Use of Gas Transported Reactants for
Uranium Remediation in Vadose Zone Sediments

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ABSTRACT

This laboratory-scale investigation is focused on decreasing mobility of uranium in subsurface contaminated sediments in the vadose zone by in situ geochemical manipulation at low water content. This geochemical manipulation of the sediment surface phases included reduction, pH change (acidic and alkaline), and additions of chemicals (phosphate, ferric iron) to form specific precipitates. Reactants were advected into 1-D columns packed with Hanford 200 area U-contaminated sediment as a reactive gas (for CO_2, NH_3, H_2S, SO_2), with a 0.1% water content mist (for NaOH, Fe(III), HCl, PO_4) and with a 1% water content foam (for PO_4). Because uranium is present in the sediment in multiple phases, changes in U surface phases were evaluated with a series of liquid extractions that dissolve progressively less soluble phases and electron microbe identification of mineral phases. In terms of the short-term decrease in U mobility (in decreasing order), NH_3, NaOH mist, CO_2, HCl mist, and Fe(III) mist showed 20% to 35% change in U surface phases. The two reductive gas treatments (H_2S and SO_2) showed little change. For long-term decrease in U transport, mineral phases created that had low solubility (phosphates, silicates) were desired, so NH_3, phosphates (mist and foam delivered), and NaOH mist showed the greatest formation of these minerals.

INTRODUCTION

Uranium Speciation in Sediment. Uranium occurs naturally in the Hanford vadose zone sediments and is also present from uranium enrichment processes (surface and subsurface discharges). Natural minerals that contain uranium include betafite C [$Ca_{0.92}U_{1.08}(Ti_2O_7)$], most likely from granitic clasts that are commonly found in Hanford sediments (15% to 35%; [1]). Uranium(IV) generally forms insoluble mineral phases, such as uraninite [$UO_{2(s)}$]. Uranium(VI) often exists in species with higher solubility such as Na-boltwoodite [$(Na, K)(UO_2)(SiO_3OH)(H_2O)_{1.5}$], uranophane [$Ca(UO_2)_2(SiO_3OH)_2(H_2O)_5$], soddyite [$(UO_2)_2SiO_4(H_2O)_2$], schoepite [$(UO_2)_8O_2(OH)_{12}(H_2O)_{12}$], and rutherfordine ($UO_2CO_3$) [2, 3].

Uranium sorption to sediment is highly dependent on pH and carbonate concentration. At the Hanford subsurface pH 7.5 – 8.0 in carbonate-saturated groundwater, U^{+6} species present are primarily $Ca_2UO_2(CO_3)_3$ (aq), $CaUO_2(CO_3)_3^{2-}$ (and to a lesser extent Mg equivalent phases), with smaller concentrations of $(UO_2)_2CO_3(OH)_3^-$ and $UO_2(CO_3)_2^{2-}$. U(VI)-carbonate anionic species (and not Ca-U-CO_3 species) would dominate the mid-pH region in low Ca/Mg systems. The Ca-U-CO_3 species are the predominant species in the Hanford natural subsurface, due to the water being saturated/oversaturated in Ca/Mg-CO_3.

Reductive Gas Treatment of Sediment. The purpose of this investigation is to evaluate the potential for candidate gas-transported reactant technologies to decrease the mobility of uranium in Hanford central plateau vadose zone sediments. The investigation is focused on assessing the reaction processes for uranium immobilization through geochemical evaluation and proof-of-principle experiments. The technologies that were evaluated include reactive gases, gas advection to deliver reactive solids (a technology currently used to deliver zero valent iron at field scale), and advection of air with small amounts of water, and/or water and a surfactant to deliver reactive solids or liquids to the vadose zone.

Two gasses (H_2S, SO_2) that create a reductive environment were evaluated. Creation of a subsurface reducing environment results in the reduction of U(VI) phases to U(IV), which typically precipitates rapidly as $U(IV)O_2$, as shown in previous studies. While this process is somewhat useful in water-saturated sediments as reducing conditions can be maintained for some period of time, when the reduced zone oxidizes, nearly all of the $U(IV)O_2$ oxidizes and is remobilized [4]. This temporary immobilization of U only during reducing conditions likely indicates this process is of limited value in unsaturated sediments, if reduction is the only process involved. *In situ* gaseous reduction (ISGR) treatment of vadose zone reduces sediments with diluted hydrogen sulfide (H_2S) [5, 6] provides a possible means for immobilization of uranium(VI) in vadose zone environment. This technology uses low concentration (~200 ppm v/v) H_2S gas as a reductant for immobilization of contaminants that show substantially lower mobility in their reduced oxidation states. It is conceivable that the ISGR approach can be used in two ways: (i) to immobilize or stabilize pre-existing contaminants in the vadose zone by direct H_2S treatment; or (ii) to create a permeable reactive barrier (PRB) in which a gaseous mixture of H_2S diluted in nitrogen or air is passed through an interval in the vadose zone to produce a volume of reduced sediment. In the vadose zone, the predicted barrier lifetime in the vadose zone for H_2S reduced sediment was estimated to range from a few years to more than 100 years [6]. There are additional processes that occur with greater contact time of U surface phases with sediment. Aging of the surface phases, even as short as 100s of hours to 1 year [4, 7, 8] decreases the mass of U that desorbs. At field scale, this significantly larger desorption Kd compared to adsorption Kd (with freshly adsorbed U) is attributed to aging of the U surface phases [1].

