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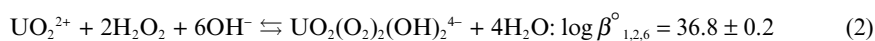
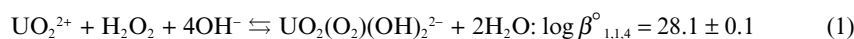
## Determination of the equilibrium formation constants of two U(VI)–peroxide complexes at alkaline pH

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The formation of uranyl-peroxide complexes was studied at alkaline media by using UV-Visible spectrophotometry and the STAR code. Two different complexes were found at a H<sub>2</sub>O<sub>2</sub>/U(VI) ratio lower than 2. A graphical method was used in order to obtain the formation constants of such complexes and the STAR program was used to refine the formation constants values because of its capacity to treat multiwavelength absorbance data and refining equilibrium constants. The values obtained for the two complexes identified were:



At hydrogen peroxide concentrations higher than 10<sup>-5</sup> mol dm<sup>-3</sup>, and in the absence of carbonate, the UO<sub>2</sub>(O<sub>2</sub>)<sub>2</sub>(OH)<sub>2</sub><sup>4-</sup> complex is predominant in solution, indicating the significant peroxide affinity of peroxide ions for uranium and the strong complexes of uranium(VI) with peroxide.

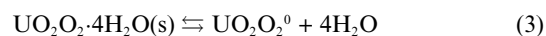
### Introduction

The dissolution of UO<sub>2</sub>(s) under oxidizing conditions controls the mobility of uranium in the environment from both natural deposits and nuclear waste repositories such as spent nuclear fuel (SNF) and transuranic wastes. Oxidizing species in the water in contact with the SNF in a High-Level Nuclear Waste (HLNW) repository might be formed as a product of the radiolysis of water.<sup>1-3</sup> In particular, hydrogen peroxide has been demonstrated to be produced by radiolysis in either alpha, beta and gamma irradiation of water.<sup>4-6</sup> In addition, hydrogen peroxide strongly affects the oxidative dissolution of SNF and UO<sub>2</sub>, by oxidizing the U(IV) of the solid to more soluble U(VI) species.<sup>7-9</sup> In this sense, different experiments have demonstrated the increase of the dissolution rates in the presence of hydrogen peroxide in a wide range of pH,<sup>8,10</sup> and the mechanism of the UO<sub>2</sub> oxidative dissolution in hydrogen peroxide has been described.<sup>9,10</sup> These results indicate that in a hypothetical future repository of HLNW, the evolution of the waste could be strongly affected by the uranium–H<sub>2</sub>O<sub>2</sub> interaction.

On the other hand, hydrogen peroxide might also affect the release of uranium from SNF by the formation of solid phases and/or uranyl–peroxide soluble complexes. The uranium peroxides studtite (UO<sub>2</sub>O<sub>2</sub>·4H<sub>2</sub>O) and metastudtite (UO<sub>2</sub>O<sub>2</sub>·2H<sub>2</sub>O)

have been identified as uranyl secondary solid phases in UO<sub>2</sub> leaching experiments under different experimental conditions and irradiations<sup>5,6,11-13</sup> and also in SNF dissolution experiments;<sup>14,15</sup> actually, the only effective source for providing a high enough hydrogen peroxide concentration for the formation of studtite is the radiolysis of water.<sup>16</sup> The solubility product of studtite<sup>16</sup> was determined to be 1.3 × 10<sup>-3</sup>, and studtite has been demonstrated to precipitate at bulk hydrogen peroxide concentrations between 10<sup>-5</sup> and 10<sup>-4</sup> mol dm<sup>-3</sup> on the UO<sub>2</sub> surface.<sup>5,11</sup>

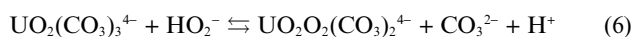
The solution chemistry of the uranyl–peroxide system is not well known because the identification and thermodynamic characterization of the U(VI)–H<sub>2</sub>O<sub>2</sub> complexes in solution has not been made yet. Moskvina<sup>17</sup> determined, from studtite dissolution experiments, the formation constants of three uranyl–peroxide complexes, but they were not considered reliable by the Nuclear Energy Agency (NEA) and have not been included in the uranium thermodynamic databases.<sup>18</sup>



Goff *et al.*<sup>19</sup> have identified by UV-vis spectroscopy the ternary complex UO<sub>2</sub>(O<sub>2</sub>)(CO<sub>3</sub>)<sub>2</sub><sup>4-</sup>, and they have determined its apparent formation constant, log K' = 4.70 ± 0.02 relative to UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>4-</sup>.

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In this work the formation of complexes in the  $\text{UO}_2\text{--H}_2\text{O}_2$  system in the absence of carbonate has been studied by UV-vis spectrophotometry at a constant pH = 12, which might be reached after the interaction of the groundwater with concrete materials of the repository.<sup>20–22</sup>

## Materials and methods

The experiments were carried out at pH = 12. The pH was buffered using a 0.01 mol dm<sup>-3</sup> tetramethylammonium hydroxide (TMAH) solution (Fluka), because of the capacity of TMAH to prevent uranate precipitation<sup>23</sup> by avoiding the presence of high concentrations of alkaline ions. The ionic strength was 0.01 mol dm<sup>-3</sup>. Stock solutions of uranyl nitrate (Panreac) and hydrogen peroxide (Merck) were prepared. Uranium content was determined by ICP-MS and the stock  $\text{H}_2\text{O}_2$  was periodically standardized with  $\text{Na}_2\text{S}_2\text{O}_3$  (Scharlau) in  $\text{H}_2\text{SO}_4$ .

