LA-UR-25-30019

Approved for public release; distribution is unlimited.

Title:	Effects of Borate and Organics on U(VI) Solubility in WIPP Brine
Author(s):	Kutahyali Aslani, Ceren
Intended for:	Report
Issued:	2025-10-08



Los Alamos
NATIONAL LABORATORY







Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by Triad National Security, LLC for the National Nuclear Security Administration of U.S. Department of Energy under contract 89233218CNA000001. By approving this article, the publisher recognizes that the U.S. Government retains nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

Notice: The current controlled version of this document is on the LCODocs website (https://lcodocs.lanl.gov/). A printed copy of the document may not be the current version.

LOS ALAMOS NATIONAL LABORATORY
CARLSBAD OPERATIONS

LCO-ACP-33, Revision 1

Effects of Borate and Organics on U(VI) Solubility in WIPP Brine

Effective Date: 11/25/2024

Originator:

Ceren Kutahyali Aslani Digitally signed by Ceren Kutahyali Aslani Date: 2024.11.22 09:46:12 -07'00'

Ceren Kutahyali Aslani, LANL-CO ACRSP Date

Approved by:

Jonathan Icenhower Digitally signed by Jonathan Icenhower Date: 2024.11.22 10:20:09 -07'00'

Jonathan Icenhower, LANL-CO ACRSP Team Leader Date

PRISCILLA YANEZ (Affiliate) Digitally signed by PRISCILLA YANEZ (Affiliate) Date: 2024.11.25 08:55:30 -07'00'

Priscilla Yanez, LANL-CO Quality Assurance Manager Date

DOUGLAS WEAVER (Affiliate) Digitally signed by DOUGLAS WEAVER (Affiliate) Date: 2024.11.25 09:54:11 -07'00'

Douglas Weaver, LANL-CO Division Leader Date

History of Revisions

Revision Number	Effective Date	Pages Affected	Description of Revision
0	12/22/2022	All	Original Release
1	11/25/2024	All	Update to include new experimental data. Added other editorial changes as needed. Complete revision, no change bars present.

TABLE OF CONTENTS

ACRONYMS AND ABBREVIATIONS 4
EXECUTIVE SUMMARY 6
1.0 INTRODUCTION 7
2.0 EXPERIMENTAL 10
3.0 RESULTS AND DISCUSSION 13
4.0 CONCLUSIONS 17
5.0 QUALITY ASSURANCE, DATA TRACEABILITY, AND DOCUMENTATION 18
6.0 REFERENCES 19

LIST OF TABLES

Table 1. Concentration Range of Acetate, Oxalate, Citrate and EDTA in the WIPP Repository Should Brine Inundation Occur (SOTERM-2019). These are Calculated Based on the Project Inventory and the Minimum Brine Volume (17,400 m^3) for DBR 9

Table 2. Compositions of the Brines used in the Experiments. Data are based on 90% Strength pC_{H+} 9 Brine. * 11

Table 3. Experimental Matrix for Model Predictions 12

LIST OF FIGURES

Figure 1. Absorption Spectrum of the Uranyl Stock Solution. The Absence of Spectral Features above 500 nm Confirmed that there was no Significant Amount of U(IV) Present. 12

Figure 2. Effect of Borate Concentration on [U] Solubility as a Function of Time in pC_{H+} 9 Brine. B Denotes Borate. 15

Figure 3. [U] Solubility as a Function of Borate Concentration in pC_{H+} 9 Brine at the end of the 609 Days of Experiments. 16

Figure 4. Effect of Presence of Organics on [U] Solubility as a Function of Time in pC_{H+} 9 Brine. (ORG: Organics, AC: Acetate, OX: Oxalate, CIT: Citrate). 17

ACRONYMS AND ABBREVIATIONS

ACRSP	Actinide Chemistry and Repository Science Program
am	amorphous
An	Actinide
ASTP	WIPP Actinide Source Term Program
°C	Degrees Celsius
$Ca(OH)_2$	Calcium hydroxide
CBFO	Carlsbad Field Office (U.S. Department of Energy)
CDP	Cellulose degradation products
CEMRC	Carlsbad Environmental Monitoring and Research Center
CFR	Code of Federal Regulations
Cl	Chlorine
cr	crystalline
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
GWB	Generic Weep Brine, a synthetic brine representative of intergranular Salado-Formation brines
HPW	High purity water
I	Ionic strength
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
K	Kelvin
kDa	kiloDalton
LANL-CO	Los Alamos National Laboratory−Carlsbad Operations
Ln	Lanthanides

ACRONYMS AND ABBREVIATIONS (cont.)

M	Molarity, moles of solute per liter of solvent
mg	Milligram
Mg	Magnesium
MgO	Magnesium oxide
µL	Microliter
mL	Milliliter
mM	Millimolar
Na	Sodium
$Na_2B_4O_7$	Sodium tetraborate
NaCl	Sodium chloride
NaOH	Sodium hydroxide
PA	Performance Assessment
pC_{H+}	negative logarithm of H^+ concentration in moles/liter
pH	negative logarithm of H^+ activity
ppb	Parts per billion
ppm	Parts per million
rpm	Revolution per minute
QAPD	Quality Assurance Program Document
SOTERM	Actinide Chemistry Source Term (Appendix in the WIPP CRA)
TRLFS	Time-Resolved Laser Fluorescence Spectroscopy
TRU	Transuranic Elements (actinides higher in atomic number than uranium)
UO_2^{2+}	Uranyl ion – Aqueous form of the uranium in the VI oxidation state
UV-Vis	Ultra-violet visible (wavelength of light detected by spectrophotometry)
WIPP	Waste Isolation Pilot Plant
XANES	X-ray absorption near edge spectroscopy
XRD	X-Ray Diffraction

EXECUTIVE SUMMARY

This report provides an update to a previously issued report on the solubility of uranium (VI) at different borate concentrations and in the presence of organics. The solubility of uranium (VI) in the Waste Isolation Pilot Plant (WIPP)-relevant brine was determined to support ongoing WIPP recertification activities (CRA-2026). This research was performed by the Los Alamos National Laboratory-Carlsbad Operations (LANL-CO) Actinide Chemistry and Repository Science Program (ACRSP).

