

Reactant Carrier Microfoam Technology for In-Situ Remediation of Radionuclide and Metallic Contaminants in Deep Vadose Zone - 10159

Shas Mattigod, Ph.D*, Lirong Zhong, Ph.D*, Danielle Jansik,*

Martin Foote, Ph.D.**, Andrea Hart**, Dawn Wellman, Ph.D.*

*Pacific Northwest National Laboratory, Richland, Washington 99352

**MSE Technology Applications, Inc., Butte, Montana 59701

ABSTRACT

The U.S. Department of Energy (DOE) is currently developing advanced remediation technologies for addressing metal and radionuclide (Cr, Tc, and U) contamination in deep vadose zone environments. One of the transformational technology alternatives being considered by the DOE Office of Environmental Management, is the use of Reactant Carrier Microfoams (RCM) as a minimally invasive method for delivery and emplacement of reagents for in-situ immobilization of contaminants. Penetration of low permeability zones deep within the subsurface for Enhance Oil Recovery (EOR) has been well-established. Use of surfactant foams have also been explored for mobilizing DNAPL from sediments. So far, the concept of using RCM for immobilizing labile metal and long-lived radionuclide contaminants in the deep vadose zone has not been explored. We, at the Pacific Northwest National Laboratory (PNNL), conducted studies to develop stable foams as a means to deliver reductive and/or precipitating reactants to the deep subsurface. To test the feasibility of this approach, we developed a preliminary foam formulation consisting of a mixture of an anionic and a nonionic surfactant with a reactant consisting of a 9:1 blend of tripoly- and orthophosphate. The MSE Technology Applications, Inc (MSE) in collaboration with PNNL, conducted a scale-up test to evaluate the efficacy of this reactant carrier foam for in-situ immobilization of U containing sediment zones in a heterogenous sediment matrix. The data indicated that successful immobilization of U contamination is feasible using specifically tailored reactant carrier foam injection technology. Studies are continuing for developing more robust optimized RCM for highly mobile contaminants such as Cr (VI), Tc (VII) in the deep vadose zone.

INTRODUCTION

Fissionable material production and processing at various U.S. Department of Energy (DOE) sites has resulted in accumulation of legacy wastes that need appropriate remediation and/or safe disposal. One of the unique challenges is finding suitable in-situ remediation methods for contaminants in deep vadose zone. A key challenge lies in delivering selected chemical fixatives to the contaminant zone to rapidly induce direct and/or reductive precipitation and coprecipitation of contaminants into limited-solubility compounds [1 -4]. Using aqueous reagents has the potential to mobilize the contamination and accelerate its movement into groundwater. Injecting foam as a carrier for chemical reagents can minimize this risk by avoiding significant increase in the inherent moisture content of contaminated vadose zone sediments. Foam injection technology for Enhance Oil Recovery (EOR) has been well-established [5 – 10]. Use of surfactant-based foams has also been explored for mobilizing DNAPL from sediments [11-15]. So far, the concept of using foam for immobilizing labile metal and long-lived radionuclide contaminants in the deep vadose zone has been briefly explored [16,17]. Recently, Pacific Northwest National Laboratory (PNNL), in conjunction with MSE Technology Applications, Inc. (MSE), conducted a study with a specific goal to develop and demonstrate the feasibility of this transformational technology for in-situ sequestration of deep vadose zone contaminants. The results of this preliminary evaluation and its potential applicability at the DOE Hanford site are presented in this paper.

REACTANT CARRIER FOAM DEVELOPMENT

Previous work with low concentrations (0.5 – 1.0 vol %) of an anionic surfactant (STEOL CS-330) indicated that the foam generated was not stable in the presence of phosphate reactant. This was due to

the foam film rupture caused by low surfactant concentrations and highly alkaline phosphate reactant. Therefore, a new series of foam tests were conducted with a mixture of STEOL and a non-ionic surfactant (NINOL 40-CO) loaded with phosphate reactant. Foams were generated by forcing the solution through a porous plate using nitrogen gas (Figure 1). The foams were collected in 2.54 cm diameter columns for a height of 10 cm and the changes in foam height as a function of time was monitored to assess the foam stability.



Figure 1. Porous Plate Apparatus for generating Surfactant Foams

The resulting foam stability data is listed in Table 1. The data showed that the most stable foams resulted when STEOL and NINOL concentrations were 4 and 2 vol % respectively with total phosphate concentrations being 0.25 and 0.5 vol% respectively. At the higher phosphate concentration (0.75 vol%) all foams displayed reduced stabilities. These data were confirmed by stability measurements conducted on foams generated by a separate method namely, high speed blending. Therefore, the foams for the scale-up tests were generating using solutions containing STEOL (4 vol%) and NINOL (2 vol%) and a total phosphate of 0.25 and 0.5 vol%.

