_3)_3^{4-}{}_{(aq)}$	−2659.5 ± 2.1	−3083.8 ± 4.4	33.9 ± 14.4
$UO_{2(s)}$	−1031.8 ± 1.0	−1085.0 ± 1.0	77.0 ± 0.2
$U(OH)_{4(aq)}$	−1452.5 ± 8.0	−1655.8 ± 10.9	40.0 ± 25.0
$U(OH)_3^+{}_{(aq)}$	−1352.6	−1213.5	18.8
$U(OH)_2^{2+}{}_{(aq)}$	−1087.6	−991.5	−69.0
$UOH^{3+}_{(aq)}$	−763.9 ± 1.8	−830.1 ± 9.5	−199.9 ± 32.5
$U_6(OH)_{15}^{9+}{}_{(aq)}$		−6638.7	
$U(CO3)_4^{4-}{}_{(aq)}$	−2841.9 ± 5.9		
$U(CO3)_5^{6-}{}_{(aq)}$	−3363.4 ± 5.8	−3987.4 ± 5.3	−83.1 ± 25.7
$U^{4+}_{(aq)}$	−529.9 ± 1.8	−591.2 ± 3.3	−416.7 ± 12.6

phase, OH^- and CO_3^{2-} that form UO_2OH^+, $UO_2(OH)_2$, the trimer $(UO_2)_3(OH)_5^+$ and UO_2CO_3, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$, depending on the pH, the temperature, the total uranium concentration and the total carbonate content [7,11–13]. The most probable aqueous species of U(IV) are $U(OH)_4$, and the carbonated species $U(CO_3)_4^{4-}$ and $U(CO_3)_5^{6-}$. The four U(IV) species: UOH^{3+}, $U(OH)_2^{2+}$, $U(OH)_3^+$ and the hexamer $U_6(OH)_{15}^{9+}$ can be further neglected.

4.3. Basic equations

Each equilibrium defined in the previous section can be characterized by a constant (K_i, β_{ij} for hydrolysis and β'_{ij} for complexation). Most of the available values are extracted from the NEA/OECD Uranium Thermodynamical Data Base [11], Baes and Mesmer [12]. Additional data are taken from some review papers [13–15] and from several classical teaching books [16,17]. The

Table 4
Saturation indexes for several possible secondary uranium phases calculated by PHREEQC [7]

Uranium compound	Oxidizing conditions (analog to test 2 [a])	Reducing conditions (analog to test 8 [b])
β-$UO_2(OH)_2$	2.27	0.17
Coffinite	−12.10	−1.13
UO_2	−11.63	−0.58
Uranophane	7.54	3.94
Na-weeksite	2.73	−1.23
Na-boltwoodite	2.25	0.43
Schoepite	0.88	−1.22
Soddyite	1.87	−2.42
Rutherfordine	−1.89	−4.34

[a] The water composition (mmol l^{-1}) is: Ca, 0.38 – Cl, 5.73 – K, 0.10 – Mg, 0.0012 – Na, 6.18 – Si, 0.99 – C, 0.52 – U, 0.28. The main parameters of the configuration are pH = 7.97, pe = 5.72, ionic strength = 0.0077, temperature = 96°C, alkalinity = 0.0011.
[b] The water composition (mmol l^{-1}) is: Ca, 0.38 – Cl, 5.73 – K, 0.10 – Mg, 0.0012 – Na, 6.18 – Si, 0.99 – C, 0.52 – U, 0.00035. The main parameters of the configuration are pH = 7.71, pe = −0.68, ionic strength = 0.0076, temperature = 96°C, alkalinity = 0.00058.

Table 5
PHREEQC concentrations of aqueous uranium species corresponding to long duration leaching tests (mol l^{-1})