Two different series of experiments were carried out. In the first series, hydrogen peroxide was kept constant ( $[\text{H}_2\text{O}_2]_{\text{tot}} = 1 \times 10^{-3}$  mol dm<sup>-3</sup>) and uranium(vi) concentration was varied between  $5 \times 10^{-6}$  and  $2 \times 10^{-4}$  mol dm<sup>-3</sup>. In the second series, uranium(vi) concentration was constant ( $2 \times 10^{-4}$  mol dm<sup>-3</sup>) and total hydrogen peroxide concentration was varied between  $1 \times 10^{-5}$  and  $1 \times 10^{-3}$  mol dm<sup>-3</sup>.

The range of uranium and hydrogen peroxide concentrations as well as the constant pH used in these experiments were chosen considering that some analytical problems are involved when studying the uranium(vi)–peroxide system. The use of the TMAH buffer avoids the precipitation of uranates. However, some other uranyl-containing solid phases are likely to precipitate if the total uranium concentration in solution, or even the total hydrogen peroxide concentration increases. In particular, the uranyl peroxide studtite ( $\text{UO}_2\text{O}_2 \cdot 4\text{H}_2\text{O}$ )<sup>11,16</sup> has been demonstrated to precipitate even at relatively low hydrogen peroxide concentrations ( $\log K_{\text{so(studtite)}}^{16}$  between -2.88 and -2.86). Avoiding the precipitation of uranyl peroxide phases as well as the uranyl hydroxide schoepite ( $\text{UO}_2(\text{OH})_2$ ) limited the range of experimental uranium and hydrogen peroxide concentrations ( $\log K_{\text{so(schoepite)}}^{18} = 4.93$ ). In this sense, the saturation indexes for these two solid phases in the experiments with the highest uranium concentration in solution ( $1 \times 10^{-4}$  mol dm<sup>-3</sup>) were determined to be -0.10 and -0.99 for studtite and schoepite, respectively.

On the other hand, the experiments have been carried out at a constant pH due to the variation of the uranium(vi) speciation with pH in the neutral to alkaline pH even in the absence of complexing agents. A constant pH was also necessary in order to keep in all the experiments a constant  $\text{H}_2\text{O}_2/\text{HO}_2^-$  ratio ( $\text{p}K_{\text{a}}$  for hydrogen peroxide is 11.6).

The experiments were carried out at  $25.0 \pm 0.1$  °C in a  $\text{N}_2$  glove-box, in order to avoid  $\text{CO}_2$  intrusion and to prevent the formation of uranyl-carbonate complexes. All the samples were closed in tubes and measured immediately after taking them out of the glovebox. A Hewlett-Packard 8453 spectrophotometer with temperature cell HP 89090A was used for the UV-vis measurements (1 cm length cell). The measurements were made by triplicate and the experiments were made twice.

## Results

The UV-vis spectra recorded from solutions with a constant hydrogen peroxide concentration and variable total uranium concentration are shown in Fig. 1. Uranium(vi) solutions at the same pH and TMAH concentration showed no absorbance in the absence of hydrogen peroxide in the range studied: 300–600 nm. The same occurred with solutions with  $\text{H}_2\text{O}_2$  and TMAH. The uranium– $\text{H}_2\text{O}_2$  solutions exhibit similar spectra with an absorbance maximum at around 350 nm, pointing to the formation of a U(vi)– $\text{H}_2\text{O}_2$  complex; in addition, there is an increase of the absorbance with the total uranium concentration in solution.

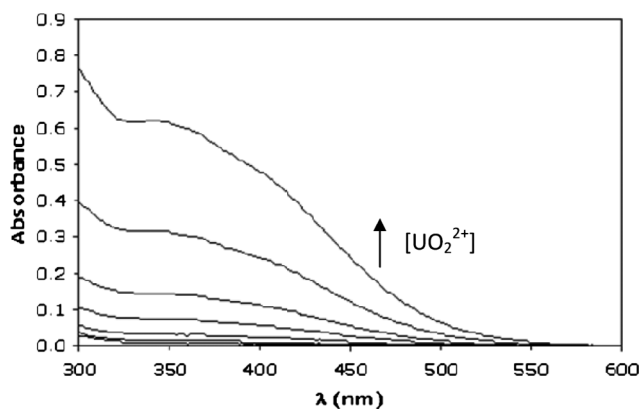


Fig. 1 Spectra recorded for the solutions with a constant hydrogen peroxide concentration ( $1 \times 10^{-3}$  mol dm<sup>-3</sup>) and a variable uranium concentration ( $5 \times 10^{-6}$  to  $2 \times 10^{-4}$  mol dm<sup>-3</sup>). pH = 12.

The spectra recorded for the solutions with a constant uranium concentration ( $2 \times 10^{-4}$  mol dm<sup>-3</sup>) and a variable initial hydrogen peroxide concentration are shown in Fig. 2. Interestingly, the solutions with hydrogen peroxide concentrations higher than total uranium concentration (this means with a  $[\text{H}_2\text{O}_2]_0/[\text{U}(\text{vi})]_0$  ratio higher than 1) present a change in the shape of the spectra. Assuming that the shape of the first spectra is due to a 1:1 U(vi): $\text{H}_2\text{O}_2$  complex, this second shape could be attributed to a 1:2 complex.

