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ABSTRACT

This project focused on the use of a sorbent, carbonated apatite, to immobilize selenium in the environment. It is know that apatite will sorb selenium and based on the mechanism of sorption it is theorized that carbonated apatite will be more effective that pure apatite. Immobilization of selenium in the environment is through the use of a sorbent in a permeable reactive barrier (PRB). A PRB can be constructed by trenching and backfill with the sorbent or in the case of apatite as the sorbent formed *in situ* using the apatite forming solution of Moore (2003, 2004). There is very little data on selenium sorption by carbonated apatite in the literature. Therefore, in this work, the basic sorptive properties of carbonated apatite were investigated. Carbonated apatite was synthesized by a precipitation method and characterized. Batch selenium kinetic and equilibrium experiments were performed. The results indicate the carbonated apatite contained 9.4% carbonate and uptake of selenium as selenite was rapid; 5 hours for complete uptake of selenium vs. more than 100 hours for pure hydroxyapatite reported in the literature. Additionally, the carbonated apatite exhibited significantly higher distribution coefficients in equilibrium experiments than pure apatite under similar experimental conditions. The next phase of this work will be to seek additional funds to continue the research with the goal of eventually demonstrating the technology in a field application.

INTRODUCTION

Selenium contamination of groundwater and surface water is a major problem in the United States. Although selenium is an essential nutrient at very low concentrations, at higher concentrations it is toxic. Major sources of selenium contamination involve US energy, agriculture and resource production including uranium, phosphate and coal mining, coal ash pile leaching at power plants, agricultural activities and hydrofracking operations. Currently, there is no inexpensive and highly effective treatment method for remediation of selenium contaminated water. It is already known that selenium in its reduced form as selenite, SeO_3^{2-}, will substitute into the pure apatite also known as hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, structure for phosphate. In this work, we investigate the use of carbonated apatite, $Ca_{10-x}Na_x(PO_4)_{6-y}(CO_3)_y(OH)_2$, for sequestering selenium as selenite. It is theorized, based on the mechanism of selenium absorption to apatite that uptake of selenium by carbonated apatite will be kinetically faster than hydroxyapatite and that the carbonated apatite may sorb more selenium than hydroxyapatite.

Current methods to remove selenium from water include phytoremediation (Esringu and Turan, 2011), biological treatment (Hageman, et al. 2013), ion exchange, evaporation, chemical treatment, filtration (Bond, 2000) and Permeable reactive barriers (Zhang et al., 2008). All of these methods with the exception of using a PRB are active treatment technologies that have significant capital costs, create a waste stream, can expose workers to the contaminant and have significant long-term operational costs. Conventional permeable reactive barriers, constructed by trenching and backfilling with a reactive media such as zero valent iron have a finite life span, have the potential to clog due to precipitation of secondary metals or biofowl, and have not been demonstrated to achieve low selenium concentration in the effluent (Sandy, T., and C. DiSante, 2010).

For permeable reactive barriers, it has been demonstrated that apatite can be formed *in situ* in sediment by injecting a solution of calcium citrate and sodium phosphate into the sediment. The indigenous soil bacteria metabolize the citrate and the calcium is released in a form that reacts with phosphate to form apatite (Moore, 2003; Moore , 2004). The technology is being used at the DOE Hanford site to remove radioactive strontium from groundwater. For selenium sorption by apatite, the selenium must be in a reduce state as selenite. The use of the indigenous soil bacteria to form apatite *in situ* in sediment results in a reducing environment in the sediment. Therefore it may be possible to use the existing technology for selenium immobilization or with an additional reducing agent.

