Solubility of Neodymium in Simulated WIPP (Waste Isolation Pilot Plant) Brines

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ABSTRACT

Neodymium is a redox-invariant analog for americium (III) and plutonium (III), which are key contaminants in the WIPP. The measurements of neodymium solubility in simulated WIPP brine is expected to verify current assumptions in WIPP Performance Assessment that were based on simplified systems.

In the present work the neodymium solubility was measured in GWB (Generic Weep Brine), ERDA-6 (Energy Research and Development Administration Well 6) Brine and 3 M NaCl as a function of carbonate concentration and pcH using an over-saturation approach. Samples were equilibrated for three months and the neodymium concentrations were measured in unfiltered and filtered aliquots using ICP-MS. Obtained results were compared with the literature data. Precipitation led to a decrease in the initial Nd concentration of ~10^{-6} M in all samples. All results reflect the expected trends. The neodymium solubility decreased with increasing pcH. The most pronounced changes are in 3 M NaCl because of the larger pcH range present. All results are consistent with the literature data. The neodymium concentrations in GWB and ERDA-6 brine, at the same pcH, are slightly greater than in 3 M NaCl solution. Experiments that provide greater detail on the aqueous and solid speciation that define solubility are in progress. Additionally, some undersaturation experiments were initiated.

Brine Composition Used in Solubility Studies

Component	ERDA-6 g/L	ERDA-6 M/L	GWB g/L	GWB M/L
NaCl	248.6	4.254	167.8	2.874
$MgCl_2 \cdot 6H_2O$	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
$Na_2B_4O_7 \cdot 10H_2O$	5.7	0.015	14.03	0.037
KCl	6.869	0.092	32.57	0.437
LiCl	-	-	0.174	0.004
$CaCl_2 \cdot 2H_2O$	1.672	0.011	1.896	0.013
Ionic strength	4.965 M		6.839 M	
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

EQUILIBRATION TIME

The kinetics of equilibration in the over-saturation approach was studied. The change in Nd concentration as a function of time for GWB and ERDA-6 brines at various pcH were measured.

GWB Brine — Nd concentration, M vs Equilibration time, days — pcH=7.48, pcH=7.93, pcH=8.42

The observed trends in the Nd concentrations with time were similar for both brines, GWB and ERDA-6.

ERDA-6 Brine — Nd concentration, M vs Equilibration time, days — pcH=7.48, pcH=7.93, pcH=8.42

The major decrease in Nd concentration occurred during the first 20 days of the solubility experiments.

EXPERIMENTAL APPROACH

Key Experimental Parameters

pH between 6 and 12
- Carbonate concentrations up to 0.01 M
- Temperature of 25 ºC ± 3 ºC
- Speciation (complexation)
- Interactions with waste components (Fe, MgO, Al, Ni, Pb and Organics)
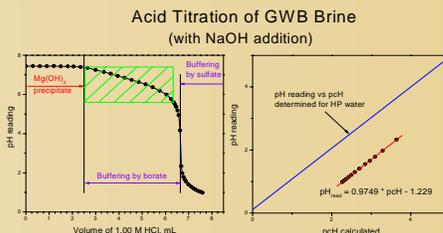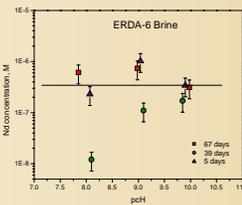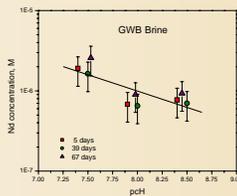
Solubility Experiments

Solubility is approached from both under-saturation and over-saturation under controlled environmental conditions and in the presence/absence of key waste components
- In over-saturation experiments, neodymium as an actinide +3 analog is added sequentially to simulated WIPP brine until a steady-state concentration is achieved
- In under-saturation experiments, the expected/predicted solid phases are prepared and contacted with simulated brine under controlled conditions until a steady state concentration is achieved
- The results of both approaches, in light of analogous modeling studies and calculations, are combined to establish the likely solubility under the expected subsurface conditions

Analytical Techniques

Total solution concentrations are determined by ICP-MS as a function of solution filtration (when applicable)
- Solids will be characterized by XRD, SEM and TEM. XANES/EXAFS analysis will be performed on selected samples to establish the near-neighbor structure of the environmentally relevant precipitates obtained by comparison to well-characterized references.

