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**SURFACE-ALTERED ZEOLITES AS PERMEABLE BARRIERS  
FOR IN SITU TREATMENT OF CONTAMINATED GROUNDWATER**

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**PHASE II TOPICAL REPORT  
CONTRACT # DE-AR21-95MC32108**

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for: **U.S. Department of Energy**  
**Office of Environmental Management**  
**Federal Energy Technology Center**  
**Pittsburgh, Pennsylvania**

# **Surface-Altered Zeolites as Permeable Barriers for In Situ Treatment of Contaminated Groundwater**

**Phase II Topical Report**

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For: U.S. Department of Energy  
Office of Environmental Management  
Federal Energy Technology Center  
Pittsburgh, Pennsylvania

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## EXECUTIVE SUMMARY

Pilot-scale tests of surfactant-modified zeolite (SMZ) permeable barriers were conducted at the Large Experimental Aquifer Facility of the Oregon Graduate Institute. The tests were performed in an 8.5-m wide, 8.5-m long, 3-m deep concrete tank. The SMZ was installed in a 1-m wide, 6-m long, 2-m deep barrier frame in the center of the tank. The rest of the tank was filled with sand to form a simulated aquifer. An array of 405 samplers was installed in the barrier and in the sand. Controlled water flow across the tank was maintained using ten upgradient injection wells and ten downgradient withdrawal wells. A specific discharge of  $0.17 \text{ m day}^{-1}$  was imposed, resulting in an average linear groundwater velocity of approximately  $0.5 \text{ m day}^{-1}$  in the sand. The upgradient wells allowed injection of a three-dimensional contaminant plume composed of  $10 \text{ mg L}^{-1}$  Cr (in the form of chromate) and  $2 \text{ mg L}^{-1}$  perchloroethylene (PCE).

Two separate pilot tests were performed. The first test required 12 metric tons of SMZ, while the second test required 8 metric tons. The SMZ was bulk-manufactured at a cost of about \$460 per metric ton (equivalent to  $\$460 \text{ m}^{-3}$ ).

In the first pilot test, 14-40 mesh (1.4-0.4 mm) SMZ was used as the barrier material. Approximately 3000 water samples were collected and analyzed over a period of eight weeks. The intensive sampling showed that much of the contaminant plume was being deflected under and around the SMZ barrier. Hydraulic testing failed to conclusively isolate the cause(s) of the flow restriction, but suggested that both low SMZ conductivity and a partially plugged barrier frame were responsible.

The 14-40 SMZ was excavated from the frame, a nylon screen on the barrier frame was removed, and two sections of the frame were refilled with 8-14 mesh (2.4-1.4 mm) SMZ. The remaining one-third of the frame was filled with iron/SMZ pellets as part of another project. After steady water flow was reestablished, chromate and PCE were injected over a period of eight weeks. A total of about 1500 water samples were collected and analyzed during contaminant injection and during an additional month when the tank was flushed with contaminant-free water.

No plume deflection occurred in the test with the 8-14 SMZ. The SMZ fully intercepted the contaminant plume and prevented migration of contaminants downgradient of the barrier. Near the end of the test chromate and PCE were detected in samplers installed in the upgradient portion of the SMZ. The estimated retardation factors for chromate and PCE in the pilot test were 44 and 39, respectively. These retardation factors are very close to the values of 42 and 29 for chromate and PCE predicted from laboratory sorption isotherm experiments.

The pilot test results demonstrate that contaminant retardation by an SMZ permeable barrier can be well-predicted from laboratory characterization of the SMZ. Furthermore, the engineered water control, sampling, and containment system developed for this project serves as a general model for testing permeable barrier performance.

## 1.0 INTRODUCTION

### A. Statement of the Waste Management Problem

Environmental cleanup of DOE and other government and military facilities has become a high priority. Disposal at many of these sites (such as Los Alamos, Hanford, Rocky Flats, Oak Ridge, and others) has resulted in low-level wastes that are distributed in shallow, broad areas. These wastes are complex mixtures that often include chromate and chlorinated and non-chlorinated organic compounds. Many sites have contamination that is spreading and needs containment. In fact, containment may be the best short- and long-term solution for many DOE, DOD, Superfund, industrial, landfill, and mining sites. Site closure and post-closure monitoring are regulatory requirements under Superfund (CERCLA and/or SARA), RCRA, and DOE Order 5820.2A. Monitoring periods extend from 30 to 100 years for hazardous and radioactive contaminants, respectively, indicating the need for long-term, low-maintenance, and low-cost solutions. The development of sorbent/reactive materials for permeable barriers will provide a better tool for dealing with these complex contamination problems.

Contaminants at the above-mentioned sites are often mixed wastes that may be mobile in groundwater, posing immediate risks to on- and off-site receptors. A particularly difficult problem is the presence of residual contamination by water-immiscible organics that cannot be removed by traditional pump-and-treat methods (Fetter, 1999). Low concentrations of organics are continuously released into the groundwater by slow dissolution of the residual liquid. Metals such as arsenic, hexavalent chromium, and selenium are also often present at these sites. These metal species are negatively charged (anionic) and are therefore mobile in most aquifers. Conventional treatment processes are typically ineffective for the removal of these anionic compounds. The use of surfactant-modified zeolite (SMZ) in permeable barriers appears to offer unique advantages over conventional processes in removal of both anionic metals as well as dissolved organic compounds from solution.

### B. Physical and Chemical Features of Surfactant-Modified Zeolites

Zeolites are hydrated aluminosilicate minerals characterized by cage-like structures, high internal and external surface areas, and high cation exchange capacities. Both natural and synthetic zeolites find use in industry as sorbents, soil amendments, ion exchangers, and molecular sieves. Clinoptilolite is the most abundant naturally occurring zeolite. It has a two-dimensional 8-ring and 10-ring channel structure with the largest cavity dimension measuring 4.4 by 7.2 Å (Newsam, 1986). The unit-cell formula is  $(\text{Ca}, \text{Na}_2, \text{K}_2)_3 [\text{Al}_6\text{Si}_{30}\text{O}_{72}] 24\text{H}_2\text{O}$ . The low cost of natural zeolites ( $\$45\text{--}\$60 \text{ ton}^{-1}$ ) makes their use attractive in water treatment applications.

Zeolite chemistry resembles that of smectite clays. In contrast to clays, however, natural zeolites can occur as millimeter- or greater-sized particles and are free of shrink-swell behavior. As a result, zeolites exhibit superior hydraulic characteristics and are suitable for use in filtration systems (Breck, 1974) and as permeable barriers to dissolved chemical migration. Internal and external surface areas up to  $800 \text{ m}^2 \text{ g}^{-1}$  have been measured. Total cation exchange capacities in natural zeolites vary from 250 to 3000 meq  $\text{kg}^{-1}$  (Ming and Mumpton, 1989). External cation exchange capacities have been

determined for a few natural zeolites and typically range from 10 to 50 percent of the total cation exchange capacity (Bowman et al., 1995).

Due to their large specific surface areas and high cation exchange capacities, natural zeolites have a high affinity for cationic heavy metals such as  $Pb^{2+}$  and  $Cd^{2+}$  (Colella et al., 1995). Zeolites have been used commercially to remove  $Pb^{2+}$  and  $NH_4^+$  from waste waters (Groffman et al., 1992; Mumpton and Fishman, 1977). However, natural zeolites have little affinity for inorganic anions such as chromate ( $CrO_4^{2-}$ ) or for dissolved organics.

Treatment of natural zeolites with cationic surfactants dramatically alters their surface chemistry. The large organic cations exchange essentially irreversibly with native cations such as  $Na^+$ ,  $K^+$ , or  $Ca^{2+}$  (Bowman et al., 1995; Li et al., 1998). Surfactant modification of zeolites enables them to sorb neutral molecules such as benzene and chlorinated hydrocarbons including perchloroethylene (PCE) and 1,1,1-trichloroethane, while retaining their ability to sorb heavy metal cations (Li and Bowman, 1998; Neel and Bowman, 1992). The sorption of target organics is little affected by the presence of other organics (Neel and Bowman, 1992). It has also been shown that strongly hydrolyzed, anionic metals such as arsenic, chromium, and selenium are selectively removed by SMZ (Haggerty and Bowman, 1994). The removal of these toxic anions is also quite dramatic. While sorption of target anions is reduced in the presence of competing anionic species, the SMZ is selective for sorption of oxyanions such as those mentioned above.

Although a variety of surfactants can be used for alteration of zeolite surface chemistry (Bowman et al., 1995), hexadecyltrimethylammonium (HDTMA) is preferred due to its ready availability and low cost. The SMZ prepared using HDTMA is stable under a wide range of pH and Eh conditions and in organic solvents, and is resistant to microbial degradation (Li et al., 1998). After the SMZ is saturated with an anion or volatile organic contaminant, it can be regenerated with little loss of sorption capacity (Bowman, 1996).

The work described above shows that SMZ is a physically and chemically stable sorbent that can simultaneously remove organics, inorganic cations, and inorganic anions from contaminated water.

### C. Intended Use of the Technology

Because of the broad sorptive capabilities of SMZ, its superior hydraulic characteristics, its low unit cost, and the historical use of zeolites in water treatment facilities, this material is very promising as a sorbent for *in situ* treatment of contaminated groundwater. Figure 1-1 shows a schematic diagram of SMZ used in a permeable barrier installation.

Barrier materials which retain organic compounds, radionuclides, and other hazardous contaminants while allowing the passage of groundwater are needed to prevent plume migration from near-surface waste sites. Such barriers will allow concentration of contaminants in a narrow zone, increasing the efficiency and lowering the costs of other *in situ* treatment methods such as enhanced biodegradation or air stripping. This project is aimed at completely characterizing the sorptive properties of SMZ and demonstrating its use as a permeable barrier in a full-scale field installation.

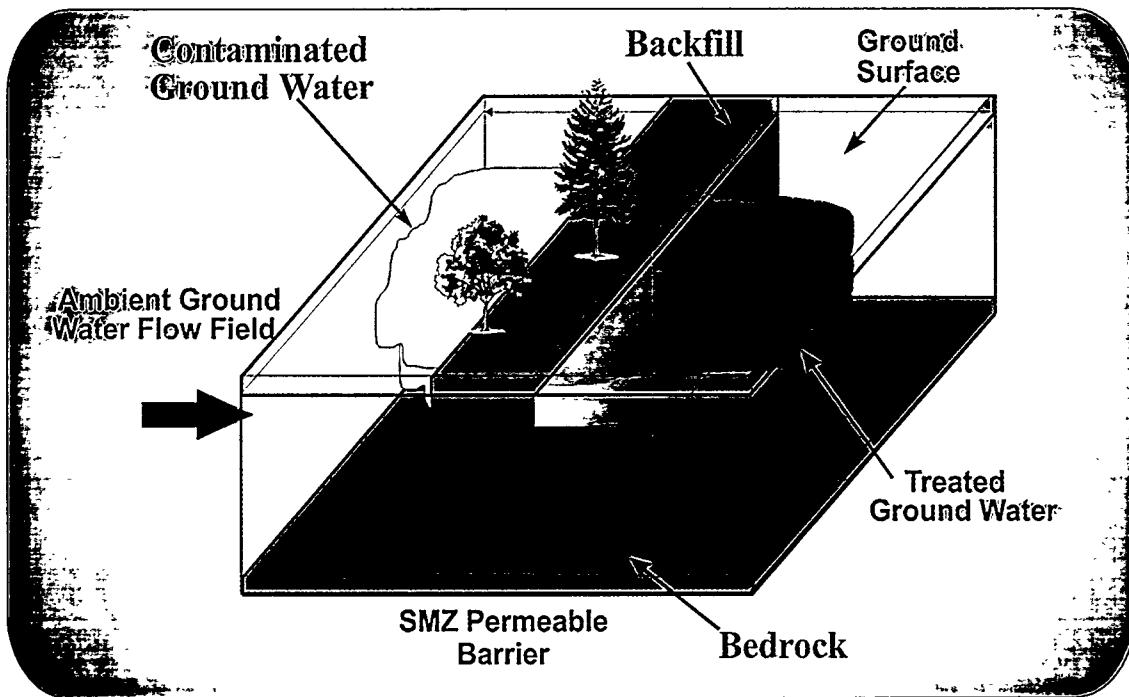


Figure 1-1. Schematic diagram of SMZ in a permeable barrier installation.

## 2.0 SCOPE OF WORK

### A. Objective

The overall objective of this effort is to develop and test a zeolite-based permeable barrier system for containing and remediating contaminated groundwater. The projected product is an engineered and tested permeable barrier system that can be adopted by the commercial sector.

### B. Phases

The project consists of three phases: a base phase (Phase I), completed in 1996 (Bowman, 1996), Phase II (which this report summarizes), and an optional Phase III. In Phase I we characterized the stability of SMZ as well as its properties with respect to sorption and transport of target groundwater contaminants. In Phase II we performed pilot-scale tests of a permeable barrier system using engineering criteria relevant to field-scale problems and developed a standard protocol for testing barrier technology. In optional Phase III, we shall test the Phase I and II barrier technology at a field demonstration site to determine its efficacy and commercial value.

The specified Tasks of the three phases are listed below.

#### **Phase I: Laboratory Bench Testing and Analysis**

- Task 1.1 Information required for the National Environmental Policy Act
- Task 1.2 Develop laboratory production of SMZ
- Task 1.3 Determine effects of site-specific water chemistry on sorption of target compounds
- Task 1.4 Determine the long-term stability of SMZ
- Task 1.5 Determine the possibility of regenerating SMZ
- Task 1.6 Determine the ability to predict contaminant movement through beds of SMZ
- Task 1.7 Topical Report

#### **Phase II: Pilot-Scale Testing of Barrier Technology**

- Task 2.1 Information required for the National Environmental Policy Act
- Task 2.2 Identify a suitable test-bed facility
- Task 2.3 Develop experimental, quality control, and analysis protocol for pilot-scale engineering testing
- Task 2.4 Develop engineering criteria for barrier technology installation
- Task 2.5 Pilot-scale testing and analysis
- Task 2.6 Topical Report

#### **Phase III: Field Demonstration**

- Task 3.1 Information required for the National Environmental Policy Act
- Task 3.2 Identify field demonstration site(s) and develop action plan for demonstrating barrier technology

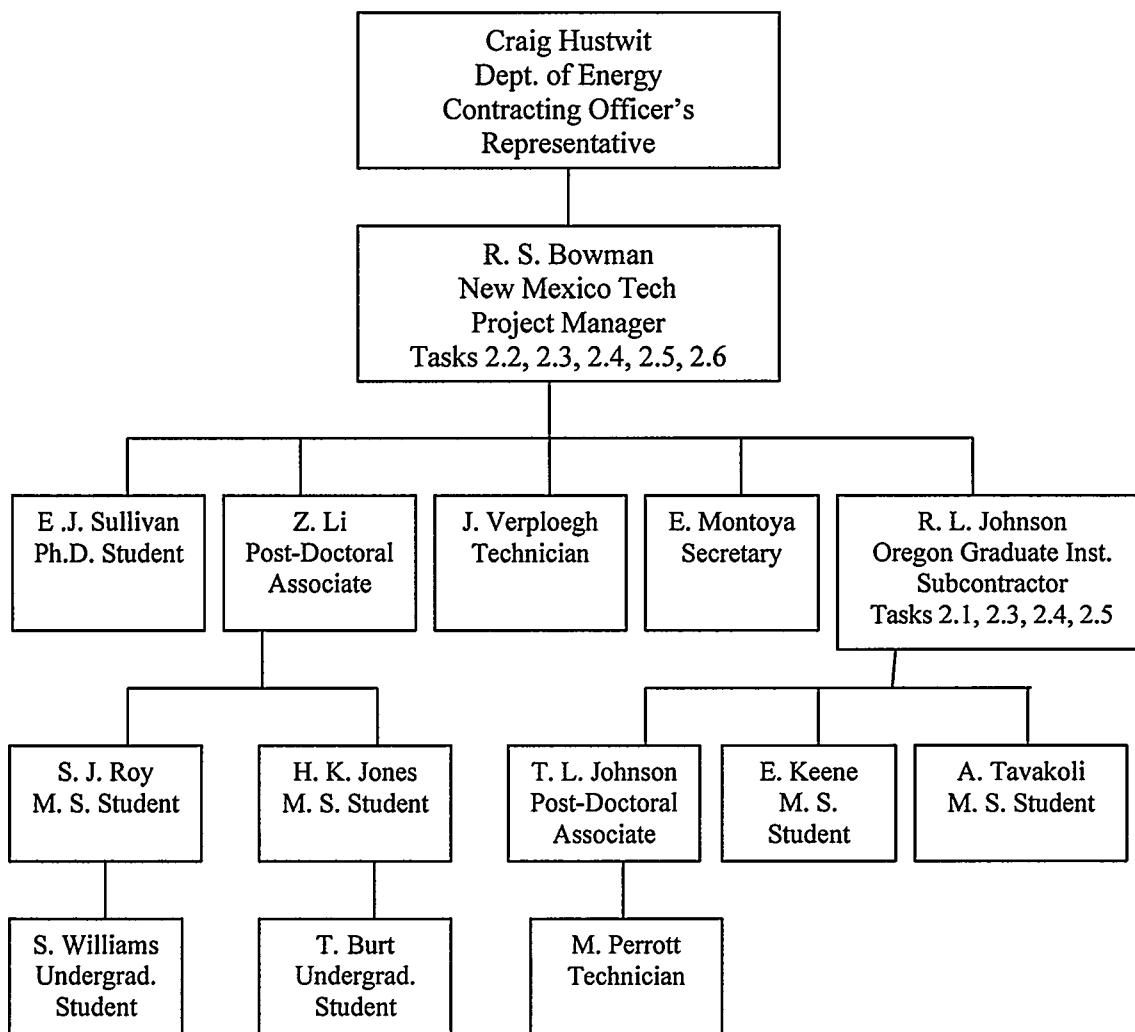
Task 3.3 Develop experimental, quality control, and analysis protocol for the field site demonstration

Task 3.4 Conduct field demonstration experiments and engineering analysis

Task 3.5 Compare Phase I, II, and III results

Task 3.6 Final Report

The personnel management plan for Phase II is presented in Figure 2.1, with primary responsibility for Phase II tasks indicated.



