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

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ACRONYMS

ACRONYM	DEFINITION
ACRSP	Actinide Chemistry and Repository Science Program
am	amorphous
An	Generic Actinide
ASTP	WIPP Actinide Source Term Program
°C	Degrees Celcius
$Ca(OH)_2$	Calcium hydroxide
CBFO	Carlsbad Field Office (U.S. Department of Energy)
CCA	Compliance Certification Application
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
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
NIST	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
ppm	Parts per million
rpm	Revolution per minute
QAPD	Quality Assurance Program Document
SOTERM	Actinide 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
WIPP	Waste Isolation Pilot Plant
XANES	X-ray absorption near edge spectroscopy
XRD	X-Ray Diffraction

EXECUTIVE SUMMARY

The solubility of uranium (VI) in Waste Isolation Pilot Plant (WIPP)-relevant brine was determined to support ongoing WIPP recertification activities. This research was performed by the Los Alamos National Laboratory Carlsbad Operations (LANL-CO) Actinide Chemistry and Repository Science Program (ACRSP).

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 within the WIPP Performance Assessment (PA) for all expected WIPP conditions (SOTERM, 2019) as selected at the recommendation of the Environment 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 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 at under-saturation approach. Experiments were equilibrated for about 135 days. Organic compounds present in WIPP waste can form strong complexes with actinides and can affect the oxidation states of actinides. 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 effects on the solubility of U(VI) 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 experiments performed were done according to the U.S. Department of Energy (DOE) approved Test Plan entitled “Experimental Strategy to Challenge Actinide Solubility Predictions” and designated 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, 2017).

1. 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 TRUs waste repository and is currently operated by the Department of Energy, Carlsbad Field Office (DOE 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.

Actinides that could potentially exist in the +VI oxidation state are U(VI), Np(VI) and Pu(VI). However, among them only U(VI) is considered in WIPP PA assumptions because both Np(VI) and Pu(VI) can be excluded, under the highly reducing conditions expected to predominate in the WIPP. Since uranium is a relatively minor contributor (~10^{-6} M) to overall potential release of actinides from the WIPP, an An(VI) actinide model was never developed (Lucchini, et al., 2013). Consequently, the solubility of U(VI) in WIPP PA was conservatively set by the Environmental Protection Agency (EPA) at 1 mM based on available literature data (EPA, 2005).

Uranium is not a TRU component but it is predominant actinide in the WIPP by mass. 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. It is not predicted to be a significant contributor to actinide release, because uranium release can occur through the Culebra in very small amounts because of its potentially high solubility and low sorption in the +VI oxidation state. (SOTERM, 2019).

In the environment, U exists only in the IV and VI oxidation state as U^{4+} and UO_2^{2+} species. U can form highly insoluble U(VI) and U(IV) phases and can persist up to mM concentrations in near-surface groundwater (SOTERM, 2019). U(III), should it be formed, is metastable and readily oxidized in aqueous solution; U(V) only exists as a very short-lived transient that is instantaneously disproportionate to U(IV) and U(VI) species in the absence of complexing ligands. Under oxidizing subsurface conditions typical of most near-surface groundwater, U(VI) as UO_2^{2+} uranyl complexes is the predominant oxidation state and is not easily reduced geochemically.

The solubility of U(VI) in the WIPP is expected to be defined by the combined contribution of hydrolysis with oxyhydroxide phase formation and carbonate complexation with U carbonate phase formation. In carbonate-free or low-carbonate solutions, the speciation of U(VI) is dominated by hydrolysis.

Hydrolysis reactions occur for the f-elements in weakly acidic to alkaline solutions in the III, IV and VI oxidation states, and often predominate over other complexation reactions in neutral and basic solutions. The hydrolysis reactions involving UO_2^{2+} can be expressed by the general reaction:

$$n\ UO_2^{2+} + q\ H_2O \Leftrightarrow \left((UO_2)_n\ (OH)_q\right)^{2n-q} + q\ H^+$$

$$^*\beta_{nq}=[((UO_2)_n\,(OH)_q)^{2n-q}]\ [H^+]^q\,/\,[UO_2^{2+}]^n$$

where $^*\beta_{nq}$ increases with increasing cationic charge density. Such hydrolysis reactions can also be described as hydroxide complexation reactions:

