The Effect of Si and Al Concentrations on the Removal of U(VI) in the Alkaline Conditions

Created by NH₃ Gas

Yelena Katsenovich^{a*}, Claudia Cardona^a, Robert Lapierre^a, Jim Szecsody^b, Leonel Lagos^a

^aApplied Research Center, Florida International University, 10555 W. Flagler Street, Miami, FL
33174, USA

^bPacific Northwest National Laboratory, PO Box 999, K3-62, Richland, WA 99352

*Corresponding author. E-mail: katsenov@fiu.edu; phone: 305-348-2338.

Abstract

Remediation of uranium in the deep unsaturated zone is a challenging task, especially in the presence of oxygenated, high-carbonate alkalinity soil and pore water composition typical for arid and semi-arid environments of the western regions of the U.S. This study evaluates the effect of various pore water constituencies on changes of uranium concentrations in alkaline conditions, created in the presence of reactive gases such as NH_3 to effectively mitigate uranium contamination in the vadose zone sediments. This contaminant is a potential source for groundwater pollution through slow infiltration of soluble and highly mobile uranium species towards the water table. The objective of this research was to evaluate uranium sequestration efficiencies in the alkaline synthetic pore water solutions prepared in a broad range of Si, Al, and bicarbonate concentrations typically present in field systems of the western U.S. regions and identify solid uranium-bearing phases that result from ammonia gas treatment. In previous studies (Szecsody et al. 2012, Zhong et al. 2015), although uranium mobility was greatly decreased, solid phases could not be identified at the low uranium concentrations in field-contaminated sediments. The chemical composition of the synthetic pore water used in the experiments varied for silica (5 to 250 mM), Al^{3+} (2.8 or 5 mM), HCO_3^- (0 – 100 mM) and U(VI) (0.0021-0.0084 mM) in the solution mixture. Experiment results suggested that solutions with Si concentrations higher than 50 mM exhibited greater removal efficiencies of U(VI). Solutions with higher concentrations of bicarbonate also exhibited greater removal efficiencies for Si, Al, and U(VI). Overall, the silica polymerization reaction leading to the formation of Si gel 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. Speciation modeling indicated that the dominant uranium species in the presence of bicarbonate were anionic uranyl

carbonate complexes ($\text{UO}_2(\text{CO}_3)_2^{-2}$ and $\text{UO}_2(\text{CO}_3)_3^{-4}$) and in the absence of bicarbonate in the solution, U(VI) major species appeared as uranyl-hydroxide ($\text{UO}_2(\text{OH})_3^-$ and $\text{UO}_2(\text{OH})_4^{-2}$) species. The model also predicted the formation of uranium solid phases. Uranyl carbonates as rutherfordine [UO_2CO_3], cejkaite [$\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$] and hydrated uranyl silicate phases as Na-boltwoodite [$\text{Na}(\text{UO}_2)(\text{SiO}_4) \cdot 1.5\text{H}_2\text{O}$] were anticipated for most of the synthetic pore water compositions amended from medium (2.9mM) to high (100mM) bicarbonate concentrations.

Key words: uranium, silica, ammonia gas, vadose zone, removal efficiency

Introduction

The legacies of uranium mining, milling waste disposable practices and past atomic weapon production activities across the U.S. Department of Energy complex has left risk-driving uranium contamination in soil and groundwater (Zachara et al. 2007, Corbin et al. 2005). This uranium contamination often originates from acidic or alkaline chemical agents that are used in conjunction with mining leaching or milling extraction methods. Alkaline solution mining is the primary uranium mining method in the U.S. (NRC 2011). Usually, alkaline carbonate-based leaching of uranium is conducted in a specific ore zone; however, uranium migration continues outside these zones under variable geochemical conditions. Analogous conditions are created at uranium disposal sites where uranium is co-disposed with alkaline solutions. These solutions influence the dissolution of soil minerals and, based on field observations, elevated concentrations of Si, Fe, and K are still observed in the contaminated groundwater about 40 years after the waste infiltration (Wan et al. 2004). After the disposal, uranium contamination, accumulated in the subsurface unsaturated zone (vadose zone), can serve as a continued “source” of U(VI) contamination for groundwater (Wellman et al. 2012). There is a concern that elevated uranium concentrations slowly infiltrate towards the water table, creating a risk of higher U concentrations reaching the groundwater and then, with groundwater flow, entering rivers and lakes. Remediation of uranium -contaminated soil is particularly challenging for deep vadose zone (VZ) environments typical for arid and semi-arid regions of the western United States where low moisture content unsaturated zones are commonly 70 to 100 m thick.

