

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/250129711>

Foam Delivery of Calcium Polysulfide to Vadose Zone for Chromium-VI Immobilization: A Laboratory Evaluation

Article in *Vadose Zone Journal* · November 2009

DOI: 10.2136/vzj2008.0124

CITATIONS

29

READS

223

5 authors, including:



Lirong Zhong

Pacific Northwest National Laboratory

96 PUBLICATIONS 739 CITATIONS

[SEE PROFILE](#)



Nikolla P Qafoku

Pacific Northwest National Laboratory

128 PUBLICATIONS 1,725 CITATIONS

[SEE PROFILE](#)



P. Evan Dresel

Victoria Department of Economic Development Jobs Transport & Resources

94 PUBLICATIONS 593 CITATIONS

[SEE PROFILE](#)



Zhuanfang Fred Zhang

Pacific Northwest National Laboratory

87 PUBLICATIONS 791 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



Catchment Scale Impacts of Land Use [View project](#)



Hanford 618 Burial Ground [View project](#)

Foam Delivery of Calcium Polysulfide to the Vadose Zone for Chromium(VI) Immobilization: A Laboratory Evaluation

Lirong Zhong,* Nikolla P. Qafoku, James E. Szecsody, P. Evan Dresel, and Zhuanfang F. Zhang

The delivery of calcium polysulfide (CPS) to the vadose zone using foam and the immobilization of Cr(VI) via reduction by the foam-delivered CPS was studied in a series of batch and column experiments. 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 a 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. Foams containing CPS with high reducing potential were prepared based on the batch tests. Sediment reduction by foam-delivered CPS was observed in the columns. Massive mobilization of Cr(VI) from sediments occurred when CPS was delivered in aqueous solution. The Cr(VI) mobilization was minimized in column tests when CPS was delivered by foams, resulting in significant Cr(VI) in situ immobilization. These results demonstrated for the first time that foam injection can be successfully used for CPS delivery to the vadose zone and that foam-delivered CPS can be applied for Cr(VI) immobilization in contaminated vadose zones.

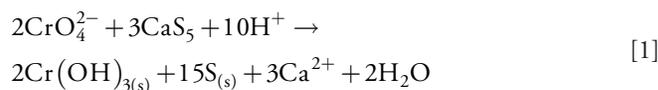
ABBREVIATIONS: CPS, calcium polysulfide; PV, pore volume; XRD, x-ray diffraction.

CHROMIUM exists mainly in two oxidation states in the environment: trivalent [Cr(III)] and hexavalent [Cr(VI)] chromium. Chromium(III) is relatively immobile and nontoxic in moderate doses. In contrast, Cr(VI) is severely toxic to plants and animals (Paschin et al., 1983; Abbasi and Soni, 1984) and is classified as a carcinogen (Ono, 1988). A number of aquatic species are sensitive to Cr(VI) exposure, including endangered fall chinook salmon (*Oncorhynchus tshawytscha*) (Olson, 1960; Dauble et al., 2003). Chromium(VI) is highly mobile in subsurfaces at circumneutral pH (Qafoku et al., 2003, 2007), thus it is easily transported with groundwater toward nearby rivers and lakes.

Chromium(VI) is one of the major contaminants in the U.S. Department of Energy's Hanford Site located along the Columbia River north of Richland, WA. The country's primary Pu production facility at the Hanford Site was operative from 1944 through

1990 (Gerber, 1996). Chromium(VI) was used as a corrosion inhibitor in the reactor cooling water, with a Cr(VI) concentration of 0.7 mg L⁻¹ (Foster, 1957). Chromium(VI) contamination was produced through spills, pipe leaks, inevitable discharges to the surface, or discard to cribs. Chromium(VI) in the vadose zone is the source of Hanford groundwater contamination. Vadose zone Cr(VI) remediation is a critical step to stop continuing groundwater contamination from the source in the vadose zone and to prevent Cr(VI) migration to the Columbia River.

Calcium polysulfide (CaS₂) may react with highly soluble metals to form less soluble and nontoxic sulfides and hydroxides, and has been used for the remediation of Cr(VI)-contaminated groundwater (Jacobs, 2001) and for Cr(VI) immobilization in chromite ore processing residues (Graham et al., 2006; Wazne et al., 2007; Moon et al., 2008). Calcium polysulfide reduces Cr(VI) to Cr(III), which is then precipitated readily as chromium hydroxide or iron chromium hydroxide [Cr_(x)Fe_(1-x)(OH)₃] with a solubility orders of magnitude lower than that of pure chromium hydroxide. The suggested redox equilibrium reaction is (Graham et al., 2006)



Other electron acceptors that might be present in the sediments, such as sorbed Fe(III) and Fe(III)-bearing minerals, may react with CPS, establishing a reduced reactive barrier within the sediment matrix. This barrier enhances the reduction and immobilization of Cr(VI).

L. Zhong, J.E. Szecsody, P.E. Dresel, and Z.F. Zhang, Energy and Environment Directorate, Pacific Northwest National Lab., P.O. Box 999, Richland, WA 99354; and N.P. Qafoku, Fundamental and Computational Sciences Directorate, Pacific Northwest National Lab., P.O. Box 999, Richland, WA 99354. *Corresponding author (lirong.zhong@pnl.gov).

Vadose Zone J. 8:976–985

doi:10.2136/vzj2008.0124

Received 29 Aug. 2008.

Published online 13 Sept. 2009.

© Soil Science Society of America

677 S. Segoe Rd. Madison, WI 53711 USA

All rights reserved. No part of this periodical may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher.

Injection of an aqueous CPS solution into the vadose zone for Cr(VI) immobilization has the potential to remediate Cr(VI) contamination. How to evenly distribute CPS solution to the vadose zone is a challenge, however, because the flow of injected liquid, which is dominantly under the control of gravity, may preferentially percolate through highly permeable pathways and bypass lower permeability zones that may contain the majority of the contamination. Furthermore, Cr(VI) sorbed to vadose zone sediments may be easily mobilized by the flushing solutions (Qafoku et al., 2003, 2007; Hanson et al., 1993). This mobilization can create a Cr(VI) moving front during the CPS solution injection, spreading contamination to the underlying aquifer.

The intrinsic challenges of preferential flow and the spreading of contamination associated with the water delivery of remedial amendments to the vadose zone can be potentially overcome by foam delivery. In contrast to the flow of a water-based solution, foam flow in the vadose zone is not dominated by gravity but can be directed by a pressure gradient. The use of foam for delivery may 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). Foam is a shear-thinning non-Newtonian fluid that enables more uniform sweeping throughout a heterogeneous system when forced through the system (Kovscek and Bertin, 2003). It was reported, from laboratory-scale testing, that the injection of a surfactant–foam mixture enhances the flooding efficiency of surfactant flushing in heterogeneous porous medium systems, resulting in better sweeping efficiency throughout the contamination zone and higher contaminant removal (Enzien et al., 1995; Jeong et al., 2000; Jeong and Corapcioglu, 2003). The permeability contrast between the zones swept by the foam was not reported. Blockage of high-permeability layers to gas flow has been reported on a laboratory system with a permeability contrast of 70:1 (Bertin et al., 1998). There should exist a limitation, however, for foam-enhanced sweeping although it is not yet available in the literature. Data on the enhanced sweeping efficiency at the field scale has not yet been reported.

