EXPERIMENTAL APPROACH : OVER-SATURATION IN CARBONATE 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 a vacuum chamber.
- Anoxic nitrogen-controlled atmosphere.
- Adjusted pCH+ 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 (± 0.3)×10^{-3} M
- Temperature of 25 (±3)°C.

Data for 337 days of the experiments are presented.

EXPERIMENTAL RESULTS

The measured solubility was approximately 10^{-3} M or less at all pCH+ 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 pCH+ ≤ 5. 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^{-4} M, the solubility was about 10^{-3} M in GWB at pCH+ ≤ 5; possibly higher than 10^{-3} M in ERDA-6 at 5 ≤ pCH+ ≤ 6 and in GWB at 6 ≤ pCH+ ≥ 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 pCH+ (data reported in our previous study [2]). This clearly demonstrates a carbonate complexation effect over hydrolysis. At pCH+ = 10.2 in ERDA-6, the measured uranium concentrations in the presence of carbonate were similar (about 10^{-3} M) to the ones collected in the absence of carbonate [2]. This establishes the predominance of hydrolysis at that pCH+ 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 predicted that the uranyl complex was mostly precipitated at low pCH+ (<4) while 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 uranyl concentrations obtained in the experiments are still below current WIPP Performance Assessment solubility assumption of 10^{-3} M. At pCH+ = 10, the uranium solubility dropped down to values close to 10^{-3} M, similar to the carbonate-free systems previously studied [2]. These experimental data are the first to determine the pCH+ boundaries of the relative contribution of hydrolysis and carbonate complexation to U(VI) solubility in WIPP brines.