TECHNICAL PROGRESS REPORT

Batch Experiments on Sodium Silicate Application on Multi-Contaminant Systems

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Table of Contents

List of Figures

List of Tables

1. Introduction

The Savannah River Site (SRS) was established as one of the major sites for the production of materials related to the U.S. nuclear program during the early 1950s. An estimated 36 metric tons of plutonium were produced during the period of 1953-1988. Since then, SRS has become a hazardous waste management facility responsible for nuclear storage and remediation of contaminated soil and groundwater from radionuclides. The groundwater at the F/H Area Seepage Basins Groundwater Operable Units at SRS was impacted by operations of the Hazardous Waste Management Facilities (HWMFs). Approximately 1.8 billion gallons (7.1 billion liters) and 1.6 billion gallons (6.0 billion liters) of low-level waste solutions have been received in the F and H Areas, respectively, originating from the processing of uranium slugs and irradiated fuel at the separation facilities. The effluents were acidic (wastewater contaminated with nitric acid) and low-activity waste solutions containing a wide variety of radionuclides and dissolved metals. Waste solutions were transported approximately 3,000 feet from each processing area through underground vitrified clay pipes to the basins. After entering the basin, the wastewater was allowed to evaporate and to seep into the underlying soil. The purpose of the basins was to take advantage of the interaction with the basin soils to minimize the migration of contaminants to exposure points. Though the seepage basins essentially functioned as designed, the acidic nature of the basin influent caused mobilization of metals and radionuclides, resulting in groundwater contaminant plumes.

Currently, more than 235 monitoring wells at the site are sampled for a variety of chemical and radioactive parameters. Groundwater monitoring results have indicated the presence of elevated levels of metals, radionuclides and nitrates. Significant chemical differences exist between the groundwater from the two areas. The F Area groundwater contains higher concentrations of dissolved metals than that in the H Area. The constituents of concern (COCs) associated with the F Area HWMF groundwater plume are tritium, uranium-238, iodine-129, strontium-90, curium-244, americium-241, technetium-99, cadmium, and aluminum. The COCs in H Area are tritium, strontium-90, and mercury.

To remove contaminants from polluted groundwater, pump-and-treat and re-inject systems were implemented. Downgrade groundwater within the system would be pumped to a water treatment facility and then re-injected upgrade within the aquifer. This system was disconnected since the process incurred the risk of exposure to workers, generated a secondary waste stream that had to be managed, was expensive, and was both time and labor intensive. In 2004, a funnel-and-gate process was implemented to carry out injections of alkaline solutions directly into the gates of the F-Area groundwater to raise pH levels. This approach allows for the creation of focused treatment zones and chemical stabilization of metals in those zones (*in situ* immobilization). The initial addition of sodium hydroxide revealed a subsequent decrease in uranium and strontium concentrations, but the concentration of iodine remained unaffected. Consequently, addition of carbonate solutions was investigated, but this solution eventually raised concerns about the re-mobilization of uranium previously contained within the treatment zone, due to the formation of highly soluble uranium-carbonate complexes. Furthermore, a systematic re-injection of carbonate solution would be required for the sustainability of circumneutral pH values in the treatment zone.

FIU-ARC is conducting research for the replacement of the injection of carbonate alkaline solutions with sodium silicate. Sodium silicate is an alkaline solution that is favorable because it is environmentally benign with moderate to low cost (Baehr & Koehl, 2007).

2. Objectives

The main objective of these studies was to assess whether sodium silicate has sufficient alkalinity to restore the natural pH of the groundwater. Silica solutions have an inherent pH ≤ 10, which complies with the regulatory constraints for injecting solutions of high pH values into subsurface systems. The optimal levels of sodium silicate for the restoration of circumneutral conditions were investigated, taking into account silica solubility levels in order to avoid clogging of the aquifer's permeability. Batch sorption and desorption kinetic experiments were performed, as well as experiments pertaining to soil characterization, in an effort to elucidate the mechanisms and provide further understanding of the process.

3. Materials and Methods

3.1 Soil samples, SRS synthetic groundwater and other stock and working solutions

Soil samples from the SRS F/H Area were sieved (USA Standard Testing Sieves, Fisher Scientific) and the fractions of mean diameter $d<0.063$, $0.063<d<0.18$ and $0.18< d<2$ mm were stored in a desiccator, which contains anhydrous calcium sulfate (Drierite, Drierite Company Inc) until further use .

Synthetic groundwater that mimics SRS groundwater characteristics was prepared according to Storm and Kabak (Storm & Kaback, 1992) by dissolving 5.4771 g $CaCl_2$, 1.0727 Na_2SO_4, 3.0943 g $MgCl_2$, 0.3997 g KCl and 2.6528 g NaCl in 1 L of deionized water (Barnstead NANOpure water purification system). One (1) mL of the stock solution was diluted into 1 L of deionized water acidified to pH 3.5 to create the working solution. Sodium silicate solutions were created by dissolving the appropriate amount of $Na_2SiO_3{\cdot}9H_2O$ (reagent grade, MP Biomedicals) in deionized water. Sodium perchlorate and calcium chloride solutions were created by dissolving the appropriate amount of $NaClO_4$ and $CaCl_2 \cdot 6H_2O$ (Acros Organics, 99+%) analytical grade in deionized water. Similarly, a Sr stock solution was prepared by dissolving the appropriate amount of $Sr(NO_3)$ (Fisher Scientific) in 2% HNO_3. Re-working solutions were prepared by appropriate dilutions from a Rhenium standard for ICP (Fluka Analytical).

