Solubility of $PuO_2(CO_3)$

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The permanent disposal of nuclear waste in repositories excavated in deep geological formation appears to be technically feasible. In the event of canister corrosion and waste failure, migration of contaminated groundwater is considered to be the principle mechanism for radionuclide transport from the underground storage site to the environment. Plutonium is one of the most toxic elements in radioactive waste. In order to predict its behaviour in a geological repository it is important to understand the solubility and the speciation of plutonium in aqueous solutions.

Complexation with natural ligands regulates the concentration of metal ions in solution. Among the inorganic ligands usually found in groundwater [1, 2] HCO_3^-; CO_3^{2-} and OH^- are of particular interest, because of the high stability constants of the complexes they form.

Solid PuO_2 can be dissolved through leaching with natural waters. Under oxidizing conditions part of the plutonium can be in the V valence. It is not easy to measure Pu(V) concentrations directly because under these conditions Pu(IV) and Pu(VI) are extensively hydrolyzed. We have planned an extensive study of plutonium chemistry in groundwaters; a first step was to study the chemistry of the Pu(VI)–CO_3^{2-} system. The experimental work in progress on the redox potentials of the Pu(VI)–Pu(V) couple will then allow us to determine the speciation and the stability domain of Pu(V).

There have been several investigations of plutonium(VI) in carbonate and bicarbonate media which indicate that the limiting complex of Pu(VI) has the same stoichiometry as found in the U(VI) system, *i.e.*, $PuO_2(CO_3)_3^{4-}$ [3, 4]. There is less agreement about the composition of the precursor to the limiting complex; in fact many authors have proposed different species formed in the Pu(VI)–H_2O–carbonate system, such as: $PuO_2(HCO_3)_i^{2-i}$ [5], $PuO_2(CO_3)_j^{2(1-j)}$ [3–6] and mixed complexes $PuO_2(OH)_x(HCO_3)_y^{2-x-y}$ [5] or $PuO_2(OH)_z(CO_3)_t^{2-z-2t}$ [6]. We have summarized the available literature information in Table I.

In the carbonate concentration range studied by Grenthe *et al.* [4], the predominant complexes were $PuO_2(CO_3)_3^{4-}$ and $(PuO_2)_3(CO_3)_6^{6-}$. As these spectrophotometric measurements were complicated by the $PuO_2(CO_3)(s)$ precipitation, they did not investigate the lower carbonate concentration region. Therefore we have studied the solubility of $PuO_2(CO_3)(s)$ in bicarbonate media, at a high ionic strength ($I = 3$ M $NaClO_4$) [controlling and varying the partial CO_2 pressure, $p(CO_2)$] to measure its solubility product and equilibrium constants.
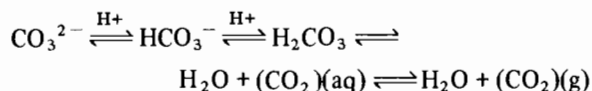

TABLE I. Pu(VI) in Carbonate Media: Logarithm of the Stability Constants and the Solubility Product

	Literature values				Calculated values[a]					
	[5]	[6]	[3]	this work	1	0.5	0.1	0	ΔZ^2	$-\Delta\epsilon$
I (mol/kg)	0.1	0.0	0.15	3.5						
$PuO_2(CO_3)(s)$		−12.8		−13.5 ± 0.3	−12.9	−13.0	−13.4	−14.2	+8	−0.37
$PuO_2(CO_3)^0$				8.6 ± 0.3	8.0	8.1	8.4	9.2	−8	+0.37
$PuO_2(CO_3)_2^{2-}$	13.1	1.51		13.6 ± 0.7	13.0	13.1	13.4	14.8	−8	+0.38
$PuO_2(CO_3)_3^{4-}$			20	18.2 ± 0.4	17.6	17.5	17.4	17.4	0	+0.23
$PuO_2(OH)(CO_3)^-$		23.9								
$PuO_2(OH)_2(CO_3)^{2-}$		23								
$PuO_2(HCO_3)^+$	2.7				$D = 0.5107 \sqrt{I}/(1 + 1.5\sqrt{I})$					
$PuO_2(HCO_3)(OH)_2^-$	20				$m = [NaClO_4]$ mol/kg					

[a]$\log \beta_i(I) = \log \beta_i(0) + \Delta Z^2 D - \Delta\epsilon\, m$ [15].