The specific study location for this investigation focusing on the stabilization of uranium contamination in the subsurface that can limit influx from the contaminated VZ to groundwater was chosen on the U.S. DOE Hanford Site in south-central Washington State. At the Hanford

Site, a significant residual mass of the disposed uranium inventory still resides in the deep vadose (Szecsody et al. 2013). 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. 2007, Szecsody et al. 2013, Zachara et al. 2005). The mobility of U(VI) is explained by the formation of highly soluble and stable uranyl-carbonato complexes (UO_2CO_3^0 , $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$) (Langmuir 1997, Guillamont et al. 2003) in the absence of calcium, and calcium-uranyl-carbonato complexes ($\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ and $\text{CaUO}_2(\text{CO}_3)_3^{2-}$) (Bernhard et al. 2001, Kalmykov and Choppin 2000). Remediation techniques for the deep VZ contaminated with radionuclides have so far received less attention although such methods are critical for protection of water resources from contaminants historically accumulated in the unsaturated subsurface environments. Remediation of deep vadose zone contamination of radionuclides can potentially be done in-situ by converting aqueous U-carbonate mobile phases to lower solubility precipitates that are stable in the natural environment. One of the potential methods to stabilize uranium in the subsurface is injection of liquid phosphorus- bearing amendments (Wellman et al. 2006). However, injection of aqueous solutions to stabilize uranium in the dry vadose zone environments may potentially mobilize uranium 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 vadose zone is a viable method to decrease uranium mobility in the contaminated subsurface via pH manipulation and creation of alkaline conditions (Szecsody et al. 2012, Zhong et al. 2015). Once injected to the vadose zone, unreacted NH_3 partitioned to the gas phase would slowly migrate upward due to a lower gas density of 0.77 kg m^{-3} compared to air density of 1.29 kg m^{-3}). Ammonia is a highly soluble gas and its injection in the vadose zone

can cause the formation of NH_4^+ (which consumes H^+) in pore water followed by a subsequent increase in pH up to 12.52 for 100% NH_3 (15.7 mol/L $\text{NH}_3(\text{aq})$), 11.87 (3.1 mol/L $\text{NH}_3(\text{aq})$) for 5% NH_3 or pH 11.02 for 0.1% NH_3 (0.063 mol/L). 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 with an increase in pH from 8 to 12 at 23°C. These dissolution reactions in alkaline conditions potentially induce the release of cations including Si, Al, Ca, Mg, Na, 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 solid phases would precipitate as a uranium-silicate such as Na-boltwoodite (Szecsody et al. 2013) or decrease U mobility by a coating of U-bearing phases forming 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 and Icenhower 2008). These chemical reactions can potentially 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 show a decrease in U mobility after ammonia gas injection in the low water content sediments (Szecsody et al. 2013). Zhong et al (2015) also 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. However, there is a lack of knowledge on how pore water constituencies in alkaline conditions where soil minerals dissolution contributes to the solution ions may affect uranium removal or precipitation.

In previous studies, uranium precipitation in alkaline waters was controlled mainly by aluminosilicate and carbonate dissolution and the presence of hydrous silicates (uranophane $[\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2 \cdot 5\text{H}_2\text{O}]$, Na-boltwoodite $[\text{Na}(\text{UO}_2)(\text{SiO}_4) \cdot 1.5\text{H}_2\text{O}]$, (Um et al. 2009); Zachara et al., 2007;) that are both natural and anthropogenic.