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 with time. Foam half-life is the time taken by the foam to reach half of its initial volume. The stability of foams is determined by the property of the foaming agent, such as a surfactant (Zhong et al., 1998), and other additions such as nonaqueous liquid and a dispersed solid-particle phase within the foaming liquid mixture (Hudales and Stein, 1990). The application of foams in environmental remediation has been evaluated for nonaqueous phase liquids removal (Hirasaki et al., 1997; Rothmel et al., 1998; Wang and Mulligan, 2004a; Mulligan and Eftekhari, 2003; Peters et al., 1994; Enzien et al., 1995; Jeong et al., 2000; Huang and Chang, 2000) and heavy metal cleanup (Mulligan and Wang, 2006; Wang and Mulligan, 2004b) from the vadose zone. In these studies, however, the surfactant–foam itself was used as the reactant but not as a delivery mechanism for other remedial amendments.

In our study, CPS was incorporated into the surfactant solutions as a remedial amendment during foam generation; the foam was then injected to packed sediments under vadose zone conditions for amendment delivery. A suitable CPS–surfactant

combination was first formulated, an appropriate foam quality and stability was identified, and an optimum foam injection protocol was developed. A series of column experiments were conducted to test the foam delivery of CPS to sediments under conditions similar to a field vadose zone to determine the rate and extent of Cr(VI) immobilization using this novel technology and to compare the remediation results with those obtained from water-based CPS delivery.

Materials and Methods

Batch Tests

The objectives of the batch tests were to identify a surfactant–CPS mixture that can be used to generate foams suitable for CPS delivery and to investigate the influence of surfactant concentration, CPS concentration, and foam quality on foam stability. A high-performance liquid chromatography pump was used to deliver the surfactant–CPS solution (Fig. 1). A gas flow controller was set up in the air–N₂ line to control the gas flow rate. The flow of surfactant–CPS solution and the flow of air or N₂ were merged and directed to a vertically mounted graduated glass column with 2.54-cm (1.0-inch) i.d. A porous plate with a characteristic pore size of 20 μm was placed at the bottom of the glass column to distribute the flow.

The surfactant sodium POE(3) laureth sulfate, or sodium lauryl ether sulfate, was tested in this study. The surfactant was produced by the Stepan Co., Northfield, IL, and received as STEOL CS-330 (3 EO). The CS-330 contains 30% sodium lauryl ether sulfate with the chemical formula of CH₃(CH₂)₁₀CH₂(OCH₂CH₂)₃OSO₃Na. It is a biodegradable anionic surfactant with a critical micelle concentration at 4.19 mmol L⁻¹ (0.18% w/w) (Rothmel et al., 1998) and a surface tension of 32.2 mN cm⁻¹. The reductant, CPS (29% w/w) was obtained from the VGS Co., Bloomington, MN. This reagent was produced for contaminated soil remediation or heavy metal removal from wastewater. We consider it representative of relatively inexpensive, commercially available, bulk chemical CPS.

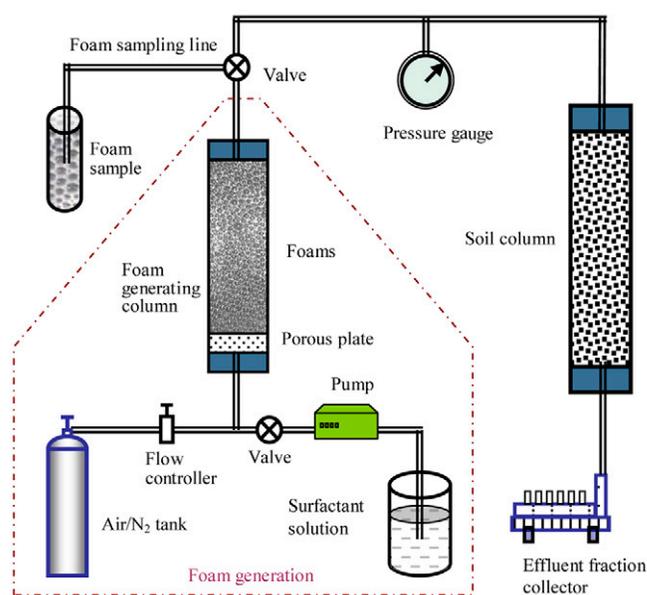


FIG. 1. Schematic of foam generation and foam flood column experiment setup.

The gas flow rate was set at 10.0 mL min⁻¹ for foam generation. The flow rate of the surfactant–CPS solution was set at a desired value so that a predetermined foam quality could be achieved. The air or N₂ flow and surfactant–CPS flow were started at the same time and were merged in a glass column where foam was generated (Fig. 1). The flows were stopped when the height of the foam in the graduated glass column reached 10 cm, and the changes in foam height, bubble size, and texture with time were monitored and recorded. The reducing potential (Eh) of the surfactant–CPS solutions and foams were measured.

Column Experiments

The objectives of the column tests were: (i) to study the pressure drop across the column during foam injection and to investigate the influence of the foam flow rate and foam quality on the injection pressure; (ii) to investigate the surfactant–CPS solution uptake in the sediment during foam flooding; (iii) to study the immobilization of Cr(VI) by foam-delivered CPS; and (iv) to demonstrate the Cr(VI) mobilization mitigation in the columns flushed by the foam-delivered CPS vs. the columns flushed by water-delivered CPS. A total of 11 bench-scale column tests in three sets were conducted (Table 1). Set I tests were performed with uncontaminated Hanford sediment to study the CPS-containing foam transport in the packed sediments and to evaluate the reduction capability of foam-delivered CPS. Set II tests were designed to investigate Cr(VI) mobilization from vadose zone sediments during water flood, or during flushing with CPS solutions, i.e., water-delivered CPS. Set III tests were performed to demonstrate that the massive mobilization of Cr(VI) at the reaction front from water-delivered CPS can be minimized and that Cr(VI) in situ immobilization can be achieved when CPS is delivered by foam. A Cr(VI)-contaminated Hanford sediment was used in the Set II and III tests.

In the Set I tests, the generated foams were delivered to a vertically mounted 30.5-cm (12.0-inch)-long and 2.54-cm (1.0-inch) i.d. column through a 0.64-cm (0.25-inch) i.d. tubing and flushed through the packed uncontaminated sediments 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 flushed through the columns were determined based on the volumes of foam under atmospheric pressure and room temperature. During foam injection, the wetting front in the column was monitored and the length of the sediment column wetted by foam-delivered liquid, the “foam-wetted length,” was measured. The injection pressure was recorded with the column effluent end open to the atmosphere. The column was disconnected from the flow system and weighed periodically to determine the liquid uptake in the sediment.

For the columns flushed with synthetic groundwater and CPS solutions (Set II tests), three polyvinyl chloride columns (2.4-cm i.d., 6.0 cm long) were uniformly dry packed with Cr-contaminated sediment. Porous plates were used at the top and bottom of each column to distribute the leaching solution at the inflow end and to collect fines (which were found to be minimal) at the column exit. High-performance liquid chromatography pumps were used to control the advective flow and yield preselected fluid residence times. Column effluent was collected in a fraction collector. The small columns were used to accommodate the limited Cr-contaminated sediment available.

