

The Effect of Ca Ions on the Removal of U(VI) via *In-Situ* Ammonia Gas Injection at the Hanford Site 200 Area-14434

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ABSTRACT

This study investigates the mechanisms and effectiveness of U removal from the solution mixture replicating the pore water composition found at the Hanford Site vadose zone (VZ). A series of batch experiments were conducted to evaluate the effect of Ca concentrations at various molar ratios of silicon to aluminum, in the presence of several bicarbonate concentrations on the removal of U(VI) and other elements. Evidently, an understanding of the role of pore water constituencies on the removal of U(VI) is needed to predict the mineralogical changes and the formation of precipitates that would be created in the treated VZ soil. For the initial experiments, the complicated pore water composition was simplified to have only five major components in the test solutions: uranium, silica, aluminum, bicarbonate and Ca. The tests were carried out with varied Si concentrations to study different Si:Al molar ratios. The Al concentration was kept constant at 5 mM and bicarbonate concentrations varied between 0 and 100 mM. To evaluate the effect of Ca, the water composition included 5 mM or 10 mM of Ca ions.

The results indicated that the percentage of U(VI) removal was largely controlled by the Si/Al ratios and calcium concentrations. The percent of U(VI) removal increased as Si/Al ratios and calcium concentrations were increased. The higher Ca concentration correlated with higher U(VI) removal, ranging between 96%-99%, at low Si/Al ratios between 1 and 10. It was clear that the increase in Ca concentration correlated with higher removal of Si from the solution mixture. When the Ca concentration was increased up to 10 mM, the percentage of silica removal at Si:Al ratio 1, the lowest ratio investigated in this study, was increased to 93-99%. In all of 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 diminutive or not observed. The results suggest the effectiveness for the potential implementation of NH₃ gas injection for the remediation of the U(VI)-contaminated VZ.

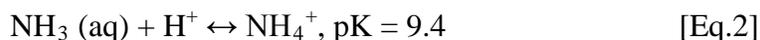
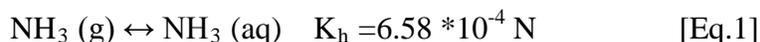
INTRODUCTION

Past uranium-plutonium extraction and enrichment processes at the Hanford Site 200 Area have left approximately 200,000 kg of legacy uranium contamination in the vadose zone (VZ). This uranium is a potential source for groundwater contamination and a risk to receptors through water uptake from contaminated wells or discharges to surface water. Despite extensive remediation efforts initiated in the early 1990s, uranium groundwater plumes identified in multiple locations around the site have persisted for many years. Uranium is present in the VZ sediment as uranyl-carbonates (liebigite and rutherfordine), co-precipitated with carbonates and hydrous silicates and Na-boltwoodite. The dominate uranium species are stable ternary calcium-

uranyl-carbonate complexes, UO_2CO_3^0 , $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$, which are highly soluble and, therefore, mobile under VZ oxidizing conditions [1, 2].

The injection of gases is simple and inexpensive method for in situ treatment of heavy metals and radionuclide contamination, which commonly resides in the vadose zone. This method is more efficient and predictable than injection of liquid or solid reagents since gas can more effectively penetrate low permeability soil and sediments [3]. The injection of reactive gases, such as ammonia gas (NH_3), is a novel technology to effectively mitigate uranium contamination in the VZ and reduce the potential for radionuclide mobility in the subsurface. This technology is able to decrease the mobility of uranium species without water addition causing undesired downward contaminant migration. The VZ at Hanford 200 area is deep, having depths between about 150 and 200 feet (46m-61m), and composed of sediments such as quartz, plagioclase, orthoclase, muscovite, biotite, hornblende, illite, calcite, montmorillonite, chlorite, kaolinite, smectite and kaolinite [4]. All of these minerals may undergo dissolution reactions in the hyperalkaline conditions increasing elemental concentrations in porewater.

