

LA-UR- 10-0817

Approved for public release;
distribution is unlimited.

<i>Title:</i>	Uranium (VI) Solubility in Carbonate-Free ERDA-6 Brine
<i>Author(s):</i>	Jean-Francois Lucchini Hnin Khaing Donald T. Reed
<i>Intended for:</i>	Material Research Society Symposium Proceedings 2010 MRS Spring meeting April 5-9, 2010 San Francisco, CA USA



Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the Los Alamos National Security, LLC for the National Nuclear Security Administration of the U.S. Department of Energy under contract DE-AC52-06NA25396. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

Uranium (VI) Solubility in Carbonate-Free ERDA-6 Brine

Jean-Francois Lucchini, Hnin Khaing and Donald T. Reed

Los Alamos National Laboratory, Earth and Environmental Sciences Division, 115 N. Main, Carlsbad, NM 88220, U.S.A.

ABSTRACT

When present, uranium is usually an element of importance in a nuclear waste repository. In the Waste Isolation Pilot Plant (WIPP), uranium is the most prevalent actinide component by mass, with about 647 metric tons to be placed in the repository [1]. Therefore, the chemistry of uranium, and especially its solubility in the WIPP conditions, needs to be well determined.

Long-term experiments were performed to measure the solubility of uranium (VI) in carbonate-free ERDA-6 brine, a simulated WIPP brine, at pC_{H^+} values between 8 and 12.5. These data, obtained from the over-saturation approach, were the first repository-relevant data for the VI actinide oxidation state. The solubility trends observed pointed towards low uranium solubility in WIPP brines and a lack of amphotericity. At the expected pC_{H^+} in the WIPP (~ 9.5), measured uranium solubility approached 10^{-7} M. The objective of these experiments was to establish a baseline solubility to further investigate the effects of carbonate complexation on uranium solubility in WIPP brines.

INTRODUCTION

In the anoxic and strongly reducing environment expected in the WIPP, tetravalent uranium will be the dominant oxidation state. As a consequence, the uranium solubility will be very low (about 10^{-8} M) [2]. However, some uranium (VI) phases and aqueous species, although not expected to predominate in the WIPP, could be present due to the localized effects of radiolysis. The WIPP Performance Assessment (PA) currently makes the conservative assumption that U(VI) species predominate in 50% of the PA vectors [1]. The solubility of U(VI) in the WIPP is expected to be defined by the combined contribution of two processes: hydrolysis with oxyhydroxide phase formation, and carbonate complexation with uranium carbonate phase formation. In the absence of WIPP-specific experimental data, the solubility of U(VI) is presently set at 10^{-3} M in the WIPP PA for all expected WIPP conditions, including the potential and likely effects of carbonate complexation [3].

This paper summarizes the results of long-term experiments to establish the solubility of U(VI) in a simulated carbonate-free WIPP brine from an over-saturation approach as a function of pH. More information on these experiments and their results can be found in [4, 5].

EXPERIMENT

The general experimental approach was to investigate uranium (VI) solubility from oversaturation, as described by Nitsche [6]. This consisted of sequentially adding dissolved uranium, as a function of experimental conditions, until precipitation was observed. Subsequently, the uranium concentration was monitored until a steady state concentration was achieved. All chemicals were reagent-grade (certified ACS) and used without further purification. Appropriate amounts of salts were dissolved in high purity 18 MΩ·cm water to prepare the simulated WIPP brine used in these experiments, ERDA-6 brine. This brine is a synthetic brine representative of fluids in Castile brine reservoirs. Its composition is listed in Table 1.

Table 1. Composition and density of ERDA-6 simulated WIPP brine (95% initial formulation).

Component	ERDA-6 brine [M]
NaCl	4.254
MgCl ₂	0.018
Na ₂ SO ₄	0.159
NaBr	0.010
Na ₂ B ₄ O ₇	0.015
KCl	0.092
CaCl ₂	0.011
Density (g/mL)	1.183
Ionic strength (M)	4.965

Significant care was taken to establish carbonate-free conditions. Polypropylene bottles were placed in a nitrogen glove box two weeks prior to use. The removal of carbonate from the brines was a two-step process. The first step consisted of acidification of the brines which converted carbonate into bicarbonate, in equilibrium with carbonic acid, then into dissolved carbon dioxide gas. The second step was to use a vacuum chamber for a slow pump-down process to smoothly remove gas from the brine. The vacuum chamber was placed in a low-flow-through high-purity-nitrogen glove box to maintain low levels of carbon dioxide. The oxygen level in the nitrogen glove box was continuously monitored, and was always lower than 10 ppm.