For Set III experiments, the foam delivery system used in the Set I tests and the sediment used in the Set II tests were utilized. The CPS-containing foams were directed to the top of the column. When a reductive barrier was needed, a section (7 cm long) of uncontaminated sediment was packed on the bottom of the column and the foam flow was first directed to the clean sediment from the bottom of the column to establish the barrier. Foams were then directed to the top of the column for the Cr(VI) mobilization–immobilization tests. When injected liquid through foam delivery reached 0.5 PV of liquid, foam injection was switched to synthetic groundwater injection to leach the column. A fraction collector was used to collect the column effluent. The effluent liquid samples were analyzed for Cr(VI) concentration and measured for pH and Eh values immediately after collection.

TABLE 1. Summary of the column tests with calcium polysulfide (CPS) delivered in foam or water.

Test name	Description	Packed sediment weight g	Pore volume mL	Porosity	Gas type	Flow rate mL min ⁻¹
Set I						
Col-CS-I	foam flow, clean sediment	305.55	49.80	0.31	air	8.08
Col-CS-II	foam flow, clean sediment	314.22	46.63	0.29	N ₂	2.53
Col-CS-III	foam flow, clean sediment	306.89	49.31	0.31	N ₂	5.05
Col-CS-IV	foam flow, clean sediment	309.04	48.52	0.30	N ₂	10.10
Set II						
Col-SGW	synthetic groundwater flush, Cr-contaminated sediment	37.17	11.86	0.47	NA [†]	0.343
Col-CPS-W-I	0.5% CPS–water delivery, Cr-contaminated sediment	37.37	10.14	0.43	NA	0.0939
Col-CPS-W-II	5.0% CPS–water delivery, Cr-contaminated sediment	37.43	9.82	0.43	NA	0.0897
Set III						
Col-CPS-F-I	5.0% CPS–foam delivery, Cr-contaminated sediment	275.95	62.65	0.39	N ₂	2.53
Col-CPS-F-Ia	repeat of Test Col-CPS-F-I	267.74	65.73	0.41	N ₂	2.53
Col-CPS-F-II	5.0% CPS–foam delivery, Cr-contaminated sediment, reduced barrier established	280.44	60.56	0.38	N ₂	2.53
Col-CPS-F-III	10.0% CPS–foam delivery, Cr-contaminated sediment, reduced barrier established	280.33	60.60	0.38	N ₂	2.53

† NA = not applicable.

An intermediate-scale column experiment was conducted to test the foam delivery distance. The column was 6.10 m (20 feet) long with 1.5-cm i.d. and was packed with the uncontaminated Hanford sediments. The sediment pack had a porosity of 32.7%. Foam of 99% quality (1% v/v liquid) was injected into the column from one end at a flow rate of 2.53 mL min⁻¹, and air was extracted from the other end of column at the same flow rate. The foam delivery distance, i.e., the foam transport length in the column, and the injection pressure were monitored. Sediment samples were taken along the column after foam flow for water content measurement.

Sediment Characterization

The uncontaminated sediment was collected from an excavation in the Hanford Site 100-D Area at approximately 1 m below the ground surface and air dried. The moisture content was 0.40% (w/w). Moisture of 1.0% (w/w) water content (with synthetic groundwater) was added before packing. The Cr(VI)-contaminated sediment was collected from a freshly contaminated surface area in the Hanford Site 100-B Area. The total Cr(VI) concentration in the sediment, determined by alkaline digestion (USEPA, 1996), was 1042.3 mg kg⁻¹. Total Cr was not determined, but x-ray fluorescence mapping indicated only traces of Cr(III) in this sediment. The sediment had a moisture content of 3.5% (w/w). Both the clean and contaminated sediments were sieved to remove grains >2 mm.

Fraction-Size Separation

The <2-mm size fraction from the contaminated sediment was air dried overnight at room temperature. A 53- μ m sieve was used to separate the <53- μ m (silt and clay) from >53- μ m (sand) fractions. The sediment materials were placed on top of the sieve and shaken by hand for 15 min. To prevent inhalation of particles contaminated with Cr(VI), the sieving process was performed in a fume hood.

Meso-Scale (Mineralogical) Characterization

The silt plus clay fraction was characterized by x-ray diffraction (XRD). The sample was analyzed using a Scintag Pad V XRD (Scintag Inc., Madison, WI) equipped with a Peltier thermoelectrically cooled detector and a copper x-ray tube. The diffractometer was operated at 45 kV and 40 mA. The diffractogram was obtained from 2 to 65° 2 θ using a step-scan increment of 0.2° and a dwell time of 2 s. Scans were collected electronically and processed using JADE XRD pattern-processing software (Materials Data Inc., Livermore, CA). Minerals identification was based on comparison of the measured XRD patterns to those of mineral powder diffraction files published by the International Center for Diffraction Data (Newtown Square, PA).

Sediment Laboratory Analysis

The Cr(VI) analyses were performed using USEPA (1992) ultraviolet-visible spectrophotometry after centrifugation, extraction into water at a water/soil ratio of 3:1, or through USEPA (1996) alkaline digestion. Centrifugation to extract soil moisture was performed at 10,000 or 16,000 rpm for 22.5 to 27 h. Moisture contents were determined gravimetrically. Soil moisture was also extracted by high-speed centrifuge and the aqueous phase was analyzed for Cr(VI).

Analytical Methods

The diphenylcarbohydrazide colorimetric method was used for Cr concentration determination (Mocák et al., 1985; American Public Health Association, 1989). Chromium(VI) reacts with 1-5-diphenylcarbohydrazide reagent to yield a complex with an absorption peak at 540 nm. This method has a Cr(VI) detection limit of 0.10 μ mol L⁻¹. The redox potentials of the foaming solution, the foam, and the effluent were measured with a Pt Eh electrode. The Eh sensor was tested against a ZoBell's standard solution before and after each set of measurements.

Results and Discussion

Sediment Characterization

The XRD analyses indicated that the mineralogy of the <53 μ m fraction from the contaminated sediment was dominated by quartz, nontronite, saponite, vermiculite, montmorillonite, muscovite, and clinocllore. Results from Cr analyses confirmed that the sediment had appreciable amount of Cr(VI) contamination, i.e., 810.4 and 1042.3 mg kg⁻¹ water- and alkaline-extractable Cr(VI), respectively. The pore-water analyses indicated that SO₄ (2218 mg L⁻¹), NO₃ (364 mg L⁻¹), and Cl⁻ (226 mg L⁻¹) were present. In addition, appreciable amounts of Ca, Mg, and Na were also present in the pore water.

Characteristics of Foaming Solution and Calcium Polysulfide Foams

Redox Potential

The interaction between the surfactant and CPS may change the properties of these chemicals. There was a concern whether the CPS could retain its reducing capacity in the foaming solutions. The measured Eh of a series of CS-330 and CPS solutions with comparison to the Eh of a CPS-water solution (Fig. 2) indicated that only a slight decrease on the solutions' Eh was observed when the surfactant was added to the solution (Fig. 2a vs. Fig. 2b, 2c, and 2d), and that the influence of surfactant concentration was minor within the 0.5% (w/w) (12.5 mmol L⁻¹) to 1.5% (w/w) (37.5 mmol L⁻¹) tested range (Fig. 2b, 2c, and 2d). 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 system shown in Fig. 1, 90% or more of the delivered gas was captured in the generated foams.

