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 H2O2/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 multilamnwleng absorbance data and refining equilibrium constants. The values obtained for the two complexes identified were:

\[ \text{UO}_2^{2+} + \text{H}_2\text{O}_2 + 4\text{OH}^- \rightleftharpoons \text{UO}_2(\text{OH})_2^{3-} + 2\text{H}_2\text{O} \quad \log \beta_{1,1,4} = 28.1 \pm 0.1 \] (1)

\[ \text{UO}_2^{2+} + 2\text{H}_2\text{O}_2 + 6\text{OH}^- \rightleftharpoons \text{UO}_2(\text{OH})_2^{4-} + 4\text{H}_2\text{O} \quad \log \beta_{1,2,6} = 36.8 \pm 0.2 \] (2)

At hydrogen peroxide concentrations higher than $10^{-2}$ mol dm$^{-3}$, and in the absence of carbonate, the UO$_2$(OH)$_2^{4-}$ 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$_2$(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.\(^{1-3}\) In particular, hydrogen peroxide has been demonstrated to be produced by radiolysis in either alpha, beta and gamma irradiation of water.\(^{4-6}\) In addition, hydrogen peroxide strongly affects the oxidative dissolution of SNF and UO$_2$, by oxidizing the U(IV) of the solid to more soluble U(VI) species.\(^{7-9}\) 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,\(^{7-9}\) and the mechanism of the UO$_2$ oxidative dissolution in hydrogen peroxide has been described.\(^{8-10}\) These results indicate that in a hypothetical future repository of HLNW, the evolution of the waste could be strongly affected by the uranium–H$_2$O$_2$ 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$_2$·4H$_2$O) and metastudtite (UO$_2$·2H$_2$O)

have been identified as uranyl secondary solid phases in UO$_2$ leaching experiments under different experimental conditions and irradiations\(^{5,6,11-13}\) and also in SNF dissolution experiments;\(^{14,15}\) actually, the only effective source for providing a high enough hydrogen peroxide concentration for the formation of studtite is the radiolysis of water.\(^{16}\) The solubility product of studtite was determined, from studtite dissolution experiments, to be $1.3 \times 10^{-5}$, and studtite has been demonstrated to precipitate at bulk hydrogen peroxide concentrations between $10^{-2}$ and $10^{-4}$ mol dm$^{-3}$ on the UO$_2$ surface.\(^{5,11}\)

The solution chemistry of the uranyl–peroxide system is not well known because the identification and thermodynamic characterization of the U(VI)–H$_2$O$_2$ complexes in solution has not been made yet. Moskvin\(^{17}\) 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.\(^{18}\)

\[ \text{UO}_2\text{O}_2^{-}\cdot4\text{H}_2\text{O}(s) \rightleftharpoons \text{UO}_2\text{O}_2^{-}\cdot4\text{H}_2\text{O} \quad (3) \]

\[ \text{UO}_2\text{O}_2^{-}\cdot4\text{H}_2\text{O}(s) + \text{H}_2\text{O} \rightleftharpoons \text{UO}_2(\text{OH})_2^{3-} + 2\text{H}^+ + 4\text{H}_2\text{O} \quad (4) \]

\[ \text{UO}_2\text{O}_2^{-}\cdot4\text{H}_2\text{O}(s) + 2\text{H}_2\text{O} \rightleftharpoons \text{UO}_2(\text{OH})_2^{4-} + 4\text{H}^+ + 4\text{H}_2\text{O} \quad (5) \]

Goff et al.\(^{19}\) have identified by UV–vis spectroscopy the ternary complex UO$_2$(OH)(CO$_3$)$_4$\(^{4+}\), and they have determined its apparent formation constant, $\log K' = 4.70 \pm 0.02$ relative to UO$_2$(CO$_3$)$_3$\(^{4+}\).
\[
\text{UO}_2(\text{CO}_3)_3^{4-} + \text{HO}_2^- \leftrightarrow \text{UO}_2\text{O}_2(\text{CO}_3)_3^{4+} + \text{CO}_3^{2-} + \text{H}^+ \quad (6)
\]

