

TECHNICAL REPORT

Effects of Ammonia on Uranium Partitioning and Kaolinite Mineral Dissolution

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Table of Contents

1.0	Introduction.....	1
2.0	Materials and Methods.....	3
2.1	Materials.....	3
2.2	Equilibrium Batch Experiments	4
2.3	Sequential Extractions.....	5
2.4	Speciation Modeling	7
3.0	Results and Discussion	8
3.1	Equilibrium Batch Experiments	8
3.1.1	Mineral Dissolution	8
3.1.2	Uranium Partitioning	10
3.2	Sequential Extractions.....	17
4.0	Conclusions.....	18
5.0	Future Work.....	19
6.0	References.....	19

Figures

Figure 1. Comparison of Si dissolution following three days of equilibration of 5 g/L kaolinite.. 9

Figure 2. Comparison of Al (*gray*) and Si (*black*) dissolution following 30 days of equilibration of 25 g/L kaolinite..... 10

Figure 3. Recovery of U in the aqueous phase for control samples 12

Figure 4. Apparent U K_d (mL/g) following a three day equilibration period 15

Figure 5. Apparent U K_d (mL/g) following a three day equilibration period 16

Figure 6. Uranium recovery for each sequential extraction step 18

Tables

Table 1. Synthetic Groundwater (SGW) Composition with Total Ionic Strength of 7.2 mM..... 4

Table 2. Sequential Extraction Methodology 7

Table 3. Summary of Saturation Indices for Minerals near Saturation in SGW at pH 11.5..... 12

Table 4. Comparison of Equilibrium Apparent U K_d 's for ~30 days and ~3 days..... 16

Table 5. Comparison of Residual and Environmentally Available U Normalized to the Initial Solid Phase U Concentration..... 18

1.0 Introduction

The Department of Energy's (DOE) Hanford Site located in Washington State has deposited over 200,000 kg of uranium (U) into the vadose zone (Corbin, Simpson et al. 2005; Zachara, Brown et al. 2007). This release occurred as a result of improper disposal of waste from plutonium production during World War II and the Cold War. U is highly mobile in the Hanford vadose zone due to the oxidizing conditions and the presence of carbonate, creating highly mobile uranyl carbonate species. 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 (Zachara, Brown et al. 2007; Szecsody, Truex et al. 2013) and the retardation factor was measured at 1.43 (Szecsody, Truex et al. 2013).

Moreover, the Hanford vadose zone is up to 255 feet thick with contamination measured down to 170 feet below the ground surface (Serne, Last et al. 2008). Therefore, there is a desire to create a remediation option that does not input additional liquid to the vadose zone as this could increase U mobility to the groundwater below. Of the remediation methods that 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 (Denham and Looney 2005; Dresel, Wellman et al. 2011).

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. However, it must be noted that geochemical changes within the subsurface are often temporary unless they are moving the system towards its natural equilibrium. Therefore, 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 (Szecsody, Truex et al. 2012).

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 (Wan, Tokunaga et al. 2004; Wan, Tokunaga et al. 2004; Szecsody, Truex et al. 2012; Szecsody, Truex

et al. 2013). This results in an increase in dissolved Si^+ and Al^{3+} as well as small increases in Na^+ , K^+ , $\text{Fe}^{2+/3+}$, Cl^- , F^- and SO_4^{2-} (Szecsody, Truex et al. 2012; Szecsody, Truex et al. 2013). Moreover, Ca^{2+} increases were reported in column experiments following injection of $\text{U} + 0.1 \text{ M NaOH} + 1 \text{ M NaNO}_3$ (Szecsody, Truex et al. 2013). The dissolution of these minerals will ultimately buffer the pH of the system (Qafoku, Ainsworth et al. 2003; Szecsody, Truex et al. 2013).

As the ammonia evaporates and the system returns to a neutral pH, U is expected to be immobilized as part of a co-precipitation process with aluminosilicate minerals. 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 (Bickmore, Nagy et al. 2001; Qafoku, Ainsworth et al. 2004; Zhao, Deng et al. 2004; Qafoku and Icenhower 2008).

A decrease in the pH of approximately two units occurred after six months in previous column experiments following ammonia gas injection (Szecsody, Truex et al. 2012). Further, Szecsody *et al.* reported that as much as 93% less U mass may be leached with 5% ammonia gas injection versus untreated sediments as evaluated in column experiments after 100 pore volumes. Similar work by Zhong *et al.* reported that 85% less U is mobilized for columns treated with 5 and 15% v/v ammonia gas (Zhong, Szecsody et al. 2015).

Nonetheless, there is a lack of understanding of the fate of U under the transient conditions caused by ammonia gas injection. Szecsody *et al.* has shown that basic solutions co-disposed with U may lead to an increase in retardation (1.76 compared to 1.43 at neutral pH) within the subsurface and that precipitation is likely (Szecsody, Truex et al. 2013). However, the high ionic strength conditions caused by mineral dissolution and greater likelihood of carbonate complexation may lead to desorption and mobilization of U. Szecsody *et al.* (2013) has shown an increase in column effluent concentrations for pH 8 versus 0.1 M NaOH with concentrations of U measured at 6.0 and 9.1 μM , respectively. There is still a need to understand the mechanisms with the greatest effect on U mobility under these conditions.

The objective of this work is to understand the partitioning of U and the mineral dissolution caused by injection of ammonia in simplified experiments. Further, samples will be prepared with a

baseline (a neutral pH representative of natural conditions), a base treatment with NaOH and a base treatment with NH_4OH . This allows for a comparison with the mainstream remediation technique of sodium hydroxide (NaOH) injection and natural conditions at the Hanford Site. Sequential extractions will also investigate the lability of U in the solid phase following treatments.

Experiments were conducted with the kaolinite mineral due to its significance at DOE sites including Hanford and its expected dissolution under alkaline pH. Kaolinite is the most significant mineral in the fine fraction of Savannah River Site sediments (Kaplan, Powell et al. 2004; Kaplan, Powell et al. 2006; Kaplan, Roberts et al. 2011; Dong, Tokunaga et al. 2012) and represents 21-28% of the clay-sized fraction of the Hanford Site vadose zone (Xue, Murray et al. 2003; Serne 2012) or 0.35% overall (Szecsody, Truex et al. 2012). Moreover, kaolinite was one of four minerals relevant to the Hanford Site that was previously identified as showing significant dissolution under basic conditions (Szecsody, Truex et al. 2010; Szecsody, Truex et al. 2012; Szecsody, Truex et al. 2013).

