STUDENT SUMMER INTERNSHIP TECHNICAL REPORT

Adsorption of Uranium to Hanford Formation Sediment in the Vadose Zone

DOE-FIU SCIENCE & TECHNOLOGY WORKFORCE DEVELOPMENT PROGRAM

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

EXECUTIVE SUMMARY

This research work has been supported by the DOE-FIU Science & Technology Workforce Development Initiative, an innovative program developed by the U.S. Department of Energy's Office of Environmental Management (DOE-EM) and Florida International University's Applied Research Center (FIU-ARC). During the summer of 2020, a DOE Fellow intern, Mariah Doughman, spent 10 weeks doing a remote summer internship with Pacific Northwest National Laboratory (PNNL) under the supervision and guidance of Dr. Nikolla Qafoku of the Environmental Subsurface Science Group. The intern's project was initiated on June 1, 2021, and continued through August 6, 2021, with the objective of elucidating uranium (U) adsorption mechanisms in the vadose zone of the 200 Area at the Hanford Site.

U adsorption onto sediment can decrease its downward migration towards groundwater at the Hanford Site vadose zone contributing to monitored natural attenuation (MNA). Previous studies have found that the presence of calcium and carbonate species have caused U complexes to become highly mobile in the environment. They have investigated the sorption of U to specific minerals and to natural sediment under these environmentally relevant conditions. Results from geochemical modeling indicate the dominant presence of neutral uranyl carbonate species which decrease its ability to adsorb onto vadose zone sediment. These results illustrate that U speciation will increase its mobility under site relevant conditions at the Hanford Site.

1. INTRODUCTION

Vadose zone uranium (U) contamination at the Hanford Site resulted from past U and plutonium enrichment activities and the intended or unintended release of 202,703 kg of U to the ground surface[1]. Once active remediation (pump and treat technology) is completed at the Hanford Site, a transition to a more passive approach such as monitored natural attenuation (MNA) is needed. Effective MNA requires an understanding of the contaminant attenuation processes that affect their mobility in the vadose zone sediment.

Uranium is normally present in the +6 oxidation state (as various complexes of UO_2^{2+}) in oxidizing/aerated conditions, such as those present in the vadose zone at the Hanford Site. Many studies have been conducted to understand the adsorption mechanisms of U onto a variety of different minerals and even natural sediment. In the pH range of 6-9, the presence of calcium carbonate in sediment (from calcite) has been shown to reduce U's ability to sorb. This is due to the blockage of reactive sites by Ca^{2+} and the formation of neutral uranyl complexes $(Ca_2UO_2(CO_3)_3^0(aq))$[2,3,4,5] which are less likely to adsorb to sediment sites due to the size of the complexes and negative charge of most sediments near neutral pH. Studies have confirmed the formation of these neutral complexes using thermodynamic modelling and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy[6,7]. This will increase U downward mobility at the site and therefore requires further examination under site relevant conditions.

The objectives of this research effort will be to provide (i) a better understanding of the species-dependent mechanisms of U interaction with sediments; (ii) the necessary parameters to predict U mobility in the vadose zone; and (iii) the technical basis for MNA at the site.

2. RESEARCH DESCRIPTION

U batch sorption experiments were initiated with uranyl nitrate hexahydrate (International Bio-Analytical Industries, Inc.) and $\leq$2 mm Hanford formation sediment fraction. Two separate batch adsorption experiments were conducted with U at lower and higher concentrations. This is due to high concentrations being observed in some wells in the 2018 groundwater and pump and treat report from the Hanford Site.[8,9]

Artificial groundwater (AGW, 2 L) used in the experiment was created using the formulation shown in Table 1. AGW was placed in 50 mL centrifuge tubes and spiked with concentrations of U and other contaminants listed in Table 2. The pH of solutions was measured using a Thermo Scientific Orion Versa Star pH meter with a Thermo electrode calibrated using standard pH buffers 4.01, 7.00, 10.00 (Fisher). After minor adjustments with NaOH (0.1 M) and HCl (1 M), the final pH for each concentration was 7.90 ± 0.03.

