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# Research Plan: Foam Delivery of Amendments to the Deep Vadose Zone for Metals and Radionuclides Remediation

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March 2009



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## Executive Summary

Research proposals were submitted to the Scientific and Technical Basis for In Situ Treatment of Metals and Radionuclides Technical Working Group under the auspices of U.S. Department of Energy (DOE) Environmental Management Office (specifically, EM-22). After a peer review and selection process, the proposal, “Foam Delivery of Remedial Amendments to Deep Vadose Zone for Metals and Radionuclides Remediation,” submitted by Pacific Northwest National Laboratory (PNNL) was selected for funding. A research plan was requested for this EM funded project and is provided in this document.

The overall objective of this project is to develop foam delivery technology for the distribution of remedial amendments to deep vadose zone sediments for in situ immobilization of metal and radionuclide contaminants. The focus of this research in FY 2009 is on the physical aspects of the foam delivery approach. Specific objectives are to 1) study the foam quality (i.e., the gas volume fraction in foam) influence on foam injection pressure, 2) study the sediment permeability influence on injection pressure, 3) investigate liquid uptake in sediment and determine whether a water front will be formed during foam delivery, 4) test amendment delivery distance (and mass) by foam from the injection point, 5) study enhanced sweeping over heterogeneous systems (i.e., low K zones) by foam delivery relative to water-based delivery under vadose zone conditions, 6) numerically simulate foam delivery processes in the vadose zone, and 7) identify techniques to monitor foam-delivery performance. Laboratory-scale experiments will be conducted at PNNL to study a range of basic physical aspects of the foam propagation in sediments including foam quality and sediment permeability influence on injection pressure, liquid uptake, and foam sweeping across heterogeneous systems. This study will be augmented with separate studies to be conducted at MSE Technology Applications, Inc. to evaluate foam transport and amendment delivery at the intermediate-scale. The results of intermediate-scale tests will be used to bridge the gap between the small-scale foam transport studies and the field-scale demonstration. Numerical simulation studies on foam delivery under vadose conditions will be performed at PNNL to simulate observed foam transport behavior under vadose zone conditions and predict foam delivery performance at field scale. A critical evaluation of existing approaches and technologies, and identification of less developed approaches providing the technical basis for monitoring the performance of foam-based delivery of remedial amendments, will be conducted at Idaho National Laboratory.



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## 1.0 Introduction

Delivery of remedial 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 permeable (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. Second, the wetting front of a water-based delivery can readily mobilize contaminants with high mobility retained in the vadose zone sediments. This potentially enhances contaminant transport to the underlying aquifer before it interacts with the amendment.

Surfactants can be used to lower the surface tension of liquids; therefore, liquids can be mixed with gases to generate foams. Foams display vastly different properties from the liquids used to produce the foam. Foam is a two-phase system where gas cells are separated by thin liquid films. The simultaneous injection of surfactant and gas (foam) enhances the delivery efficiency of remedial amendments when injected through unsaturated, heterogeneous environments. The flow of foam through a vadose zone environment can be directed by pressure gradient in the sediments rather than being dominated by gravity. The low volume of liquid in foam (usually < 3% vol.) required for remedy delivery and emplacement enables mitigation of contaminant mobilization from the vadose zone.

Foam delivery can potentially distribute remedial amendments to the deep vadose zone for site remediation with minimal change in water content and can achieve relatively more uniform distribution. Development of amendment foam delivery technology is proposed for vadose zone metals and radionuclides remediation. This technology development will be a multiple step process—demonstrating the physical feasibility of using foam transport in the vadose zone for amendment distribution is the first step. Foam injection pressure as a function of foam quality and sediment air permeability, foam sweeping behavior over heterogeneous systems, and the amendment/liquid distribution in the foam-swept zones will be studied and evaluated in the first stage of development. These initial studies are the focus of this research plan. The results will be used to evaluate the physical aspects of foam delivery for vadose zone remediation. The study and optimization of the interactions of remedial amendments with foaming reagent, vadose zone sediments, and target contaminants will be performed in future projects. The most effective amendment delivery approach can therefore be developed. Development of a numerical model that can be used to simulate and predict foam delivery performance at the field-scale will be carried out before this technology is applied in field deployment.

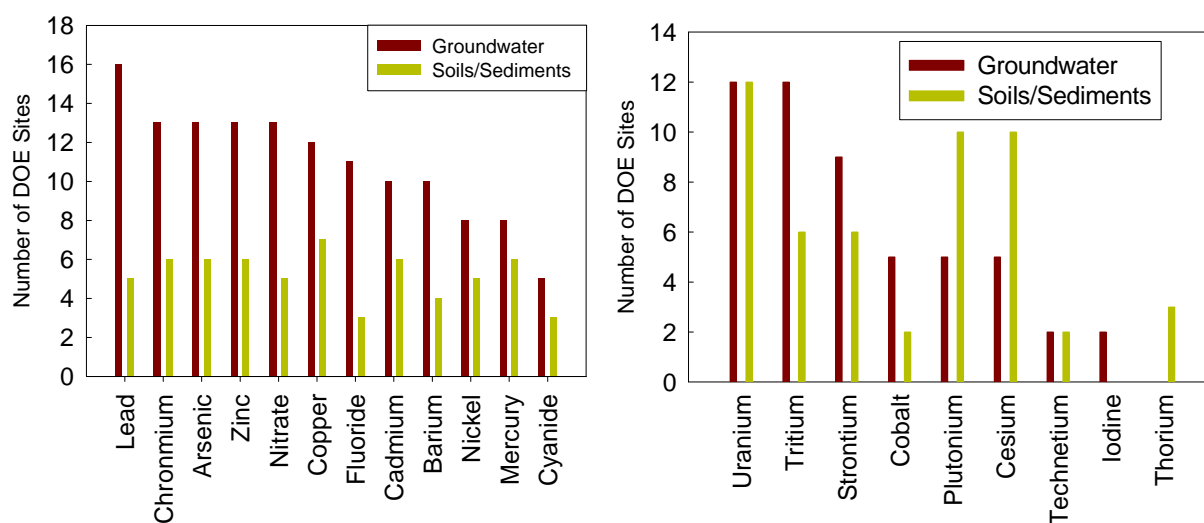
After discussing the background of vadose zone metals and radionuclides remediation and the advantages of using foam flow for the delivery of amendments to the vadose zone, this research plan describes the work elements associated with research on the physical aspects of foam delivery of remedial amendments to the vadose zone for metals and radionuclides remediation, including laboratory-scale experiments and intermediate-scale testing. The initiation of a numerical simulation study is also described. The chemical interactions between the remedial amendments and foaming reagents, sediment minerals, and target contaminants will be studied in future research.



## 2.0 Background

### 2.1 Vadose Zone Metals and Radionuclides Remediation

Nuclear fuel and weapons production have resulted in a legacy of subsurface contamination across the U.S. Department of Energy (DOE) complex. The DOE manages approximately 79 million cubic meters of contaminated solid media (primarily soils and sediments) and 1,800 million cubic meters of contaminated water (mostly groundwater) (DOE 1997) at 64 environmental management sites in 25 states including Colorado (Rocky Flats), Florida (Pinellas), Idaho (Idaho Site), Kentucky (Paducah), Ohio (Fernald, Mound, and Portsmouth), South Carolina (Savannah River Site), Missouri (Weldon Springs), Nevada (Nevada Test Site), Tennessee (Oak Ridge), Texas (Pantex), Utah (Fry Canyon), and Washington (Hanford Site). Figure 2.1 presents the metals and radionuclides most commonly reported in sediments and groundwater (Riley et al. 1992). Disposition of metal and radionuclide contaminants is generally related to process containment facilities such as tanks, cribs, trenches, and process ponds located at or within the ground surface. Many of these containment facilities have been breached or failed resulting in migration of metals and radionuclides into the vadose zone. Primary vadose zone metal and radionuclide contaminants include technetium-99 (Tc-99), uranium, strontium-90, plutonium, and chromium.



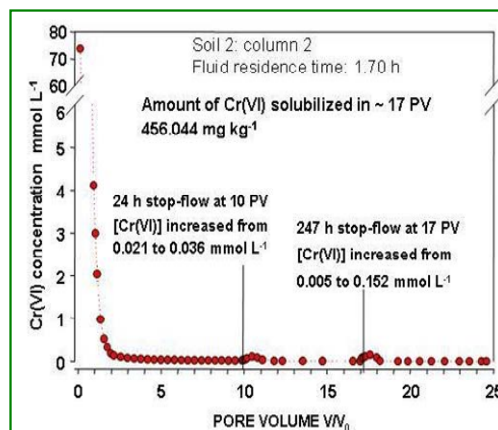
**Figure 2.1.** Plot of the Frequency of Select Metal and Radionuclide Contaminants at DOE Sites

Due to the mobility of the contaminants, vadose zone metals and radionuclides remediation is critical to stop groundwater contamination sourcing from the vadose zone and to prevent contaminants from migrating to nearby surface waters. It is well acknowledged that remediating vadose zone sites contaminated with metals and radionuclides presents one of the greatest challenges within the field of environmental remediation. A National Research Council (2001) report recognized that much of the contamination in the vadose zone at DOE sites will not be removed by any active remediation efforts due to the high cost and technological limitations. Alternatively, in-situ stabilization is expected to become one of the most important remediation strategies. This is particularly true in the deep vadose zone. Chemical fixation, including direct reaction, chemical induced precipitation and co-precipitation, and sorption to precipitates, is the most commonly used approach for metals and radionuclides in-situ

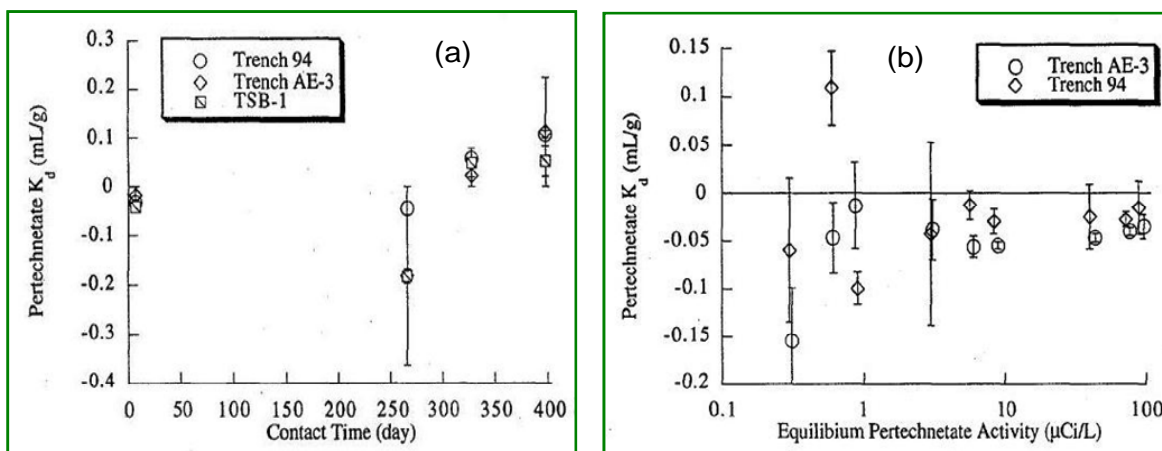
immobilization (Moore et al. 2001, Yang et al. 2007, Szecsody et al. 2007, Wellman et al. 2007). Innovative delivery approaches for in-situ treatment of specific metals and radionuclides in subsurface environments are a critical need for remediation of vadose zone contamination.

