Actinide (III) Solubility in WIPP Brine:

Data Summary and Recommendations

WIPP Facility and Stratigraphic Sequence

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Marian Borkowski

Jean-Francois Lucchini

Michael K. Richmann

Donald T. Reed

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ACRONYMS

ACRONYM	DEFINITION
ACRSP	Actinide Chemistry and Repository Science Program
ASTP	WIPP Actinide Source Term Program
CBFO	Carlsbad Field Office (U.S. Department of Energy)
CCA	Compliance Certification Application
CEMRC	Carlsbad Environmental Monitoring and Research Center
CFR	Code of Federal Regulations
CRA	Compliance Recertification Application
DBR	dissolved brine release
DOE	U.S. Department of Energy
EDTA	ethylenediaminetetraacetic acid
EPA	U.S. Environmental Protection Agency
ERDA-6	U.S. Energy Research and Development Administration Well 6, a synthetic brine representative of fluids in Castile brine reservoirs
EXAFS	extended x-ray absorption fine structure
FMT	Fracture-Matrix Transport (code used to calculate actinide speciation for CRA)
GWB	generic weep brine
ICP-MS	inductively coupled plasma mass spectroscopy
LANL-CO	Los Alamos National Laboratory–Carlsbad Operations
NIST database	National Institute of Standards and Technology database
PA	performance assessment
PAVT	Performance Assessment Verification Test
pC_{H+}	negative logarithm of H^+ concentration in moles/liter
pH	negative logarithm of H^+ activity
QA	quality assurance
QAPD	Quality Assurance Program Document
SNL	Sandia National Laboratories
SOTERM	Actinide Source Term (appendix in the WIPP CRA)
TRU	transuranic (actinides higher in atomic number than uranium)
WIPP	Waste Isolation Pilot Plant
XANES	x-ray absorption near edge spectroscopy
XRD	x-ray diffraction

EXECUTIVE SUMMARY

The solubility of actinides in the +3 oxidation state is an important input into the Waste Isolation Pilot Plant (WIPP) performance assessment (PA) models that calculate potential actinide release from the WIPP repository. In this context, the solubility of neodymium(III) was determined as a function of pH, carbonate concentration, and WIPP brine composition. Additionally, we conducted a literature review on the solubility of +3 actinides under WIPP-related conditions. Neodymium(III) was used as a redox-invariant analog for the +3 oxidation state of americium and plutonium, which is the oxidation state that accounts for over 90% of the potential release from the WIPP through the dissolved brine release (DBR) mechanism, based on current WIPP performance assessment assumptions. These solubility data extend past studies to brine compositions that are more WIPP-relevant and cover a broader range of experimental conditions than past studies.

The experiments were performed by the Los Alamos National Laboratory-Carlsbad Operations (LANL-CO) Actinide Chemistry and Repository Science Program (ACRSP) as part of a larger effort to establish the conservatisms related to actinide chemistry in the current WIPP PA model and establish a more robust WIPP chemistry model to support ongoing WIPP recertification efforts. The experiments were performed under the U.S. Department of Energy (DOE) approved test plan "Solubility of Neodymium(III) in WIPP Brines," LCO-ACP-03. All data reported were generated under the LANL-CO WIPP Quality Assurance (QA) Program, which is compliant with the DOE Carlsbad Field Office (CBFO) Quality Assurance Program Document (QAPD). The data summarized in this report are supported by QA documentation, which is maintained in the LANL-CO Records Center.

There are a number of key results and observations from the neodymium(III) solubility experimental study and corresponding literature review. The most important of these are as follows:

1) There were no surprises discovered in the literature review that was centered on the solubility of Am(III) and Pu(III) in brine systems. There are little, if any, new data that bear directly on the measurement and calculation of the solubility of +3 actinides in brine systems since the Compliance Certification Application (CCA).

2) The solubility data we report for neodymium(III) in WIPP-relevant brine systems supports current WIPP PA calculations of the +3 actinide solubility in that the calculated values remain conservative for the referenced WIPP conditions.

3) Specific observations and results that relate to the Nd^{+3} solubility data that were obtained by ACRSP include the following:

   o Excellent agreement with comparable literature values for Nd^{+3} solubility in the carbonate-free, simplified 5 M NaCl brine study was obtained. This provides an external corroboration of our experimental approach for the only system we investigated that can be directly compared to other non-WIPP studies.

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- o Excellent agreement was obtained in all of our experiments between our over- and undersaturation approaches. This is a strong indicator that the solubility, rather than steady-state metastable concentrations, was being measured.

- o The solubility of neodymium(III) in simulated WIPP brine was not strongly influenced by the range of carbonate concentrations considered (as high as a total concentration of 0.01 M). This is largely due to the complexation of neodymium(III) by borate, already present in WIPP brine at much higher concentrations, which masks the effects of carbonate. The plots of neodymium solubility as a function of pC_{H+} in two simulated WIPP brines, generic weep brine (GWB) and U.S. Energy Research and Development Administration Well 6 (ERDA-6) brine, were essentially the same in the presence and absence of carbonate.

- o The solubility of neodymium, in the simplified and simulated brine systems considered, does not exhibit amphoteric behavior. In this context, the solubility of neodymium at $pC_{H+} >10$ is mostly controlled by hydroxide concentration and decreases with increasing pC_{H+}. A shoulder to a varying degree, however, is noted in the neodymium solubility graphs for $7.5 < pC_{H+} < 10.5$ because of complexation present in all three of the brines investigated.

- o We established that the shoulder in the neodymium solubility data for GWB and ERDA-6 brine is caused by borate complexation. This establishes borate as the predominant complexant in brine in the pC_{H+} range of 7.5 to 10 (this includes the current reference pC_{H+}). We have estimated the formation constant for this complex to be log K of ~3 to 4.

There are two key recommendations to WIPP PA for the solubility of the +3 actinides based on our experimental results and literature review:

1) ***There should be no significant change to the +3 solubility concentrations used in WIPP PA for the reference case.*** The WIPP-relevant data summarized in this report support current PA calculations performed with the use of the Pitzer model (Compliance Recertification Application 2004, Attachment SOTERM) for the values of 3 x 10^{-7} M and 1.7 x 10^{-7} M in GWB and ERDA-6 brine, respectively, at pH = 8.7 (pC_{H+} ~9.2). Our data show that this solubility is at or near the maximum solubility over a wide range of pH, brine composition, and carbonate concentrations.

2) ***The +3 actinide speciation model should be modified to account for the effects of borate complexation.*** Borate is, in fact, the key complexant in WIPP brine for +3 actinides and should be reflected in the model to properly account for the solubility trends and effects of pH and carbonate concentration on the solubility of +3 actinides. We should proceed with developing the needed Pitzer parameters and a Quality Level 1 determination of the formation constant for incorporation in the WIPP speciation model for the +3 actinides.

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1.0   INTRODUCTION

The objectives of this technical summary report are to provide the following:

1) An updated literature review for the solubility of key Waste Isolation Pilot Plant (WIPP) transuranics in the +3 oxidation state

2) A summary of WIPP-specific data obtained by the Los Alamos National Laboratory-Carlsbad Operations (LANL-CO) Actinide Chemistry and Repository Science Program (ACRSP) team over the past two years on the solubility of neodymium(III) in simulated WIPP brine, where neodymium(III) was used as an oxidation state invariant analog for the key +3 actinides in the WIPP

3) An assessment and comparison of the literature and WIPP-specific results with the WIPP performance assessment (PA) position established in the 2004 Compliance Recertification Application (CRA-2004) documentation

This report will provide, in part, a basis for WIPP PA analysis of +3 actinide solubility for the ongoing WIPP recertification activities. More specifically, this report supports Appendix SOTERM-2009 in the CRA-2009 application, with the second WIPP recertification decision anticipated in 2010.

The WIPP, which is located in the northern portion of the Delaware Basin in southeastern New Mexico east of Carlsbad, continues to be the only operating transuranic (TRU) waste repository in the world. Owned by the U.S. Department of Energy (DOE), it was first certified by the U.S. Environmental Protection Agency (EPA) in May 1998. The regulatory guidelines for the WIPP are given in Title 40 Code of Federal Regulations (CFR), Parts 191/194 (U.S. EPA 1993 and U.S. DOE 1996). Based on these regulations, the WIPP is required to undergo recertification by the EPA every five years. The first CRA (CRA-2004) was submitted in 2004 and was approved in April 2006.

The WIPP-relevant solubility studies summarized in this report were performed by the ACRSP team at the Carlsbad Environmental Monitoring and Research Center (CEMRC). The overall research goals of ACRSP are (1) establish the conservatisms of the current WIPP PA calculations of actinide solubility, (2) establish a more robust WIPP chemistry model, and (3) extend past research to conditions that better simulate potential brine environments in the WIPP. This is being done by a combination of redox invariant analog studies and actinide studies in two simulated WIPP brines, generic weep brine (GWB) and U.S. Energy Research and Development Administration Well 6 (ERDA-6) brine, which bracket the range of brine composition expected in the WIPP. Both under- and oversaturation approaches are being used. All WIPP-relevant results reported were performed under the LANL-CO WIPP Quality Assurance Plan, which is compliant with the DOE Carlsbad Field Office (CBFO) Quality Assurance Program Document (QAPD).

In this context, neodymium(III) was used as a redox-invariant analog for the +3 oxidation state of americium and plutonium in the WIPP, which is the oxidation state that accounts for over 80% of the potential release from the WIPP through the dissolved brine release (DBR) mechanism. The +3 actinide solubilities reported, therefore, address a key actinide release consideration in WIPP PA, based on current assumptions.

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2.0 SUMMARY OF WIPP PA POSITION ON +3 ACTINIDE SOLUBILITY

A significant amount of research was performed during the 1990s as part of the WIPP Actinide Source Term Program (ASTP) managed by Sandia National Laboratories (SNL) to support the certification of the WIPP. Experimental methods—such as potentiometric titration, extraction, spectroscopy, and solubility measurements—were deployed for collection of the laboratory data for the ASTP at Florida State University and several national laboratories. The range of investigated parameters included inorganic ligand concentration (i.e., brine composition), pC_{H+} 3 to 10, presence and absence of oxygen and carbonate, and four organic ligands: acetate, oxalate, citrate, and ethylenediaminetetraacetic acid (EDTA) (Choppin et al. 2001; Giambalvo 2003).

The key sections on plutonium and americium in the Actinide Source Term (CRA-2004, Attachment SOTERM) are summarized in this section. Based on SOTERM, the following is an overview of the relative importance of the predominant actinides and oxidation states in the WIPP:

Importance of the actinide solubility to DBR release: Pu ≈ Am >> U > Th >> Np, Cm

Importance of the oxidation state: An(III) > An(IV) >> An(VI) >> An(V)

The most important difference between the Compliance Certification Application (CCA) (completed for the initial certification) and CRA-2004 in this area is the increased importance of americium as an actinide of concern and, correspondingly, the increased importance of the +3 oxidation state.

2.1 Current (CRA-2004) WIPP Position on Plutonium Solubility

Plutonium is the most important transuranic in the WIPP, and its potential release to the environment is a key concern for WIPP PA. This importance is consistently established in internal assessments of WIPP actinide issues, and plutonium remains the actinide of most concern in public perception. The current WIPP PA position on the plutonium source term is addressed in the following excerpt from SOTERM (CRA 2004, Attachment SOTERM):

SOTERM-4.4 Plutonium

> *Pu can exist in the +III, +IV, +V, +VI, and +VII oxidation states (Katz et al. 1986, 781). Pu(III) is the favored oxidation state in acidic solutions, but oxidation of Pu(III) to Pu(IV) becomes progressively easier with increasing pH. This occurs because Pu(IV) features a very strong tendency to undergo hydrolysis, which has the effect of reducing the solution concentration of the free Pu(IV) ion Pu^{4+}. As the pH of a Pu solution is raised from acidic to neutral, Pu(IV) begins to precipitate, resulting in a shift of equilibrium concentrations of Pu(III) to Pu(IV). Consequently, Pu(III) is not a thermodynamically stable oxidation state in the basic environment that will be established by MgO in the WIPP (see Reaction 5 above). Although Pu(III) is unstable under expected WIPP conditions, Felmy et al. (1989) observed Pu(III) in PBB1 and PBB3 brines at neutral and slightly basic conditions.*

Pu(V) and Pu(VI) can be produced from Pu(IV) under oxidizing conditions. It is not possible to produce Pu(V) by direct oxidation of Pu(IV) because the oxidation potential that must be applied exceeds the potential required for the oxidation of Pu(V) to Pu(VI). Therefore, in a solution with oxidizing conditions, any Pu(V) that arises from the oxidation of Pu(IV) will be immediately oxidized to Pu(VI). Pu(V) can be produced in solution only by first producing Pu(VI), followed by a carefully controlled reduction of Pu(VI) to Pu(V). Pu(V) may persist in neutral to basic solutions even when it is not the thermodynamically stable oxidation state, because of the reduction reaction's inverse fourth power dependence on the concentration of H^+, which can make the reduction of Pu(V) to Pu(IV) kinetically slow. Neither Pu(V) nor Pu(VI) will persist in significant quantities in the repository, because oxidizing conditions are required to produce them. Pu(VI) was shown to form complexes with Cl- under oxic conditions in high-ionic-strength NaCl solutions (Clark and Tait 1996). Clark and Tait (1996) and Reed et al. (1996) showed the reduction of Pu(VI) to Pu(IV) by Fe and other reductants under expected WIPP repository conditions. Metallic Fe and Fe^{2+} reduce Pu(VI) in WIPP brines to either Pu(IV) or Pu(III). Clark and Tait (1996) and Felmy et al. (1996) experimentally observed the reduction of Pu(VI)-CO_3^{2-} complexes to Pu(IV) by either metallic Fe or Fe^{2+}. Reduction of Pu(VI) was also observed in the absence of CO_3^{2-}, but the oxidation state of the resulting species was not determined because the concentration was below the analytical detection limit, ca. 10^{-9} M. Neretnieks (1982) showed that dissolved actinides are reduced to a less soluble oxidation state and precipitated from moving groundwater upon coming in contact with Fe(II).

Pu(VII) can be produced in concentrated OH- solutions that are also highly oxidizing. Pu(VII) will not be formed in the WIPP.

The DOE determined (Weiner 1996) that Pu(IV) will be the dominant oxidation state under WIPP conditions, but the possibility of the existence of Pu(III) cannot be excluded. As a result, Pu is modeled as Pu(III) in half of the PA vectors, and as Pu(IV) in half of the vectors.

In summary, SOTERM (CRA 2004, Attachment SOTERM) makes the assumption that only Pu(IV) species exist in 50% of the PA vectors and only Pu(III) species exist in the other 50% of the PA vectors. This is, in part, based on the important role that excess iron in the WIPP has in establishing reducing conditions but is also consistent with the effects of microbiological processes on multivalent actinides (e.g., bioreduction). The lower oxidation states of plutonium have a lower solubility in the expected WIPP brine and are used to calculate releases from the repository. That higher oxidation states of plutonium may prevail in the presence of excess iron, which is recognized as a possibility in localized zones, is likely to be quickly overwhelmed by the overall reducing conditions present.

2.2   Current (CRA-2004) WIPP Position on Americium Solubility

Americium, from the perspective of dissolved brine release, is of approximately equal importance to plutonium in WIPP PA. The current WIPP position on the speciation and

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solubility of americium is defined in the following excerpt from SOTERM (CRA 2004, Attachment SOTERM):

SOTERM-4.5 Americium

Am(III) is the most stable aqueous oxidation state of Am (Katz et al. 1986, 912), and will be the only oxidation state of Am in the WIPP. Am(III) is not easily oxidized in aqueous solution (Hobart et al. 1982); however, Am(V) and Am(VI) are accessible at high pH under highly oxidizing conditions. Am(V) and Am(VI) are not stable in natural waters and are readily reduced. Am(V) and Am(VI) can oxidize water, and as a result, they are thermodynamically unstable in aqueous solutions. Am(V) may be formed by oxidation of Am(III) by radiolysis products in NaCl solutions (Runde and Kim 1994), which may occur in micro- environments within WIPP disposal rooms, but Am(V) would not be stable in the homogeneous mixture of waste and brine. Solubility studies carried out by Pryke and Rees (1986) and Felmy et al. (1990) indicated that Am(V) is unstable in brine above pH 9 and reduces to Am(III). These studies also showed significant instability of Am(V) at pH 7. Because of the thermodynamic instability of Am(V) and Am(VI) in aqueous solution, and the lack of a credible mechanism for maintaining the highly oxidizing conditions necessary for persistence of these two oxidation states, Am(III) is the only oxidation state that is used in modeling the speciation and solubility of this element in the repository.

