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Enhanced remedial amendment delivery to subsurface using shear thinning fluid and aqueous foam

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ABSTRACT

A major issue with *in situ* subsurface remediation is the ability to achieve an even spatial distribution of remedial amendments to the contamination zones in an aquifer or vadose zone. Amendment delivery to the aquifer using shear thinning fluid and to the vadose zone using aqueous foam has the potential to enhance the distribution. 2-D saturated flow cell experiments were conducted to evaluate the enhanced fluid sweeping over heterogeneous system, improved contaminant removal, and extended amendment presence in low-permeability zones achieved by shear thinning fluid delivery. Unsaturated column and flow cell experiments were conducted to investigate the improvement on contaminant mobilization mitigation, amendment distribution, and lateral delivery implemented by foam delivery. It was demonstrated that the shear thinning fluid injection enhanced the fluid sweeping and increased the delivery of remedial amendment into low-perm zones. The presence of amendment distributed by the shear thinning fluid in the low-permeability zones was increased. Foam delivery was shown to mitigate the mobilization of highly mobile contaminant from sediments. It also achieved more uniform amendment distribution in a heterogeneous unsaturated system, and demonstrated remarkable increasing in lateral distribution of the injected liquid compared to direct liquid injection.

1. Introduction

In many contamination sites, removal of contaminants by any active remediation efforts is not practical due to the high cost and technological limitations [1]. Alternatively, *in situ* remediation is expected to be the most important remediation strategy. Delivery of reactive amendment into the contamination zone is essential for the reactions between the contaminants and remedial amendments to proceed *in situ*.

Effective delivery of remedial amendment to the subsurface contamination zone is a challenge when the source zone is either in an aquifer or in a vadose zone. In aquifer, heterogeneity induces fluid bypassing by creating preferential flow channels in the high-permeability pathways during subsurface fluid injection, leaving the low-permeability (low-perm) zones bypassed. The heterogeneity-induced bypassing places certain contaminated areas inaccessible to the remedial amendment delivered by fluid injection, thus inhibiting the success of remedial operations, as reported in pump-and-treat systems [2], *in situ* redox manipulation [3], surfactant-enhanced aquifer remediation [4], and delivery of bio-amendments [5]. The adverse effect can considerably delay the completion of a remedial operation and significantly increase the cost or simply make the remediation goals unachievable.

Methods of forcing fluids into low-permeability flow paths in saturated formations have been developed and widely implemented to solve the heterogeneity-induced bypassing problems encountered during oil recovery, e.g. [6]. Two methods of the enhanced low-perm zone sweeping have been developed. One of them is to use a water-soluble polymer to increase the viscosity of the injectate so that the *in situ* pore pressure is raised, and cross-flow between layers with different permeability occurs [7]. The majority of the polymer solutions used in oil-field applications is non-Newtonian fluids exhibiting shear-thinning (pseudoplastic) behavior [8]. The other method uses surfactant–foam floods to generate foam in high permeable zones *in situ*; therefore, the injected fluid is forced into the low-permeable areas [9]. Recently, polymer solutions with shear thinning property were studied as a delivery means for micro- and nano- particles to subsurface for remediation [10,11].

For vadose zone *in situ* remediation, remedial amendments are usually injected or infiltrated using water as the carrier. To achieve a uniform distribution of the remedial amendment in the vadose zone, especially in the deep vadose zone is a challenge. The injected/infiltrated liquid preferentially percolates downward

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through some high permeable pathways and migrates laterally in the lower permeable compartments due to the higher capillary force. The uneven flow of liquid results in non-uniform distribution of amendment. Furthermore, highly mobile contaminants such as hexavalent chromium [Cr(VI)] and technetium (Tc-99) sorbed to the vadose zone sediment is easily mobilized by the flushing water. It was shown that at least 95% of Cr(VI) was leached out in the first 2 pore volumes of water-based solution leaching [12]. This mobilization forms a Cr(VI)/Tc-99 moving front during amendment injection. The movement of this front is out of control and likely to cause a spreading of contamination. The primary issue with water-based amendment delivery systems in the vadose zone is that gravitational and capillary forces have a dominating influence over the flow direction of the injected fluids. The flow is hard to manipulate, resulting in non-uniform amendment distribution and inducing risk of contamination spreading.

Aqueous foam can be used to improve the delivery of remedial amendments in the vadose zone. Foam-delivery has several significant advantages over water-based delivery owing to the foam transport properties. First, foam flow in the vadose zone is not dominated by gravity but can be directed by applied pressure gradient. Foam flow is much easier to manipulate than the liquid flow. Foam flow has the high potential to transport and deliver amendment laterally. Second, when amendments are delivered by foams, the contaminant mobilization can be remarkably minimized due to the low water content in foam (1–3 vol.%), thus considerably increase *in situ* immobilization. Third, the injection of foam, a shear thinning fluid (STF), can achieve more uniform sweeping than solution injection over heterogeneous systems.

In this work, laboratory 1-D column and 2-D flow cell experiments were conducted to characterize the mechanisms, process interactions, and quantify amendment spatial distributions by STF delivery under saturated conditions, and by foam enhanced delivery under unsaturated conditions. For STF injection into saturated sediments, the processes investigated include: (a) fluid sweeping over heterogeneous porous medium; (b) amendment delivery into low-perm zones and improved contaminant removal; (c) prolonged presence of delivered amendment. For foam delivery in unsaturated sediments, processes investigated include: (a) mobilization mitigating of highly mobile contaminant; (b) delivery into high-perm zones; (c) enhanced lateral delivery.

2. Experimental

2.1. STF enhanced delivery under saturated conditions

2.1.1. Materials

Flow cell experiments were conducted in 0.5 m by 0.4 m by 0.05 m nominal 2-D sand box. The front and back of the flow cell was made of glass. Heterogeneous porous media system was packed in the flow cell using Accusand at 3 different size grades, 20/30 (0.72 mm average grain size), 30/40 (0.51 mm), and 40/50 (0.36 mm). Two packing configurations were applied, as schematically shown in Fig. 1. Configuration A was used to study enhanced sweeping over a heterogeneous system and configuration B was used to investigate enhanced amendment delivery into low-perm zones.

