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EIS Name: Jean-Francois Lucchini
EIS Znumber: 190867
EIS Group: EES-12
EIS MS: A141
EIS Phone: +1.505.234.5556
EIS Fax: +1.505.887.3051
EIS Email: lucchini@lanl.gov

SOLUBILITY OF URANYL IN BRINE

HIROMICHI YAMAZAKI
TOHOKU UNIVERSITY
FACULTY OF ENGINEERING
DEPARTMENT OF NUCLEAR ENGINEERING
SENDAI, JAPAN

BO LAGERMAN
ROYAL INSTITUTE OF TECHNOLOGY
DEPARTMENT OF INORGANIC CHEMISTRY
S-100 44 STOCKHOLM, SWEDEN

VASSILIOS SYMEOPOULOS
UNIVERSITY OF PATRAS
DEPARTMENT OF CHEMISTRY
RADIOCHEMISTRY AND RADIATION CHEMISTRY LAB.
PATRAS, GREECE

AND GREGORY R. CHOPPIN*
DEPARTMENT OF CHEMISTRY
FLORIDA STATE UNIVERSITY
TALLAHASSEE, FLORIDA 32306-3006
(904) 644-3875

ABSTRACT

The solubility of UO_2^{2+} has been measured in a synthetic brine solution at pcH values between 6.4 and 12.4. The solubility is greater at pcH 8.4 (ca. 2 X 10^{-3} M) than at 6.4 (ca. 3 X 10^{-6} M) but is lower at 10.4 (ca. 2 X 10^{-7} M) and 12.4 (ca. 2 X 10^{-7} M). The nature of the solid was studied by X-ray diffraction and seems to be a Schoepite at pcH < 9 and $K_2U_2O_7$ above pcH 10. Modelling calculations indicate formation of $UO_2(CO_3)_3^{4-}$ accounts for the increased solubility at pcH < 9. The decreased solubility above that value can be associated with removal of CO_3^{2-} from solution via $CaCO_3$ precipitation which results in the less soluble $UO_2(OH)_3^-$ becoming the dominant solution species.

I. INTRODUCTION

Disposal of radioactive waste in salt formations is being evaluated in several countries. An important question is that of the solubility of the radionuclides in the saturated brine in inclusions in the salt. The problems of redox speciation of plutonium increases significantly the problems of interpretation of solubility measurements of that element. To aid in the latter, oxidation state analogs such as Nd(III), Th(IV), Np(V), and U(VI) can be studied in place of Pu(III)-(VI). These analogs resist change in oxidation state while closely resembling the chemical behavior of Pu in that oxidation state.

We have conducted such analog studies in a synthetic brine which is representative of those in the WIPP repository site. In this paper, we report the results of the investigation of the solubility of uranyl (UO_2^{2+}) in the brine at pH values between 6.4 and 12.4.

II. EXPERIMENTAL

A. Brine

The synthetic brine was prepared according to the formulation in Table 1. The solubility for each set of conditions was measured in twin experiments in 2 liter plastic beakers with a loose fitting top. The contents were stirred at 60 rpm. In the pcH 10 and 12 experiments, N_2 was passed continuously through the volume above the liquid to present uptake of CO_2. Several types of solubility experiments were performed. The "oversaturation" experiments involved dissolution of the precipitated uranyl. The uranyl was added to a brine solution and the pH was adjusted to the desired value, inducing precipitation.