Species	Test 2	Test 5	Test 6	Test 8	Test 11
UO_2^{2+}	3×10^{-11}	2.3×10^{-13}	1.7×10^{-13}	1.2×10^{-13}	9×10^{-15}
$UO_2(CO_3)_2^{2-}$	2.6×10^{-5}	4.7×10^{-5}	3.3×10^{-5}	1.5×10^{-7}	1.3×10^{-6}
$UO_2(OH)_3^-$	1.4×10^{-6}	1.7×10^{-9}	1.1×10^{-9}	1.3×10^{-7}	5.3×10^{-11}
$(UO_2)_3(OH)_5^+$	8.3×10^{-5}	1.5×10^{-12}	5.3×10^{-13}	3.2×10^{-13}	5.5×10^{-17}
UO_2OH^+	4.9×10^{-7}	2×10^{-9}	1.4×10^{-9}	1.6×10^{-10}	6.8×10^{-11}
UO_2CO_3	1.8×10^{-7}	1.9×10^{-8}	1.4×10^{-8}	1.3×10^{-9}	5.8×10^{-10}
$UO_2(CO_3)_3^{4-}$	7.1×10^{-8}	2.5×10^{-6}	1.7×10^{-6}	6.8×10^{-8}	7.8×10^{-8}
$U(OH)_4$				8.3×10^{-12}	3.5×10^{-16}

temperature dependence of the various equilibrium constants has been evaluated using the formalism developed in [18]:

$$\log K^o(T) = \log K^o(T_0) \\ - [(\Delta r H_m^o(T_0)/2.303\,R)\,(1/T - 1/T_0)] \\ - 1/2.303\,RT \int_{T_0}^{T} \Delta r C_{p,m}^o \, dT \; 1/2.303\,R \int_{T_0}^{T} \Delta r C_{p,m}^o/T \, dT.$$

(1)

From equilibria (I)–(V) we can write

$$K_1^o = [UO_{2(aq)}^{2+}]/[H_{(aq)}^+]^2[pO_2]^{1/2},$$ (2)

$$K_2^o = [H_{(aq)}^+]^2/[UO_{2(aq)}^{2+}],$$ (3)

$$K_3 = [H_{(aq)}^+][OH_{(aq)}^-],$$ (4)

$$K_{4,1} = [HCO_{3(aq)}^-][H_{(aq)}^+]/[CO_{2(aq)}],$$ (5)

$$K_{4,2} = [CO_{3(aq)}^{2-}][H_{(aq)}^+]/[HCO_{3(aq)}^-],$$ (6)

$$K_{4,3} = K_{4,1}K_{4,2} = [CO_{3(aq)}^{2-}][H_{(aq)}^+]^2/[CO_{2(aq)}],$$ (7)

$$\beta_{11}^o = [UO_2OH_{(aq)}^+][H_{(aq)}^+]/[UO_{2(aq)}^{2+}],$$ (8)

$$\beta_{12}^o = [UO_2(OH)_{2(aq)}][H_{(aq)}^+]^2/[UO_{2(aq)}^{2+}],$$ (9)

$$\beta_{35}^o = [(UO_2)_3(OH)_{5(aq)}^+][H_{(aq)}^+]^5/[UO_{2(aq)}^{2+}]^3,$$ (10)

$$\beta_{11}'^o = [UO_2CO_{3(aq)}]/[UO_{2(aq)}^{2+}][CO_{3(aq)}^{2-}],$$ (11)

$$\beta_{12}'^o = [UO_2(CO_3)_{2(aq)}^{2-}]/[UO_{2(aq)}^{2+}][CO_{3(aq)}^{2-}]^2,$$ (12)

$$\beta_{13}'^o = [UO_2(CO_3)_{3(aq)}^{4-}]/[UO_{2(aq)}^{2+}][CO_{3(aq)}^{2-}]^3.$$ (13)

From equilibria (VI)–(IX), we can also write

$$K_1^R = [U_{(aq)}^{4+}]K_3^4/[H_{(aq)}^+]^4,$$ (14)

$$\beta_{11}^R = [UOH_{(aq)}^{3+}][H_{(aq)}^+]/[U_{(aq)}^{4+}],$$ (15)

$$\beta_{12}^R = [U(OH)_{2(aq)}^{2+}][H_{(aq)}^+]^2/[U_{(aq)}^{4+}],$$ (16)

$$\beta_{13}^R = [U(OH)_{3(aq)}^+][H_{(aq)}^+]^3/[U_{(aq)}^{4+}],$$ (17)

$$\beta_{14}^R = [U(OH)_{4(aq)}][H_{(aq)}^+]^4/[U_{(aq)}^{4+}],$$ (18)

$$\beta_{615}^R = [U_6(OH)_{15(aq)}^{9+}][H_{(aq)}^+]^{15}/[U_{(aq)}^{4+}]^6,$$ (19)

$$\beta_{14}'^R = [U(CO_3)_{4(aq)}^{4-}]/[U_{(aq)}^{4+}][CO_{3(aq)}^{2-}]^4,$$ (20)

$$\beta_{15}'^R = [U(CO_3)_{5(aq)}^{6-}]/[U_{(aq)}^{4+}][CO_{3(aq)}^{2-}]^5.$$ (21)