Biopolymer xanthan gum (Kelco Oil Field Group, Houston) was used to form the STFs. Surfactant sodium dihexyl sulfosuccinate (MA-80) was the remedial amendment used to mobilize dense non-aqueous phase liquid (DNAPL) trichloroethylene (TCE). TCE was packed into the low-perm zones in configuration B (Fig. 1), occupying 12% (v/v) of the pore space. Xanthan solution at 600 ppm concentration with 400 ppm Na^+ was used in the enhanced sweeping test. Solution with 4.0% (w/w) MA-80 surfactant, 600 ppm xanthan, and 6000 ppm Na^+ was used in the TCE removal experiments to demonstrate enhanced delivery in the low-perm zones. This solution was identified to have a favorable phase behavior in contact with TCE and have the lowest interfacial tension with TCE [13]. The polymer and the polymer-surfactant solutions were dyed with Brilliant Blue FCF (50 ppm), and TCE was colored with Oil Red O dye (50 ppm). All the chemicals, except for the xanthan, were obtained from Aldrich Chemical Company (Milwaukee, WI).

2.1.2. Procedures

The heterogeneous Accusand system was wet-packed, i.e. packed under saturated conditions, and kept saturated with water after packing. Eight high-precision pumps were use to pump fluids into the flow cell through 8 evenly distributed injection ports. Outflow also flowed through 8 evenly distributed effluent ports connected to a constant-head chamber. The fluid level in the chamber was set at the same elevation as the top of the flow cell. The total flow rate was 5 ml/min for all the STF flow cell tests.

In all tests, the fluid displacing fronts could be monitored and pictured because the displacing fluid had a different color from the fluid being displaced. The removal of red-dyed TCE could also be visually observed. Pictures were taken through the test duration.

2.2. Foam enhanced delivery under unsaturated conditions

2.2.1. Materials

Anionic surfactant sodium lauryl ether sulfate [$CH_3(CH_2)_{10}CH_2(OCH_2CH_2)_3OSO_3Na$] was used as the foaming agent. The surfactant was produced by the Stepan Company, Northfield, IL, and received as STEOL CS-330 (3 EO). It is a biodegradable surfactant with a critical micelle concentration at 4.19 mmol/L (0.18 wt.%) [14]. A surfactant concentration of 0.5% (w/w) was used in all experiments. Calcium polysulfide (CPS) was added to the foaming liquid as the amendment to reduce Tc(VII) to Tc(IV) therefore to immobilize technetium in the column experiments. CPS as obtained from the VGS Company, Bloomington, MN. Sodium phosphate (Na_2HPO_4, Aldrich, Milwaukee, WI) was the chemical amendment used in flow cell tests. Nitrogen and air was the foaming gas used in the column and 2-D cell experiments, respectively. Uncontaminated Hanford Formation sediment from the Hanford Site of the U.S. DOE located at the southeast of Washington State with sizes between 0.053 and 2.0 mm was used as the packing matrix with medium permeability (med-K). Fine sand (#70, 0.21 mm) and coarse sand (#16, 1.2 mm) were used to pack the low-permeability (low-K) and high-permeability (high-K) zones, respectively.

2.2.2. Procedures

2.2.2.1. Foam generation. The foam generation method established in our previous work [12] was used to produce foams in this study. In brief, a flow of surfactant solution containing remedial amendments and a flow of gas (air or nitrogen) were combined and directed through a porous plate to generate foam. Foam was then injected into columns or flow cells by the gas pressure.

2.2.2.2. Tc-99 immobilization. Three column tests, Tc-Col-I, II, III, were conducted to illustrate the enhanced Tc-99 immobilization by foam-delivered CPS. Glass columns (2.4 cm ID, 13.0 cm long) were uniformly dry-packed with Tc-99-contaminated sediments. Porous plates were used at the top and bottom of each column to distribute the foam flow at the inflow end and to collect fines at the column exit. In Tc-Col-I, synthetic groundwater with 5% (w/w) dissolved CPS was injected from the top of column through the sediment. Injection rate was 0.04 ml/min. In Tc-Col-II, foam generated from 0.5% (w/w) STEOL CS-330 surfactant solution at foam quality of 98% (0.04 ml/min liquid flow rate and 2.0 ml/min nitrogen flow rate)

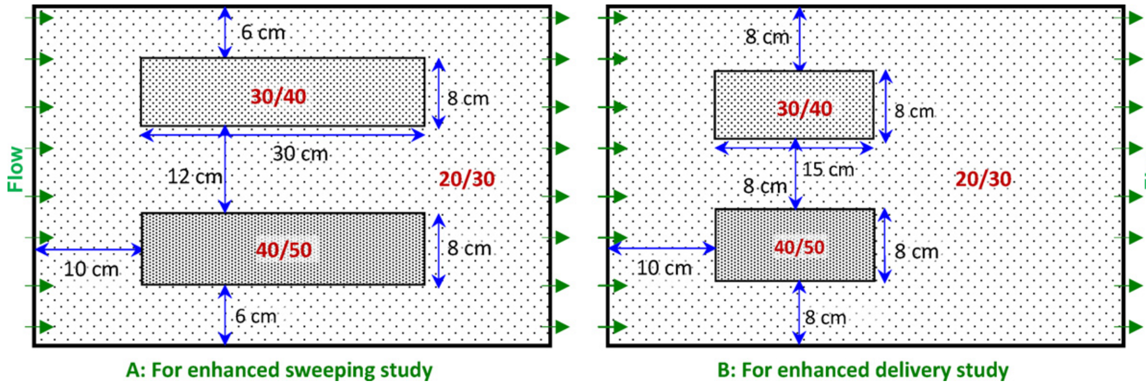

Fig. 1. Schematic of heterogeneous packing in flow cell. Accusand of different grade levels are labeled as 20/30, 30/40, and 40/50.

was used to deliver CPS to sediment for reductive immobilization of Tc-99. The foaming solution contained 5% (w/w) of CPS. After 2.5 PV of liquid delivery through foam injection, synthetic groundwater (SGW) was injection through the column to evaluate the Tc-99 remobilization. In Tc-Col-III, the same procedure used in Tc-Col-II was applied, except that before the SGW injection, about 3000 PV of air was flushed through the foam-CPS-treated column to oxidize the reduced sediment. Column effluent was collected with a fraction collector. All the column experiments were performed inside a controlled radioactive contamination area. The activity of Tc-99 in the effluent samples was determined using a liquid scintillation counter.

