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LA-UR-25-30122

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Title:	Effect of Citrate on the Solubility of Uranium (VI) in WIPP Brine
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Intended for:	Report
Issued:	2025-10-13

LOS ALAMOS NATIONAL LABORATORY
CARLSBAD OPERATIONS

LCO-ACP-43, Revision 0

Effect of Citrate on the Solubility of Uranium (VI) in WIPP Brine

Effective Date: 04/10/2025

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History of Revisions

Revision Number	Effective Date	Pages Affected	Description of Revision
0	04/10/2025	All	Original Release

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ACRONYMS AND ABBREVIATIONS

ACRSP	Actinide Chemistry and Repository Science Program
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
Cl	Chlorine
CRA	Compliance Recertification Application
Da	Dalton
DBR	Direct Brine Release
DOE	U.S. Department of Energy
EDTA	Ethylenediaminetetraacetic Acid
EPA	U.S. Environmental Protection Agency
EXAFS	Extended X-ray Absorption Fine Structure
FTIR	Fourier Transform Infrared Spectroscopy
GWB	Generic Weep Brine, a synthetic brine representative of intergranular Salado-Formation brines
HCl	Hydrogen chloride
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
M	Molarity, moles of solute per liter of solvent
mg	Milligram
Mg	Magnesium

ACRONYMS AND ABBREVIATIONS (cont.)

MgO	Magnesium oxide
µL	Microliter
mL	Milliliter
mM	Millimolar
Na	Sodium
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)
TRU	Transuranic Elements (actinides higher in atomic number than uranium)
U	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

EXECUTIVE SUMMARY

The Waste Isolation Pilot Plant (WIPP) is the only active deep geological repository in the United States for the disposal of defense-related transuranic (TRU) waste, located in the northern part of the Delaware Basin in southeastern New Mexico, approximately 26 miles east of Carlsbad. The repository is situated 2,150 feet (about 610 meters) underground within the Salado Formation, a thick layer of stable salt deposits. This unique geological formation provides a secure and long-term environment for isolating TRU waste, ensuring its safe containment for thousands of years.

WIPP-relevant solubility studies are important for evaluating the long-term safety and stability of the repository. In particular, the effect of citrate on uranium (VI) solubility was investigated, and the results are summarized in this report. The main goal of this study is to perform screening experiments that account for the contributions of organics on uranium solubility. The solubility of U(VI) was determined in pC_{H+} specific WIPP brines (pC_{H+} 7, 9 and 11) as well as 5 M NaCl in the presence or absence of organics using an under-saturation approach. The results confirmed a significant impact of citrate on the solubility of U(VI).

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 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-} (SOTERM, 2019).

The experiments were performed 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). Furthermore, the experiments will be continued, characterization studies will be performed, and more detailed and comprehensive results will be presented in subsequent reports.

1.0 INTRODUCTION

In the environment, uranium 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 is 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 (Ferguson et al., 2022).

Uranium is not a TRU component, but it is a predominant actinide in the WIPP based on mass. Although its specific activity is low (U-238, 3.36×10^{-7} Ci/g), its projected release into the Culebra in the event of an intrusion is high (Bethune, 2023). The salt formations at WIPP are designed to provide a natural barrier to the migration of water and contaminants, owing to their capacity to act as an impermeable barrier that limits fluid movement. In the event of brine intrusion into WIPP, the potential for subsequent migration of radioactive materials could occur. Therefore, comprehensive monitoring and long-term studies focusing on the behavior of radionuclides and the chemical interactions within the repository are very important (Silva and Nitsche, 1995; Runde, 2000).

Solubility studies relevant to WIPP are essential for predicting the long-term stability of the repository and ensuring the safe containment of radioactive waste. These studies help to understand the behavior of the waste materials when they come into contact with brine. However, determining the solubility of any species in a complicated matrix such as WIPP brine is not straightforward. The brine contains various dissolved chemical constituents, forming a highly complex system. This complexity makes predicting the solubility behavior of waste species much more difficult compared to simpler solutions.