This report differs from the previous one in that longer time solubility experiments are included, i.e., 609 days instead of 135 days. The main goal of this study is to perform screening experiments that account for the contributions of organics and borate on uranium solubility. In this report, the solubility of U(VI) was determined at pC_{H+} 9 WIPP brine in the absence or presence of borate and organics using an under-saturation approach.

Organic compounds present in WIPP waste can form strong complexes with actinides and may affect the oxidation states of actinides (Suzuki et al., 2006; Srivastava et al., 2017) The organic compounds addressed in WIPP Performance Assessment include EDTA (ethylenediaminetetraacetic acid), oxalate, citrate, and acetate (SOTERM, 2019). These data quantify the effects of WIPP-relevant concentrations of borate and organics on the solubility of U(VI) to discuss the predictions of the WIPP actinide model and inform decisions and recommendations made in the upcoming recertification of the WIPP Compliance Recertification Application (CRA-2026). The WIPP Actinide Source Term Program (ASTP) did not develop a model for the solubility of actinides in the VI oxidation state. The solubility of UO_2^{2+}, in the absence of WIPP-specific data, is presently set to be equal to a conservatively high 1 mM concentration within the WIPP Performance Assessment (PA) for all expected WIPP conditions (SOTERM, 2019) as selected at the recommendation of the Environmental Protection Agency (EPA) (EPA, 2005). According to the current WIPP chemistry model assumptions and conditions, the expected pC_{H+} is about 9.5 and controlled by MgO buffering CO_3^{2-}. The results of the experiments in this report show that the solubility data trend remains the same at the end of the 609 days within the uncertainty limits and the differences are almost indistinguishable. These results demonstrate that equilibrium conditions prevailed over the experimental duration.

The experiments performed were completed according to the U.S. Department of Energy (DOE) approved Test Plan entitled “Experimental Strategy to Challenge Actinide Solubility Predictions” (LCO-ACP-26). All data reported were obtained under the LANL-CO Quality Assurance Program, which is compliant with the DOE Carlsbad Field Office, Quality Assurance Program Document (CBFO/QAPD) (QAPD, 2023).

1.0 INTRODUCTION

The Waste Isolation Pilot Plant (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, 26 miles 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 U.S. Department of Energy (DOE), Carlsbad Field Office (CBFO). WIPP-relevant U(VI) 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.

In the environment, U exists only in the IV and VI oxidation state as U^{4+} and UO_2^{2+} species. Uranium can form highly insoluble U(VI) and U(IV) phases and can persist up to mM concentrations in near-surface groundwater (SOTERM, 2019). If U(III) forms, it is metastable and quickly oxidized in aqueous solution. U(V) exists as a very short-lived transient that instantly disproportionates to U(IV) and U(VI) species in the absence of complexing ligands. U(VI) as uranyl (UO_2^{2+}) complexes predominate under the oxidizing subsurface conditions typical of most near-surface groundwater and is not reduced easily.

In the WIPP TRU repository, U(VI) is the only An(VI) actinide considered in Performance Assessment (PA) because both Np(VI) and Pu(VI) can be excluded under the highly reducing conditions expected to predominate. An actinide (VI) model was never developed because the uranium contribution is relatively minor (~10^{-6} M) to overall potential release of actinides from the WIPP (Lucchini et al., 2013b). Based on available literature data, the solubility of U(VI) in WIPP PA has been conservatively set by the EPA at a concentration of 1 mM to account for the lack of data on the effects of carbonate (EPA, 2005). Uranium is not a TRU component, but it is a predominant actinide in the WIPP by mass. In addition, it is potentially useful as a +VI analog for Pu(VI) species. Currently, U is conservatively assumed to be U(VI) in 50% of the PA vectors (set at a 1 mM solubility) and U(IV) in 50% of the PA vectors. Although its specific activity is low (3.36×10^{-7} Ci), its projected release into the Culebra in the event of an intrusion is high (Bethune, 2023).

A detailed review and data summary with recommendations regarding An (VI) solubility was reported by the ACRSP group (Lucchini et al., 2010; 2013b). They reported the solubility of uranium (VI) in WIPP-relevant brines as a function of pC_{H+} and ionic strength, both in the absence and presence of carbonate. The uranium (VI) solubilities measured in their experiments were about 10^{-6} M in GWB brine at $pC_{H+} \geq 7$ and about 10^{-8} - 10^{-7} M in ERDA-6 at $pC_{H+} \geq 8$. At the expected pC_{H+} in the WIPP (~ 9.5), measured uranium solubility approached ~ 10^{-7} - 10^{-6} M. They concluded that the solubility trends observed in carbonate-free solutions pointed towards lower uranium solubilities in WIPP brine, a lack of significant amphotericity, an insignificant effect of borate complexation, and a predominance of hydrolysis at $pC_{H+} > 10.5$. According to

experiments on the effect of carbonate on uranium solubility in WIPP brines, the highest uranium solubility obtained experimentally was ~ 10^{-4} M with the highest carbonate concentration (2×10^{-3} M) investigated, which is ~ 10 times higher than the carbonate concentration predicted by WIPP PA.