In highly concentrated brines, the measurement of the hydrogen ion concentration is difficult because of their high ionic strength that affects the activity coefficients and because of the presence of a high sodium concentration that introduces junction potentials. However, reliable hydrogen ion concentrations can be calculated from the measured/observed pH (pH_{obs}) by the following equation based on modified Gran titration method [7]: $pC_{H^+} = pH_{obs} + K$, where pC_{H^+} is the negative logarithm of the hydrogen concentration in molarity (mol/L or M) units, and K is an experimentally determined constant. The correction factor K was found to be (0.94 ± 0.02) for ERDA-6 [8].

The pH of the brine solutions was measured with a sealed Orion-Ross combination glass electrode calibrated against NIST-certified pH buffers. Adjustments of pH were made in the anoxic carbon dioxide-free glovebox with low carbonate sodium hydroxide (50 weight%) to minimize the re-introduction of carbonate in solution. From this point, all brine solutions were

kept in polypropylene bottles, tightly capped, in an anoxic carbon dioxide-free glovebox (MBraun Labmaster 130 with a nitrogen atmosphere and with an oxygen purification system).

Our source of uranyl ion was a depleted uranium (VI) nitrate hexahydrate that was converted to a nitrate-free hydrochloric acid solution with an oxidation-state purity of greater than 99% for UO_2^{2+} . Appropriate amounts of this U(VI) stock solution were volumetrically pipetted into an aliquot of brine at a pH of ~ 3 -4 and checked for precipitation. This step led to properly diluted carbonate-free solutions to use as uranyl spikes in the pC_{H^+} -adjusted brines.

The experiments were initiated by the addition of uranyl spiked brine into the pC_{H^+} -adjusted solutions. The initial uranyl concentration in all of the brine experiments was $(1.7 \pm 0.3) \times 10^{-5}$ M. All the experiments were carried out at $(25 \pm 4)^\circ\text{C}$. Once underway, aliquots were periodically removed (0.3 mL) and centrifuged at 8,000 or 13,500 rpm for 15 minutes. Supernatants were filtered through Microcon® Millipore centrifugal filters with a nominal molecular weight limit of 30,000 Daltons. This filtration step removed potential uranium colloids or particulates bigger than 5 nm from the sample aliquots.

Filtrates were analyzed for uranium content using an inductively coupled plasma mass spectrometer (ICP-MS) Elan model 6000. Aliquots of the filtrates were diluted 50 or 100 times in nitric acid due to the high salt concentration and to establish uranium concentrations within the range of the ICP-MS calibration. The detection limit by ICP-MS for uranium was $\sim 5 \times 10^{-12}$ M, which was effectively $\sim 2.5 \times 10^{-10}$ M or $\sim 5 \times 10^{-10}$ M for our experiments due to the sample dilutions made. After 216 days of experiment, a second uranyl spike was added to every solution to re-establish over-saturation with respect to uranium concentration. This second uranium addition was $(8.6 \pm 1.7) \times 10^{-5}$ M, which was about 5 times the initial uranium spike.

RESULTS AND DISCUSSION

The uranium concentration data measured as a function of time in carbonate-free ERDA-6 brine placed in a nitrogen-controlled atmosphere throughout the 705 days of the experiments are shown on Figure 1.

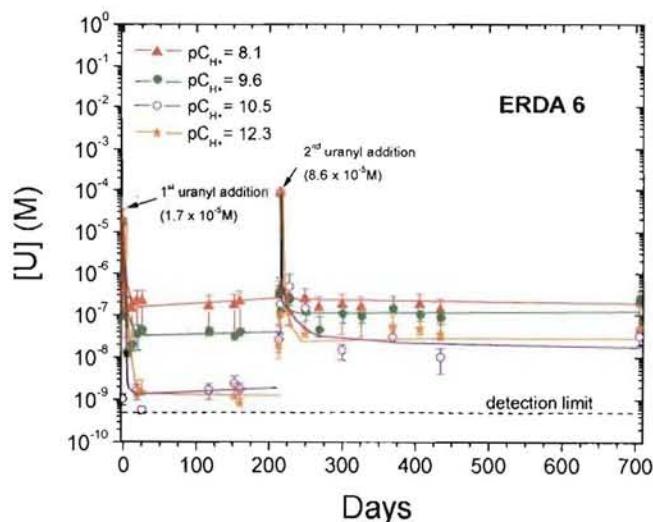


Figure 1: Uranium concentration in carbonate-free ERDA-6 brine in a nitrogen-controlled atmosphere as a function of time. Data shown are for $\text{pC}_{\text{H}^+} = 8.1$,

9.6, 10.5 and 12.3 from top to bottom of the legend. These data correspond to 19 samplings performed throughout 705 days of the experiments.

