Advanced Remedial Methods for Metals and Radionuclides in Vadose Zone Environments – 11026

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ABSTRACT

Functionally, the methods for addressing contamination must remove and/or reduce transport or toxicity of contaminants. This problem is particularly challenging in arid environments where the vadose zone can be up to hundreds of feet thick, rendering transitional excavation methods exceedingly costly and ineffective. Delivery of remedial amendments is one of the most challenging and critical aspects for all remedy-based approaches. The conventional approach for delivery is through injection of aqueous remedial solutions. However, heterogeneous vadose zone environments present hydrologic and geochemical challenges that limit the effectiveness. Because the flow of solution infiltration is dominantly controlled by gravity and suction, injected liquid preferentially percolates through highly permeable pathways, bypassing low-permeability zones which frequently contain the majority of the contamination. Moreover, the wetting front can readily mobilize and enhance contaminant transport to underlying aquifers prior to stabilization. Development of innovative, in-situ technologies may be the only way to meet remedial action objectives and long-term stewardship goals.

Shear-thinning fluids (i.e., surfactants) can be used to lower the liquid surface tension and create stabile foams, which readily penetrate low permeability zones. Although surfactant foams have been utilized for subsurface mobilization efforts in the oil and gas industry, so far, the concept of using foams as a delivery mechanism for transporting reactive remedial amendments into deep vadose zone environments to stabilize metal and long-lived radionuclide contaminants has not been explored. Foam flow can be directed by pressure gradients rather than being dominated by gravity, and, foam delivery mechanisms limit the volume of water (< 20% vol.) required for remedy delivery and emplacement, thus mitigating contaminant mobilization. We will present the results of an integrated laboratory- / intermediate-scale investigation to simulate, develop, demonstrate, and monitor (using advanced geophysical techniques and natural marker monitoring) foam-based delivery of remedial amendments to stabilize metals and radionuclides in vadose zone environments.

INTRODUCTION

Deep vadose zone environments can be a primary source and pathway for contaminant migration to groundwater. These environments present unique characterization and remediation challenges that necessitate scrutiny and research. The thickness, depth, and intricacies of the deep vadose zone, combined with a lack of understanding of key subsurface processes (e.g., biogeochemical and hydrologic processes) affecting contaminant migration, make it difficult to create validated conceptual and predictive models of subsurface flow dynamics and contaminant behavior across multiple scales. These factors also make it difficult to design and deploy sustainable remedial approaches and monitor long-term contaminant behavior after remedial actions.

Delivery of amendments within vadose zone environments is a challenging and critical aspect for all remedy-based remediation approaches. The conventional approach for amendment delivery is through injection or infiltration of chemical solutions. However, delivery of remedial solutions through a heterogeneous deep vadose zone environment encounters hydrologic and geochemical challenges.

First, because the flow of solution infiltration is dominantly controlled by gravity and suction, preferential flow paths of the solution in the deep vadose zone are very difficult to overcome. Injected liquid preferentially percolates through the high permeability (high-k) pathways at high infiltration rates potentially bypassing low-permeability

(low-k) zones, which may contain the majority of contamination. Generally, vertical migration is observed through high-k zones and lateral migration observed deeper in the low-k zones of the vadose zone [1].

Second, the wetting front of a water-based delivery can readily mobilize contaminants with high mobility retained in the vadose zone sediments. Once the pore water is mobilized by the injected solution, it moves downwards to the aquifer. This potentially enhances contaminant transport to the underlying aquifer before it interacts with the amendment.

FOAM DELIVERY SYSTEMS FOR REMEDIAL AMENDMENTS

Foam is a dispersed phase of gas in a liquid. Foam formation is a dynamic process in which a non-wetting gas is dispersed in a continuous surfactant-laden liquid phase. It is an emulsion-like, two-phase system in which gas cells are dispersed in a liquid and separated by thin liquid films called lamellae [2]. The non-Newtonian, shear-thinning fluid [3, 4] provides enhanced migration through low-permeability, heterogeneous porous media resulting in better sweeping efficiency over the contaminated zone [3, 5].

Foams generally are classified into two broad categories: polyhedral foam and microfoam [6]. Polyhedral foams consist of polyhedral bubbles that are separated by thin liquid films. Microfoams consist of very small spherical bubbles with bimolecular oriented surfactant shells [7-17]. A comparison of the characteristics of the two types of foam is presented in Table 1.

