Ammonia gas Treatment for Uranium Immobilization at DOE Hanford Site – 17067

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ABSTRACT

Ammonia gas is a potential uranium (U) remediation technique for the vadose zone at the Department of Energy's (DOE) Hanford Site in Washington State via pH manipulation. The objective of this work was to investigate U removal from the aqueous phase and mineral dissolution with either NaOH or NH_4OH in order to understand ammonia as a remediation technique for the vadose zone. Batch experiments were designed to investigate the fate of U and mineral dissolution upon treatment with either NaOH or NH_4OH. These experiments investigated mineral dissolution and U partitioning in the presence of pure minerals (quartz, kaolinite, illite, montmorillonite, muscovite) and sediments relevant to the Hanford site in either NaCl or synthetic groundwater formulated based on the Hanford site groundwater components. Analysis of mineral dissolution via measurement of major cations has demonstrated that there is a significant increase in dissolution of minerals with basic treatment and likely greater secondary precipitation for the NH_4OH as compared to NaOH treatment for clay minerals and Hanford sediments.

INTRODUCTION

The Department of Energy's (DOE) Hanford site in Washington State has deposited over 200,000 kg of uranium (U) into the vadose zone [1, 2]. This release occurred largely as a result of improper disposal of waste from plutonium production during World War II and the Cold War. Further, U is mobile within the site due to oxidizing conditions and the presence of carbonate creating highly mobile uranyl carbonate species. For example, the partitioning coefficient (K_d) for U was previously measured in the range of 0.11 – 4 mL/g at pH 8 for Hanford sediments and groundwater and the retardation factor was measured at 1.43 [2, 3].

Moreover, the Hanford vadose zone is 255+ feet thick with contamination measured down to 170 feet below the ground surface [4]. Therefore, there is a desire to create a remediation option that does not input additional liquid to the vadose zone as this could increase flux of U to the groundwater below. Of the remediation methods that the DOE is currently considering, ammonia gas injection appears to be a favorable option. Gas injection has been previously described as a viable remediation technique for inorganic radionuclides because they are highly affected by solution chemistry [5, 6].

The goal of the remediation technique is to remove U from the aqueous phase by raising the pH of the system leading to immobilization as insoluble precipitates or

strongly sorbed species. Basic injections, including the injection of the weak base NH_3, may lead to the slow dissolution of silica-containing minerals such as quartz, montmorillonite, muscovite and kaolinite [3, 7-9]. This results in an increase in dissolved Si^{4+} and Al^{3+} as well as small increases in Na^+, K^+, $Fe^{2+/3+}$, Cl^-, F^- and SO_4^{2-} [3, 9]. Moreover, Ca^{2+} increases were reported in column experiments following injection of U + 0.1 M NaOH + 1 M $NaNO_3$ [3]. The dissolution of these minerals will ultimately buffer the pH of the system [3, 10].

However, it must be noted that geochemical changes within the subsurface are often temporary unless they are moving the system towards its natural equilibrium. The injection of ammonia gas for remediation is designed to temporarily raise the pH of the aqueous phase to dissolve natural aluminosilicate minerals. Based on preliminary laboratory scale experiments, it is expected that the system may reach a pH of 11 – 13 [9]. Then, as the system returns to a neutral pH as the ammonia evaporates, U is expected to be immobilized as part of a co-precipitation process with aluminosilicate minerals. As ammonia gas evaporates and the pH returns to neutral, there are two phenomena that are expected to decrease the mobility of U (1) U precipitation as solubility of Si, Al and similar ions decreases and (2) U (co)precipitates are coated with non-U, low solubility precipitates. Some of the low solubility precipitates that are expected to form include cancrinite, sodalite, hydrobiotite, brucite and goethite [11-14].

It is important to understand the impact of mineral dissolution and secondary precipitation processes on the fate of U during and after remediation. The objective of this research is to investigate the partitioning of U and the mineral dissolution upon pH manipulation with base treatment via addition of either NaOH or NH_4OH. Experiments focused on simplified batch experiments with pure minerals (quartz, kaolinite, illite, montmorillonite, muscovite) and Hanford sediments in order to determine the minerals controlling the dissolution and precipitation processes for the Hanford sediments.