Table 1. Stability Data for Reactant Carrier Foams

STEOL Vol %	NINOL Vol (%)	Tot P* Vol %	Foam (t ₅₀)** (min)
2	1	0.25	300
2	1	0.50	300
2	1	0.75	130
4	2	0.25	410
4	2	0.50	375
4	2	0.75	220
8	4	0.25	270
8	4	0.50	80
8	4	0.75	150

*9:1 mixture of monosodium phosphate and sodium tripolyphosphate

**Time for foam height to decrease by 50%

REACTANT FOAM INJECTION SCALE-UP TESTS

A set of scale-up tests were conducted at the MSE Test Facility in Butte, Montana. The objectives were to assess the factors such as, 1) appropriate foam flow rate, 2) flow paths through heterogeneous sediments, 3) the effectiveness of foam transport of polyphosphate through sediments and, 4) potential in-situ immobilization of U-contaminated material by phosphate-bearing foam. The results of the first three tests in the series are presented and discussed in a companion paper¹. In this paper we will describe how the fourth test, namely, the potential immobilization of U in sediments by the polyphosphate reactant foam was conducted and discuss the results.

Description of the Test Bed

The scale-up testing was performed in a 2-D flow test bed that is described in detail by Foote et al¹. For the U-immobilization test described in this paper, the following changes were made in the test bed configuration:

- The solid PVC portions of the extraction systems in the previous experiments were replaced with PVC well screens so that the entire length of the extraction system (except for the upper few inches) was screened.
- A group of three extraction tubes were arranged at 2.5, 25 and 45 cm from the bottom of each box to extract foam.
- The foam generation system for one of the boxes was modified to allow incorporation of an inert tracer gas such as helium into the foam injected at the inlet end and a SUMMA Canister sampling assembly to the outlet tube of the extraction system to allow samples of tracer gas to be collected.
- Finer porous plates (15 µm) were substituted for generating foams with smaller bubble size instead of the 35 µm porous plates used in previous experiments.

Heterogeneous Sediments Properties

Three sediments designated as K1, K2 and K3 from the Hanford area were used for these tests. The particle size distribution of these materials was determined by wet-sieving. The particle size distribution of these sediments is shown in Figure 2.

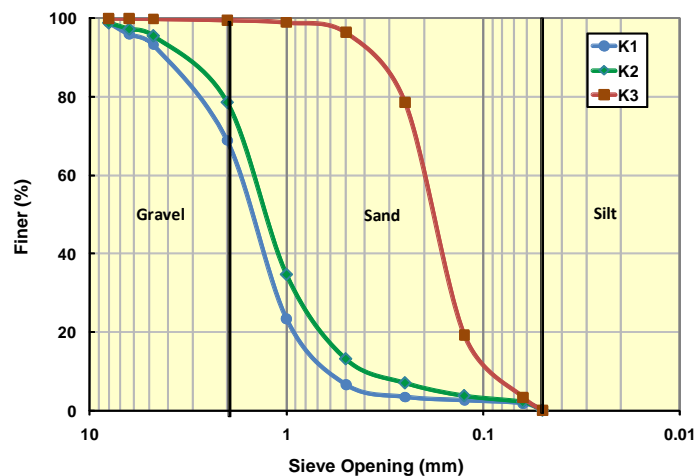


Figure 2. Particle size Distribution of Hanford Sediments (K1, K2, K3)

¹ Foote et al, Paper #10040

Both the K1 and K2 sediments were coarse textured with gravel contents of approximately 30 and 20% by mass respectively. Comparatively K3 sediment was relatively fine-textured sediment fraction with the dominant fraction being fine to very fine sand. The hydraulic conductivities and initial moisture content of these materials were determined. The sediment characteristics are summarized in Table 2.

Table 2. Characteristics of Hanford Sediments used in the 2-D Flow Test Bed

Sediment	Texture	Volumetric Moisture Content (%)	Porosity	Hydraulic Conductivity (cm/s)
K1	Gravelly Sand	3.5	0.305	0.1150
K2	Gravelly Sand	5.0	0.296	0.0469
K3	Fine Sand	9.0	0.310	0.0029

Sediment Packing into Test-Beds

Both of the boxes were packed with sediments to produce two rectangular heterogeneous zones (one with K1 and another with K) in a matrix of K2 sediment. One of the boxes had the zone with fine-grained K3 sediment in the upper part, while the other box had the K3 zone in the lower part as shown in Figure 3. Instrumentation was completed before sediments were packed into the boxes.