Table 1. Comparison of Foam Characteristics

Characteristics	Polyhedral Foam	Microfoam
Bubble size	0.5 – 10 cm	10 – 300 µm
Liquid Content	0.5 – 5%	10 – 50%
Micelle Conc	Low	High
Half life	Min - hr	Days - months
Surface Tension	High	Low
Ostwald Ripening	Rapid	Slow
Reactant Stability	Low	High
Electrical Conductivity	Low	High
Deformability	High	Low

In comparison to polyhedral foams, microfoams are more stable and have, therefore, been used in applications such as soil remediation for mobilizing dense non-aqueous phase liquid (DNAPL) from sediments [5, 18-21] and enhanced oil recovery. Initial results support the concept of using foam for distribution of remedial amendments within vadose zone environments as this method involves minimal change in water content and can achieve more uniform distribution relative to other methods [22-24].

In contrast to solution flow in water-based delivery systems, foam flow under vadose zone conditions is not dominated by gravity; rather, it can be directed by pressure gradients in the sediments. This allows resolution of uneven remedial fluid distribution in heterogeneous subsurface environments. Furthermore, the use of foam also provides better control on the volume of fluid (< 20% vol.) required for remedy delivery and emplacement, thereby minimizing the potential for contaminant mobilization [25].

The objective of this initiative is to transform foam technology into a viable method for delivering remedial amendments to vadose zone environments. Critical to successful implementation of this technology is the ability to monitor delivery, placement and contaminant plume behavior for real-time optimization in deep subsurface environments. Therefore, advanced geophysical methods are being developed to characterize controlling properties and induced processes at a high enough spatial resolution for accurate assessment of foam-based delivery technologies for deep vadose zone treatments. Furthermore, the addition of microbial community markers provides additional, contextual information that can be used for monitoring fate and efficacy of remedial treatments.

REACTIVE CARRIER MICROFOAMS

Two-dimensional flow cell systems were used to develop and optimize foam-based delivery technology in this investigation. The flow cell had dimensions of $l = 100$ cm, $h = 90$ cm, $w = 15$ cm wide and contained approximately 255 kg of sediment. The flow cell was packed with sediments representative deep vadose zone sediments found in 200 East Area at Hanford, Washington. Two rectangular heterogeneous zones (sediments K1 and K3 with hydraulic conductivities of 0.1150 and 0.0029 cm/s, respectively) were embedded in a matrix of a third sediment, K2 (hydraulic conductivity = 0.0469 cm/s). Approximately 300 mg/kg of uranium-rich calcite [26] was positioned in a specific location to produce a zone of enrichment (Fig. 1).

Foam was generated in a porous plate apparatus (15 µm pore opening) using an aqueous solution consisting of 4% by volume of STEOL CS-330, 2% by volume of NINOL 40-CO (NINOL 40-CO is the trade name for a mixture of surfactant, cocamide DEA [CAS# 68603-42-9], glycerine [CAS# 56-81-5], and diethanolamine [CAS# 111-42-2]) and 0.25% by volume (9:1 mixture of ortho- and tripolyphosphate). The specific phosphate reagent composition was based on previous tests that demonstrated effective propagation of phosphate through Hanford sedimentary materials [26]. The rate of foam injection was 175 mL/min at about 6 psi; air was extracted from the extraction side at the same rate. After the test was completed, samples of the sediments were collected in a grid-like pattern throughout the flow cell. These samples were analyzed for moisture content, pH, surfactant concentration, total and leachable uranium.

The results indicated that the final moisture content was dependent upon the texture of the sediment, with the fine textured sediment possessing the highest, 12%, moisture content (Fig. 2).

The pH values of samples of post-test sediments indicated that foam infusion did not significantly change the pH values due the inherent buffering capacity of the sediments. However, a slight increase in pH value was observed at the extraction side of the test cell indicating that these sediment samples were enriched in phosphate amendment. Also, the fluid/foam emerging from the extraction well had pH values approaching 9 SU (Fig. 3).