**Figure 2-1. Phase II personnel management, with primary responsibility for Phase II tasks indicated.**

### 3.0 PHASE II TASKS, METHODOLOGY, AND RESULTS

#### Task 2.1 Information required for the National Environmental Policy Act

The appropriate documentation was submitted prior to initiation of the Phase II pilot-test experiments.

#### Task 2.2 Identify a Suitable Test-Bed Facility

In the investigation of suitable facilities the Project Manager contacted seven organizations and made site visits to most of them. From these investigations the following organizations emerged as the most suited for meeting Phase II objectives. They are listed in order of preference:

1. Oregon Graduate Institute, Beaverton, Oregon
2. University of Wyoming, Laramie, Wyoming
3. Los Alamos National Laboratory, Los Alamos, New Mexico

Other organizations investigated and found not to be suitable were:

Dover Air Force Base, Dover, Delaware  
Oak Ridge National Laboratory, Oak Ridge, Tennessee  
Pacific Northwest Laboratory, Richland, Washington  
University of Waterloo, Waterloo, Canada

Below the ranking of the acceptable facilities is justified. Each facility operator indicated that he could provide the required level of Phase II support within the budget for the subcontract.

##### A. Oregon Graduate Institute, Beaverton, Oregon

Oregon Graduate Institute (OGI) offered the most suitable test bed facility and support structure for Phase II. OGI had the largest facility, an 8.5-m by 8.5-m by 3-m deep test bed which could be packed with any desired aquifer material. The facility was outdoors, but could be shielded from precipitation. An outdoor facility was important for Phase II in order to test barrier installation under realistic field conditions. The OGI facility was set up for complete control of water input and extraction rates and allowed straightforward installation of contaminant monitoring devices. The facility was specifically designed for testing of innovative remediation technologies. The staff, under the direction of facility operator Dr. Richard Johnson, had an extensive track record in performance-testing and validation of such technologies using their facility. The staff had experience handling large volumes of contaminated water and providing safe procedures for test operation and for treatment and disposal of wastes. Operating in a university environment, the facility director was relatively free from external pressures which would adversely affect project scheduling. OGI was the subcontractor most able to meet the timeline outlined in the Phase II Milestone Schedule. OGI was expected to

be a true collaborator in the Phase II tasks and thus maximize the chances for a successful and extensive pilot test.

**B. University of Wyoming, Laramie, Wyoming**

The University of Wyoming had a smaller test bed facility (8-m by 3-m by 3-m deep). The facility was designed for evaluating leachate generation from oil shale wastes. The facility was indoors, which was advantageous for control of environmental variables but which would have prevented the realistic simulation of field installation of permeable barriers. The facility could have been modified to allow groundwater flow control similar to what was available at OGI. The facility director, Dr. Quentin Skinner, and his staff had little experience in using the facility for testing remediation technologies, and could not readily provide the level of Phase II support offered by OGI. The staff at Wyoming would have, initially at least, required much more direction from the Project Manager.

**C. Los Alamos National Laboratory, Los Alamos, New Mexico**

The Los Alamos facility was much smaller than either the OGI or Wyoming facilities, measuring only 2-m by 1.5-m by 1.5-m deep. The small scale of the facility would have provided a much less realistic simulation of field-scale barrier installation and performance. The facility operators (Drs. H. Jake Turin and David Janecky) did have extensive experience with remediation technologies and instrumentation. Due to the high cost of performing work at national laboratories, the much smaller-scale pilot test at Los Alamos would have cost as much as the tests at OGI or Wyoming. Both of the Los Alamos facility operators had existing commitments to other DOE projects. Given that prioritization among these projects was at least partially beyond their control, there were concerns about their ability to meet Phase II milestones.

### Task 2.3: Develop Experimental, Quality Control, and Analysis Protocol for Pilot-Scale Engineering Testing

#### A. Pilot-test tank design

The pilot test was conducted at the Large Experimental Aquifer Program (LEAP) site at OGI. The LEAP tank is an 8.5-m wide, 8.5-m long, 3-m deep concrete pool. The permeable barrier was 1-m wide, 6-m long, and 2-m deep, and designed to simulate a real-world application where the barrier was not keyed in to a low-permeability layer. A schematic diagram of the pilot test facility is shown in Fig. 3-1.

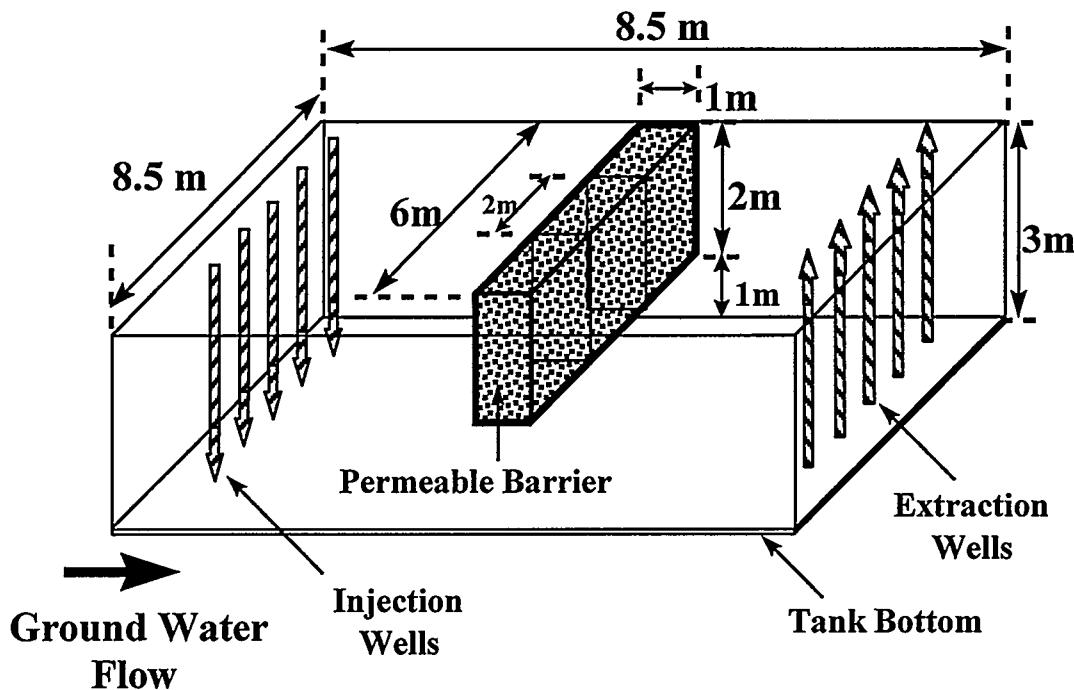
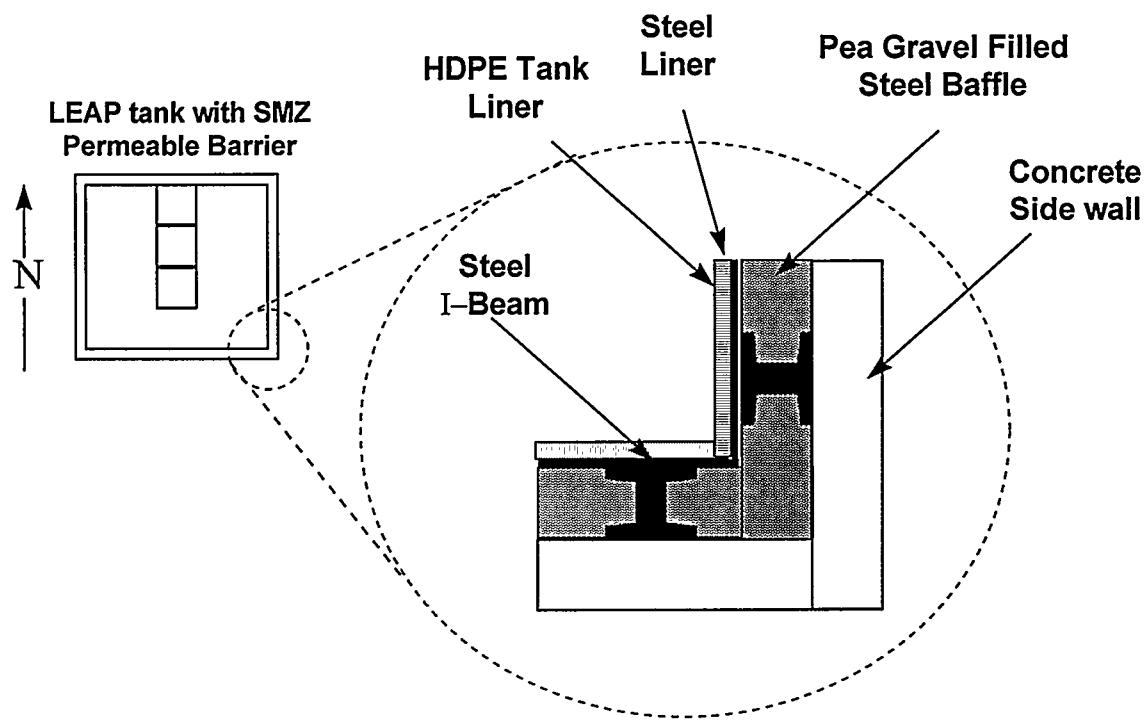


Figure 3-1. Schematic diagram of the pilot-test tank at OGI's LEAP facility.

A steel liner reinforced with a steel I-beam baffle was installed in the LEAP tank for secondary containment of the experiment. The primary liner was a 0.64-cm thick welded seam HDPE liner installed within an outer steel liner (Fig. 3-2). The baffles in the steel liner were backfilled with pea gravel and contained eight fully screened 5-cm ID wells. These wells could be used for leak detection as well as mitigation by inducing a hydraulic gradient into the tank. The finished interior dimensions of the tank were 8.5-m wide, 8.5-m long, and 3-m deep.



**Figure 3-2. Detail of the pilot-test tank wall construction.**

#### B. Barrier construction and installation

A steel frame was constructed to hold the SMZ and to allow for media replacement. The frame was constructed of 5-cm steel angle iron and 2.5-cm and 7.6-cm square steel tube. The frame had solid floor and end walls (1.3-cm thick steel plates) to divide it into three distinct modules, and perforated metal walls (0.16-cm thick perforated steel sheets with 0.64-cm holes covering 50% of the surface area) transverse to the direction of flow. A schematic diagram of the barrier frame is shown in Fig. 3-3. The entire cell was professionally painted with high quality rust resistant paint. The barrier frame was placed in the pilot test tank in three sections on top of a 1-m depth of aquifer sand previously added to the tank. The three sections were bolted together after applying a silicone caulk (Sika-Flex™) for sealing. The end of the barrier in contact with the side of the tank was sealed to the HDPE liner with Sika-Flex™ and a silicone-based glue. To prevent sand from flowing into the barrier when it was empty, the interior and exterior perforated metal walls of the frame were covered with 100-mesh nylon screen, attached with silicone-based glue. The arrangement of the barrier frame within the tank is detailed in Fig. 3-4.

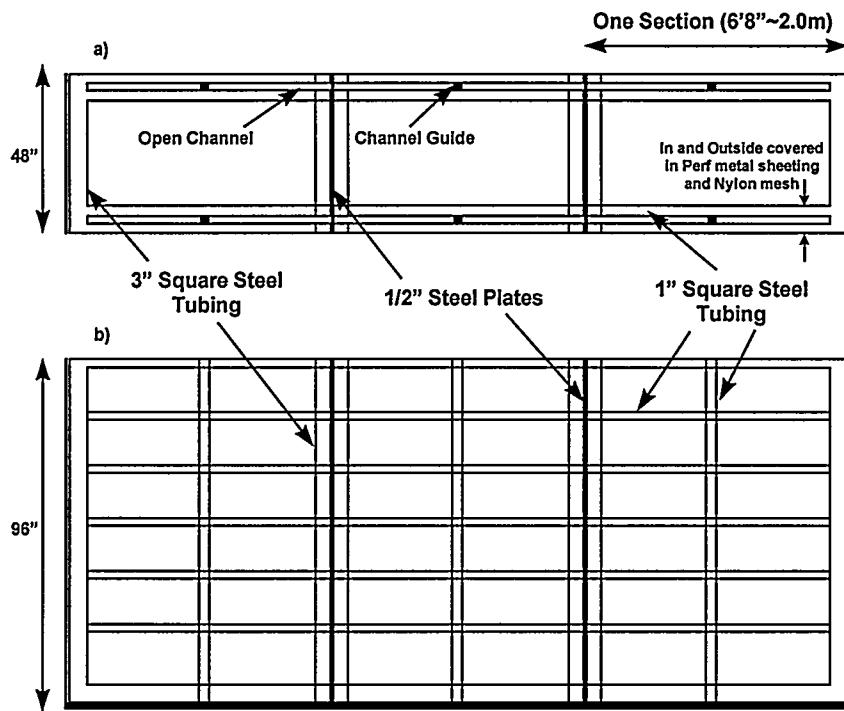


Figure 3-3. Schematic diagram of the barrier frame construction.

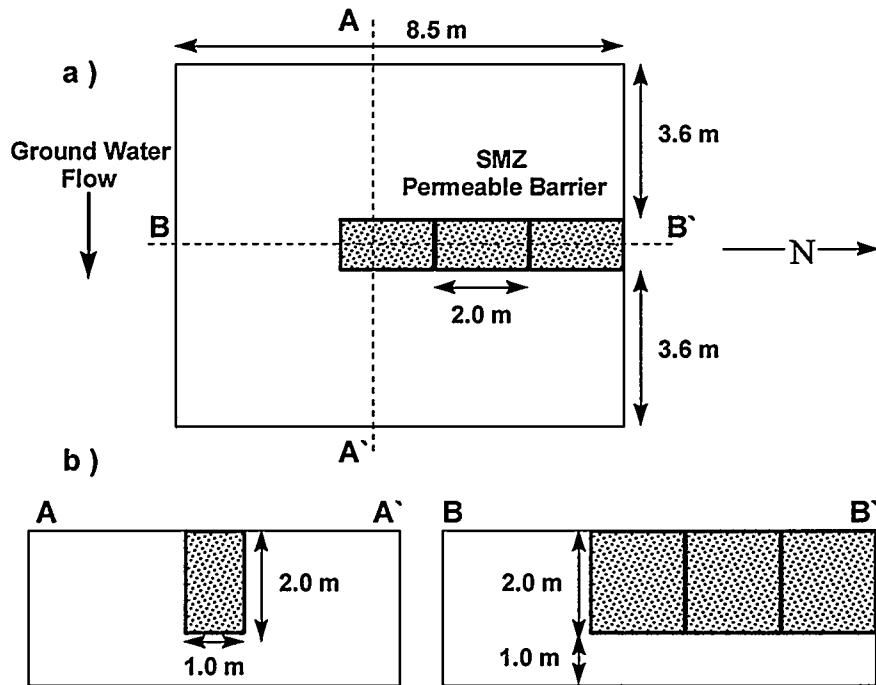


Figure 3-4. Geometry of the pilot-test tank and barrier.