MATERIALS AND METHODS

Materials

Experiments were conducted with the minerals kaolinite (Alfa Aesar), illite (IMt-2, Clay Minerals Society), montmorillonite (SWy-2, Clay Minerals Society), muscovite (Ward Scientific, <2 mm size fraction) and quartz (Ottawa Sand Standard passed through 20-30 mesh, Fisher) due to their significance at DOE's Hanford site. Montmorillonite, muscovite and kaolinite are common in the clay-sized fraction of sediments at the site and were previously observed to undergo significant dissolution under basic conditions [9]. Quartz represents the most significant fraction of the bulk sediments [4]. Additional experiments were also conducted with clean sediments collected by Dr. Jim Szecsody from the ERDF pit at a depth of 6.1 meters for comparison. Further characterization of this sediment has been published previously [3].

Minerals and sediments were washed and equilibrated with the either NaCl or synthetic groundwater prior to experiments based on the methods outlined in Table I below. Following the steps in Table I, the solids were dried at 35°C for ~3 days and lightly crushed with a mortar and pestle to homogenize. Surface area for the aforementioned minerals was measured in m^2/g based on the BET method (Table II). Two solutions were formulated to describe the Hanford groundwater, (1) a simplified synthetic groundwater as described in Table II and (2) NaCl solution of similar ionic strength (~3.2 mM) for comparison. The simplified synthetic groundwater in Table III is based on correspondence with Dr. Szecsody and previous work [15].

TABLE I: Summary of Mineral Washing Methods

Mineral	Method	Reference
Quartz (Ottawa Sand)	(1) Mix 100 g/L suspension in 0.01 M NaOH for 60 minutes, (2) Centrifuge, decant, replace liquid with 0.01 M HCl, mix 60 minutes, (3) Centrifuge, decant, replace with Nanopure (>18 MΩ) H_2O and mix 3 minutes, (4) repeat step three two more times	[16]
Montmorillonite	(1) Mix 100 g/L suspension in 0.001 M HCl for 30 minutes, (2) Add 0.5 mL H_2O_2 and mix an additional 30 minutes, (3) Centrifuge 6 hours at 4500 rpm, decant aqueous and replace with 0.01 M NaCl (or synthetic groundwater) and mix overnight, (4) Repeat four times, (5) Centrifuge, decant and replace with Nanopure H_2O, (6) Repeat at least four times (until excess ions are removed)	[16]
Kaolinite	(1) Mix 100 g/L suspension in 1 M NaCl (or synthetic groundwater) for 30 minutes, (2) Centrifuge, decant and repeat four more times, (3) Centrifuge, decant and replace with Nanopure H_2O, (4) repeat four more times	[17]
Illite	(1) Mix 100 g/L suspension with 1 M NaCl (or synthetic groundwater) for three hours and allow to flocculate overnight, (2) Decant and replace with 1 M NaCl (or synthetic groundwater) and mix, (3) Repeat two more times, (4) Decant and replace with Nanopure H_2O, (5) Repeat until excess ions are removed	[18]

TABLE II: BET surface area for relevant minerals and Hanford sediments

Mineral ID	m²/g
Hanford Sediment	17.4
Quartz	0.046
Kaolinite	17.9
Muscovite	0.096
Illite	19.1
Montmorillonite	23.8

TABLE III: Synthetic groundwater composition with total ionic strength of 3.2 mM

Element	(mmol/L)
Na^+	1.1
K^+	0.22
Ca^{2+}	1.4
Mg^{2+}	0.6
HCO_3^-	1.32
Cl^-	3.9

Batch Experimental Protocol

Batch experiments were conducted in triplicate at pH ~7.5 in the presence of 100 g/L quartz, 5 g/L kaolinite, illite, muscovite, montmorillonite, or 25 g/L Hanford sediment and either synthetic groundwater (Table II) or NaCl at similar ionic strength (3.2 mM). An aliquot of U (Spex Certiprep, New Jersey) was added following equilibration of samples at pH ~7.5 to reach 500 ppb U. After equilibration with U for three days on an end over end tube revolver at 40 rpm (Thermo Scientific), a homogenous aliquot was removed for analysis for both controls (without mineral) and samples.

Samples were centrifuged at 5000 rpm for 30 minutes (18100 rcf, Thermo Scientific, Corvall ST 16R centrifuge) to remove particles >100 nm based on Stoke's law as described by Jackson [19]. Then, the supernatant was acidified in 1% HNO_3 (Fisher, ACS Plus) for analysis by kinetic phosphorescence analyzer (KPA-11, Chemchek) for U and inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin Elmer, Optima 7300 DV) for major cations (Ca^{2+}, Mg^{2+}, $Fe^{2+/3+}$, $H_4SiO_4^+$ as Si, Al^{3+}, Na^+, K^+). Al and Si were analyzed to track dissolution of the minerals throughout these experiments.