2.2.2.3. Delivery to heterogeneous vadose zone system. A liquid infiltration test was conducted in a 2-D cell packed with heterogeneous sediment system, and a foam injection test was performed in a 2-D cell with similar packing to reveal the improved amendment distribution in foam delivery. The sediment system contains random low-K and high-K zones and lenses distributed in the matrix with med-K medium, which tends to occur in the fluvial deposited sediment found in the 100-N Area at the Hanford Site. Phosphate solution with concentration of 47 mM was infiltrated into the sediment through a point at the up-left corner of the cell at a rate of 21 ml/min. Phosphate at the same concentration was added to the foaming liquid in the foam injection experiment. Foam with quality of 96.2% (i.e. 3.8% of the total foam volume was liquid) was injected through a vertical well installed at the left side of the cell at a rate of 26 ml/min. An 80 cm injection interval in the well was located 20 cm from the top and 20 cm from the bottom of the flow cell. There were 17 evenly distributed injection points on the well. Vacuum at 25 mm Hg was applied to an extraction well at the right side of the cell. The extraction point distribution on the extraction well was the same as on the injection well. When infiltration or foam injection was finished, the test cell was disassembled and sediment samples were taken for water content and phosphate concentration determination. Pictures of the flow cells were taken through the test duration. The liquid and chemical distribution in the heterogeneous sediment system was compared in order to evaluate the two approaches of remedial chemical delivery.

2.2.2.4. Enhanced lateral delivery by foam injection. Experiments on foam and liquid injection into uniformly packed sand box were performed to demonstrate enhanced lateral delivery by foam injection. Foams were generated by injecting 1% (w/w) STEOL CS-330 surfactant solution and nitrogen gas simultaneously into a foam-generating system similar to the one described by Zhong et al. [12]. Three 60 mesh stainless wire screens were placed at both ends of the foam generation column. Coomassie brilliant blue (0.05%, w/w) was added into the surfactant solution as a tracer. The foam was

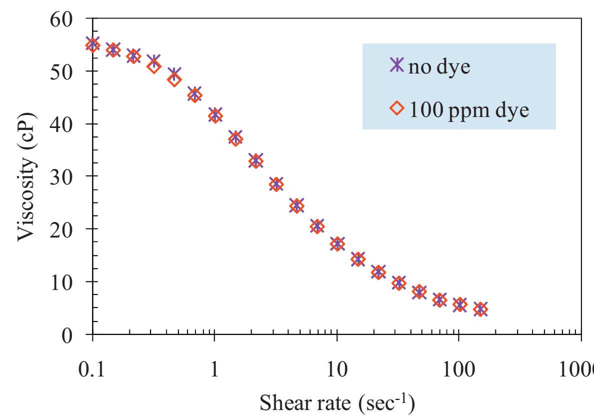

Fig. 2. Shear thinning behavior of the 600 ppm xanthan gum 400 ppm Na^+ solution and the influence of Brilliant Blue FCF dye.

introduced into a sand box of 30 cm × 30 cm × 3 cm packed with dry quartz sand with a size range of 0.8–1.25 mm. Vacuum was applied to the outlet of the flow cell. In the liquid injection test, the solution with the same surfactant concentration as in the foaming solution was directly pumped into the flow cell. In both injection modes, liquid flow rate was 8.5 ml/min. The gas flow rate was 100 ml/min (corresponding to a foam quality of 92.2%). The outlet vacuum was set at 0.08 Mpa for both liquid and foam injections. The transport of liquid solution and foam was monitored using a camera.

3. Results and discussions

3.1. Enhanced sweeping by STF injection

The shear thinning behavior of the 600 ppm xanthan 400 ppm Na^+ solution is shown in Fig. 2. The rheological behavior of the same solution but with 100 ppm Brilliant Blue FCF dye was also plotted in this figure to illustrate the influence of the dye. The polymer solution showed considerable shear thinning. At 0.1 s^{-1} shear rate, its viscosity was 55 cP. When the shear rate approached 100 s^{-1}, the viscosity reduced to less than 5 cP. The addition of 100 ppm blue dye to the solution had negligible influence on its rheological property.

Subsurface formation sweeping efficiency was defined as the portion of a formation volume contacted by the fluid at any stage of the injection [15]. There was remarkably improved sweeping efficiency over a heterogeneous system by STF injection (Fig. 3a) compared to water injection (Fig. 3b). For the 30/40 (0.51 mm) grade Accusand, about 90% of the total area was swept in the water injection at 0.95 PV injection; while 100% percent of this insertion

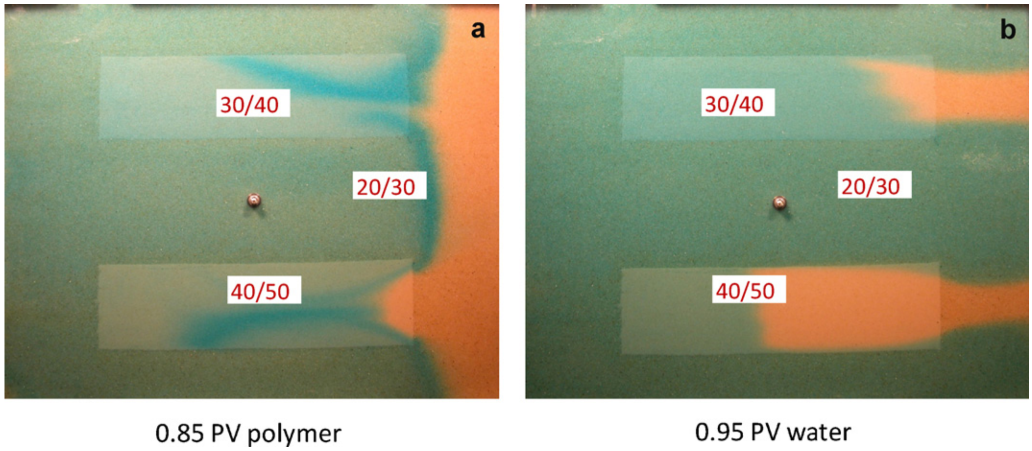

Fig. 3. Enhanced sweeping. (a) Water displaced by blue-dyed 600 ppm xanthan gum solution; (b) water displaced by blue-dyed water. Water injection was conducted first, followed by STF injection at the same system. Numbers in the pictures indicate the particle size grade of the Accusand. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

was swept at 0.85 PV of injection in the STF injection. For the 40/50 (0.36 mm) grade Accusand insertion, about 45% area was swept by displacing water at 0.95 PV injection; while about 95% area was swept by the displacing STF at 0.85 PV injection.