Only a few studies are reported on the sorption of selenium by apatite. $Ca_{10}(PO_4)_6(OH)_2$) has been reported substitute for phosphate in the apatite structure. Monteil-Riveria et al. (1999; 2000) studied the sorption by selenium by hydroxyapatite. The results indicate selenium as selenite substitutes for phosphate in the apatite lattice. Substitution of selenite, a +3 ion, for phosphate, a +4 ion, must be balanced in the apatite structure for charge neutrality. Thus, selenite substitution for phosphate is accompanied by a monovalent ion, typically sodium, substituting for calcium. It is theorized that if a divalent oxyanion, carbonate, is substituted into the apatite structure along with an equal number of monovalent cations, sodium, then incorporation of the divalent selenite ion into the apatite structure will be a single substitution mechanism and with much faster kinetics and potentially greater uptake of selenium. The kinetics of selenium substitution into apatite must be fast for applications of permeable reactive barriers where groundwater flow in the region is rapid. Duc et al., (2003) reports on the sorption of selenium by apatites and iron oxides. The authors performed batch sorption studies with hydroxyapatite, fluorinated apatite, goethite and Hematite. The authors concluded from their results that sorption kinetics for selenium on iron oxides was kinetically faster than apatites, however in the long term the use of apatite as a sorbent may be more favorable because the selenium is incorporated into the apatite lattice and not superficially sorbed to the iron oxide surface.

The long term goal of this work is to develop a material that can be used in permeable reactive barriers to permanently immobilize selenium from groundwater or at least slow down its release to acceptable concentrations. In this first phase of the work, the sorptive ability of carbonated apatite for selenium as selenite was investigated. A carbonated apatite was synthesized by a precipitation method and batch sorption experiments to determine sorption kinetic and uptake experiments as a function of pH were performed. The results indicate the carbonate apatite used in this work exhibits much faster kinetics for selenite sorption and significantly outperforms hydroxyapatite for selenium uptake. Additional research is needed for engineering a method for use of carbonated apatite in a permeable reactive barrier.

EXPERIMENTAL/METHOD

Although it has been demonstrated that apatite can be formed in sediment to form a permeable reactive barrier and the technology is in use at the Hanford 100 N site, little information is available concerning the formation of carbonated apatite. Experiments forming apatite using the method described by Moore et al. (2003, 2004) with a synthetic Hanford groundwater containing significant amounts of carbonate have been performed by Szecsody (2014). Although the carbonate concentration in the groundwater was relatively high, very little carbonate was incorporated into the apatite. In another study by Szecsody (2014), an attempt was made to make carbonated apatite *in situ* in sediment by modification of the method of Moore (2003, 2004) by adding sodium bicarbonate to the formulation. No carbonated apatite and very little apatite were formed. The main product of the synthesis was calcium carbonate. These results are interesting because it is typically easy to incorporate carbonate into apatite using a precipitation method by simply adding a carbonate compound to the calcium and phosphate reagents (LeGeros, 1991). The *in situ* method of Moore (2003, 2004) for precipitating apatite in sediment is much more complicated than simple precipitation methods in laboratory synthesis and a significant amount of work may be required to modify the method for precipitating carbonated apatite in sediment. If it is determined forming carbonated apatite *in situ* is not feasible then carbonated apatite can be used in conventional permeable reactive barriers constructed by trenching and backfilling. However, fundamental information is first needed on the sorptive ability of carbonated apatite for selenium. Therefore, in this first stage of the work, experiments focused on sorption kinetics and equilibrium distribution of selenium by carbonated apatite.

Preparation of Carbonated Apatite

All chemicals used were of reagent grade and used without further purification. Water used was treated by reverse osmosis followed by filtration through activated carbon. Carbonated apatite was prepared using a modification of the precipitation method described by Frank-Kamenetskaya (2014). A 0.35L solution containing 0.053 M $CaNO_3$ was mixed with 0.35L of a solution containing 0.017 M $NaHPO_4$ and 0.021M $NaHCO_3$ over a 4 hours period in a 1L flask. The solution was prepared by degassing the water by boiling and sparging with nitrogen. The initial pH of each solution was adjusted to 7.4 using either 0.01 to 0.1 M HCl and/or NaOH solutions. The solutions containing calcium citrate and sodium phosphate with sodium carbonate were steadily introduced into the reaction vessel using a peristaltic pumps. The pH was constantly monitored and maintained at 7.4 by adding NaOH. Dry ultrapure nitrogen was sparged through the mixture of reagents at all times. The reacting solution was constantly stirred and the temperature was maintained at 38°C. After all chemical reagents had been added, the solution with precipitate was maintained at 38°C overnight. The precipitate was separated from the solution by vacuum filtration and rinsed with distilled water and dried under vacuum at ambient temperature for 24 hours. The precipitate was ground into a fine powder.