2.0 Materials and Methods

2.1 Materials

Kaolinite (Alfa Aesar) was washed and equilibrated with the synthetic groundwater as described previously (Heidmann, Christl et al. 2005; Heidmann, Christl et al. 2005). Briefly, a 100 g/L suspension in 1 M NaCl or synthetic groundwater (SGW) was mixed for 30 minutes, then centrifuged for 30 minutes at 5000 rpm (18100 rcf, Thermo Scientific, Corvall ST 16R centrifuge) and decanted. These three steps were repeated three times. Then, the process was repeated four more times with $>18 \text{ M}\Omega\cdot\text{cm}$ H_2O (Barnstead NANOpure). Finally, the solid was dried at 35°C for ~ 3 days and lightly crushed with a mortar and pestle to homogenize. The surface area was measured at $17.59 \text{ m}^2/\text{g}$ based on the BET method.

Two solutions were formulated to describe the Hanford groundwater: 1) a simplified synthetic groundwater (SGW) as described in Table 1, and 2) an NaCl solution of similar ionic strength for comparison. The simplified SGW in Table 1 is based on correspondence with Dr. Szecsody and previous work (Szecsody, Cantrell et al. 1998).

Table 1. Synthetic Groundwater (SGW) Composition with Total Ionic Strength of 7.2 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

2.2 Equilibrium Batch Experiments

Initial batch experiments were conducted in triplicate at pH ~7.5 in the presence of 5 g/L kaolinite and either synthetic porewater (Table 1) or NaCl at similar ionic strength (~0.007 M). An aliquot of U (Spex Certiprep) was added following equilibration of the 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 kaolinite) and samples.

The 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 (Jackson 1985). Then, the supernatant was acidified in 1% HNO₃ (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 Al and Si). Al and Si were analyzed to track dissolution of the kaolinite mineral throughout these experiments. In addition, appropriate control samples without the solid were prepared with negligible losses (within error of the measurements) to the vial walls at pH ~7.5.

Following equilibration at pH ~7.5, the pH of each sample was raised with either 2.5 M NH₄OH or 2.5 M NaClO₄ + 0.025 M NaOH. Samples adjusted with NH₄OH were immediately capped and wrapped with parafilm following addition to reduce volatilization as NH₃ gas. The pH adjusted solutions were prepared to allow for similar ionic strength and base adjusting power. In addition, the adjustment by either NH₄OH or NaOH allows for comparison of both options as a possible step to raise the pH during remediation of the subsurface. After adjustment, the samples were equilibrated for three days before analysis as described above for U, Al, and Si and additional

analysis for total ammonia. The control samples analyzed at elevated pH showed considerable losses from the aqueous phase and will be discussed with the results below.

2.3 Sequential Extractions

Sequential extraction procedures were completed in triplicate on 40 mL suspensions equilibrated for ~30 days with 25 g/L kaolinite, 500 ppb U, and either synthetic porewater or NaCl initial solutions to better define the changes in availability of U following treatment with NaOH or NH₄OH to pH~11.5 or under simulated natural conditions near pH~7.5. The steps were chosen based on previous work as described below and each step dissolves increasingly less soluble phases. However, it must be noted that each of these phases are operationally defined and may not necessarily be representative of the specific fraction.

The sequential extraction procedures were completed following the ~30 day equilibration period with the aqueous phase being centrifuged at 5000 rpm for 30 minutes and decanted. The aqueous phase was then analyzed for U, Al and Si as described above. Each solid sample was then dried in an oven at 30°C for ten days before the procedure was initiated. The solid to liquid ratio was 1:40 for each of the extraction steps with the exception of the residual step which was 1:25.

An additional wash step was conducted after each fractionation step where 5 mL of >18 MΩ*cm H₂O was mixed, re-centrifuged, and decanted. The majority of the previous sequential extraction procedures utilized ultrapure water for the wash step (Tessier, Campbell et al. 1979; Lee, Yoon et al. 2004; Vandenhove, Van Hees et al. 2007; Beltrán, de la Rosa et al. 2010). However, some researchers used Ca(NO₃)₂, but significant evidence was not provided to suggest it as a better wash solution (Clark, Johnson et al. 1996; Serkiz, Johnson et al. 2007).

The first extraction step is defined as the aqueous U phases. Therefore, the synthetic groundwater, either NaCl or the SGW formulation in Table 1, were used for this step as they are most representative of the aqueous groundwater. The second step is expected to remove U weakly adsorbed by electrostatic interactions and ion exchange processes with previous work using salts with little reactivity with the elements of concern (Gleyzes, Tellier et al. 2002). Some of the previous salts utilized include MgCl₂, Mg(NO₃)₂, Ca(NO₃)₂, and NH₄-acetate (Tessier, Campbell et al. 1979; Clark, Johnson et al. 1996; Kurosaki, Asbury et al. 2002; Galan, Gomez-Ariza et al. 2003; Lee, Yoon et al. 2004; Alam and Cheng 2014).

However, Filgueiras previously noted that nitrate salts are less reactive than chloride and acetate salts and, because no major metal complexation takes place, cation exchange is the major mechanism (Filgueiras, Lavilla et al. 2002). Previous researchers have also utilized a carbonate extraction to identify the adsorbed/exchangeable fraction (Kohler, Curtis et al. 2004; Szecsody, Truex et al. 2010; Szecsody, Truex et al. 2012; Wan, Tokunaga et al. 2012; Alam and Cheng 2014). However, Kohler *et al.* found that a 120 hour contact time was necessary to reach steady state (Kohler, Curtis et al. 2004). Therefore, the 1 M MgNO_3 solution was chosen for the second step for this work.

Although conventional extraction schemes generally also include a step for other operationally defined phases, like amorphous and crystalline iron oxides and organics, these steps were not included in the procedure in this work as they are not present in the kaolinite system. The third extraction step (1 M sodium acetate adjusted to pH 5) was originally defined to remove carbonates by Tessier (Tessier, Campbell et al. 1979) with a similar formulation of 1 M ammonium acetate at pH 5 used by other researchers (Kurosaki, Asbury et al. 2002; Lee, Yoon et al. 2004). However, work by Szecsody defined this fraction as removing a portion of the carbonate or ‘rind’ on carbonates (Szecsody, Truex et al. 2010). Contaminants removed during the first three extraction steps are considered environmentally available, meaning they could be mobilized in the groundwater (Serkiz, Johnson et al. 2007; Szecsody, Truex et al. 2010).

