

The Effect of Si and Al Concentration Ratios on the Removal of U(VI) under Hanford Site 200 Area Conditions-12115

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ABSTRACT

Injection of reactive gases, such as NH_3 , is an innovative technique to mitigate uranium contamination in soil for a vadose zone (VZ) contaminated with radionuclides. A series of experiments were conducted to examine the effect of the concentration ratio of silicon to aluminum in the presence of various bicarbonate concentrations on the co-precipitation process of U(VI). The concentration of Al in all tests remained unchanged at 2.8 mM. Experiments showed that the removal efficiency of uranium was not significantly affected by the different bicarbonate and U(VI) concentrations tested. For the lower Si:Al molar ratios of 2:1 and 18:1, the removal efficiency of uranium was relatively low ($\leq 8\%$). For the Si:Al molar ratio of 35:1, the removal efficiency of uranium was increased to an average of $\sim 82\%$ for all bicarbonate concentrations tested. At higher Si:Al molar ratios (53:1 and above), a relatively high removal efficiency of U(VI), approximately 85% and higher, was observed. These results demonstrate that the U(VI) removal efficiency is more affected by the Si:Al molar ratio than by the bicarbonate concentration in solution. The results of this experiment are promising for the potential implementation of NH_3 gas injection for the remediation of U(VI) –contaminated VZ.

INTRODUCTION

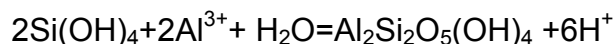
Uranium - plutonium extraction and enrichment processes at the 200 East and 200 West Areas at DOE's Hanford Site have resulted in the release of $\sim 200,000$ kg of uranium to the ground surface [1]. This release of radioactive materials onto the ground's surface have directly impacted the vadose zone (VZ) by creating a potential future source for groundwater contamination and risk to receptors through water uptake from contaminated wells or discharge to surface water. Despite extensive remediation efforts initiated in the early 1990s, persistent groundwater plumes containing uranium concentrations exceeding 30 ppb, the U.S. Environmental Protection Agency (EPA) standard for drinking water supplies, have formed in multiple locations at Hanford. The protection of water resources across the DOE complex from contaminated groundwater resulting from past, present, and future operations at the Hanford Site, is a key element of the overall Hanford cleanup efforts. One of the elements of these efforts is the evaluation of various treatment alternatives targeted to reduce potential contaminant migration from the VZ to the groundwater. Injection of reactive gases such as NH_3 is an innovative technology for a VZ contaminated with radionuclides, shown to mitigate uranium contamination in soil. The injection of a NH_3 gaseous mixture causes the

formation of NH_4OH and a subsequent increase in pH. This manipulation can significantly alter the pore water chemistry and promote the formation of various aluminosilicates during recrystallization of minerals followed by co-precipitation of U(VI) [as uranyl (UO_2^{2+})] and Al at higher pH conditions. These chemical reactions can potentially control the mobility of uranyl cations in soil systems since co-precipitated contaminants are less available for migration [2]. This study evaluates the role of major pore water constituents such as Al and Si, and their concentration ratios in the presence of various concentrations of bicarbonate on the formation of uranium – bearing precipitates created after NH_3 gas injection.

SILICATE CHEMISTRY: INTERACTION WITH ALUMINUM AND URANIUM

Silicates are one of the most abundant compounds found in the earth crust. The soluble form of silica is monomeric with one silicon atom formulated as $\text{Si}(\text{OH})_4$, which is generally called monosilicic acid. The structure of silicates involves silicon surrounded by four oxygen atoms and the silicon atom shares an electron with each of the four oxygens. Having two valence electrons, oxygen can form an additional bond with another metal atom or a bond with second silicon. This possibility leads to polymerization reactions initially forming polysilicic acids, the hydrated silica polymers with molecular weights up to $\sim 100,000$ consisting of dense spherical particles less than about 50A in diameter. The highly polymerized species form colloidal particles with a size larger than 50A. The soluble silica remains in the monomeric state for a long period of time with a concentration lower than about $2 \times 10^{-3}\text{M}$, but polymerizes rapidly at higher concentrations, initially forming polysilicic acids of low molecular weight and then larger polymeric species or colloidal silica particles. Under alkaline conditions from pH 9 to 10.7, the solubility of amorphous silica is increased due to the formation of silicate ion in addition to the monomer that is in equilibrium with the solid phase. Silica polymerization is a reversible process. At pH above 10.7, the amorphous silica dissolves to form soluble silicate, and no amorphous solid remains in equilibrium [3].