Four key organic complexants are co-disposed with WIPP waste and play a critical role in the behavior of the waste and its long-term stability within the repository. These complexants include acetate ($C_2H_3O_2^{-}$), oxalate ($C_2O_4^{2-}$), citrate ($C_6H_8O_7$) and ethylenediaminetetraacetic acid (EDTA ($C_{10}H_{16}N_2O_8^{4-}$)) (SOTERM, 2019). These organic complexants can bind to metal ions, such as uranium, plutonium, and americium, forming stable metal-organic complexes that can influence the mobility and solubility of radioactive materials (EPA, 2021; Suzuki et al., 2006; Srivastava et al., 2017). It is assumed that these complexants will not degrade under the expected conditions within the repository, such that their concentration is determined by their initial inventory, except for oxalate, which is solubility-limited (SOTERM, 2019). This increase in solubility could potentially enhance the mobility of radionuclides, affecting their migration behavior and the overall performance of the WIPP repository in containing radioactive materials over the long term.

A large number of studies have been conducted to investigate the effects of organics in uranium complexation. Among these, citrate is an important complexing agent (Hummel et al., 2005) and that could play an important role towards the migration of uranium. Previous studies in the literature show that citrate forms strong complexes with both U(VI) and U(IV) over a wide range of pH (Kantar et al., 2005; Kretzschmar et al., 2021). Citric acid is a nontoxic, tricarboxylic acid commonly used as a chelating agent for metal ions. Under oxidizing conditions, citrate primarily forms a binuclear complex with uranyl-$(UO_2\text{-citrate})_2^{2-}$ and to a lesser extent, a tridentate complex, $UO_2\text{-citrate}^{1-}$ (Huang et al., 1998).

Interactions between citric acid and uranium have been investigated by several researchers in previous studies using various techniques determining the speciation of uranium and citrate, such as: spectrophotometry and potentiometry (Heitner and Bobtelsky, 1954; Feldman et al., 1954), EXAFS (Allen et al., 1996), Raman and FTIR (Pasilis and Pemberton, 2003). The uranyl citrate system exhibits complex behavior, in particular pH-dependent changes in stoichiometry and the coordination environment of UO_2^{2+} in an aqueous medium (Srivastava et al., 2017). Therefore, the authors made a comprehensive investigation on the speciation and redox behavior of UO_2^{2+} with varying physicochemical conditions in aqueous citrate medium. They investigated the reduction behavior of UO_2^{2+} in citrate media at pH 2-7. At pH 2.0, UO_2^{2+} was reduced to U(IV) through a one-step reduction process, while it was reduced to U(IV) through a two-step reduction process at pH 3.0–5.0. The reduction potential of UO_2^{2+} shifted to lower values with an increase in pH from 2.0 to 7.0. UV-visible spectroscopy and speciation calculations of UO_2^{2+} in citrate media indicated that uranium existed as a mixture of UO_2^{2+}, $[UO_2Cit]^-$ and $[(UO_2)_2Cit_2]^{2-}$ at pH 2–3, and a predominant species at pH 3–5 was $[(UO_2)_2Cit_2]^{2-}$ (H_3Cit: citric acid). At pH 5–7, polymeric complexes, probably, $[(UO_2)_3Cit_3]^{3-}$ and $[(UO_2)_6Cit_6(OH)_{10}]^{16-}$ were present. Absorption spectra of the reduced complexes showed that U(IV) forms soluble complexes with citric acid at pH 2.0–5.0, and presence of U(V) species was not observed during the reduction of UO_2^{2+}. Bailey et al., (2005) investigated the speciation and structure of uranyl-citrate complexes formed in aqueous solutions temperatures between 25 and 200 °C, at pH 0.8 - 3.7 and at citrate/U ratios between 0.5 - 50 using U L_{III}-edge X-ray absorption spectroscopy (XAS).

The literature review reveals a significant lack of studies on the solubility of uranium in the presence of citrate. A couple of studies include dissolution of the minerals (Ferguson et al., 2022) or soils (Lozano et al., 2011). Ferguson et al. (2022) investigated citrate-promoted dissolution of a uranyl phosphate mineral, chernikovite $[(H_3O)(UO_2)(PO_4)\ 3H_2O]$, by determining the extent of uranium release from chernikovite at a wide range of citrate concentrations. Experiments indicate that increasing citrate concentrations from 0.1 mM to 50 mM increases the concentration of dissolved uranium. Lozano et al. (2011) evaluated citrate, EDTA, and EDDS (the [S,S]-stereo-isomer of ethylenediaminedisuccinic acid) as chelating agents for the solubilization of uranium from granitic soil. They found that the most efficient chelating agent to solubilize uranium from a granitic soil was citrate. It was more effective at all four soil pH ranges (4-8) tested, and comparatively for all concentrations (5-50 mmol kg^{-1}).