Acidic Treatment of Sediment. Carbon dioxide gas injection and aqueous 0.5M HCl injection as a 0.1% liquid mist (by volume) were evaluated to dissolve and reprecipitate a mineral phase to coat adsorbed U(VI) species or incorporate U(VI) into a less mobile precipitate phase. The injection of CO_2 gas leads to mildly acidic conditions (pH 5.5 to 7), which causes some dissolution of carbonate minerals, although this aqueous dissolution reaction would likely be significantly more limited at low water content. A subsequent increase in pH (by air or N_2 injection) leads to carbonate mineral precipitation, that could coat $U(IV)O_2$ precipitates and possibly adsorbed U(VI) species. In water-saturated systems, advection of aqueous complexes in the porous media redistributes reactant mass, so carbonates dissolved in one location can coat surface phases in another location. At low water saturation, the very slow advection of water near surfaces will result in significantly less redistribution of reactants (i.e., more

difficulty in carbonate precipitates coating other phases without a mechanism for redistribution). Carbonate coatings on mineral phases have been previously observed to influence U(VI) adsorption [9]. The slow time scale for carbonate dissolution/precipitation of weeks or longer (although pH dependent,[10]) may be of concern.

Alkaline Treatment of Sediment. Ammonia gas injection and aqueous 0.5M NaOH injection as a 0.1% liquid mist (by volume) were evaluated as a remediation technology, as alkaline conditions result in aluminosilicate dissolution, and subsequent pH neutralization results in precipitation of sodalite and and cancrinite [11] in Hanford sediments. The increase in pH and aluminosilicate dissolution and subsequent precipitation has been previously observed in water saturated Hanford sediment under highly alkaline conditions (pH 14, 4M NaOH) and is somewhat effective for Tc immobilization. In that study, injection of a high-NaOH solution through sediments caused the dissolution of several mineral phases as evidenced by aqueous Si, Al, and Fe effluent concentrations. There was significant mobilized silica (up to 10 g/L). The released ferrous iron was sufficient to reduced the pertechnetate ($Tc(VII)O_4-$) to $Tc(IV)O_2$, which precipitated in the system. As the pH was subsequently reduced to natural groundwater (pH 8), only 23% of the TcO_2 precipitate was remobilized upon reoxidation. Thus, 77% of the technetium remained immobilized in the oxic environment, presumably by aluminosilicate mineral phase coatings.

Phosphate Addition to Sediment. The formation of a $Ca-U-PO_4$ mineral phase autunite $[Ca(UO_2)_2(PO_4)_2 \cdot XH_2O]$ by injection of sodium phosphate or polyphosphate mixture into sediment is well established in water-saturated sediment as well as in unsaturated sediment [12, 13]. In this study, an aqueous phosphate solution was injected into unsaturated sediment at low water saturation as a mist (0.1% liquid by volume), and with foam formed by the use of a surfactant (~1% water content in the foam).

Ferric Iron Addition to Sediment. Laboratory experiments in water-saturated sediments have demonstrated that a ferric nitrate solution will result in ferric oxide precipitation, which will co-precipitate U(VI) in the iron oxide structure. The injection of ferric nitrate into unsaturated sediments at low water content could be accomplished using 1% water content with primarily air injection. Ferric iron is kept in solution at a pH of 1.5, so this treatment technology will additionally dissolve mineral phases before a NaOH solution (as a mist) is subsequently injected to neutralize the pH and cause precipitation.

EXPERIMENTAL AND MODELING METHODS
Sediment Reaction Experiments. Because the intended use of these treatment technologies is in the vadose zone, treatment technologies was conducted at low water content. Treatments were conducted with an initial water content of 5 wt% (approximate field conditions) and 15 wt% (about half saturation) in separate sets of columns. Three different U-contaminated subsurface sediments from the U.S. DOE Hanford 200E area (BX and TX tank farm) were used for these experiments, with varied U mass and speciation. Sediment 1 (total U 377 ug/g) and sediment 2 (74.4 ug/g) both were

dominated by U in carbonate (74 to 80%), with lesser amounts of U in oxides (8 – 14%), silicates (5.1 – 6.5%), and adsorbed (1.1%). In contrast, sediment 3 (total U 28.1 ug/g) contained significant (29%) U as a thin surface carbonate (or "rind"), compared with 2.8 to 3.8% U in rind carbonate for sediments 1 and 2. The balance of the U surface phases for sediment 3 were in the carbonate (34%), oxides (6.1%), silicates (15%), and adsorbed (16%).