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.\textsuperscript{20–22}

Materials and methods

The experiments were carried out at pH = 12. The pH was buffered using a 0.01 mol dm\(^{-3}\) tetramethylammonium hydroxide (TMAH) solution (Fluka), because of the capacity of TMAH to prevent uranate precipitation\textsuperscript{23} by avoiding the presence of high concentrations of alkaline ions. The ionic strength was 0.01 mol dm\(^{-3}\). 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 \(([\text{H}_2\text{O}_2]_{\text{tot}} = 1 \times 10^{-3}\ \text{mol dm}^{-3})\) and uranium(VI) concentration was varied between \(5 \times 10^{-4}\) and \(2 \times 10^{-4}\ \text{mol dm}^{-3}\). In the second series, uranium(VI) concentration was constant \((2 \times 10^{-4}\ \text{mol dm}^{-3})\) and total hydrogen peroxide concentration was varied between \(1 \times 10^{-5}\) and \(1 \times 10^{-3}\ \text{mol dm}^{-3}\).

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 studite \((\text{UO}_2\text{O}_3\cdot 4\text{H}_2\text{O})\)\textsuperscript{11,16} has been demonstrated to precipitate even at relatively low hydrogen peroxide concentrations \((\log K_{\text{precipitation}}\) between −2.88 and −2.86). Avoiding the precipitation of uranyl peroxide phases as well as the uranyl hydroxide schoepite \((\text{UO}_2\text{O}_3\text{OH})_2\) limited the range of experimental uranium and hydrogen peroxide concentrations \((\log K_{\text{sol}}\) (schoepite)\) = 4.93). In this sense, the saturation indexes for these two solid phases in the experiments with the highest uranium concentration in solution \((1 \times 10^{-3}\ \text{mol dm}^{-3})\) were determined to be −0.10 and −0.99 for studite 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 \((pK_w\) for hydrogen peroxide is 11.6).

The experiments were carried out at 25.0 ± 0.1 °C in a N\(_2\) glove-box, in order to avoid 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 initial 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 \(\text{U(VI)}-\text{H}_2\text{O}_2\) complex; in addition, there is an increase of the absorbance with the total uranium concentration in solution.

![Fig. 1](image-url) Spectra recorded for the solutions with a constant hydrogen peroxide concentration \((1 \times 10^{-3}\ \text{mol dm}^{-3})\) and a variable initial uranium concentration \((5 \times 10^{-4}\ \text{mol dm}^{-3})\) to \(2 \times 10^{-4}\ \text{mol dm}^{-3}\). pH = 12.

The spectra recorded for the solutions with a constant uranium concentration \((2 \times 10^{-4}\ \text{mol dm}^{-3})\) 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 \([\text{H}_2\text{O}_2]_0/[\text{U(VI)}]\) 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 \(\text{U(VI)}:\text{H}_2\text{O}_2\) complex, this second shape could be attributed to a 1 : 2 complex.

![Fig. 2](image-url) Spectra recorded for the solutions with a constant uranium concentration and a variable initial hydrogen peroxide concentration (hydrogen peroxide concentration between 1 \(\times 10^{-4}\) and 1 \(\times 10^{-3}\ \text{mol dm}^{-3}\), and uranium concentration of 2 \(\times 10^{-4}\ \text{mol dm}^{-3}\); pH = 12).
These changes might also be seen in Fig. 3, that shows the variation of the absorbance with 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.

Graphical determination of the formation equilibrium constant of the first U(VI)–H₂O₂ 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 [H₂O₂]/[U(VI)] = 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 slope of the curve changes at pH = 5 and is very low at pH > 2. As above, these changes in the slope are assumed to be due to the formation of two complexes of different stoichiometry.