The hydraulic conductivity (K) contrast between the 20/30 (0.72 mm) sand and 30/40 (0.51 mm) sand was 1.7–1, and that between 20/30 (0.72 mm) and 40/50 (0.36 mm) sand was 3.5–1 [16]. Fig. 3 demonstrates that at higher K contrast, the sweeping enhancement was more significant. The same observation was reported by [17]. Blue dye redistribution was observed in Fig. 3a. Since the dye at concentration of 100 ppm showed negligible influence on the rheological behavior of the shear thinning fluid (Fig. 2), this redistribution should not affect the enhanced sweeping performance of the fluid.

3.2. STF delivery into low-perm zones and enhanced DNAPL removal

When a surfactant solution possesses optimum phase behavior with a NAPL comes in contact with the NAPL trapped in saturated porous medium, mobilization of the NAPL will be observed immediately due to the ultra-low interfacial tension between the solution and the NAPL [13,18]. Therefore the TCE mobilization from the low-perm zones observed in the flow cell tests reported here is an indication of the arrival of surfactant amendment.

In the surfactant delivery tests, the TCE trapped in the low-perm zones was mobilized earlier and was removed faster when STF was used for delivery (Fig. 4). Improved distribution of surfactant into both 30/40 (0.51 mm) and 40/50 (0.36 mm) sand low-perm zones was observed before the injection reached 1 PV (not shown in Fig. 3). Enhanced amendment delivery into low-perm zones and improved NAPL removal by the STF injection was clearly demonstrated in the 40/50 (0.36 mm) sand at 1 PV injection. The TCE removal was about 35% from the 40/50 (0.36 mm) sand in the water delivery test, while the removal was about 65% from the 40/50 (0.36 mm) sand in STF injection test (Fig. 3A and C).

It should be noted that downward TCE migration after mobilization was observed in the flow cell tests, which presents negative impact in remediation. The purpose of the surfactant-polymer tests reported here was to demonstrate enhanced amendment delivery into lower-permeability zones using the STF while optimization of remediation was not our intent. Other remediation techniques that minimize downward migration of DNAPL after mobilization, such as density manipulation [19,20] and upward flow to capture the mobilized DNAPL [21,22], are needed in order to minimize the negative potential of TCE mobilization observed in the surfactant-polymer solution injection.

3.3. Extended presence of amendment in saturated low-perm zones

After amendment solution was delivered into the low permeability zones, the STF containing the amendment tends to remain in the low-perm zones during the natural groundwater flow since the shear rate in the solution decreased and the viscosity increased when the injection was stopped. In Fig. 4B, at 2.1 PV (1.1 PV water injection), surfactant solution was washed out from the whole (100%) area in the 30/40 (0.51 mm) sand zone, and about 30% area in the 40/50 (0.36 mm) sand when the amendment was delivered by water. In comparison, at the same pore volumes of injection, surfactant solution was washed out from only 10% area in the 30/40 (0.51 mm) sand and 15% area in the 40/50 (0.36 mm) sand zone when the amendment was delivered into the low-perm zones by STF (Fig. 4D).

Further understanding on the extended presence of amendment in the low-perm zones can be revealed by looking at the mobility ratio (M) of the resident and displacing fluids. This ratio is defined as the mobility of the displaced, or resident, phase over that of the displacing phase, where the mobility is equal to the effective permeability of each phase divided by the viscosity of that phase. The mobility ratio can be simplified as the ratio of the resident fluid viscosity, μ_R, to the displacing fluid viscosity, μ_D, when the flow is confined in a uniform porous medium [23–25].

$$M = \frac{\mu_R}{\mu_D} \tag{1}$$

When the displacing fluid is more viscous than the resident fluid, $M < 1$, the displacement is considered favorable and stable displacement front is observed. When the displacing fluid is less viscous than the displaced fluid, $M > 1$, the displacing is typically unstable and the displacement is considered unfavorable. The mobility ratio was unfavorable for the natural groundwater flow to displace the emplaced more viscous polymer solution in the matrix sand since the static viscosity of the surfactant-polymer solution was about 40 times higher than that of water. This explains the observed evident displacement fingering in Fig. 4D. In the low-perm zones, the fluid flow is slower than that in the matrix sand resulting lower shear rate and higher viscosity of the STF. The mobility ratio is even higher than that in the matrix indicating more unfavorable displacing condition; therefore the displacement of the amendment emplaced in

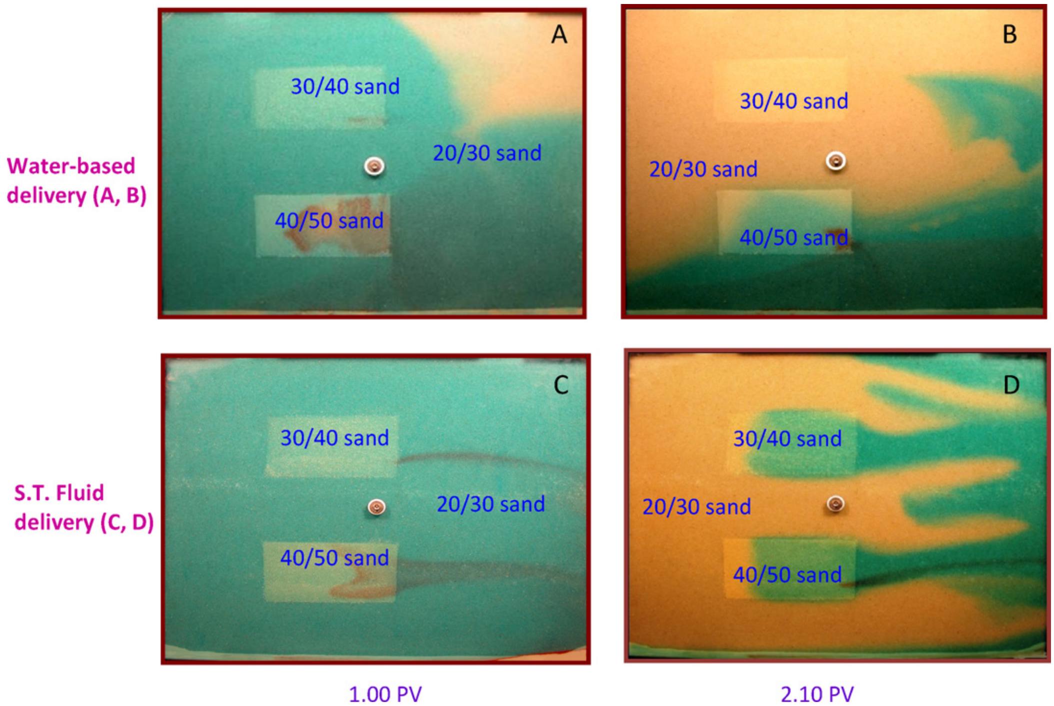

Fig. 4. Enhanced amendment delivery into low-K zone (A vs. C), and extended presence of amendment solution in low-K zones after STF injection (B vs. D) demonstrated in flow cell experiments. The red color fluid is TCE. The flow cell was first saturated using water with TCE trapped in the low-K zones. Surfactant amendment was delivered to the flow cell using water (dyed blue; A and B) and polymer solution (dyed blue; C and D). After 1 PV surfactant solution or surfactant-polymer solution injection, water (without dye) injection was started to displace the surfactant solution. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the low-perm zones is further delayed. Water will bypass the zones occupied by polymer solution until the polymer is either diluted or biodegraded.