Treatment times of 1, 2, and 3 months were used, with sequential liquid extractions used to evaluate changes in uranium mobility. The following sequential extraction tests were used to evaluate the change in uranium mobility of the control and treated columns for each aging treatment: a) aqueous U by addition of Hanford groundwater, b) readily desorbed uranium by 1M Mg-nitrate batch extraction, c) dissolution of the thin rind of U-carbonate precipitate (acetate at pH 5, 1 h), d) dissolution of most carbonates (acetic acid, pH 2.3, 1 week), e) dissolution of amorphous oxides (0.1M oxalic acid), and f) dissolution of hard to extract U in oxides, silicates, and phosphates (8 M nitric acid, 95°C, 2 h) for total uranium. Uranium (VI) was measured by kinetic phosphorescence analysis (KPA). Electron microprobe analysis of thin sections of treated sediments that are likely to contain different U surface phases or coatings on uranium were also conducted for positive identification of the U surface phase changes.

Simulation of Uranium Transport.   Gas delivery technologies were simulated to quantify long-term effectiveness at a large scale, based on uranium surface phase changes characterized in laboratory experiments. Simulation cases were selected from existing simulations from the hydrostratigraphy at the BX-BY tank farm [14], with surface backfill (269 to 260 ft elevation), H2 gravelly sand (235 to 260 ft), H2 sand (170 to 235 ft), H3 gravelly sand (51 to 170 ft), a silty sand (51 to 31 ft), and the aquifer at a 10 ft elevation. Unsaturated physical properties are based on laboratory measurements and values used in prior simulations [15, 16]. The actual uranium contamination profile in the B-BX-BY is located at 99 to 170 ft elevation, with additional mass at 185 to 200 ft elevation, but for this study, a uniform mass of uranium at 99 to 170 ft elevation was used in order to evaluate breakthrough curves due to the change in mass between different surface phases, rather than the distribution vertically in the sediment profile. Water infiltration at 60 mm/year (high due to the surface gravel) results in a tracer in the 99 to 170 ft U-laden zone reaching the water table in 90 years.

The geochemical reactions used for these preliminary simulations are relatively simple, and are representative of some aspects of uranium phases and transport. One equilibrium reaction (U(VI) sorption) and four kinetic reactions were used in this modeling approach. Dissolution reactions were used to represent precipitates that contained uranium, and included carbonates (U in a thin surface rind or within most of the carbonate), silicates/phosphates, and reduced U(IV) phases that are subsequently oxidized over time. The kinetic reactions included rind carbonate dissolution (dissolution half-life 1800 y), total carbonate dissolution (half-life 10,500 yr), silicate/phosphate dissolution (half-life 18,000 yr), and time-delayed sorption (100 yr lag for reduced U(IV) phases). Although these simulations are more informative than a model that includes only sorption (i.e., Kd model), results are approximate behavior, as these simulations do not include aqueous

speciation, nor the behavior that would be observed for multiple species sorption or transformation, nor slow diffusion release of U from sediment, all of which influence the actual observed field-scale U migration.

RESULTS AND DISCUSSION
Reductive Gas Treatment of Sediment. Hydrogen sulfide has been used at the laboratory and field scale to create weak iron reducing conditions in different sediments [6] including Hanford sediments. The hydrogen sulfide treatment has been applied and successfully treated chromate at the White Sands, New Mexico field site Uranium requires a greater reduction potential than chromate to reduce mobile U(VI) carbonate phases to U(IV) phases [UO_2 (ppt)]. In addition, when the sediment system becomes oxidized over time, U(IV) phases are reoxidized. Therefore, the reduction in U mobility associated with hydrogen sulfide gas treatment is mainly dependent on the rate at which the sediment is reoxidized at the field scale. Aging of the surface phases, even as short as 100s of hours to 1 year [7, 8] decreases the mass of U that desorbs. Therefore, the use of hydrogen sulfide gas for uranium remediation would be dependent on several processes that would be difficult to quantify: a) field scale oxidation rate of the reduced sediment zone (years to 10s of years), and b) rate of transformation of reduced U phases to other surface phases that are less mobile (also years to 10s of years).

In this study, hydrogen sulfide treatments were conducted on small sediment columns to keep the sediment reduced for 1 or 2 months, with changes in U surface phases characterized by the sequential extractions. A concentration of 200 ppm (by volume) H_2S was used at a flow rate of 6 pore volumes per hour for 24 hours.
After 1 month of reduction, and after 1 or 2 additional months of oxidation, there little change in the six different uranium surface phases were observed (Figure 1a). The bar graph represents the fraction of U in different phases from the most mobile phase (aqueous U) in red, adsorbed in dark orange, rind carbonate-U in orange, carbonate U in yellow, oxide U in light green, and silicate/phosphate U in dark green. These operationally defined phases were based on the six sequential extractions, as described in the experimental section. The colors were used to be representative of the mobile/labile phases (red/orange) and surface phases with less and less solubility (green). Hydrogen sulfide gas treatment to sediment does result in mildly reducing conditions, as an Eh of -40 to -50 mV was measured for water contents of 2% to 15%. The reductive capacity of the H_2S reduced sediment was small (1.2 umol/g), based on oxidation in a water-saturated system in which air-saturated water (8.2 mg/L dissolved oxygen) was slowly pumped into the column (70 h/pore volume,), with dissolved oxygen being monitored at the effluent using two separate microelectrodes. In contrast, the same sediment reduced with an aqueous reductant (sodium dithionite) had a reductive capacity of 11.3 umol/g [17].

