

Foam-Delivery of Remedial Amendments for Enhanced Vadose Zone Metals and Radionuclides Remediation - 9465

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ABSTRACT

The remediation of metals and radionuclides contamination, such as Cr(VI), Tc-99, and Sr-90 in the U.S. DOE Hanford Site vadose zone is a critical need. Water-based remedial amendments delivery to the deep vadose zone is facing significant technical challenges. Water-based delivery will easily leach out the highly mobile pollutants therefore contaminate the underlying aquifer. Preferential flow of the amendment-laden solution in the vadose zone due to the formation heterogeneity is difficult to overcome, resulting in bypassing of the less permeable zones. Foam has unique transport properties in the vadose zone that enable mitigation on the mobilization of mobile contaminants and enhance the sweeping over heterogeneous systems. Calcium polysulfide (CPS) is a remedial amendment that can be used to reduce and immobilize hexavalent chromium [Cr(VI)] and other redox-sensitive radionuclides/metals in the vadose zone. The delivery of CPS to the vadose zone using foam and the immobilization of Cr(VI) via reduction by the foam-delivered CPS was investigated in this study. Batch tests were conducted to select the foam-generating CPS-surfactant solutions, to determine the solution foamability and the reducing potential of CPS-containing foams, and to study the influence of foam quality, surfactant concentration, and CPS concentration on foam stability. Column experiments were performed to test the foam delivery of CPS to sediments under conditions similar to field vadose zone, to study the foam transport and interaction with sediments, and to determine the extent of Cr(VI) immobilization using this novel delivery approach. CPS-containing foams with high reducing potential were prepared based on the batch tests. Sediment reduction by foam-delivered CPS was observed in the column studies. Significant mobilization of Cr(VI) from sediments occurred when CPS was delivered in aqueous solution. The Cr(VI) mobilization was minimized when CPS was delivered by foams, resulting in significant Cr(VI) *in-situ* immobilization. Foam delivery of citrate-phosphate mixture to vadose zone sediments for apatite precipitation was also tested in preliminary column and 2-D flow cell tests. The results of this study demonstrated for the first time that foam injection can be successfully used for CPS delivery and that foam-delivered CPS can be applied for Cr(VI) immobilization in contaminated vadose zones. A second solution (Ca-citrate-PO₄) was also foam-delivered into vadose zone sediments. This sediment will result in precipitation of apatite, which then adsorbs and incorporates Sr (and Sr-90) into the structure. 1-D and 2-D foam injection experiments resulted in a wide area of apatite precipitate.

INTRODUCTION

Nuclear weapons production at US DOE's Hanford site (north of Richland, WA) generated hundred millions of gallons waste containing radionuclides and toxic metals. Some of the waste has leaked into the vadose zone, resulted in subsurface distribution of radionuclides and toxic metals. For example, chromate was used throughout the Hanford 100 Areas as a corrosion inhibitor in reactor cooling water with 0.7 to 2.0 mgL⁻¹ chromium. Cr(VI) contamination was produced through spills, pipe leaks, inevitable discharges to surface, or discard to cribs. The recently observed high Cr(VI) concentration (>10 mgL⁻¹) in

groundwater demonstrates that the chromate is not come from the cooling water but from a more concentrated source in the vadose zone. Cr(VI) is one of the major metal contaminants that the DOE is trying to characterize and aim to remediate. Tc-99 is a widespread radionuclide contaminant in the Hanford vadose zone due to the release from waste tank leaks, liquids leaked to the ground, and buried solid wastes. Tc-99 poses a special concern to the long-term risk assessments due to its long half-life ($T_{1/2} = 2.1 \times 10^5$ yrs) and the high mobility of pertechnetate [$^{99}\text{TcO}_4^-$] under oxidizing environments. Sr-90 is present in vadose zone sediments and in groundwater near the Columbia River as the result of reactor discharge to trenches. Sr-90 is slowly leaching into the Columbia River.

Deep vadose zone metals and radionuclides remediation is a critical and imminent step to take in order to stop groundwater contamination sourcing from the vadose zone and to prevent contaminants migration to the Columbia River. A National Research Council report recently recognized that much of the contamination in the subsurface at DOE sites will not be removed by any active remediation efforts due to the high cost and technological limitations. Alternatively, *in-situ* stabilization is expected to become one of the most important remediation strategies. This is particularly true in the deep vadose zone. Delivery of remedial amendments to the vadose zone is required for *in-situ* remediation.