The concentration of surfactants in the fluid/foam emerging from the test cell was depleted relative to the concentrations in the influent foam, indicating that a fraction of the surfactants had adsorbed onto the sediments (Fig. 4). To confirm this observation, sediment samples were analyzed to determine the adsorbed surfactant concentrations. The data indicated that higher concentrations of 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 about 250 – 300 ppm and the fine-grained K3 sediment could adsorb up to about 400 ppm.
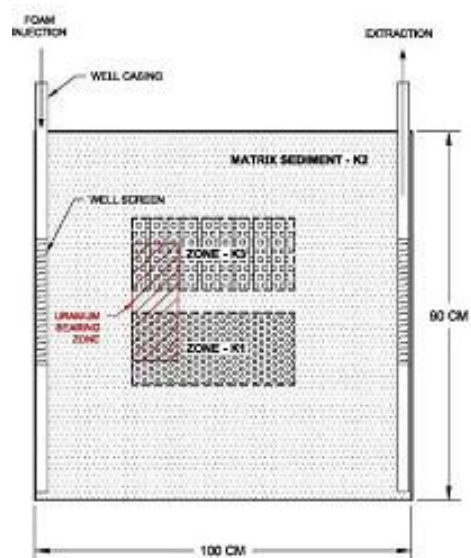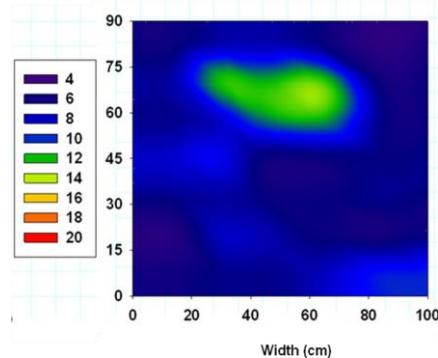

Fig. 1. 2D flow cell configuration

Fig. 2. Moisture content distribution subsequent to foam-delivery of polyphosphate for in situ uranium immobilization
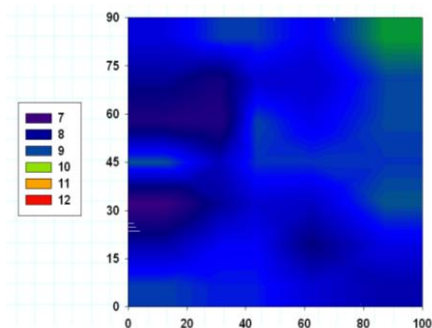

Fig. 3. Distribution of pH values throughout 2D test cell subsequent to foam-delivery of polyphosphate for in situ uranium immobilization

The total and leachable concentrations of uranium indicated that the bulk of the uranium had remained within the original zone, suggesting potential in-situ stabilization (Fig. 5). Less than 3% of the uranium had moved 6 cm and <0.5% of the uranium was detected about 25 cm from the contaminated zone. Beyond this range, uranium concentrations were at background levels (0.5 – 0.7 ppm). Also, the fluid/foam collected from the extraction port contained very low uranium concentration (0.8 ppb).
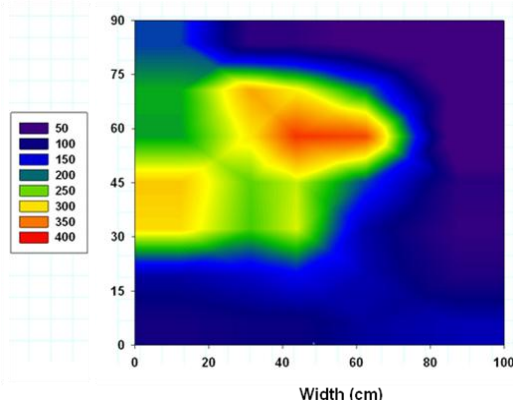

Fig. 4. Surfactant distribution throughout 2D
test cell subsequent to foam delivery of
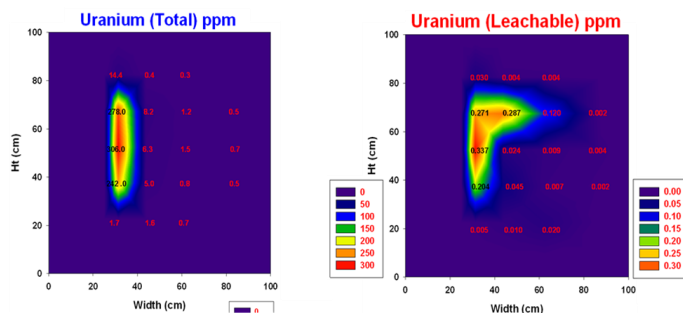polyphosphate for in situ uranium immobilization

Fig. 5. Total and leachable U concentrations (ppm).