$$n\ UO_2^{2+} + q\ OH^- \Leftrightarrow \left((UO_2)_n\ (OH)_q\right)^{2n-q}$$

$$^*\beta_{nq}=[((UO_2)_n\,(OH)_q)^{2n-q}]\,/\,[UO_2^{2+}]^n\ [OH^-]^q$$

with $K_W = [H^+][OH^-]$, this becomes

$$\beta_{nq}= \beta_{nq}/\ K^q{}_W$$

In the absence of other complexing ligands, carbonate complexation will dominate the speciation of the uranyl ion under near-neutral pH conditions as long as there is ample carbonate-bicarbonate available (Clark, et al., 1995). Three monomeric complexes, $UO_2(CO_3)$, $UO_2(CO_3)_2^{2-}$, and $UO_2(CO_3)_3^{4-}$ are predicted to be present. At uranyl concentrations above 10^{-3} M, the trimeric cluster $(UO_2)_3(CO_3)_6^{6-}$ is present in significant concentrations. When the uranyl ion concentration exceeds the carbonate concentration, hydrolysis competes with carbonate complexation and plays an increasingly important role (Clark, et al., 1995).

In this work, we focused on the two key scientific issues which are borate and organics effects to determine the effective 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 establish 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 under-saturation approaches.

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 the organic complexants are given on Table 2. 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). Moreover, little attention has been dedicated so far to the possible complexation of borate species with actinides.

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). 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 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 1.

Table 1. 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.

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}

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) (Novak, et al., 1996) (Bronikowski, et al., 1999) (Borkowski, et al., 2001) (Choppin G.R., et al., 2001). The studies show the complexation behavior of U(VI) with organic ligands in the acidic pH region between 5 and 7, not representative for WIPP relevant conditions. Other studies (Felipe-Sotelo, et al., 2015) (Felipe-Sotelo, et al., 2017) observed of U(VI) in 95%-saturated $Ca(OH)_2$ (pH 12.3) in the presence of organic ligands and CDP (cellulose degradation products). The 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.

A very detailed review and data summary and recommendations regarding An (VI) solubility was reported by ACRSP group (Lucchini, et al., 2010) (Lucchini, et al., 2013) as part of WIPP reports. In the study, the solubility of U(VI) in the absence and the presence of carbonate has since been more extensively studied in simulated GWB (Generic Weep Brine) and ERDA-6 (U.S. Energy Research and Development Administration Well 6) brine. Their studies reported that the solubility of U(VI) in WIPP-relevant brines as a function of pC_{H+} and ionic strength, in the absence of carbonate. In the absence of carbonate, the measured U(VI) solubilities 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 (~9.3), the measured uranium solubility approaches ~10^{-7} M and 10^{-6} M.

Xiong and Wand obtained solubility constants at infinite dilution for solid uranyl oxalates, $UO_2C_2O_4 \bullet 3H_2O$, based on the solubility data over a wide range of ionic strengths (Xiong & Wang, 2021). The developed model will enable for the accurate stability assessment of oxalate complexes affecting uranium mobility under a wide range of conditions including those in deep geological repositories.

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

Rao et al. 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 effects at higher temperatures and can be explained by the effect of temperature on the solvent structure and a simple electrostatic model (Rao, et al., 2005).

A PhD. Thesis from The Institute for Nuclear Waste Disposal of the Karlsruhe Institute of Technology (KIT-INE) 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. EXPERIMENTAL

In this work, borate and organics effects on solubility for U(VI) in pC_{H+} 9 WIPP specific brine were investigated using an under-saturation experimental approach. In the experiments, synthesized (Figure 1) uranyl hydroxide was used as the solid phase. HPW was bubbled with high-purity nitrogen to remove dissolved oxygen, and 25 µL concentrated HCl (Fisher Scientific, lot # 4108010) was added to remove carboxyl 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 ~135 days at an adjusted pC_{H+} of 9 with carbonate free NaOH (Fisher Scientific, lot # 000381) and HCl (Fisher Scientific, 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. Acetate (Sodium Acetate, Aldrich lot# 01103TZ) and oxalate (Oxalic Acid, lot# 05829CH) 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.