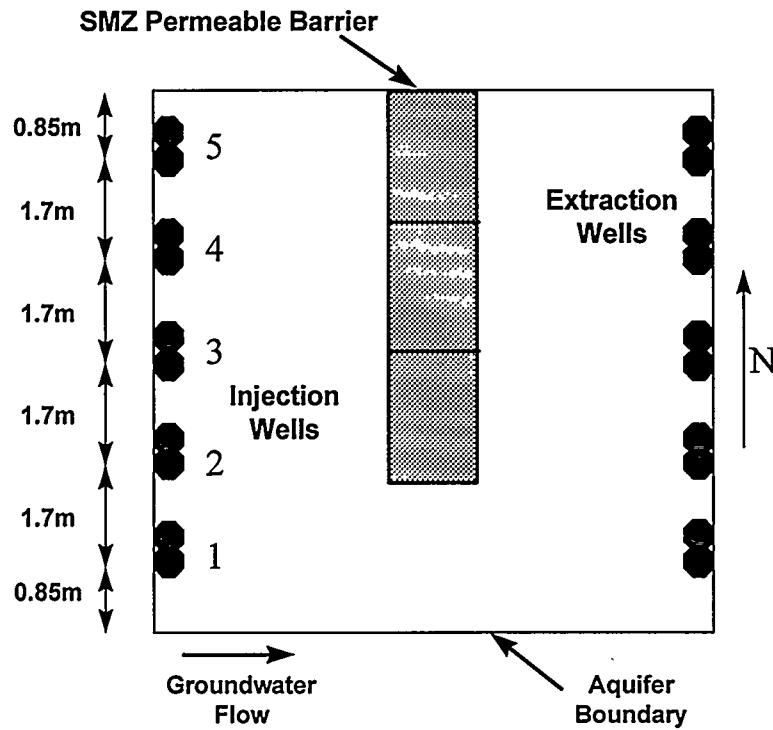
After the barrier frame was in place, pipes for the injection/extraction wells, piezometers, and the sampling network were suspended in the tank from cables (Fig. 3-5). Sand was then added to fill the remaining aquifer portion of the tank. After the aquifer material was in place the SMZ was packed into the permeable barrier frame. The pipes were buried in place as the tank and frame were filled.



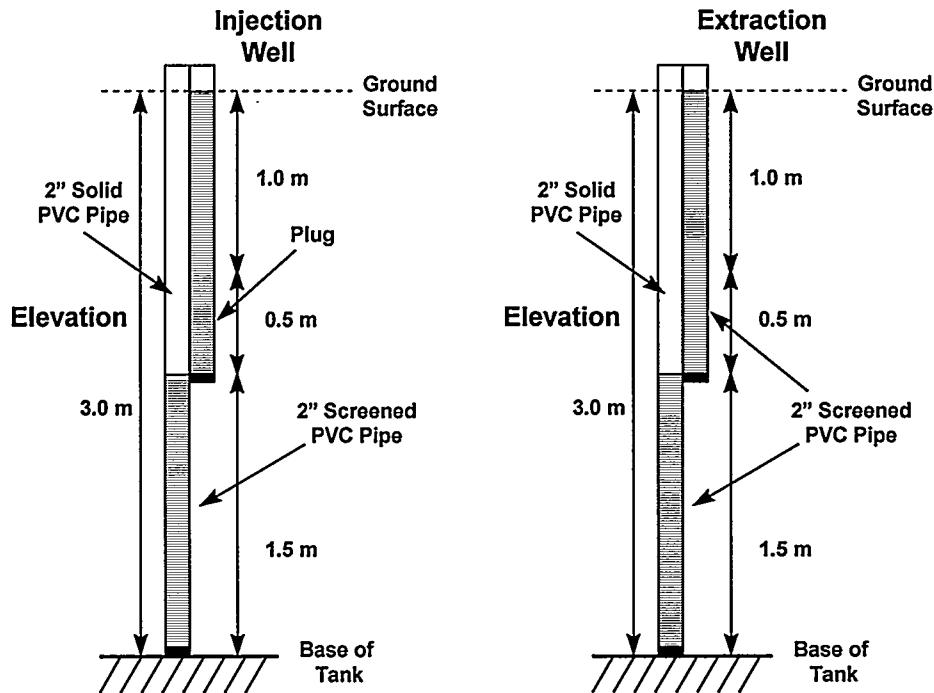
**Figure 3-5. Photograph of the barrier frame and pilot-test instrumentation during tank filling.**

### **C. Water injection/extraction system**

Ten injection and ten extraction wells were used to control water flow within the tank and to inject contaminants. The wells were bundled in pairs, with five pairs at the upgradient end of the tank and five pairs at the downgradient end (Fig. 3-6). In each pair, one well controlled water flow in the lower half of the tank while the other controlled flow in the upper half. All wells were constructed of 5-cm ID schedule 40 PVC. The lower wells were 3-m long and screened over the bottom 1.5 m while the upper wells were 1.5-m long and screened over the entire length (Fig. 3-7). A moveable packer ("plug") in the upper injection wells allowed control of the contaminant injection interval.



**Figure 3-6. Locations of the injection and extraction wells in the pilot-test tank.**



**Figure 3-7. Schematic diagrams of the injection and extraction well construction.**

**D. Water pressure monitoring system**

Eight piezometers were installed to monitor water pressures within and outside the barrier (Fig. 3-8). Piezometers were constructed of 1-in (2.5-cm) ID schedule 40 PVC of 1-m length screened over the bottom 0.17 m (Fig. 3-9).

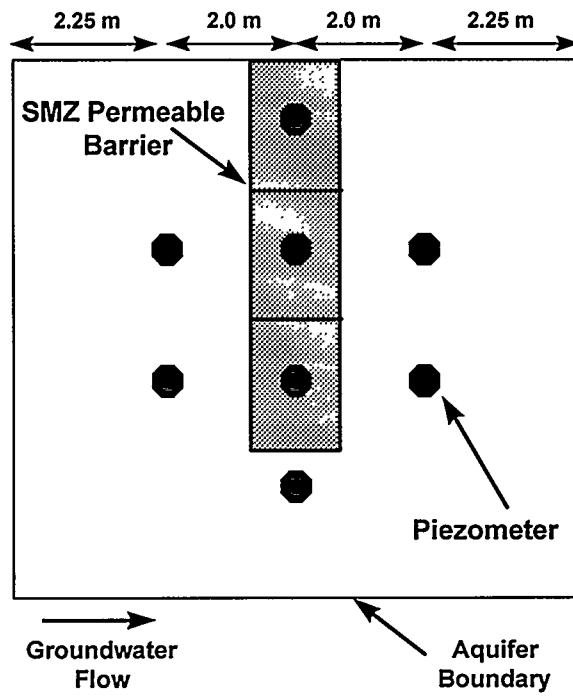
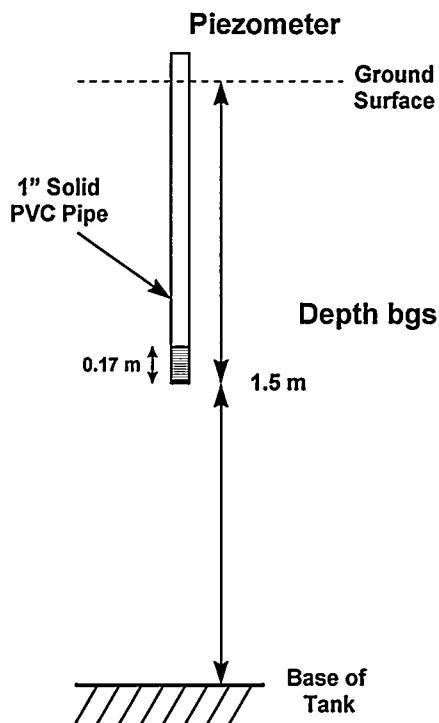


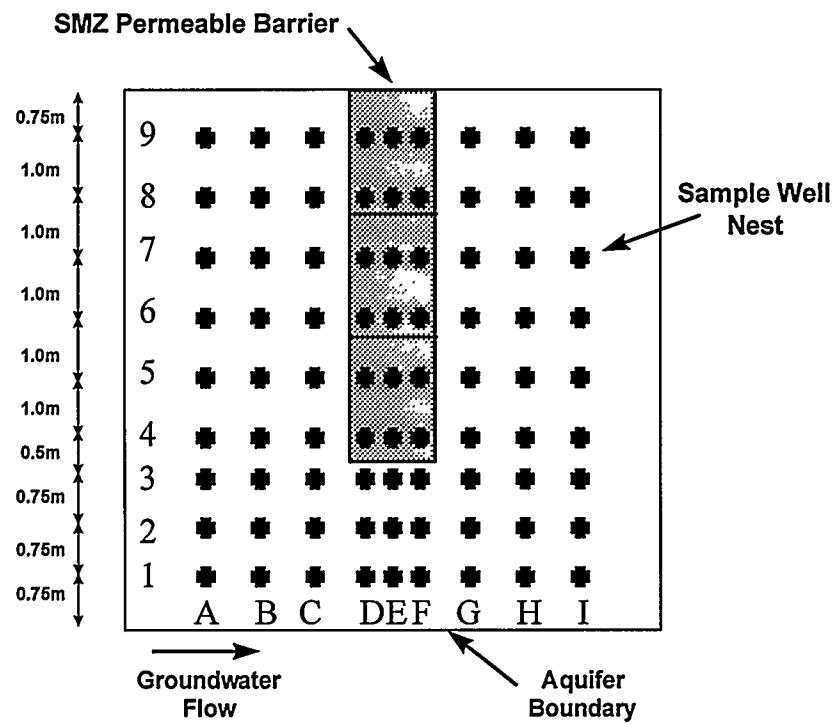
Figure 3-8. Locations of the piezometers in the pilot-test tank.



**Figure 3-9. Schematic diagram of piezometer construction and installation.**

#### E. Sampling system

The sampling system consisted of a 9 x 9 grid of multi-level samplers with 5 depths each (Fig. 3-10), for a total of 405 sampling locations. The physical locations of the samplers are provided in Table 3-1. The sampler construction consisted of 1.25-cm PVC stock to which was attached HDPE tubing terminating at successive 0.5-m depths below the surface. The ends of all of the sample tubes were wrapped in 100-mesh nylon screen attached with an HDPE ziptie. The 18 sample nests within the SMZ barrier had four of the sampling levels inside the barrier and one sampling level penetrating the solid base to a depth of 0.5 m below the barrier. A small hole was drilled into the bottom of the barrier during construction and the appropriate sample tubes were inserted through the holes and sealed into place with Sika-Flex™. Details of sampler construction are shown in Fig. 3-11. The samplers were labeled using a letter (column), number (row), and color (depth) system. For example, sampler designation A3B translates to column A, row 3, depth black. The depth roughly corresponded to the color spectrum, beginning with the red (deepest), followed by yellow, green, black, and white (shallowest). Color coding the samplers and bottles significantly increased accuracy in collecting and analyzing large numbers of samples.



**Figure 3-10. Locations of the sampler nests in the pilot-test tank.**

**Table 3-1. Locations of multi-level samplers in the pilot-test tank.**

<u>Column</u>	<u>X (m)</u>	<u>Row</u>	<u>Y (m)</u>
A	1.25	1	0.75
B	2.25	2	1.50
C	3.25	3	2.25
D	4.00	4	2.75
E	4.25	5	3.75
F	4.50	6	4.75
G	5.25	7	5.75
H	6.25	8	6.75
I	7.25	9	7.75

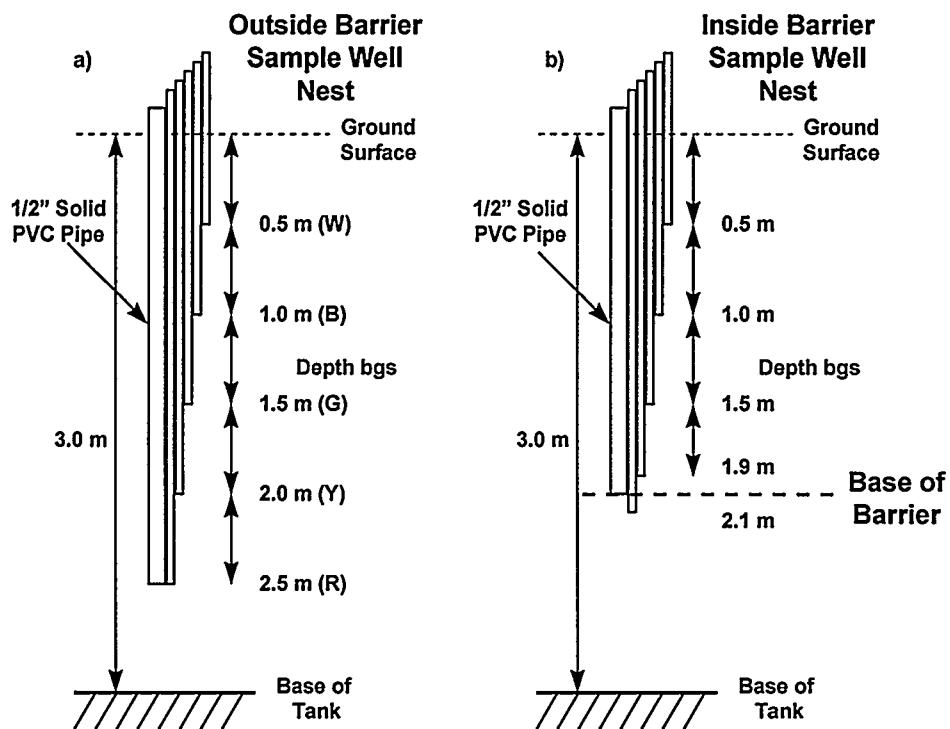


Figure 3-11. Schematic diagrams of the sampler construction and installation.

#### F. Flow Control and Contaminant Injection Systems

Figure 3-12 is a schematic diagram of the pilot-test flow control system. The flow in the pilot-test tank was stratified into lower and upper zones created by the five upper injection/extraction wells and the five lower injection/extraction wells. The feed water was dispensed through a flow totalizer into the injection wells via a manifold and a series of ten controllable flow meters. The lower injection wells were fed directly with Beaverton city water. The upper injection wells were fed from three 6800-L tanks (Fig. 3-13). Using three tanks allowed one tank to be actively supplying feed water, one to be full with the appropriate input solution, and one to be receiving tank effluent. Water for the upper injection wells was supplied under gravity pressure. Water was removed from the extraction wells using five Cole-Parmer Masterflex® L/S™ Variable-Speed Standard Console 1/10 hp drives, each capable of operating four peristaltic pump heads from 1 to 100 rpm. Injection and extraction rates were controlled manually using valves. These rates, as well as the water levels in the feed tanks and pilot test tank, were monitored continuously using HPVee™ Software. Redundant float switches connected to automatic cutoff valves protected against fluid escapes from the system.

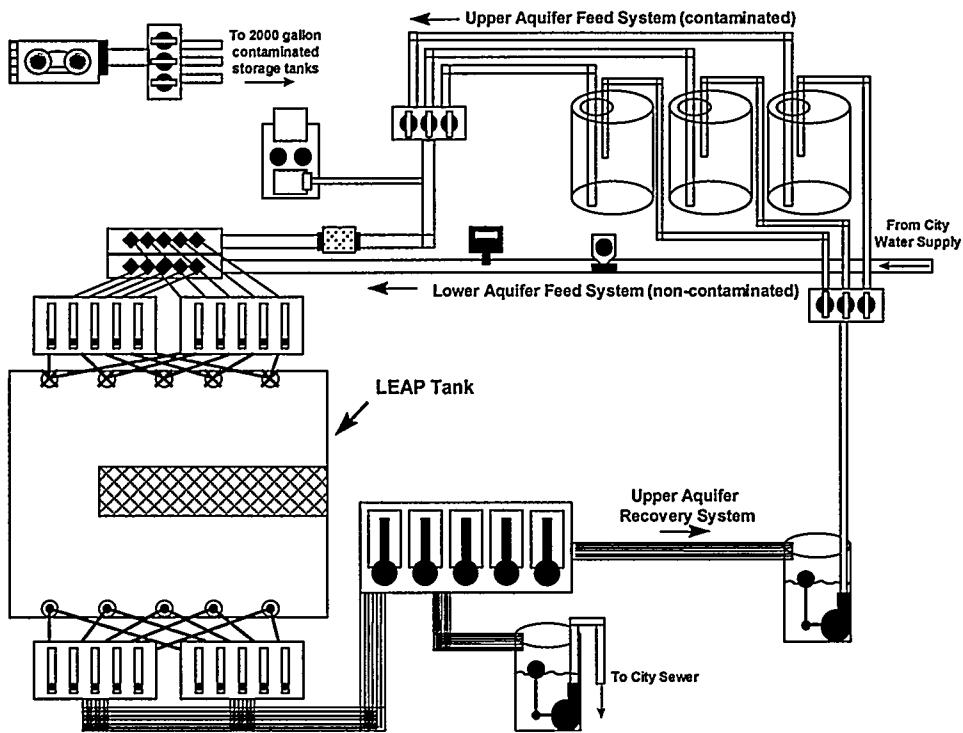


Figure 3-12. Schematic diagram of the pilot-test flow control system.