The objective of this study was to quantify the role of major pore water constituents on uranium (VI) precipitation/removal from NH_3 -treated synthetic pore water solutions. This was accomplished by characterizing the influence of differing U(VI), silicon, aluminum, and bicarbonate concentrations present in the synthetic pore water composition on the U(VI) removal and studying the formation of uranium-bearing solid phases that would be created as a result of the NH_3 treatment. An understanding of the role of pore water constituencies on the removal of U(VI) is needed to identify controlling geochemical processes that would occur in NH_3 -treated alkaline sediments with a composition typical for arid and semiarid regions of the western U.S. that received differing U-laden wastes.

Material 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 the purpose of these experiments, the complicated pore water composition was simplified to have four major components in the test solutions: uranium, silica, aluminum, and bicarbonate. Two relatively low concentrations of U(VI), 0.0021mM and 0.0084 mM (0.5 mg/L and 2 mg/L), and six different bicarbonate concentrations (0.0, 2.9, 25, 50, 75 and 100 mM) were tested. The silica concentration was varied (5, 50, 100, 150, 200, 250 mM) given 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 (Zhong et al. 2015). This concentration was then gradually decreased after 24 h (Zhong

et al. 2015). The same highest Si concentration of 100 mM with the total cation 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. 2004) or up to 0.8 mM in 10% NH₃-treated sediment, justifying the fact that Al concentration is smaller than Si. Based on these results, two concentrations of Al (2.8 mM and 5 mM) were tested. Both Si and Al concentrations tested are orders of magnitude greater than U; that can lead to the potential U precipitation as U-silicates from the Si and Al rich solutions.

In addition, several analogous controls were prepared without Al in the solution mixture, helping to evaluate its effect on the removal of U(VI). The experiments were run by limiting the 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, the pore water concentration of aqueous carbonate will be considerably increased, justifying the wide range of bicarbonate concentrations tested in the experiments. Stock solutions of Al (50 mM), Si (422 mM), and HCO₃⁻ (400 mM) were first prepared in deionized water (DIW) from the salts Al(NO₃)₃·9H₂O, Na₂SiO₃·9H₂O, and KHCO₃, respectively, reaching the desired concentrations in 50 mL volume. Sodium metasilicate, Na₂SiO₃·9H₂O, and potassium bicarbonate, KHCO₃, were also served as a source of sodium and potassium in the solution mixture. The 100 µg stock solution of uranyl nitrate dissolved in DIW was prepared fresh from a uranyl nitrate hexahydrate 1000 µg standard before use (Fisher Scientific).

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 vadose zone (Serne et al. 2008, Zachara et al. 2005).

Then, NH_3 gas (0.1% NH_3 + 99.9% N_2) was injected into each solution through a metal gas sparger (Mott Corporation, 20 μm pores) until the pH of the solution reached approximately 11 (0.063 mol/L (aq)). 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 mg/L and the other three samples were each amended with a U(VI) concentration of 2 mg/L. Control samples were prepared in DIW amended with U(VI) at concentrations of 0.5 mg/L and 2 mg/L 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 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 (Table 1).

Analytical Procedures

Samples of the supernatant from each vial were analyzed using a kinetic phosphorescence analyzer (KPA-11, Chemchek 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) (PerkinElmer). 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 $\alpha = 0.05$.