The fourth extraction step is 1.45 M acetic acid at pH 2.3. A similar extraction solution, 0.44 M acetic acid + 0.5 M $\text{Ca}(\text{NO}_3)_2$ adjusted to pH 2.5, was used previously to remove acid soluble or inner sphere sorbed species (Clark, Johnson et al. 1996; Serkiz, Johnson et al. 2007). Further, 0.44 M acetic acid + 0.1 M KCl was used previously to remove carbonates (Xu, Kaplan et al. 2015). It is assumed that the solution is removing the remaining carbonates as well as boltwoodite and uranophane precipitates based on previous work on similar systems (Szecsody, Truex et al. 2010; Szecsody, Truex et al. 2012).

The final step is defined as the residual step which is expected to include primary and secondary minerals and contaminants bound within their structure (Tessier, Campbell et al. 1979). Uranium released with this step is not expected to be released to the groundwater under normal environmental conditions.

Table 2. Sequential Extraction Methodology

Operationally-defined Fraction	Extraction Conditions	References
(1) Aqueous	Synthetic groundwater	(Clark, Johnson et al. 1996, Szecsody, Truex et al. 2010, Szecsody, Truex et al. 2012)
(2) Adsorbed/Exchangeable	1 M MgNO ₃ at pH 7 for 16 hours	(Tessier, Campbell et al. 1979, Clark, Johnson et al. 1996, Serkiz, Johnson et al. 2007, Alam and Cheng 2014)
(3) Some Carbonates	1 M Sodium Acetate adjusted to pH 5 with Acetic Acid for 1 hour	(Tessier, Campbell et al. 1979, Beltrán, de la Rosa et al. 2010, Szecsody, Truex et al. 2010, Szecsody, Truex et al. 2012)
(4) Remaining Carbonates	1.45 M Acetic Acid at pH 2.3 for 5 days	(Szecsody, Truex et al. 2010, Szecsody, Truex et al. 2012)
(5) Residual	8 M HNO ₃ @ 95°C for 2 hours	(Szecsody, Truex et al. 2010, Szecsody, Truex et al. 2012)

2.4 Speciation Modeling

A chemical equilibrium computer program named Visual Minteq 3.0 was used to model aqueous speciation in these systems (Gustafsson 2005). The thermos.vdb database was utilized for all simulations. The code was originally developed by the U.S. Environmental Protection Agency (USEPA) and is currently maintained by John Petter Gustafsson. The Davies equation was used for calculation of activity coefficients. This method is generally considered to be applicable up to 0.7 mol/kg (Langmuir 1997). However, it must be noted that some solutions in this work are slightly higher with the highest ionic strength near 0.8 mol/L for the highest pH treatments. The total carbonate concentration was fixed at 0.22 mmol/L in the model to represent initial equilibrium with the atmosphere at pH 7.5. It is assumed that the initial solution at pH 7.5 is in equilibrium with the atmosphere prior to the addition of treatments and capping of the vials. The modeling of the treated system is assumed to be closed from the atmosphere and, therefore, maintains the 0.22 mmol/L total carbonate from the initial conditions.

3.0 Results and Discussion

3.1 Equilibrium Batch Experiments

3.1.1 Mineral Dissolution

Figure 1 below shows the dissolution of Si from 5 g/L kaolinite suspensions following three days of equilibration in SGW (Table 1) or 3 mM NaCl following base addition via 2.5 M NH₄OH or 2.5 M NaClO₄ + 0.025 M NaOH. The dissolution of kaolinite clearly increases with pH as expected. Moreover, the initial electrolyte (either SGW or a composition of 3 mM NaCl) do not significantly affect the dissolution as confirmed with the data points for 3 mM NaCl following the trend for the SGW (Figure 1). It is important to note that both initial solutions are a similar ionic strength (7.2 versus 3 mM), but the SGW is more complex with a significant contribution from divalent cations. However, the base treatment appears to have a significant effect on the concentration of Si in the aqueous phase with the 2.5 M NaClO₄ + 0.025 M NaOH treatment leading to a significant increase in Si in the aqueous phase near pH 10.5-11 as compared to the NH₄OH treatment. The 2.5 M NH₄OH treatment did not reach similar Si concentrations until almost pH 12.

Al is not shown for the three-day equilibration because the majority of the measured concentrations for the three-day equilibration period and 5 g/L kaolinite were near the analytical limit of detection (LOD) of the ICP-OES of ~17 ppb. Previous work by Szecsody *et al.* also noted that less dissolution of Al occurred than Si for NaOH treatment (Szecsody, Truex et al. 2013). However, a similar correlation was noted for the 30-day equilibration period for the samples prepared for sequential extraction (Figure 2) (i.e., an increase in dissolution with respect to pH with the NaOH treatment leading to greater dissolution than the NH₄OH treatment). Moreover, the data shown in Figure 2 is only for SGW as the error was too large to confirm significant differences in the 7 mM NaCl samples. This is the first body of work to directly compare the two treatment methods under saturated conditions.

The differences in dissolved concentrations of Si and Al as compared to the NaOH and NH₄OH treatments is likely due to ionic strength effects of molecular versus ionic species. The total ionic strength was similar at the highest pH (~11.8) with triplicate samples estimated at 0.82±0.14 and 0.77±0.14 for the NH₄OH and NaOH treatments, respectively. However, for the NH₄OH

treatment, 99.7% of the total ammonia is present as a molecular, uncharged NH_3 species at pH ~ 11.8 . The ammonia is a major contribution to the total ionic strength. The major contribution to the ionic strength in the two treatments is uncharged for NH_4OH treatment and $+1/-1$ for the 2.5 M $\text{NaClO}_4 + 0.025$ M NaOH treatment. In general, the solubility of charged ions increases with ionic strength while molecular species decreases (Langmuir 1997). However, research is ongoing to delineate the theoretical effects from molecular versus charged species on the solubility of kaolinite.