## 2.2 Water-based Amendment Delivery

Injection or infiltration of chemical solutions into the vadose zone is the conventional approach for amendment delivery. However, uniform delivery of the solutions to the heterogeneous vadose zone, especially to the deep vadose zone, is a challenge because the injected liquid preferentially percolates through the high- permeable pathways but can travel into low- permeability zones at low infiltration rates. What is generally observed in the field is vertical migration in high K zones and lateral migration deeper in the vadose zone (lower infiltration rates at this point) in low K zones (Ward et al. 2004). Furthermore, mobile contaminants retained in the vadose zone sediments are easily mobilized by the flushing of water-based solution. As shown in Figure 2.2, at least 95% of Cr(VI) was leached out in the first two pore volumes of flushing. This mobilization will form a significant Cr(VI) moving front during the solution injection (Hanson et al. 1993). The movement of this front is out of control and may cause a spread of contamination, consequently causing significant contamination to the underlying aquifer. The significant mobilization problem with Tc-99 will be as serious due to its high mobility. The adsorption distribution coefficient ( $K_d$ ) for the pertechnetate anion ( $^{99}\text{TcO}_4^-$ ) in Hanford sediments at neutral to slightly alkaline pH is nearly zero or even negative due to anion exclusion effects, as illustrated in Figure 2.3 (Kaplan et al. 1996), indicating Tc-99 simply stays in the pore water and is not sorbed to the soil in the vadose zone. Once the pore water is mobilized by the injected solution, it moves downwards to the aquifer.



**Figure 2.2.** Column Leaching of Cr(VI) from Vadose Zone Sediments Collected from a ~40-year Old Spill Zone at the Hanford Site (Dresel et al. 2008).



**Figure 2.3.** Pertechnetate Distribution Coefficient ( $K_d$ ) Values of Hanford Sediments as a Function of Contact Time (a) and Solution Pertechnetate Activity (b). (Kaplan et al. 1996)

In summary, the conventional water-based remedial amendment delivery approach to the vadose zone faces significant challenges. First, when the contaminants are mobile, the wetting front of a water-based delivery easily mobilizes these pollutants, thus potentially enhancing contaminant transport to the underlying aquifer before interaction with the amendment. Second, because the flow of solution infiltration is dominantly controlled by gravity and suction, preferential flow paths of the solution in the vadose zone are very difficult to overcome, resulting in bypassing of less permeable zones, which may contain the majority of contamination.

## **2.3 Foam-based Amendment Delivery**

In contrast to the 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. Foam is a shear, thinning fluid (Schramm and Wassmuth 1994, Kovscek and Bertin 2003) that provides improved sweeping efficiency when injected into heterogeneous systems. Furthermore, the limited amount of water (usually < 3% vol.) in foam minimizes the potential for contaminant mobilization. Foam-aided remedial amendment delivery technology could resolve both the uneven remedial fluid distribution and the significant contaminant mobilization front issues encountered in water-based delivery.

Foam is a disperse phase of gas in a liquid. 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 (Bikerman 1973). Surfactants are usually used as the foaming agent to lower the surface tension of the liquid to create and stabilize foam. Foam formation is a dynamic process, and foam is thermodynamically unstable. Aqueous surfactant foam is formed by dispersing non-wetting gas within a continuous surfactant-laden liquid phase. Foams may be created either by simultaneous injection of gas and liquid or by injection of alternating slugs of liquid and gas into porous media. Foam quality and stability are two important parameters used for foam characterization. Foam quality is defined as the percentage of gas volume in the total foam volume. Foam stability is usually measured by the volume or height change of foam in a container over time. Foam half-life is the time taken by the foam to reach half of its initial volume or height.

Foams display properties that are vastly different from the liquids used to produce them (Chowdiah et al. 1998). Simultaneous injection of surfactant and air will enhance the flooding efficiency of surfactant flushing even in a heterogeneous porous medium resulting in better sweeping efficiency over the contamination zone and higher contaminant removal (Jeong et al. 2000, Kovscek and Bertin 2003). The use of foam can also provide better control on the volume of fluid injected and the ability to contain the migration of contaminant-laden liquid (Chowdiah et al. 1998). The stability of foams is determined by the property of the foaming agent, such as surfactants (Zhong et al. 1998). Surfactant foam has been used to remove metal, organic, and nonaqueous phase liquids from contaminated soil (Mulligan and Eftekhari 2003, Wang and Mulligan 2004, Rothmel et al. 1998, Peters et al. 1994). However, a systematic study on the influence of foam quality, sediment air permeability, foam stability, and foam flow rate on the pressure gradient in soil is not available in the literature. Furthermore, foam has not been characterized as an amendment delivery vehicle for deep vadose zone remediation.

Preliminary research on amendment foam-delivery has been conducted under a Pacific Northwest National Laboratory (PNNL) Laboratory Directed Research and Development (LDRD) Program funded

project. Calcium polysulfide (CPS) was the remedial amendment to be delivered. Two surfactants, Steol CS-330 and Tween-80, were tested as the candidates for the foaming agent. 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, CPS concentration, and pH on foam stability. It was demonstrated that surfactant Steol CS-330 is a good foaming agent. Additionally, Dr. George Hirasaki at Rice University was consulted for the final selection of surfactant. Dr Hirasaki has decades of research experience on foam transport in porous media and foam application in the petroleum recovery and environmental remediation areas. He recently led a U.S. Department of Defense Strategic Environmental Remediation and Development Program project on the foam delivery of hydrogen to the saturated zones for enhanced bioremediation of chlorinated solvents (Hirasaki et al. 2005). Surfactant Steol CS-330 was selected as the foaming agent.

The stability of all foams decreased with increasing quality. Foam stability generally increases when the surfactant concentration in the foaming solution increases up to 1.5%. The increase in CPS concentration significantly decreased the foam stability. The decrease in pH of the foaming solution decreased the foam stability within a tested range between pH 11 and 7.5. More details can be found in Zhong et al. (2009).

Characterization of the physical aspects of foam transport in porous media is critical to the evaluation of the amendment foam-delivery remediation approach. These aspects include the foam quality/stability influence on foam injection pressure, the sediment air permeability influence on foam injection pressure, the sediment initial water content influence on water-front formation and liquid uptake in the sediment, and the distance the foam-delivery can achieve. No systemic studies have been conducted to address these issues. Additionally, numerical simulation on foam transport in the vadose zone is essential to predict foam-delivery performance at the field-scale before implementation.

### 3.0 Objectives

The overall objective of this project is to develop foam delivery technology for the distribution of remedial amendments to the deep vadose zone for in-situ immobilization of metal and radionuclide contaminants in the sediments. The focus of this research is on the physical aspects of remedial amendment foam delivery, the simulation of foam transport in the vadose zone, and identification of techniques to monitor the performance of foam delivery. Specific objectives include:

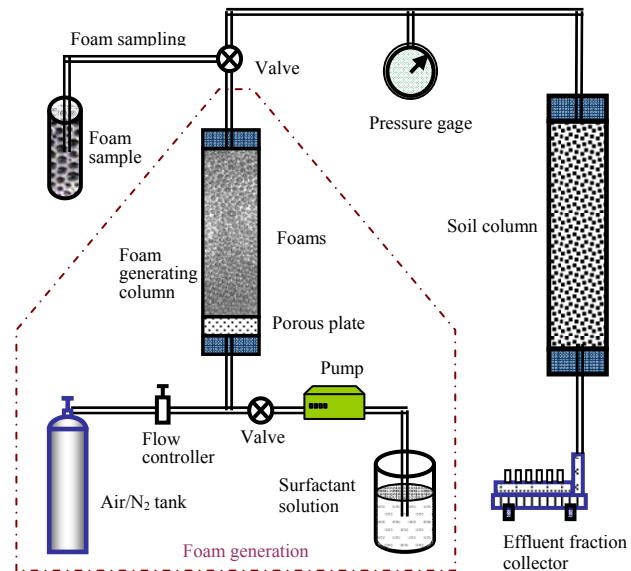
- Quantify the influence of foam quality on foam injection pressure in column tests (laboratory-scale tests: PNNL).
- Quantify the influence of sediment air permeability on foam injection pressure in column experiments (laboratory-scale tests: PNNL).
- Quantify the change in sediment moisture content as a function of the initial sediment water content and injection rate (laboratory-scale tests: PNNL) and evaluate whether a water front will be formed during foam injection (laboratory-scale tests: PNNL; intermediate-scale tests: MSE).
- Quantify the lateral extent of foam-based mass transport for remedial amendments (intermediate-scale tests: MSE).
- Study enhanced sweeping over heterogeneous systems by foam flushing under vadose zone conditions. The delivered fluid into zones with different permeability will be quantified to demonstrate enhanced sweeping (laboratory-scale tests: PNNL; intermediate-scale tests: MSE).
- Conduct a literature survey regarding simulation of foam transport in porous media to provide the technical basis for developing a numerical model to simulate foam transport in unsaturated media (modeling: PNNL).
- Identify techniques to monitor the spatial and temporal distribution of foam and amendments in the vadose zone during and after injection; provide a technical basis for monitoring the performance of foam-based delivery of remedial amendments (Monitoring: INL).





## 4.0 Research Plan

Laboratory-scale testing and intermediate-scale experiments will be conducted to study the physical aspects of foam delivery in vadose zone sediments. Laboratory-scale tests will be conducted at PNNL to study the foam quality and sediment air permeability impact on foam injection pressure, evaluate the influence of sediment particle size and size distribution on liquid uptake, investigate foam sweeping over heterogeneous systems, and test the delivery distance foam injection can achieve. The intermediate-scale tests will be conducted at MSE Technology Applications, Inc. and will be used to study foam delivery physical behavior at a larger scale. The focus of testing on a larger scale will be on enhanced sweeping of foam delivery in heterogeneous systems and the delivery distance. Modeling studies will be conducted at PNNL to simulate foam transport in the vadose zone.

