LA-UR-22-32478

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Title:	Solubility of An(OH)3 (am) and An(OH)3 (cr) in the presence of Citrate and EDTA
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Intended for:	Report
Issued:	2022-11-30

LOS ALAMOS NATIONAL LABORATORY
CARLSBAD OPERATIONS

LCO-ACP-29, Rev 0

Solubility of $An(OH)_{3\ am}$ and $An(OH)_{3\ cr}$ in the presence of Citrate and EDTA

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Effective Date: 11-30-2022

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History of Revision/Change

Revision Number	Effective Date	Pages Affected	Description of Revision
0	11/30/2022	All	Original Release

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ACRONYMS

ACRONYM	DEFINITION
ACRSP	Actinide Chemistry and Repository Science Program
ASTP	WIPP Actinide Source Term Program
am	amorphous
Am	Americium
An	Generic Actinide
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
cr	crystalline
CRA	Compliance Recertification Application
DBR	Dissolved Brine Release
DFT	Density Functional Theory
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
FMT	Fracture-Matrix Transport (code used to calculate actinide speciation for CRA)
GWB	Generic Weep Brine, a synthetic brine representative of intergranular Salado-Formation brines
HPW	High purity water
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
LANL-CO	Los Alamos National Laboratory−Carlsbad Operations
$\log_{10} K^0_{s0}$	Solubility constant
$\log {}^*\beta_1'$	Formation constants of the first hydrolysis species
M	molarity, moles of solute per liter of solvent
NIST	National Institute of Standards and Technology
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)

TRLFS	Time-Resolved Laser Fluorescence Spectroscopy
TRUs	Transuranic Elements (actinides higher in atomic number than uranium)
WIPP	Waste Isolation Pilot Plant
XANES	X-ray absorption near edge spectroscopy
XAS	X-ray absorption spectroscopy
XRD	X-Ray Diffraction

EXECUTIVE SUMMARY

The solubility of An(III), which pertains to Pu(III), Am(III), and Cm(III), in brine is an important contributor in WIPP (Waste Isolation Pilot Plant) performance assessment (PA) models to calculate the potential release of transuranic elements in the near-field environment of the WIPP repository. Americium, although present in much smaller quantities than plutonium (~ 336 kg on year 2033 is potentially WIPP-bound primarily as Am-241), has a significant impact on release due to its higher activity during the earlier times of repository history (~26% initially, decreasing to 17% and ~0% at 1000 and 10,000 years after emplacement) (SOTERM, 2019). Lanthanide analogues such as Nd^{3+} possess physical and chemical characteristics that allow them to be used to examine the chemical behavior of trivalent actinides (Lucchini, et al., 2007).

Organic compounds present in WIPP waste can form strong complexes with metals and actinides. The organic compounds addressed in WIPP performance assessment include EDTA (Ethylenediaminetetraacetic Acid), oxalate, citrate, and acetate. Among them, only citrate and EDTA are predicted to form strong enough complexes to influence the speciation of the trivalent actinides and potentially increase actinide solubility under the expected conditions in the WIPP (SOTERM, 2019).

Actinide minerals also will have different morphologies, and the choice of which mineral to represent in the PA will affect the degree of a release. For example, the Am solid phase expected at the WIPP, $Am(OH)_3$, can either be amorphous (am) or crystalline (cr) and will dissolve to release soluble Am(III). In this work, EDTA and citrate effects on solubility for both amorphous and crystalline phases in brines as a function of two constant ionic strengths (low-0.1 M and high-5 M NaCl) and pC_{H+} specific brines were investigated by an under-saturation approach. In the experiments, commercially available crystalline neodymium hydroxide and synthesized amorphous neodymium hydroxide were used as the solid phases. Experiments were equilibrated for about 250 days at an adjusted pC_{H+} 7, 9 and 11. The results from the experiments show that Nd (III) solubility is higher with crystalline phase in the presence of the organics. These data quantify the effects of WIPP-relevant concentrations of EDTA and Citrate on the solubility of An(III) to challenge the predictions of the WIPP actinide model and inform decisions and recommendations made in the upcoming recertification of the WIPP (CRA-2024). The information obtained in this report applies, by analogy, to the trivalent actinides present in the WIPP.

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 conceptual model to support ongoing WIPP recertification efforts. The experiments were performed under the U.S. Department of Energy (DOE) approved test plan “Experimental Strategy to Challenge Actinide Solubility Predictions” LCO-ACP-26. 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) (QAPD, 2017).

1.0 INTRODUCTION

WIPP is the only operating transuranic (TRU) waste deep geologic repository in the United States and is located in the northern portion of the Delaware Basin in southeastern New Mexico east of Carlsbad. It was certified by the Environmental Protection Agency (EPA) in May 1998 as a TRU waste repository and is currently operated by the Department of Energy, Carlsbad Field Office (DOE CBFO). WIPP-relevant Nd(III) solubility studies were performed by the ACRSP team at the Carlsbad Environmental Monitoring and Research Center (CEMRC) and the results were summarized in this report.

All experiments were performed under the DOE approved test plan "Experimental Strategy to Challenge Actinide Solubility Predictions" LCO-ACP-26. The resulting data establish the solubility of Nd(III), as an analog for Am(III), in low and high ionic strength simplified brines and simulated WIPP brines at pC_{H+} 7, 9, 11, as well as in the presence of EDTA and Citrate under-saturation approaches.

Determining the solubility of any species in a complicated matrix such as WIPP brine is not straightforward. To better control each organic ligands affecting solubility, we used NaCl as simplified brine. For the chosen experimental conditions, the influence of major organic ligands such as citrate and EDTA on neodymium solubility were investigated.

The solubility and speciation of multivalent actinides are often investigated with lanthanide and actinide analogs. Using redox-invariant analogs for the multivalent actinides helps provide information to determine oxidation-state-specific properties (e.g., solubility or complexation). Lanthanides, in general, are excellent analogs for actinides because they possess f-electrons, and their physical and chemical characteristics are similar to the actinides. They also have similar ionic radius for coordination number 6 (CN=6); as for Am(III) is 97.5 picometers (pm), Pu(III) is 100 pm, Cm(III) is 97 pm, and Nd (III) is 98.3 pm *(Shannon, 1976)*. In this context, Nd(III) is a good non-radioactive analog for the chemical behavior of An(III) *(Choppin, 2007)*.