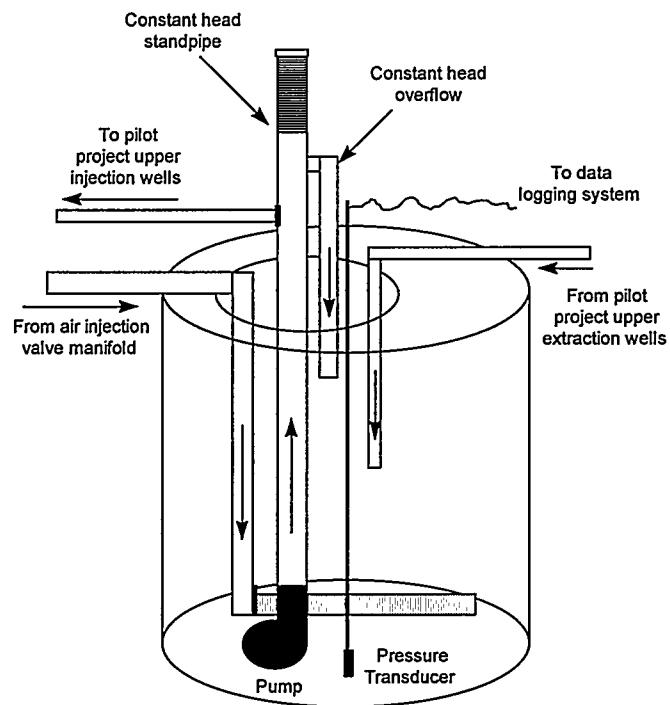


Figure 3-13. Schematic diagram of a water feed/standby/receiving tank.

During pilot-test tank saturation and flushing, the feed tank contained Beaverton city water. During contaminant injection, the feed tank also contained the target input concentration of chromate. A 9:1 methanol: PCE mixture was injected into the feed line via an HPLC pump to yield the appropriate PCE input concentration. The target contaminant concentrations in the injection wells were 10 mg/L Cr(VI) as chromate and 1.8 mg/L PCE. Effluent from the extraction wells was checked for chromate and PCE concentrations and discharged to the municipal sewage system if it met regulatory standards. Effluent not meeting standards was directed to a receiving tank where it was air-stripped of PCE (Fig. 3-13). Chromate was then added as necessary to establish the correct input concentration. This tank was now ready to serve as a feed tank. In this manner each of the three tanks served alternately as a feed, standby, or receiving tank.

#### G. Sample Collection

Samples were collected in 40-mL VOA vials (Fig. 3-14) using dedicated tubing and a 5-head peristaltic pump. To collect a representative sample and to prevent volatilization losses of PCE, several fluid volumes were flushed through the vials prior to sealing with zero headspace. Synoptic samples were taken within different subsets of the 405 samplers depending upon the stage of the experiment. The frequency of sampling ranged from semi-weekly to monthly, again depending upon the stage of the experiment.

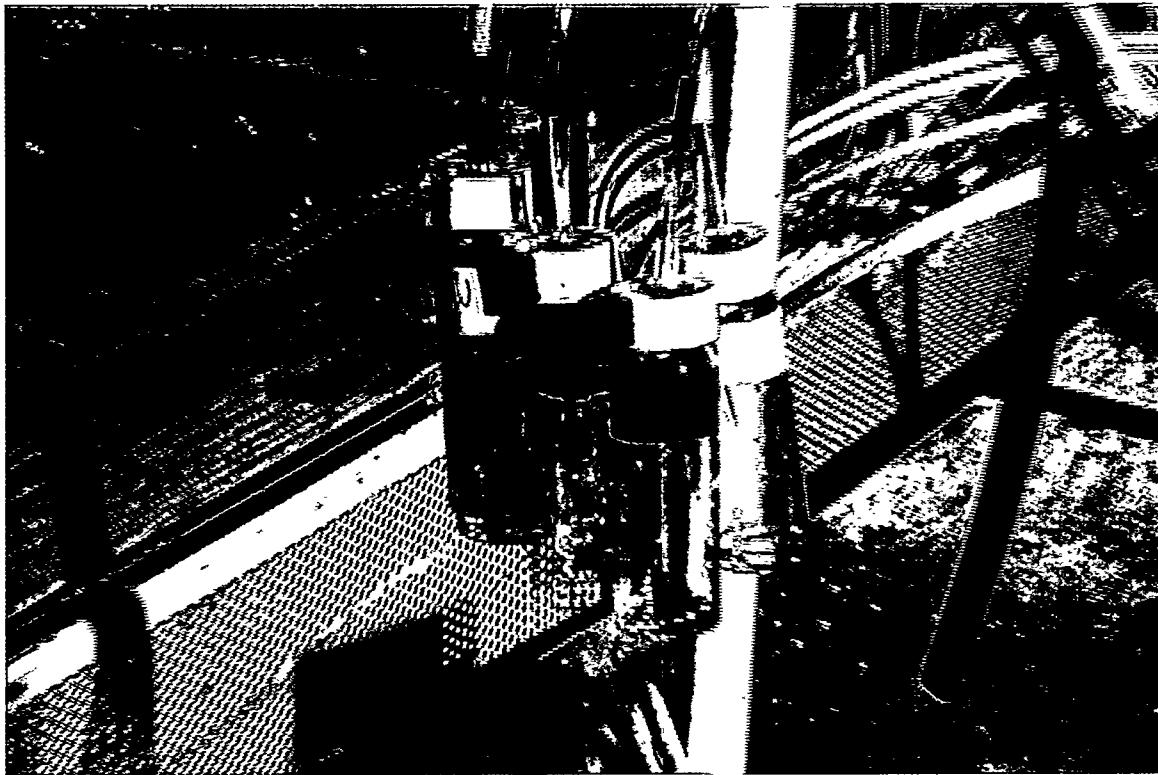


Figure 3-14. Photograph showing sample collection bundle with color-coded vials.

## H. Chemical Analyses

Samples from the 40-mL VOA vials were split for chromate and PCE analyses and typically analyzed within 48 h of collection. Chromate concentration was determined via an HPLC method using a Gilson Model 116 UV detector set at 365 nm and a 2- by 150-mm Waters Nova-Pak® C18 60A HPLC column packed with 4- $\mu$ m particles. The mobile phase consisted of 5-mM tert-butylammonium hydrogen sulfate buffered to pH 4.4 with NaOH with 10 % acetonitrile (v/v) as a modifier. The eluent flow rate was 0.8 mL min<sup>-1</sup>. Samples were filtered through a 0.45- $\mu$ m filter as they were injected by an Alcott 708 autosampler with a 0.1-mL sample loop. The typical run time was 4 min with a calibration range of 0.05 to 20 mg/L Cr as chromate.

The PCE concentration was determined by a headspace method using an HP5890 Series II GC with an HP7694 autosampler. A sample volume of 750  $\mu$ L was injected onto a 30-m by 0.53-mm ID DB-1 column at an oven temperature of 140 °C. Detection was by electron capture with a calibration range of 1 to 2500  $\mu$ g/L and a 3-min run time.

## Task 2.4 Develop Engineering Criteria for Technology Installation

### A. Characterization of Aquifer Sand

The aquifer material was a silica beach sand from the Columbia River basin in Oregon. The well-sorted sand had less than 1 % by weight of organic matter and less than 1 % by weight of iron oxide-cemented aggregates. The hydraulic conductivity of the sand was determined at NMT using a constant-head permeameter (Fig. 3-15) and at OGI using a falling-head permeameter. The mean hydraulic conductivities determined using the two laboratory methods were  $5*10^{-4}$  m sec<sup>-1</sup> and  $2*10^{-4}$  m sec<sup>-1</sup>, respectively.

To test the interaction of the contaminants with the aquifer sand, complete sorption isotherms for both chromate and PCE were prepared. The results showed that the sand had negligible sorption capacity for either contaminant.

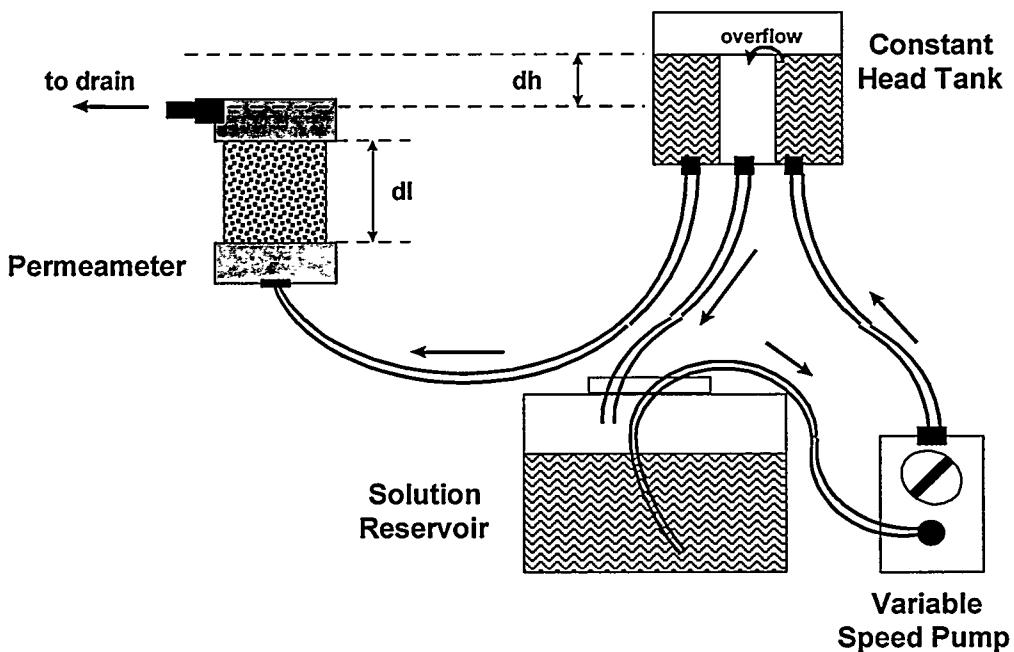


Figure 3-15. Schematic diagram of the constant-head permeameter.

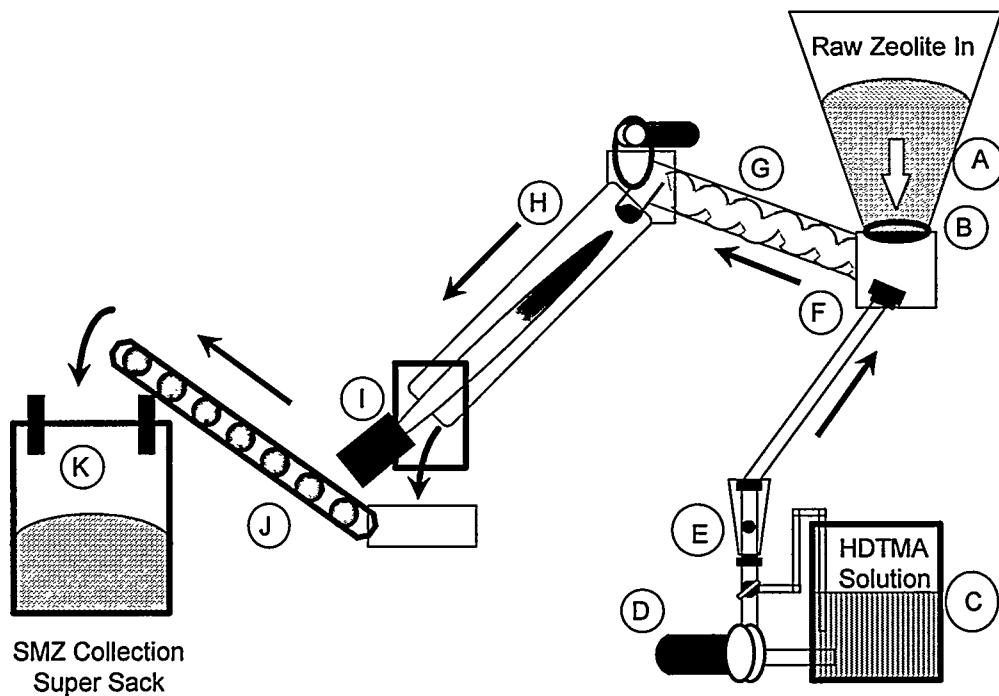
### B. Preparation of SMZ

We used a natural clinoptilolite-rich zeolite from the St. Cloud deposit near Winston, New Mexico, for the pilot test. The material was ground and screened at the St. Cloud mine to the appropriate size, either 14-40 mesh (1.4 to 0.4 mm), or 8-14 mesh (2.4 to 1.4 mm). The mineral content of the zeolite, based on internal standard XRD analysis (Chipera and Bish, 1995; Sullivan et al., 1997), was 74 % clinoptilolite, 5 % smectite, 10 % quartz plus cristobalite, 10 % feldspar, and 1% illite. The zeolite had an internal (zeolitic) cation exchange capacity (CEC) of 800 meq kg<sup>-1</sup> and an external (nonzeolitic) cation exchange capacity (ECEC) of 100 meq kg<sup>-1</sup>, as determined using a method modified from that of Ming and Dixon (Li and Bowman, 1997; Ming and Dixon, 1987). The external surface area using nitrogen adsorption was 15.7 m<sup>2</sup> g<sup>-1</sup> (Sullivan et al.,

1997). The porosity of the zeolite aggregates was 0.6, and the dry bulk density was 1 kg L<sup>-1</sup>.

The SMZ was bulk-produced in an existing batch plant at the St. Cloud mine. The sequence of steps used to produce the SMZ is illustrated in Fig. 3-16. Raw zeolite (A) was metered (B) into a mixing chamber (F) where HDTMA solution (C), fed by pump (D) and monitored with a flow meter (E), was added. The mixture was further homogenized and fed by a screw-auger (G) into a rotating dryer (H) heated by a propane burner (I). The mixture exited the dryer onto a conveyor belt (J) leading to a 1-m<sup>3</sup> "supersack" storage container (K).

Two separate large-scale batches of SMZ were manufactured. In February 1997, 20 m<sup>3</sup> (about 20 metric tons) of 14-40 mesh SMZ was prepared at the St. Cloud facility. In May 1998, 9 m<sup>3</sup> (9 metric tons) of 8-14 mesh SMZ was prepared. In each case, SMZ was manufactured at a rate of 3-4 m<sup>3</sup> h<sup>-1</sup>. A 30 % (by weight) aqueous HDTMA-Cl solution from Lonza Chemical Co. was used as the feed solution for both batches. The target HDTMA loading for the 14-40 batch was 180 mmol kg<sup>-1</sup>, while the target HDTMA loading for the 8-14 batch was 140 mmol kg<sup>-1</sup>.