Table 2. WIPP-relevant Brine Compositions of the Brines used in the Experiments. Data are based on 90% Strength

	Element/Species - Measured Concentrations (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

UV-Vis spectroscopy confirms the stock solution is primarily 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). $UO_2(OH)_2$ was precipitated from a stock solution with 1

M carbonate free NaOH. After centrifugation (6 min., 3000rpm) the precipitate was washed with HPW. This washing step was performed twice. Precipitate was dissolved in 0.1 M HCl. 100 µl intervals of 0.1M and/or 1 M NaOH (Acros Organics, lot# A0277324) was added until a permanent precipitate appeared. 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).

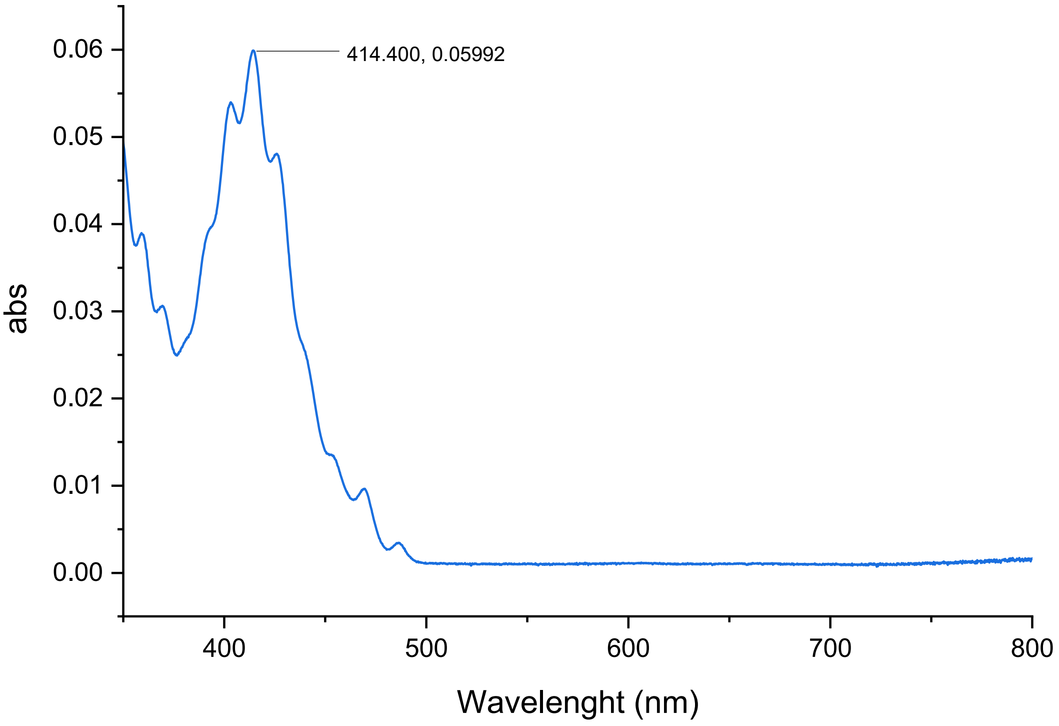

Figure 1. Absorption spectrum of the uranyl stock solution. The absence of spectral features above 500 nm confirmed that there was no significant amount of U(IV) present.

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”.

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
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 298 K. In the experiments, approximately 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, 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+}). 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^+. Concentration of uranium 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% HNO_3 (Fisher Scientific, lot# 1218110) with 300 ppb of an indium internal standard (Agilent High Purity Standards, lot# 2013216) to provide a final dilution of 1:180 in triplicate for ICP-MS analysis.

3. RESULTS AND DISCUSSION

In this work, U(VI) effective 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 is obvious that the presence of borate in the solutions increases the solubility. At the beginning of the experiments (6 days), absence of borate shows the lowest uranium solubility whereas WIPP brine with the highest borate content has the highest solubility. Second sampling that performed around 35 days, all U concentrations are lower than the first sampling. In the third sampling (72 days) an increase was observed in the U concentration except 100 mM borate presence. In the last two sampling period, experiments with 100 mM borate concentration and WIPP brine show slight increase towards last sampling, conversely with smaller borate concentrations decrease was observed. Lucchini et al. 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 were observed after 55 d, indicating the formation of a complex anion of U(VI) with tetraboric anion (Lucchini, et al., 2013).