Sulfur dioxide treatment of sediment also produced slightly reducing conditions in sediments (Eh = -25 to -45 mV), as some ferric oxide phases are slightly reduced. In contrast to hydrogen sulfide, sulfur dioxide has not been used previously for field reduction experiments. Uranium extractions on the SO_2-treated sediment after 1 month (Figure 1b) showed an increase in aqueous and ion exchangeable uranium fractions, but

then at 2 and 3 months returned to conditions nearly the same as the untreated sediment (first column in all plots in Figure 1). This performance was similar to that of the H_2S-treated sediments.
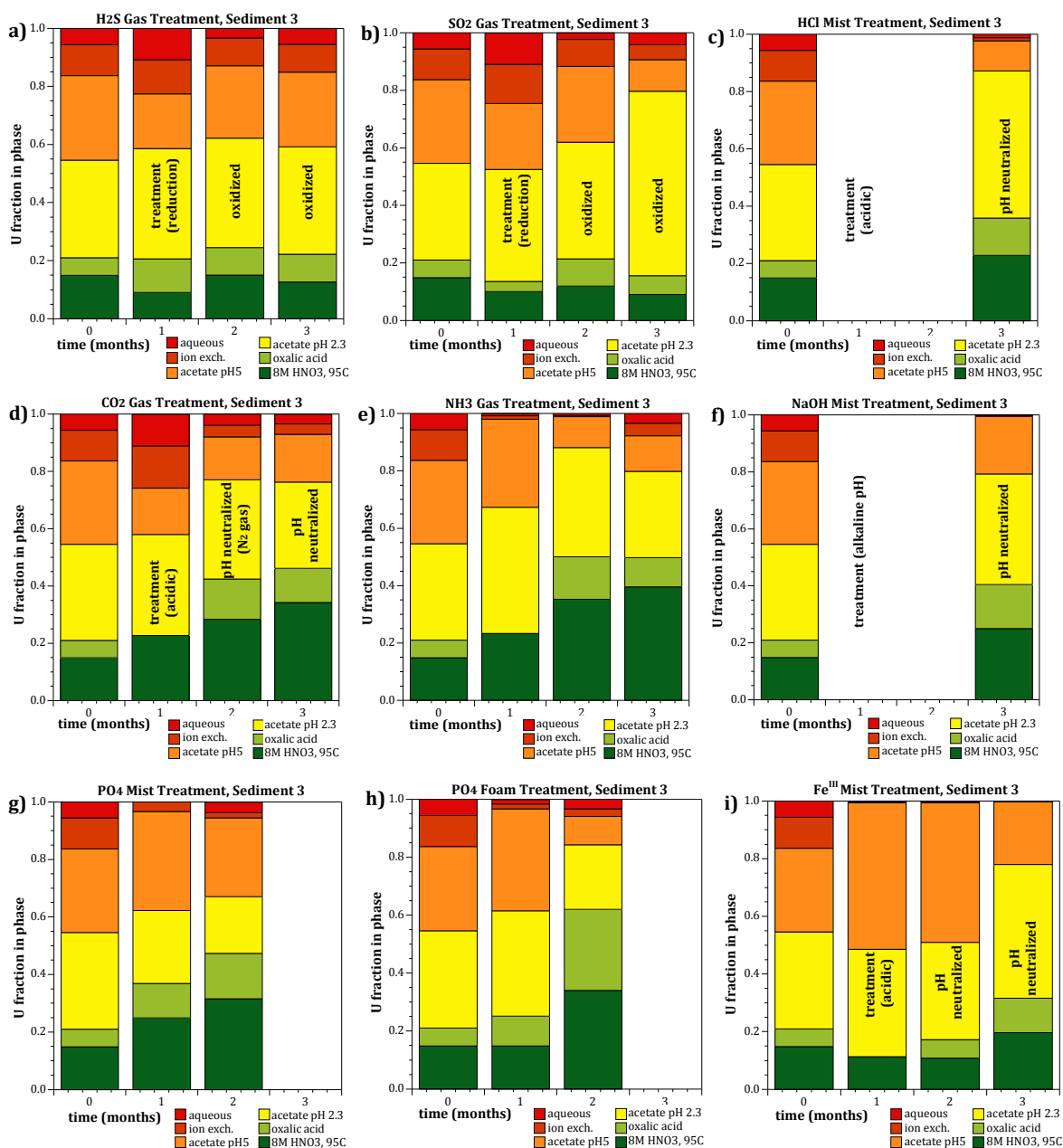

Figure 1. Sediment 3 treatment by: a) H_2S gas, b) SO_2 gas, NH_3 gas, c) HCl mist, d) CO_2 gas, e) NH_3 gas, f) NaOH mist, g) PO_4 mist, h) PO_4 foam, and i) ferric iron mist.

