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Solubility of Uranium (VI) in Brine

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ABSTRACT

Uranium (VI) solubility in very low carbonate WIPP brines under an air or nitrogen atmosphere at different high basic pH's was investigated from an over-saturation approach.

Preliminary data, based on 27-day experiments, are presented. Carbonate was removed from the solutions, and a carbon dioxide free environment was maintained in the nitrogen atmosphere samples. The initial uranium concentration in GWB and ERDA-6 brine was 1.7×10^{-5} M.

Uranium concentrations in the solutions investigated have not yet reached equilibrium. Uranium (VI) solubility was higher in GWB (high magnesium brine) than in ERDA-6 (low magnesium brine).

Uranium concentration used in GWB brine did not reach saturation, except for pcH 9. In ERDA-6 brine, uranium solubility decreased when pcH increased because of hydrolysis. At pcH greater than 9, uranium was likely to co-precipitate with magnesium hydroxide, and form insoluble uranyl precipitates at pcH 12. Uranium solubility at pcH 11 and 12 was four orders of magnitude less than the initial uranium concentration.

The absence of carbonate lowered uranium (VI) solubility by two orders of magnitude in ERDA-6 at pcH greater than 9. These data on solubility of uranium (VI) in brines are the first at high pcH under what we believe to be a truly CO_2-free atmosphere.

EXPERIMENTAL APPROACH : OVER-SATURATION IN CARBONATE FREE BRINES AS FUNCTION OF pcH

Key Experimental Parameters

- Carbonate removed initially from brines by acidification of the brines and slow "pump-down" of the above atmosphere in vacuum chamber.
- Air or nitrogen-controlled atmosphere.
- Adjusted pcH between 6 and 12 with low carbonate NaOH.
- Temperature of 23 (±2) °C.

Over-saturation Experiments

- Initial addition of uranyl spiked brine: [U] = 1.7 (± 0.3) × 10^{-5} M
- Uranium will be added sequentially in WIPP brine samples until a concentration equilibrium is achieved and precipitation is observed.

Analytical Techniques

- 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.

Data for the first 27 days of the experiments are presented.

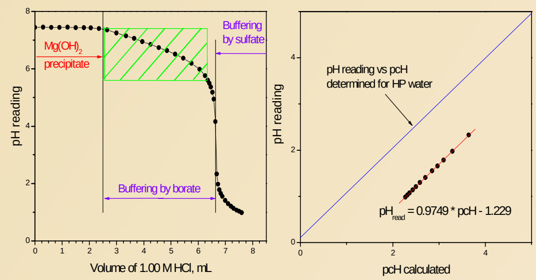
pcH MEASUREMENT in BRINES

The measurement of hydrogen ion concentration (pcH) 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:

$$pcH = pH_{obs.} + K$$

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

Acid Titration of GWB Brine
(with NaOH addition)

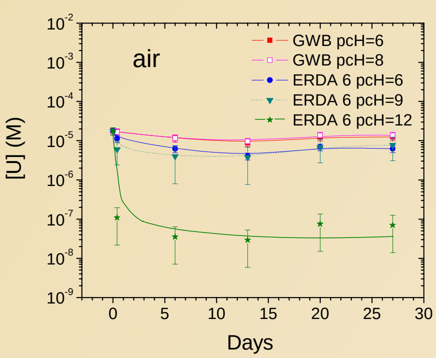


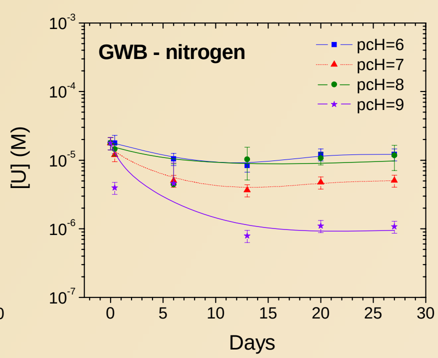
Brine Composition				
	ERDA-6		GWB	
Component	g/L	M	g/L	M
NaCl	248.6	4.254	167.8	2.874
$MgCl_2.6H_2O$	3.667	0.018	193.4	0.953
Na_2SO_4	22.52	0.159	23.61	0.166
NaBr	1.074	0.010	2.565	0.025
$Na_2B_4O_7.10H_2O$	5.7	0.015	14.03	0.037
KCl	6.869	0.092	32.57	0.437
LiCl	-	-	0.174	0.004
$CaCl_2.2H_2O$	1.672	0.011	1.896	0.013
Ionic strength (M)	4.965		6.839	
Density (g/mL)	1.183		1.216	