In summary, americium will predominantly exist as a complexed americium(III) species in the WIPP. This remains a strong and supportable assumption, although there are results published since CRA-2004 that show that AmO_2^+ species can be formed due to radiolytic processes in high sodium chloride solutions similar to WIPP brine. These higher oxidation- state species will, however, be unstable and are not predicted to prevail in the expected reducing conditions.

2.3   Speciation and Importance of the +3 Actinide Oxidation State in the WIPP

The +3 actinides of interest to the WIPP are Am(III), Pu(III), and to a much lesser extent, Cm(III). Data for An(III) and the +3 lanthanides are the most extensive when considering all of the oxidation states of interest, and these data form the basis for modeling the solubility of An(III) in the WIPP. On the basis of the recently reviewed literature data reported in Section 3 and our recently generated data, the following are the major reactions of An(III) expected in WIPP brine that affect An(III) solubilities, as written for Am(III):
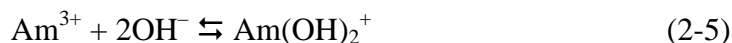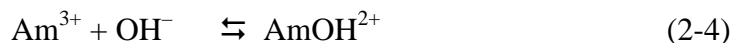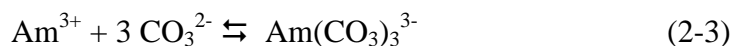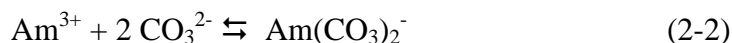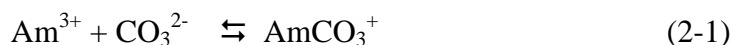
$$Am^{3+} + CO_3^{2-} \leftrightarrows AmCO_3^+ \qquad (2\text{-}1)$$

$$Am^{3+} + 2\,CO_3^{2-} \leftrightarrows Am(CO_3)_2^- \qquad (2\text{-}2)$$

$$Am^{3+} + 3\,CO_3^{2-} \leftrightarrows Am(CO_3)_3^{3-} \qquad (2\text{-}3)$$

$$Am^{3+} + OH^- \leftrightarrows AmOH^{2+} \qquad (2\text{-}4)$$

$$Am^{3+} + 2OH^- \leftrightarrows Am(OH)_2^+ \qquad (2\text{-}5)$$

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$$Am^{3+} + 2OH^- \leftrightharpoons Am(OH)_2^+ \qquad\qquad (2\text{-}5)$$

$$Am^{3+} + 3OH^- \leftrightharpoons Am(OH)_3(s) \qquad\qquad (2\text{-}6)$$

$$Am^{3+} + OH^- + CO_3^{2-} \leftrightharpoons AmOH\,CO_3(s) \qquad\qquad (2\text{-}7)$$

$$Am^{3+} + PO_4^{3-} \leftrightharpoons Am\,PO_4(s) \qquad\qquad (2\text{-}8)$$

$$Am^{3+} + B(OH)_4^- \leftrightharpoons Am\,B(OH)_4^{2+} \qquad\qquad (2\text{-}9)$$
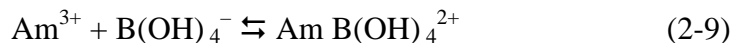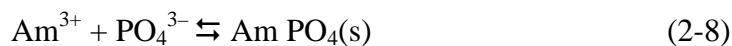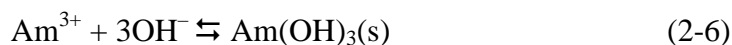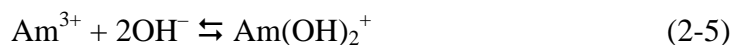
The An (III) model used in WIPP PA was demonstrated to describe the chemical behavior of both Am(III) and Pu(III). In these calculations, reactions 2-1 through 2-8 were considered. These model calculations, however, were not experimentally verified for WIPP relevant brine. There are also some limitations to the existing literature data on An (III) complexation with carbonate (see Section 3), which are only available to $pC_{H+} = 10$. Lastly, complexation with borate, probably the predominant complexant at $pC_{H+} \sim 8-9$, was not considered in the model.

The solubility of An^{3+} species in WIPP brine calculated in the various WIPP PA analyses are tabulated in Table 2-1. The calculated solubility of +3 actinides has been fairly consistent and is 0.31 μM for Salado brine (analogous to GWB simulated brine composition) and 0.17 to 0.18 μM for Castile brines (analogous to ERDA-6 simulated brine composition). This is over an order of magnitude more soluble than the corresponding +4 actinide species. In this context, the +3 actinides account for ~100% of the dissolved americium species and over 90% of the dissolved plutonium species predicted to be present, according to current WIPP PA assumptions.

Table 2-1. **Actinide Solubilities (M) Calculated (+III, +IV, and +V) or Estimated (+VI) for the CRA-2004 PA, the 1997 PA Verification Test (PAVT), and the CCA PA (Table SOTERM-2) (CRA 2004). The CRA calculations reflect the inclusion of organic complexation and updated chemical conditions for microbial and nonmicrobial vectors.**

Actinide Oxidation State and Brine	CRA-2004 Solubilities, Microbial Vectors	CRA-2004 Solubilities, Nonmicrobial Vectors	PAVT Solubilities	CCA Solubilities
+III, Salado brine	3.07×10^{-7}	3.07×10^{-7}	1.2×10^{-7}	5.82×10^{-7}
+III, Castile brine	1.69×10^{-7}	1.77×10^{-7}	1.3×10^{-8}	1.3×10^{-8}
+IV, Salado brine	1.19×10^{-8}	1.24×10^{-8}	1.3×10^{-8}	4.4×10^{-6}
+IV, Castile brine	2.47×10^{-8}	5.84×10^{-9}	4.1×10^{-9}	6.0×10^{-9}
+V, Salado brine	1.02×10^{-6}	9.72×10^{-7}	2.4×10^{-7}	2.3×10^{-6}
+V, Castile brine	5.08×10^{-6}	2.13×10^{-5}	4.8×10^{-5}	2.2×10^{-6}
+VI, Salado brine	8.7×10^{-6}	8.7×10^{-6}	8.7×10^{-6}	8.7×10^{-6}
+VI, Castile brine	8.8×10^{-6}	8.8×10^{-6}	8.8×10^{-6}	8.8×10^{-6}

3.0 LITERATURE BACKGROUND: SOLUBILITY OF Pu(III) AND Am(III)

Many of the scientific issues that define the mobility and solubility of actinides in the WIPP are ubiquitous to all existing and potential subsurface actinide contamination problems throughout the DOE complex (Choppin et al. 2001). Since the CCA, there is little that is new in the literature that directly pertains to the solubility of the +3 actinides in WIPP brine. There are, however, new data on the potential for radiolytically induced oxidation of americium and by association, other multivalent actinides, which is an important issue that is outside the scope of this report because we are dealing with oxidation-state-specific solubility. Reducing anoxic conditions, such as those expected in the WIPP, will lead to a prevalence of lower oxidation states and correspondingly, a low solubility and potential for actinide mobility/release from the WIPP (Nitsche et al. 1994; Runde 2000).

In this section, we provide an update and summary of the literature pertaining to the solubility of Am(III) and Pu(III), which are the key +3 actinides of concern in the WIPP.

3.1 Solubility of Plutonium(III) in Brine

Plutonium(III), as an aqueous species, is relatively unstable under a wide range of environmentally relevant pH and Eh regimes. It is, however, predicted to prevail under highly reducing conditions, as shown in Figure 3-1 (Runde et al. 2002), and WIPP PA makes the assumption that the solubility of plutonium in half the dissolved brine vectors is defined by plutonium(III) species. Because this solubility is over 10 times that of comparable Pu(IV) species, the Pu(III) species, from the perspective of predicted release, is the predominant aqueous plutonium species in the WIPP.

It is very difficult to measure the solubility of Pu(III) with confidence, however, because of its redox instability under laboratory conditions. For this reason, there are essentially no good direct measurements of Pu(III) solubility in the pH regime expected in the WIPP. The solubility of Pu(III) in brine is predicted to be in the nano- to micro-molar concentration range, which is below the sensitivity of most direct speciation methods. The potential oxidation of aqueous plutonium(III) and, correspondingly, the conversion of Pu(III) solids to phases with other oxidation states, lead to significant experimental uncertainty. In WIPP PA, which uses the approach generally taken in the modeling of Pu(III) systems, speciation reactions and solubilities of plutonium species are based on analog studies with redox-invariant +3 analogs—therefore, we have employed the same approach in our experimental work.

It is important to note, although it is somewhat outside of the scope of this report, that there is a question about the durability and long-term stability of Pu(III) phases in the pH range of 6 to 10. Most general reviews and studies (Runde et al. 2002; Choppin 2006; Rard 1997; Silver 2002) acknowledge the possibility of Pu(III) species, but experimentally, we routinely only identify Pu(IV) solid and aqueous species in WIPP-related studies (Reed et al. 2006). Anaerobic bacteria typical of low ionic strength groundwater systems have been shown to reduce Pu(V) to Pu(III) when complexants prevent Pu(IV) precipitation (Reed et al. 2007). The redox distribution of plutonium under WIPP-related conditions is the subject of ongoing ACRSP studies. For these reasons, current WIPP PA assumptions about the prevalence of Pu(III) continue to be viewed as conservatively high for the expected WIPP environment.
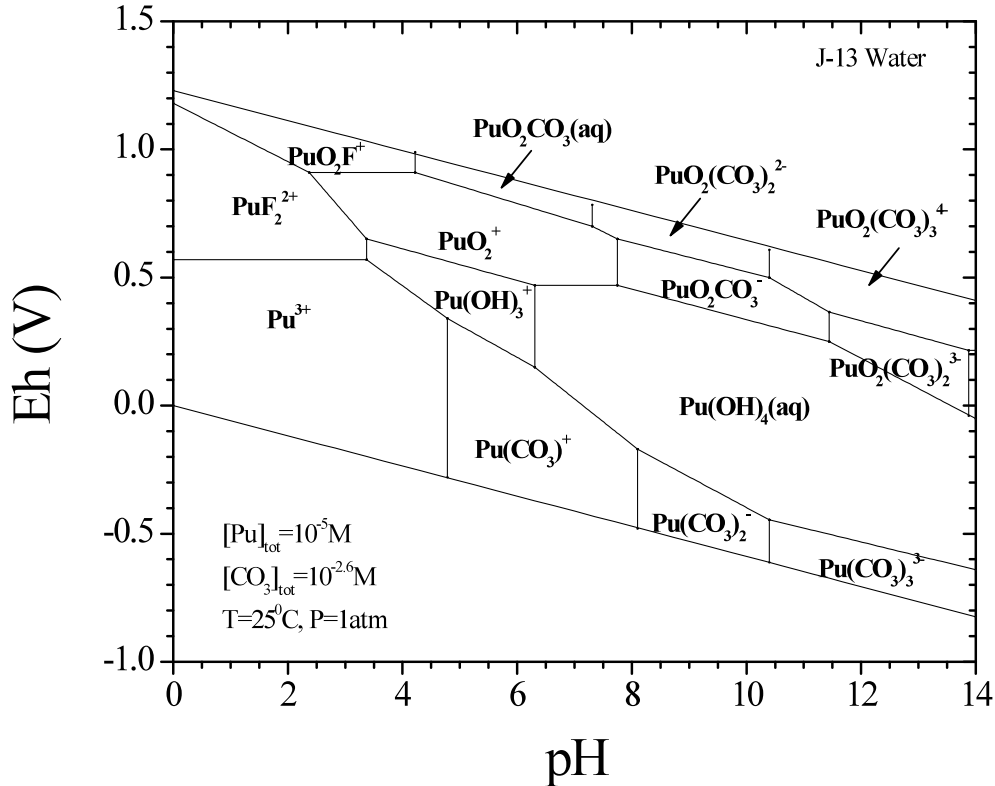
Figure 3-1.   Speciation diagram for plutonium in groundwater (based on data from Runde et al. 2002).

3.2   Solubility of Americium(III) in Brine

Unlike plutonium, the +3 oxidation state of americium is very stable over a wide range of conditions. For this reason, a number of solubility studies exist with americium, and the direct measurement of americium solubility is relatively straightforward. The most important factors that pertain to Am(III) solubility in the WIPP are as follows:

- The relative contribution of hydrolysis and carbonate complexation as a function of pH. Specifically, when does hydrolysis begin to predominate over carbonate complexation, and what controls pH in the subsurface environment?

- The relative impact of radiolytic products on redox conditions and possible generation of higher oxidation states of americium that might complicate Am(III) solubility studies.

- The contributions to solubility of complexants present in WIPP brine.

3.2.1 Hydrolysis of Americium(III)

The most important complexation reactions with americium in natural waters and alkaline pH are hydrolysis, carbonate complexation, and the solubility of the products of these reactions. The literature values for americium(III) hydrolysis (see reaction 3-1) are listed in Table 3-1.

$$Am^{3+} + nH_2O \leftrightarrows Am(OH)_n^{(3-n)} + nH^+ \qquad (3-1)$$
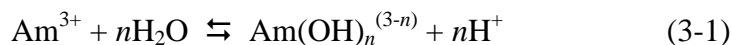
Table 3-1.	Hydrolysis Constants in Logarithmic Units of Americium(III) Corresponding to Eq. 3-1.			
AmOH^{2+}	**Am(OH)$_2^+$**	**Am(OH)$_{3,(aq)}$**	**Medium**	**Reference:**
-7.93 ± 0.35	-14.77 ± 0.25	-24.71 ± 0.11	0.1 M NaClO$_4$	(Kim et al. 1984)
-7.5 ± 0.3	-15.4 ± 0.4	-26.9 ± 0.5	0.1 M NaClO$_4$	(Stadler and Kim 1988)
-7.8 ± 0.4	-15.4 ± 0.5	-26.9 ± 0.5	0.1 M NaCl	(Stadler and Kim 1988)
-8.1 ± 0.3	-15.8 ± 0.4	-27.0 ± 0.5	0.6 M NaCl	(Stadler and Kim 1988)
-7.7 ± 0.3	-16.7 ± 0.7	-25.0 ± 0.3	0.1 M NaClO$_4$	(Silva 1982)
-6.9 ± 0.2		-23.8 ± 0.9	0.1 M NaClO$_4$	(Rösch et al. 1989)
<-8.2	-17.1 ± 0.7	<-27.0	I → 0	(Rai and Strickert 1982)
-6.40 ± 0.11	-13.40 ± 0.16	-20.31 ± 0.17	3 M NaClO$_4$	(Pazukhin and Kochergin 1989)
Recalculated from literature data				
-7.0 ± 0.4	-15.1 ± 0.4	-26.4 ± 0.5	0.1 M NaClO$_4$	(Silva et al. 1995)

For the reaction

$$Am(OH)_3(s) + 3H^+ \leftrightarrows Am^{3+} + 3H_2O_{3,(aq)} \qquad (3-2)$$
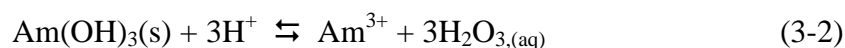
the reported equilibrium constants measured in 0.1 M NaClO$_4$ solution are log K = 13.7 ± 0.2 to 15.9 ± 0.6. With the use of the above data, the distribution diagram of the americium hydrolysis

species at 25°C in standard aqueous solutions (I = 0) in the range $6 \leq pH \leq 12$ were calculated (Silva et al. 1995) and are presented in Figure 3-2.
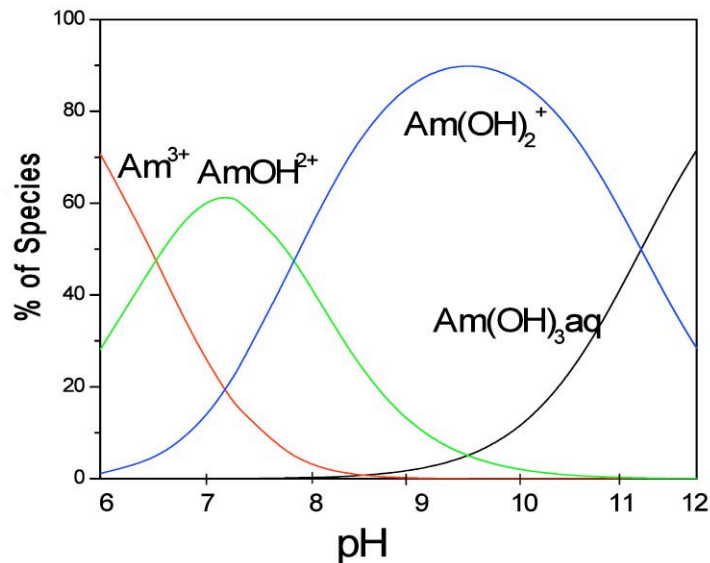
Figure 3-2. Calculated distribution diagram of americium species at 25°C (based on data published by Silva et al. 1995). The precipitation of solid phases has not been considered.