Extended presence of amendment in the low-perm zone has an important implication in remediation. In heterogeneous systems, contaminants can diffuse or slowly advect into low permeability zones and the contamination in the low-perm zones presences a challenge to remediation [26]. The prolonged presence of amendment provides additional time for chemical reaction or microbial interactions to occur in the low-perm zones, therefore improve the remediation. The xanthan gum polymer solution has been shown to preserve up to 60% of its initial viscosity 300 days after injection for enhanced oil recovery application [27]. Faster biodegradation of the xanthan gum is anticipated in a groundwater setting [28] and the xanthan gum may serve as a long-term carbon source to support continued biodegradation reactions in applicable cases.

3.4. Mobilization mitigation of contaminants by foam delivery

Using the foam-delivered calcium polysulfide (5%, w/w), 68% of the total Tc-99 in the contaminated sediment was immobilized, while less than 9% of total Tc-99 was immobilized when CPS was delivered by water (Fig. 5a). Only 3.61% of the immobilized Tc-99 was remobilized by infiltrating 6 pore volumes of groundwater after 3000 pore volumes of air was flushed through the treated column (Fig. 5b).

When amendment is delivered to the vadose zone sediment using foam, bubbles break at the foam flow front and liquid is leased to coat and wet the sediment [29], while the amendment reacts with contaminants. With more bubbles breakdown, liquid carried by foam gradually saturate the sediment pore space and the amendment delivery front moves forward. This process provides more time for the reactions between amendment and contaminant to proceed compared to that when the amendment is delivered using

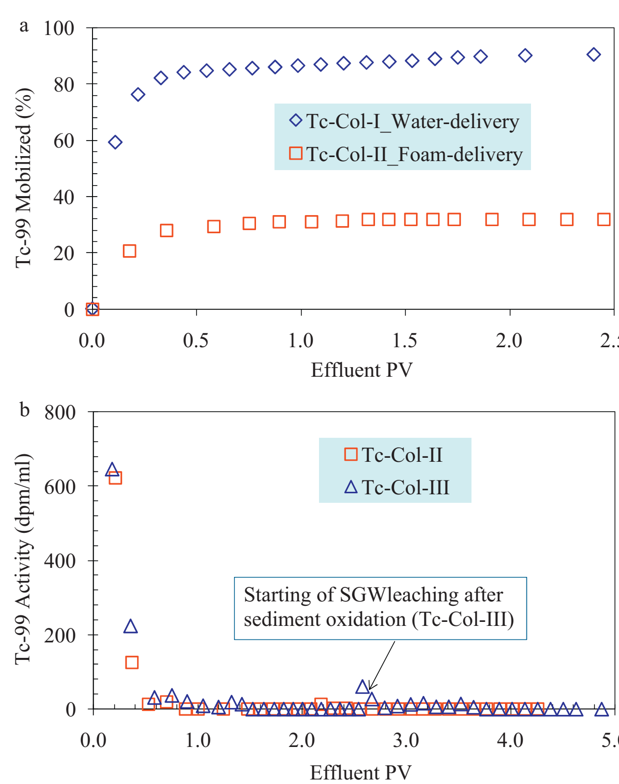

Fig. 5. Accumulative mobilized Tc-99 (a) and effluent Tc-99 activity (b) from technetium immobilization column tests.

water. Improved Cr(VI) immobilization by foam delivered CPS over water-delivered CPS was reported by Zhong et al. [12].

It has been reported [30] that the reaction between technetium and sulfide in aqueous solution under anaerobic conditions produces Tc_2S_7, according to the reaction:

$$2TcO_4^- + 7HS^- + H_2O \leftrightarrow Tc_2S_7 + 9OH^- \quad (2)$$

Tc_2S_7 has very low solubility in water under reducing conditions [31] and oxidizes more slowly than TcO_2 [32]. However, under aerobic conditions, the dissolution of Tc_2S_7 was significant in relative short time scale (100 days) [30]. In the test reported here, it was speculated that after 3000 PV air flush through the column, the sediment still kept a reducing environment therefore the remobilized Tc-99 was minimal. The air flushing intended to oxide the treated sediment was conducted at relatively high flow rate. The oxidation procedure was concluded in 4 h.

3.5. Improved amendment distribution by foam delivery

The fluid distribution indicated by sediment wetting in the whole flow cell in the liquid infiltration and foam injection tests are illustrated in Fig. 6. In the infiltration test, the solution migrated vertically with little lateral spreading in the matrix (med-K) sediment. At 4-h infiltrating, liquid content accumulated at the bottom of the cell with sediment saturated while the liquid was distributed only about halfway across the sediment in majority of the cell. At 4-h injection in the foam delivery flow cell test, liquid distribution covered more than half of the sediments across the flow cell while no liquid had reached the bottom of the cell. In the infiltration test, liquid transport was controlled dominated by gravity therefore mainly migrate downward. In the foam injection test, liquid transport was controlled dominantly by the pressure gradient, which was in the horizontal direction. The injection pressure was applied via the foaming gas. Pressure in the injection well increased from zero to 2.5 psi in 2 h after foam injection was started, and stayed at 2.5 ± 0.2 psi until the completion of the test at 5.5 h. Foam delivery achieved more uniform liquid distribution in the sediment.

In a heterogeneous system, capillary force plays an important role in pulling more liquid into the low-K zones/lenses in solution infiltration. As shown in Fig. 6, solution migrated laterally twice the distance in low-K zones compare to that in the med-K matrix. It was also observed that lateral movement of water in low-K zone resulted in additional water saturation in the med-K sediment near to low-K zone. In the high-K zones/lenses, liquid distribution was limited and liquid transport fingering was clearly observed as shown in the close-up picture in Fig. 7a. The solution was infiltrating through the high-K zones in discontinuous pathways, leaving low residual water content. This would result in lower amendment concentration in the high-K zones [33].

