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Uranium Sequestration by pH Manipulation using NH₃ Injection in the Vadose Zone of Hanford Site 200 Area

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

URANIUM SEQUESTRATION BY PH MANIPULATION USING NH_3 INJECTION
IN THE VADOSE ZONE OF HANFORD SITE 200 AREA

A dissertation submitted in partial fulfillment of the

requirements for the degree of

DOCTOR OF PHILOSOPHY

in

CIVIL ENGINEERING

by

Claudia Cardona

2017

To: Dean John L. Volakis
College of Engineering and Computing

This dissertation, written by Claudia Cardona, and entitled Uranium Sequestration by pH Manipulation Using NH₃ Injection in the Vadose Zone of Hanford Site 200 Area, having been approved in respect to style and intellectual content, is referred to you for judgment.

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The dissertation of Claudia Cardona is approved.

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Florida International University, 2017

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DEDICATION

I dedicate this dissertation to my son, Nicolas, my parents, my husband, my sisters and brothers, but especially to my grandmother, Esther, who is looking me from the heavens.

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I owe a great of gratitude to many of people who supported me from a different point of view while I completed my doctoral studies. First, I wish to thank the members of my dissertation committee, Dr. Walter Tang, Dr. Yelena Katsenovich, Dr. Shonali Laha, Dr. Bernin Tansel, and Dr. Michael Sukop; their orientations and support were always presented for me. I am pleased to express, my most sincere gratitude to my advisor Dr. Walter Z. Tang, who encouraged me throughout my graduate student career that started many years ago after I just arrived from a foreign country. His valuable suggestions and endless support began since I was a Master student, and once again when I decided to go forward through my Ph.D.

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ABSTRACT OF THE DISSERTATION

URANIUM SEQUESTRATION BY PH MANIPULATION USING NH_3 INJECTION

IN THE VADOSE ZONE OF HANFORD SITE 200 AREA

by

Claudia Cardona

Florida International University, 2017

Miami, Florida

Professor Walter Z. Tang, Major Professor

Past nuclear weapon production activities have left a significant legacy of uranium (U) contamination in the vadose zone (VZ) of the Department of Energy (DOE) Hanford Site. This U is a source of groundwater (GW) contamination. There is a concern that elevated U concentration would slowly infiltrate through the VZ, reach the GW water table, and then end up in nearby rivers and lakes. Remediation of U-contaminated low moisture content soil is a challenging task considering the VZ depth, where contamination is found between 70 and 100 m below the ground surface, and the formation of highly soluble and stable CaUO_2CO_3 complexes is influenced by Hanford's soil rich in carbonate.

Injection of reactive gasses (e.g., NH_3) is a promising technology to decrease U migration in through the VZ. The NH_3 injection creates alkaline conditions that would alter the pore water chemistry (e.g., dissolving some aluminosilicates). Over time as the pH neutralizes, U(VI) could precipitate as uranyl mineral (e.g., Na-boltwoodite). Also, the dissolved U(VI) could be incorporated into the structure of some mineral phases or be coated by non-U minerals. These chemical reactions could control the U(VI) mobility to

the GW. However, there is a lack of knowledge on how the VZ pore water constituents (e.g., Si, Al^{3+} , HCO_3^- , and Ca^{2+}) would affect U(VI) removal/precipitation in alkaline conditions.

This study quantified the role of the major pore water constituents on the U(VI) removal and evaluated the uranyl minerals that could precipitate from a variety of SPW solutions. Results showed that the percentage of U(VI) removal was controlled by Si/Al ratios and Ca^{2+} concentration regardless of HCO_3^- concentrations tested. XRD revealed the presence of uranyl minerals by analyzing precipitates formed from SPW solutions, but none of them were identified as uranyl silicates as expected from speciation modeling. The SEM images displayed dense amorphous regions high in silica content, where EDS elemental analysis unveiled higher U atomic percentage in some samples. U(VI) silicate and carbonate minerals were predicted by the speciation modeling.

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ABBREVIATIONS AND ACRONYMS

BET	Brunauer–Emmett–Teller (Surface Area Measurement)
DO	Dissolved Oxygen
DOE	Department of Energy
DOM	Dissolved Organic Matter
EDS	Energy dispersive X-ray analysis
EPA	Environmental Protection Agency
HWL	High Level Waste
HCO ₃	Bicarbonate
H _x SiO ₄	Hydrous Silicates
IC	Inorganic Carbon
TOC	Total Organic Carbon
NEA	Nuclear Energy Agency
OECD	Organization for Economic Co-operation and Development
SEM	Scanner Electron Microscope
SI	Saturation Index
SPW	Synthetic Pore Water
PNNL	Pacific Northwest National Laboratory
TDS	Total Dissolved Solids
VZ	Vadose Zone
XRD	X-ray Diffraction

SYMBOLS

Al	Aluminum
C	Carbon
Ca	Calcium
Cl	Chloride
K	Potassium
NH ₃	Ammonia
Na	Sodium
Si	Silica
SiO ₂	Silicon Dioxide
U	Uranium
U(IV)	Uranium (IV)
U(VI)	Uranium (VI)
a_i	Activity of species i in aqueous phase
C_i	Concentration of species i
Eh	Redox potential
IAP	Ion activity product
K_d	Distribution coefficient
T	Temperature
m.s ⁻¹	meters per second
mLg ⁻¹	milliliters per gram

1. INTRODUCTION

1.1 Motivation

Large volumes of radioactive and hazardous waste were disposed of or stored during World War II and the Cold War at the U.S Department of Energy (DOE) facilities. These facilities, located in 13 states in the United States, were developed for researching, producing, assembling, and testing nuclear weapons. The Hanford Site facility was home to the first full-scale plutonium production reactor and produced plutonium for most of the nuclear weapons manufactured in the U.S during over 40 years of operations. The plutonium production and separation created large volumes of high-level nuclear waste containing uranium (U) and other constituents. The Hanford Site, divided into 100, 200, 300, and 1100 Areas, is placed on the National Priority List of the Environmental Protection Agency (EPA) due to the known radioactive and hazardous waste released to the environment. Approximately 200,000 kg of U has been reported as released in vadose zone (VZ) (Simpson , Corbin, Anderson , & Kindcaid, 2006) which leads to a risk to the human health and the environment through discharge to surface water or contaminated wells.

The 200 Area in the Northwest of the site, divided into the 200 East and 200 West, has an area of approximately 60 square miles and is known as the Central Plateau (Figure 1.1). This site is associated with the removal of plutonium from the uranium fuel rods after the radioactive decay process of U in the 100 Area reactor (Serne, et al., 2008), causing a high level of groundwater and soil contamination in the area. The most concentrated of these waste, classified as high-level waste (HLW), is stored in underground storage tanks known as “Tank Farms.” There are 177 underground storage tanks, 149 single-shell tanks

(SSTs) and 28-double-shell tanks (Mann, et al., 2001); Johnston et al., 2002), 67 SSTs have been found to be leaking into the subsurface (Gephart & Lundgren, 1998). The leaks of U to the surrounding soil led to waste streams causing widespread subsurface contamination including the VZ. Several projects have taken place to clean up the radionuclide waste in the VZ; these projects include laboratory studies of emerging technologies for in-situ remediation. The injection of NH_3 gas is a promising technology to decrease the highly mobile aqueous U(VI) complexes and the mobility of present U precipitates in the subsurface area (Szecsody et al., 2010; Szecsody et al., 2012; Zhong, Szecsody, Truex, Williams, & Liu, 2015). However, this technology needs additional studies to comprehend better the effects of the pore water constituents on the removal of U and the formation of stable precipitates after the NH_3 gas treatment.

Figure 1-1 Hanford Site – Location 200 East and West Areas
Source: Hanford Reach National Monument Maps, 2006

1.2 Overview of the vadose zone of the 200-Area in Hanford Site

The migration of the U contamination in the VZ of the 200-area at the Hanford Site could reach the water table below and then end up in the Columbia River. The mobility of U is not easy to categorize in this area because of its heterogeneity and anisotropic geological conditions. In addition, the complicated uranium chemistry makes it difficult to predict its transport through the VZ accurately (Cantrell, Zachara, Dresel, Krupka, & Serne, 2007). The sediment composition in the subsurface can enormously influence the U contamination concentration and its mobility. An overview of the present of U conditions and the geological characteristics in the VZ of the 200-area of Hanford is needed for a better understanding of the U contamination migration in the area.

1.2.1 Geological Conditions

The Hanford Site is in southeastern Washington State, within the central Pasco Basin in the Columbia Basin, known as the Central Plateau. The Hanford Site is the result of millions of years of geologic history shaping the soil and sediment composition within the basin. From the lowest to the highest layer the site was constituted geologically by the Miocene period, which is the older formation. It corresponds to the formation of the Columbia River basalt within the basin that is a bedrock that separates different layers of sedimentary rocks. The next is the Ringold Formation, between the Miocene and Pliocene ages. Unconsolidated alluvial-lacustrine deposits shape it. This formation contains the records of the river and streams migrations (Cantrell et al., 2007). The third unit, named as the Cold Creek unit, was created during the Pliocene and Pleistocene periods, it consists of deposits of basaltic to quartzitic gravels, sands, silts, and clays covered by calcareous soil. The concentration of calcite in the calcareous soil imparts a high moisture-retention

capacity to this unit. Its depth is approximately between 70 and 100 m and mainly marks the boundary between the unsaturated and saturated zones.

The Hanford Formation is the following unit and is the result of the Pleistocene-age cataclysmic flood deposits in the Pasco Basin. Its formation is primarily of rock fragments, gravel, silt sand, and silt. The gravel was deposited as consequence of flood water events while the silt, fine sand, and coarse sand were primarily deposited after flooding ceased and the water gradually went away (Baker et al., 1991; Lindsey et al., 1994). The earliest unit belongs to the Holocene age, and it is composed of surficial deposits. Gravel is found throughout the area representing the fast-flowing water from the main floods. Silts and sands are found throughout the area away from the main flood channels, and fine-grained silt and sand are around the basin borders.

The VZ lies mainly within the Hanford Formation, but it can extend to the Cold Creek unit and Ringold Formation in locations such as the 200 West Area. The thickness of the VZ in the 200-area varies from about 50 m in part of the 200 West Area to 104 m in places of the 200 East Area. Contaminants mobility is influenced by the geologic conditions found in each unit (Cantrell et al., 2007). U contamination has mainly been found in the Hanford Formation unit. Figure 1-2 shows a general representation of stratigraphic units within the Central Pasco Basin, and Figure 1-3 displays the general stratigraphy of the of the sediments in Hanford Site.

Figure 1-2. Generalized Stratigraphy of the Sediments
(Source: Reidel and Chamness, 2007), modified to locate the vadose zone

Figure 1-3 General representation of stratigraphic units in the Central Pasco Basin
(Source: Bjornstad, 2006)

1.2.2 Sediments Composition

The Hanford formation sediment consists of the glacio-fluvial material deposited through the geological periods. The mineralogy of the sediment formation is highly variable depending on the time formed and grain size. Different spectroscopic techniques have characterized the sediments mineralogy of the different units. In general, these minerals are quartz, calcite, plagioclase, K-feldspar, micas (muscovite, biotite, illite, montmorillonite) and other clays. Also, some analysis shows that the bulk sediment samples contain minor amounts of mica, chlorite, amphibole, smectite, and calcite. Calcite is dominant in the sediment samples, especially in the lower Cold Creek unit (Qafoku, Ainsworth, Szecsody, & Qafoku, 2004; Serne, et al., 2008). The concentration of calcium carbonate can vary over a wide range and can be as much as 70 percent by weight (Reidel & Chamness, 2007). In the Ringold Formation unit, the sediment minerals are mostly quartz and feldspar, which are derived from weathering of silicic plutonic rocks. The presence of dissolved silica in the pore water and sediments can result in the complexation of metals and radionuclides as well as in the precipitation of silica-containing phases (Bjornstad, 2006). Also, small percentages of magnetic, iron-rich mineral fraction containing magnetic and reactive iron-bearing minerals such as Fe(II)/Fe(III)-phyllosilicates have been characterized in the Hanford sediments (Zachara et al., 2007), but generally the composition in Hanford Site is characterized as about 50% of rock fragments and 50% quartz-feldspar (Tallman et al. 1979). The deposits of the Hanford formation reportedly have a low organic carbon content, less than 0.1% by weight and low and low-to-moderate cation exchange capacity. The sediment has a slightly basic pH if wetted. The moisture content of the VZ sediments is about 5 to 7 percent of the total

sediments by weight. The contaminant distribution coefficient (K_d) values are classified from high to low depending on the potential for migration through the VZ or GW. The K_d of U ranks between 0.2 and 4 mLg⁻¹ in natural conditions, which means U transport under natural conditions will be from high to moderate (Cantrell et al., 2003).

Most of the contamination at the Hanford Site occurs in the Hanford formation unit. Also, U is known to react strongly with the sediments in the Cold Creek unit, by binding and retarding uranium migration deeper into the subsurface. The distribution of uranium in an unsaturated and saturated porous media as consolidated by Giammar in 2001 is displayed in Figure 1-4.

Figure 1-4. Overview of the U distribution pore water media (Giammar et al., 2001)

1.2.3 *The presence of uranium contamination in the VZ of Hanford Site*

Uranium waste was released as a variety of aqueous solutions that percolated into the soil causing the contamination of the VZ (Simpson et al., 2006). The total amount of U released is unknown (Serne et al., 2008). Pacific Northwest National Laboratory (PNNL) scientists have conducted extensive evaluations of the contaminated areas of the 200-area. Measurements of the U concentration in the pore water have been reported in the range of 0.3 ppm to 500 ppm (Serne et al., 2008; Simpson et al., 2006).

Under the VZ natural conditions, U is found as U(VI) mainly as calcium uranyl carbonate complexes, as neutral $[\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0]$ and anionic $[\text{CaUO}_2(\text{CO}_3)_3^{2-}]$, because of the Hanford's Ca-rich carbonate environment. As shown by the leaching of sequential liquid extractions through sediment and subsurface pore water phases that concluded these complexes dominated at pH of 8 (Liu, Zachara, Qafoku & Wang, 2008). However, under more alkaline conditions the main uranyl aqueous species were found to be anionic calcium uranyl carbonate $[\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^{2-}]$ and uranyl tricarbonate $[\text{UO}_2(\text{CO}_3)_3^{4-}]$ (Zachara et al., 2007). Peterson et al. (2008) performed different thermodynamic speciation modeling using the Geochemistry Workbench (GWB), simulating U(VI) concentrations of 0.1 μM , 1 μM , and 10 μM in pore water solutions with 0.05 M NaNO_3 ionic strength. The CO_3^{2-} concentration in the solution was in equilibrium with $\text{CO}_{2(\text{g})}$ pressure of $10^{-3.5}$ atmospheres. The UO_2^{2+} and CO_3^{2-} species were plotted as a function of pH, between 6.0 and 9.0. The speciation with the lower total U(VI) concentration, 0.1 $\mu\text{mol/L}$, predicted the U(VI) speciation dominated by a mononuclear hydrolysis species (UO_2OH^+) below pH 6.5 and by the $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ species from pH 6.5 to 7.8. At pH greater than 7.8, the anionic uranyl carbonate complexes $[\text{UO}_2(\text{CO}_3)_2^{2-}]$ and $[\text{UO}_2(\text{CO}_3)_3^{4-}]$ predominated in the

speciation. Increasing the total U(VI) concentration expands the region dominated by the $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ species at the expense of uranyl carbonate species at both low and high pH. When U(VI) is increased above 10 $\mu\text{mol/L}$, the multinuclear $(\text{UO}_2)_3(\text{OH})_5^+$ species become more important at lower pH. The effect of U(VI) is minor above pH 7.0 because U(VI) aqueous speciation stabilized with high carbonate concentrations and strong carbonate complexes [e.g., $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$] (Figure 1-5). However, in the presence of Ca_2^+ (not shown) significant changes in uranyl aqueous speciation above pH of 7 were predicted. Below pH 6.5, Ca_2^+ has no effect, and U(VI) speciation is dominated by species $\text{Ca}_2\text{UO}_2(\text{CO}_3)^0$ from pH 7 to 8. Above pH 8, a combination of the $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ species were predicted.

Figure 1-5. U speciation as a function of pH and CO_3 in Hanford Sediment Pore Water. $\text{CO}_2(\text{g})$ pressure of $10^{-3.5}$ atmospheres.
(Source: Peterson et al, 2008)

The uranyl minerals in the natural and contaminated sediments are identified as the hydrous silicates such as Na-boltwoodite and uranophane (Szecsody et al., 2012). Crystallized precipitates found in fractures of plagioclase feldspar were suggested to be uranyl silicates (Catalano et al., 2004). The uranyl carbonate minerals, liebigite and rutherfordine, were characterized in sediments at medium and high CO_3^{2-} concentrations. Also, co-precipitated minerals with carbonates and hydrous silicates have been identified as uranophane and Na-boltwoodite (Zachara et al., 2007; Um et al., 2009; Szecsody et al., 2012; Szecsody et al., 2013). Uranophane and Na-boltwoodite are the more common uranyl solid phases associated as alteration products of spent nuclear fuel in oxidized zones (Finch & Ewing, 1992; Wronkiewicz et al., 1992; Wronkiewicz et al., 1996).

1.3 Injection of ammonia gas

Ammonia (NH_3) gas injection to promote the alteration on subsurface geochemistry and sequester uranium is a promising technology that has been evaluated by PNNL scientists to apply as in-situ remediation of inorganic contaminants in unsaturated sediments of the VZ (Szecsody et al., 2010; Szecsody et al., 2012; Szecsody et al., 2013; Zhong et al., 2015). Ammonia is a highly soluble gas and its injection in an unsaturated porous medium causes a formation of NH_4OH and consequently the incremental increase in the pore water pH. The aqueous speciation reactions caused by the NH_3 partitioning into liquid are written as follows:

Where K_h of 6.58×10^{-4} is the dimensionless Henry's Law partition coefficient and pK is the negative logarithm of the dissociation constant. From the equations 2.1 and 2.2, the NH_4^+ aqueous species predominates at $pH < 9.4$ while $NH_{3(aq)}$ is the major species at higher pH conditions. Because of its low Henry's constant (K_h), large ammonia partitions into the pore water when NH_3 gas is injected. Experimental results showed that by injecting 5% NH_3 and 95% N_2 gas mixture to VZ sediments with water content of 4% (w/w), the mass of ammonia was 99.7% ($NH_{3(aq)} = 3.1 \text{ mol/L}$) in the pore water when it reached a pH of 11.8. Also, these experiments showed a decrease in U mobility (Szecsody et al., 2010; Szecsody et al., 2012).

Changes in the pore water pH can profoundly affect the dominant soil minerals such as calcite, feldspar, iron oxides, and quartz that are present in the Hanford Site vadose zone. Chou and Wollast (1984) previously illustrated that the rate of feldspar dissolution increased by two to three orders of magnitude with increase pH from 8 to 12 at 23°C (Chou & Wollast, 1984). These dissolution reactions potentially induce the release of cations such as Si, Al, Ca, Mg, Na, and K from soil minerals to pore water. The subsequent decrease in pH to natural conditions would lead to precipitation of magnesium silicate and aluminosilicates that could possibly sequester contaminants in a process called co-precipitation (Szecsody et al., 2010 a, b). Another possible mechanism that can decrease U mobility is coating by a low solubility non-U precipitate, such as cancrinite (Bickmore et al. 2001), sodalite, hydrobiotite, brucite, and goethite, as observed in water-saturated systems (Qafoku et al. 2004, Qafoku & Icenhower, 2008). This technology has significant uncertainties at the 200-area vadose zone-specific conditions and requires additional testing in the laboratory to understand the effect of various environmental factors on the

formation and precipitation of uranium-bearing mineral phases. Particularly, what requires clarification is the role of major pore water constituents and the formation of precipitates after the NH_3 injection. Figure 1.6 displays an overview of the processes that occurs with NH_3 injection into unsaturated uranium contaminated Hanford Site sediments (Zhong et al., 2015).

Figure 1-6 Overview of the processes occurring with NH_3 injection
(Source: Zhong et al., 2015)

2. RESEARCH OBJECTIVES AND APPROACH

2.1 Research objectives

The objectives of this dissertation are to quantify the role of major pore water constituents on uranium (VI) precipitation/removal and identify the uranyl minerals that could precipitate from NH_3 -treated synthetic pore water (SPW) solutions under alkaline conditions. This work is accomplished by characterizing the influence of different Si/Al ratios and varied concentration of HCO_3^- , Ca^{2+} , and U(VI) in the SPW solutions. These components are essential in the VZ pore water composition. Therefore, their effect on the U(VI) removal and in the formation of uranium-bearing solid phases that could create due to the NH_3 treatment is evaluated. The first aim of this research is to quantify the removal of U(VI) at different Si/Al ratios in varied HCO_3^- concentration, characterizing Hanford Site conditions. The study also evaluated the effect of the divalent metals ions such as Ca^{2+} on U(VI) removal in alkaline conditions as the second aim. The third objective is to perform characterization to the precipitates formed in the SPW samples injected with NH_3 . The last objective is to conduct a thermodynamic speciation modeling to compare the results obtain by the batch experiments and spectroscopic analysis. In addition to add additional thermodynamic parameters of uranium species under alkaline condition, the database that is used to conduct speciation modeling is customized. The customized U(VI) database includes the most recent published experimental thermodynamic parameters for U(VI) aqueous species and uranyl mineral phases. A summarized of the objectives of this study is as follows:

- a) To quantify the role of the Si/Al ratio and HCO_3^- on the removal of uranium. A batch experiment is conducted preparing different SPW samples that include the main

constituents characterized in the VZ pore water. These SPW samples are injected with NH_3 gas. The samples preparation and the NH_3 injection are performed imitating the Hanford Site conditions.