Silva (1982) measured solubility of $^{243}Am(OH)_3(cr)$ and $Nd(OH)_3(cr)$ in 0.1 M $NaClO_4$ solutions at (25 ± 1)°C within the pH range 6 to 10. This is the only study with americium hydroxide using an x-ray characterized crystalline solid. The solid phase was prepared by rigorously controlled high-temperature transformation of $Am(OH)_3(am)$. Optical viewing by scanning electron microscopy of $Nd(OH)_3(cr)$ samples at the end of the solubility experiments showed no changes in the crystal. The use of the americium-243 isotope diminished α-radiation damage of the crystal because of the lower specific activity (by a factor of 17) compared to americium-241. The limitation of this experiment was the relatively short time of equilibration—only 48 days. The following equilibrium constants for reaction 3-1 were reported:

$$\log_{10} K_{s,0} = 16.6 \pm 0.4$$
$$\log_{10} \beta_1 = -(7.7 \pm 0.3)$$
$$\log_{10} \beta_2 = -(16.7 \pm 0.7)$$
$$\log_{10} \beta_3 = -(25.0 \pm 0.3)$$
$$\log_{10} \beta_4 = -34.9$$

(3-3)

Similar values of hydrolysis for Nd(III) were derived from the $Nd(OH)_3(cr)$ solubility measurements.

Stadler and Kim (1988) investigated the pH dependence of $Am(OH)_3(s)$ solubility in 0.1 M $NaClO_4$ and more concentrated sodium chloride and perchlorate solutions at 25 ±0.5°C. The effect of α-induced radiolysis on solubility was also studied using different total concentrations of americium-241. The solid phase was not characterized in this work. Although the solid was different than that used by Silva (1982), the reported solubility products are in good agreement. It is unclear, however, if the same phase controls the americium solubility in the two cases because of the markedly different conditions used to prepare the starting solids. The results of the solubility measurements in this work are presented in Figure 3-3.
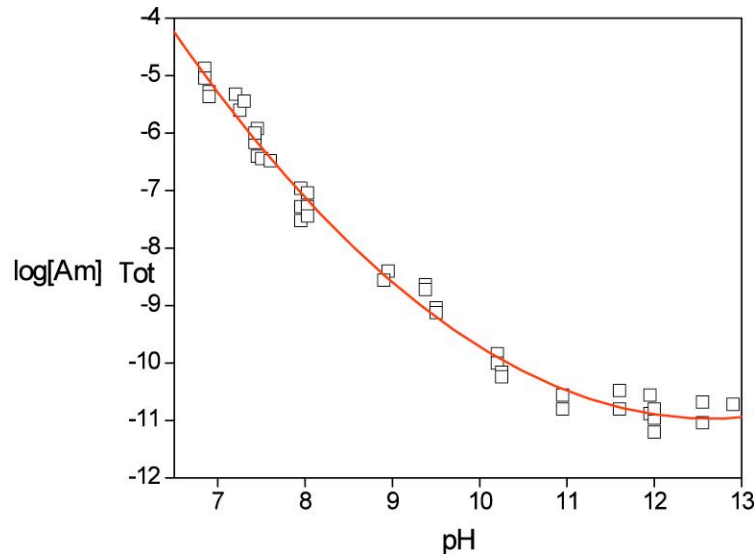
Figure 3-3.   Solubility measurements of Am(III) hydroxide based on data published by Kim et al. (1984).

3.2.2   Carbonate Complexation of Americium(III)

Americium complexation by carbonate has been investigated by solvent extraction, spectrophotometry, electromigration, and solubility (Kim et al. 1984; Robouch 1989; Felmy et al. 1990; Meinrath and Kim 1991; Nitsche et al. 1989). Several soluble species were proposed for the americium-water-carbonate system. These include carbonate, and/or bicarbonate, and/or mixed hydroxy-carbonate complexes. The literature data were carefully reviewed (Silva et al. 1995) and reinterpreted. The existence of $Am(CO_3)_n^{(3-2n)}$ with $n = 1, 2$, and 3 was proposed as the predominant species. There is no experimental evidence for the existence of a complex with $n = 4$, even at the highest carbonate concentrations. After the reinterpretation of literature data, Silva et al. (1995) found no evidence for the formation of Am(III)-bicarbonate or hydroxo-carbonate complexes in the solution. Some of the reported literature stability constants for various reactions are listed in Table 3-2.

Lundquist (1982) and Nitsche et al. (1989) showed, using two different CO_2 partial pressures, that bicarbonate complexes must be much weaker than reported by Bidolgio (1982); however, his conclusion that the predominant species is $Am(CO_3)_2^-$ at $8 \leq pH \leq 9$ and $-4.4 \leq \log_{10}[CO_3^{2-}] \leq -3$ is in agreement with the observations of other researchers.

Table 3-2.	Literature Equilibrium Constants for the Americium(III)-Carbonate-Water System	
$\log_{10}K$	Medium	Reference
$Am^{3+} + CO_3^{2-} \leftrightarrows AmCO_3^+$		
7.6	$I = 0$	(Felmy et al. 1990)
7.7 ±0.18	0.1 NaCl	(Giffaut and Vitorage 1993)
5.3 ±0.25	4 M NaCl	(Giffaut and Vitorage 1993)
$Am^{3+} + 2CO_3^{2-} \leftrightarrows Am(CO_3)_2^-$		
12.3	$I = 0$	(Felmy et al. 1990)
11.21 ±0.21	0.1 NaCl	(Giffaut and Vitorage 1993)
9.2 ±0.36	4 M NaCl	(Giffaut and Vitorage 1993)
8.92 ±0.15	3 M $NaClO_4$	(Robouch 1989)
9.27 ±2.2	0.1 – 0.3 M $NaClO_4$	(Kim et al. 1984)
$Am^{3+} + 3CO_3^{2-} \leftrightarrows Am(CO_3)_3^{3-}$		
15.2	$I = 0$	(Felmy et al. 1990)
12.8 ±0.25	0.1 NaCl	(Giffaut and Vitorage 1993)
11.4 ±0.25	4 M NaCl	(Giffaut and Vitorage 1993)
11.44 ±0.12	3 M $NaClO_4$	(Robouch 1989)

3.2.3   Solubility of Americium(III) in the Presence of Carbonate

Kim et al. (1984) measured the solubility of solid $Am(OH)_3(s)$ at $I = 0.1$ and 0.3 M $NaClO_4$, at $pCO_2 = 10^{-3.5}$ atm and interpreted their solubility data assuming the presence of hydroxy, carbonato, and mixed americium hydroxy-carbonato complexes. Several investigators have shown that changes of solid phase in aqueous suspensions of Am(III) hydroxide because of aging conditions become evident in hours and continue for weeks. No characterization of the solid was reported in this work, but it is likely $AmCO_3OH(s)$. The solubility data of americium(III) (reported in Kim et al. 1984) in the presence and absence of CO_2 are presented in Figure 3-4.
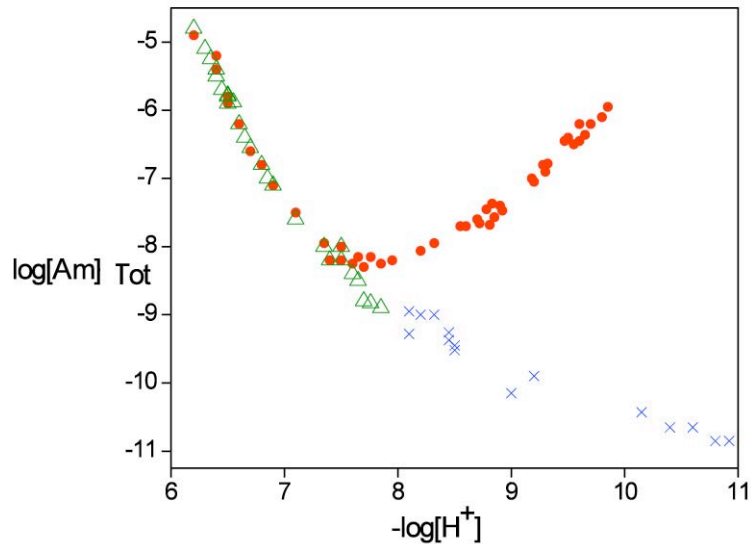
Figure 3-4.   Solubility of americium(III) (based on data published by Kim et al. 1984)
in the absence of CO_2(Δ at pH <8, and $\times$ at pH $\geq$ 8) and the presence of
CO_2 (•) in 0.1−0.3 M $NaClO_4$.

Similar work was reported by Felmy et al. (1990). These authors measured solubility of
$AmCO_3OH$(cr) at $p_{CO2} = 10^{-3}$ atm. The changes in total americium concentration measured in
this work as a function of pH are presented in Figure 3-5.

The effect of carbonate on the solubility of americium(III) was also studied by Meinrath and
Kim (1991). They measured solubility of $Am_2(CO_3)_3$(cr) for pH < 8 at I = 0.1 M $NaClO_4$ and for
pH $\geq$8 at I = 0.3 M $NaClO_4$ under a CO_2 partial pressure of 0.01 atm and 25°C. The results of
these measurements are presented in Figure 3-6.

Nitsche et al. (1994) measured the solubility of Am/Nd [(neodymium (III), as in many other
papers, as the analog of americium(III)] in modified UE-25p #1 groundwater from the Yucca
Mountain, Nevada, region at 60°C at three pH values (6, 7, and 8.5). Torretto et al. (1995)
measured the solubility of Am/Nd at the same pHs in a neutral electrolyte, 0.18 M $NaClO_4$,
containing a total carbonate concentration similar to Yucca Mountain groundwater at 25°C.
These experiments lasted over 300 days, and the final results of Am/Nd concentrations are
shown in Table 3-3. The solids from over- and undersaturation experiments were analyzed to be
a mixture of orthorhombic $NdOHCO_3$ and $Nd_2(CO_3)_3 \cdot 2H_2O$ with possibly varying water content.
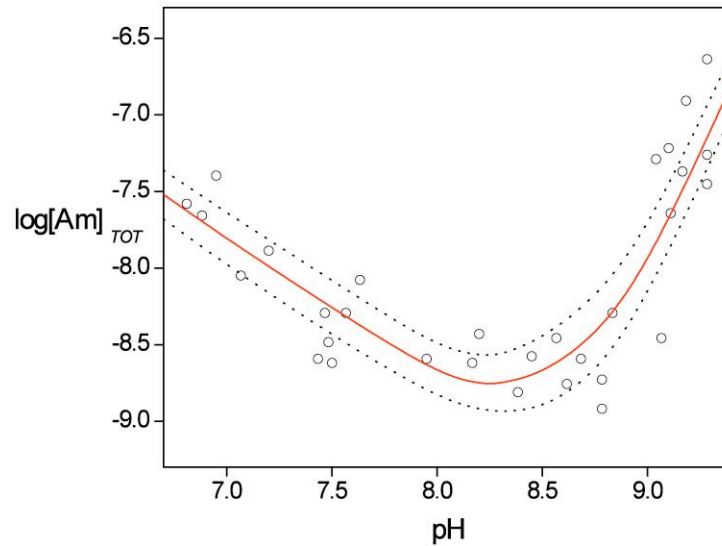
Figure 3-5.   Solubility of $AmCO_3OH(cr)$ as a function of pH (based on data from Felmy et al. 1990). The circles represent the experimental points; the continuous line represents the values calculated with the equilibrium constants given in Tables 3.1 and 3.2; and the dotted curves show the associated uncertainty of the calculation.
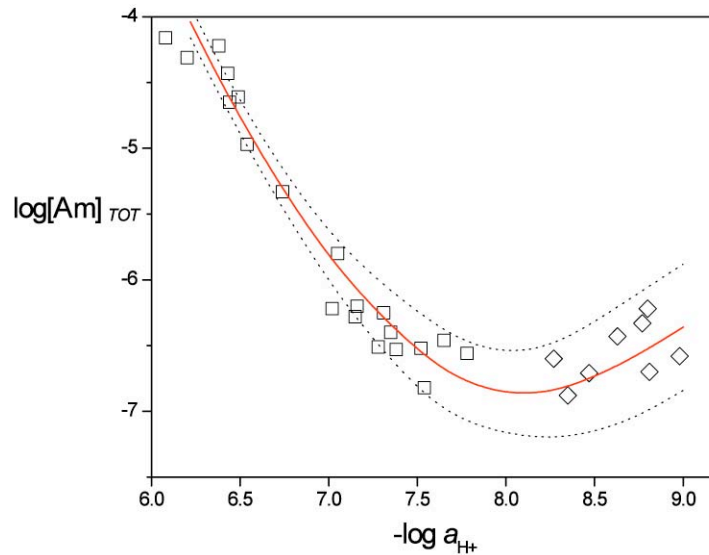
Figure 3-6.   Solubility of $Am_2(CO_3)_3(cr)$ as a function of pH (based on data published by Meinrath and Kim 1991).

Solubility of americium in groundwater and saline solution was modeled by Bruton (1995), and the results have been compared with those obtained by Bruno and Sellin (1992). They used equilibrium constants for hydrolysis and complexation reactions involving $AmCO_3^+$, $Am(CO_3)_2^-$, $AmOHCO_3(s)$, and other species from the GEMBOCHS database (version R16). The total

americium concentrations calculated by Bruton were about 2 to 3 times larger than those of Bruno and Sellin and were on the level of 10^{-7} M (~1.5 times greater in saline solution than in ground water) for Eh = 650 and –250 mV. Bruno and Sellin stated that aqueous speciation of americium is not affected by the salinity of the water. However, calculations with the GEMBOCHS database suggest that in fresh water, 100% of the americium is complexed by carbonate, but only about 50% is complexed by carbonate in saline waters.

Table 3-3.	**Results of Americium Solubility Measurements under Conditions Relevant to Yucca Mountain Groundwater (Torretto et al. 1995; Nitsche et al. 1995)**		
pH	Am(III) concentration (M)		
	Groundwater undersaturation exp.	Groundwater oversaturation exp.	0.18 M NaClO$_4$ oversaturation exp.
6	$(7.0 \pm 7.3) \times 10^{-10}$	$(2.7 \pm 0.4) \times 10^{-9}$	$(6.00 \pm 4.23) \times 10^{-6}$
7	$(4.6 \pm 2.0) \times 10^{-10}$	$(7.1 \pm 0.5) \times 10^{-10}$	$(3.04 \pm 1.44) \times 10^{-7}$
8.5	$(8.4 \pm 1.8) \times 10^{-11}$	$(7.8 \pm 4.3) \times 10^{-9}$	$(2.99 \pm 1.68) \times 10^{-10}$

4.0   WIPP-RELEVANT EXPERIMENTAL RESULTS: SOLUBILITY OF NEODYMIUM(III) IN BRINE

WIPP-relevant solubility data obtained since the CRA-2004 submittal for the solubility of +3 actinides are summarized in this section. All experiments were performed under the DOE-approved test plan "Solubility of Neodymium(III) in WIPP Brines," LCO-ACP-03. The resulting data establish the solubility of neodymium(III), as an analog for plutonium(III) and americium(III), in simulated WIPP brines over a broad range of pH and carbonate concentrations. Both under- and oversaturation approaches were used. As a consequence of these experimental results, we can define a more robust and repository-relevant understanding of the solubility of actinides in the +3 oxidation state.

4.1   Neodymium(III) as a Redox-Invariant Analog for Plutonium(III) and Americium(III)

The use of redox-invariant analogs for solubility studies is not always a straightforward argument since, ideally, the best data are obtained using the actual actinide of interest. The solubility and speciation of multivalent actinides (with plutonium as the best example of this) are best investigated by oxidation state analogy to eliminate the uncertainty of changes in the oxidation state during the experiment. This is especially true when trace-level concentrations are being considered and leads to a considerably simpler experimental design with far less ambiguity and uncertainty about the oxidation state distribution at the point of equilibration. Also, the nature of the solubility-controlling solid phases is more certain (Choppin 1999; CRA 2004, Attachment SOTERM).

For the two +3 actinides of interest to the WIPP (Pu^{3+} and Am^{3+}), neodymium, as Nd^{3+}, is probably the best choice for a redox-invariant analog. Lanthanides, in general, are excellent analogs for actinides because they possess f-electron physical and chemical characteristics that allow them to be used to study the chemical behavior of actinides. In the WIPP, the most important complexes are hard-donor (oxygen) ligands. The formation of complexes of these ligands with *f*-elements is due to the electrostatic attraction between the metal and the electron donating the functionality of the ligand molecule. Because of the similarity of ionic radii— Am(III) = 97.5 picometers (pm), Pu(III) = 100.0 pm, and Nd(III) = 98.3 pm for 6-coordinated species (Shannon 1976)—the magnitude of electrostatic attraction between metal ions and corresponding ligands is similar, yielding comparable thermodynamic stabilities.