The An(III) of interest to the WIPP are Am(III), Pu(III), and to a much lesser extent, Cm(III). Am is a 5f electron element and, can exist in aqueous solution in several oxidation states and the trivalent state of Am is the most stable aqueous oxidation state (SOTERM, 2019). Due to its chemical properties it can be used as an analog for Pu(III), which has a similar ionic radius. In the WIPP, americium will predominantly exist as a partially hydrolyzed $Am(OH)_2^+$ species in equilibrium with an $Am(OH)_3$ solid (Domski and Sisk-Scott 2019).

The speciation of Am in groundwater under mildly alkaline conditions is primarily defined by hydrolysis and carbonate complexation. Hydrolysis is generally represented by the following reaction:

$Am^{3+} + nH_2O \leftrightarrow Am(OH)_n^{(3-n)} + nH^+$

Silva, (Silva, 1982) reported solubilities of crystalline $Nd(OH)_3$ and $Am(OH)_3$ in 0.1 M $NaClO_4$. MINEQL was used for analyses of the solubility data and estimated the solubility product constants, K_{s10}, and the second and third hydrolysis constants, K_{12} and K_{13}, for Nd^{3+} and Am^{3+}. For Nd, they are: log K_{s10}=16.0± 0.2, log K_{12}= -15.8± 0.5, log K_{13}= -23.9± 0.2. For Am, they are: log K_{s10}=15.9± 0.4, log K_{12}= -16.0± 0.7, log K_{13}= -24.3± 0.3.

The distribution diagram of americium hydrolysis species at 25°C in standard aqueous solutions (I = 0) in the range of 6 ≤ pH ≤ 12 were calculated and is presented in Figure 1.

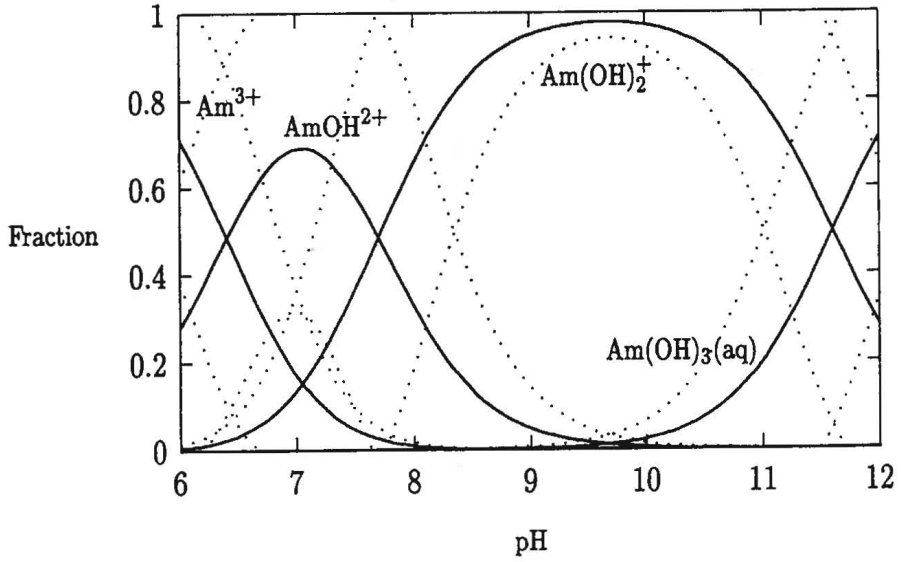

Figure 1. Calculated distribution diagram of americium species at 25°C in standard aqueous solutions (I=0) in the range of 6 ≤ pH ≤ 12 *(Silva, et al., 1995)*. The precipitation of solid phases has not been considered. *(Silva, 1982)*

An extensive literature search was performed and summary was reported in SOTERM -2019. In this report the latest literature reviews from selected publications are included.

A very detailed review and data summary and recommendations regarding An (III) solubility was reported by Borkowski et al. 2009 (Borkowski, et al., 2009) as part of a WIPP report. In this report, Nd(III) was used as a redox-invariant analog for Am(III) and Pu(III) in the WIPP. The solubility of Nd(III) in 5 M NaCl, which is a simplified WIPP brine, was done to establish the effects of brine constituents on brine solubility. Additionally, 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. They noted that a decrease in the neodymium

solubility pC_{H+}>10. This decrease was due to the predominance of hydrolysis over carbonate complexation.

Xiong et al. (Xiong, et al., 2017), presented solubility data at 298.15 K in high ionic strength NaCl solutions as $\log_{10} K^0_{s0} = 16.85 \pm 0.2$, which is slightly lower than the values in the literature, for the reaction of

$Nd(OH)_3$ (am) + $3H^+ = Nd^{3+} + 3H_2O$ (l)

In their study, the experimental results from long-term solubility experiments up to 1146 days on micro-crystalline neodymium hydroxide, $Nd(OH)_3$(micro-cr), under well-constrained conditions, were presented. They concluded that the value can be applied to amorphous americium hydroxide, $Am(OH)_3$(am), using Nd(III) as an analog to Am(III).

A conventional, speciated Pitzer ion-interaction model at 298 K and 0.1 MPa is presented by Oakes et al., (Oakes, et al., 2021) for the $NdCl_3$+H_2O system and mixtures containing HCl, NaCl, KCl, and $CaCl_2$. The resulting thermodynamic model accurately reproduces the properties of $NdCl_3$(aq), and mixtures containing evaporite salts, over a range of pH, including those typical of geologic nuclear waste repositories that use engineered chemical barriers to minimize transport of An(III).

One of the latest studies was published by Cho et. al. 2022 (Cho, et al., 2022) where the hydrolysis of Pu(III) and the solubility of $Pu(OH)_3$(am) were investigated at various temperatures (10−40 °C) in 0.1 M $NaClO_4$. The formation constants of the first hydrolysis species, log $*\beta_1'$, and the solubility products of $Pu(OH)_3$(am), log $*K'_{s,0}$, at 10, 17, and 40 °C were experimentally determined using spectrophotometry, laser-induced breakdown detection, and radiometry.

Diblasi et al., 2022 (DiBlasi, et al., 2022) work on the impact of calcium on the solubility, redox behavior, and speciation of the An(III)–EDTA (An= Pu or Cm) system under reducing, anoxic conditions, by X-ray absorption spectroscopy (XAS), density functional theory (DFT), and time-resolved laser fluorescence spectroscopy (TRLFS). They reported the possible existence of four major complex types within Ca–An(III)–EDTA systems: An(III)–EDTA, An(III)–OH–EDTA, Ca–An(III)–EDTA, and Ca–An(III)–OH–EDTA.