In this work, we focused on the two key scientific issues, which are the effects borate and organics, to determine the solubility of U(VI) under conditions that simulate the expected environment in the WIPP. All experiments were performed under the DOE approved test plan "Experimental Strategy to Challenge Actinide Solubility Predictions" (LCO-ACP-26). The resulting data established the solubility of U(VI) in simulated WIPP brine at pC_{H+} 9, as well as in the presence and absence of borate and organics using an under-saturation approach.

Determining the solubility of any species in a complicated matrix such as WIPP brine is not straightforward. The four organic chelating agents addressed by PA are acetate, oxalate, citrate and ethylenediaminetetraacetic acid (EDTA). Concentrations of these organic complexants are given in Table 1. These are assumed to not degrade under the expected WIPP conditions. Under WIPP conditions, their concentrations are defined by their inventory (except for oxalate, which is solubility limited); these complexing agents can form actinide complexes that increase their solubility in the source term (SOTERM, 2019).

Organic compounds are expected to 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). 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 1). The complexation of chelating agents with actinides has a significant effect on the actinide concentrations in brine. The organic inventories are also important as they, in many cases, define the predominant aqueous speciation predicted. These inventories are updated in each CRA cycle. The CRA-2019 (SOTERM, 2019) projected inventories lead to the concentrations shown in Table 1. The borate complexation effect in WIPP brine was demonstrated on neodymium (III) by Borkowski et al. (2009). Later, Borkowski et al. (2010) focused on actinide-borate complexation in WIPP-related environments. Even though the borate contribution is negligible according to current modeling assumptions (SOTERM, 2019), their results showed that borate affects actinide solubility.

Table 1. Concentration Range of Acetate, Oxalate, Citrate and EDTA in the WIPP Repository Should Brine Inundation Occur (SOTERM-2019). These are Calculated Based on the Project Inventory and the Minimum Brine Volume (17,400 m^3) for DBR.

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}

The importance of this work is to reveal the effect of borate and organics on the solubility in WIPP-relevant brine. Previous studies shows that the presence of borate and organics increases uranium solubility. But those studies (see below) are mostly in simple brines with lower ionic strengths or lower pH values and not representative of WIPP. In this study, we demonstrated the effect of the presence of organics in the WIPP brine medium. As discussed in the Test Plan "Experimental Strategy to Challenge Actinide Solubility Predictions" (LCO-ACP-26), it is aimed to address the missing gaps specific to the WIPP repository, which are uranium solubility in varying concentrations of borate and organics in brine solution separately and all organics together in the brine solution. The results of this report will give us an overview of the magnitude of the increase in uranium solubility and will indicate which organic content is the most important in terms of solubility increase. In light of these results, a more accurate assessment can be made of the 1 mM uranium solubility was conservatively set by EPA.

Previous Work

A series of studies was conducted at Florida State University as part of the WIPP ASTP program to determine the strength of organic complexes under conditions relevant to the WIPP (Borkowski et al., 1996, 2001; Novak et al., 1996; Bronikowski et al., 1999; Choppin et al., 2001). The studies show the complexation behavior of U(VI) with organic ligands in the pH region between 5 and 7, which are not representative of WIPP-relevant conditions. Other studies (Felipe-Sotelo et al., 2015, 2017) investigated the solubility of U(VI) in 95%-saturated $Ca(OH)_2$ (pH 12.3) in the presence of organic ligands and cellulose degradation products (CDP). These studies show that solubility increases up to 3 orders of magnitude in the presence of citrate and an order of magnitude in the presence of CDP.

Xiong and Wang (2021) obtained solubility constants at infinite dilution for solid uranyl oxalates, $UO_2C_2O_4 \cdot 3H_2O$, based on the solubility data over a wide range of ionic strengths. Their model set the stage for developing a detailed understanding of how oxalate complexes affect

uranium mobility over a wide range of geochemical conditions, including those pertinent to WIPP.

Yalcintas et al. (2017) investigated the impacts of EDTA on the solubility and speciation of uranium as a function of ionic strength, redox conditions, and pC_{H+}. As a result of their experiments, they reported a significant increase in U(VI) solubility by increasing EDTA concentration. Their under-saturation experiments, (where [EDTA]=0.001 and 0.05 M), were investigated at a constant ionic strength (I = 0.5 and 5.0 M). The results show an order of magnitude increase of the [U] in solution in 5 M NaCl in the presence of EDTA.

Rao et al. (2005) studied the complexation of U(VI), Th(IV), and Nd(III) with acetate from 10 to 70 °C. In this work, the formation constants and the enthalpies of complexation were determined by titration potentiometry and calorimetry. They found that the complexes with acetate became stronger as the temperature increased, despite the enthalpy of complexation becoming more endothermic and unfavorable to the complexation at higher temperatures. The enhancement of the complexation is mainly due to a larger entropy effect at higher temperatures and can be explained by the effect of temperature on the solvent structure and a simple electrostatic model.

A PhD. thesis from The Institute for Nuclear Waste Disposal of the Karlsruhe Institute of Technology (KIT-INE) reported the interaction of borate with Ln (III) and An (III, IV, V, VI) in dilute to concentrated saline solutions (NaCl and $MgCl_2$) with various $[B]_{tot}$ concentrations (Hinz, 2015). In the case of U(VI), borate showed an increase in U(VI) solubility in NaCl systems at $7.5 \leq pC_{H+} \leq 9$ for $[B]tot \geq 0.04$ M likely caused by the formation of aqueous U(VI)-borate complexes. Borates tend to form polymeric networks containing the polymerized BO_3 and BO_4 units which build layers between the UO_2^{2+} cations.