A report was published about a series of studies conducted at Florida State University as part of the WIPP ASTP program to comply with the quality assurance and traceability criteria established for data used in PA calculations for WIPP. It was reported that apparent stability constants were measured for the complexation of UO_2^{2+} by acetate, lactate, oxalate, citrate, and EDTA using a tracer level solvent extraction method in 0.3-5 m NaCl at 25°C (Choppin et al., 2001). Felipe-Sotelo et al. (2015) 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 increased up to 3 orders of magnitude in the presence of citrate and an order of magnitude in the presence of CDP.

In the previous study conducted at ACRSP (Kutahyali Aslani, 2024), the effects of organic compounds present in the WIPP, specifically EDTA, oxalate, citrate, and acetate, were investigated. U(VI) solubility was determined in WIPP brine at pC_{H+} 9, both in the presence and absence of these organic compounds, using an under-saturation approach. The results of the study were derived from solubility experiments conducted over a period of 609 days, with the objective of evaluating the contribution of organic complexants to uranium solubility. The findings revealed that organic complexation significantly enhanced uranium solubility, with U solubility reaching as high as approximately 10^{-6} M when all organic complexants were present. Among the organic complexants tested, citrate demonstrated the most pronounced effect on increasing U solubility.

Based on these findings, our current study focuses on the influence of citrate and varying pC_{H+} levels on U(VI) solubility under WIPP-relevant conditions. Experiments were conducted in both WIPP-specific brines and 5 M NaCl, with pCH^+ ranging from 7 to 11. All experiments were performed under the DOE approved Test Plan "Experimental Strategy to Challenge Actinide Solubility Predictions" (LCO-ACP-26). The data derived from this study quantify the influence of WIPP-relevant organic concentrations on the solubility of U(VI), offering insights that can inform solubility parameter recommendations for future WIPP recertifications.

2.0 SUMMARY OF EXPERIMENTS

NaCl, HNO_3, NaOH, HCl, $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 2H_2O$, LiCl, KCl, NaBr, Na_2SO_4 (Fisher Scientific), oxalic acid, Na_4EDTA, sodium acetate (Sigma-Aldrich), citric acid anhydrous (Fluka), and $Na_2B_4O_7 \cdot 10H_2O$ (Acros Organics) were used in this study. Synthesized uranyl hydroxide was used as the solid phase. High purity water (HPW) was sparged with high-purity nitrogen to remove dissolved oxygen, and 25 µL concentrated HCl 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 experiments. All solution preparations, experimental setup and sampling were performed in a nitrogen atmosphere glovebox. Samples vials were kept in airtight jars to prevent any exposure and sample evaporation.

The predicted range in brine composition expected in the WIPP is shown in Table 1. 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. The 30 mL polypropylene bottles were conditioned with brine solutions for 2 weeks before experiments began. Brines were prepared according to procedure ACP-EXP-001, *Brine Preparation*.

Table 1. Target and weighed concentrations of WIPP brine components used in uranium solubility experiments. Data are based on 90% Strength.

Ion	**90% GWB* [I_{tot}]: 6.34 (M) ******		**90% pC_{H+} 9 ** [I_{tot}]: 5.40 (M) ******		**90% pC_{H+} 11*** [Itot]: 5.06 (M) ******		**5 M NaCl [Itot]: 5.00 (M) ******	
	target	**actual**	**target**	**actual**	**target**	**actual**	**target**	**actual**
Li^+	3.89×10^{-3}	4.00×10^{-3}	3.38×10^{-3}	3.51×10^{-2}	3.19×10^{-3}	3.18×10^{-3}	-	-
Na^+	3.13	3.17	3.15	3.00	4.46	4.71	5.00	5.00
Mg^{2+}	9.01×10^{-1}	9.15×10^{-1}	9.27×10^{-1}	9.27×10^{-1}	9.99×10^{-3}	1.0×10^{-2}	-	-
K^+	4.14×10^{-1}	4.20×10^{-1}	4.12×10^{-1}	4.12×10^{-1}	4.04×10^{-1}	4.04×10^{-1}	-	-
Ca^{2+}	1.22×10^{-2}	1.28×10^{-2}	1.22×10^{-2}	1.21×10^{-2}	9.81×10^{-3}	9.82×10^{-3}	-	-
Cl^-	4.96	4.10	4.89	4.78	4.78	4.76	5.00	5.00
$B_4O_7^{2-}$	3.49×10^{-2}	3.53×10^{-2}	3.50×10^{-2}	3.51×10^{-2}	2.75×10^{-2}	2.74×10^{-2}	-	-

*GWB: Generic Weep Brine.