Table 6 gives the calculated values of the different equilibrium constants for $T = 298$ K and the corresponding values at 369 K. These values have not been corrected for the ionic strength effect. Then, the application of both charge (including the cations and the anions present in the water) and mass conservation principles gives some complex equations, as for example, under oxidizing conditions:

Table 6
Equilibrium constants at $T = 298$ K and $T = 369$ K

Reaction	K^{298}	K^{369}
K_1^o	1.41×10^{15}	1.53×10^{11}
K_2^o	1.35×10^{12}	2.09×10^{15}
K_3	1.00×10^{-14}	6.07×10^{-13}
K_p	3.37×10^{-2}	7.25×10^{-3}
$K_{4,1}$	4.46×10^{-7}	4.00×10^{-9}
$K_{4,2}$	4.67×10^{-11}	7.59×10^{-11}
β_{11}^o	6.31×10^{-6}	1.17×10^{-3}
β_{12}^o	$<5.01 \times 10^{-11}$	2.75×10^{-10}
β_{35}^o	2.82×10^{-16}	6.08×10^{-9}
$\beta_{11}'^o$	4.79×10^9	7.05×10^9
$\beta_{12}'^o$	8.71×10^{16}	3.66×10^{17}
$\beta_{13}'^o$	3.98×10^{21}	1.90×10^{20}
β_{11}^R	2.88×10^{-1}	1.39×10^{-5}
β_{14}^R	2.88×10^{-5}	1.3×10^{-2}
β_{15}^R	1.0×10^{-12}	1.7×10^{-9}
β_{615}^R	1.26×10^{-17}	5.0×10^{-34}
$\beta_{14}'^R$	1.55×10^{-10}	1.13×10^{-9}
$\beta_{15}'^R$	7.24×10^{-24}	2.5×10^{-21}

$$[OH^-_{(aq)}] + 2[CO^{2-}_{3(aq)}] + [HCO^-_{3(aq)}] + 2[UO_2(CO_3)^{2-}_{2(aq)}]$$

$$+ 4[UO_2(CO_3)^{4-}_{3(aq)}] + [Cl^-_{(aq)}] + 2[SO^{2-}_{4(aq)}] + [Al(OH)^-_{4(aq)}]$$

$$= [Na^+_{(aq)}] + 2[Mg^{2+}_{(aq)}] + 2[Ca^{2+}_{(aq)}]$$

$$+ [K^+_{(aq)}] + [H^+_{(aq)}] + 2[UO^{2+}_{2(aq)}]$$

$$+ [UO_2(OH)^+_{(aq)}] + [(UO_2)_3(OH)^+_{5(aq)}], \qquad (22)$$

$$C(U(VI))_{total} = [UO^{2+}_{2(aq)}]$$

$$+ [UO_2(OH)_{2(aq)}] + [UO_2(OH)^+_{(aq)}]$$

$$+ [UO_2CO_{3(aq)}] + 3[(UO_2)_3(OH)^+_{5(aq)}]$$

$$+ [UO_2(CO_3)^{2-}_{2(aq)}] + [UO_2(CO_3)^{4-}_{3(aq)}]. \qquad (23)$$

Under reducing conditions, considering the sulfur contribution restricted as $[S^{2-}]$, we can deduce

$$[OH^-_{(aq)}] + 2[CO^{2-}_{3(aq)}] + [HCO^-_{3(aq)}] + 4[U(CO_3)^{4-}_{4(aq)}]$$

$$+ 6[U(CO_3)^{6-}_{5(aq)}] + [Cl^-_{(aq)}] + 2[S^{2-}_{(aq)}] + [Al(OH)^-_{4(aq)}]$$

$$= [Na^+_{(aq)}] + 2[Mg^{2+}_{(aq)}] + 2[Ca^{2+}_{(aq)}] + [K^+_{(aq)}] + [H^+_{(aq)}]$$

$$+ 4[U^{4+}_{(aq)}] + 3[UOH^{3+}_{(aq)}] + 2[U(OH)^{2+}_{2(aq)}]$$

$$+ [U(OH)^+_{3(aq)}] + 9[U_6(OH)^{9+}_{15(aq)}], \qquad (24)$$

$$C(U(IV))_{total} = [U^{4+}_{(aq)}] + [UOH^{3+}_{(aq)}] + [U(OH)^{2+}_{2(aq)}]$$