NH_3 is a highly soluble gas and its injection in the VZ causes the formation of ammonia hydroxide (NH_4OH) and a subsequent increase in pH. The NH_3 gas rapid partition into liquid results in the aqueous speciation reactions written as [4]:



Where K_h is the dimensionless Henry's Law partition coefficient and pK is the negative logarithm of the dissociation constant.

The alkaline conditions can greatly enhance the solubility rates of most Si-containing soil minerals such as feldspar and quartz present in the Hanford Site vadose zone. Chou and Wollast (1984[5]) previously illustrated that the rate of feldspar dissolution has been shown to increase by two to three orders of magnitude with an increase in pH from 8 to 12 at 23°C. 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 following decrease in pH as the system stabilizes and reaches natural equilibrium will cause uranium co-precipitation during the recrystallization of minerals. Szecsody et al, (2010b [6]) hypothesized that under alkaline conditions aluminosilicates originated from the dissolution of some specific clays might precipitate and coat surface of U-bearing phases. There is a need for a better understanding of the effects of pore water constituencies on the U co-precipitation process. Previous short-term laboratory evaluation showed a decrease in U mobility after ammonia gas injection in the low water content sediments [7]. This technology has significant uncertainty under the 200 Area VZ 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 solid phases. Particularly, what requires clarification is the role of major pore water constituents on the removal of uranium and the formation of precipitates after the NH_3 injection. This investigation is focusing on the effect of concentration ratios of silicon to aluminum, in the presence of various bicarbonate and

calcium concentrations, on the removal of U(VI) under conditions imitating the pore water composition of the Hanford Site 200 Area vadose zone.

MATERIAL AND METHODS

The composition of borehole 299-E33-45 pore water has been previously characterized for major cations (Ca^{2+} , Na^+ , K^+ , Mg^{2+} , Fe^{2+} , Al^{3+} , and Si^{4+}), anions (F^- , Cl^- , NO_2^- , Br^- , SO_4^- , NO_3^-), and pH [8]. In the test solutions used for these experiments, the pore water composition was simplified to contain only five elements such as silica, aluminum, uranium, bicarbonate and calcium. Previous studies confirmed the increase of Si concentrations in the sediments as high as 10 g L^{-1} caused by the injection of a concentrated NaOH solution through sediments [6]. The maximum concentration of Si in experiments with water-saturated column experiments using NH_3 -treated Hanford sediments was observed as 30mM [4]. So, the experimental test solutions were prepared in a wide range of Si concentration using 5 mM, 50 mM, 100 mM, 150 mM, 200 mM, and 250 mM to analyze different Si:Al ratios at varied between 0 mM and 100 mM bicarbonate concentrations. The Al concentration was kept constant at 5 mM. To evaluate the effect of calcium ions on the U(VI) removal, two concentrations of Ca were tested in the experiments, 5 mM and 10mM. The concentration of U(VI) in the experimental solutions was kept constant at 2 ppm. Experimental matrix is presented in TABLE 1.

TABLE 1. Experimental Matrix

Batch number	HCO_3^- , mM	Si:Al molar ratio (Ca=5mM and Ca=10mM)					
1	0	1	10	20	30	40	50
2	2.9	1	10	20	30	40	50
3	25	1	10	20	30	40	50
4	50	1	10	20	30	40	50
5	75	1	10	20	30	40	50
6	100	1	10	20	30	40	50

Stock solutions of 422.24 mM of Si ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$), 50mM of aluminum ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), 400mM bicarbonate (KHCO_3), and 1250mM of Ca ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) were used as starting reagents for solutions formulations. Uranyl nitrate hexahydrate was used as a source of U(VI).