Calcium polysulfide (CPS) is a remedial amendment that has been used for aquifer heavy metal removal (Petersen and Hedquist, 2006). CPS precipitates highly soluble metals as less soluble and non-toxic sulfides and hydroxides. For example, it reduces Cr(VI) to Cr(III), which is then precipitated readily as chromium hydroxide and/or as iron chromium hydroxide [$\text{Cr}_x\text{Fe}_{(1-x)}(\text{OH})_3$] with resultant solubility orders of magnitude lower than that of pure chromium hydroxide. Several site CPS applications were reported. Dissolved CPS was injected into the chromium contaminated soil in a wood treating plant at Ukiah, CA for Cr(VI) remediation (Jacobs, 2001). The highest reduction rate (70%) was observed during the first six months. In about 18 months, 99% of Cr(VI) in the groundwater was reduced. In this work, higher injection tip pressures were used to induce hydrofracturing in low permeability sediments, allowing for movement of the treatment chemicals into the target zone. Calcium polysulfide was also used to treat Cr(VI)-contaminated soil in a wood treatment site located at Windsor, California (CA Regional Water Quality Control Board, 2006). Remedial performance evaluation showed that the treatment was effective but was limited to about 5 feet of depth. CPS solution was used to mix with the groundwater pumped out from the DOE Hanford Site 100-K Area to remove Cr(VI), and the groundwater was then injected back into the aquifer (Petersen and Hedquist, 2006). According to the U. S. EPA (2000), the CPS remediation technology was also used to remediate chromium contaminated sites in Indiana, Maryland, and Maine. Redox-sensitive mobile technetium [$^{99}\text{Tc(VII)}$] and uranium in the Hanford vadose zone is also potentially to be reduced by CPS to less soluble $^{99}\text{Tc(IV)}$. *In-situ* immobilization of Tc-99 can be achieved.

Injection of CPS solution into Hanford vadose zone was proposed as a remediation technology to treat the Cr(VI) contamination. However, uniform delivery of CPS solution to the heterogeneous vadose zone, especially to the deep vadose zone is a challenge because the injected liquid preferentially percolates through the high permeable pathways in the vadose zone. Furthermore, Cr(VI) sorbed to the vadose zone soil is easily mobilized by the flushing water (Hanson *et al.*, 1993). At least 95% of Cr(VI) was leached out in the first 2 pore volumes of flushing. This mobilization will form a significant Cr(VI) moving front during the CPS solution injection. The movement of this front is out of control and may cause a spread of contamination, consequently even a significant contamination to the underlying aquifer. The massive mobilization problem with Tc-99 will be as serious due to its high mobility. The adsorption distribution coefficient (K_d) for Tc-99 in Hanford soil is zero or even negative due to anion exclusion effects (Kaplan *et al.*, 1996), indicating Tc-99 simply stays in the pore water but not sorbed to the soil in the vadose zone. Once the pore water is mobilized, it moves downwards to the aquifer.

The primary problem with water-based delivery systems for remedial amendments in the vadose zone is that gravitational forces have a dominating influence over the direction of flow and it is very hard to control, resulting in risk of contamination spreading. In summary, water-based remedial amendments delivery to the DVZ is facing significant technical challenges that are difficult to overcome.

In contrast to water-based delivery systems, foam flow in vadose zone is not dominated by gravity but can be directed by differences of pressure and resistance to flow in the soil. Foam is a shear thinning fluid Schramm and Wassmuth, 1994 which provides improved sweeping efficiency when injected into heterogeneous systems. Furthermore, the limited amount of liquid in foam enables the contaminant mobilization mitigation. Foam-aided calcium polysulfide delivery technology can resolve both the uneven remedial fluid distribution and the significant Cr(VI)/Tc-99 mobilization front issues.