Organic compounds form strong complexes with metals and actinides. These large molecules often have multiple binding sites allowing them to attach to a metal at multiple locations. As a result, organic ligands, or chelates, tend to form very stable complexes (EPA, 2021). Chelates can increase the solubility of a metal. Some important organic compounds associated with the WIPP include EDTA ($C_{10}H_{16}N_2O_8^{4-}$), oxalate ($C_2O_4^{2-}$), citrate ($C_6H_8O_7$) and acetate ($C_2H_3O_2^-$) (Table 2). There are a very limited number of studies in the literature related to the organics complexation with An(III). Brown et al., (Brown, et al., 2014) studied the aqueous complexation

of Nd(III) and Am(III) with anions of citrate by potentiometry, absorption spectrophotometry, microcalorimetry and XAS. Using potentiometric titration data fitting the metal–ligand (L) complexes that were identified for Nd(III) were NdHL, NdL, $NdHL_2$ and NdL_2. Fröhlich, et al. (Fröhlich, et al., 2015) studied the complexation of acetate with Am(III) as a function of the pH (1–6) by extended XAS. The molecular structure of the Am(III)–acetate complexes determined from Am L_{III}-edge EXAFS spectra are in very good agreement with the thermodynamic model calculations (NIST database) based on the Am^{3+}, $AmAc^{2+}$ and $AmAc_2^{+}$ species from pH 1 to 6.

The effect of organic complexation on the concentration of neodymium, as the An(III) analog, was also evaluated for each key chelating agent (DOE, 2014). These data are shown in (SOTERM, 2019). They show a strong effect of citrate and EDTA where a 1:1 complex with the neodymium is being formed and the concentration of the neodymium is approximately the concentration of EDTA in ERDA-6 brine and approximately 50% of the concentration of EDTA in GWB brine. These data also illustrate the important effect that competition has on the observed effects on solubility.

2.0 EXPERIMENTAL

In this work, EDTA and citrate effects on solubility for both amorphous and crystalline phases of $Nd(OH)_3$ in brines at two ionic strengths (0.1 M and 5 M NaCl) (NaCl, Fisher Chemical, lot# 193467) and WIPP specific brines were investigated using an under-saturation experimental approach. In the experiments, synthesized amorphous (Figure 2) and commercially available crystalline neodymium hydroxide (Aldrich, lot# 14713PEV) were used as the solid phase. The HPW were bubbled with high-purity nitrogen to remove dissolved oxygen and carbon dioxide prior to placement in a nitrogen glove box (<0.1 ppm O_2) for the duration of the experiment. Experiments were equilibrated for ~250 days at an adjusted pC_{H+} of 7, 9 and 11 with carbonate free 50% NaOH (ACROS, lot # A0277324) and HCl (Fisher lot# 4108010). 0.01 M EDTA (Na_4EDTA, Aldrich, lot# MKBS6945V) and 0.1 M citrate (citric acid anhydrous, Fluka, lot# 447332/1 21403229) were prepared as stock solutions. Appropriate dilutions were made from these stocks for the experiments.

Amorphous $Nd(OH)_3$ was synthesized by dissolving 1.9210 g $NdCl_3 \cdot 6H_2O$ (Sigma-Aldrich, lot# MKCH0593) in 10 ml high purity water (HPW, 18.2 MΩ) and adding carbonate free 50% sodium hydroxide (Acros Organics, lot# A0277324) dropwise to a pH of 10 in a nitrogen glovebox. Powder X-ray Diffraction (XRD) analysis confirmed the structure of the solid (Figure 2). Figure 2 shows XRD patterns of the commercial crystalline and synthesized amorphous $Nd(OH)_3$ solids. According to the XRD patterns as a comparison with the crystalline pattern, amorphous phase is microcrystalline.

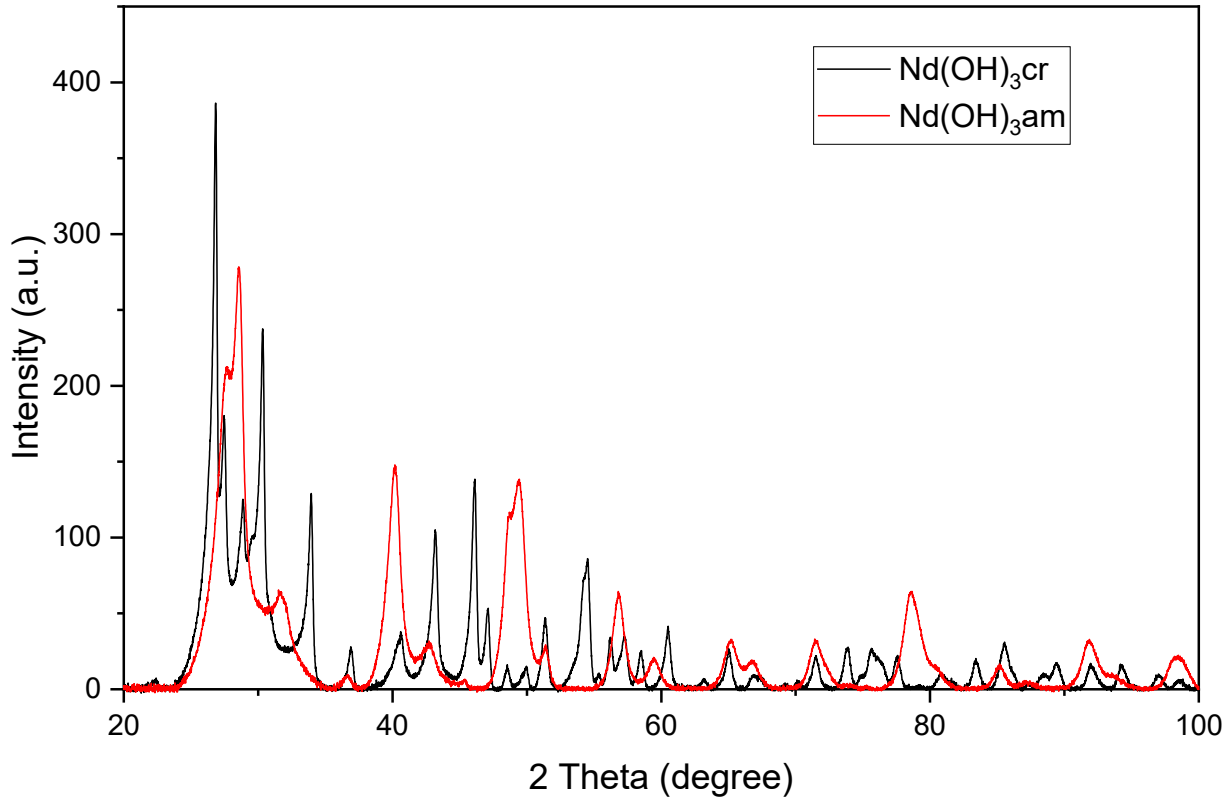

Figure 2. XRD pattern of $Nd(OH)_3$. Microcrystallinity is observed in the amorphous structure.