3.2 Sorption, desorption and sequential extraction experiments

All sorption experiments were performed by mixing solid (different fractions of SRS soil or mixtures of pure minerals in order to mimic SRS soil composition - Ottawa Sand standard 20-30 mesh by Fisher and $Al_2Si_2O_7 \cdot 2H_2O$ by Alfa Aesar) and SRS synthetic groundwater, resulting in a ratio of 20 g L^{-1} soil suspensions. Each sample was spiked with the appropriate volume from a freshly prepared sodium silicate solution in order to achieve a final sodium silicate concentration of 70 mg L^{-1}. Preliminary experiments revealed that 70 mg L^{-1} sodium silicate is the appropriate amount in order to achieve circumneutral conditions. The initial concentration of uranium in all samples was 500 μg L^{-1}, whereas in the case of strontium and rhenium, the initial concentration was 100 μg L^{-1}. Vials were agitated on a platform shaker at 120 rpm and all experiments were performed in triplicate. In order to study the effect of ionic strength, samples were spiked with the appropriate amount of $NaClO_4$ in order to obtain a final concentration of 0.001, 0.01 and 0.1 M. Similarly, in order to study the potential competition of uranium with calcium as far as sorption is concerned, appropriate amounts of $CaCl_2$ were added to the samples and a range of 0.00001 to 0.1 M Ca^{+2} was achieved.

Desorption experiments were performed by replacing the metal-bearing aqueous phase past the equilibration, by an equal volume of deionized water or SRS synthetic groundwater.

Sequential extraction experiments followed Community Bureau of Reference (BCR) protocol. More specifically, after the initial sorption step, 1 g of the metal-laden solid was suspended in 40 ml 0.11 M CH_3COOH and was shaken at room temperature for 16 h at 120 rpm. The extract was separated from the solid residue by centrifugation for 10 min (5000 rpm) and decanted into a polyethylene container and stored in a refrigerator at 4ºC for analysis. The residue was washed with 10 ml of deionized water by shaking for 10 min, centrifuged, and the washings discarded. Step 1 aims to determine the exchangeable and acid soluble fraction of sorbed uranium. The second step involved the suspension of the solid in 40 mL of 0.5 M hydroxylamine hydrochloride ($H_2NO \cdot HCl$, Alfa Aesar), pH 1.5, acidified with HCl; the extraction procedure was then performed as described above. The goal of step 2 is the determination of the amount of uranium bound to Fe and Mn oxides. Subsequently, the solid was treated with 10 mL of H_2O_2 for 1h at room temperature, followed by a 1-hour treatment with an 85ºC water bath, until the reduction of the initial volume to less than 2 ml. Fifty (50) mL of $NH_4CH_3CO_2$ 1M, pH 2 adjusted with HNO_3 acid, were then introduced. The suspension was shaken for 16 h at room temperature at 120 rpm and the extraction procedure was repeated, as described above. Step 3 provides information on the oxidizable fraction of sorbed uranium. The residual amount of retained uranium was calculated by subtracting the sum of the fractions mentioned above from the total mass of sorbed uranium (Rauret et al., 1999). The steps are summarized in Table 1.

Table 1. Procedure of BCR Sequential Extraction (He et al., 2013; Zemberyova et al., 2006)

Target phase	Reagents	Conditions
Exchangeable, water and acid-soluble	40 mL 0.11M CH_3COOH	16 h, room temperature
Reducible (Fe and Mn oxides)	40 mL 0.5M NH_2OH-HCl (pH 1.5)	16 h, room temperature
Oxidizable (Organic matter and sulfides)	10 mL 8.8M H_2O_2, 50 mL 1M $NH_4CH_3CO_2$ (pH2)	1 h, room temperature 1 h, 85°C
Residual	HNO_3-HCl digestion	

3.3 SEM-EDS analysis

The morphology and elemental composition of the SRS soil fractions were investigated using scanning electron microscopy equipped with energy dispersive spectroscopy (SEM-EDS) at the Florida Center for Analytical Electron Microscopy located on the Florida International University Modesto A. Maidique Campus. Samples were initially dried in a conventional oven at 30^{o}C for a period of 5 days. Specific amount of each SRS soil fraction was placed on a stainless steel stub and the exact weight was recorded. Any required gold coating was done with an SPI-Module Control and Sputter unit for 2 minutes to produce a thin layer of gold. The SEM system used was a JOEL-5910-LV with acceleration potentials ranging from 10 to 20 kV. EDS analysis was produced using an EDAX Sapphire detector with UTW Window controlled through Genesis software.

3.4 Elemental analysis

The residual uranium concentration in the samples was analyzed by means of kinetic phosphorescence analysis (KPA-11, Chemchek Instruments Inc.). Iron, calcium, magnesium, strontium and rhenium were determined by means of inductively coupled plasma - optical emission spectroscopy (ICP-OES 7300 Optima, Perkin Elmer). Rhenium (Re) was chosen as a chemical analog of technetium (Tc) under oxidizing conditions, due to their similarities in cationic radius and geochemical behavior (Icenhower et al., 2008).

4. Results and Discussion

4.1 Kinetic experiments with SRS soil

SRS soil was sieved and the fractions of average particle diameter d<63 µm, 63 µm<d<180 µm and 180 µm<d<2 mm (called fine, intermediate and coarse fraction, respectively from now on) were obtained and stored in a desiccator containing anhydrous calcium sulfate (Drierite, Drierite Company Inc.), until further use. The results of uranium retention by each soil fraction as a function of time are presented in Figure 1.

The establishment of equilibrium is achieved within 24h for the coarse fraction; whereas the equilibrium for the fine and the intermediate fraction is almost instantaneous (equilibrium is achieved within 1h). Furthermore, the uranium removal efficiency at equilibrium varies: 60%, 80% and 100% for the coarse, intermediate and fine fraction, respectively. Despite having used the same amount of mass in each experiment, the surface area among the different fractions varies significantly. Hence, the results were expressed as percent uranium removal and not as *q* (mg U(VI) sorbed per g of soil). Nevertheless, it is clear that in the case of the intermediate and fine fractions, all of the experimental points in the figure are part of the equilibrium, whereas, in the case of the coarse fraction, there is a gradual increase of uptake up to 24 h.