Foam is a disperse phase of gas in a liquid. It is an emulsion-like two-phase system where air cells is dispersed in a liquid and separated by thin liquid films called lamellae. Surfactants are usually used as the foaming agent to lower the surface tension of the liquid therefore to create or stabilize foams. Foam formation is a dynamic process and foams are thermodynamically unstable. Aqueous surfactant foam is formed by dispersing non-wetting gas within a continuous surfactant-laden liquid phase. They may be created either by simultaneous injection of gas and liquid or by injection of alternating slugs of liquid and gas into porous media. Foams display properties that are vastly different from the liquids used in the production of the foams (Chowdiah *et al.*, 1998). The simultaneous injection of surfactant and air will enhance the flooding efficiency of surfactant flushing even in a heterogeneous porous medium, resulting in better sweeping efficiency over the contamination zone and higher contaminant removal (Jeong *et al.*, 2000; Kovscek and Bertin, 2003). The use of foam can also provide a better control on the volume of fluids injected and the ability to contain the migration of contaminant-laden liquids (Chowdiah *et al.*, 1998). The stability of foams is determined by the property of the foaming agent, such as surfactant (Zhong *et al.*, 1998). Surfactant-foam was used to remove metal, organic, and nonaqueous phase liquids (NAPLs) from contaminated soil (Mulligan and Eftekhari, 2003; Wang and Mulligan, 2004; Rothmel *et al.*, 1998; Peters *et al.*, 1994). The influence of surfactant concentration, foam quality, foam stability, and foam flow rate on the pressure gradient in soil was reported in these literatures. Relative low foam flow rate and high foam quality was suggested in order to avoid high pressure in soil during foam flushing (Mulligan and Eftekhari, 2003).

Foam quality and stability are two important parameters used for foam characterization. Foam quality is defined as the percentage of gas volume in the total foam volume. Foam stability is usually measured by the volume or height change of foam in a container over time. Foam half-life is the time taken by the foam to reach half of its initial volume.

In this study, CPS was incorporated into surfactant solutions as a remedial amendment during foam generation; the foam was then applied to deliver CPS to unsaturated sediments. A series of column experiments were conducted to test the foam-delivery of CPS under conditions similar to field vadose zone, to determine the extent of Cr(VI) immobilization using this novel delivery technology, and to compare the Cr(VI) sequestration results with those obtained from tests with water-based CPS delivery.

A remediation technology focused upon sequestration of radionuclides Sr-90 and uranium in groundwater at the Hanford Site has been developed. This technology is based on the injection of an aqueous apatite mixture into the aquifer. In situ apatite formation and subsequent Sr-90 sequestration by this technology occurs by the following steps (Szecsody *et al.*, 2007) : 1) injection of Ca-PO₄ citrate solution (with a Ca-citrate solution complex), 2) in situ biodegradation of citrate which slowly releases the Ca required for apatite [Ca₆(PO₄)₁₀(OH)₂] precipitation (amorphous, then crystalline), 3) adsorption of Sr-90 to the apatite surface, 4) apatite recrystallization with Sr-90 substitution for Ca (permanent), and 5) radioactive decay of Sr-90 to Y-90 to Zr-90.

Sequestration of Sr-90 and uranium in the vadose zone using apatite formation was also proposed; therefore an effective delivery of the apatite-foaming formulation into the vadose zone is in demand. As an individual task in this study, foam-delivery of Ca-PO₄-citrate solution was tested using long column tests and 2-D flow cell experiments.

EXPERIMENT SECTION

Batch and “Bottle” Tests

“Bottle Tests” were conducted to select the foaming solution for foam generation, to study the foam stability property, and to study the foam aging behavior. A HPLC pump was used to deliver surfactant-CPS solution, and a line connected to a building air or a nitrogen tank was used to deliver air/N₂. A gas flow meter/controller was set up in the air/N₂ line. The flow of surfactant-CPS solution and the flow of air/N₂ were combined and delivered to a vertically mounted glass column with 1-in inner diameter (ID). A porous plate was placed on the bottom of the glass column. The gas flow rate was set at 10.0 ml/min for foam generation. The flow rate of the surfactant-CPS or surfactant-citrate-phosphate solutions was set at a desired value so that a predetermined foam quality could be achieved. The flows were stopped when the height of foam in the glass column reached 10 cm and the changes in foam height, bubble size, and texture with time were monitored – at this stage the graduated column was used as a “bottle” in the bottle tests. Surfactant and CPS were mixed in batch tests to measure the solutions’ redox potential (Eh), and to study the influence of surfactant addition on Eh changes to CPS solutions.