$$+ [U(OH)^+_{3(aq)}] + [U(OH)_{4(aq)}]$$

$$+ [U(CO_3)^{4-}_{4(aq)}] + [U(CO_3)^{6-}_{6(aq)}]$$

$$+ 6[U_6(OH)^{9+}_{15(aq)}]. \qquad (25)$$

It is suggested by many authors that the probability of formation of polymeric species by hydrolysis of U(VI) and U(IV) strongly decreases with temperature [7,11,13]. Then, it is possible to neglect the corresponding terms further, especially $(UO_2)_3(OH)^+_5$ and $U_6(OH)^{9+}_{15}$ [19,20]. The occurrence of mixt U(IV) OH–CO₃ aqueous complexes will not be taken into account [11,21]. The above basic relations can be thus simplified. Combining Eqs. (2–13), (14–21) and (22–25), we can summarize four general expressions:

$$[UO^{2+}_{2(aq)}] = f \ ([H^+_{(aq)}]),$$

$$C(U(VI))_{total} = [UO^{2+}_{2(aq)}]f'([H^+_{(aq)}]),$$

$$[U^{4+}_{(aq)}] = g([H^+_{(aq)}]),$$

$$C(U(IV))_{total} = [U^{4+}_{(aq)}]g'([H^+_{(aq)}]),$$

where $f ([H^+_{(aq)}])$, $f' ([H^+_{(aq)}])$, $g ([H^+_{(aq)}])$ and $g' ([H^+_{(aq)}])$ are $[H^+_{(aq)}]$ polynoms of variable degree n with proportionality factors exclusively depending on K_i, β_{ij} and β'_{ij}.

4.4. Application examples of the model

The simple model as described above contains a general approach that can be applied to any case of secondary phase formation, provided that the corresponding thermodynamical data are available. In the following, we are going to illustrate the feasability of the model to leaching conditions and results corresponding to those detailed in Section 2, in the case of the formation of $UO_2(OH)_2$ under oxidizing conditions.

Using the parameters corresponding to the leaching test 2, that means pH, pCO₂ (400 ppm volumic or $10^{-2.4}$ atm.) and total aqueous carbonate concentration according to the following relation:

$$(C_{CO_3})_{total} = [CO^{2-}_{3(aq)}] + [HCO^-_{3(aq)}] + [CO_{2(aq)}], \qquad (26)$$

it is possible to deduce the total aqueous uranium concentration in the leachate. The estimated uranium concentration is

$$C(U)_{total} = 2.00 \ \times \ 10^{-3} \text{mol l}^{-1}.$$

5. Discussion

In the case of the leaching test 2, taking into account the uncertainties admitted for S^o_m and K^{298} values (Tables 3 and 5), the experimental value of 2.77×10^{-4} mol l⁻¹ has to be compared with the concentration predicted by our model 2.00×10^{-3} mol l⁻¹ and the result from PHREEQC simulation 2.2×10^{-7} mol l⁻¹. The experimental value and the model prediction are quite comparable considering both the approximations presented in Section 4.2 and the accuracy of thermodynamical data. The simulation from PHREEQC leads to a lower concentration than the two previous results but it has to be noticed that the geocode take into account the polymeric species and the correction for ionic strength effect. Moreover in PHREEQC, the ionic species contained in the water are not only considered as free basic ions.

Theoretical predictions from PHREEQC concerning the main U-species present in the aqueous solution can be also compared with the results of our model, as it is shown in Table 7 under oxidizing conditions. The model predictions and PHREEQC calculations are in a fairly good agreement except for one U(VI) aqueous specimen $UO_2(OH)_2$. It appears that the three dominant U(VI) aqueous species are $UO_2(OH)^-_3$, $UO_2(CO_3)^{2-}_2$ and $(UO_2)_3(OH)^+_5$ under oxidizing conditions. The relatively high concentration of the polymeric specie $(UO_2)_3(OH)^+_5$ seems to prove that the application of the assumption suggested in [7,10,12] should not be valid.