The precipitate was examined using several analytical techniques commonly used for examining apatites including Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), Fourier Transform-Infrared Spectroscopy (FT-IR) and X-Ray Diffraction (XRD). The surface area of the precipitate was determined by Brunauer, Emmett and Teller (BET) analysis. The amount of carbonate in the apatite was determined using a thermogravimetric method where a known amount of the carbonated apatite was placed in a crucible in a tube furnace. Dry ultrapure nitrogen was continuously passed through the furnace. The carbonated apatite sample was heated to different temperatures and then weighed. These temperatures were 160°C to remove water adsorbed to the carbonated apatite surface, 400°C to remove additional water inside the carbonated apatite structure and 950°C where all carbonate in the structure is converted to carbon dioxide.

Solubility Experiments

The solubility of the carbonated apatite was determined at pH values of 5, 6, 9, and 11. Experiments were performed by placing 40 mg of carbonated apatite in 20 L of D.I water and gently shaking for 7 days. The pH of the solution was measured and if necessary adjusted each day with HCl and/or NaOH. After 5 days no further change in pH was observed. Calcium and phosphate concentrations were determined by ion chromatography.

Batch Sorption Experiments

Kinetic Experiment

Kinetic experiments were performed by adding 40 mg of carbonated apatite to 20 mL of a 0.1 KNO_3 solution. It is known that potassium and nitrate does not strongly interact with apatite, carbonated apatite or selenium. A significant quantity of background electrolyte is needed for an accurate pH measurement. The pH of the solution was maintained at 8.0 and allowed to equilibrate for 7 days prior to initiation of the kinetic experiment. Selenium was added into the mixture and samples of the liquid phase were withdrawn periodically and then filtered through 40 μm syringe filters. The amount of selenium in the samples was determined by ICP-MS. A blank containing no carbonated apatite was performed to ensure selenium was not sorbing to the container walls. No change in the amount of selenium in the blanks samples was detected.

Equilibrium Experiments

Equilibrium sorption experiments were performed by adding 40 mg of carbonated apatite into 20 mL solution of 0.1M KNO_3. The solutions were allowed to equilibrate for 7 days prior with the pH adjusted each day if necessary. Selenium (IV) as Na_2SO_3 was added to each vessel and the vessels gently agitated on a shaker table for 5 days. The pH of each vessel was monitored and adjusted if necessary. At the end of 5 days, samples were withdrawn then filtered through 40 μm syringe filters. The amount of selenium in the samples was determined by ICP-MS. A blank containing no carbonated apatite was run to ensure selenium was not sorbing to the container walls. No change in the amount of selenium in the blanks samples was detected.

RESULTS

Analysis of Carbonated Apatite

Carbonate can substitute into the apatite structure for phosphate groups or hydroxyl groups. Substitution of carbonate for hydroxyl groups is characterized by larger a- and smaller c- axis dimensions than hydroxyapatite, whereas substitution of carbonate for phosphate groups is characterized by substitution of CO_3 for PO_4 and substitution of Na for Ca. The structure and composition of the carbonated apatite was examined using several different analytical techniques.

XRD is used for identification, determining purity and crystallinity, lattice parameters and the presence of mixed phases for calcium phosphates. Figure 1 is an XRD plot of 2θ vs. intensity for the carbonated apatite. The XRD analysis indicates the carbonated apatite is poorly crystallized. Poor crystallinity is typical for apatites prepared at low temperature and for highly substituted apatites (LeGeros, 1991).

The FT-IR pattern for the carbonated apatite is given in figure 2. The pattern is typical for carbonated apatite with IR vibrational bands for carbonated apatite shown at 873 and 1400-1550 cm^{-1}.

Analysis of the carbonated apatite by the thermogravimetric method indicated the material contains 6% water sorbed onto the surface, 3.5% water in the structure of the material and 9.4% carbonate that has been substituted for phosphate. BET analysis indicated the material has a surface area of 210.2 m^2/g.