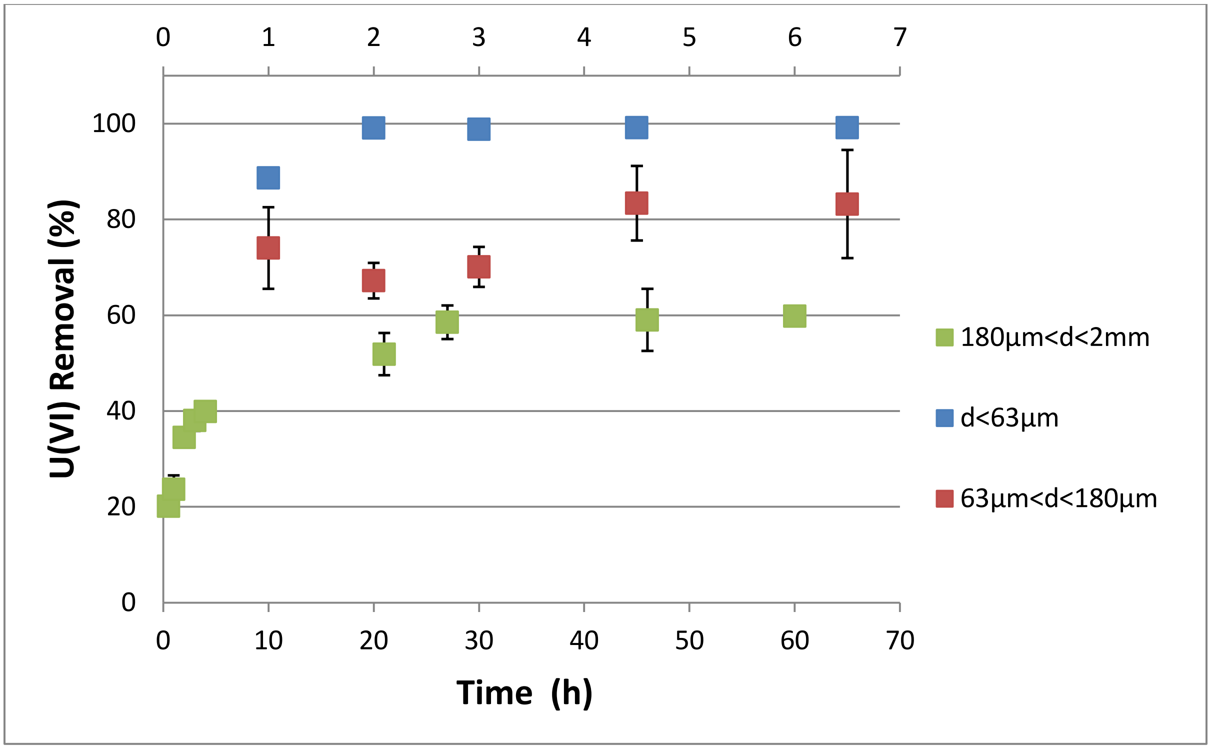

Figure 1. Uranium removal as a function of time for different fractions of SRS soil.

4.2 SEM-EDS analysis of different soil fractions

A specific mass of each soil fraction was placed on SEM stubs on an analytical scale and the exact mass was recorded. Triplicate samples were prepared for each fraction and EDS analysis was performed in multiple locations of each sample. In Table 2, the elemental analysis of each fraction for Fe, Al and Si is presented.

Table 2. Concentration of Fe, Al and Si for each SRS Fraction Followed by Relative Standard Deviation

SRS Soil Fraction	U(VI) % Removed	[Fe] (mg/g)	[Al] (mg/g)	[Si] (mg/g)
d<63μm	99±0.2	89±2	72±4	396±3
63μm<d<180μm	79±8	70±11	71±5	389±4
180μm<d<2mm	59±1	40±4	54±13	416±37

The concentration of Fe differs significantly among the three fractions, whereas the concentration of Al and Si remains statistically the same throughout the fractions. The presence of Al and Si is due to kaolinite and quartz, whereas the presence of Fe is associated with goethite. Table 2 reveals a trend of higher uranium removal when the average particle diameter of the soil decreases. Nevertheless, the increase in uranium uptake could be attributed to two factors: the increase of iron concentration and/or the increase of surface area. It can be seen clearly in the SEM photos of different fractions that the smaller the average particle diameter, the larger the surface area (Figure 2).

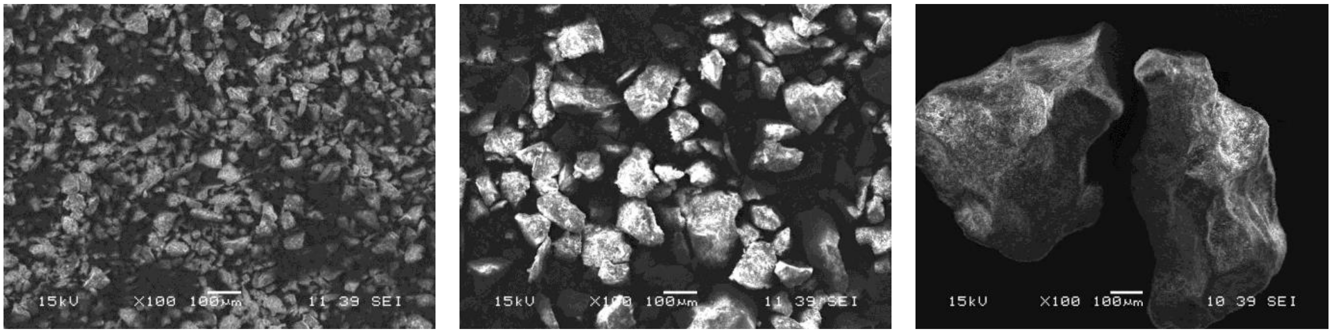

Figure 2. SRS soil fraction d<63 μm (left), 63<d<180 μm (middle) and 180 μm<d<2mm (right).