Surfactant sodium POE(3) laureth sulfate was used in this study. The surfactant was produced by the Stepan Company, Northfield, IL, and received as STEOL CS-330 (3 EO). CS-330 contains 30% of sodium lauryl ether sulfate, CH₃(CH₂)₁₀CH₂(OCH₂CH₂)₃OSO₃Na. It is a biodegradable anionic surfactant with critical micelle concentration (CMC) at 4.19 mmol/L (0.18 wt%) and surface tension of 32.2 dyne/cm. The reductant, calcium polysulfide (CPS, 29% by weight) was obtained from the VGS Company, Bloomington, MN. This reagent was produced for contaminated soil remediation or heavy metal removal from wastewaters. We consider it representative of relatively inexpensive commercially available bulk chemical CPS. Chemicals citrate and phosphate were purchased from Aldrich Chemical Company (Milwaukee, WI).

Column Tests

Column tests were used to study the foam transport in sediment and foam-delivery of CPS and citrate-phosphate mixture. Column experiments were also used to study Cr(VI) immobilization by foam-delivered CPS. In the foam transport experiments, the generated foams were delivered to a vertically mounted 12-inch long and 1-inch ID column packed with clean Hanford sediment through a ¼-inch ID tubing and flushed through the sediment pack from top to bottom. The pore volume (PV) of a column was either measured by weighing the dry and water-saturated column, or calculated based on the bulk density, particle density, and water content of the sediment. The PVs of foam (PV-foam) flushed through the columns were determined based on the volumes of foam under atmospheric pressure and room temperature. During foam flushing, the wetting front in the column was monitored and the length of sediment column wetted by foam, termed as “foam-wetted-length”, was measured. In the Cr(VI) immobilization tests, Cr(VI) contaminated sediments were packed in the column. CPS-containing foam was injected through the column. The liquid effluent was collected and analyzed for Cr(VI) concentration, solution Eh and pH. In order to compare the Cr(VI) mobilization and immobilization behavior observed in the CPS foam-delivery tests with that in CPS water-delivery tests, column tests were conducted in

which CPS was delivered using water solutions. Total of 6 column tests were performed as summarized in Table 1.

For the Ca-PO₄-citrate delivery column test, a 7.5 m long column with ¾-in ID was set up horizontally. The column was packed with Hanford sediments. Ca-PO₄-citrate-containing foam was injected from one end of the column while air was extracted from the other end. The injected solution mass, the foam-wetted-length, and the injection pressure were monitored. After foam injection, the sediment was sampled at desired locations for water content and PO₄ concentration determination.

Flow Cell Tests

A flow cell with dimensions of 1.4 m by 0.4 m was used for Ca-PO₄-citrate foam delivery test. An injection well was setup at the center of the cell with an injection interval of 15 cm started from the bottom of the flow cell. An extraction well was established at each end of the cell. The same sediment used in the long column test was used to pack the flow cell. A higher permeability zone was packed at the left side of the cell and two lower permeability zones were packed in the right side of the cell (see Fig. 4 for the dimensions and packing configurations). The sediment was sampled at desired locations for water content and PO₄ concentration determination after foam delivery.

Table 1. Summary of the column tests

Test name	Description	Packed sediment weight (g)	PV (ml)	Porosity	Gas type	Flow rate (ml/min)
GW Flushing test	Synthetic groundwater flush; Cr-contaminated sediment.	37.17	11.86	0.47	NA	0.343
Water deli -- I	0.5% CPS--water delivery; Cr-contaminated sediment.	37.37	10.14	0.43	NA	0.0939
Water deli -- II	5.0% CPS--water delivery; Cr-contaminated sediment.	37.43	9.82	0.43	NA	0.0897
Foam deli -- I	5.0% CPS--foam delivery; Cr-contaminated sediment.	275.95	62.65	0.39	N ₂	2.53
Foam deli -- II	5.0% CPS--foam delivery; Cr-contaminated sediment; a reduced barrier established	280.44	60.56	0.38	N ₂	2.53
Foam deli -- III	10.0% CPS--foam delivery; Cr-contaminated sediment; a reduced barrier established	280.33	60.60	0.38	N ₂	2.53

Analytical Methods

The diphenylcarbohydrazide (DPC) colorimetric method was used for chromium concentration determination. Cr(VI) reacts with 1-5, diphenylcarbohydrazide reagent to yield complex with an absorption peak at 540 nm. This method has a Cr(VI) detection limit of $0.10 \mu\text{M}$. PO_4^- was analyzed colorimetrically by an amino acid method (Hach 8178, Loveland, CO). The redox potential of the foaming solution, the foam, and the effluent was measured with a platinum Eh electrode. The Eh sensor was tested against a ZoBell's standard solution before and after each set of measurements.