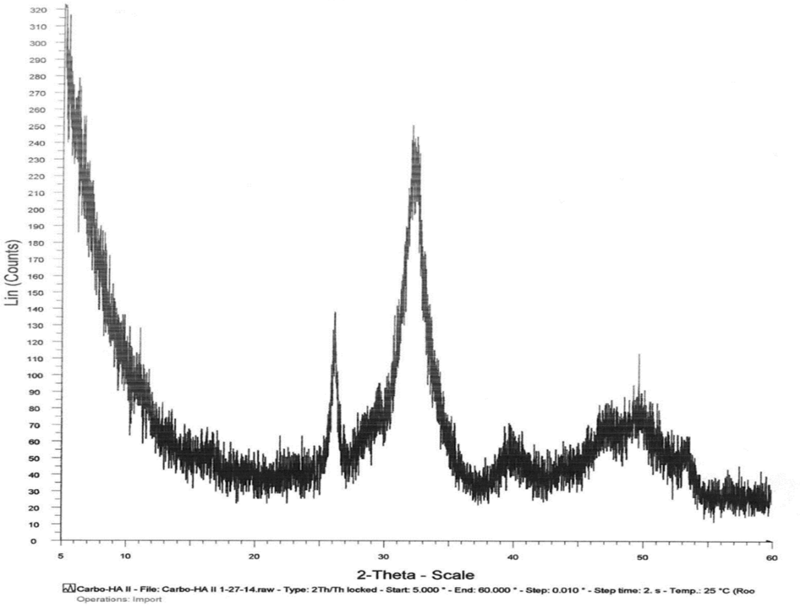

Figure 1. XRD pattern for carbonated apatite synthesized in this work.

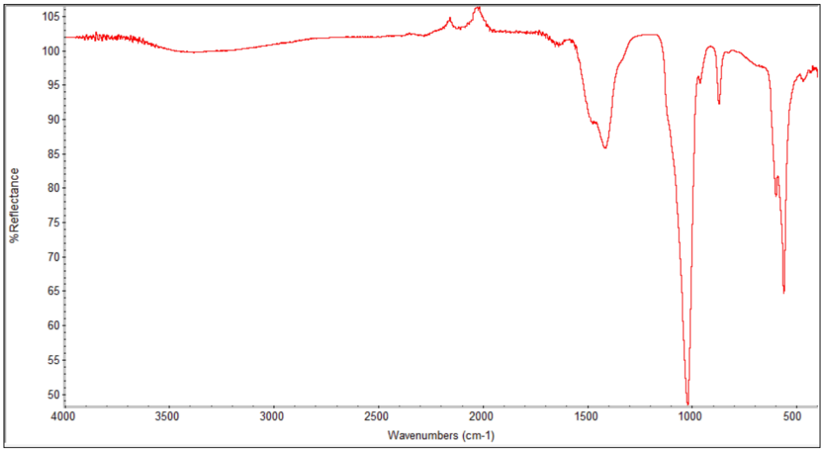

Figure 2. FT-IR pattern for carbonated apatite in this work

Hydroxyapatite with a high crystallinity is acicular crystals. Substitution of carbonate into the apatite structure changes the morphology to hexagonal plates that are clear to see if the material is highly crystalline. For poorly crystallized, highly carbonated apatite the morphology is plate shaped but irregular in shape. Figure 3 is a SEM image of the carbonated apatite. The material is composed of small irregular shaped particles.

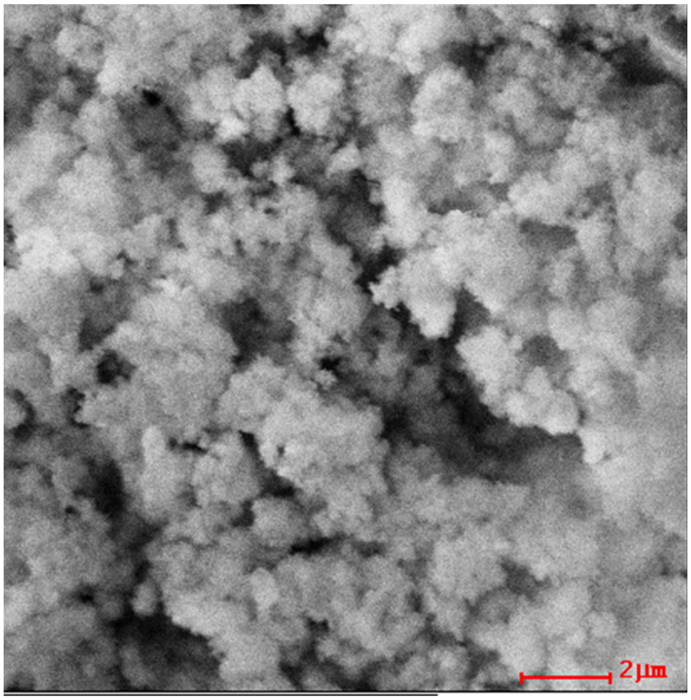

Figure 3. SEM image of carbonated apatite.