- b) To quantify the effect of the divalent metals ions such as Ca^{2+} on the removal of uranium under alkaline conditions. The SPW samples include two Ca concentration which are in the range of the Ca concentration found in the VZ.
- c) To characterize the uranyl minerals that could be formed in the precipitated samples, the morphology and elemental composition are evaluated using the SEM-EDS by producing micrographs from the precipitated samples, locating the uranium crystals or amorphous formations, and collecting the chemical composition in the located areas or points using the EDS.
- d) The thermodynamic speciation modeling is conducted using the Geochemist Workbench speciation model. The GWB's thermo-minteq database is customized including uranium species that could be present in alkaline conditions, based on the most recent uranium thermodynamic data published. The database updates stability and solubility constants and include uranyl aqueous and minerals species that are significant for this study.

This work is accomplished by characterizing the influence of different silicon-aluminum ratios and varied concentrations of bicarbonate, calcium, and U(VI) in the SPW solutions. These components are essential in the VZ pore water composition. Therefore, their effect on the U(VI) removal and in the formation of uranium-bearing solid phases that could create due to the NH_3 treatment is evaluated.

2.2 Uranium geochemistry in aqueous systems

One of the most important factors affecting the uranium solubility in an aqueous system is the oxidation/reduction potential; the oxidation state of uranium (U) is a good indicator of the uranium behavior in the aqueous environment, where U can exist as four oxidation states U^{3+} , U^{4+} , U^{5+} , and U^{6+} . The trivalent (U^{3+}) cations are unstable in the water, whereas the pentavalent uranyl cation (UO_2^+) has minor importance due to its rapid disproportionation into U(VI) and U(IV) in most of the aquatic conditions.

Under reducing conditions, U exists as uranous oxide (UO_2) or tetravalent state (U^{4+}); U(IV) is insoluble and sparsely mobile with a strong tendency to precipitate as U(IV) (e.g. uraninite). Only the U(IV)-fluoride and U(IV)-hydroxide complexes are dissolved under this condition (Gascoyne et al., 1989). The enrichment uranium in a subsurface under a low redox potential can occur primarily due to the U(IV) precipitation (Osmond and Cowart, 1992). Also, the reduction from the U(VI) to U(IV) oxidation state can be present by microbial mediation. Iron and sulfate reducing bacteria are organisms that have shown reduced U(IV) to U(VI) (Lovley et al., 1991; Lovley & Phillips, 1992; Spear et al., 2000).

Under oxidic conditions the hexavalent state, as uranyl dioxo ion (UO_2^{2+}) species, is more mobile and highly soluble in an aqueous system. The UO_2^{2+} ion forms a variety of aqueous uranyl complexes depending on pH, U concentration, and at the presence of complexes such as carbonate ion (CO_3^{2-}) and Ca^{2+} . The aqueous speciation of a solution in 0.01 mM of U(VI), absence of CO_3^{2-} and under low pH ($pH < 5$) can form mostly UO_2^{2+} ions, slightly species of the mononuclear cation UO_2OH^+ species, and insignificant polynuclear cation $(UO_2)_2(OH)_2^{2+}$ species. Under moderate alkaline conditions, the $(UO_2)_2(OH)_2^0$ and $(UO_2)_3(OH)_5^+$ species are present, but it is strongly predominated by the

$\text{UO}_2(\text{OH})_2^0$ species. Also, the negatively charged species (e.g. $\text{UO}_2(\text{OH})_8^{2-}$) starts to be formed. Under alkaline solutions, $\text{pH} > 10$, insignificant species of $(\text{UO}_2)_3(\text{OH})_{10}^{4-}$ and predominance of $\text{UO}_2(\text{OH})_3^-$ exist in the solution. However, these species decrease when $\text{pH} > 12$. In carbonate solutions in contact with the atmosphere (an open system), the content of carbonates, in the aqueous phase, is controlled by the dissolution of the atmospheric carbon dioxide. In a closed system and under low pH conditions, UO_2^{2+} is still in the solution although CO_3^{2-} is in the solution. It might be due to the greater amount of dissolved CO_3^{2-} as $\text{CO}_2(\text{aq})$ species. However, under moderate alkaline conditions, the $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3$ specie is present, and its concentration reach the higher peak between pH of 7 and 8. As pH increases, $\text{pH} > 8$, most of U is transformed to $\text{UO}_2(\text{CO}_3)_3^{4-}$ and $\text{UO}_2(\text{CO}_3)_2^{2-}$ complexes, only these species are formed above pH of 10 due to the high dissolved total carbonates concentration in the aqueous phase. The $\text{UO}_2(\text{CO}_3)_3^{4-}$ complex is the more thermodynamic stable chemical uranium species formed in a carbonated and contaminated uranyl aqueous system (Gorman-Lewis, 2008). Therefore, the presence of CO_3^{2-} in an aqueous system plays a significant role in the UO_2^{2+} geochemical speciation since it facilitates the formation of stable complexes.

2.3 Calcium, Silica, and Aluminum aqueous reactions under alkaline conditions

The presence of Si, Al^{3+} , and Ca^{2+} constituents in a contaminated solution, under alkaline conditions, can affect the uranium mobility in the aqueous system because these constituents can influence to the formation of aqueous mobile species and/or precipitation of U-bearing mineral phases. The formed reactions can alter the U speciation in a natural or a contaminated aqueous environment. Si, Al^{3+} , and Ca^{2+} are characterized as present in the pore water of the VZ of Hanford Site, and they were included in the evaluated synthetic

pore water (SPW) solutions. Their reactions in an aqueous environment are reviewed as follows:

2.3.1 Calcium (Ca^{2+})

Calcium is a common aqueous cation found in equilibrium with calcite ($CaCO_3$) in the pore water and groundwater at many U contaminated sites, the Ca^{2+} ions can complex with uranyl in bicarbonate solutions to form calcium-uranyl-carbonate complexes [e.g., $Ca_2UO_2(CO_3)_3^0$ and $CaUO_2(CO_3)_3^{2-}$]. These species possess large stability constants (log K) that favor the U(VI) transportation in the pore water and groundwater system (Guillaumont et al., 2003). The mobility of the U(VI) in the environment is highly related to its complexation with Ca^{2+} and CO_3^{2-} ions under high alkaline conditions. Calcium concentration in carbonate aqueous is usually large because of reactions between carbonate minerals and carbon dioxide (CO_2). Reaction 2.3 helps to understand dissolution and precipitation of calcite in aqueous systems.

An increase in $CO_{2(g)}$ concentration due to oxidation process causes dissolution of $CaCO_3$ while degassing of $CO_{2(g)}$ causes calcite precipitation. According to Kellermeier et al. (2010), under alkaline pH, precipitation of the amorphous calcium carbonate in Si-rich solutions induces dissociation of HCO_3^- and the release of protons. Consequently, local pH decreases near the growing carbonate phases:

2.3.2 Silicon (Si)

Silicate (SiO_4^{4-}) as one of the most abundant natural compound found in the earth's crust can be presented in amorphous and crystalline forms. The presence of dissolved silica in the aqueous solution can result in the complexation of metals and radionuclides and the precipitation of silica-containing phases. The basic chemistry of silica is complex due to the variety of species in aqueous solution that depend on pH, ionic strength and temperature. Forms of silica that are soluble and stable for a long period in solutions with low dissolved concentrations $> 0.1\%$ are monomeric such as $\text{H}_4\text{SiO}_{4(\text{aq})}$, H_3SiO_4^- , and $\text{H}_2\text{SiO}_4^{2-}$. However, when the solution is supersaturated with respect to amorphous silica, extensive polymerization occurs because of the condensation of the silanol (Si-OH) group. It forms polymeric species that includes dimeric, trimer, tetrameric, and hexameric species and amorphous ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$ or $\text{SiO}_{2-x}(\text{OH})_{2x} \cdot 2\text{H}_2\text{O}$): silica precipitates) (Busey and Mesmer 1977, Choppin et al., 2011, Felmy et al., 2001). The polymerization of orthosilicic acid, $\text{Si}(\text{OH})_4$, involves nucleation. Nucleation implies the formation of critical clusters called nuclei after; the crystal growth occurs spontaneously (Stumm and Morgan, 1996). Thermodynamically nucleation or seeding of some chemical reactions can result in a lowering of the activation energy associated with the reaction (Mattus et al., 2002). The presence of impurities such as alkali metal ions and aluminum (Al), which precipitates by reacting with silicate, can accelerate polymerization reactions and the rate of silica precipitation (Iler 1979; Gallup 1997).

The monomeric silicate specie, $\text{Si}(\text{OH})_4$, is the more important specie for this reaction, given that the other monomeric silicate species (H_3SiO_4^- , and $\text{H}_2\text{SiO}_4^{2-}$) are negatively charged, preventing them from encountering $\text{Al}(\text{OH})_4^-$. However, the reaction of

these two species are considered in this study because of their importance at 25°C environments (Felmy et al., 2001), and their importance in the formation of uranyl silicate minerals. Negatively charged colloidal silica particles can also flocculate through reaction with alkaline earth metals. Also, divalent ions, such as Ca^{2+} , interact with silica surfaces through displacement of a proton as shows by Equation 2.5

Silicate species respond to these local pH changes by polymerization reactions following by particle aggregation and flocculation (Equation 2.6) (Iler, 1979; Kellermeier et al., 2010).

Therefore, lowering pH caused by the precipitation of carbonate increases the local supersaturation of silicic acid in the surroundings of the growing carbonate phases, thus, provoking precipitation of silica (García-Ruiz et al., 2009). When a soluble silicate is mixed with solutions containing metals other than the alkali metal group, insoluble amorphous metal silicates along with other elements are precipitated out of solution (Iler, 1975). Iler (1975) proposed mechanisms of silica coagulation by calcium ions leading to precipitation of those elements from solution. The adsorption of a calcium ions on the negatively charged silica surface liberates by ion exchange only one hydrogen ion, thus creating one additional negative site on the Si surface. This negative site is neutralized by one adsorbed calcium ion that retains a single positive charge.

Iler (1975) assumed that a possible mechanism of Si coagulation is through interparticle bonding that involves bridging by positively charged calcium ions and attraction between surfaces bearing a mosaic of positive and negative site. This can cause Si aggregation reactions to convert it to calcium silicate nuclei. As nucleus mass continues to grow, it results in flocculation and precipitation reactions (Dove and Nix, 1997).

2.3.3 Aluminum (Al^{3+})

Under alkaline conditions, Al(III) is present in the tetrahedral $Al(OH)_4^-$ form. The reaction between the uncharged silica species $Si(OH)_4$ and the negative charged alumina species $Al(OH)_4^-$ will form aluminosilicate chains joined by shared oxygen atoms. The presence of aluminum in the pore water solutions is important due its iteration with silicate. Aluminate ions make important modifications to the silica surface. Geometrically, the aluminate ion $Al(OH)_4^-$ is depicted by a regular tetrahedron, with the aluminum atom located in the center and the hydroxide ions forming the corner points (Gasteiger et al., 1992). Polymerization reactions of aluminum and silicon tetrahedra create an aluminosilicate anion; excess silica must be present at the reaction (Iler, 1979). The alumina-modified colloidal silica are negatively charged in a wide range of $pH < 3$, compared to pure silica, which is negatively charged by the adsorption of hydroxyl ions above pH of 7, but losing the charge in acidic solutions. Iler (1975) observed that surface aluminosilicate complexes reduce silica solubility and dissolution. Previous estimates of the reduction in silica dissolution rate by aluminum range from three to five orders of magnitude (Hurd 1973; Iler 1975).

2.4 Chemical speciation modeling

A chemical speciation determines the distribution of an element with all possible reactions present in a system. The results from a speciation modeling depend on the reliable input data and consistent and accurately database to model the equilibria. The output from the speciation modeling helps to interpret and a better understanding of experimental and analytical results. The calculation of chemical equilibria derives from thermodynamics supported mathematically to solve the complicated chemical equilibrium equations that are presented. These mathematical equations are derivations from several texts that detailed the development of the determination of chemical equilibria from the thermodynamics basics (Zeggeren & Storey, 1970). In the last decades, a large variety of models and computer models has been developed to solve chemical equilibrium calculations. There are several software packages, both commercial and public domain packages. Among the well-known are MINTEQA2 (Allison, 1991), PHREEQC (Parkhurst and Appelo, 1999), WATEQ4F (Ball & Nordstrom, 1991), Geochemist's Workbench (Bethke, 2007). No single to simulate could meet all the research requirements. However, GWB has capability to simulate chemical reaction as the ammonia gas reaction in a simple manner, the enabling to evaluate and modify the database, allowing to perform for more completed chemical analyzes from the results displayed, and superior output graphics capabilities. GWB is based on the Law of Mass Action approach, which is common and available in several thermodynamic computer programs. The mathematical treatment of the equilibrium speciation problem yields nonlinear equation systems that can only be solved iteratively using numerical methods such as Newton-Raphson method. In this work GWB v6.02 STD has been chosen as the tool to conduct the simulation of ammonia gas injection and uranium

speciation in the synthetic porewater solutions. GWB is used to calculate saturation indices (SI) and the distribution of aqueous species.

In GWB the analytical data for mole balances can be specified for any valence states of an element and distribution of redox elements among the different valence states that are determined based on specified pE or any redox couple. The concentration of an element can also be adjusted to obtain equilibrium with a specified phase. In batch reaction calculations, both equilibrium and non-equilibrium reactions can be modeled. In an equilibrium calculation, the total moles of an element are distributed among different phases to attain system equilibrium. Non-equilibrium reactions, such as aqueous-phase mixing can also be modeled in GWB where mole balances on hydrogen and oxygen allow the calculation of pE and mass of water in the aqueous phase. To conduct speciation calculations in GWM, water composition is input and the program then calculates the ion activities and saturation states of the relevant minerals. A solution can also be brought to equilibrium with a specified mineral in GWB.

The law of mass action provides a fundamental description of equilibrium in water. Considering a generalized reaction $aA + bB \rightleftharpoons cC + dD$, the distribution of species at equilibrium is governed by equation 2.8.

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (2.8)$$

K is the equilibrium constant (which depend on temperature) and the bracketed quantities denote activities or effective concentrations. GWB uses the Debye-Huckel and Davies equations to calculate activity coefficients. Once the activities of free ions in

solution are calculated, the saturation of a water sample can be calculated in terms of saturation index (SI) given in equation 2.9.

$$SI = \log\left(\frac{IAP}{K}\right) \quad (2.9)$$

Where: IAP: Ion activity product, is expressed like solubility product but involves the actual activities that used are in the solution sample, it may not be in state of equilibrium.

K, thermodynamic solubility product or equilibrium constant for dissolution reaction

SI: Saturation index denotes the tendency of a mineral phase to be in equilibrium, or towards to dissolution (undersaturated) or may be precipitated (supersaturated). For GWB, SI between -0.5 and 0.5, the mineral is generally considered to be near in equilibrium with the solution, whereas SI more negative values ($SI < -0.5$) reflects under-saturation, and SI more positive values ($SI > 0.5$) are considered super-saturation.

The GWB package consists of ten modules: The geochemist's spreadsheet (GSS). Balance reactions (Rxn) that automatically balances chemical reactions, calculates equilibrium constants and equations and solves for the temperatures at which defined reactions are in equilibrium. Activity, stability, and solubility diagrams (Act2) that calculates and plots stability diagrams on activity and fugacity axes. It can also project the traces of reaction paths calculated using the React program. Temperature and activity diagrams (Tact) that calculates and plots temperature-activity and temperature-fugacity diagrams. Calculate speciation in solution (SpecE8) that calculates species distributions in aqueous solutions and computes mineral saturations and gas fugacity, SpecE8 can also

account for sorption of species onto mineral surfaces per a variety of methods, including surface complexation and ion exchange. Trace reaction processes (React), React has the capabilities of SpecE8, but it also calculates traces reaction paths involving fluids, minerals and gasses. Furthermore, react module can predict the fractionation of stable isotopes during reaction processes. Plot geochemical data and reactions paths (Gtplot), 1D reactive transport (X1t), 2D reactive transport (X2t), and render reactive transport results (Xtplot) (Bethke, 2007).

2.5 Analytical techniques

2.5.1 Analytical techniques for elemental determination

a.) Kinetic phosphoresce analyzer (KPA):

Kinetic phosphoresce analyzer (KPA-11, Chemchek) and inductively Couple plasma mass spectrometry (ICP-OES, Perkin Elmer, Optima 7300 DV) are used for analyzing the concentration removal of hexavalent uranium U(VI) and the other interested elements contained in the supernatant solutions that are attained from the tested synthetic porewater. Although there are several analytical techniques for the determination of uranium removal, the KPA permits determinate the uranium concentration in the aqueous samples rapidly with a good accuracy. In KPA a laser pulse is used to electronically excite uranyl in the presence of a property phosphate-based complexing solution. The KPA measures the time-dependent decay of light intensity (lifetime approximately 250 μ s) and, by extrapolation to time zero computes the initial intensity, which is proportional to the uranium concentration. The results are an averaged of multiples laser pulses that are used for each measurement, so it makes the KPA has a good precision. The interferences of other species and dropping effects are controlled with the time-resolved technique. The

detection limit of KPA is around of 50 ng l⁻¹. However, the optimal results depend on the control of some interferences (e.g., calcium) and a good calibration performed before each analysis is conducted. A calibration containing a least five (5) points, 0.05, 0.1, 0.2, 0.5, 1.0 ppm of the standard uranium is conducted before each analysis, a method to fit the calibration should choose to fit the curve. Also, samples for quality control checks need to be prepared, this quality control samples must fit in the range of the calibration curve. All samples and quality control samples are analyzed in 1% nitric acid. All samples are triplicated to analyze the accuracy of each concentration measured.

b.) Inductively Coupled Plasma-Optical Emission Spectroscopy:

The instrument Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES Perkin Elmer, Optima 7300 DV) is used to measure the concentration of Si, Al, and Ca in the supernatant solutions. Using the ICP-OES the sample is decomposed by intense heat into a cloud of hot gases containing free atoms and ions of the interested elements. Because of the high temperatures used for the analyses, the sample atoms produce large amounts of ionization and excessive collision. This excitation in atoms and ions can decay to lower states through thermal or radioactive (emission) energy transitions. During ICP-OES analysis the intensity of the light emitted at specific wavelengths is measures and used to determine the concentration of the elements of interest. In ICP-OES analysis the thermal excitation sources can populate large number of different energy levels for several different elements at the same time. All the excited atoms and ions can then emit their characteristic radiation at the same time. This results in the flexibility to choose from several different emissions concurrently and allows detection of multiple elements concurrently. For optimal results operating the ICP-OES, a curve calibration for each element to analyze

should be performed. The calibration curve should cover a least five (5) points, 0.05, 0.1, 0.2, 0.5, 1.0 ppm of the standard element, and then a calibration linear fit of the curve must be chosen in the software. Also, samples for quality control checks need to be prepared, this quality control samples must fit in the range of the calibration curve. All samples and quality control samples are analyzed in 2% nitric acid. The accuracy of the concentration measurements is determined by replicated analysis of samples prepared from standards solutions (Fitzsimmons, J., 2015).

2.5.2 *Spectroscopic techniques*

a.) Power X-ray diffraction (XRD):

This analytical technique is mainly used for identification of a crystalline material. As each crystalline solid has its own distinct combination of chemical composition and crystal structure, its lattice spacing (d-spacing) and their relative intensities from a distinct pattern that is produced by the constructive interference of a beam of monochromatic X-ray diffused at specific angles to the family of d-spacing that constitutes the sample. Comparison of d-spacing of an unknown to those tabulated for known provides a means to identify the unknown. Rapid comparison is facilitated by different software's computer. The samples need to be grounded into a fine powder using a mortar and pestle into 1 or 0.5 mm depending on the availability of the sample. Samples should have a smooth plane surface to attain a random distribution of all possible planes, it means that crystallinities are reflected planes parallel to the specimen surface will contribute to the reflected intensities. Samples are conducted setting the XDR with 35 kV and 40 mA, programming to run over a 2-theta (2θ) range from 5° to 70° with a 0.02° step size and 3 second counting per step, and collecting patterns using a copper Cu $K\alpha$ radiation source ($\lambda=0.154056$ nm)

with a tungsten filter. For this study, the files provide by the Joint Committee on Powder Diffraction Standards (JCPDS), the International Center for Diffraction Data's Power Diffraction (ICDD) files are used for the identification of possible uranyl phases in the precipitated samples. XRD analysis is performed in the Advanced Materials Engineering Research Institute (AMERI) at Florida International University (FIU) using a Brucker 5000D X-ray Diffractometer.

b.) Scanner Electron Microscope - Energy Dispersive Spectroscopy (SEM-EDS):

The Scanning Electron Microscopy (SEM) is a technique that uses electrons instead of light to obtain images from a sample. The signals reveal information about the morphology, chemical composition, and crystalline structure of materials of the sample. SEM measurements include mainly the use of secondary electrons (SE) and backscattered electrons (BSE) for imaging samples. SE gives the morphology and topography while BSE is mainly used to demonstrate the contrast in composition of the mixed phases in the sample. Because of their greater cross-sectional area, larger atoms with a greater atomic number have a higher probability of producing an elastic collision. The number of BSE detected is proportional to the mean atomic number constituting the sample. Thus, a "brighter" and "darker" BSE intensity correspond to an element of greater and lower atomic number respectively. Therefore, BSE mode helped to identify particles containing in U. BSE images provide high-resolution compositional sample. Electron microscopy analysis is performed using a JEOL-5910-LV with accelerative potentials between 10 kV and 20 kV. For conduction purposes, all samples are gold coated using an SPI-Module Control and Sputter unit. EDS analysis is accomplished using an EDAX Sapphire detector with UTW Window paired with Genesis software. Micrographs are prepared in both SE and

BSE modes with the objective lens aperture 2 at 30 μm diameter and the spot sizes (condenser lens) ranging from 35 to 40 μm .

