

Sr-90 Immobilization by Infiltration of a Ca-Citrate-PO₄ Solution into the Hanford 100-N Area Vadose Zone

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ABSTRACT

This project was initiated to develop a strategy for infiltration of a Ca-citrate-PO₄ solution in order to precipitate apatite [Ca₁₀(PO₄)₆(OH)₂] in desired locations in the vadose zone for Sr-90 remediation. Laboratory experiments have demonstrated that infiltration of a Ca-citrate-PO₄ solution into sediments at low and high water saturation results in citrate biodegradation and formation of apatite. The citrate biodegradation rate was relatively uniform, in spite of the spatial variability of sediment microbial biomass, likely because of microbial transport processes that occur during solution infiltration. The precipitate was characterized as hydroxyapatite, and the Sr-90 substitution into apatite was shown to have a half-life of 5.5 to 16 months. 1-D and 2-D laboratory infiltration experiments quantified the spatial distribution of apatite that formed during solution infiltration. Slow infiltration in 2-D experiments at low water saturation show the apatite precipitate concentrated in the upper third of the infiltration zone. More rapid 1-D infiltration studies show the apatite precipitate concentrated at greater depth.

INTRODUCTION

Strontium-90 (Sr-90) discharge from former liquid waste disposal sites in the Hanford 100-N Area have resulted in Sr-90 release to groundwater, the Columbia River, and biota along the river bank. Although liquid discharges were terminated in 1993, Sr-90 adsorbed on aquifer solids remains as a continuing source of contamination to the Columbia River. Sr-90 is found primarily adsorbed to sediments by ion exchange (99% adsorbed, <1% in groundwater) in the upper portion of the unconfined aquifer and lower vadose zone. Although primarily adsorbed, Sr-90 is still considered a high mobility risk as it is mobilized by seasonal river stage increases and by plumes of higher ionic strength relative to groundwater. The lower part of the unconfined aquifer in the 100N area consists of sandy gravel (Ringold Fm), which is overlain by more permeable (~3x) sandy gravel (Hanford Fm). A series of 10 wells screened in both formations along a 300-ft-long section of shoreline with high Sr-90 contamination have received injections of a Ca-citrate-PO₄ solution to treat Sr-90 primarily in the water-saturated Ringold sediments. Sr-90 sequestration by this technology occurs by in situ biodegradation of citrate resulting in apatite[Ca₁₀(PO₄)₆(OH)₂] precipitation, adsorption of Sr-90 to the apatite, and then apatite recrystallization with partial isomorphic substitution (permanent) of Sr-90 for Ca, and natural radioactive decay of Sr-90. Because most (50 – 70%) of the Sr-90 contamination is in the shallow, variably saturated Hanford Formation which can only be partially treated through aquifer injections, the most efficient means of treating this zone may be surface infiltration of the apatite-forming solution.

Previous research has demonstrated the viability of using Ca-citrate-PO₄ solutions to form apatite in situ in water-saturated zones. This remediation technology relies upon the Ca-citrate-PO₄ solution forming apatite precipitate [Ca₁₀(PO₄)₆(OH)₂], which incorporates some Sr-90 during initial precipitation and additionally slowly incorporates Sr-90 by solid phase substitution for Ca. Sr substitution occurs because Sr-apatite is thermodynamically more stable than Ca-apatite. Once the Sr-90 is in the apatite structure, Sr-90 will decay to Y-90 (29.1 y half-life) then Zr-90 (64.1 h half-life) without the potential for migration into the Columbia River. Injection of a Ca-citrate-PO₄ solution into saturated sediment results in biodegradation of the citrate within a few days in both oxic and anoxic environments, forming low molecular weight organic acids (acetate, formate) and finally CO₂. Upon citrate biodegradation, the slow release of Ca from the Ca-citrate complex results in the formation of apatite. Because the citrate biodegradation depends on subsurface microbial activity, there should be a direct correlation between the microbial biomass and the citrate biodegradation rate, which varies considerably in the vadose zone. Some Sr-90 in the injection zone (30% to 70%) is incorporated into apatite during the initial precipitation phase (i.e., within days), although the majority of Sr-90 incorporation is from the adsorption of Sr-90 onto the apatite surface, then slow solid phase substitution of Sr for Ca in the apatite structure. Two factors that control the viability of this technology in a specific field site are: a) sufficient apatite needs to be emplaced to incorporate Sr and Sr-90 for 300 years (~10 half-lives of Sr-90 decay), and b) the rate of incorporation needs to exceed the natural groundwater flux rate of Sr in the 100-N Area.

This study is focused on testing whether a Ca-citrate-PO₄ solution can be infiltrated into sediment at low water saturation, apatite can be formed with a relatively uniform spatial distribution, and that Sr-90 adsorption and substitution into apatite occurs at a rate more rapid than the Sr-90 subsurface migration rate in the aquifer and overlying vadose zone. It is hypothesized that the citrate biodegradation rate will decrease with infiltration distance from the surface, due to the decrease in the microbial population, which may lead to an uneven spatial distribution of apatite precipitate. Experiments are, therefore, conducted at differing water saturations and microbial population density to assess their influence on the apatite precipitation rate. Once the apatite is formed, it is likely that Sr-90 substitution is relatively independent of water saturation. It is further hypothesized that the distribution of apatite precipitate will be dependent on the infiltration rate. Because the field site contains significant low-K and high-K layering (fluvial deposits), nonuniform infiltration profiles would result in uneven apatite precipitation distributions. 1-D and 2-D laboratory infiltration experiments are used to quantify the spatial distribution of apatite that formed during solution infiltration. Because low-K zones are likely to contain higher concentrations of Sr-90 in the field, 2-D experiments are used to investigate changes in the infiltration rate in order to manipulate the spatial distribution of the solution within low-K zones in order to have a somewhat more uniform spatial distribution of apatite. Through the development of an understanding of the apatite-forming processes, evaluation of infiltration tests in laboratory 1-D and 2-D flow systems, and reactive transport modeling, the results of this study will be used to design an efficient and effective infiltration strategy that will be tested at field scale.