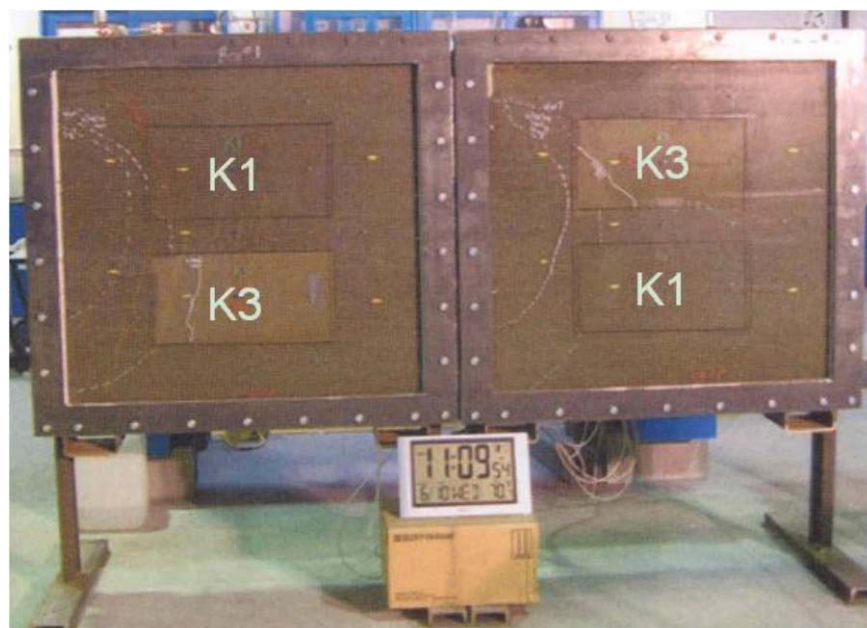


Figure 3. Heterogeneously-packed 2-D Flow Test Beds used in Reactant Foam Injection Tests

Additionally, uranium-rich calcite [18] was added to the sediments in a specific location within each test box to produce a zone of enrichment with a uranium concentration of approximately 300 mg/kg. The configuration of the U-enriched zone in each of the boxes is shown in Figure 4.

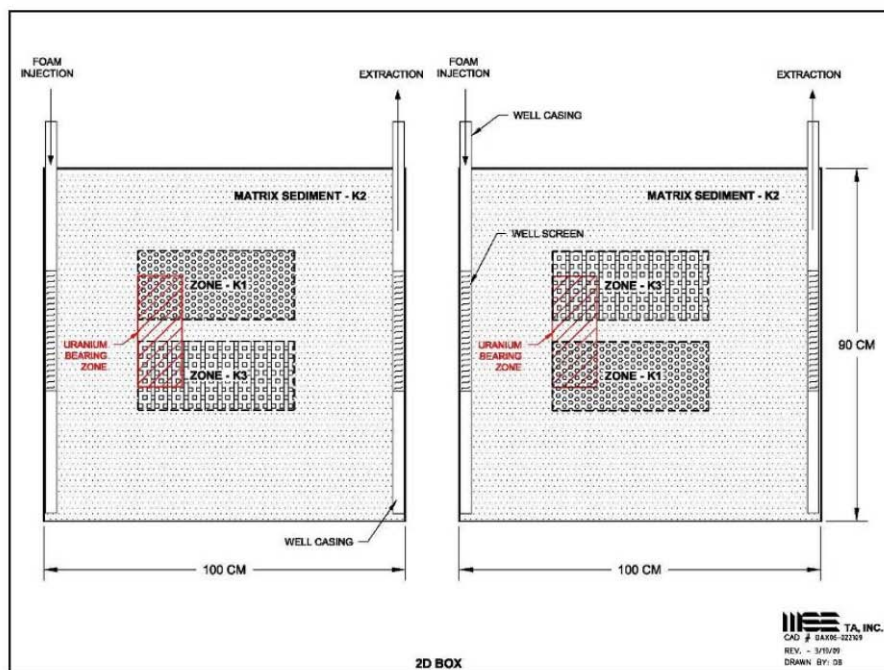


Figure 4. Frontal view of the Test Beds

Foam Injection

Data from the foam stability test was used to formulate the foam composition for injection into the test bed. The foam was generated using an aqueous solution consisting of 4% by volume of STEOL CS-330 and a 2% by volume of NINOL 40-CO. The foaming solution for the first box contained phosphate concentration of 0.25% by volume of phosphate solution (9:1 mixture of ortho- and tripoly phosphate), and for the second box contained 0.5% by volume of phosphate solution. The specific phosphate reagent composition used in this test was based previous tests that demonstrated effective propagation of phosphate through Hanford sedimentary materials [18]. Foam was injected into both boxes at a rate of 175 mL/min, while air was pumped out from the extraction side of the boxes at the same rate. The flow rate used in this test was based on a set of preliminary tests conducted to determine the optimal foam flow rate for similarly packed test bed. The operational conditions for the test are listed in Table 3. During test, all the operating parameters including the internal box pressures were continuously monitored.