Following equilibration at pH ~7.5, the pH of each sample was raised with either 2.5 M NH_4OH or 2.5 M NaCl + 0.025 M NaOH. It must be noted that NaCl is included in the NaOH solution to maintain similar ionic strength for both solutions allowing for a more representative comparison. Samples adjusted with NH_4OH were immediately capped and wrapped with parafilm following addition to reduce

volatilization of NH_3 gas. Ammonia volatilization increases by an order of magnitude for every unit above pH 6.0 and, therefore, is expected to be higher in alkaline soil suspensions [20, 21]. The adjustment by either NH_4OH or NaOH allows for comparison of both options as a possible step to raise the pH (Thermo Scientific, 8175BNWP) during remediation of the subsurface. After adjustment, samples were equilibrated for three days before analysis as described above for U and major cations.

DISCUSSION

Mineral Dissolution

Fig. 1 represents dissolution of Hanford sediments as determined by aqueous Al and Si measurements in 25 g/L batch reactors in the presence of synthetic groundwater. Base treatment significantly increased both Si and Al concentrations in the aqueous phase as compared to initial conditions at pH 7.5. It should be noted that aqueous Al was below detection limits for ICP-OES for the initial conditions at pH 7.5 (LOD 41 ppb for Al). However, significantly greater Si is present in the aqueous phase than Al for all conditions. Previous work by Szecsody *et al*. noted that less Al was measured in the aqueous phase than Si with base treatment [3].
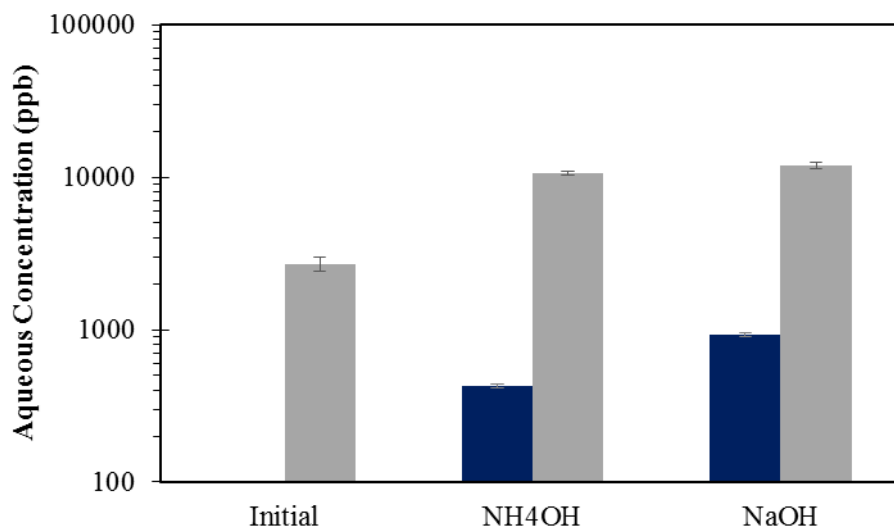

Fig. 1: Aqueous Al (blue) and Si (gray) dissolved from Hanford sediment (25 g/L) in synthetic groundwater with pH at ~11.5 via adjustment with either NaOH or NH_4OH or at ~7.5 to represent initial conditions prior to base treatment, Note: Al measurements at pH 7.5 were below detection limits

Figs. 2-5 compare pure mineral dissolution with respect to base treatment where Figs. 2-3 represent minerals in the presence of 3.2 mM synthetic groundwater and Figs. 4-5 in the presence of 2.5 M NaCl + 0.025 M NaOH. Mineral dissolution is estimated based on aqueous cation measurements by ICP-OES. Synthetic

groundwater is representative of the Hanford site groundwater, and NaCl represents the simplest chemical system at a similar ionic strength to synthetic groundwater. The NaCl solution allows for a better understanding of the fate of U without the more complex divalent cations present in the actual and synthetic groundwater.