The predicted range in brine composition expected in the WIPP is shown in Table 1. In the WIPP, high ionic strength brines will form when the intruded brine reacts with the emplaced materials. These brines are Na/Mg/Cl dominated with lesser amount of calcium, borate, sulfate, potassium, lithium, bromide, and carbonate. In long-term experiments, 90% strength compositions are used to prevent salt precipitation and minimize mineral colloid and pseudo-colloid formation. This dilution is a necessary step for anoxic experiments. Brines were prepared according to procedure ACP-EXP-001.

Table 1. WIPP-relevant Brine Compositions as a Function of pC_{H+}. Data are based on 90% Strength.

pC_{H+} or Brine	**Element/Species - Measured Concentrations (M)**						
	Na^+	**K^+**	**Mg^{2+}**	**Ca^{2+}**	**Li^+**	**$B_4O_7^{2-}$**	**Cl^-**
GWB	3.17	0.42	0.92	1.28×10^{-2}	4.00×10^{-3}	3.53×10^{-2}	3.83
9	3.03	0.42	0.94	1.2×10^{-2}	3.9×10^{-3}	3.5×10^{-2}	3.7
11	4.71	0.40	0.01	0.98×10^{-3}	3.2×10^{-3}	2.74×10^{-2}	4.5
NaCl	5.02	-	-	-	-	-	5.02

The complexation of chelating agents with actinides has a significant impact on the concentrations of actinides in brine. The organic inventories are also important as they, in many cases, define the predominant aqueous speciation predicted. These inventories updated in each CRA cycle. The CRA-2019 (SOTERM, 2019) projected inventories lead to the concentrations shown in Table 2. Especially, at the pH of interest to the WIPP PA, EDTA and citrate complexation is strong enough to impact the actinide solubility.

Table 2. Concentration Range of Acetate, Oxalate, Citrate and EDTA in the WIPP Repository Should Brine Inundation Occur *(Van Soest, 2018)*. These are Calculated Based on the Project Inventory and the Minimum Brine Volume (17,400 m^3) for DBR *(SOTERM, 2019)*

Organic Complexant	**Concentration at 1X dilution, M**
Acetate	2.83×10^{-2}
Oxalate	1.13×10^{-2}
Citrate	2.30×10^{-3}
EDTA	7.92×10^{-5}

Experiments were conducted on neodymium (III), by analogy americium (III) within the range of conditions expected in the WIPP. Table 3 shows the experimental matrix using for the test plan "Experimental Strategy to Challenge Actinide Solubility Predictions" LCO-ACP-26 in "Subtask 1.4: Solubility of $Am(OH)_3$ am and $Am(OH)_3$ cr in the presence of Citrate and EDTA".

Table 3. Experimental Matrix for Model Predictions using EDTA and Citrate

Experiment Designation	Solid Phase	Medium	Complexant	pC_{H+}	Comment
Nd-am-01-"pH"	$Nd(OH)_3$ am	0.1 m NaCl	Inventory defined EDTA/ Citrate	7, 9, 11	Low I model challenge
Nd-am-5-"pH"	$Nd(OH)_3$ am	5.0 m NaCl	Inventory defined EDTA/ Citrate	7, 9, 11	High I model challenge
Nd-cr-01-"pH"	$Nd(OH)_3$ cr	0.1 m NaCl	Inventory defined EDTA/ Citrate	7, 9, 11	Low I model challenge
Nd-cr-5-"pH"	$Nd(OH)_3$ cr	5.0 m NaCl	Inventory defined EDTA/ Citrate	7, 9, 11	High I model challenge
Nd-am-Brine	$Nd(OH)_3$ am	WIPP Brine	Inventory defined EDTA/ Citrate	7, 9, 11	High I model challenge

am: amorphous, cr: crystalline.

The effect of organic ligands complexation on neodymium solubility was experimentally determined in 0.1 M NaCl, 5 M NaCl and WIPP-relevant brines as a function of pC_{H+} (7, 9, 11) under simulated WIPP conditions. The effects of EDTA/Citrate of high-pH speciation were investigated. Experiments were performed including inventory defined EDTA/Citrate except for control experiments with excluding organics. Nomenclature is shown in Table 4.

Table 4. Experiment Designation and Conditions for the Nd(III) Solubility Determination in Brine as a Function of pC_{H+}

Medium / pC_{H+}	0.1 M NaCl		5 M NaCl		pC_{H+} Brines
7	Nd-am-01-7	Nd-cr-01-7	Nd-am-5-7	Nd-cr-5-7	Nd-am-pCH-7
9	Nd-am-01-9	Nd-cr-01-9	Nd-am-5-9	Nd-cr-5-9	Nd-am-pCH-9
11	Nd-am-01-11	Nd-cr-01-11	Nd-am-5-11	Nd-cr-5-11	Nd-am-pCH-11

am: amorphous, cr: crystalline.

Under-saturation experiments were conducted at 298 K. In the experiments, approximately 5 mg of $Nd(OH)_3$(cr) or $Nd(OH)_3$(am) were placed into bottles along with 20 mL solution. Sample solutions were periodically withdrawn from the experiments, approximately one month period to

determine whether the system had reached equilibrium. Sampling was performed using 10K (Pall-type filters, Omega-modified polyethersulfone) filtration at 13,000 RPM centrifugation during 30 minutes. pH readings and corrections were performed at each sampling period. The pH was measured with an Orion-Ross combination pH glass electrode, coupled with Mettler Toledo FiveGo pH meter that was calibrated with three pH buffers (Fisher Chemical, lot# 216233, 217475, and 214692 for pH 4, pH 7, and pH 10, respectively). The measured pH readings were converted to negative logarithm of hydrogen ion concentrations on a molar scale (i.e., pC_{H+}) (Borkowski, et al., 2009). Concentration of neodymium was determined in each sample using ICP-MS (ACP-EXP-011). 100 µL from each 1:10 dilution was added to 1700 µL of 2% HNO3 (Fisher Scientific, lot# 1218110) with 300 ppb of an indium internal standard (High Purity Standards, lot# 2013216) to provide a final dilution of 1:180 in triplicate for ICP-MS analysis.