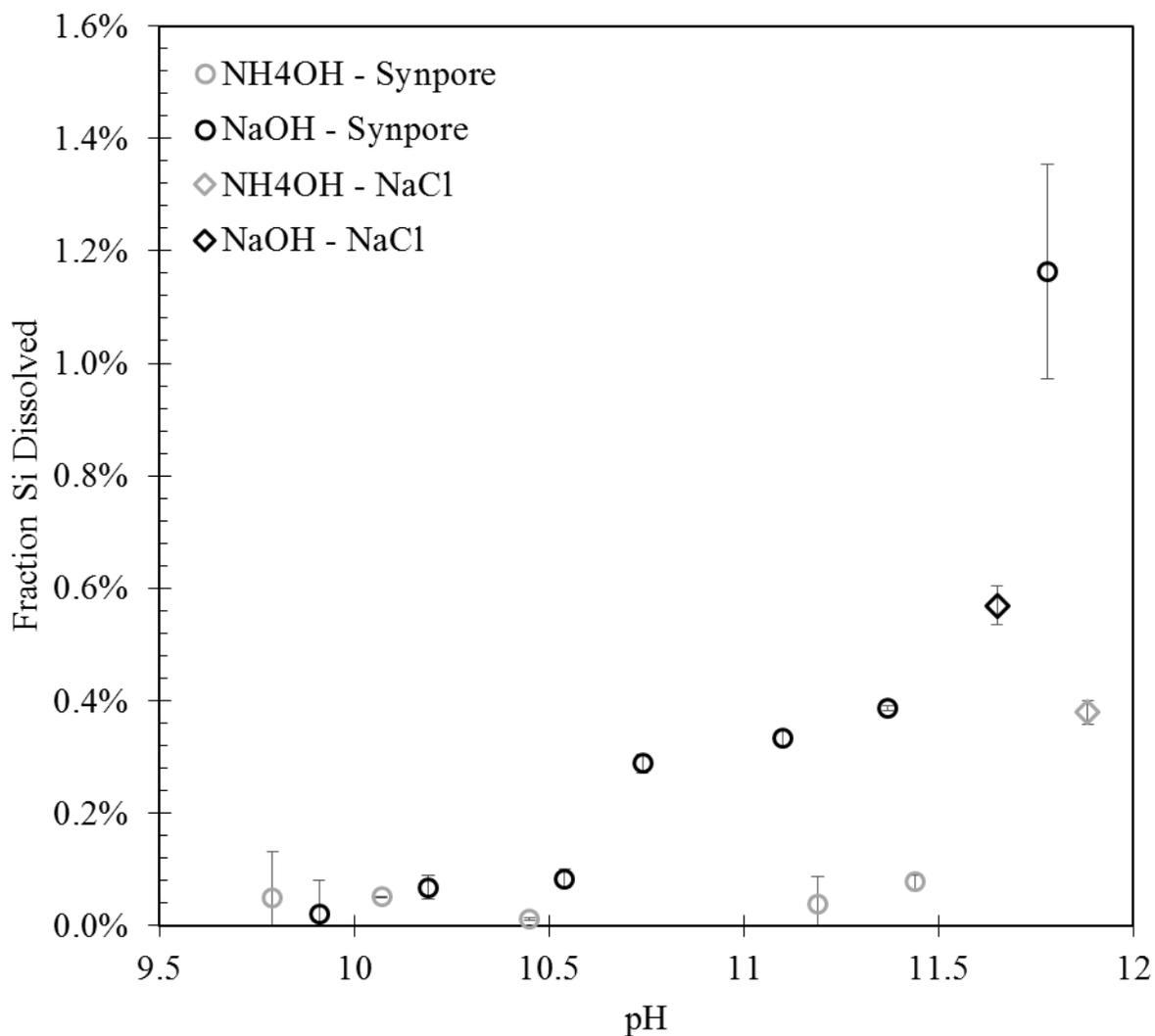


Figure 1. Comparison of Si dissolution following three days of equilibration of 5 g/L kaolinite in SGW (Table 1, circles) or 3 mM NaCl (diamonds) at variable pH following treatment with either 2.5 M NH_4OH (gray) or 2.5 M $\text{NaClO}_4 + 0.025$ M NaOH (black), Note: Al is not shown as dissolution was similar for both treatments. Error bars are based on triplicate samples.

