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Solubility of Nd^{3+} and UO_2^{2+} in WIPP brine as oxidation-state invariant analogs for plutonium

Jean-Francois Lucchini^a, Marian Borkowski^{a,*}, Michael K. Richmann^a,
 Sally Ballard^b, Donald T. Reed^a

^a Los Alamos National Laboratory, Earth and Environmental Sciences Division, Carlsbad, NM 88220, USA

^b Carlsbad Environmental Monitoring and Research Center, New Mexico State University,
 Carlsbad, NM 88220, USA

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Abstract

A general status of the Waste Isolation Pilot Plant (WIPP), as it relates to plutonium chemistry and inventory, is given. We also report on the results of two redox-invariant studies, Nd^{3+} and UO_2^{2+} , that are being investigated as analogs for Pu(III) and Pu(VI) chemistry under WIPP-relevant conditions. The WIPP repository is the only working repository for TRU waste in the world and continues to perform above expectations. Recertification of the WIPP was recently received in April 2006 and plutonium research to support these ongoing recertification activities continues.

As oxidation-state analogs for plutonium, the solubility of uranium(VI) and neodymium(III) were established in long-term experiments as a function of pC_{H^+} for two WIPP simulated brines that bracket the range in brine composition expected. The solubility of uranium(VI) measured at high pC_{H^+} in the absence of carbonate was $\sim 2 \times 10^{-7}$ M in ERDA-6 brine. This is almost 100 times lower than the uranium solubility published in the literature for carbon dioxide-free systems and is almost four orders of magnitude lower than current assumptions in the WIPP Performance Assessment (PA). The Nd^{3+} solubility determined was $\sim 1 \times 10^{-7}$ M. There was essentially no significant effect of carbonate on the solubility measured for Nd^{3+} . Taking into consideration experimental errors in our data, the neodymium solubilities determined in the present work are in good agreement with the solubilities calculated by WIPP PA.

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1. Introduction and WIPP project update

The solubility of plutonium in groundwater defines its mobility and migration when it is present as a contaminant in the subsurface. This solubility, and correspondingly the speciation of plutonium, is complex and intricately linked to its redox chemistry; oxidation-state specific complexation and sorptive interactions; and microbial interactions. In our research, which is performed in support of the recertification activities of the Waste Isolation Pilot Plant (WIPP), the strategy is to establish the overall solubility of plutonium by a combination of oxidation-invariant analog studies with plutonium solubility studies—where redox reactions can occur.

Herein we report on the overall status/progress of the WIPP transuranic (TRU) repository from the perspective of plutonium chemistry and provide initial data on two oxidation-state plutonium analog studies: U(VI) and Nd(III) for Pu(VI) and Pu(III). The solubility of uranium(VI) in two simulated WIPP brines was determined and evaluated as an analog for Pu(VI). These uranium results apply most directly to the solubility of uranium in the WIPP, which is an actinide of concern in its own right, since Pu(VI) is only expected as a transient oxidation-state for plutonium given the reducing conditions expected. The solubility of neodymium(III), which is a redox-invariant analog for americium(III) and plutonium(III), was also determined to extend past work to a higher pH range and to the more complex simulated, rather than simplified, WIPP brines. Plutonium(III), under the conditions expected in the WIPP, is predicted by current WIPP model, but its role and importance in the WIPP has not been experimentally proven. These WIPP-relevant data are used in the

* Corresponding author. Tel.: +1 5052345554; fax: +1 5058873051.

E-mail address: marian@lanl.gov (M. Borkowski).

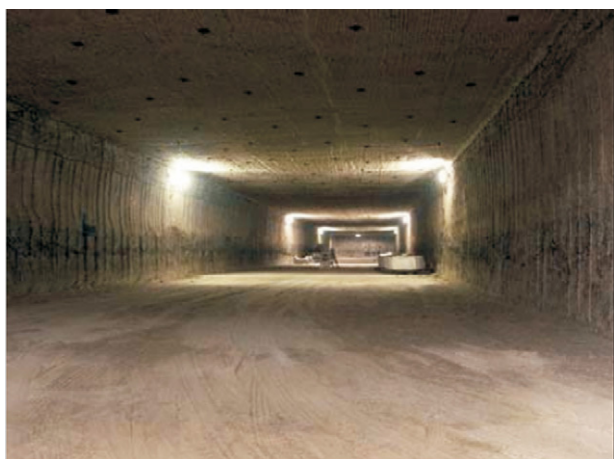


Fig. 1. View of an excavated disposal room in the WIPP underground. These are approximately 4 m high, 10 m wide and 100 m long.

recertification effort to support and assess current assumptions in WIPP performance assessment models.