4.3 BCR sequential extraction experiments

The theory behind sequential extraction protocols is that most mobile metals are removed in the first fraction and continue in order of decreasing of mobility (Zimmerman & Weindorf, 2010). In an attempt to provide an internationally accepted sequential extraction protocol, a modified BCR (Community Bureau of Reference or now the Standards, Measurements and Testing Program of the European Commission) sequential extraction procedure was developed (Rauret et al., 1999). This procedure is largely similar to that produced by Tessier (Tessier et al., 1979), with the chief difference in the first fraction of the procedure. Instead of evaluating the exchangeable and carbonate bound separately, the BCR procedure combines both in the first fraction (Ure et al., 1993). The results of BCR sequential extraction for U(VI) sorbed on SRS soil are presented at Table 3.

Table 3. Percentage of U(VI) Recovered in each Stage of BCR Sequential Extraction Protocol

BCR target phase	U(VI) recovery %
Exchangeable, water and acid soluble	83 ± 7
Reducible form - bound to Fe and Mn oxides	10 ± 1
Oxidizable form – bound to organic matter and sulfides	2 ± 1
Residual	5 ± 4

The majority of the uranium that was retained by SRS soil was recovered in the first step of the process, indicating that uranium that is uptaken by the soil is found mostly in acid soluble form. Nevertheless, the preliminary desorption experiments that involved uranium-loaded soil and deionized water (pH 6.5) as a desorbing agent revealed practically no recovery of uranium. These results suggest that sorbed uranium on SRS soil may be re-mobilized only by acidic agents, such as 0.11 M CH_3COOH, that was used during step 1. Ten (10) percent of the total uranium retained is associated with iron oxides, since SRS background soil from the F/H Area does not contain a significant amount of manganese oxides, as can be seen in Table 4. The amount of uranium in oxidizable and residual form was found to be practically zero, given the experimental error. The background soil from SRS F/H Area is a low organic, quartz dominated soil (Dong et al., 2012), hence the experimental results were rather as expected. Typically, metals of anthropogenic activity tend to accumulate in the first three phases and metals found in the residual fraction are metals of natural occurrence incorporated in the crystal lattice of the parent rock (Ratuzny et al., 2008; Tessier et al., 1979).

Table 4. Adaptation of Elemental Composition of SRS F/H Area Background Soil Obtained by Means of X-Ray Fluorescence (courtesy of Dr. Miles Denham)

Mineral phase	SRS F/H area soil percentage (%)
Quartz	92 ± 4
Kaolinite	6 ± 2
Goethite	2.0 ± 0.5
MnO_2	<0.01

4.4 Kinetic experiments with mixtures of pure minerals

This set of experiments comprised of 2 different batches: the first contained plain quartz (Ottawa sand, 20-30 mesh) and the second contained 95% of quartz and 5% of kaolinite ($Al_2Si_2O_7 \cdot 2H_2O$), a concentration mimicking the ratio of quartz and kaolinite in the actual SRS F/H Area (see Table 4). The results of the batch kinetic experiments are presented in Figure 3. The kinetic results, including those of the coarse fraction of the SRS soil (180 μm<d<2 mm) for comparison reasons, are presented in Figure 4.

The uranium removal efficiencies of quartz and the quartz and kaolinite mixture at equilibrium are quite close: 16% and 20%, respectively. Results suggest that the presence of kaolinite does not contribute significantly in uranium removal under the conditions studied (pH 6.7, 5% kaolinite in the mineral mixture). In the case of quartz, equilibrium is established within 1 h, whereas in the case of the quartz and kaolinite mixture, equilibrium is gradually established after 3-4 h. The initial slope of the line before the establishment of equilibrium is 3.2 h^{-1} for quartz and kaolinite and 13 h^{-1} for plain quartz. The lower uptake rate for quartz and kaolinite, as well as the larger amount of time required to reach equilibrium, may be indications of diffusion phenomena, due to coating of the surface of quartz by fine kaolinite particles. Similarly, the uptake of U(VI) by the coarse fraction of SRS soil was even slower (equilibrium was reached after 24 h). On the other hand, the removal efficiency at equilibrium was much higher (60%). This result suggests that the presence of goethite in SRS soil enhances the U(VI) uptake at circumneutral conditions.