Acidic Treatment of Sediment. The use of a mist containing 0.5M HCl to acidify sediment was originally intended to parallel the CO_2 gas phase treatment of sediment. The HCl mist provides a similar pH decrease to the CO_2 gas, but does not increase the carbonate concentration in the sediment. Mist injection is a high volume of air injected

into sediment with a small amount of water. Mist injection into a 160 cm long column (Figure 2a) at 329 mL/min air flow and 1.0 mL/min water flow (0.3% water by volume) showed the mist was exiting the column, and after 10 minutes, a relatively uniform water content of 2% was observed to 100 cm, beyond which there was a decrease in water content. In a second mist injection experiment into a 610 cm long (25 ft) column, mist injection was not as uniform, although there were problems with the venturi used to atomize the water in the gas stream. Mist injection of HCl at 0.1% water content by volume into a 160 cm long sediment column resulted in a nonuniform spatial distribution of the final pH (Figure 2b), with greater deposition of the acid near the injection location. The sediment pH at the injection point was 5.06, and gradually increased to ~8.0 by 100 cm (natural sediment pH).

The changes in uranium surface phases for sediment that was treated with a 0.5M HCl mist for 1 month, after which time 0.5M NaOH was injected into the column as a mist. The uranium extractions were conducted only after 3 months. The results (Figure 1c) showed large decreases in aqueous, ion exchangeable, and CO_3 rind-associated uranium (mobile and labile phases), and an increase in uranium associated with carbonate-, oxide-, and hard to extract phases.
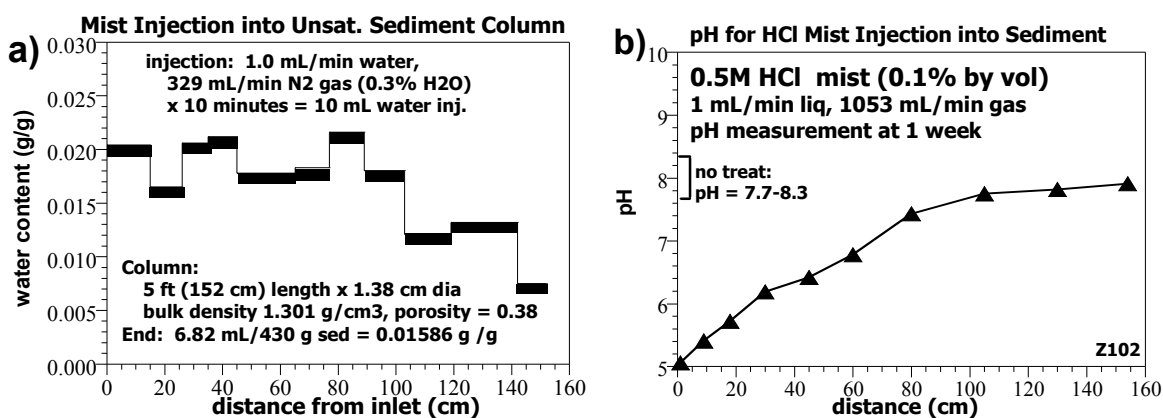

Figure 2. Mist injection into a 160 cm long column showing: a) final water content, b) pH.

A comparison of the changes in uranium mobility for CO_2 gas treatment (Figure 1d) to HCl mist treatment (Figure 1c) show significant differences. Although both ultimately decreased aqueous and ion exchangeable U phases, the CO_2 gas treatment actually decreased the total U associated with carbonates (both rind and total carbonate) in contrast to HCl treatment resulted in a significant increase in U associated with total carbonate. The U associated with oxides (extraction #5) decreased for the CO_2 gas treatment (8%), versus a 7% increase for the HCl treatment. Finally, both resulted in a 33% change in U phases extracted, and both increased the less mobile phases (total carbonate, oxide and hard to extract phases). For field scale application, the CO_2 gas treatment would be easier to implement. One potential down side of the CO_2 gas treatment is the initial large increase in aqueous U (samples after 1 month) before the CO_2 gas was removed.

Alkaline Treatment of Sediment. In this study, 10% ammonia (balance N_2) was injected into small sediment columns at a flow rate of 6 pore volumes per hour for 24 hours. Three columns at different initial water content (2%, 7%, 15%) showed that a pH of 11.5 to 12 was achieved. Three additional sediment columns at 7% initial water content were treated with ammonia gas and analyzed for pH over 3 months. These results showed that the pH was returning to the natural sediment pH (pH = 10 by 1 month, pH = 9.5 by 3 months). Therefore, neutralization of the alkaline conditions may be possible with just the natural sediment buffering capacity. The changes in uranium surface phases for sediment #3 were quantified using the sequential liquid extractions (Figure 1e). There were consistent decreases in the aqueous, adsorbed, and carbonate-rind associated U, and a significant increase in hard to extract U phases (8M HNO_3, silicates) for sediment 3 at 5% initial water content (Figure 1e), as well as other sediments tested (not shown).