The Eh of the foams generated from 1% (w/w) (25 mmol L⁻¹) CS-330 and 5% CPS (Eh = -516 mV) at 99% foam quality was -496 mV, and the Eh of the liquid drained from this foam in an open-atmosphere environment was -502 mV. During the Eh measurement of the foams, the reading was slightly fluctuating due to the connection between the 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 in the Eh from the foaming solution to the foam-drained solution was probably due to the interaction between the foam and O₂ in the air during the bubble breakdown.

Foam Texture and Aging

The foam bubble size and texture changed during aging, as illustrated in Fig. 3. The foam bubbles were in "ball foam" shape with diameters around 2 mm when first generated. During aging

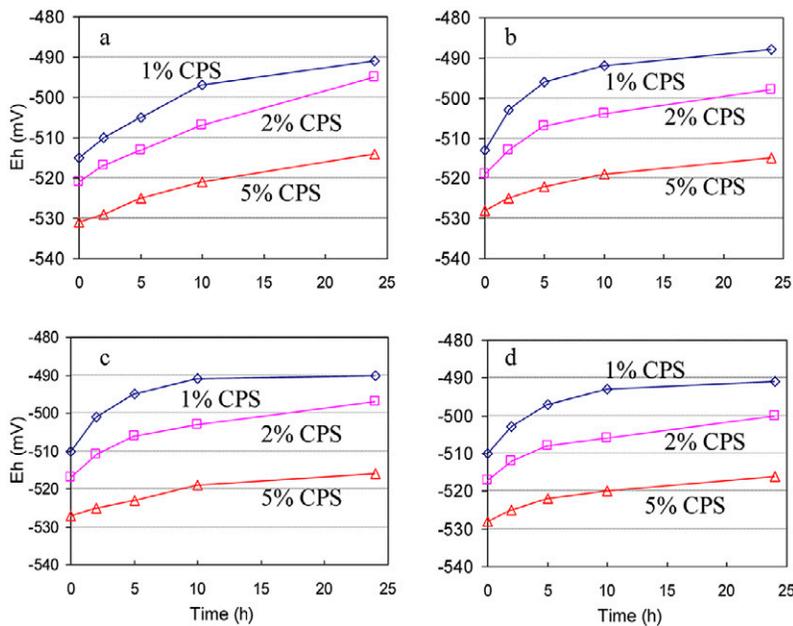


FIG. 2. Redox potential comparison between calcium polysulfide (CPS) solutions with and without CS-330 surfactant: (a) in water (0% CS-330), and in (b) 0.5%, (c) 1.0%, and (d) 1.5% CS-330 surfactant solution.

in the foam generation column (Fig. 1), 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 size increased from ~ 2 to ~ 10 mm due to the gas-diffusion-caused foam coalescence (Bikerman, 1973, p. 33–64; Chambers and Radke, 1991; Schramm and Wassmuth, 1994). Figure 3 is an example of foam bubble size and texture changes obtained from foam with 99% initial quality.

Foam Stability

For the purpose of vadose zone remediation, foam will be generated ex situ and then injected into the subsurface. Foams should be stable enough for injection. Foam stability also influences the 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, a function of the foam quality, surfactant concentration, and CPS concentration.

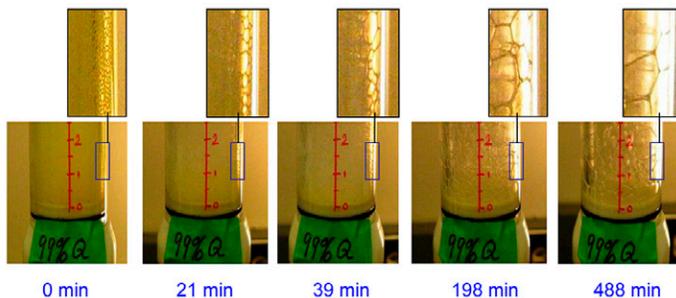


FIG. 3. Bubble size and texture of foams with 99% quality during aging.

The stability of all foams decreased with increasing quality (Fig. 4). In foams of higher quality, the bubble films were thinner than those in foams of lower quality. With the gravity drainage of the foaming liquid, the higher quality foams ruptured sooner. For this reason, the foam stability increased when the quality decreased. There is a quality threshold point, however, below which the foam stability decreases. When the foam quality is below this threshold, the foam is too heavy for the lamella to support and it therefore collapses quickly. Wang and Mulligan (2004a) reported that the foam generated using a biosurfactant was less stable at 90% quality than at 95% quality. The threshold value for the CS-330 surfactant–CPS foam was not determined in this work.

The influence of surfactant concentration on foam stability was insignificant. In all the qualities tested, the stability of foams generated from 1% (w/w) (25 mmol L⁻¹) CS-330 solution was slightly more stable than the foams generated from the 0.5% (w/w) (12.5 mmol L⁻¹) CS-330 solution, which was slightly more stable than that of foams generated from the 1.5% (w/w) (37.5 mmol L⁻¹) CS-330 solution. Generally, foam stability increases when the surfactant concentration in the foaming solution increases up to 1.5% (Wang and Mulligan, 2004b). No clear correlation was seen in this study, probably due to the fact that 0.5% (w/w) (12.5 mmol L⁻¹) was out of the concentration range in which the concentration influence on foam stability can be readily observed.

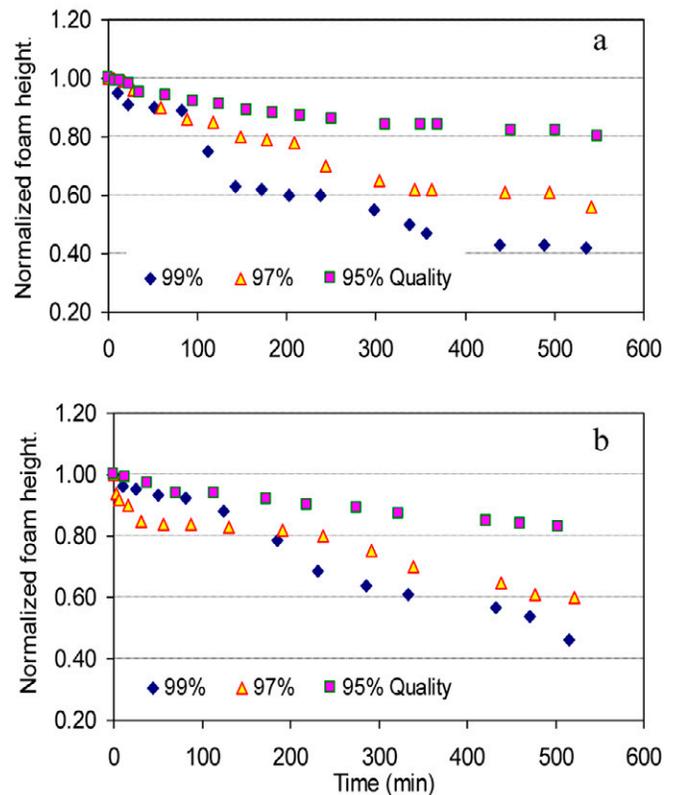


FIG. 4. Foam stability: effects of foam quality. Foam was generated using solutions with 2% calcium polysulfide (CPS) and (a) 0.5% and (b) 1% CS-330 surfactant solution.