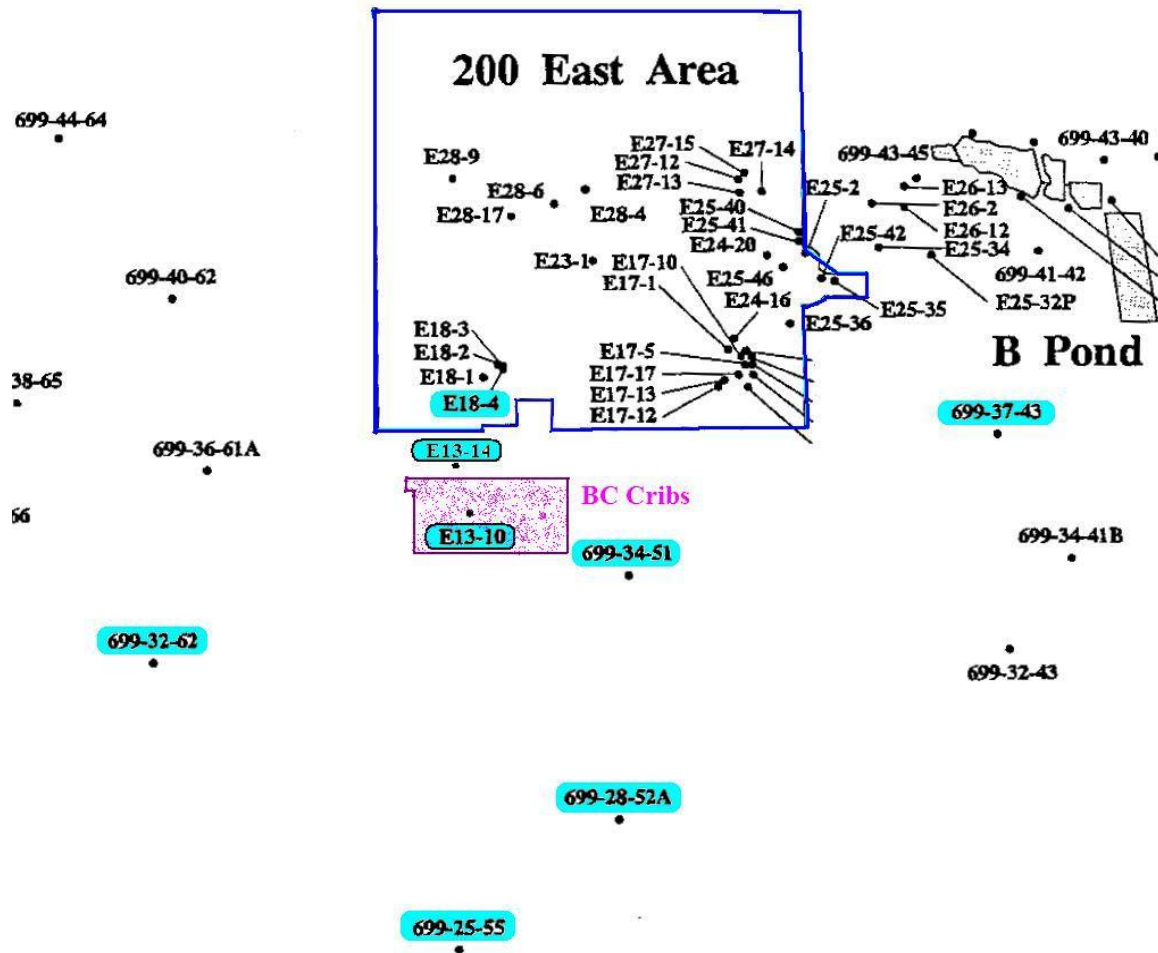


**Figure 4.1.** Schematic of Foam Generation and Foam Flood Column Experiment Setup

In the PNNL LDRD-supported project entitled “Foam Delivery of Calcium Polysulfide to Hanford Deep Vadose Zone for Cr(VI)/Tc-99 Remediation,” foaming solutions were identified, and a foam generation system was set up. In the EM-funded research described here, the same surfactant used in the LDRD project will be used, but no specific remedial amendment will be used in testing. The foaming system used in the LDRD project (Figure 4.1) will be used for the EM research and modified, if necessary, to meet specific goals of the EM project.

The surfactant to be used is sodium POE(3) laureth sulfate. This surfactant is produced by the Stepan Company (Northfield, Illinois) and received as STEOL CS-330 (3 EO). CS-330 contains 30% sodium lauryl ether sulfate,  $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2(\text{OCH}_2\text{CH}_2)_3\text{OSO}_3\text{Na}$ . It is a biodegradable, anionic surfactant with critical micelle concentration (CMC) at 4.19 mmol/L (0.18 wt%) (Rothmel et al. 1998) and has a surface tension of 32.2 dyne/cm.

Sediments with particle size distribution characteristics similar to that in the sediments in and around the Hanford Site BC Cribs Area will be used in this research. The particle size distribution data from eight boreholes in and around the BC Cribs Area (Figure 4.2) was collected and analyzed to obtain the range of the sediment particle size distribution in this area. The percentage of total gravel, fine pebble, very fine pebble, total sand, and total fines (silt/clay) was used in the analysis. Based on the particle size distribution analysis, three mixtures of sediments, K1, K2, and K3, were selected as the sediments to be used in this project (Table 4.1). The K2 mixture represents the average of the sediment particle size distribution and saturated hydraulic conductivity. The K1 and K3 sediments have saturated hydraulic conductivities of 10 times and 1 tenth of that of K2, respectively. The moisture retention characteristics and hydraulic conductivity of the sediments will be determined per PNNL technical procedure UFA-SK-01.



**Figure 4.2.** Locations of wells in and around the Hanford Site BC Cribs Area from which sediment particle size distribution data were used for sediment selection. The wells are highlighted in green. The complete names of E13-10, E13-14, and E18-4 are 299-E13-10, 299-E13-14, and 299-E18-4, respectively.

**Table 4.1.** Particle Size Distribution of Sediment Mixtures Selected for Tests of K1, K2, and K3

Particle Sizes (mm)	8~4 (%)	4~2 (%)	2~1 (%)	1~0.5 (%)	0.5~0.25 (%)	0.25~0.125 (%)	0.125~0.0625 (%)	<0.0625 (%)
<b>K1</b> ( $K=0.556^{(a)}$ ; $0.193^{(b)}$ cm/s)	56.8	31.1	4.6	3.4	1.9	0.8	1.0	0.4
<b>K2</b> ( $K=0.0568^{(a)}$ ; $0.0173^{(b)}$ cm/s)	12.8	22.0	25.6	27.1	8.0	1.8	1.1	1.6
<b>K3</b> ( $K=0.00567^{(a)}$ ; $0.00215^{(b)}$ cm/s)	0.4	8.5	14.3	19.2	22.0	21.1	6.0	8.5

(a) Saturated hydraulic conductivity estimated using modified Hazen formula

(b) Saturated hydraulic conductivity using modified Masch and Denny formula

## 4.1 Laboratory-Scale Testing

### 4.1.1 Foam Quality Influence on Injection Pressure

Pressure gradient in the sediment is one of the key considerations in the application of foam delivery. The surfactant concentration in the foaming solution influences the injection pressure for foam transport in porous media. Higher surfactant concentration resulted in stronger foams and higher injection pressure (Mannhardt and Svorstøl 2001). Based on the previous LDRD research results, 0.1 wt% surfactant concentration will be used in this project. Foam quality has a significant influence on the foam stability (Zhong et al. 2009). Therefore, foam quality affects the pressure gradient in foam flow as reported by Chowdiah et al. (1998) and Zhong et al. (2009). The foam injection pressure as a function of foam quality has to be studied for an effective foam delivery design.

Column experiments will be performed to test the foam quality influence on injection pressure. A glass column with dimensions of 30.48 cm long with a 2.54 cm internal diameter will be packed with K2 sediment with average permeability in the BC Cribs Area. Foams at qualities of 93%, 95%, 97%, and 99% will be injected into the column using a fixed injection rate. The same column with similar packing will be used for all the injections. The injection pressure, pressure gradient in the column, the injected liquid amount, and the foam wetted length in the column will be recorded by measurement of the volumetric water content for specified samples along the column length and the injection pressure at different locations along the column length. The tests are summarized in Table 4.2.

**Table 4.2.** Summary of Column Experiments for Injection Pressure vs. Foam Quality Testing

Test Name	Foam Quality <sup>(a)</sup>	Flow Rate (ml/min)
FQ-P-Col-1	93%	2.5
FQ-P-Col-2	95%	2.5
FQ-P-Col-3	97%	2.5
FQ-P-Col-4	99%	2.5
(a) Foam quality: percentage of gas volume in the total foam volume		

### 4.1.2 Sediment Air Permeability Influence on Injection Pressure

The response of injection pressure to the vadose zone sediment air permeability determines whether the foam delivery approach can be used at a specific site. Laboratory-scale column tests will be applied to study the relationship between air permeability and foam injection pressure. A column with dimensions of 30.48 cm long x 2.54 cm will be packed with the selected sediments (Table 4.3). The column will be flushed with foams of the quality to be dictated by the best results from the previous task. The same injection rate will be used in all the columns tests. The experiment layout is listed in Table 4.3. The injection pressure, the liquid uptake, and the foam wetted length in the column will be recorded during the tests.

**Table 4.3.** Summary of Column Experiments for Injection Pressure vs. Permeability Testing

Test Name	Sediments	Flow Rate (ml/min) and Foam Quality (%)
K-P-Col-1	Sediment K1	3.0 & TBD
K-P-Col-2	Sediment K2	3.0 & TBD
K-P-Col-3	Sediment K3	3.0 & TBD
K-P-Col-4	Sediment K4	3.0 & TBD

### 4.1.3 Liquid Uptake in Sediments and Water Front Formation

When foam flows through the sediment column, the bubbles break and the liquid phase is deposited to the sediment grains while the gas phase flows through the pore space. The liquid uptake in sediment determines the amount of the remedial reagent delivered to the contamination zone, which is a critical design parameter in remediation. Foam flow in the sediments is a fluid transport with low water content; therefore, foam delivery is expected to mitigate the mobilization of high mobility metals and radionuclides. However, if there is a water front formed ahead of the foam transport, the mobilization mitigation may not be achieved. Column experiments will be designed to study the liquid content change in sediments during foam flow and to determine whether a water front will be formed ahead of the foam sweeping zone. The influence of foam injection rate on the liquid uptake will be studied.

A transparent column with dimensions of 91.44 cm long and 2.54 cm will be packed with Hanford sediments mixture K2. Foams with the best quality (Table 4.1) will be injected at the rates listed in Table 4.4. The influence of the initial sediment water content on the liquid uptake will be tested. The wetting front in the sediment will be monitored visually and recorded. The injection will be stopped just before the wetting front reaches the column effluent end. The amount of injected liquid will be recorded during injection. The sediment across the column will be sampled for liquid content measurement to determine the liquid uptake and to verify the non-existing water front.