Carbonate Apatite Solubility

The solubility of the carbonated apatite is given graphically in figure 4 as a plot of calcium and phosphate concentration in solution as a function of pH. The solubility of the carbonated apatite is relatively high in acidic solution but rapidly drops off in basic solution. This is typical for apatites in general (LeGeros, 1991)

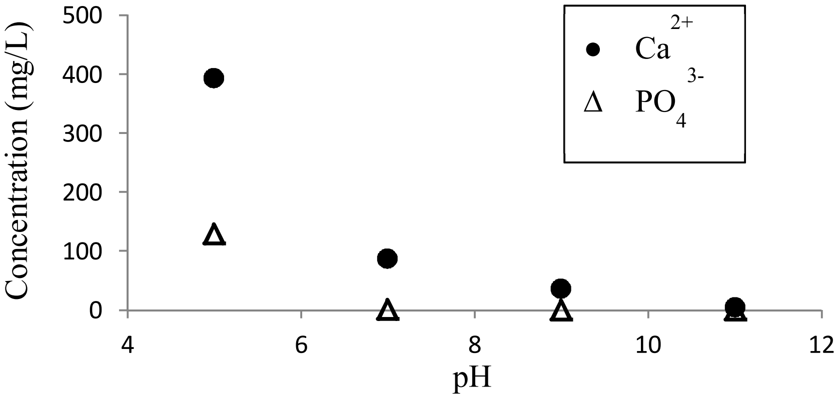

Figure 4. Solubility of apatite represented by calcium and phosphate concentration in solution at different pH. Concentrations were measured using ion chromatography.

Selenium Sorption Experiments

Kinetic Experiment

Kinetic experiments were performed by equilibrating the carbonated apatite with the 0.1M KNO_3 solution prior to adding the selenium. This step ensures dissolution is not the limiting process in reaching equilibrium (Monteil-Rivera et al., 2000). The results from a single kinetic experiment are given graphical in figure 5. Uptake of selenium was complete in approximately 300 min.

Equilibrium Experiments

Distribution coefficient, K_d, is defined as:

$$K_d = [Se]_{sorbed} / [Se]_{liquid\ phase}$$

K_d values were determined over a pH range of 6 to 12 with two different initial concentrations of selenium(IV) of 0.00633 moles/L and 0.0242 moles/L, both in 20 mL of 0.1M KNO_3 solution with 40 mg carbonated apatite. The results are given graphically in figure 6. Maximum selenium sorption occurs between pH 8.5 and 9 and drops off as the solution is more acidic or basic.