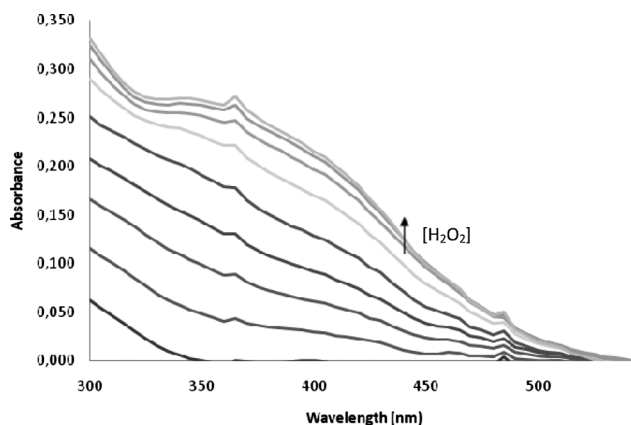
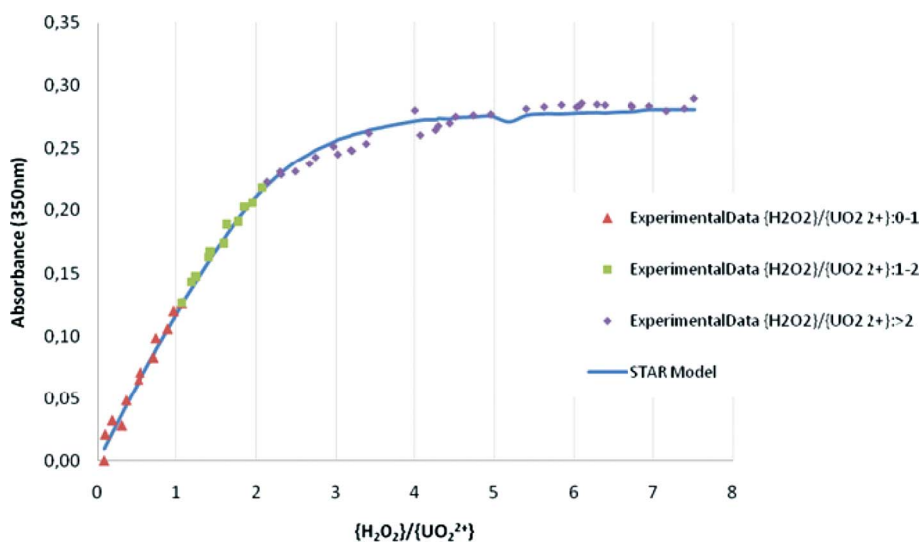


Fig. 2 Spectra recorded for the solutions with a constant uranium concentration and a variable initial hydrogen peroxide concentration (hydrogen peroxide concentration between  $1 \times 10^{-5}$  and  $1 \times 10^{-3}$  mol dm<sup>-3</sup>, and uranium concentration of  $2 \times 10^{-4}$  mol dm<sup>-3</sup>; pH = 12).



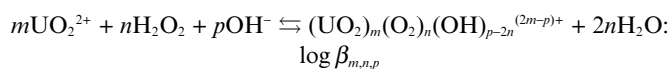
**Fig. 3** Variation of the absorbance with the ratio of activities ( $[\text{H}_2\text{O}_2]_0 = 1 \times 10^{-5}$  to  $1 \times 10^{-3}$  mol dm $^{-3}$ ,  $[\text{U}(\text{VI})]_0 = 2 \times 10^{-4}$  mol dm $^{-3}$ , pH = 12). The line represents the fitting of the data considering the equilibrium constants determined with the STAR program.

These changes might also be seen in Fig. 3, that shows the variation of the absorbance with the  $\{\text{H}_2\text{O}_2\}_0/\{\text{U}(\text{VI})\}_0$  ratio. The slope of the curve changes at  $\{\text{H}_2\text{O}_2\}_0/\{\text{U}(\text{VI})\}_0 = 1$  and it is very low at  $\{\text{H}_2\text{O}_2\}_0/\{\text{U}(\text{VI})\}_0 > 2$ . As above, these changes in the slope are assumed to be due to the formation of two complexes of different stoichiometry.

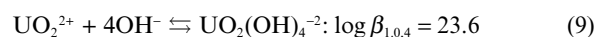
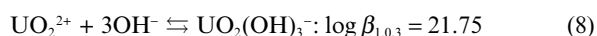
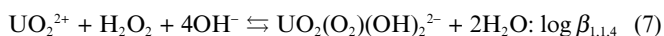
#### Graphical determination of the formation equilibrium constant of the first U(VI)–H<sub>2</sub>O<sub>2</sub> complex

A graphical method was used to determine the equilibrium constant of the first U(VI)–peroxide complex. This value was afterwards used as an input to be refined with the STAR program (see below).