** pC_{H+} 9: Specific brine at pH 9.

***pC_{H+} 11: Specific brine at pH 11.

****Ionic Strength calculated via the EQ3\6 software [Wolery 2008]. Using the Sandia National Laboratories FMT database [Xiong 2011].

$UO_2(OH)_2$ was prepared from $UO_2(NO_3)_2.6H_2O$ (Spectrum, batch-202-U). Approximately 1 g $UO_2(NO_3)_2.6H_2O$ was weighed and put in a Pyrex beaker by adding 1 M HCl to dissolve the uranium, followed by heating on a hotplate to facilitate evaporation. The temperature was gradually increased to approximately 210 °C until the solution was fully evaporated to dryness. The process was repeated three times, with the addition of 1 M HCl and subsequent heating to dryness after each cycle. After the final evaporation, the stock solution was prepared by dissolution in 3 mL of 0.1 M HCl. The oxidation state purity of this solution was confirmed by UV-vis spectroscopy. Spectrophotometric measurements were performed using a Cary 5000

(Varian) UV-VIS-NIR spectrometer in double-beam mode. Measurements were conducted in gas-tight cuvettes. Spectra were recorded with a 0.2 nm data interval, a scan rate of 60 nm•min^{-1} and a slit-width of 0.6 nm. Figure 1 confirms the stock solution primarily contains U(VI). If any U(IV) is present, it is below the limit of detection.

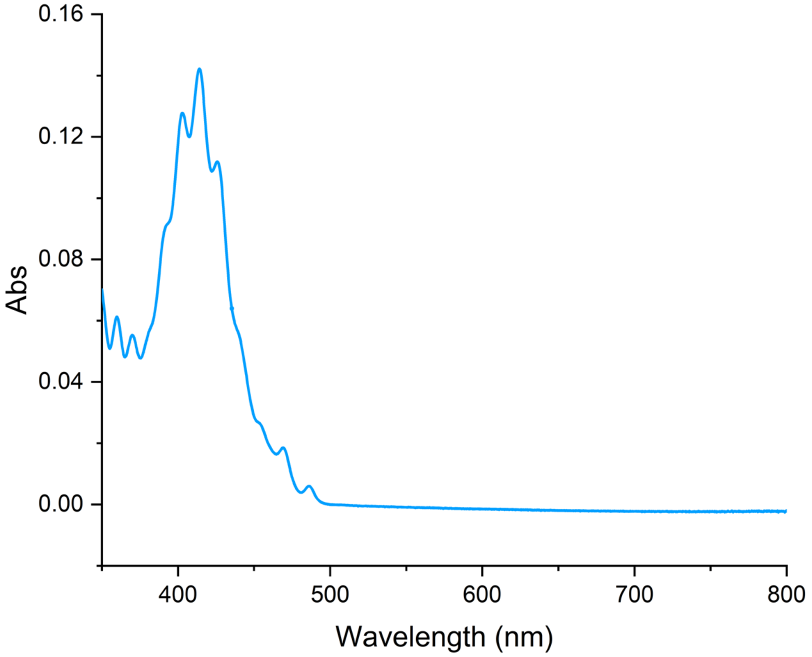


Figure 1. Absorption Spectrum of the Uranyl Stock Solution. The Absence of Spectral Features above 500 nm Confirmed that there was no Significant Amount of U(IV) Present.

For the solubility experiments, $UO_2(OH)_{2\ (am)}$ was precipitated by titrating the stock solution with carbonate-free NaOH. A yellow precipitate was observed at approximately pH 7.5. The yellow solid phase was separated by decanting and washed three times with carbonate-free water.

In this study, the effects of organics on the solubility of U(VI) in anoxic pC_{H+} 7-11 WIPP-specific brines and 5 M NaCl at room temperature were investigated using an under-saturation experimental approach. Samples were equilibrated in three synthetic WIPP brines (GWB at pC_{H+} 7, transitional brines at pC_{H+} 9 and 11) and 5 M NaCl at pC_{H+} 7, 9, and 11, separately. Samples were monitored for pC_{H+} and E_h. Uranium concentrations were determined using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

Table 2 and Table 3 show the CRA-2019 (SOTERM, 2019) organic concentrations based on the projected inventory and the experimental matrix used for the experiments, respectively. All experiments were performed in duplicate samples.