In the presence of synthetic groundwater solution, the greatest fraction of Si entered the aqueous phase at elevated pH for kaolinite, as shown in dark blue for Fig. 2. In addition, aqueous Si fractions are similar for each of the other clays. Based on Fig. 3, muscovite resulted in the highest fractions of Al in the aqueous phase. However, in general, each of the minerals had similar aqueous Al concentrations. Furthermore, there is not a clear difference between the aqueous cation concentrations with the base treatments.

The greater aqueous Si as compared to Al for the clay minerals (kaolinite, illite, muscovite, and montmorillonite) is similar to results for Hanford sediments (Fig. 1) and confirms results from previous work by Szecsody *et al* [3]. Moreover, a comparison of the ratios of Al to Si measured in the aqueous phase with the theoretical ratios based on the minerals investigated (Table IV) suggests that incongruent dissolution is occurring. Therefore, it is likely that a secondary precipitate is forming following dissolution of the clay minerals.

Furthermore, Figs. 4 and 5 represent the results for mineral dissolution in the presence of 3.2 mM NaCl solution for kaolinite, illite, quartz and montmorillonite. It should be noted that Fig. 4 indicates an increase in Si in the aqueous phase for NaOH-treated samples as compared to NH_4OH. This effect can be explained by the different impacts of the two treatments on mineral solubility. The addition of NaOH adds singly charged ions (Na^+) to solution. However, the addition of NH_4OH adds greater than 99% molecular species (NH_3) at pH ~11.5 based on ammonia/ammonium speciation. For the charged ions (NaOH), solubility increases with ionic strength while molecular species (NH_3) decreases [22]. Therefore, it is expected that the increase in molecular species for the NH_4OH treatment would result in a significant decrease in solubility especially of Si as it is most likely to dissolve as a molecular species (H_4O_4Si). The trend for Al in Fig. 5 is not as clear.
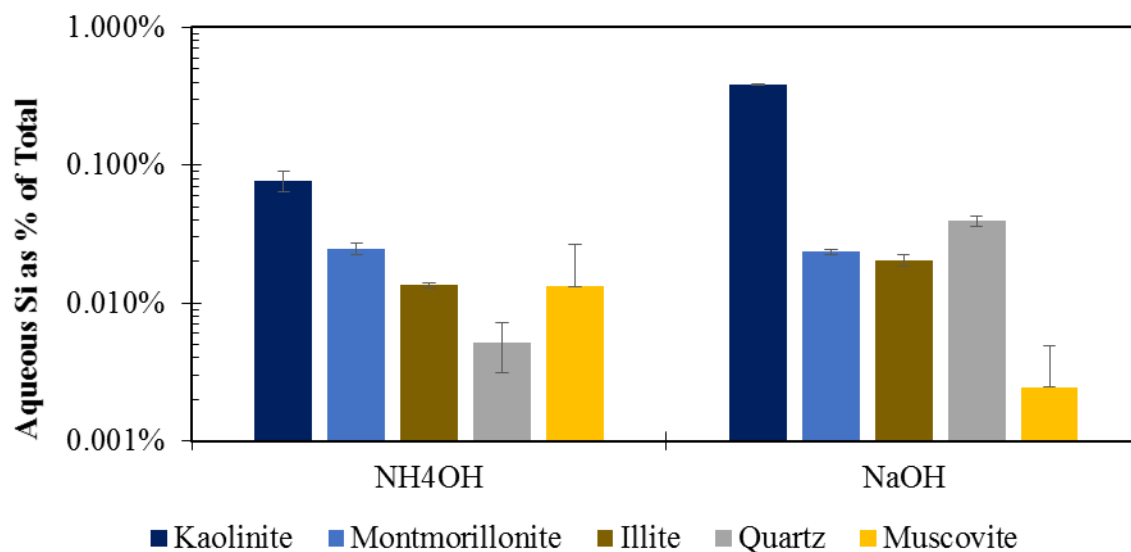
Fig. 2: Aqueous Si as a percentage of total initial Si based on initial minerals (layer silicate clays and quartz) in the presence of synthetic groundwater with aqueous measurements by ICP-OES
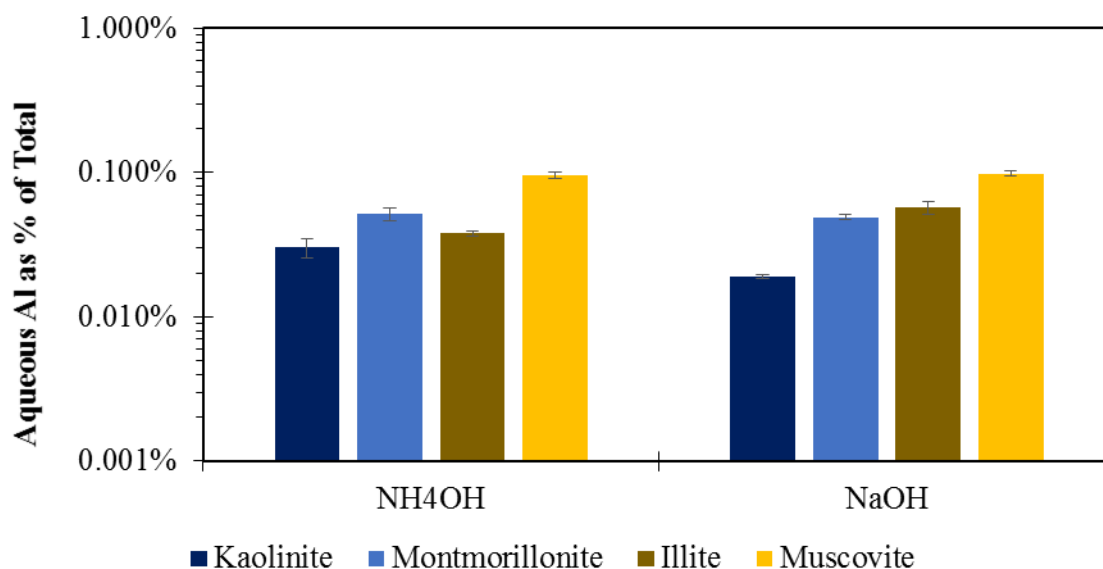