At the experimental conditions of  $[\text{H}_2\text{O}_2]_0/[\text{U}(\text{VI})]_0 < 2$  and pH = 12, hydroxyl concentration (about  $10^{-2}$  mol dm $^{-3}$ ) is two orders of magnitude higher than both uranium and hydrogen peroxide concentrations, and it can be supposed to be constant. Under the experimental conditions of this work, the equilibria involving uranium(VI) that have to be considered can be expressed in a general reaction:



and are:<sup>18,24</sup>



The concentration of the complexes in solution at equilibrium will be:

$$[\text{UO}_2(\text{OH})_3^-] = \beta_{1,0,3}[\text{UO}_2^{2+}][\text{OH}^-]^3 \quad (10)$$

$$[\text{UO}_2(\text{OH})_4^{2-}] = \beta_{1,0,4}[\text{UO}_2^{2+}][\text{OH}^-]^4 \quad (11)$$

$$[\text{UO}_2(\text{O}_2)(\text{OH})_2^{2-}] = \beta_{1,1,4}[\text{UO}_2^{2+}][\text{H}_2\text{O}_2][\text{OH}^-]^4 \quad (12)$$

Considering the mass-balances of uranium(VI) and hydrogen peroxide in solution:

$$[\text{UO}_2^{2+}] = [\text{UO}_2^{2+}]_0 - [\text{UO}_2(\text{O}_2)(\text{OH})_2^{2-}] - [\text{UO}_2(\text{OH})_3^-] - [\text{UO}_2(\text{OH})_4^{2-}] \quad (13)$$

$$[\text{H}_2\text{O}_2] = [\text{H}_2\text{O}_2]_0 - [\text{UO}_2(\text{O}_2)(\text{OH})_2^{2-}] \quad (14)$$

The addition of eqn (10) and (11) gives the total concentration of the uranyl hydroxo-complexes, as a function of free uranyl concentration, which has been obtained from eqn (13). This gives:

$$\frac{[\text{UO}_2(\text{OH})_3^-] + [\text{UO}_2(\text{OH})_4^{2-}]}{1 + (\beta_{1,0,3} + \beta_{1,0,4}[\text{OH}^-])[\text{OH}^-]^3} = \frac{(\beta_{1,0,3} + \beta_{1,0,4}[\text{OH}^-])([\text{UO}_2^{2+}]_0 - [\text{UO}_2(\text{O}_2)(\text{OH})_2^{2-}])[\text{OH}^-]^3}{1 + (\beta_{1,0,3} + \beta_{1,0,4}[\text{OH}^-])[\text{OH}^-]^3} \quad (15)$$

The concentration of the uranyl–peroxide complex is given by the combination of eqn (12) and (14) and the addition of the concentrations of the uranyl–hydroxide complexes by eqn (13). The expression obtained is:

$$\frac{1}{[\text{UO}_2(\text{HO}_2)(\text{OH})_2^{2-}]} = \frac{1}{[\text{UO}_2^{2+}]_0} + \frac{1 + (\beta_{1,0,3} + \beta_{1,0,4}[\text{OH}^-] + \beta_{1,1,4}[\text{UO}_2^{2+}]_0[\text{OH}^-])[\text{OH}^-]^3}{\beta_{1,1,4}[\text{OH}^-]^4[\text{UO}_2^{2+}]_0} \cdot \frac{1}{[\text{H}_2\text{O}_2]_0} \quad (16)$$

According to the Lambert–Beer equation, the absorbance is proportional to the concentration of the uranyl–peroxide complex:

$$A = \varepsilon l [\text{UO}_2(\text{O}_2)(\text{OH})_2^{2-}] \quad (17)$$

where  $A$  is the absorbance,  $\varepsilon$  is the molar extinction coefficient and  $l$  is the cuvette length. Combining eqn (16) and (17):

$$\frac{1}{A} = \frac{1}{\varepsilon l [\text{UO}_2^{2+}]_0} + \frac{1 + (\beta_{1,0,3} + \beta_{1,0,4} [\text{OH}^-] + \beta_{1,1,4} [\text{UO}_2^{2+}]_0 [\text{OH}^-]) [\text{OH}^-]^3}{\varepsilon l \beta_{1,1,4} [\text{OH}^-]^4 [\text{UO}_2^{2+}]_0} \cdot \frac{1}{[\text{H}_2\text{O}_2]_0} \quad (18)$$

The representation of  $1/A$  vs.  $1/[\text{H}_2\text{O}_2]_0$  is shown in Fig. 4. The lineal regression of the data allowed to determine the molar extinction coefficient,  $(1.7 \pm 0.9) \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ , as well as the value of the formation constant of the complex:  $\log \beta_{1,1,4} = 27.1 \pm 0.5$ .

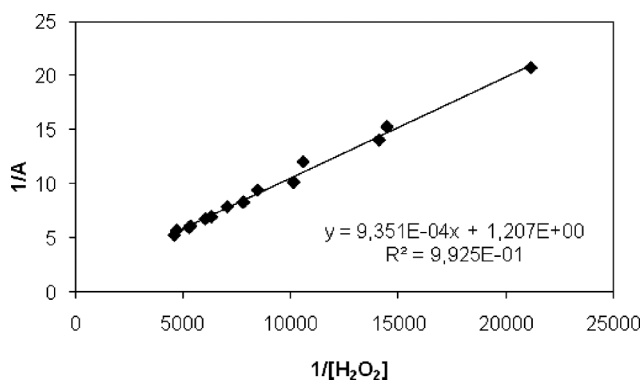


Fig. 4 Representation of  $1/\text{Absorbance}$  vs.  $1/[\text{H}_2\text{O}_2]_0$ , for  $[\text{H}_2\text{O}_2]/[\text{UO}_2^{2+}]$  ratio  $< 1$ .

The equilibrium constant obtained was corrected considering the ionic strength of the solution by using the Debye–Hückel approximation,<sup>18</sup> the value obtained was:  $\log \beta_{1,1,4}^0 = 27.2 \pm 0.5$ .