1.1. Overall status of the WIPP repository

The Waste Isolation Pilot Plant (WIPP), which is located 26 miles east of Carlsbad in Southeastern New Mexico, has been in operation for almost 7 years and remains a cornerstone of the U.S. Department of Energy's (DOE) nuclear waste management effort. Its purpose is to permanently dispose of defense-generated transuranic waste that is a by-product of the many past nuclear weapons activities. This TRU waste is currently stored at various DOE sites and plutonium is almost always the key component of concern.

Waste disposal operations began at the WIPP on 26 March 1999 after approvals by the Environmental Protection Agency (EPA) and the New Mexico Environment Department (NMED). A requirement of the WIPP license is that the WIPP needs to be recertified every 5 years for its TRU disposal operations. The first recertification of the WIPP was received in April 2006. Currently, efforts are underway to prepare for the second WIPP recertification that is due in March 2009. This recertification effort includes confirmatory actinide solubility studies that are being conducted by the Los Alamos Actinide Chemistry and Repository Science Program (ACRSP) team at the Carlsbad Environmental Monitoring and Research Center operated by New Mexico State University. ACRSP is part of a larger multidisciplinary Los Alamos National Laboratory group working in Carlsbad, NM, to provide laboratory research and program support on actinide-related issues to the DOE Carlsbad Field Office (DOE CBFO) to maintain the certification of the WIPP.

The WIPP repository itself is organized into five large panels that are comprised of seven disposal rooms in each panel. An excavated disposal room is shown in Fig. 1. These panels and disposal rooms are located in Salado salt formation at an average depth of 650 m. Currently the first two panels are completely filled with TRU waste and the disposal of waste in the third panel is underway. In all, over 5000 TRU waste shipments have been processed by the WIPP resulting in the emplacement of

Table 1

Total amount (in kg) of key waste package components and actinides present in WIPP Panels 1 and 2 [1]

Radionuclides	Amount (kg)	Materials	Amount (kg)
Panel 1			
Am-241	34.6	Iron based metal alloys	3,327,871
Pu	2,571	Aluminum base metal alloys	5,459
Pu-239	2,416	Other metal alloys	46,793
U	22,232	MgO	4,482,355
U-238	22,170	Cellulosics	706,141
Np-237	0.6	Plastic	522,688
Panel 2			
Am-241	9.2	Iron based metal alloys	4,922,035
Pu	1,405	Aluminum base metal alloys	17,730
Pu-239	1,306	Other metal alloys	121,526
U	6,850	MgO	6,667,625
U-238	6,808	Cellulosics	477,213
Np-237	1.2	Plastic	876,399

82,575 waste containers and a total waste volume of 41,877 m³ [1].

1.2. Plutonium in TRU waste

Transuranic waste placed in the WIPP consists mainly of clothing, tools, rags, debris and other disposable items that are radioactively contaminated. This is truly waste that has no commercial or marketable value. From an actinide perspective, TRU waste must contain more than 100 nCi of transuranic elements (e.g., Pu, Np and Am) per gram of waste [2]. The actual actinide inventory, along with key waste components, that was emplaced in the two completed panels is given in Table 1. From the perspective of mass, uranium is by far the most prevalent actinide (~83% by mass) and plutonium is the most prevalent TRU component (most of which is Pu-239). From the perspective of Ci content, both plutonium and americium are approximately equal and are together by far, the most important contributors to the potential actinide release calculations. The overall ranking of actinides, from the perspective of potential contribution to release from the WIPP, is: Pu ~ Am > U ≫ Th and Np.