In the "undersaturation" experiments, after equilibrium had been obtained at some pH, the supernatant solution was adjusted to the new pH

Table 1

Components of Synthetic Brine

Compound	Grams per Liter
NaCl	100.1 (1.71 M)
Na_2SO_4	6.2 (0.044 M)
$NaHCO_3$	0.96 (0.011 M)
NaBr	0.52 (0.005 M)
KCl	57.2 (0.767 M)
$CaCl_2$	1.66 (0.015 M)
$MgCl \cdot 6H_2O$	292.1 (1.44 M)
$Na_2B_4O_7 \cdot 10H_2O$	2.0 (0.005 M)

and new measurements begun. These experiments involved dissolution of precipitated uranyl. At pH ≥ 10, massive precipitation of $Mg(OH)_2$ occurs. For pH 10 and 12, the solubility was measured in the presence of this solid and in a sample of the filtrate with no $Mg(OH)_2$ residue. In all experiments, duplicate samples were taken and the values averaged. The pcH values were checked at the time of sampling and, when necessary, adjusted. There was no significant trend in the small pcH variations.

B. Solubility

The experimental procedures were the following.

1) pcH 6, oversaturation experiment: 1.3 ml of the brine was added to each of the two beakers followed by 6.2 mmoles of $UO_2(NO_3)_2$. The pcH was adjusted to 6.37 with concentrated acid.

2) pcH 8, undersaturation experiment: after equilibrium was reached at pcH 6, the pH of the brine was adjusted to ca. pcH 8 with saturated NaOH solution.

3) pcH 8, oversaturation experiment: 1.3 ml of the brine was added to two beakers followed by 6.2 mmoles of $UO_2(NO_3)_2$. The pcH was adjusted to 8.37 with the saturated NaOH solution.

4) pcH 10, oversaturation experiment: In this experiment, two kinds of brine were used.

a) Without massive brine solids: 6 ml of brine had the pcH adjusted to ca. 10 by adding saturated NaOH solution. NaCl, 198 grams, were added to the alkaline brine to readjust the ionic strength. The solid $Mg(OH)_2$ was filtered and 0.5 ml of the filtrate transferred to two beakers where 2.4 mmoles $UO_2(NO_3)_2$ were added. The pcH was adjusted to 10.37.

b) With massive brine solids: The pcH's in the two beakers, each containing 1.3 ml of the brine plus 6.2 mmoles of $UO_2(NO_3)_2$, were shifted to 10.37 without removal of the solids.

5) pcH 12, oversaturation experiment: Two kinds of brine were used similarly to the experiment at pcH 10.

a) Without massive brine solids: The solution from the pcH 10.4 experiment was used and the pcH shifted from 10.37 to 12.37.

b) With massive brine solids: The brine was made in the same way as 4b and the pcH made 12.37 without solid removal.

C. pcH

A glass combination electrode was used in which the original KCl solution in the reference cell was replaced by a solution similar in composition to the brine but without sulfate, bicarbonate, and borate and with the inlet hole of the reference cell closed to prevent flow of the reference solution into the test solution. These procedures minimized liquid junction potential variations. The dependence of the liquid junction potential on H^+ was measured to be $Ej = -22 \cdot [H^+]$ so it had no significant effect on the pH measurements. The electrode was calibrated to the hydrogen ion concentrations by the Gran method (1) and all data is reported in terms of pcH (= -log (H^+ concentration)). The electrode was recalibrated every 90-100 days and over a year showed no significant change.

D. Separation of the Uranium

Separation of uranium from brine constituents: Samples of brine containing uranium were removed and centrifuged prior to filtration through 0.2 μm-filter (acrylic). A portion of each sample was acidified by adding 0.1 ml volume of 6 M HCl. This was placed on a column of 2 g of Dowex-1X10 in the Cl^- form (0.8 cm in diameter and 12 cm in height). The column was pre-equilibrated by passage of 60 ml of 6 M HCl for separation of samples at pcH < 8.4, and of 3 M HCl in the case of samples at pcH > 10.4. The loading volume of the samples was 5-10 ml (pcH 6.4 samples), 1-10 ml (pcH 8.4 samples). Samples with high uranium concentration were diluted tenfold. After loading, the column had 40 ml of 6 M HCl passed to separate the brine constituent from the uranium; then, the uranium fraction was eluted by 64 ml of 0.001 M HCl after washing it with 6 ml H_2O. The flow rate was controlled to 0.3-0.4 ml/min in the elution. The eluted fraction of uranium was evaporated to dryness and dissolved in a small volume of 0.01 M HCl (<8 ml).

