FIELD DEMONSTRATION OF PERMEABLE REACTIVE BARRIERS TO CONTROL URANIUM CONTAMINATION IN GROUND WATER

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ABSTRACT

Permeable Reactive Barriers show promise as an inexpensive and effective remediation technology alternative to Pump and Treat for removal of a wide range of contaminants including radionuclides from groundwater. Reactions within a reactive barrier either degrade contaminants to non-toxic forms or transfer contaminants to an immobile phase. Three permeable reactive barriers (PRBs) were installed near Fry Canyon, Utah, in August 1997. The overall objective of this project is to demonstrate the use of PRBs to control the migration of uranium (U) in ground water. A funnel and gate design was used to construct the three PRBs, which consist of (1) bone-char phosphate (PO₄), (2) zero-valent iron (ZVI) pellets, and (3) amorphous ferric oxyhydroxide (AFO). During the first 28 months of PRB operation (September 1997 through December 1999), the ZVI PRB was the most effective at lowering U concentrations in the contaminated ground water. The median U removal in the ZVI PRB was higher than 99.5 percent, in the AFO barrier 95 percent, and in the bone-char phosphate barrier, 81 percent. Geochemical modeling techniques were used to define and quantify the amount and type of mineral precipitates that may be forming in the ZVI PRB. Modeling results indicate that most of the mineral precipitation occurs within the first 1.0 foot of barrier material. On the basis of water-chemistry data collected during May 1999, the downgradient two-thirds of the ZVI PRB has not been affected by mineral precipitation. Geochemical modeling results were consistent with solid-phase analyses of reactive material collected from the ZVI PRB.

INTRODUCTION

The use of permeable reactive barriers (PRBs) as an alternative to for the remediation of ground water contaminated with chlorinated organics has received considerable attention in recent years (Gu et al., 1999). In contrast, the application of PRBs to remove uranium (U) and other radionuclides from ground water has been limited. As of 1999, 46 field projects utilized PRBs to treat contaminated ground water; however, only 7 of these field projects are treating U in water.

One of these field projects is located near Fry Canyon, Utah (Figure 1). Three PRBs were installed at this site in August 1997 to determine if long-term treatment of U-contaminated ground water would occur. Funding and overall
management of this PRB demonstration project was provided by the U.S. Environmental Protection Agency (USEPA)/Office of Radiation and Indoor Air, and the Office of Emergency and Remedial Response.

**Objectives**

The overall objective of this project is to demonstrate the use of three different PRBs to control the migration of U in ground water. Specific objectives of this paper are to (1) present the initial results of PRB performance for each of the three PRB materials during the first 28 months of field operation and (2) utilize geo-chemical modeling techniques to determine chemical reactions that may potentially decrease the long-term effectiveness of the zero-valent iron (ZVI) PRB. Results contained in this report will be useful to personnel involved with the clean up of ground water contaminated with uranium and (or) the plugging and passivation of ZVI PRBs.

**Site Description**

A shallow colluvial aquifer contaminated by previous U-upgrading operations near Fry Canyon, Utah (Figure 1), was selected for the long-term field demonstration of selected PRBs. This site is located on land managed by the U.S. Bureau of Land Management (BLM).

The shallow colluvial aquifer consists of silt to gravel-size particles derived from nearby sandstone and shale formations. Maximum saturated thickness of the colluvial aquifer ranges from about 2 to 5 feet (ft). Based on laboratory and field tests, hydraulic-conductivity values range spatially from 5 to 85 feet per day (ft/d) and transmissivity values range spatially from 10 to 200 square feet per day (ft²/d). The in-situ effective porosity for the aquifer is estimated to be 20 to 25 percent (Freethey, Spangler, and Monheiser, 1994). Underlying the colluvial aquifer is the Permian Cedar Mesa Sandstone, which is virtually impermeable compared to the colluvial aquifer. Concentrations of U in the contaminated part of the colluvial aquifer exceeded 16,000 micrograms per liter (µg/L). These concentrations were
substantially higher than background U concentrations, which ranged from 60 to 80 µg/L.

**METHODOLOGY**

**PRB Installation**

A funnel and gate design was chosen to demonstrate the three PRBs. This design consists of three "permeable windows" or gates in which each of the reactive materials is placed. Each gate is separated by an impermeable wall, and impermeable wing walls are installed on each end of the multigate structure to channel the ground water into the PRBs. Dimensions of each gate structure are 7 ft long by 3 ft wide by about 4 ft deep. The three PRBs and no-flow walls were placed into the upper parts of the bedrock (Cedar Mesa Sandstone) underlying the colluvial aquifer. A 1.5-ft-wide layer of pea gravel was placed on the upgradient side of the PRBs to facilitate uniform flow of contaminated ground water into each gate structure. The three gates contained (1) bone-char phosphate (PO₄); (2) ZVI pellets; and (3) amorphous ferric oxyhydroxide (AFO).

