URANIUM (VI) SOLUBILITY BEHAVIOR IN WIPP-SPECIFIC BRINE AND IN THE PRESENCE OF WIPP-RELEVANT ORGANICS

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Introduction

The Waste Isolation Pilot Plant (WIPP), located in the northern portion of the Delaware Basin, 26 miles east of Carlsbad in Southeastern New Mexico, is the only deep geologic repository for the disposal of transuranic (TRU) waste in the United States. It was certified by the Environmental Protection Agency (EPA) in May 1998 and is the first operational salt-based deep geologic transuranic (TRU) radioactive waste repository in the world.

The only important An(VI) actinide in the WIPP's performance assessment (PA) is U(VI), because both Np(VI) and Pu(VI) can be excluded under the highly reducing conditions expected to predominate in the WIPP. Due to its low specific activity, U(VI) has a minor contribution to radioactive release scenarios in the WIPP PA. 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 [1,2] to account for the lack of data on the effects of carbonate. Uranium, predominantly as the U-238 isotope, is also the most prevalent actinide (~ 83%) from the perspective of mass although, due to its low specific activity, it is not predicted to be a large contributor to potential release.

Aim of the study

Organic compounds present in WIPP waste can form strong complexes with metals and actinides. The most abundant of these organic complexants in the WIPP inventory are EDTA, citrate, oxalate, and acetate that impact solubility of the actinides. Thus, we aimed to perform screening experiments that account for the contributions of organics to the observed WIPP-relevant uranium concentrations.

Experimental

- Organics effects on solubility for U(VI) in pC_{H+} 9 WIPP specific brine were investigated using an under-saturation experimental approach.
- Synthesized uranyl hydroxide ($UO_2(OH)_2$) was used as the solid phase.
- Organic effects were investigated at WIPP-relevant concentrations (Table 2).
- Experiments were performed over 609 days from an under-saturation approach in a nitrogen glove box (<0.1 ppm O_2) at 23 ± 2°C.
- Uranium concentrations were determined by ICP-MS in filtered aliquots (10 kDa Pall-type filters).
- The brine compositions used in the uranium solubility experiments are shown in Table 1.

Table 1. WIPP-relevant Brine Composition of the Brines used in the Experiments. Data are based on 90% Levels of Saturation

	Element/Species - Measured Concentrations (M)						
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Li^+	$B_4O_7^{2-}$	Cl^-
pC_{H+} 9	3.03	0.42	0.94	1.2×10^{-2}	3.9×10^{-3}	3.5×10^{-2}	3.7

Table 2. Concentrations of Acetate, Oxalate, Citrate and EDTA in the WIPP Repository Should Brine Inundation Occur [3]. These are Calculated Based on the Projected Inventory and the Minimum Brine Volume (17,400 m^3) for DBR [1]

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}

U(VI) Solubility in the presence of organics

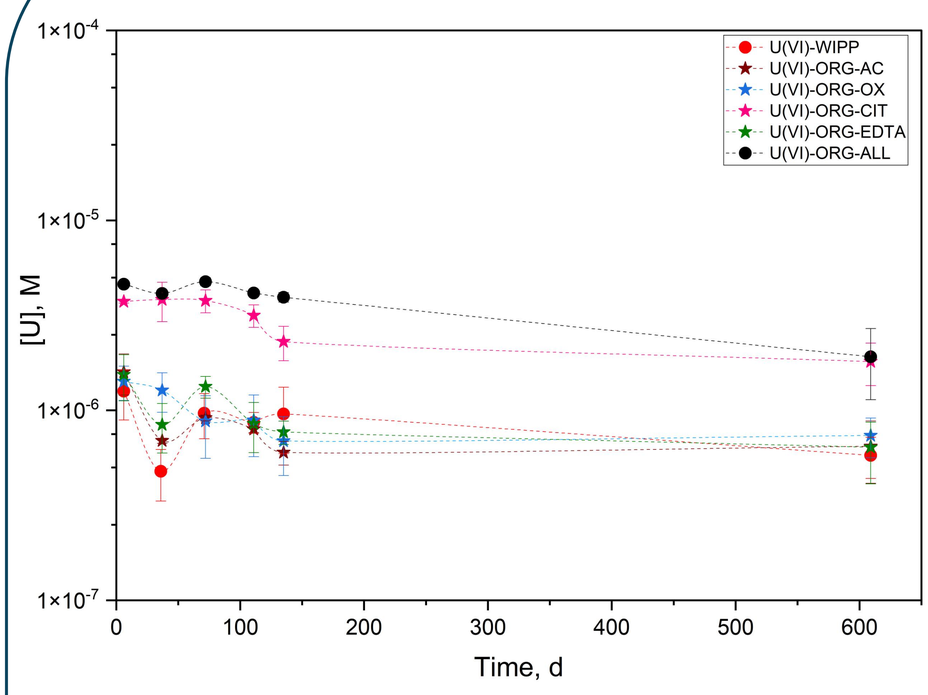
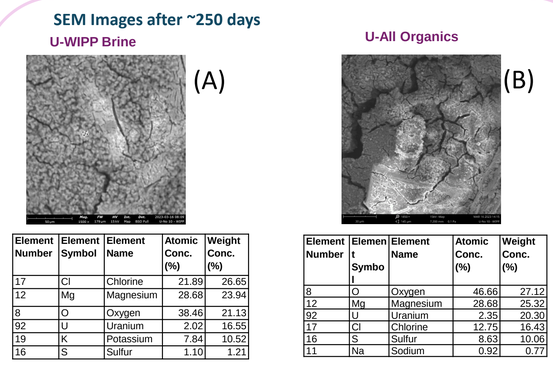


Figure 1. Effect of presence of organics on [U] solubility as a function of time in pC_{H+} 9 brine. ORG: Organics, AC: Acetate, OX: Oxalate, CIT: Citrate)

Figure 1 shows the uranium concentration as a function of time in the presence of organics.