Geochemical Modeling

Geochemist's Workbench (GWB) 10.0 (Bethke, University of Illinois) React Module was used for the geochemical equilibrium modeling to predict the formation of uranium aqueous species and solid phases likely to be present as a result of NH₃ gas injections in the synthetic pore water solutions. The React Module allowed for varying the pH levels, simulating the addition of ammonia. This modeling was conducted for a system closed to the exchange of CO₂ with the atmosphere. A closed system is also more applicable to field treatment where the 95% N₂, 5% NH₃ gas will be injected into a zone. With a NH₃ gas retardation of 300 to 400 depending on water content (Szecsody et al., 2012), there will eventually be a large zone where the pore gas is flushed out and replaced with N₂ as well as a smaller zone where NH₃ gas is in equilibrium with

ammonia in the pore water. This effectively is a closed system in terms of CO₂ partitioning, at least for the short term (i.e., several months). Over a longer time span (i.e., years), due to gas diffusion, atmospheric gas will eventually equilibrate with the treated zone. The simulated pore water solutions included four cations and three anions at an initial pH of 8. The H₂SiO₄²⁻ was assumed to represent all the silica species in the solution at 25°C (Felmy et al. 2001). Dissolved oxygen was set as 8.4 mg/L at a constant temperature 25°C and the concentration of U(VI) was kept constant at 2 mg/L in all simulations. In the Reactants pane, experimental conditions were simulated by sliding pH from 8 to 11.02 for 0.1% of NH₃. Simulations were then repeated by sliding pH from 8 to 11.87, imitating the pH values reached after the injection of 5% of NH₃. This would result in the React Module simulating the concentration of aqueous ammonia as 0.063 mol/L and 3.1 mol/L in the solutions at equilibrium. The thermodynamic databases supplied with the GWB software were modified to include revised thermodynamic data for aqueous and mineral uranium species of interest (Felmy, Xia and Wang 2005, Guillaumont et al. 2003). The aqueous uranium species and minerals uranium species were identified and graphed as a function of the pH. These speciation models assumed that ammonia would 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 of nitrate with uranyl standard and 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).

Characterization of Uranium-Bearing Precipitates

The sample preparation process used to prepare samples for characterization closely mirrored those previously described. Synthetic pore water solutions were prepared using a combination of stock solutions at varying concentrations. These stock solutions were combined in a ratio such

that the final concentrations of the major constituents were 100 mM for Si, 5 mM for Al, and either 50 mM or 3 mM for bicarbonate (HCO_3^-). Nitric acid (HNO_3^-) was used to adjust the pH of sample synthetic porewater solutions to the 7-8 range found in the Hanford vadose zone. The remediation method was then applied by the sparging of ammonia gas (NH_3) through the adjusted solutions until the pH was elevated to the 11-12 range. Lastly, a small volume of high concentration uranyl nitrate solution was added to the samples such that the uranium concentration would be approximately 0.84 mM (200 mg/L). Solutions were left at room temperature over a 2 day reaction period. After this stage, the samples were decanted to isolate the precipitate and supernatant solutions for further testing. The recovered solids were allowed a period of time to dry in preparation for SEM-EDS and X-ray diffraction analysis while the supernatants were set aside for uranium concentration analysis by KPA.

Electron microscopy was performed using a JEOL-5910-LV with accelerative potentials between 10 kV and 20 kV. For conduction purposes, all samples were gold coated using an SPI-Module Control and Sputter unit. The energy dispersive spectroscopy (EDS) analysis was accomplished using an EDAX Sapphire detector with UTW Window paired with Genesis software.

Micrographs were prepared in both secondary electron and backscatter modes with the objective lens aperture 2 at 30 μm diameter and the spot sizes (condenser lens) ranging from 35-40.

X-ray diffraction analyses were performed on the dried precipitates at 35 kV and 40 mA via Bruker 5000D XRD instrument. Diffraction patterns were obtained using a copper $\text{Cu K}\alpha$ radiation source ($\lambda=0.154056 \text{ nm}$) 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.

Selected precipitate samples were carefully ground into a fine powder using a mortar and pestle

in anticipation of the analysis. The pulverized sample was packed into the small recess of a plastic sample holder that was designed specifically for the small amount available.

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 initial concentration of silica on the x-axis (Figure 1, Figure 1S, Figure 2S).