This analogy would not hold for soft donors (e.g., nitrogen, sulfur, and thiocyanate). In these soft-ligand systems, a significant contribution of covalency to the metal-ligand bonding is observed, which results in so-called "covalent shortening." In such systems, the actinides have much smaller effective ionic radii than the corresponding lanthanides and would exhibit significantly different chemical behavior. This difference is the basis of the separation of lanthanides from actinides and yttrium (Moore 1964). In the WIPP, the key complexants that define solubility are carbonate, hydroxide, sulfate, borate, and chloride, which are all hard-donor complexants.

Lastly, neodymium exists primarily in the +3 oxidation state over a wide range of Eh and pH; therefore, there is no question about its oxidation state in the solid and liquid phases. There are no examples in the literature where other oxidation states of neodymium will be prevalent under groundwater or repository-relevant conditions.

Actinide (III) Solubility in WIPP Brine:
Data Summary and Recommendations

4.2   Experimental Goals and Test Matrices

Neodymium, as aqueous neodymium(III), was used as a redox-invariant analog for the solubility of americium(III) and plutonium(III) species in WIPP brine. The most important experimental goals of these solubility studies were the following:

- Verify and support WIPP PA calculations of the solubility of trivalent actinides at the current reference WIPP conditions using the Pitzer model in simulated brines that more realistically represent what is expected in the WIPP.

- Make more robust the current WIPP position on the +3 actinide solubility under WIPP-relevant conditions. More specifically,

    o   Establish the importance and relative contribution of hydrolysis and carbonate complexation over a broader range of pH. Specifically, when does hydrolysis begin to predominate over carbonate complexation?

    o   Establish the measured contribution of carbonate complexation to neodymium solubility in WIPP brines over a range of carbonate values in the WIPP.

    o   Confirm that the current WIPP PA model reflects +3 complexation trends in WIPP brine in that the contributions of all key complexants are included.

The Nd^{+3} test plan (LCO-ACP-03) consisted of the following four subtasks:

Subtask 1: Solubility of neodymium(III) using an oversaturation approach in carbonate-free WIPP brine (see Table 4-1 for the experimental matrix)

Subtask 2: Solubility of neodymium(III) using an oversaturation approach in carbonate-containing WIPP brine (see Table 4-2 for the experimental matrix)

Subtask 3: Solubility of neodymium(III) using an undersaturation approach in carbonate-free WIPP brine (see Table 4-3 for the experimental matrix)

Subtask 4: Solubility of neodymium(III) using an undersaturation approach in carbonate-containing WIPP brine (see Table 4-4 for the experimental matrix)

Table 4-1.	Experiment Designation and Conditions for the Neodymium(III) Solubility Determination in Brine from Oversaturation as a Function of pC_{H+} in a Carbonate-Free Environment (Subtask 1)		
Medium pC_{H+}	5 M NaCl	ERDA-6	GWB
~8.0	N8CF-x	E8CF-x	G8CF-x
~9.0	-	E9CF-x	G9CF-x
~10.0	N10CF-x	E10CF-x	G10CF-x
~12.0	N12CF-x	Not available	Not available

where x = 1, 2 denotes the numbering of replicate experiments.

Table 4-2.	Experiment Designation and Conditions for the Neodymium(III) Solubility Determination in Brine from Oversaturation as a Function of pC_{H+} and Carbonate Concentration (Subtask 2)								
Medium	5 M NaCl			ERDA-6			GWB		
Carbonate pC_{H+}	$\sim 10^{-3}$ M	$\sim 10^{-4}$ M	$\sim 10^{-5}$ M	$\sim 10^{-3}$ M	$\sim 10^{-4}$ M	$\sim 10^{-5}$ M	$\sim 10^{-3}$ M	$\sim 10^{-4}$ M	$\sim 10^{-5}$ M
~8.0	N8C1-x	N8C2-x	N8C3-x	E8C1-x	E8C2-x	E8C3-x	G8C1-x	G8C2-x	G8C3-x
~9.0	-	-	-	E9C1-x	E9C2-x	E9C3-x	G9C1-x	G9C2-x	G9C3-x
~10.0	N10C1-x	N10C2-x	N10C3-x	E10C1-x	E10C2-x	E10C3-x	G10C1-x	G10C2-x	G10C3-x
~12.0	N12C1-x	N12C2-x	N12C3-x	Not available	Not available	Not available	Not available	Not available	Not available

where x = 1, 2 denotes the numbering of replicate experiments.

Actinide (III) Solubility in WIPP Brine:
Data Summary and Recommendations

Table 4-3.	Experiment Designation and Conditions for the Neodymium(III) Solubility Determination in Brine from Undersaturation as a Function of pC_{H+} in a Carbonate-Free Environment (Subtask 3)		
Medium pC_{H+}	5 M NaCl	ERDA-6	GWB
~8.0	UN8CF-x	UE8CF-x	UG8CF-x
~9.0	-	UE9CF-x	UG9CF-x
~10.0	UN10CF-x	UE10CF-x	UG10CF-x
~12.0	UN12CF-x	Not available	Not available

where x = 1, 2 denotes the numbering of replicate experiments.

Table 4-4.	Experiment Designation and Conditions for the Neodymium(III) Solubility Determination in Brine from Undersaturation as a Function of pC_{H+} and Carbonate Concentration (Subtask 4)								
Medium	5 M NaCl			ERDA-6			GWB		
Carbonate pC_{H+}	~10^{-3} M	~10^{-4} M	~10^{-5} M	~10^{-3} M	~10^{-4} M	~10^{-5} M	~10^{-3} M	~10^{-4} M	~10^{-5} M
~8.0	UN8C1-x	UN8C2-x	UN8C3-x	UE8C1-x	UE8C2-x	UE8C3-x	UG8C1-x	UG8C2-x	UG8C3-x
~9.0	-	-	-	UE9C1-x	UE9C2-x	UE9C3-x	UG9C1-x	UG9C2-x	UG9C3-x
~10.0	UN10C1-x	UN10C2-x	UN10C3-x	UE10C1-x	UE10C2-x	UE10C3-x	UG10C1-x	UG10C2-x	UG10C3-x
~12.0	UN12C1-x	UN12C2-x	UN12C3-x	Not available	Not available	Not available	Not available	Not available	Not available

where x = 1, 2 denotes the numbering of replicate experiments.

Actinide (III) Solubility in WIPP Brine:
Data Summary and Recommendations

4.3 Experimental Approach, Limitations, and Error Analysis

4.3.1 Experimental Approach

The solubility of neodymium(III) [as an oxidation-state invariant analog for plutonium(III) and americium(III)] was measured as a function of pC_{H+} and carbonate concentration in 5 M NaCl, GWB, and ERDA-6 brine using both an over- and undersaturation approach. The general conditions of these studies were as follows:

- pC_{H+} between 6.5 and 10.5

- carbonate-free to 0.01 M carbonate concentrations

- temperature of 25 ± 3°C

Determining the solubility of any species in a complicated matrix such as WIPP brine is not straightforward. The Nd(III) solubility was measured from over- and undersaturation as described by Nitsche et al. (1995) and Torretto et al. (1995). The oversaturation approach consists of sequentially adding dissolved neodymium until precipitation and steady neodymium concentration are observed. Subsequently, the neodymium concentration was monitored until steady-state concentrations were achieved. A stock solution of 10^{-2} M neodymium at pH~4 (in dilute hydrochloric acid) was used as the spike in the oversaturation approach. After the first addition, the initial neodymium concentration in the brine was 5×10^{-5} M. The amount of precipitates generated in this approach was very small, so solids that were either synthesized or procured (when available) were used as the source solid phase to establish the solubility from undersaturation.

The experimental approach used in the neodymium solubility experiments was as follows:

1) Two simulated brines (GWB and ERDA-6) and one simplified brine (5 M NaCl) were prepared according to procedure ACP-EXP-001. These were at 95% of saturation to prevent salt precipitation during the solubility experiments.

2) The pH of the brine was varied as a parameter. The pC_{H+} in brines was determined according to procedure ACP-EXP-010: "Determination of Hydrogen Ion Concentration in Brines."

3) The stock solution was prepared by the dissolution of high-purity neodymium chloride at pH ~ 4.

4) All atmospheric-controlled experiments were performed in a controlled-atmosphere glove box to eliminate carbon dioxide from the system. The gas-phase environment was monitored throughout the experiment by a gas analyzer.

5) Carbonate concentration and pC_{H+} were expected to be the most important parameters that define the solubility of neodymium (III). Carbonate was added to the brine directly (i.e., not by equilibration with a carbon dioxide gas) as a spike.

6) Throughout the solubility experiments, the neodymium concentration was analyzed by inductively coupled plasma mass spectroscopy (ICP-MS) to establish the steady-state concentration as a function of time and as a function of the size distribution in the brine that was established by sequential filtration (0.22 μm, ~30 nm, and ~ 5 nm).

7) The sequential addition of neodymium led to its precipitation as a solid. Because of the

low solubility ($\sim10^{-9}$-10^{-7} M) of neodymium(III), the amount of precipitate generated was not enough to perform the undersaturation experiments.

8) The solid phases, such as $Nd(OH)_3$, $Nd_2(CO_3)_3$, or mixed $NdOH(CO_3)$ (commercially available or prepared individually), were used for the undersaturated experiments.

A more detailed description of key aspects of the experimental approach is provided in the following sections:

Removal and Addition of Carbonate in the Brine Studies

Significant care was taken to remove carbonate from the brines to perform the carbonate-free experiments. The brine solution was acidified to $pC_{H+} \sim$ 3-4 and bubbled with high-purity nitrogen to remove residual air. This deaerated brine was placed in a pump-down box to evacuate/remove all dissolved gases and subsequently was transferred to a nitrogen glovebox with an anoxic, carbonate-free atmosphere, which was controlled for the duration of the experiment. The desired pC_{H+} was established in each solution by the addition of carbonate-free sodium hydroxide and/or hydrochloric acid. A carbonate-free neodymium stock solution was added in the carbonate-free brine as a spike to initiate the oversaturation solubility experiments. The corresponding neodymium undersaturation, carbonate-free experiments were initiated by adding a commercially available solid hydroxide to the brine, and solid was contacted with simulated brine under controlled conditions (nitrogen glovebox) until a steady-state neodymium concentration was achieved.

The effect of carbonate was investigated in similar systems. Carbonate was added to the carbonate-free brines as a dissolved carbonate spike, rather than equilibration with a carbon dioxide partial pressure. Experiments were maintained in gas-tight polypropylene bottles to prevent the loss of carbon dioxide because of outgassing. The effect of carbonate was determined at four carbonate concentrations: 10^{-2}, 10^{-3}, 10^{-4}, and 10^{-5} M. The corresponding undersaturation experiments were performed using a mixed neodymium 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 200 to 350 days. The total neodymium concentrations were determined by ICP-MS (Elan 6000) after the filtration of each sample with 30,000 Dalton cutoff centrifuge filters (Millipore Microcon). The precipitates, when possible, were recovered and analyzed, using x-ray absorption near edge spectroscopy (XANES) and extended x-ray absorption fine structure (EXAFS), at the Advance Photon Source at Argonne National Laboratory to try to obtain structural and phase information.

Preparation of the NdCO₃OH Solid

A mixed hydroxy carbonate phase of neodymium was expected to be the predominant phase in WIPP brine when carbonate was present at high pH. For the undersaturation studies, this solid was prepared by adding a solution containing 4.6 mM neodymium chloride to a 50 mL solution consisting of 5.0 mM sodium carbonate and 5.7 mM sodium hydroxide. This was done slowly with continuous stirring. After the addition was complete, the solution was heated to 80°C and kept for one hour. This solution with the solid was transferred to a centrifuge vial and centrifuged for 15 minutes. The supernatant was decanted, and the solid was washed and

recentrifuged three times with high-purity water. The pH of the final wash was 9.2. The recovered solid was dried in a glass beaker at 105°C overnight. The mass of solid recovered was 1.011 g, corresponding to a synthetic yield (based on $NdCO_3OH$) of 99.3%. This solid, as well as the other neodymium solids used, was analyzed using the x-ray diffraction (XRD) technique on our Bruker XRD (see Figure 4-1). Analysis of the characteristic lines confirmed the predominance of a neodymium mixed hydroxy-carbonate phase. This solid was subsequently used in the undersaturation experiments when carbonate was present.

Sequential Filtration

Sequential filtration was performed for all of the neodymium brine systems investigated to establish the extent that a neodymium suspension or colloid might be present. The presence of suspended neodymium, which would not be a "truly" dissolved solid, is a key consideration for WIPP PA and could interfere with our neodymium concentration measurements. In this context, the neodymium concentrations were measured in unfiltered brine solution and in brine solution filtered using filters of three pore sizes: 0.22 µm, 100,000 nominal molecular weight limit (~ 30 nm), and 30,000 nominal molecular weight limit (~ 5 nm). Six randomly chosen samples of 5 M NaCl, GWB, and ERDA-6 brine, equilibrated with neodymium from over- and undersaturation, were tested. The results of these measurements are presented in Figure 4-2.