[\text{UO}_2(\text{OH})_3^{2-}] = \beta_{1,0} [\text{UO}_2^{2+}] [\text{OH}^-]^4 \quad (11)

\[ \text{UO}_2(\text{O}_2\text{OH})_2^{5-} = \beta_{1,1,4} [\text{UO}_2^{2+}][\text{H}_2\text{O}_2][\text{OH}^-]^4 \quad (12) \]

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

\[ [\text{UO}_2]^{2+} = [\text{UO}_2^{2+}]_0 - [\text{UO}_2(\text{O}_2\text{OH})_2^{5-}] - [\text{UO}_2(\text{OH})_3^{2-}] \quad (13) \]

\[ [\text{H}_2\text{O}_2] = [\text{H}_2\text{O}_2]_0 - [\text{UO}_2(\text{O}_2\text{OH})_2^{5-}] \quad (14) \]

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:

\[ [\text{UO}_2(\text{OH})_3] + [\text{UO}_2(\text{OH})_3] = \frac{[\beta_{1,0} + \beta_{1,4,0}[\text{OH}^-][\text{UO}_2^{2+}]_0 - [\text{UO}_2(\text{O}_2\text{OH})_2^{5-}] - [\text{UO}_2(\text{OH})_3]}{1 + [\beta_{1,0} + \beta_{1,4,0}[\text{OH}^-][\text{OH}^-]]} \quad (15) \]

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:

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

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

\[ A = \varepsilon ([\text{UO}_2(\text{O}_2\text{OH})_2]_0) \quad (17) \]
where $A$ is the absorbance, $e$ is the molar extinction coefficient and $l$ is the cuvette length. Combining eqn (16) and (17):

$$\frac{1}{A} = \frac{1}{el[\text{UO}_2^{2+}]_0} + \frac{1 + (\beta_{0,0} + \beta_{1,0} [\text{OH}^-] + \beta_{1,1} [\text{UO}_2^{2+}]_0 [\text{OH}^-]^2)}{el\beta_{1,1} [\text{OH}^-]^2 [\text{UO}_2^{2+}]_0} \frac{1}{[\text{H}_2\text{O}]_0}$$

(18)

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

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)$^{26}$ 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$^{27}$ 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$^{28}$ by numerical differentiation, until a minimum in the sum of squares residuals ($U$) is attained. This function is defined as

$$U = \sum_{i=1}^{n_o} \sum_{j=1}^{n_w} (r_{ij})^2 = \sum_{i=1}^{n_o} \sum_{j=1}^{n_w} (A_{i,j,exp} - A_{i,j,calc})^2$$

(25)

where $n_o$ 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.$^{27}$

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

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

(21)

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

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

$$e = \frac{1}{\text{O.O.}[\text{UO}_2^{2+}]_0}$$

(22)

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

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

(23)

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

(24)

Finally the uncertainty value for log $\beta_{1,1,4}^o$ 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)$^{26}$ 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.

The error in the measurement of the hydroxyl concentration was $2\times10^{-4}$. In the case of divergence in the refinement procedure, the method is modified to optimize the “shifts” of the constants.$^{27}$
In this procedure, the COGS routine of the COMICS program total concentrations of the components and the pH of the solution. To avoid negative values, the mass balance equations of the system spectra, these are calculated by multilinear regression, damped to CALCABS, from the calculated concentrations of each species and these are obtained with the STAR program, the fitting of the model while skewness, kurtosis and Pearson’s χ² test optimal values for a Gaussian distribution with six degrees of freedom and 95% of confidence level are 0, 3 and 12, respectively.

The values of 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.