3. THE EFFECT OF Si AND Al CONCENTRATIONS ON THE REMOVAL OF U(VI) IN THE ALKALINE CONDITIONS CREATED BY NH₃ GAS

3.1 Abstract

Injection of reactive gasses, such as NH₃, is an innovative technology to mitigate uranium contamination in a high carbonate deep vadose zone (VZ), where the U contamination is a potential source of groundwater pollution. The objective of this experiment was to quantify the uranium sequestration efficiency in the synthetic pore water (SPW) solutions under alkaline conditions. The SPW solutions were prepared in a wide-ranging concentration of Si and HCO₃⁻ and with the present of Al³⁺, typical in the VZ contaminated sediments. The SPW composed of the primary compounds in the VZ were prepared with Si (5 to 250 mM), Al³⁺ (2.8 or 5 mM), HCO₃⁻ (0 – 100 mM) and U(VI) (0.0021-0.0084 mM) in the solution mixture. Experiments suggested that solutions with Si concentrations higher than 50 mM exhibited greater sequestration efficiencies of U(VI) whereas solutions with higher HCO₃⁻ concentrations showed greater removal efficiencies for Si, Al, and U(VI). Overall, silica polymerization reaction leading to the formation of Si gel correlated with the removal of U(VI), Si, and Al from the tested solutions. If no Si polymerization was observed, there was no U removal from the supernatant solutions.

3.2 Introduction

Atomic weapons production at the Hanford Site has left over 200,000 kg of legacy uranium contamination as a result of radioactive waste released to the ground surface (Corbin et al., 2005; Zachara et al., 2007). The release of radionuclides led to widespread uranium contamination that poses significant threats to the groundwater at the site. Despite extensive remediation efforts initiated in the early 1990s, the U contamination is still

characterized at multiple locations around the site that includes the VZ. The contaminated VZ is one of the primary challenges for the U.S. Department of Energy cleanup program, especially at the Hanford Site 200-area, where the VZ is 80 to 100 m thick with only 5-7% moisture content and the presence of co-contaminants. There is a concern as elevated uranium concentrations slowly migrate downward, creating a risk of higher U concentrations, reaching the groundwater and ending up the Columbia River. The mobility of uranium in the oxidizing, carbonate-rich Hanford subsurface at pH ~8.0 is relatively high, with a low U(VI) adsorption distribution coefficient (K_d) averaging 0.11 - 4 L/kg (Zachara et al., 2005; Zachara et al., 2007; Szecsody et al., 2013). The mobility of U(VI) can be explained by the formation of highly soluble and stable uranyl-carbonate complexes such as UO_2CO_3^0 , $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ (Langmuir, 1997; Guillaumont et al., 2003) whereas Ca^{2+} is not present in the aqueous environment. Contamination of radionuclides in a deep VZ, as at the Hanford Site, can be done by in-situ remediation converting aqueous U-carbonate mobile phases to lower solubility precipitates which are more stable in the natural environment. One of the potential methods to stabilize uranium in the subsurface is the injection of liquid phosphorus- bearing amendments (Wellman et al., 2006). However, injection of aqueous solutions to stabilize uranium in the dry VZ environments may potentially mobilize U and other co-contaminants by increasing the sediment water content leading to downward U(VI) migration with the aqueous phase.

Injection of NH_3 gas to the VZ is a viable method to decrease U mobility in the contaminated subsurface (Szecsody et al., 2012; Zhong et al., 2015). Ammonia is a highly soluble gas, and its injection in the VZ can cause the formation of NH_4^+ (which consumes H^+) followed by a consequent pH increment up to 12.52 for 100% NH_3 (15.7mol/L $\text{NH}_{3(\text{aq})}$),

11.87 (3.1mol/L NH_3 (aq)) for 5% NH_3 or pH 11.02 for 0.1% NH_3 (0.063mol/L NH_3 (aq)).

The total porosity and soil moisture content can potentially define the amount of gas needed to reach NH_3 gas/liquid equilibrium in a sediment/pore water system (Zhong et al., 2015).

This manipulation can significantly alter the pore water chemistry due to dissolution of the dominant soil minerals such as calcite, feldspar, iron oxides, and quartz present in the VZ soil. Chou and Wollast (1984) previously illustrated that the rate of feldspar dissolution may increase by two to three orders of magnitude increasing the pH from 8 to 12 at 23°C. These dissolution reactions in alkaline conditions induce the release of cations including SiO_4^{4-} , Al^{3+} , Ca^{2+} , Mg^{2+} , Na^{2+} , and K^{+} from soil minerals to pore water (Zhong et al., 2015). Then, upon the re-establishment of natural pH conditions, various silica and aluminosilicate solids would precipitate as a uranium-silicate such as Na-boltwoodite (Szecsody et al., 2013) or decrease U mobility by coating of U-bearing phases forming a low solubility, non-U precipitates, such as cancrinite sodalite, hydrobiotite, brucite, and goethite, as observed in water-saturated systems (Bickmore et al., 2001; Qafoku et al., 2004; Qafoku and Icenhower, 2008). These chemical reactions could control the mobility of uranyl cations and limit their downward migration to the underlying groundwater aquifer (Szecsody et al., 2012). Previous short-term laboratory evaluations showed decreasing U mobility after NH_3 gas injection in low water content sediments (Szecsody et al., 2013; Zhong et al., 2015), also this study reported that the mass of U leaching from NH_3 -treated U-contaminated sediment was significantly less compared to the mass leached from the untreated sediment.

The objective of this study was to quantify the role of major pore water constituents on uranium (VI) removal from NH_3 -treated SPW solutions. This was accomplished by

characterizing the influence of different Si to Al ratios and varied HCO_3^- concentrations on the removal of U(VI) in the SPW solutions treated with NH_3 gas. An understanding of the role of pore water constituents on the removal of U(VI) is needed to identify controlling geochemical processes that would occur in NH_3 -treated sediments with a composition typical for the arid and semiarid regions of the western U.S. that received different U-laden wastes (Katsenovich et al., 2016). Parallel studies focused on the characterization of the formed uranium-bearing solids that were created from the tested SPW solutions in this chapter. This characterization is discussed in chapter 5, section 5.6.1 of this work.

3.3 Materials and methods

The composition of pore water at the Hanford site has been previously characterized in terms of concentrations of major cations, anions, and pH (Serne et al. 2008). For these experiments, the complicated pore water composition was simplified to have only four five major elements in the test solutions: U(VI), Si, Al^{3+} , and HCO_3^- . Two relatively low concentrations of U(VI), 0.5 ppm and 2 ppm (0.0021- 0.0084 mM), and six different HCO_3^- concentration (0.0, 2.9, 25, 50, 75 and 100 mM) were tested. Si was represented by H_4SiO_4 salt in the mixture solution, it was varied (5, 50, 100, 150, 200, 250 mM) because of past observations of 30 mM in 5% NH_3 treated sediment (Szecsody et al., 2012), and reached up to 100 mM in 10% NH_3 treated sediment. This concentration was then gradually declined after 24 h (Zhong et al., 2015). The same highest Si concentration of 100 mM with the total cations values of 250 mM was noted by Szecsody et al., (2010). Past observations also showed that the concentration of Al released during the soil treatment by 1 mol L^{-1} NaOH is relatively small, resulting in ~5.1 mM of Al in the soil solution (Qafoku et al., 2003) or up to 0.8 mM in 10% NH_3 -treated sediment. Based on

these results, two concentrations of Al^{3+} (2.8 mM and 5 mM) were tested. Both Si and Al^{3+} concentration tested are orders of magnitude greater than U. Therefore, it can lead to the potential U precipitation as U-silicates from the Si and Al^{3+} rich solutions. Detailed composition of SPW solutions are provided in Appendix 1 (Table A1-1).

In addition, several analogous control samples were prepared without Al^{3+} in the solution mixture which served to evaluate its effect on the removal of U(VI). The experiments were run by limiting Si concentration to a maximum of 250 mM, because preliminary experiments did not show any significant difference in results of U(VI) removal for Si values higher than 250 mM. In addition, carbonate solubility is much higher under alkaline conditions; so, at pH 11 pore water concentration of aqueous carbonate will be considerably increased justifying of wide range of bicarbonate concentrations tested in the experiments. Stock solutions of Al (50 mM), Si (422 mM), and HCO_3^- (400 mM) were first prepared in deionized water (DIW) from the salts $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, and KHCO_3 , respectively, reaching the desired concentrations in 50 mL volume. The 100-ppb stock solution of uranyl nitrate dissolved in DIW was prepared fresh from a uranyl nitrate hexahydrate 1000-ppb standard before use (Fisher Scientific). Detailed chemicals as stock solutions and the used formulations are provided in Appendix 1 (Table A1-2).

For each bicarbonate concentration, six different test solutions with varying Si concentrations were prepared and each was formulated at both 2.8 and 5.0 mM Al concentrations. Each of these test solutions was prepared by mixing a precise volume of the silicate stock solution with a measured volume of the aluminum stock solution. This mixture was then added to the test solution with a measured volume of the appropriate bicarbonate stock solution (unless no bicarbonate was used). Deionized water (DIW) was

added to each test solution to reach a total final volume of 49 mL leaving 1 mL of volume for the pH adjustment. Then the pH of the resulting solution was adjusted to 8.0 by titration with concentrated nitric acid and DIW was added to end up with a final volume of 50 mL in each tube. The pH value of 8.0 is consistent with values previously observed in the Hanford Site 200-area VZ (Zachara et al., 2007; Serne et al., 2008).

Then, NH_3 gas (0.1% NH_3 + 99.9% N_2) was injected into each solution through a metal gas sparger (Mott Corporation, dL of 5 μm pores in average) until the pH of the solution reached approximately 11. Afterwards, triplicate test samples, each with a volume of 5 mL, were extracted from each test solution and added to individual polyethylene 15 mL tubes. Three of the samples were each amended with a U(VI) concentration of 0.5 ppm and the other three samples were each amended with a U(VI) concentration of 2 ppm. Control samples were prepared in DIW amended with U(VI) at concentrations of 0.5 ppm and 2 ppm U(VI) to test for U(VI) losses from the solutions due to sorption to tube walls and caps. All control and experimental tubes were capped and placed and experimental in an incubator/shaker at 100 rpm at a temperature of 25 °C. After two days, the solutions were centrifuged for 15 minutes at 4000 rpm and supernatant solutions were withdrawn to analyze for U(VI), Si, and Al. Each set had six distinctive test solutions, each prepared at a different Si concentration, for a total of thirty-six test solutions each prepared in triplicate for each Al concentration. The matrix of solution prepared are detailed in appendix 1 (Table A1-3). In this study, it is assumed that in conditions created in vials, ammonia will not reduce U(VI) to U(IV). The reduction of U(VI) by ammonia is strongly hindered by the presence of air, which is 21% oxygen, in the headspace of capped vials, the addition the nitrates in the solution through the uranyl standard used and pH adjustment.

Figure 3-1 Sample preparation procedure, effect of Si and Al

3.4 Analytical procedure

Samples of the supernatant from each vial were analyzed using a kinetic phosphorescence analyzer (KPA-11, Chemcheck Instruments, Richland, WA) instrument to determine the remaining U(VI) concentration left in the solution. The residual Al and Si concentrations in each solution were measured using inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Perkin Elmer). The initial Al and Si stock solutions were also analyzed periodically with ICP-OES to confirm concentrations.

For analysis with the KPA instrument, an aliquot was extracted from the supernatant of each test sample and diluted with 1% nitric acid between 5 and 100 times. For analysis with the ICP-OES, an aliquot extracted from the supernatant of each test sample was diluted with DIW in conical polypropylene tubes between 100 and 200 times.

To examine the results on the effect of U(VI) concentration on its removal, One Way ANOVA statistics were used. All statistical tests were investigated by Sigma plot 11.2 (Systat Software Inc.). Significant levels were set to $\alpha = 0.05$.

3.5 Results and discussion

Experimental results were calculated as percent removal of the elements of interest from the supernatant solutions: U(VI), Al and Si. The removal values for each element were plotted on the y-axis against the Si concentration on the x-axis. These graphs were used to compare results for each data set prepared with different U(VI) and bicarbonate concentrations ranging between 0 and 100 mM. The results for the removal of elements in 2.8 mM Al, amended solutions for 0.5 ppm and 2 ppm U(VI), at varied HCO_3^- and Si concentration are presented in Figures 3-2 and Figures A-2-1 (Appendix 2). A reduction in Si content in the supernatant from the solutions initially amended with 2.8 mM of Al and 0.5 ppm (Figure A-2-2A) or 2 ppm of U(VI) (Figure 3-2-A) was observed for most of the initial Si concentrations tested. Si polymerization leading to the formation of silica gel always coincided with a lowering of the pH of aqueous solution mixtures from 11, where all the Si is dissolved as silicate ion, between 10.6 and 10.7. The change in the pH led to Si supersaturation and then nucleation and deposition of monomeric silica (H_3SiO_4^-) and $\text{H}_2\text{SiO}_4^{2-}$) from the solution.

In SPW solutions with HCO_3^- concentrations between 0 mM and 25 mM and an initial Si concentrations less than 100 mM, the removal efficiency of Si showed relatively low values that ranged from 0 to 50%. However, the increasing of HCO_3^- concentration up to 100 mM correlated with an enhanced Si removal with up to 91% removed from solution. Experiments using greater Si content of 200 mM and 250 mM resulted in high Si removal

efficiencies of up to 97% from the supernatant solutions. Solutions at HCO_3^- concentrations above 100 mM did not appear to alter the efficiency of Si removal. Overall, these results suggest that the percent removal of Si increases at higher Si and HCO_3^- concentrations until the removal stabilizes in the range from 95 to 97% (Figure 3-2-A and Figure A-2-A).

The percentages of Al removal in test solutions with U(VI) concentrations of 0.5 ppm (Figure A-2-B) and 2.0 ppm (Figure 3-2-B) were in the range of 98.2 - 99.7%. U(VI) removal (Figure 3-2-C; Figure A-2-1; Figure A-2-2C) from the SPW samples over the range of U(VI). HCO_3^- solution concentrations showed similar trends as Si and Al removal. The results also indicated that the initial U(VI) concentration (0.5 ppm) did not appear to affect the efficiency of U(VI) removal (Figure A-2-1).

Data analysis of U(VI) removal showed that the maximum percent removal of U(VI) was near to 98% for the solution prepared with Si concentration over 150 mM (Figures 3-2-C and A-2-1). At low Si concentration, 5 mM, there was no observed reduction in the U(VI) concentration in the supernatant solutions; therefore, the process of U(VI) removal does not seem to be efficient when the concentration of Si is less than 50 mM. This Si concentration is higher than the solubility of amorphous silica observed at pH 10.6 as 876 mg/L (31.1mM) at 25°C (Iler, 1979).

The solubility of Si increases at high pH due to the formation of silicate (SiO_4^{4-}) due to addition of Si(OH)_4 in solution. The increment of HCO_3^- in solution appeared to alter the efficiency of Si removal at lower Si concentration. Samples containing HCO_3^- higher than 50 mM revealed considerable changes in the percent removal of U(VI) compared to samples amended with 25 mM or less in HCO_3^- solutions. In those samples,

the removal of U(VI) from the supernatant solutions was increased between 80% and 99%, but it was not affected by the varied HCO_3^- concentration tested in solutions.

Figure 3-2 Removal of Si from solution prepared with 2.8 mM Al and 2 ppm U

Experimental results for both concentration of U(VI) followed the same trend: insignificant removal of U(VI) from solutions containing initial Si concentration ranging

between 5 mM and 50 mM, the removal increased to 78% - 94% at Si concentration of 100 mM and increased again to 95-99% at Si concentration between 150 mM and 250 mM. This trend for U(VI) removal is like that of Si. Also, statistical analysis indicated substantial evidence that there was not a concentration dependence on U(VI) removal based on the experiments at 0.5 ppm and 2.8 ppm U(VI) ($P < 0.05$) (not shown). The U(VI) removal increased to 78-95% when the solution mixture contained HCO_3^- concentration higher than 50 mM. Due to similar results on U(VI) removal at both U(VI) concentration tested, U(VI) of 2 ppm was employed in all further experiments. The concentration of Al^{3+} was increased to 5 mM and the removal efficiency of U(VI) from the Si-Al- HCO_3^- mixture was evaluated across the HCO_3^- concentration tested previously at 2.8 mM.

The experiments suggested that the removal of Si from the solution mixture in the presence of 5 mM and 2.8 mM of Al showed a similar trend. However, the addition of 5 mM of Al produced more consistent results for the Si removal at a low Si/Al ratio of 10 (50 mM of initial Si in the solution) and generally was found between 75 and 89% compared to values obtained for the batch amended with 2.8 mM of Al (Figure 3-1-A, Figure A2). The set amended with 25 mM HCO_3^- and 5 mM Al showed a relatively low removal of Si with a calculated value of 6.2%. In opposition, the removal of Si obtained for 2.8 mM of Al at the same initial Si in the solution was much lower, especially in the range of 0 to 25 mM HCO_3^- (Figure 3-2-A, Figure A-2-A) and Figure A-2 shows a similar pattern for the U(VI) removal at Al/Si ratio 1.0 (5 mM of Si) with the higher removal obtained at 75 mM HCO_3^- and 100 mM HCO_3^- amended solutions. The concentrations of Al were not detectable in the supernatant (detection limit for Al -20 ug/L or 0.74 uM) when Si was higher than 100 mM (Figure 3-2-B and Figure 3-3-B).

Figure 3-3. Si, Al, and U(VI) removal from solutions prepared with 5 mM of Al

In the presence of 5 mM of Al, a similar trend was noticed between the removal of U(VI) and Si when Si initial concentrations in the solution were > 50 mM. In the set amended with 25 mM of HCO₃⁻, the decreased removal of Si correlated with only 7.5% removal of U(VI) from the supernatant (Figure 3-3-A). For the rest of the bicarbonate concentrations tested, the removal of U(VI) ranging between 71% and 98.5% showed a good correlation with the 90-95% removal of Si from the supernatant solutions (Figure 3-3-C).

The effect of Al on the removal of 2 mg/L of U(VI) was further evaluated in a series of experiments using solutions of Si, HCO₃⁻, and U(VI) salts and amended with and without Al. For this assessment, only two concentrations of bicarbonate solutions were tested, 2.9

mM and 50 mM, to investigate a lower and upper bicarbonate range. The concentrations of Al in the trials were 0, 2.8 and 5 mM.

As shown in Figure 3-3-D, the U(VI) removal was delayed when the solution mixture for both HCO_3^- concentrations was prepared in the absence of Al. At low HCO_3^- and without Al, the U(VI) removal of $81 \pm 0.9\%$ was observed at $\text{Si} \geq 150$ mM. Similar solution mixtures containing low HCO_3^- concentrations and Al at 2.8 mM exhibited $79.5 \pm 1.7\%$ U(VI) removal starting from 150 mM of Si. The increase in Al concentration up to 5 mM resulted in 9.5% -16% higher U(VI) removal compared to values obtained with 2.8 mM of Al. At 50 mM HCO_3^- and no Al present in the solution, the notable U(VI) removal of $94.6 \pm 1.1\%$ was observed at $\text{Si} \geq 50$ mM. In the mixture with the same high HCO_3^- (50 mM) and 5 mM of Al, the U(VI) removal efficiency of $86.7 \pm 0.7\%$ was observed at 50 mM of Si (Figure 3-3-D). Hence, the higher Al and HCO_3^- concentrations triggered silica polymerization reactions at lower concentrations, which coincides with a simultaneous lowering of U(VI) content of the solution mixture.

When the Si-free solution mixture contained 2.8 mM of Al, the percentage of uranium removal exponentially declined with an increase in the concentration of HCO_3^- in the solution composition. This phenomenon might be explained by the competitive adsorption of HCO_3^- and U(VI) on Al hydroxide created in the solution (Su & Suarez 1997) at alkaline pH in addition to the presence of soluble uranyl carbonate complexes in the solution composition. The higher concentration of bicarbonate solutions correlated with a lower U(VI) removal from the solution (Figure 3-4).

Figure 3-4 Removal of Al from solution prepared with 5mM of Al

Su and Suarez (1997) proposed a ligand exchange reaction to describe the interaction of bicarbonate and carbonate ions with the surface functional groups of Al. These reactions could potentially limit the competitive adsorption of U(VI) on the surface of Al hydroxide, which is defined by speciation modeling as a major species of Al at alkaline pH. In addition, U(VI) adsorption is decreased in the presence of carbonate due to the formation of negatively charged uranyl carbonate complexes in the solution (Zheng, Tokunaga & Wan, 2003; Um, Serne and Krupka, 2007).