Uncertainties have been estimated in order to make a propagation of error analysis on the experimental data. Uncertainties from the origin ordinate and the slope have been estimated considering the equations related to the regression line.<sup>25</sup>

$$\Delta a = \left[ \frac{\sum_{i=1}^N (y_i - ax_i - b)^2}{(N-2) \sum_{i=1}^N (x_i - \bar{x})^2} \right]^{1/2} \quad (19)$$

$$\Delta b = \left[ \left( \frac{1}{N} + \frac{\bar{x}^2}{\sum_{i=1}^N (x_i - \bar{x})^2} \right) \left( \frac{\sum_{i=1}^N (y_i - ax_i - b)^2}{N-2} \right) \right]^{1/2} \quad (20)$$

where  $\Delta a$  is the slope error,  $\Delta b$  is the origin ordinate error,  $\bar{x}$  is the mean value of  $x$ , and  $N$  is the number of values.

The absolute errors estimated for the origin ordinate and the slope are  $1.5$  and  $5.6 \times 10^{-4}$ , respectively.

The error of the initial concentration of uranium has been estimated measuring six samples of uranium with the same concentration ( $2 \times 10^{-4} \text{ mol dm}^{-3}$ ), the standard deviation was  $5.5 \times 10^{-6}$ . The error in the measurement of the hydroxyl concentration was estimated from seven pH measurements, which gave a standard deviation of  $4.3 \times 10^{-4}$ . The uncertainties of the  $\beta_{1,0,3}^0$  and  $\beta_{1,0,4}^0$  constants have been obtained from the literature.<sup>24</sup>

With those estimated uncertainties, propagation of error analysis was made, using the following equation:

$$e_F = \sqrt{\left( \frac{\partial F}{\partial x} \right)^2 e_x^2 + \left( \frac{\partial F}{\partial y} \right)^2 e_y^2 + \left( \frac{\partial F}{\partial z} \right)^2 e_z^2 + \dots} \quad (21)$$

where  $F$  is the equation used to find the value of its uncertainty,  $x$ ,  $y$ ,  $z$ , ... are the parameters of this equation and  $e_i$  is the uncertainty of the parameter.

For example in the case of the molar extinction coefficient ( $\varepsilon$ ):

$$\varepsilon = \frac{1}{\text{O.O.} [\text{UO}_2^{2+}]_0} \quad (22)$$

where O.O. is the origin ordinate and  $[\text{UO}_2^{2+}]_0$  is the initial concentration of  $\text{UO}_2^{2+}$ .

$$e_\varepsilon = \sqrt{\left( \frac{\partial \varepsilon}{\partial \text{O.O.}} \right)^2 e_{\text{O.O.}}^2 + \left( \frac{\partial \varepsilon}{\partial [\text{UO}_2^{2+}]_0} \right)^2 e_{[\text{UO}_2^{2+}]_0}^2} \quad (23)$$

$$e_\varepsilon = \sqrt{\left( \frac{-1}{\text{O.O.}^2 [\text{UO}_2^{2+}]_0} \right)^2 e_{\text{O.O.}}^2 + \left( \frac{-1}{\text{O.O.} [\text{UO}_2^{2+}]_0^2} \right)^2 e_{[\text{UO}_2^{2+}]_0}^2} \quad (24)$$

Finally the uncertainty value for  $\log \beta_{1,1,4}^0$  is 0.5.

#### Determination of the formation constants of the two $\text{UO}_2^{2+}$ - $\text{H}_2\text{O}_2$ complexes by using the STAR program

The graphical method described above did not allow the determination of the formation constant of the second complex. Numerical methods are more reliable and accurate than most of the graphical methods and in this work the program STAR (STability constants by Absorbance Reading)<sup>26</sup> was used. While in the graphical method 18 experimental points were used to fit the model, in the STAR program 2500 experimental points have been used, minimizing the effect from experimental data uncertainties in the model. The STAR program also allows the refinement of up to ten constants at the same time and, in addition, the program tries different models and wavelengths ranges and allows finding the best chemical model for a given system.

In addition to the experimental spectra, the STAR program needs an input data file with information of the components and species assumed to be in solution at equilibrium as well as the equilibrium formation constants of such species.<sup>27</sup> The program calculates a model to represent the theoretical spectra and the residuals.

The refinement of equilibrium constants is done by the procedure REFINE, using the Gauss–Newton non-linear least-squares algorithm<sup>28</sup> by numerical differentiation, until a minimum in the sum of squares residuals ( $U$ ) is attained. This function is defined as

$$U = \sum_{i=1}^{n_s} \sum_{j=1}^{n_w} r_{i,j}^2 = \sum_{i=1}^{n_s} \sum_{j=1}^{n_w} (A_{i,j,\text{exp}} - A_{i,j,\text{calc}})^2 \quad (25)$$

where  $n_s$  and  $n_w$  are the number of solutions and the number of wavelengths, respectively. The minimization process is repeated until the relative change of  $U$  between two iterations is less than 0.01%. In the case of divergence in the refinement procedure, the method is modified to optimize the “shifts” of the constants.<sup>27</sup>

**Table 1** Species in the chemical equilibrium. Constants are referenced to zero ionic strength at 25 °C, but before their incorporation to the STAR code database, the equilibrium constants were extrapolated to the experimental ionic strength, using the Debye-Hückel approximation<sup>18</sup>