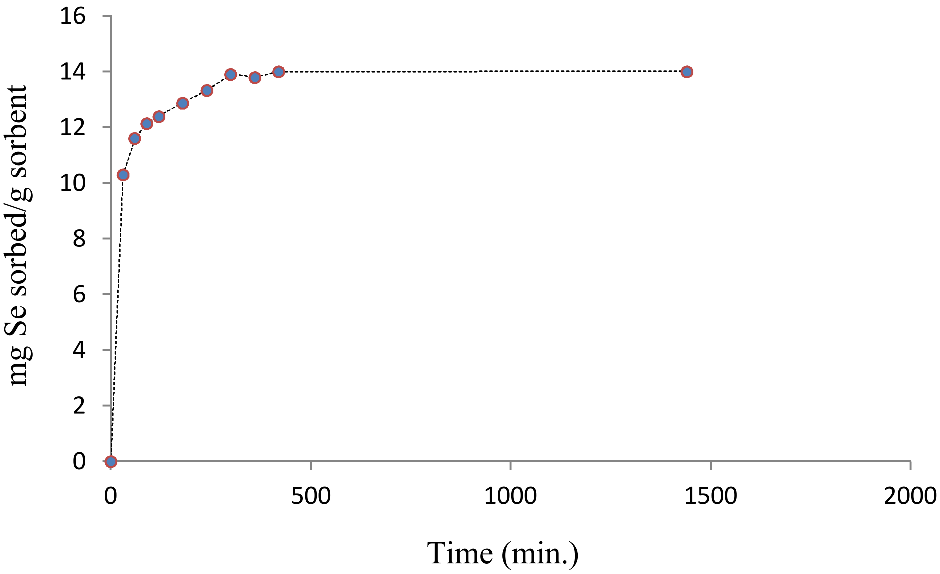

Figure 5. Sorption of selenium(IV) as a function of time. 40 mg of carbonated apatite was placed in 20 mL of 0.1M NKO_3 solution. Selenium in the solution phase was determined by ICP-MS.

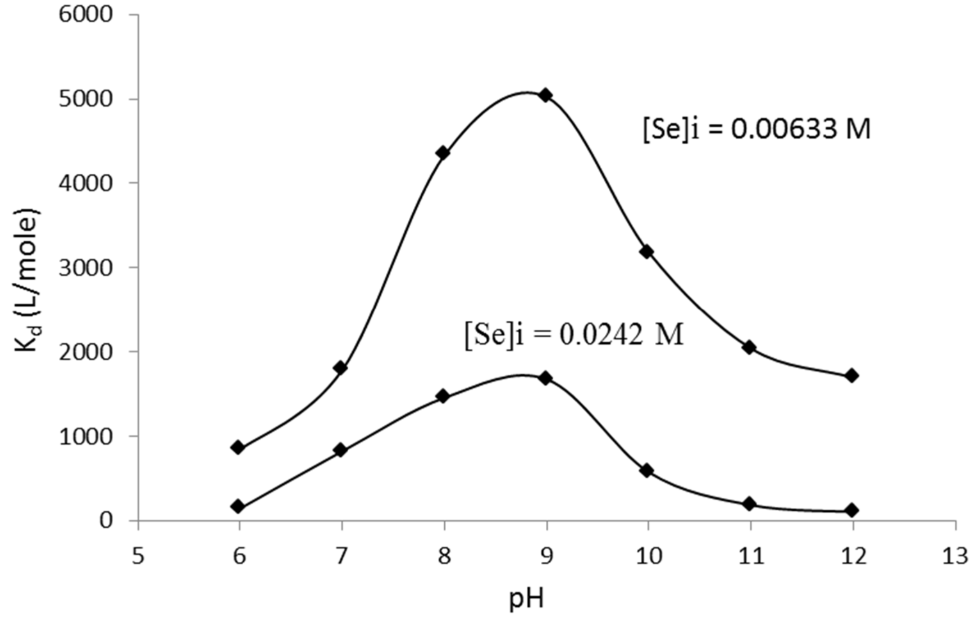

Figure 5. Distribution coefficient vs pH for selenium(IV) sorption by carbonated apatite. Two different initial concentrations of selenium were investigated, 0.00633 moles/L and 0.0242 moles/L, both in 20 mL of 0.1M KNO_3 solution with 40 mg carbonated apatite.

Much more information is required on carbonated apatite characterization and sorption of selenium for engineering a permeable reactive barrier. In this initial scoping study, there were limited resources and additional data could not be collected. Data are needed on the effects of groundwater on carbonated apatite stability and selenium desorption. Desorption experiments need to evaluate the effect of specific ions on selenium desorption. Additionally, the data collected by Szescody for *in situ* formation in of apatite and carbonated apatite in sediment needs further examination and additional experiments need to be performed to understand the interaction of the media and condition for carbonated apatite formation.

DISCUSSION

The theory behind using carbonated apatite instead of hydroxyapatite for selenium sorption is based on the fact that apatite substituted with a divalent oxyanion, carbonate, along with a monovalent cation, sodium, would exhibit faster kinetics for selenium sorption than hydroxyapatite. This because the mechanism of selenium substitution into carbonate apatite consists of a single substitution step, whereas substitution of selenium whereas substitution of selenium for phosphate also involves the substitution of a monovalent cation for calcium.

