

Uranium (VI) Solubility from Over-saturation in Carbonate-free Brines

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INTRODUCTION

The environmental chemistry and the subsurface mobility of actinides are important considerations for a transuranic waste repository such as the Waste Isolation Pilot Plant (WIPP). The uranium (VI) solubility estimate used by WIPP Performance Assessment (PA) in the initial license application was $(8.8 \pm 0.1) \times 10^{-6} \text{ M}^{[1]}$. In the most recent WIPP PA recertification, this was increased to 10^{-3} M on the recommendation of the EPA to establish a conservative upper limit that accounts for the potential effects of carbonate complexation on uranium solubility. These values however have not been experimentally confirmed under the WIPP specific conditions (highly concentrated brines at $\text{pH} \leq 12$). At high pH, carbonate complexation is expected to compete with hydrolysis, leading to lower uranyl U(VI) solubility in the absence of an amphoteric effect^[2]. Determination of the relative importance of these two processes is the objective of our experimental program. This study was conducted with carbonate-free simulated WIPP brines to establish a baseline for the effect of carbonate on the solubility of the +VI oxidation state of actinides (including Pu) in the WIPP. Herein we present the results of uranium (VI) solubility experiments, performed using the over-saturation approach in two simulated WIPP brines, for 325 days, at $\text{pH}=6-12$ and in the absence of carbonate.

^[1] Hobart, D.E., Moore, R.C.: Analysis of Uranium (VI) Solubility Data for WIPP Performance Assessment. Unpublished report, May 28, 1996. Albuquerque, NM: Sandia National Laboratories. WPO 39856.

^[2] Clark, D.L., Hobart, D.E., Neu, M.P.: Actinide carbonate complexes and their importance in actinide environmental chemistry, Chemical Reviews 95, 25 (1995).

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

Key Experimental Parameters

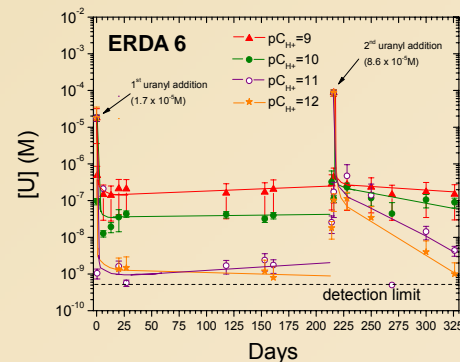
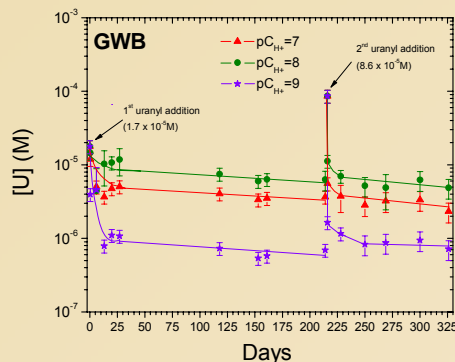
- Carbonate is removed initially from brines by acidification of the brines and slow "pump-down" of the atmosphere above in a vacuum chamber.
- Nitrogen-controlled atmosphere all the time (oxygen level < 10 ppm, insignificant carbon dioxide level).
- Adjusted pC_{H^+} between 6 and 12 with low carbonate NaOH.
- Temperature of 25 (± 2) °C.

Over-saturation Experiments

- Initial addition of uranyl spiked brine: $[\text{U}] = 1.7 (\pm 0.3) \times 10^{-5} \text{ M}$.
- Uranium is added sequentially in WIPP brine samples until a concentration equilibrium is achieved and precipitation is observed.
- Second addition of uranyl spiked brine: $[\text{U}] = 8.5 (\pm 0.3) \times 10^{-5} \text{ M}$.

Analytical Technique

- Total uranium concentrations determined by ICP-MS in filtered aliquots (30,000 Dalton).
- Detection limit for U is $5 \times 10^{-10} \text{ M}$, due to the necessary dilution of the high salt-concentrated samples.



TWO SIMULATED WIPP BRINES : ERDA-6 AND GWB

ERDA-6 brine is a multi-component sodium chloride-based brine at ionic strength = 5.0 M. GWB brine is a multi-component magnesium chloride-based brine at ionic strength = 6.8 M.

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	

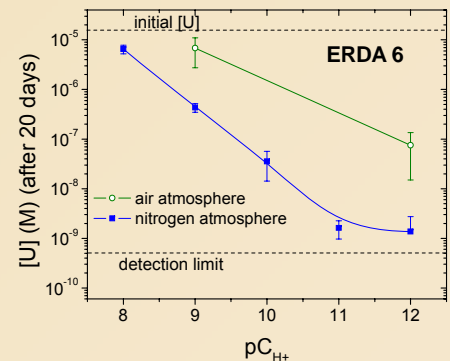
ERDA-6 - Energy Research and Development Administration Well 6 represents the fluids in Castle brine reservoirs
GWB - Generic Weep Brine represents brine from the Salado Formation

Significant effort was made to establish carbonate-free conditions.

DISCUSSION

- Steady state uranium concentrations are observed in all solutions. The U(VI) concentrations decrease to the apparent equilibria obtained before the second uranyl addition, and yellow precipitates (presumably a uranyl hydroxide phase) are observed in these solutions.
- Uranium (VI) solubility in carbonate-free ERDA-6 decreases when pC_{H^+} increases. This pH dependence was mostly a hydrolysis effect.
- Uranium (VI) does not exhibit amphoteric behavior under the conditions investigated. This is confirmed by the uranium concentration trends observed over time at pC_{H^+} values up to 12 in carbonate-free ERDA-6 brine.
- Our techniques to remove carbonate from the solutions and to maintain a CO₂-free environment are satisfactory. The uranium solubility data measured in our ERDA-6 experiments at $\text{pC}_{\text{H}^+}=9$ are lower by two orders of magnitude than the most similar published work, performed by Diaz Arocas and Grambow^[3].
- Carbonate complexation in ERDA-6 at pC_{H^+} greater than 9 increases uranium (VI) solubility by two orders of magnitude. Some identical experiments were performed with less stringent CO₂ controls in sealed vessels kept in room air, leading to CO₂ uptake during sampling. The uranium concentrations obtained were two orders of magnitude higher than in our nitrogen-controlled atmosphere and comparable with Diaz and Grambow's data^[3].

^[3] Diaz Arocas, P., Grambow, B.: Solid-liquid Phase Equilibria of U(VI) in NaCl Solutions, Geochimica et Cosmochimica Acta 62/2, 245 (1998).



CONCLUSIONS

- Based on this work, the uranium (VI) solubility is about 10^{-6} - 10^{-9} M in carbonate-free GWB at $\text{pC}_{\text{H}^+} \geq 7$, and below 10^{-6} M in carbonate-free ERDA-6 at $\text{pC}_{\text{H}^+} \geq 9$. These are lower than current PA assumptions.
- These data on solubility of uranium (VI) in WIPP brines are the first at high pC_{H^+} , under what we believe to be a truly carbonate-free system. They establish a uranium solubility, in the absence of carbonate, that is 10-100 times lower than published results.
- These estimated values define a "baseline" carbonate-free uranium solubility that will be used to evaluate the effect of carbonate on uranium (VI) solubility in future studies.

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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 (shown here in GWB) were used to establish a correction factor (K) for the specific pH electrode and brine according to the following general equation:

$$\text{pC}_{\text{H}^+} = \text{pH}_{\text{reading}} + K$$

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