RESULTS AND DISCUSSION

Foam Property – Aging and Stability

The foam bubble size and texture changed during aging. The foam bubbles were in “ball foam” shape with diameters around 2 mm when first generated. During aging in the foam generation column, the individual bubble size increased and the bubbles gradually changed from “ball” shape to polyhedral shape. After aging for 450 min, the individual bubble dimension could reach about 10 mm. The changes in bubble size and texture revealed the increasing foam quality, i.e. more liquid had drained from the foam (Kovscek and Radke, 1994) as indicated by the accumulation of liquid on the bottom of the column. The number of bubbles per unit volume decreased while the individual bubble sizes increased from ~2mm to ~10 mm, due to the gas-diffusion caused foam coalescence (Bikerman, 1973; Chambers and Radke, 1991; Schramm and Wassmuth, 1994).

Foams should be stable enough for injection because for the vadose zone remediation purpose, foam will be generated *ex-situ* and then injected into the subsurface. Foam stability also influence foam injection pressure. More stable foam may require a higher injection pressure (Chowdiah et al., 1998). Foam stability was described with the normalized foam height. It was a function of the foam quality, surfactant concentration, and remedial amendment concentration. Foam stability decreased with the foam quality in the 95% and 99% tested range. Foam stability decreased considerably when the concentration of CPS in the foaming solution increased from 1 wt% to 5 wt% (Fig. 1). However, the stability increased when the Ca- PO_4 -citrate concentration increased from 30 mM to 60 mM, as illustrated in Fig. 1.

There was a concern whether the CPS can retain its reducing capacity in the foaming solutions. The measured redox potential, Eh, of a series of CS-330 and CPS solutions with comparison to the Eh of CPS-in-water solution indicated that only a slight decrease on the solutions' redox potential was observed when surfactant was added to the solution, and that the influence of surfactant concentration was minor within the 0.5 wt% (12.5 mM) to 1.5 wt% (37.5 mM) tested range. The redox potential of the foams generated from 1 wt% (25 mM) CS-330 and 5% CPS (Eh = -516 mV) at 99% foam quality was -496 mV, and the redox potential of the liquid drained from this foam in open atmosphere environment was -502 mV. During the redox potential measurement of the foams, the reading was slightly fluctuating due to the connection between Eh probe and the foams. It was clear that during the foaming process, the fluid kept most of its initial reducing potential. The slight decrease on the reducing potential from the foaming solution to the foam-drained solution was probably due to the interaction between foam and oxygen in the air during the bubble breakdown.

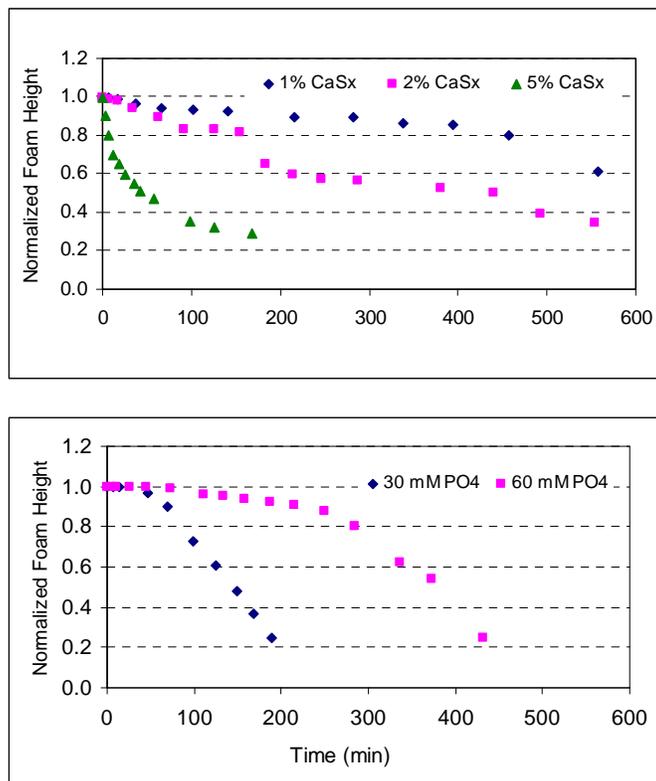


Fig. 1.
remedial amendment concentration on foam stability

Influence of

The surfactant-CPS solutions were ready for foaming when gas was delivered into the fluids. Based on the gas flow rates and the foam volume generated from the gas flow using the foam generation system, 90% or more of the delivered gas was captured in the generated foams.