The use of a mist containing 0.5M NaOH to create alkaline conditions in the low water saturation sediment was intended to parallel the ammonia gas phase treatment of sediment. The changes in uranium surface phases for sediment #3 (at 5% water content) for NaOH mist injection was conducted on a single sediment column in which the NaOH mist treatment remained in the column for 1 month, then an HCl mist was used to neutralize the pore water pH. Uranium sequential extractions were conducted after 3 months (Figure 1f). In general, the NaOH mist treatment resulted in similar U surface phase changes as the ammonia gas, with losses in the aqueous, adsorbed, and CO_3 rind phases, and a gain in the oxide and phosphate/silicate phases. The total change in uranium surface phases (as a fraction of the total extractable,) was 25%, as compared to 29% for the ammonia gas for the same sediment (#3) at the same initial water content (5%).

Phosphate Addition to Sediment. The addition of phosphate to sediment either by a liquid mist (this section) or by foam injection (following section) will result in the formation of autunite [$Ca(UO_2)_2(PO_4)_2 \cdot XH_2O$] and excess phosphate will form mono- or di-calcium phosphate and apatite [$Ca_{10}(PO_4)_6 \cdot 2H_2O$] in this mid-pH range. Phosphate injection as a mist (0.1% liquid by volume) into a 160 cm column resulted in a roughly uniform moisture distribution, averaging 6% water content (initial water content was < 1%), but with greater moisture at 20 to 60 cm. Phosphate adsorbs to sediment quickly and slowly precipitates (hours to 100s of hours), so lags relative to a conservative tracer. For this mist injection of phosphate, there was a decreasing amount of phosphate from 0 to 90 cm, with the highest concentration of 0.85 mg PO_4/g of sediment at 0 to 10 cm (Figure 3a). The calculated phosphate mass injected into the column, based on the concentrations analyzed within the column, was within 20% of the phosphate mass injected. The foam injection technology uses 0.5% sodium laureth sulfate solution (30% purity) containing the phosphate mixture to inject a 0.5% to 1% water content foam into sediment [18]. The foam itself has a high viscosity so requires pressure to be advected through the sediment. For 50 mM phosphate injection with foam generated by the surfactant in the 1% water, although the foam front reached 40 cm and the pore water was in front of this foam front, the phosphate only reached 10 cm (Figure 3b). For a 250

mM phosphate injection at a higher foam flow rate, the foam front reached 105 cm, with the phosphate reaching 30 cm.

Results of the U phase changes over 1 to 3 months for these PO_4 injections using foam (Figure 1h) were similar to the phase changes for the PO_4 mist injections (Figure 1g). The most mobile aqueous and adsorbed U phases generally increased, but there was an apparent significant loss in carbonate associated U and a significant increase in oxide and PO_4/silicate U phases. Because the phosphate solution is at pH 7.5, carbonates are not dissolved, but the phosphate precipitate is most likely coating carbonate surfaces, so the carbonate extraction(s) show an apparent loss. This hypothesis will be investigated further with electron microbe analysis. Compared to the PO_4 injected with a mist, the foam-injected PO_4 experiments resulted in smaller increases in the immobile U phases, and there were larger gains in the aqueous and adsorbed U fractions. This appears to indicate that the presence of the surfactant may increase the uranium mobility.
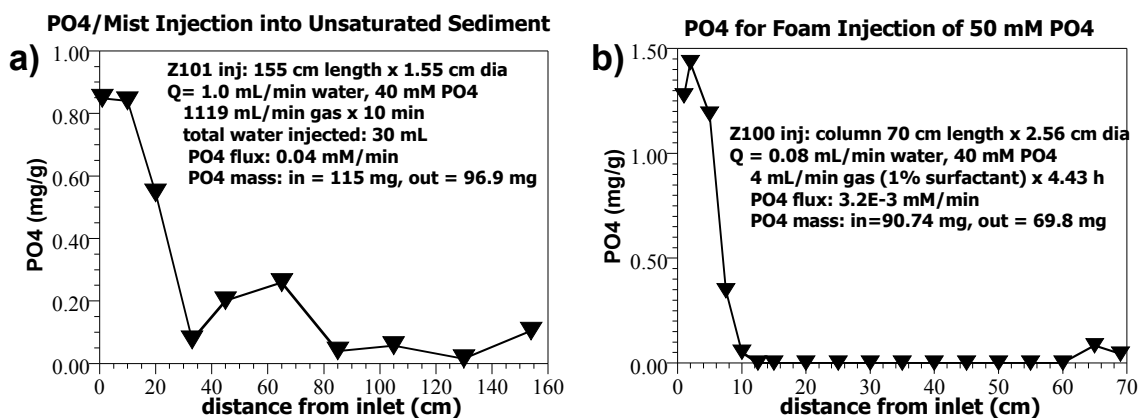

Figure 3. Phosphate injection by: a) 0.1% aqueous mist in gas, and b) foam advection.

Ferric Iron Addition to Sediment. Aqueous ferric iron can only occur under highly acidic conditions (pH < 2.0), as it will precipitate under pH neutral to alkaline conditions of the natural Hanford sediment (pH 7.7 to 8.3). Under oxic conditions, addition of ferric iron (in this case as ferric nitrate) at pH 1.5 as a mist (Figure 2) is then pH neutralized with the mist injection of a 0.5M NaOH solution to cause precipitation insitu. Because the spatial distribution of the water content after the first mist injection influences the spatial deposition of the NaOH during the second mist injection, there is incomplete pH neutralization spatially. At field scale, this multiple step mist injection would be complicated.