The CPS concentration significantly changed the foam stability. The normalized height of foams generated from 1.5% (w/w) (37.5 mmol L⁻¹) CS-330 surfactant solutions with 1.0, 2.0, and 5.0% (w/w) CPS is shown in Fig. 5. The foam stability decreased with increasing CPS concentration. When the foam quality increased, the influence of CPS concentration became more significant. The CPS did not react with the surfactant in such a way as to change its amphiphilic property; therefore, it did not destroy the foamability of the CPS–surfactant mixture. The addition of CPS to the surfactant solution did, however, slightly change the property of the foam solution. The CPS might have increased the surface tension, decreased surface elasticity, decreased surface viscosity, or decreased surface potential. One of the changes or combination of changes to a foaming solution destabilized the foams generated from that solution (Schramm and Wassmuth, 1994), as was observed here.

Foam Transport in Packed Sediments

The foam bubble sizes were >2 mm in the tubing before the bubbles were driven into the sediment column. Flow of foam bubbles with dimensions <2 mm was observed in the sediment column, while the effluent foam had bubbles >2 mm, indicating that foam breakdown and regeneration occurred during transport. This behavior was reported by Holm (1968). A plot on the typical relationship among the injection pressure, foam-wetted length, liquid uptake, and PV of foam from Col-CS-I is shown in Fig. 6.

Pressure Drop

The flow rate and foam quality both had significant influence on the injection pressure drop (Fig. 7). When the quality of injected foam decreased, the pressure drop increased. A near-linear relationship between the foam quality and pressure drop was observed. At higher foam quality, the impact of the flow rate was less than when the foam quality was lower. At a higher flow rate, the pressure drop was more sensitive to the foam quality change.

At higher foam quality, the foam stability was lower (Fig. 4) and the bubbles had thinner films that 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. The influence of surfactant concentration on the foam stability was minor. Therefore it is predicted that the surfactant concentration will not affect the foam injection pressure significantly, as was reported by Wang and Mulligan (2004a).

Foam flow rate and quality are the two major factors that determine the injection pressure. To keep the injection pressure low, high foam quality and a relatively low flow rate are desirable. When the injection pressure is limited due to the foam delivery setup 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, when foam with 99% quality was injected at a rate of 2.53 mL min⁻¹, or 0.92 m h⁻¹ pore velocity, into the sediment, the pressure drop was around 49.9 kPa m⁻¹ (2.2 psi foot⁻¹).

If the injection pressure is scaled up to a 9.1-m (30-foot)-long column, the injection pressure will be about 456 kPa (66 psi). This observation from the bench-scale tests implies that the foam injection is practical when scaled up to field remediation. In the intermediate-scale long column test, the foam delivery distance reached 5.4 m (17.7 feet) with a maximum injection pressure of

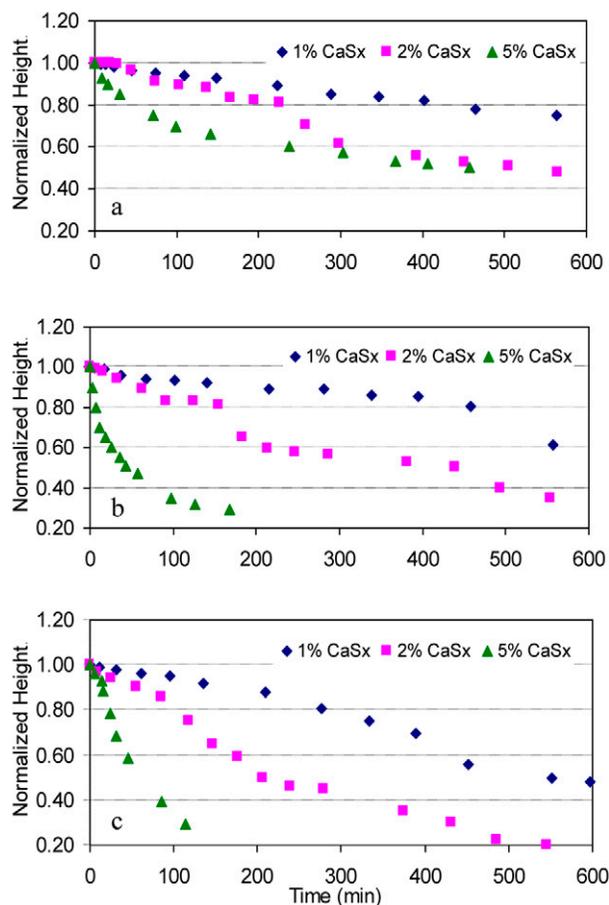


FIG. 5. Foam stability: effects of calcium polysulfide (CaSx) concentration. The solutions contained 1.5% CS-330 (37.5 mmol L⁻¹) surfactant with a foam quality of (a) 95%, (b) 97%, and (c) 99%.

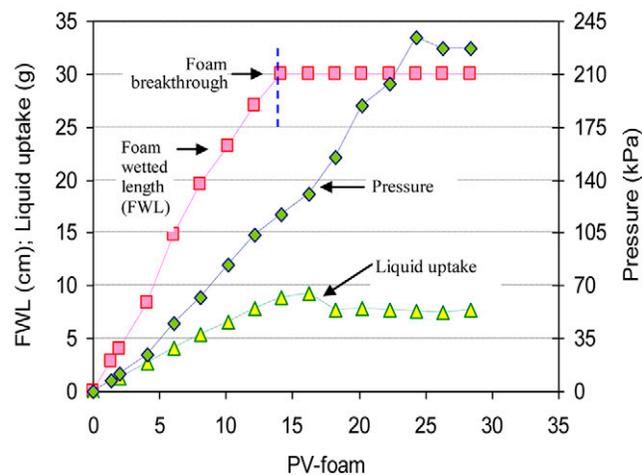


FIG. 6. Injection pressure, foam-wetted length (FWL), and liquid uptake during a typical foam flushing column test (Col-CS-I); PV is pore volume.

366.2 kPa (53 psi) at a foam flow rate of 2.53 mL min⁻¹, or 2.63 m h⁻¹ pore velocity. It is worthwhile to mention that the foam flow rate was higher than that commonly used in field applications. At a lower foam injection rate, the injection pressure will be lower (Fig. 7). Therefore, it is reasonable to state that foam delivery is feasible at the field scale. It should be pointed out

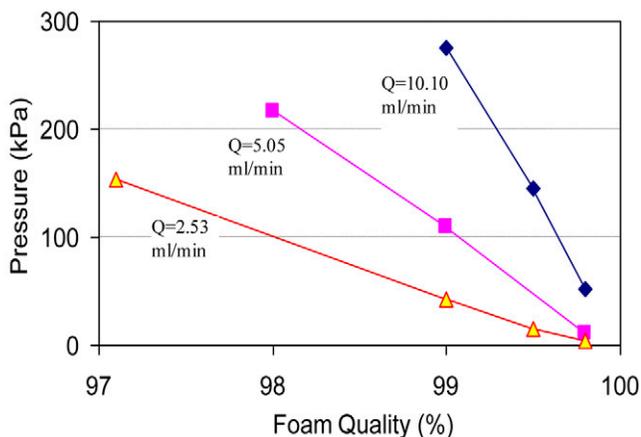


FIG. 7. Foam flow rate (Q) and foam quality effect on the pressure drop across the sediment column.

that during field deployment, foam propagates in three dimensions. The pressure buildup in three-dimensional foam transport will probably be less than that in a one-dimensional column test, as was observed by Tanzil (2001). Additional two- and three-dimensional scale-up tests (including radial flow geometry) and numerical simulation studies are needed and planned before this foam-delivery technology can be deployed in the field.