CALCULATED An(III) SOLUBILITY*

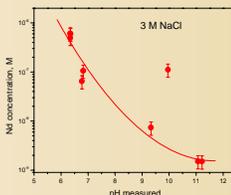| Brine	Estimated with Microbial Presence	Estimated with Microbial Absence
Salado Formation Brine	3.07×10^{-7} M	3.07×10^{-7} M
Castile Brine	1.69×10^{-7} M	1.77×10^{-7} M

*Brush L.H., and Xiong Y, Actinide Solubility for the WIPP PAB Calculations, unpublished analysis (2005)

pcH DEPENDENCE

The experimentally available pcH ranges in GWB and ERDA-6 brines are limited at higher pcH by precipitation of magnesium hydroxide and at lower pcH by the steep slope when small amounts of acid are added (green area in the graph above). Nd(III) concentrations were measured at three equilibration times as a function of pcH. All plots are consistent with data reported in the literature for americium.

ERDA-6 Brine — Nd concentration, M vs pcH — 67 days, 39 days, 5 days

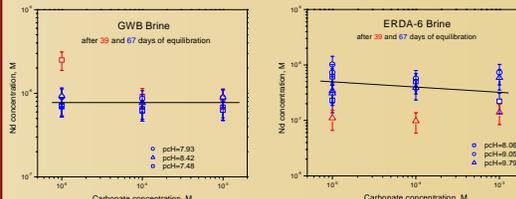GWB Brine — Nd concentration, M vs pcH — 5 days, 39 days, 67 days

The neodymium solubilities decreased with increased pH. The most pronounced changes were in 3 M NaCl because of the larger range of pH investigated. The decrease from 10^{-6} M at pH~6 to 10^{-9} M at pH~11 in low carbonate solution is consistent with the literature data. The neodymium concentrations in GWB and ERDA-6 brines, for the same pH, are slightly greater than in 3 M NaCl solution. It is possible, however, that the equilibration process may be slower in solutions at higher ionic strength.

3 M NaCl — Nd concentration, M vs pH measured

pH MEASUREMENTS in BRINE SYSTEMS

The extension of commonly used analytical techniques and approaches to brine systems is often problematic and not straightforward. Significant effort is required to confirm and develop experimental protocols that work for brine systems. For example the measurement of hydrogen ion concentration (pH), which is a critical parameter for actinide solubility in geochemical systems, is made difficult by the high ionic strength and buffer capacity of the brines used. In concentrated brines, variations in activity coefficients, the formation of species such as HSO_4^- and $H_2B_4O_7$ that can consume protons during electrode standardization procedures, and potentially large junction potentials all add to the difficulty in the pH measurement.

Acid Titration of GWB Brine (with NaOH addition)

The Gran-type titrations shown above were done with HCl with/or without addition of NaOH. Extra precautions were required to determine pH shifts for electrolytes that react with H^+ or OH^- [e.g., sulfate ions and magnesium brines for the precipitation of $Mg(OH)_2$]. These titrations, performed in all the brines investigated, were used to establish a correction factor (K) for the specific pH electrode and brine according to the following general equation:

$$pcH = pH_{read} + K$$

Brine	Correction factor, K
ERDA-6 brine	0.944 ± 0.023
GWB brine	1.23 ± 0.010

EFFECT OF CARBONATE

Neodymium solubility in GWB and ERDA-6 brine at a constant pcH but with varied carbonate concentrations and various equilibration times were investigated. The neodymium concentrations in these samples were measured using ICP-MS after 39 and 67 days of equilibration.

GWB Brine after 39 and 67 days of equilibration — Nd concentration, M vs Carbonate concentration, M — pcH=7.93, pcH=8.42, pcH=7.48

ERDA-6 Brine after 39 and 67 days of equilibration — Nd concentration, M vs Carbonate concentration, M — pcH=8.06, pcH=9.05, pcH=9.79

Only a very weak influence of carbonate on neodymium solubility was observed. This observation is also in agreement with the literature data. *Meinrath G. and Kim J.I. The Carbonate Complexation of the Am(III) Ion. Radiochimica Acta 46, 185-189, 1991.*
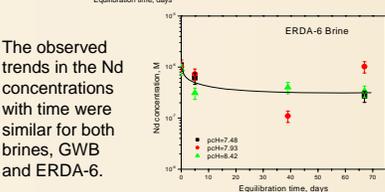
CONCLUSIONS

- Neodymium solubility in brine decreases in the following order: GWB>ERDA-6>3M NaCl and at pcH=8 are equal to $8(3) \times 10^{-7}$M; $3(1) \times 10^{-7}$M and $5(2) \times 10^{-8}$M, respectively,
- Neodymium solubility decreases slightly with increased pcH,
- Carbonates of the range of 10^{-3} to 10^{-5} M have almost no effect on neodymium solubility in GWB and ERDA-6 brines,
- These results are in good agreement with current PA estimations.

ACKNOWLEDGEMENT