Fig. 3. Aqueous Al as a percentage of total initial Al based on initial minerals (kaolinite, montmorillonite, illite and muscovite) in the presence of synthetic groundwater based on aqueous measurements by ICP-OES

TABLE IV: Comparison of Al:Si molar ratios measured in the aqueous phase for base treatment with NH_4OH and NaOH in the presence of synthetic groundwater with theoretical ratios, Note: ratio not included for illite-NH_4OH because Si was below detection limit

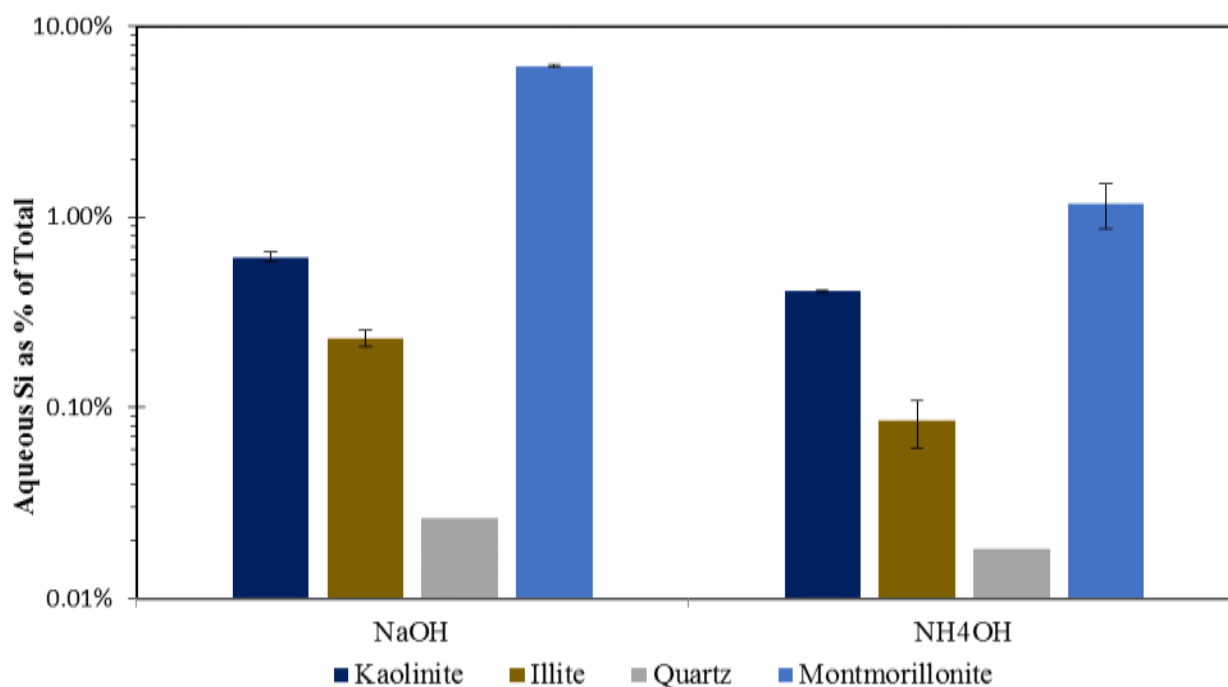| Mineral	NH₄OH	NaOH	Theoretical
Kaolinite	0.049	0.098	1
Illite	-	0.053	0.5
Montmorillonite	0.089	0.019	0.5
Muscovite	0.532	0.646	1