Overall, the silica polymerization reaction leading to the formation of amorphous Si gel always correlated with the removal of U(VI), Si, and Al from the solution. If Si polymerization and gel formation was not observed, there was no removal of U from the supernatant. The efficiency of U(VI) removal was affected by the Si concentrations and accelerated by the presence of Al and bicarbonate salts supplemented in the solution.

Overall, the silica polymerization reaction leading to the formation of amorphous Si gel always correlated with the removal of U(VI), Si, and Al from the solution. If Si polymerization and gel formation was not observed, there was no removal of U from the supernatant. The efficiency of

U(VI) removal was affected by the Si concentrations and accelerated by the presence of Al and bicarbonate salts supplemented into the solution.

3.6 Conclusions

The experimental results provided details on the effect of various silicon, aluminum and bicarbonate concentrations on the removal of uranium from the supernatant solution because of silica polymerization reactions. The removal efficiency of uranium was not significantly affected by U(VI) concentrations tested (0.5 ppm and 2.0 ppm). Experimental results showed evidence that solutions with higher concentrations of Si, Al, and HCO_3 tended to have more significant removal efficiencies of U(VI). The highest percentage removal of U(VI), 95-99%, was observed at Si concentrations between 150 mM and 250 mM. The process of U(VI) removal did not appear to be efficient when the concentration of Si was less than 50 mM. Solutions with higher concentrations of bicarbonate exhibited larger removal efficiencies for Si, Al, and U(VI). The increase in Al concentration up to 5mM resulted in 9.5%-16% higher U(VI) removal compared to values obtained with 2.8mM of Al. Overall, the formation of amorphous Si always correlated with the removal of U(VI), Si, and Al from the solution. If no Si polymerization was observed, there was no U removal from the supernatant solution.

4. THE EFFECTS OF DIVALENT CATIONS (Ca^{2+}) ON THE REMOVAL OF U(VI) IN THE ALKALINE CONDITIONS CREATED BY NH_3 GAS

4.1 Introduction

In Ca-rich carbonate-bearing subsurface environments, typical for western U.S arid and semi-arid regions including Hanford Site, U(VI) speciation lead to the formation of highly soluble and stable calcium-uranyl-carbonate complexes [$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0(\text{aq})$, $\text{CaUO}_2(\text{CO}_3)_3^{2-}$] (Bernhard et al., 2001; Kalmykov & Chopin, 2000; Davis et al., 2004). The formation of these complexes can explain the high mobility of U in the VZ sediments given its low partition coefficient (K_d) values ranging between 0.2 to 4 mL/g (Cantrell et al., 2003; Szecsody et al. 2013; Zachara et al., 2005, 2007). The uranyl minerals and their stabilities can be influenced by the pH conditions and co-precipitated in the presence of complexing anions such as carbonate (CO_3^{2-}) and hydrous silicates such as H_3SiO_4^- and $\text{H}_2\text{SiO}_4^{2-}$ forming uranyl carbonate and uranyl silicate minerals.

The uranophane and boltwoodite are the more common uranyl silicate minerals associated as alteration products in nuclear fuel in oxidized zones (Bernhard et al., 2001; Finch & Ewing, 1992; Wronkiewicz et al., 1992, 1996). Also, these minerals have been found as uranium-bearing precipitates in the VZ of Hanford Site (Catalano et al., 2004) and their formation are related to the uranyl co-precipitation with CO_3^{2-} and hydrous silicates (Szecsody et al., 2012; Um et al., 2009; Wellman et al., 2006; Zachara et al., 2007). The liebigite and rutherfordine (uranyl carbonate minerals) have been found at medium to a high concentration in the VZ sediments (Szecsody et al., 2012). The injection of a highly soluble ammonia gas to VZ prompts the formation of NH_4OH following a subsequent increase in pH from 8 to about pH 11.02.

The objective of this chapter is to examine the effect of Ca^{2+} on the removal of U(VI) in varied SPW compositions treated with NH_3 gas. This study quantifies the removal of U(VI) in the presence of Ca^{2+} , HCO_3^- and Si/Al ratios. The SPW solutions were prepared with two Ca^{2+} concentrations to examine its effects on the removal of U(VI). Also, the tested solutions contained different Si to Al ratios, HCO_3^- and U(VI). The sample preparation mimicked the VZ pore water characterization and conditions at Hanford Site, as explained previously in Section 3.3 in Chapter 3. Manipulations with pore water constituents can simulate the conditions occurring in the subsurface and explain changes in the removal of elements through co-precipitation with silica and aluminosilicates. The precipitates formed from the SPW solutions were collected to be evaluated using the spectroscopic analyses. The detailed characterization of the uranium-bearing precipitates created after ammonia gas injection in samples including Ca^{2+} is described in detailed and discussed in the chapter 5.

4.2 Material and methods

The composition of the pore water at Hanford Site has been characterized in terms of concentrations of major cations, anions, alkalinity and pH (Serne et al., 2008). In this experiment, the complicated pore water composition was simplified to contain five major components including Ca^{2+} in the SPW solutions. Therefore, silica, aluminum, uranium, calcium, and bicarbonate and the main components in the SPW solutions. As previously Si composition, Si concentrations were based on previous studies (Katsenovich et al., 2016; Qafoku et al., 2004; Szecsody et al., 2010b, 2012; Zhong et al., 2015). These experiments were conducted by limiting Si concentrations to a maximum of 250 mM (7.0 g L^{-1}) since previous studies suggested that the increase in Si concentration up to 10 g L^{-1} hasn't

affected the removal of uranium. Al concentration was kept constant at 5mM, which is slightly higher than was observed in the batch experiments conducted by (Zhong et al., 2015). Both, Si and Al concentrations, are orders of magnitude greater than U, so these systems can lead to U precipitation as U-silicate species since solutions are rich in Si and Al. Due to abundance of calcite in Hanford's sediments, CO_3^- and HCO_3^- are the major anions in the groundwater and porewater (Qafoku and Icenhower, 2008; Serne et al., 2008). For this experiment, SPW compositions contained, six Si (5, 50 100, 150, 200, and 250 mM), six HCO_3^- (0, 2.9, 25, 50, 75, and 100 mM) and two Ca^{2+} (5 mM and 10mM) concentrations; the U concentration was kept constant as 0.0084mM (2 ppm) in all SPW tested. The experimental results provide a complete range of data for U(VI) removal in the presence of 5mM of Al across all Si and HCO_3^- concentration tested in addition to Ca^{2+} commonly present in the pore water composition. In this study, the SPW solutions preparation followed same guidelines as in the experiment discussed in chapter 3. Therefore, a detailed of the stock solutions, formulations, and concentration used in this experiment is found in the Appendix 1 (Table A1-1, A1-2, A1-3).

4.3 Samples preparation and procedures

Stock solution consisted in 50mL of Al (50 mM), Si (420 mM), HCO_3^- (400 mM), and 20mL of Ca (500 mM) which were prepared by dissolving individually the correspondent salt, 0.94g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 5.99g of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, 2.0g of KHCO_3 and 2.19g of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in 100 mL graduated tubes with distilled deionized water (DIW). $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ and KHCO_3 served also as sources of Na^+ and K^+ in the pore waters. A 100-ppm stock solution of uranyl nitrate stock solution was prepared fresh by dissolving the appropriated amount of uranyl $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1000 ppm, Fisher Scientific) in DIW.

All other reagents were of analytical grade. Sample preparation procedures at different molar ratios of Si/Al followed the same route as described in (Katsenovich et al., 2016) by mixing the appropriated volume of stock solutions and injecting NH_3 gas (5% NH_3 in 95% N_2) through averaged 5 μm pores of a metal gas sparger (Mott Corporation) until the pH of the solutions reached a value of 11.02 (0.063 mol/L of $\text{NH}_{3(\text{aq})}$). Triplicate synthesized pore water samples of 5 mL were prepared by extracting the correspondent amount of volume from NH_3 -laden aluminum-silicate-carbonate test solutions to 15-mL individual polyethylene tubes and mixing rapidly with CaCl_2 stock solution (50 and 100 μL). All tested samples were amended with 0.0084 mM (2 ppm) of U(VI) by adding 100 μL from the prepared uranyl nitrate. U(VI) control samples were prepared at the same concentration, 0.0084 mM (2 ppm), in DIW to test U(VI) losing from the solutions due to sorption to tube walls and caps. All samples and control tubes were vortexed and kept in an incubator/shaker at 100 rpm at a temperature of 25 °C. After two days, the solutions were centrifuged for 15 minutes at 4000 rpm (Thermo Scientific, Corvall ST 16R centrifuge) and supernatant solutions were withdrawn to analyze for U(VI), Si, Al, Ca, IC (inorganic carbon). Preliminary experiments showed that the removal efficiency of U(VI) reached a plateau after two days of agitation on the shaker. A total of 72 triplicated samples of 5 mL were prepared, each Si/Al molar ratio (1, 10, 20, 30, 40, and 50) by each bicarbonate concentration (0, 2.9, 25, 50, 75, and 100 mM), and each calcium concentration (5 and 10 mM). All mixed with 0.0084 mM (2 ppm) of U(VI).

Figure 4-1 Sample preparation procedure, effects of divalent cations (Ca²⁺)

4.4 Analytical procedures

The supernatant was analyzed by kinetic phosphorescence analyzer (KPA-11, Chemchek) for U, inductively coupled plasma emission spectroscopy (ICP-OES, Perkin Elmer, Optima 7300 DV) for Si, Al³⁺, and Ca²⁺, and Shimadzu TOC analyzer with an autosampler (TOC-V CSH) for Total Organic Carbon (TOC).). In addition, the accuracy of the initial stock solution concentration was tested with ICP-OES. For better precision, the concentration of elements was analyzed using different dilutions factors. For analysis with KPA, an aliquot was extracted from the supernatant of each test sample and diluted with 1% HNO₃ between 5 to 100 times. For analysis with the ICP-OES, an extracted aliquot was diluted with DIW in conical polypropylene tubes between 100 to 200 times. The total organic carbon (TOC) of the supernatant solutions was analyzed using a Shimadzu TOC analyzer with an autosampler (TOC-V CSH). Each analysis was repeated until the standard deviation was less than 3%.

4.5 Results and Discussions

Experimental results were evaluated based on the percent removal of the elements of interest: U(VI), Si, Al, and Ca. Figures 4.1 to 4.4 depict the removal percentage of these components in solutions with an increased pH above 11 after NH_3 injection.

As explained in chapter 2 (section 2.3.2), the removal of U(VI) involves a phenomenon of Si precipitation following trapping of U by the co-precipitation process (Allard et al., 1999). It is known that dissolved silica polymerizes in Si-rich alkaline solutions. This process involves nucleation reactions and the formation of amorphous silica particles by polymerization of $\text{Si}(\text{OH})_4$ (Iler 1979). In addition, amorphous Si precipitates can be formed by aggregation of colloidal particles due to the coagulation of alkaline earth metal carbonates (Kellermeier et al., 2010; Voinescu et al., 2007). The addition of divalent ions such as calcium are commonly used for coagulation of colloidal silica from water. These divalent ions flocculate colloidal silica along with other suspended or precipitated matter (Sheikholeslami & Bright, 2002).

The experimental results indicate that the percentage of U(VI) removal was mainly controlled by the Si/Al ratios and Ca concentrations (Figure 4.1). Furthermore, regardless of HCO_3^- concentration tested, the percent of U(VI) removal increased as Si/Al ratios were increased. The removal of U(VI) varied between 87% and 100% starting at Si/Al ratio 10 for the six HCO_3^- concentrations tested. The higher Ca concentration correlated with higher U(VI) removal at low Si/Al ratios ranging from 96% to 99%. Possible mechanisms responsible for the U(VI) removal include the cumulative effect of nucleation reactions forming calcium carbonate clusters upon mixing CaCl_2 and Na_2CO_3 and then uptake of uranyl by co-precipitation with calcium carbonate (Reeder et al., 2000; Reeder et al., 2001).

The following deposition of hydrated amorphous silica layers on the precipitated calcium carbonate grains creates silica layers coating on the aggregates (Kellermeier et al., 2010; Klein and Walter, 1995; Voinescu et al., 2007). Previous studies on U(VI) trapping in natural Si/Al-rich gels were consistent with a co-precipitation process of U(VI), Si and Al^{3+} that discussed encapsulation of U(VI) within a silicate polymer (Katsenovich et al, 2016; Allard et al., 1999).

Figure 4-2. Removal of U(VI) from SPW prepared with Ca^{2+} 5 mM (right) and 10mM (left)

Also, the low solubility calcium carbonate may evolve from the SPW solutions amended with HCO_3^- , Ca^{2+} , and Si at pH values between 10 and 11. According to (Kellermeier et al., 2010). Under alkaline pH, precipitation of the amorphous calcium carbonate in Si-rich solutions induces dissociation of HCO_3^- and the release of protons results in decreasing pH near the growing carbonate phases. Silicates (SiO_4^{4-}) species respond to these local pH changes by polymerization reactions following by particle aggregation and by flocculation (Equations 2.2 and 2.3, section 2.3.2). Therefore, the decreasing pH caused by the precipitation of carbonate increases the local supersaturation of silicic acid in the surroundings of the growing carbonate phases, thus, provoking precipitation of silica (García-Ruiz et al., 2009).

When a soluble silicate is mixed in solutions containing metals other than the alkali metal group, insoluble amorphous metal silicates along with other elements are precipitated out of solution (Iler, 1979). (Iler, 1975) proposed mechanisms of silica coagulation by Ca^{2+} ions leading to precipitation of those elements from solution. The adsorption of Ca^{2+} on the negatively charged silica surface liberates by ion exchange only one hydrogen ion, thus creating one additional negative site on the Si surface (Iler, 1975). This negative site is neutralized by one adsorbed Ca^{2+} that retains a single positive charge (Equation 2.5 and Equation 2.6, Section 2.3.2). Iler (1975) assumed that a possible mechanism of Si coagulation is through interparticle bonding that involves bridging by positively charged calcium ions and attraction between surfaces bearing a mosaic of positive and negative sites. The equilibrium distribution of dissolved aqueous and solid phase species is discussed later in this dissertation.

The removal of silica concentrations from the tested solutions indicated that in bicarbonate-free and 2.9 mM HCO_3^- SPW amended with 5 mM of Ca^{2+} , the percentage of silica removal at Si/Al ratios of 1 and 10 remained between 13% and 40% (Figure 4.2). At higher Si/Al ratios greater than 10, the percentage of Si removal was found between 89% and 99% for all HCO_3^- concentration solutions tested; increasing Ca^{2+} concentration correlated with higher removal of Si from the solution. When the Ca^{2+} concentration was increased up to 10 mM, the percentage at Si/Al ratio 1 increased to 93-99%. The precipitates formed after combining all stock solutions are usually not homogeneous in composition. This depends on the degree of Si polymerization and precipitation reactions that occur in the solution mixture. This causes some discrepancies in the results between replicate samples, especially those prepared for low Si/Al ratios (Figure 4.2). In all the

experiments, the removal of Si correlated with the removal of U(VI) from solutions. If the supernatant solutions showed a small decline in Si concentrations, the removal in U(VI) was insignificant or not observed. The unique chemical affinity between Si and Al^{3+} is responsible for the removal of aluminum from the solution. Monomeric silica, $Si(OH)_4$, reacts with Al^{3+} ions to form aluminum silicate, which tends to precipitate (Iler, 1979): According to (Iler, 1979), SiO_2 surfaces exposed to solutions containing aluminum form aluminosilicate surface complexes by reaction with the following stoichiometry:

Figure 4-3. Removal of Si from SPW prepared with Ca^{2+} 5mM (right) and 10mM (left)

The presence of Al^{3+} can radically affect the amorphous silica surface properties due to formation of aluminosilicate surface complexes that results in an entire armored surface coating, which is extensive enough to reverse the net negative silicate (SiO_4^{4-}) surface charge to positive (Dove & Rimstidt, 1994). (Iler, 1979) also demonstrated that low Al^{3+} concentration can give a significant reduction in solubility of silica gel. Figure 4.3 shows the removal of Al^{3+} , from the tested SPW prepared with 5 and 10 mM of Ca^{2+} , as a function of the range of Si to Al ratios.

Figure 4-4. Removal of Al from SPW prepared with Ca²⁺ 5mM (right) and 10mM (left)

The removal of Ca²⁺ ion from the solution is apparently due to the precipitation of CaCO₃ (e.g. calcite) and silica coagulation reactions initiated upon addition of Ca²⁺ ions. So, the addition of CaCl₂ to the SPW solution containing sodium silicate and bicarbonate ions influences silica coagulation reaction with the formation of Si-based multicomponent precipitates, which could retain co-precipitated uranium (as U silicate or/and carbonate) within its amorphous structure.

Another possible mechanism for Ca²⁺ removal from the solution mixture is the adsorption of Ca ions on the silica amorphous surface (Figure 4.4). The adsorption of a divalent cation on the surface of amorphous silica may increase the development of positive charge sites making a bridge by reacting with two particles at their point of contact. The adsorption of metal ions on the silica surface may also affect the surface properties and, in addition, displace H⁺ into the solution (Dove & Rimstidt, 1994; Iler, 1975)

Figure 4-5. Removal of Ca from SPW solution prepared with Ca^{2+} 5mM (up) and 10mM (down)

(Kellermeier et al., 2012) examined the formation of cluster-like species grown when alkaline-earth carbonates and silica are co-precipitated at elevated pH. Silica was coagulated by the addition of CaCl_2 in experiments conducted by Kellermeier (2008). Analyses of the flocculated material showed that it essentially consisted of amorphous silica, with minor amounts of calcium entrapped between the coagulated particles. They ruled out precipitation of calcium-rich silica particles in the samples and expected that the major fraction of the Ca^{2+} ions to be free and available for interaction with carbonate under

the experimental conditions. This removal can be due to the saturation of CaCO_3 species such as calcite in the SPW solutions (Equation 2.2, Section 2.3.1).

4.6 Conclusions

The experimental results indicate that the percentage of U(VI) removal was controlled by the Si/Al ratios and Ca^{2+} concentration. Furthermore, regardless of HCO_3^- concentration tested, the percent of U(VI) removal increased as Si/Al ratios were increased. The removal of (VI) was always greater than 87% at Si/Al ratios ≥ 10 (50 mM Si and 5 mM Al) for the six HCO_3^- concentrations tested. The higher Ca^{2+} concentration correlated with higher U(VI) removal at low Si/Al ratios. The uranium removal could be due to the saturation of CaCO_3 species in the SPW solutions since possible mechanisms responsible for the U(VI) removal include the cumulative effect of nucleation reactions forming calcium carbonate clusters upon mixing CaCl_2 and then uptake of uranyl by co-precipitation with calcium carbonate (Reeder et al., 2000; Reeder et al., 2001).

5. CHARACTERIZATION OF URANYL MINERAL

5.1 Abstract

Laboratory batch experiments to quantify the role of major pore water constituents on uranium (VI) precipitation/removal in synthesized pore water samples injected with NH_3 gas were completed in (Chapter 1 and Chapter 2). The formation of U(VI) minerals that would be present in the precipitate samples formed from these synthesized pore water solutions is fundamental to determine the uranyl mineral that could have been formed after the SPW solutions were treated by the injection of NH_3 .

The combination of the XRD and SEM-EDS analyzes were used to find a correlation with the results obtained in the batch experiments and the speciation modeling (Chapter 6). SEM/EDS images and elemental composition analyzes for precipitated samples with low and elevated uranium following by XRD analysis were conducted. The results helped in a better understanding of the uranyl mineral formation in the precipitate samples. The formation of amorphous Si correlated with the removal of U(VI), Si, and Al from the solution. With Ca presence, the SEM images displayed dense amorphous regions high in silica content, where EDS elemental analysis delivered higher U atomic percentages in some samples. XRD revealed the presence of uranyl minerals, but none of them were uranyl silicate minerals as expected. The formation of uranium phases could not be identified in U(VI) low content precipitates.

5.2 Introduction

The injection of the reactive NH_3 gas to boost the pH in the VZ contaminated sediments until reached alkaline conditions, it is a promising technology to decrease the uranium mobility in the unsaturated area. It is thought that this injection into the VZ

promotes partial dissolution of subsurface minerals. Once the environmental conditions are re-establishment to neutralize pH, the re-precipitation of mineral phases could reduce the mobility of uranium phases likely by physically containing them. PNNL scientists have evaluated this technology at laboratory scale, based on the laboratory results, the NH_3 injection has been associated with a reduction in uranium mobility (Zhong et al., 2015; Szecsody et al., 2012). Laboratory results suggested that after the treatment, Na-boltwoodite could co-precipitate, as the pH is neutralized. Also, it is suggested that in pore water composition at high carbonate concentration and initial alkaline conditions, existing uranyl minerals could dissolve in the aqueous environment.

Studies have been dedicated to evaluating the formation of uranyl minerals creating by U(VI) chemical species and other components that are present in a composition (Burns, R. Finch, 1999); the XRD and SEM-EDS analyzes could support to determine the formation of the uranyl minerals in the exanimated precipitate samples. The batch experimental results (chapter 3 and 4) suggested that the U(VI) retained in some of precipitate samples could be U silicate or/and U carbonate into an amorphous structure formed most likely from SPW solutions prepared at $\text{Si} \geq 50 \text{ mM}$, 5 mM of Al, 5 and 10 mM of Ca, and low and high bicarbonate concentrations.