Methodology

The carbonate ion is a base:

$$CO_3^{2-} \overset{H^+}{\rightleftharpoons} HCO_3^- \overset{H^+}{\rightleftharpoons} H_2CO_3 \rightleftharpoons$$
$$H_2O + (CO_2)(aq) \rightleftharpoons H_2O + (CO_2)(g)$$

If a metal M^{z+} is complexed by OH^-, HCO_3^- and/or CO_3^{2-} we obtain the following complex: $M_p(OH)_x(HCO_3)_y(CO_3)_t$ which is equivalent to $M_p(CO_2)_q(OH)_r$, where $q = t + y$ and $r = x + y + 2t$ (we have omitted the charges). This way of writing equilibria indicates that it is impossible to determine stoichiometric coefficients of a complex in OH^-–HCO_3^-–CO_3^{2-} media from experimental data obtained in equilibrium with air (where $p(CO_2)$ is roughly constant; $p(CO_2) \cong 10^{-3.5}$ atm). Hence, the experimental parameters that must be controlled during a solubility study in carbonate media are: the total metal concentration, the partial pressure of CO_2 $[p(CO_2)]$ and the pH. The concentrations of the ligands are governed by the acid dissociation constants: $K_1 = [HCO_3^-]/([H^+][CO_3^{2-}])$ and $K_{p1} = [H^+][HCO_3^-]/p(CO_2)$ and cannot be varied independently. When $p(CO_2)$ is known we have $[CO_3^{2-}] = (K_{p1}/K_1)p(CO_2)/[H^+]^2$. In a solution of ionic strength 3 M, we use the following values: $\log K_{p1}$ (3 M) = 7.99 and $\log K_1$ (3 M) = −9.62 [7].

Experimental

In order to determine the free carbonate concentration we have to measure the hydrogen concentration [H^+]. This was done potentiometrically by using a combined glass electrode (Tacussel TCBC 11/HS/sm with an Ag–AgCl reference halfcell). The original reference solution was replaced with a (0.01 M NaCl + 2.99 M NaClO$_4$) solution. We calibrated the electrode (*versus* [H^+]) using the following buffers: 0.01 M HClO$_4$ + 2.99 M NaClO$_4$; 0.1 M NaHCO$_3$ + 2.9 M NaClO$_4$ ($p(CO_2)$ = 1 atm); and 0.05 M(NaHCO$_3$ = Na$_2$CO$_3$) + 2.85 M NaClO$_4$. These gave $\log [H^+]$ = −2.00, −7.00 and −9.62, respectively.

The Pu(VI) perchlorate solution was prepared from an acid stock solution by evaporation of HClO$_4$ until most of the excess acid had been removed. The concentrated solution was dissolved in 0.1 M HClO$_4$, to obtain more than 99.7% of Pu(VI). The solid Pu(VI)O$_2$CO$_3$(s) was then precipitated by addition of NaHCO$_3$ to the fresh perchlorate solution in order to avoid reduction by radiolysis. The light tan precipitate was dissolved in a 0.1 M NaHCO$_3$ + 2.9 M NaClO$_4$ solution . The carbonate concentration was sufficiently high to ensure that the limiting complex was formed. This green stock solution (50 ml) was introduced into a cell through which was bubbled a pre-equilibrated (in 3 M NaClO$_4$) mixture of CO$_2$ + Ar ($p(CO_2)$ = 0.1, 0.3, 1.0 atm). Keeping agitation constant, we measured pH (and [CO_3^{2-}]). When at a given pH the solubility was constant, we added 3 M HClO$_4$ or 1 M NaHCO$_3$ in order to vary [CO_3^{2-}], keeping the ionic strength constant (I = 3 M Na$^+$). The Pu(VI) concentration was determined by acidifying the sample with HClO$_4$ and measuring the light absorption of PuO$_2^{2+}$ using a Cary 17 D spectrometer at 830.4 nm [8] (ϵ = 532 in 3 M HClO$_4$).