Very little is known about the coordination chemistry of tetraborate ($B_4O_7^{2-}$), particularly with actinides. Sodium tetraborate decahydrate (borax), $Na_2B_4O_7\cdot10H_2O$, is better formulated as $Na_2[B_4O_5(OH)_4]\cdot8H_2O$, because the structure of the $[B_4O_5(OH)_4]^{2-}$ ion can be easily identified with two four coordinate boron atoms (two BO_4 tetrahedra) and two three coordinate boron atoms (two BO_3 triangles). The acid form of the tetraborate ion 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., 2013). 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).

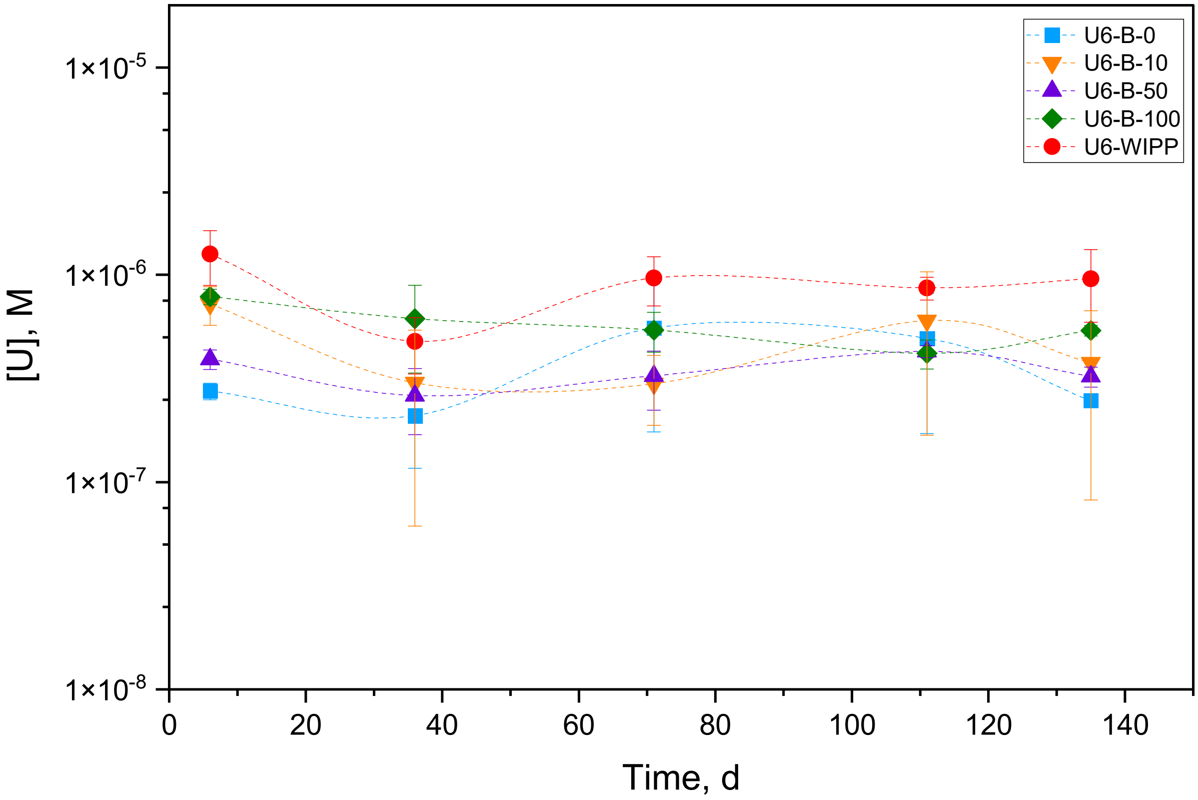

Figure 2 Effect of borate concentration on [U] solubility as a function of time in pC_{H+} 9 brine. B denotes borate.