The mechanism of U removal in each of the PRBs is a function of the type of barrier material. The PO₄ barrier material consists of pelletized bone charcoal...
that facilitates surface complexation of U (Fuller et al., 1999). The ZVI barrier material consists of pelletized iron designed to remove U by reduction of U (VI) to the less soluble U (IV). The AFO barrier material consists of pea gravel coated with amorphous ferric oxyhydroxide that removes U by adsorption. Materials were pelletized or used as a coating on gravel to increase the permeability of the gate structure relative to the permeability of the native aquifer material.

Water Sampling and Analysis

An extensive monitoring network was installed in each PRB consisting of 16, 0.25-inch- (in.) diameter poly vinyl chloride (PVC) wells located along 2 parallel flow paths and 4, 2-in-diameter PVC wells (Figure 2) for sample collection and monitoring of water levels and selected water-quality parameters. Because of the proximity of wells to one another, limited purge volumes were extracted prior to sample collection. One gallon (gal) of water was removed from the 2-in-diameter monitoring wells and 0.26 gal of water was removed from the 0.25-in-diameter monitoring wells.
Fig. 3. Box plots showing the percentage of input uranium removed for each permeable reactive barrier during the first 28 months of operation at Fry Canyon, Utah.
After purging, water samples were filtered on site using a 0.45-micrometer (µm) capsule filter and collected in field-rinsed polyethylene bottles. Samples for analysis of U, calcium (Ca), iron (Fe), potassium (K), magnesium (Mg), and sodium (Na) were acidified on site with ultra-pure concentrated nitric acid. Each monitoring point contains a dedicated sampling tube to minimize cross contamination.

Water analyses were conducted at the U.S. Geological Survey (USGS) Research Laboratories in Menlo Park, California. Dissolved U was measured by kinetic phosphorescence analysis (KPA). Ca, Fe, Mg, and Na concentrations were measured by inductively coupled plasma optical emission spectrometry (ICP/OES) using a Thermo Jarrel Ash ICAP 61 (Standard Methods, 1992). The K concentration was measured by direct air-acetylene flame atomic absorption spectrometry (AA) using a Perkin Elmer AA 603. Sulfate (SO₄) concentrations were measured by ion chromatography (IC) using a Dionex Chromatograph CHB (Standard Methods, 1992).

The pH, Eh, and temperature of each water sample were measured in a flow-through chamber by using a Yellow Springs Instrument 600XL minimonitor that was calibrated daily with respect to pH and weekly with respect to Eh. Total alkalinity (as CaCO₃) of filtered (0.45 µm) water samples was measured on site by using a HACH digital titrator and 1.6 normal sulfuric acid.

RESULTS AND DISCUSSION

U Removal

The percentage of input U removed by each of the PRBs was determined for water samples collected during the first 28 months of PRB operation (September 1997 through December 1999) (Figure 3). The ZVI PRB was the most efficient of the three PRBs for reducing input U concentrations. The median percentage of U removal was always higher than 99.5 percent during the 11 monitoring periods (Figure 3). Although the median values for percentage of U removal were less in the PO₄ and AFO PRBs, substantial decreases in U concentration still occurred during the first 28 months of operation (Figure 3). The median values for percentage of U removal in the PO₄ PRB decreased to less than 70 percent in September 1998; however, there has been a steady increase in the percentage of U removed from December 1998 to December 1999. The AFO PRB has had a steady decrease in the median percentage of U removal since installation (Figure 3). The median percentage of U removal after 28 months of operation is 70 percent.

Plugging Reactions in Zero-Valent Iron PRB

ZVI PRB is removing the highest percentage of input U; however, core analysis from this barrier indicates that mineral precipitation is occurring. Minerals qualitatively identified in cores collected from the ZVI PRB during May 1999 included iron sulfide, calcite, and metallic iron (ZVI material). Mineral
precipitation can decrease the permeability and reactivity of the ZVI barrier material and result in a decrease in contaminant removal efficiencies (Gu et al., 1999). In a series of laboratory column experiments, Gu et al. (1999) identified a number of mineral precipitates forming in ZVI material. Mineral precipitates included iron hydroxides, carbonates, and sulfides.