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 mg/L U(VI) at variable bicarbonate and silica concentrations are presented in the Supplementary Materials file (Figure 1S, Figure 2S). A reduction in Si content in the supernatant from the solutions initially amended with 2.8 mM of Al and 0.5 mg/L (Figure 2S (A)) or 2 mg/L of U(VI) (Figure 1A) 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 silica is dissolved as silicate ion, to 10.6- 10.7. The change in the pH led to silica supersaturation and then nucleation and deposition of monomeric silica from the solution.

At bicarbonate concentrations between 0 mM – 25 mM and initial Si concentrations below 100 mM, the removal efficiency of Si showed relatively low values, ranging between 0 and 50%. However, the increase in bicarbonate (HCO_3^-) solution concentrations up to 100 mM correlated with an enhanced Si removal with up to 91% removed from solution. Experiments using greater Si content of 200 and 250 mM resulted in high Si removal efficiencies of up to 97% from the supernatant solutions. Bicarbonate solution 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 of 95-97% (Figure 1A; Figure 2S(A)).

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

Data analysis of U(VI) removal showed that the maximum percent removal of U(VI) was close to 98% for the initial Si concentrations over 150 mM used for the solution preparations (Figure 1C, Figure 1S). At low Si concentrations, 5 mM and 50 mM, there was no observed reduction in the U(VI) concentrations 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 silica increases at high pH because of the formation of silicate ion in addition to Si(OH)_4 in solution. The increase in HCO_3^- solution concentrations appeared to alter the efficiency of Si removal at lower Si concentrations. 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^- solution concentrations. In those samples, the removal of U(VI) from the supernatant solutions was increased to 80-99% and was not affected by the different HCO_3^- solution concentrations tested. Experimental results for both concentrations of U(VI) followed the same trend: insignificant removal of U(VI) from solutions containing initial Si concentrations ranging between 5 mM and 50 mM, removal

increased to 78% -94% at a Si concentration of 100 mM and increased again to 95-99% at Si concentrations between 150 mM and 250 mM. This trend for U(VI) removal is similar to that of Si. In addition, statistical analysis indicated strong evidence that there was not a concentration dependence on U(VI) removal based on experiments at 0.5 and 2.0 mg/L U(VI) ($P < 0.05$) (Figure 1S in Supplementary Materials). The U(VI) removal increased to 78-95% when the solution mixture contained higher than 50 mM HCO_3^- . Based on the modeling predictions, in the absence of carbonate in solution, U(VI) major species appear as uranyl-hydroxide $\text{UO}_2(\text{OH})_3^-$ and $\text{UO}_2(\text{OH})_4^{2-}$. The addition of 2.9 mM of HCO_3^- causes the formation of negatively charged anionic uranyl carbonate complexes, $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$, which are highly soluble. At $\text{HCO}_3^- \geq 25$ mM, the soluble $\text{UO}_2(\text{CO}_3)_3^{4-}$ species become predominant and account for 99.9% at alkaline conditions. These species should be present in the solution as dissolved uranyl carbonate species. However, our data demonstrated an increase in the U(VI) removal in the supernatant as the concentration of bicarbonate solutions rises.

Due to similar results for the removal of U(VI) at different concentrations, 2 mg/L of U(VI) was employed in all further experiments. The concentration of Al 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^- concentrations tested previously at 2.8 mM Al.

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 to be between 75-89% compared to values obtained for the batch amended with 2.8 mM of Al (Figure 1A, Figure 2A). 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 for the range of 0-25 mM HCO_3^- . Figure 1A, Figure 1S(A) and Figure 2A show 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 1B and Figure 2B).

In the presence of 5 mM of Al, a similar trend was noted 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 HCO_3^- , the decreased removal of Si correlated with only 7.5% removal of U(VI) from the supernatant (Figure 2C). 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 2C).