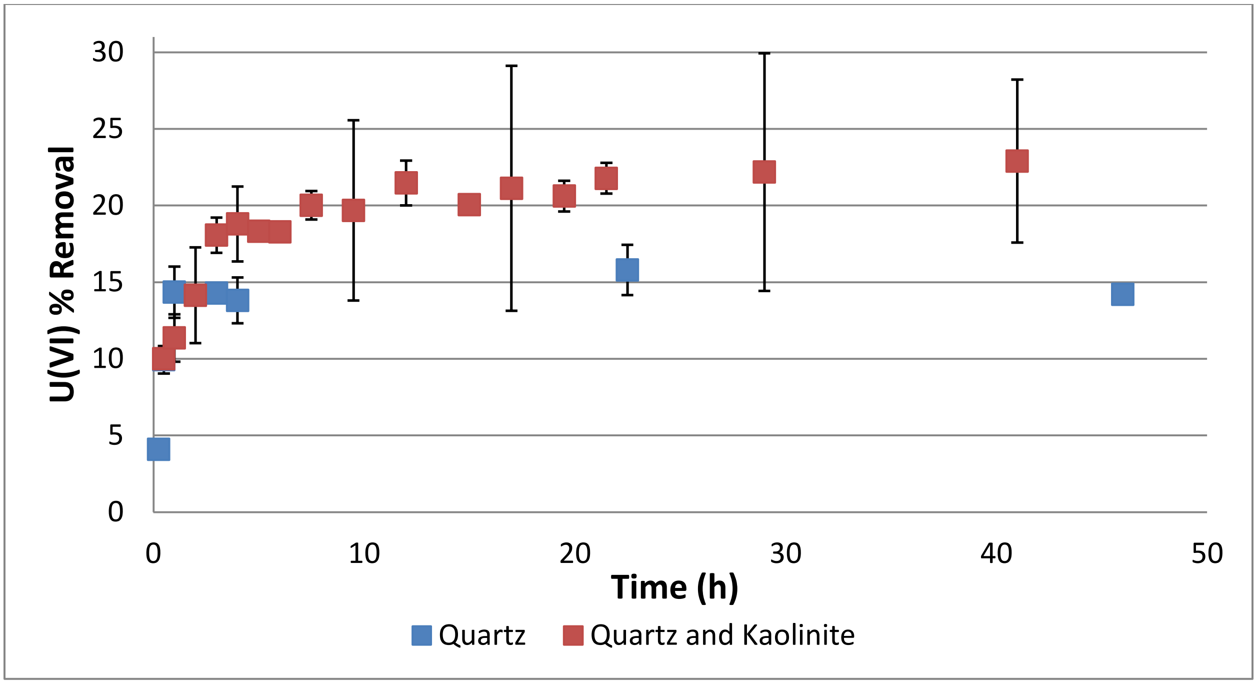

Figure 3. U(VI) percent removal as a function of time for pure quartz and quartz and kaolinite mineral mixtures.

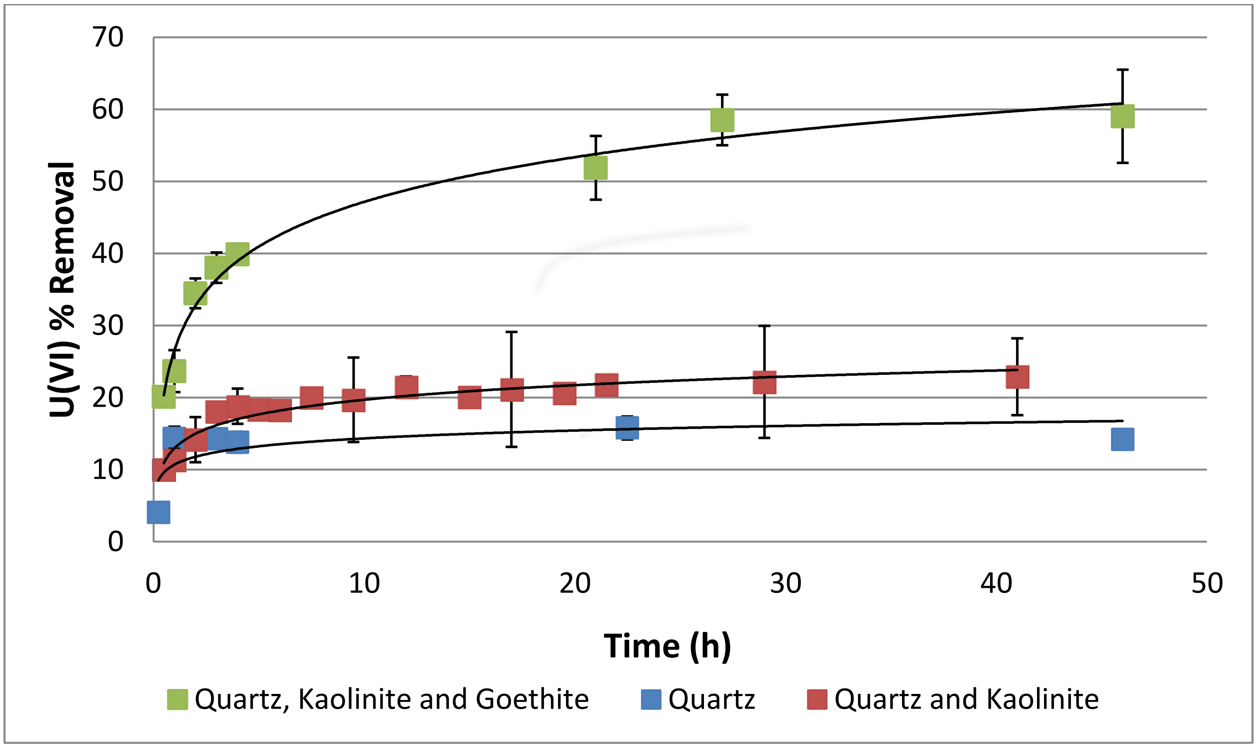

Figure 4. U(VI) percent removal as a function of time for pure quartz and quartz and kaolinite mixtures, as well as SRS soil coarse fraction (180 µm<d<2 mm).

4.5 Desorption experiments

After the establishment of the sorption equilibrium for the mixtures of pure minerals and the SRS coarse fraction, the supernatant was discarded and 10 ml of synthetic SRS groundwater were reintroduced. The new mixture was left to equilibrate for another 24 hours at room temperature and the U(VI) concentration released in the aqueous phase was determined. Results are summarized in Table 5.

Table 5. U(VI) Removal by each Experimental Set, Followed by the Percentage of U(VI) Released in the Aqueous Phase, as a Result of Contact with SRS Synthetic Groundwater (Desorption).