For each bicarbonate concentration, six different test solutions were prepared at different Si:Al ratios by mixing measured volumes of the silicate and aluminum stock solutions. The mixture was then amended with the measured volume of appropriate bicarbonate stock solution and the pH of the resulting solution was adjusted to 8.0 by titrating with concentrated nitric acid. This pH was previously measured in the pore water composition [8]. The deionized water (DIW) was added to bring the final volume of the each test solution to 50mL. Then, NH_3 gas (5% NH_3 in 95% N_2) was injected into each solution through 20 μm pores of a metal gas sparger (Mott Corporation) until the pH of the solution reached a value of approximately 11. Three test samples, each with a volume of 5 mL, were extracted from each test solution and transferred to individual polyethylene 15mL tubes and then spiked with corresponding concentration of Ca and U(VI). Control samples amended with U(VI) at concentrations of 2 ppm were prepared in DIW

to test for U(VI) losses from the solutions due to sorption to tube walls and caps. All control and experimental tubes were kept in an incubator/shaker at 100 rpm and at a temperature of 25°C. After two days, tubes were centrifuged for 5 minutes at 2000 rpm and supernatant solutions were analyzed for U(VI), Si, Al, and Ca. Si, Al, and Ca were measured using an inductively coupled plasma optical emission spectrometer (ICP-OES, OPTIMA 7300DV, Perkin-Elmer). Aqueous uranium U(VI) concentrations were analyzed via a Kinetic Phosphorescence Analyzer KPA-11 (Chemcheck Instruments, Richland, WA). For analysis with the KPA, an aliquot was extracted from the supernatant of each test sample and diluted with 1% nitric acid between 5 to 100 times. For analysis with the ICP-OES, an aliquot extracted from the supernatant of each test sample was diluted in conical polypropylene tubes between 100 to 200 times with DIW. For better accuracy, the concentration of elements was analyzed using different dilutions factors.

The predominant uranium species in the solutions were calculated via Visual MINTEQ equilibrium modeling software (v. 3.0, maintained by J.Gustafsson at KTH, Sweden), and updated with the Nuclear Energy Agency’s thermodynamic database for uranium [2] and calcium-uranyl-carbonate complexes from [9]. The software calculated uranium speciation in the elements of interest and saturation indexes for solid phases.

RESULTS

Experimental results were evaluated based on the percent removal of the elements of interest: U(VI), Si, Al, Ca, and inorganic carbon (IC). Fig.1 – Fig.3 depict the percent removal of these elements in solutions where pH was increased up to 11 as a result of NH₃ gas injection.

