Influence of Carbonate on Uranium Solubility in the WIPP

Jean-Francois Lucchini[1], Sally Ballard[2], and Hnin Khaing[3]

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

[2] Carlsbad Environmental Monitoring and Research Center, New Mexico State University, 1400 University Drive, Carlsbad, NM 88220, U.S.A.

[3] URS, Washington Safety Management Solutions, 1400 University Drive, Carlsbad, NM 88220, U.S.A.

ABSTRACT

In the performance assessment (PA) for the Waste Isolation Pilot Plant (WIPP), the solubility of uranium (VI) was conservatively set at 10^{-3} M for all expected WIPP conditions, including the potential and likely effects of carbonate complexation [1]. Under WIPP-relevant conditions, long-term experiments were performed to establish the uranium (VI) solubility limits in WIPP-simulated brine over a broad range of pC_{H+} values [7.5-12.5] and to evaluate the contribution of carbonate complexation and hydrolysis to uranium (VI) speciation. Data obtained in carbonate-free ERDA-6 brine, a simulated WIPP brine, were reported earlier [2]. In the absence of carbonate, uranium solubility approached 10^{-7} M at the expected pC_{H+} in the WIPP (~ 9.5). In the presence of a significant amount of carbonate (millimole levels), recent experimental results showed that uranium (VI) concentrations will not exceed 10^{-4}M. This measured solubility limit is an order of magnitude lower than the uranium solubility value currently used in the WIPP PA [3]. A small effect of borate complexation was found in the pC_{H+} range [7.5-10]. At $pC_{H+} \geq$ 10, hydrolysis overwhelmed carbonate effects, and no amphoteric effect was observed.

INTRODUCTION

In the anoxic and strongly-reducing environment expected in the WIPP, tetravalent uranium (IV) is predicted to be the dominant oxidation state and will establish uranium solubility at a very low value (about 10^{-8}M) [4]. However, some uranium (VI) phases and aqueous species, although not expected to predominate in the WIPP, could be present due to localized oxidation effects. Consequently, in WIPP PA, both IV and VI oxidation states of uranium are considered. Uranium is assumed to be uranium (VI) in 50% of the PA vectors and uranium (IV) in 50% of the PA vectors [2]. The solubility of uranium (VI) was conservatively set at 10^{-3} M in WIPP PA for all expected WIPP conditions, including the potential and likely effects of carbonate complexation [1].

The solubility of uranium (VI) in the WIPP is expected to be defined by the combined contribution of hydrolysis and carbonate complexation. Experimental data published in previous papers [2, 5, 6] were obtained under carbonate-free conditions, so they provided a baseline for carbonate effects on uranium (VI) solubility. In this paper, some results of long-term

experiments carried out in the presence of a significant amount of carbonate (up to millimole levels) are given.

EXPERIMENT

Long-term experiments to establish the solubility of uranium (VI) in the presence of carbonate were performed in ERDA-6 and GWB brines, two simulated WIPP brines, at pC_{H+} values between 7.5 and 12.5.

The general experimental approach was to investigate uranium (VI) solubility from over-saturation. The two simulated WIPP brines, GWB and ERDA-6, were prepared at 95% of initial formulations, using reagent-grade chemicals without further purification (Table 1). GWB brine simulates intergranular brines from the Salado formation at, or near, the stratigraphic horizon of the repository. ERDA-6 brine is representative of fluids in the Castile brine reservoirs that underlie the repository horizon. These two simulated brines bracket the expected range in WIPP brine composition [3]. The source of uranyl ion was depleted uranium (VI) nitrate hexahydrate that was converted to a nitrate-free chloride form with an oxidation-state purity of ~ 100% for UO_2^{2+}.

Table 1. Composition and ionic strength of ERDA-6 and GWB, two simulated WIPP brines (95% initial formulation), and pH correction factor for each brine.