2.0 EXPERIMENTAL

In this work, borate and organics effects on the solubility of U(VI) in anoxic pC_{H+} 9 WIPP-specific brine at room temperature were investigated using an under-saturation experimental approach. In the experiments, synthesized uranyl hydroxide was used as the solid phase. High purity water (HPW) was bubbled with high-purity nitrogen to remove dissolved oxygen, and 25 µL concentrated HCl (Fisher Scientific) was added to remove carbonic acid in brine solution prior to placement in a nitrogen glove box (<0.1 ppm O_2) for the duration of the experiment. Experiments were equilibrated for ~609 days at an adjusted pC_{H+} of 9 with carbonate free NaOH (Fisher Scientific) and HCl (Fisher Scientific). 0.01 M EDTA (Na_4EDTA, Aldrich) and 0.1 M citrate (citric acid anhydrous, Fluka) were prepared as stock solutions. Appropriate dilutions were made from these stocks for the experiments. Acetate (sodium acetate, Aldrich) and oxalate (oxalic acid) were added to solutions by weighing appropriate amounts. Borate free pC_{H+} 9 brine was used for borate effect experiments. Appropriate dilutions were performed from WIPP-specific pC_{H+} 9 brine for adjusting borate concentrations.

The predicted range in brine composition expected in the WIPP is shown in Table 2. 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, and bromide. 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, *Brine Preparation*.

Table 2. Compositions of the Brines used in the Experiments. Data are based on 90% Strength pC_{H+} 9 Brine. *

	Element/Species in M						
	Na^+	**K^+**	**Mg^{2+}**	**Ca^{2+}**	**Li^+**	**$B_4O_7^{2-}$**	**Cl^-**
pC_{H+} 9-borate free	2.93	0.41	0.93	1.2×10^{-2}	3.4×10^{-3}	-	3.7
pC_{H+} 9	3.03	0.42	0.94	1.2×10^{-2}	3.9×10^{-3}	3.5×10^{-2}	3.7

For details on the chemical composition, see Scientific Notebook SN-CKA-1 and ACP-26-1B.

UV-Vis spectroscopy was used to confirm that the stock solution is primarily contains U(VI) (Figure 1). If any U(IV) is present, it is below the limit of detection. The spectrum was taken using a Varian CARY 5000 dual beam instrument (ACP-EXP-006, *UV-VIS-NIR Spectrophotometer Calibration and Performance Check*). $UO_2(OH)_2$ was precipitated from a stock solution with 1 M carbonate free NaOH. After centrifugation (6 min., 3000 rpm), the precipitate was washed with HPW. This washing step was performed twice. The precipitate was dissolved in 0.1 M HCl. 100 µl aliquots of 0.1M and/or 1 M NaOH (Acros Organics) was added until a permanent precipitate appeared. The solid was allowed to settle overnight to complete precipitation. After measuring the final pH, it was washed twice with high purity water (HPW, 18.2 MΩ cm).

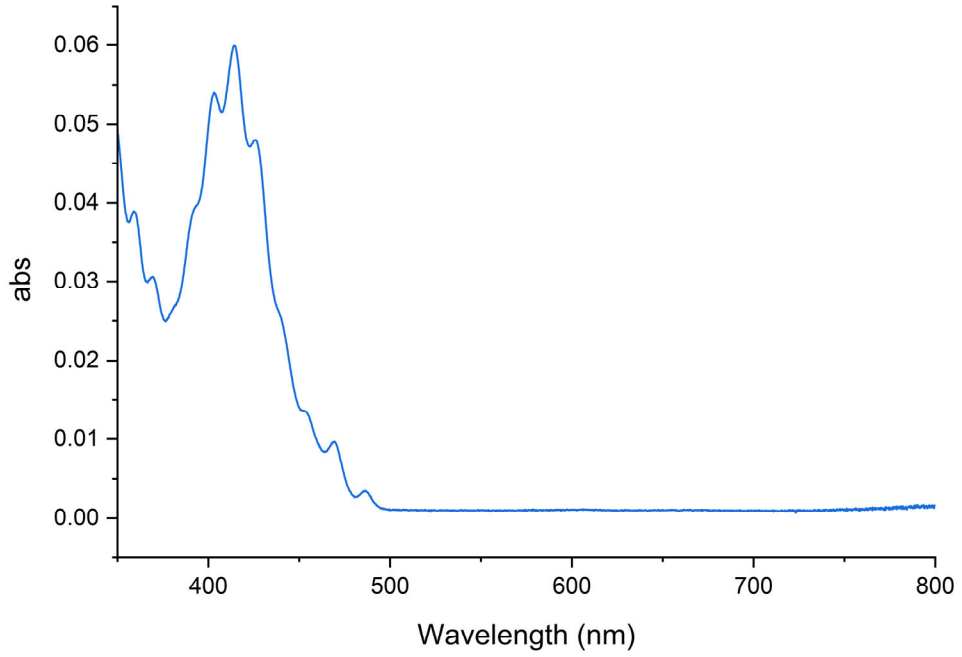


Figure 1. Absorption Spectrum of the Uranyl Stock Solution. The Absence of Spectral Features above 500 nm Confirmed that there was no Significant Amount of U(IV) Present.

Experiments were conducted on U(VI), 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 4.1: Effects of borate and organics on the solubility of U(VI) for the expected conditions in the WIPP." Experiments were performed in duplicate.

Table 3. Experimental Matrix for Model Predictions

Experiment Designation	Complexant	Medium	pC_{H+}	Comment
Borate Effects				
U6-B-0	0 mM borate	pC_{H+} Specific Brine*	9	Control
U6-B-10	10 mM borate	pC_{H+} Specific Brine*	9	Borate effects
U6-B-50	50 mM borate	pC_{H+} Specific Brine*	9	Borate effects
U6-B-100	100 mM borate	pC_{H+} Specific Brine*	9	Borate effects
U6-B-WIPP	Brine	pC_{H+} Specific Brine	9	WIPP-relevance

Table 3. Experimental Matrix for Model Predictions (cont.)