These results suggest that the foam-based delivery of remedial amendments has the potential to advance remediation strategies for effective treatment of contaminants and mitigate the contaminant flux from the deep vadose zone to groundwater.

ADVANCED MONITORING APPROACHES FOR SUBSURFACE EMPLACEMENT AND PERFORMANCE OF REMEDIAL AMENDMENTS

Integral to the successful development of any remedial technology is the ability to monitor, and eventually predict, the delivery, emplacement, and long-term performance of the treatment. In general, such monitoring is complicated by subsurface heterogeneity and by the disparity of scales across which hydrological properties span because these properties control the distribution of the remedial amendment and thus the location of subsequent transformations. Conventional techniques for subsurface hydrobiogeochemical monitoring rely on wellbore-based approaches to collect samples or make measurements. Because of their limited spatial extent, these methods often cannot provide sufficient information to describe key controls on subsurface flow and transport. This is especially true in the vadose zone, where vertical infiltration pathways can form as a result of variable saturation and heterogeneity and where fluid recovery for sampling can be challenging.

The inability to conventionally characterize controlling properties and induced processes at a high enough spatial resolution, and over a large enough spatial extents, prohibits accurate assessment of foam-based delivery technologies for deep vadose zone treatments. To this end, we are advancing the application of radar and complex resistivity methods, which encompass three different geophysical attributes.

Briefly, radar methods are expected to provide information about the dielectric constant, which is sensitive to soil moisture and may also respond to the reactive foam. Complex resistivity measures both the frequency-dependent electrical conductivity and induced phase response of the media to an external current. The electrical conductivity is expected to be useful primarily for monitoring the change in saturation and total dissolved solids (TDS) associated with the reactive foam.

Finally, microbial markers will be used as a long-term monitoring approach to assess the effectiveness of remedial treatment and reaction of community dynamics. This profiling can be performed rapidly at the point source and at downstream gradients where microbial community changes may occur in advance of measurable geochemical

metrics; thereby, providing a highly sensitive "warning" of possible changes in contaminant plume behavior or the need for additional in situ remediation.

ADVANCED GEOPHYSICAL APPROACHES

Geophysical methods have been used in recent years to improve the characterization of near subsurface properties and processes [27]. Because geophysical data can be collected from many different platforms (such as at the ground surface, between wellbores, and within wellbores), they can interrogate subsurface variability over a variety of spatial scales and resolutions. The main advantage of using geophysical data over conventional measurements is that geophysical methods can provide spatially extensive information about the subsurface in a minimally invasive manner at a comparatively high resolution.

A particularly attractive feature of geophysical methods for subsurface process monitoring is the ability to collect a suite of continuous datasets at the same location as a function of time. Time-lapse geophysical imaging can be extremely useful for monitoring the temporal evolution of a process because it effectively "removes" the response of the geophysical signatures to the components of the system that are static (such as lithology) and illuminates the components of the system that change over time. These approaches have been effectively used for hydrological investigations to monitor vadose zone water infiltration [28, 29] and to track the spatiotemporal distribution of a polylactate amendment into Cr(VI)-contaminated groundwater and associated biogeochemical responses [30]. Hubbard et al. [30] also highlighted the significant control of heterogeneity on the location of amendment and biogeochemical transformations. Recent efforts have explored how geophysical methods can be used to track the evolution of pore structures and field-scale flow paths associated with remediation-induced end-products, such as precipitates or gases (e.g., [30-32]). Current studies also have illustrated that strong feedbacks occur between remediation-induced biogeochemical transformations and flow characteristics at the field scale [33, 34].

The ability to meaningfully interpret the geophysical data in terms of flow and transport parameters requires an understanding of how geophysical signatures respond to a variety of subsurface alterations associated with the remedial treatment. One such alteration is the introduction of the remedial treatment into porous medium and the subsequent biogeochemical transformations that occur as a result of the treatment. The ability to geophysically distinguish processes associated with a remedial treatment is a function of many factors, including: (1) the geophysical method and acquisition geometry that is employed; (2) the contrast in geophysical properties induced by different components of the treatment process; and (3) the scale of the region that is impacted relative to the footprint of the geophysical method.

Application of complex resistivity and radar methods encompass three different geophysical attributes that may be useful for quantifying foam distribution and reactivity: radar velocity, complex resistivity phase response, and electrical conductivity. These methods are briefly described below.