In all the experimental solutions, steady state uranium concentrations were achieved in about 50 days. This rate was quite long, because of the high ionic strength of the brine. However, the U(VI) steady state concentrations were not all reproducible after the first and the second uranyl additions. Only at $pC_{H^+} = 8.1$ and, to some extend at $pC_{H^+} = 9.6$, the steady state U(VI) concentrations were the same after the first and after the second uranyl additions. At $pC_{H^+} = 8.1$, the U(VI) concentration found in solution was established at about 2×10^{-7} M, whatever the uranium addition was. At $pC_{H^+} = 9.6$, the steady state U(VI) concentration was about 10^{-7} M after the second uranyl addition, that was only two times more than the concentration established before the second uranyl addition. Discrepancies in the steady state U(VI) concentrations were noticed at the two highest pC_{H^+} values investigated (10.5 and 12.3). One order of magnitude difference was found between the steady state U(VI) concentrations obtained before the second uranyl concentration ($\sim 10^{-9}$ M) and after the second uranyl addition ($\sim 2 \times 10^{-8}$ M). These values of pC_{H^+} were on the edge of or beyond the chemical stability range of the brine, so there were compositional changes in the brine that were the likely cause of the increased concentrations.

Yellow precipitates were generated in all ERDA-6 solutions a few days after the second uranyl addition. These were U(VI) hydroxide phases that were undergoing phase transformations over time. For example, the precipitate observed at $pC_{H^+} = 10.5$ turned from yellow to white about 40 days after the addition of the second uranyl spike. Some solid characterization was carried out by Scanning Electron Microscopy (SEM) using a Hitachi model S-3400N Type II scanning electron microscope equipped with an Energy-Dispersive x-ray Spectrometer (EDS - Thermo Electron NORAN System Six 300). Figure 2 shows different SEM images of the precipitate obtained in ERDA-6 solution at $pC_{H^+} \sim 12$.



Figure 2: Scanning Electron Microscopy images of the precipitate obtained in ERDA-6 solution at $pC_{H^+} \sim 12$ at three different magnifications: 84 \times (left picture), 248 \times (middle picture), and 348 \times (right picture). These pictures clearly show a halite (NaCl) deposit on brucite (Mg(OH)₂).

Two phases could be identified by EDS. The two solid phases were mostly sodium chloride (NaCl) and magnesium hydroxide (Mg(OH)₂). At $pC_{H^+} \sim 12$, the formation of brucite (or magnesium hydroxide) was expected, unlike halite (or sodium chloride). We assume that halite deposited on brucite during the preparation (dryness step) of the precipitate for solid characterization. Uranium was not detected by EDS. We assume that the uranium phases were embedded in the brucite phase.

Figure 3 gives the U(VI) solubility estimates obtained in the experiments using the over-saturation approach. These results will need to be confirmed using the under-saturation approach. However, the data obtained are considered reliable when the concentration reached a steady state over time and precipitation occurred in solution.

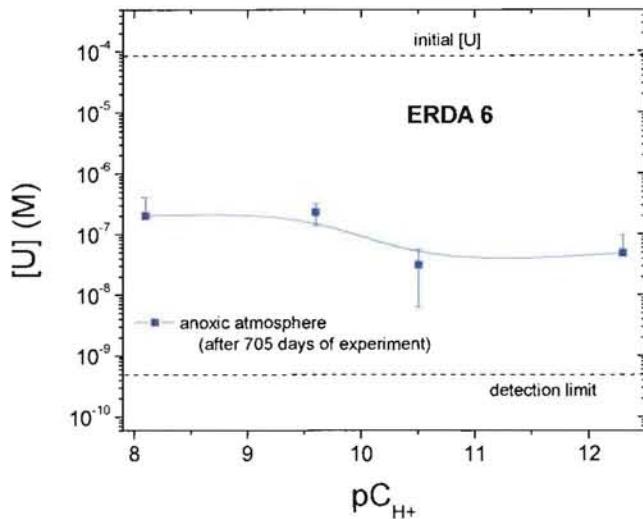


Figure 3: Uranium (VI) solubility estimates in carbonate-free ERDA-6 brine solutions versus pC_{H+} . The curve compiles data obtained from the solutions kept in a nitrogen-controlled atmosphere throughout the 705 days of the experiment.

From pC_{H+} 8 to 11, the solubility of U(VI) in carbonate-free ERDA-6 brine was between 3.1×10^{-8} M and 2.3×10^{-7} M. This solubility decreased slightly from $pC_{H+} \sim 8$ to $pC_{H+} \sim 11$. At $pC_{H+} \sim 12.3$, which is beyond the chemical stability of ERDA-6, the solubility of U(VI) was $\sim 4.8 \times 10^{-8}$ M. This solubility was within the range of the data measured at lower pC_{H+} . The presence of a precipitate from the brine components prior to the beginning of the experiments and the first addition of uranium in solution did not enhance the solubility of uranium (VI).