Table 2. 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 (Van Soest, 2018) 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}

Table 3. Experimental Matrix for Model Predictions

Experiment Designation	Complexant	Medium	pC_{H+} value at ~126 days	Eh (mV) at 200-250 days
U6-Control-7-1	0	pC_{H+} 7 Brine	6.92	-
U6-Control-7-2	0	pC_{H+} 7 Brine	6.95	-
U6-CIT-7-1	Citrate	pC_{H+} 7 Brine	7.01	-8.8
U6-CIT-7-2	Citrate	pC_{H+} 7 Brine	6.95	11.1
U6-ORG-ALL-7-1	ALL ORGANICS	pC_{H+} 7 Brine	6.89	11.2
U6-ORG-ALL-7-2	ALL ORGANICS	pC_{H+} 7 Brine	6.87	4.1
U6-Control-9-1	0	pC_{H+} 9 Brine	8.82	288.8
U6-Control-9-2	0	pC_{H+} 9 Brine	8.82	-
U6-CIT-9-1	Citrate	pC_{H+} 9 Brine	8.87	215.5
U6-CIT-9-2	Citrate	pC_{H+} 9 Brine	9.02	222.0
U6-ORG-ALL-9-1	ALL ORGANICS	pC_{H+} 9 Brine	8.94	220.7
U6-ORG-ALL-9-2	ALL ORGANICS	pC_{H+} 9 Brine	9.13	-
U6-Control-11-1	0	pC_{H+} 11 Brine	10.85	169
U6-Control-11-2	0	pC_{H+} 11 Brine	10.85	169.2
U6-CIT-11-1	Citrate	pC_{H+} 11 Brine	11.19	171.3
U6-CIT-11-2	Citrate	pC_{H+} 11 Brine	11.11	172.7
U6-ORG-ALL-11-1	ALL ORGANICS	pC_{H+} 11 Brine	11.18	194.7
U6-ORG-ALL-11-2	ALL ORGANICS	pC_{H+} 11 Brine	11.11	174.3
U6-Control-5M NaCl-7-1	0	5 M NaCl	6.95	240.8
U6-Control-5M NaCl-7-2	0	5 M NaCl	7.04	-
U6-CIT-5M NaCl-7-1	Citrate	5 M NaCl	7.13	-183.4
U6-CIT-5M NaCl-7-2	Citrate	5 M NaCl	6.95	-116.5

Experiment Designation	Complexant	Medium	pC_{H+}value at ~126 days	Eh (mV) at 200-250 days
U6-ORG-ALL-5M NaCl-7-1	ALL ORGANICS	5 M NaCl	7.18	-66.5
U6-ORG-ALL-5M NaCl-7-2	ALL ORGANICS	5 M NaCl	7.14	-102.5
U6-Control-5M NaCl-9-1	0	5 M NaCl	9.00	-
U6-Control-5M NaCl-9-2	0	5 M NaCl	9.14	-
U6-CIT-5M NaCl-9-1	Citrate	5 M NaCl	9.13	-
U6-CIT-5M NaCl-9-2	Citrate	5 M NaCl	9.11	-
U6-ORG-ALL-5M NaCl-9-1	ALL ORGANICS	5 M NaCl	9.06	-
U6-ORG-ALL-5M NaCl-9-2	ALL ORGANICS	5 M NaCl	8.85	-23.6
U6-Control-5M NaCl-11-1	0	5 M NaCl	10.9	-
U6-Control-5M NaCl-11-2	0	5 M NaCl	10.95	-
U6-CIT-5M NaCl-11-1	Citrate	5 M NaCl	11.03	-
U6-CIT-5M NaCl-11-2	Citrate	5 M NaCl	10.92	-
U6-ORG-ALL-5M NaCl-11-1	ALL ORGANICS	5 M NaCl	10.91	-
U6-ORG-ALL-5M NaCl-11-2	ALL ORGANICS	5 M NaCl	11.05	-

Under-saturation experiments were conducted at ambient temperature (23 ± 5 °C). An approximate total mass of 25 mg of uranium was placed into polypropylene bottles, along with 20 mL of solution. Sample solutions were periodically withdrawn from the experiments at approximately one-month intervals to determine whether the system had reached equilibrium. 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 using calibration 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 accounting for the liquid junction potential of the electrode and the activity coefficient of H^+. ΔpH is 1.11, 1.12, 0.87 and 0.82 for GWB, pC_{H+} 9, 11 and 5 M NaCl, respectively.