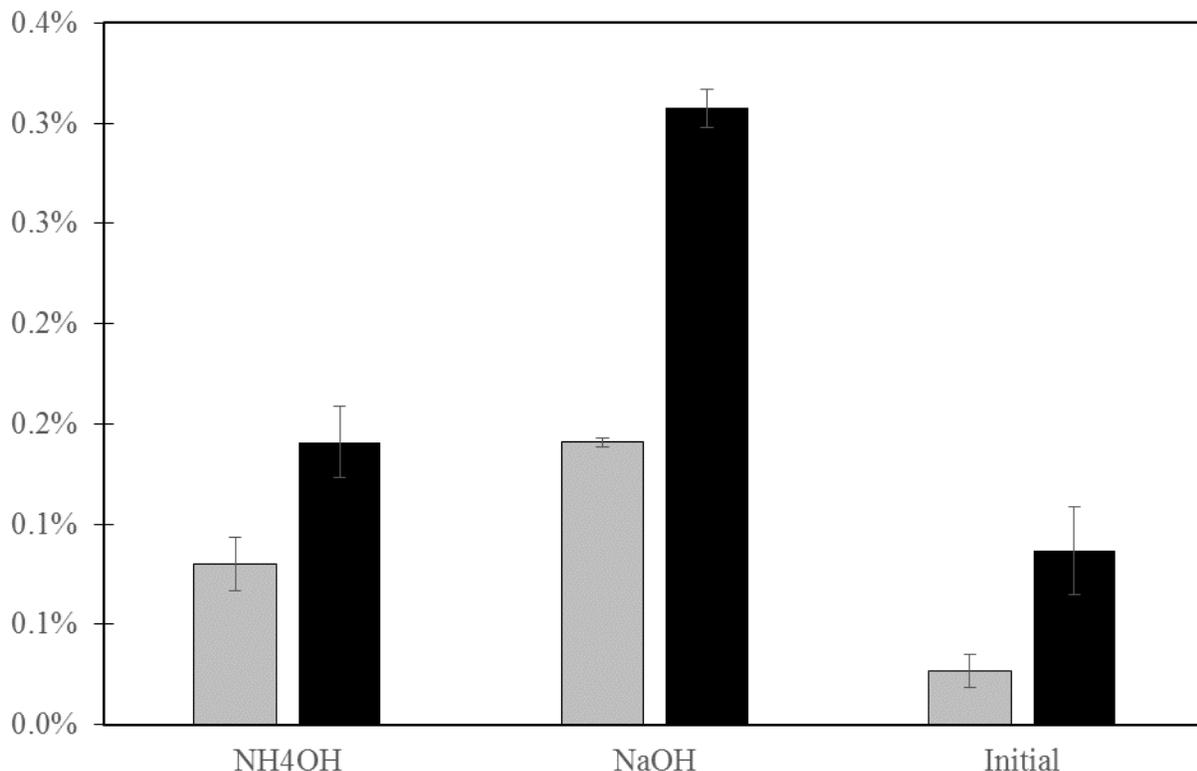


Figure 2. Comparison of Al (*gray*) and Si (*black*) dissolution following 30 days of equilibration of 25 g/L kaolinite in SGW (Table 1) at pH ~7.5 for initial conditions and ~11.5 for treatment with either 2.5 M NH₄OH or 2.5 M NaClO₄ + 0.025 M NaOH. Note: Error bars are based on triplicate samples.

3.1.2 Uranium Partitioning

3.1.2.1 Control U Recovery

The recovery of U in the aqueous phase in control (without kaolinite mineral) samples prepared in triplicate for the SGW (Table 1) is presented in Figure 3. The fraction of U remaining in the aqueous phase for the initial samples at neutral pH (~7.5) are nearly 100% (96±6%). Therefore, the batch data presented in Figures 4 and 5 is corrected for the control recovery for the initial conditions as pH ~7.5 as it is assumed these are losses due to sorption to vial walls and/or pH adjustment.

However, the aqueous phase recovery after treatment at pH near 11.5 is similar to or less than the recovery in the presence of the kaolinite mineral. For comparison, aqueous phase recovery was 1.2±0.2% versus 2.5±0.4% for the NH₄OH treatment for the control and with kaolinite, respectively. For the NaOH treatment, recovery was 8.7±5.6% and 11.8±3.6%, respectively. These

samples were not corrected for the recovery of U in the controls at elevated pH as the system appears more complex with precipitation and sorption occurring simultaneously and likely at different levels than samples with kaolinite.

Because of the likelihood of precipitation in both controls and in the presence of kaolinite, the batch equilibrium data presented in Figures 4-5 represents an apparent K_d as it includes both precipitation and sorption processes in the overall partitioning coefficient. However, it is notable that precipitation is similar or slightly greater in the control samples. This shows that there is possibly a reduction of precipitation in the presence of the kaolinite mineral likely due to sorption of cations that would otherwise precipitate and remove U as part of a co-precipitation process.

Speciation modeling conducted via Visual Minteq predicts that the aqueous SGW solutions are saturated with respect to several magnesium (artinite, brucite, dolomite and magnesium hydroxide) and calcium (calcite, dolomite and vaterite) minerals for both treatments at pH ~11.5. The system is not saturated with respect to any minerals at the neutral pH of the initial conditions. Table 3 represents a summary of minerals near or above saturation in the systems treated to pH 11.5 based on their saturation indices. A saturation index greater than zero is expected for precipitation.

The saturation indices are higher (suggesting greater precipitation may occur) for the calcium and magnesium minerals for the 2.5 M NH_4OH treatment as compared to the 2.5 M NaClO_4 + 0.025 M NaOH treatment. The differences between the two treatments are likely a phenomena due to the different effects of molecular and charged ions on the activity and, therefore, solubility of ions as discussed above. Although the software does not explicitly predict precipitation of uranium in these systems, it is likely that a co-precipitation process occurs with the calcium and magnesium minerals that are predicted to precipitate under these conditions. Moreover, previous research confirms that these co-precipitation processes are possible and remove the actinides (Goncharova, Ruzankin et al. 1975; Reeder, Nugent et al. 2000; Reeder, Nugent et al. 2001).

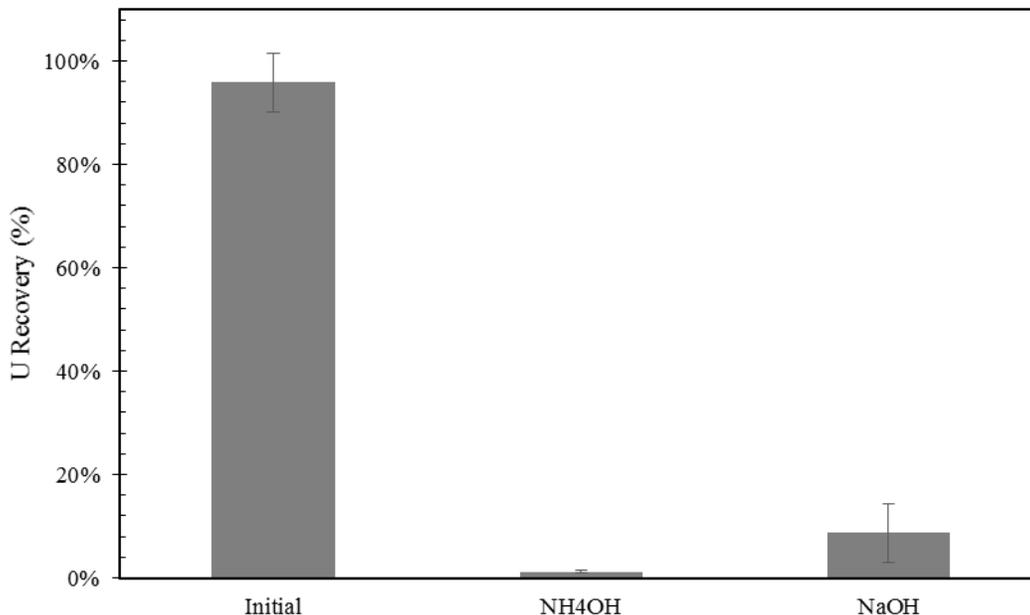


Figure 3. Recovery of U in the aqueous phase for control samples (without kaolinite mineral) following three days of equilibration in SGW. Note: Only neutral pH (initial) samples were adjusted for recovery as it is likely that precipitation occurred at elevated pH. Error bars are based on triplicate samples.