Table 1: AGW Formulation[10]

Constituent	formula weight (g/mol)	Conc. (mmol/L)	Mass (g/L)
$NaHCO_3$	84.006	1.586	0.1333
$KHCO_3$	100.114	0.1231	0.0123
$MgSO_4 \cdot 7H_2O$	246.466	0.3660	0.0902
$MgCl_2 \cdot 6H_2O$	203.351	0.2468	0.0502
$CaCl_2 \cdot 2H_2O$	147.036	1.0708	0.1574
1M HCl add 0.150 mL for pH 7.8			

Table 2: Concentrations of Each Contaminant Used in Experiments[11,9]

Contaminant	I-127, µg/L	Tc-99, µg/L	Cr(VI) µg/L	NO_3^- µg/L	U(VI) mg/L	U(VI) µg/L
1	100	2.6	532	1990	99	9000
2	80	2.6	400	1600	80	5000
3	60	2.6	300	1200	60	2500
4	40	2.6	200	800	40	1000
5	20	2.6	100	400	20	100
6						50

Tabletop dried sediment (0.752 g $\pm$ 0.001 g) was placed in 15 mL polypropylene centrifuge tubes in triplicate. Spiked AGW (0.750$\pm$ 0.001 mL) was added to the sediments. A control without any sediment was also prepared to measure the amount of U absorbed on the tube and the cap or lost during pH measurement. Centrifuge tubes were placed on an end-over-end tube revolver at 8 rpm, as shown in Figure 1.
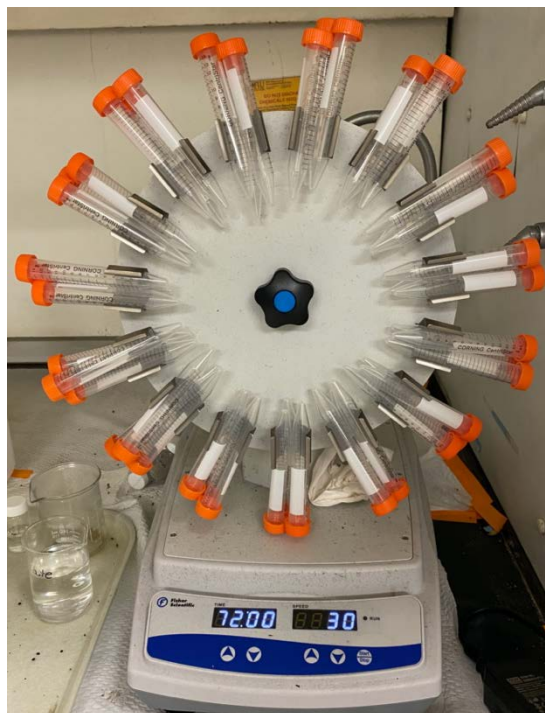
Figure 1: Sediment samples in an end-over-end tube revolver at 8 rpm.

For preliminary sorption equilibrium experiments, samples were sacrificed (to ensure a constant solid:solution ratio) at the following times to establish equilibrium time: 1 hour, 3 hours, 8 hours, 1 day, 2 days, 3 days, 4 days, 5 days, 7 days, and 14 days after the addition of the spiked AGW to sediment. During these sampling times, the samples were centrifuged at 4,500 RPM for 30 minutes (Sorvall ST Thermo Scientific Centrifuge). The supernatant was removed from the sediment and placed in a new vial for storage. Samples (186) were stored in the refrigerator before chemical analyses.

Samples collected during the batch adsorption experiment were diluted with 2% nitric acid (HNO_3) prior to analyses on the ThermoFisher Scientific iCAP RQ inductively coupled plasma - mass spectrometer (ICP-MS). This instrument was calibrated with U standards (0.1-100 ppb) that were prepared from 1000 ppm commercial uranyl nitrate stock solution. U samples (9000-1000 ppb and 100-50 ppb) were diluted 100x, and 10x with 2% HNO_3 respectively.

Geochemical speciation modeling using the Geochemist's Workbench software (version 12) was conducted to determine the distribution of uranyl aqueous species and to analyze the saturation state of uranium in AGW. Visual MINTEQ (thermo-minteq) thermodynamic database formatted by Jon Petter Gustafsson (KTH Royal Institute of Technology) was used in this modeling. Artificial groundwater composition included four cations and one anion along with counter ions. Concentrations of uranium ranged from 50 ppb-99 ppm. Dissolved oxygen was set at 8.0 mg/L at a constant temperature of 25°C. The speciation modeling assumed that the system was open to the atmosphere by including the presence of carbon dioxide. This best represents the environment in the vadose zone at the Hanford Site.