The column separations gave 96-102% recovery in a series of tests with standards.

E. Analysis of Uranium

The concentration of the uranium in the dilute HCl solution from the dissolution after separation was determined by measuring the absorption spectral intensity at 578 nm after adding 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (2). This method had a maximum sensitivity of 0.16 mg U with an uncertainty of ± 80% at this lowest level. The spectral measurements were conducted on a computer interfaced, rebuilt (On Line Instr. Sys., Inc.) Cary 14. The

spectrophotometer was calibrated by measuring the absorbance of a solution of $8.3X10^{-6}$ g U in 25 ml of 0.1 M HCl. The spectrometer was calibrated before each series of samples and found to be constant over the 12 months of the study.

F. X-ray Measurements

Samples of the solid present at equilibrium were washed with distilled water briefly, dried, and studied by X-ray diffraction on a Siemens D-5000 diffractometer using Cu K_α line at 1.514 Å.

III. RESULTS AND DISCUSSION

The time required to reach a constant value of uranyl in the solution phase was a function of time and method of measurement. Figure 1 shows the measured solubility as a function of time at pcH 8.4 in twin experiments. The two series of values overlap in the oversaturation system in which equilibrium is reached rather quickly - ca. 60 days. There is about a 30% difference in the values for the two solutions in the undersaturation experiments and equilibrium has not been attained within the time span of our experiments (still continuing). However, the curves indicate that in ca. 3 years, the solubility will reach the equilibrium value observed in oversaturation experiments. This trend to much slower equilibrium for the dissolution was observed also in measurements of the solubilities of Nd^{3+} and Th^{4+} in these brines (3).

The measured solubilities are listed in Table 2. Except for the pcH 8.4 oversaturation experiments, the other systems had reached constant solubility values. The relative solubilities with and without solids are reversed for pcH 10.4 and 12.4.

The values are at the lower end of the sensitivity of our method and the differences most likely reflect experimental uncertainties rather than significant solubility differences.

The X-ray diffraction patterns provide information on the chemical nature and crystallinity of the solid phases. At pcH 6.4 (oversaturation) after 30 days, the solids seemed to have poor crystallinity which improved with time. The crystalline solid (90 days aging) cannot be assigned unambiguously to either a simple uranyl carbonate such as Rutherfordine or to a pure uranium oxide hydrate such as α-Schoepite. The principle peaks in the diffraction spectra correlated with those expected for β-Shoepite while some smaller peaks generally agreed with the α-Schoepite. We conclude

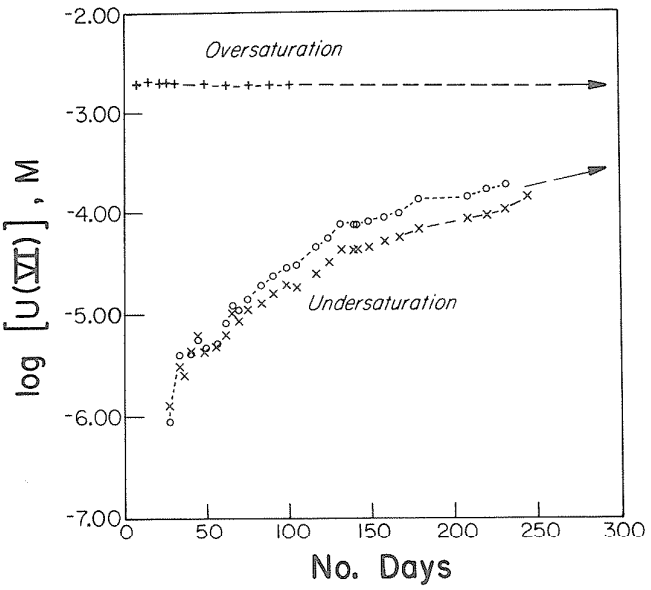

Figure 1. Measured solubility of uranyl in the brine at pcH 8.4 as a function of time.