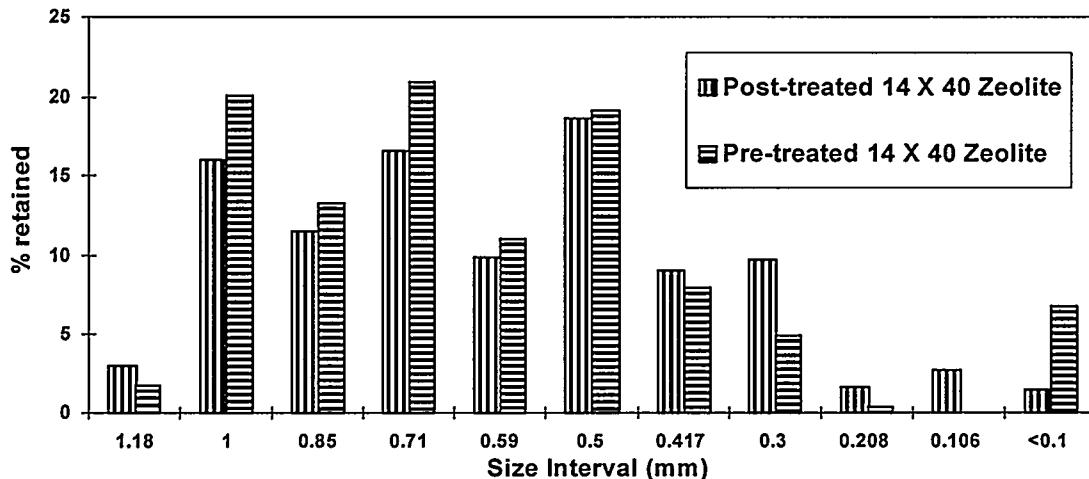


**Figure 3-16. Schematic diagram of the process for bulk production of SMZ.**

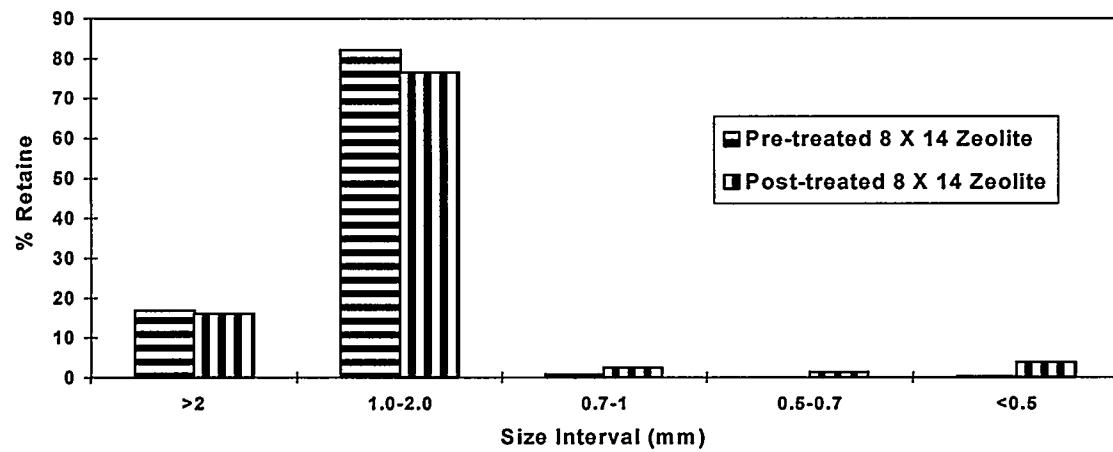
### C. Physical and Chemical Characterization of SMZ

The grain size distributions, determined by sieve analysis, for the two batches of zeolite are shown in Figs. 3-17 and 3-18. In both cases the grain size distribution of the SMZ is almost the same as that of the raw zeolite, demonstrating that the SMZ

manufacturing process caused little breakdown of zeolite aggregates. This preservation of size distribution is important for manufacturing SMZ with specific hydraulic characteristics. Using the constant-head apparatus shown in Fig. 3-15, we determined a hydraulic conductivity of  $20*10^{-4}$  m sec $^{-1}$  for the 14-40 SMZ and a much higher value (difficult to measure accurately with this apparatus) for the 8-14 SMZ. Using their falling-head permeameter, OGI determined a conductivity of  $10*10^{-4}$  m sec $^{-1}$  for the 14-40 SMZ.



**Figure 3-17. Grain size distribution of 14-40 zeolite before and after surfactant treatment.**



**Figure 3-18. Grain size distribution of 8-14 zeolite before and after surfactant treatment.**

The chromate sorption isotherms for the 14-40 and the 8-14 SMZ are shown in Fig. 3-19. The sorption of chromate on SMZ was Langmuirian with sorption maxima of 12 mmol kg<sup>-1</sup> for the 14-40 SMZ and 9 mmol kg<sup>-1</sup> for the 8-14 SMZ. These values are similar to those measured for SMZ prepared in the laboratory during Phase I of this project (Bowman, 1996; Li and Bowman, 1997).

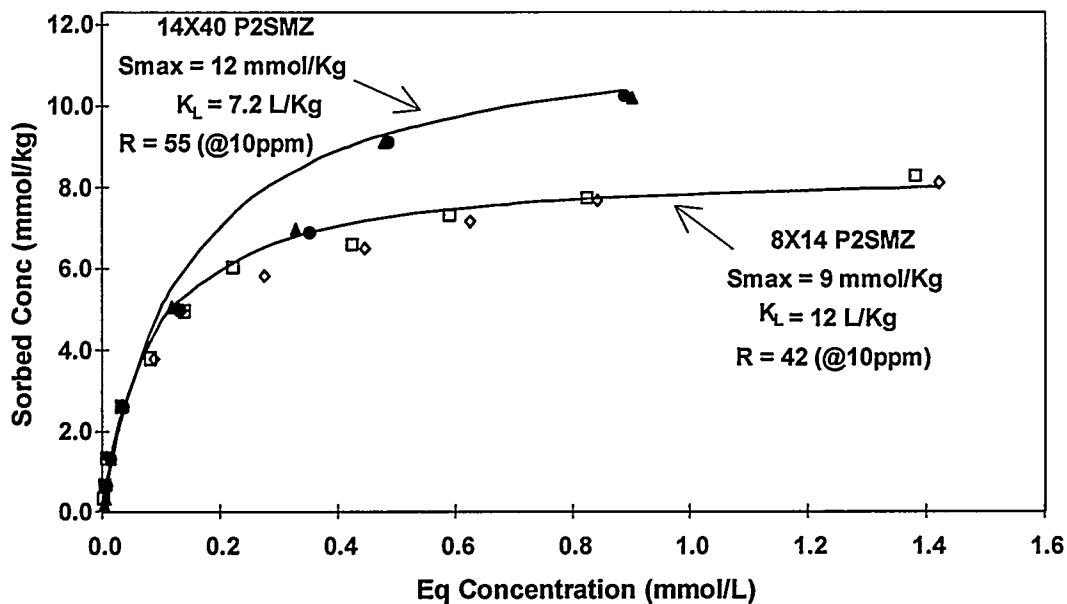


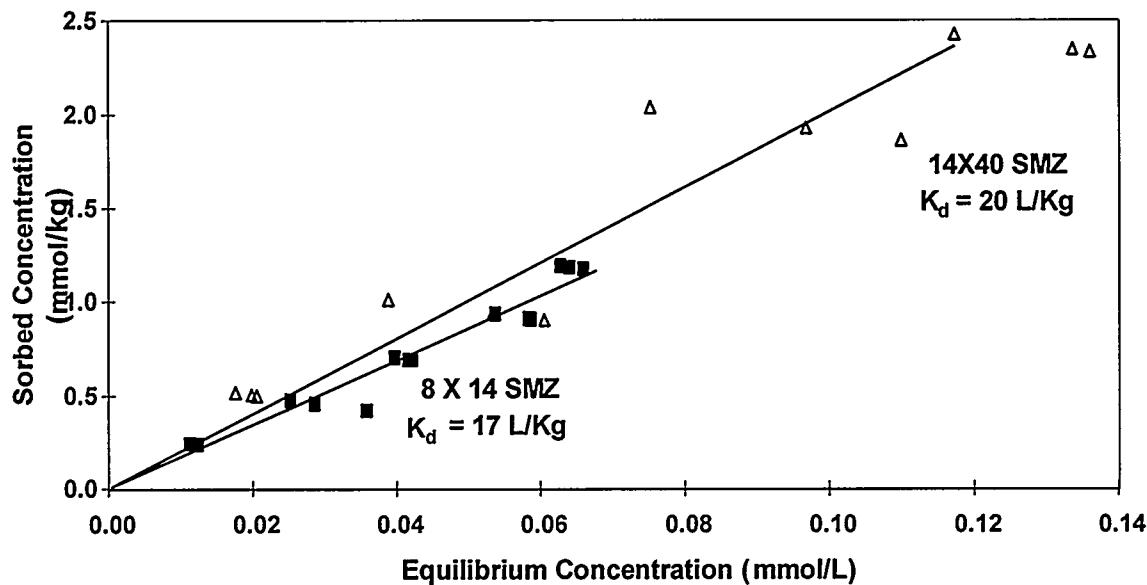
Figure 3-19. Sorption isotherms for chromate on 14-40 and 8-14 SMZ.

The retardation factor (R) for a chemical undergoing Langmuir-type sorption is:

$$R = 1 + \frac{\rho K_L \beta}{\theta (1 + K_L C)^2}$$

where  $\rho$  is the bulk density (M L<sup>-3</sup>),  $\beta$  is the sorption maximum (M/M),  $\theta$  is the porosity (L<sup>3</sup> L<sup>-3</sup>), C is the aqueous concentration (M L<sup>-3</sup>), and  $K_L$  is the Langmuir sorption coefficient (L<sup>3</sup> M<sup>-1</sup>). The chromate  $K_L$  values were 7.2 L mmol<sup>-1</sup> for the 14-40 SMZ and 12 L mmol<sup>-1</sup> for the 8-14 SMZ. Given the measured SMZ properties of 1 kg L<sup>-1</sup> for  $\rho$  and 0.6 for  $\theta$ , and assuming a chromate concentration of 10 mg L<sup>-1</sup> (equivalent to 4.5 mg L<sup>-1</sup> Cr), the estimated R values for chromate are 55 for the 14-40 SMZ and 42 for the 8-14 SMZ.

The PCE sorption isotherms for the 14-40 and the 8-14 SMZ are shown in Fig. 3-20. The sorption of PCE for both samples was well described by linear sorption isotherms. The linear sorption coefficient ( $K_d$ ) was 20 L kg<sup>-1</sup> for the 14-40 SMZ and 17 L kg<sup>-1</sup> for the 8-14 SMZ. Again, these values are similar to PCE sorption coefficients measured in Phase I (Bowman, 1996; Li and Bowman, 1998).



**Figure 3-20. Sorption isotherms for PCE on 14-40 and 8-14 SMZ.**

The retardation factor for a chemical undergoing linear-type sorption is:

$$R = 1 + \frac{\rho K_d}{\theta}$$

Again assuming that  $\rho$  equals  $1 \text{ kg L}^{-1}$  and  $\theta$  equals 0.6, the estimated R values for PCE are 34 for the 14-40 SMZ and 29 for the 8-14 SMZ, regardless of PCE input concentration.

The retention of both chromate and PCE is similar for the two size fractions of SMZ, with the 14-40 material showing about 20-30 % greater sorption and retardation. This greater retention by the 14-40 material is consistent with its 30 % greater loading of HDTMA.

#### D. Installation of Sand and SMZ in the Pilot-Test Tank

After manufacture and characterization, the SMZ was shipped to OGI on flatbed trucks in  $1\text{-m}^3$  supersacks. As described under Task 2.3, the sand and SMZ were packed into the pilot test tank in lifts around the previously installed instrumentation. The aquifer sand was placed into a hopper with a small end-loader, then traveled up a conveyor and down a large tube to the approximate location where it was needed in the tank (Fig. 3-21). The sand was then further spread and leveled by hand. The SMZ was added to the barrier in a similar manner. The final depth of aquifer sand was 3.0 m while the depth of the SMZ was 2.0 m.

## Task 2.5 Pilot-Scale Testing and Analyses

### A. Overview

Two separate pilot tests were performed, one using the 14-40 SMZ and a second using the 8-14 SMZ. The original intent was to perform a single, long-term test using the 14-40 SMZ only. However, due to the hydraulic and operational problems described below, the decision was made to remove the 14-40 material and replace it with the coarser 8-14 SMZ.

### B. Pilot Test with 14-40 SMZ

#### 1. *In Situ* Hydraulic Testing.

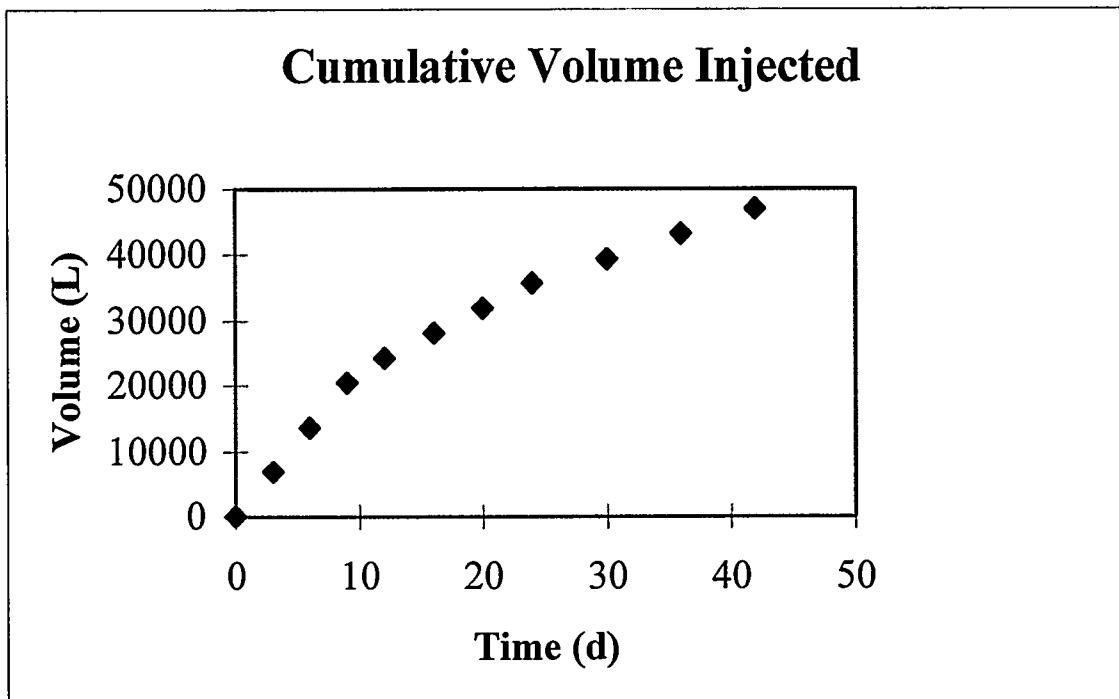
Soon after saturation of the pilot-test tank and establishment of the flow regime, *in situ* hydraulic tests (slug tests) were performed to characterize the properties of the aquifer sand and the SMZ. The average results from these tests along with the laboratory-derived values determined under Task 2.4 are shown in Table 3-2. Whereas the laboratory tests showed a desired hydraulic conductivity contrast of about 5:1, the *in situ* tests showed essentially identical hydraulic conductivities for the sand and the SMZ. The major change was a much lower conductivity of the SMZ in the barrier than what had been determined in the laboratory. The explanation for this decreased conductivity is not certain. At the time, it was thought that entrapped air, which would slowly dissolve under sustained water flow, might be responsible for the decreased conductivity of the SMZ. Another potential explanation was that some compaction of the SMZ had occurred during barrier filling. The decision was made to proceed with the pilot test even though the sand/SMZ permeability contrast was lower than desired.

**Table 3-2. Hydraulic conductivity of the 14-40 SMZ measured in the laboratory and after installation in the pilot-test tank.**

Material	NMT Lab k (m/sec * 10 <sup>-3</sup> )	OGI Lab k (m/sec * 10 <sup>-3</sup> )	Field k(m/sec * 10 <sup>-3</sup> )
sand	0.5	0.2	0.2
SMZ	2.0	1.0	0.2

#### 2. Pilot Test Operation.

A steady flux rate of 0.17 m day<sup>-1</sup>, resulting in an average linear groundwater velocity of approximately 0.5 m day<sup>-1</sup>, was established in the tank. Beginning on 27 December 1997, 10 mg L<sup>-1</sup> Cr (in the form of chromate) and 1.8 mg L<sup>-1</sup> of PCE were injected through all five upper injection wells. The same flux of contaminant-free water was provided to the bottom half of the aquifer. Contaminant injection continued through 12 February 1998. The cumulative volume of contaminant solution injected is shown in Fig. 3-22. The schedule of contaminant feed tank switches with the corresponding cumulative masses of contaminant injected is shown in Table 3-3.