Foam Transport in Packed Sediments – flow rate, injection pressure, liquid uptake

Flow rate and foam quality had significant influence on the injection pressure drop. When the quality of injected foam decreased, the injection pressure increased. At a fix flow rate, a near-linear relationship between the foam quality and pressure drop was observed. At higher foam flow rate, the impact of foam quality was higher. At higher foam quality, the foam stability was lower and the bubbles had thinner films which collapsed more easily when being pushed through the sediment pack (Chowdiah et al., 1998). This observation explains the decreased pressure drop at higher foam quality.

In order to keep low the injection pressure, high foam quality and relatively low flow rate are desirable. When the injection pressure is limited due to the foam delivery set up or the vadose zone depth, these two factors have to be compensated so that the injection pressure won't be excessive. In the column tests conducted here, when the foam injection rate was 2.53 ml/min, or 0.92 m/h flow rate in the sediment, the pressure drop was around 15.2 kP/ft (2.2 psi/ft). The foam injection is practical when scale up to field remediation.

When foam bubbles break, the liquid is up taken by the sediments. The liquid uptake in sediment determines the amount of the remedial reagent delivered to the contamination zone, which is a critical

design parameter in remediation. Before liquid effluent breakthrough, the uptake rate was the same as the surfactant-CPS liquid injection rate. In Fig. 2, a linear relationship between the foam-wetted-length and PV-foam was observed, meaning the foam front progressed into the sediment column at a constant velocity. This suggested that the liquid uptake content was uniform across the foam flushed column. The uptake reached a steady and usually the maximum value at a few PVs after foam breakthrough (Fig. 2). Liquid uptake between 15% and 65% of the column pore volume was observed in the tested sediments. The maximum liquid uptake was influenced by the foam flow rate and the foam quality. The results showed that under a fixed foam quality, the liquid uptake decreased with increasing flow rate. The same relationship between the foam flow rate and fluid uptake in sediment columns was also observed in a previous study (Chowdian et al., 1998).

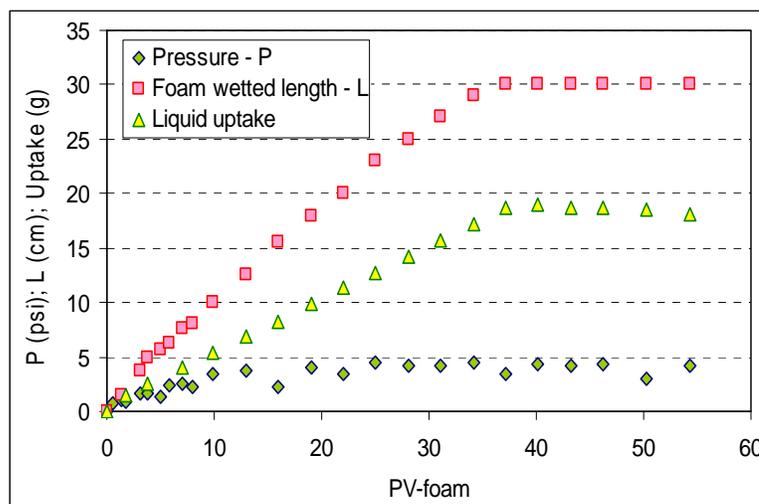


Fig. 2. Injection pressure, foam-wetted-length, and liquid uptake during a foam injection column test

Cr(VI) Remediation – Mitigated mobilization and *in-situ* immobilization

In column tests when water-delivered CPS was flushed through the sediments, significant Cr(VI) mobilization occurred. The mobilization was considerably mitigated when CPS was delivered by foams. Fig. 3 shows the column effluent Cr(VI) concentration for the column tests listed in Table 1. The mobilized Cr(VI) mass was calculated based on the effluent liquid volume and Cr(VI) concentration. When synthetic groundwater was used to flush the column (GW flush), more than 98% of the total water-leachable Cr(VI) mass was mobilized out from the sediment at 1 PV. When 0.5% and 5% CPS solutions were used in the column flood (Foam deli--I, Foam deli--II), 90% and 77% of the total Cr(VI) mass was mobilized, respectively, when 1 PV or less solution was flushed through the column. When CPS was delivered to the sediment using N₂- generated foams from 5% CPS solution (Foam deli--I), the amount of mobilized Cr(VI) was much lower (28.9%), thus much more of the chromium was immobilized *in situ*.