EXPERIMENTAL AND MODELING METHODS

Infiltration Solution Composition and Batch Experiments

This technology uses a Ca-citrate-PO₄ solution that does not precipitate until the citrate is biodegraded. The composition of the infiltrating solution consisted of: 1.0 mM calcium chloride, 2.5 mM trisodium citrate, 8.1 mM disodium phosphate, 1.4 mM sodium phosphate, and 0.5 mM diammonium phosphate, or a general composition of 1 mM Ca, 2.5 mM citrate, and 10 mM PO₄, at pH 7.8. The proportions of the different phosphate chemicals were used to obtain pH 7.8, as well as provide a small N source for the microbes. The chemical composition of apatite [Ca₁₀(PO₄)₆(OH)₂] has a Ca:PO₄ molar ratio of 1.67:1, so the solution composition used is Ca deficient (i.e., Ca:PO₄ ratio is 1:10) in order to utilize the significant Ca and Sr available from ion exchange sites on sediment. The ratio of citrate:Ca is defined by how much citrate is needed to complex the Ca (at equilibrium, 2.5:1). Previous field injections in the Hanford 100N area utilize this (or a similar) Ca-citrate-PO₄ solution composition at a large scale by delivery of concentrated chemicals that are mixed with Columbia River water upon injection. Because microbes in the river water used in the infiltrated/injected solution will degrade the citrate, the final solution was mixed immediately before use. Delivery in laboratory infiltration experiments consisted of an automated multiport pump and mixing system using one concentrated solution containing CaCl₂ and Na-citrate, a second concentrated solution containing the PO₄, and the third solution of river water.

Batch experiments were focused on quantifying rates of citrate biodegradation (and subsequent apatite precipitate) rate and long-term Sr-90 uptake by the solid phase apatite. Citrate biodegradation experiments consisted of mixing Hanford 100N sediment at specific water content (not dried, as to maintain the microbial population) with the Ca-citrate-PO₄ solution at different concentrations and monitor carbon dioxide (i.e., mineralization) of the citrate over 100s of hours. In water-saturated systems, the citrate biodegradation pathway could be monitored. In these previous studies citric acid is utilized by many organic systems as part of the TCA (Krebs) respiration process, where the citrate (a C₆ organic acid) is converted to C₆, C₅, and C₄ organic acids producing CO₂ and H⁺, then cycled from oxaloacetic acid (C₄) to citric acid (Bailey and Ollis 1986). Citrate can also be further degraded to acetic acid (C₂), formaldehyde, formic acid (C₁) and CO₂. In those studies, it was determined that citrate was degraded in both aerobic and anaerobic systems. For these studies at low water saturation, there was very little pore water that could be extracted for analysis, so CO₂ was measured using radiolabeled ¹⁴C-citrate and CO₂ traps in the vial headspace. These citrate mineralization experiments typically consisted of 1 to 5 g of sediment at a specific water content in a 20 mL septa top vial and a 0.25 mL CO₂ trap filled with 1M NaOH, which was periodically sampled without opening the vial during the experiment (i.e., using a needle through the septa). The cumulative percentage of the total ¹⁴C from the citrate was plotted over time to quantify the citrate mineralization rate and final extent.

Strontium-90 uptake into apatite occurs by two processes; during the initial precipitation phase, and a solid phase substitution of Sr for Ca in the apatite. Experiments conducted

to measure the Sr-90 uptake during initial precipitation consisted of utilization of Sr-90 in the initial sediment/water and subsequent Ca-citrate-PO₄ treatment, with periodic monitoring of the Sr-90 remaining in solution over time. Solid phase samples (i.e., sediment/apatite) were also needed in order to quantify the mass of Sr-90 sorbed on the sediment, sorbed onto the apatite, and finally, incorporated into the apatite. Sorption on sediment or apatite was quantified by ion exchanging the Sr-90 off the sediment using a 0.5M KNO₃ solution, and measurement of the amount removed. Previous studies (Moore et al., 2006) have shown that >90% of the Sr-90 is held on the sediment by ion exchange. The amount of Sr-90 incorporated in apatite was quantified by dissolving the apatite in 4M HNO₃ for 24 h at 80C, then measuring the Sr-90 removed. Strontium-90 uptake studies by solid phase substitution were similar, but started with solid phase apatite (rather than a Ca-citrate-PO₄ solution), with ion exchangeable Sr-90 and solid phase Sr-90 measurements by solid phase sampling at periodic intervals. Both ¹⁴C and ⁹⁰Sr concentrations were quantified by liquid scintillation counting.

1-D and 2-D Infiltration Experiments

Several different 1-D column systems were used for infiltration experiments. Some 1-D column experimental systems used in these experiments consisted of both simple 1-D columns (50-cm length, 1.5-cm diameter) with no sampling along the length of the column. In these columns, the apatite precipitate mass was quantified by two methods: a) a 10-pore-volume flush of groundwater after the infiltration experiment was used to elude PO₄ that did not precipitate, and b) PO₄ extractions on sediment samples taken along the length of the column after the infiltration experiment. For other 1-D experiments, a larger diameter column was used (50 cm length, and a square cross section 5 cm by 5 cm) which enabled additional characterization by: a) nonintrusive water content measurement of the moisture front during the experiment by gamma attenuation, and b) sampling ports along the length of the column. The infiltration rate in the 1-D experiments was varied from 0.4 to 4.0 cm/h, and composition was varied from a 10 mM PO₄ to 20 mM PO₄ solution of Ca-citrate-PO₄.