Oxidation-reduction potential measurements were performed with a Mettler Toledo InLab glass redox microelectrode with a platinum ring. Corrections from redox potential to E_h were made by adding the Ag/AgCl redox potential from the meter reading Zobell solution (LabChem). In E_h measurements, especially in solutions with high ionic strength, the uncertainty can be up to 200 mV. After each measurement, the electrode was washed with 1 M HCl and 1 M NaOH, and finally with water.

Concentration of uranium was determined in each sample using ICP-MS (Agilent 7900). The detection limit by ICP-MS for uranium is ~10^{-12} M, our experimental results were within ~1×10^{-10} M to 1×10^{-11} M. 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 organic ligands under conditions that simulate the expected environment in the WIPP were investigated. This study addressed the effects of organics and their influence on U solubility, specifically citrate. In order to investigate the citrate effect on U(VI) solubility, the experiments were designed for $UO_2(OH)_2$ in GWB, pC_{H+} 9-11 WIPP brine and 5 M NaCl.

Figure 2 shows the solubility of uranium in the presence and absence of citrate in undersaturation experiments in WIPP brines. Figure 2 (a) shows the results as a function of time. It appears that the highest solubility was observed at pC_{H+} 7 in the presence of citrate and all organic compounds in the solution. Although this pC_{H+} value does not fully represent the conditions at WIPP, the effect of organics is clearly evident, as their presence increased the solubility of uranium nearly two orders of magnitude as compared with the control. At pC_{H+} 9, similar observations were made at pC_{H+} 7, where the presence of organics enhanced the solubility of uranium by one order of magnitude. As shown in Figure 2 (a), both citrate alone and the presence of all organic components in the solution yielded similar results. This further supports the conclusion that citrate itself contributes to the increase in solubility at pC_{H+} 9. Unlike pC_{H+} 7 and 9, pC_{H+} 11 exhibits a different trend. Upon examining the results, it is observed that the presence of all organics and citrate still leads to the highest solubility. However, the difference between the effects of the organics and the control experiments is not as pronounced as in the experiments conducted at pC_{H+} 7 and 9. Figure 2 (b) shows the results after approximately 125 days of experimentation. At all three pC_{H+} values, the presence of organics enhances the solubility of uranium. Furthermore, this enhancement is primarily attributed to the citrate content in the solution.

