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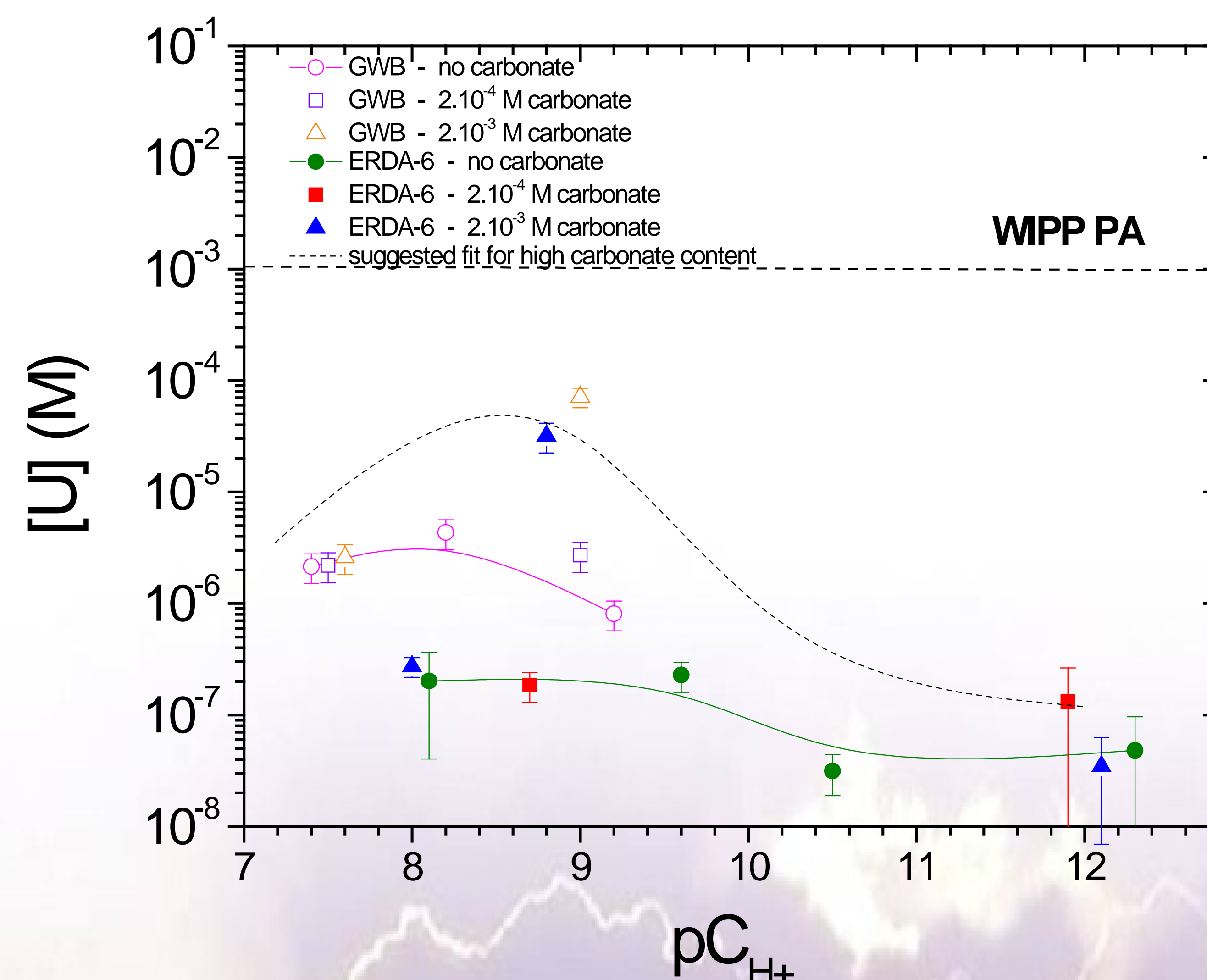
Introduction

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 were reported in earlier publications [2, 3]. They are summarized herein.

Composition and ionic strength of ERDA-6 and GWB, two simulated WIPP brines (95% 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 ₂ SO ₄	0.159	0.166
NaBr	0.010	0.025
Na ₂ B ₄ O 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

In high ionic strength: $pC_{H^+} = pH_{measured} + K$



Uranium concentration 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 ($2 \cdot 10^{-4}$ M and $2 \cdot 10^{-3}$ M) at the beginning of the experiments [3].

Description of the work

The general experimental approach was to investigate uranium (VI) solubility from over-saturation in the two simulated WIPP brines, GWB and ERDA-6 (95% of initial formulations). Carbonate was first removed from the brines using a two-step process: acidification of the brines, and a slow pump-down process to smoothly remove CO₂ gas from the brines. The hydrogen ion concentration of the brines was then adjusted with low-carbonate sodium hydroxide (50 weight%). The level of carbonate in the experiments was established by the addition of a small volume of an appropriate intermediate carbonate solution to achieve the desired initial concentration of carbonate in solution: $2 \cdot 10^{-4}$ M or $2 \cdot 10^{-3}$ M. The experiments were initiated by the addition of uranyl-spiked brine into the pC_{H^+} -adjusted brine solutions containing no carbonate or a known amount of carbonate. Aliquots were periodically removed, centrifuged and filtered through Microcon® Millipore centrifugal filters (30,000 Daltons). Filtrates were analyzed for uranium content using an inductively-coupled plasma mass spectrometer (ICP-MS).

Results

In the absence of carbonate, the measured U(VI) solubilities were about 10^{-6} M in GWB brine at $pC_{H^+} \geq 7.5$ and about 10^{-8} - 10^{-7} M in ERDA-6 at $pC_{H^+} \geq 8$. These results put an upper bound of $\sim 10^{-5}$ M for the solubility of uranyl in the carbonate-free WIPP brines for the investigated range of experimental conditions. At the expected pC_{H^+} in the WIPP (~ 9.4), the measured uranium solubility was between 10^{-7} M and 10^{-6} M.

In the presence of carbonate, the highest uranium solubility obtained experimentally was $\sim 10^{-4}$ M, under WIPP-related conditions ($pC_{H^+} \sim 9$). This is an order of magnitude lower than the uranium (VI) solubility currently assumed by WIPP PA and mandated by the EPA. This high uranium solubility value was obtained at the highest carbonate concentration ($2 \cdot 10^{-3}$ M) investigated which is ~ 10 times higher than the carbonate concentration predicted by WIPP PA.

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Conclusion

The 1 mM value for uranium (VI) solubility used in WIPP PA is confirmed to be conservative, by over a factor of 50, relative to the experimental results. These experimental data clearly support the current position on An(VI) solubility under WIPP-relevant conditions. In the broader consideration of a high level waste repository, uranium chemistry has a bigger importance. Consequently, these experimental data could support the disposal of radioactive waste present in a uranium dioxide-like matrix in underground saline formations similar to the Salado and Castile formations.

References

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