**Figure 3-22. Cumulative volume of contaminant solution injected for the 14-40 experiment.**

**Table 3-3. Dates of feed tank switches and cumulative contaminant injections for the 14-40 experiment.**

<u>Date</u>	<u>Time (d)</u>	<u>Cum vol. (L)</u>	<u>Cr (g)</u>	<u>PCE (g)</u>
27-Dec	0	0	0	0
30-Dec	3	6800	68	12.24
2-Jan	6	13600	136	24.48
5-Jan	9	20400	204	36.72
8-Jan	12	24200	242	43.56
12-Jan	16	28000	280	50.40
16-Jan	20	31800	318	57.24
20-Jan	24	35600	356	64.08
26-Jan	30	39400	394	70.92
1-Feb	36	43200	432	77.76
7-Feb	42	47000	470	84.60

### 3. Contaminant Sampling.

At approximately weekly intervals, samples were collected from transects parallel to the water flow direction to monitor the performance of the SMZ barrier. As standard practice Transects (rows) 2, 5, 7, and 9 were sampled. This scheme provided one transect within the barrier-free portion of the tank and one transect through each of the

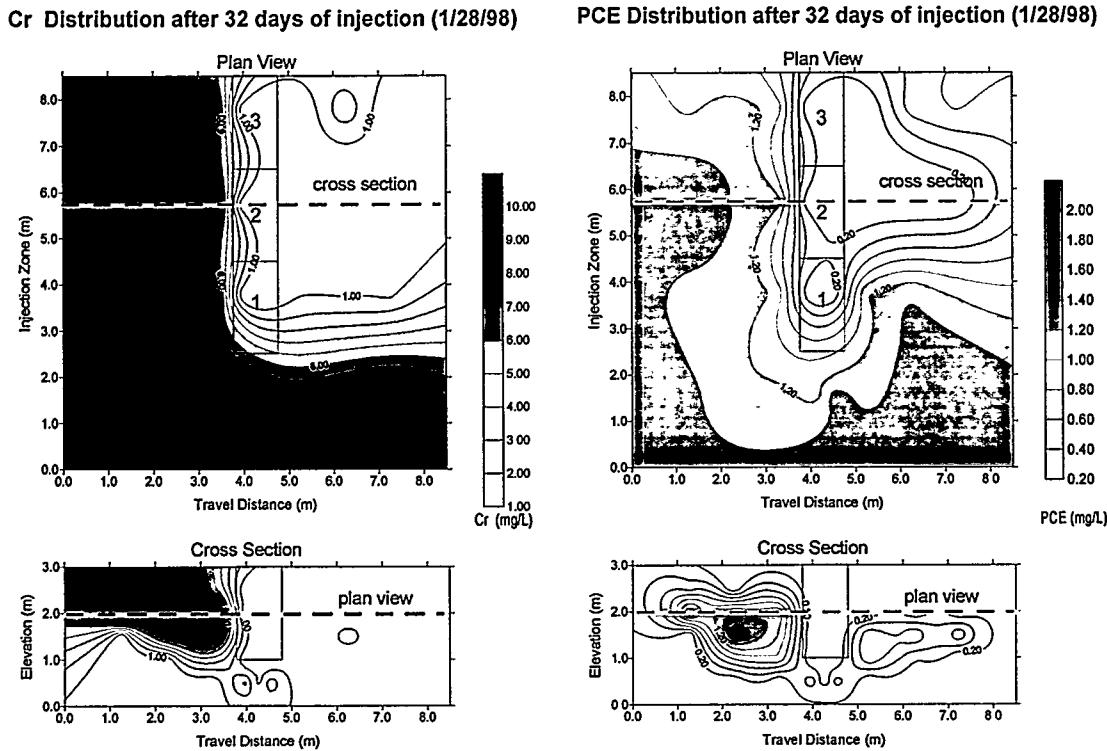
three barrier cells. Depending upon the previous week's results, additional locations were sampled to provide a detailed picture of selected flow regions.

Eight sampling rounds were performed over a period of six weeks. During this period approximately 3000 samples were collected and analyzed for PCE and chromate.

#### 4. Results and Discussion.

The chromate/PCE plume contacted the barrier during the second week of contaminant injection. The barrier-free portion of the aquifer (the control section) saw free migration of both contaminants across the tank. By the beginning of the third week, contaminants had migrated completely through the control section and were being recovered from the extraction wells at the downgradient end of the tank. Conversely, by late January 1998, neither chromate nor PCE had migrated through the SMZ barrier. At the end of the fourth week, PCE had been detected in the upgradient sampling nests in the barrier for the first time at a concentration of  $20 \mu\text{g L}^{-1}$ , while chromate still had not been detected in the barrier.

Within two weeks following contaminant injection, however, both chromate and PCE were detected below the barrier. As the experiment progressed, it became clear that the contaminants (and hence the flow field) were being deflected beneath and around the barrier. Figure 3-23, which shows the chromate and PCE distributions after five weeks of injection, illustrates the deflection of the plume. The contaminant distributions indicated that the barrier frame or the SMZ or both were causing a hydraulic restriction resulting in the plume deflection. Since evaluation of the SMZ performance depended upon accurate knowledge of the amount of chromate and PCE entering the barrier, contaminant injection was terminated. Attempts were then made to ascertain and ameliorate the cause(s) of the hydraulic restriction.



**Figure 3-23. Chrome and PCE distributions following 32 days of contaminant injection, 14-40 experiment.**

Spring of 1998 was spent evaluating the hydraulics of the tank/barrier system. The most likely causes of plume deflection were considered to be changes in the conductivity of the aquifer sand or SMZ (due to compaction or particle breakdown) or plugging of the barrier frame's nylon screen (by mobilized fines, precipitates, or biological growth). New slug tests in the SMZ and the aquifer material resulted in values similar to those obtained prior to contaminant injection. Localized pumping tests seemed to indicate a restriction at the up-gradient face of the barrier frame. Several tracer tests with fluorescein were conducted in an attempt to determine whether the low barrier conductivity was localized or consistent across the barrier. Two-meter long laboratory columns were packed with SMZ and subjected to high water flows. These column tests showed decreasing hydraulic conductivity of the SMZ over time, due to compaction or collection of fines at interfaces.

Based on the assumption that much of the flow restriction was due to plugging of the upgradient barrier screen, the sand in the barrier frame annulus was removed and an attempt made to flush the screen with high-pressure water jets. Additional tracer tests conducted after the jetting showed that a hydraulic restriction was still present. Since the cause of the hydraulic restriction could not be unambiguously determined or ameliorated, the decision was made to replace the 14-40 SMZ with the higher hydraulic conductivity 8-14 SMZ, and at the same time to remove the 100-mesh screen from the barrier frame.

Although the plume deflection during this phase of the experiment was a setback and a disappointment, it illustrated the value of an intensive sampling array in assessing barrier performance. With less spatial resolution of the contaminant plume, we may have reached the erroneous conclusion that contaminants were passing through, rather than around, the barrier. In fact, the SMZ barrier performed as expected with respect to contaminant retardation, preventing any down-gradient contaminant migration.

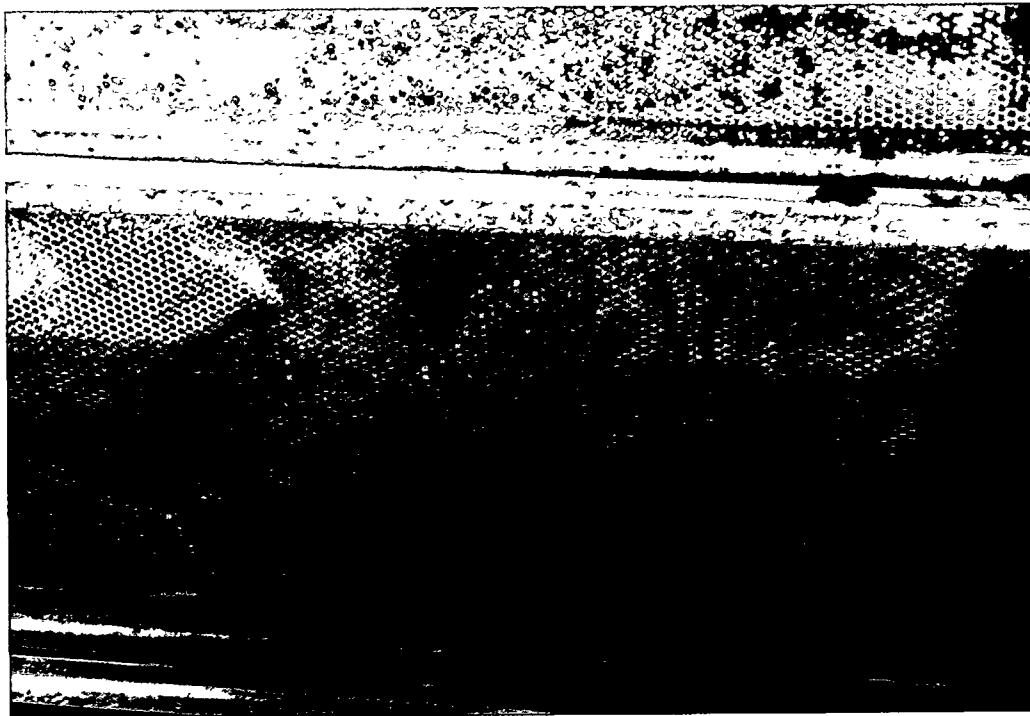
### C. SMZ Replacement and Barrier Retrofit

#### 1. Removal of 14-40 SMZ.

Clean water was flushed through the tank for several weeks in order to reduce contaminant concentrations. Water was then pumped from the tank to lower the water table to the 1-m depth in preparation for excavation of the 14-40 SMZ. The 14-40 SMZ was manually excavated from the barrier cells starting with the Cell 1 (farthest away from the tank wall). Two methods of emptying the cells were used. The first method involved using a small trash pump capable of pumping slurries. This method was somewhat effective and could be used successfully in larger-scale applications where full-size pumps could be employed. The effluent from the trash pump was placed in a supersack, which acted as a filter to remove the SMZ from the water stream. The second, and more effective, method of SMZ removal was manual excavation from the cell into supersacks for disposal.

#### 2. Modification of Barrier Frame.

Once a cell was empty, the interior 100-mesh nylon screen was removed. The inner perforated metal was then removed by cutting or breaking off the bolts holding it to the barrier frame. The perforated metal on the outer barrier frame was thus left exposed, with the outer nylon screen accessible through the perforations. This outer nylon screen, directly adjacent to the aquifer sand, was removed by burning it off through the holes in the perforations using a propane torch. The method was quite effective and left only a small amount of charred material (Fig. 3-24). The upper 30 cm of sand adjacent to the frame exterior was excavated to examine the burn results and to manually remove the remaining screen.



**Figure 3-24. Photograph showing barrier frame with the nylon mesh screen partially burned away.**

### **3. Barrier Refilling.**

Cells 1 and 2 of the barrier frame were filled with 8-14 SMZ while Cell 3, adjacent to the pilot-test tank wall, was filled with iron/surfactant-modified zeolite pellets (Fe/SMZ pellets, see below). During refilling, sheets of plywood were temporarily placed against the inner faces of the barrier frame to retain the fill material (Fig. 3-25). The SMZ was transferred using a conveyor belt that ran from the outside the pilot-test tank to the appropriate cell (Fig. 3-25). While the SMZ was loaded in the barrier frame the samplers were re-installed in their original positions. The annular space between the plywood and the outer perforated metal of the frame was filled with aquifer sand. The plywood was then pulled out of the cell using a jack and appropriate blocking.



**Figure 3-25. Photographs showing barrier Cell 1 refilled with 8-14 SMZ (left), and the conveyor system for transporting SMZ to the barrier frame (right).**

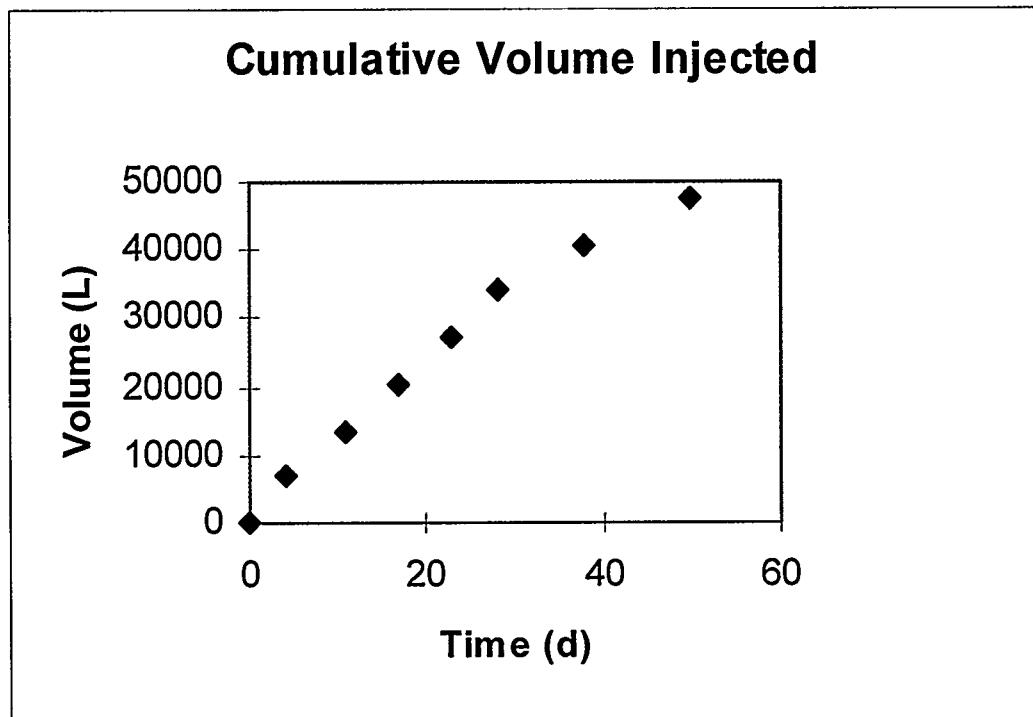
The refilling of the barrier provided the opportunity to test Fe/SMZ pellets along with the SMZ. The Fe/SMZ allows both sorption and chemical reduction of PCE and chromate and shows promise for enhancing contaminant removal and reducing the thickness of permeable barriers (Burt et al., 1999; Jones et al., 1998; Li et al., 1997). The Fe/SMZ pellets arrived at the site in 55-gal drums with removable tops. The drums were placed next to the pilot-test tank and the pellets transferred manually into Cell 3. Due to limited pellet availability, an Fe/SMZ barrier thickness of 0.5 m, rather than 1.0 m, was used. For Cell 3, the plywood retainers were used to split the cell into equal halves. The Fe/SMZ pellets were placed in the upgradient half while the downgradient 0.5-m width was simultaneously filled with aquifer sand. Samplers were re-installed in their original locations, resulting in four sampling locations in the Fe/SMZ and two sampling locations in the downgradient sand of Cell 3.

#### **D. Pilot Test with 8-14 SMZ**

##### **1. Pilot Test Operation.**

Following the barrier retrofit and replacement of the reactive media, the pilot-test tank was slowly resaturated and the flow regime reestablished. The same injection and extraction rates were used as in the 14-40 experiment, resulting in the same volumetric water flux and linear velocity. After several days of steady flow, contaminant injection began. In this case, only the three upper injection well directly upgradient from the barrier (Wells 3, 4, and 5), received chromate and PCE, while upper injection Wells 1 and 2 as well as all the lower injection wells received contaminant-free water. This

configuration resulted in a plume that could be completely captured by the barrier. Contaminant injection began on 10 July and ended on 11 September 1998. Due to budgetary and schedule constraints, a longer injection period could not be sustained. The cumulative volume of contaminant solution injected is shown in Fig. 3-26. The schedule of contaminant feed tank switches is shown in Table 3-4.



**Figure 3-26. Cumulative volume of contaminant solution injected for the 8-14 experiment.**

**Table 3-4. Dates of feed tank switches for the 8-14 experiment.**

Date	Time (d)	Cum vol. (L)	Cr (g)	PCE (g)
6-Jul	0	0	0	0
10-Jul	4	6800	68	12.24
17-Jul	11	13600	136	24.48
23-Jul	17	20400	204	36.72
29-Jul	23	27200	272	48.96
3-Aug	28	34000	340	61.20
13-Aug	38	40800	408	73.44
25-Aug	50	47600	476	85.68

Following cessation of chromate and PCE injection, contaminant-free water was injected at the same rate through all wells for an additional six weeks to flush

residual contaminants from the aquifer sand. Sampling continued during this period, allowing further characterization of the SMZ's ability to retard the chromate and PCE.