Table 3. Operational Conditions for the Test Bed

Box #	Injection Pressure (psi)	Foam Quality (%)	Foam Stability (hour)	Foam pH (SU)	Bubble Size (mm)	Gas Flow Rate (mL/min)	Flow Rate (mL/min)	Extraction Rate (mL/min)
1	6.0	97	> 2	6.79	< 1	175	4.6	175
2	7.0	97	> 2	6.53	< 1	175	4.6	175

After the tests were completed, samples of the sediments were collected from a grid-like pattern through each box. These samples were then analyzed for a number of parameters such as, moisture content, pH, surfactant concentration, total and leachable U.

RESULTS AND DISCUSSION

The foam spread through the sediments as an arcuate front that increased in size with injection time. Bulk of the foam appeared to move horizontally to the extraction end with some portion of the foam moving in both upward and downward from the elongate injection port. The foam front in each test box reached the extraction end, and fluid resulting from displaced inherent soil moisture and potential film drainage from foam was extracted after ~ 28 hours of injection into the first box and ~31 hours of injection into the second box.

During the test, the movement of foam bubbles could be readily observed within the coarse-grained sediments (K1 and K2) behind the arcuate wetting front; however, no foam movement could be discerned within the fine-grained sediment (K3). The shapes of the foam fronts appeared to be influenced by the heterogeneous sedimentary zones. As the foam wetting front contacted the heterogeneous zones, the fine-grained zone was wetted by the foam while no excess wetting could be discerned in the coarse-grained zone. However, as the test progressed, the wetness of the fine-grained sediments decreased but remained above that of the coarse-grained sediments. The final moisture content measurements confirmed the visual observations conducted during the test (Figure 5).

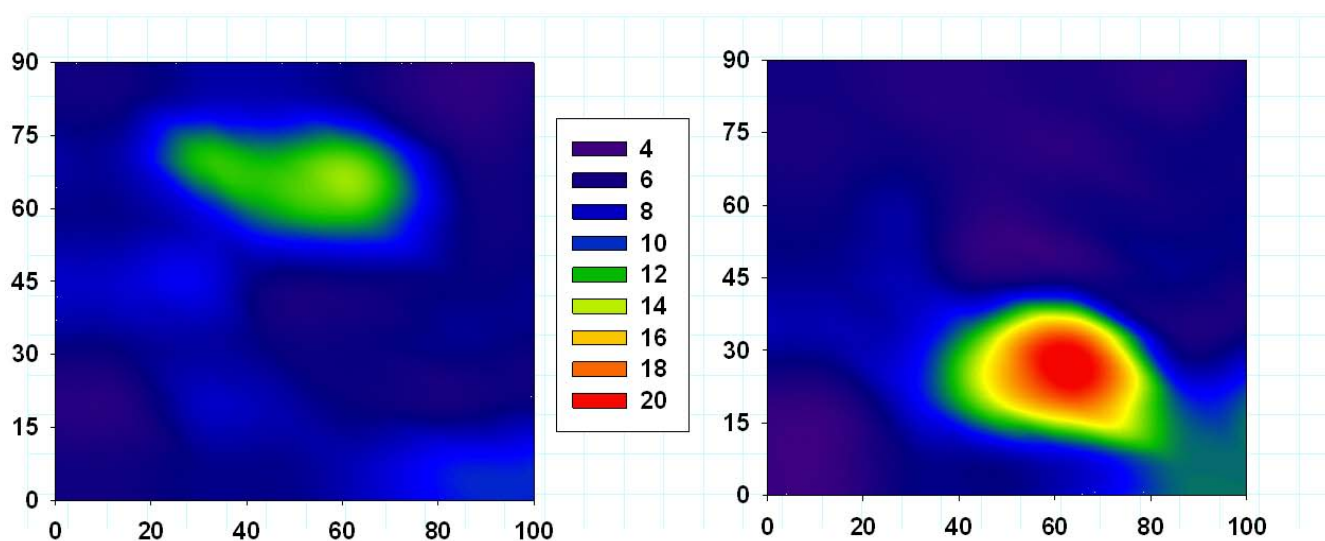


Fig. 5. Post-Test Volumetric Moisture Contents (%) of the Sediments in Box 1 (left) and Box 2 (right). The height (Y axis) and the width (X axis) of the boxes are in cm.