Mass-balance modeling techniques were used to define and quantify the amount and type of mineral precipitates that may be forming in the ZVI PRB at Fry Canyon. The USGS geo-chemical model NETPATH (Plummer, Prestemon, and Parkhurst, 1994) was used to determine the quantity of each phase (mineral or gas) that would likely form or dissolve in ground water flowing between monitoring wells in the ZVI PRB. The general chemical reaction for this modeling is in the form of:

Initial solution composition + “Reactant Phases” Þ Final solution + “Product Phases” (Eq. 1)

where the terms “Reactant Phases” and “Product Phases” refer to phases entering or leaving the water during the course of a chemical reaction. The possible “Reactant” and “Product” phases were based on the qualitative mineralogical analysis of the ZVI material, speciation calculations (Table I), geo-chemical inferences made from the anaerobic and aerobic corrosion of Fe, and qualitative observations made during field visits.

Water samples collected during May 1999 from wells along three different hydrologic flow paths in the ZVI PRB were used in the NETPATH modeling. The wells from each flow path in upgradient to downgradient order are: (flow path 1) ZVIT1 Þ ZVIR1-2 Þ ZVIR1-3 Þ ZVIR1-6; (flow path 2) ZVIT2 Þ ZVIT3 Þ ZVIFS1; and (flow path 3) ZVIT2 Þ ZVIR2-2 Þ ZVIR2-5 (Figure 2).

Six chemical constraints and eight plausible phases were considered during the NETPATH modeling. The six chemical constraints included carbon (C), sulfur (S), Ca, Mg, and Fe concentrations and the term referred to as redox state (RS). The RS is a method of keeping track of electron transfer in the redox reactions considered in the NETPATH modeling. Conventions defining RS can be found in Plummer, Peterson, and Parkhurst (1994). The eight plausible phases considered during the NETPATH modeling are (1) calcite (precipitation (ppt.) only); (2) magnesite (ppt. only); (3) dissolved organic carbon (DOC) (dissolution (diss.) only); (4) siderite (ppt. only); (5) zero-valent iron (diss. only); (6) hydrogen gas (ppt. only); (7) iron sulfide; and (8) dissolved oxygen (diss. only).

On the basis of the chemical constraints and plausible phases that were selected, the small amount of dissolved oxygen (0.8 mg/L) in the input water was consumed by the aerobic corrosion of the ZVI material (Figure 4). Anaerobic corrosion of the ZVI material caused the generation of hydrogen gas accompanied by the precipitation of carbonate minerals (calcite, magnesite, and siderite). Oxidation of DOC in conjunction with the observed decrease in total inorganic carbon accounted for the relatively large amounts of carbonate precipitation along each flow path. The observed decrease in SO₄ concentration along each flow path.
was accounted for by microbial mediated sulfate reduction and the formation of iron sulfide. Electron donors used during the \( \text{SO}_4 \) reduction were a combination of DOC and hydrogen gas.

This geo-chemical model is not the only set of plausible phases that can explain the observed changes in water quality along the hydrologic flow paths; however, other data also support this model. The generation of hydrogen gas has been indirectly confirmed by the observation of gas bubbles in water from wells.
completed in the ZVI PRB. The corrosion of Fe is supported by the 10 to 15 percent decrease in Fe concentration from cores collected in the ZVI PRB relative to un-reacted ZVI material. The precipitation of calcite in the ZVI PRB is supported by scanning electron microscope images in combination with energy dispersive analysis of core samples collected from the barrier. In addition, total inorganic carbon concentration increased from 718 milligrams per kilogram (mg/kg) in an un-reacted sample of ZVI material to 7,780 mg/kg in a core sample collected from the ZVI PRB during May 1999. Selected samples from the ZVI material indicate up to a six-fold increase in Ca and two-fold increase in Mg concentration relative to the un-reacted ZVI material. The DOC concentration in ZVI feed water has not been measured; however, leaching of the bone-char phosphate may produce high DOC concentrations. Tracer tests conducted in April 1999 indicate that water from the PO\textsubscript{4} PRB is moving along the gravel pack and entering the ZVI PRB. The total organic carbon concentration decreased from 19,600 mg/kg in un-reacted bone-char barrier material to 3,660 mg/kg in a core sample collected from the PO\textsubscript{4} PRB during May 1999 (20-month time period). Sulfate reduction is supported by the detection of iron sulfide solid phases using SEM/EDA in core samples from the ZVI PRB. Additional confirmation of the NETPATH modeling is provided by the computer program WATEQF (Plummer, Jones, and Truesdell, 1976). The program was used to calculate the ionic activities in water samples upgradient and within the ZVI PRB (Table I). The degree of saturation, defined as the ratio of the ion-activity product divided by the equilibrium constant for the specific mineral, was determined for each mineral considered as a plausible source or sink for selected chemical constituents. The log of this ratio is referred to as the saturation index (SI). A positive SI indicates that thermodynamic conditions favor mineral precipitation from solution, whereas a negative SI indicates conditions that favor mineral dissolution. A SI near zero indicates that the solution is in equilibrium with respect to the mineral of interest.