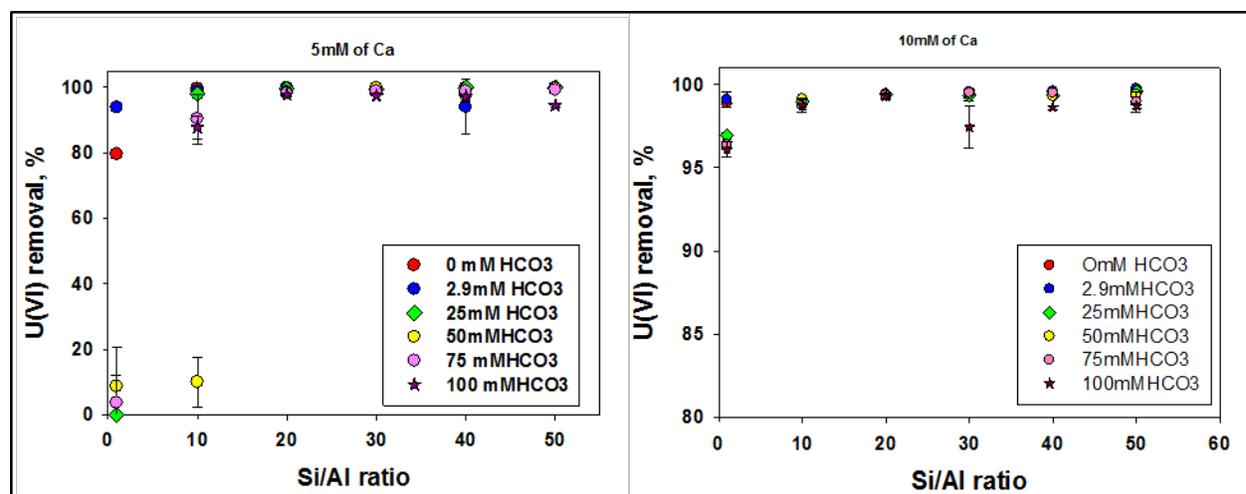


Fig.1. Removal of U(VI) in the solution mixture prepared with 5 mM and 10 mM of Ca.

The results indicated that the percentage of U(VI) removal was largely controlled by the Si/Al ratios and calcium concentrations. The percent of U(VI) removal increased as Si/Al ratios and calcium concentrations were increased. As noted from the results, the higher Ca concentration correlated with greater U(VI) removal, ranging between 96%-99%. This was especially notable at low Si/Al ratios between 1 and 10 (Fig. 1). Without Ca there was no observed reduction in the U(VI) concentration in the supernatant solutions at low Si/Al ratios [10]. Besides, starting from the Si/Al ratio 20 (Si ≥100mM), the removal of U(VI) yielded 98%-99%, which seemed to

have overshadowed previous results without Ca ions introduced in the solution. Compare to samples without Ca, samples amended with Ca have not revealed significant changes in the percent removal of U(VI) in respect to increasing bicarbonate concentrations [10].

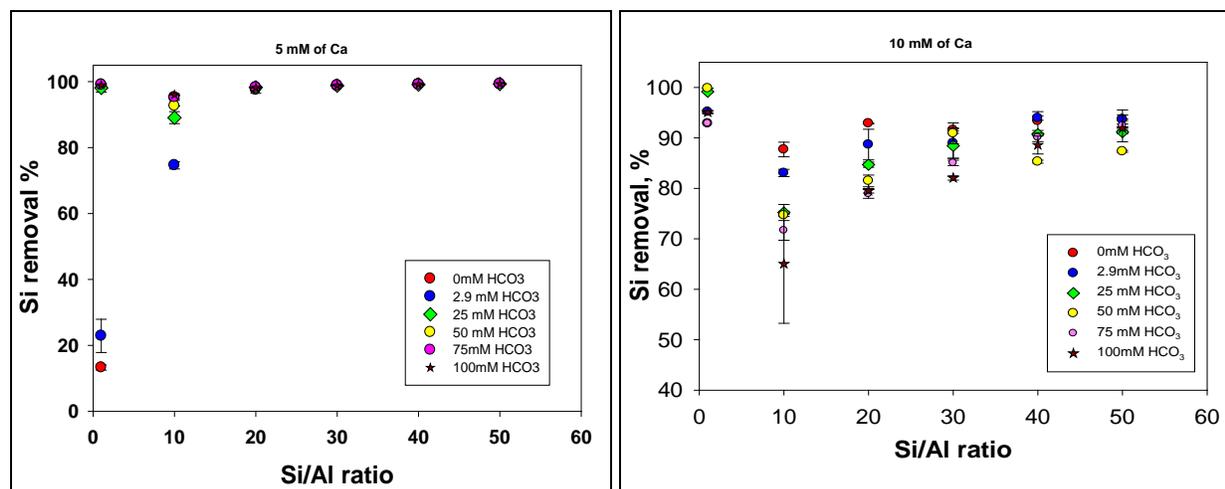
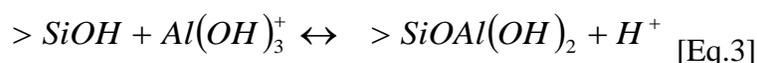


Fig. 2. Removal of Si in the solution mixture prepared with 5 mM of Ca and 10mM of Ca.