The purpose of a mist injection of the ferric iron in this study is that U(VI) will substitute for the ferric iron, forming a mixed oxide $[(Fe_{1-x}, U_x)(OH)_3]$. In one 160 cm long column, ferric nitrate (pH 1.3) was injected as a mist (0.1% water content by volume), then a week later the pH was neutralized by the injection of an NaOH mist. Three untreated sediment samples were used to quantify the natural ferric and ferrous iron surface phases. Untreated sediment averaged 15.2 ± 0.7 mg ferric iron per gram of sediment and for the 10 samples taken in the ferric nitrate-treated column averaged 17.4 ± 1.1 mg per gram of sediment. The average ferrous iron in the untreated sediment was

4.56 ± 0.42 mg/g, and the treated column averaged 3.14 ± 0.65 mg/g. This decrease in ferrous iron may have been caused by some unidentified dissolution/precipitation during the pH changes. The changes in uranium surface phases for sediments #2 and #3 were characterized by sequential extractions. Overall, there was 23% to 26% change in uranium in surface phases, with decreases in aqueous and adsorbed U, and an increase in oxide U.

Simulation of Uranium Transport. Laboratory experiments with the different sediment treatments quantified some aspects of the change in sediment geochemical and physical environment and changes in uranium surface phases. Although it is intuitive that it is desired to decrease the most mobile surface phases (aqueous, adsorbed, rind-CO_3) and increase less mobile surface phases (U associated with total carbonates, oxides, silicates, and phosphates), simulations were used to provide an estimate of the long-term impact of these phase changes. The hypothetical plume is based on a profile from BX-BY, with uniform uranium (in multiple phases) at an elevation of 99 ft to 170 ft (land surface at 270 ft, water table at 17 ft). For the base case (no treatment), the uranium laden zone has a total of 160 ug U/g of sediment (327.5 ug U/cm3), partitioned between 5.4% aqueous, 14% adsorbed, 33% rind-CO_3, 40% balance of the CO_3, and 7.6% oxide/silicate/ phosphate. A total of five uranium phases were used in this modeling (aqueous U, adsorbed U, rind-CO_3, carbonate-CO_3, and oxide/silicate/PO_4 associated U, as described in detail in the experimental/modeling section. There is downward migration of the different phases due to infiltration of precipitation (6 cm/year) and the slow dissolution/ reprecipitation of carbonate and oxide phases.

The sediment treatments previously described in the results section move U mass between the different surface phases. If adsorbed/aqueous mass is transformed into oxide/silicate/ phosphate mass, two changes occur: a) the timing of when the U mass eludes at the water table increases from 100s to 1000s of years, and b) the U concentration decreases. A comparison of the transport of just the adsorbed fraction of uranium to the 27 ft elevation (Figure 4a) was based on simulations of the U surface phase changes that occurred for seven different treatments. Simulations for H_2S and SO_2 treated sediments are not shown, as there were nearly no surface phase changes. The base case (solid red line, Figure 4a), phosphate by mist and foam, and CO_2 gas treatments all had similar uranium peak concentration, as according to the sequential extractions there were minimal changes in the fraction of uranium in aqueous and adsorbed phases. It should be noted that the phosphate and CO_2 treatments did effect major changes in other surface phases, which do highly influence the leaching of U at later time periods. Ammonia gas and NaOH mist decreased the U aqueous concentration 50%, and HCl mist and ferric iron mist decreased the U aqueous concentration by 75%

The total cumulative mass of aqueous and all solid phases that have migrated to the 27 ft depth for all treatment cases illustrates (Figure 4b) that the performance of a treatment varies with time. The Fe(III) mist and HCl mist, which showed the greatest decrease in aqueous peak concentration (< 400 years) have only moved this U mass to rind CO_3, so are the worst performers at > 3000 years. Ammonia gas shows the greatest lag in mass of any of the treatments over most of the time period (2000 to 10,000 years). Phosphate