5.3 Material and Method

Samples was prepared with low and elevated uranium concentrations for XRD and SEM/EDS analysis. The procedures for sample preparation followed the same routine as previously described in Chapter 3 and 4. However, for one additional set, two uranium concentrations were injected, 200 ppm for solution free of Ca^{2+} and 400 ppm for solution containing Ca^{2+} . The composition of samples was comprised of the salt solutions described

in appendix 1, Table A1-3. These solutions were consistent across the samples with the only difference being the bicarbonate (HCO_3^-) and calcium (Ca_2^+) content added. The concentrated stock solutions were prepared such that the desired concentration would be reached after mixing in the solutions.

5.4 Sample preparation

The XRD and SEM-EDS analysis were performed to the precipitates samples that were formed from SPW solutions in high (50mM) and low (3.0mM) bicarbonate concentrations. The procedure began with concentrated solutions of KHCO_3 , Na_2SiO_3 , and $\text{Al}(\text{NO}_3)_3$ combined in a 50-mL vial to form the base of the various synthetic pore water solutions. The base solution would then be pH adjusted using nitric acid to reach a value of about 8, consistent with the pH of pore water in the Hanford vadose zone. The synthetic pore water solutions were then bubbled with ammonia gas until the system reached a treatment pH range around 11. Immediately following this step, the base solutions were broken up into 10-mL aliquots in 15-mL vials with caps perforated to allow some air exchange. The final components, CaCl_2 and $\text{UO}_2(\text{NO}_3)_2$, were added in small volumes of highly concentrated solutions to reach desired concentrations when diluted. The synthetic pore water pH was monitored as the samples re-established the pre-treatment pH range through the partitioning and liberation of the dissolved NH_3 gas. After three weeks, the samples were transferred to an orbital shaker and agitated gently for a fourth week. The solid precipitate phase and supernatant were separated by vacuum filtration using disposable 0.22 μm nitrocellulose filters. Then, supernatant was decanted and reserved for analysis via KPA while solids were dried in an oven at 30°C for two weeks in preparation for the spectroscopic analysis. The collected precipitate samples were duplicated.

5.5 Analytical procedure

The mineralogical and morphological characteristics of the dried uranium-bearing precipitates were analyzed using Scanning Electron Microscope-Energy Dispersive Spectroscopy (SEM-EDS) and powder X-Ray Diffraction (XRD). The samples' surface composition and the development of crystalline structures were monitored by means of SEM-EDS. The spectroscopy analytical and the speciation modeling (Chapter 6. Section 6.5) results helped to identify the possible U(VI) mineral phases that could be presented present in precipitate samples.

X-ray diffraction analyses were performed at 15 kV (low bicarbonate) and 35 kV (high bicarbonate); 40 mA via Bruker 5000D XRD instrument. Diffraction patterns were obtained using a copper Cu K α radiation source ($\lambda=0.154056$ nm) with a tungsten filter. The XRD was programmed to run over a 2-theta (2θ) range from 5° to 70° with a 0.02° step size and 3 second counting per step. Precipitate samples were carefully ground into a fine powder using a mortar and pestle. Then the pulverized sample was packed into the small recess of a plastic sample holder that was designed specifically for the small amount of sample available. Two method blanks, prepared identically to the experimental sample except for uranium were also ground and analyzed. Identification of the uranyl mineral phases was based on a comparison of the XRD patterns measured for the selected precipitate samples with the mineral powder diffraction files (PDF) published by the Joint Committee on Powder Diffraction Standards (JCPDS) International Center for Diffraction Data (ICDD). The XRD images display the diffractogram of sample on left y-axis and ICDD reference on right-y-side.

Scanning Electron microscopy (SEM) was performed using a JEOL-5910-LV with acceleration potentials between 10 and 20 kV. For conduction purposes, all samples were gold coated using an SPI-Module Control and Sputter unit. EDS analysis was accomplished using an EDAX Sapphire detector with UTW Window paired with Genesis software. Micrographs were prepared in both secondary electron (SE) and complemented with backscatter secondary electron (BSE) mode to discern better the areas with the higher average atomic mass that would be most likely rich in uranium; white areas in micrographs indicate areas containing heavier elements because of their stronger backscatter of electrons. Therefore, the primary interest in the precipitate samples during the SEM observations was to locate the points and areas that were shown bright and white, as an indication of containing high uranium concentration. The content of this uranium was detected by the EDS analysis, collecting weight and atomic percentages of the elements presented at located points and areas, which were considered as rich in uranium and silica content.

5.6 Results and discussions

5.6.1 Effect of Si and Al concentrations on the removal of U(VI)

The XRD and SEM-EDS analysis were performed to the precipitate samples that were formed from SPW solutions with HCO_3^- , in high (50 mM) and low (3.0 mM) concentrations (Table A1-3). The micrographs for the high concentration of HCO_3^- samples showed rich-uranium formations of crystalline structures that seen as within or growing from the precipitate sample. Also, these micrographs displayed amorphous uranium areas that looked incorporated into the sample (Figure A-3-1). Therefore, it could be assumed that both uranium structures could be formed in the precipitate samples containing high

HCO₃ concentration. The micrographs producing crystal-like structures (Figure 5-1 left) showed in the EDS analysis weighty contents of potassium, nitrogen, oxygen, sodium, and silica (Figure 5-1 right). However, their ratios were not related to a known uranium mineral.

The powder X-ray diffraction analysis of the high concentration of HCO₃ samples revealed defining peaks (Figure 5-2) which confirmed the presence of some crystalline material in this precipitate sample. The resultant diffraction patterns were compared to the patterns of the predicted speciation modeling uranium minerals compiled in the ICDD database. The compared diffraction patterns didn't match with a known uranium mineral pattern; it matched for nitratine (NaNO₃) which was contained in synthetic pore water samples (Figure 5-2). It could be that the presence of uranium minerals in the sample was minimum related to the bulk sample that any uranium form could be detected by powder XRD.

Figure 5-1. SEM-EDS of precipitate formed at high bicarbonate concentration
(Source: Katsenovich et. el., 2016)

Figure 5-2. XRD of precipitate formed at high bicarbonate concentration
(Source: Katsenovich et. el., 2016)

Different to micrographs produced for the low bicarbonate (3 mM) bicarbonate precipitate samples which didn't distinguish uranium-rich areas, there was not crystalline, or another form high in uranium content detected for these samples (A-3-2). Therefore, the XRD analysis was not preformed to the precipitate samples formed at low bicarbonate content.

5.6.2 *Effect of divalent cations (Ca^{2+}) on the removal of U(VI)*

The primary SEM imagen produced for the precipitate sample prepared with high bicarbonate concentration (50 mM) showed the uranium-bearing crystal-like structures or uranium dense regions of the amorphous collection; the EDS analysis resulted in uranium weight percentages between 14.8% and 29.7% for the samples containing 10 mM and 15 mM of Ca respectively (Figures 5-3 and 5-5). The compared XRD diffraction patterns results of those samples, having the only difference in composition by calcium

concentrations, revealed potential matches for Grimselite ($\text{K}_3\text{Na}(\text{UO}_2)(\text{CO}_3)_3 \cdot \text{H}_2\text{O}$), along with calcite (Figures 5.4 and 5.6). The SEM image produced for the grounded sample composed at mM concentration of 50 Si, 5 Al, 10 Ca and 50 HCO_3 , did not show the formation of a crystal-like phase (Figure 5-5). However, the XRD pattern of this sample suggested the presence of Grimselite mineral (Figure 5.6), correlating with the mineral pattern displayed for the sample at high bicarbonate (50mM) concentration and 15 mM of Ca shown in Figure 5-4.

Figure 5-3. SEM-EDS of precipitate formed at high HCO_3 and 15 mM of Ca

Figure 5-4. XRD of precipitate formed at high HCO_3 and 15 mM Ca

Figure 5-5. SEM-EDS of precipitate formed at high HCO_3 and 10 mM of Ca

Figure 5-6. XRD of precipitate formed at high HCO_3 and 10 mM of Ca

Whereas the SEM images produced for samples at high bicarbonate displayed some crystal-like formations; the images for low bicarbonate (3.0 mM) revealed significant amorphous uranium-dense areas, where the EDS analysis generated U weight percentages (U-Wt%) between 14.0% and 11.4% for samples with Ca concentrations of 15 mM and 10 mM (Figure 5.7 and Figure 5.9). These U-Wt% coincided with higher Si weight percentages (Si-Wt%), which ranged from the levels of 19% and 21%. The XRD pattern produced a broad, undefined single peak between 2θ between 12 and 22 which suggested the presence in the sample of amorphous materials as well as well-defined peaks representative for crystalline forms. Also, XRD identified the formation of a uranyl carbonate mineral known as Andersonite [$\text{Na}_2\text{CaUO}_2(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$] in the sample prepared at 15mM of Ca (Figure 5.8).

Figure 5-7. SEM-EDS of precipitate formed at low HCO_3 and 15 mM of Ca

Figure 5-8. XRD of precipitate formed at low HCO_3 and 15 mM of Ca

Figure 5-9. SEM-EDS of precipitate sample at low HCO_3 and 10 mM of Ca

5.7 Conclusions

The SEM analysis produced crystal-like structures identified as bright spots using backscatter electron capture mode, also the images produced displayed high amorphous areas for samples composed at high bicarbonate concentrations. Energy dispersive spectroscopy (EDS) analysis was used to confirm the presence and estimate the abundance of the components in the analyzed points; the EDS analysis could not extract consistent quantitative data probably due to the precipitate sample was not polished thin slice; however, the results of these analyses provided valued information. The samples prepared with high bicarbonate concentrations showed the uranium-bearing crystal-like structures or uranium dense regions of amorphous collection. EDS analysis of the amorphous areas resulted in high silica content and high uranium weight percentages (U-Wt%). The X-ray diffraction (XRD) analysis of those samples identified the formation of Grimselite, a uranyl carbonate mineral. However, it didn't show a pure mineral intensity. Low bicarbonate samples showed only amorphous uranium-dense areas with U-Wt% that coincided with higher Si weight percentage (Si-Wt%). The XRD pattern produced a broad, undefined

single peak between 2θ between 12 and 22 suggesting the presence in the sample of amorphous materials as well as well-defined peaks representative for crystalline forms. The formation of uranyl silicates could not be detected by SEM-EDS or identified by the XRD analysis perhaps due to amorphous nature of these solid phases. Micrographs produced by SEM analysis conducted to precipitate samples high in silica (100 mM), bicarbonate-free, and at low U(VI) concentration (2ppm) did not show areas of concentrated uranium, crystalline or otherwise in the precipitate formed from the SPW with this composition (A-3-2). Due to the low uranium concentration (2ppm), the U(VI) could not be detectable for the instrument. Therefore, the preparation of precipitate samples high in U(VI) were needed to complete the characterization. The micrographs produced for the precipitate samples at the lower bicarbonate and Ca concentration (10 mM) didn't distinguish uranium-rich regions. Therefore, these samples were not analyzed by the XRD.

6. URANIUM THERMODYNAMIC SPECIATION MODELING

6.1 Introduction

The chemistry of uranium is a complicated subject, U(VI) can form relevant aqueous complexes and uranyl phases that can contribute to the increasing of U solubility in the natural oxidic aquatic environments and contaminated systems (e.g., ligand complexes, uranyl structure). Nowadays, the thermodynamic of uranium species is a subject of study because there is a concern to control the long-term mobility of uranium in surface waters. In the last decade, there have been multiple studies evaluating the uranium species that could be present in the aquatic environments, but there have been a few studies considering these species in alkaline conditions. There has not been an official thermodynamic database created for uranium species in alkaline conditions, additionally, some relevant species were found to be present in this condition (e.g., Ca-U(VI)-CO₃) (Bernhard et al., 2001) and are not yet included database because there is not enough evidence of their existence or because there were inconsistencies found while the data was collected for the experiments (Gorman-Lewis, Burns, & Fein, 2008). Therefore, the prediction of uranyl species in solutions after the injection of NH₃ in the VZ of Hanford Site is a challenging task in this study. There is a need to customize a database that includes crucial uranyl species expected to be present after the NH₃ gas treatment. In this study, crucial uranyl species for this study were evaluated and included in a customized database. Only uranium species and formation constants related to the major constituents of VZ of Hanford Site and species contained in the salts used in the experiment which are listed in this work (e.g., hydroxide, silicate, aluminum, carbonate, calcium, and sodium). First, the databases are reviewed including the most recent published experimental studies. Then,

uranium species are carefully selected depending on the precipitate species that could be present in alkaline conditions, from these findings a customized database is created.

6.2 Uranium thermodynamic databases

Uranium thermodynamic databases are available by various agencies. The most recognized is the Nuclear Energy Agency (NEA), within the Organization for Economic Co-operation and Development (Grenthe et al., 1992), which is charged with providing reliable nuclear data to the participating countries. In addition, there are other agencies and institutes that provide consistent uranium data. These agencies collect the uranium thermodynamic data and associated values for equilibrium constants that have been published; experts in the area evaluate the compiled data for consistency and quality. These agencies work together to provide a consistent uranium database. However, they have discrepancies in some uranium species, it might be because of lack of information, or the methods used for the measurements, are not into the agency's standard. The Paul Scherrer Institute - Nagra Chemical Thermodynamic Database (PSI PSI/Nagra) (Thoenen al. et., 2014). The thermodynamic Reference Database (THEDERA) (Richter al. et., 2015) is a project conducted by a group of European institutions that have as a goal to collect and evaluate data to assure a consistently and quality database for relevant elements including uranium. These databases experts that evaluate all the uranium publications and consider if the specific specie should be included into the database.

6.3 Uranium aqueous species

The Geochemist Workbench' thermo-minteq database includes most of these species. However, some of the formation constants are updated, and a few species are needed to include in the customized database. Only uranium aqueous complexes and their

formation constants for these constituents (hydroxide, carbonate, calcium, silicate, sodium, and aluminum). Although uranium species with nitrate and chloride are present in the tested solutions, these species have shown only small tendency to complex with uranium (Reference) and therefore were not reviewed, however the nitrate served as a balance specie in the thermodynamic speciation modeling.

6.3.1 *Hydrolysis Species*

The uranyl hydroxide aqueous complexes have been reported to occur as soon as the uraninite (precipitation of U^{4+}) is oxidized in U deposits (Gorman-Lewis et al., 2008 a,b). Diluted UO_2^{2+} changes to uranyl oxy-hydroxide complexes which predominate in natural fresh surface waters. In neutral and weakly alkaline solutions, the formation of polymeric uranyl hydroxide species, such as $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_3(OH)_5^+$, $(UO_2)_4(OH)_7^+$, and $(UO_2)_3(OH)_7^-$, occur depending on the U concentrations. The monomeric and anionic species as $UO_2(OH)_2(aq)$, $UO_2(OH)_3^-$, and $UO_2(OH)_4^{2-}$ predominate at greater U concentrations. The UO_2OH^+ and $(UO_2)_3(OH)_5^+$ species can also occur, but generally in small amounts except in an environment of low or free carbonate solutions. The GWB thermo-minteq database contained most of the monomeric and polymeric uranyl hydrolysis species; only the $UO_2(OH)_2$ specie is included and formation constant of two (2) polymeric uranyl hydrolysis species are updated in the customized database. The formation constants reported for the hydrolysis species have been determined by careful approaches and the measures have been compared by spectroscopic analyzes.

6.3.2 *Carbonate Complexes*

The uranyl carbonate complexes, including calcium uranyl carbonates, are the most significant uranyl aqueous complexes in this study. The mobility in the aqueous

environment can change significantly when these complexes are formed because their stability constants ($\log K$) are the greatest compared to other U(VI) aqueous complexes. It may be in part to its tendency to form anionic carbonate complexes like uranyl tricarbonate [e.g., $\text{UO}_2(\text{CO}_3)_3^{4-}$, $\text{CaUO}_2(\text{CO}_3)_3^{2-}$] which are extremely soluble and stable in the aqueous system. The polynuclear mixed U(VI) hydroxide-carbonate complex, $(\text{UO}_2)_{11}(\text{CO}_3)_6(\text{OH})_{12}^{2-}$ is found as a minor aqueous specie and considered to represent in a 15% of the total uranium in slightly concentrated solutions (Gorman Lewis, 2008, Grenthe et al.1992). In the presence of calcium, as most of the typical natural water systems in the western of the United States, including Hanford Site contaminated water systems; the formation of ternary aqueous complexes with Ca^{2+} ions, U(VI) and carbonates are facilitated (Bernhard et al., 1996, Kalmykow & Choppin, 2000, Guillaumont et al., 2003; Dong & Brooks, 2006). The thermo-minteq data base contain in most of these species, but for the customized database the thermodynamic stability constants of few species, Ca-U(VI)- CO_3 and UO_2 - CO_3 are updated following recent publications and thermodynamic database.

6.3.3 *Silicate and aluminum complexes*

The GWM thermos-minteq data uses the polymer H_4SiO_4 specie as the silica basic component and two-monomeric silica reactions ($\text{H}_2\text{SiO}_4^{2-}$, H_3SiO_4^-). Since the presence of the polymers of silica species are in the database, the Al-Si, and $\text{UO}_2\text{H}_3\text{SiO}_4^+$ complexes are also evaluated. Although monometer, dimer, and trimer silica species are reactions that are present when the solutions contain high silica concentrations, dimer and trimer silica reactions are not important at the temperature setting conditions in this work (Xiong, Y., 2013). Since the $\text{Al}(\text{OH})_4^-$ is existing in solutions, the formation of $\text{AlH}_3\text{SiO}_4^{2+}$ is evaluated,

but aluminum polymeric species may not be important at the presence of high concentration of silica since the formation of the $\text{AlH}_3\text{SiO}_4^{2+}$ complex requires aluminum concentrations greater or equal than 1.5 m compared to the silica concentration in neutral and basic solutions (Moolenaar et. el., 1970; Baes & Mesmer, 1976). The $\text{UO}_2\text{H}_3\text{SiO}_4^+$ complex specie can be only present. The table 3.1 displays the aqueous uranium complexation reactions and the thermodynamic stability constants) and table 3.2 displays the thermodynamic stability constants for auxiliary reactions.

Table 3.1: Aqueous phase uranium complexation reactions and thermodynamic stability constants (T=25°C, I=0).