After about 2 weeks of experiments the solubility measurements gave some unexpected results in the $5 \leqslant pH \leqslant 6$ region. A rapid return to pH = 7 gave an apple green solution, with some precipitate present. This would not dissolve even in 1 M HCl, indicating the existence of polymerized Pu(IV) hydroxide. This was confirmed by spectrophotometry. The formation of a Pu(IV) colloid may be due to radiolytic reduction of the Pu(VI) solid in aqueous carbonate media [9]. We reoxidized the polymeric Pu(IV) hydroxide in the following way: (a) HNO$_3$ was added until [HNO$_3$] = 4 M; (b) the solution was heated at 75 °C for 3 h [10]; (c) the solution was oxidized with AgO; (d) the silver was eliminated by adding the correct amount of HCl; (e) PuO$_2$(CO$_3$)(s) was precipitated by adding NaHCO$_3$; (f) the precipitate was dissolved, as before, in 0.1 M NaHCO$_3^-$ + 2.9 M NaClO$_4$ solution. This green solution (new stock solution) was shown by spectrophotometry to contain only the limiting complex PuO$_2$(CO$_3$)$_3^{4-}$ [4, 11].

Results

We have verified that PuO$_2$(CO$_3$)(s) can be obtained by precipitation of Pu(VI) either from acidic medium by HCO$_3^-$ addition or from bicarbonate medium by H$^+$ addition. PuO$_2$(CO$_3$)(s) is isostructural with UO$_2$(CO$_3$)(s) [12]. Extra lines in the X-ray diffraction pattern appeared several days after the precipitation of PuO$_2$(CO$_3$)(s). We noticed that this solid is most stable under a vacuum. It changes within 2 weeks in an HCO$_3^-$ solution, and is not stable at all in contact with air (changes in less than 24 h).

The X-ray spectra of the solid used in the solubility experiments were recorded several times during the experiment. They always corresponded to PuO$_2$(CO$_3$)(s). The slope of the solubility curve ($\log S$) *versus* $\log [CO_3^{2-}]$ in the low carbonate concentration range is equal to −1. This indicates that the soluble species present in solution is PuO$_2^{2+}$. This confirms the X-ray result.

The experiments run at different $p(CO_2)$ and pH gave a reproducible solubility curve *versus* $\log [CO_3^{2-}]$. At a constant free carbonate concentration, the solubility does not depend on the bicarbonate
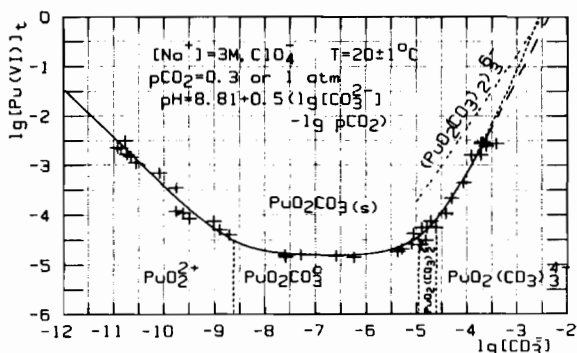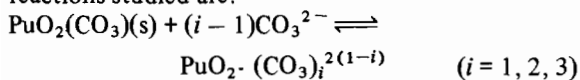
Fig. 1. Solubility of $PuO_2(CO_3)(s)$ in carbonate media at $I = 3$ M $NaClO_4$ and 20 ± 1 °C: Experimental measurements and calculated solubility curve. Calculation of the influence of $(PuO_2(CO_3)_2)_3^{6-}$ ($= T$) [4]:
Solubility: $- - -$ without T; $\cdots$ with T; $- \cdot - \cdot -$ $3[T] = [PuO_2(CO_3)_3^{4-}]$.

concentration, pH or $p(CO_2)$. Then the solubility reactions studied are:

$$PuO_2(CO_3)(s) + (i-1)CO_3^{2-} \rightleftharpoons$$
$$PuO_2 \cdot (CO_3)_i^{2(1-i)} \qquad (i = 1, 2, 3)$$

All the experimental solubility measurements obtained spectrophotometrically in a 1-cm cuvette are presented in Fig. 1. The full-drawn curve is the calculated solubility curve. In the pH range $5 \leqslant pH \leqslant 6$ we had to measure the solubility by using 10-cm cuvettes in order to attain a sufficiently large precision. The solubility experiments with a given solid must not continue longer than 2 weeks in order to avoid the transformation of the solid through radiolysis.