## 2. Contaminant Sampling.

Samples were collected approximately weekly during the first several weeks, with a decreasing frequency later in the experiment. Transects (rows) 3, 5, 7, 8, and 9 were sampled. This scheme provided one transect within the barrier-free portion of the tank, one transect through each of the two SMZ-filled barrier cells, and two transects through the Fe/SMZ cell.

Eleven sampling rounds were conducted over a period of 16 weeks. During this period approximately 1500 samples were collected and analyzed for PCE and chromate.

## 3. Results and Discussion.

The migration of the chromate and PCE plumes during the two months of contaminant injection are shown in Figs. 3-27 through 3-35. The chromate/PCE plume contacted the barrier during the second week of contaminant injection. In contrast to the earlier experiment with the 14-40 SMZ, no deflection of the contaminant plume occurred. All of the chromate and PCE entered the barrier and both were retarded in their movement relative to water flow. After 56 d (equivalent to 20 pore volumes of contaminated water passing through the barrier), low concentrations of chromate and PCE were detected in the in-barrier samplers, but no contamination was detected downgradient of the SMZ. Chromate broke through the Fe/SMZ section of the barrier after about 20 d of contaminant injection, while PCE began to break through after about 56 d. The results for the Fe/SMZ pellets are described in detail in a separate report (Bowman et al., 1999).

Quantitative evaluation of barrier performance would have required several additional months of contaminant injection in order to collect complete contaminant breakthrough profiles for the in-barrier and downgradient samplers. Budgetary and time constraints prevented such longer-term monitoring. Nonetheless, a semi-quantitative evaluation of the SMZ performance was made by comparing the velocities of the contaminant contours in the aquifer sand upgradient from the barrier with the arrival times of specific contaminant concentrations at the in-barrier samplers. Using this approach, the estimated velocity of contours for both contaminants in the aquifer sand was about  $0.35 \text{ m d}^{-1}$ . The velocity of chromate within the barrier, obtained by tracking concentration contours, was about  $0.008 \text{ m d}^{-1}$ . The PCE velocity within the barrier was about  $0.009 \text{ m d}^{-1}$ .

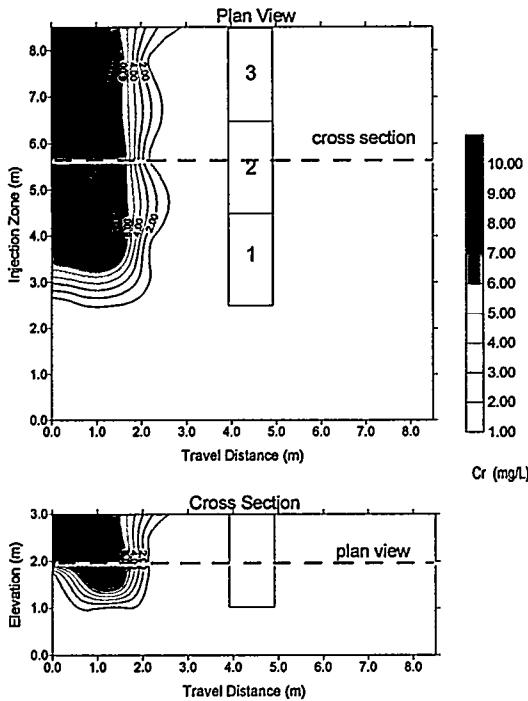
The retardation factors of the contaminants in the SMZ are simply the ratios of the velocities in the aquifer sand and the SMZ:

$$R = V_{\text{sand}}/V_{\text{SMZ}}$$

Using the above equation we calculated retardation factors of 44 for chromate and 39 for PCE. These pilot-test retardation factors are very close to the

estimates of 42 and 29 calculated for chromate and PCE based upon their laboratory sorption isotherms. The pilot test results thus confirm that the field barrier performance of SMZ may be predicted reasonably well from laboratory characterization of contaminant interactions.

Cr Distribution after 4 days of injection (7/14/98)



PCE Distribution after 4 days of injection (7/14/98)

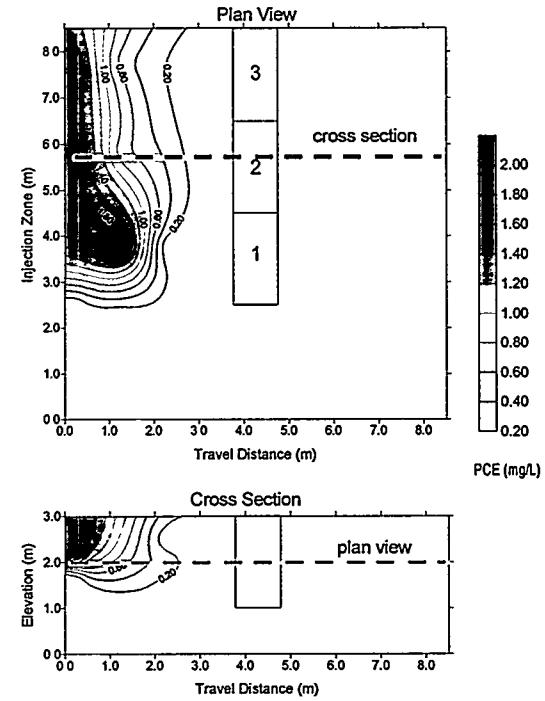
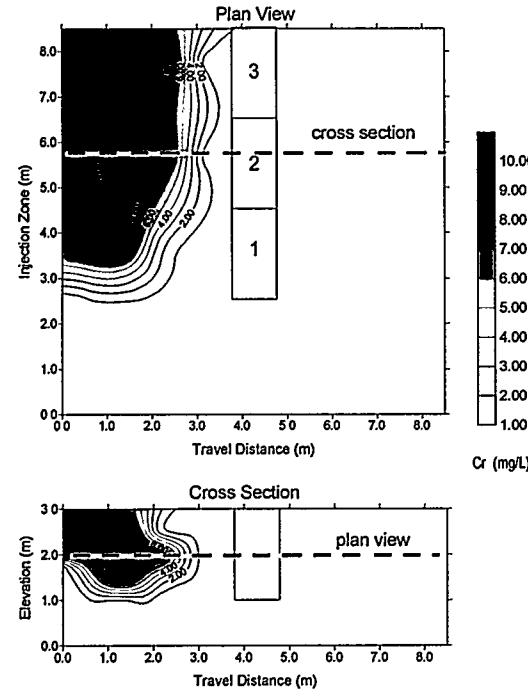


Figure 3-27. Chrome and PCE distributions following 4 days of contaminant injection, 8-14 experiment.

Cr Distribution after 7 days of injection (7/17/98)



PCE Distribution after 7 days of injection (7/17/98)

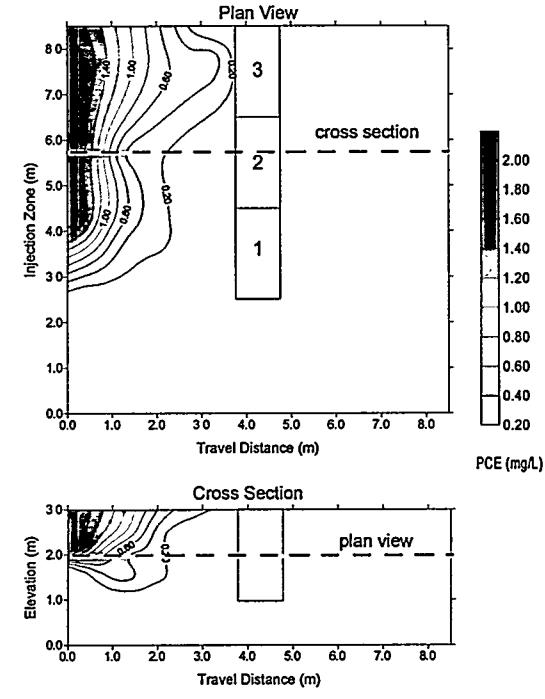
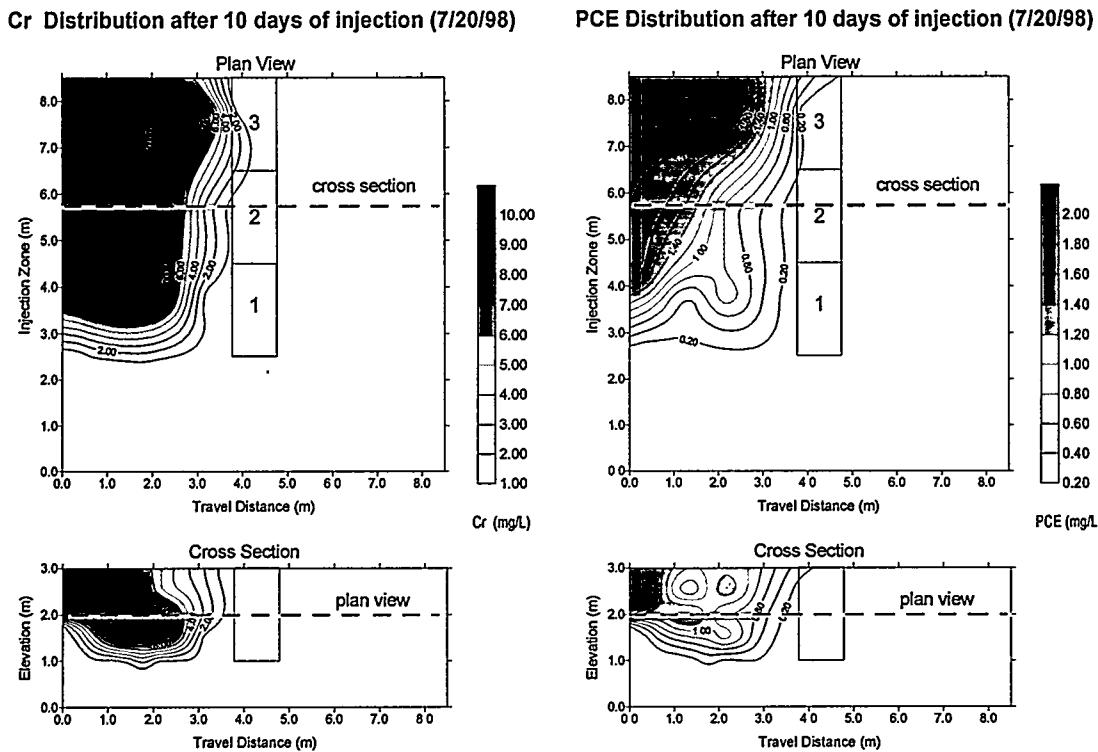
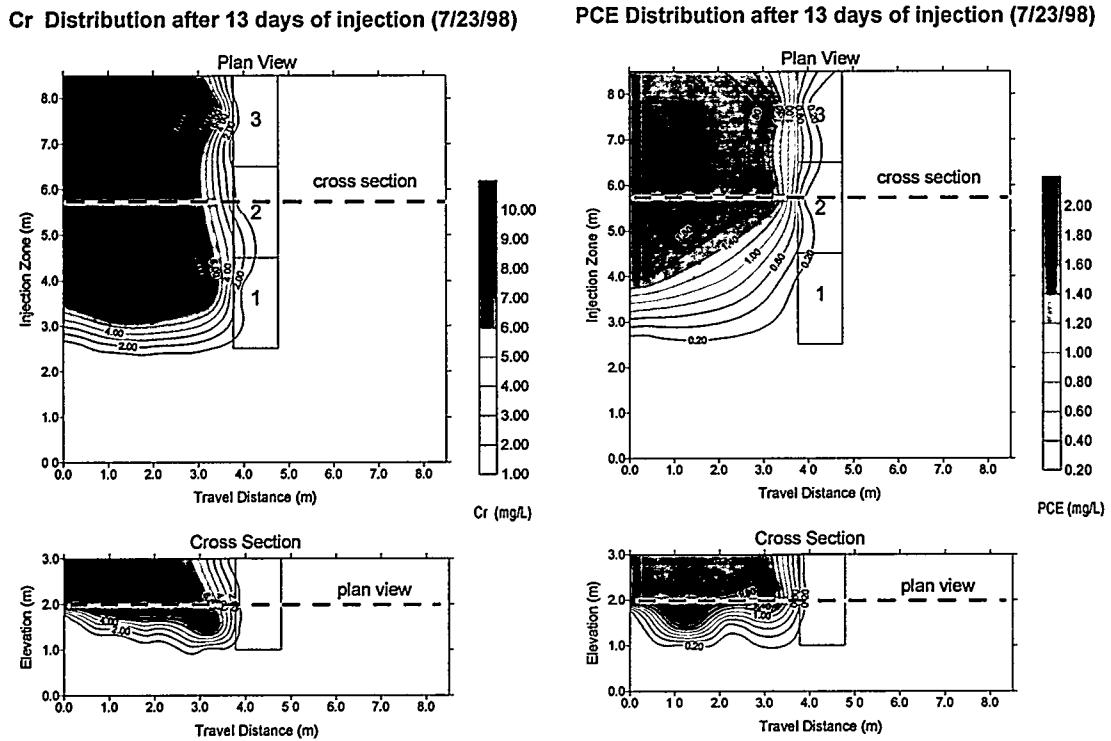


Figure 3-28. Chrome and PCE distributions following 7 days of contaminant injection, 8-14 experiment.

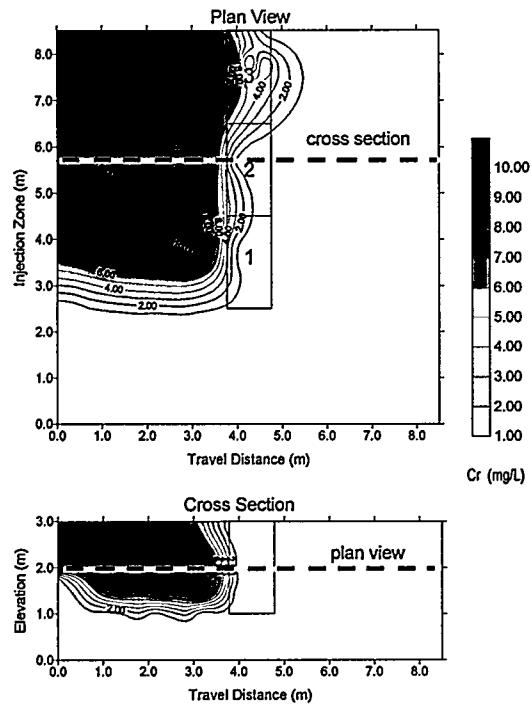


**Figure 3-29. Chrome and PCE distributions following 10 days of contaminant injection, 8-14 experiment.**



**Figure 3-30. Chrome and PCE distributions following 13 days of contaminant injection, 8-14 experiment.**

Cr Distribution after 20 days of injection (7/30/98)



PCE Distribution after 20 days of injection (7/30/98)

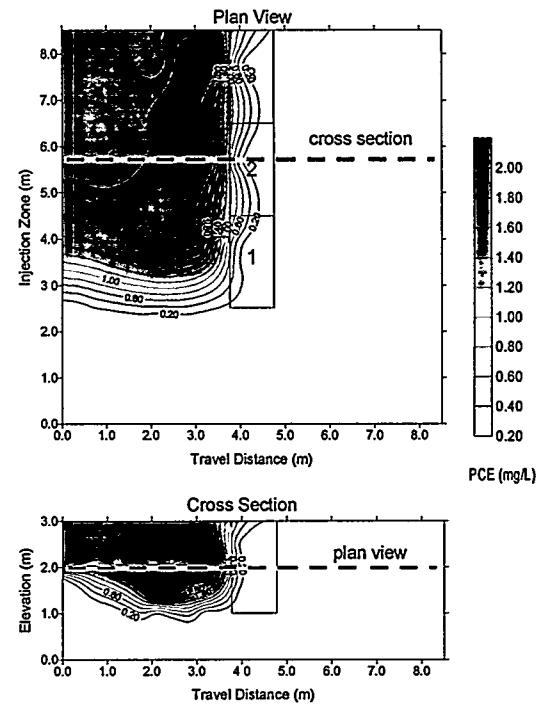
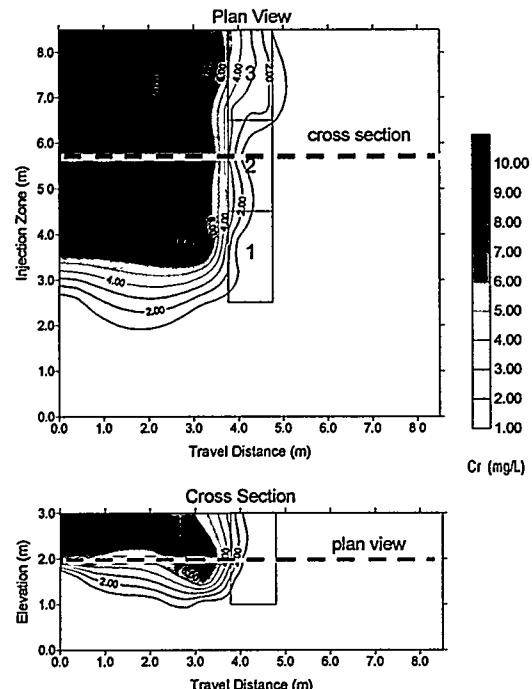


Figure 3-31. Chrome and PCE distributions following 20 days of contaminant injection, 8-14 experiment.

