32

Neodymium Analog Study of An(III) Solubility in WIPP Brine

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Introduction: The solubility of An(III) and An(IV) in brine is important to the Waste Isolation Pilot Plant, WIPP, primarily from the point of view of potential release of transuranium elements to the near-field environment. The solubility of Am(III) and Nd(III), which is an established analog for Am(III), was measured in low ionic strength solutions[1-6], as well as in 3-4 M NaCl and NaClO4 solutions[7,8]. These data were used by WIPP PA for modeling An(III) solubility in brines[9]. The goal of the present work, conducted using an Nd(III) analog, was to measure the effect of pC_{H+}, carbonate concentration, and brine composition on Nd(III) solubility to verify model calculations. Long term experiments (>150 days) were performed in three kinds of brine: ERDA-6, GWB and in 5 M NaCl in the basic pC_{H+} range, in the presence and absence of carbonate ions at a temperature of ~25 ºC. The carbonate free experiments were designed to provide baseline data for the effect of carbonate. Both over-saturation and under-saturation approaches were used.

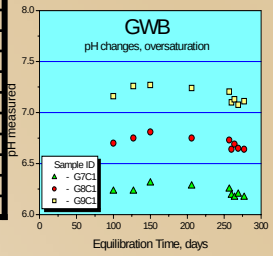
Experimental: Carbonate was carefully removed from the brine. The brine solution was acidified and bubbled with high-purity nitrogen. Then brine was placed in a nitrogen glove box and the atmosphere was controlled for the duration of the experiment. The desired pC_{H+} was adjusted in each bottle and a stock neodymium solution at pH~4 (HCl) was used as a spike in the over-saturation approach. For the under-saturation experiments, commercially-available neodymium hydroxide was used as the solid phase.

The carbonate effect was measured in similar systems. Four concentrations of total carbonate were used: 10^{-2}, 10^{-3}, 10^{-4} and 10^{-5} M. In each sample, pC_{H+} was adjusted to the desired value and stock neodymium solution at pH~4 (HCl) was used as a spike in the over-saturation approach. The initial neodymium concentration was equal to $5x10^{-5}$ M. For under-saturation experiments, $NdCO_3OH$, prepared in our laboratory, was used as a solid phase.

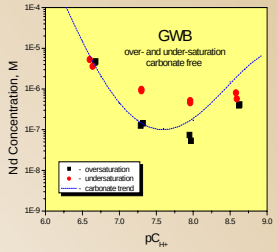
GWB

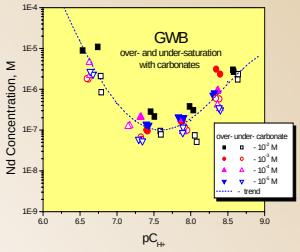
GWB brine composition

Component	g/L	M
NaCl	167.8	2.874
$MgCl_2$	90.57	0.953
Na_2SO_4	23.61	0.166
NaBr	2.565	0.025
$Na_2B_4O_7$	7.402	0.037
KCl	32.57	0.437
LiCl	0.174	0.174
$CaCl_2$	1.431	0.013
Ionic Strength	6.839	
Density g/mL	1.216	



Neodymium solubility was measured after 150 days of equilibration (2 additions in over-saturation experiments). Changes of pC_{H+} were very small during the entire period of equilibration.



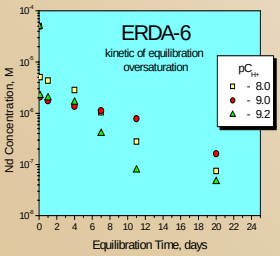


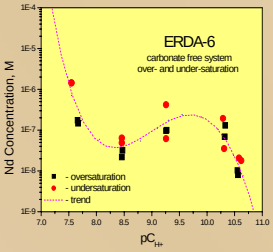
Neodymium concentrations measured from over-saturation and under-saturation were very close to each other indicating that steady state was achieved. Neodymium solubility limit was changed with pC_{H+}. Different concentrations of carbonate did not affect the neodymium solubility limit in the GWB brine.

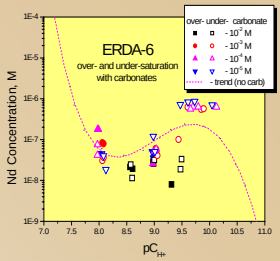
ERDA-6

ERDA-6 brine composition

Component	g/L	M
NaCl	248.6	4.254
$MgCl_2$	1.718	0.018
Na_2SO_4	22.52	0.159
NaBr	1.074	0.010
$Na_2B_4O_7$	3.007	0.015
KCl	6.869	0.092
$CaCl_2$	1.262	0.011
Ionic Strength	4.965	
Density g/mL	1.183	



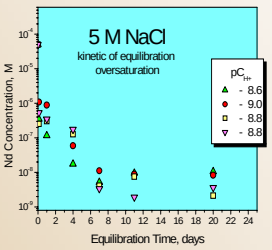


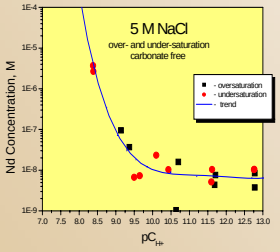


At pC_{H+} ~8.5, the likely value expected in the WIPP, the lowest Nd(III) solubility was found in ERDA-6 (the low magnesium brine) and was almost one order of magnitude lower than in GWB (high magnesium brine). The shoulder observed for ERDA-6 brine with a maximum at pC_{H+} = 9.6, can be assigned to neodymium complex formation with brine components. 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.

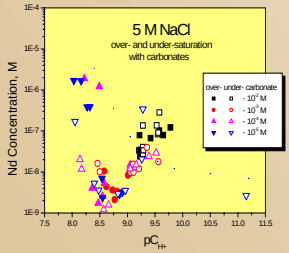
5 M NaCl

Kinetic data for all brines tested indicate that from over-saturation the steady state is achieved after 30 days of equilibration. From under-saturation a longer time is required.





The pC_{H+} neodymium concentration trend for 5 M NaCl is analogous to the Am(III) solubilities reported for low ionic strength solutions[1-4] but is shifted up by about two orders of magnitude.



The change in neodymium solubility observed in the 5 M NaCl solution with carbonate, reported also in the literature[5] for lower NaCl concentration, can be explained by carbonate complexation, although this effect did not increase with the increase of carbonate concentration.

Conclusions:

- The Nd(III) complexation with carbonate ion does not appear to play a significant role for neodymium solubility in the 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 neodymium solubility plot was found in some cases. These shoulders were assigned to complexation of neodymium with carbonate ion or with brine component (e.g. borate) in carbonate free system. These observations are consistent with the literature data[4,6]. However, the literature data were reported for low ionic strength solutions and hydroxyl ion concentrations used were not high enough to observe the further decrease we noted at higher pC_{H+}.
- Characterization of solids controlling solubility collected in broad range of pC_{H+} will give us more information to better explain this phenomenon.
- The An(III) solubilities calculated in GWB and ERDA-6 brines using the Pitzer model[9] at pC_{H+}~8.5 are equal to $3x10^{-7}$ M and $1.7x10^{-7}$ M respectively and are in good agreement with the neodymium solubility data measured in the present work.

References:

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