The kinetic experiment performed in this work exhibited significantly faster kinetics than published data for selenium substitution for hydroxyapatite. However, there is not sufficient information to state the mechanism of substitution is responsible or partly responsible for the faster kinetics. This is because there are other factors than can affect substitution into the apatite structure. These include:

- Crystallinity
- Solubility
- The presence of other ions in the structure
- The composition of the solution phase

Monteil-Rivera et al (2000) studied the sorption of selenium by hydroxyapatite. The authors used a commercially available hydroxyapatite from Bio-Rad Laboratories. Characterization of the material indicated it was spherical with a surface of 77 m^2/g as determined by BET. The authors did not perform their own characterization of the apatite but indicated from the work of others on this same commercially available material that the composition was given by two limiting formulae:

$$Ca_{9.3}\,Na_{0.48}\,(PO_4)_6\,(OH)_{1.1} \bullet 12H_2O$$

$$Ca_{9.9}\,Na_{0.048}\,(PO_4)_{5.1}\,(HPO_4)_{0.9}\,(OH)_2 \bullet 1.8\,H_2O$$

Kinetic experiments were performed with a solution to solid ratio of 250 mL/g. In the present work the solution to solid ratio was 500mL/g. Both studies were performed at a pH of 8.0. In the Monteil-Rivera work, kinetics experiments were performed with initial selenium concentrations of 1×10^{-5} molar and 1×10^{-3} molar as compared to 2.22×10^{-4} molar in the present work. The work of Monteil-Rivera et al (2000) for both initial concentrations complete uptake of selenium took approximately 100 to 160 hours. In the present work uptake was complete in approximately 5 hours. This is a very significant difference. However a direct comparison between the results of the two studies is difficult because of the other factors that can affect sorption such as the large difference in surface area between the two materials.

Direct comparison of equilibrium distribution coefficients, K_d, is also difficult and many times can be because experiments are typically performed under varying circumstances that can significantly affect the values. However, certain information can sometimes be obtained. Experimental conditions in this work were similar in certain ways to the Montiel-Rivera study with the exception of the large difference in surface area and the uncertainty in the difference in solubility of the two materials. In this study and the Montiel-Rivera study the solution to sorbent ratios of 500:1 and 250:1 and the initial concentration of selenium were within the same order of magnitude. The background electrolyte for both studies was 0.1molar KNO_3 and both sets of experiments were performed at ambient temperature.

Sorption of selenium in the Montiel-Rivera study was at a maximum at pH 7.8 to 8.0. In the present study, the maximum selenium sorption was observed between pH 8.5 and 9.0. This difference is relatively small compared to difference in distribution coefficients measured in the two studies. In the Montiel-Rivera study, the highest values are reported to be approximately

200L/mole and 800L/mole for initial selenium concentrations of 1 x 10^{-3} molar and 1 x 10^{-6} molar, respectively. In this study, the maximum values are approximately 1800L/mole and 5300 L/mole for initial concentrations of 6.33 x 10^{-3} moles/L and 2.42 x 10^{-2} moles/L, respectively. The difference between the two studies is approximately an order of magnitude. Additional work is required to separate the effects of surface area, solubility and other factors that can affect selenium sorption for more insight into the effect of the substitution mechanism on selenium sorption.

Despite the need for additional research, the carbonated apatite did exhibit very rapid kinetics for selenium sorption compared to hydroxyapatite and large distribution coefficients. The data indicate carbonate apatite may be a good candidate for use in permeable reactive barrier for immobilization of selenium. Other than its affinity for selenium sorption, carbonated apatite is common throughout the environment, has a low aqueous solubility in the neutral to highly basic region.

ANTICIPATED IMPACT

Selenium contamination of groundwater has become a major problem in the U.S. Selenium is a necessary trace nutrient, but highly toxic in larger amounts. Major sources of selenium contamination are from phosphate and coal mining and hydrofracking operations. The problem at phosphate mines is particularly significant. Phosphate rock is the number two produced chemical in the U.S. with the majority of mines located in the Western Phosphate Field located in Northwestern. Phosphate mining in this area has resulted in significant selenium contamination of groundwater. Selenium is easily taken up by plants that are consumed by animals. Significant livestock, elk, deer and fish kills have been documented (U.S. G.A.O. report to Congress, May 2012).

EPA has stated that the need for long-term water treatment to remove Selenium can be the most costly remediation action at phosphate mines and cleanup activities may take more than 100 years to complete. Additionally, EPA has stated that the Selenium water quality standard may be more stringent in the future increasing the level of cleanup required. The proposed injectable permeable reactive barrier would provide a simple and inexpensive solution to the problem.