All the neodymium concentrations determined in filtered samples and unfiltered samples (with one exception) were in good agreement and within experimental error. This indicates that colloids or a fine particle suspension were not formed during the solubility experiments. The solids formed were crystalline with a readily filterable grain size. This was consistent with our observations when the solids were recovered for characterization. Only one data point for ERDA-6 brine in an unfiltered sample [note circled point in Figure 4-2(A)] had a higher neodymium concentration. This data point corresponds to an unfiltered sample, where it is likely that a small grain of suspended solid was taken with the solution because of sample perturbation during the sampling process.
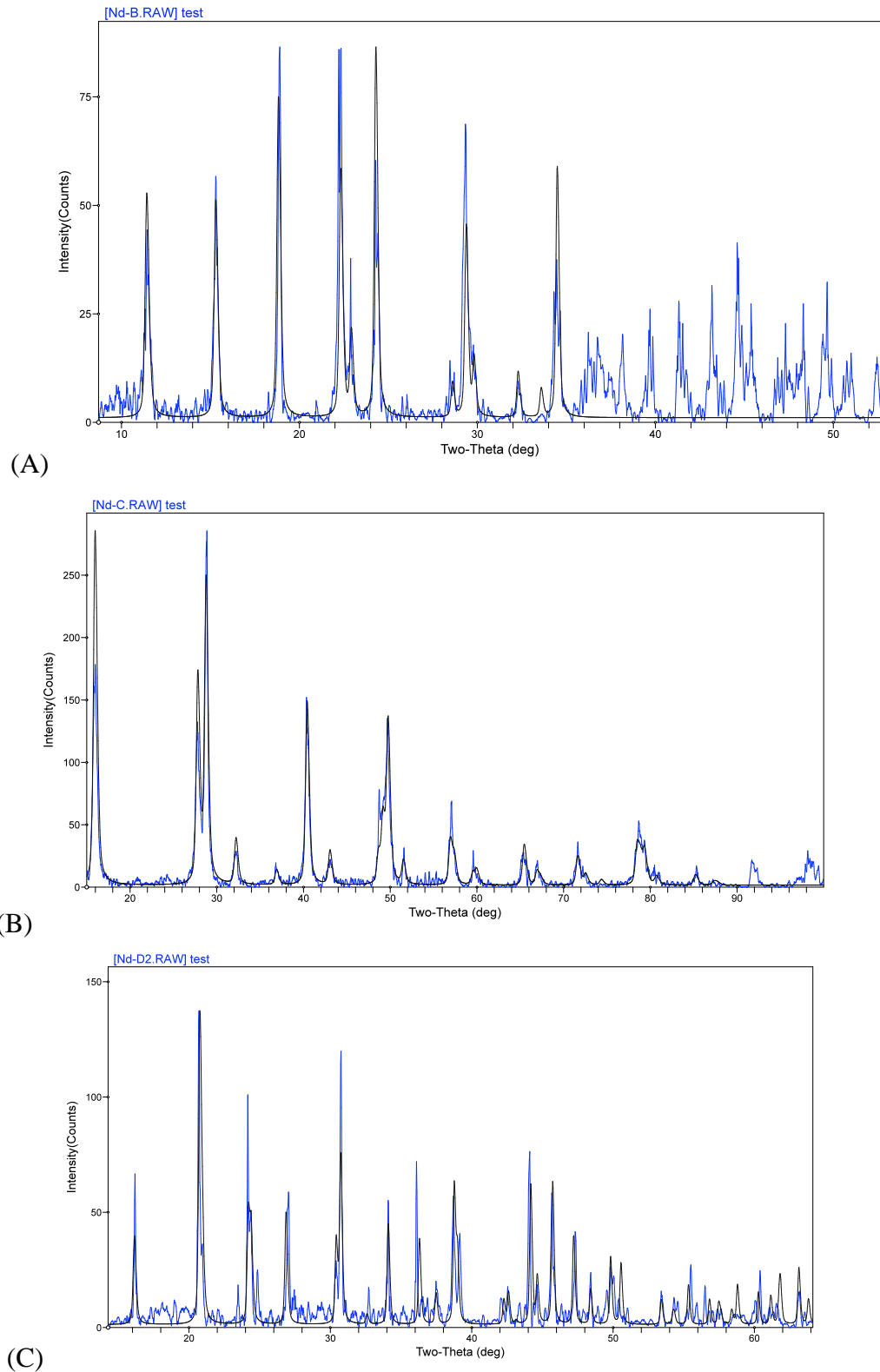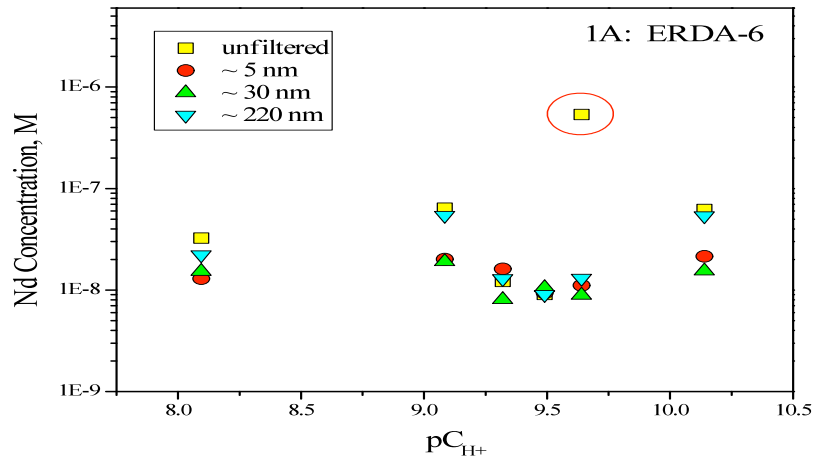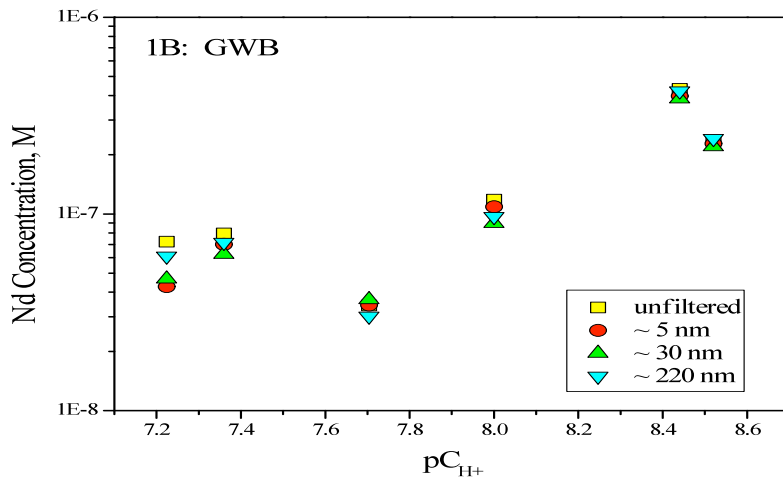
Figure 4-1.   XRD analysis of neodymium hydroxide solid (A - top), hydrated neodymium carbonate solid (B - middle), and the in-lab synthesized mixed hydroxy-carbonate phase (C - bottom).
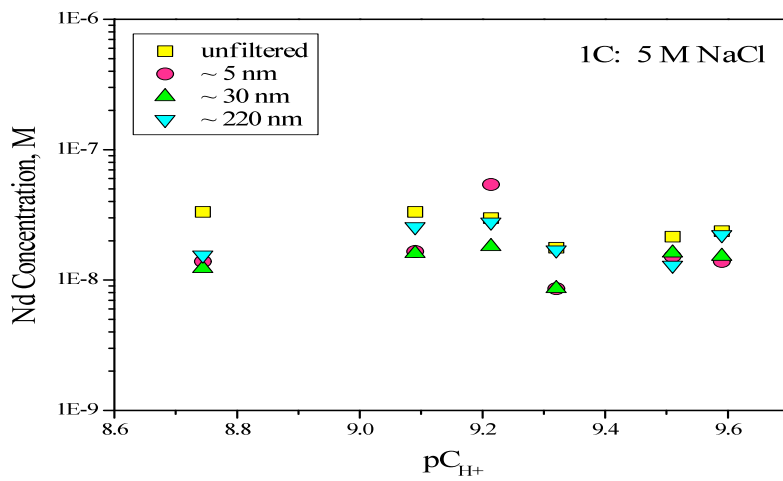
(A)

(B)

(C)

Figure 4-2.   Results of sequential filtration of neodymium samples in ERDA-6 brine
            (A), GWB (B), and 5 M NaCl (C).

Actinide (III) Solubility in WIPP Brine:
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4.3.2 Experimental Limitations

There were a number of limitations on the experiments performed. The most important of these are described in the following sections:

pC_{H+} range

Two simulated WIPP brines were used in our studies. These brines were based on a high-magnesium GWB and a low-magnesium ERDA-6 brine. The composition and key properties of these simulated brines are given in Table 4-5.

Table 4-5.   Composition and Density of GWB and ERDA-6 Simulated WIPP Brines

Component	GWB	ERDA-6 brine
	(M)	(M)
NaCl	2.874	4.254
$MgCl_2$	0.953	0.018
Na_2SO_4	0.166	0.159
NaBr	0.025	0.010
$Na_2B_4O_7$	0.037	0.015
KCl	0.437	0.092
$CaCl_2$	0.013	0.011
LiCl	0.004	-
Density g/mL	1.216	1.183

In high ionic strength media, where activity coefficients of species are often not well known, the measurement of pH (logarithm of hydrogen ion activity) is not straightforward. In these media, the pH reading of a glass combination electrode calibrated with low ionic strength pH buffers can be related to the hydrogen ion concentration, pC_{H+}. According to our measurements, the relationship between the pH reading and pC_{H+} is, to a good approximation, a linear function of the ionic strength (see Figure 4-3). In this context, the following empirical formula was used to calculate the hydrogen ion concentration using pH reading:

$$pC_{H+} = pH \ reading + K, \hspace{3cm} 4\text{-}1$$

where K is a brine-specific constant. The values of K obtained for the three brines investigated were: 0.82 ± 0.03 for 5 M NaCl, 0.94 ± 0.02 for ERDA-6, and 1.23 ± 0.01 for GWB. This experimental approach to measure pC_{H+} in the brine systems established a reproducible electrode-independent approach that can be consistently compared over time. The theoretically calculated pH in terms of hydrogen activity, however, is estimated to be ~0.5 pH units lower that the measured pC_{H+} (H^+ concentration in M). In this context, a measured pC_{H+} of 9.0 correlates to a calculated pH of 8.5.
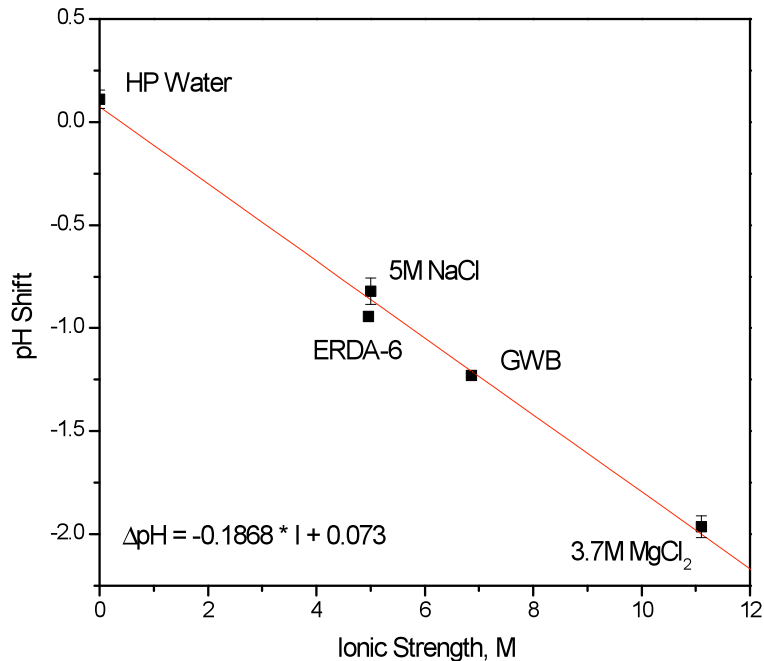
Figure 4-3.   Correlation between the pH adjustment and ionic strength of the brine to determine the pC_{H+}. A good linear fit was found with a correlation factor of 0.997. We established that the values of the pH adjustment may be obtained by multiplying the ionic strength in molar units by 0.1868 ± 0.0082. The value of the slope is in good agreement with those reported by Rai et al. (1995).

Both brines, GWB and EDRA-6, contain significant amounts of magnesium and calcium cations. Magnesium and calcium form hydroxides at higher pH that are poorly soluble in water. Each brine, GWB and EDRA-6, was titrated with either sodium hydroxide or hydrochloric acid. The goal of the titration with sodium hydroxide was to determine the cloud point at which precipitates were observed leading to a change in the brine composition. During titration with the base, a cloud point was observed at $pC_{H+} = 8.7$ in GWB brine and at $pC_{H+} = 10.8$ in ERDA-6 brine. During the titration with acid, the jump in pH was observed at $pC_{H+} \sim 5.5$ in both brines and was assigned to the end point of borate titration. A good correlation was found between the amount of acid added and the concentration of borate in the brine. The operational pC_{H+} range established was 6.0 to 8.7 for GWB, and 7.0 to 10.8 for ERDA-6 brine.

Limitations in Carbonate Concentration

Carbon dioxide is generated in the WIPP as the result of microbial degradation of coexisting organic waste. This carbon dioxide will potentially dissolve in brine and react with the engineered barrier, MgO, to form an insoluble magnesium carbonate. Calcium and iron(II) are also present in the WIPP and will form insoluble carbonates. The key thermodynamic solubility terms (NIST Database 2004) for these reactions are: $\log K_s = -10.8$ for ferrous carbonate, $\log K_s = -8.48$ for calcite, and $\log K_s = -7.46$ for magnesium carbonate ($\log K_s = -4.6$ for hydrous

magnesium carbonate). The formation of these insoluble carbonates will define the concentration of carbonate in the brine. To experimentally establish this concentration, we titrated each brine with sodium carbonate. For both brines, GWB and ERDA-6, significant carbonate precipitation was observed when the concentration of sodium carbonate was increased above 4×10^{-2} M. This carbonate concentration defined our operational limit in our brine experiments.

Limitations in the Detection of Neodymium Using ICP-MS

The concentration of neodymium in all of the solubility experiments was determined using ICP-MS (Elan 6000). To obtain good consistency and account for matrix effects, an internal standard (indium-115) was used in these analyses. The range of recovery for this standard recommended by the manufacturer was 40% to 125%. To accomplish this requirement, we had to dilute each brine solution by a factor of 100 to get a recovery within the recommended range. This dilution also helped to avoid the plugging of the capillary tubing and nebulizer during the analysis. High-purity nitric acid (99.9999% purity, Alfa Aesar) and water (18 M-ohm) was used to dilute the brine samples to ~0.5% nitric acid for ICP-MS analysis. The actual detectivity of the ICP-MS to neodymium concentration under these conditions was ~4×10^{-11} M. This led to an effective detectivity of ~4×10^{-9} M in the brines because of the necessary dilutions made in sample preparations.

4.3.3 Experimental Error Analysis

The neodymium concentration, as a function of the several parameters investigated, was the final result of all of the measurements made in these solubility studies. This number was derived from a number of measurements that are potential sources of error. The biggest contribution to the uncertainty in the neodymium concentration determination was ICP-MS analysis. This was especially true when the neodymium concentrations measured approached our detection limit. Systematic error was present in these analyses because of a small neodymium impurity found in the super-pure nitric acid used for ICP-MS sample preparations. This error increased neodymium concentration by approximately 100% at the detection limit (4×10^{-9} M)—about 40% at 10^{-8} M and about 4% at 10^{-7} M neodymium. The linearity of the mass spectrometric measurements was checked using 10 samples and was always equal to or better than 0.9999 in the range of neodymium concentrations from 0.5 ppb to 200 ppb.

To monitor the reproducibility of ICP-MS analysis over time, neodymium secondary standards were reanalyzed. During the nine-month duration of the experiments, the secondary standard solution N1 had an average neodymium concentration of 9.83×10^{-6} M with a standard deviation ±4.53%; the secondary standard solution N2 had an average neodymium concentration of 1.03×10^{-6} M with a standard deviation of ±3.91%; and the secondary standard solution N3 had an average neodymium concentration that was equal to 2.93×10^{-7} M with a standard deviation ±3.80%. The experimental error attributed to pipeting and weighing was approximately 1% for each operation. Because of the high ionic strength, each sample was 100-fold diluted, and this operation contributed about 10% to the error in the ICP-MS analysis.

Given these sources of uncertainty, the overall uncertainty in the neodymium concentration determination was estimated to be 15% at 10^{-6} M, 25% at 10^{-7} M, 50% at 10^{-8} M, and 100% for neodymium concentrations below 7×10^{-8} M. The pC$_{H+}$ was measured with the precision of

0.05 pH units. These errors, although present, are not included in the graphs in order to preserve their clarity.

4.4   Results and Discussion

4.4.1   Solubility of Neodymium(III) in 5 M Sodium Chloride

The solubility of neodymium(III) in 5 M NaCl, which is a simplified WIPP brine, was done to establish the effects of brine constituents on brine solubility and link to existing literature data in this medium. Carbonate-free experiments provided baseline data for the effects of carbonate complexation on solubility. Carbonate was carefully removed from the brine. The brine was then placed in a nitrogen glove box, and the atmosphere was controlled for the duration of the experiment. Five M NaCl has no limitation in respect to the pC_{H+} used; however, it does not have any buffering capacity, and pC_{H+} could not be easily controlled. In the carbonate-free system, pC_{H+} was relatively stable. The samples were equilibrated over 330 days. The results of the last two samplings in the carbonate free system after 300 days of equilibration are presented in Figure 4-4. The data points determined from over- and undersaturation overlap well and indicated that a steady-state neodymium concentration, as a function of pC_{H+}, was achieved. The literature data used by Giambalvo for the model correction (Giambalvo 2003) are placed in the graph for comparison, and they are in very good agreement with the data measured in the present work. For $pC_{H+}>11$, the literature data are lower than measured in the present work.

Measurements of neodymium(III) solubility in 5 M NaCl containing various carbonate concentrations as a function of pC_{H+} were more complex than in carbonate-free systems. Sodium chloride solution does not have a significant pH buffer capacity. The addition of sodium carbonate solutions, which are basic, to 5 M NaCl solution caused a slow drift in the pH after initial adjustment. Over time, the pC_{H+} was defined by the carbonate concentration added. In all cases, after eight months of equilibration, the final pC_{H+} was close to 9.5.

The effect of carbonate on neodymium solubility was studied in 5 M NaCl solution using four total carbonate concentrations: 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 added as a spike in the oversaturation approach. The initial neodymium concentration was equal to 5×10^{-5} M. After 200 days of equilibration, a second neodymium concentration spike was added to each oversaturation experiment. In the undersaturation experiments, $NdCO_3OH$ (prepared in our laboratory) was used as a solid phase. Solutions were periodically sampled and filtered, and the neodymium concentrations were measured from over- and undersaturation as a function of pC_{H+} and carbonate concentration in a 5 M NaCl solution.
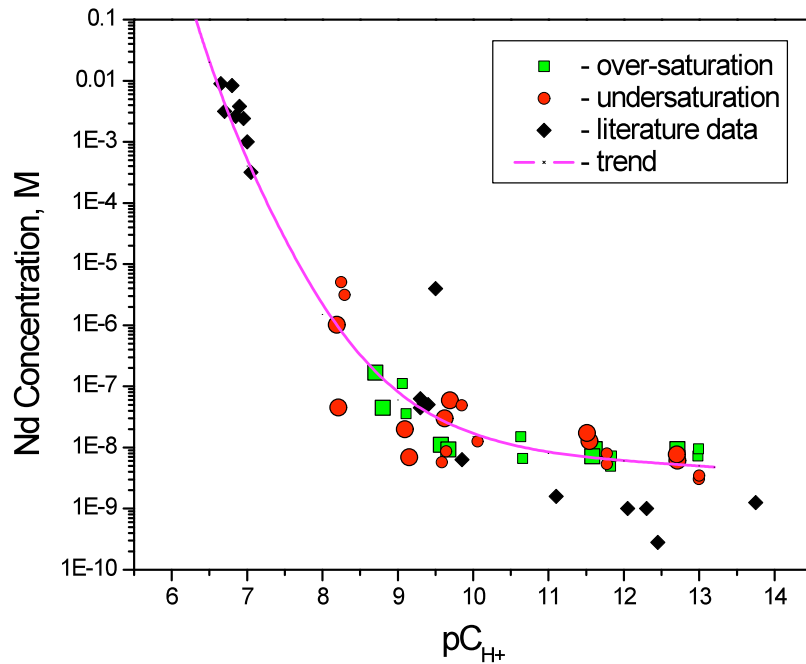
Figure 4-4.   Neodymium(III) solubility in carbonate-free 5 M NaCl as a function of pC_{H+}. Data points: ● - undersaturation experiments; ■ - oversaturation experiments; ♦ - literature data used by Giambalvo for the model correction (Giambalvo 2003).