In foam injection, the liquid flow and distribution in the high-K zones were enhanced as demonstrated in Fig. 7. In the high-K zone, the resistance to foam transport is less than in the matrix, resulted in enhanced foam flow. More flowing foam bubbles were observed in the high-K sediment than in the matrix sediment, while no flowing bubbles could be seen in the low-K layers/zones. The preferential flow of foam in high-K media is highly useful since it brings remedial amendment into the high-K layers/zones that will be largely “by-passed” in liquid infiltration.

In the foam delivery flow cell test, capillary suction also played a role in collecting liquid into the low-K zones. The wetting front in the low-K zones was ahead of that in the matrix (Fig. 6). Under unsaturated conditions, the bubbles at the foam front break and the foaming liquid accumulated in the sediment at the front [29]. The higher capillary suction in the low-K zones moves the accumulated liquid into these zones, resulted in a higher moisture content than that in the matrix sediment (Figs. 6 and 7b).

The moisture content and phosphate concentrations were measured in sediment samples collected from 3 horizontal zones in the matrix (Matrix-1, Matrix-2, Matrix-3; 30, 51, 84 cm from the top of the flow cell, respectively), 3 high-K layers (HKL-1, HKL-2, HKL-3; 35, 64, 100 cm from the top of the flow cell), and 3 low-K layers (LKL-1, LKL-2, LKL-3; 16, 47, 80 cm from the top of the flow cell). In each zone, multiple samples at different distance from the injection well were analyzed (Fig. 8).

Liquid was distributed across the flow system where the wetting front had reached. The low-K zones had the highest moisture content while the high-K zones had the lowest (Fig. 8, A1, A2, A3). Although foam flow rate was higher in the high-K layers, these layers did not retain higher water content due to the lower capillary force and the fluid displacement from pore space by foam flow [29]. Nevertheless, the moisture content in the high-K zones was still higher than that in the high-K zones obtained in the infiltration test [33].

The phosphate distribution clearly showed the advantage of foam injection in delivery amendment into high-K zones. PO_4 concentration higher than 100 mmol/L was obtained in the high-K layers (Fig. 8, B2), while in the infiltration test, PO_4 was nearly absent from the high-K zones due to very low water content reached those zones [33].

It should be noticed that the measured pore water PO_4 concentration in some locations was higher that the injected concentration. When the phosphate-laden foaming solution was injected into the flow system, PO_4 reacted with calcium and precipitated as apatite [33]. The precipitates accumulated on the sediment surface when the solution continued to flow through the porous medium, resulted in the extracted PO_4 concentration higher than the injected concentration.

The shape of the PO_4 concentration profile of a zone/layer did not match the moisture content profile of the same zone/layer (Fig. 8, A1 vs. B1, A2 vs. B2, A3 vs. B3). The moisture distribution was relatively uniform across the zones or layers, while the PO_4 concentrations were often higher near the injection well and dropped fast in locations away from the injection well. It is also worth to note that PO_4 concentrations in the low-K layers were much lower than that in the matrix and the high-K layers (Fig. 8, B1, B2, B3). The PO_4 distribution patterns were resulted from the retardation of PO_4 during the foam delivery. The retardation factor of PO_4 was 1.6–2.4 due to sorption to the sediments [33].

In foam-delivery of amendment into heterogeneous vadose zone systems, the distribution into med-K, high-K, and low-K zones was achieved. The more uniform amendment distribution obtained in foam-delivery is expected to benefit vadose remediation.

3.6. Enhanced lateral delivery in vadose zone sediments

The comparison of lateral delivery between liquid injection and foam injection is illustrated in Fig. 9. During liquid injection, the solution transported predominantly in the vertical direction. Lateral spreading of liquid completely stopped 15 min after injection. Liquid accumulated at the bottom of the sand box, saturating the porous medium. The maximum distance solution transported laterally was around 5 cm. In contrast, liquid transported in the sand box in both lateral and vertical directions during foam injection. Foam injection spreads liquids much faster at the lateral direction even though the liquid injection rate in the foam experiment was the same as in the liquid injection experiment. At the initial stage of injection, foam injection formed a half-circle “plume”. In 130 s injection, liquid had distributed through more than halfway (>15 cm) across the sand box, while very little liquid has accumulated at the bottom of the flow cell. In less than 5 min, foam reached the outlet at the center of the effluent side (photo not included in Fig. 9). Foam flow has a much strong potential to transport laterally.