Component	ERDA-6 (M)	GWB (M)
NaCl	4.25	2.87
$MgCl_2$	0.018	0.953
Na_2SO_4	0.159	0.166
NaBr	0.010	0.025
$Na_2B_4O_7$	0.015	0.037
KCl	0.092	0.437
$CaCl_2$	0.011	0.013
LiCl	---	0.004
ionic strength (M)	4.97	6.84
pH correction factor (K)	0.94 ± 0.02	1.23 ± 0.01

Similarly to the carbonate-free experiments [2], carbonate was first removed from the brines using a two-step process: acidification of the brines, which ultimately converted carbonate into dissolved carbon dioxide gas, and a slow pump-down process to smoothly remove gas from

the brine. From this point, all brine solutions were kept in polypropylene bottles, tightly capped, in an anoxic carbon dioxide-free glovebox, and at a temperature of (25 ± 4) ºC. The hydrogen ion concentration of the brines were adjusted with low-carbonate sodium hydroxide (50 weight%) and measured with a sealed Orion-Ross combination glass electrode calibrated against NIST-certified pH buffers. The effect of the high ionic strength of the two simulated WIPP brines was taken into consideration in the determination of reliable hydrogen ion concentrations, using the following equation based on a modified Gran titration method [7]: $pC_{H+} = pH_{obs} + K$, where pC_{H+} is the negative logarithm of the hydrogen ion concentration in molarity (mol/L or M) units, pH_{obs} the measured/observed pH and K an experimentally determined constant. The correction factor K was found to be (0.94 ± 0.02) for ERDA-6 and (1.23 ± 0.01) for GWB [8]. The level of carbonate in the experiments was maintained by the addition of a small volume of an appropriate intermediate carbonate solution to achieve the desired concentration of carbonate in solution: 2×10^{-4} M or 2×10^{-3} M. The intermediate carbonate solution was prepared by dissolving a known amount of sodium carbonate in a determined volume of brine.

The experiments were initiated by the addition of uranyl-spiked brine into the pC_{H+}-adjusted brine solutions containing a known amount of carbonate. Aliquots were periodically removed, centrifuged and filtered through Microcon® Millipore centrifugal filters with a nominal molecular weight limit of 30,000 Daltons. Filtrates were analyzed for uranium content using an inductively-coupled plasma mass spectrometer (ICP-MS). Over time, three additions of uranyl were performed to every solution to re-establish over-saturation with respect to uranium concentration: $[U]=1.48 \times 10^{-5}$ M at day 0 (initial), $[U]=1.0 \times 10^{-4}$ M at day 231, and $[U]=1.2 \times 10^{-3}$ M at day 675. These additions of uranyl, performed in small volumes, didn't change the pH of the solutions.

When the experiments were complete, the total carbonate concentration in solutions was measured using gas chromatography. It was found that about 90% of carbonate initially added to the brines was present at the end of the experiments. A loss of carbonate from solutions at $pC_{H+} >$ 8 was not expected, because the partial pressure of carbon dioxide over the solution was very small and the vessels were kept closed during the experiment.

RESULTS AND DISCUSSION

Figure 1 shows the uranium concentrations measured in ERDA-6 and GWB brines as a function of pC_{H+}. The data obtained when carbonate was present correspond to 17 samplings performed throughout 994 days of experiments. The data in carbonate-free brines are presented elsewhere [2, 9], but they are reproduced in Figure 1 for comparison purposes.
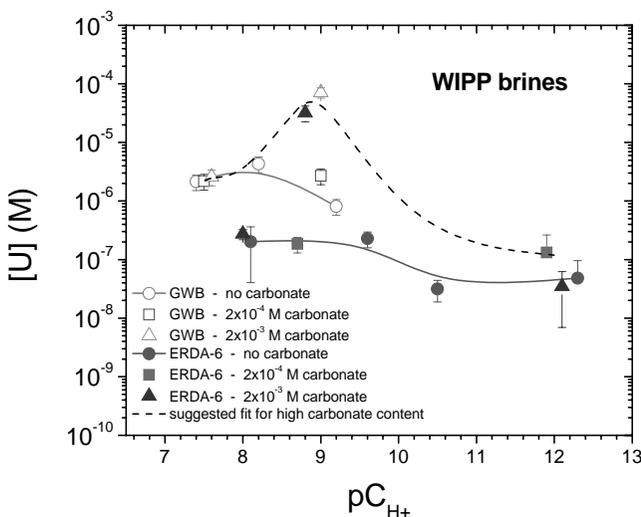
Figure 1. Uranium concentrations in ERDA-6 (filled symbols) and GWB (open symbols) versus pC_{H+} in nitrogen-controlled atmosphere, in the absence of carbonate or in the presence of two concentrations of carbonate (2×10^{-4} M and 2×10^{-3} M) at the beginning of the experiments.