**Table 4.4.** Column Experiments for Liquid Uptake and Water Front Study

Test Name	Sediments/Water Content	Flow Rate (ml/min)
Uptake-Col-1a	Sediment K2/2%	2.0
Uptake-Col-1b	Sediment K2/4%	2.0
Uptake-Col-1c	Sediment K2/6%	2.0
Uptake-Col-2	Sediment K2/2%	4.0
Uptake -Col-3	Sediment K2/2%	8.0

### 4.1.4 Foam Sweeping over Vadose Zone Heterogeneous Systems

Foam has a shear thinning property that enables enhanced sweeping of foam flow across heterogeneous systems. Foam shear thinning has been applied extensively in the petroleum industry for enhanced oil recovery (Yan et al. 2006) and also utilized in aquifer remediation (Hirasaki et al. 1997). All the applications reported in the literature were under saturated conditions. The shear thinning

behavior of foam under unsaturated conditions has not been studied. Column tests and two-dimensional (2-D) flow cell experiments will be conducted to investigate foam shear thinning and enhanced sweeping behavior under vadose zone conditions.

#### 4.1.4.1 Parallel Column Tests

Two columns packed with sediments of different particle sizes will be tested in parallel. The most and the least permeable sediment mixtures, K1 and K3, will be packed in column 1 and 2, respectively. Foams will be forced into the columns through a common injection head. Pressure across each column and flow rate through each sediment pack will be monitored during the testing process until a steady state is reached in both columns. The effective viscosity of the foam in each column can be calculated using Equation 4.1 (Chowdiah et al. 1998); therefore, foam shear thinning behavior can be evaluated.

$$\mu_{eff} = \frac{kA}{q_{foam}} \frac{\Delta P}{\Delta L} \quad (4.1)$$

Where  $\mu$  is viscosity (cp),  $k$  is permeability (Darcy),  $q$  is flow rate (cm<sup>3</sup>/s),  $A$  is the column cross-section area (cm<sup>2</sup>),  $\Delta L$  is column length (cm), and  $\Delta P$  is pressure drop across the column (atm).

#### 4.1.4.2 Laboratory-Scale, 2-D Flow Cell Experiments

A flow cell with dimensions of 80 cm x 50 cm x 5 cm heterogeneously packed with sediments will be used in testing. Heterogeneity will be introduced by packing lenses/layers of sediments with permeability higher and lower than that of the matrix. Foam will be injected through one end of the flow cell and air will be pulled from the other end through an extraction well. The foam injection rate will be matched by the extraction rate. The foaming solution will be dyed to enhance visual observation of foam transport and the liquid wetting front (foam sweeping front).

The pressure gradient across the flow cell will be monitored through the tests. A dual-energy, gamma radiation system (Oostrom et al. 2003, Oostrom and Lenhard 2003) will be used to determine water saturations in the flow cell during the foam delivery experiments.

## 4.2 Intermediate-Scale Testing

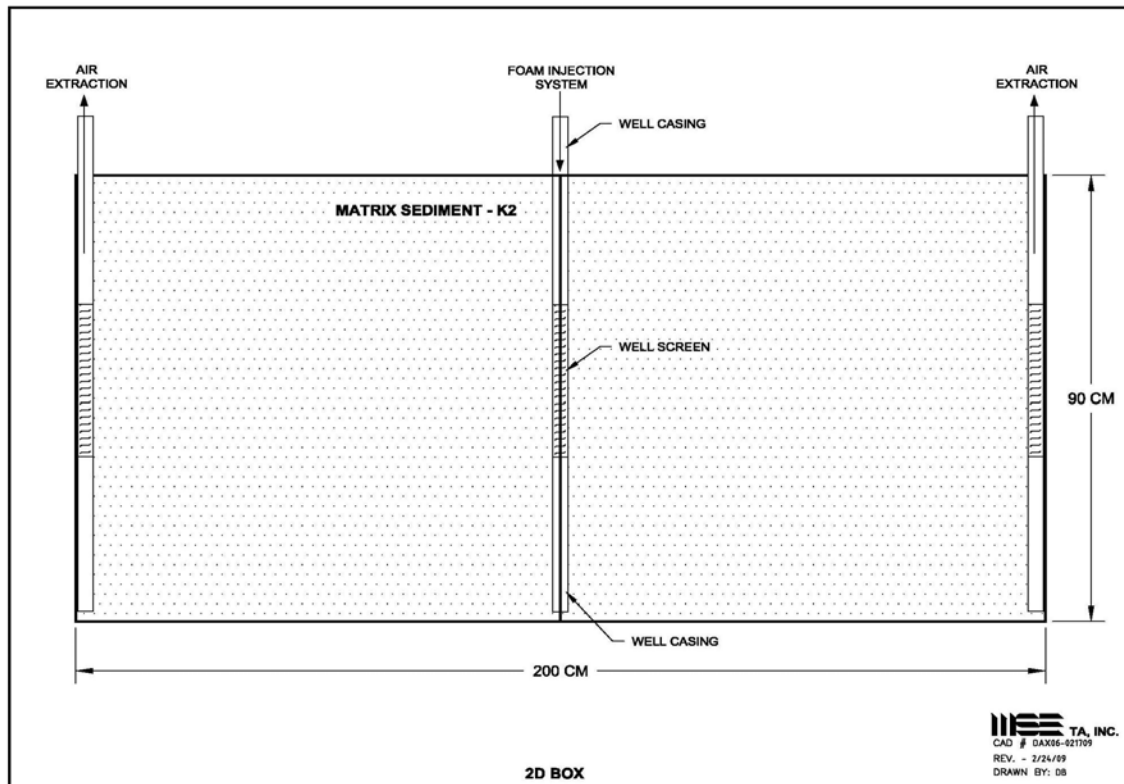
Intermediate-scale testing will be conducted at MSE using a separate funding source. The primary objectives of the intermediate-scale testing to be conducted at MSE are:

- Conduct foam injection test(s) using an appropriate test bed(s) to investigate the effects of sediment heterogeneities on the ability of foam to propagate through a sedimentary mass. This primary objective will be studied by visually observing the sweeping of the foam through the sedimentary material and collecting samples with associated analyses and instrument data to assist in the determination of several parameters specifically associated with the movement of foam. Among these parameters are:
  - changes in the injection pressure throughout the test period(s) at the point of injection into the test bed;

- the pressure gradient(s) established throughout the test bed during the testing periods;
  - the distribution of the moisture in the sediments during and after the test period(s);
  - the uptake of liquid from the foam by the sediment;
  - the extent of any water front formed during foam injection;
  - the ability of the foam to sweep through heterogeneous masses within the sediments; and
  - the effect of gravity on the propagation of the foam.
- Conduct injection test(s) using the foam as a carrier of a treatment reagent in appropriate test bed(s). These tests will investigate the effects of sediment heterogeneities on the ability of the foam to carry a treatment reagent through a sedimentary mass. In addition, these tests will determine the potential mobilization of a contaminant of concern by the foam and the ability of the treatment reagent to immobilize that contaminant of concern within the deep vadose zone. This objective will be studied by comparing the sweeping ability of the foam with the reagent to that without the reagent. The same data will be collected in these tests as were described above to assist in the determination of the aforementioned parameters associated with the movement of foam. In addition, to the samples and data collected earlier, samples of the sediments will be collected subsequent to the testing to ascertain the following information:
    - distribution of the treatment reagent throughout the mass of sediments
    - changes in mobility of the contaminants by interaction with the treatment reagent and foam-based reagent carrier.

#### **4.2.1 Two-Dimensional Test Bed Development**

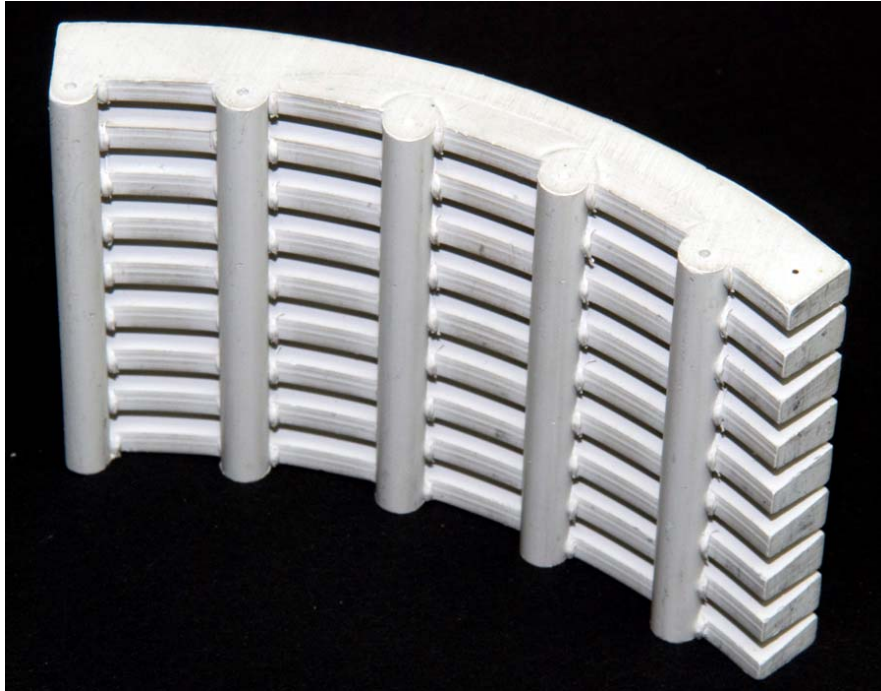
A test bed will consist of two closed boxes with overall dimensions of 200 cm long by 90 cm high by 15 cm wide. A frontal-view, schematic of the test bed is shown in Figure 4.3. This test bed will be divided vertically into two equal sized sub-boxes. The front wall of the closed boxes of the test bed will be constructed of transparent materials and have a removable lid to allow for the loading and sampling of the test bed. In addition each of the sub boxes will be surrounded by an external frame. This frame will be designed to provide the box with the ability to withstand the pressures that will develop during the testing sequence. Overall, the external box of the test bed will be designed to withstand an internal pressure of 61 kilopascals (Kpa) (10 psi) without excessive deformation and leaking.



**Figure 4.3.** Schematic diagram of the 2-D test bed

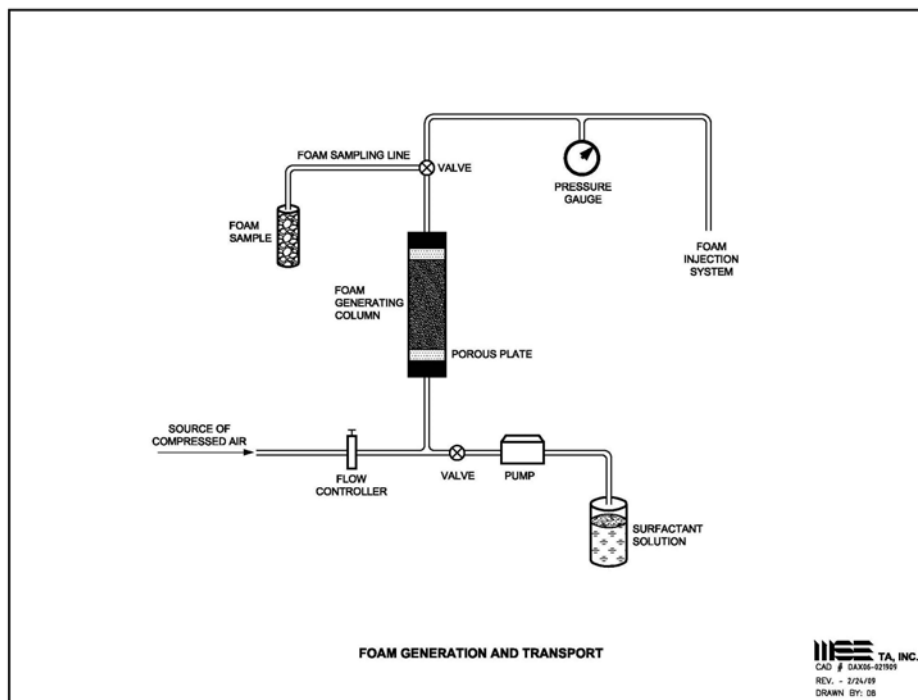
Each of the sub-boxes will have a foam injection configuration immediately adjacent to the central divider wall. This system will consist of three sections (Figure 4.3). The uppermost and lowermost sections will comprise a slice of well casing with a radius significantly larger than the width of the test bed. The center section will be formed of a well screen with a radius equal to the well casing (Figure 4.4). The size of the slots of the well screen will be defined by the grain size distribution of the sedimentary material in contact with the well screen.