RADAR METHODS. Time-Domain Reflectometer (TDR) and radar methods will be used to measure electromagnetic wave propagation characteristics over the approximately $100 - 1000$ MHz range at the laboratory and field scales, respectively. TDR methods involve propagating an electromagnetic signal along waveguides inserted into the material of interest, and measuring the velocity and amplitude of the traveling wave [35]. Radar data acquisition consists of placing a transmitter and a receiver in separate locations, and moving them successively until many transmitter and receiver locations have been occupied. The travel time of the direct arrival and associated amplitude information is extracted from the recorded waveforms, and inversion algorithms are used to transform this information into estimates of velocity and attenuation. This is illustrated in Peterson's 2001 study [36].

At the frequency of operation for TDR and radar systems, the separation (polarization) of opposite electric charges within a material subjected to an external electric field dominates the electrical response. The dielectric constant (κ), which used to describe these high-frequency electrical properties, can be approximated from the velocity (V) of the radar signal [37] by:

$$\kappa \approx \left(\frac{c}{V}\right)^2 \tag{Eq. 1}$$

where c is the propagation velocity of electromagnetic waves in free space. The dielectric constant obtained from travel times is often used within dielectric mixing models to explore the dielectric contribution from a variety of components (Wharton et al., 1980) such as the idealistic expression for a three-component, soil-water-air system:

$$\kappa = \left(Sn\kappa_w^\gamma + (1-n)\kappa_g^\gamma + n(1-S)\kappa_a^\gamma \right)^{\frac{1}{\gamma}}$$ (Eq. 2)

In Equation (3), S is water saturation; n is the soil porosity; κ_w, κ_g and κ_a are the unitless dielectric constant values of pore water, soil grains, and air, respectively. γ is a factor that accounts for the orientation of the electrical field with respect to the geometry of the medium (which is commonly assumed to be 0.5 for an isotropic medium). Given that the dielectric constant of water (80) is high relative to typical values for grains (4-8) and air (1), the mixing formula shown in (2) is commonly used for moisture content estimation. In addition to monitoring moisture in this project, if the dielectric constant of the reactive foam differs dramatically from air, then radar methods might additionally respond to the distribution of foam.

It is critical to perform laboratory analyses that closely mimic experimental conditions in the field. The results will determine the optimal geophysical monitoring approaches for quantifying the geophysical attribute sensitivities to various processes associated with the remediation method.

COMPLEX ELECTRICAL METHODS. The complex electrical method will be used to measure frequency-dependent electrical responses over the range of 0.1-1000 Hz using non-polarizing Ag/AgCl electrodes. This method involves injecting current of different frequencies into a sample volume and measuring the responses relative to a reference resistor to yield phase and electrical conductivity as a function of frequency. Information about both electrical conductivity and the phase response can be obtained from the complex electrical signature. Typically, the obtained electrical conductivity estimate is used to provide information about pore space variations (water content and total dissolved solids) whereas the phase is used to infer information about interactions occurring near the interface of the grains and pore fluids [38]. Archie's Law [39] is commonly used to relate the measured effective conductivity (σ_{eff}) to porosity (n), the electrical conductivity of the pore water (σ_w), and the electrical conductivity associated with surface conduction ($\sigma_{surface}$) as:

$$\sigma_{eff} = \sigma_w n^m + \sigma_{surface} \,,$$ (Eq. 3)

where m is Archie's exponent. Neglecting changes associated with surface conduction, cementation and porosity, equation (3) suggests that if an amendment having a higher electrical conductivity replaces pore water, the effective electrical conductivity will increase. The phase response (or induced polarization [IP]) is generated by the existence of the electrical double layer (EDL) at the grain/pore fluid interface.

Phenomenological formulations, such as the Cole-Cole relaxation model, are often used to model complex electrical response, because theoretically based models for predicting the spectral-induced polarization or phase response are lacking (or extremely difficult to parameterize). Inversion of the complex resistivity data yields estimates of the Cole-Cole parameters chargeability and time constant, similar to those seen in Chen, Kemna, and Hubbard [40], which can, in turn, be related to pore and grain geometric characteristics as well as pore-grain interfacial phenomena. Interpretation of phase response or Cole-Cole parameters in terms of near-subsurface biogeochemical properties and processes is a relatively new area of biogeophysical research. Recent experimental research suggests that changes in phase response tracks the onset, aggregation, and aging of remediation-induced precipitates [32, 41] and that phase response can be useful for quantifying the volume of remediation-induced precipitates and concomitant reduction in permeability [42].