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, HCO_3^- , 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 2D, 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 $\text{Si} \geq 100 \text{ mM}$. In the mixture with the same high HCO_3^- and 5 mM of Al added, the U(VI) removal efficiency of $86.7 \pm 0.7\%$ was observed at 50 mM of Si (Figure 2D). 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 from the solution mixture.

When the Si-free solution mixture contained 2.8 mM of Al, the uranium percent removal exponentially declined with an increase in the concentration of HCO_3^- in the solution composition (Figure 2E). This phenomenon might be explained by the competitive adsorption of HCO_3^- and U(VI) on Al hydroxide created in the solution (Su and 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 mixture (Figure 2E).

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 and 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.

Several important aspects should be considered to explain these findings. One of them is the formation of aluminosilicate chains upon mixing silicate ions and $\text{Al}(\text{OH})_3$. Iler (1979) described the affinity between aluminum and silicon ions and proposed the formation of aluminosilicate surface complexes according to a reaction between monomeric silica $\text{Si}(\text{OH})_4$ and $\text{Al}(\text{OH})_3$ (Iler 1979).

The presence of the aluminum reverses the negative net of Si surface charge to positive (Iler 1973, Dove and Rimstidt 1994). The release of hydrogen ions contributes to the conversion of soluble silica to amorphous silica. The formation of amorphous silica particles by polymerization of $\text{Si}(\text{OH})_4$ involves some aspects of the theory of nucleation (Iler 1979). Aluminosilicate impurities serve as nucleation sites or “seeds,” accelerating Si polymerization reactions. The formation of aluminosilicate impurities is complemented by the dissociation of bicarbonate ions, provoking a local decrease in pH. In this condition, silica speciation shifts towards a higher degree of protonation that in turn triggers silica polymerization reactions. The release of hydrogen ions reduces the solubility of Si at alkaline pH, leading to Si polymerization reactions according to previous work (Iler 1979, Kellermeier et al. 2010):

Therefore, the decrease in pH triggered by the release of hydrogen ions increases the local supersaturation of silicic acid in the surrounding environment, subsequently provoking precipitation of silica (García-Ruiz et al. 2009). In addition, the process of dissociation intensifies at higher bicarbonate ion concentrations that induce a local decrease in pH. This shifts

the silica speciation towards a higher degree of protonation effectively facilitating silica polymerization reactions (Kellermeier et al. 2010). As a result, silica polymerizes around the developing nano size clusters with the formation of coatings, consisting of massive dense amorphous silica as shown on SEM micrograph (Figure 3S in Supplementary Materials file). The adsorption of alkali metals onto the silica polymer chain with the release of hydrogen ions is another possible mechanism that contributes to heterogeneous nucleation (Iler 1975). Several studies have confirmed the tendency of silica-mediated deposition at high pH onto amorphous calcium carbonate grains (García-Ruiz et al. 2009, Kellermeier et al. 2010, Ruiz 1998, Lakshtanov and Stipp 2010). Ammonia gas injection, through altering the pH in the soil pore water, can potentially induce the dissolution of Si, Al and other elements from soil minerals. This study began to probe the effect of Si, Al, and bicarbonate ions dissolved from soil minerals on the U co-precipitation process in alkaline conditions by showing a clear correlation between Si and U precipitation from solution.

Characterization of the Uranium- Bearing Precipitates.

The scanning electron microscope imaging and energy dispersive spectroscopy were used to compare and evaluate precipitate morphology and elemental content for high (50 mM) and low (3 mM) bicarbonate samples. The primary points of interest during this sample investigation were areas of high uranium concentration, which were identified as bright, white areas indicative of areas containing heavier elements due to their stronger backscatter of electrons. The elevated uranium content was confirmed by comparison of spectroscopy data collected at the points of interest to that of the rest of the silica-rich sample. Alongside the uranium content, the EDS analysis of these areas indicated significant atomic percentages of potassium, sodium, nitrogen, silica, and carbon, though the ratios were inconsistent.