We also observed an increase in the injection pressure after foam breakthrough (Fig. 6). More bubbles could be trapped in the pores after breakthrough, which probably was the cause of the increase in injection pressure (Kovscek and Radke, 1994; Bikerman, 1973, p. 184–213).

Liquid Uptake

When foam flows through the sediment column, the bubbles break and the liquid phase is sorbed to the sediment grains while the gas phase flows through the pore space. The liquid uptake by the 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. 6, a linear relationship between the foam-wetted length and foam PV was observed, meaning that 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. In the intermediate-scale column test, the liquid content of 20% was relatively uniform across the 5.4 m of foam-flushed sediment length. This observation verifies a uniform liquid distribution. The uptake reached a steady and usually the maximum value at a few PVs after foam breakthrough (Fig. 6). 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 at 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 (Chowdiah et al., 1998).

Since the amount of remedial amendment delivered to the vadose zone is proportional to the liquid volume taken up by the sediment, this observation implies that a large variation in the remedial amendment amount can be added to the sediment by manipulating the foam flow rate, foam quality, and remedial amendment aqueous concentration. The required amendment amount will be determined by the concentration of the target contaminant and the consumption of amendment by the reactive components in the sediment.

Sediment Reduction and Chromium(VI) Immobilization

Sediment Reduction

With N_2 -generated CPS foams flowing through the sediment column, the sediment was gradually reduced, as indicated by a color change from brown to green, a typical color observed when Fe^{2+} is present. When more foam was flushed through the column, the sediment color changed from light green to dark green, as shown in Fig. 8. The reduction of the sediment was further proven by the changes in the Eh of the effluent liquid (see below). The effluent solution had a positive Eh at breakthrough, indicating that the Eh of the fluid was consumed by the sediment. When more CPS foam was pushed through the sediment, the Eh value of the effluent gradually decreased and turned into a reducing state. In a test with air-generated foams forced through the column (Col-CS-I), no sediment reduction was observed because the reducing capacity of the foam-delivered CPS was consumed by the O_2 in the air.

Chromium(VI) Immobilization

Significant Cr(VI) mobilization caused by water-delivered CPS flushing occurred (Fig. 9). When synthetic groundwater was used to flush the column (Col-SGW), >98% of the total water-leachable Cr(VI) mass was mobilized out of the sediment at 1 PV. When 0.5 and 5% CPS solutions were used in the column flood (Col-CPS-W-I and Col-CPS-W-II, respectively), 90 and 77%, respectively, of the total Cr(VI) mass was mobilized when 1



Time (min)	0	109	171	229	320	452
PV-foam	0	11.16	17.51	23.45	32.77	46.29
PV-liquid	0	0.11	0.18	0.23	0.33	0.46

FIG. 8. Column of Hanford sediment reduction by foam-delivered CPS: time series (Col-CS-III). Listed under the columns are the times when pictures were taken and the pore volumes (PV) of foam and liquid flushed through the column.

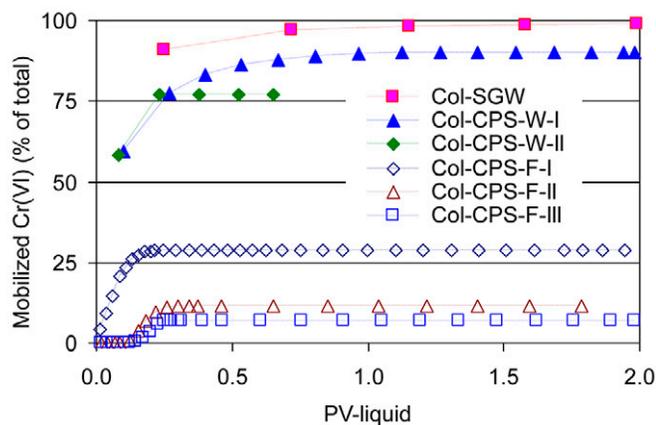


FIG. 9. Accumulative mass of mobilized Cr(VI) in effluent from column tests: a comparison of calcium polysulfide (CPS)-containing foam flow, CPS solution flush, and synthetic groundwater (SGW) flush. See Table 1 for test descriptions; PV is pore volume.

PV or less solution was flushed through the column. When CPS was delivered to the sediment using N_2 -generated foams from a 5% CPS solution (Col-CPS-F-I), the amount of mobilized Cr(VI) was much lower (28.9%), thus much more of the Cr was immobilized in situ. This test was repeated (Col-CPS-F-Ia, Table 1). In the repeat test, 26.5% of the total Cr(VI) was mobilized and the effluent Cr(VI) concentration vs. liquid PV curve shape was close to identical to that of Col-CPS-F-I. The repeatability of testing was thus verified.

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 injecting the same foam from the top of the column to immobilize Cr(VI) (Col-CPS-F-II and Col-CPS-F-III). Only 11.5 and 7.1% of the total Cr(VI) contaminant mass was mobilized in Tests Col-CPS-F-II and Col-CPS-F-III, respectively (Fig. 9). When 1.5 PV of 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 the foam-delivered CPS.

The Cr(VI) concentrations and Eh values of the column effluent liquid from Tests Col-CPS-F-I and Col-CPS-F-II are shown in Fig. 10. The effluent peak Cr(VI) concentrations and the peak Eh value corresponded with each other, indicating that, when more Eh of the fluid was consumed by the sediment, the corresponding effluent Cr(VI) concentration was higher. For Test Col-CPS-F-I, as the fluid carried by foam flowed through the column, the reducing capacity of the fluid front was consumed by the Cr(VI) and sediment. Therefore the liquid front mobilized Cr(VI), producing the peaks of Cr(VI) concentration and Eh at breakthrough. For Test Col-CPS-F-II, the liquid first released from the column was the fluid retained in the reduced barrier at the bottom of the column, thus Cr(VI) was undetectable. As more liquid was flushed out, the front of the CPS solution produced from foam rupturing during the downward flushing eluted the column. Within this front, the reducing capacity was consumed by the Cr(VI) and Fe oxides in the sediment. This front created a peak Eh value and Cr(VI) concentration for the effluent liquid. After the front had passed, the effluent returned to higher reducing potential (lower Eh values) and zero Cr(VI)