Table 2

Solubility of UO_2^{+2} in Brine

T = 22 ± 2°C

pcH	Solubility (M)	Time (d)	Condition
6.4	a)$3.4(\pm0.5)X10^{-6}$ b)$3.3(\pm0.4)X10^{-6}$	24	Oversat.
8.4	a)$1.82(\pm0.0)X10^{-3}$ b)$1.81(\pm0.0)X10^{-3}$	100	Oversat.
8.4	a)$1.4(\pm0.05)X10^{-3}$ b)$1.8(\pm0.05)X10^{-3}$	244	Undersat.
10.4	a)$1.8(\pm0.3)X10^{-7}$ b)$1.8(\pm0.3)X10^{-7}$	113	Oversat. w/o solids
10.4	a)$3.8(\pm0.4)X10^{-7}$ b)$3.1(\pm0.3)X10^{-7}$	150	Oversat. w/ solids
12.4	a)$1.8(\pm0.3)X10^{-7}$ b)$1.7(\pm0.3)X10^{-7}$	60	Undersat. w/o solids
12.4	a)$7(\pm2)X10^{-8}$ b)$8(\pm2)X10^{-8}$	65	Undersat. w/ solids

that this solid is a mixture of α- and β-Schoepite.

The undersaturation experiments at pcH 8.4 began with the solid from the pcH 6.4 experiments while the solid still exhibited poor crystallinity (ca. 25 days) and little further change in crystallinity was observed over the next 250 days (in contrast to the improvement in crystallinity with time at pcH 6.4). Consequently, the solid seems to be a mixture of α- and β-Schoepite with more of the latter. In the oversaturation experiments, at pcH 8.4 a very broad diffraction pattern was observed which corresponds to α-Schoepite based on the relative intensity of the two peaks at around 12° and 23°. The diffraction peaks became slightly sharper after 61 days due to aging of the solid but the crystallinity was not changed appreciably with time. We conclude that poorly crystalline α-Schoepite controls the uranium solubility in the uranium oversaturated brine at pcH 8.4.

For the oversaturation experiments at pcH 10.4 in the absence of the precipitated solid ($Mg(OH)_2$), the X-ray diffraction measurement showed that a mixture of crystalline $Mg(OH)_2$ and $K_2U_2O_7$ was present at pcH 10.4 after 55 days of equilibration (Fig. 2). Therefore, the solid phase controlling uranium solubility changed from poorly crystalline Schoepite at pcH 8.4 to potassium diuranate at pcH 10.4. The equilibrating time was much longer at pcH 10.4 than at lower pcH, which may be due to the phase transformation of the uranium solid formed. In the experiment with massive solid, the diffraction pattern was dominated by the $Mg(OH)_2$ solid but small peaks confirmed the presence of $K_2U_2O_7$.

The X-ray diffraction measurement of the solid (equilibrated for 35 days) revealed that crystalline $K_2U_2O_7$ controlled the uranium concentration in brine at pcH 12.4 as at pcH 10.4.

Modelling calculation of uranium solubility in the standard recipe brine was carried out by taking into account the reactions of uranyl ions with hydroxide, carbonate, chloride and sulfate ions in contact with crystalline UO_2CO_3, $UO_3 \cdot 2H_2O$, and $K_2U_2O_7$ as the uranium(VI) solid phases. As the effective carbonate concentration in brine depends on the extent of a carbonate complexation and precipitation by Mg^{2+} and Ca^{2+}, three different sets of solid phase formation constants of magnesium and calcium carbonates were checked: (a) metastable carbonate phases; (b) stable carbonate phases; (c) metastable $MgCO_3 \cdot 3H_2O(s)$ plus stable $CaCO_3(s)$. Other reactions of Mg^{2+} and Ca^{2+} with the