The major distinguishing characteristic observed in comparing micrographs was the presence of those targeted uranium-rich regions. The majority of high bicarbonate samples produced some distinguishable uranium-rich phases, as confirmed by EDS. Typically, those samples produced unmistakably crystalline uranium solids; made obvious by the needle like structures pictured in Figure 3. Though the uranium-bearing crystal structures displayed in Figure 3 were the most prevalent in the 50 mM bicarbonate samples, either or both forms could be present in these samples.

In contrast, under these experimental conditions, there were no areas of concentrated uranium, crystalline or otherwise, detected in the low bicarbonate samples (image not shown). As such, no 3 mM bicarbonate samples were selected for continued analysis by XRD.

The powder X-ray diffraction analysis of the select samples consistently resulted in the well-defined peaks for all samples tested, confirming the presence of some crystalline material. The resultant diffraction patterns were compared to reference data for various minerals using both the automated *Match!* software and manually comparing against the data for predicted minerals found in an ICDD database. No diffraction pattern generated produced a sufficient match to any referenced uranium mineral. There was, however, a near perfect match for nitratine (NaNO_3), a likely product for the contents of the synthetic porewater solution (Figure 4). It is likely that, at the concentration added, any uranium minerals present in the sample were too miniscule, relative to the bulk sample, to be detected with any certainty by powder XRD.

Geochemical Modeling Results

According to 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, aqueous uranium carbonates species, $\text{UO}_2(\text{CO}_3)_3^{4-}$ and $\text{UO}_2(\text{CO}_3)_2^{2-}$, dominated uranium

speciation at both 0.1% (0.063 mol/L NH₃(aq) and 5% (3.1 mol/L NH₃(aq) of NH₃. However, the concentration of uranyl carbonates species was noted to decrease above pH 9.5; the decrease of UO₂(CO₃)₃⁴⁻ and UO₂(CO₃)₂²⁻ was more pronounced at 2.9 mM HCO₃⁻ when using 5% of NH₃ (Figure 4S (B1)) compared to 0.1% of NH₃ (Figure 5-B1). At higher bicarbonate concentrations, the concentration of UO₂(CO₃)₃⁴⁻ species was almost unchanged over a pH range from 8 to 11 in both ammonia gas concentrations but, at the pH above 11.5, their concentrations were slightly decreased with treatment of 5% NH₃ (Figure 5C1, Figure 4S (C1)). The modeling also predicted the formation of uranyl silicate Na-boltwoodite [(Na)(UO₂)(HSiO₄) · 0.5H₂O] and uranyl carbonate solid phases such as cejkaite [Na₄ (UO₂)(CO₃)₃] and rutherfordine [UO₂(CO₃)] in addition to gummite and schoepite [(UO₂)₈O₂(OH)₁₂(H₂O)₁₂], [UO₂(OH)₃ (beta)]. Na-boltwoodite, cejkaite, gummite, schoepite, and [UO₂(OH)₃ (beta)] were present in all of the conditions tested while rutherfordine was seen only in the presence of bicarbonate in the solution. The formation of uranyl hydroxide minerals, schoepite and [UO₂(OH)₃ (beta)], were favored under bicarbonate-free and low 2.9 mM bicarbonate concentrations; however, their saturation indices decreased as the concentration of bicarbonate ions increased for both 0.1% and 5% of NH₃. Overall, saturation indices for Na-boltwoodite were found to be the highest for all of the conditions tested. This correlates with previous geochemical equilibrium modeling results based on the samples analyzed 24 h after NH₃ treatment suggesting Na-boltwoodite as the predominant phases even in the presence of the high carbonate concentration (Szecsody et al. 2013). The increase in silica concentration from 50 mM to 100 mM has not affected the speciation and the saturation indices of formed minerals (Figure 5S - 10S).