The opposite end of each of the sub-boxes will be occupied by a foam/gas/fluid extraction configuration that will be composed of the same materials in the same orientation as the aforementioned injection configuration. Suction will be applied to this configuration so as to remove air, foam, and fluid from the test bed during testing. The foam/gas/fluid extraction system will also include a gas-fluid separating vessel to capture water-based fluids that are extracted from the test bed and to determine the volume of those fluids. By using this injection/extraction arrangement, it is intended that foam will be injected into and extracted from primarily the central, horizontal region of each sub-box.



**Figure 4.4.** Photograph of a Section of Representative Well Screen

In addition to the previously described aspects, the test bed will include two foam generating systems that will produce foam and deliver it to the foam injection configuration of each sub-box. This system will be similar to that shown in Figure 4.5 and will include devices to measure the injection pressure and injection rate of the foam and take samples of the foam before injection into the test bed.



**Figure 4.5.** Schematic Diagram of the Foam Generating System



A number of spigots will be incorporated into the back wall of the test bed. These devices will be used to acquire samples of the foam as it travels through the test bed sediment. Lastly, the test bed will include an appropriate instrumentation package for determining the real-time pressure gradient, moisture distribution, and ground potential within each sub-box during the testing sequences.

The instrument package will include pressure transducers, time domain reflectometry (TDR) probes, and electrodes near the injection and extraction configurations for determining the ground potential across the sub-box. The TDR probes, pressure transducers and ground potential electrodes will be designed to communicate with a personal computer (PC), which will be used as a data collection and retrieval system.

All of the penetrations of the sub-boxes, including spigots and instruments, will be located on the back of each sub-box to allow visual observations to be made at the front. The front section of each sub-box will be scored both vertically and horizontally to allow for a more quantitative visual assessment of foam movement.

It is planned that one complete 2-D test bed with two sub-boxes will be designed and constructed for the project. The test bed will be fabricated and constructed by MSE in accordance with the aforementioned design package.

#### **4.2.2 Acquisition of Sediments**

The quantity of sedimentary materials required for loading the 2-D test beds will be collected from an area chosen by PNNL that is immediately adjacent to the Hanford Site having uncontaminated sediments. PNNL will assist MSE with activities associated with the collection. The materials collected in the field will be screened to remove the larger cobble-sized material (greater than 64 mm) before packaging for shipment. The collected sedimentary material will be transported to the MSE Test Facility at Butte, Montana.

Once the collected sediments arrive at the MSE Test Facility, they will be thoroughly mixed and screened to remove remaining particles that are larger than 8 mm. This sediment will be considered as the matrix sediment denoted as K2 in Figure 4.3. The K2 sediment will be sampled and tested for moisture. The initial moisture content for the K2 sediment will be established as between 5 and 7%, which is appropriate for similar vadose zone sediments from the Hanford Site. If the material arriving from the field contains more moisture than the prescribed amount, it will be air-dried to reach the required moisture concentration. In addition, samples of the K2 material will be tested on MSE's ELE triaxial compression, saturated hydraulic conductivity permeameter to determine the permeability of the material. Once known, it will be used as the baseline permeability for the development of other sediment mixtures that will be used to develop heterogeneous zones within the test bed.

Two mixtures of heterogeneous sediments having ten-fold greater and ten-fold lesser permeabilities than the K2 sediment will be developed using grain size distributions produced by the formula developed by Masch and Denny (1966). Specific formulas for grain size distribution will be developed and documented to produce each of the heterogeneous mixtures. The first mixture (designated as K1) will be developed with permeability approximately 10 times the permeability of the K2 material and with an initial moisture content of between 3 and 5%. This value is also appropriate for similar vadose zone sediments from the Hanford Site. The second mixture (designated as K3) will be developed with permeability approximately one tenth of the permeability of the K2 material and with an initial moisture

content of approximately 10%. This value is again appropriate for similar vadose zone sediments from the Hanford Site. Once the K1 and K3 materials are developed, the permeabilities of these materials will be tested again using the permeameter. Should it be required, the grain size formula for each heterogeneous zone will be adjusted and new samples prepared and tested. Once the correct permeabilities have been realized, the grain size formulas will be used to produce the required amounts of each of the K1 and K3 mixtures.

#### **4.2.3 Test Bed Loading**

The initial testing sequence calls for the sub-boxes to be loaded in a homogenous manner with only K2 sediment. This material will be loaded into the test bed using the standard operating procedure (SOP) for packing the test bed. The subsequent testing sequences require that heterogeneous zones based on differences in permeability be developed within the test bed. In this case the test beds used for these tests will be loaded so that portions of the K1 and K3 heterogeneous zones are placed within the direct foam injection/extraction path of the test bed (see Figure 4.6).

The uranium-bearing hot spots will be produced by mixing an appropriate amount of uranium-rich calcite with a quantity of each sediment type as denoted in the SOP in Appendix B. The uranium-rich calcite will be produced by PNNL. Discussions between PNNL and MSE will define the concentration of the uranium in the calcite as well as the appropriate concentration of the calcite in the sediment for the development of representative hot spots. To prevent excess evaporation of moisture from the loaded test beds, the test beds will be sealed and the foam injection testing commenced as soon as reasonable after test bed loading.

#### **4.2.4 Surrogate Groundwater**

The dissolved chemistry of groundwater from the Hanford Site is presented in Table 4.5. These data will be used in formulation of the surrogate groundwater for use in the foam production. The surrogate groundwater that will be used for the testing will be prepared in the following manner. The reagent salts and amounts to make 25 L of surrogate groundwater are listed in Table 4.6.

1. Add 25 L of de-ionized water to an appropriate sized polyethylene tank and set up stirring apparatus.
2. Accurately weigh out each chemical reagent listed in Table 4.6 and transfer each weighed portion of reagent to the aforementioned container while stirring.
3. After all the reagents have appeared to dissolve, check the solution pH and specific conductance.

**Table 4.5.** Groundwater Chemistry of the Hanford Site

Analytes	Average Value	Units
HCO <sub>3</sub>	10.3	x 10 <sup>-4</sup> mol/L
CO <sub>3</sub>	0.11	x 10 <sup>-4</sup> mol/L
Calcium	5.97	x 10 <sup>-4</sup> mol/L
Bromide	6.23	x 10 <sup>-4</sup> mol/L
Magnesium	5.29	x 10 <sup>-4</sup> mol/L
Nitrate	5.71	x 10 <sup>-4</sup> mol/L
pH	8.05	standard units
Potassium	4.30	x 10 <sup>-4</sup> mol/L
Sodium	15.3	x 10 <sup>-4</sup> mol/L
Ionic Strength	59.3	x 10 <sup>-4</sup> mol/L
Sulfate	9.81	x 10 <sup>-4</sup> mol/L

After more than 24 hours recheck the solution pH and specific conductance. The surrogate is equilibrated in ambient air for at least 24 hours to reach saturation with calcium and stabilize the carbonate concentration. Solution pH and alkalinity may be adjusted if necessary by varying the amount of NaHCO<sub>3</sub> added to the solution.

**Table 4.6.** Reagents Used to Produce 25 L of Hanford Site Surrogate Groundwater

Reagent	Mass	Units
CaCl <sub>2</sub> •2H <sub>2</sub> O	12.68	Grams
CaCO <sub>3</sub>	17.75	Grams
Ca(NO <sub>3</sub> ) <sub>2</sub> •4H <sub>2</sub> O	23.25	Grams
MgSO <sub>4</sub> •7H <sub>2</sub> O	42.86	Grams
NaHCO <sub>3</sub>	12.68	Grams
H <sub>2</sub> SO <sub>4</sub> (concentrated)	10.79	Grams

#### 4.2.5 Two-Dimensional Foam testing

The 2-D testing is planned in test beds that are configured in the form of boxes that are each 200 cm long by 90 cm high by 15 cm wide. Each of the test beds will be divided into two sub-boxes 100 cm long by 90 cm high by 15 cm wide.

Before injection testing begins, a testing apparatus will be produced to determine the viability of acquiring samples of the foam from within the sub-boxes. This test apparatus will consist of a 15 cm long x 2.5 cm internal diameter tube with a sampling spigot penetrating the wall of the tube. The tube will be packed with sediment having a particle size of less than 2 mm. Foam of the same quality as will be used in the injection tests will be injected into the tube. As the foam is being injected into the tube, the

sampling spigot will be opened to collect samples of the foam from inside the tube. The flow rate of the foam from the spigot, as well as the foam quality from the spigot, will be determined. Once this test is completed, the viability of the foam sampling procedure will be examined and potentially altered as required. Should the foam sampling procedure be made viable, spigots will be applied to each sub-box for the acquisition of samples from within the sub-boxes.

A total of eight sub-box tests are planned, to be arranged into four tests. During each test, foam will be injected into each sub-box at a specific rate. The injection rate of foam will be matched by the extraction rate of air. Each test will be run until a quasi-steady state is reached. This quasi-steady state will be determined when the quantity of solution being extracted from the foam/gas/fluid extraction system does not change by more than 10% in one hour of operation. Due to the small quantity of water contained in the foam, the times required to reach the aforementioned quasi-steady state will be largely a function of the foam quality. As an example, if the injected foam is at a rate of 125 ml/min and a foam quality of 99%, the time required to reach a quasi-steady state is calculated to be greater than 85 hours. If the injected foam quality is 97%, the time required to reach a quasi-steady state is calculated to be greater than 30 hours. The foam quality that will be used in these tests will be determined through preliminary tests, as previously stated; once this factor is determined, it will be incorporated into the testing approach and a calculated time of injection will be determined. Relative to the length of time required for each test, the sequence of the testing is to load a set of sub-boxes, which will then be sealed and allowed to stand for 48 hours before the specific injection test.