The 2-D infiltration studies contained Hanford sediment with either homogenous or heterogeneous packing. Homogeneous 2-D infiltration experiments were conducted in several systems that were all 55 cm vertical height and 1 cm in thickness, but varied in lateral dimensions (38 cm, 70 cm, 120 cm or 140 cm). Other 2-D systems were used in which the moisture content was monitored were 5.0 cm in thickness to provide sufficient attenuation due to the water content. The objective of these 2-D studies with homogeneous packing was to determine optimal flow rates that resulted in a relatively uniform apatite spatial distribution vertically as well as laterally. The infiltration rate in these 2-D experiments varied from 8.3 mL/h to 0.28 mL/h, so the time to reach a 55 cm depth varied from 15 h to 400 h. At the end of the experiment, sediment samples were taken at depth and laterally under the infiltration point, with measurements of moisture content, aqueous PO₄, and apatite precipitate. The apatite was extracted from the sediment by a 15 minute extraction with 0.5M HNO₃. A calibration curve was established with known quantities of apatite added to the sediment.

RESULTS AND DISCUSSION

Low Water Content Ca-citrate-PO₄ Solution Infiltration and Apatite Formation

To determine if the sediment water content influenced the processes involved in apatite formation from the Ca-citrate-PO₄ solution, batch experiments were conducted at differing water content to measure the rate of citrate biodegradation to CO₂. In addition, precipitates were analyzed by multiple techniques to insure that apatite was formed. Mineralization of ¹⁴C-labeled citrate was examined over a range of initial citrate concentrations (5, 10, 25 and 125 mM) and percent water saturation of the composite 100-N sediment (35 to 100%) at 22°C. These Ca-citrate-PO₄ solutions contained the proportions of constituents described in the experimental section. Citrate was mineralized at all water saturations from 35% to 100% at 10 mM citrate initial concentration, although there were differences in mineralization rate and extent. At moderate to high water content (i.e., 65% to 100% water saturation), there was little difference in the mineralization rate (half-life averaged 37.3 ± 3.8 h) and extent (averaged $75.0 \pm 4.1\%$), but lower water contents (50% saturation and 35% saturation) showed slower mineralization rates and smaller mineralization extent. The cause of this may simply be the more limited mixing of the solution in the sediment at low water content. Similar experiments conducted at higher initial citrate concentrations (25, 125 mM) showed no consistent trends between water content and the mineralization rate or extent. The most significant conclusion was all citrate concentrations and all water contents showed some citrate mineralization. Citrate mineralization rates slowed at higher initial concentrations, but extent remained the same. The experimental data suggests that higher water saturations would produce better results (i.e., greater and more rapid citrate mineralization, so greater and more rapid apatite precipitation). Higher (nearly saturated) water conditions may also be required to drive the system anaerobic, which may be needed for the most rapid apatite formation. Infiltration simulations (not shown) show that more rapid infiltration rates achieve higher water saturations, even at steady state.

The concentrations of the Ca-citrate-PO₄ solution result in a low concentration of apatite in the sediment. Two factors control the amount of apatite needed to sequester Sr-90 in the Hanford 100-N Area. First, from a mass balance perspective, a specific amount of apatite is needed that will remove all Sr and Sr-90 from groundwater and the vadose over the next 300 years (i.e., 10 half lives of Sr-90 decay, half-life 29.1 years). This calculation is dependent on the crystal substitution of Sr for Ca in apatite. If 10% substitution is assumed, then 1.7 mg of apatite is sufficient to sequester Sr and Sr-90 in the saturated zone. This calculation assumes an average groundwater flow rate of 0.3 m/day and a 10-m thick apatite-laden barrier. The 1.7-mg apatite/g of sediment does occupy some pore space in the aquifer, which is calculated at 13.6% of the 20% pore space, so there should be some decrease in permeability. In the vadose zone, vertical water flux from precipitation is minimal (0.1 to 1 cm/year estimated infiltration rate), but there will also be some horizontal movement of pore water in the vadose zone, especially in higher saturation areas near the water table. Given that the water table in this aquifer zone near the Columbia river varies a few feet seasonally, an upper bound for flux of Sr and Sr-90 in the vadose zone is the 1.7 mg apatite/g of sediment calculated for the saturated zone. The second factor that controls the amount of apatite needed to sequester

Sr-90 is the rate of incorporation. For this technology to be effective, both sufficient apatite needs to be emplaced in sediments to incorporate Sr and Sr-90 for 300 years, and the rate of incorporation needs to exceed the natural groundwater flux rate of Sr in the 100-N Area. The rate of incorporation of Sr-90 into the apatite is described in a following results section.

Given the relatively small concentrations of Ca-PO₄ precipitate formed from the Ca-citrate-PO₄ solution, there are limitations on the techniques that can be used to identify this phase as apatite. In water-saturated systems, precipitation formed from Ca-citrate-PO₄ solutions have been positively identified as hydroxyapatite using X-ray powder diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) (Moore et al., 2004, 2007). For low concentrations of apatite formed in sediment (such as from these experiments), scanning electron microscope with EDS and elemental detectors have been used to identify both the percentage of apatite formed and positively identify that the crystal structure is hydroxyapatite (Szecsody et al., 2007). Hydroxyapatite (apatite) has very low solubility (Heslop et al., 2005), so is stable over the 300 years needed for decay of Sr-90 that is incorporated into apatite.