Fig. 4: Aqueous Si as a percentage of total initial Si based on initial minerals (layer silicate clays and quartz) in the presence of 3.2 mM NaCl with aqueous measurements by ICP-OES
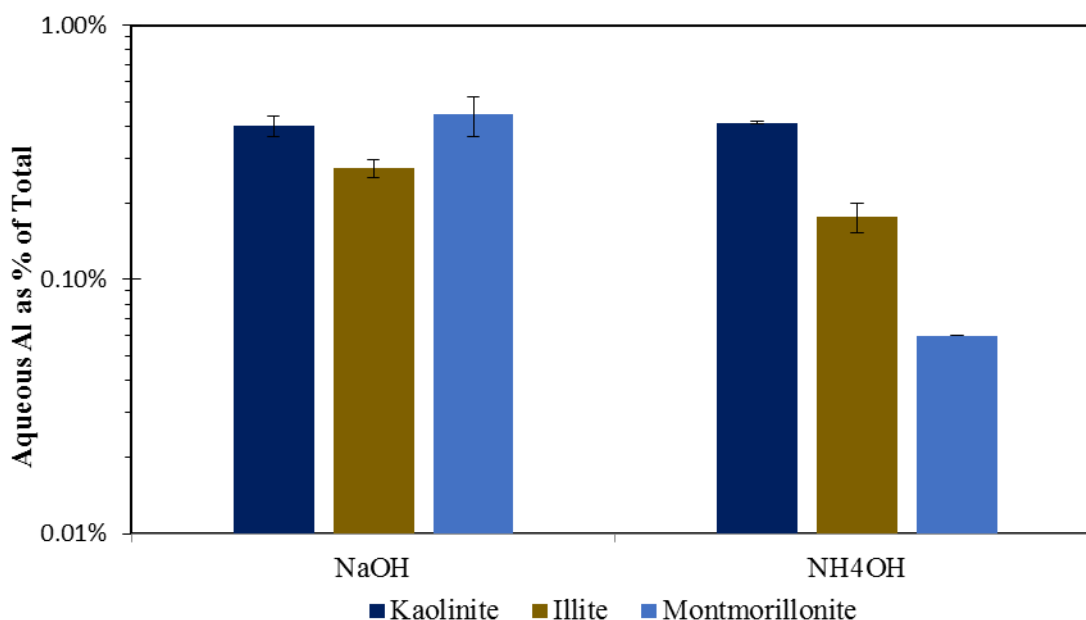
Fig. 5: Aqueous Al as a percentage of total initial Al based on initial minerals (kaolinite, montmorillonite, illite and muscovite) in the presence of 3.2 mM NaCl based on aqueous measurements by ICP-OES

Figs. 6 and 7 represent the fraction of Si and Al in the aqueous phase, respectively, from 5 g/L kaolinite after three days of equilibration in synthetic groundwater (circles) or NaCl (diamonds) after base addition of aliquots of 2.5 M NH_4OH or 2.5 M NaCl + 0.025 M NaOH to reach variable basic pH values. The dissolution of kaolinite clearly increases with pH as expected. Moreover, the initial electrolytes (either synthetic groundwater or a composition of NaCl) do not significantly affect the dissolution. It is important to note that both initial solutions are at a similar ionic strength (7.2 versus 3.2 mM), but the synthetic groundwater is more complex with a significant contribution from divalent cations such as Mg and Ca (Table III).