Table 3. Summary of Saturation Indices for Minerals near Saturation in SGW at pH 11.5 with Treatment via 2.5 M NH₄OH or 2.5 M NaClO₄ + 0.025 M NaOH

Mineral	Saturation Index	
	NaClO ₄ -NaOH	NH ₄ OH
Artinite	0.706	1.639
Brucite	2.006	2.025
CaCO ₃ xH ₂ O(s)	-1.119	-0.372
Calcite	0.217	0.963
Dolomite (disordered)	-0.524	1.138
Dolomite (ordered)	0.026	1.688
Mg(OH) ₂ (active)	0.312	0.331
Vaterite	-0.35	0.397

Note: a positive value represents a saturated solution with respect to that mineral

3.1.2.2 Equilibrium U Apparent Partitioning Coefficients (K_d 's)

Equilibrium partitioning of U is presented below in terms of an apparent partitioning coefficient (K_d) as shown in equation 1 where U_{sol} and U_{aqu} represent the concentrations of U in the solid phase and aqueous phase, respectively.

$$K_d = \frac{[U]_{sol}}{[U]_{aq}} \quad \text{Eqn. 1}$$

Because both precipitation and sorption processes are likely occurring simultaneously as discussed above, this is described as an apparent partitioning coefficient. Moreover, Table 4 below compares apparent K_d 's for the partitioning of 500 ppb U in the presence of 5 g/L kaolinite after three days of equilibration and of 25 g/L kaolinite after 30 days of equilibration. The similarity of the results provides ample evidence that equilibrium was reached in the three day samples. Further, data is presented for both SGW (Table 1) and 3 mM NaCl as well as for comparison with the two base treatments described in the Materials and Methods section, 2.5 M NH_4OH and 2.5 M $NaClO_4$ + 0.025 M $NaOH$.

For the SGW (described in Table 1), U removal from the aqueous phase is significantly increased from the baseline (initial, neutral pH ~ 7.5) by base treatment with either $NaOH$ or NH_4OH as shown by the 2 – 2.5 orders of magnitude increase in apparent K_d 's. The neutral pH initial conditions with the SGW represent the lowest removal of U from the aqueous phase of all conditions investigated.

This is due to formation of uranyl carbonate or ternary calcium uranyl carbonate complexes which are less likely to sorb (Clark, Hobart et al. 1995; Silva and Nitsche 1995; Dong and Brooks 2006; Fox, Davis et al. 2006). The presence of bivalent cations like Ca have been previously hypothesized to affect U sorption in the following ways: 1) competing for sorption sites, 2) change the surface charge or potential of minerals, 3) affecting aqueous speciation, and 4) ionic strength affects (Fox, Davis et al. 2006). However, Fox *et al.* concluded that their effect on aqueous speciation was the determining factor in sorption. The two major aqueous species predicted by Visual Minteq at pH 7.5 in the SGW are $Ca_2UO_2(CO_3)_3$ at 66% and $CaUO_2(CO_3)_3^{-2}$ at 29%.

Further, U partitioning for both base treatments in the SGW is similar up to pH 10.5 (Figure 4). This is likely also the point where co-precipitation begins to occur as suggested by the abrupt decrease in apparent K_d near pH 10.5. However, at this point, a divergence occurs where removal appears to be slightly greater for the NaOH treatment for pH 10.7 – 11.5. This represents 24.5 versus 11.4% remaining in the aqueous phase for NH_4OH and NaOH treatments, respectively, at pH ~11.4. Finally, at pH ~11.8, U removal becomes greater for the NH_4OH treatment. Again, it is expected that the effects on partitioning are likely due to effects of molecular versus ionic species on the co-precipitation processes occurring in the system.

The U partitioning in the simpler NaCl system is significantly different from that for the SGW as depicted in Figure 5. The initial mobility of U is lower at neutral pH (K_d is higher) with the NaCl electrolyte than the SGW composition. However, as the pH increases with the two treatment methods, the mobility increases and the K_d decreases for the NaCl. This is due to the formation of negatively charged uranyl carbonate species at elevated pH which decreases the likelihood of sorption. Although carbonate was not added to the initial suspensions, it is assumed that these solutions are initially in equilibrium with the atmosphere with respect to dissolved carbonate at pH 7.5. Then, the system is assumed to be closed (vials are capped) following addition of 2.5 M NH_4OH or 2.5 M NaClO_4 + 0.025 M NaOH. The Visual Minteq simulations predict a complex speciation at pH 7.5 with mostly uranyl carbonate dominating the speciation [48% as $\text{UO}_2(\text{CO}_3)_2^{-2}$, 27% as $\text{UO}_2(\text{CO}_3)$, 8% as $\text{UO}_2(\text{OH})_2$ and 6% as $\text{UO}_2(\text{CO}_3)_3^{-4}$] but nearly 100% of the U is present as $\text{UO}_2(\text{CO}_3)_3^{-4}$ at pH 11.5.