Sr-90 Incorporation Mass and Rate Into Apatite

Sr-90 is incorporated into apatite by two mechanisms: a) during initial precipitation of apatite (time scale of days, Raicevic et al., 1996), and b) slow recrystallization of Sr-laden apatite (time scale of months to years). Sr-90 incorporation in apatite is somewhat difficult to measure, as it needs to be separated from Sr-90 adsorption on sediment and Sr-90 adsorption onto apatite surfaces (both of which can be ion exchanged off the surfaces). The initial incorporation (Figure 1b, black triangles and circles) occurs within days and typically incorporates a fraction of the Sr-90 mass equal to the fraction Ca uptake in apatite (i.e., Ca and Sr and Sr-90 behave similarly). The Sr-90 incorporation rate into solid phase apatite is observed at times scales of months by: a) additional decrease in aqueous Sr-90 (Figure 1a, red triangles), b) decrease in adsorbed Sr-90 on sediment (Figure 1a, purple circles), c) decrease in Sr-90 sorbed on apatite (Figure 1a, blue diamonds), and d) increased Sr-90 in apatite (Figure 1a, green triangles and Figure 1b, triangles and circles). On an equivalent mass basis, Sr-90 adsorption to apatite is 55 times stronger than adsorption onto the Hanford sediment, so even a small amount of apatite in the sediment will adsorb the Sr-90 (and eventually be incorporated into the apatite structure).

Simulation of Ca-Sr-Na ion exchange in sediment, Ca-Sr-Na ion exchange on apatite, and Sr incorporation in apatite was conducted to quantify the incorporation rate in this specific laboratory system (Figure 1a). In addition, simulations were conducted at the much higher sediment/water ratio of the field system. Because Sr-90 incorporation is dependent on Sr-90 being sorbed to the apatite surface, it was hypothesized that the Sr-90 incorporation rate could slow with less Sr-90 sorbed on apatite. At high sediment/water ratios in field sediments, there is proportionally greater Sr-90 sorption on sediment relative to apatite. The field scenario simulation using the total apatite needed in the field showed the same time scale for Sr-90 incorporation into apatite as the laboratory

experiment, so incorporation was not dependent on the amount of Sr adsorbed onto apatite.

Long-term experiments

(Figure 1) showed the Sr-90 incorporation into apatite was as high as 98% by 15 months. The Sr-90 incorporation rate into solid-phase apatite (i.e., not including more rapid incorporation during initial precipitation) averaged $2.7 \pm 2.6 \times 10^{-5} \text{ h}^{-1}$ (half-life 1080 days, $1.42 \times 10^{-8} \text{ mg Sr/day/mg apatite}$). This long-term solid phase Sr-90 incorporation rate was used to calculate the Sr uptake rate in a 30-ft wide (diameter) apatite barrier to compare with the natural groundwater flux rate of Sr. For 10 mM PO_4 injected (0.34 mg apatite/g sediment), the Sr uptake rate was $8.8 \times 10^{-6} \text{ mmol Sr/day/cm}^2$. This Sr incorporation rate into

apatite was 6.5 times greater than the average natural Sr groundwater flux rate ($1.4 \times 10^{-6} \text{ mmol Sr day}^{-1} \text{ cm}^{-2}$, assumes 1 ft/day groundwater flow rate, Szecsody et al., 2007). This indicates Sr would be sequestered in the apatite-laden zone for the average Sr groundwater flux rate, but zones of higher groundwater flux (10x to 100x) would exceed the barrier uptake rate for this low apatite loading (0.34 mg apatite/g sediment). In addition, this low apatite loading would also not be able to incorporate Sr and Sr-90 for 300 years. From a mass balance perspective, approximately 3.4 mg apatite per gram of sediment is needed to incorporate Sr and Sr-90 for 300 years (assumes 10% Sr substitution for Ca in apatite). At this higher apatite loading, the Sr uptake rate during initial precipitation ($5 \times 10^{-3} \text{ mmol Sr day}^{-1} \text{ cm}^{-2}$) is 3600x more rapid than the average Sr groundwater flux rate and the Sr uptake rate during solid phase incorporation ($7.8 \times 10^{-5} \text{ mmol Sr day}^{-1} \text{ cm}^{-2}$) is 57x more rapid than the average Sr groundwater flux rate, so the barrier will effectively remove all Sr except in extreme high groundwater flow conditions. Because vadose zone pore water flux rates are typically orders of magnitude slower than groundwater flow rates, a lower mass of apatite be emplaced in the vadose zone to sequester Sr-90. In the lower portion of the vadose zone, which becomes water saturated due to seasonal river water fluctuations, the amount of apatite would need to be equal to this mass calculated for the saturated zone.

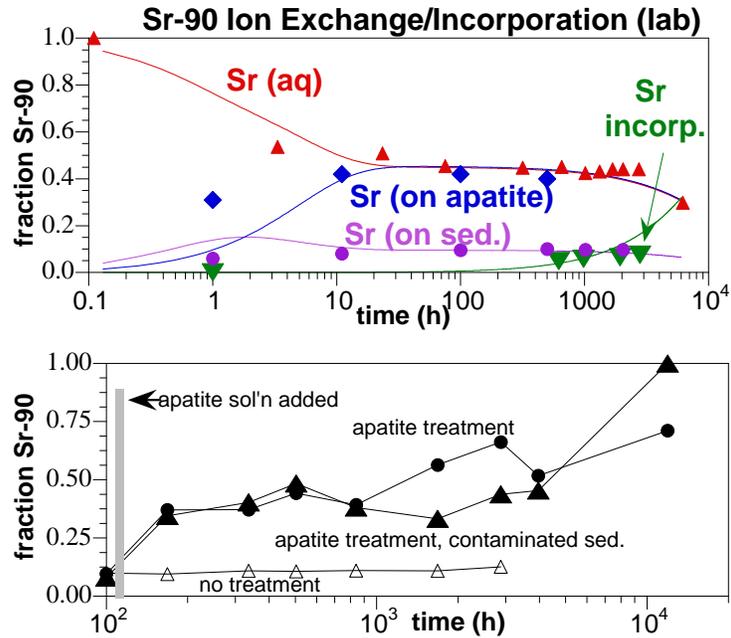


Figure 1. Sr uptake from: a) groundwater suspension of 0.34 g/L apatite and 20 g/L sediment at 82°C with solid phase apatite added, and b) Ca-citrate- PO_4 solution added.