Organic Effects				
U6-ORG-AC	Acetate**	pC_{H+} Specific Brine	9	Organic effects
U6-ORG-OX	Oxalate**	pC_{H+} Specific Brine	9	Organic effects
U6-ORG-CIT	Citrate**	pC_{H+} Specific Brine	9	Organic effects
U6-ORG-EDTA	EDTA**	pC_{H+} Specific Brine	9	Organic effects
U6-ORG-ALL	All Organics**	pC_{H+} Specific Brine	9	Organic effects
*pH-specific brine at pC_{H+} = 9 w/o borate **at the predicted maximum 1 X concentration in CRA-2019		B: Borate; ORG: Organics: AC: Acetate; OX: Oxalate; CIT: Citrate:		

Under-saturation experiments were conducted at ambient temperature (23 ± 5 °C). In the experiments, between 3 and 9 mg of $UO_2(OH)_2$ solid were placed into polypropylene bottles along with 10 mL and 30 mL solutions, for borate and organics experiments, respectively. Sample solutions were periodically withdrawn from the experiments at approximately one-month intervals to determine whether the system had reached equilibrium (first sampling was made after 6 days). Sampling was performed using 10 kDa (Pall-type filters, Omega-modified polyethersulfone) filtration at 13,000 RPM centrifugation for 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 Thermoscientific OrionStar T940 pH meter that was calibrated with three pH buffers (Fisher Chemical, for pH 4, pH 7, and pH 10). The measured pH readings were converted to negative logarithm of hydrogen ion concentrations on a molar scale (i.e., pC_{H+}). The hydrogen ion concentration was determined according to $pC_{H+} = pH_{exp} + \Delta pH$ as described previously in the literature (Borkowski et al., 2009), where pH_{exp} is the measured pH value and ΔpH is the empirical correction factor entailing the liquid junction potential of the electrode and the activity coefficient of H^+. ΔpH is 1.12 for pC_{H+} 9 in this study. Concentration of uranium was determined in each sample using ICP-MS (ACP-EXP-011, *Inductively Coupled Plasma-Mass Spectrometry*). 100 µL from each 1:10 dilution was added to 1700 µL of 2% HNO_3 (Fisher Scientific) with 300 ppb of an indium internal standard (Agilent High Purity Standards) to provide a final dilution of 1:180 in triplicate for ICP-MS analysis. The detection limit by ICP-MS for uranium was ~10^{-12} M, which was ~1×10^{-10} M to 1×10^{-11} M for our experiments. Uncertainties were calculated based on the standard deviation from the mean of the ICP-MS measurements.

3.0 RESULTS AND DISCUSSION

In this work, U(VI) solubility in the presence/absence of borate and organic ligands under conditions that simulate the expected environment in the WIPP were investigated. This study

addressed the effects associated with complexation by borate and organics and their influence on U solubility. In order to investigate the effect of borate and organics, on U(VI) solubility, the experiments are designed for $UO_2(OH)_2$ in pC_{H+} 9 WIPP brine.

The solubility of U(VI) in pC_{H+} 9 brine in the presence of borate can be seen in Figure 2. It appears that the solubility of uranium increases with increasing borate concentration. Six samplings were carried out at different times throughout the experiments. The last one was at 609 days. The reader can see from the Figure 2, at the beginning of the experiments (6 days), uranium concentration is the lowest in the absence of borate, whereas the highest uranium concentration was observed in WIPP brine with the highest borate content. This trend remained almost unchanged in all samples. The final sampling shows that the experiments reached equilibrium within 609 days (Figure 2). Experiments with 100 mM borate concentration and experiments in WIPP brine eventually exhibited slightly higher solubility (Figure 3), than experiments in lower borate concentrations. At lower borate concentrations, apparent solubilities are indistinguishable from one another suggesting that the effect of low borate concentrations (10 – 50 mM) is minor on U solubility. Lucchini et al. (2013a) investigated the effect of borate on U(VI) solubility in their work by saturating three ERDA-6 brine solutions at an initial pC_{H+} of 8.1, 9.6, and 10.5 with sodium tetraborate solid, reaching a total concentration of $\sim 5\times10^{-2}$ M tetraborate in solution. A significant increase was observed after 55 d at I=5.0 M, indicating the formation of a complex anion of U(VI) with tetraboric anion (Lucchini et al., 2013a).

There is little information on the coordination chemistry of tetraborate, especially with actinides. Borkowski et al. (2010) investigated the effect of borate on Nd (III) solubility in dilute to concentrated NaCl solutions at $pC_{H+} = 8.6$ and $0 \leq [B]_{tot} \leq 0.16$ M. A small increase was observed in the Nd concentration in the range of $5.0 \times 10^{-8} – 2.5 \times 10^{-7}$ M. Schott et al. (2015) studied the Eu (III)-borate interaction. The formation of a Eu(III) solid phase involving polyborates was observed. In aqueous solution, polyborates show weak complexation of Eu(III). In view of the lack of a systematic study on An(III)-borate interactions, Hinz et al. (2015) investigated the interaction of Nd (III) and Cm (III) with borate. The experiments in dilute to concentrated NaCl, $MgCl_2$ and $CaCl_2$ solutions under near neutral pH conditions and $[B]_{tot} \geq$ 0.04 M were performed. They observed no increase in solubility for $Nd(OH)_3(am)$ in the presence of $[B]_{tot} \leq 0.4$ M, but 2-4 orders of magnitude drop occurred at $6 \leq pH_c \leq 9$.