Similar observations were made for Si removal (Fig. 2). The results suggest that the percent removal of Si increases with an increase in Si concentration in solution and the increase in Ca concentration correlated with higher removal of Si from the supernatant of the solution mixtures at low Si/Al ratios. When the Ca concentration was increased up to 10 mM, the percentage of silica removal at Si:Al ratio 1, the lowest ratio investigated in this study, was increased to 93-99%. In all of 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 diminutive or not observed.

Under alkaline conditions, $Al(OH)_4^-$ is the dominant species for Al. Its concentration at Si/Al = 1 showed some variability, but when the concentration of Si increased at Si/Al molar ratio ≥ 10 , Al concentration dropped to almost undetectable level. Monomeric silica reacts with Al^{3+} ions following its precipitation due to a reaction between $Si(OH)_4$ and crystalline $Al(OH)_3$. When the silica concentration is below the solubility of amorphous silica in water, no polymerization occurs except when alumina is added. Iler (1979[11]) proposed that SiO_2 surfaces exposed to solutions containing aluminum formed aluminosilicate surface complexes by reaction with the hypothetical stoichiometry:



The formation of aluminosilicate chains upon mixing monosilicic acid and $Al(OH)_3$ acting as nuclei or “seeds” can accelerate Si polymerization reactions. The presence of aluminum results in an entire armored surface coating, which is extensive enough to reverse a net negative Si surface charge to positive [11,12].

According to speciation modeling, the dominant Ca species in the solution at the tested conditions are free Ca^{2+} ions, CaHCO_3^+ , CaCO_3 with minor formation of CaNH_3^{+2} , $\text{Ca}(\text{NH}_3)_2^{+2}$ and Ca-U-CO_3 . The speciation modeling hasn't predicted the formation of calcium silicate at this elevated pH condition and the removal of Ca^{2+} ion from the solution apparently is mostly due to the precipitation of calcium carbonate (Fig. 3).

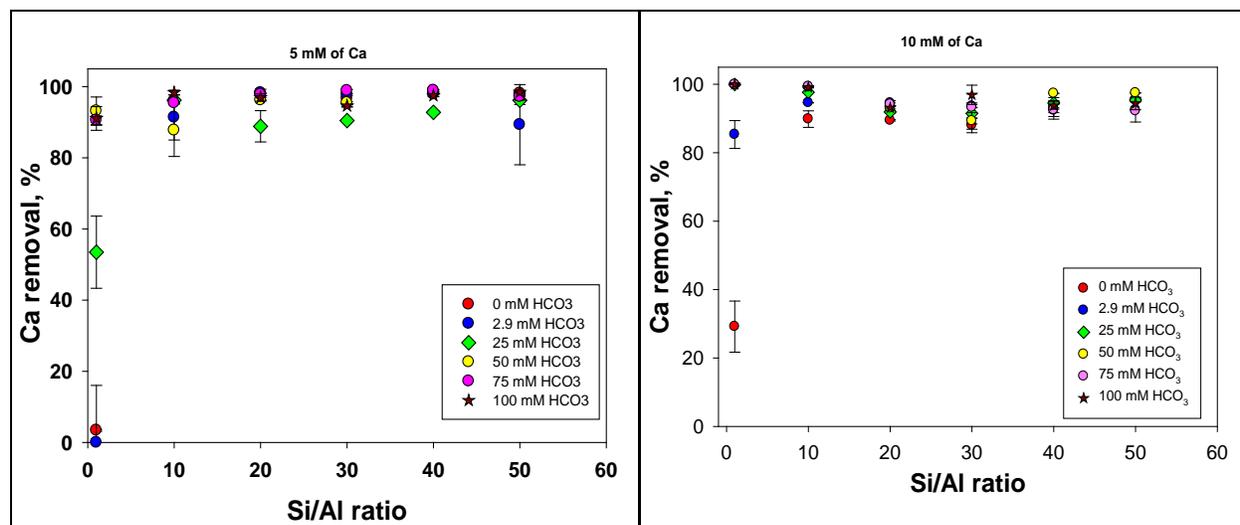


Fig. 3. Removal of Ca from the solution mixture prepared with 5 mM of Ca and 10mM of Ca.