The data indicated that the final moisture content of the fine sediment (K3) zone depended on its location in the Box. In Box 1, K3 zone in the upper part of the box contained up to 12% moisture whereas, in Box 2, K3 zone located in the lower section, contained significantly more moisture (up to 20%). These positional differences in K3 moisture content can be attributed to the gravitational drainage of fluids resulting from both displaced original moisture and release of fluid from foam coalescence. Also, the gas collected from Box 2 at the end of ~5 hr of foam injection contained ~49% helium (used as a tracer) that confirmed the occurrence of foam coalescence and film drainage. In the U-contaminated zone however, the moisture content differences were smaller between coarse and fine sediments.

The pH values of samples of post-test sediments are shown as contour plots (Figure 6). The data indicated that foam infusion did not significantly change the pH values due the inherent buffering

capacity of the sediments. However, slight increases in pH values were observed at the extraction end of both boxes indicating that these sediment samples were enriched in tripolyphosphate. This is likely due to more rapid reaction of orthophosphate with the sediment minerals with concomitant tripolyphosphate enriched foam. Also, the fluid/foam emerging from the extraction well had pH values approaching 9 SU.

The concentration of the surfactants in the fluid/foam emerging from both the boxes were depleted relative to the concentrations in the influent foam indicating that a fraction of the surfactants had adsorbed on to the sediments. To confirm this observation, sediment samples were analyzed to determine the adsorbed surfactant concentrations. The data indicated (Figure 7) that higher concentrations of the surfactants were associated with fine-grain material (K3). Also many of the sediment samples closer to the influent end contained relatively higher surfactant concentrations. The distribution of surfactant in the test bed showed that the saturation levels for the coarse grained sediments (K1 and K2) were ~ 250 – 300 ppm and the fine-grained K3 sediment could adsorb up to ~400 ppm. The total and leachable concentrations of U in the sediment samples were measured to determine the effectiveness of the

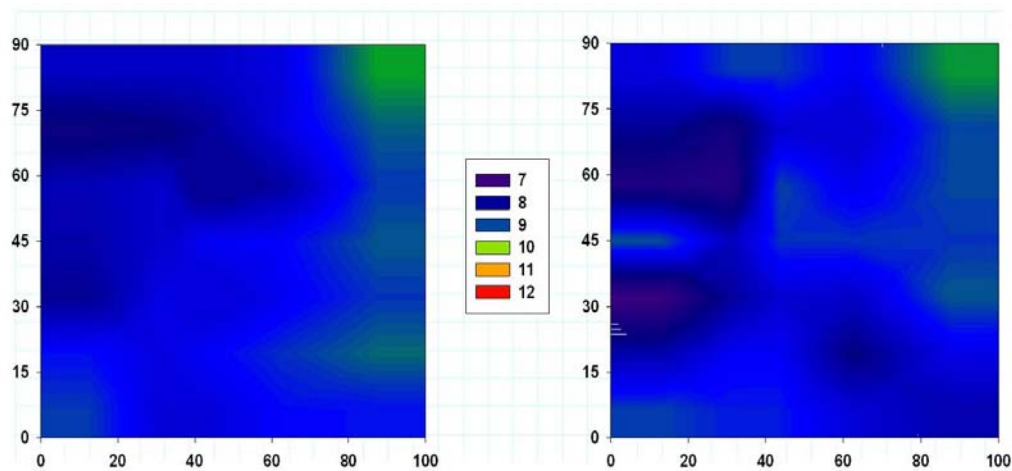


Fig. 6. Post-Test pH Values (SU) of the Sediments in Box 1 (left) and Box (2) right. The height (Y axis) and the width (X axis) of the boxes are in cm.

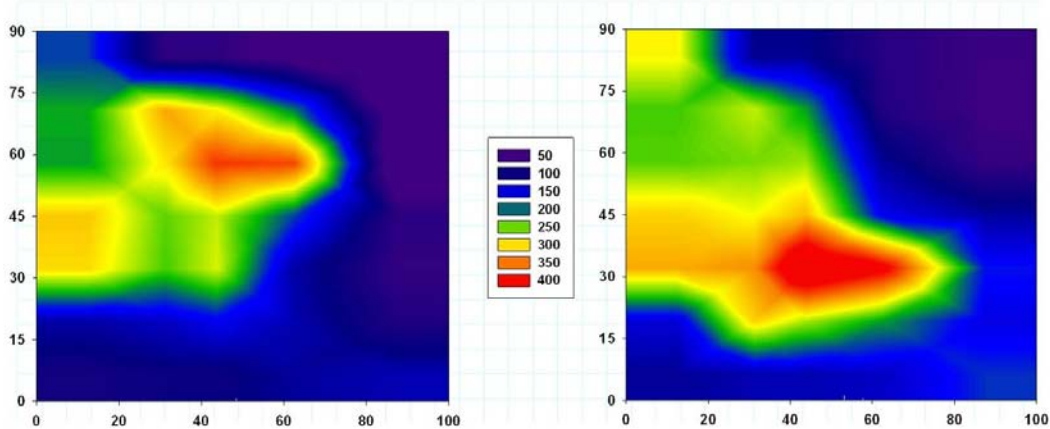


Fig. 7. Surfactant Concentration (ppm) in the Sediments in Box 1 (left) and Box (2) right. The height (Y axis) and the width (X axis) of the boxes are in cm.