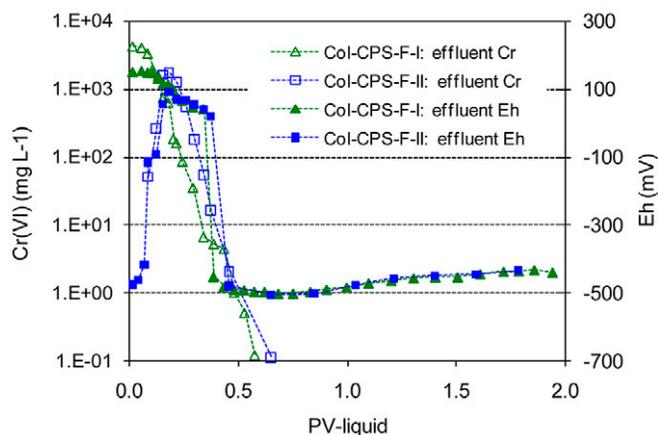


FIG. 10. Column effluent Cr(VI) concentration and redox potential (Eh) from column tests Col-CPS-F-I and Col-CPS-F-II. See Table 1 for test descriptions; PV is pore volume.

concentration. Following the foam injection was an infiltration of synthetic groundwater from the top of the column. The infiltrated water washed out the CPS solution from the sediment. Consequently, the Eh of the effluent gradually increased as more water infiltrated through the column (Fig. 10). At the same time, the Cr(VI) concentration remained at zero, indicating that the reduced Cr(VI) was not reoxidized.

Tests Col-CPS-F-II and Col-CPS-F-III revealed that the amount of mobilized Cr(VI) can be decreased by establishing a reduced sediment barrier. The mobile Cr(VI) will be reduced and captured as downward percolating moisture passes through this barrier. It is reasonable to assume that, when the length or thickness of the barrier increases, even less Cr(VI) will be mobilized. It is worth noting that it is realistic to establish a reduced sediment barrier below the contaminated zones by injecting CPS-containing foam through a section of the sediment because foam flow can be controlled by manipulating the pressure gradient in the vadose zone. In contrast, it is very challenging if a CPS solution is used to generate a reduced barrier in the vadose zone under the contamination zones. In any case, the CPS foam delivery resulted in lower mobilization of Cr(VI) than single-phase CPS water delivery.

In Test Col-CPS-W-I, the effluent pH values varied between 8.31 and 9.79, and those of Col-CPS-W-II varied between 11.45 and 12.08, which is consistent with the influent pH values. In the CPS foam-delivery column tests (Col-CPS-F-I, Col-CPS-F-II, and Col-CPS-F-III), the pH of the foaming solutions varied between 11.42 and 11.58 while the effluent pH varied between 7.58 and 11.30. As pH increases, the sorption extent of an anion (such as CrO_4^{2-}) should decrease since an increase in pH causes an increase in the pH-dependent surface (in this case, negative) charge on variable-charge soil particles and hydroxyl surface reactive groups (Qafoku et al., 2004). Therefore, if the sorption extent of Cr(VI) in the sediment was affected by the pH change during the CPS foam injection, it did not contribute to the observed Cr(VI) immobilization in this study.

We speculate that the mechanism of Cr(VI) immobilization by foam-delivered CPS is dependent on the physical delivery of the foam, the interaction of the CPS foam with the sediment moisture, and the chemical reaction with the Cr(VI). At the front

of foam flow, the reducing CPS solution contained in the lamella sorbed to the sediment grains after foam breakdown. The CPS in the liquid that is taken up reacts with Cr(VI) or Fe oxides, while the N₂ gas flows through the pores. With an increasing collapse of foam bubbles at the front, more Cr(VI) and Fe oxides are reduced. When the liquid content becomes high enough, either the incoming bubbles do not collapse or the bubbles break and reform. Therefore, foam is transported forward and Cr(VI) and sediment reduction proceeds to the downstream end of the column.

Summary and Conclusions

A series of batch and column tests were conducted to study the foam delivery of CPS to sediments under vadose zone conditions and to evaluate Cr(VI) immobilization by foam-delivered CPS. The results from the laboratory-based experiments clearly showed that CPS can be efficiently delivered to unsaturated sediments to immobilize Cr(VI) in situ and to minimize the Cr(VI) mobilization at the reaction front that is encountered when CPS is delivered in a water-based single-phase solution. The results indicate that foam delivery of CPS is a promising approach for vadose zone Cr(VI) immobilization and remediation, although further development is needed to assess the methodology for heterogeneous sediments in three-dimensional systems. Generation of foam with N₂ as the gas component decreases the oxidation of the CPS by air during injection through the sediments.

Importantly, foam injection can potentially be used to deliver a range of remedial amendments to the vadose zone for heavy metal and radionuclide immobilization. In addition, foam may also be used to deliver nutrients to enhance biodegradation of organic contaminants.

ACKNOWLEDGMENTS

Support for this research was provided by the Pacific Northwest National Laboratory (PNNL) Laboratory Directed Research and Development program and from the Department of Energy (DOE) Environment Management program. We appreciate the discussions on this research that we had with Dr. Phil Gauglitz at PNNL and Dr. George Hirasaki at Rice University. The PNNL is operated by Battelle for the U.S. DOE.