There are a number of acceptable ways to package TRU waste. An example of actually emplaced waste is shown in Fig. 2 that is comprised of bundled 55 gallon drums that are stacked three-high. A magnesium oxide overpack is placed above these bundled drums as an engineered barrier to control and buffer the pH (~8.5–9.0) and sequester carbon dioxide that may be generated due to microbial degradation of the emplaced organic waste. In both cases the overall purpose of the engineered barrier is to maintain an environment that promotes low actinide solubility.

The performance assessment calculations for the potential release of plutonium from the WIPP repository show that the release of plutonium to the accessible environment is highly unlikely. This assessment is based on the following key assumptions:

- Higher-valent plutonium, specifically PuO₂⁺ and PuO₂²⁺ species, do not contribute to the overall solubility of pluto-



Fig. 2. Actual TRU waste disposed in 55 gallon drum bundles stacked three-high. The MgO sacks are seen placed on top of each TRU waste bundle set.

nium in the WIPP. Although it is recognized that localized oxidizing zones may exist, these are overwhelmed by the highly reducing environment established by the waste components (e.g., Fe and Pb) and anticipated microbiology (e.g. sulfate reduction and methanogenesis).

- The expected plutonium solubility is comprised of Pu^{3+} species in half the PA vectors and Pu^{4+} in the other half. This is a conservative assumption that reflects the possible formation of $\text{Pu}(\text{III})$, which is ~ 10 times more soluble than $\text{Pu}(\text{IV})$, in the expected redox environment.
- The PA calculated oxidation-state solubility of plutonium is [3]:
 - Pu^{3+} : 1.7×10^{-7} M to 3.1×10^{-7} M depending on brine composition.
 - Pu^{4+} : 5.8×10^{-9} M to 2.5×10^{-8} M depending on brine composition.

In this context, the Nd^{3+} analog provides key data on the most soluble form of plutonium that is considered by WIPP PA. Conversely, the UO_2^{2+} solubility data are a contingency to the current speciation assumptions since PuO_2^{2+} is not expected to be present in significant amounts in the expected WIPP environment.

2. Experimental approach

2.1. WIPP simulated brines

Two simulated WIPP brines were used in our studies. These brines were based on a high magnesium Generic Weep Brine that is designated as GWB, and a low magnesium Energy Research and Development Administration Well 6 brine that is designated as ERDA-6. The composition (95% formulation) and key properties of these simulated brines are given in Table 2. Reagent grade chemicals (all from Fisher except sodium tetraborate from Acros Organics, all >99% purity) were used to make these brines with no additional purification.

Significant care was taken to remove carbonate from the brines for the carbon dioxide-free experiments performed. The brine solution was acidified to $\text{pC}_{\text{H}^+} \sim 3\text{--}4$ and bubbled with high-purity nitrogen to remove residual air. This de-aerated brine was placed in a pump-down box to evacuate/remove all dissolved gas and subsequently transferred to a nitrogen glovebox with an anoxic carbon dioxide-free atmosphere that was controlled for the duration of the exper-

Table 2

Composition and key properties of GWB and ERDA-6 simulated WIPP brines (95% formulation)

Component	GWB brine		ERDA-6 brine	
	g/L	M	g/L	M
NaCl	167.8	2.874	248.6	4.254
MgCl ₂	193.4	0.953	3.667	0.018
Na ₂ SO ₄	23.61	0.166	22.52	0.159
NaBr	2.565	0.025	1.074	0.010
Na ₂ B ₄ O ₇	14.03	0.037	5.70	0.015
KCl	32.57	0.437	6.869	0.092
LiCl	0.174	0.004	–	–
CaCl ₂	1.896	0.013	1.672	0.011
Ionic strength		6.839		4.965
Density (g/mL)	1.216		1.183	

iment. The desired pC_{H^+} was established in each solution by the addition of carbon dioxide-free sodium hydroxide. A carbon dioxide-free neodymium or uranyl stock solution was added to the carbon dioxide-free brine as a spike to initiate the over-saturation solubility experiments. For the neodymium experiments, the corresponding under-saturation experiments were initiated by adding a commercially available hydroxide (Alfa Aesar, 99% purity) to the brine system. The effect of carbonate was also investigated in these systems. Carbonate was added to the carbon dioxide-free brines as a dissolved carbonate spike rather than through equilibration with a carbon dioxide partial pressure. Experiments were maintained in gas-tight polypropylene bottles to prevent loss of carbon dioxide due to out-gassing.