3. RESULTS AND ANALYSIS

Speciation results presented in Figure 2 predicted that $Ca_2UO_2(CO_3)_3^0$ (aq) and $CaUO_2(CO_3)_3^{2-}$ are the dominant uranyl aqueous species present in the AGW. The speciation modeling predicted the over saturation/precipitation formation (Q/K >1) of swartzite (calcium magnesium uranyl carbonate mineral). This indicates that not all aqueous U removal is due to adsorption, and some is due to precipitation in the form of these minerals. All other minerals were considered undersaturated in the system (Q/K <1).
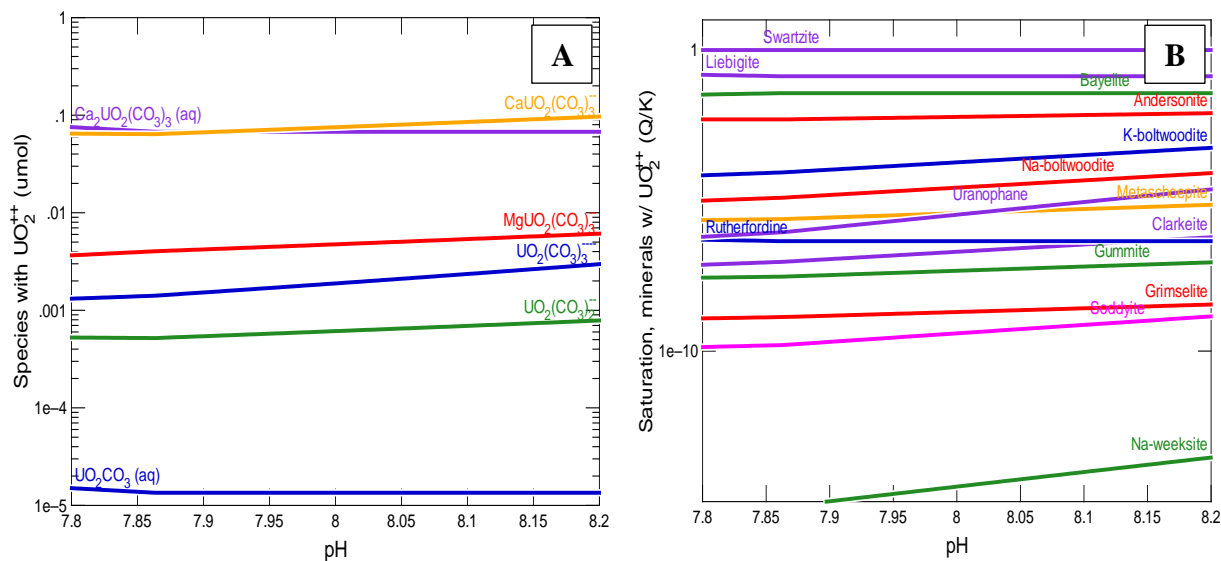
Figure 2. A: Uranium aqueous species and B: Saturation indices of uranium-bearing mineral phases as a function of pH. Sample composition includes 1.586 mmol/L of Na$^+$, 0.1231mmol/L K$^+$, 0.62 mmol/L Mg^{2+}, 1.0708 mmol/L Ca^{2+}, 0.366 mmol/L SO$_4{}^{2-}$, and 10 g of quartz.