Conclusions

Our results provide details on the effect of various silicon, aluminum and bicarbonate concentrations on the removal of uranium from the supernatant solution as a result of silica polymerization reactions. The removal efficiency of uranium was not significantly affected by the different U(VI) concentrations tested (0.5 mg/L and 2.0 mg/L). From the experiments, it is evident that solutions with higher concentrations of Si, Al and bicarbonate tended to have greater removal efficiencies of U(VI). The highest percent 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 5 mM resulted in 9.5%-16% higher U(VI) removal compared to values obtained with 2.8 mM 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. Diagrams with aqueous uranium species plotted as a function of pH showed $\text{UO}_2(\text{CO}_3)_3^{-4}$ and Na-boltwoodite to be present as the higher uranyl aqueous and mineral species presence in the solutions. The characterization of the solid samples using scanning electron microscopy and energy dispersive spectroscopy conclusively showed that solid uranium phases were being formed with the precipitation of samples. Under the tested conditions, the importance of bicarbonate concentration could be inferred based on the lack of any distinguishable uranium phase in the low bicarbonate samples. This reasoning is consistent with the aforementioned finding that uranium removal from the supernatant solution increased with the increase in bicarbonate. Despite the qualitative evidence of solid uranium phases, X-ray diffraction data produced no identification of the uranyl phases due to their low

concentrations. This analysis requires an increased uranium concentration to attempt to maximize the analyte yield. In addition, the research is ongoing to investigate the effect of divalent calcium and magnesium ions on the co-precipitation process of U(VI) under conditions imitating the pore water composition typical for arid and semi-arid environments throughout the western United States. The results from these experiments are promising for the potential implementation of the NH₃ gas injection technology to sequester U(VI) in the deep vadose zone sediments.

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Table 1. 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

Figure 1

Figure 2

Figure 3

<i>Element</i>	<i>Point 1</i>		<i>Point 2</i>	
	<i>Wt%</i>	<i>At%</i>	<i>Wt%</i>	<i>At%</i>
<i>C-K_α</i>	13.35	22.92	03.06	07.04
<i>N-K_α</i>	06.28	09.25	05.16	10.17
<i>O-K_α</i>	38.09	49.09	26.08	45.01
<i>Na-K_α</i>	13.96	12.52	06.48	07.78
<i>Al-K_α</i>	00.76	00.58	00.84	00.86
<i>Si-K_α</i>	01.78	01.31	06.59	06.48
<i>Cl-K_α</i>	00.00	00.00	00.30	00.23
<i>U-M_α</i>	21.02	01.82	23.60	02.74
<i>K-K_α</i>	04.76	02.51	27.88	19.68

Figure 4

Figure 5

Figure 1. Percent removal of each element tested at variable bicarbonate and silica concentrations in 2.8 mM Al amended solutions containing 2 mg/L U(VI). (A) Removal of Si; (B) Removal of Al ; (C) Removal of U(VI) .

Figure 2. Percent removal of each element tested at variable bicarbonate and silica concentrations in 5 mM Al amended solutions containing 2 mg/L U(VI); A) Percent removal of Si concentrations from the solution mixture; B) Removal of Al concentrations from the solution mixture; C) Removal of U(VI) from the solution mixture; D) The effect of Al and HCO_3^- concentrations on the percent removal of U(VI); E) Percent removal of U(VI) from the solution mixture with no Si.

Figure 3. SEM image and EDS data for precipitates formed from solutions containing high bicarbonate (50 mM) concentration.

Figure 4. Comparison of diffraction data for nitratine to that of precipitates formed using high bicarbonate (50 mM) pore water solution.

Figure 5. Diagrams of uranium aqueous species and saturation indices of some of uranium-bearing mineral phases plotted as a function of pH for 0.1% of NH_3 (0.063 mol/L $\text{NH}_3(\text{aq})$). Sample composition includes 50mM of Si and varied HCO_3^- concentrations. The first row shows diagrams for HCO_3^- —free samples (A1, A2), the 2nd and 3rd row show the diagrams for 2.9mM (B1, B2) and 50mM of HCO_3^- (C1, C2).