Although untested, the phase response (or induced polarization [IP]) is generated by the existence of the electrical double layer (EDL) at the grain/pore fluid interface. Recent research has revealed that phase responses can be particularly useful for monitoring remediation-induced, biogeochemical transformations that impact the pore-grain interfacial region, such as the onset, distribution, and aging of precipitates (e.g., [31, 41, 43]). Although untested, the phase responses may also be useful for monitoring the distribution, drainage, and breakdown of foam. This

hypothesis is based on previous studies that indicate that the zeta potential (ξ-potential) at gas/liquid interfaces is on the magnitude of tens of milivolts [44, 45], which is compatible to responses observed in association with solid/liquid interfaces. Although the phase responses associated with solid/liquid interfaces have been subjected to intensive studies, similar research for gas/liquid interfaces is absent from our knowledge. If proven sensitive, the phase response could provide a unique technology for the characterization and monitoring of the fate of the reactive foam.

MICROBIAL MARKERS FOR LONG-TERM MONITORING

Remediation of contaminant plumes, such as technetium and uranium, in the vadose zone has been challenging with respect to site characterization prior to and following remedial activities, design for treatability, and monitoring of treatment efficacy, to name a few. Characterization of physical and geochemical properties is achieved through advances in sensor technologies, modeling, and well placement. However, the biotic composition within the subsurface is also an important component that adds an additional biochemical contribution not currently being assessed. Remedial agent(s) and the long-chain surfactants used to provide the foam-delivery media will come into contact with, not only the targeted contaminant plume, but indigenous microorganisms as well.

Microorganisms almost never exist as single species in nature, but as integrated communities that process available nutrient resources which impact their environment. There is little information for understanding the community dynamics that maintain stable metabolic outputs or produce changes in the environment. Microorganisms adhere directly to surfaces and are the initial contact surface between solid and fluid phase environments. Changes in the environment have impacts to the composition of microbial communities at this solid/fluid phase interface.

The introduction of the remedial amendments may provide an abundant food source for microorganisms in the vadose zone and alter community dynamics. Such changes to the microbial community composition may have dramatic effects on bulk community biochemistry, which in turn may affect the quality of the remedial treatment in terms of effectiveness and transport through the altered environment. Data are needed to enable quantitative field-scale measurement and modeling capabilities of subsurface microbial communities in the vadose zone for baseline characterization, monitoring of treatment impacts, and long-term monitoring of environmental stability. Moreover, baseline assessment of microbial community structure with depth across the remedial area will be compared with relative geochemistry to determine profiling of community composition with available environmental resources. Introduction of remedial and delivery agents will likely cause short-term community changes that can be monitored and assessed concomitant with contaminant fate and transport. Continued monitoring of community shift and stabilization will also be compared with contaminant tracking to assess effectiveness of remedial treatment and reaction of community dynamics. This profiling can be performed rapidly at the point source, and at downstream gradients where microbial community changes may occur in advance of measurable geochemical metrics, thereby, providing an highly sensitive "warning" of possible changes in contaminant plume behavior or the need for additional in situ remediation.