The four tests will take place as follows:

- Test 1 – both of the sub-boxes will be loaded in a homogeneous manner with only K2 sediment. Foam will be injected into one of the sub boxes at a rate of 125 ml/min while air is extracted from that sub-box at a rate of 125 ml/min. Foam will be injected into the second sub-box at a rate of 250 ml/min while air is extracted at a rate of 250 ml/min. Due to the variation in the injection rate, the period of time required to reach the aforementioned quasi-steady state will be different for each sub-box. The sub-box that is injected at a rate of 250 ml/min will be tested for a period of time approximately one-half as long as the sub-box that is injected at a rate of 125 ml/min.
- Test 2 – both of the sub-boxes will be loaded primarily with K2 sediment. In addition, two rectangular heterogeneous zones (one zone with K1 sediment and one with K3 sediment) will be developed in each of the boxes. Foam will be injected into each of these sub-boxes simultaneously at a rate of 125 ml/min while air is extracted from both sub-boxes at a rate of 125 ml/min.
- Test 3 – both sub-boxes will be loaded in the same manner as in Test 2. Foam will be injected into each of these sub-boxes simultaneously at a rate of 125 ml/min while air is extracted from both sub-boxes at a rate of 125 ml/min. However, the foam for this test will contain a 9:1 mixture of sodium phosphate and sodium tripolyphosphate. The results of this test will support the development of foam-based delivery for remediation of radionuclides in the deep vadose zone, as well as support and integrate with the on-going investigation by the Hanford Central Plateau Remediation Contractor – Deep Vadose Zone Treatability Test Plan.
- Test 4 – both sub-boxes will be loaded in the same manner as in Test 2. In addition, eight known locations of each of the sediment masses will contain hot spots of known uranium concentration formed from mixing uranium rich calcite into the sediment mixture. Again, foam containing a 9:1 mixture of sodium phosphate and sodium tripolyphosphate will be injected into each of these sub-

boxes simultaneously at a rate of 125 ml/min while air is extracted from both sub-boxes at a rate of 125 ml/min.

The configuration of each of the sub-boxes associated with each of the tests is shown in Table 4.7.

The foam used in the testing will be produced by combining a biodegradable, anionic surfactant known as STEOL CS-330 with water and air. The active ingredient in CS-330 is a sodium salt of laureth sulfate. The surfactant will be dissolved in a surrogate groundwater to the required concentration (the specific concentration to be determined). The gas used to produce the foam will be air provided by the MSE service and instrument air system located in the test facility, which is capable of controlling the air moisture content. The injected foam will be colored with food coloring to enhance its visibility as it moves through the test bed sediment.

**Table 4.7.** Testing Sub-Box Configuration

Test	Sub-Box Orientation	Sediment Loading	Injection Extraction Rate ml/min	Treatment Reagent	Contaminant Hot Spots
1	Left	Homogenous	125	No	No
	Right	Homogenous	250	No	No
2	Left	Heterogeneous	125	No	No
	Right	Heterogeneous	125	No	No
3	Left	Heterogeneous	125	Yes	No
	Right	Heterogeneous	125	Yes	No
4	Left	Heterogeneous	125	Yes	Yes
	Right	Heterogeneous	125	Yes	Yes

#### 4.2.6 Measurements and Analyses

Before injection testing begins, samples of the final sediment mixtures for the K1, K2 and K3 materials will be submitted to PNNL for development of a moisture retention curve for each of the mixtures.

Numerous manual and automated measurements will be collected during and after each of the tests conducted within the project. These measurements will be acquired at a number of places within and adjacent to each test bed. Quantitative measurements that will be acquired throughout each of the testing sequences are:

- The concentration of surfactant in the foam generating fluid
- The surface tension of the foam generating fluid
- The flow rates of both the foam generating fluid and the foam producing gas
- The volume of foam generating fluid that is injected into the test bed
- The initial foam quality, stability and bubble size
- The injection pressure of the foam

- The pressure gradient throughout the test bed during the foam injection period
- The distribution of sediment moisture throughout the test bed during the foam injection period
- The position within the test bed of the foam wetting front
- The duration of the foam injection period
- The quality and stability of the foam within specific regions of the test bed during foam injection
- The foam quality, foam stability and bubble size of the foam being extracted from the sub-boxes during the tests
- The amount of treatment reagent (if any) reporting to the extraction system during those tests that include treatment reagent
- The amount of uranium (if any) reporting to the extraction system during those tests that include treatment reagent
- The rate of removal of materials from the extraction system of the test bed during foam injection.

Semi-quantitative and qualitative measurements that will be acquired throughout each of the testing sequences are:

- The sweeping characteristics of the injected foam within the sediments of the test bed as discerned by visual and digital video information
- The size of the bubbles within the foam at various positions within the test bed
- The possible production of an autunite mineral-like phase in the “hot spot” locations of test 4 by ultraviolet fluorescence.

Subsequent to each of the test sequences, the test beds will be disassembled and samples of the sediments taken. These sediment samples will be analyzed for a number of parameters depending on the specific test sequence.

- Test 1 and 2 – contained moisture and surfactant, moisture/surfactant retention curves
- Test 3 – contained moisture, surfactant and phosphate concentration
- Test 4 – contained moisture, surfactant, phosphate concentration and total and leachable uranium.

For manual measurements, each of the test time periods will be segmented into several measurement intervals (Table 4.8). Manual measurements that will be collected during each of the measurement intervals for each of the sub-boxes within each of the test pairs is shown in Table 4.9.

**Table 4.8.** Manual Measurement Intervals

Measurement Interval	Time After Initiating Foam Injection
1	0 minutes
2	30 minutes
3	1 hour

4	2 hours
5	4 hours
6	8 hours
7	24 hours
8	32 hours
9	48 hours
10	56 hours
11	72 hours
12	80 hours
13	96 hours

**Table 4.9.** Manual Test Measurements Collected During the Test Period

Measurement Interval	Injection Pressure	Inj. and Ext. Foam Quality	Inj. And Ext. Foam Stability	Inj. And Ext. Foam Bubble Size	Gas Flow Rate	Foam Solution Flow Rate	Extraction Rate	Extracted Solution Volume	Spigot Foam Quality	Spigot Foam Stability	Phosphate Concentration in Extracted Fluid	Uranium Concentration in Extracted Fluid
1	X	X	X	X	X	X	X					
2	X	X	X	X	X	X	X					
3	X	X	X	X	X	X	X	X	X	X	X	X
4	X	X	X	X	X	X	X	X	X	X	X	X
5	X	X	X	X	X	X	X	X	X	X	X	X
6	X	X	X	X	X	X	X	X	X	X	X	X
7	X	X	X	X	X	X	X	X	X	X	X	X
8	X	X	X	X	X	X	X	X	X	X	X	X
9	X	X	X	X	X	X	X	X	X	X	X	X
10	X	X	X	X	X	X	X	X	X	X	X	X
11	X	X	X	X	X	X	X	X	X	X	X	X
12	X	X	X	X	X	X	X	X	X	X	X	X
13	X	X	X	X	X	X	X	X	X	X	X	X

The instruments within each of the sub-boxes (time domain reflectometry devices and pressure sensors) will be connected to personnel PCs that will function as data collection and storage devices. These PCs will be programmed to collect data readings from each of the instruments within the sub-boxes at 30-min intervals beginning at the initiation of foam injection and lasting throughout each test period.

Table 4.10 contains information related to the qualitative and visual measurements that will be taken during each test.

**Table 4.10.** Qualitative and Visual Test Measurements Collected During the Test Period

Measurement Interval	Foam Wetting Front Location	Foam Bubble Size Determination	Zones of Foam Movement and Stagnation
1	X	X	X
2	X	X	X
3	X	X	X
4	X	X	X
5	X	X	X
6	X	X	X
7	X	X	X
8	X	X	X
9	X	X	X
10	X	X	X
11	X	X	X
12	X	X	X
13	X	X	X

In addition to those qualitative data collections denoted in Table 4.10, a digital video apparatus will be collecting continuous information throughout the period of each test. Subsequent to the completion of each test period, the test beds will be opened and sediment samples collected from within each sub-box. Several analytical measurements will be performed on each of the sediment samples collected from the sub-boxes. Table 4.11 provides the types and numbers of analyses that will be performed on the sediment samples after each test is completed. In addition, post-test sediment samples will be collected from each of the sediment zones and sent to PNNL for the determination of moisture/surfactant retention curves. By developing these curves subsequent to the injection of foam, the effects of the surfactant will be determined on the ability of the specific sediments to retain moisture.

**Table 4.11.** Post Test Measurements

Test	Sub-Box Orientation	Sediment Moisture	Sediment Surfactant Concentration	Sediment Phosphate Concentration	Sediment Total Uranium Concentration	Sediment Leachable Uranium Concentration
1	Left	24	24			
	Right	24	24			
2	Left	24	24			
	Right	24	24			



3	Left	24	24	24		
	Right	24	24	24		
4	Left	24	24	24	8	8
	Right	24	24	24	8	8

#### 4.2.7 Quantitative Measurements

Before sub-box testing begins, a series of foam-generating fluids will be produced. Each of these fluids will contain a known concentration of surfactant—1000 mg/L, 5000 mg/L, 10,000 mg/L, 15,000 mg/L and 20,000 mg/L. Samples of each fluid will be collected and sent to PNNL for analysis of the fluid surface tension.

The quantitative data collected for each test sequence will be tabulated versus the time of injection through the test period and, if appropriate, tabulated against the physical position of the specific sensor being read or sample collected. These data will be analyzed to discern definable trends that occurred throughout the test period. The injection pressure and pressure gradient within the test bed are direct measurements of the ease of injection of the foam and are also directly related to the foam quality. The variation in foam quality will be kept to a minimum throughout each of the test sequences. Should significant changes in the foam quality being injected into the test bed occur, the flow rates of the driving gas and the foam producing fluid will be adjusted to maintain the foam quality as near as possible to that initially being injected. Therefore, changes in the injection pressure and the pressure gradient should be directly relatable to changes in the foam permeability of the test bed. As the pores between the grains in the test bed fill with fluid and reduce the foam permeability of the sediments, the injection pressure should rise, and the orientation of the pressure gradient within the test bed should shift.

Changes in moisture within the test bed will be analyzed and related to the movement of the foam front and foam flow pattern(s) as each test progresses. Trends in the moisture distribution data will be used to discern the arrival of the foam wetting front at any point in the test bed and the presence, position, and extent of any water front that may form during foam delivery. These data will also be used to determine the extent of liquid uptake by the sediment. Data from post-test samples of the sediment will be used to augment the final position of the foam wetting front as well as any water front that may form during a test. This information will also be used to define and quantify the extent of the surfactant separation from the foam generating fluid and uptake by the sediments as well as the extent of liquid uptake by the sediment.

Samples of the foam collected from within the test bed will be analyzed for foam quality and foam stability. These data, along with qualitative data related to the size of the foam bubbles within various portions of the test bed, will be used to augment the conclusions reached. In addition, samples of the foam collected from the extraction configuration of each sub-box will be analyzed for foam quality, foam stability, and bubble size. These data will be used to augment the conclusions reached. In addition, these data will be used by the PNNL modeling group to develop a model describing the subsurface movement of foam.