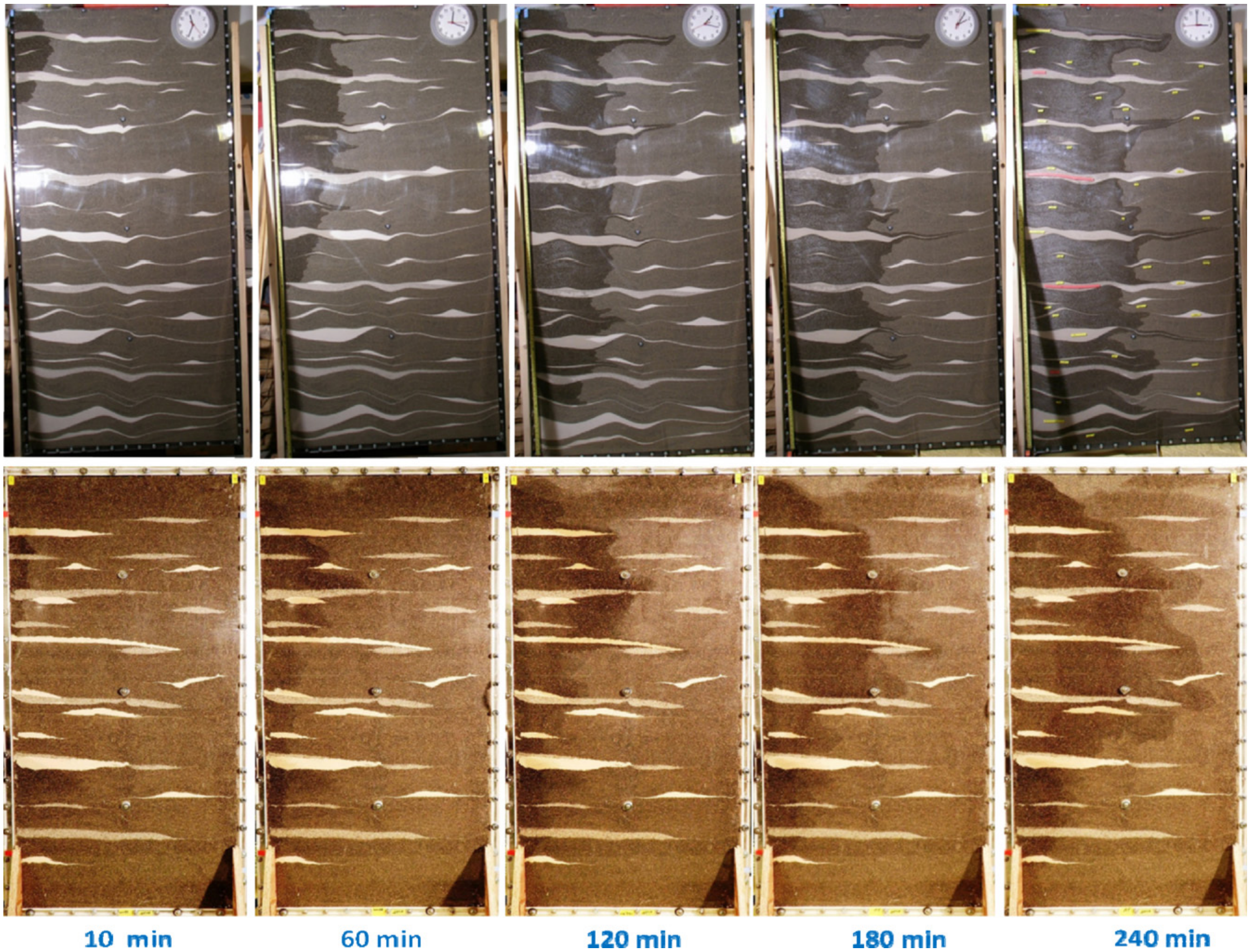

Fig. 6. Liquid distribution in heterogeneous vadose zone sediment systems: infiltration (top photos) vs. foam injection (bottom photos). Infiltration system was 8 ft (vertical) by 4 ft; foam injection system was 4 ft (vertical) by 2 ft.

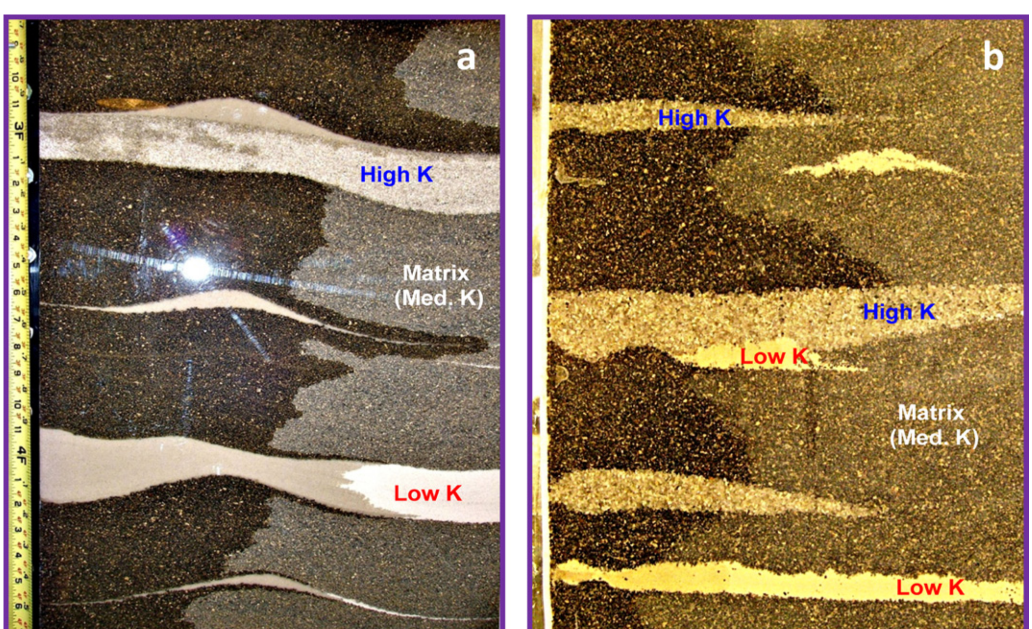

Fig. 7. Close-up view of liquid distribution in sediment matrix, high-K, and low-K layers and lenses during liquid infiltration (a) and foam injection (b).