The concentration of neodymium as a function of time in the presence of various carbonate concentrations is shown in Figure 4-5. In many cases, these data were overlapping. The plot for a particular carbonate concentration could not be distinguished; therefore, the same statistical weight was assumed for each point. The neodymium concentrations determined from an oversaturation approach were similar to those determined from undersaturation. The pC_{H+} in this system was difficult to control because of the lack of buffering capacity in 5 M NaCl. Other than this complexity, however, the data collected were acceptable. The results in Figure 4-5 show significant differences from those shown in Figure 4-4 (in the absence of carbonate). The increase in neodymium concentration for $9 < pC_{H+} < 10$ is consistent with what is reported in the literature. It is important to note that at $pC_{H+} > 10$, a further decrease in the neodymium concentration was noted in 5 M NaCl. This decrease was due to the predominance of hydrolysis over carbonate complexation. This observation benefits the WIPP because it extends current data to a pH range that is higher than the current reference case, and there is some possibility under repository-relevant conditions that a higher pC_{H+} can exist as a transient condition (e.g., should CaO present in MgO preferentially dissolve during the initial phase of brine equilibration with the engineered barrier). Our results show that at this higher pC_{H+}, the neodymium +3 (and by analogy, +3 actinides) have a lower, not higher, solubility, and there is no evidence of amphoteric behavior.
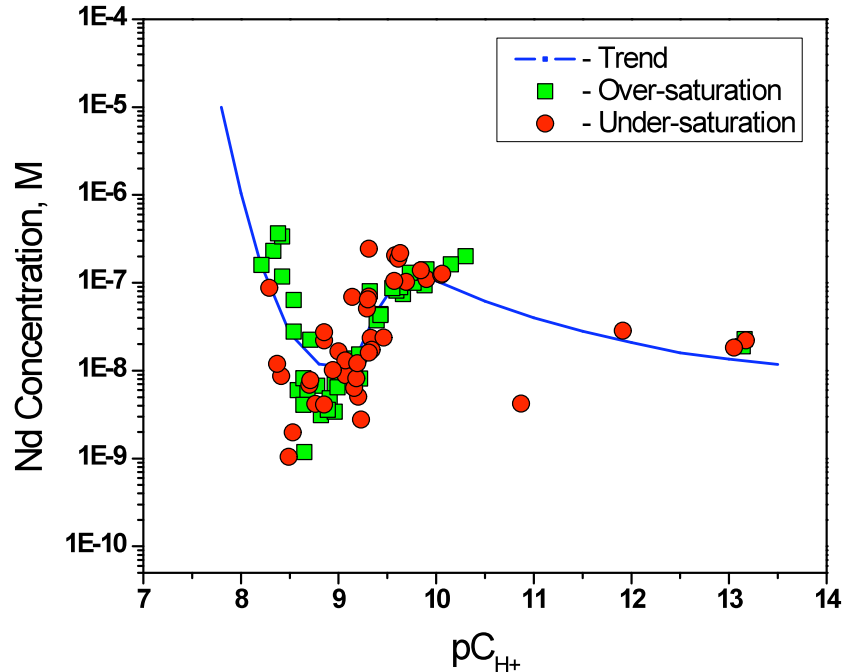
Figure 4-5. Neodymium(III) solubility in 5 M NaCl measured in the presence of carbonate as a function of pC_{H+}. Data points in which the pC_{H+} was initially adjusted to cover the broad range of pC_{H+} investigated were suppressed. A shoulder with a maximum at pC_{H+} ~10 is due to the formation of a carbonate complex with neodymium.

These results also compare favorably with those reported by others in the literature (section 3.2) for americium. Kim et al. (1984) measured the solubility of $Am(OH)_3(s)$ at I = 0.1 and 0.3 M $NaClO_4$, in the absence of CO_2 and at $pCO_2 = 10^{-3.5}$ atm and attributed the solubility measured in terms of contributions from the hydroxy, carbonato, and mixed americium hydroxy-carbonato complexes. The solubility data of americium(III) reported by Kim et al. (1984) in the absence and presence of CO_2 are presented in Figure 3-4. No characterization of the solid was reported in this work, but it was assumed to be $AmCO_3OH(s)$. It was found by several investigators that changes in the solid phase in aqueous suspensions of Am(III) hydroxide because of aging conditions become evident in hours and continue for weeks. Similar work was reported by Felmy et al. (1990). These authors measured the solubility of $AmCO_3OH(cr)$ at $pCO_2 = 10^{-3}$ atm. The change in total americium concentration measured in this work as a function of pH was similar to that reported by Kim et al. and also similar to the plot in the present work (Figure 4-4); however, neodymium concentrations for the corresponding pC_{H+} in the present work are 2 to 3 orders of magnitude greater due to the higher ionic strength present.

Data reported by Kim et al. clearly indicate that up to pC_{H+} ~ 7.5 – 8.0, the carbonate complexation does not affect the solubility of americium(III). For the higher pC_{H+}, the presence of carbonate in 0.1−0.3 M $NaClO_4$ increases the solubility of americium(III) relative to carbonate-free systems, and at pC_{H+} ~10, this difference is equal to almost 4 orders of magnitude. For pC_{H+} greater than 10, there are no solubility data in the presence of carbonate. The pC_{H+} range of 7.5 to 10 is where carbonate effects are expected to predominate relative to hydroxide

because of the pK_a of carbonic acid. For higher pC_{H+}, hydroxide effects prevail over the carbonate effects.

4.4.2   Solubility of Neodymium(III) in GWB and ERDA-6 WIPP Brines

The composition of GWB is most typical of the brine composition expected in the WIPP after equilibration and reaction with emplaced MgO. In the undersaturation experiment, the GWB and ERDA-6 brine were equilibrated with neodymium solids for approximately 350 days. Total experiment duration in the oversaturation experiments was even longer (a total of 450 days) and was divided into two neodymium additions. The first neodymium addition was equilibrated for 210 days, with the second neodymium addition equilibrated for an additional 240 days. During these experiments, the brine was periodically sampled to check pC_{H+} and measure the neodymium concentration.

There are some important differences in the experimental approach between GWB and ERDA-6 brines and 5 M NaCl. In contrast to 5 M NaCl, GWB and ERDA-6 brines have a high buffer capacity; therefore, the initial adjustment to the desired pC_{H+} was very stable and did not change throughout the experiment. Typical pC_{H+} profiles, as a function of time, in the oversaturation experiments are shown in Figure 4-6. A small decrease in the pC_{H+} was noted immediately after the second neodymium addition, but, in time, the pC_{H+} returned to the initially adjusted value. Overall, in GWB and ERDA-6 brine, the pC_{H+} was within $\pm$ 0.1 pC_{H+} units throughout the entire experiment (450 days).

Time profiles of the neodymium concentration in the over- and undersaturation experiments are shown in Figure 4-7. In the undersaturation experiment data presented in Figure 4-7(A), there are two features of interest to point out. First, the concentration of neodymium was much higher initially than that observed at the end of the experiment. In these experiments, we had, in fact, expected to see a dissolution process that slowly approached the neodymium(III) solubility limit. The observed trend, however, indicated that the solid used in these experiments (neodymium hydroxy-carbonate) is not the solid that eventually defined the neodymium solubility. The hydroxy-carbonate phase is more soluble, leading to the initially high concentrations. The second feature is that the time of equilibration (flat area of the curve) was over 170 days. For the samples UG6C3-1 and UG9C2-2, a slightly decreasing neodymium(III) concentration was noted even after 350 days of equilibration. This decrease, however, is so small that it may be within experimental error. The equilibration in GWB and ERDA-6 brine in the oversaturation experiments [as shown in Figure 4-7(B)] had a completely different trend. The highest change in concentration was observed during the first 30 days after the addition of neodymium to the brine. In these systems, steady-state concentrations were observed in about 100 days. After each of the two additions, the final neodymium concentration was the same.
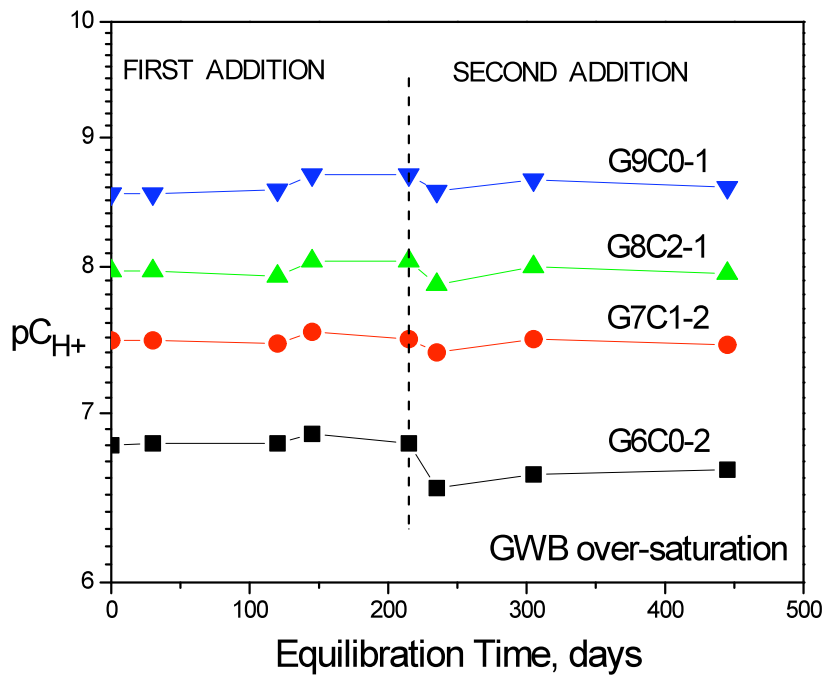
Figure 4-6.   Change in pC_{H+} for GWB as a function of time in the oversaturation experiments.

The solubility data determined from over- and undersaturation as a function of pC_{H+} for various carbonate concentrations and in the absence of carbonate in GWB and ERDA-6 brine are shown in Figures 4-8, 4-9, 4-10, and 4-11.

The results of the over- and undersaturation experiments for GWB (shown in Figures 4-8 and 4-9) are essentially the same, which indicates that steady-state concentrations were achieved in these experiments. The solubility of neodymium measured in GWB as a function of pC_{H+} with variable carbonate concentration shows very little dependence on the carbonate concentration. The decrease in neodymium concentration observed up to $pC_{H+} = 7.5$ was similar to that observed in the 5 M NaCl system. At $pC_{H+} > 7.5$, a further increase in the neodymium concentration was observed. This increase was independent of carbonate concentration and was due to complexation of the neodymium with a GWB component.

The neodymium concentrations measured in the over- and undersaturation experiments for ERDA-6 brine (shown in Figures 4-10 and 4-11) are very close each other, indicating that steady-state concentrations in these experiments were achieved. The solubilities of neodymium measured in ERDA-6 brine as a function of pC_{H+} containing various carbonate concentrations and in the carbonate-free experiments exhibit, to a good approximation, the same dependence. This is analogous to what was seen in the GWB experiments.
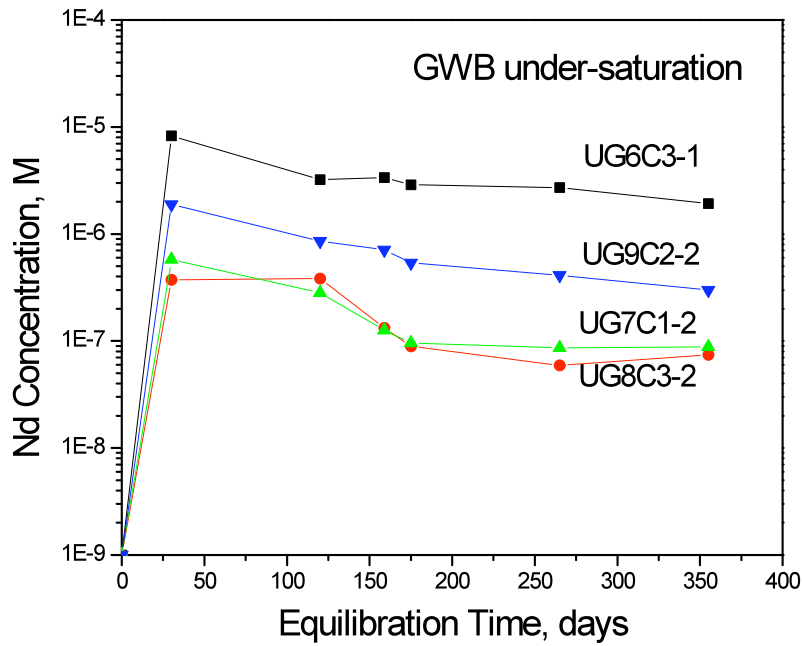
(A)
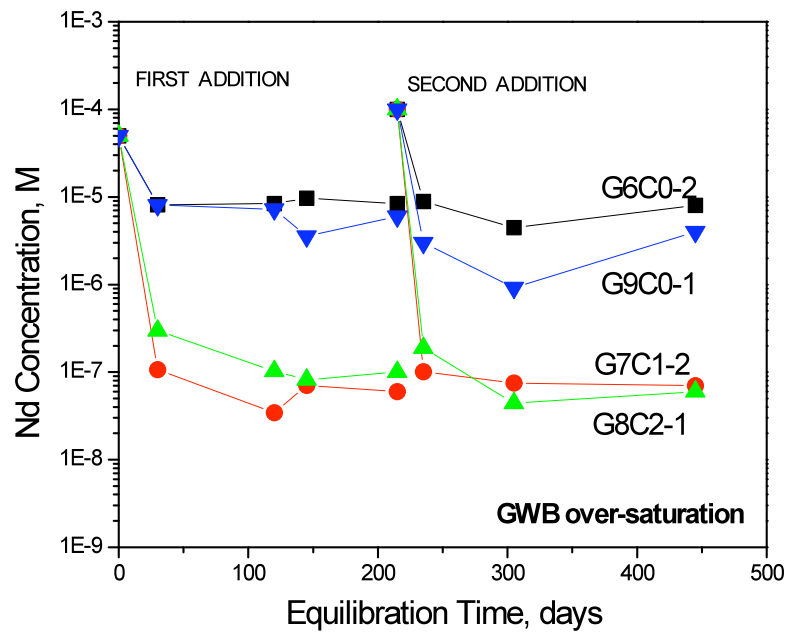
(B)

Figure 4-7.　　Neodymium concentration in GWB as a function of time in the undersaturation experiments (A) and oversaturation experiments (B).

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The effect of carbonate concentration on neodymium solubility was negligible under all conditions investigated. The neodymium concentration initially decreased to an observed minimum at pC_{H+} = 8.3. Increased pC_{H+} values showed a "hump" in the solubility profile, with a maximum at pC_{H+} = 9.7, and a further decrease in neodymium concentration with increased pC_{H+}. We believe that this solubility profile is due to complexation with borate. Boric acid is the only brine component that has a pK_a value in this pC_{H+} region. As reported in the literature, the pK_a value of boric acid at I = 5.0 M is 9.02 (NIST Database 2004). In comparison, the pK_a of carbonic acid at I = 5.0 M is 9.67. For the highest concentration of carbonate used in our experiments, the concentration of free borate ion was ~10 fold higher. Stability constants for the neodymium-borate complex are not available in the literature, which makes it difficult to compare the effect of this complexant to carbonate complexation. In GWB, because of the limitation in the range of pC_{H+} we could investigate, we only saw an increasing slope above pC_{H+} = 7.5. The expectation is that this trend will reverse itself at higher pC_{H+} because hydrolysis effects will predominate. The overall solubility trend is consistent with that observed in ERDA-6, where this same "hump" probably existed but could not be measured because of limitations in the range of pC_{H+} that we could investigate.