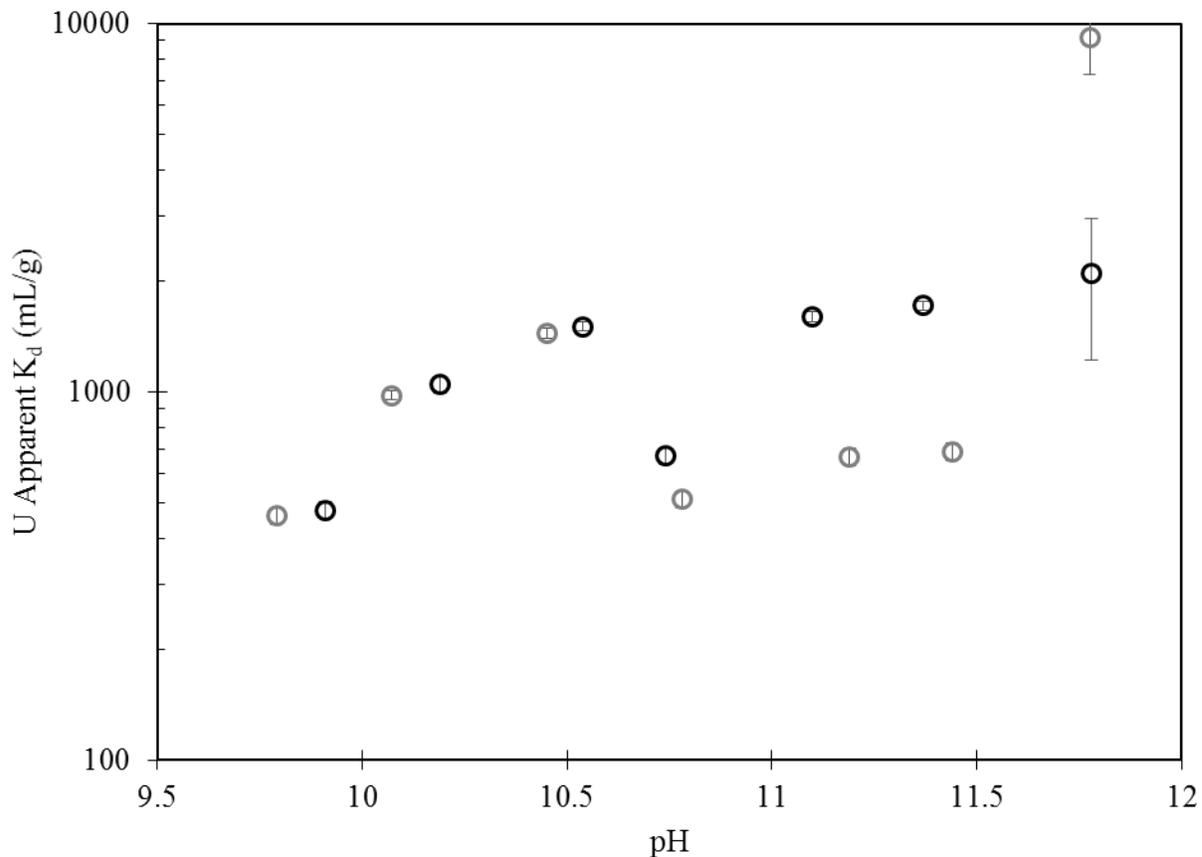


Figure 4. Apparent U K_d (mL/g) following a three day equilibration period with 500 ppb U in SGW (Table 1) in the presence of 5 g/L kaolinite with treatment by either 2.5 M NH_4OH (gray) or 2.5 M $NaOH$ + 0.025 M $NaOH$ (black). Note: Error bars are based on triplicate samples.

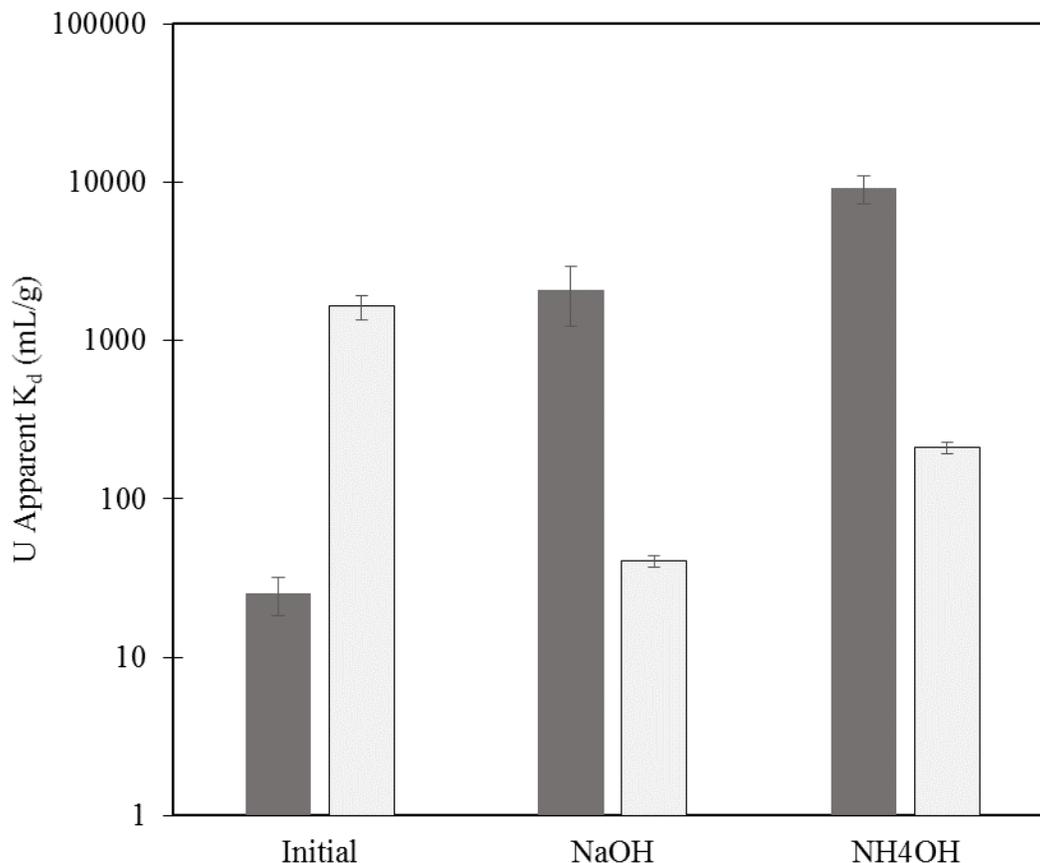


Figure 5. Apparent U K_d (mL/g) following a three day equilibration period with 500 ppb U in SGW (Table 1, gray) or 3 mM NaCl (white) in the presence of 5 g/L kaolinite with treatment by either 2.5 M NH₄OH or 2.5 M NaOH + 0.025 M NaOH, Note: equilibrium pH was pH 7.4±0.1, 11.7±0.1 and 11.8±0.1 for initial, NaOH and NH₄OH treatments, respectively. Error bars are based on triplicate samples.

Table 4. Comparison of Equilibrium Apparent U K_d 's for ~30 days and ~3 days for 500 ppb U in the presence of 25 and 5 g/L kaolinite, respectively, with synthetic porewater or 0.007 M NaCl at neutral pH (~7.5) or treated with NH₄OH or NaOH, Note: mineral dissolution is not shown but was also comparable at 3 and 30 days. Error bars are based on triplicate samples.