The chemical formula of borax is $Na_2[B_4O_5(OH)_4].8H_2O$, and it can also be written as $Na_2B_4O_7.10H_2O$. The structure of the $[B_4O_5(OH)_4]^{2-}$ ion can be identified with two four coordinate boron centers and two three coordinate boron centers and it is the dominating polymeric anion formed in the simulated brines when the pC_{H+} increases from neutral to mildly basic values (7−9) (Lucchini et al., 2013a). Monomeric species $B(OH)_3(aq)$ and $B(OH)_4^-$ have been reported to have a low tendency to complex hard Lewis acids such as actinide cations (Pearson, 1995). Polyborate species, $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$ and $B_5O_6(OH)_4^-$, are known to

form with increasing boron concentrations (Hinz, 2015). These species have been postulated to form stronger complexes with actinides than the corresponding monomeric species (Borkowski et al., 2010).

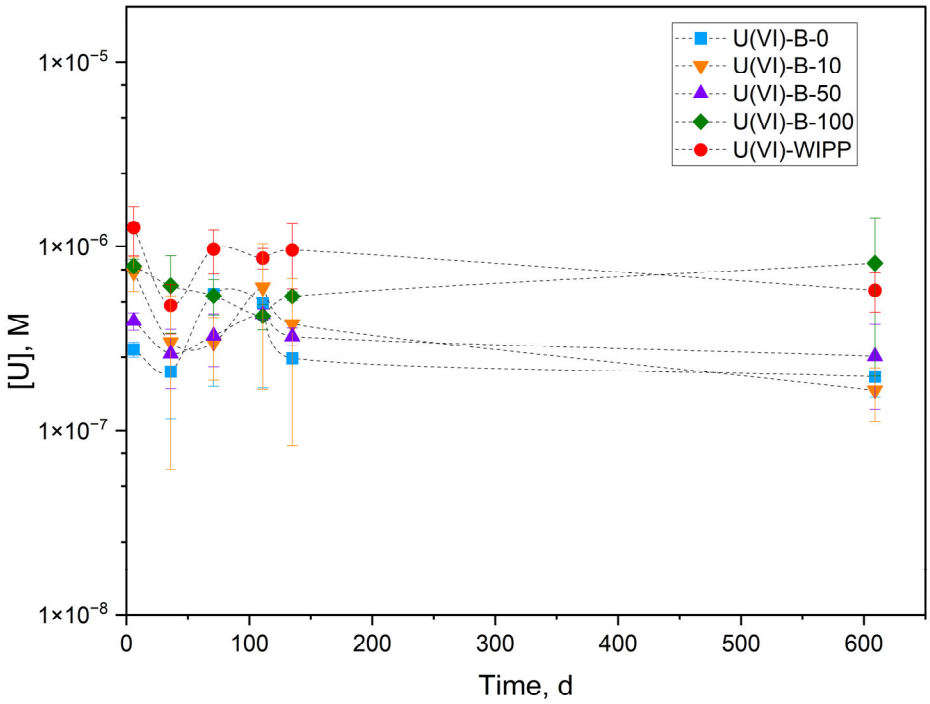


Figure 2. Effect of Borate Concentration on [U] Solubility as a Function of Time in pC_{H^+} 9 Brine. B Denotes Borate.

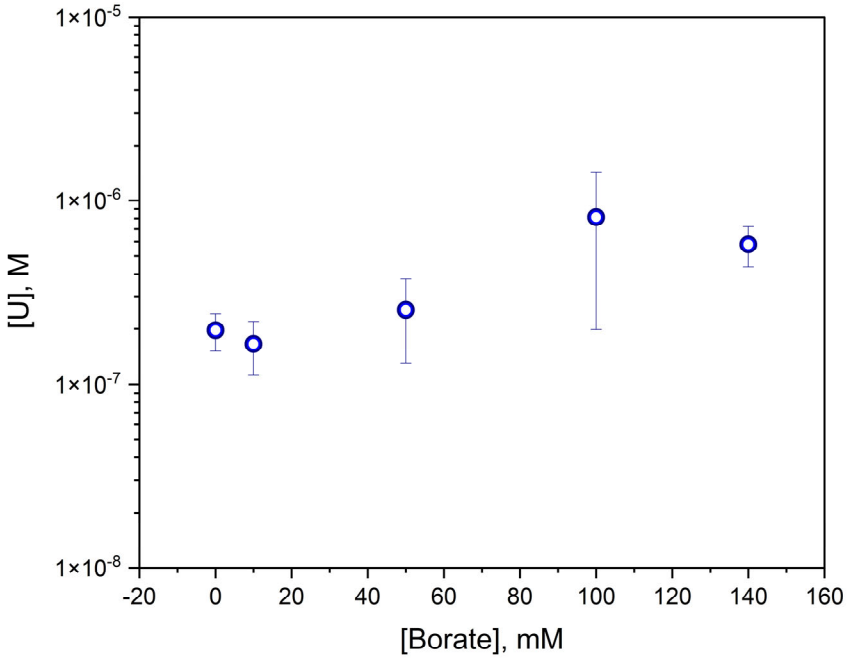


Figure 3. [U] Solubility as a Function of Borate Concentration in pC_{H+} 9 Brine at the end of the 609 Days of Experiments.

Figure 4 shows the effect of organics on uranium solubility as a function of time in the presence of organics. At the beginning of the experiments (6 days), the presence of all organics together (ORG-ALL) and citrate shows the highest uranium concentration in the solution. This trend remains unchanged throughout all the sampling periods except the last sampling (609 days). U concentrations in the experiments with citrate are slightly lower than the experiments with all organics together in the solution, but the final sampling shows that the solubilities of both are so close that the difference is almost indistinguishable. Experiments with other organics (acetate, oxalate and EDTA) exhibit solubilities that are almost indistinguishable from each other, although there are slight fluctuations over 609 days. In summary, the solubility of uranium was ~3 times higher when all WIPP-relevant organics were present. This, as shown in the organic-specific experiments, was predominantly due to citrate complexation. U(VI)-organic speciation data are a key gap in available high pH data for uranyl in WIPP brine.