Reaction	Log K
Hydrolysis	
$(\text{UO}_2)_{11}(\text{CO}_3)_6(\text{OH})_{12}^{2-} + 12\text{H}^+ = 11\text{UO}_2^{2+} + 6\text{CO}_3^{2-} + 12\text{H}_2\text{O}$	-36.43
$(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^- + 3\text{H}^+ = 2\text{UO}_2^{2+} + \text{CO}_3^{2-} + 3\text{H}_2\text{O}$	0.861
$(\text{UO}_2)_2(\text{OH})_2 + 2\text{H}^+ = 2\text{UO}_2^{2+} + 2\text{H}_2\text{O}$	5.620
$(\text{UO}_2)_2\text{OH}^{3+} + \text{H}^+ = 2\text{UO}_2^{2+} + \text{H}_2\text{O}$	2.700
$(\text{UO}_2)_3(\text{CO}_3)_6^{6-} = 3\text{UO}_2^{2+} + 6\text{CO}_3^{2-}$	-54.00
$3\text{UO}_2^{2+}(\text{OH})_4^+ + 4\text{H}^+ = 3\text{UO}_2^{2+} + 4\text{H}_2\text{O}$	11.90
$(\text{UO}_2)_2\text{OH}^{3+} + \text{H}^+ = 2\text{UO}_2^{2+} + \text{H}_2\text{O}$	15.55
$(\text{UO}_2)_4(\text{OH})_7^+ + 7\text{H}^+ = 4\text{UO}_2^{2+} + 7\text{H}_2\text{O}$	21.90
Carbonate	
$(\text{UO}_2)_3(\text{CO}_3)_6^{6-} = 3\text{UO}_2^{2+} + 6\text{CO}_3^{2-}$	32.20
$(\text{UO}_2)_3\text{CO}_3(\text{OH})_3^+ + 3\text{H}^+ = 3\text{UO}_2^{2+} + \text{CO}_3^{2-} + 3\text{H}_2\text{O}$	-0.649
$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq}) = \text{UO}_2^{2+} + 3\text{CO}_3^{2-} + 2\text{Ca}^{2+}$	-30.60
$\text{Ca UO}_2(\text{CO}_3)_3^{2-} = \text{UO}_2^{2+} + 3\text{CO}_3^{2-} + \text{Ca}^{2+}$	-27.18
$\text{Mg UO}_2(\text{CO}_3)_3^{2-} = \text{UO}_2^{2+} + 3\text{CO}_3^{2-} + \text{Mg}^{2+}$	-26.11
$\text{U}(\text{CO}_3)_4^{4-} = \text{UO}^{4+} + 4\text{CO}_3^{2-} + \text{H}_2\text{O}$	-1.120
$\text{U}(\text{CO}_3)_5^{6-} = \text{UO}^{4+} + 5\text{CO}_3^{2-}$	-34.00
$\text{UO}_2(\text{CO}_3)^{2-} = \text{UO}_2^{2+} + 2\text{CO}_3^{2-}$	-16.61
$\text{UO}_2(\text{CO}_3)^{4-} = \text{UO}_2^{2+} + 3\text{CO}_3^{2-}$	-21.84
$\text{UO}_2(\text{OH})_2(\text{aq}) + 2\text{H}^+ = \text{UO}_2^{2+} + 3\text{H}_2\text{O}$	12.15
$\text{UO}_2(\text{OH})_2^- + 3\text{H}^+ = \text{UO}_2^{2+} + 2\text{H}_2\text{O}$	20.25
$\text{UO}_2(\text{OH})_4^{2-} + 4\text{H}^+ = \text{UO}_2^{2+} + 4\text{H}_2\text{O}$	31.92
$\text{UO}_2\text{Cl}^+ = \text{Cl}^- + \text{UO}_2^{2+}$	-0.170
$\text{UO}_2\text{Cl}_2(\text{aq})^+ = 2\text{Cl}^- + \text{UO}_2^{2+}$	1.100
$\text{UO}_2^{2+} + \text{CO}_3^{2-}$	-9.940
Silicates, aluminums, and nitrate	
$\text{UO}_2^{2+} + \text{H}_4\text{SiO}_4$	1.840
$\text{UO}_2\text{NO}_3^+ = \text{NO}_3^- + \text{UO}_2^{2+}$	-0.300
$\text{UO}_2\text{OH}^+ + \text{H}^+ = \text{UO}_2^{2+} + \text{H}_2\text{O}$	5.250

Table 3.2: Thermodynamic stability constants for general reactions (T=25°C, I=0)

Reaction	Log K
$\text{H}_2\text{O} = \text{OH}^- + \text{H}^+$	-14.00
$\text{CO}_2(\text{g}) + \text{H}_2\text{O} = \text{H}_2\text{CO}_3^{**}$	01.48
$\text{CO}_3^{2-} + 2\text{H}^+ = \text{H}_2\text{CO}_3^*$	16.68
$\text{CO}_3^{2-} + \text{H}^+ = \text{HCO}_3^-$	10.33
$\text{H}_4\text{SiO}_{4(\text{aq})} = \text{H}_3\text{SiO}_4^- + \text{H}^+$	-9.930
$\text{H}_4\text{SiO}_{4(\text{aq})} = \text{H}_2\text{SiO}_4^{2-} + 2\text{H}^+$	-21.62
$\text{Ca}^{2+} + \text{H}_2\text{O} = \text{CaOH}^+$	-12.60
$\text{Ca}^{2+} + \text{CO}_3^{2-} + \text{H}^+ = \text{CaHCO}_3^+$	11.33
$\text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_3(\text{aq})$	-3.150

6.4 Uranyl Minerals

The U^{6+} cation as $(\text{U}^{6+}\text{O}_2)^{2+}$ is the main constituent of most of the U(VI) minerals. Due to its valent as 2^+ , it must be coordinated by four, five, or six ligands (O^{2-} , OH^- , and H_2O) in a crystal structure that are arranged at the equatorial corners forming bipyramid structures to interlayer the existing ligands. There are reported six uranyl mineral groups that are chemically grouped owning a distinct structure and chemical composition that depend on the chemical conditions during their formation. Therefore, these minerals are good indicators of the geochemical environment conditions. However, the lack of purity in uranyl natural mineral, since the variation in their compositions can influence in large differences in the measurements of thermodynamic parameters including solubility. Additionally, synthetic phases analyzed in the laboratory don't know correspond to know minerals, it is maybe to insufficient knowledge about the compositions of many uranyl minerals (Finch & Murakani, 1999). This study shows only the uranyl minerals that contain the constituents used in the preparation of the studied synthetic porewater (SPW)

6.4.1 *Uranyl oxide hydrates*

These group of uranyl minerals are classified based on their structure that contains a divalent cation (Ca^{2+} , Pb^{2+} , Ba^{2+} , Sr^{2+} , and K^{+}). The uranyl oxide hydrates evaluated in this study are schoepite, meta-schoepite, becquerelite, compreignacite, and clarkeite. These minerals shared the same anionic sheet containing only triangles and pentagons that are arranged in a specific way connecting the bonds. The schoepite structural formula is $(\text{UO}_2)_8\text{O}_2(\text{OH})_{12}(\text{H}_2\text{O})_{12}$, its sheets are connected by bonding hydrogen to interchange H_2O molecules. The meta-schoepite structure $[(\text{UO}_2)_4\text{O}(\text{OH})_6(\text{H}_2\text{O}) - (\text{H}_2\text{O})_5]$ is like the schoepite, but it varies only in the quantity of H_2O molecules that are loosen in the schoepite crystallization process. The uranyl oxide hydrates are considered the first alteration product to appear when uraninite is oxidized in U deposits (Finch et al., 1992) due to the early formation of schoepite in the alteration of uraninite, this mineral is commonly replaced by uranyl silicates and carbonates (Finch et al., 1992 a, b; Finch et al., 1994). Becquerelite $[\text{Ca}(\text{UO}_2)_6\text{O}_4(\text{OH})_6(\text{H}_2\text{O})_8]$, compreignacite $[\text{K}_2(\text{UO}_2)_4\text{O}_4(\text{OH})_6(\text{H}_2\text{O})_7]$, and clarkeite $\text{Na}[(\text{UO}_2)\text{O}(\text{OH})](\text{H}_2\text{O})_{0.1}$ have structures very similar the only difference is the interlayer divalent cation and the H_2O molecules containing in their structure (Gorma-Lewis et al., 2008).

6.4.2 *Uranyl carbonates*

The uranyl carbonate minerals belonging to the second group are identified as andersonite $[\text{Na}_2\text{CaUO}_2(\text{CO}_3)_36\text{H}_2\text{O}]$, cejkaite $[\text{Na}_4\text{UO}_2(\text{CO}_3)_3]$, grimselite $[\text{NaK}_3\text{UO}_2(\text{CO}_3)_3\text{H}_2\text{O}]$, liebigite $[\text{Ca}_2\text{UO}_2(\text{CO}_3)_310\text{H}_2\text{O}]$, and rutherfordine $[\text{UO}_2\text{CO}_3]$. These minerals can occur as mono, di, and tri- carbonate species; monocarbonate species are insoluble, but di-and-tricarbonate species can precipitate from an acid system to an

alkaline system if the aquatic system exposed to fresh water. Most of these minerals, except of rutherfordine, contain the uranyl tricarbonate complex $[(\text{UO}_2)(\text{CO}_3)_3]^{4-}$ in their structural formula, so the solubility product constants (logKs) are the largest compared to other uranyl minerals considered in this research. Due to these solubility complex in their chemical formula, these minerals may precipitate when there are significant evaporation conditions, and the fugacity of carbonate dioxide (CO_2) is greater than the atmospheric pressure in the environment (Gorman-Lewis et al., 2008). Also, uranyl minerals containing the tricarbonate complex in their structure have larger solubility compared to other uranyl minerals (e.g., uranyl silicates). Therefore, these species have been reported to behave like transitory phases in the alteration process when uraninite $[\text{U(IV)}]$ oxidizes changing the uranium solubility (Gorman-Lewis et al., 2008). The liebigite and rutherfordine minerals has been found in Hanford site as medium and high concentrations.

6.4.3 *Uranyl silicates*

Over the last two decades, uranyl silicates have been the focus for several studies (Burns & Finch, 1999). These uranyl minerals group represents the most abundant uranyl minerals because of the predominance of Si in several of the aquatic environments. Studies have evaluated how these minerals could incorporate non-uranium radionuclides into their structure (Burns, 1999b, 2004; Douglas et. al., 2005; Kingensmith and Burns, 2007). The minerals group identified in this work are soddyite $[\text{UO}_2)_2\text{H}_4\text{SiO}_4 \cdot 2\text{H}_2\text{O}]$, (Na-K)-boltwoodite $[(\text{Na-K}) \text{HSiO}_4 \text{UO}_2 \cdot 1.5\text{H}_2\text{O}]$, uranophane $[\text{Ca}(\text{UO}_2)_2(\text{HSiO}_4)_2 \cdot 5\text{H}_2\text{O}]$, and Na-weeksite $[\text{Na}_2(\text{UO}_2)_2(\text{Si}_2\text{O}_5)_3(\text{H}_2\text{O})_4]$. The elemental composition of these minerals is Ca^{2+} , Si, Na^+ , K^+ , which are described as the major constituents in the pore water in Hanford site and the presence of U(VI). Near to neutral to alkaline conditions in aqueous environments

containing dissolved Si and Ca^{2+} , uranophane is the most common uranyl mineral precipitated. Uranyl silicate minerals may release some Ca^{2+} and Si when exposed to carbonate-free aqueous environments, and these releasing would facilitate the formation of uranophane and soddyite minerals. In alkaline rich-carbonate aqueous environments as the study in this work, uranyl minerals may lose U(VI) that could alter the microcrystalline and amorphous silica.

The surface charges (zeta potential) of uranyl silicate minerals have been showed similar behavior to the clay (montmorillonite) minerals while measured as decreasing with increasing pH (Yuklen & Erzin, 2008, Saka & Guler, 2006). Also, measurements conducted by the BET method to determine the surface areas in these minerals have shown large surface area like the natural clay minerals ($\sim 31\text{m}^2\text{ g}^{-1}$ for Na-boltwoodite) (Gurses et al., 2006, Wall, N. et al., 2010). Na-weeksite is also reviewed as a part of the database, but it is not included due to its formation in mostly at high temperature (Nguyen et al., Reference). Studies have shown that near the neutral pH condition, like the pH conditions in the VZ of Hanford site 200 Area, the solubility of these minerals have a smaller value than the solubility values of carbonate and oxide hydrates (Wronkiewicz et. al., 1992). The Na-boltwoodite and uranophane minerals have been reported as found in contaminated sediment in VZ of Hanford site (Catalano et al., 2004; Um et al., 2009).

Table 3.3: Uranyl mineral and dissolution reactions (T=25°C, I=0)

Mineral Phase	Structural Formula	Log K _{sp}
<i>Uranyl Carbonates</i>		
Andersonite	Na ₂ CaUO ₂ (CO ₃) ₃ 6H ₂ O	-37.50
Cejkaite	Na ₄ UO ₂ (CO ₃) ₃	-27.18
Grimselite	NaK ₃ UO ₂ (CO ₃) ₃ H ₂ O	-37.10
Liebigite	Ca ₂ UO ₂ (CO ₃) ₃ 10H ₂ O	-36.90
Rutherfordine	UO ₂ CO ₃	-14.46
<i>Uranyl hydroxides</i>		
Becquerelite	Ca (UO ₂) ₆ O ₄ (OH) ₆ (H ₂ O) ₈	40.50
Clarkeite	Na(UO ₂)O(OH)	9.400
Schoepite	(UO ₂) ₈ O ₂ (OH) ₁₂ (H ₂ O) ₁₂	6.430
Metaschoepite	(UO ₂) ₈ O ₂ (OH) ₁₂ (H ₂ O) ₁₀	5.350
<i>Uranyl Silicates</i>		
Soddyite	(UO ₂) ₂ H ₄ SiO ₄ 2H ₂ O	6.090
K-Boltwoodite	KH ₄ SiO ₄ UO ₂ 1.5H ₂ O	4.120
Na-Boltwoodite	NaHSiO ₄ UO ₂ 1.5H ₂ O	6.070
Uranophane	Ca(UO ₂) ₂ (HSiO ₄) ₂ 5H ₂ O	10.82

6.4.4 Paragenesis of U(VI) minerals

Many studies have reported that the schoepite mineral may be the first uranyl mineral to be formed in the alteration process after the uraninite oxidation (Finch R.J. et, el., 1992, Gorma-Lewis el. et., 2008). Due to the instability and tendency to lose interlayers water, metaschoepite could form with only difference of two water molecules. However, the formation of metaschoepite reported as the dehydration of schoepite without possibility to return at any temperature (Gorma-Lewis et al., 2008). Finding by Schimmak (2006), another phase that could be formed after the schoepite is becquerelite. This mineral was found due to the Ca presence in aqueous environments (Schimmak et. el., 2006). Under oxidation conditions and dissolved silica presence, the uranyl silicates minerals are the last minerals reported to be formed in the paragenesis alteration of spent nuclear fuel. Near the neutral pH conditions, uranyl silicates are less soluble than uranyl carbonates or uranyl oxide hydrates. The sediments composition and water chemistry play a role for the formation. Some studies of UO₂ in Si-rich water and under oxidation conditions have

showed the formation of the uranyl-silicates (Wronkiewicz et al. 1992, Wronkiewicz et al. 1996). In addition, boltwoodite and uranophane were found as uranium-bearing precipitates in the vadose zone of the Hanford Site (Catalano et al. 2004, Um et al. 2009). Therefore, the presence of these minerals in a natural and contaminated environment is important because they can serve as control of U concentrations on the aqueous phases.

Uranyl minerals are significant in the defining the U mobility in an oxidization environment where dissolved silica is present (Gorman-Lewis et al., 2008). The Hanford subsurface is also rich with carbonates and calcite. Thus, thermodynamic parameters of relevant uranyl silicates, uranyl carbonates and uranyl oxides hydrates phases were reviewed to be included or modified in the database.

6.5 Thermodynamic speciation modeling

6.5.1 Speciation modeling procedure

The speciation modeling included five cations and four anions, concentrations of uranium aluminum, and silica were kept constant in all simulations as 2ppm, 5mM, and 50mM, respectively, varied bicarbonate concentration as 0, 2.9 and 50mM, and 5 and 10 mM of Ca if the effect of Ca ions were evaluated. Dissolved oxygen (DO) was set as 8.4 mg/L at a constant temperature of 25 °C. In the GWB Reactants pane, the experimental conditions to conduct two simulations to model the injection 0.1% and 5% NH₃ were created by sliding the pH from 8 to 11.02 and 8 to 11.87 because of the pH reached for the NH₃ injection of 0.1% [0.063 mol/L of NH₃(aq)] and 5% [3.1 mol/L of NH₃ (aq)] respectively (Zhong et al., 2015). The NH₃(aq) concentrations were assumed at equilibrium in the pore water solutions. The speciation modeling was conducted as a system closed to the exchange of CO₂ with the atmosphere because of more applicable to the NH₃ injection

condition in the field. These speciation models assumed that ammonia would not reduce U(VI) to U(IV). The process of uranium reduction by ammonia is strongly impeded by the presence of air, which is 21% oxygen, in the headspace of capped vials, the addition of nitrate ions by uranyl nitrate as standard and HNO₃ to pH adjustment solutions, and by the stabilizing effect of bicarbonate in the bicarbonate-amended solutions due to the formation of uranyl-carbonate complexes (Campbell et al., 2015). Based on this assumption, additional U(IV) aqueous species were not considered in this study. The uranium aqueous species and Saturation indexes (SI) of mineral phases were calculated and graphed as function of the pH, if SI of uranyl minerals were calculated as greater than 0.5, the mineral was considered supersaturated and could be precipitated from the solution.

6.5.2 *The effect of Si and Al on the Removal of U(VI)*

Per the speciation modeling, in bicarbonate-free synthetic solutions, $\text{UO}_2(\text{OH})_3^-$ and $\text{UO}_2(\text{OH})_4^{2-}$ were the predominant aqueous uranium species. In the presence of bicarbonate uranium carbonates $\text{UO}_2(\text{CO}_3)_3^{4-}$ and $\text{UO}_2(\text{CO}_3)_2^{2-}$ dominated at both, 0.1% NH₃ (0.063 mol/L (NH₃(aq))) and 5% NH₃ (3.1mol/L (NH₃(aq))). The concentration of uranyl carbonates species was noted to start decreasing above pH 9.5 at low bicarbonate. However, the $\text{UO}_2(\text{CO}_3)_3^{4-}$ specie prevailed over the pH range at high bicarbonate, it slightly increased and state stable when increased the bicarbonate concentration. The decreasing of $\text{UO}_2(\text{CO}_3)_3^{4-}$ and $\text{UO}_2(\text{CO}_3)_2^{2-}$ species were more pronounced at 2.9 mM HCO₃ when using 5% of NH₃. The formation of the aqueous uranyl silicate specie, $\text{UO}_2\text{H}_3\text{SiO}_4$, was favored at Ca-free, but its concentration was still insignificant (Figure 6-1-A1 and Figure A-4-1).

The speciation modeling also predicted the formation of uranyl minerals such as Na-boltwoodite [(Na)(UO₂)(HSiO₄)·1.5H₂O], clarkeite [Na(UO₂)O(OH)], metaschoepite

[(UO₂)₈O₂(OH)₁₂(H₂O)₁₀], soddyite [(UO₂)₂H₄SiO₄ · 2H₂O], gummite (a mixed of uranyl silicates such as soddyite), rutherfordine [UO₂(CO₃)], and cejkaite. The predicted uranyl minerals' SI were computed lower than 0.5 (SI>0.5). Uranyl hydroxide minerals, clarkeite and mataschoepite were favored under neutral bicarbonate and lower bicarbonate; decreasing slightly when increasing bicarbonate concentrations at both, 0.1 and 5% of NH₃. Finch and Ewing, 1992 and O'Hare et al, 1988 suggested that under lower silica saturation conditions the initial precipitation of mixed schoepite (metashoepite) is favored. The precipitation of these uranyl hydroxides is a result of the dehydration and restructure of the schoepite with the formation of dehydrate schoepite. The modeling predicted the Na-boltwoodite saturation indexes, SI=1 (oversaturated), it was stable at bicarbonate-free. In the presence of bicarbonate and pH 8, the Na-boltwoodite SI predicted was lower, but in low and high bicarbonate, its SI was increasing as the pH was increasing. The formation of Na-boltwoodite was favored at low bicarbonate and pH>9.5, as monomeric hydrous silicates increased (H₂SiO₄⁻, H₂SiO₄²⁻). Na-boltwoodite was more diluted at high bicarbonate concentrations.

6.5.3 *Effect of divalent cation (Ca²⁺) on the removal of (U(VI))*

GWB thermodynamic speciation modeling (SM) simulations for experimental SPW were conducted in this study. The SM predicted the formation of the uranyl aqueous species and solid phases for the SPW containing mM concentrations of Si (50 mM), Al (5 mM), two of Ca (5 mM and 10mM); and varied with three bicarbonate concentrations, free (0 mM), low (2.9 mM) and high (50 mM). The SM results predicted similar results in simulation containing SPW at Ca concentrations of 5 mM and 10mM. Therefore, the

predicted species for SPW containing 10 mM of Ca are discussed in this chapter, and the results for SPW containing 5 mM of Ca are presented in Appendix 4.

In SPW bicarbonate-free, the aqueous uranyl species, $\text{UO}_2(\text{OH})_3^-$ and $\text{UO}_2(\text{OH})_4^{2-}$, predominated at the higher pH (Figure 6-1-A1), but their concentrations are shown lower than these species at neutral calcium and bicarbonate. Simulated SPWs, treated with NH_3 and composed with low and high bicarbonate, predicted the presence of U(VI) mostly as $\text{UO}_2(\text{CO}_3)_3^{4-}$. The speciation showed that adding calcium to the SPW favored the formation of calcium uranyl complexes [e.g. $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ and $\text{CaUO}_2(\text{CO}_3)_3^{2-}$] in samples at low bicarbonate concentration and for both, 0.1% and 5%, of NH_3 injection. The $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$, $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ drastically decreased at low bicarbonate and above pH of 8.5, at high bicarbonate, the $\text{UO}_2(\text{CO}_3)_3^{4-}$ remained almost unchanged whereas increasing the pH. The formation of the aqueous uranyl silicate specie, $\text{UO}_2\text{H}_3\text{SiO}_4$, was insignificant at both bicarbonate concentrations.