Treatment	>30 days, 25 g/L	3 days, 5 g/L
NaCl-NH ₄ OH	313±26	210±20
NaCl-NaOH	119±2	40±3
NaCl-Initial	1510±550	1650±290
SGW-NH ₄ OH	3560±90	10030±1970
SGW-NaOH	2670±250	2280±950
SGW-Initial	126±11	25±7

3.2 Sequential Extractions

A summary of the U recovery within the sequential extractions is shown below in Figure 6. As described above in the Materials and Methods section, the environmentally available fraction is assumed to be represented by the first three extraction steps (aqueous + exchangeable + some carbonates extraction). Upon treatment with base, the available fraction appears to increase based on Figure 6. Further, a comparison of the residual and available fractions normalized to the initial solid phase concentration (Table 5) appears to suggest an increase in mobility of U with the base treatments. It must be noted that the error within the NaCl samples was too large to differentiate changes between initial and following base treatment. Further, the results are also not statistically different between the two base treatments.

In Figure 6, the recovery from all of the washes is combined. However, it is important to note that the recovery from all washes excluding the wash after the third extraction step (1 M sodium acetate adjusted to pH 5 with acetic acid for 1 hour) was <3%. The wash step after the third extraction step recovered an average of $25\pm 6\%$ of the total U from the kaolinite. Further, the aqueous U concentration in these washes was as high as 1500 ppb in 5 mL of total volume. It is hypothesized that the 1 M sodium acetate extraction step either: 1) solubilized a significant fraction of the U which then precipitated on the surface, or 2) removed precipitates on the outer surface exposing a more soluble phase. Szecsody *et al.* (2010) previously reported that this extraction step removed some carbonates or the ‘rind’ of carbonates. Then, when the ultrapure water was added for the wash step, these precipitates were quickly dissolved into the aqueous phase. If one of these phenomena occurred, it is likely that the U in these precipitates would have been removed by the fourth extraction step had the wash step not dissolved the U.

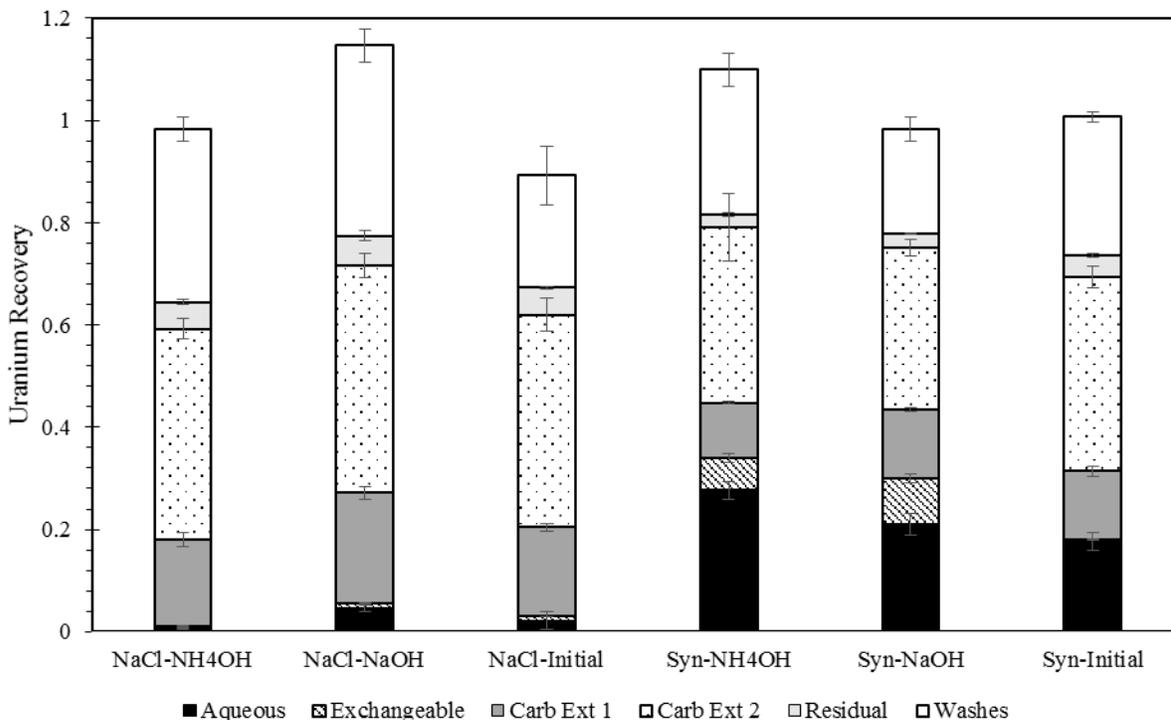


Figure 6. Uranium recovery for each sequential extraction step across the two different initial solutions (7 mM NaCl and SGW per Table 1) and three different treatments (initial – neutral pH ~ 7.5, treated with either 2.5 M NH₄OH or 2.5 M NaClO₄ + 0.025 M NaOH). Notes: overall recovery of U was 102±9% across all experimental conditions. Error bars are based on triplicate samples.

Table 5. Comparison of Residual and Environmentally Available U Normalized to the Initial Solid Phase U Concentration

Treatment	Available (%)	Residual (%)
NaCl-NH ₄ OH	18±7	5.2±0.5
NaCl-NaOH	27±6	5.8±1.0
Syn-NH ₄ OH	45±7	2.4±0.4
Syn-NaOH	43±6	2.8±0.1
Syn-Initial	31±5	4.2±0.4
NaCl-Initial	20±16	5.3±0.3

4.0 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 above shows that the equilibrium K_d increases with treatment for a system with

divalent cations and carbonate present initially (for SGW) and decreases with a simple NaCl system with less carbonate initially present. Further, while sequential extractions are not statistically different between the two base treatments, it appears that the overall availability of U is initially increased following treatment for the SGW. However, following evaporation of ammonia gas and the expected co-precipitation processes, it is still unclear whether U mobility will be decreased.

5.0 Future Work

In the future, the solid phase of the kaolinite before and after reactions will be characterized following treatments by XRD, SEM-EDS, and BET surface area to confirm any changes in mineralogy and available surface area due to dissolution and precipitation reactions. Further, additional experiments will investigate the equilibrium partitioning of U and mineral dissolution after ammonia has evaporated and the pH of the samples have reached conditions near that of the initial samples.

Future experiments will focus on gathering data for a suite of minerals common to Department of Energy sites for non-equilibrium conditions. Non-equilibrium conditions may be important for understanding these processes based on previous work (Szecsody, Truex et al. 2013). The results will be compared with kaolinite and used to better understand the applicability of base injection for remediation of uranium and other cations.

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