PHREEQC calculations conducted under reducing conditions and assuming the equilibrium

Table 7
Concentrations (mol l^{-1}) of the main U-aqueous species for test 2: Comparison between our model and PHREEQC calculations

Species	Test 2 model/PHREEQE
$[UO_2^{2+}{}_{(aq)}]$	$9.65 \times 10^{-12}/3 \times 10^{-11}$
$[UO_2OH^+_{(aq)}]$	$1.1 \times 10^{-6}/4.96 \times 10^{-7}$
$[UO_2(OH)_{2(aq)}]$	$2.7 \times 10^{-5}/3.98 \times 10^{-10}$
$[UO_2(OH)_3^-{}_{(aq)}]$	$/1.39 \times 10^{-6}$
$[UO_2CO_{3(aq)}]$	$5.2 \times 10^{-7}/1.77 \times 10^{-7}$
$[UO_2(CO_3)_2^{2-}{}_{(aq)}]$	$1.99 \times 10^{-4}/2.6 \times 10^{-5}$
$[UO_2(CO_3)_3^{4-}{}_{(aq)}]$	$7.8 \times 10^{-7}/7.1 \times 10^{-8}$
$(UO_2)_3(OH)_5^+$	$/8.3 \times 10^{-5}$

$$UO_{2(s)} + nH_2O \leftrightarrow UO_2, nH_2O_{(s)}$$
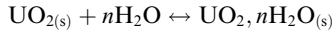
with a constant K^o derived from [11] and [22], assuming log $K^o = 0.5 \pm 0.3$, finally gives a total aqueous uranium concentration about 10^{-7} mol l^{-1}. This result is in good agreement with our experimental values which ranged from 10^{-7} to 10^{-6} mol l^{-1} and data previously published by Bruno and coworkers [23], in which they discussed the formation of crystalline UO_2 and rejected the formation of $U(OH)_{4(am)}$.

From the different key parameters available (pH, total carbonate concentration), it is possible to deduce $UO_2(OH)_2$ and UO_2 solubility limits. Applying a simple formalism derived from Ringbom theory [24] in which each U(VI) or U(IV) aqueous specie is taken into account, typical expressions can be written:

$$C(U(VI)_{total}) = K_{s(UO_2(OH)_2)}F_{ij}[H^+_{(aq)}]^2 \qquad (27)$$

with $K_{s(UO_2(OH)_2)} = 1/K_2^o$,

$$F_{ij} = \beta_{11}^o/[H^+_{(aq)}] + \beta_{12}^o/[H^+_{(aq)}]^2 + \beta_{11}^{\prime o}[CO_{3(aq)}^{2-}]$$
$$+ \beta_{12}^{\prime o}[CO_{3(aq)}^{2-}]^2 + \beta_{13}^{\prime o}[CO_{3(aq)}^{2-}]^3, \qquad (28)$$

$$C(U(IV)_{total}) = K_{s(UO_2)}[H^+_{(aq)}]^4 G_{ij} \qquad (29)$$

with $K_{s(UO_2)} = K_1^R K_3^4$,

$$G_{ij} = \beta_{11}^R/[H^+_{(aq)}] + \beta_{12}^R/[H^+_{(aq)}]^2 + \beta_{13}^R/[H^+_{(aq)}]^3$$
$$+ \beta_{14}^R[H^+_{(aq)}]^4 + \beta_{14}^{\prime R}[CO_{3(aq)}^{2-}]^4 + \beta_{15}^{\prime R}[CO_{3(aq)}^{2-}]^5. \qquad (30)$$

In the case of the formation of uranyl hydrate, we have found a solubility value, $s = 2.2 \times 10^{-6}$ mol l^{-1} that is in good agreement with data given by De Pablo [25]. In the case of the formation of UO_2, we have obtained $s = 1.7 \times 10^{-8}$ mol l^{-1} that is in good agreement with commonly admitted values [26].

6. Conclusion

A simple thermodynamical model has been built, presented and tested to describe the alteration mechanisms of sintered uranium dioxide by a synthetic granitic groundwater, under oxidizing or reducing conditions. The basis of this model is the formation of a secondary uranium phase able to control the total aqueous uranium concentration in the leachate.

The agreement between experimental data, model predictions and theoretical calculations is far from perfect in all cases. Some approximations that have been done as for example to neglect polymeric species, to neglect the effect of the ionic strength, to neglect mixt hydroxo-carbonate complexes, to simplify the speciation of mineral species in the water or to neglect the redox potential temperature correction could partly explain these discrepancies.