Aluminate ions make important modifications of the silica surface. Hingston and Raupach [4] investigated the reaction between aqueous silica and the crystalline aluminum hydroxide [$\text{Al}(\text{OH})_3$] surface, which resulted in multiple layers of silicic acid that eventually sorbed onto the aluminum hydroxide surface, with maximum sorption at pH 9.2. Monomeric silica, $\text{Si}(\text{OH})_4$ reacts with Al^{3+} ions, and precipitate forming colloidal aluminum silicate of the halloysite compositions.



As a result of the reaction, several layers of SiO_2 were built up with the simultaneous decrease in pH of the suspension [3].

The behavior of uranium in the solution is greatly affected by the presence of carbonates since uranium tends to form carbonate complexes with carbonate ions. At high pH (between 9 and 11) and in the presence of bicarbonate, most actinides reside as negatively charged hydroxide or carbonate (CO_3^{2-}) species, such as $(\text{UO}_2)_2(\text{OH})_5^-$

and $\text{UO}_2(\text{CO}_3)_3^{4-}$. The surfaces of most solids are negatively charged at these pH values and are unlikely to adsorb ionic species, which can explain why the formation of negatively-charged, highly soluble U(VI)-carbonate species typically suppress U(VI) sorption in alkaline conditions. An increase in pH following the injection of ammonia gas in a VZ has been proposed to affect mineral phases, which can potentially induce the dissolution of silica and aluminum from soil minerals [2]. The subsequent decrease in pH due to natural conditions would lead to precipitation of aluminosilicates that could possibly coat adsorbed U(VI) species in a process called co-precipitation.

MATERIALS AND METHODS

The composition of borehole 299-E33-45 pore water that has been previously characterized in terms of concentrations of major cations (Al, Ba, Ca, Fe, K, Mg, Na, Si, Sr), anions (NO_3 , F, NO_2 , Cl, SO_4 , PO_4 , HCO_3), and pH [5], was used to prepare the Synthetic Pore Water (SPW) formulation. In initial experiments, only four components were used in the test solutions: uranium, silica, aluminum and bicarbonate. Past observations showed that the concentration of Al released during the dissolution from soil by 1 mol L^{-1} NaOH is relatively small, resulting in 5.1 mM of Al in the soil solution [6]. On the other hand, as a result of increasing soil pH, the concentration of Si in pore water was observed to be as high as 10 g L^{-1} [2]. For these reasons, the tests were performed with varied Si concentrations to study different Si:Al molar ratios, including 1.8:1, 18:1, 35:1, 53:1, 70:1, and 88:1. The concentration of Al in all tests remained unchanged at 2.8 mM. This concentration of Al represents a value that is the highest observed Al concentration in the pore water of the Hanford Site 200 Area, which is about 0.8 mM Al, and the concentration of Al released during the dissolution from soil by 1 mol L^{-1} NaOH reported by Qafoku et al. [6], which was 5.1 mM Al.

Stock solutions of Al (28.4 mM), Si (350 and 420 mM), and HCO_3^- (29 and 100 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 (Table I). The stock solution of uranyl nitrate dissolved in DIW was prepared from uranyl nitrate hexahydrate 1000 ppm stock (Fisher Scientific).

Table I. Stock Solutions Used to Prepare Various Si/Al Molar Ratios

Stock solutions	
Solutions	Concentration
Aluminum	28.4 mM
Silicate	350-420 mM
Bicarbonate	29 mM
	100 mM
Uranium	100 ppm

Two relatively low concentrations of U(VI) (0.5 ppm and 2.0 ppm) and four bicarbonate concentrations (0 mM, 2.9 mM, 25 mM, and 50 mM) were tested. These U(VI)

concentrations were considered as preliminary concentrations to test the potential remediation technique of NH₃ gas injection into contaminated solutions.

For each bicarbonate concentration, six different test solutions were prepared. Each of these test solutions had a different molar ratio of Si:Al, prepared by mixing a measured 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). The pH of the resulting solution was adjusted to 8 by titration with concentrated nitric acid, and DIW was added to each test solution so that each test solution had a total final volume of 50 mL. The pH value of 8 was previously observed in pore water composition in the Hanford Site 200 Area VZ [5]. After that, NH₃ gas (5% NH₃ in 95% N₂) 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. Then, six test samples, each with a volume of 5 mL, were extracted from each test solution and added to individual polyethylene 15mL 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 kept in an incubator/shaker at 100 rpm and at a temperature of 25 °C. After two days, the solutions were centrifuged for 5 minutes at 2000 rpm and analyzed for U(VI), Si, and Al.