Influence of Biomass Variability on Apatite Precipitate Spatial Distribution

The rate of citrate biodegradation, and the subsequent rate of apatite precipitation is dependent on the microbial biomass. Because the natural microbial biomass in the sediment decreases with depth, it is hypothesized that the citrate mineralization rate will decrease with depth, leading to a nonuniform apatite spatial distribution. To investigate this, the spatial variations in microbial population in Hanford 100-N sediments was investigated as a function of depth and location in sediments from monitoring and injection wells along the Columbia River shoreline at the 100-N remediation site. In addition, the citrate mineralization rate was investigated as a function of the microbial biomass. The microbial population in sediment samples from three wells decreased with increasing depth (one shown in Figure 2a). Populations per gram of sediment, reported as cell equivalents or colony forming units (cfu), decreased by 5 orders of magnitude in these wells and were higher in the Hanford formation than in the deeper Ringold formation. The vadose zone population decreased from $\sim 5 \times 10^8$ cfu/g at shallow depth to $\sim 10^6$ cfu/g at the water table (15 to 20 ft).

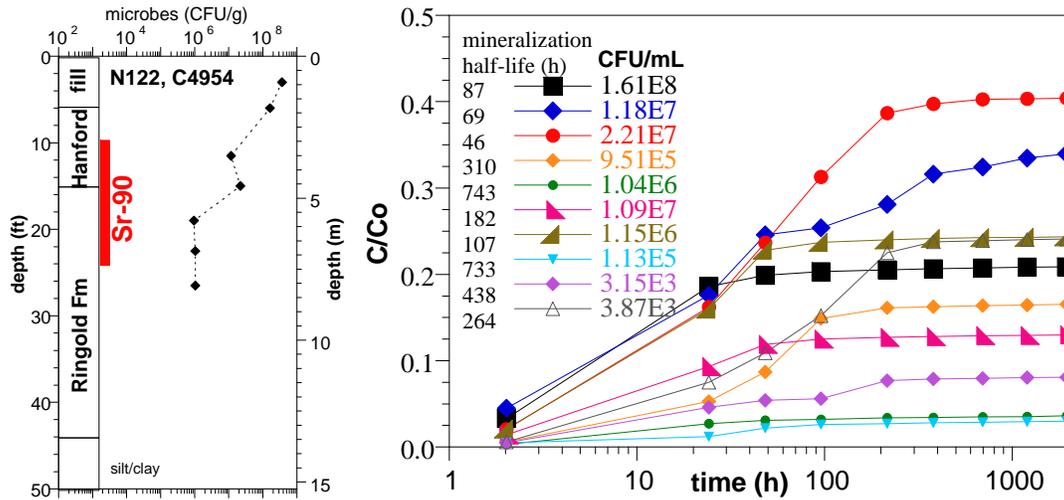


Figure 2. Natural microbial biomass concentration in Hanford sediment at different depth (a), and citrate mineralization rate correlation with biomass (b).

Citrate biodegradation depends on subsurface microbial activity, and there should be a direct correlation between the microbial biomass and the citrate biodegradation rate. As expected, microbial biomass decreased significantly with depth from 10^8 cells/g at 6 ft depth to 10^5 cells/g at a 25 ft depth to $<10^3$ cells/g at a 40 ft depth. However, the citrate mineralization rate decreased only one order of magnitude for a five order of magnitude decrease in biomass (Figure 2b), indicating likely significant control by another process. The likely cause of the relative uniformity of the citrate biodegradation rate in sediments is the movement of in situ microbes and the mass of microbes in the injection solution. Microbes attach by multiple and dynamic mechanisms, so when injected are not evenly distributed in the subsurface (or during infiltration). For batch laboratory experiments, the biomass in the infiltration water is evenly distributed throughout the sediment. For

infiltration experiments, the higher ionic strength of the Ca-citrate-PO₄ solution will cause some desorption of in situ microbes. The net result is the citrate mineralization rate and extent (i.e., fraction CO₂ produced) decreased only slightly with depth (Figure 2b, citrate mineralization half-life average 250 ± 114 h, range 87 h to 743 h), indicating there should be no significant trends with lateral distance along the injection barrier. The conclusion of these citrate mineralization studies is that there will be relatively uniform citrate degradation observed in field-scale injection at different locations and at different depth, and subsequently the in situ biomass variability contributes little to the expected apatite precipitate spatial distribution.

1-D/2-D Infiltration Studies and the Spatial Distribution of Apatite Precipitation

Four 1-D unsaturated column experiments were conducted in which the infiltration rate was varied from 0.4 to 4.0 cm/h, and the Ca-citrate-PO₄ solution concentration was varied from 10 mM PO₄ (i.e., 1 mM Ca, 2.5 mM citrate, and 10 mM PO₄) to 20 mM PO₄. The initial water content was 0.16 g water/g sediment (66% water saturation). The solution was infiltrated for 12 to 100 h, then the remaining aqueous PO₄ and precipitated PO₄ was measured. The aqueous PO₄ was measured by a 10-pore volume flush of groundwater and effluent samples collected for PO₄ analysis. The mass of PO₄ calculated from the breakthrough curve is the mass of PO₄ that did not precipitate. In addition, ten samples were taken in each column and PO₄ extracted from the sediment.