treatments (delivered in a mist or by foam advection), do not decrease aqueous U mass (< 400 years), but are among the best performers to delay mass breakthrough over most of the time period. In general, most treatments delayed 50% of the mass breakthrough from 700 years (untreated sediment) to 2300 to 2800 years (excluding phosphate treatments). This 4x delay does not illustrate the risk decrease, which is dependent on the U aqueous concentration that result from the delayed movement of these U solid phases to the water table.
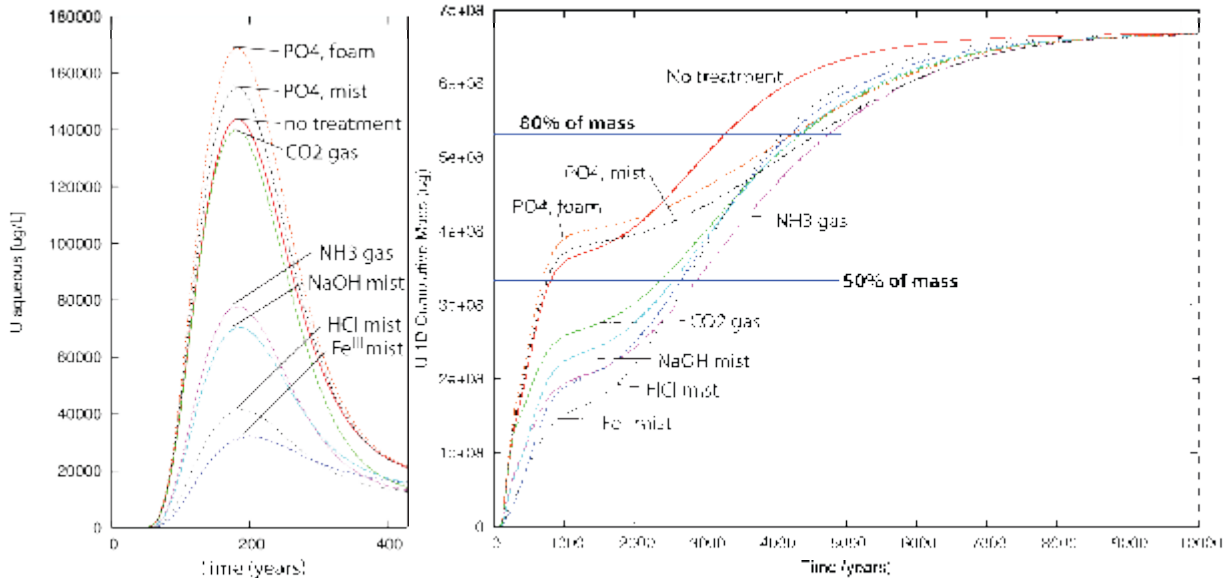

Figure 4. Simulation of downward migration of U phases showing: a) vadose zone pore water U concentration at 27 ft (10 ft above water table), and b) total cumulative U mass at 27 ft.

CONCLUSIONS

This project was initiated to evaluate the potential for candidate gas-transported reactant technologies to decrease the mobility of uranium in Hanford central plateau vadose zone sediments. The investigation is focused on assessing the geochemical reaction processes for uranium immobilization through geochemical evaluation and proof-of-principle experiments. Although the project is focused on changes in uranium mobility, some of the geochemical changes that result from injection of the reactive gasses and liquid do not directly affect uranium, yet still have a significant influence on uranium mobility. For example, aluminosilicate precipitates produced from ammonia gas (and subsequent pH neutralization) likely coat uranium surface phases such as carbonates. Sequential extractions showed general changes in U surface phases, but do not correctly identify surface coatings of less soluble minerals on more soluble minerals. Positive identification of U surface phases by the described technologies is currently in progress using electron microprobe techniques.

Reactive gasses, mist-advected reactants, and foam-advected reactants were compared in terms of: a) the measured changes in short-term U mobilization (as measured mainly by sequential liquid extractions), b) estimated long term changes in U mobilization, as predicted from vadose zone simulation given the changes in U surface phases, c)

advection aspects of the technology, and d) potential issues associated with field scale implementation. Short-term changes are U surface phases that are transported somewhat retarded relative to a tracer, so include the aqueous, adsorbed and rind carbonate U phases. In the vadose zone simulations of downward migration of U phases due to infiltration of precipitation, the tracer reaches the water table in 90 years, adsorbed/aqueous uranium reaches the water table in 180 years (i.e., $Rf = 2$), and rind-CO_3 associated U reaches the water table in 800 years (i.e., $Rf = 10$).

In terms of the short-term decrease in U mobility (in decreasing order), NH_3, NaOH mist, CO_2, HCl mist, and Fe(III) mist resulted in moderate to high decrease. Phosphates (mist or foam advected) showed inconsistent change in aqueous and adsorbed U. For long-term estimated change in U reduction, mineral phases created that had low solubility (phosphates, silicates) were desired, so phosphates (mist and foam delivered), NH_3, and NaOH mist showed the greatest formation of these minerals. The evaluation of the physical transport of the reactants into the sediment packed in columns was based on the ease of treatment in laboratory experiments as well as any associated issues. The four gasses (NH_3, CO_2, H_2S, SO_2) were the easiest to advect. Mist delivered reactants was more difficult to implement, due to inconsistent mist formation. Foam advection was relatively easy to implement, but foam advection is a complex process, and the additional presence of the surfactant has somewhat unknown influence on U mobility. Evaluation of the ability to treat sediment at field scale with the current technologies was the highest for CO_2 and NH_3 gas. Mist delivery, although being implemented at field scale for other purposes, is likely to be more limited in areal extent. Foam delivery may be feasible but requires more development and potentially a different foam than the one used in these studies.

Overall, the ammonia and carbon dioxide gas had the greatest overall geochemical performance and ability to implement at field scale. Corresponding mist-delivered technologies (NaOH mist for ammonia and HCl mist for carbon dioxide) performed as well or better geochemically, but are not as easily upscaled. Phosphate delivery by mist was rated slightly higher than by foam delivery simply due to the need for more information about foam injection and the unknown effect of U mobility in the presence of the surfactant.

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