Sorption becomes weaker at higher initial U concentrations as can be seen in Figure 3. This agrees with previous observations.[12,13,14,15,3]
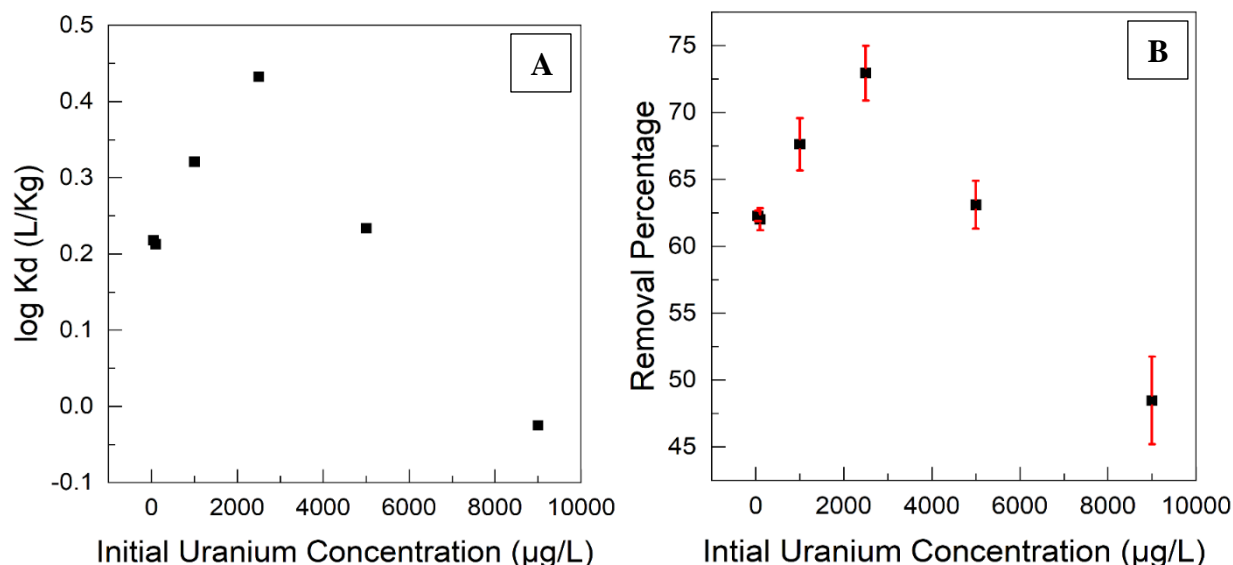
Figure 3. A: Log K_d(L/Kg) and B: Removal percentage vs initial U concentration (µg/L) in AGW onto Hanford formation sediment.

The small amount of adsorption observed in batch experiments can be assumed to be due to the dominant $Ca_2UO_2(CO_3)_3^0$(aq) and $CaUO_2(CO_3)_3^{2-}$ species. It is unlikely that $Ca_2UO_2(CO_3)_3^0$(aq) will be able to adsorb well to the surface of quartz due to its neutral charge and is unlikely to bond with the surface via the Ca atoms because they are already bonded to oxygen atoms of the carbonate anions.[7] For these same reasons, $CaUO_2(CO_3)_3^{2-}$ is also unlikely to bond to the surface of quartz.

Iron (Fe) oxides were most likely responsible for the majority of U adsorption to Hanford formation sediment. This is due to their high specific areas, as high as several hundreds of m^2g^{-1}, and their point of zero charge being located in the neutral or slightly basic pH range.[16,17,18] Unlike quartz, Ca has the ability to adsorb to the surface of ferrihydrite.[19,20,21] This can lead to a change in surface charge on ferrihydrite and also cause a decrease in U ability to adsorb to its surface.

Pseudo-first and pseudo-second order kinetic models were investigated. The pseudo-second order gave the best fit; kinetic correlation coefficients are illustrated in Table 3. This agreed with previous findings.[22]

Table 3: Pseudo-First Order (Solid Lines) and Pseudo-Second Order (Dashed Lines) Kinetics of U Spiked AGW Adsorption onto Hanford formation Sediment.

Concentration (ppb)	Pseudo-first order r^2	Pseudo-second order r^2
9000	0.91	0.95
5000	0.90	0.96
2500	0.91	0.96
1000	0.89	0.95
100	0.91	0.96
50	0.92	0.97

4. CONCLUSION

Uranium (VI) adsorption to Hanford formation sediment under site relevant conditions is minimal. This is due to the slightly alkaline pH and the presence of calcium and carbonate causing the formation of $Ca_2UO_2(CO_3)_3^0(aq)$ and $CaUO_2(CO_3)_3^{2-}$. These species make it difficult for U to sorb to minerals present in the sediment. Overall, this indicates that U(VI) present in the vadose zone at the Hanford Site is relatively mobile. This should be considered while developing future MNA procedures.

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