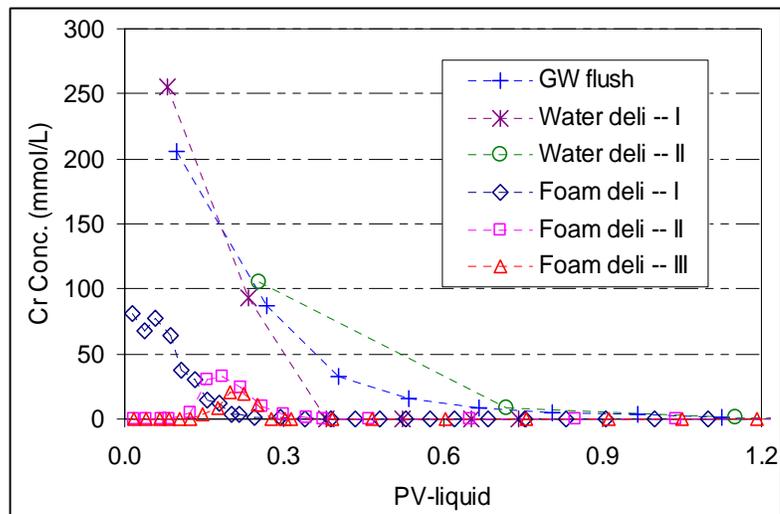


Fig. 3.
Comparison of effluent Cr(VI) concentration in column effluent in water flushed, water-delivered CPS flush, and foam-delivered CPS flush tests.

A strategy to further lower the Cr(VI) mobilization was tested using 5% and 10% CPS generated foam to establish a reductive barrier at the bottom of the contaminated sediment column, followed by flushing the same foam from the top of the column to immobilize Cr(VI). Only 11.5% and 7.1% of the total Cr(VI) contaminant mass was mobilized in Test Foam deli--I and Foam deli--II, respectively (Fig. 3). When 1.5 PV synthetic groundwater was flushed through the sediment column following the foam flood, no Cr(VI) was detected in the effluent, indicating the immobilization of Cr(VI) by foam-delivered CPS.

Ca-PO₄⁻-Citrate Distribution by Foam Delivery

In the Ca-PO₄⁻-citrate foam delivery long column (7.6 m) test, the fluid was delivered 6.5 m into the column with injection pressure of 60 psi. The water content in the sediment in the foam swept section was around 15% of the pore volume. The remedial amendment was distributed 1.5 m into the column from the injection end. Retardation of the remedial amendment in the sediment was observed which merits future study.