The phosphate breakthrough curves showed that varying the infiltration rate by only an order of magnitude (0.4 to 4 cm/h) did not change the amount of PO₄ precipitate (76%). In each case 8-10 mM of PO₄ was injected into the column and 2 to 2.4 mM of PO₄ was eluded (i.e., still aqueous). These results are not surprising, given that the infiltration time scale did not significantly change between experiments. The PO₄ extraction from the 10 samples for each sediment column showed a possible trend of increasing precipitate with depth, but also showed a high concentration near the surface. This PO₄ extraction consisted of a 3.0 g sediment sample extracted for 15 minutes with 0.5M HNO₃.

A 1-D infiltration experiment conducted with a higher solution concentration (2 mM Ca, 5 mM citrate, and 20 mM PO₄) showed that 90% of the PO₄ injected precipitated (i.e., only 10% was eluded). In this case, the amount of PO₄ precipitated per gram of sediment was about 40% of the background PO₄ from the sediment, and the vertical profile in the 50-cm long column did show increasing PO₄ with increasing depth. Uniform apatite precipitate would result in 0.42 mg PO₄/g of sediment. The profile shows that PO₄ varies from a relatively uniform 0.25 mg PO₄/g sediment for the upper 30 cm, then increases to 1.0 mg PO₄/g sediment for the last 10 cm. The increase in apatite precipitate concentration with depth is not a function of the water content in the sediment. This column showed a high uniform water content for the upper 45 cm of the column (14.6% water content), with the lowest 5 cm at a slightly lower water content (11.2%), so the moisture levels do not correspond to the PO₄ mass change (which occurs from 35 cm to 50 cm depth). An alternate hypothesis is that microbes are transported with the infiltration front (i.e., higher ionic strength solution will desorb microbes off surfaces), so there could be a higher microbial population in the lower portion of the sediment column.

2-D experiments were initiated to quantify Ca-citrate-PO₄ solution infiltration and spatial variability of apatite precipitate vertically (as in 1-D studies) and also laterally. The overall goal of the infiltration studies is to develop an infiltration strategy (i.e., constant or varying flow rate, concentration, etc.) to effectively precipitate apatite in desired locations. In general, an even apatite precipitate distribution is desired, and initial 2-D experiments are conducted in systems that are homogeneously packed. However, vertical profiles of the Sr-90 distribution show 50% to 70% of the Sr-90 located in the more permeable Hanford formation, which overlies the remaining Sr-90 mass in the upper 10 to 15 ft of the Ringold Formation. During most of the year, the groundwater level is roughly at the Ringold/Hanford contact, although during spring runoff (high river stage), the water table is a few feet into the Hanford formation. Therefore, the zone of expected Ca-citrate-PO₄ treatment by infiltration is essentially the lower half of the vadose zone. As the river (and aquifer) water level rises, additional Sr-90 mass enters the aquifer in some wells, likely due to Sr-90 entrapped in pore water in the vadose zone. Over the decades of these water level change cycles, some Sr-90 mass in the vadose zone has leached away, although it is hypothesized that a higher proportion of Sr-90 mass is in low hydraulic conductivity layers in the vadose zone, due simply to lower leaching rates. Therefore, 2-D experiments are focused on delivering a relatively even Ca-citrate-PO₄ solution in low-K layers, and underneath low-K layers.

Initial 2-D experiments conducted in homogeneous sediment packing were conducted varying the infiltration rate from 0.3 to 9 mL/h in order to vary the time for the solution to reach a 55 cm depth from 400 h to 17 h. One 2-D infiltration experiment was conducted in which a 30 mM PO₄ solution was infiltrated into the upper left corner of the flow system at 3.2 mL/h for 44 h (Figure 3). The initial water content in this 2-D experiment of 0.02 g/g (9% water saturation) was much lower than in the 1-D experiments. The final water content in the 2-D experiment (Figure 3a) showed that the solution had migrated to the 55 cm depth of the system, and was at a higher water content at depth (0.06 g/g or 26% saturation). Although the Ca-citrate-PO₄ solution did migrate to depth, most of the citrate biodegradation and subsequent apatite precipitate formation occurred at shallow depth (first 30 cm of depth and 20 cm of width). The 30 mM PO₄ (or 950 mg/L) injected was largely precipitated, as aqueous PO₄ measurements (Figure 3b) varied from 1 to 110 mg/L (i.e., <12% of the initial concentration). Apatite precipitate extracted from the sediment (with 0.5M HNO₃), and after subtracting the amount of aqueous PO₄, showed that the precipitate was generally in the upper third of the infiltrating plume. If all of the 30 mM PO₄ precipitated in the pore space, there should be 0.34 mg of apatite per gram of sediment. Results (Figure 3c) show that the amount of apatite varied from a high of 0.96 mg/g at the infiltration point to 0.05 mg/g at depth.

Water-saturated experiments of Ca-citrate-PO₄ solution injection into the same sediment show a similar trend to that observed for the 2-D unsaturated experiments, namely phosphate adsorption/precipitation results in an apparent retardation of 1.6 to 2.4. The difference between the results of the 1-D infiltration experiments (showing more precipitate at depth) and the 2-D infiltration experiment (Figure 3, showing more precipitate at shallow depth) is likely the residence time of the solution in a specific location and the ability of microbes to degrade the citrate, which results in the formation

of the apatite precipitate. At significantly higher water saturation (66%) in 1-D experiments, some of the Ca-citrate-PO₄ solution infiltrated to a 50 cm depth within 12 h, but then filled additional pore space by 25 h, when the experiment ended. In contrast, the infiltration solution in the 2-D experiment (Figure 3) reached the 55 cm depth (and 30 cm width) by 44 h, and only a small portion of the pore space was filled with this solution (final water saturations 2% to 12%). Therefore, the apatite precipitation buildup was in the location of greatest PO₄ mass and contact time (time needed to degrade the citrate), which was near the infiltration point in the 2-D experiment, and at depth in the 1-D experiment. The role of migration of microbes, either initially in the sediment, or introduced in the river water used in the infiltration solution, is under investigation.