3.0 RESULTS AND DISCUSSION

In this work, neodymium effective solubility in the presence of organic ligands and by analogy, the effective solubility of trivalent actinides under conditions that simulate the expected environment in the WIPP were investigated. Because the complicated matrix of the WIPP brine, solubility determination of any species is not straightforward. For that reason, we used simplified brines for the solubility experiments. This study addressed the effects associated with complexation by citrate and EDTA ions and their influence on neodymium solubility. In order to investigate the effect of EDTA and citrate, which are known as strong complexants, impacting neodymium solubility, the experiments are designed for both initially amorphous and crystalline phases of $Nd(OH)_3$ in 0.1 M, 5 M NaCl and simulated WIPP brines.

The solubility of neodymium (III) with the amorphous and crystalline phase of $Nd(OH)_3$ in 5 M NaCl and 0.1 M NaCl can be seen in Figure 3. It is obvious that the presence of organics in the solution increases the solubility. Nd solubility is almost the same at pC_{H+} 7, 9 and 11 when organics are present. There is only a slight decrease in 5 M NaCl at pC_{H+} 9 and 11. This indicate no dependence of solubility on pC_{H+}. However, a sharp decrease is observed in the solubility at higher pH values when organics are not present. This trend was observed in the literature (Neck, et al., 2009), (Silva, 1982), (Rao, et al., 1996). In both experiments the crystalline phase shows higher solubility.

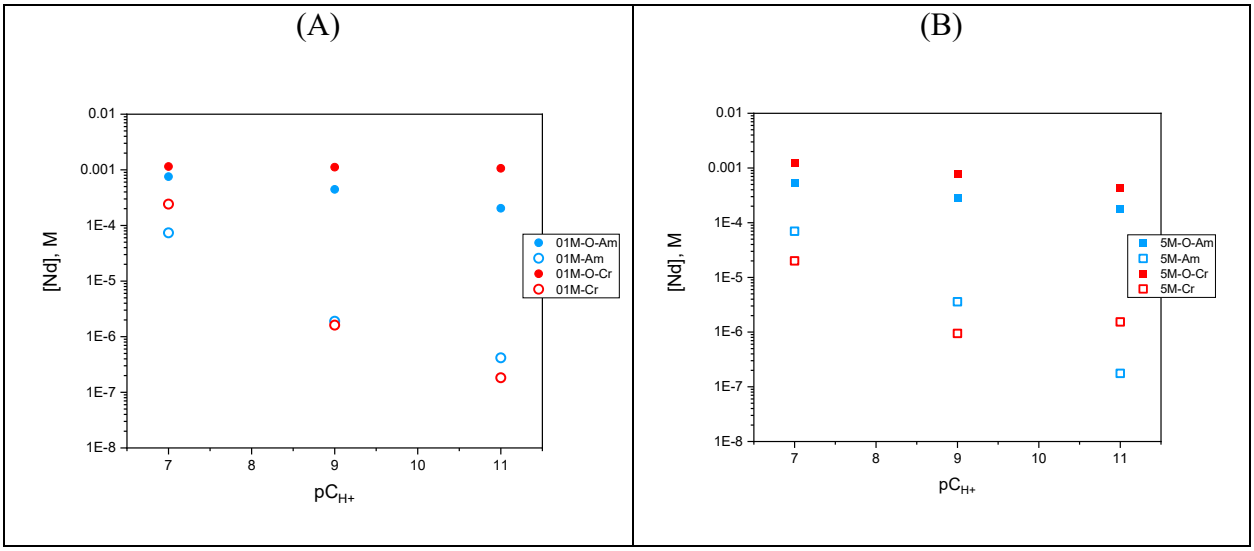

Figure 3. [Nd] as a function of pC_{H+} in 0.1 M NaCl (A) and 5 M NaCl (B). 01M and 5M denotes 0.1 M and 5 M NaCl, O denotes organics, Am and Cr denotes amorphous and crystalline, respectively (after ~250 days of equilibration).

Effect of organics expected in the WIPP, on neodymium solubility under repository conditions with presence and absence of organics are presented in Figure 4 as a function of pC_{H+}. Figure 4 shows that the solubility is higher with organics present at all pC_{H+}s.

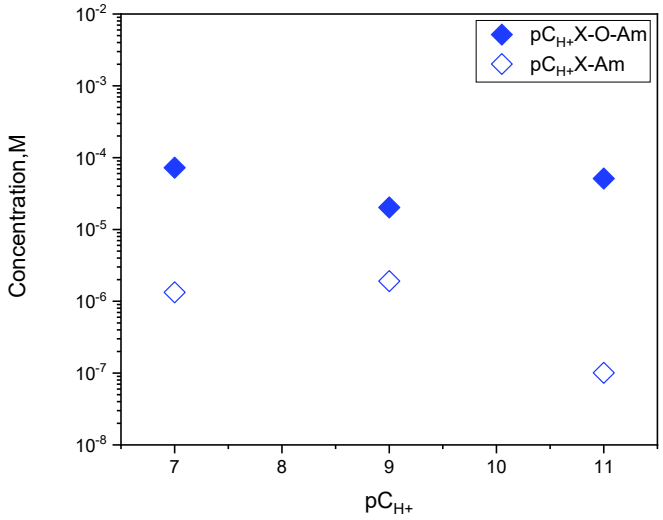

Figure 4. [Nd] as a function of pC_{H+} specific WIPP Brines. X denotes pC_{H+}7, 9 and 11, O denotes organics and Am denotes amorphous (after ~250 days of equilibration).

Figure 5 and Figure 6 show the comparison of the experimental results in this study with the literature data. The results from this study included into the figures with a comparison of the results from literature (Borkowski, et al., 2009), (Neck, et al., 2009), (Xiong, et al., 2017), (Sisk-Scott, 2019). Figure 5 shows the literature data and the data from this study in 5 M NaCl. Borkowski et al. (2009) found lower Nd concentration in solution in comparison with the data plots from Neck et al. (2009) and the data from this work. Neck et al. (2009) found Nd(III) concentrations ~2 orders of magnitude higher than our data at low pC_{H+}, conversely their Nd(III) concentration at pC_{H+} 11 are lower.