There were a total of eight experimental sets, each with a different combination of U(VI) concentration and bicarbonate concentration. Each set had six different test solutions (each test solution with a different Si:Al molar ratio), for a total of forty eight test solutions. A description of the experimental matrix is shown in Table II.

Table II. Experimental Matrix

Batch number	HCO ₃ , mM	Si:Al molar ratio (Al=2.8mM)					
		1.8	18	35	53	70	88
1	0	1.8	18	35	53	70	88
2	2.9	1.8	18	35	53	70	88
3	25	1.8	18	35	53	70	88
4	50	1.8	18	35	53	70	88

The sodium metasilicate used to prepare the silicate stock solution has a high solubility in water, up to 61 wt % (percent by weight) at 30°C. However, the experiments were run by limiting the Si:Al molar ratio to a maximum of 88:1, which corresponds to a Si concentration of about 7.0 g L⁻¹.

ANALYSIS PROCEDURES

Samples of the supernatant from each vial were analyzed to determine the remaining U(VI) concentration in each solution using a Kinetic Phosphorescence Analyzer KPA-11 (Chemcheck Instruments, Richland, WA) instrument, and to determine the remaining Al and Si concentrations in each solution, using inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) (PerkinElmer). In addition, the accuracy of the initial Al and Si stock solutions, prepared by weight, were tested with ICP-OES.

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 to 100 times. For analysis with the ICP-OES instrument, an aliquot was extracted from the supernatant of each test sample and diluted 30 times with DIW in polypropylene tubes.

RESULTS AND DISCUSSION

As discussed above and as outlined in the experimental matrix in Table II, eight sets of experiments with two different uranium concentrations and four different bicarbonate concentrations were performed. Presented results are based on the percentage removal of the elements of interest: U(VI), Al and Si. The results of the analysis are summarized in the following plots. Fig. 1 represents the percent reduction of Si in solutions that had U(VI) concentrations of 0.5 ppm and 2 ppm.

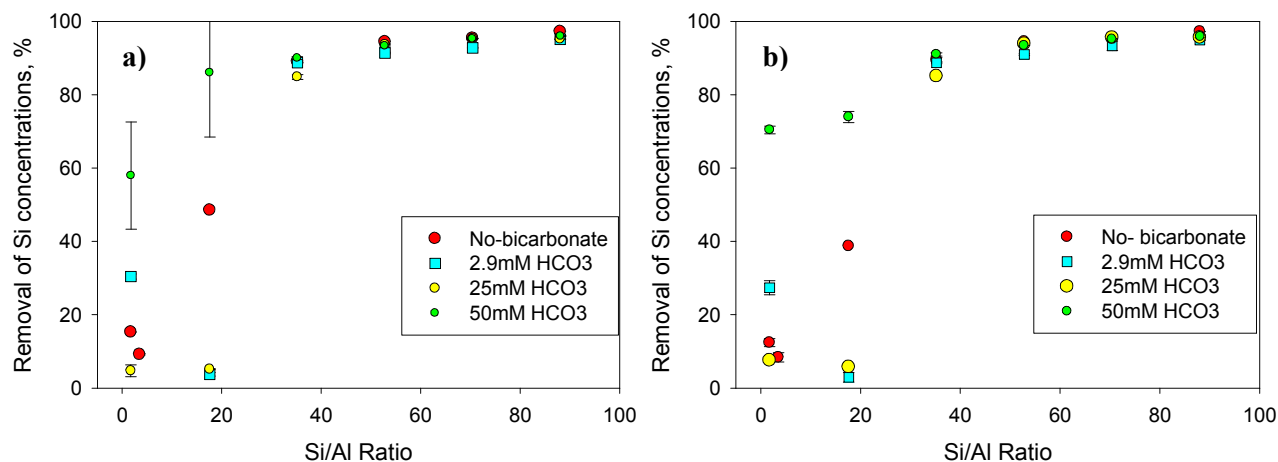


Fig. 1. Reduction of Si concentration in solution for U(VI) of a) 0.5ppm b) 2ppm.