In these high ionic-strength brine systems, the hydrogen ion concentration cannot be directly measured. For this reason, Gran-type titrations [4] were performed in all the brines investigated to calculate a correction factor (K) for the Ross-type pH electrodes (Orion glass combination, model 8103) used according to the following:

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

where, pC_{H^+} denotes the negative logarithm of the hydrogen ion concentration, pH_{read} the actual pH indicated by the in-calibration pH electrode and K is the ionic strength correction factor. For the two simulated brines we used, the correction factors were 1.23 ± 0.01 and 0.94 ± 0.02 for GWB and ERDA-6 respectively.

2.2. Neodymium +3 experiments

The solubility of $\text{Nd}(\text{III})$, as an oxidation-state invariant analog for Pu^{3+} and Am^{3+} , was determined as a function of pC_{H^+} and carbonate concentration in GWB and ERDA-6 simulated WIPP brines using both an over-saturation and an under-saturation approach. The general conditions of these studies were:

- pC_{H^+} between 6.5 and 10.5.
- Carbon dioxide-free to 0.01 M carbonate concentrations.
- Temperature of 25 ± 3 °C.

A stock solution of 10^{-2} M neodymium at $\text{pH} \sim 4$ (in hydrochloric acid) was used as the spike in the over-saturation approach. The initial neodymium concentration in the brine, after the first addition, was 5×10^{-5} M. In the under-saturation experiments, commercially available neodymium hydroxide was used as the solid phase in the carbon dioxide-free experiments and contacted with simulated brine under controlled conditions until a steady state concentration is achieved. All carbonate free experiments were carried out in a nitrogen glove box, and the nitrogen atmosphere was monitored throughout the experiment. The effect of carbonate was determined at four carbonate concentrations: 10^{-2} , 10^{-3} , 10^{-4} and 10^{-5} M. The corresponding under-saturation experiments were performed using a mixed hydroxy carbonate (NdCO_3OH), prepared in our laboratory, as the solid phase.

In each experiment, pC_{H^+} was adjusted to the desired value, neodymium was added and the solution was equilibrated for over 200 days. The total neodymium concentrations were determined by ICP-MS (Elan 6000) before and after filtration with 30,000 Da cut-off centrifuge filters (Millipore Microcon).

2.3. Uranium +6 experiments

The uranium(VI) solubility experiments were performed using an analogous approach to the neodymium over-saturation experiments just described. Experiments in GWB and ERDA-6 brines were conducted for 250 days, at $pC_{H^+} = 7-12$, a temperature of $25 \pm 3^\circ\text{C}$, and in the absence of carbonate in an anoxic carbon dioxide-free glovebox (MBraun Labmaster 130 with an oxygen purification system). A uranyl brine stock solution was added to each pC_{H^+} -adjusted brine experiment to establish an initial uranyl concentration of 1.7×10^{-5} M. The solutions were periodically sampled, filtered using centrifuge filters (30,000 Da cut-off), and analyzed for uranium content by ICP-MS. Once steady-state uranium concentrations were observed, a second addition of uranyl-spiked brine (8.6×10^{-5} M) was performed into the pC_{H^+} -adjusted brines at day 215. It was verified that the pC_{H^+} of the brine experiments did not change during the 250 days of the experiment.

3. Results and discussion

The solubility and speciation of multivalent actinides, especially plutonium, are often investigated by oxidation-state analogy, which states that lanthanides and actinides that are in the same oxidation-states have similar chemical behavior. Redox-invariant analogs can considerably simplify experimental design and consequently improve reliability of experimental data.