Current methods to remove selenium from water include phytoremediation (Esringu and Turan, 2011), biological treatment (Hageman, et al. 2013), ion exchange, evaporation, chemical treatment, filtration (Bond, 2000) and Permeable reactive barriers (Zhang et al., 2008). All of these methods with the exception of using a PRB are active treatment technologies that have significant capital costs, create a waste stream, can expose workers to the contaminant and have significant long-term operational costs. Conventional Permeable reactive barriers, constructed by trenching and backfilling with a reactive media such as zero valent iron have a finite life span, have the potential to clog due to precipitation of secondary metals or biofowl, and have not been demonstrated to achieve low selenium concentration in the effluent (Sandy, T., and C. DiSante, 2010).

The data collected in this work indicates the kinetics of selenium sorption by carbonated apatite are much faster than for hydroxyapatite. The use of hydroxyapatite for selenium uptake is much too slow in areas of fast groundwater flow rates for use in a permeable reactive barrier. Carbonated apatite may be much more promising.

If the formulation of Moore (2003, 2004) can be modified to produce carbonated apatite *in situ* then construction of a permeable reactive barrier for selenium would have significant advantages over conventional construction methods such as trench and backfill. The advantages of in situ barrier construction include:

- Inexpensive to implement,
- Forms a continuous permeable reactive barrier of nano-size apatite crystals that do not decrease soil porosity resulting in groundwater bypass of the barrier,
- Apatite forming solution flows into areas with highest porosity in the soil (i.e. more apatite is formed in areas of preferential flow of contaminated groundwater),
- Contaminate(s) is kept underground. No above ground equipment (ion exchange, filters, etc.) are required except optional monitoring equipment,
- The technology can be used deep underground and under large obstacles such as buried waste tanks and piping systems where conventional construction techniques are not possible,
- No operational expences for the barrier,
- Workers are not exposed to contaminants unlike above ground treatment or construction of a permeable reactive barrier using conventional trenching and backfilling with a reactive media,
- Disposal costs for contaminated soil and the contaminant are eliminated.

A presentation and a white paper on the use of *in situ* formed apatite and the potential to use a carbonated form of apatite for selenium immobilization in the environment have already been given to the Members of the U.S. EPA, Idaho EPA, and Idaho state regulators. Additional funding to continue this work will be through proposals to federal, state and local agencies.

In addition to immobilization of selenium, there are other sites that could benefit from the use of carbonate apatite as a sorbent in permeable reactive barriers. Among the other contaminants is technetium a significant problematic radionuclide at the DOE Hanford Site and other DOE sites. At the Hanford site, technetium is the primary risk driver for tank closure at the Hanford Site. A technetium management program utilizing a modified apatite sorbent to address the challenges at Hanford has recently been accepted for funding. In preliminary experiments performed by

Washington River Protection Solutions, a reducing agent with apatite exhibited a very strong affinity for soption of technetium over a pH range, 2 to 12, and outperformed other sorbents and/or reducing agents when used as an immobilizing agent in leaching tests for cementitious waste forms. It may be possible to adapt carbonated apatite for use as a sorbent for separation processes, groundwater treatment, waste forms and permeable reactive barriers for technetium management at the Hanford site. Similar to selenium, technetium must first be in a reduced form for sorption by apatite.

CONCLUSIONS

The goal of this work was to examine the potential use of carbonated apatite as a sorbent for selenium for environmental applications. It is know that apatite will sorb selenium and based on the mechanism of sorption it is theorized that carbonated apatite would be more effective that pure apatite. In this work, carbonated apatite was synthesized by a precipitation method and characterized. Batch selenium kinetic and equilibrium experiments were performed. The results indicated the synthesized carbonated apatite contained 9.4% carbonate and uptake of selenium as selenite was rapid; 5 hours to complete uptake vs. more than 100 hours for pure hydroxyapatite reported in the literature. Additionally, the carbonated apatite exhibited significantly higher distribution coefficients in equilibrium experiments than pure hydroxyapatite under similar experimental conditions. The next phase of this work will be to seek additional funds to continue the research and eventually demonstrate the technology in a field application.

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