It is important to notice that under these experimental conditions we did not see evidence for amphotericity in the long-term. Our data also show that U(VI) solubility in high ionic strength brine when carbonate was carefully excluded can be 10-100 times lower than any reported in the literature for similar systems [9]. Diaz-Arocas performed uranium (VI) solubility experiments in 5 M sodium chloride at 25°C and different basic pH values, under an argon atmosphere using an over-saturation approach. They reported a uranium solubility of $(2.8 \pm 1.8) \times 10^{-5}$ M at $pC_{H+} = 8.9$ in 5 M NaCl with a similar experimental approach using argon bubbling to remove carbonate. Our data obtained in a nitrogen glovebox with a carbonate-free atmosphere were more than two orders of magnitude lower than Diaz-Arocas data. We believe that our lower uranium concentrations reported herein reflects the greater extent that carbon dioxide was removed from the brine solutions at the beginning of the experiments, along with a better control of the carbon dioxide-free environment throughout our experiment.

CONCLUSIONS

Our solubility data for uranium (VI) provides the first WIPP-relevant data for the VI actinide oxidation state that establish the solubility of uranium (VI) over an extended pC_{H+} range for ERDA-6 brine in the absence of carbonate. These data are the first data generated at high pC_{H+} under what we believe to be a truly carbonate-free system. They establish uranium solubility, in the absence of carbonate that is 10-100 times lower than published results. The

uranium (VI) solubility measured in our experiments was about 10^{-8} - 10^{-7} M in ERDA-6 at $p\text{C}_{\text{H}^+} \geq 8$. At the expected $p\text{C}_{\text{H}^+}$ in the WIPP (~ 9.5), measured uranium solubility approached 10^{-7} M.

ACKNOWLEDGMENTS

This work was supported by the United States Department of Energy- Carlsbad Field Office. This research was performed by the Los Alamos National Laboratory Actinide Chemistry and Repository Science Program in Carlsbad, NM in support of the ongoing recertification activities for the WIPP transuranic repository. The authors are grateful to S. Ballard (New Mexico State University, Carlsbad Environmental and Monitoring Research Center) for the technical support (brine preparation, $p\text{C}_{\text{H}^+}$ adjustments) and to P. Cooke (NMSU, Electron Microscopy Laboratory) for SEM/EDS analysis.

REFERENCES

1. U.S. Department of Energy (DOE). 2009. *Title 40 CFR Part 191 Subparts B and C Compliance Recertification Application for the Waste Isolation Pilot Plant. Appendix SOTERM-2009*. DOE/WIPP 2009-3424. Carlsbad, NM: Carlsbad Field Office.
2. Neck, V., and J.I. Kim. 2001. "Solubility and Hydrolysis of Tetravalent Actinides." *Radiochimica Acta*, vol. 89: 1–16.
3. U.S. Environmental Protection Agency (EPA). 2005. Teleconference with U.S. Department of Energy (DOE), Sandia National Laboratories (SNL), and Los Alamos National Laboratory (LANL) re: Change in U(VI) Solubility Assumption to a Concentration to 1 mM. 2 March 2005.
4. Lucchini, J.F., M. Borkowski, M.K. Richmann, S. Ballard, and D.T. Reed. 2007. "Solubility of Nd^{3+} and UO_2^{2+} in WIPP Brine as Oxidation-State Invariant Analogs for Plutonium." *Journal of Alloys and Compounds*, vol. 444/445: 506–11.
5. Lucchini, J.F., H. Khaing, M. Borkowski, M.K. Richmann, and D.T. Reed. 2010. *Actinide (VI) Solubility in Carbonate-free WIPP Brine: Data Summary and Recommendations*. LCO-ACP-10, LANL\ACRSP Report. LA-UR-10-00497. Los Alamos, NM: Los Alamos National Laboratory.
6. Nitsche, H., Muller, A., Standifer, E.M., Deinhammer, R.S., Becroft, K., Prussin, T., Gatti, R.C.: Dependence of Actinide Solubility and Speciation on Carbonate Concentration and Ionic-Strength in Groundwater, *Radiochim. Acta* 58/59, 27 (1992).
7. Rai D., A.R. Felmy, S.P. Juracich, and L.F.Rao, Estimating the Hydrogen Ion Concentration in Concentrated NaCl and Na_2SO_4 electrolytes, Report SAND94-1949, Sandia National Laboratories, Albuquerque, NM. 1995.
8. Borkowski, M., J.F. Lucchini, M.K. Richmann, and D.T. Reed. 2009. *Actinide (III) Solubility in WIPP Brine: Data Summary and Recommendations*. LCO-ACP-08, LANL\ACRSP Report. LA- 14360. Los Alamos, NM: Los Alamos National Laboratory.
9. Diaz Arocas, P., and B. Grambow. 1998. "Solid-liquid Phase Equilibria of U(VI) in NaCl Solutions." *Geochimica et Cosmochimica Acta*, vol. 62: 245–63.