Soil Type	U(VI) % Removal	U(VI) % Recovery
Quartz	16±2	109±13
Quartz and Kaolinite	22±1	99±12
Quartz, Kaolinite, Goethite (SRS soil, 180 μm<d<2 mm)	59±6	61±5

The results indicate that when the mineral mixture comprises of quartz and kaolinite, the amount of uranium removed is much lower compared to the removal percentage of SRS background soil. This suggests that goethite is the most reactive mineral phase towards U(VI) under circumneutral conditions, as discussed above. Furthermore, the amount of U(VI) sorbed is quantitatively released in the aqueous phase, upon contact with SRS synthetic groundwater in the case of quartz and quartz and kaolinite mixture. On the other hand, desorption was significantly less in the experiments with SRS background soil, which contains goethite as well, indicating that goethite contributes to stronger binding of U(VI). Possible reasons contributing to higher U (VI) sorption and lower desorption may be the higher surface area provided by goethite particles, as well as Fe-U(VI) interactions (Cornell & Schwertmann, 2003; Jolivet et al., 2000).

4.6 Investigation of ion exchange mechanism

In order to investigate if ion exchange is involved in the retention of U(VI) by SRS background soil from the F/H Area, different sample sets were prepared: batch experiments were conducted in the presence of sodium silicate (pH ~6.5) and without sodium silicate (pH ~3.5), as well as with and without uranium. The purpose was to track the amount of Ca, Mg, Al and Fe in the aqueous phase in the presence and absence of uranium to investigate if they affect the removal of uranium. The different sample sets are summarized in Table 6.

Table 6. Schematic Representation of the Different Batch Experiments Conducted in Order to Investigate the Effect of Cations on the Uranium Sorption onto SRS Sediment

Code	U(VI), 0.5 ppm	Sodium silicate (70ppm) amendment	Medium	pH
A	x		SRS GRW	3.5
B	x	x	SRS GRW	6.5
C			SRS GRW	3.5
D		x	SRS GRW	6.5

In Table 7, the average concentration of Ca and Mg in the aqueous phase is presented, followed by the standard deviation for all samples (A-D). A comparison of the concentration of Ca and Mg reveals that there are significantly greater concentrations of these cations in the supernatant solution compared to the composition of synthetic SRS groundwater. This result suggests that amounts of Ca and Mg could leach from the soil into the aqueous phase, despite the fact that calcium and magnesium oxides comprise a very small fraction of SRS sediment. Furthermore, results suggest that the amount of calcium and magnesium in the aqueous phase is not pH dependent, since the pH at code samples A and C is 3.5, whereas at code samples B and D, the pH value is 6.5 (sodium silicate amendment). Similarly, the presence of uranium in the samples does not seem to affect the amount of magnesium in the aqueous phase (code samples C and D do not contain uranium). Uranium removal for the code A samples (pH 3.5) was found to be zero while for code B samples (pH 6.5), the uranium removal was found to be 60 ± 4%, consistent with all of our previous experiments. On the other hand, a small difference in the amount of calcium released in the aqueous phase was observed in the presence of uranium, implying that there may be some limited ion-exchange between calcium and uranium during uranium sorption. Finally, there seems to be no difference between the different time intervals (day 1 and 2), something rather expected since, in previous kinetic experiments, the equilibrium was found to be established in less than 24 hours.

In Table 8, the average concentration of Al and Fe in the aqueous phase is presented, followed by the standard deviation for all samples (A-D). The presence of Al and Fe in solution can be traced back to the soil composition (kaolinite and goethite, respectively), since SRS synthetic groundwater does not contain any of these elements.

Table 7. Ca and Mg Concentrations Detected in the Aqueous Phase Followed by Relative Standard Deviation

		A	**B**	**C**	**D**
Day 1	Ca (ppm)	2.2 ± 0.1	2.6 ± 0.3	1.8 ± 0.1	1.7 ± 0.1
	Mg (ppm)	0.8 ± 0.01	0.8 ± 0.03	0.70 ± 0.01	0.70 ± 0.02
Day 2	Ca (ppm)	2.1 ± 0.3	2.0 ± 0.1	1.7 ± 0.01	1.6 ± 0.04
	Mg (ppm)	0.72 ± 0.01	0.71 ± 0.04	0.67 ± 0.01	0.68 ± 0.03
SRS.GRW	Ca (ppm)	0.50 ± 0.03			
	Mg (ppm)	0.35 ± 0.01			

Table 8. Al and Fe Concentration Detected in the Aqueous Phase Followed by Relative Standard Deviation

		A	**B**	**C**	**D**
Day 1	Al (ppm)	0.71 ± 0.08	0.66 ± 0.07	0.66 ± 0.09	0.56 ± 0.1
	Fe (ppm)	0.32 ± 0.1	0.39 ± 0.01	0.28 ± 0.1	0.41 ± 0.2
Day 2	Al (ppm)	0.51 ± 0.04	0.44 ± 0.05	0.51 ± 0.01	0.42 ± 0.1
	Fe (ppm)	0.12 ± 0.09	0.25 ± 0.1	0.13 ± 0.03	0.20 ± 0.1
SRS.GRW	Al (ppm)	0			
	Fe (ppm)	0			

The levels of iron and aluminum are similar across all the groups at day 1, indicating that the leaching of iron and aluminum into the aqueous phase is not pH dependent and is not affected by the presence of uranium in the aqueous phase. On the other hand, the levels of iron and aluminum during the second day, although similar across the samples, are lower than the respective values of the first day. A possible explanation for this pattern may be the secondary precipitation of iron and aluminum at the respective pH values.

Finally, identical batch experiments (pH 3.5 and 6.5 after sodium silicate amendment) were carried out, but instead of using SRS synthetic groundwater, deionized water

(DIW) was introduced in the samples. In the sorption experiments of U onto SRS sediment in deionized water with and without the addition of sodium silicate (pH 3.5 and 6.5, respectively), U(VI) removal was very similar when compared to the experiment with SRS synthetic groundwater: at pH 3.5, removal was zero, while at pH 6.5, removal was 64±7%. This implies that the presence of several cations in the SRS synthetic groundwater, like Na^+, K^+, Ca^{2+} and Mg^{2+}, has little or no interference with U(VI) sorption onto the sediment. The amount of calcium, magnesium, aluminum and iron leached from the sediment in the aqueous phase (DI water) is summarized in Table 9.