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REFERENCES

1. Ward, AL, GW Gee, ZF Zhang, and JM Keller. 2004. "Vadose Zone Contaminant Fate-and-Transport Analysis for the 216-B-26 Trench." PNNL-14907, Pacific Northwest National Laboratory, Richland, Washington.
2. Bikerman, JJ. 1973. *Foams*, Springer-Verlag, New York.
3. Kovscek, AR and HJ Bertin. 2003. "Foam Mobility in Heterogeneous Porous Media: (II: Experimental observations). "*Trans. Porous Med*. 52:37-49.
4. Schramm, LL and F Wassmuth. 1994. *Foams: Basic Principles. In Foams - Fundamentals and Applications in the Petroleum Industry*, American Chemical Society, Washington, DC.
5. Jeong, SW, MY Corapcioglu, and SE Roosevelt. 2000. "Micromodel Study of Surfactant Foam Remediation of Residual Trichloroethylene." *Environ. Sci. Technol.* 34:3456-3461.
6. Schramm, LL. 2005. *Emulsions, Foams, and Suspensions.* Wiley-VCH Verlag, GmbH & Co., Morlenbach, Germany.
7. Alargova, RG, DS Warhadpande, VN Paunov, and OD Velev. 2004. "Foam Superstabilization by Polymer Microrods." *Langmuir* 22:10371-10374.
8. Kim, S, H Barrazza, and OD Velev. 2009. "Intense and Selective Coloration of Foams Stabilized with Functionalized Particles. "*J. Mat. Chem*. 19:7043-7049.
9. Larmignat, S, D Vanderpool, HK Lai, and L Pilon. 2008. "Rheology of Colloidal Gas Aphrons (Microfoams)." *Colloids and Surfaces A-Physicochemical and Engineering Aspects* 322(1-3):199-210.
10. Lim, KS, and M Barigou. 2005. "Ultrasound-Assisted Generation of Foam." *Ind. Eng. Chem. Res*. 44:3312-3320.
11. Sebba, F. 1971. "Microfoams - an Unexploited Colloidal System." *J. Coll. Interface Sci.* 35:643-646.
12. Sebba, F. 1985. "An Improved Generator for Micron-Sized Bubbles." *Chem. Ind.* 3:91-92.
13. Sebba, F. 1994. *Foams and Biliquid Foams - Aphrons.* John Wiley, New York.
14. Tsai, YJ, FC Chou, and SJ Cheng. 2009. "Using Tracer Technique to Study the Flow Behavior of Surfactant Foam," *J. Haz. Mat*. 166:1232-1237.
15. Wan, J, S Veerapaneni, F Gadelle, TK Tokunaga. 2001. "Generation of Stable Bubbles and Their Transport through Porous Media." *Water Resources Research* 37:1173-1182.
16. Wege, H, S Kim, VN Paunov, Q Zhong, and OD Velev. 2008. "Long-Term Stabilization of Foams and Emulsions with in-Situ Formed Microparticles from Hydrophobic Cellulose." *Langmuir* 24:9245-9253.
17. Wheatley, MA, and S Singhal. 1995. "Structural Studies on Stabilized Microbubbles: Development of a Novel Contrast Agent for Diagnostic Ultrasound." *Reactive Polymers* 25:157-166.
18. Mulligan, CN and F Eftekhari. 2003. "Remediation with Surfactant Foam of Pcp-Contaminated Soil." *Eng. Geol* 70:269-279.
19. Rothmel, RK, RW Peters, E St. Martin, and MF Deflaun. 1998. "Surfactant Foam/Bioaugmentation Technology for in Situ Treatment of Tce-Dnapls." *Environ. Sci. Technol.* 32:1667-1675.
20. Roy, D, RR Kommalapati, KT Valsaraj, and WD Constant. 1995. "Soil Flushing of Residual Transmission Fluid: Application of Colloidal Gas Aphron Suspensions and Conventional Surfactant Solutions." *Water Research* 29(2):589-595.
21. Wang, A, and CN Mulligan. 2004. "An Evaluation of Surfactant Foam Technology in Remediation of Contaminated Soil." *Chemosphere* 57:1079-1089.
22. Szecsody, JE, MD Williams, CA Burns, DC Girvin, RC Moore, JP Mckinley, JS Fruchter, MJ Truex, VR Vermeul, JL Phillips. 2007. "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.
23. Zhong, L, NP Qafoku, JE Szecsody, PE Dresel, and ZF Zhang. 2009. "Foam Delivery of Calcium Polysulfide to the Vadose Zone for Chromium(Vi) Immobilization: A Laboratory Evaluation." *The Vadose Zone Journal* 8: 976-985.
24. Zhong, L, JE Szecsody, DM Wellman, F Zhang, S Mattigod, and E Pierce. 2009.
25. Chowdaiah, P, BR Mishra, JJ Kilbane II, VJ Srivastava, and TD Hayes. 1998. "Foam Propagation through Soils for Enhanced In-situ Remediation." *J. Haz. Mat*. 62:265-280.
26. Wellman, DM, EM Pierce, DH Bacon, M Oostrom, KM Gunderson, SM Webb, CC Bovaird, E Cordova, ET Clayton, KE Parker, RM Ermi, SR Baum, VR Vermeul, and JS Fruchter. 2008. "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.

27. Rubin, Y and S Hubbard. 2005. *Hydrogeophysics*, *Water and Science Technology Library*, Springer, Netherlands.

28. Hubbard, S, JE Peterson, E Majer, PT Zawislanski, J Roberts, KH Williams, and F Wobber. 1997. "Estimation of Permeable Pathways and Water Content Using Tomographic Radar Data." *The Leading Edge of Exploration* 16(11):1623-1628.