Figure 3 shows the uranium concentration as a function of time in the presence of organics. Figure 3shows that the organics increase the uranium solubility. At the beginning of the experiments (6 days), presence of all organics together and citrate shows the highest solubility. This trend remains unchanged throughout the all sampling periods. Over all sampling periods, U concentration in the experiments with the presence of citrate is slightly lower than the experiments with all organics together in the solution. U solubility is almost the same in the experiments individually having all other organics in the first sampling. In the second sampling, (35 days) WIPP brine without organics have the lowest U solubility. Nevertheless, solubility is lower than the first sampling in all samples. In the third sampling (72 days) an increase is observed in the U concentration for all organics except oxalate and citrate. In the last sampling (135 days) solubilities of the samples has slight differences, but are almost indistinguishable.

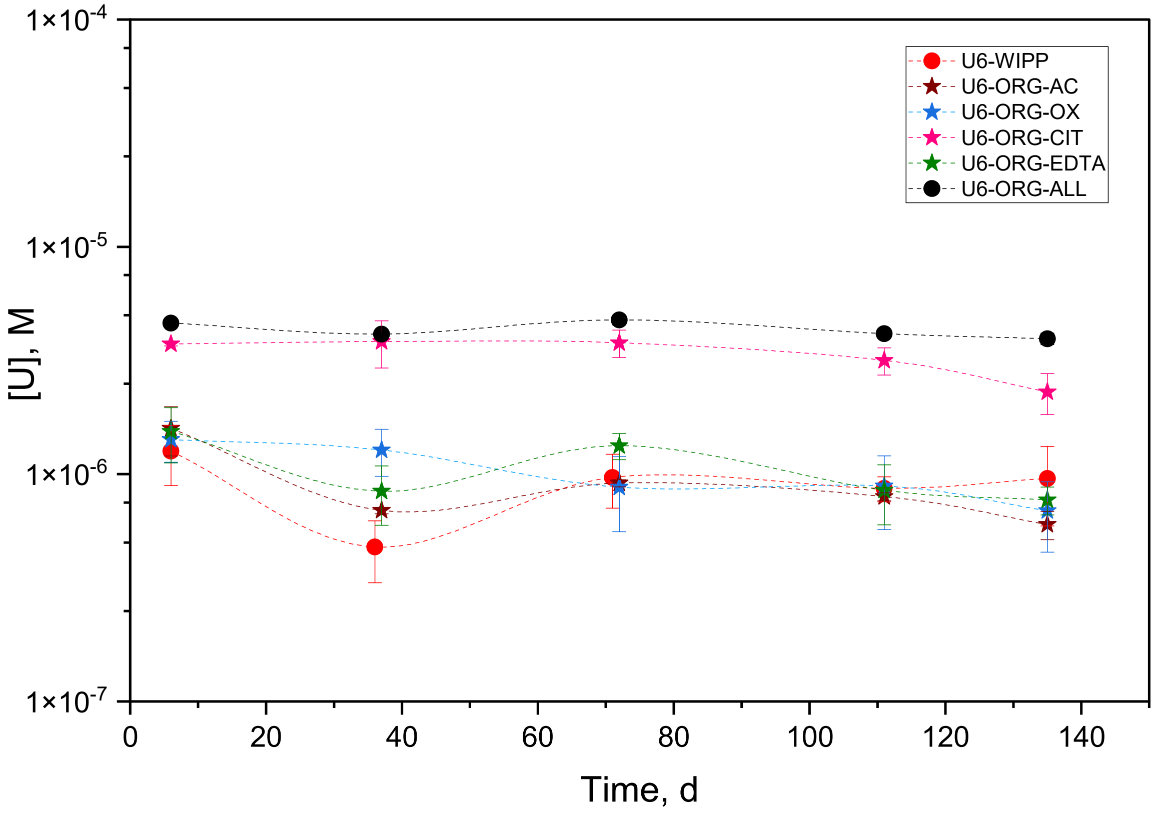

Figure 3. Effect of presence of organics on [U] solubility as a function of time in pC_{H+} 9 brine. ORG: Organics, AC: Acetate, OX: Oxalate, CIT: Citrate)

4. 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 at ~ 10^{-6} M.

Organic complexation increased uranium solubility in the experiments, with U solubility as high as ~$4x10^{-6}$ 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.

5. 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-26-4, developmental notebook designated SN-CKA-1 and ACP-26-1B.

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