

Effect of Carbonate on U(VI) Solubility in WIPP Brine



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INTRODUCTION

Carbonate complexation is of major importance in uranium environmental chemistry [1]. The goal of our research was to experimentally determine the realistic contribution of carbonate complexation to the long-term solubility of U(VI) in the Waste Isolation Pilot Plant (WIPP).

The solubility of U(VI) in two WIPP simulated brines (GWB and ERDA-6) was investigated in long-term experiments (more than 330 days), as a function of pC_{H^+} (6-11) and in the presence of two carbonate concentrations (2×10^{-3} M and 2×10^{-4} M), using an over-saturation approach. Data are compared with similar experiments performed in carbonate-free brines [2]. These experimental results were modeled to give us a better understanding of the brine chemistry at high pC_{H^+} , and to try to establish the relative contribution of hydrolysis and carbonate complexation to U(VI) solubility as a function of pC_{H^+} in our high ionic strength brines.

pC_{H^+} MEASUREMENT in BRINES

The measurement of hydrogen ion concentration (pC_{H^+}) is made difficult by the high ionic strength and buffer capacity of brine components. The Gran-type titrations were used to establish a correction factor (K) for the specific pH electrode and brine according to the following general equation:

$$pC_{H^+} = pH_{obs.} + K$$

Brine	Correction factor, K
ERDA-6	0.94 ± 0.02
GWB	1.23 ± 0.01

Brine Composition

Component	ERDA-6		GWB	
	g/L	M	g/L	M
NaCl	248.6	4.254	167.8	2.874
MgCl ₂ ·6H ₂ O	3.667	0.018	193.4	0.953
Na ₂ SO ₄	22.52	0.159	23.61	0.166
NaBr	1.074	0.010	2.565	0.025
Na ₂ B ₄ O ₇ ·10H ₂ O	5.7	0.015	14.03	0.037
KCl	6.869	0.092	32.57	0.437
LiCl	-	-	0.174	0.004
CaCl ₂ ·2H ₂ O	1.672	0.011	1.896	0.013
Ionic strength (M)	4.965		6.839	
Density (g/mL)	1.183		1.216	

ERDA-6 - Energy Research and Development Administration Well 6 represents the fluids in Castile brine reservoirs
GWB - Generic Weep Brine represents brine from the Salado Formation

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EXPERIMENTAL APPROACH : OVER-SATURATION IN CARBONATE BRINES AS FUNCTION OF pC_{H^+}

Key Experimental Parameters

- Carbonate removed initially from brines by acidification of the brines and slow "pump-down" of the above atmosphere in a vacuum chamber.
- Anoxic nitrogen-controlled atmosphere.
- Adjusted pC_{H^+} between 6 and 11 with low carbonate NaOH.
- Addition of carbonate in solutions to desired concentration (2×10^{-3} M or 2×10^{-4} M).
- Initial addition of uranyl spiked brine: $[U] = 1.5 (\pm 0.3) \times 10^{-5}$ M.
- Temperature of 25 (± 3) °C.

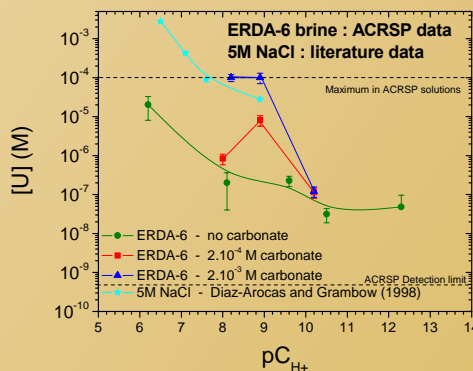
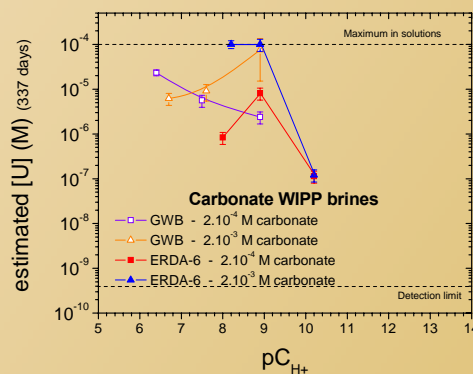
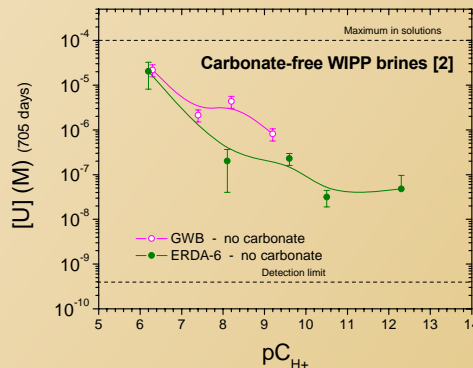
Over-saturation Experiments