phosphate-bearing foam to immobilize in-situ the U contamination. The data indicated that bulk of the U in each box had remained within the emplaced zone suggesting potential in-situ immobilization (Figure 8). Less than ~2 -3% of the U had moved about 6 cm and < 0.5% of the U was detected ~25 cm from the contaminated zone. Beyond this range, U concentrations were at the sediment background levels (0.5 – 0.7 ppm)

Leachable U concentrations indicated that less than ~ 3% of the total U was leachable from the enriched zone (Figure 8)². Measurable (0.01 – 0.3 ppm) concentrations of leachable U were found at distances of 6 and 25 cm downstream respectively from the U-enriched zone in the fine grain sediment. Sediment samples obtained further downstream contained leachable U at the background levels. Also, the fluid/foam collected from the extraction port contained very low U concentrations (0.8 ppb and 1.8 ppb)

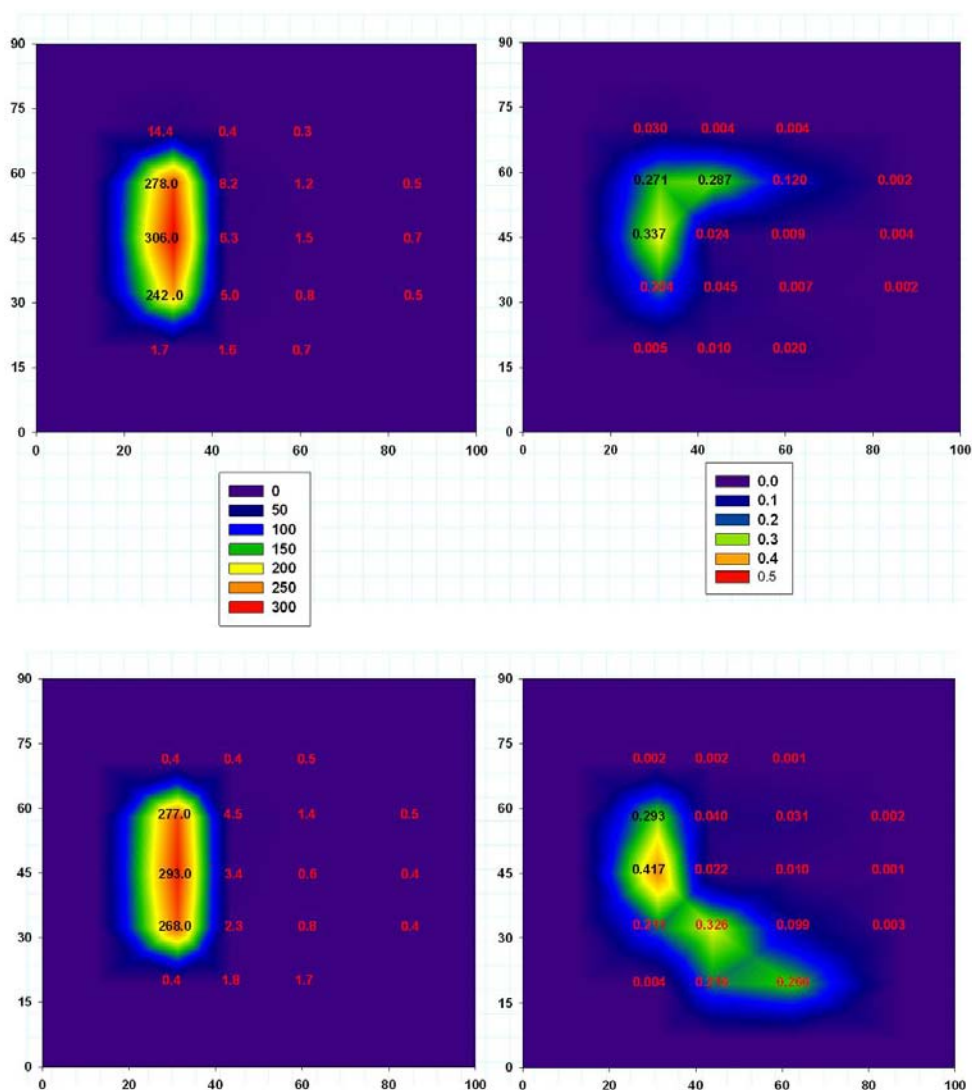


Fig. 8. Total and Leachable U Concentrations (ppm). Box 1 Sediments (Top left and Top Right respectively) and Box 2 Sediments (Bottom Left and Bottom Right respectively). The height (Y axis) and the width (X axis) of the boxes are in cm.