For tests that involve the use of treatment reagents, the post-test sediment sample analyses will be used to determine the separation of the treatment reagent from the foam-generating fluid processes, which are related to the dispersive characteristics and the adsorptive characteristics of the reagent onto the

sediments. The use of a contaminant (uranium) as hot spots within the test bed during the final test sequence will allow determination of the ability of foam propagated reagents to react with adsorbed contaminants and reduce their mobility. Should the immobilized form of the contaminant be a fluorescent mineral-like species, the ability to qualitatively monitor that fluorescence will allow the development of that species to be monitored throughout the test sequence.

#### **4.2.8 Qualitative Measurements**

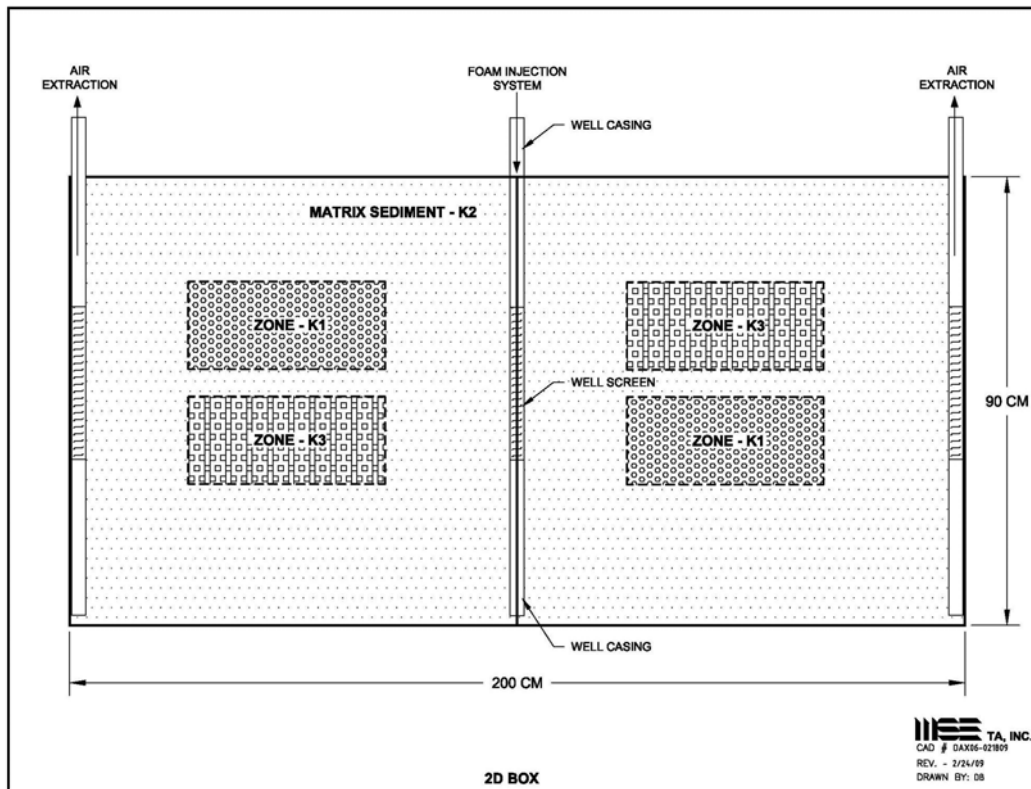
The qualitative data collected throughout the test sequences, including visual observations and semi-quantitative video data, will augment the quantitative data and the conclusions supported by that quantitative data. As was stated earlier, these qualitative data will also be tabulated through the test period. In much the same manner as the previously described positional data, the physical location of the foam wetting front will be tabulated versus the time of injection. The sweeping characteristics of the foam will also be denoted throughout the test period

#### **4.2.9 Sample Collection**

##### **4.2.9.1 Foam/Fluid Samples**

Samples of the foam before injection will be collected from the tube used to introduce the foam to the foam injection system. Approximately 25 mL of this foam will be collected at the appropriate times. The time required for the foam to collapse will be denoted and used to determine foam stability. The volume of liquid residual after the collapse of the foam and the initial foam volume will be used to determine the foam quality.

Samples of the foam will also be collected from the spigots located on the test beds. Approximately 10 mL of this foam will be collected from the spigots at the defined times.



**Figure 4.6.** Schematic Diagram of the Heterogeneously Loaded Test Bed

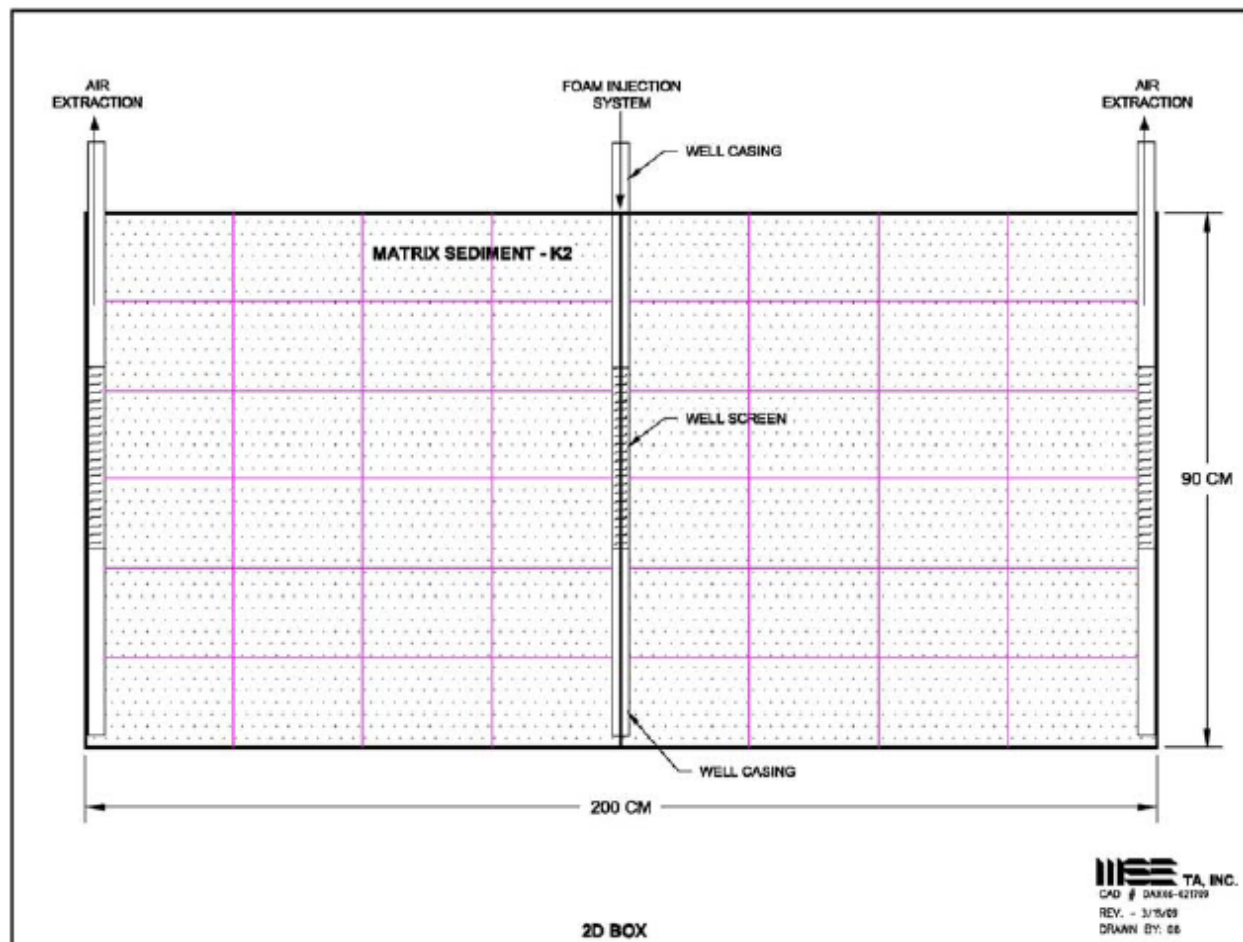
The time required for the foam to collapse will be denoted and used to determine foam stability. The volume of liquid residual after the collapse of the foam and the initial foam volume will be used to determine foam quality.

Samples of the extracted fluid will be collected from the sample collection device associated with the foam/gas/fluid extraction system and prepared for laboratory analysis of surfactant, phosphate, and uranium.

#### 4.2.9.2 Sediment Samples

Sediment samples will be obtained from the material within the test beds at the conclusion of each test. Once the test has been completed, the lid of the test bed will be removed and the sediment material from the proper sampling locations will be scooped out of the test bed with a clean sampling device. A sufficient mass of material will be collected to satisfy all the tests that will be performed on each sample. The sample will be placed into a clean, labeled, sealable plastic bag. Approximately 100 g of each sample will be removed from the sample bag and placed in a tared drying pan. The moist weight of each sample will then be recorded. The drying pans will then be placed in the drying oven, which will have been pre-heated to 40°C for a period of no less than 12 hours. The remaining portion of each sediment sample will be transferred to the MSE Analytical Laboratory for analysis.