Species	log $K^\circ$	Reaction
UO <sub>2</sub> (OH) <sub>3</sub> <sup>-</sup>	-20.25 ± 0.42	3H <sub>2</sub> O(l) + UO <sub>2</sub> <sup>2+</sup> ↔ 3H <sup>+</sup> + UO <sub>2</sub> (OH) <sub>3</sub> <sup>-</sup>
UO <sub>2</sub> (OH) <sub>4</sub> <sup>2-</sup>	-32.40 ± 0.68	4H <sub>2</sub> O(l) + UO <sub>2</sub> <sup>2+</sup> ↔ 4H <sup>+</sup> + UO <sub>2</sub> (OH) <sub>4</sub> <sup>2-</sup>
UO <sub>2</sub> OH <sup>+</sup>	-5.25 ± 0.24	H <sub>2</sub> O(l) + UO <sub>2</sub> <sup>2+</sup> ↔ H <sup>+</sup> + UO <sub>2</sub> (OH) <sup>+</sup>
UO <sub>2</sub> (OH) <sub>2</sub>	-12.15 ± 0.07	2H <sub>2</sub> O(l) + UO <sub>2</sub> <sup>2+</sup> ↔ 2H <sup>+</sup> + UO <sub>2</sub> (OH) <sub>2</sub>
(UO <sub>2</sub> ) <sub>2</sub> OH <sup>3+</sup>	-2.70 ± 1.00	H <sub>2</sub> O(l) + 2UO <sub>2</sub> <sup>2+</sup> ↔ H <sup>+</sup> + (UO <sub>2</sub> ) <sub>2</sub> (OH) <sup>3+</sup>
(UO <sub>2</sub> ) <sub>2</sub> (OH) <sub>2</sub> <sup>2+</sup>	-5.62 ± 0.04	2H <sub>2</sub> O(l) + 2UO <sub>2</sub> <sup>2+</sup> ↔ 2H <sup>+</sup> + (UO <sub>2</sub> ) <sub>2</sub> (OH) <sub>2</sub> <sup>2+</sup>
(UO <sub>2</sub> ) <sub>3</sub> (OH) <sub>4</sub> <sup>2+</sup>	-11.90 ± 0.30	4H <sub>2</sub> O(l) + 3UO <sub>2</sub> <sup>2+</sup> ↔ 4H <sup>+</sup> + (UO <sub>2</sub> ) <sub>3</sub> (OH) <sub>4</sub> <sup>2+</sup>
(UO <sub>2</sub> ) <sub>3</sub> (OH) <sub>5</sub> <sup>+</sup>	-15.55 ± 0.12	5H <sub>2</sub> O(l) + 3UO <sub>2</sub> <sup>2+</sup> ↔ 5H <sup>+</sup> + (UO <sub>2</sub> ) <sub>3</sub> (OH) <sub>5</sub> <sup>+</sup>
(UO <sub>2</sub> ) <sub>3</sub> (OH) <sub>7</sub> <sup>-</sup>	-32.20 ± 0.80	7H <sub>2</sub> O(l) + 3UO <sub>2</sub> <sup>2+</sup> ↔ 7H <sup>+</sup> + (UO <sub>2</sub> ) <sub>3</sub> (OH) <sub>7</sub> <sup>-</sup>
(UO <sub>2</sub> ) <sub>4</sub> (OH) <sub>7</sub> <sup>+</sup>	-21.90 ± 1.00	7H <sub>2</sub> O(l) + 4UO <sub>2</sub> <sup>2+</sup> ↔ 7H <sup>+</sup> + (UO <sub>2</sub> ) <sub>4</sub> (OH) <sub>7</sub> <sup>+</sup>
HO <sub>2</sub> <sup>-</sup>	-11.60	HO <sub>2</sub> <sup>-</sup> + H <sup>+</sup> ↔ H <sub>2</sub> O <sub>2</sub>
O <sub>2</sub> <sup>2-</sup>	-36.60	O <sub>2</sub> <sup>2-</sup> + 2H <sup>+</sup> ↔ H <sub>2</sub> O <sub>2</sub>
UO <sub>2</sub> (O <sub>2</sub> )(OH) <sub>2</sub> <sup>2-</sup>	Unknown	2H <sub>2</sub> O(l) + UO <sub>2</sub> <sup>2+</sup> + H <sub>2</sub> O <sub>2</sub> ↔ 4H <sup>+</sup> + UO <sub>2</sub> (O <sub>2</sub> )(OH) <sub>2</sub> <sup>2-</sup>
UO <sub>2</sub> (O <sub>2</sub> ) <sub>2</sub> (OH) <sub>2</sub> <sup>4-</sup>	Unknown	2H <sub>2</sub> O(l) + UO <sub>2</sub> <sup>2+</sup> + 2H <sub>2</sub> O <sub>2</sub> ↔ 6H <sup>+</sup> + UO <sub>2</sub> (O <sub>2</sub> ) <sub>2</sub> (OH) <sub>2</sub> <sup>4-</sup>

The values of  $A_{\text{calc}}$  are obtained by Beer's law in the procedure CALCABS, from the calculated concentrations of each species and their molar absorptivities. For the species which have unknown spectra, these are calculated by multilinear regression, damped to avoid negative values. The mass balance equations of the system are solved in the COMPLEX procedure, from the given model, the total concentrations of the components and the pH of the solution. In this procedure, the COGS routine of the COMICS program<sup>29</sup> and a damped Newton non-linear method<sup>30</sup> are used alternatively. This approach has been applied successfully to the simulation of complex equilibria in multi-metal-multi-ligand systems.<sup>30</sup>