References

- Abbasi, S.A., and R. Soni. 1984. Teratogenic effects of chromium(VI) in the environment as evidenced by the impact of larvae of amphibian *Rana tigrina*: Implications in the environmental management of chromium. *Int. J. Environ. Stud.* 23:131–137.
- American Public Health Association. 1989. Standard methods for the examination of water and wastewater. 17th ed. APHA, Washington, DC.
- Bertin, H.J., O.G. Apaydin, L.M. Castanier, and A.R. Kovscek. 1998. Foam flow in heterogeneous porous media: Effect of crossflow. p. 255–264. *In Proc. SPE/DOE Improved Oil Recovery Symp.*, 11th, Tulsa, OK. 19–22 Apr. 1998. Soc. Pet. Eng., Richardson, TX.
- Bikerman, J.J. 1973. *Foams*. Springer-Verlag, Berlin.
- Chambers, K.T., and C.J. Radke. 1991. Capillary phenomena in foam flow through porous media. p. 191–255. *In N.R. Morrow (ed.) Interfacial phenomena in petroleum recovery*. Marcel Dekker, New York.
- Chowdhia, P., B.R. Misra, J.J. Kilbane, II, V.J. Srivastava, and T.D. Hayes. 1998. Foam propagation through soils for enhanced in situ remediation. *J. Hazard. Mater.* 62:265–280.
- Dauble, D.D., G.W. Patton, T.M. Poston, and R.E. Peterson. 2003. Evaluation of the effects of chromium on fall chinook salmon in the Hanford Reach of the Columbia River: Integration of recent toxicity test results. PNNL-14008. Pac. Northw. Natl. Lab., Richland WA.
- Enzien, M.V., D.L. Michelsen, R.W. Peters, J.X. Bouillard, and J.R. Frank. 1995. Enhanced in situ bioremediation using foams and oil aphrons. p. 503–509. *In R.E. Hinchee et al. (ed.) In-situ aeration: Air sparging, bioventing, and related remediation processes*. Battelle Press, Columbus, OH.
- Foster, R.F. 1957. Recommended limit on addition of dichromate to the Columbia River. HW-49713. General Electric Co., Richland, WA.
- Gerber, M.A. 1996. The plutonium production story at the Hanford Site: Processes and facilities history. WHC-MR-0521 Rev 0. Westinghouse Hanford Co., Richland, WA.
- Graham, M.C., J.G. Farmer, P. Anderson, E. Paterson, S. Hillier, D.G. Lumsdon, and R.J.F. Bewley. 2006. Calcium polysulfide remediation of hexavalent chromium contamination from chromite ore processing residue. *Sci. Total Environ.* 364:32–44.
- Hanson, A.T., B. Dwyer, Z.A. Samani, and D. York. 1993. Remediation of chromium-containing soils by heap leaching: Column study. *J. Environ. Eng.* 119:825–841.
- Hirasaki, G.J., C.A. Miller, R. Szafranski, J.B. Lawson, and N. Akiya. 1997. Surfactant/foam process for aquifer remediation. p. 471. *In Proc. SPE Int. Symp. on Oilfield Chemistry*, Houston, TX. 18–21 Feb. 1997. Soc. Pet. Eng., Richardson, TX.
- Holm, L.W. 1968. The mechanism of gas and liquid flow through porous media in the presence of foam. *J. Pet. Technol.* 8:359–369.
- Huang, C.W., and C.H. Chang. 2000. A laboratory study on foam-enhanced surfactant solution flooding in removing *n*-pentadecane from contaminated columns. *Colloids Surf. A* 173:171–179.
- Hudales, J.B.N., and H.N. Stein. 1990. The influence of solid particles on foam and film drainage. *J. Colloid Interface Sci.* 140:307–313.
- Jacobs, J.A. 2001. In situ delivery methods for remediation of hexavalent chromium in soil and groundwater. *In Abstracts of the Association of Engineering Geologists and American Institute of Professional Geologists*, St Louis, MO. 5 Oct. 2001. Assoc. Eng. Geol., Denver.
- Jeong, S.W., and M.Y. Corapcioglu. 2003. Physical model analysis of foam-TCE displacement in porous media. *AIChE J.* 49:782–788.
- Jeong, S.W., M.Y. Corapcioglu, and S.E. Rosevelt. 2000. Micromodel study of surfactant foam remediation of residual trichloroethylene. *Environ. Sci. Technol.* 34:3456–3461.
- Kovscek, A.R., and H.J. Bertin. 2003. Foam mobility in heterogeneous porous media: II. Experimental observations. *Transp. Porous Media* 52:37–49.
- Kovscek, A.R., and C.J. Radke. 1994. Fundamentals of foam transport in porous media. p. 115–164. *In L.L. Schramm (ed.) Foams: Fundamentals and applications in the petroleum industry*. Am. Chem. Soc., Washington, DC.
- Mocák, J., M. Vaníková, and J. Labuda. 1985. Determination of extractable chromium(VI) in the presence of large excess of chromium(III) in solid materials. *Mikrochim. Acta* 11:231–246.
- Moon, D.H., M. Wazne, S.C. Jagupilla, C. Christodoulatos, M.G. Kim, and A. Koutsospyros. 2008. Particle size and pH effects on remediation of chromite ore processing residue using calcium polysulfide (CaS₂). *Sci. Total Environ.* 399:2–10.
- Mulligan, C.N., and F. Eftekhari. 2003. Remediation with surfactant foam of PCP-contaminated soil. 2003. *Eng. Geol.* 70:269–279.
- Mulligan, C.N., and S. Wang. 2006. Remediation of a heavy metal-contaminated soil by a rhamnolipid foam. *Eng. Geol.* 85:75–81.
- Olson, P.A. 1960. Toxicity of chromium to fish. HW-SA-1956. General Electric Co., Richland, WA.
- Ono, B.I. 1988. Genetic approaches in the study of chromium toxicity and resistance in yeast and bacteria. p. 351–368. *In J.O. Nriagu and E. Nieboer (ed.) Chromium in the natural and human environments*. John Wiley & Sons, New York.
- Paschin, Y.V., V.I. Kozachenko, and L.E. Sal'nikova. 1983. Differential mutagenic response at HGPRT locus in V-79 and CHO cells after treatment with chromate. *Mutat. Res.* 122:361–365.
- Peters, R.W., M.V. Enzien, J.X. Bouillard, J.R. Frank, V.J. Srivastava, J. Kilbane, and T. Hayes. 1994. Nonaqueous phase liquids contaminated soil/groundwater remediation using foams. p. 1067–1088. *In G.W. Gee and N.R. Wing (ed.) In-situ remediation: Scientific basis for current and future technologies*. Battelle Press, Columbus, OH.
- Qafoku, N.P., C.C. Ainsworth, and S.M. Heald. 2007. Cr(VI) fate in mineralogically altered sediments by hyperalkaline waste fluids. *Soil Sci.* 172:598–613.
- Qafoku, N.P., C.C. Ainsworth, J.E. Szecsody, and O.S. Qafoku. 2003. Effect of coupled dissolution and redox reactions on Cr(VI)_{aq} attenuation during transport in the Hanford sediments under hyperalkaline conditions. *Environ. Sci. Technol.* 37:3640–3646.

- Qafoku, N.P., E. Van Ranst, A. Noble, and G. Baert. 2004. Variable charge soils: Their mineralogy, chemistry and management. *Adv. Agron.* 84:159–215.
- Rothmel, R.K., R.W. Peters, E.S.T. Martin, and M.F. DeFlaun. 1998. Surfactant foam/bioaugmentation technology for in situ treatment of TCE-DNAPLs. *Environ. Sci. Technol.* 32:1667–1675.
- Schramm, L.L., and R. Wassmuth. 1994. Foams: Basic principles. p. 3–46. *In* L.L. Schramm (ed.) *Foams: Fundamentals and applications in the petroleum industry*. Am. Chem. Soc., Washington, DC.
- Tanzil, D. 2001. Foam generation and propagation in heterogeneous porous media. Ph.D. diss. Rice Univ., Houston, TX.
- USEPA. 1992. Hexavalent chromium by UV-visible spectrophotometry. Method 7196A. *In* Test methods for evaluating solid waste: Physical/chemical methods. EPA SW-846. USEPA, Washington, DC.
- USEPA. 1996. Alkaline digestion for hexavalent chromium. Method 3060A. *In* Test methods for evaluating solid waste: Physical/chemical methods. EPA SW-846. USEPA, Washington, DC.
- Wang, S., and C.N. Mulligan. 2004a. An evaluation of surfactant foam technology in remediation of contaminated soil. *Chemosphere* 57:1079–1089.
- Wang, S., and C.N. Mulligan. 2004b. Rhamnolipid foam enhanced remediation of cadmium and nickel contaminated soil. *Water Air Soil Pollut.* 157:315–330.
- Wazne, M., S.C. Jagupilla, D.H. Moon, C. Christodoulatos, and M.G. Kim. 2007. Assessment of calcium polysulfide for the remediation of hexavalent chromium in chromite ore processing residue (COPR). *J. Hazard. Mater.* 143:620–628.
- Zhong, L., S. Siddiqui, and M.R. Islam. 1998. A new method for screening surfactants for foam diversion applications. *Energy Sources* 21:191–213.