The SM predicted the formation of uranophane [$\text{Ca}(\text{UO}_2)_2(\text{HSiO}_4)_2 \cdot 5\text{H}_2\text{O}$] and Na-boltwoodite [$\text{Na H}_4\text{SiO}_4 \text{UO}_2 \cdot 1.5\text{H}_2\text{O}$] in free-bicarbonate SPW (Figure 6-1-A2 and Figure 6-2-A2). The calculated SI of uranophane was computed greater than 0.5, indicating that it is supersaturated, so it maybe would be precipitated from those SPW. SI of Na-boltwoodite was computed at equilibrium (SI=0.31) remaining constant over the pH range (Figure 6-2-B2); this might have been due to the increment of hydrous silicates (H_3SiO_4^- , $\text{H}_2\text{SiO}_4^{2-}$) as pH was greater (no shown) and the absence of uranyl carbonate species. The solubility of Na-boltwoodite is higher than uranyl oxide hydrated (metaschopite and clakeite), this maybe be due to the formation of $\text{UO}_2\text{H}_3\text{SiO}_4$ was insignificant over the pH range (Gorman-Lewis, 2008). At low-bicarbonate concentration, the solid uranyl silicate species

started to form after $\sim \text{pH} > 8.8$, (Na-K) boltwoodite with the higher SI (K-boltwoodite as 0.94 and uranophane as 1), followed by the uranyl carbonate (andersonite, liebigite, grimselite, and rutherfordine) and uranyl oxide hydroxide (clarkeite and metaschopite) minerals, which remained undersaturated above pH 9.0 (Figure 6-1-B2). The activity of hydrous silicates increased with higher pH (shown in supporting information Appendix 4, figure A-4-3), and a decreasing of $\text{UO}_3\text{CO}_3^{4-}$ concentrations was also observed so there is not carbonate (CO_3^{2-}) activity that lead the formation of uranyl silicate phases. SM also predicted the formation of uranyl oxide hydrated (clarkeite and metaschopite), favored under bicarbonate-free and low-bicarbonate concentrations (Figures 6-1-A2 and 6-1-B2). At high bicarbonate concentration, the grimselite and andersonite were found as the main uranyl minerals at the initial reaction (pH=8.0), probably leading to the presence of the high concentration of $\text{UO}_2(\text{CO}_3)_3^{4-}$ (Figures 6-1-C1 and 6-1-C2). However, immediately the pH was increasing, andersonite decreased; maybe due to the precipitation of U-free calcium minerals (aragonite, calcite, $\text{CaCO}_3 \cdot x\text{H}_2\text{O}$). Grimselite prevailed as the only uranium-bearing solid phase supersaturated over the wide pH from 8 to 11.02, its SI was computed as 1. As SI of andersonite decreased, the liebigite's SI started dropping above pH of 8.8 and favoring the formation of boltwoodites. It agreed with the decreased of solubility of the calcium uranyl carbonate complexes (Figure 6-2-B1), and constant increment of hydrous silicates species (H_3SiO_4^- , $\text{H}_2\text{SiO}_4^{2-}$) as the pH increased (Figure A-4-4). The SI of uranophane increased at pH 9.0 starting to be higher than the SI of rutherfordine after pH reached 10.4 (no shown). Also, at pH > 10, small increments of the $\text{UO}_2\text{H}_3\text{SiO}_4^+$ concentration were observed agreeing with higher SI of uranyl silicates but smaller of uranyl carbonates. Therefore, it is assumed that only a minimum concentration

of UO_2^{2+} is needed for the formation of these minerals. As observed, while synthesizing sodium boltwoodite and uranophane in the laboratory, only between 5% and 11%, of the amount of uranyl moles, could be incorporated in the structure of uranyl silicates (Wall, Nathalie et al., 2010). Similar results were obtained in the speciation modeling conducted for 5 mM of Ca, the results indicated a slightly decreased in the Ca-U(VI)- CO_3 complexes as well as of the uranyl silicate minerals formed after reaching pH of 9. The finding of grimselite mineral from the precipitate formed by the SPW solution at “high” bicarbonate agreed with the XRD analyses (Figure 6.3).

Figure 6-1. Predicted U(VI) aqueous speciation and SI of some U(VI) minerals (Ca^{2+} - free) SPW composition: Ca-free, 50 mM of Si, 5 mM of Al and varied HCO_3^- , reacting with 0.1% NH_3 . Diagrams show species (left) and SI (right). First row for SPW free- HCO_3^- (A1, A2), the 2nd row for 2.9 mM (B1, B2), and 3rd 50 mM (C1, C2) of HCO_3^-

Figure 6-2. Predicted U(VI) aqueous species and SI of some U(VI) minerals (10 mM of Ca) SPW composition: 10 mM of Ca, 50 mM of Si, 5 mM of Al, and varied HCO_3^- , reacting with 0.1% NH_3 . Diagrams show aqueous species (left) and SI (right). First row for SPW free- HCO_3^- (A1, A2), the 2nd row for 2.9 mM (B1, B2) and 3rd 50 mM (C1, C2) of HCO_3^-

Figure 6-3. Predicted SI (Q/K) of some U(VI) minerals
 SPW composition: 10 mM of Ca, 50 mM of Si, 5 mM of Al, and 50 mM of HCO_3^- , reacting with
 5% NH_3 gas

7. CONCLUSIONS AND RECOMMENDATIONS

The removal efficiency of uranium was not significantly affected by U(VI) concentrations tested (0.5 ppm and 2.0 ppm). It was evident that solutions with higher concentrations of Si, Al and bicarbonate tended to have greater removal of U(VI). The process of U(VI) removal did not appear to be efficient when the concentration of Si was less than 50mM. Solutions with higher concentrations of bicarbonate exhibited larger removal efficiencies for Si, Al^{3+} , and U(VI). Overall, the silica polymerization reaction leading to the formation of amorphous Si gel always correlated with the removal of U(VI), Si, and Al^{3+} from the solutions. If no Si polymerization and gel formation was observed, there was no removal of U from the supernatant solution. The Si concentration and the acceleration because of presence of Al^{3+} and HCO_3^- in the pore water solutions affected the efficiency of the U(VI) removal from the supernatant solutions tested.

The effects of Ca^{2+} in the synthesized pore water, indicated that the percentage of U(VI) removal was controlled by the Si/Al ratios and Ca^{2+} concentration. Furthermore, regardless of HCO_3^- concentration tested. The percent of U(VI) removal increased as Si/Al ratios were increased; the uranium removal was always greater at Si/Al ratios ≥ 10 for all HCO_3^- tested. The higher Ca^{2+} concentration (10 mM) correlated with higher U(VI) removal at low Si/Al ratios.

The SEM analysis for samples prepared with high HCO_3^- concentration showed the uranium-bearing crystal-like structures or uranium dense regions of amorphous collection where EDS analysis of the amorphous areas resulted in high silica content (Wt%) and uranium atomic percentages (At%). The X-ray diffraction analysis of those samples identified the formation of grimselite, but it didn't identify the formation of uranyl silicate

minerals perhaps due to amorphous nature of these solid phases. However, the presence of boltwoodite and uranophane were predicted by the speciation modeling in most of the modeled synthesized pore water solutions. The SI of these uranyl silicate minerals were computed greater in neutral and low bicarbonate pore water solutions. In low bicarbonate concentration and the presence of Ca ions, the computed SI of uranyl carbonate minerals (liegibite, andersonite, grimselite, and rutherfordine) were computed supersaturated (SI=1) at pH near to 8.0. However, these SI started to decrease above pH of 9.0 (Figure 6.2-B2). Also, it is observed that the hydrous silicate species (H_3SiO_4^- and $\text{H}_2\text{SiO}_4^{2-}$) were constantly increasing over pH 8.0 to 11.02/11.87 (shown in supplementary information, Appendix 4, figure A4-3). The decreasing of $\text{Ca-UO}_3\text{-CO}_3$ concentration and SI of uranyl carbonate minerals, in modeled pore water in low bicarbonate concentration, was probably because their large solubility constant product, and they could act as transitional phases that are formed in the system and induced to the formation of the uranyl silicate minerals (Gorman-Lewis et al., 2008). In samples prepared with high HCO_3^- concentration, SEM-EDS showed uranium-bearing crystal-like structures or uranium dense regions of amorphous collection, whereas the X-ray diffraction analysis identified the formation of grimselite in the precipitate. These results were accorded with the speciation modeling results conducted for “high” HCO_3^- samples, which predicted grimselite as the prevalent uranyl mineral. The SI of grimselite was computed as supersaturated between pH of 8 and 11.75. At this pH, the SI of grimselite started to decrease (Figure 6.3); suggesting that dissolution of UO_2^{2+} could be occurred in high alkaline conditions (Zhong et al., 2015).

Additional analysis using the electron microprobe and produce two-dimensional maps of the main pore water elements studied in this dissertation. This analysis will

indicate the association of the elements studies with the formed U(VI) mineral phases. The mapping analysis should be conducted to the precipitate samples in high and low bicarbonate concentrations and the presence of 5 mM and 10 mM of Ca^{2+} . The microprobe mapping would produce images that could show the distribution and relative amount of U as well as the other components that would be presented in the precipitate sample. The mapping would display the location of all components in the point or area selected because of the high content uranium, each component, in a different color, would be located on an individual micrograph. This can be done by using the tricolor function of the SMAK software. With all the components differentiated, the components that would be proximal to U(VI) would be identified. Also, the correlation module could plot graphs of each element that could be overlaid to observe the correlation with U(VI). The microprobe analysis combined with the work already conducted in this dissertation would help to a better understanding of the role of the main components in the studied synthetic pore water and in the formation of uranyl minerals that could have been formed from the solutions after the NH_3 gas injection.

LIST OF REFERENCES

- Afonso, M., & Silveira Jr., V. (2005). Characterization of equilibrium conditions of adsorbed silica-gel/water bed according to Dubinin-Astakhov and Freundlich. *Engenharia Térmica (Thermal Engineering)*, 4 (1), 3-7.
- Allard, T., Ildefonse, P, Beaucaire, C., Calas, G. (1999). Structural chemistry of uranium associated with Si, Al, Fe gels in a granitic uranium mine. *Chemical Geology* 158, 81-103.
- Allison J. D., Brown D. S. and Novo-Gradac K. J. (1990). MINTEQA2 - A geochemical assessment model for environmental systems, Version 3.0 user's manual: Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, Georgia, 106 p.
- Altmaier, M., Gaona, X. & Fanghänel, T. (2013). Recent advances in aqueous actinide chemistry and thermodynamics. *Chemical Reviews*, 113 (2), 901-943.
- Baes, C. F. & Mesmer, R.E. (1976). *Hydrolysis of cations*. Oak Ridge National Laboratory. New York, NY. John Wiley & Sons.
- Baker, V., Bjornstad, B., Busacca, A., Fecht, K., Kiver, E., Moody, U., Rigby, J., Stradling, D.F., & Tallman, A. (1991). Quaternary Geology of the Columbia Plateau, in Morrison, R.B., ed., Quaternary Nonglacial Geology Conterminous U.S., K-2: Boulder, Colorado, Geological Society of America, p. 215–250.
- Ball, J.W. & Nordstrom, D. K. (1991). User's manual for WATEQ4F, Rev. thermodynamic database and test cases for calculating speciation of major, trace, and redox elements in natural waters. Menlo Park: U.S. Geological Survey Open-File Report. 91-193.
- Bernhard, G., Geipel, G., Brendler, V., & Nitsche, H. (1996). Speciation of uranium in seepage waters of a mine tailing pile studied by time-resolved laser-induced fluorescence spectroscopy (TRLFS). *Radiochim Acta*, 74, 87–91

- Bernhard, G., Geipel, G., Reich, T., Brendler, V., Amayri, S., & Nitsche, H. (2001). Uranyl (VI) carbonate complex formation: Validation of the $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ species. *Radiochimica Acta*, 89 (8), 511-518.
- Bethke, C. M. (Ed.). (2010). *Geochemical and biogeochemical reaction modeling* (2nd ed). University of Illinois, Urban Champaign.
- Bickmore, B. R., Nagy, K. L., Young, J. S., & Drexler, J. W. (2001). Nitrate-cancrinite precipitation on quartz sand in simulated Hanford tank solutions. *Environmental Science & Technology*, 35, 4481-4486.
- Bjornstad, B.N. (2006). *On the Trail of the Ice Age Floods: A Geological Field Guide to the Mid-Columbia Basin*. Sandpoint, Idaho. Keokee Co. Publishing, Inc.
- Blum, A.E. & Stillings, L.L. (1995). Feldspar dissolution kinetics. p. 291-351. In A.F. White and S.L. Brantley (ed.). *Reviews in mineralogy*. Vol. 31. Chemical weathering rates of silicate minerals. Mineralogical Soc. of Am., Washington, DC.
- Brimblecombe, P. & Dawson, G.A. (1984). Wet removal of highly soluble gases. *Journal of Atmospheric Chemistry*, 2 (1), 95–107.
- Bruno J., Casas I., Finch R. J., Cera E. and Ewing R. C. (1994). Kinetic and thermodynamic studies of uranium minerals. Assessment of the long-term evolution of spent nuclear fuel. *SKB Tech. Rep. 94*, 73.
- Burns P. C. (1998). The structure of boltwoodite and implications of solid solution toward sodium boltwoodite. *Can. Mineral.* 36, 1069–1075.
- Burns P. C. (2005). U^{6+} minerals and inorganic compounds: insights into an expanded structural hierarchy of crystal structures. *Can. Mineral.* 43, 1839–1894.
- Busey, K.H. & Mesmer, R.E. (1997). Ionization equilibria of silic acid and polysilicate formation in aqueous sodium chloride solution to 300 °C. *Inorganic Chemistry*, 16, 2444-2450.

- Campbell, K., Gallegos, T., Landa, E. (2015). Biogeochemical aspects of uranium mineralization, mining, milling, and remediation. *Applied Geochemistry*, 57, 206-235.
- Cantrell, K.J., Serne, R.J., & Last, G.V. (2003). *Hanford Contaminant Distribution Coefficient Database and Users Guide* (PNNL-13895). Richland, Washington: Pacific Northwest National Laboratory.
- Cantrell, K.J., Zachara, J.M., Dresel, P.E., Krupka, K.M., & Serne, R.J. (2007). *Geochemical Processes Data Package for the Vadose Zone in the Single-shell Tank Waste Management Area at the Hanford Site* (No. PNNL-16663). Richland, Washington: Pacific Northwest National Laboratory.
- Catalano, J.G., Heald, S.M. Zachara, J.M. & Brown, Jr., G.E. (2004a). X-ray spectroscopic and diffraction study of uranium speciation in contaminated vadose zone sediments from the Hanford site Washington State. *Environ. Sci. Technol.* 38(10), 2822-2828.
- Cejka J. (1999). Infrared spectroscopy and thermal analysis of the uranyl minerals. *Rev. Mineral.* 38, 521–622
- Chou, L. & Wollast, R. (1984). Study of the weathering of albite at room temperature and pressure with a fluidized bed reactor. *Geochimica et Cosmochimica Acta*, 48(11), 2205-2217.
- Choppin, G., Liljezin, J.O., Rydberg, J. (2003). Behavior of radionuclides in the environment (4th edition), *Radiochemistry and Nuclear Chemistry* (pp. 753-788).
- Choppin, G., Pathak, P. & Thakur, P. (2011). Polymerization and Complexation Behavior of Silicic Acid: A Review. *Main Group Metal Chemistry*, 31(1-2), pp. 53-72.
- Choppin, G., Pathak, P., & Thakur, P. (2008). Polymerization and Complexation Behavior of Silicic Acid: A Review. *Main Group Metal Chemistry*, 31(1-2), *radiochemistry and Nuclear Chemistry*, 653-685.

- Davis, J.A., Meece, D.E., Kohler, M., Curtis, G.P. (2004). Approaches to surface complexation modeling of uranium (VI) adsorption on aquifer sediments. *Geochimica et Cosmochimica Acta*, 68 (18), 3621-3641.
- Douglas, M., Clark, S., Friese, J., Bruce, B., Buck, E., Hanson, B., Utsunomiy, S., & Ewing, R. Microscale characterization of uranium (VI) silicate solids and associated neptunium(V). *Radiochimica Acta*, 63 (5), 265-272.
- Dove, P. M & Rimstidt, J. D. (1994). Silica-water interactions. *Reviews in Mineralogy and Geochemistry*, 29(1), 259-308.
- Dove, P.M. & Nix, C.J. (1997). The influence of the alkaline earth cations, magnesium, calcium, and barium on the dissolution kinetics of quartz. *Geochimica et Cosmochimica Acta*, 61 (16), 3329-3340.
- Dong, W. & Brooks, S. C. (2006). Determination of the formation constants of ternary complexes of uranyl and carbonate with alkaline earth metals (Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+}) using anion exchange method. *Environmental Science and Technology*, 40 (15), 4689-4695.
- Felmy, A. R., Cho, H., Rustad, J. R., & Mason, M. J. (2001). An aqueous thermodynamic model for polymerized silica species to high ionic strength. *Journal of Solution Chemistry*, 30 (6), 509-525.
- Felmy, A.R., Xia, Y., Wang, Z. (2005). The solubility product of $NaUO_2PO_4 \cdot xH_2O$ determined in phosphate and carbonate solutions. *Radiochimica Acta*, 93 (7), 401-408.
- Finch, R. J. & Ewing, R. C (1992). The corrosion of uraninite under oxidizing conditions. *Journal of Nuclear Materials*, 190, 133-156.
- Finch, R. J. & Murakani, T. (1999). Uranium: Mineralogy, Geochemistry and the Environment (P.C. Burns & R. Finch, eds.). *Systematics and paragenesis of uranium minerals*. Reviews in Mineralogy and Geochemistry, 38, 91-180.

- Fitzsimmons, J. (2015). Analytical method Validation: ICP-OES. *Journal of Analytical Atomic Spectrometry*, 1-9.
- Gallup, D.L. (1997). Aluminum silicate scale formation and inhibition: scale characterization and laboratory experiments. *Geothermics*, 26 (4), 483-499.
- Garcia-Ruiz, J.M. (1998). Carbonate precipitation into alkaline silica-rich environments. *Geology*, 26(9), 843-846.
- García-Ruiz, J. M., Melero-García, E., Hyde, S.T. (2009). Morphogenesis of self-assembled nanocrystalline materials of barium carbonate and silica. *Science*, 323(5912), 362-365.
- Gascoyne M (1989). High levels of Uranium in groundwaters at Canada's underground research laboratory, Lac du Bonnet, Manitoba, Canada. *Appl. Geochem.*, 4, 577-591.
- Gascoyne M (2004). Hydrogeochemistry, groundwater ages and sources of salts in a granitic batholith on the Canadian Shield, southeastern Manitoba. *Appl. Geochem.*, 19, 19–560
- Gephart, R.E & Lundgren, R.E. (1998). Hanford tank cleanup: a guide to understanding the technical issues. Battelle Press, Columbus Ohio.
- Gasteiger, H.A., Frederick, W.J., Streisel, R.C. (1992). Solubility of aluminosilicates in alkaline solutions and a thermodynamic equilibrium model. *Ind. Eng. Chem. Res.* 31, 1183-1190.
- Giammar, D. Geochemistry of uranium at mineral-water interfaces: rates of sorption-desorption and dissolution-precipitation reactions (Doctoral dissertation). California Institute of Technology. Retrieved from Dissertations and Theses database.
- Gorman-Lewis, D., Burns, P. C., & Fein, J. B. (2008). Review of uranyl mineral solubility measurements. *Journal of Chemical Thermodynamics*, 40(3), 335-352.

- Grenthe, I., Fuger, J., Konings, R. J., Lemire, R.J., Muller, A.B., Nguyen-Trung, C., & Wanner, H. (1992). *Chemical thermodynamics of uranium* (OECD Nuclear Energy Agency, Data Bank). Issy-les-Moulineaux, France. Nuclear Energy Agency Data Bank Organisation for Economic Co-operation and Development.
- Guillaumont, R., Fanghänel, T., Fuger, J., Grenthe, I., Neck, V., Palmer, D., & Rand, M. (2003). *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium* (OECD Nuclear Energy Agency, Data Bank). Issy-les-Moulineaux, France. Nuclear Energy Agency Data Bank Organisation for Economic Co-operation and Development.
- Hummel, W., Berner, U., Curti, E., Pearson, F., & Thoenen, T. (2014). *PSI/Nagra Chemical Thermodynamic Database 12/07*. Paul Scherrer Institut, Villigen PSI, Switzerland: Nuclear Energy and Safety Research Department Laboratory for Waste Management (LES).
- Hurd, D.C. 1973. Interactions of biogenic opal, sediments and seawater in the central equatorial Pacific. *Geochim.Cosmochim. Acta*, 37, 2257-2282.
- Iler, R.K. (1973). Effect of adsorbed alumina on the solubility of amorphous silica in water. *Journal of Colloid and Interface Science*, 43(2), 399-408.
- Iler, R.K. (1975). Coagulation of colloidal silica by calcium ions, mechanism, and effect of particle size. *Journal of Colloid and Interface Science*, 53(3), 476-488.
- Iler, R.K. (1979). *The chemistry of silica: solubility, polymerization, colloid and surface properties and biochemistry of silica* (p. 886). John Wiley & Sons Inc.
- Johnston, C.T., Agnew, S.F., Schoonover, J.R., Kenney, J.W., Page, B., & Schott, J. and Corbin, R. (2002). Raman study of aluminum speciation in simulated alkaline nuclear waste. *Environmental Science and Technology*, 36 (11), 2451–2458.

- Kalmykov, S. N., & Choppin, G. R. (2000). Mixed $\text{Ca}^{2+}/\text{UO}_2^{2+}/\text{CO}_3^{2-}$ -complex formation at different ionic strengths. *Radiochimica Acta*, 88 (9), 603-606.
- Katsenovich, Y. P., Cardona, C., Lapierre, R., Szecsody, J., & Lagos, L. (2016). The effect of Si and Al concentrations on the removal of U (VI) in the alkaline conditions created by NH_3 gas. *Applied Geochemistry*, 73, 109-117.
- Kellermeier, M. (2011). Co-mineralization of alkaline-earth carbonates and silica (Doctoral dissertation), Universität Regensburg.
- Kellermeier, M., Gebauer, D., Melero-García, E., Klein, R., Drechsler, M., Talmon, Y., Kienle, L., Cölfen, H., García-Ruiz, J.M., Kunz, W. (2012). Colloidal Stabilization of Calcium Carbonate Prenucleation Clusters with Silica. *Adv. Funct. Mater.* 22, 4301–4311.
- Kellermeier, M., Melero-García, E., Glaab, F., Klein, R., Drechsler, M., Reinhard, R., García-Ruiz, J.M., Kunz, W. (2010). Stabilization of amorphous calcium carbonate in inorganic silica-rich environments. *Journal of the American Chemical Society*, 132(50), 17859-17866.
- Kitano, Y., Okumura, M. & Idogaki, M., 1979. Behavior of dissolved silica in parent solution at the formation of calcium carbonate. *Geochemistry Journal.*, 13, 253-260.
- Klein, R T. & Walter, L.M. (1995). Interactions between dissolved silica and carbonate minerals: An experimental study at 25-50°C. *Chemical Geology*, 125, 29-43.
- Smith, K. F., Bryan, N. D., Swinburne, A. N., Bots, P., Shaw, S., Natrajan, L.S., Mosselmans, J. F., Livens, F. R., Katherine, M. (2015). U(VI) behaviour in hyperalkaline calcite systems, *Geochimica et Cosmochimica Acta*, 148, 343-359.
- Lakshtanov, L., Stipp, S.L.S., 2010. Interaction between dissolved silica and calcium carbonate: 1. Spontaneous precipitation of calcium carbonate in the presence of dissolved silica. *Geochimica et Cosmochimica Acta*, 74(9), 2655-2664.