With the chemical species postulated for the model of the chemical equilibrium (shown in Table I), the values of the formation constants obtained with the STAR program are  $\log^* \beta_{1,1,4} = -28.10 \pm 0.14$  and  $\log^* \beta_{1,2,6} = -46.9 \pm 0.2$  (the STAR program calculates formation constants referred to the formation or consumption of H<sup>+</sup>, instead of OH<sup>-</sup>, even at alkaline pH). By using the water dissociation constant, the values obtained are:  $\log \beta_{1,1,4} = 27.9 \pm 0.1$  and  $\log \beta_{1,2,6} = 37.1 \pm 0.2$ . The extrapolation of these equilibrium constants to zero ionic strength, using the Debye-Hückel approximation, resulted in:

$$\log \beta_{1,1,4}^\circ = 28.1 \pm 0.1$$

$$\log \beta_{1,2,6}^\circ = 36.8 \pm 0.2$$

The variation of the absorbance with the [H<sub>2</sub>O<sub>2</sub>]/[U(VI)] ratio has been modeled considering the values of the equilibrium constants obtained with the STAR program, the fitting of the model to the absorbance data is shown in Fig. 3.

Table 2 shows the statistic parameters obtained. The most important parameters are the sum of squared residuals, the standard deviation of residuals, and the residual mean. A fit is considered good when the standard deviation of residuals is lower than 0.005. The perfect fit will have a residual mean and a sum of squared residuals equal to 0. In our case all are optimal values. These parameters give information about the fitting of the model while skewness, kurtosis and Pearson's  $\chi^2$  tests evaluate the distribution of the residuals. Skewness, kurtosis and Pearson's  $\chi^2$  test optimal values for a Gaussian distribution with six degrees of freedom and 95% of confidence level are 0, 3 and 12, respectively.

**Table 2** Statistic parameters from the STAR calculations for the H<sub>2</sub>O<sub>2</sub>-UO<sub>2</sub> system

	Value
Sum of squared residuals	0.0044761
Standard deviation of residuals	0.002936743
Mean residual	0.002220761
Residual mean	-0.000215541
Chi-squared test	19.0000000
Skewness	0.1655885
Kurtosis	2.9626457

Skewness and kurtosis are very close to the optimal value, while Pearson's  $\chi^2$  test is a little bit higher than the optimal value but it is also statistically acceptable.

The STAR program includes the STARFA utility, which determines the number of absorbing species by a factor analysis of the absorbance data matrix.<sup>26</sup> The rank of this absorbance matrix gives the minimum number of absorbing species in solution. In the plot  $s_k(A)$  vs.  $k$ , the rank of our matrix corresponds to the greater  $k$  with  $s_k(A) > s_{\text{inst}}(A)$ .  $s_k(A)$  is the calculated standard deviation of absorbance as estimated by factor analysis of the absorbance matrix ( $A$ ),  $k$  is the rank of the matrix and  $s_{\text{inst}}(A)$  is the instrumental error. We have taken as instrumental error the maximum value of absorbance (0.00112) in the range between 300 and 500 nm, for a TMAH solution without uranium and hydrogen peroxide. The results obtained are shown in Fig. 6 and confirm the likely existence of two different U(VI)-hydrogen peroxide complexes.

### Impact of the existence of U(VI)-H<sub>2</sub>O<sub>2</sub> complexes on the uranium(VI) chemical speciation in solution

In order to know the relative strength of the uranyl-H<sub>2</sub>O<sub>2</sub>-OH complexes described in this work, a theoretical study of the influence of these complexes on the chemical speciation of uranium(VI) at alkaline pH has been done, using specific software to simulate the speciation at different conditions.

Fig. 6 shows the predominance diagram at pH = 12 which is found to depend on both total carbonate concentration and total hydrogen peroxide concentration. The predominance diagram was made by using the MEDUSA code,<sup>31</sup> including the species shown in Table I and the formation constant of the UO<sub>2</sub>O<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub><sup>4-</sup>

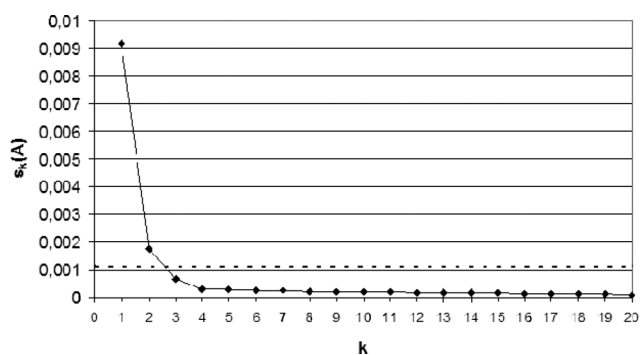


Fig. 5 Standard deviation of the absorbance vs. rank of the absorbance matrix. The dotted line represents instrumental error (see text).