From Fig. 1, a reduction in Si concentration can be observed for most of the molar ratios of Si:Al. The experimental runs with Si:Al molar ratios below 35:1 had relatively low values in the range of 0-50% for the removal efficiency of Si concentration. The exception is 50mMHCO₃ set where the removal of Si concentration was observed 86±17.7% and 73.9±1.55% for 0.5ppm and 2ppm, respectively. On the other hand, the experimental runs with higher Si:Al molar ratios had relatively high removal efficiencies reaching up to 97% removal of Si concentration. Concentrations of bicarbonate (HCO₃⁻) up to 50 mM did not appear to alter the efficiency of removal of Si concentration at higher molar ratios of Si:Al. These results suggest that the percent removal of Si increases with an increase in Si concentration in solution until it is stabilized to a

constant value. Nevertheless, future experiments with higher HCO_3^- concentrations will be performed to provide further results for Si removal efficiency.

Fig. 2 corresponds to the percent reduction of Al in test solutions with U(VI) concentrations of 0.5 ppm and 2.0 ppm. For solutions that had no bicarbonate, the results for Al removal (Fig. 2) were found to be more consistent than the results for Si removal (Fig. 1) over the various molar ratios of Si:Al.

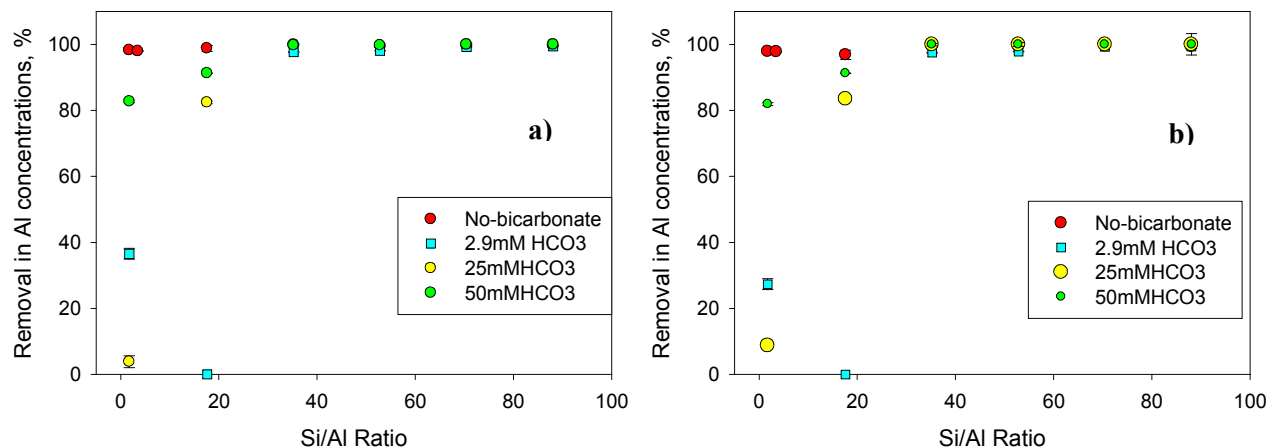


Fig. 1 Fig. 2. Reduction of Al concentration in solution for U(VI) of a) 0.5ppm b) 2ppm

From Fig. 2, it can be observed that different HCO_3^- (bicarbonate) concentrations in the test solutions affected the removal efficiency of Al. In solutions that did not contain HCO_3^- , the overall removal efficiency of Al was close to 98%-99% for all the molar ratios of Si:Al. However, when HCO_3^- was present in the solutions, percent removal of Al deviated. For the molar ratio of Si:Al at 1.8:1, the removal efficiencies for Al exhibited a decline except values observed for 50mM HCO_3^- . Solutions with higher concentrations of bicarbonate tended to have a sharper increase in removal efficiencies for Al. Future experiments with HCO_3^- concentrations of 75 mM, and 100 mM will provide more results and further conclusions. Fig. 1 and Fig. 2 both suggest that the increase in pH as a result of the NH_3 addition to the test solutions resulted in the removal of Si and Al from the supernatant solutions.

Fig. 3 presents the analyses for the percent removal of U(VI) from the test samples at the two different concentrations of U(VI) of 0.5 ppm and 2 ppm over the range of HCO_3^- concentrations tested. Results obtained for both of the tested U(VI) concentrations showed similar trends, indicating that the chosen range of initial U(VI) concentration did not appear to affect the efficiency of U(VI) removal.