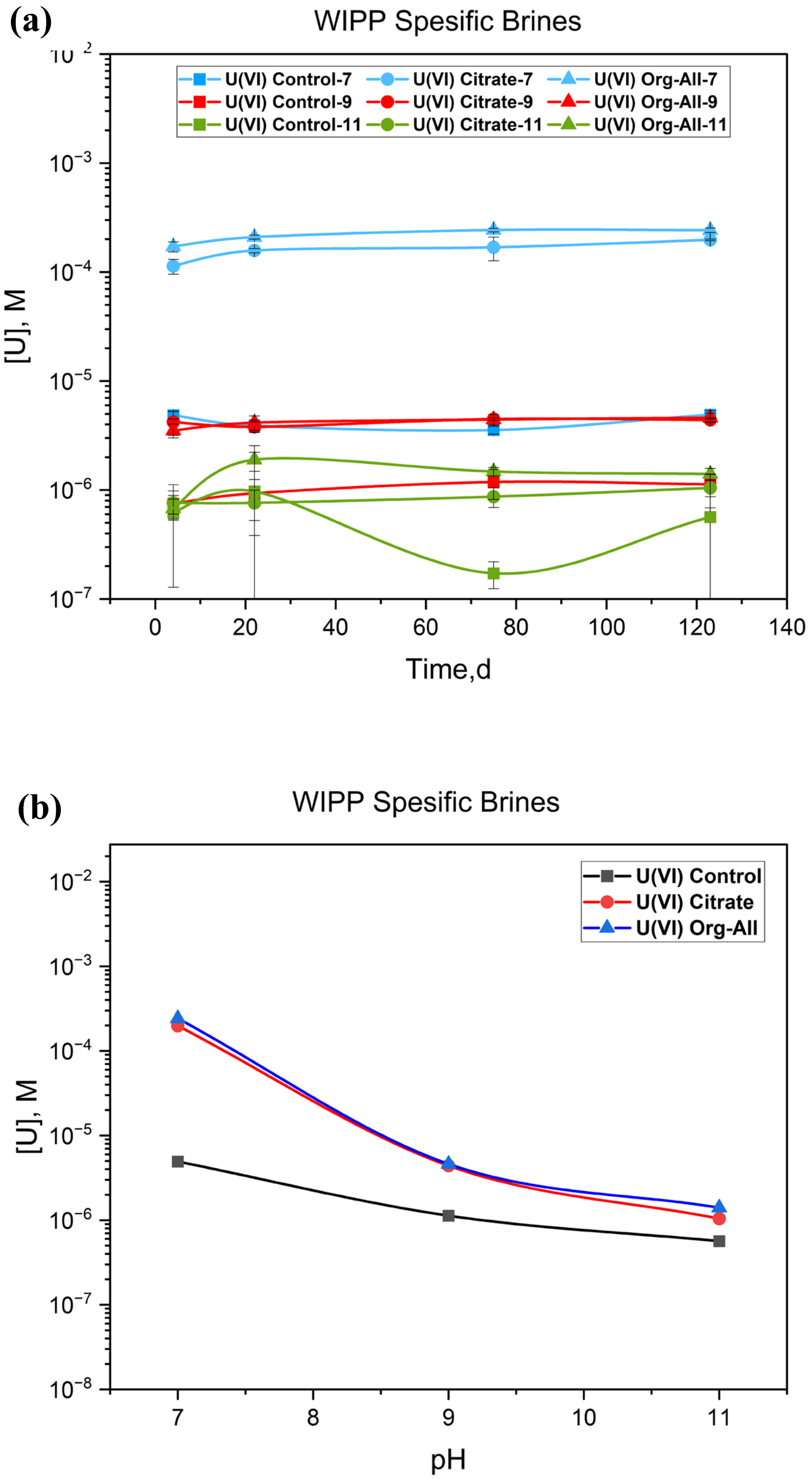
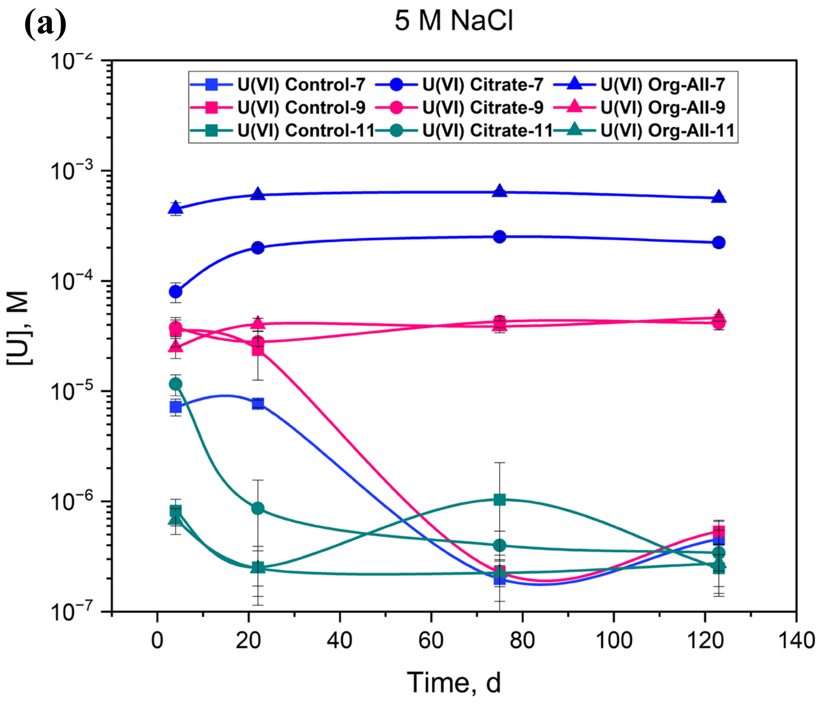


Figure 2. Effect of Presence of Citrate alone and all Organics on [U] Solubility as a Function of Time (a) and pC_{H+} (b) in WIPP Specific Brines.

Figure 3 (a) illustrates the solubility of uranium in the presence and absence of citrate in undersaturation experiments conducted in 5 M NaCl. Figure 3 (a) presents the results as a function of time. The highest solubility was observed at $\mathrm{pC_{H+}}$ 7 in the presence of all organic compounds in the solution. Under the same conditions, the uranium concentration measured in the solution with the citrate complexant was lower. At $\mathrm{pC_{H+}}$ 9, the highest concentration values were observed in both citrate and all organic systems. In contrast, $\mathrm{pC_{H+}}$ 11 exhibited a different trend compared to the previous experimental results. At $\mathrm{pC_{H+}}$ 11, although the presence of citrate had the highest effect at the beginning of the experiment, the complexants showed no significant difference by the end of the experiment.