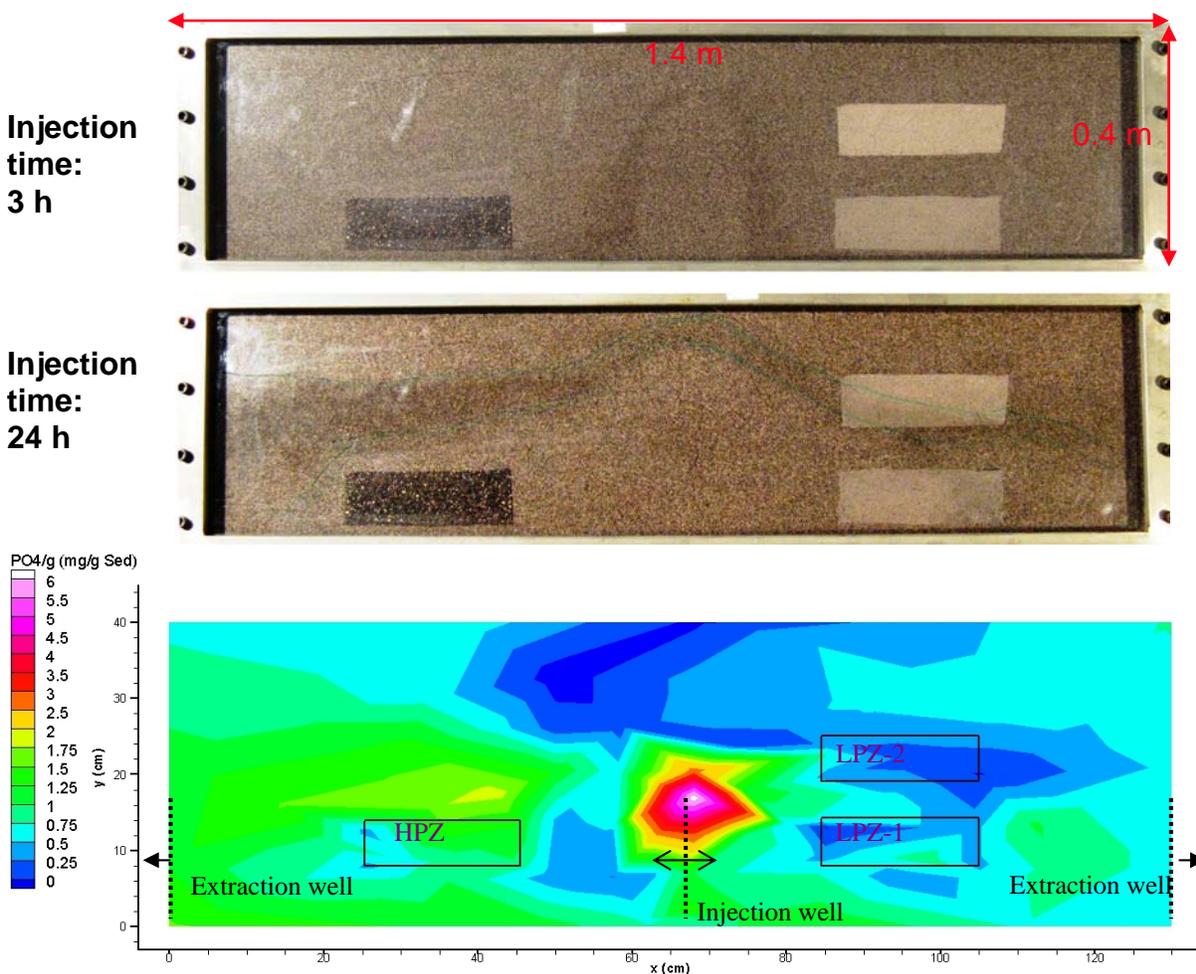


Fig. 4. Flow cell packing configuration and liquid, PO_4 distribution in sediments after foam flushing. HPZ – high permeability zone; LPZ – low permeability zone

The foam-wetted sediment section layout and the PO_4^- distribution in the 2-D flow cell foam injection test are shown in Fig. 4. Foam injection can sweep the sediment laterally. Higher flow in the high K zones was observed. Higher apatite precipitation was measured in high-K zones and zones close to the injection well. This is a preliminary flow cell test. Better defined tests with finer sampling will be performed to further study the distribution of foam-delivered amendments.

CONCLUSION

Batch tests were conducted for the selection of foaming solutions and to study the properties of CPS-containing foams. Column tests were conducted to study foam transport in sediments under vadose zone conditions, to investigate the feasibility of foam delivery of calcium polysulfide to sediments under vadose zone conditions, to evaluate the Cr(VI) immobilization by foam-delivered CPS, and to test the delivery of citrate-phosphate amendment. A flow cell test was performed to test the delivery of citrate-phosphate in 2-D setup. A foam generation and foam injection setup was established. Results from the column experiments clearly showed that CPS can be efficiently foam-delivered to unsaturated sediments to immobilize Cr(VI) *in-situ* and to minimize Cr(VI) mobilization at the reaction front as encountered

when CPS is delivered in a water-based single-phase solution. The results indicated that foam delivery of CPS is a promising approach for vadose zone Cr(VI) immobilization and remediation. Retardation of remedial amendment merits further investigation in order to better understand the distribution of the reactants delivered by foam. The flow cell test result indicated the laterally sweeping of injected foams over heterogeneous sediment systems, while further testing is needed in order to better understand the foam sweeping behavior across heterogeneous settings under vadose zone conditions.

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