3.1. Solubility of uranium +6

The concentration of uranium as a function of time is shown in Fig. 3 for carbon dioxide-free GWB brine and in Fig. 4 for carbon dioxide-free ERDA-6 brine. These data show that steady state uranium concentrations are rapidly achieved (less than 20 days) in both brines. These concentrations were re-confirmed by the second uranium addition although slower kinetics were

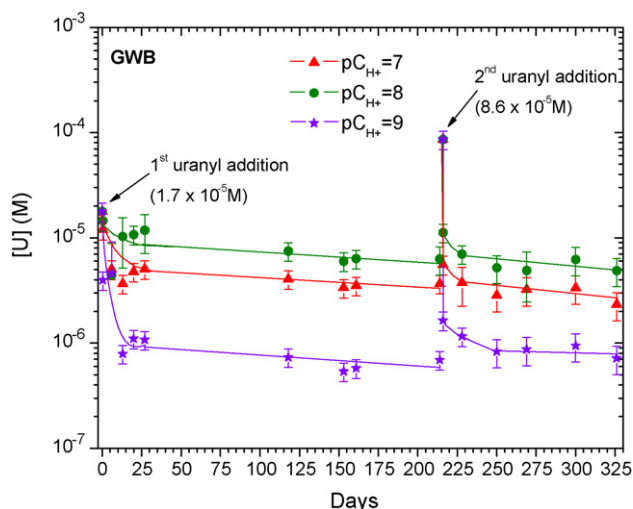


Fig. 3. Concentration of uranium(VI) in GWB brine as a function of time. *The effective detection limit of uranium in brine with our sampling protocols is 5×10^{-10} M.

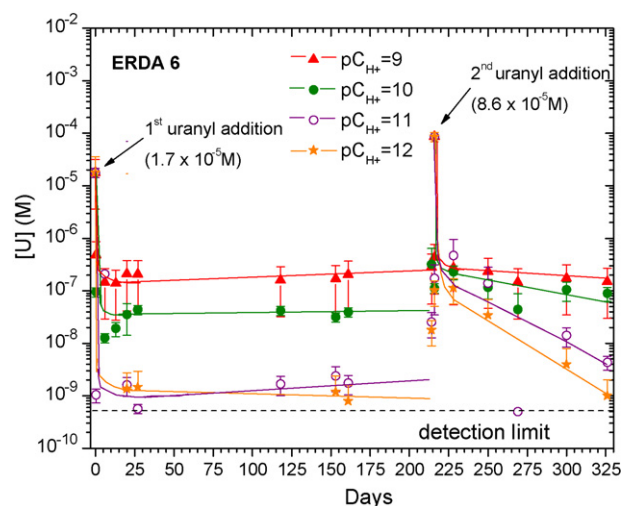


Fig. 4. Concentration of uranium(VI) in ERDA-6 brine as a function of time. *The effective detection limit of uranium in brine with our sampling protocols is 5×10^{-10} M.

observed at the higher pH. Yellow precipitates (presumably a uranyl hydroxide phase) were observed in all brine systems after the second addition. Based on these results, the uranium(VI) solubility in carbon dioxide-free brines at high pC_{H^+} is about 10^{-6} to 10^{-5} M in GWB brine and below 10^{-6} M in ERDA-6 at $pC_{H^+} \geq 9$. At the same pC_{H^+} , the solubility of uranium is slightly higher in GWB than in ERDA-6, which we attribute to differences in the ionic strength and complexant concentrations (Table 1).

The solubility of U(VI) in these carbon dioxide-free systems clearly depends on the pC_{H^+} . Uranium(VI) solubility was consistently lower when pC_{H^+} was increased, presumably due to increased complexation with hydroxide and subsequent precipitation of uranyl-hydroxide phases. The uranium concentration trends observed over time at pC_{H^+} values up to 12 in carbon dioxide-free ERDA-6 brine indicate that uranium(VI) does not exhibit amphoteric behavior under the conditions we investigated. Work is ongoing to characterize the solids formed in our experiments although XANES analysis performed at the Argonne Advanced Photon Source confirmed that we are not getting measurable reduction in these systems.