However, the type of base treatment appears to have an effect on the concentration of Si in the aqueous phase as compared to the initial electrolyte while the Al concentration in the aqueous phase is similar for each treatment (Figs. 6 and 7, respectively). Further, the 2.5 M NaCl + 0.025 M NaOH treatment led to a significant increase in Si in the aqueous phase near pH 10.5-11 as compared to the NH_4OH treatment. The 2.5 M NH_4OH treatment did not reach similar Si concentrations until almost pH 12. Again, this can be attributed to the effects of molecular versus ionic species on solubility as discussed above and likely indicates greater precipitation of silicon-containing solids with NH_4OH treatment as compared to NaOH.
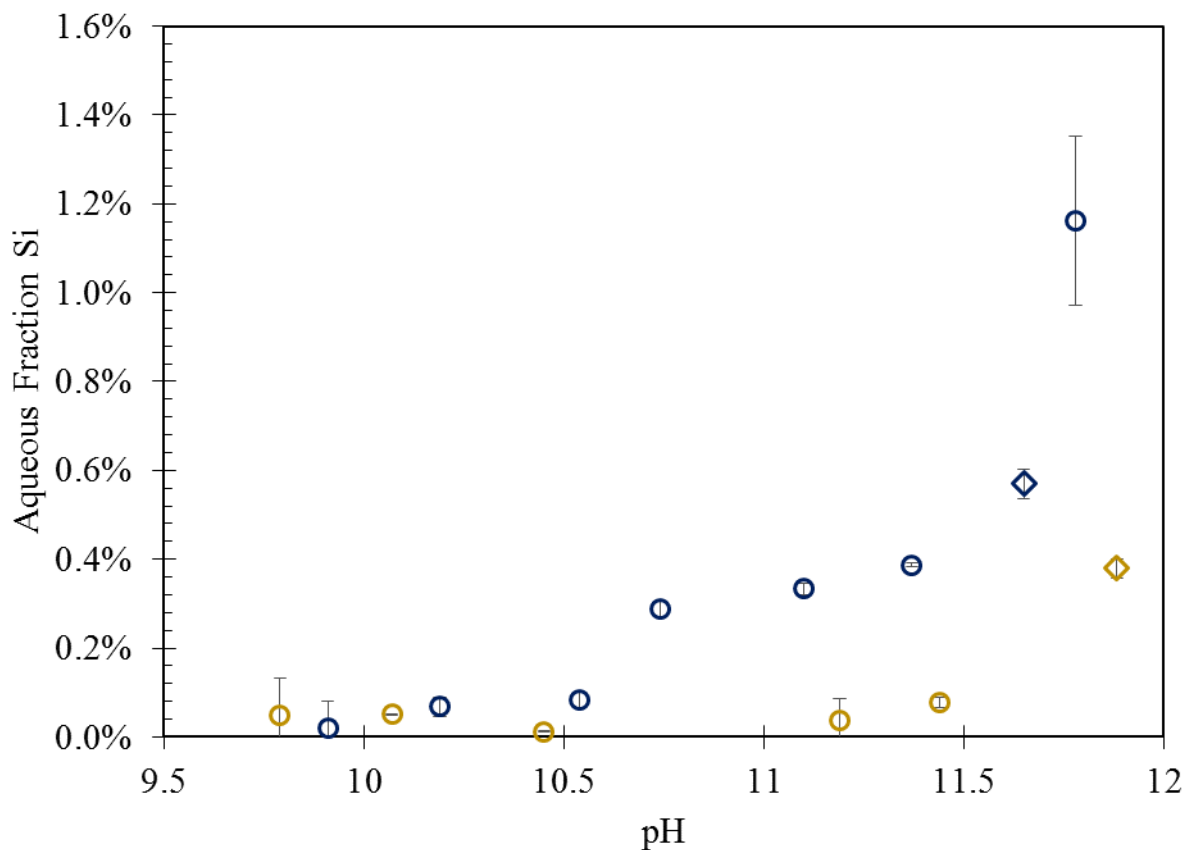
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Fig. 6. Comparison of aqueous Si as a fraction of the total based on the initial kaolinite mineral concentration following three days of equilibration of 5 g/L kaolinite in synthetic groundwater (circles) or 3.2 mM NaCl (diamonds) at variable pH following treatment with either 2.5 M NH_4OH (yellow) or 2.5 M NaCl + 0.025 M NaOH (blue)
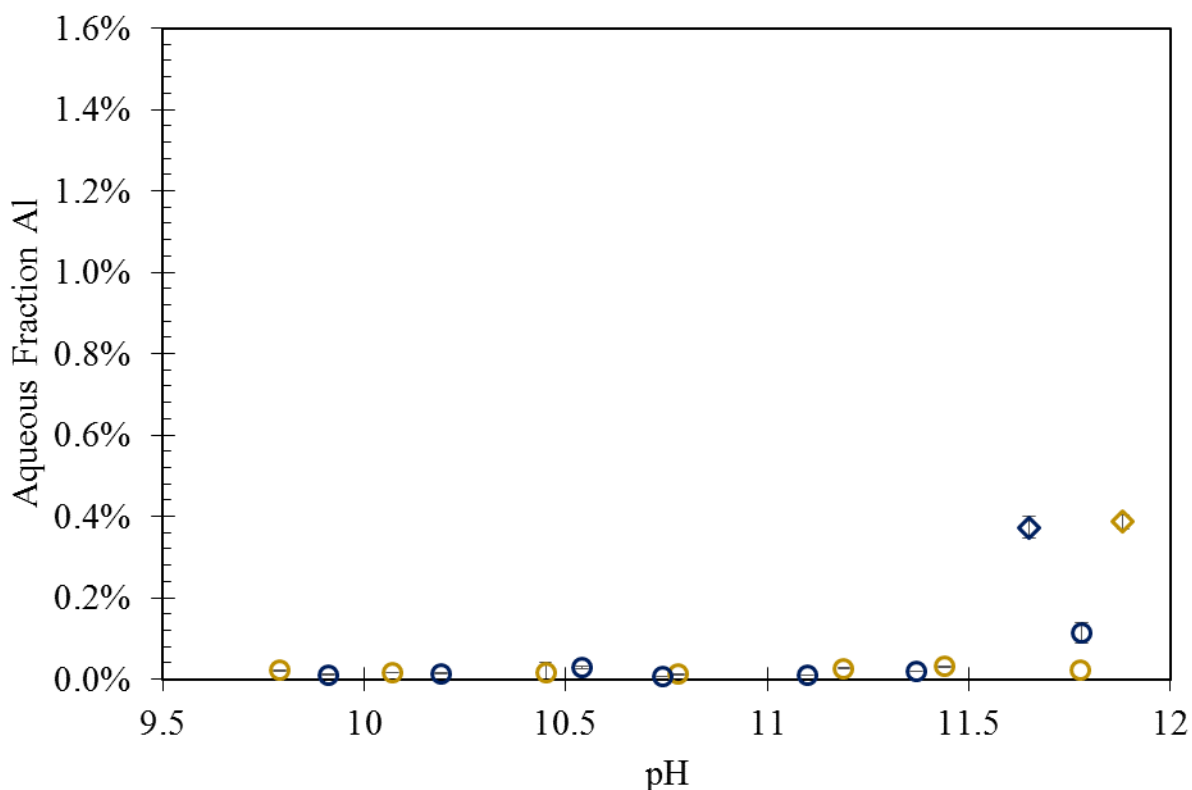
Fig. 7: Comparison of aqueous Al as a fraction of the total based on the initial kaolinite mineral concentration following three days of equilibration of 5 g/L kaolinite in synthetic groundwater (circles) or 3.2 mM NaCl (diamonds) at variable pH following treatment with either 2.5 M NH_4OH (red) or 2.5 M NaCl + 0.025 M NaOH (black)

CONCLUSIONS

The work presented above is part of a larger, ongoing effort to understand the long term fate of uranium at the Hanford site if ammonia gas injection is chosen as a remediation technique. The data presented examines the dissolution behavior of minerals and sediments with significant relevance to Washington State's Hanford site. Upon base treatment with either NaOH or NH_4OH, quartz and aluminosilicate clays dissolve. Although the NaCl versus synthetic groundwater for initial ionic strength did not significantly affect mineral dissolution, some differences were observed with base treatments. In the case of montmorillonite, illite and kaolinite, significantly greater aqueous Si was observed for NH_4OH treatment versus NaOH treatment. However, aqueous Al measurements were similar for both treatments.

It is still unclear whether U mobility will be decreased long term, but it is expected that these precipitation processes could remove additional U from the aqueous phase and coat precipitated uranyl phases with lower solubility precipitates.

Investigations of these processes and characterization of solid phases to confirm previous work and model predictions is the subject of ongoing and future work.

ACKNOWLEDGEMENTS

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