Figure 6 shows the experiments conducted in 0.1 M NaCl for the comparison of our data with the literature. For pC_{H+} value at 7, the data of Neck et al. (2009) plotting Nd(III) concentrations ~2 orders of magnitude higher than our data. At pC_{H+} 9 and 11 the data from this study in both crystalline and amorphous phases are higher than the plots of Neck et al (2009) and Sisk-Scott (2019). Sisk-Scott (2019) comments on the variability in Nd concentration data as variability in $Nd(OH)_3$ size and crystallinity, presence of colloids or very fine particles.

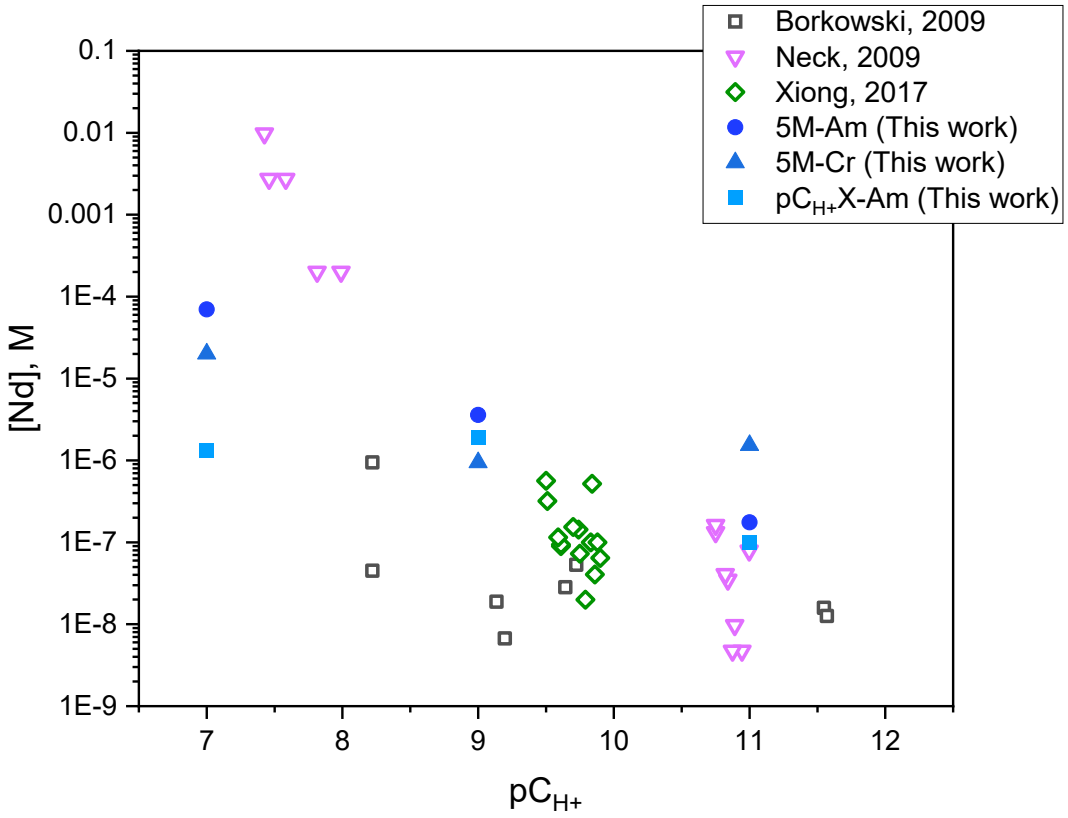

Figure 5. [Nd] in 5 M NaCl with comparison of literature data.

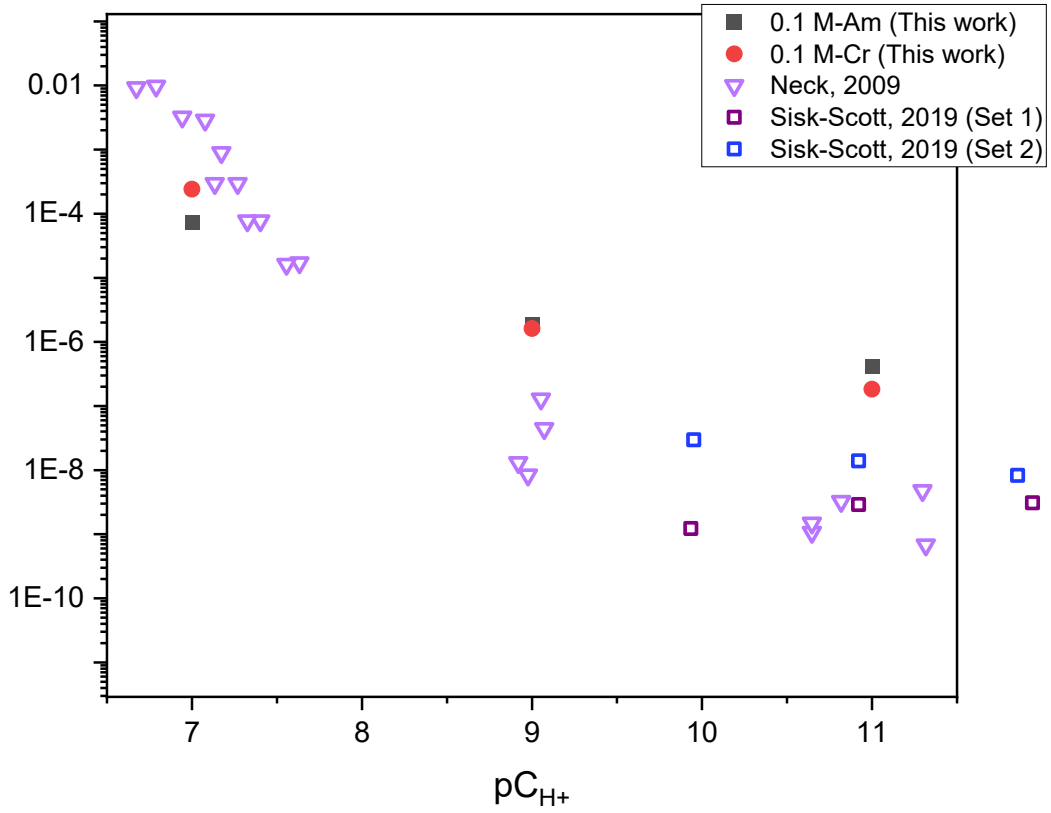

Figure 6. [Nd] versus pC_{H+} for literature data.