Analogous experiments were performed with less stringent CO_2 controls in sealed vessels kept in room air rather than a carbon dioxide-free glovebox. Under these conditions a small uptake of CO_2 was possible during the time of sampling when the experiment container was open for a short time. This small change in protocol led to uranium concentrations that were up to two orders of magnitude higher than in our nitrogen-controlled atmosphere experiments, and were comparable to those reported by Diaz and Grambow [5] who reported a uranium solubility of $(2.8 \pm 1.8) \times 10^{-5}$ M at $pC_{H^+} = 8.9$ in 5 M sodium chloride with a similar experimental approach using only argon bubbling to remove carbonate. In contrast to this, the solubility of uranium in our carbon dioxide-free ERDA-6 brine was $(2.0 \pm 1.7) \times 10^{-7}$ M. We believe that the lower uranium concentrations we report reflects the better efficiency we had in removing carbonate from the brine solutions at the beginning of

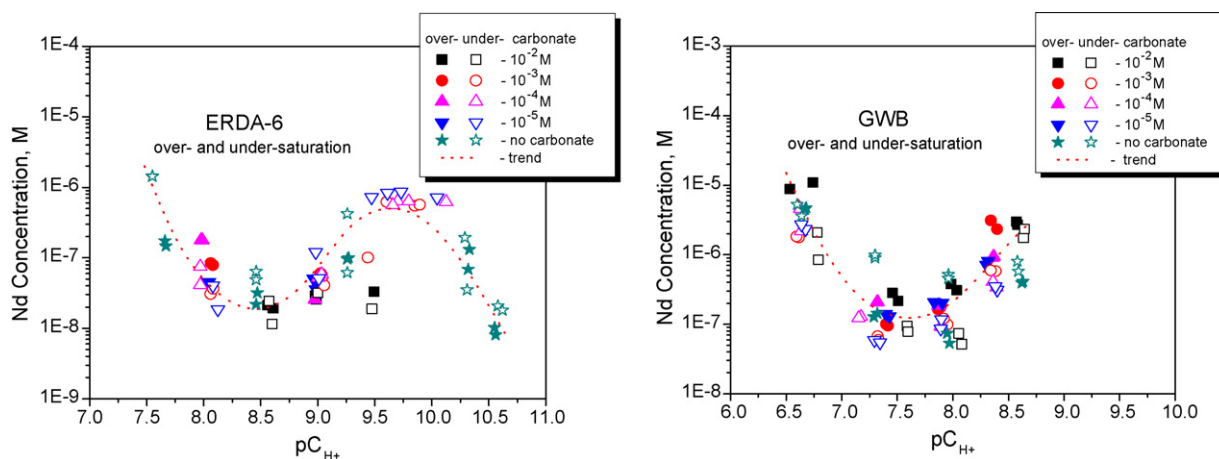


Fig. 5. Solubility of neodymium in ERDA-6 and GWB brines as a function of pC_{H^+} and carbonate concentration.

the experiments, as well as better controls to maintain a carbon dioxide-free environment throughout our experiments.

The impact of these results on WIPP performance assessment of the potential for plutonium release, as mentioned earlier, is not straightforward since Pu(VI) species are not predicted to be prevalent in the WIPP. That Pu(VI) can be reduced by Fe(II) and Fe(0) under WIPP relevant conditions was established [6,7]. Additionally, it is not clear that U(VI) is a good analog for Pu(VI), regardless of the importance of Pu(VI) in WIPP PA, due to significant difference in hydrolytic tendencies and the tendency of Pu(VI) to persist as a metastable species in brine systems. Nevertheless, our data show that U(VI) is less soluble in WIPP brine than previously thought and for the reference case WIPP scenario, the anticipated solubility of U(VI) is below 10^{-5} M, which is considerably less than the current PA assumption of 10^{-3} M that was mandated by the EPA.

3.2. Solubility of neodymium +3

The key factors that define the long-term solubility of Nd(III) in the WIPP are pH and complexation by anions. The contribution of carbonate complexation to the solubility of Nd(III) has already been investigated by others in low ionic strength solutions [8–15]. The goal of our study was to extend these results to higher ionic strength brines to determine the realistic effect of hydrolysis and carbonate complexation on Nd(III) solubility as a function of pH in simulated ERDA-6 and GWB brines. The results of our experiments are presented in Fig. 5.