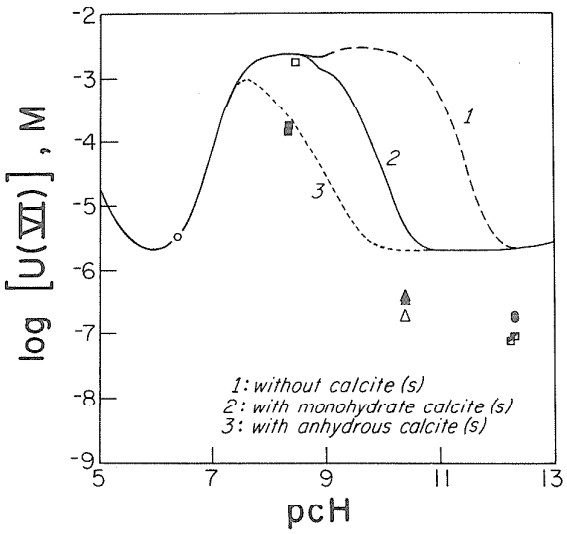

Figure 2. Calculated curves and experimental solubilities of UO_2^{+2} in brine; pcH 6.4, O; pcH 8.4, ■ undersat., □ oversat.; pcH 10.4, ▲ with solid, △ without solid; pcH 12.4, □ with solid, ● without solid.

brine anions were taken into consideration in order to estimate the effective carbonate concentration.

The ionic strength correction of the thermodynamic data at zero ionic strength was based on the specific interaction theory (4), which was simplified by neglecting the contributions of all minor species. Although the specific interaction theory should be limited to media with ionic strength < 3 M, it was applied to 7 M medium in the absence of alternate ionic

strength corrections of the equilibrium constants (5). Based on the results of the X-ray diffraction studies, $UO_3 \cdot 2H_2O$ and $K_2U_2O_7$ were chosen as the solids which limit the solubility of the uranium. As the formation free energy of crystalline $K_2U_2O_7$ was not available, the value of crystalline $Cs_2U_2O_7$, -3029.5 + 4.5 kJ/mol, was substituted. The computer codes used for speciation were Haltafall (6) and Solgaswater (7).

To consider the competition between uranium and calcium (and magnesium) for the carbonate, three different cases are plotted in Figure 2: (1) without any calcium carbonate solid; (2) with $CaCO_3$(s) (calcite); (3) with $CaCO_3 \cdot H_2O$(s). The increase in solubility between pcH 6.4 and 8.4 is related to the formation of $UO_2(CO_3)_3^{4-}$. In the region of pcH > 9, carbonates are removed from solution by precipitation of $CaCO_3$ resulting in constant solubility between pcH 10 and 12. The solubility in this region seems to be governed by the pcH independent dissolution reaction:

$$K_2U_2O_{7(s)} + 3H_2O = 2K^+ + 2UO_2(OH)_3^-$$

The calculations also agree with our observations that the insoluble uranium phase is $UO_3 \cdot 2H_2O$ below pcH 9.3 and $K_2U_2O_7$ above that value. The sharp decrease in uranium solubility above pcH 9 is related to the decreased carbonate concentration as $CaCO_3$ precipitates. This results in dissociation of the strong $UO_2(CO_3)_3^{4-}$ complex and a sharp decrease in solubility as $UO_2(OH)_3^-$ and $UO_2(OH)_4^{2-}$ become the dominant solution phase species.

In summary, uranium solubility increases in the brine from pcH 6 to 8 due to formation of $UO_2(CO_3)_3^{4-}$. The decrease in solubility above pcH 8 is related to the shift from $UO_2(CO_3)_3^{4-}$ to $UO_2(OH)_n^{2-n}$ in the solution phase as precipitation of $CaCO_3$ removes carbonate from solution and to conversion of the limiting solid to $K_2U_2O_7$.

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