² The background concentrations of U in the sediments ranged from 0.4 – 0.7 ppm of which 0.001 – 0.004 ppm was extractable (0.3 – 0.8%).

from Box 1 and 2 respectively) indicating the relative immobility of U in the sediments. The negligible leachability of U irrespective of the sediment texture differences indicated that the immobilization reaction was more rapid than the migration of any soluble fraction. The moisture content data (Fig 5) also adds credence to such rapid immobilization reaction for U.

Currently, studies are continuing to identify the stable U phases that may have formed in the contaminated zone from reactions with phosphate-bearing foam.

CONCLUSIONS

A set of tests were conducted to demonstrate the feasibility of using reactant carrier foam to immobilize in-situ U contamination in deep vadose sediments. The results from these tests indicate that:

- Relatively stable reactant carrier foams can be formulated using a mixture of an anionic surfactant (STEOL CS-330) and a non-ionic surfactant (NINOL CO-40) in concentrations of 4 and 2 vol % respectively and total phosphate concentrations 0.25 and 0.5 vol% (9:1 monosodium phosphate:sodium tripolyphosphate).
- Reactant carrier foam injection into heterogeneous sediments (in a 2-D test bed) was accomplished successfully using relatively low injection pressures (6 – 7 psi) for flow rates of 175 ml/min).
- The volumetric moisture content distribution in the test bed reflected sediment porosity. The moisture content in the fine-grain sediment varied according to its location in the test bed. Film drainage causes fine sediment (K3) located in the lower part of the test bed to have higher moisture content as compared to K3 zone location in the upper part of the box.
- Reactant carrier foam infusion did not significantly change the pH values due the inherent buffering capacity of the sediments. Slight increases in pH values observed at the extraction end sediment samples are attributable to foam enriched in tripolyphosphate. Such enrichment is the likely result of more rapid reaction of orthophosphate with the sediment minerals resulting in foam being depleted of orthophosphate and enriched with tripolyphosphate.
- The distribution of surfactant in the test bed showed that some of the surfactant had adsorbed on to the sediments. The saturation levels for the coarse grained sediments (K1 and K2) were ~ 250 – 300 ppm and that fine-grained K3 sediment could adsorb up to ~400 ppm.
- The test confirmed that bulk of the U in each box had remained within the emplaced zone suggesting potential in-situ immobilization. Less than 3% of the total U was leachable from the immobilized zone confirming feasibility of using phosphate reactant carrier foam for in-situ immobilization of U is feasible.
- Reactant carrier foam injection technology has the potential to help advance remediation strategy for effective treatment of contaminants and mitigate the contaminant flux from deep vadose zone. Current studies include, testing new RCM formulations, identifying geophysical techniques for monitoring foam mobility and reactivity, and modeling of foam behavior in vadose zone sediments.

ACKNOWLEDGEMENTS

Funding for this project was provided by the U.S. Department of Energy (DOE) Office of Environmental Management (EM) - Office of Technology Innovation and Development (EM-30), Soil and Groundwater Remediation Technology Development Program (EM-32). This work was conducted by PNNL under

contract DE-AC05-76RL01830 for the U. S. Department of Energy. Additional support was provided by the PNNL LDRD funding. The MSE part of the work was conducted through the DOE Environmental Management Consolidated Business Center at the Western Environmental Technology Office under DOE Contract Number DE-AC09-96EW96405.