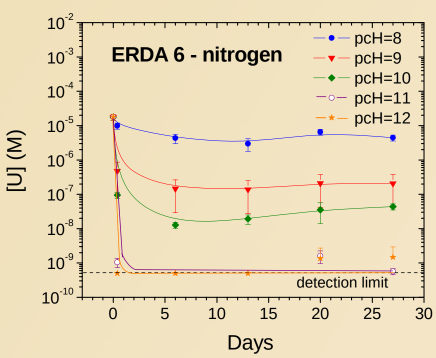
ERDA-6 - Energy Research and Development Administration Well 6 represents the fluids in Castile brine reservoirs
GWB - Generic Weep Brine represents brine from the Salado Formation

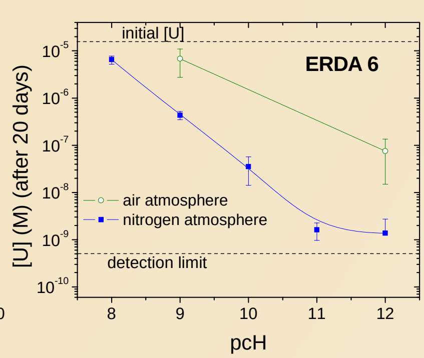
EXPERIMENTS IN GWB

- In an air atmosphere, data points at pcH 6 and 8 overlapped, and were very close to the initial uranium concentration. The same result was observed in a nitrogen-controlled atmosphere at pcH 6, 7 and 8. This means that uranium (VI) solubility is likely higher than 1.7×10^{-5} M at these conditions. Further uranium additions will confirm this statement.
- In the nitrogen-controlled atmosphere at pcH 9, the solubility of uranium (VI) decreased, due to hydrolysis, to a uranium concentration (at 13 days) that was about one order of magnitude lower than the initial uranium concentration.









EXPERIMENTS IN ERDA-6

In air atmosphere:

- At pcH 6 and 9, there was no difference with initial uranium concentration. Uranium solubility in air atmosphere is higher than 1.7×10^{-5} M.
- At pcH 12, uranium concentration was two orders of magnitude lower than what was initially present. Hydrolysis lowered uranium solubility.

In nitrogen-controlled atmosphere:

- Solubility of uranium (VI) was lower when pcH increased, because of hydrolysis effects.
- Precipitation of magnesium hydroxide occurred irreversibly at pcH above 10.4 in ERDA-6 due to instability in the simulated brine formulation. There is experimental concern that uranium may have co-precipitated under these conditions to artificially lower the uranium concentrations measured. Future work with a "high-pH" brine formulation is planned to avoid this experimental complexity.
- At pcH 12, a yellow precipitate was observed. We believe this to be a uranyl precipitate based on past observations.
- Data comparison between air and nitrogen-controlled atmosphere shows the impact of carbonate complexation. Uranium concentrations at any fixed pcH were lower in a CO_2-free atmosphere than in a non-controlled atmosphere.
- These experiments demonstrate an efficient method to remove CO_2 from brine solutions, and a good control of CO_2-free environment in brine samples.

CONCLUSIONS

Our techniques to remove carbonate from the solutions and to maintain a CO_2-free environment are satisfactory.

- At the same pcH, Uranium (VI) solubility is slightly higher in GWB (high magnesium brine) than in ERDA-6 (low magnesium brine).
- In carbon-dioxide free atmosphere, uranium (VI) solubility in ERDA-6 decreases when pcH increases due to hydrolysis. At pcH above 10, uranium may also co-precipitate with magnesium hydroxide. At pcH 12, a yellow precipitate is observed (uranyl phase ?).
- Carbonate complexation in ERDA-6 at pcH greater than 9 increases uranium (VI) solubility by two orders of magnitude.

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