In all of the experimental solutions containing carbonate, a yellow precipitate could be observed, and the uranium concentrations measured in solution reached a steady state over time. Therefore, the uranium concentrations measured in carbonate systems shown in Figure 1 can be considered as reliable estimates of uranium (VI) solubility.

Based on the experimental data in Figure 1, the impact of carbonate on uranium (VI) solubility in WIPP-simulated brines depends on pC_{H+}. Three pC_{H+} regions were noted.

First region

From pC_{H+} 7.5 to 8, the uranium concentrations were stable in both brines and independent of the carbonate concentration. However, there were differences in the uranium solubility due to differences in the composition of the brine: $\sim 10^{-6}$ M in GWB and $\sim 10^{-7}$ M in ERDA-6. These data indicated a possible effect of a ligand present in higher amounts in GWB than in ERDA-6, and an effect of the difference in ionic strength between the two brines. Based on our previous investigation of neodymium solubility [8], we postulated that borate may play a role in defining the uranium (VI) solubility in this pC_{H+} region ($7.5 \leq pC_{H+} \leq 8$). Three carbonate-free ERDA-6 solutions at an initial pC_{H+} of 8.1, 9.6 and 10.5 were saturated with a sodium tetraborate solid, reaching a total concentration of $\sim 5\times10^{-2}$ M tetraborate in solution [9]. A significant increase of uranium in solution (up to 10^{-4} M) and a shift of pC_{H+} to values close to

the pK_a (9.02) of boric acid at ionic strength of 5.0 M were observed after 55 days of experiments. Borate complexation was demonstrated to influence uranium solubility in WIPP-simulated brines at pC_{H+} values between 7.5 and 10.

Second region

The second pC_{H+} region of interest, $8 \leq pC_{H+} \leq 10$, was directly relevant to the WIPP. In this pC_{H+} region, not only was there a compositional effect between the two brines studied (higher uranium concentrations in GWB than in ERDA-6 for identical carbonate content) due to borate, but carbonate also had an impact on the observed uranium solubility in both brines. With high carbonate content (2×10^{-3} M), the uranium concentrations reached 10^{-4} M, which was two or more orders of magnitude higher than in the absence of carbonate. The low carbonate content data (2×10^{-4} M) did not reflect a strong influence of carbonate on uranium solubility, since these data were similar to the ones obtained in carbonate-free systems. The maximum concentration of total carbon species that could be present in the WIPP brine is predicted to be 4×10^{-4} M [3]. With this concentration of bicarbonate-carbonate species in brines at pC_{H+} values between 8 and 10, our experimental data demonstrate that carbonate complexation will not have a significant impact on uranium concentration and uranium solubility will be 10^{-4} M or less.

Third region

Lastly, the third pC_{H+} region of interest was at $10 \leq pC_{H+}$. In that pC_{H+} region, the uranium concentrations were stable around 10^{-7}- 10^{-8} M, and similar to the values obtained in carbonate-free systems. In this pC_{H+} region, hydrolysis clearly overwhelmed any other possible effects on uranium solubility. It is important to note that under these experimental conditions, we did not see evidence for amphotericity of uranium (VI) in the long term experiments.

CONCLUSIONS

The solubility data presented herein were the first WIPP repository-relevant data for uranium (VI) in the presence of carbonate. The uranium (VI) solubility measured in our experiments did not exceed 10^{-4} M for all investigated conditions: $pC_{H+} \geq 7.5$ and the absence or presence of carbonate up to millimole levels (5 times more than the maximum concentration of carbon species predicted in WIPP PA [3]). This uranium solubility limit is an order of magnitude lower than the uranium solubility value currently used in the WIPP PA [3]. Therefore, the results of these experiments confirm the conservatism of the uranium solubility value currently used in the WIPP PA.

These data provided some information on the chemistry of uranium in WIPP-simulated brine in the presence of carbonate. Carbonate complexation can overwhelm borate effects in the pC_{H+} range [7.5 - 10]. Hydrolysis will overwhelm carbonate complexation at a higher pC_{H+}. The future direction of this work will be to define the uranium speciation under these experimental conditions, using numerical simulation.

ACKNOWLEDGMENTS

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