REFERENCES

1. R. C. Moore, C. Sanchez, J. Schelling, J. Jones, D. R. Anderson, F. Salas, D. Lucero, and K. Holt, *Bench-Scale Testing of in-Situ Formation of Apatite in Hanford Soils for Sorption of Uranium and Technetium*, SAND2001-3001, Sandia National Laboratories, Albuquerque, New Mexico (2001).
2. L. Yang, R. J. Donahoe, and J. C. Redwine, "In Situ Chemical Fixation of Arsenic-Contaminated Soils: An Experimental Study," *Science of the Total Environment*. 387:28-41 (2007).
3. J. E. Szecsody, M. D. Williams, C. A. Burns, D. C. Girvin, R. C. Moore, J. P. McKinley, J. S. Fruchter, M. J. Truex, V. R. Vermeul, and J. L. Phillips, *Hanford 100-N Area Apatite Emplacement: Laboratory Results of Ca-Citrate-PO₄ Solution Injection and Sr-90 Immobilization in 100-N Sediments*, PNNL-16891, Pacific Northwest National Laboratory, Richland, Washington (2007).
4. D. M. Wellman, E. M. Pierce, E. L. Richards, B. C. Butler, K. E. Parker, J. N. Glovack, S. D. Burton, S. R. Baum, E. T. Clayton, and E. A. Rodriguez, *Interim Report: Uranium Stabilization through Polyphosphate Injection - 300 Area Uranium Plume Treatability Demonstration Project*. PNNL-16683, Pacific Northwest National Laboratory, Richland, Washington (2007).
5. G. J. Hirasaki, G. Hughes; and A.M. Clarence. *Foam Delivery of Hydrogen of Enhanced Aquifer Contacting and Anaerobic Bioremediation of Chlorinated Solvents*. SERDP final report, project number CU-1203. (2005).
6. G. J. Hirasaki, C.A. Miller; R. Szafranski; D. Tanzil; J.B. Lawson; H.W. Meinardus; M. Jin; J.T. Londergan; R.E. Jackson; G.A. Pope; and WH Wade. Field demonstration of the surfactant/foam process for aquifer remediation. Paper SPE 39292 presented at the 1997 SPE Annual Technical Conference and Exhibition, San Antonio, Texas, 5-8 October. Society of Petroleum Engineers, Richardson, Texas. (1997)
7. A. R. Kovscek, and C. J. Radke. J. Fundamentals of Foam Transport in Porous Media. In *Foams – Fundamentals and Applications in the Petroleum Industry*; Schramm, L.L. Ed.; American Chemical Society, Washington, DC (1994).
8. R. K. Rothmel, R. W. Peters, E. S. T. Martin, M. F. DeFlaun. Surfactant foam/bioaugmentation technology for in situ treatment of TCE-DNAPLs. *Environ. Sci. Technol.* 32:1667–1675 (1998)
9. L. L. Schramm, and F. Wassmuth. Foams: Basic Principles. In *Foams – Fundamentals and Applications in the Petroleum Industry*; Schramm, L.L. Ed.; American Chemical Society, Washington, DC (1994).
10. W. Yan, C.A. Miller and G.J. Hirasaki. Foam sweep in fractures for enhanced oil recovery. *Colloids and Surfaces A-Physicochemical and Engineering Aspects.* 282:348-359, (2006).
11. D. Roy, R. R. Kommalapati, K. T. Valsaraj, and W. D. Constant, "Soil Flushing of Residual Transmission fluid: Application of Colloidal Gas Aphron Suspensions and Conventional Surfactant Solutions." *Wat. Res.* 29:589-595 (1995).
12. R. K. Rothmel, R. W. Peters, E. St. Martin, and M. F. DeFlaun. Surfactant Foam/Bioaugmentation Technology for In Situ Treatment of TCE-DNAPLs. *Environ. Sci. Technol.* 32:1667-1675 (1998).
13. S. W. Jeong, M. Y. Corapcioglu and S. E. Roosevelt. Micromodel Study of Surfactant Foam Remediation of Residual Trichloroethylene. *Environ. Sci. Technol.* 34:3456-3461 (2000)
14. C. N. Mulligan, and F. Eftekhari. "Remediation with Surfactant Foam of PCP-Contaminated Soil." *Eng. Geol.* 70:269-279 (2003).
15. A. Wang, and C. N. Mulligan. An Evaluation of Surfactant Foam Technology in Remediation of Contaminated soil. *Chemosphere.* 57:1079-1089. (2004)
16. L. Zhong, N.P. Qafoku, J.E. Szecsody, P.E. Dresel, and Z.F. Zhang. Foam delivery of calcium polysulfide to the vadose zone for chromium (VI) immobilization: A laboratory evaluation. *The Vadose Zone Journal*. Vol. 8 No.4, (2009).

17. L. Zhong, J. Szecsody, D. Wellman, F. Zhang, S. V. Mattigod, E. Peirce. Foam Application in Vadose Zone Remediation: Transport; Amendment Delivery; and Technetium-99 Immobilization. American Geophysical Union 2009 Fall Meeting. Dec. 14-19, San Francisco. (2009)
18. D. M. Wellman, E. M. Pierce, D. H. Bacon, K. E. Parker, M. Oostrum, K. M. Gunderson, S. M. Webb, C. C. Bovaird, E. A. Cordova, E. T. Clayton, R. M. Ermi, S. R. Baum, V. R. Vermeul, and J. S. Bruchter, *300 Area Treatability Test: Laboratory Development of Polyphosphate Remediation Technology for In-situ Treatment of Uranium Contamination in the Vadose Zone and Capillary Fringe*, PNNL-17818, Pacific Northwest National Laboratory, Richland, Washington (2008).