Figure 7 shows the Nd(III) solubility trends under all conditions investigated as a function of pC_{H+}. The highest Nd(III) concentration in the solution was found in 0.1 M NaCl and 5 M NaCl of crystalline $Nd(OH)_3$ at pC_{H+}7 with presence of organics. At all conditions organics presence have a positive effect of the solubility except 0.1 M NaCl, crystalline phase without organics. This point is higher than the pC_{H+} 7 brine while it is lower in all other simplified brines. Overall, WIPP specific brines have the lowest solubility under most conditions.

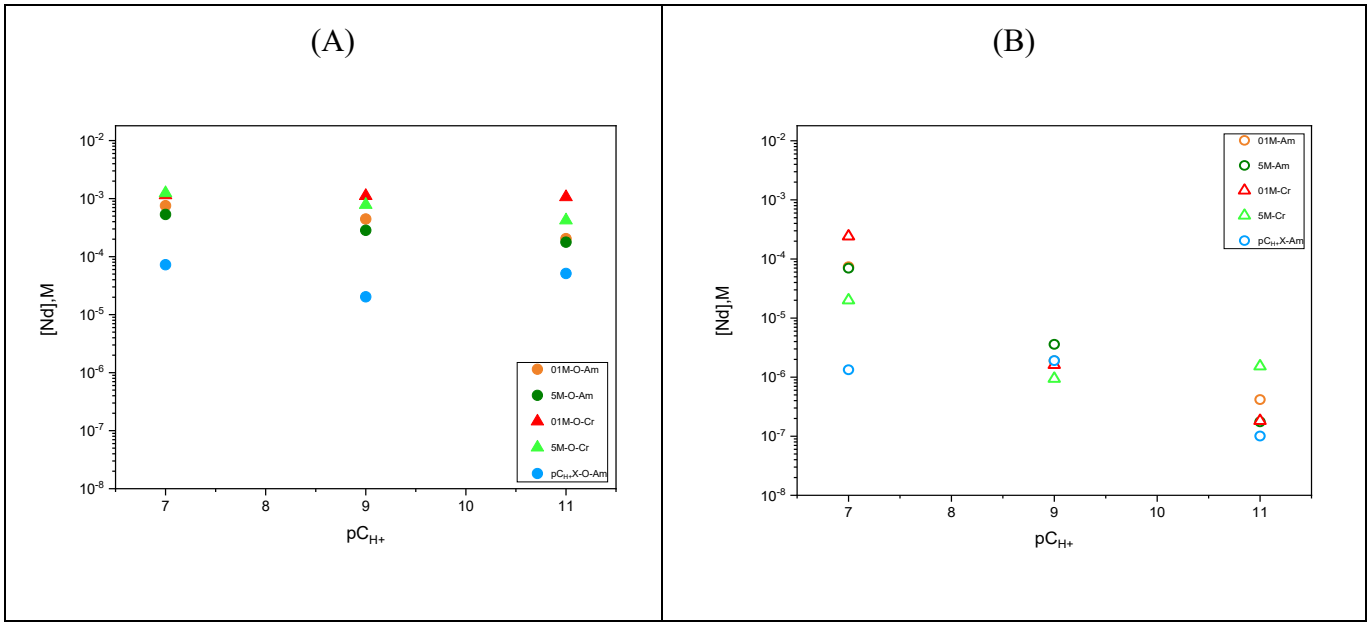

Figure 7. [Nd] as a function of pC_{H+} under all conditions. (A) [Nd] as function of pC_{H+} with organics (B) [Nd] as function of pC_{H+} without organics. 01M and 5M denotes 0.1 M and 5 M NaCl, O denotes organics, Am and Cr denotes amorphous and crystalline, respectively (after ~250 days of equilibration).

Figure 8 and Figure 9 show the Nd(III) concentration as a function of time in 0.1 M NaCl and 5 M NaCl with and without organics. In both conditions pC_{H+} 7 and 9 with organics and crystalline phase show the highest solubility effect. Over approximately 250 days there are not significant change of the solubility in the presence of organics. These data show that steady state Nd concentrations are rapidly achieved in the brines investigated. Moreover, when the experiments were performed without organics the changes are observed during this time. The biggest difference is observed in 0.1 M NaCl, pC_{H+} 9 with crystalline phase. A sharp decrease can be seen after the first sampling. Conversely, in 5 M NaCl, pC_{H+} 9 and amorphous phase a significant difference is observed during the experimental period.

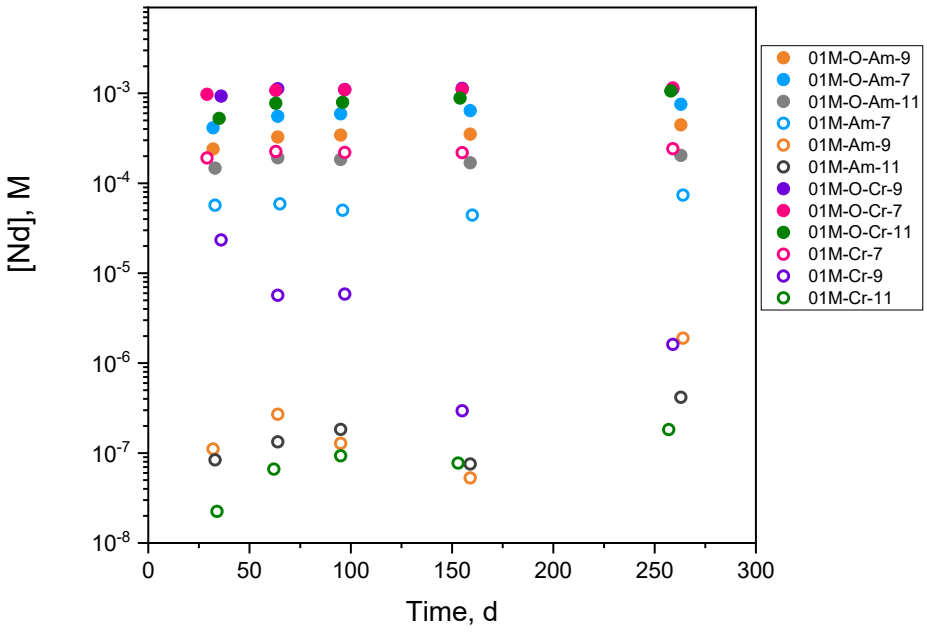

Figure 8. [Nd] concentration as a function of time in 0.1 M NaCl. 01M denotes 0.1 M NaCl, O denotes organics, Am and Cr denotes amorphous and crystalline, respectively.