- Langmuir, D. (Ed.). (1997). *Aqueous environmental geochemistry* Prentice Hall, Upper Saddle River, NJ.
- Langmuir, D., 1978. Uranium solution–mineral equilibria at low temperatures with application to sedimentary ore deposits. *Geochimica et Cosmochimica Acta* 42, 547-569.
- Lindsey, K. A., Slate, J. L. Jaeger, G. K. Swett, K. J., & Mercer, R. B (1994). *Geologic setting of the low-level burial grounds* (No. WHC-SD-TI-290). Westinghouse Richland, Washington: Westinghouse Hanford Co.
- Liu, C., Zachara, J. M., Qafoku, O., McKinley, J. P., Heald, S. M., & Wang, Z. (2004). Dissolution of uranyl microprecipitates in subsurface sediments at Hanford site, USA. *Geochimica Et Cosmochimica Acta*, 68, 4519-4537.
- Liu, C., Zachara, J. M., Qafoku, O., Wang, Z., (2008). Scale-dependent desorption of uranium contaminated subsurface sediments. *Water Resources Research* 44, 2454-2461
- Lovley, D., Phillips, E., Gordy, R. & Landa, R. (1991). Microbial reduction of uranium. Bioremediation of uranium contamination with enzymatic uranium reduction. *Nature*, 350, 413–416.
- Lovley, D. & Phillips, E. (1992). Bioremediation of uranium contamination with enzymatic uranium reduction. *Environ. Sci. Technol.*, 26 (11), 228–2234.
- Mann, F., Burgard, K., Root, W., Puigh, R., Finfrock, S., Khaleel, R., LaMont, P. (2001). *Hanford Immobilization Low-Activity Tank Waste Performance Assessment*. Richland, Washington: US Department of Energy, Office of River Protection.
- Mattus, A.J., Mattus, C.H., Hunt, R.D. (2002). *Investigation into the control and kinetics of aluminosilicate formation on stainless steel surfaces at 100C* (ORNL/TM2002/47). Oak Ridge National Laboratory.

- Moolenaar, R.J., Evans, J.C., McKeever, L.D. (1970). The structure of the aluminate ion in solutions at High pH. *The Journal of Physical Chemistry* 74 (20), 3629–3636.
- Nguyen S. N., Silva R. J., Weed H. C. & Andrews J. E. (1992). Standard Gibbs free-energies of formation at the temperature 303.15 K of four uranyl silicates – soddyite, uranophane, sodium boltwoodite, and sodium weeksite. *J. Chem. Thermodyn.* 24, 359–376.
- Parkhurst, D.L., Thorstenson, D.C., & Plummer, L.N., (1980). PHREEQE–A computer program for geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 80-96, pp. 195 (Revised and reprinted August, 1990).
- Peterson, R.E. , Rockhold, M.L. , Serne, R. J. , Thorne, P.D. , & Williams, M. D. (2008). *Uranium Contamination in the Subsurface Beneath the 300 Area, Hanford Site, Washington* (PNNL-17034). Richland, Washington: Pacific Northwest National Laboratory.
- Qafoku, N. P., Ainsworth, C. C., Szecsody, J. E., & Qafoku, O. S. (2003). Aluminum effect on dissolution and precipitation under hyperalkaline conditions. *Journal of Environmental Quality*, 32, 2354-2363.
- Qafoku, N. P., Ainsworth, C. C., Szecsody, J. E., & Qafoku, O. S. (2004). Transport-controlled kinetics of dissolution and precipitation in the sediments under alkaline and saline conditions. *Geochimica Et Cosmochimica Acta*, 68, 2981-2995.
- Qafoku, N. P., & Icenhower, J. P. (2008). Interactions of aqueous U (VI) with soil minerals in slightly alkaline natural systems. *Reviews in Environmental Science and Bio/Technology*, 7, 355-380.
- Reeder, R.J., Nugent, M., Lamble, G.M., Tait, C.D., & Morris, D.E. (2000). Uranyl incorporation into calcite and aragonite: XAFS and luminescence studies. *Environmental Science and Technology*, 34(4). 638-644.

- Reeder R. J., Nugent M., Tai, C. D., Morris, D. E., Heald S. M., Beck K. M., Hess W. P., & Lanzirotti A. (2001). Coprecipitation of uranium (VI) with calcite: XAFS, micro-XAS, and luminescence characterization. *Geochimica et Cosmochimica Acta*, 65, (20), 3491-3503.
- Reidel, S.P. & Chamness, M.A. (2007). *Geology Data package for the Single-Shell Tank Waste Management Areas at the Hanford Site* (PNNL-15955). Richland, Washington: Pacific Northwest National Laboratory.
- Richter, A., Bok, F., & Brendler, V. (2015). *Data compilation and evaluation for U(IV) and U(VI) for the thermodynamic reference database THEREDA* (No. HZDR-065). Dresden: Helmholtz Zentrum Dresden - Rossendorf.
- Schlosser, F., Moskaleva, L.V., Kremleva, A., Kruger, S and Rosch, N. (2010). Comparative density functional study of the complexes $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ and $[(\text{UO}_2)_3(\text{CO}_3)_6]^{6-}$ in aqueous solution. *Dalton Trans.*, 39, 5705–5712.
- Serne, R., Bjornstad, B., Horton, D., Lanigan, D., Lindenmeier, C., Lindberg, M., . . . Baum, S. (2004). *Characterization of vadose zone sediments below the TX tank farm: Boreholes C3830, C3831, C3832 and RCRA borehole 299-W10-27* (PNNL-14594): Richland, Washington. Pacific Northwest National Laboratory.
- Serne, R., Last, G. V., Horton, D., Gee, G. W., Schaef, D. E., Lanigan, D. C., Orr, R. D. (2008). *Characterization of vadose zone sediment: Borehole 299-E33-45 near BX-102 in the B-BX-BY waste management area* (PNNL-14083). Richland, Washington: Pacific Northwest National Laboratory.
- Sheikholeslami, R. & Bright J. (2002). Silica and metals removal by pretreatment to prevent fouling of reverse osmosis membranes. *Desalination*, 143(3). 255-267.
- Shvareva, T. Y., Mazeina, L., Gorman-Lewis, D., Burns, P. C., Szymanowski, J. E., Fein, J. B., & Navrotsky, A. (2011). Thermodynamic characterization of boltwoodite and

uranophane: Enthalpy of formation and aqueous solubility. *Geochimica Et Cosmochimica Acta*, 75(18), 5269-5282.

Simpson B.C., Corbin, R.A., Anderson M.J., & Kincaid C.T. (2006). *Hanford soil Inventory Model (SIM)* (PNNL-16663). Richland, Washington: Pacific Northwest National Laboratory.

Spear, J.R., Figueroa, L.A. & Honeyman, B. D. (2000). Modeling Reduction of Uranium U(VI) under Variable Sulfate Concentrations by Sulfate-Reducing Bacteria. *Applied Environmental Microbiology*, 66 (9), 151-175.

Stefaniak E.A., Alsecc A., Frost R., Mathe Z., Sajo I.E., Torok S., Worobiec A., Van Grieken R. (2009). Combined SEM/EDX and Micro-Raman spectroscopy analysis of uranium minerals from a former uranium mine. *Journal of Hazardous Materials*, 168, 416-423.

Stumm, W. & Morgan, J.J. Aquatic Chemistry (1996): Chemical Equilibria and Rates in Natural Waters, New York: John Wiley & Sons.

Su, C.M. & Suarez, D.L., 1997. In Situ Infrared Speciation of Adsorbed Carbonate on Aluminum and Iron Oxides. *Clays and Clay Minerals*, 45(6), 814-825.

Szecsody, J. E., Truex, M. J., Qafoku, N. P., Wellman, D. M., Resch, T., & Zhong, L. R. (2013). Influence of acidic and alkaline waste solution properties on uranium migration in subsurface sediments. *Journal of Contaminant Hydrology*, 151, 151-175.

Szecsody, J. E., Truex, M. J., Zhong, L., Qafoku, N., Williams, M. D., McKinley, J. P.,...Phillips, J. L. (2010). *Remediation of uranium in the Hanford vadose zone using ammonia gas: laboratory-scale experiments* (PNNL-20004). Richland, Washington: Pacific Northwest National Laboratory.

Szecsody, J. E., Truex, M. J., Zhong, L., Johnson, N. P., Qafoku, N. P., Williams, M. D.,...Faurie, D. K. (2012). Geochemical and geophysical changes during ammonia gas

- treatment of vadose zone sediments for uranium remediation. *Vadose Zone Journal*, 11(4), 1-13.
- Tallman, A.M., Fecht, K.R., Marratt, M.C., Last, G.V (1979). *Geology of the Separation Areas, Hanford site, South-Central Washington* (RHO-ST-23). Richland, Washington: Rockwell International Corp., Rockwell Hanford Operations.
- Um, W., Serne, R.J., Krupka, K.M. (2007). Surface Complexation modeling of U(VI) sorption to Hanford sediment with varying geochemical conditions. *Environ. Sci. Technol.*, 41, 3587-3592.
- Zeggeren, F.V. & Storey, S.H. (1970). *The computation of chemical equilibria*. New York, NY: Cambridge University Press.
- Voinescu, A.E., Kellermeier, M., Bartel, B., Carnerup, A. M., Larsson, A. K., Touraud, D., Kunz, W., Kienle, L., Pfitzner, A., & Hyde, S. T. (2007). Inorganic Self-Organized Silica Aragonite Biomorphonic Composites. *Crystal Growth & Design*, 8 (5), 1515-1521.
- Wan, J., Tokunaga, T.K., Larsen, J.T., Serne, R.F. (2004). Geochemical evolution of highly alkaline and saline tank waste plumes during seepage through vadose zone sediments. *Geochimica et Cosmochimica Acta*, 68 (3), 491-502.
- Wronkiewicz D. J., Bates J. K., Gerding T. J., Veleckis E. & Tani B. S. (1992) Uranium release and secondary phase formation during unsaturated testing of uranium dioxide at 90 °C. *Journal of Nuclear Materials*. 190, 107–127.
- Wronkiewicz D. J., Bates J. K., Wolf S. F. and Buck E. C. (1996) Ten-year results from unsaturated drip tests with UO₂ at 90: implications for the corrosion of spent nuclear fuel. *Journal of Nuclear Materials*. 238, 78–95.
- Wellman, D.M., Freshley, M.D., Johnson, T.C., Miracle, A.L., 2012. Contaminants in Vadose Zone Environments. *Vadose Zone Journal*, 11(4).

- Wellman, D.M., Icenhower, J.P., Gamberdinger, A.P., Forrester, S.W., 2006. Effects of pH, temperature, and aqueous organic material on the dissolution kinetics of meta-autunite minerals, (Na, Ca) $2-1 [(UO_2)(PO_4)] \cdot 2 \cdot 3H_2O$. *American Mineralogist*, 91(1), 143-158
- Zachara, J. M., Brown, C., Christensen, J., Davis, J. A., Dresel, E., Liu, C., . . . Um, W. (2007). *A site-wide perspective on uranium geochemistry at the Hanford site* (PNNL-17031). Richland, Washington: Pacific Northwest National Laboratory.
- Zachara, J. M., Davis, J. A., McKinley, J. P., Wellman, D. M., Liu, C., Qafoku, N. P., & Yabusaki, S. (2005). *Uranium geochemistry in vadose zone and aquifer Sediments from the 300-area uranium plume* (PNNL-15121). Richland, Washington: Pacific Northwest National Laboratory.
- Zheng, Z.P., Tokunaga, T.K., Wan, J.M., 2003. Influence of calcium carbonate on U(VI) sorption to soils. *Environmental Science & Technology*, 37(24), 5603-5608.
- Zhong, L., Szecsody, J. E., Truex, M. J., Williams, M. D., & Liu, Y. (2015). Ammonia gas transport and reactions in unsaturated sediments: Implications for use as an amendment to immobilize inorganic contaminants. *Journal of Hazardous Materials*, 289, 118-119.

APPENDICES

Appendix 1

Experimental samples preparation - Supporting information

Table A1-1. Stock Solutions Used to Prepare Various Si/Al Molar Ratios

Stock Solution	Salt Used	MW of Salt (g/mol)	Stock Solution (mM)	50 mL (g)
Bicarbonate	KHCO ₃	100.114	400.00	2.002
Metasilicate	Na ₂ SiO ₃ ·9H ₂ O	284.196	422.24	5.998
Aluminum	Al(NO ₃) ₃ ·9H ₂ O	375.129	50.00	0.938
Calcium	CaCl ₂ ·2H ₂ O	147.01	1250.0	9.188

Table A1-2. Experimental matrix

Batch number	HCO ₃ , mM	Initial Si concentrations in the solution mixture, mM					
1	0	5	50	100	150	200	250
2	2.9	5	50	100	150	200	250
3	25	5	50	100	150	200	250
4	50	5	50	100	150	200	250
5	75	5	50	100	150	200	250
6	100	5	50	100	150	200	250

Table A1-3. Stock Solution & Synthetic Pore Water Concentrations

Stock Solution	Concentration (mM)	Synthetic Pore Water Concentrations (mM)
CaCl ₂ ·6H ₂ O	500.00	0/5/10/15
KHCO ₃	400.00	3.0/50
Na ₂ SiO ₃ ·9H ₂ O	422.24	50
Al(NO ₃) ₃ ·9H ₂ O	50.00	5
UO ₂ (NO ₃) ₂ ·6H ₂ O	210.06	200/400 ppm U*
0.1% NH ₃ in N ₂ (gas)	Bubbled into solution until pH ≈ 11	

*200 ppm was used for characterized samples in the batch experiment in Chapter 3

Table A1-4. Synthetic Pore Water Formulation used for the Speciation Modeling

Sample ID	Samples Concentration (mM)			
	Bicarbonate	Metasilicate	Aluminum	Calcium
1	2.9	50	5	0
3	2.9	50	5	5
3	2.9	50	5	10
4	50	50	5	0
5	50	50	5	5
6	50	50	5	10

Appendix 2

Chapter - Supplementary information

Figure A-2-1. Removal of U(VI) in 2.8 mM Al amended solutions
U(VI) concentrations of 0.5 and 2 ppm.

Figure A-2-2. Removal of Si in 2.8 mM Al amended solutions for 0.5 ppm U(VI) at varied HCO₃, Removal of Si (A), Removal of Al (B), Removal of U(VI) (C).

Appendix 3

Uranyl mineral characterization - Supplementary information

Figure A-3-1. SEM Precipitate Ca^{2+} - free Sample - Amorphous U-bearing dense regions

<i>Element Line</i>	<i>Weight %</i>	<i>Atom %</i>
<i>C K</i>	29.63	41.50
<i>O K</i>	36.21	38.08
<i>Na K</i>	2.000	1.460
<i>Al K</i>	0.790	0.490
<i>Si K</i>	30.62	18.34
<i>K K</i>	0.230	0.100
<i>U M</i>	0.520	0.040
<i>Total</i>	100.00	100.00

A-3-2. SEM-EDS, precipitate formed at 100 Si + 5 Al + 0 HCO_3 (mM) + 2 ppm U(VI)

The SEM did not show areas of concentrated uranium, crystalline or otherwise for this composition of SPW. Because of the small amount of U(VI) concentration (2ppm), the uranium is not visible for the instrument. This can be explained by Si polymerization around the developing nano size clusters with the formation of coatings consisting on massive dense amorphous silica as shown on SEM micrograph (Figure A-3-2).

Appendix 4

Predicted speciation modeling - Supplementary information

Figure A-4-2. Predicted U(VI) aqueous species and SI of some U(VI) minerals (5 mM of Ca) SPW composition: 5 mM of Ca, 50 mM of Si, 5 mM of Al, and varied HCO_3^- , reacting with 5% NH_3 . Diagrams show aqueous species (left) and SI (right). First row for SPW free- HCO_3^- (A1, A2), the 2nd row for 2.9 mM (B1, B2) and 3rd 50 mM (C1, C2) of HCO_3^-

Figure A-4-3. Predicted U(VI) aqueous species and SI of some U(VI) minerals (10 mM of Ca) SPW composition: 10 mM of Ca, 50 mM of Si, 5 mM of Al, and varied HCO_3^- , reacting with 5% NH_3 . Diagrams show aqueous species (left) and SI (right). First row for SPW free- HCO_3^- (A1, A2), the 2nd row for 2.9 mM (B1, B2) and 3rd 50 mM (C1, C2) of HCO_3^-

Figure A-4-4. SI of some u(VI) minerals plotted as a function of pH for 5% of NH_3 [3.1 mol/L $\text{NH}_3(\text{aq})$]. Sample composition includes 10 mM of Ca, 50 mM of Si and varied HCO_3^- concentrations.

Figure A-4-5. Diagrams of Hydrous silicas species (left) and oxidation potential (Eh) (right) as a function of pH. Sample composition 10mM of Ca, 50 mM of Si and 2.9 HCO_3^- reacting with 5% of NH_3 gas

Appendix 5

Ammonia Gas Simulation Using Geochemist Workbench

The primary focus of the simulation was on the application of the geochemical equilibrium modeling software, Geochemist's Workbench (GWB) version 10.0 (Bethke, University of Illinois) to predict the formation of uranium aqueous species and solid phases likely to be saturated in the post-NH₃ gas-treated pore water and observed the NH₃ gas reaction to estimate the mass of NH₃ in a treatment.

The modeling was conducted by combining the concentrations of four cations and three anions to reproduce the experimental synthetic pore water solutions. The divalent Ca²⁺ was not considered initially in this modeling. The GWB React Module was used to simulate the NH₃ gas reaction in multiple synthetic pore water solutions. The pH was fixed from 8 to 11.02 and then repeated from 8 to 11.87, simulating the pH values reached after the 0.1% and 5% of NH₃ gas injection. The concentrations of aqueous ammonia in the solutions at equilibrium for each reaction were set as 0.063M and 3.1M, respectively. A dissolved oxygen concentration equivalent to the typical on-site conditions was set as 8.4 ppm at constant temperature of 25°C. The concentration of uranium was kept constant at 2ppm in all simulations. The aqueous uranium species and mineral uranium species were identified and graphed as a function of the pH. The React module was used for modeling multiple synthetic pore water solution simulations using 0.1% and 5% concentrations of NH₃. The major pore water components dissolved in the synthetic pore water were represented by H₂SiO₄, K⁺, Na²⁺, Al³⁺, UO²⁺, HCO₃⁻ and NO₃²⁻. The simulation considered a small concentration of NH₄⁺ as an initial input to initiate the simulation of the NH₃ gas reaction. The basic section included all other component concentrations for the specific

pore water solution system, the H^+ activity of 8, and the mass solvent water (1 kg by default). The temperature was set up at 25°C and the density and total dissolved solids (TDS) were kept “auto”. The NH_3 gas reaction was simulated in the reactants section sliding pH to 11.02 and then to 11.87; the NH_3 aqueous total mass to react was set up to 0.063 and 3.1M, respectively. The partitioning of 0.1% and 5% of NH_3 gas into the pore water solutions and the resulting pH were modeled to observe the mass of NH_3 in the pore water after the partitioning. The simulation started by adding an initial amount of 1×10^{-10} mol/L of NH_4^+ to the solution at pH 8 as initial condition and until the NH_3 gas reaction is reached, 0.063mol/L and 3.1mol/L, which are equivalent to 0.1% and 5% of NH_3 respectively. Figure A-5-1 shows the 5% of NH_3 gas partitioning between an initial pH of 8 (natural conditions) and the resulting pH of 11.87.

Figure A-5-1. 5% of the NH_3 gas partitioning into water and the resulting pH.

Figure A-5-2. 5% of the NH_3 gas partitioning into water resulting $\text{NH}_{3(\text{aq})}$

VITA

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1992-1997	B.S. in Civil Engineering EAFIT University Medellin, Colombia
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PUBLICATIONS AND PROFESSIONAL PRESENTATIONS

Katsenovich, Y.P., Cardona, C., Lapierre, R., Szecsody, J., Lagos, L.E., 2016. The effect of Si and Al concentrations on the removal of U (VI) in the alkaline conditions created by NH₃ gas. *Applied Geochemistry*, 73: 109-117

Katsenovich, Y.P., Cardona, C., Szecsody, J. (2017) “Assessment of calcium addition on the removal of U(VI) in the alkaline conditions created by NH₃ Gas”. (In-preparation Publication)

Removal of U(VI) in the Alkaline Conditions Created by NH₃ Gas. Professional Presentation #17288. WM 2017; Phoenix, Arizona, March 2017.

The solubility of uranium species using the Isopiestic Method. Poster Presentation. Department of Energy Fellowship Poster Exhibition. Florida International University September 2014. The Effect of Ca Ions on the Removal of U(VI) via In-Situ Ammonia Gas.

Injection at the Hanford Site 200 Area. Professional Presentation #14434. WM 2014; Phoenix, Arizona.