<table>
<thead>
<tr>
<th>Species</th>
<th>log K°</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO₂(OH)⁻</td>
<td>-20.25 ± 0.42</td>
<td>3H₂O(l) + UO₂⁺ ↔ 3H⁺ + UO₂(OH)⁻</td>
</tr>
<tr>
<td>UO₂(OH)²⁻</td>
<td>-32.40 ± 0.68</td>
<td>4H₂O(l) + UO₂⁺ ↔ 4H⁺ + UO₂(OH)²⁻</td>
</tr>
<tr>
<td>UO₂(OH)³⁻</td>
<td>-5.25 ± 0.24</td>
<td>2H₂O(l) + UO₂⁺ ↔ 2H⁺ + UO₂(OH)²⁻</td>
</tr>
<tr>
<td>UO₂(OH)⁴⁻</td>
<td>-12.15 ± 0.07</td>
<td>H₂O(l) + 2UO₂⁺ ↔ H⁺ + (UO₂)₂(OH)³⁻</td>
</tr>
<tr>
<td>UO₂(OH)⁵⁻</td>
<td>-2.70 ± 1.00</td>
<td>2H₂O(l) + 2UO₂⁺ ↔ 2H⁺ + (UO₂)₂(OH)³⁻</td>
</tr>
<tr>
<td>(UO₂)₂(OH)⁻</td>
<td>-5.62 ± 0.04</td>
<td>4H₂O(l) + 3UO₂⁺ ↔ 4H⁺ + (UO₂)₂(OH)³⁻</td>
</tr>
<tr>
<td>(UO₂)₂(OH)²⁻</td>
<td>-11.90 ± 0.30</td>
<td>5H₂O(l) + 3UO₂⁺ ↔ 5H⁺ + (UO₂)₂(OH)³⁻</td>
</tr>
<tr>
<td>(UO₂)₂(OH)³⁻</td>
<td>-15.55 ± 0.12</td>
<td>7H₂O(l) + 3UO₂⁺ ↔ 7H⁺ + (UO₂)₂(OH)³⁻</td>
</tr>
<tr>
<td>(UO₂)₂(OH)⁴⁻</td>
<td>-32.20 ± 0.80</td>
<td>7H₂O(l) + 4UO₂⁺ ↔ 7H⁺ + (UO₂)₂(OH)³⁻</td>
</tr>
<tr>
<td>(UO₂)₂(OH)⁵⁻</td>
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<td>HO₂⁻ ↔ H⁺ + (UO₂)₂(OH)³⁻</td>
</tr>
<tr>
<td>HO₂⁻</td>
<td>-11.60</td>
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</tr>
<tr>
<td>O₂²⁻</td>
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<td>O₂²⁻ ↔ 2H⁺ ↔ H₂O</td>
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<tr>
<td>UO₂(OH)₂(OH)²⁻</td>
<td>Unknown</td>
<td>2H₂O(l) + UO₂⁺ ↔ H₂O ↔ 4H⁺ + UO₂(OH)²⁻</td>
</tr>
<tr>
<td>UO₂(OH)₂(OH)³⁻</td>
<td>Unknown</td>
<td>2H₂O(l) + UO₂⁺ ↔ 2H₂O ↔ 6H⁺ + UO₂(OH)²⁻</td>
</tr>
</tbody>
</table>

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 $s_k(A) > s_{max}(A)$. $s_k(A)$ 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 $s_{max}(A)$ 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)–H₂O₂ complexes on the uranium(vi) chemical speciation in solution

In order to know the relative strength of the uranyl–H₂O₂–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, including the species shown in Table I and the formation constant of the UO₂(OH)(CO₃)⁴⁺.
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⁻³ ionic strength.

Fig. 7  Fraction diagram of the uranium(VI) species in solution at [CO₃²⁻] = 10⁻⁴ mol dm⁻³; pH = 12 and 0.01 mol dm⁻³ 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 [H₂O₂]ₜₒₜ > 10⁻³ mol dm⁻³.

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 UO₂²⁺–H₂O₂–OH⁻ complexes, which would increase the solubility of the UO₂ 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⁻³), 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 UO₂²⁺–H₂O₂–OH⁻ complexes were considered at pH 12 according to UV-vis spectrophotometric data on uranium solutions titrated with H₂O₂. The proposed formation reactions are:

\[
\text{UO}_2^{2+} + \text{H}_2\text{O}_2 + 4\text{OH}^- \rightleftharpoons \text{UO}_2(\text{O}_2)(\text{OH})_2^{2-} + 2\text{H}_2\text{O} \quad \beta^{1,1,4}_{1,2}(26)
\]

\[
\text{UO}_2^{2+} + 2\text{H}_2\text{O}_2 + 6\text{OH}^- \rightleftharpoons \text{UO}_2(\text{O}_2)_2(\text{OH})_2^{4-} + 4\text{H}_2\text{O} \quad \beta^{1,2,6}_{1,2,6}(27)
\]

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

Considering their formation constants, the ternary complexes UO₂(Ο₂)(ΟΗ)²⁻ and UO₂(Ο₂)₂(ΟΗ)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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