Table 9. Ca, Mg, Al and Fe Concentrations in the Aqueous Phase Followed by Relative Standard Deviation for All the Samples

	pH 3.5	**pH 6.5**
Ca (ppm)	2.7±0.3	2.8±0.2
Mg (ppm)	0.75±0.2	0.72±0.1
Al (ppm)	0.40±0.03	0.44±0.01
Fe (ppm)	0.24±0.08	0.36±0.1

4.7 Effect of ionic strength

The experiments were conducted to bring 400 mg of SRS soil of mean particle diameter 0.18<d<2mm in contact with 20 ml of SRS synthetic groundwater pH 3.5 bearing 500 ppb of U(VI). Seventy (70) ppm of sodium silicate was added to achieve circumneutral conditions and then different quantities from stock solutions of $CaCl_2$ and $NaClO_4$ were added in order to achieve the desired electrolyte concentrations. The concentrations of $CaCl_2$ and $NaClO_4$ were 0.001, 0.01 and 0.1 M. Control samples (no addition of electrolyte) were also studied, which already contain a concentration of $CaCl_2$ 10^{-5} M. The results are presented in Figure 5.

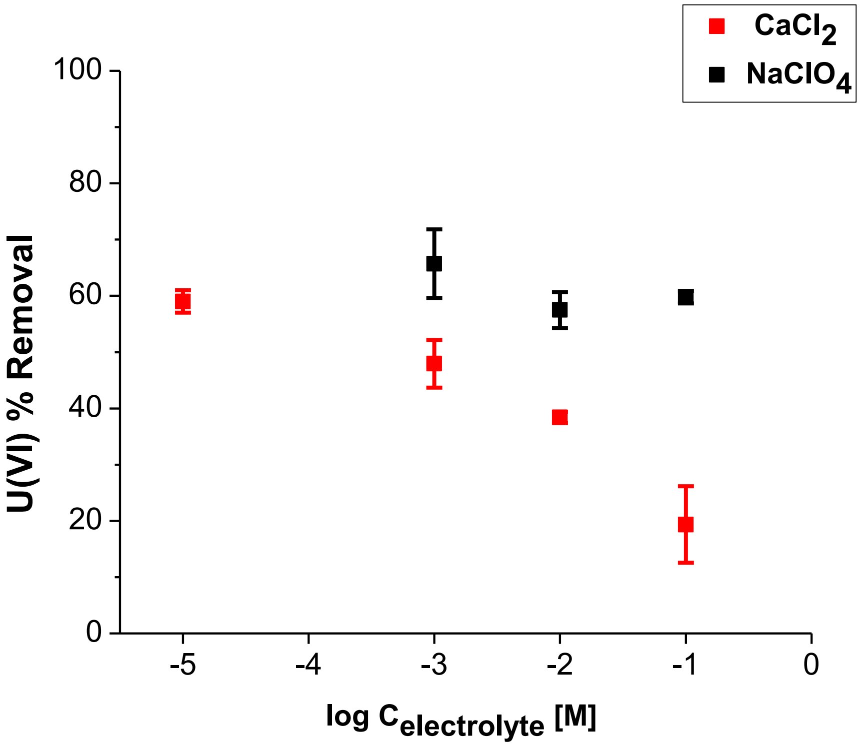

Figure 5. U(VI) percent removal as a function of electrolyte concentration using $CaCl_2$ and $NaClO_4$ (x-axis is in logarithmic scale). Error bars represent relative standard deviation.

The retention of cations from mineral surfaces is frequently described by the surface complexation model. Surface complexation involves the formation of direct bonds between metal cations and surface –OH groups and/or O atoms and comprises of two different types of complexes: the outer-sphere complexes and the inner-sphere complexes (Wu et al., 1999). In the case of inner-sphere complexation, the ions are bound directly to the surface site (Figure 6). On the other hand, in outer-sphere complexation, the ion is presumed to bind to the surface site by chemical bonds without losing the hydration shell, meaning that the water molecule is located between the ion and the binding site (Figure 6). The distance to the surface is larger and the bond strength is weaker in comparison to inner-sphere complexation (Worch, 2015). Outer-sphere complexation takes place in the double layer (as opposed to inner-sphere complexation, which takes place on the surface), where an excess of counter-ions are located, neutralizing the surface charge. The double layer decreases with ionic strength (electrolyte concentration) increase and, hence, outer-sphere complexes are presumed to be susceptible to coulombic interactions (Sherwood Lollar, 2005).

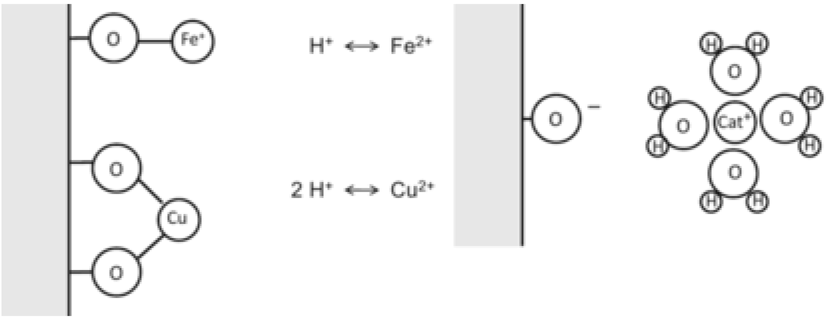

Figure 6. Example of inner-sphere complexation (left) and outer-sphere complexation (right), as adapted by Sigg and Stumm, Aquatic Chemistry (Sigg & Stumm, 2011).