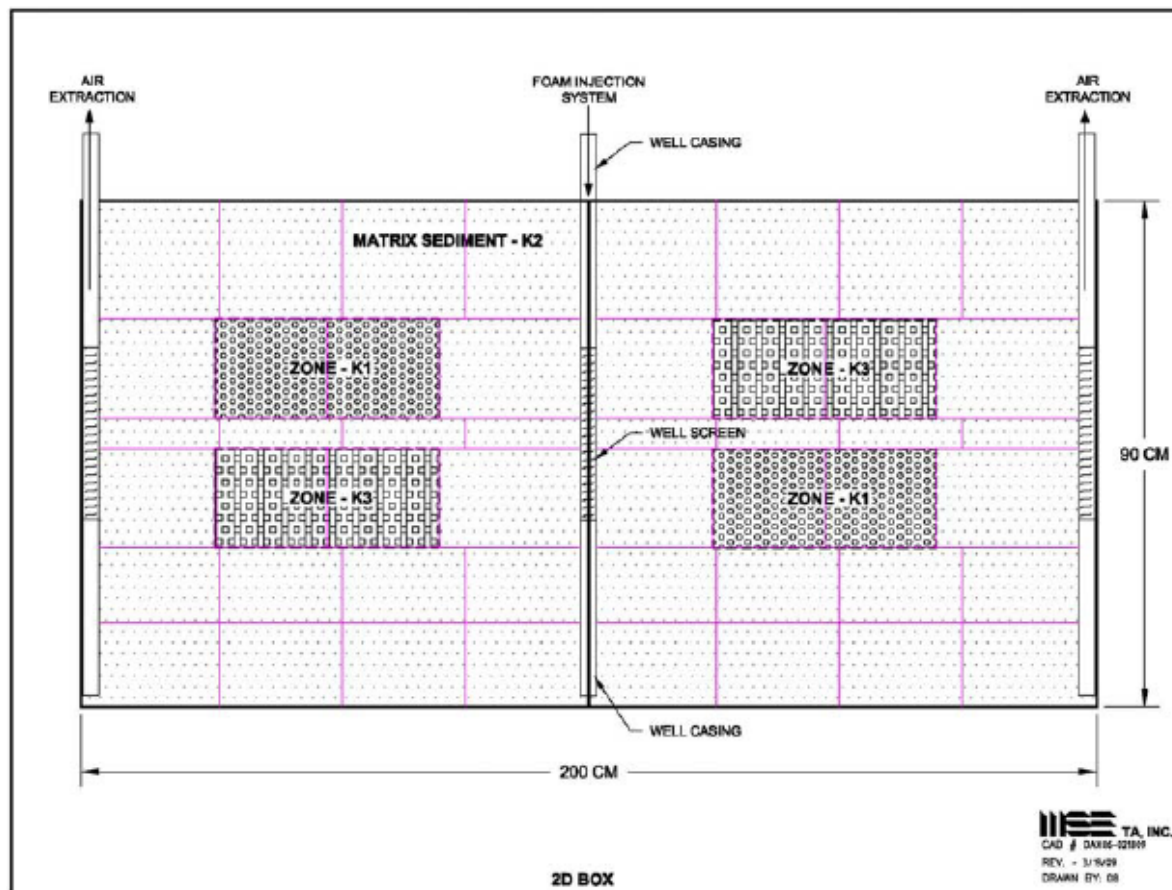
For the sub-boxes that are loaded homogeneously, four sediment samples approximately 15 cm long will be collected from each of six 15-cm-deep layers throughout each sub-box (Figure 4.7). The four samples will be taken from equidistant positions across the horizontal length of each sub-box. As such, 24 sediment samples will be taken from each of the homogeneously loaded sub-boxes. The final position of the foam wetting front within the sediment mass of the sub-box will determine the actual number of samples that are acquired. Should a portion of the sediment remain dry, that dry sediment will not be sampled. The final position of the foam wetting front will be determined before the post-test activities. Relative to this position, the actual number of samples that are taken will be at the discretion of the sampler.



**Figure 4.7.** Schematic Diagram Showing the Sample Positions for the Homogeneously Loaded Test Bed

For sub-boxes loaded heterogeneously, four sediment samples approximately 15 cm long will again be collected from each of six 15-cm-deep layers throughout each sub-box (Figure 4.8). The uppermost, central, and lowermost layers will be largely within K2 sediment, and as such, samples will be taken from equidistant positions across the horizontal length of each sub-box within those layers. For the layers that contain the heterogeneous zones, a single sample will be collected from the injection portion of the K2 sediment, two samples will be collected from within each of the heterogeneous zones, and a single sample will be collected from the extraction portion of the K2 sediment. For this sample collection scenario, a total of 16 samples will be collected from the K2 sediment and four each will be collected from the K1

and K3 sediments. Again, relative to the final position of the foam wetting front, the actual number of samples that are taken will be at the discretion of the sampler.



**Figure 4.8.** Schematic Diagram Showing the Sample Positions for the Heterogeneously Loaded Test Bed.

### 4.3 Foam Transport Simulation

A pertinent aspect of the delivery/remedial technology development is the ability to simulate foam transport. A variety of empirical and theoretical methods for modeling foam displacement are available in the literature. These include population-balance methods (Falls et al. 1988, Kovscek et al. 1995), percolation models (Rossen 1990, Rossen and Gauglitz 1990), fractional flow theories (Zhou and Rossen 1994), and semi-empirical alteration of gas-phase mobilities (Liu and Brigham 1992, Mohammadi et al. 1993). Of these four methods, only the population balance method and percolation models arise from first principles of mass conservation.

Much of the work on foam transport to date has been carried out in fully saturated systems and for the purpose of high recovery of petroleum. As noted in the literature, there are several challenges in developing conceptual and mathematical models for simulating foam transport (a non-Newtonian fluid) in porous media. Specifically, foam properties need to be characterized, which are dynamically dependent on foam and water velocities, and the viscosity of the foam. Furthermore, the surfactant concentration and type used to generate the foam and the interaction between foam and soil water can also impact foam properties. For example, trapped foam can block the channels that otherwise carry gas. During transport,

foam continuously breaks down and regenerates. The net rate of these two processes needs to be represented to model foam displacement.

A numerical challenge in simulating foam transport is the instability associated with the physical discontinuity occurring near the critical capillary pressure. In an unsaturated system, foam breaks down abruptly near the critical capillary pressure or saturation. This is an important issue in the development of the mathematical model. A recent publication by Kam (2008) presents an algorithm that utilizes the population balance approach and can deal with the instability and divergence issues associated with the physical discontinuity that occurs near the critical capillary pressure. This algorithm is more appropriate for foam transport in the vadose zone, in which the existence of critical pressure or saturation is common.

The tasks needed to develop a simulation capability for foam transport are listed below.

1. Develop the conceptual and mathematical models. The conceptual model will describe the foam generation, destruction, transport, trapping under different physical (e.g., pore size, permeability, and wetness) and operational (e.g., gas and water velocity) conditions. The mathematical model will describe the relationships between foam properties (e.g., quality, texture, and viscosity) with the soil properties and system conditions and the relationships for the kinetic processes of foam generation and destruction. Data resulting from the experiments in this work, as well as relationships identified in the literature, will be used to establish a set of differential equations for the transport of water, gas, and the dissolved surfactant. An additional differential equation will be used to describe the bubble population. The mass exchange between the foam and the liquid phase will also be considered.
2. Develop an analytical model for foam displacement. Analytical solutions will be developed for foam transport in homogeneous soil based on the piston-flow assumption. The solutions will describe the position of the foam front and the pressure distribution within the foam-occupied region. It is expected that the analytical solutions will be useful for examining the effects of different factors on foam transport, quick scoping analyses, and verifying numerical models.
3. Develop a numerical model for foam transport. Numerical experimentation is highly instructive for understanding the physics of foam displacement and allows for transport predictions to be made for conditions that extend beyond those used at the bench-scale. To obtain this capability, a mathematical model for foam transport can be incorporated into existing codes simulating the subsurface transport of gas and water. In this study, the water-air mode of STOMP (White and Oostrom 2006, Nichols, 1997) will be used for this purpose. Differential equations developed in Task 1 will be incorporated into the simulator, though only primary processes driving foam transport will be included. The method of the population balance equation in combination with the mass balance equations of gas, water, and surfactant will be used because they provide a general framework where the relevant physics of foam generation, coalescence, and transport can be expressed. Moreover, the equations in this method are similar to the mass balance equations already used in STOMP. It is anticipated that the foam simulation capability in STOMP will be used to help identify critical design parameters for both bench- and field-scale applications.
4. Perform verification studies. Once the equations have been incorporated into the STOMP simulator, verification testing will be performed based on the one-dimensional column experiments carried out in this study. Analytical solutions will also be used to aid in the verification of the foam transport capability.

## **4.4 Performance Monitoring**

Performance monitoring will support the specific objectives outlined above in Section 3.

The first monitoring task will be supporting the selection of instrumentation for monitoring parameters including foam pressure, quality, and distribution; water content and distribution; and, potentially, the distribution of reactive components in the foam that may modify parameters including Eh, pH, viscosity, and surface tension.

The second monitoring task will be reviewing the performance of the instrumentation used and reporting on the technical basis for monitoring and performance of the final deliverable (see Section 5).





## **5.0 Expected Deliverables**

The expected output from this research plan is a data package that includes 1) laboratory- and intermediate-scale tests results, 2) conceptual and mathematical models for foam transport and an initial simulation code, 3) an evaluation of existing approaches and technologies and identification of less developed approaches providing the technical basis for monitoring the performance of foam-based delivery of remedial amendments (to be provided by Idaho National Laboratory), and 4) conclusion and recommendations on the utility and efficacy of foam-based delivery of remedial amendments for metals and radionuclides in vadose zone environments.



## 6.0 Budget and Schedule

The estimated project cost and project schedule are shown in Table 6.1 and Table 6.2.

**Table 6.1.** Estimated Cost by Tasks

Task	Cost (\$K)	Comments
<b>Laboratory Scale Tests</b>		
Foam Quality Influence on Injection Pressure	21	
Sediment Air Permeability Influence on Injection Pressure	20	
Liquid Uptake in Sediments and Water Front Formation	20	
Foam Sweeping over Vadose Zone Heterogeneous Systems	45	
<b>Intermediate-Scale Testing</b>		MSE funded and conducted
2-D Sand Box Experiment	15	PNNL, including travel expense to MSE
Large Horizontal Column Tests	14	PNNL, including travel expense to MSE
Foam Transport Simulation	25	Plus additional pending funding from Advanced Modeling TWG.
Performance Monitoring	50	Funding at Idaho National Laboratory
Project Management and Reporting	15	
<b>Total</b>	<b>225</b>	

**Table 6.2.** Foam-Delivery Project Schedule (Starting time: March 2009)

Task	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec	Jan	Feb
<b>Lab Scale Tests (PNNL)</b>												
Foam Quality Influence	■	■	■									
Permeability Influence			■	■	■	■						
Liquid Uptake and Water Front					■	■	■	■	■			
Foam Enhanced Sweeping						■	■	■	■	■	■	■
<b>Inter-Scale Tests (MSE)</b>												
2-D Sand Box Experiment	■	■	■	■	■	■	■	■	■	■	■	■
Large Horizontal Column Tests	■	■	■	■	■	■	■	■	■	■	■	■
<b>Foam Transport Simulation</b>	■	■	■	■	■	■	■	■	■	■	■	■
<b>Performance Monitoring (INL)</b>	■	■	■	■	■	■	■	■	■	■	■	■
<b>Reporting (PNNL, MSE, INL)</b>										■	■	■



## **7.0 Quality Assurance**

The work will be conducted in accordance with the Columbia River Protection Quality Assurance Project Plan (PNNL 2008). All instrument calibrations and materials will be traceable, test procedures and associated training activities will be documented in detail, and test methods will comply with established plans and procedures. The PNNL Standards-Based Management System subject area, “Software,” will be followed for the data analysis software used to store, sort, and reduce data.

All staff members contributing to the work specified in this research plan will have received proper technical and quality assurance training. Staff executing routine, analytical procedures shall comply with Hanford Analytical Services Quality Assurance Requirements Documents, Volume 1: Administrative Requirements, and Volume 4: Laboratory Technical Requirements (Hyatt 1997). Any analytical procedural deviations shall be documented in the narrative of the data report with a justification, unless these deviations result from updated versions of the procedures. All data not meeting the quality control requirements shall be properly noted, and the associated quality control failures will be documented and reported. Individuals who have not completed the appropriate training will not conduct the work.



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