Felipe-Sotelo et al. (2015) studied the influence of anthropogenic organic complexants (citrate, EDTA and DTPA from 0.005 to 0.1 M) on the solubility of nickel(II), thorium(IV) and uranium (U(IV) and U(VI)). Experiments were carried out in 95%-saturated $Ca(OH)_2$ solutions. They found citrate had the greatest effect on the solubility of Th(IV) and U(IV)/(VI). Their results show that presence of citrate increases the concentration of U(VI) in solution by 3 orders of

magnitude. Lozano et al. (2011) tested citrate, EDTA and EDDS ([S,S]-stereo-isomer of ethylenediaminedisuccinic acid) as chelating agents on the solubilization of uranium from a granitic soil. In their work, the most efficient chelating agent to solubilize uranium was found to be citrate, while EDTA was unsuccessful. These findings are in agreement with the data from our experiments.

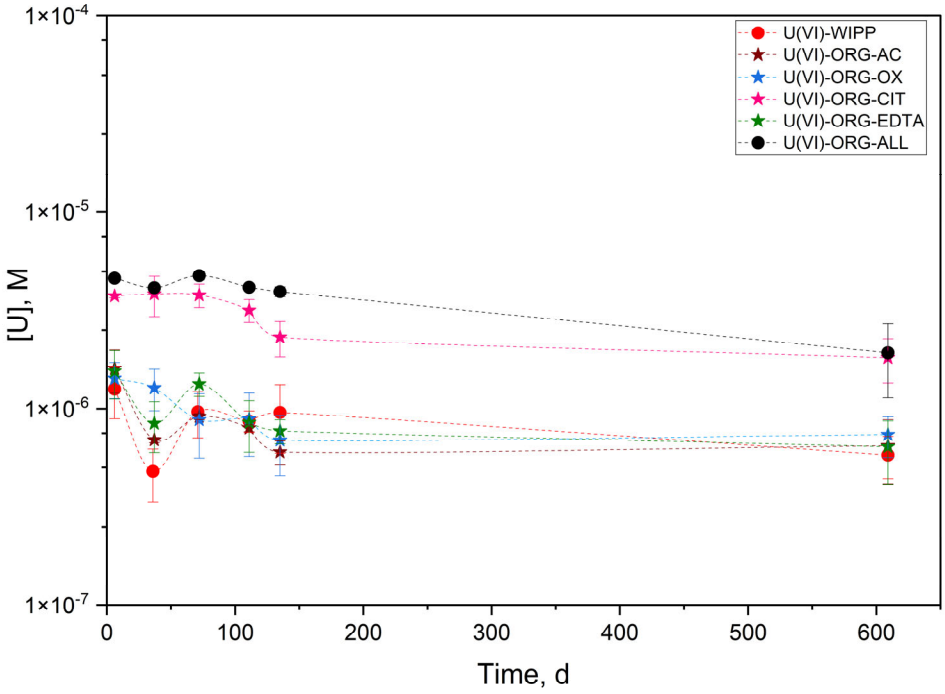


Figure 4. Effect of Presence of Organics on [U] Solubility as a Function of Time in pC_{H+} 9 Brine. (ORG: Organics, AC: Acetate, OX: Oxalate, CIT: Citrate).

4.0 CONCLUSIONS

In this report, WIPP-relevant data for uranium (VI) solubility at pC_{H+} 9 brine in the absence or presence of borate and organic complexants as a function of time are provided. In the absence of borate, uranyl concentrations are ~10^{-7} M and in WIPP conditions it is slightly higher. Organic complexation increased uranium solubility in the experiments, with U solubility as high as ~10^{-6} M when all organic complexants were present. Similarly, citrate individually has the highest impact on the U solubility amongst all organic complexants used.

In conclusion, the experiments show that U(VI) solubility is ~10^{-6} M with either borate or organics present. This result is much lower than the 1 mM assumption used in PA. The data we reported in this document showed that the 1 mM value for uranium (VI) solubility used in WIPP

PA is conservative, relative to our experimental results. If feasible, the solid phase will be characterized further.

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 CBFO QAPD. 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-26-4, developmental notebook designated SN-CKA-1 and ACP-26-1B.

6.0 REFERENCES

Bethune, J., Analysis Report for Culebra Flow and Transport in the Replacement Panels Planned Change Request, 2023, Sandia National Laboratories, Waste Isolation Pilot Plant, ERMS 579725.

Borkowski, M., Lis, S., Choppin, G. R., 1996. Complexation study of NpO^{2+} and UO_2^{2+} ions with several organic ligands in aqueous solutions of high ionic strengh. Radiochim. Acta, 74, 117.

Borkowski, M., Moore, R.C., Bronikowski, M.G., Chen, J.F, Pokrovsky, O.S, Xia, Y.X.; Choppin, G.R., 2001. Thermodynamic modeling of actinide complexation with oxalate at high ionic strength. J. Radioanal. Nucl. Chem, 248, 2.

Borkowski, M., Lucchini, J.-F., Richmann, M. K., Reed, D. T., 2009. Actinide (III) Solubility in WIPP Brine: Data Summary and Recommendations, Los Alamos National Laboratory; Carlsbad, NM. LA-UR-10-14360.

Borkowski, M., Richmann, M., Reed, D. T., Xiong, Y., 2010. Complexation of Nd(III) with tetraborate ion and its effect on actinide(III) solubility in WIPP brine. Radiochimica Acta, 98, 577-582.