Ions that form outer-sphere complexes exhibit reduced sorption with ionic strength increase whereas ions that form inner-sphere complexes are usually not affected by the fluctuation of ionic strength (Bachmaf & Merkel, 2010). The removal of U(VI) by SRS soil remained unaffected when ionic strength was adjusted with the addition of $NaClO_4$, implying that U(VI) removal under the conditions studied may be mainly attributed to the formation of inner-sphere complexes. $NaClO_4$ was chosen because it is an inert electrolyte: it exhibits practically no complexation with metals present in the aqueous form and the sorption of ClO_4^- on oxide surfaces is minimal (Morales et al., 2011; Zebardast et al., 2014). Similar results were reported by Guo (Guo et al., 2009) who found that the sorption of U(VI) on goethite was insensitive to the fluctuation of ionic strength, adjusted with NaCl.

On the other hand, removal decreases significantly with the increase of calcium chloride concentration. The speciation of the soluble U(VI) species under the conditions studied is presented at Table 10 (10^{-5} M $CaCl_2$ is the concentration of SRS synthetic groundwater, without any further addition of calcium chloride). The speciation for most species remains the same across the range of concentrations studied, with the exception of the percentage of the $Ca_2UO_2(CO_3)_3$ and $(UO_2)_3(OH)_5^+$ species, between 0.01 and 0.1 M $CaCl_2$ concentrations. Nevertheless, the decrease in the uranium removal across the wide range of concentrations studied is not likely to be largely dependent on speciation. A possible explanation for the reduced removal at high calcium chloride concentrations may be the competition of calcium ions and uranium complexes for the same or neighboring binding sites, resulting in a reduced uranium sorption. The uptake of calcium by goethite has been documented in literature and it has been found that calcium binds on goethite both as an outer- and inner-sphere complex (Rahnemaie et al., 2006; Rietra et al., 2001) based on the following scheme: $=SO\text{-}Ca^+$ (Sverjensky, 2006), where S stands for the solid surface and O is the oxygen atom. Goethite may constitute only a small fraction of SRS soil; nevertheless, it is very reactive towards metal cations in the solution. Taking into consideration the results of Guo (Guo et al., 2009) who showed that when ionic strength is adjusted with NaCl, U(VI) sorption on goethite remains the same, it may be concluded that high calcium concentration plays an important role in inhibiting U(VI) sorption on SRS soil in circumneutral conditions. As calcium concentration increases (0.1M), the decrease in U(VI) sorption is even more sharp (from 40% down to 18%), perhaps due to the formation of $Ca_2UO_2(CO_3)_3$, which may not be available for further complexation by the binding sites. Nevertheless, that does not seem to be the case for low calcium concentrations: uranium removal was found to be 59 ± 6% and 64 ± 7% when sorption experiments were performed in synthetic SRS groundwater (Ca^{2+} 10^{-5} M) and deionized water, respectively.

Table 10. Speciation of U(VI) Soluble Species for All the Calcium Concentrations Studied (as provided by Visual Minteq)

$CaCl_2$ concentration (M)			
10^{-5}	**10^{-3}**	**10^{-2}**	**0.1**
47.3% $(UO_2)_3(OH)_5^+$	46.9 % $(UO_2)_3(OH)_5^+$	44.5 % $(UO_2)_3(OH)_5^+$	21.7 % $(UO_2)_3(OH)_5^+$
14.5 % UO_2OH^+	14.8 % UO_2OH^+	15.6 % UO_2OH^+	13.5 % UO_2OH^+
4.1% $(UO_2)_4(OH)_7^+$	4.0% $(UO_2)_4(OH)_7^+$	3.6 % $(UO_2)_4(OH)_7^+$	1.3 % $(UO_2)_4(OH)_7^+$
7.8 % $UO_2H_3SiO_4^+$	8.0 % $UO_2H_3SiO_4^+$	8.4 % $UO_2H_3SiO_4^+$	7.7 % $UO_2H_3SiO_4^+$
18.7 % UO_2CO_3	18.4 % UO_2CO_3	17.3 % UO_2CO_3	12.3 % UO_2CO_3
5.6 % $UO_2(OH)_2$	5.5 % $UO_2(OH)_2$	5.2 % $UO_2(OH)_2$	3.7 % $UO_2(OH)_2$
		1.9 % $Ca_2UO_2(CO_3)_3$	34.4 % $Ca_2UO_2(CO_3)_3$

Experiments with elevated calcium and magnesium concentrations will be repeated using $Ca(NO_3)_2$ and $Mg(NO_3)_2$ as electrolytes, in order to investigate the effect of the counter-ion (Cl^- versus NO_3^-) in the process.

4.8 Multi-contaminant batch sorption experiments

In this set of experiments, the liquid phase contained 0.5 ppm of U(VI), 0.1 ppm of Sr and 0.1 ppm of Re. U(VI) removal was found to be 59±5%, whereas there was zero retention of strontium and rhenium. Rhenium under oxidizing conditions is found as perrhenate (ReO_4^-) and can be used as a chemical analog for technetium (TcO_4^-). Pertechnetate is highly soluble, does not sorb onto sediments and migrates at the same velocity as groundwater (Kaplan et al., 1998). Hence, the experimental results for rhenium were rather expected. Strontium has similar physicochemical properties with calcium and although calcium has been reported to be retained by goethite (Rahnemaie et al., 2006; Rietra et al., 2001; Sverjensky, 2006), no such behavior was observed for strontium under the conditions studied.

5. Future Work

Future work will include the determination of the surface area of different SRS soil fractions and normalization of U(VI) retention per area unit. Furthermore, desorption experiments will be performed on the intermediate and fine soil fraction of SRS soil in an effort to compare recovery among different SRS fractions and provide better understanding of the role of Fe concentration and area in U(VI) retention across a range of particle sizes.

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