29. Kowalsky, MB, S Finsterle, J Peterson, S Hubbard, E Majer, A Ward, and G Gee. 2005. "Estimation of Field-Scale Soil Hydraulic and Dielectric Parameters through Joint Inversion of Gpr and Hydrological Data." *Water Resources Research* 41(W11425).

30. Hubbard, SS, K Williams, M Conrad, B Faybishenko, J Peterson, J Chen, P Long, and T Hazen. 2008. "Geophysical Monitoring of Hydrological and Biogeochemical Transformations Associated with Cr(Vi) Biostimulation." *Environmental Science & Technology* 42 (10):3757–3765.

31. Williams, K, A Kemna, M Wilkins, J Druhan, E Arntzen, L N'guessan, P Long, S Hubbard, and J Banfield. 2009. "Geophysical Monitoring of Coupled Microbial and Geochemical Processes During Stimulated Subsurface Bioremediation." *Environ. Sci. Technol*. 43(17):6717-23.

32. Williams, KH, D Ntarlagiannis, LD Slater, A Dohnalkova, SS Hubbard, and JF Banfield. 2005. "Geophysical Imaging of Stimulated Microbial Biomineralization." *Environ. Sci. Technol*. 39(19):7592-7600.

33. Englert, A, SS Hubbard, KH Williams, L Li, and CI Steefel. 2009. "Feedbacks between Hydrological Heterogeneity and Bioremediation Induced Biogeochemical Transformations." *Environ. Sci. Technol.* 43(14): 5497-5204.

34. Li, L, CI Steefel, KH Williams, MJ Wilkins, and SS Hubbard. 2009. "Mineral Transformation and Biomass Accumulation During Uranium Bioremediation at Rifle, Co." *Environ. Sci. Technol*. 43(14):5429-5435.

35. Topp, CG, JL Davis, AP Annan. 1980. "Electromagnetic Determination of Soil Water Content: Measurements in Coaxial Transmission Lines." *Water Resources Research* 16(3):574-582.

36. Peterson, JE. 2001. "Pre-Inversion Processing and Analysis of Tomographic Radar Data." *Journal of Environ. Eng. Geophysics* 6(1):1-18.

37. Davis, JL, and AP Annan 1989. "Ground Penetrating Radar for High Resolution Mapping of Soil and Rock Stratigraphy." *Geophysical Prospecting* 37(5):531-551.

38. Binley, A, and A Kemna. 2005. Hydrogeophysics, Springer, Dordrecht, Dc Resistivity and Induced Polarization Methods. It seems like something is missing here.

39. Archie, G. 1942. "The Electrical Resistivity Log as an Aid in Determining Some Reservoir Characteristics." *Trans. Amer. Inst. Mining Metallurgical and Petroleum Engineers* 146:54-62.

40. Chen, JD, A Kemna, and S Hubbard. 2008. "A Comparison between Gauss-Newton and Markov-Chair Monte Carlo-Based Methods for Inverting Spectral Induced-Polarization Data for Cole-Cole Parameters." *Geophysics* 73(6): F247-F259.

41. Wu, Y, SS Hubbard, K Williams, and J Ajo-Franklin. 2010. "On the Complex Conductivity Signatures of Calcite Precipitation." *J. Geophys. Res*. 115: G00G04.

42. Chen, J, SS Hubbard, KH Williams, S Pride, L Li, and L Slater. 2009. "A State-Space Bayesian Framework for Estimating Biogeochemical Transformations Using Time-Lapse Geophysical Data." *Water Resources Research* 45: W08420.

43. Williams, JM, B Rowland, MT Jeffery, GS Groenewold, AD Appelhans, GL Gresham, and JE Olson. 2005. "Degradation Kinetics of Vx on Concrete by Secondary Ion Mass Spectrometry" *Langmuir* 21:2386-2390.

44. Gracia, A, G Morel, P Saulner, J Lachaise, and S Schecter. 1995. "The z-Potential of Gas Bubbles." *Journal of Colloid and Interface Science* 172:131-136.

45. Yang, C, D Tedeusz, D Li, J Czarnecki, and JH Masliyah. 2001. "Measurement of the Zeta Potential of Gas Bubbles in Aqueous Solutions by Microelectrophoresis Method." *Journal of Colloid and Interface Science* 243: 128-135.