The formation of $UO_2(OH)_2$ under oxidizing conditions gives an excellent fit between experimental data, geochemical simulations and thermodynamical model predictions. Under reducing conditions, the assumptions of the formation of $UO_{2(s)}$ or $U(OH)_{4(am)}$ do not fit well with the experimental data. The presence of an intermediate U(IV) specie such as UO_2, nH_2O with $n \leqslant 2$ could probably control the uranium oxide solubility.

References

[1] J. Bruno, I. Casas, E. Cera, J. De Pablo, J. Gimenez, M.E. Torrero, in: Materials Research Society Symposium Proceedings, vol. 353, part I, 1995, p. 601.

[2] R.J. Finch, J. Suksi, K. Rasilainen, R.C. Ewing, in: Materials Research Society Symposium Proceedings, vol. 353, part I, 1995, p. 647.

[3] R. Wang, Y.B. Katayama, Nucl. Waste Management 3 (1982) 83.

[4] D.J. Wronkiewicz, J.K. Bates, T.J. Gerding, E. Veleckis, B.S. Tani, J. Nucl. Mater. 190 (1992) 107.

[5] C. Cachoir, M.J. Guittet, J.P. Gallien, P. Trocellier, Radiochim. Acta 74 (1996) 59.

[6] C. Cachoir, J.P. Gallien, P. Trocellier, Durabilité chimique d'un oxyde d'uranium placé dans des conditions de stockage en milieu géologique: remobilisation de l'uranium, Paper accepted for publication in Ann. Chim.: Sci. Matér., 1996.

[7] D.L. Parkhurst, User's guide to PHREEQC: A computer program for speciation, reaction-path, advective transport

and inverse geochemical calculations, US Geological Survey Water Res. Invest. Report 95-4227, 1995.

[8] P. Trocellier, J.P. Gallien, C. Cachoir, in: Materials Research Society Symposium Proceedings, vol. 353, part I, 1995, p. 585.

[9] C. Cachoir, PhD thesis, Orsay, 1997.

[10] J.P. Gallien, PhD thesis, Orsay, 1994.

[11] H. Wanner, I. Forest (Eds.), Chemical Thermodynamics, vol. 1: Chemical Thermodynamics of Uranium, Chaired by I. Grenthe, Nuclear Energy Agency, Organisation for Economic Co-operation and Development, North-Holland, Amsterdam, 1992.

[12] C.F. Baes Jr., R.E. Mesmer, The Hydrolysis of Cations, Wiley, New York, 1976.

[13] J.P. McKinley, J.M. Zachara, S.C. Smith, G.D. Turner, Clays Clay Miner. 43 (5) (1995) 586.

[14] D. Langmuir, Geochim. Cosmochim. Acta 42 (1978) 547.

[15] P. Taylor, R.J. Lemire, D.D. Wood, in: Proc. High Level Radioactive Waste Management Workshop, Las Vegas, The influence of moisture on air oxidation of UO_2: Calculations and observations, 1992, p. 1442.

[16] M. Bernard, F. Busnot, Chimie Générale et Minérale, Dunod, Paris, 1978.

[17] O. Kubaschewski, E.L.L. Evans, C.B. Alcock, Metallurgical Thermochemistry, Pergamon, Oxford, 1967.

[18] I. Grenthe, I. Puigdomenech, Temperature corrections to thermodynamic data and enthalpy calculations in modelling in Aquatic Chemistry; OECD/NEA, Paris, 1997.

[19] P.L. Brown, J. Ellis, R.N. Sylva, J. Chem. Soc. Dalton Trans. (1983) 31.

[20] S. Hietanen, Acta Chem. Scand. 10 (1956) 1531.

[21] K. Spahiu, personal communication.

[22] J. Bruno, D. Ferri, I. Grenthe, F. Salvatore, Acta Chem. Scand. A 40 (1986) 428.

[23] J. Bruno, I. Casas, I. Puigdomenech, Radiochim. Acta 44&45 (1988) 11.

[24] J. Trémillon, Electrochimie analytique et réactions en solution, tome 1, manuel d'enseignement, Masson, Paris, 1993.

[25] J. De Pablo, J. Giménez, M.E. Torrero, I. Casas, in: Materials Research Society Symposium Proceedings, vol. 353, part 1, p. 609, 1995.

[26] K. Ollila, Solubility of UO2 under reducing conditions, Communication to the 1997 Spent Fuel Workshop, Avignon (France), 21–23 April 1997.