The precipitation of calcium carbonate controls the removal of inorganic carbon from the aqueous solution. Speciation modeling suggested that calcium carbonate accounts for 19.1-68.1%, 14.1-20.5%, and 8.0-19.0% of the total bicarbonate concentrations present initially in the solution at the 3 mM, 25 mM and 50-100 mM range, respectively. However, experimental results showed that the removal of inorganic carbon is much higher reaching at some instances 80%. We hypothesized that the discrepancies between MINTEQ- predicted formation of CaCO_3^{2-} and the experimental removal of inorganic carbon are coagulation and encapsulation within the silicate polymer that retained carbonate solids with polymerized silica gel. Precipitation of CaCO_3 and its encapsulation within Si sols cause changes in the carbonate system due to the decrease in the calcium carbonate saturation state. It is especially noticeable at higher Si and HCO_3^- concentrations in solution. In previous studies, silica uptake onto calcium carbonate was shown to increase in higher-ionic-strength solutions and higher silica aqueous concentration [13].

According to the speciation modeling predictions, at 0 mM HCO_3^- , U(VI) is present in the solution dominantly as $\text{UO}_2(\text{OH})_3^-$. In the solutions amended with bicarbonate, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ and $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ are the predominant species accounting for 30%- 84% of the total uranium species. Saturation indexes showed that potential U-bearing secondary phases as becquereline, gummite, rutherfordine, and schoepite are undersaturated at all conditions tested. However, speciation modeling predicted the formation of aragonite and calcite in addition to various aluminosilicate and aluminum hydroxide solid phases created out of elements present in the solution. These solid phases can serve as potential nuclei that trigger Si polymerization reactions. This leads to the co-precipitation of U solids (as U hydroxide and/or Ca-U-CO_3) within the amorphous structure of Si-Al-CaCO_3 precipitates.

CONCLUSIONS

Our results provided details on the effect of various Si/Al ratios and calcium concentrations on the removal of uranium from the synthetic solution mixture. From the experiments, it is evident that solutions with higher concentrations of Si and Ca tended to have greater removal efficiencies of U(VI) reaching up to 98-99%. In the presence of 5 mM and 10mM of Ca, the removal of U(VI) have overshadowed previously obtained results without Ca ions introduced in the solution. When the Ca concentration was increased up to 10 mM, the percentage of silica removal at Si:Al ratio 1, the lowest ratio investigated in this study, was increased to 93-99%. Higher Si removal in the presence of Ca^{2+} ions was probably due to silica coagulation by calcium ions leading to precipitation of those elements from the tested solutions [11]. However, the geochemical equilibrium modeling hasn't predicted the formation of calcium silicate species limiting Ca species only to CaHCO_3^+ , CaCO_3 , CaNH_3^{+2} , $\text{Ca}(\text{NH}_3)_2^{+2}$, and Ca-U- CO_3 complexes. Overall, the formation of precipitate always correlated with the removal of U(VI), Si, Al and Ca from the solution. If no precipitate formation was observed, there was no U removal from the supernatant solution. Visual Minteq modeling predicted that U(VI) present in solution dominantly as $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ and $\text{CaUO}_2(\text{CO}_3)_3^{-2}$ and Ca-UO₂-CO₃ ternary complexes constitute up to 84% of uranyl species. The solid phase characterizations of uranium-bearing precipitates prepared with Ca are ongoing by means of X-ray diffraction and SEM/EDS techniques. These results further our understanding of uranium removal after the ammonia gas injection in the Hanford VZ.

ACKNOWLEDGEMENTS

Funding for this work was provided by the U.S. Department of Energy Office of Environmental Management under grant DE-EM0000598.

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