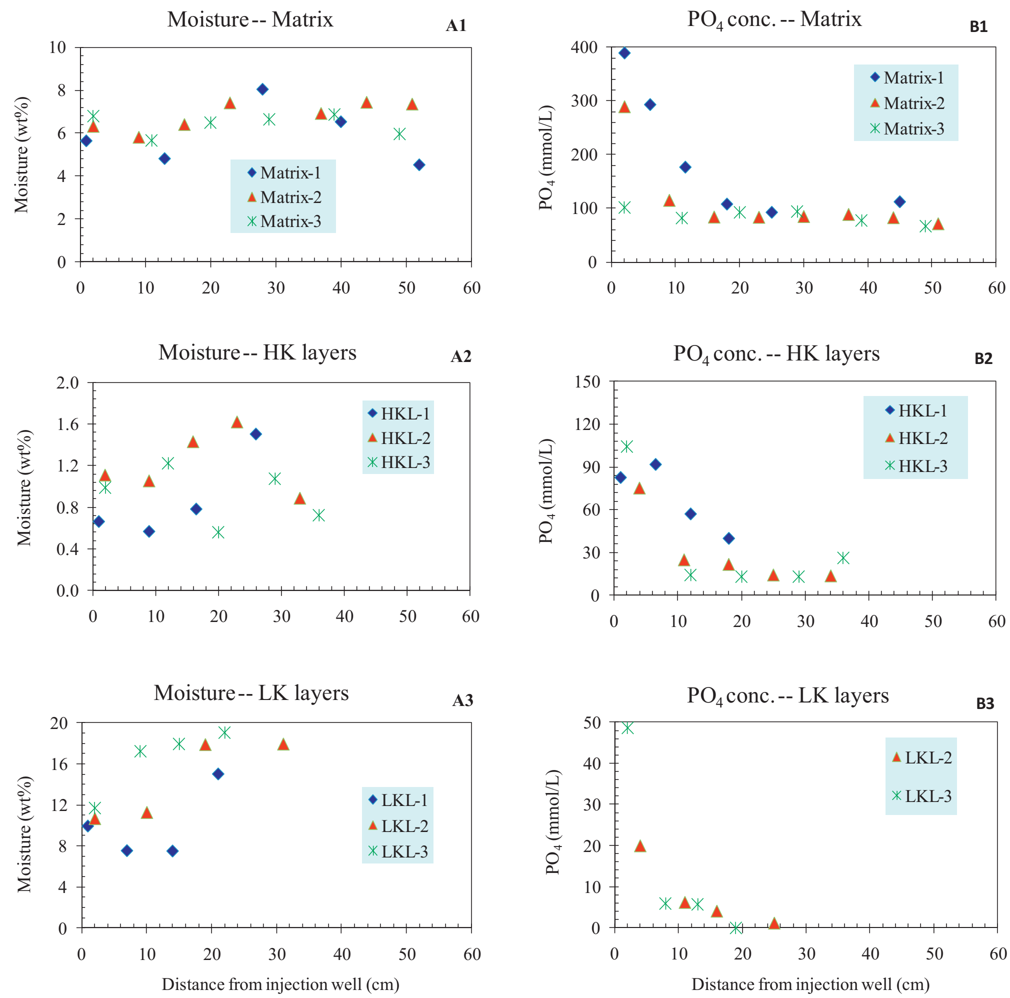

Fig. 8. Moisture and phosphate distribution in matrix, high-K, and low-K sediments in foam injection flow cell. A1, A2, A3: moisture in matrix (med-K) sediments, high-K layers, and low-K layers, respectively; B1, B2, B3: phosphate concentration in matrix (med-K) sediments, high-K layers, and low-K layers, respectively. LKL-1 was not included in B3 since no injected fluid reached this layer therefore no samples were taken.

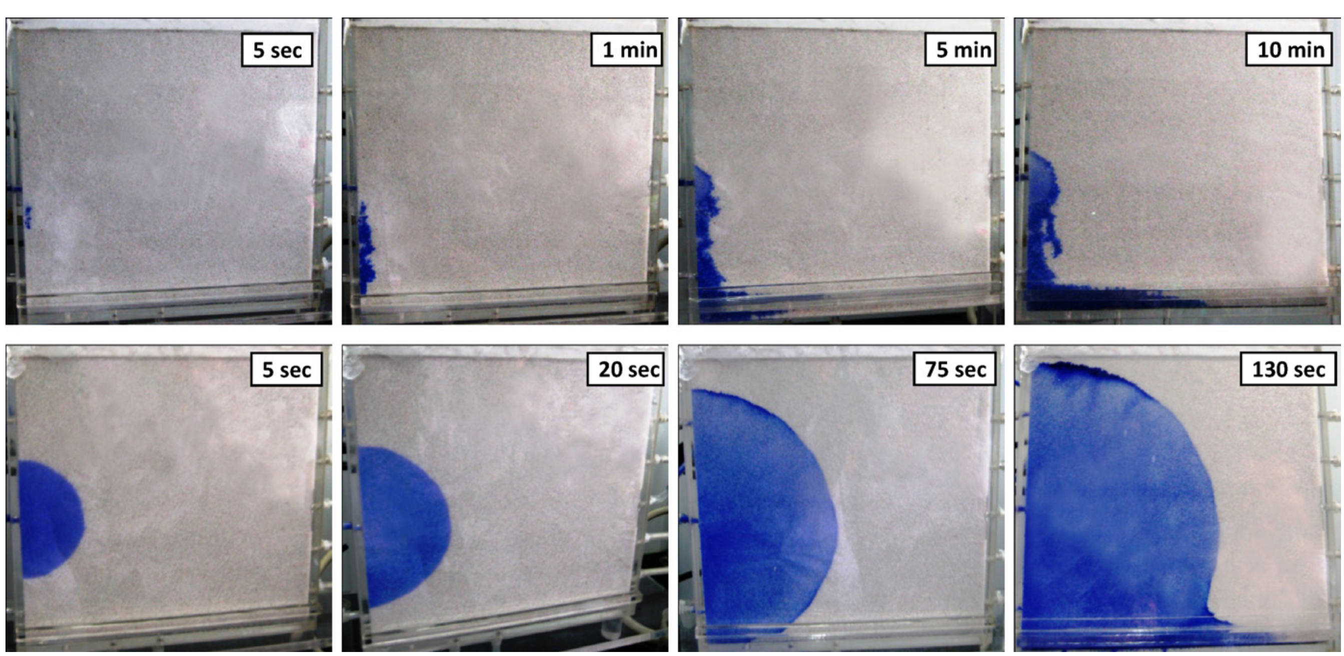

Fig. 9. Enhanced lateral delivery in foam injection. The top 4 photos show liquid injection, and the bottom 4 photos record the foam injection. In both injections, the liquid flow rate was the same. The dimensions of the flow cell was 30 cm × 30 cm × 3 cm.

For vadose zone *in situ* remediation, amendment delivered by liquid injection or infiltration will transported mostly in the vertical direction. In a vadose zone heterogeneous formation, the low-K zones accumulate liquids while the high-K zones are largely bypassed. Foam delivery not only improves the amendment delivery into the high-K zones therefore obtain a more uniform distribution; it also spreads the amendment further laterally so that the influence radius of a delivery well is increased.

4. Conclusions

Amendment delivery to the contamination zones is one of the most important steps in subsurface *in situ* remediation. Uniform distribution of amendments and reactants delivery into target zones is usually a challenge task. STF delivery and aqueous foam delivery was studied for delivery improvement to aquifer and vadose zone, respectively. STF delivery improved the weeping over a heterogeneous system by the injected liquid and enhanced the amendment distribution into the low-perm zones. It also prolonged the stay of amendment distributed into the low-perm zones. Attributed to the properties of aqueous foam flow in porous medium, foam delivery has shown to improve the uniformity of liquid distribution in heterogeneous vadose zone sediments. Especially, foam injection increased the amendment distribution to the high-permeability zones. Foam injection also demonstrated its high potential in spreading liquid laterally. Owing to the low water content in foam, foam delivery was able to mitigate the mobilization of highly mobile contaminants from the sediment. All these aspects achieved by the STF delivery and foam delivery are beneficial to the remedial processes and will improve the subsurface remediation.

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