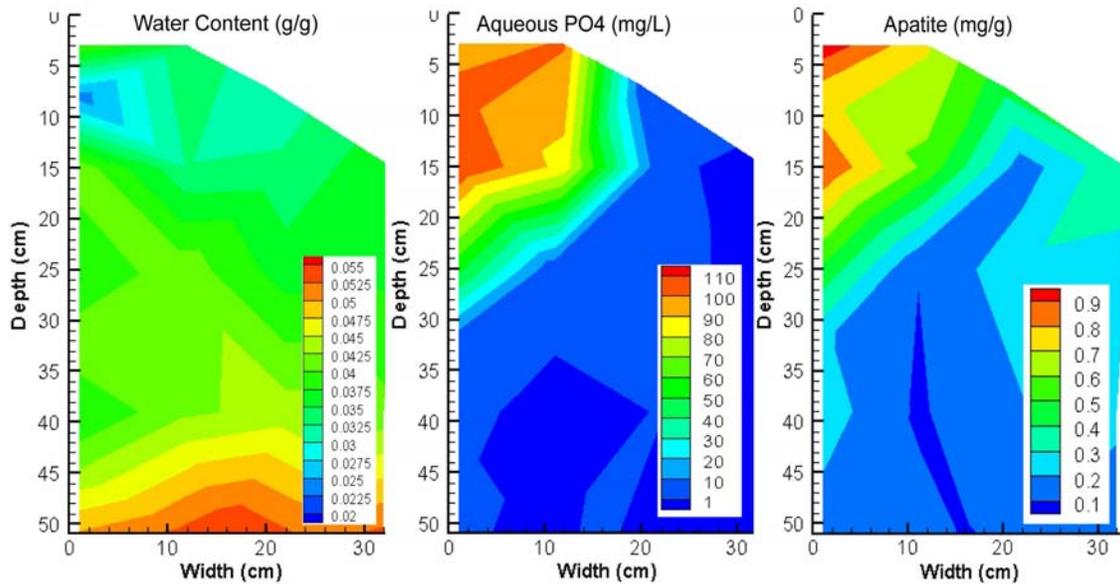


Figure 3. 2-D unsaturated column experiments of infiltration of 30 mM PO₄ at a rate of 3.2 mL/h. showing final: a) water content, b) aqueous PO₄, and c) apatite (mg/g).

A 2-D visualization experiment was conducted to demonstrate the process of varying the infiltration rate of a solution to achieve solution coverage in desired areas (Figure 4). Constant infiltration rate into homogeneous and heterogeneous (low-K lens) are shown in the left panels. Infiltration at a constant rate results in some lateral spreading and incomplete coverage in the low-K layer (Figure 4c). At later times, infiltration below the low-K zone is also incomplete. In contrast, by varying the infiltration rate (Figure 4, right panels), the low-K unit was fully saturated with the infiltrating solution and nearly all the area under the low-K unit was also saturated. To achieve this spatial solution coverage, the rate of infiltration of the solution was slowed during the time period when the solution was infiltrating within the low-K unit (Figure 4b and 4d) as capillary forces controlled lateral solution movement. Once the solution had nearly saturated the low-K lens with some solution, the infiltration rate was increased to exceed the infiltration rate of the low-K unit, thereby forcing lateral transport of water at high saturation across the top of the low-K unit and down the sides (Figure 4f). This resulted in multiple locations that were infiltrating into the sediment under the low-K lens (Figure 4h).