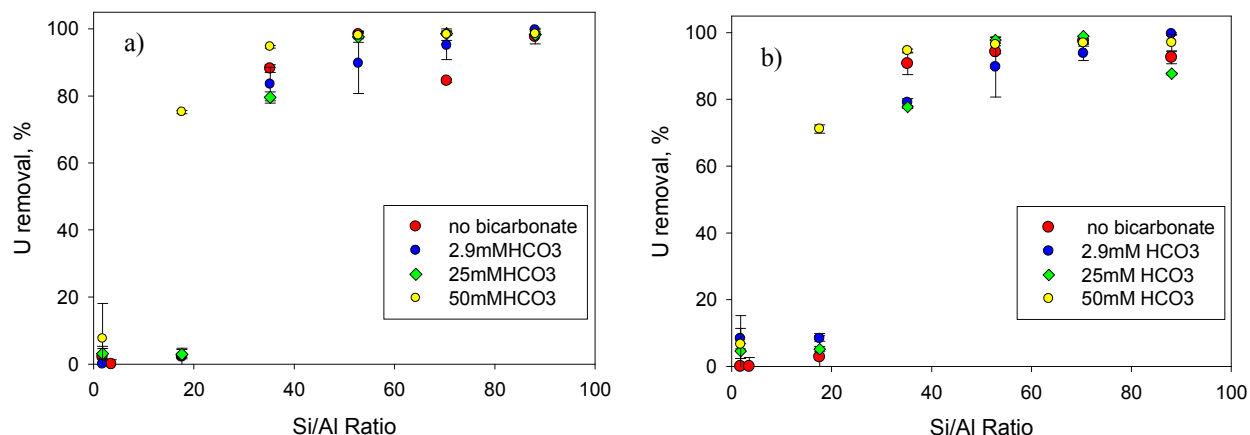


Fig. 3. Reduction of U(VI) concentrations a) 0.5ppm & b) 2ppm.

Data analysis of U(VI) reduction in the supernatant solutions, presented in Fig. 3, shows that the maximum percent removal of U(VI) was close to 98% for molar ratios of Si:Al over 53:1. For the HCO_3^- concentrations up to 25mM, at Si:Al molar ratios of 1.8:1 and 18:1, there was no observed reduction in the U(VI) concentration in the supernatant solutions; therefore, the process of U(VI) removal does not appear to be efficient when the concentration of Si is up to 10 times higher than the concentration of Al in solution. Samples containing 50mM HCO_3^- revealed significant changes in the percent removal of U(VI) compared to 25mM concentrations or less. Experimental runs for both concentrations of U(VI) that were tested followed the same trend: no observed reduction of U(VI) concentrations at Si:Al molar ratios of 1.8:1, then a percent removal of U(VI) between 72% -75% at a Si:Al molar ratio of 18:1, and then the highest percent removal of U(VI) at Si:Al molar ratios of 53:1, 70:1 and 88:1.

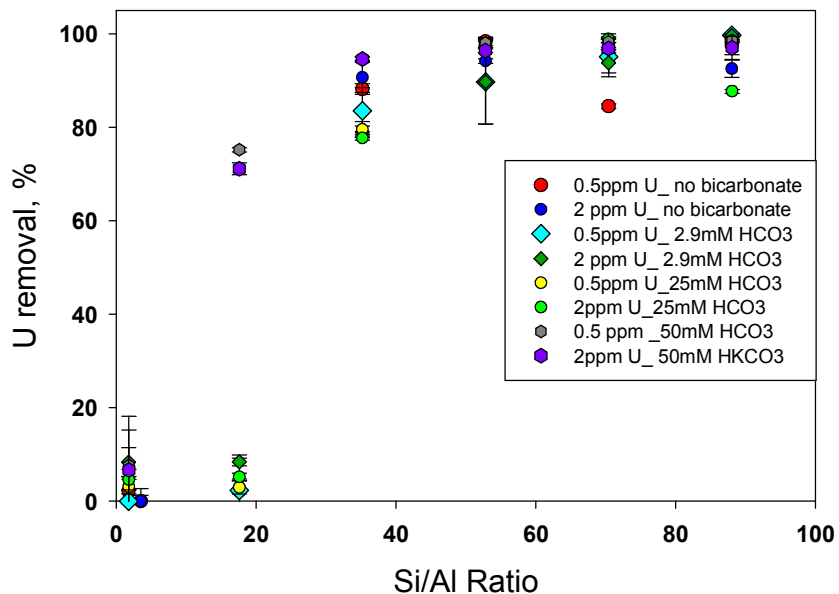


Fig. 4 illustrates the comparison between the eight sets of the experiments that have been performed thus far in the present study. It is evident that results of the eight sets of experiments follow a similar path with relatively small deviations between triplicate samples.