The neodymium solubility measured in ERDA-6 brine was lower than in GWB but higher than that measured in 5 M NaCl solution for comparable pC_{H+} and carbonate levels. This is explained by the differences in hydroxyl ion activity and borate concentrations in the three brine systems.
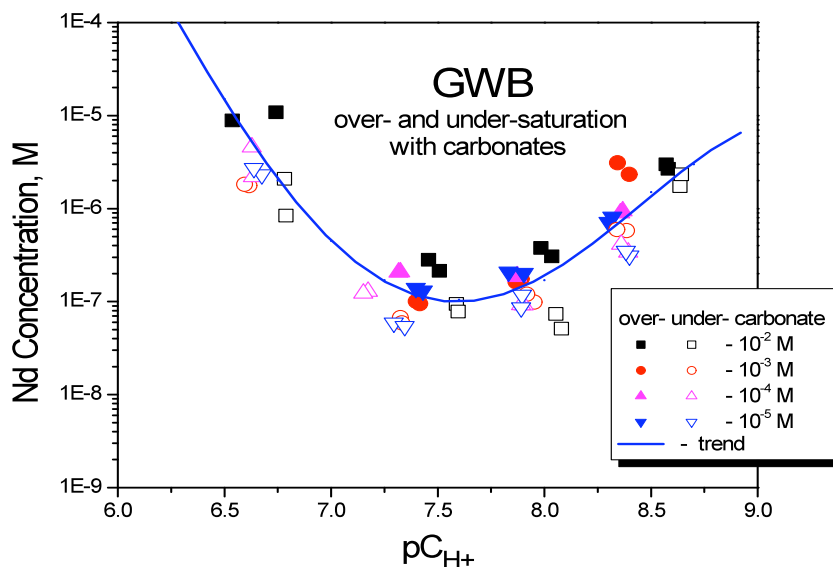
Figure 4-8.   Neodymium solubility in GWB as a function of pC_{H+} and total initial carbonate concentration. The line shown in the graph defines the border between oversaturation (filled points) and undersaturation (open points) experiments.

Figure 4-9.   Neodymium solubility in carbonate-free GWB as a function of pC_{H+}. The dotted line in this graph is transferred from Figure 4-8 for comparison.

Figure 4-10.   Solubility of neodymium as a function of pC_{H+} in carbonate-free ERDA-6 brine. The line in the graph is drawn to show the trends for both oversaturation (squares) and undersaturation (circles) experiments.
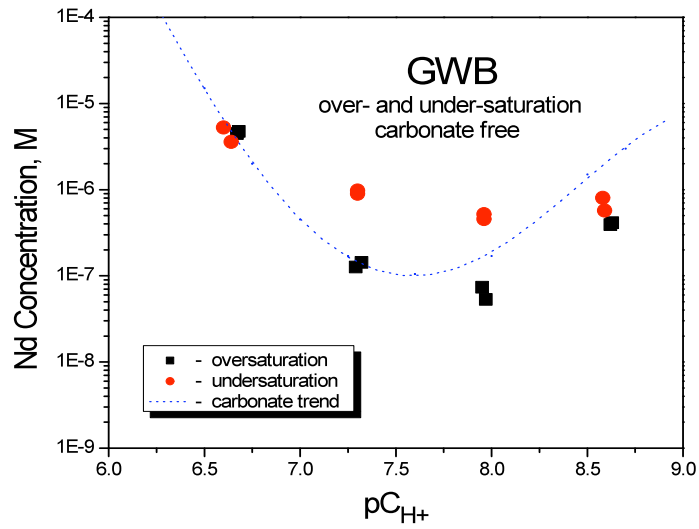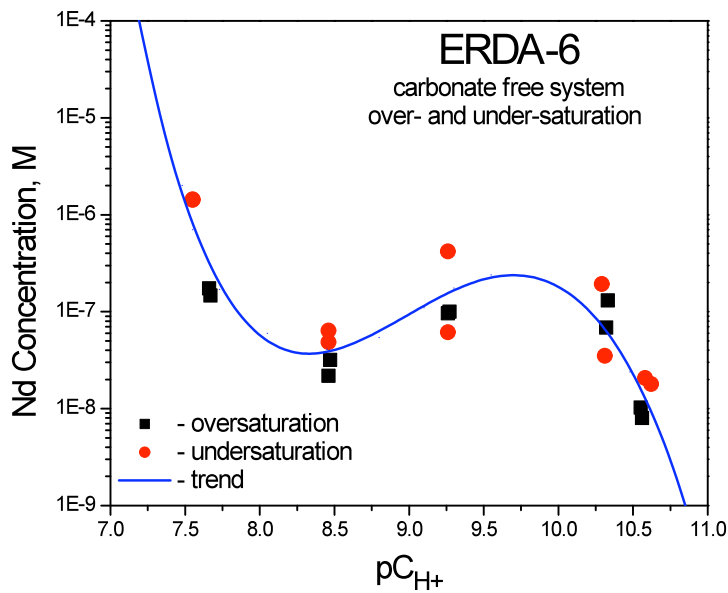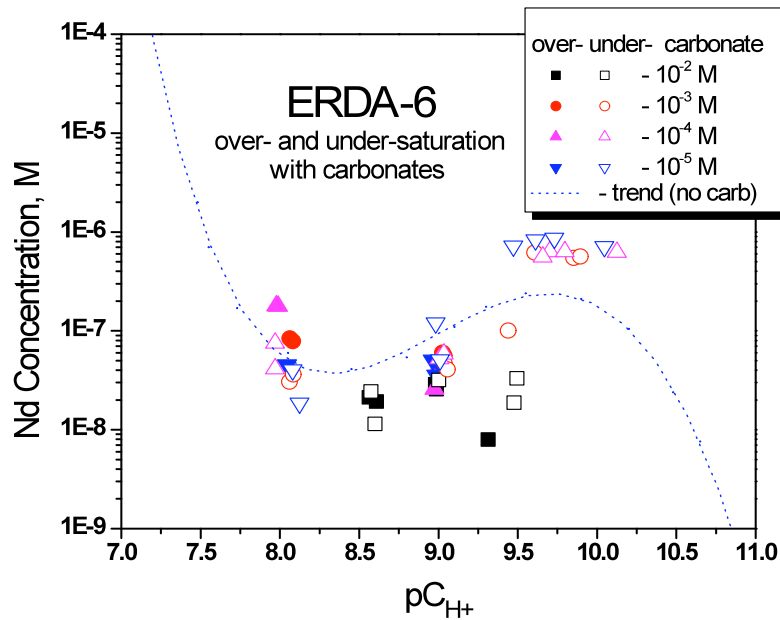
Figure 4-11. Solubility of neodymium in ERDA-6 brine as a function of pC_{H+} and initial carbonate concentration. The dotted line in this graph is transferred from Figure 4-9 for comparison. Additional experiments are needed to verify the trends above $pC_{H+} \sim 10$.

4.4.3   Effect of Solids on the Kinetics of Neodymium(III) Equilibration

The goal of these experiments was to establish the influence of Nd(III) solids such as $Nd(OH)_3$ and $Nd_2(CO_3)_3$ (previously $NdCO_3OH$ was used in the undersaturation experiments) on the kinetics of equilibration and final neodymium steady-state concentration as a function of pC_{H+}, carbonate concentration, and brine. The results of the neodymium over- and undersaturation solubility experiments in GWB, which were just presented, are in good agreement. For this reason, GWB was the brine selected for these experiments.

In GWB, the solubility of neodymium was measured in the presence of all solids, at three pC_{H+} values, with a 0.01 M carbonate concentration. Samples were equilibrated for 118 days and were periodically sampled. The neodymium concentrations measured as a function of time are shown in Figures 4-12(A) and (B). In GWB, the change in pC_{H+} was negligible, with only small changes noted at the beginning of the experiments. Significant changes in the concentration of neodymium, however, were observed for up to 70 days. These changes were different for $Nd(OH)_3$ and $Nd_2(CO_3)_3$ solids. It was typically observed that there was a fast increase in neodymium concentrations during the first several days (up to 20 days) of equilibration. After reaching a maximum concentration, a continuous decrease of up to 2 orders of magnitude in neodymium concentration was noted. The plot of the change in neodymium concentration with
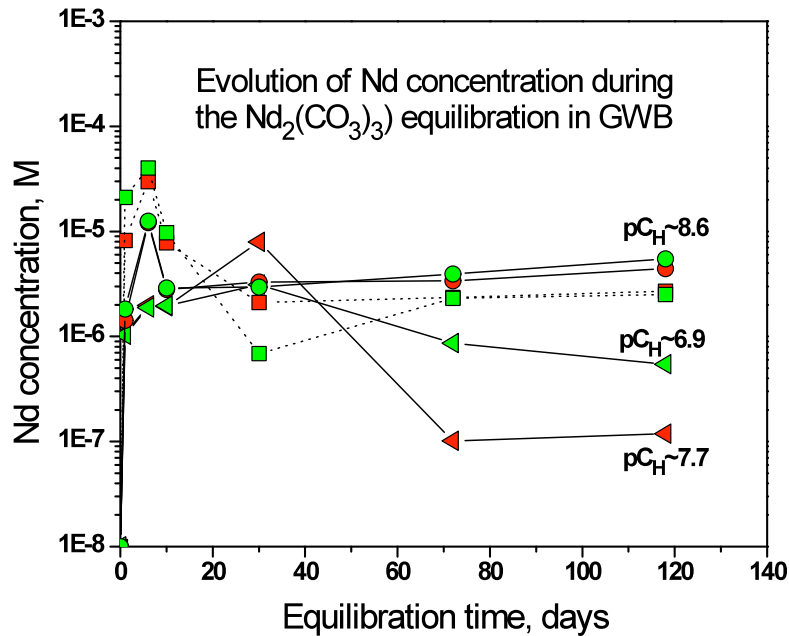
(A)
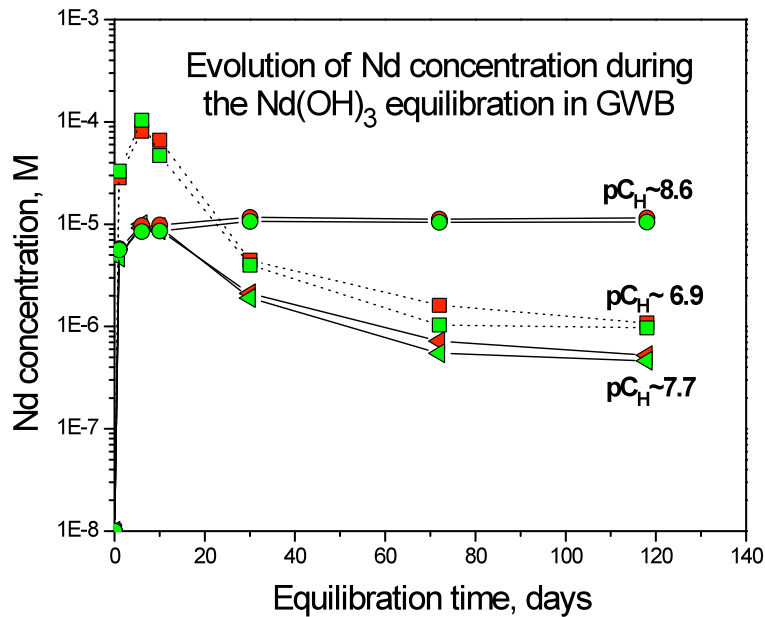
(B)

Figure 4-12.   Neodymium concentration in GWB as a function of time (duplicate
                samples) using $Nd_2(CO_3)_3$ as the solid (A) and $Nd(OH)_3$ as the solid (B).

time was similar to that obtained when $NdCO_3OH$ solid was equilibrated with brine
[Figure 4-7(A)]. This trend is best explained as evidence that the solid phase controlling
neodymium solubility is different than the solid initially added and we are observing the
conversion of this solid into the one that controls solubility. A slightly different trend is seen at
pC_{H+}~8.5 for the $Nd(OH)_3$ solid. In this case, a maximum concentration was not observed. This

is best interpreted as evidence that the solubility-controlling phase under these conditions is neodymium hydroxide, which is in agreement with thermodynamic data in the literature.

The dependence of neodymium solubility on pC_{H+} for the $Nd(OH)_3$ and $Nd_2(CO_3)_3$ solids measured in these experiments is presented in Figure 4-13. After 118 days of equilibration in GWB, the neodymium concentration in the $Nd(OH)_3$ or $Nd_2(CO_3)_3$ solid experiments were within an order of magnitude of the solubility obtained in the undersaturation experiments with $NdCO_3OH$ solid and the oversaturation experiments. Given that the long-term trend (up to 400 days) in neodymium concentration is to decrease with time in the undersaturation experiments, the overall agreement among all of the measured solubility values is very good.
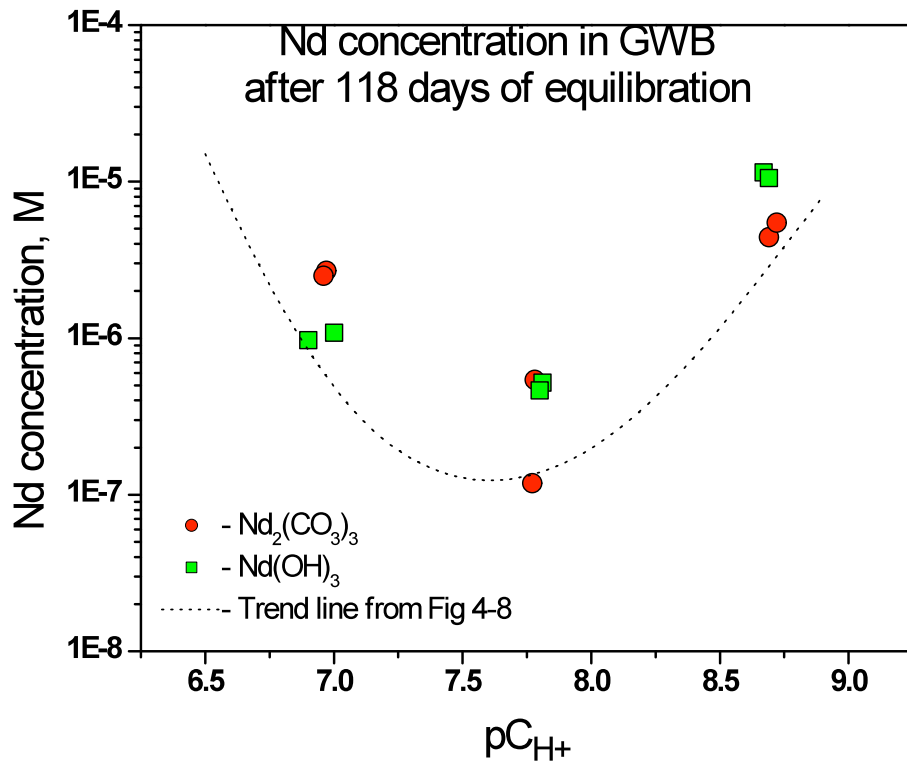
Figure 4-13.   Comparison of the neodymium concentrations measured in GWB for $Nd(OH)_3$ and $Nd_2(CO_3)_3$ with the data presented in Figure 4-8.

4.4.4   Neodymium Reactions in Brine

GWB and ERDA-6 brine are very complex media, and neodymium is involved in many reactions. Our goal was to distinguish the neodymium reactions that play important roles in solubility processes in these particular media. Among other reactions, the reactions listed below in the basic solutions were considered of primary importance:

$$Nd^{3+} + OH^- \quad \rightleftarrows \quad NdOH^{2+} \qquad (4\text{-}2)$$

$$Nd^{3+} + 2OH^- \quad \rightleftarrows \quad Nd(OH)_2^+ \qquad (4\text{-}3)$$

$$Nd^{3+} + CO_3^{2-} \quad \rightleftarrows \quad NdCO_3^+ \qquad (4\text{-}4)$$

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$$Nd^{3+} + 2CO_3^{2-} \quad \rightleftharpoons \quad Nd(CO_3)_2^- \qquad (4\text{-}5)$$

$$Nd(OH)_3 \text{ (s)} \quad \rightleftharpoons \quad Nd(OH)_2^+ + OH^- \qquad (4\text{-}6)$$

$$Nd_2(CO_3)_3 \text{ (s)} \quad \rightleftharpoons \quad Nd_2(CO_3)_2^{2+} + CO_3^{2-} \quad (4\text{-}7)$$

$$NdCO_3OH \text{ (s)} \quad \rightleftharpoons \quad NdCO_3^+ + OH^- \qquad (4\text{-}8)$$

These reactions are well known, and literature values for the corresponding stability constants can be found (NIST Database 2004). These systems were modeled using the Geochemist's Workbench computer code (Bethke 2005). According to these modeling results, in high ionic strength (NaCl, MgCl$_2$) solution (I >5M), only hydrolytic species are present in the absence of carbonate. The dominant hydrolytic species is Nd(OH)$_2^+$ for pC$_{H+}$ greater than 6. The addition of carbonate led to a slight increase in the neodymium concentration because of the formation of the Nd$_2$(CO$_3$)$_2^{2+}$ complex for pC$_{H+}$>9. As previously indicated, in GWB and ERDA-6 brine, the complexation of neodymium with tetraborate is likely to be very significant at 7.5 < pC$_{H+}$ <10.5. Unfortunately, there are no literature values for the neodymium borate stability constant, so we could not account for this effect using the existing speciation database.