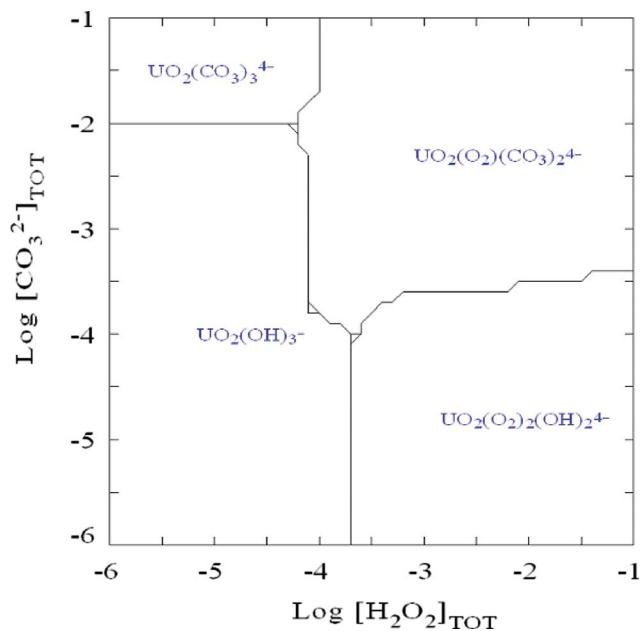


Fig. 6 Predominance diagram of the uranium(VI) species in solution at pH = 12 and 0.01 mol dm<sup>-3</sup> ionic strength.

complex.<sup>19</sup> Solid species have not been included, in order to evaluate only the chemical speciation in solution.

It can be seen that the  $\text{UO}_2(\text{O}_2)_2(\text{OH})_2^{4-}$  complex predominates at hydrogen peroxide concentrations higher than  $10^{-4}$  mol dm<sup>-3</sup> at total carbonate concentrations lower than  $5 \times 10^{-4}$  mol dm<sup>-3</sup>. Peroxide easily replaces the hydroxyl ion in the complexes to form the U(VI)-H<sub>2</sub>O<sub>2</sub>-OH<sup>-</sup> ternary complexes in a similar way that it replaces the carbonate ion to form mixed complexes with uranium<sup>19</sup> and plutonium.<sup>32</sup> The final picture is that at hydrogen peroxide concentrations higher than  $10^{-4}$  mol dm<sup>-3</sup>, the mixed complexes predominate, and the predominant ternary complex depends on carbonate concentration in solution.

On the other hand, a fraction diagram corroborates the importance of the mixed complexes on the U(VI) speciation in the presence of H<sub>2</sub>O<sub>2</sub>, because it allows the elucidation of not only the predominant complexes but all the complexes present at equilibrium in solution. Fig. 7 shows the uranium(VI) fraction diagram at pH = 12 and a  $10^{-4}$  mol dm<sup>-3</sup> carbonate concentration. As can be seen, at hydrogen peroxide concentrations higher than  $10^{-5}$  mol dm<sup>-3</sup>, the complexes with peroxide (both the

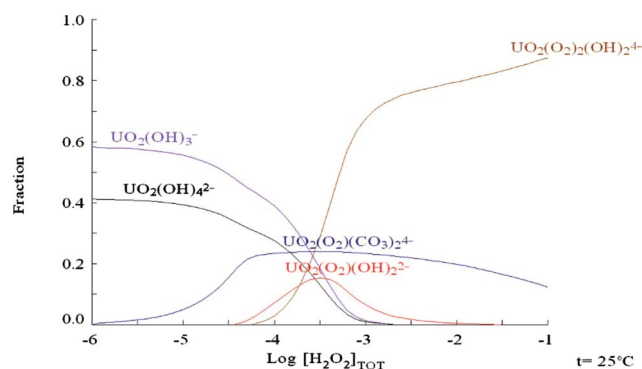


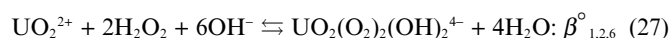
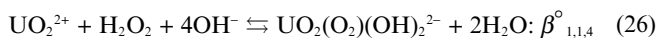
Fig. 7 Fraction diagram of the uranium(VI) species in solution at  $[\text{CO}_3^{2-}] = 10^{-4}$  mol dm<sup>-3</sup>, pH = 12 and 0.01 mol dm<sup>-3</sup> ionic strength.

two complexes described in this work and the ternary complex identified by Goff *et al.*) are present in solution; these complexes account for almost all the uranium in solution at  $[\text{H}_2\text{O}_2]_{\text{tot}} > 10^{-3}$  mol dm<sup>-3</sup>.

This theoretical study on the uranium(VI) speciation in solution corroborates the high affinity of peroxide ion for actinides, in particular for uranium. The strong  $\text{UO}_2^{2+}\text{-H}_2\text{O}_2\text{-OH}^-$  complexes, which would increase the solubility of the  $\text{UO}_2$  and the uranium secondary solid phases (specially studtite, whose solubility could increase an order of magnitude at pH = 13 and hydrogen peroxide concentrations between  $10^{-5}$  and  $10^{-4}$  mol dm<sup>-3</sup>), would have a significant impact on the migration of uranium in a deep geological repository for SNF.

## Conclusions

The speciation of uranium(VI) in the presence of hydrogen peroxide was studied in alkaline conditions and in the absence of carbonates. Two  $\text{UO}_2^{2+}\text{-H}_2\text{O}_2\text{-OH}^-$  complexes were considered at pH 12 according to UV-vis spectrophotometric data on uranium solutions titrated with H<sub>2</sub>O<sub>2</sub>. The proposed formation reactions are:



The equilibrium constants for both reactions were determined by using the STAR program:  $\log \beta_{1,1,4}^\circ = 28.1 \pm 0.1$  and  $\log \beta_{1,2,6}^\circ = 36.8 \pm 0.2$ .

Considering their formation constants, the ternary complexes  $\text{UO}_2(\text{O}_2)(\text{OH})_2^{2-}$  and  $\text{UO}_2(\text{O}_2)_2(\text{OH})_2^{4-}$  would have a significant impact on the uranium(VI) migration in solution, which is especially important in a High-Level Nuclear Waste Repository.

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