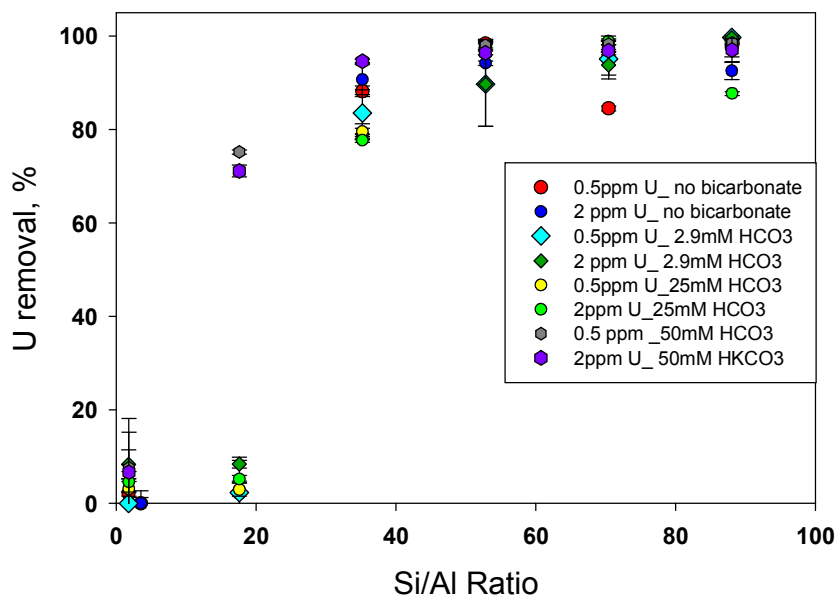


Fig. 4. Reduction of U concentration for initial U concentrations of 0.5 ppm & 2 ppm.

Future experiments will explore the effect of higher concentrations of bicarbonate (up to 100 mM) on the U(VI) co-precipitation process with Al and Si, and examine the mineralogy and microstructure of the formed precipitate.

CONCLUSION

From the data presented above, the removal efficiency of uranium (Fig. 3) was not significantly affected by the different bicarbonate concentrations tested thus far, which were 0 mM, 2.9 mM, 25 mM and 50mM bicarbonate. Moreover, the removal efficiency of uranium was not significantly affected by the different U(VI) concentrations tested: 0.5 ppm and 2.0 ppm. For bicarbonate concentrations up to 25mM at lower Si:Al molar ratios of 1.8:1 and 18:1, the removal efficiency of uranium was relatively low ($\leq 8\%$ or less). For the following Si:Al molar ratio of 35:1, the removal efficiency of uranium increased to average $\sim 82\%$ for all three initial bicarbonate concentrations tested. For the higher Si:Al molar ratios of 53:1, 70:1, and 88:1, the removal efficiency of uranium increased to between $\sim 85\%$ and $\sim 97\%$. At 50mM of HCO_3^- , there was no observed reduction of U(VI) concentrations at Si:Al molar ratios of 1.8:1, then a percent removal of U(VI) was increased to 72% -75% at a Si:Al molar ratio of 18:1.

For the test solutions with 2.9 mM and 25 mM bicarbonate, there was a decrease and then a sharp increase in Si removal efficiency over the first two tested molar ratios of Si:Al, followed by slightly increasing Si removal efficiency over the higher Si:Al molar ratios. At the lower Si:Al molar ratios of 1.8:1 and 18:1, the removal efficiency of Si was higher for higher bicarbonate concentrations. For the test solutions without bicarbonate, the removal efficiency of Al was relatively high, around 98%, for all the Si:Al molar ratios that had been tested. For the test solutions with 2.9 mM and 25 mM bicarbonate, a decrease and then a sharp increase in removal efficiency of Al was observed over the first three tested Si:Al molar ratios, followed by constant or slightly increasing Al removal efficiency over the higher Si:Al molar ratios. In addition, the removal efficiency of Al was higher for the solutions with the higher bicarbonate concentration of 50 mM. The removal efficiency of Al appeared to increase with increasing bicarbonate concentration. The formation of gel in the experimental tubes always correlated with the reduction of U(VI) and the removal of Si and Al from the solution. If no Si polymerization and gel formation was observed, there was no U removal.

From the above results, it appears that U(VI) removal efficiency is affected more by the Si:Al molar ratio in solution than by the bicarbonate concentration in solution. At the higher Si:Al molar ratios (35:1 and above), a relatively high removal efficiency of U(VI) (approximately 93% and higher) was observed. These results are promising for the potential implementation of NH_3 gas injection in the VZ for removal of U(VI) from pore water.

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