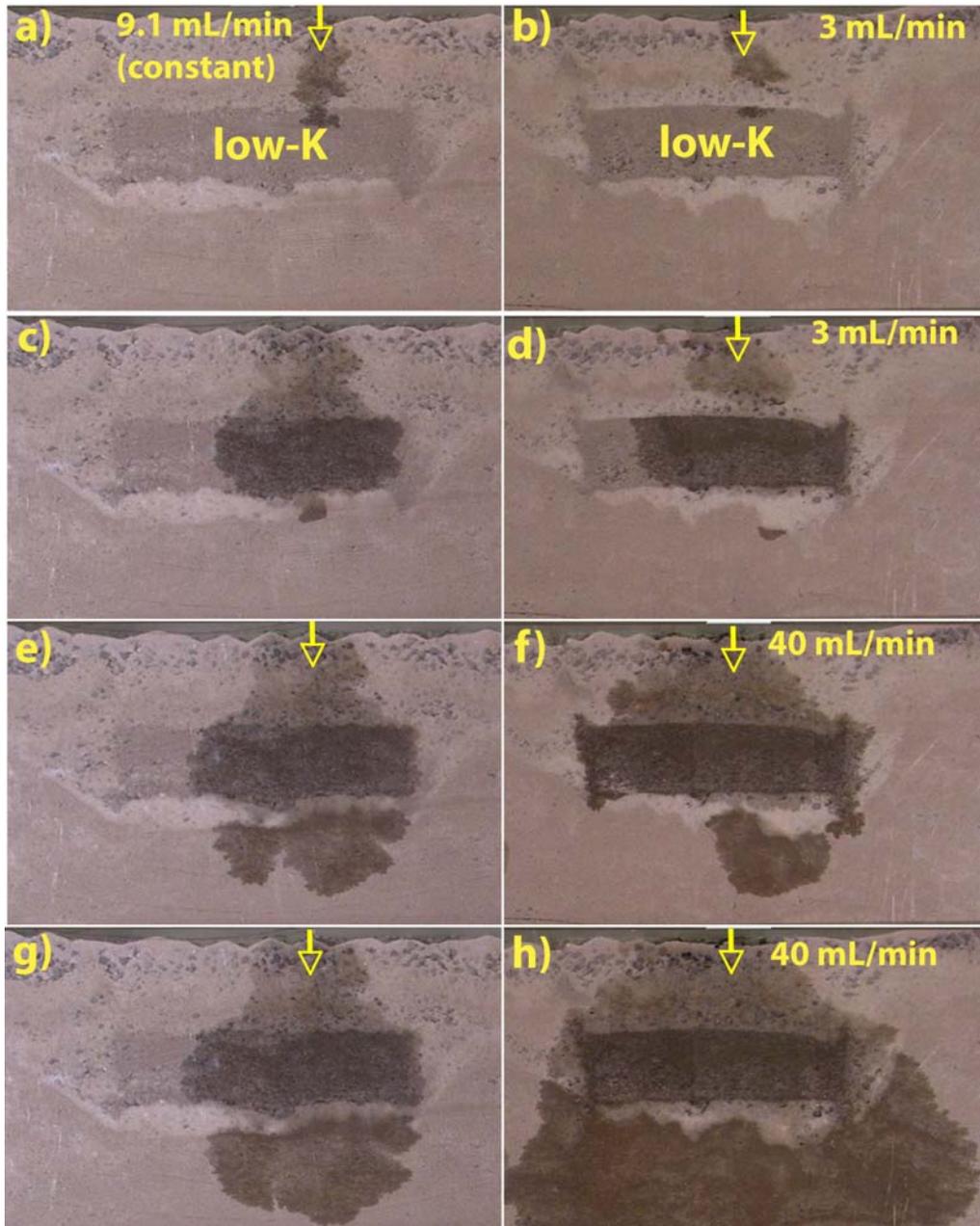


Figure 4. 2-D unsaturated infiltration into a low-K zone at constant infiltration rate (left panels) and at varying infiltration rate (right panels).

CONCLUSIONS

This project was initiated to develop a strategy for infiltration of a Ca-citrate- PO_4 solution in order to precipitate apatite $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ in desired locations in the vadose zone. Apatite is used for remediation of Sr-90 subsurface contamination at the U.S. DOE Hanford site, as over time Sr-90 is incorporated into apatite. Sr substitution occurs because Sr-apatite is thermodynamically more stable than Ca-apatite (Geochem

Software, 1994). This technology has previously been used to precipitate apatite in water-saturated sediments. The objectives of this study are to quantify the precipitation rate and spatial variability of apatite formation and Sr sequestration processes under variably saturated (low water saturation) conditions. Small-scale batch and column studies, intermediate-scale 2-D experiments, and numerical modeling were performed to quantify individual and coupled processes associated with apatite formation and Sr-90 transport during and after infiltration of the Ca-citrate-PO₄ solution.

Laboratory studies have demonstrated that: a) apatite precipitation occurs under variable water saturation, b) the small mass of apatite precipitate formed can be measured by multiple methods, and c) Sr-90 is slowly incorporated into the apatite structure. The apatite precipitation rate is controlled primarily by the in-situ biodegradation of citrate, where the initial Ca-citrate complex prevents immediate precipitation of apatite. Citrate degradation to CO₂ quantified over a range of initial citrate concentrations (5, 10, 25 and 125 mM) and water saturation of the sediment (35 to 100%) generally showed no consistent trends between water content and the mineralization rate or extent. At low citrate concentration (5 to 10 mM), mineralization rates were slower at water saturations below 65%. The 48 h to 70 h citrate degradation half-life (at aquifer temperature and sediment/water ratio) provides sufficient time for the infiltrating solution to reach the location where apatite precipitate is needed. Although microbial biomass decreases by five orders of magnitude with depth, transport of shallow in situ microbes and biomass associated with the river water used during infiltration results in citrate biodegradation rates that vary by less than one-order-of-magnitude. Apatite precipitate in sediment was characterized by electron microprobe analysis with elemental P and Ca detection, aqueous phosphate extraction of sediment, and fluorescence detection of substituted apatite. Sr-90 substitution in apatite was measured by sequential aqueous extractions to measure Sr-90 adsorbed on the sediment, Sr-90 adsorbed on the apatite, and finally (with acid dissolution of the apatite) Sr-90 incorporation in apatite. Long-term experiments showed that the half-life for Sr-90 incorporation into apatite was 5.5 to 16 months.

1-D and 2-D laboratory infiltration experiments quantified the spatial distribution of apatite that formed during solution infiltration. 1-D infiltration studies demonstrated that zones of higher apatite formation resulted where there was sufficient residence time (and higher water saturation) of the Ca-citrate-PO₄ solution. 2-D infiltration studies in progress are evaluating the vertical and unconstrained lateral infiltration of the Ca-citrate-PO₄ solution and resulting spatial distribution of apatite formation in heterogeneous systems. Factors that control the spatial distribution of apatite include adsorption/precipitation of injected phosphate, the rate of citrate biodegradation, and microbial transport processes. Preliminary 2-D experiments show the apatite precipitate concentrated in the upper third of the area of solution infiltration, indicating the infiltration rate was slower than the apatite precipitation rate. Because it is hypothesized that there are likely higher concentrations of Sr-90 in low-K zones of the vadose zone, 2-D experiments are focused on the spatial distribution of apatite that precipitates in these low-K zones. 2-D experiments have demonstrated that changes in the infiltration rate can be used to manipulate the spatial distribution of the solution within low-K zones. Through the development of an understanding of the apatite-forming processes,

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evaluation of infiltration tests in laboratory 1-D and 2-D flow systems, and reactive transport modeling, the results of this study will be used to design an efficient and effective infiltration strategy that will be tested at field scale.

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