- 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



Element Number	Element Symbol	Element Name	Atomic Conc. (%)	Weight Conc. (%)
17	Cl	Chlorine	21.89	26.65
12	Mg	Magnesium	28.68	23.94
8	O	Oxygen	38.46	21.13
92	U	Uranium	2.02	16.55
19	K	Potassium	7.84	10.52
16	S	Sulfur	1.10	1.21

Element Number	Element Symbol	Element Name	Atomic Conc. (%)	Weight Conc. (%)
8	O	Oxygen	46.66	27.12
12	Mg	Magnesium	28.68	25.32
92	U	Uranium	2.35	20.30
17	Cl	Chlorine	12.75	16.43
16	S	Sulfur	8.63	10.06
11	Na	Sodium	0.92	0.77

Figure 2. SEM Images of the solid phase after ~250 days. (A) In WIPP Brine (B) In WIPP brine with organics.

Solid phase characterization

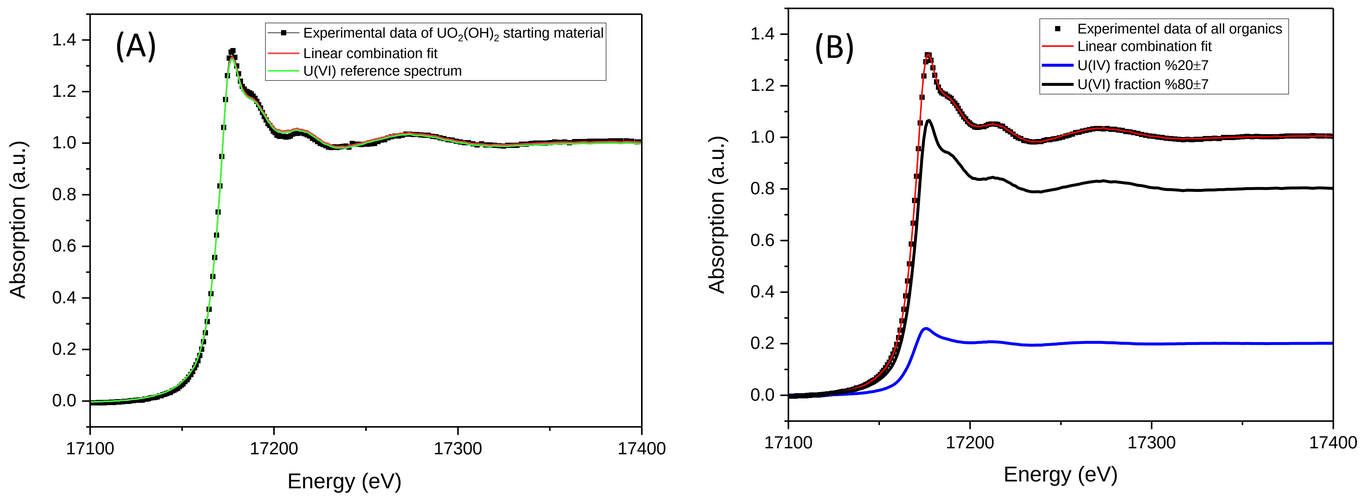


Figure 3. Experimental U L_{III}-edge XANES spectra. All experimental data are calculated to corresponding linear combination fits of U(IV) and U(VI). (A) $UO_2(OH)_2$ starting material, (B) Presence of all organics together

- Figure 2 shows the SEM-EDX Analyses of the solid phase after ~250 days.
- Figure 3 shows the U L_{III}-edge XANES spectra of the selected solid phases, including reference spectra of U(IV) and U(VI).
- The oxidation state of U in the samples was determined by fitting the XANES region between 17160 and 17200 eV by a linear combination of reference spectra for U(IV) and U(VI).
- Linear combination fitting analysis, based on the reference spectra, shows that starting material consisted of 100% U(VI).
- U L_{III}-edge XANES analysis of the solid phase in the experiments where all the organics were present showed the oxidation state distribution to be 20% U(IV) and 80% U(VI) with ±7% error.
- Steudtner and Geipel [4] observed the reduction of U(VI) to U(IV) by citric acid with ~22.3% reduction rate at pH 9. This result is very similar to the presented work.

Conclusions

- WIPP relevant data for uranium (VI) solubility at pC_{H+} 9 brine in the absence or presence of organic complexants as a function of time are provided.
- Organic complexation increased uranium solubility to as high as ~2×10^{-6} M when all organic complexants were present.
- Similarly, citrate individually has the highest impact on the U solubility amongst all organic complexants investigated.
- The data presented above (Fig. 1) indicates that the solubility of uranium is < 10^{-5} M. This value is >100x lower than EPA limit of 1 mM in PA.

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3. Van Soest, G. D., 2018. Periormance Assessment Inventory Report, s.l.: LANL-CO. INV-PA-18, Revision 0.
4. Steudtner, R., Geipel, G., Reduction of uranium(VI) by citric acid, Forschungszentrum Dresden-Rossendorf Institut für Radiochemie, Annual Report 2008.

Acknowledgement
Los Alamos National Laboratories is a multidisciplinary multi-mission laboratory managed and operated by Triad National Security, LLC for the U.S. Department of Energy's (DOE) National Nuclear Security Administration under contract 89233218CNA000001. This research is funded by WIPP Programs, administered by the DOE Office of Environmental Management.

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LA-UR-24-29582