The solubility of neodymium measured as a function of pC_{H^+} in GWB and ERDA-6 brines for all carbonate concentrations used, reproduces to a good approximation the dependencies found in the carbonate free experiments. Based on thermodynamic data, Nd(OH)₃ should be the equilibrium solid phase in this system. At $pC_{H^+} \sim 8.5$, which is the reference case for the WIPP, the Nd(III) solubility in ERDA-6 (the low magnesium brine) was almost one order of magnitude lower than in GWB (high magnesium brine). The shoulder observed for ERDA-6 brine with a maximum at $pC_{H^+} = 9.6$, is best understood as the formation of a neodymium complex with brine components and not an effect of carbonate complexation since it is not sig-

nificantly affected by increasing carbonate levels. The An(III) solubilities calculated for GWB and ERDA-6 brines using the Pitzer model [3] at $pC_{H^+} \sim 8.5$ are 3×10^{-7} and 1.7×10^{-7} M, respectively. The neodymium solubility measured was slightly greater in GWB brine and slightly lower in ERDA-6 brine. Taking into consideration experimental errors, however, the neodymium solubilities determined in the present work are in good agreement with the calculated values for both brines.

Lanthanide analogs such as Nd³⁺ possess physical and chemical characteristics that allow them to be used to examine the chemical behavior of trivalent actinides. Complex formation for most ligands with f-elements is due to the electrostatic attraction between the metal and the electron donating functionality of the ligand molecule. Due to the similarity of ionic radii (for coordination number = 8: Am(III) = 109 pm and Nd(III) = 111 pm [16]), the magnitude of electrostatic attraction between metal ions and corresponding ligands is similar, yielding comparable thermodynamic stabilities. Pu(III), having an ionic radius of 100 pm and a slightly higher charge density does not differ significantly from the chemical properties of Nd(III). In this context, the neodymium(III) data are analogous to the Pu(III) case and support current WIPP PA assessment calculations for the solubility of Pu³⁺.

4. Conclusions

The WIPP continues to perform above expectations as a repository for TRU waste as DOE site cleanup efforts continue. A large fraction of the expected plutonium inventory is already emplaced in the WIPP. Ongoing research to support the recertification activities continues to show that the WIPP has very favorable properties with respect to plutonium solubility and speciation under the expected environment in the WIPP.

Data from two redox-invariant analog studies for plutonium were reported. The solubility data for uranium(VI) in carbon dioxide-free WIPP brines presented herein are the first at high pC_{H^+} under what we believe to be a truly carbon dioxide-free system. They establish a uranium solubility, in the absence of carbonate, of $\sim 2 \times 10^{-7}$ M for ERDA-6 brine, which is 10–100 times lower than published results and almost four orders of

magnitude below current WIPP PA assumptions. Since significant amounts of Pu(VI) are not expected in the WIPP, the uranium(VI) data serve as a contingency that provides an estimate for Pu(VI) solubility for simulated WIPP brine under WIPP-relevant conditions should this be needed. Future studies will extend these data to include the effects of carbonate on the solubility of U(VI) in WIPP brines.

The second redox-invariant analog for plutonium was Nd(III). Pu(III) is currently an expected oxidation-state in WIPP PA so these data are highly relevant to current PA calculations. Our results show that complexation with carbonate does not appear to play a significant role for neodymium solubility in WIPP brine. The solubility of neodymium is mostly controlled by the hydroxyl ion concentration and decreases as pC_{H^+} increases. For $8.5 < pC_{H^+} < 10.5$, a shoulder in the plot of neodymium solubility was found in ERDA-6 brine. This shoulder can be assigned to the complexation of neodymium with brine components (most likely borate) or conversion of a solid in this pC_{H^+} range. Characterization of solids controlling solubility collected in a broad range of pC_{H^+} will provide more information to better understand the thermodynamics of this process. Overall, these data support the WIPP PA calculations for Pu(III) and extend past work to more WIPP-relevant brine systems, higher pC_{H^+} , and higher carbonate concentrations. Future research will be more focused on the long-term stability of Pu(III) phases and species in the WIPP towards oxidation to form lower solubility Pu(IV) species.

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