- Uranium was added sequentially to the solutions until a concentration equilibrium was achieved and precipitation was observed.
- Second addition of uranyl spiked brine: $[U] = 1.0 (\pm 0.3) \times 10^{-4}$ M.
- Yellow precipitates were then observed in all solutions but in GWB at $pC_{H^+} = 6.7$ (no precipitate) and in ERDA-6 at $pC_{H^+} = 10.2$ (white precipitate).

Analytical Technique

- Total uranium concentrations determined by ICP-MS in filtered aliquots (30,000 Dalton).
- Detection limit is 5×10^{-10} M, due to the necessary dilution of the high salt-concentrated samples.
- A technique to measure low amount of carbonate ($\sim 10^{-5}$ M) in solution is under development in our laboratory.

Data for 337 days of the experiments are presented.



EXPERIMENTAL RESULTS

The measured solubility was approximately 10^{-5} M or less at all pC_{H^+} values in both brines when the total carbonate concentration was 2×10^{-4} M. This was similar to the solubility observed in carbonate-free brines [2], with the exception of ERDA-6 at $pC_{H^+} = 9$. In this case, the presence of carbonate increased the uranium concentration by nearly two orders of magnitude. At a total carbonate concentration of 2×10^{-3} M, the solubility was about 10^{-5} M in GWB at $pC_{H^+} \leq 8$; possibly higher than 10^{-4} M in ERDA-6 at $8 \leq pC_{H^+} \leq 9$ and in GWB at $pC_{H^+} \geq 8$. These uranium concentrations in the presence of carbonate were at least one order of magnitude higher than in the absence of carbonate at a fixed pC_{H^+} (data reported in our previous study [2]). This clearly demonstrates a carbonate complexation effect over hydrolysis. At $pC_{H^+} = 10.2$ in ERDA-6, the measured uranium concentrations in the presence of carbonate were similar (about 10^{-7} M) to the ones collected in the absence of carbonate [2]. This establishes the predominance of hydrolysis at that pC_{H^+} value. Our data were compared with the closest published work, performed in NaCl by Diaz Arocas and Grambow [4]. The presence of carbonate and the absence of compounds other than NaCl in their solutions may explain the difference in uranium solubilities.

MODELING

Modeling was performed using the Geochemist's Workbench program [3]. Precipitation, when experimentally observed, was confirmed by the calculations. The model predicts that the uranyl chemistry is dominated by the trimer $(UO_2)_3(OH)_7$ in carbonate-free brines. In the presence of 200 μ M carbonate, the major uranyl species in solution are expected to be $(UO_2)_2(CO_3)(OH)_5$ at the lower range of investigated pC_{H^+} , and $UO_2(CO_3)_3^{4-}$ at $pC_{H^+} > 7$. For higher carbonate concentration, the triscarbonato uranyl complex is responsible for the relatively high uranium concentration in solutions. The uranium profiles obtained by the experiments are close to the trends estimated by modeling, with the exception of GWB at $pC_{H^+} = 9$: the solubility calculations do not predict an increase of U solubility.

CONCLUSION

These data help establish the effect of carbonate on the solubility of uranyl in WIPP-specific brines. In all cases, except at high pC_{H^+} (≥ 10), the presence of carbonate increased the uranium solubility by forming mostly the triscarbonato uranyl complex. This was expected according to the literature [5], and the modeling performed with the Geochemist's Workbench program [3]. The uranium concentrations obtained in the experiments are still below current WIPP Performance Assessment solubility assumption of 10^{-3} M. At $pC_{H^+} \geq 10$, the uranium solubility dropped down to values close to 10^{-7} M; similar to the carbonate-free systems previously studied [2]. These experimental data are the first to determine the pC_{H^+} boundaries of the relative contribution of hydrolysis and carbonate complexation to U(VI) solubility in WIPP brines.