Discussion

Gel'man et al. [6] studied the solubility of $(NH_4)_2Pu_2O_7$ at different $[CO_3^{2-}]$ and at constant pH; they could not establish the hydroxide dependence. We therefore do not consider the evidence of the mixed complexes to be reliable. The spectra given at $[CO_3^{2-}] \geqslant 0.5$ M [6] are similar to those reported in 1 M $NaHCO_3$ and 1 M Na_2CO_3 [13] and to those we obtained. At such a high carbonate concentration only the limiting complex can be the major species present; we believe that this is $PuO_2(CO_3)_3^{4-}$ and not $PuO_2(CO_3)_2^{2-}$ as proposed by Gel'man et al.

Woods et al. [3] studied the complexation of Pu(VI) in carbonate media by spectrophotometry (at $I = 0.15$ M). Newton and Sullivan's estimation [14] of $\log \beta_3 = 20 \pm 2$ ($\beta_3 = [PuO_2(CO_3)_3^{4-}]/([PuO_2^{2+}] \cdot [CO_3^{2-}]^3)$) for the formation of $PuO_2(CO_3)_3^{4-}$ from PuO_2^{2+} and CO_3^{2-} is in good agreement with our experimental result. By using the ionic strength (I) correction ($\log \beta_3(I) = \log \beta_3(0) + 0.23I$) [15] and our measured value ($\log \beta_3(3 \text{ M}) = 18.2 \pm 0.3$), we ob-

tain $\log \beta_3(0.15 \text{ M}) = 17.8 \pm 0.5$, a value that is within the prediction interval of ref. 14.

Sullivan et al. [5] studied the Pu(VI) complexation in HCO_3^- media at pH = 8.3 ($I = 0.1$ M). They interpret the spectrophotometric results in terms of $PuO_2(OH)_2(HCO_3)^-$ and $PuO_2(CO_3)_2^{2-}$. As with Gel'man's results, it is not possible to prove the existence of a mixed complex at constant pH. This complex must be considered as uncertain. We would rather propose the complexes: $PuO_2(CO_3)(aq)$ and $PuO_2(CO_3)_2^{2-}$.

Grenthe et al. [4] studied the formation of the trinuclear complex:

$$3PuO_2(CO_3)_3^{4-} \rightleftharpoons (PuO_2(CO_3)_2)_3^{6-} + 3CO_3^{2-}$$
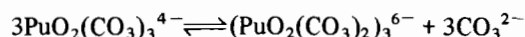
The equilibrium constant they found at $I = 3$ M $NaClO_4$ was $\log K = -7.3$. Working at the same ionic strength ($I = 3$ M), we did not observe this trinuclear complex because this species predominates in oversaturated solutions (Fig. 1) with higher concentrations of Pu(VI).

As we determined the formation constant of the limiting complex (β_3), we propose the equilibrium constant ($\beta_{3,6}$) of the following reaction:

$$(PuO_2(CO_3)_2)_3^{6-} \rightleftharpoons 3PuO_2^{2+} + 6CO_3^{2-}$$
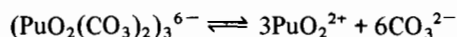
$$\log \beta_{3,6} = \log K(\beta_3^3) = 47.3 \pm 0.5$$

The solubility of $PuO_2(CO_3)(s)$ can be interpreted by the formation of the $PuO_2(CO_3)_i^{2(1-i)}$ ($i = 1, 2, 3$) complexes. Our model can be used to interpret the different results of the literature, even when the authors propose other (not proven) interpretations of their results.

Electrochemical experiments on the Pu(VI)/Pu(V) redox system in carbonate media are in progress. The solubility data we have on Pu(VI) and the redox results we will obtain will give information on the Pu(V) speciation, and will allow us to determine Pu(V) stability in leaching waters of nuclear wastes.

Acknowledgements

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