The likely importance of borate complexation is qualitative, based on our observed data trends. The expected concentration of free tetraborate ion for GWB and ERDA-6 brine is much greater than the expected free carbonate ion under WIPP-related conditions. Boric acid is a very weak acid and acts exclusively by hydroxyl ion acceptance rather than proton donation. There are many polyforms of boric acid. In our work, the tetraborate form was used. Usually, anions of weak acids form strong complexes with metals. The tetraborate reactions that likely affect neodymium solubility in GWB and ERDA-6 brine are:

$$Nd^{3+} + B_4O_7^{2-} \quad \rightleftharpoons NdB_4O_7^{1+} \qquad (4\text{-}9)$$

$$Nd^{3+} + 2B_4O_7^{2-} \quad \rightleftharpoons Nd(B_4O_7)_2^{1-} \qquad (4\text{-}10)$$

Both reactions 4-9 and 4-10 may be responsible for the observed concentration trends in the neodymium solubility observed in carbonate-free GWB and ERDA-6 brine in the pC$_{H+}$ range of 7.5 to 10.5. In contrast, no such trend is observed in the 5 M NaCl solution. In the pC$_{H+}$ range of 7.5 to 10.5, neodymium complexation with tetraborate predominates over neodymium complexation with carbonate. This was observed as a "hump" in the neodymium concentration trends in carbonate-free brine and the absence of a solubility increase when carbonate was added to GWB and ERDA-6 brine. When the pC$_{H+}$ was increased above 10, hydrolysis of neodymium becomes dominant under all investigated conditions (including the addition of carbonate).

The pK$_a$ of boric acid has been well established (NIST Database 2004) and is shown as a function of ionic strength in Figure 4-14. In a series of low ionic strength developmental experiments, we observed an increase in the neodymium solubility as the tetraborate con-centration was increased. This dependence is shown in Figure 4-15. On the basis of these data, the stability constant for the neodymium-borate complex was estimated to be log β$_1$ ~ 3.5. This value is consistent with the observed effects on neodymium solubility observed in GWB and ERDA-6 brine. It is our plan to determine this formation constant more accurately as a function of ionic strength in experiments that are ongoing under the test plan "Effect of Acetate, Citrate, EDTA, Oxalate and Borate Ions on Neodymium Solubility in WIPP Brine," LCO-ACP-07.
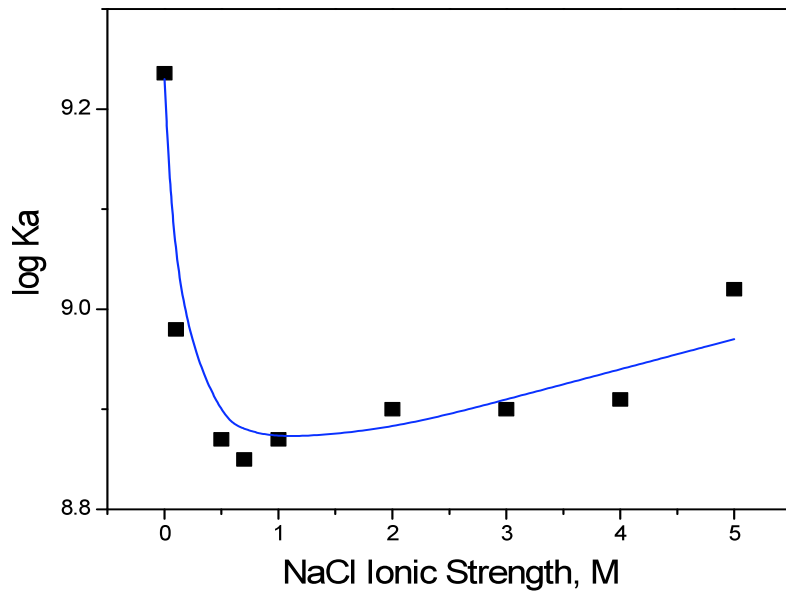
Figure 4-14.   The pK$_a$ for boric acid as a function of ionic strength (NIST Database 2004).
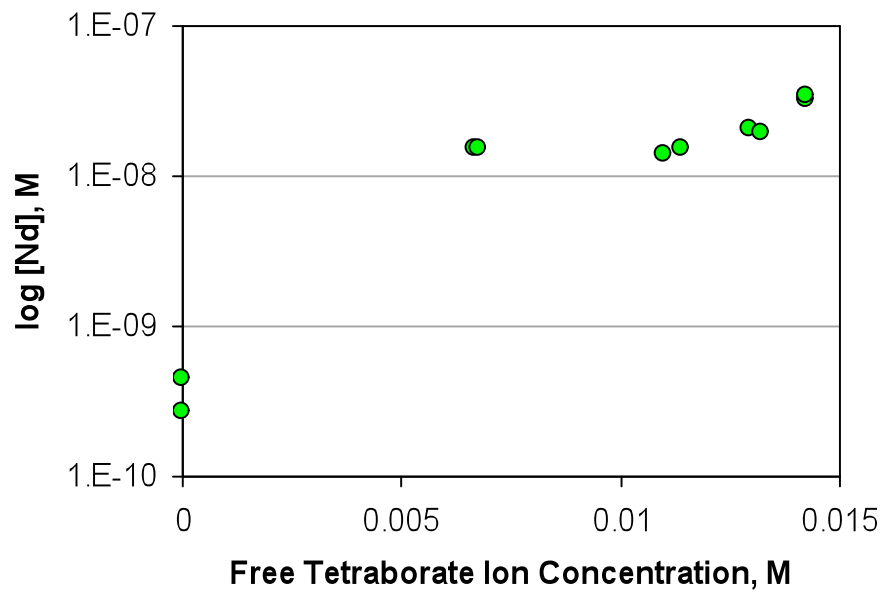

Figure 4-15.   Dependence of neodymium solubility on tetraborate concentration in low ionic strength solution.

4.5   Summary of Experimental Results and Conclusions

In the research just described, neodymium(III) was used as a redox-invariant analog for americium(III) and plutonium(III). Both of these oxidation states contribute significantly to actinide release in the WIPP PA; therefore, these data are highly relevant to current PA calculations. The key results from our literature review and solubility experiments are as follows:

1) There were no surprises discovered in the literature review. This review was centered on the solubility of Am(III) and Pu(III) in brine systems. There are little, if any, new data that bear directly on the measurement and calculation of the solubility of +3 actinides in brine systems since the CCA.

2) The solubility data we report for neodymium(III) in WIPP-relevant brine systems supports current WIPP PA calculations of the +3 actinide solubility in that the calculated values remain conservative for the referenced WIPP conditions.

3) Specific observations and results that relate to the Nd^{+3} solubility data that were obtained by ACRSP include the following:

    o   Excellent agreement with comparable literature values for Nd^{+3} solubility in the carbonate-free, simplified 5 M NaCl brine study was obtained. This provides an external corroboration of our experimental approach for the only system we investigated that can be directly compared to other non-WIPP studies.

    o   Excellent agreement was obtained in all of our experiments between our over- and undersaturation approaches. This is a strong indicator that the solubility, rather than steady-state metastable concentrations, was being measured.

    o   The solubility of Nd(III) in simulated WIPP brine was not strongly influenced by the range of carbonate concentrations considered (as high as a total concentration of 0.01 M). This is largely due to the complexation of neodymium(III) by borate, already present in WIPP brine at much higher concentrations, which masks the effects of carbonate. The plots of neodymium solubility as a function of pC_{H+} in both GWB and ERDA-6 brine were essentially the same in the presence and absence of carbonate.

    o   The solubility of neodymium, in the simplified and simulated brine systems considered, does not exhibit amphoteric behavior. In this context, the solubility of neodymium at $pC_{H+} > 10$ is mostly controlled by hydroxide concentration and decreases with increasing pC_{H+}. A shoulder to a varying degree, however, is noted in the neodymium solubility graphs for $7.5 < pC_{H+} < 10.5$ because of complexation in all three brines investigated. This shoulder was likely a result of the complexation of neodymium with carbonate ion for 5 M NaCl. This observation is consistent with observations reported in the literature (Felmy et al. 1990; Kim et al. 1984) at low ionic strength and near-neutral pH.

    o   The shoulder in the neodymium solubility in GWB and ERDA-6 brine, however, was likely caused by a different mechanism. The maximum observed at $pC_{H+} = 9.7$ for ERDA-6 brine and the increased solubility observed in GWB for $pC_{H+} > 7.5$ were likely a result of the neodymium complexation with borate (a brine component) and not carbonate. This complex was predominant over complexation with carbonate for the carbonate concentrations investigated. The

neodymium-borate or tetraborate stability constant is not available in the literature because it is very difficult to measure. On the basis of our data, we estimate this to be log K of about 3 to 4. The pK_a value for boric acid is 0.65 log units smaller than the second pK_a of carbonic acid, and the borate concentration in the two simulated brines investigated is higher than carbonate. Although estimated, this formation constant explains the neodymium solubility trends observed in both GWB and ERDA-6 brine. Our data, which extend to higher pH, show that hydroxide complexation prevails at higher pH.

o The An(III) solubilities in GWB and ERDA-6 brine calculated by the WIPP PA using the Pitzer model (SOTERM 2003) are 3×10^{-7} M and 1.7×10^{-7} M, respectively, at pH = 8.7 (pC_{H+}~9.2). These agree quite well with the neodymium solubility data measured in the present work.

5.0 WIPP ASSESSMENT AND RECOMMENDATIONS

The solubility of neodymium(III) was determined as a function of pH, carbonate concentration, and WIPP brine composition. Additionally, we conducted a literature review on the solubility of +3 actinides under WIPP-related conditions. Neodymium(III) was used as a redox-invariant analog for the +3 oxidation state of americium and plutonium, which is the oxidation state that accounts for over 80% of the potential release from the WIPP through the DBR mechanism, based on current WIPP PA assumptions.

The WIPP-relevant solubility data we compiled accomplished two main objectives:

o   Past solubility studies in simplified WIPP brine were extended to simulated brines, specifically GWB and ERDA-6, that bracket the range of brine compositions expected in the WIPP. Performing these studies in more complicated media provided more realistic data on the solubility of +3 actinides in the WIPP.

o   A broader range of pC_{H+} and carbonate concentrations was addressed in the experiments performed. This provided needed baseline data to establish a more robust chemistry model of the +3 actinides in the WIPP. A composite of all of the measured concentration data is shown in Figure 5-1.
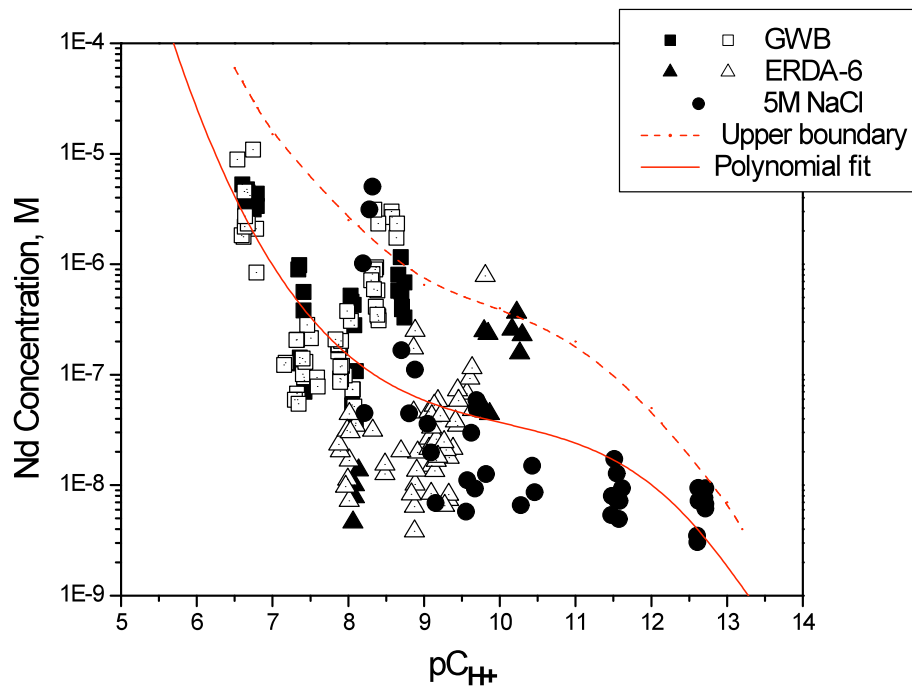

Figure 5-1.   Composite of neodymium solubility trends under all conditions investigated. Open symbols correspond to undersaturation experiments and closed symbols correspond to oversaturation experiments.

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A key observation that has come from our investigation is that the most important complexant for the +3 actinides is not currently accounted for in the WIPP database. The observed maximum at pC_{H+} = 9.7 for ERDA-6 brine, and the increased solubility observed in GWB at pC_{H+} > 7.5 are caused by the presence of borate. The neodymium-borate or tetraborate stability constant is not available in the literature because it is very difficult to measure. On the basis of our developmental data, we estimate this to be a log K of about 3 to 4. The pK_a value for boric acid is 0.65 log units smaller than the second pK_a of carbonic acid, and the borate concentration in the two simulated brines investigated is higher than carbonate concentration expected in the WIPP. Although estimated, this formation constant explains the neodymium solubility trends observed in both GWB and ERDA-6 brine.

A second observation is that we still do not have a complete picture of the long-term solubility-controlling phases for the +3 actinides, although some progress was made. $Nd(OH)_3$ solid appears to control solubility in these brines at pC_{H+} > 9. Dissolution kinetics of the various solids, namely $Nd_2(CO_3)_3$, $Nd(OH)_3$, and $NdOHCO_3$, have maxima on the beginning of equilibration and a further decrease in neodymium concentration, indicating that these solids are more soluble than the solid that will eventually control the neodymium solubility for pC_{H+} < 9.

Overall, there are two key recommendations to WIPP PA for the solubility of the +3 actinides based on our experimental results and literature review:

1) ***There should be no significant change to the +3 solubility concentrations used in WIPP PA for the reference case.*** The WIPP-relevant data summarized in this report support current PA calculations performed with the use of the Pitzer model (SOTERM 2003) for the values of 3×10^{-7} M and 1.7×10^{-7} M in GWB and ERDA-6 brine, respectively, at pH = 8.7 (pC_{H+}~9.2). Our data show that this solubility is at or near the maximum solubility over a wide range of pH, brine composition, and carbonate concentrations.

2) ***The +3 actinide speciation model should be modified to account for the effects of borate complexation.*** Borate is, in fact, the key complexant in WIPP brine for +3 actinides and should be reflected in the model to properly account for the solubility trends and effects of pH and carbonate concentration on the solubility of +3 actinides. In the longer term, we should proceed with developing the needed Pitzer parameters and a Quality Level 1 determination of the formation constant for incorporation in the WIPP speciation model for the +3 actinides.

6.0   QUALITY ASSURANCE, DATA TRACEABILITY, AND DOCUMENTATION

All of the data presented in Section 4 were generated under the LANL-CO WIPP Quality Assurance (QA) Program, which is compliant with the CBFO QAPD. The experiments were performed under the DOE-approved test plan "Solubility of Neodymium(III) in WIPP Brines," LCO-ACP-03. The documentation for the experiments is found in the test plan-specific scientific notebook designated LCO-ACP-03/1 and a series of data packages designated Nd 1 to Nd 47. Copies of the scientific notebook and the data packages were submitted to the LANL-CO Records Center.

Linkage of the figures published in this summary to the data submitted to the LANL-CO Record Center.

Figure #	Document containing the data submitted to Record Center
4-2	Data Package Nd 38
4-3	SN MB-1 pp. 1-50
4-4	Data Package Nd 42 and Nd 43
4-5	Data Package Nd 8, Nd 9, and Nd 46
4-6	Data Package Nd 2, Nd 6, Nd 7, Nd 24, Nd 28, Nd 39, Nd 40, and Nd 44
4-7A	Data Package Nd 4 Nd 27, Nd 28, Nd 41, Nd 43, and Nd 45
4-7B	Data Package Nd 2, Nd 6, Nd 7, Nd 24, Nd 28, Nd 39, Nd 40, and Nd 44
4-8	Data Package Nd 41 and Nd 45
4-9	Data Package Nd 42
4-10	Data Package Nd 26 and Nd 27
4-11	Data Package Nd 17
4-12A and B	Data Package Nd 30, Nd 31, Nd 32, Nd 33, Nd 34, and Nd 46
4-13	Data Package Nd 33
4-14	Literature data
4-15	SN MB-1 p. 86
5-1	Collection of the data from figures in Section 4.

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