Figure 3 (b) shows the results after approximately 125 days of experimentation. At all three $\mathrm{pC_{H+}}$ values, the presence of organics enhances the solubility of uranium, except at $\mathrm{pC_{H+}}$ 11. As observed in previous experiments, this enhancement is primarily attributed to the citrate content in solution. However, at $\mathrm{pC_{H+}}$ 11, it was evident that the presence of organic complexants had no significant effect on the solubility at the end of the 125-day period.



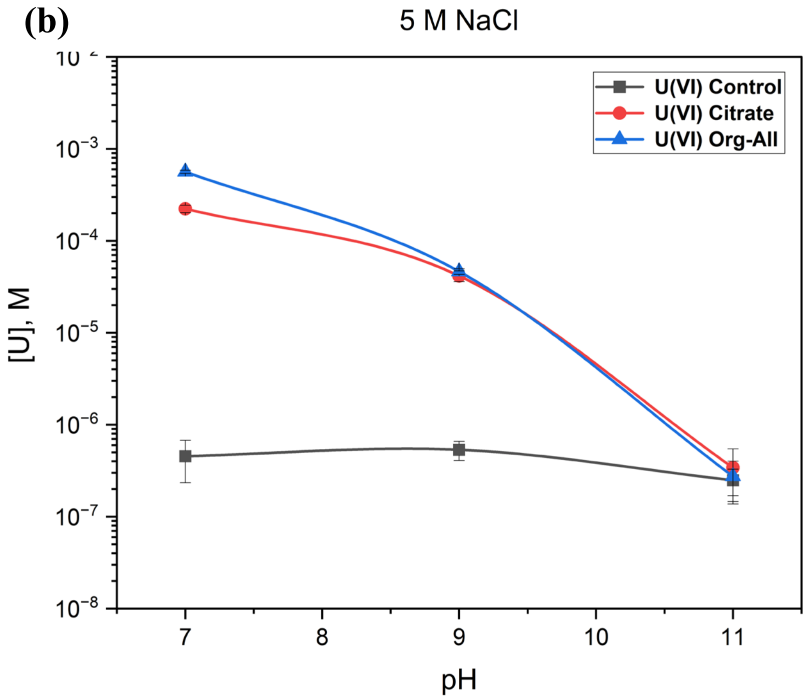


Figure 3. Effect of Presence of Citrate alone and all Organics on [U] Solubility as a Function of Time (a) and pC$_{H+}$ (b) in 5 M NaCl.

Comparing the WIPP-specific brines to 5 M NaCl under WIPP conditions, especially at pC$_{H+}$ 9, 5 M NaCl exhibits a solubility that is one order of magnitude higher than the WIPP-specific pC$_{H+}$ 9 brine. This higher solubility can be attributed to several factors related to the composition of the two solutions. WIPP-specific brine contains various dissolved minerals and salts, such as calcium, magnesium, and sulfate ions, which may interact differently with uranium and other solutes. These ions can form insoluble complexes or precipitates, thereby reducing the solubility of uranium. In contrast, 5 M NaCl, being a simpler solution with a single salt (NaCl), may not form such complexes, allowing more uranium to remain in the dissolved state and contributing to higher solubility (Hummel et al., 2005; SOTERM, 2019). Besides, the WIPP-specific brine might have a different pH buffering capacity compared to 5 M NaCl, affecting the speciation of uranium. Examining the E$_h$ values, particularly at pC$_{H+}$ 9, the WIPP-specific brine exhibits slightly lower E$_h$ in the presence of organic complexants, which may indicate the occurrence of reducing conditions. A more comprehensive interpretation can be made following solid-state analysis.

4.0 CONCLUSIONS

In this report, WIPP-relevant data for uranium (VI) solubility in WIPP specific brines and 5 M NaCl in the absence or presence of organic complexants are provided. 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 at pC_{H+} 9, which is the WIPP-relevant pC_{H+} with/without organics present. This result is much lower than the 1 mM assumption used in PA. The data we reported in this report showed that the 1 mM value for uranium (VI) solubility used in WIPP PA is conservative, relative to our experimental results.

Future work should address remaining gaps, such as examining uranium solubility in low ionic strength NaCl systems at higher pH in the presence of citrate. Long-term experiments should be conducted to monitor changes in solubility behavior over extended timeframes. If feasible, solid-phase characterization (e.g., XRD, XAS, SEM) should be incorporated to better understand structural and redox changes in the solid phase. Such analyses could help determine whether reduction processes are occurring and contributing to observed solubility trends. We anticipate reporting our future findings in a comprehensive report.

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

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