Cr Distribution after 27 days of injection (8/06/98)



PCE Distribution after 27 days of injection (8/06/98)

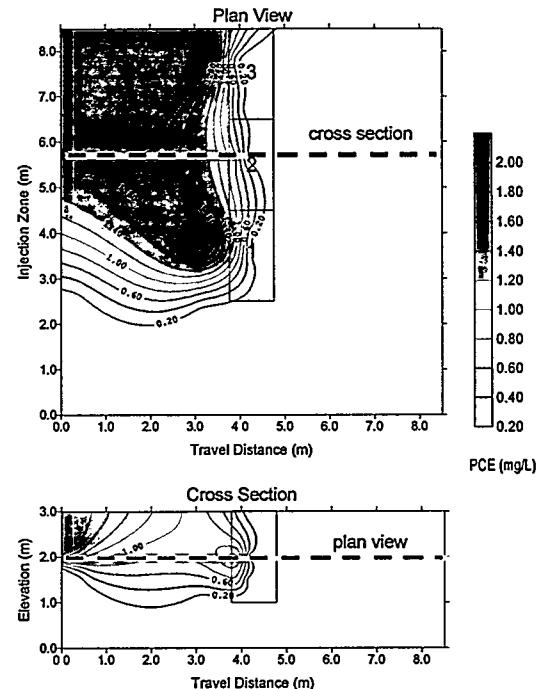
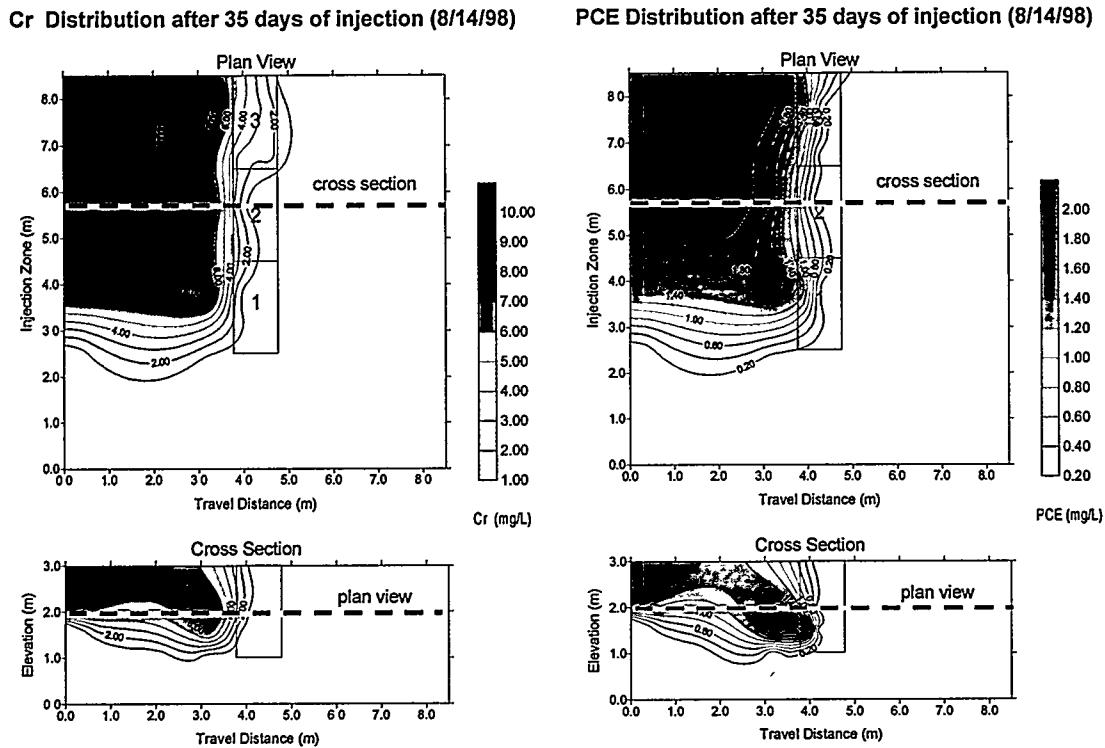
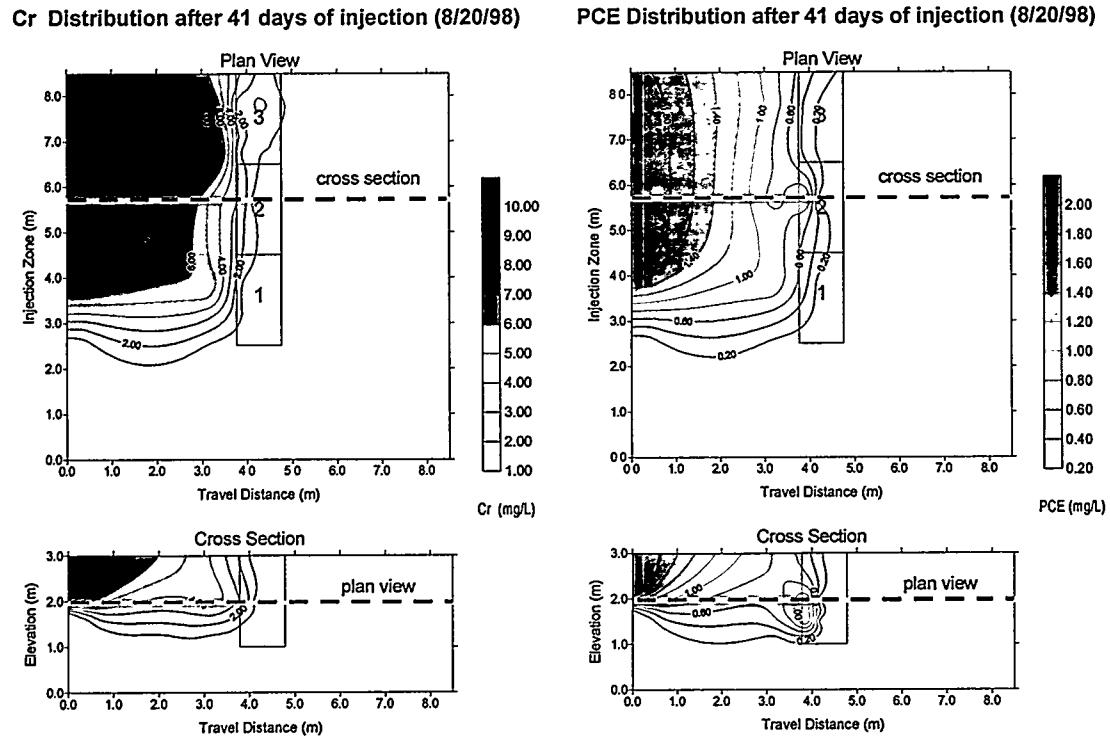


Figure 3-32. Chrome and PCE distributions following 27 days of contaminant injection, 8-14 experiment.

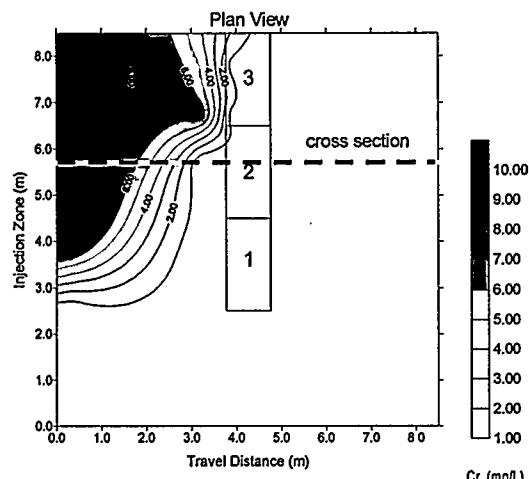


**Figure 3-33. Chrome and PCE distributions following 35 days of contaminant injection, 8-14 experiment.**

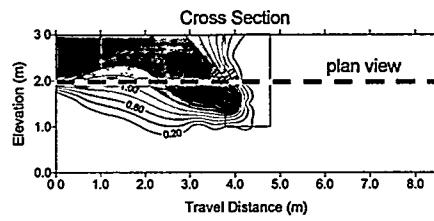
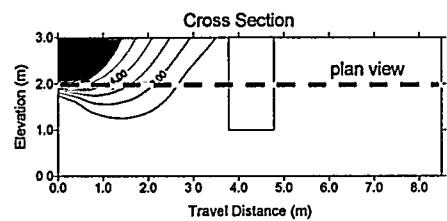
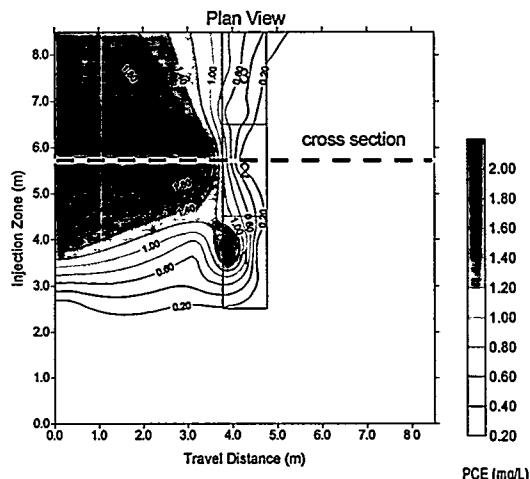


**Figure 3-34. Chrome and PCE distributions following 41 days of contaminant injection, 8-14 experiment.**

Cr Distribution after 56 days of injection (9/04/98)



PCE Distribution after 56 days of injection (9/04/98)



**Figure 3-35. Chrome and PCE distributions following 56 days of contaminant injection, 8-14 experiment.**

## 4.0 ECONOMIC ANALYSIS

The preparation of more than 30 tons of SMZ provided solid information on the cost of bulk production of the material. The major cost of the final product was associated with the price of the raw surfactant. Using 14-40 SMZ (with about 5 % HDTMA-Cl by weight) as an example, the per-ton production cost was about \$45 for raw zeolite, \$300 for HDTMA, and \$75 for processing, for a total cost of about \$420 ton<sup>-1</sup> (\$0.46 kg<sup>-1</sup>). Since the dry bulk density of SMZ is about 1 g cm<sup>-3</sup>, the cost on a unit volume basis was about \$13 ft<sup>3</sup> (\$460 m<sup>3</sup>).

In this project, we used high-purity HDTMA to manufacture the SMZ, since all of our laboratory testing had been done using this surfactant. Clearly, the bulk cost of SMZ could be greatly reduced if a less expensive surfactant were used. Surfactant mixtures which contain lower molecular-weight cationic surfactants, in addition to HDTMA, are available at lower cost. Limited experimentation with these lower-purity formulations indicated they produced SMZ that was less stable chemically and had a lower contaminant sorption capacity than SMZ prepared with pure HDTMA. The effectiveness of SMZ prepared from these alternative surfactant formulations warrants further examination, however.

Table 4-1 compares the cost of SMZ to other materials currently used or proposed for use in permeable reactive barriers. The most effective material for a particular barrier application will depend upon the material's unit cost and upon the contaminants to be controlled. Installation costs should be similar for each material.

In determining the material cost for a barrier of a given geometry, it is the cost per unit volume, rather than per unit weight, that is important. One clear advantage of SMZ is that its cost per unit volume is one-half to one-tenth that of the other materials listed in Table 4-1.

**Table 4-1. Costs of potential permeable reactive barrier materials.**

<u>Medium</u>	<u>Cost per Ton</u>	<u>Cost per Cubic Foot</u>
Granular Activated Carbon	\$1300-5000	\$20-60
Ion Exchange Resins	\$3000-6000	\$90-140
Iron Metal	\$300-400	\$30-35
Organoclay	\$1500-4000	\$30-90
SMZ	\$400-450	\$11-14

## 5.0 CONCLUSIONS

### A. Installation and Testing of Permeable Barriers

- An SMZ permeable barrier can be successfully deployed under field-like conditions while providing hydraulic containment.
- A highly automated water and chemical delivery system can be designed to provide uniform water flows and contaminant plumes of defined geometries, while minimizing contaminant discharges.
- Intensive sampling can and should be performed when evaluating prospective permeable barrier systems. Without an extensive sampling array and close monitoring of contaminant plumes, barrier performance will be difficult to evaluate.
- Extreme care must be taken to prevent hydraulic restrictions at barrier/aquifer interfaces.

### B. SMZ as a Permeable Barrier Material

- SMZ can be manufactured in multi-ton quantities at a cost of about \$460 m<sup>-3</sup> (\$460 per metric ton).
- The bulk-produced SMZ has physical and chemical properties essentially identical to SMZ prepared in the laboratory. In particular, the contaminant (chromate and PCE) sorption characteristics of bulk- and laboratory-produced SMZ are the same.
- Compaction of SMZ under the loading conditions of a permeable barrier is a potential problem. Since the hydraulic conductivity of SMZ can be tailored by varying the particle size, SMZ with a laboratory conductivity at least 100 times greater than that of the aquifer material should be used.
- Based upon the pilot-test data collected, it appears that contaminant retention by SMZ in a permeable barrier can well-predicted from laboratory sorption measurements.

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## 7.0 APPENDICES

### A. Publications and Reports Resulting from This Project

#### 1. Refereed Publications in Journals

Sullivan, E.J., J.W. Carey, and R.S. Bowman. 1998. Thermodynamics of cationic surfactant sorption onto natural clinoptilolite. *J. Colloid Interface Sci.* 206:369-380.

Li, Z., and R.S. Bowman. 1998. Sorption of chromate and PCE by surfactant-modified clay minerals. *Environ. Eng. Sci.* 15:237-245.

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Haggerty, G.M., and R.S. Bowman. 1994. Sorption of inorganic anions by organo-zeolites. *Environ. Sci. Technol.* 28:452-458.

#### 2. Book Chapters:

Bowman, R.S., E.J. Sullivan, and Z. Li. 1999. Mechanisms of surfactant and contaminant sorption by surfactant-modified zeolite (SMZ). In C. Collela, (ed). *Zeolite '97*. International Committee on Natural Zeolites, Brockport, NY (submitted).

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### 3. Symposia Proceedings:

Bowman, R. S., Z. Li, S. J. Roy, T. A. Burt, R. L. Johnson, and T. L. Johnson. 1999. A pilot-scale test of a surfactant-modified zeolite permeable barrier. *In Proc. WERC Conf. On the Environment, 26-29 April 1999, Albuquerque, NM (in press).*

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#### **4. Research Reports:**

Bowman, R.S. 1996. Surface-altered zeolites as permeable barriers for in situ treatment of contaminated groundwater. Phase I Topical Report. U.S. Department of Energy, Office of Environmental Management, Morgantown, WV. 40 p.

#### **5. Abstracts of Papers Presented at Professional Meetings:**

Bowman, R.S. 1999. Mechanisms of contaminant and surfactant sorption by surfactant-modified zeolite. 3<sup>rd</sup> Mesilla Chemistry Worksop, Mesilla, NM, 7-9 Feb. 1999.

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**B. List of Acronyms**

CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act of 1983
DOD	Department of Defense
DOE	Department of Energy
GC	Gas chromatography
HDPE	High-density polyethylene
HPLC	High performance liquid chromatography
HDTMA	Hexadecyltrimethylammonium
LEAP	Large Experimental Aquifer Program
NMT	New Mexico Tech
OGI	Oregon Graduate Institute
PCE	Perchloroethylene
PVC	Polyvinyl chloride
RCRA	Resource Conservation and Recovery Act of 1976
SARA	Superfund Amendments and Reauthorization Act of 1986
SMZ	Surfactant-modified zeolite