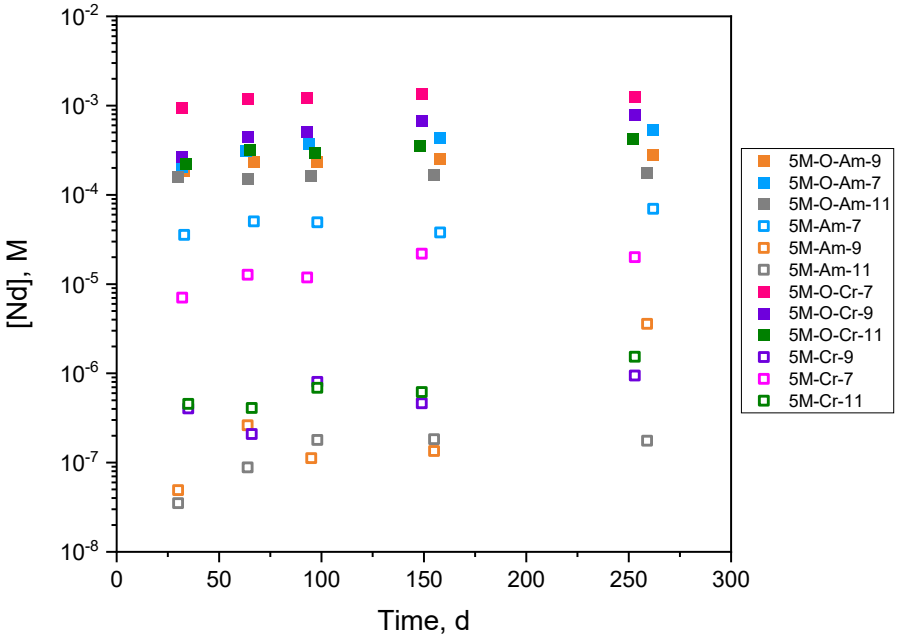

Figure 9. [Nd] concentration as a function of time in 5 M NaCl. 5M denotes 5 M NaCl, O denotes organics, Am and Cr denotes amorphous and crystalline, respectively.

Figure 10 shows the time effect on the solubility of Nd(III) in the pC_{H+} specific brines under repository conditions, with presence and absence of organics. As mentioned earlier, the presence of organics increases the solubility. The highest solubility is observed in pC_{H+} 7 brine with organics, the lowest is the pC_{H+} 11 brine without organics.

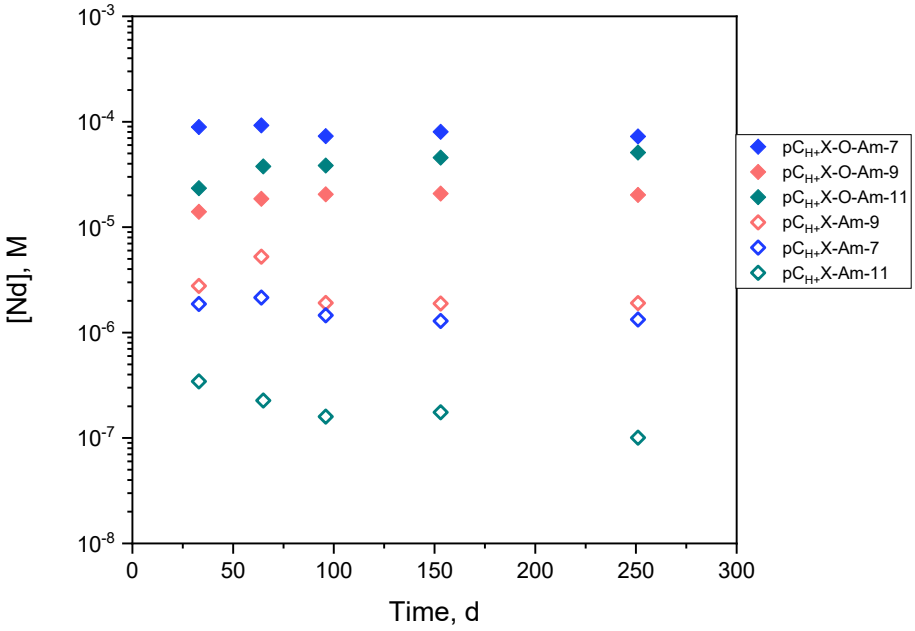

Figure 10. [Nd] concentration as a function of time in pC_{H+} specific brines. X denotes 7, 9 and 11, O denotes organics and Am denotes amorphous.

4.0 CONCLUSIONS

Nd(III) solubility was investigated with 60 samples over approximately 250 days until the experiments reach equilibrium. 0.1 M NaCl, 5 M NaCl, pC_{H+} specific brine at pH 7, 9 and 11 were used as the experimental conditions. Amorphous and crystalline $Nd(OH)_3$ phase were used for the experiments. Experiments were performed in anoxic conditions at room temperature. Effect of organics (EDTA and citrate) were examined.

According to our experimental results, citrate and EDTA obviously have a measurable impact on neodymium solubility as they are known strong complexants. In most cases, a higher effective solubility was noted when the crystalline $Nd(OH)_3$ phase was initially present. When the experiments in 0.1 M and 5 M NaCl with organics are compared as a function of time, the impact on Nd solubility for the crystalline phase between pC_{H+} 7 and 9 is higher for 5 M NaCl.

Furthermore, the presence of organics show an enhanced Nd solubility in pC_{H+} specific brines, too. Accordingly, we can conclude that organics clearly play a significant role for neodymium solubility.

Through repeated cycles of partial re-dissolution and re-forming of bonds, amorphous compounds eventually become crystalline, following Ostwald's step rules (Sisk-Scott, 2019). As a result of that our experimental results showed that Nd (III) solubility is higher with a crystalline starting phase and in the presence of organics.

These data quantify the effects of WIPP-relevant concentrations of EDTA (7.9×10^{-5} M) and Citrate (2.3 mM) on the solubility of An(III) to challenge the predictions of the WIPP actinide model and inform decisions and recommendations made in the upcoming recertification of the WIPP (CRA-2024).

5.0 QUALITY ASSURANCE, DATA TRACEABILITY, AND DOCUMENTATION

All of the data presented in this report, unless specified otherwise, were generated as Quality Level-1 data, in accordance with the WIPP Quality Assurance Program Document. Experiments were performed under the test plan, "Experimental Strategy to Challenge Actinide Solubility Predictions" (LCO-ACP-26). Descriptions of the experiments can be found in the scientific notebook designated ACP-26-1B, developmental notebook designated SN-CKA-1 and data package designated ACP-2211-05-09-01.

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