Bronikowski, M. G., Pokrovsky, O. S., Borkowski, M., Choppin, G. R., 1999. UO_2^{2+} and NpO^{2+} complexation with citrate in brine solutions. In: Actinide Speciation in High Strength Ionic Media. New York: Kluwer Academic Plenum Publisher, pp. 177-185.

Choppin G.R., Bond , A.H, Borkowski, M., Bronikowski, M.G., Chen, J.F, Labonne-Wall, N,A, Lis, S., Mizera, J.J., Pokrovsky O.S, Xia, Y., Moore, R.C, 2001. Waste Isolation Pilot Plant Source Term Test Program:Solubility studies and development of modeling parameters, Albuquerque, NM: SAND-99-0943. Sandia National Laboratory.

EPA, 2005. Performance Assessment Issues. Letter from E. Cotsworth, U.S. Environmental Protection Agency Office of Radiation and Indoor Air, Washington DC, to Ines Triay, U.S. Department of Energy Carlsbad Field Office, March 4, 2005.

EPA, 2021. The Geochemistry of the Waste Isolation Pilot Plant, EPA-402/R-21/002.

Felipe-Sotelo, M., Edgar, M., Beattie, T., Warwick, P., Evans, N.D.M., Read,. D., 2015. Effect of anthropogenic organic complexants on the solubility of Ni,Th, U(IV) and U(VI). Journal of Hazardous Materials, 300, 553-560.

Felipe-Sotelo, M., Hinchliff, J, Field, L.P., Milodowski, A.E., Preedy, O., Read, D., 2017. Retardation of uranium and thorium by a cementitious backfill developed for radioactive waste disposal. Chemosphere, 179, 127-138.

Hinz, K., 2015. Interaction of Ln(III) and An(III/IV/V/VI) with borate in dilute to concentrated NaCl, $CaCl_2$ and $MgCl_2$ solutions. PhD Thesis.

Hinz, K. Altmaier, M., Gaona, X., Rabung, T., Schild, D., Richmann, M., Reed, D.T., Alekseev, E.V., Geckeis., H., 2015. Interaction of Nd(III) and Cm(III) with borate in dilute to concentrated alkaline NaCl, $MgCl_2$ and $CaCl_2$ solutions: solubility and TRLFS studies. New J. Chem., 39, 849--859.

Lozano, J. C., Blanco Rodríguez, P., Vera Tomé, F., Prieto Calvo, C., 2011. Enhancing uranium solubilization in soils by citrate, EDTA, and EDDS chelating amendments. Journal of Hazardous Materials, 198, 224-231.

Lucchini, J.-F., Khaing, H., Borkowski, M., Richmann, M. K., Reed, D. T., 2010. Actinide (VI) Solubility in Carbonate-free WIPP Brine: Data Summary and Recommendations, Carlsbad, NM: Los Alamos National Laboratory; LCO-ACP-10.

Lucchini, J.-F., Borkowski, M., Richmann, M. K., Reed, D. T., 2013a. Uranium(VI) solubility in carbonate-free WIPP brine. Radiochimica Acta, 101, 391-398.

Lucchini, J.-F., Richmann, M. K., Borkowski, M., 2013b. Uranium (VI) Solubility in WIPP Brine, Carlsbad, NM: Los Alamos National Laboratory, LCO-ACP-14..

Novak, C. F., Borkowski, M., Choppin, G. R., 1996. Thermodynamic Modeling ofNeptunium(V)-Acetate Complexation in Concentrated NaCl Media. Radiochim. Acta, 74, 111.

Pearson, R., 1995. The HSAB principle - More quantitative aspects. Inorganica Chimica Acta, Volume 240, pp. 93-98.

QAPD, 2023. Quality Assurance Program Document, DOE/CBFO-94-1012, Rev.13.

Rao, L., Zanonato, P., DiBernardo, P., 2005. Interaction of actinides with carboxylates in solution: complexation of U(VI), Th(IV), and Nd(III) with acetate at variable temperatures. Journal of Nuclear and Radiochemical Sciences, 6, 31-37.

Schott, J., J., Kretzschmar, J., Tsushima, S., Drobot, B., Acker, M., Barkleit, A., Taut, S., Brendlera,. V., Stumpf, T., 2015. The interaction of Eu(III) with organoborates – a further approach to understand the complexation in the An/Ln(III)–borate system. Dalton Trans, 44, 11095-11108.

SOTERM, 2019. Title 40 CFR Part 191 Subparts B and C Compliance Recertification Application 2019, Appendix SOTERM-2019.

Srivastava, A., Satpati, A.K., Singh, R., Kumar, P., Kumar, S., Tomar, B.S., 2017. Redox speciation of uranyl in citrate medium: kinetics and reduction mechanism with in situ spectroelectrochemical investigation. New J.Chem., 41, 15094-15104.

Suzuki, Y., Nankawa, T., Yoshida, T., Ozaki, T., Ohnuki, T., Francis, A.J., Tsushima, S., Enokida, Y., Yamamoto, I., 2006. Reduction behavior of uranium in the presence of citric acid. Radiochim. Acta, 94, 579-583.

Van Soest, G. D., 2018. Performance Assessment Inventory Report, LANL-CO. INV-PA-18, Revision 0.

Xiong, Y., Wang, Y., 2021. Uranyl oxalate species in high ionic strength environments: stability constants for aqueous and solid uranyl oxalate complexes. Radiochim. Acta, 109, 177-185.

Yalcintas, E., Reed, D. T., Gaona, X., Altmaier, M., 2017. Impact of EDTA on the solubility and redox behaviour of uranium in dilute to concentrated NaCl solutions. Barcelona, Spain (LA-UR-17-27827).