Table I. Saturation indicies of selected plausible phases in water samples upgradient and within the zero-valent iron permeable reactive barrier in Fry Canyon, Utah, during May 1999.

<table>
<thead>
<tr>
<th>Well number</th>
<th>Calcite</th>
<th>Siderite</th>
<th>Gypsum</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZVIT1</td>
<td>0.495</td>
<td>0.240</td>
<td>-0.257</td>
</tr>
<tr>
<td>ZVI T2</td>
<td>0.468</td>
<td>0.350</td>
<td>-0.388</td>
</tr>
<tr>
<td>ZVIT3</td>
<td>1.143</td>
<td>1.687</td>
<td>-1.287</td>
</tr>
<tr>
<td>ZVIFS1</td>
<td>1.396</td>
<td>1.180</td>
<td>-1.472</td>
</tr>
<tr>
<td>ZVIR1-2</td>
<td>0.616</td>
<td>1.673</td>
<td>-0.470</td>
</tr>
<tr>
<td>ZVIR1-3</td>
<td>0.923</td>
<td>1.732</td>
<td>-0.997</td>
</tr>
<tr>
<td>ZVIR1-6</td>
<td>1.017</td>
<td>1.549</td>
<td>-1.299</td>
</tr>
<tr>
<td>ZVIR2-2</td>
<td>0.610</td>
<td>1.665</td>
<td>-0.479</td>
</tr>
<tr>
<td>ZVIR2-5</td>
<td>0.668</td>
<td>1.751</td>
<td>-0.513</td>
</tr>
</tbody>
</table>

The likely formation of calcite and siderite is supported by the larger positive SIs observed for these minerals in water samples from wells completed in the ZVI PRB (Table I) relative to wells completed in the upgradient gravel pack (ZVIT1 and ZVIT2). Although magnesite is used in the NETPATH model to account for Mg loss along each of the flow paths, it is likely that magnesium is substituting in the calcite mineral phases that are observed. The SI for gypsum
(Table I) is negative, indicating that the observed decrease in sulfate concentration along each flow path is the result of sulfate reduction and not gypsum precipitation.

Results from the NETPATH model indicate that most of the mass transfer occurs along the first 1.0 ft in each hydrologic flow path (Figure 4). For example, 16.81 millimoles per kilogram of water (mmol/kg H₂O) of carbonates and sulfides are precipitated along the first 1.0 ft in flow path 1 compared with only 2.67 mmol/kg H₂O in the 1.0-to-2.0-ft section (Figure 4). This pattern of mineral precipitation indicates that approximately two-thirds of the ZVI PRB has not been affected by mineral precipitation.

The amount of carbonate and sulfide precipitation indicated by the NETPATH modeling results can be used to estimate the rate of porosity reduction in the first 0.5 ft of flow path 1 in the ZVI PRB. By using a calculated groundwater input of 9.7 cubic feet per day (ft³/d) into the ZVI PRB (Table II), approximately 0.0017 cubic feet per day of ZVI PRB porosity is consumed by carbonate and sulfide mineral phases in the first 0.5 ft of reactive material. The total porosity in the first 0.5 ft of un-reacted ZVI material along flow path 1 was 1.70 ft³ (0.5 ft thick by 2.3 ft width by 3.7 ft deep by 40 percent total porosity). With the porosity reduction rate of 0.0017 ft³/d, over 30 percent of the ZVI porosity will be lost each year. The yearly rate of porosity reduction will probably not be linear. As mineral precipitation continues, less of the ZVI material will be available for reaction causing the precipitation reactions to migrate farther into the PRB.

Table II. Data used to calculate the volume of carbonate and sulfide mineral precipitates along flow path 1 in the zero-valent iron permeable reactive barrier, Fry Canyon, Utah.

<table>
<thead>
<tr>
<th>Groundwater input (ft³/d)</th>
<th>Carbonate precipitated (mmol/d)</th>
<th>FeS (trolite) precipitated (mmol/d)</th>
<th>Calcite density (g/cm³)</th>
<th>FeS (trolite) density (g/cm³)</th>
<th>Calcite volume (ft³/d)</th>
<th>FeS volume (ft³/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.7</td>
<td>933</td>
<td>785</td>
<td>2.71</td>
<td>4.61</td>
<td>0.0012</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

*Based on tracer test conducted during April 1999.

CONCLUSIONS

The PRBs installed at Fry Canyon were demonstrated to be highly effective in removing Uranium and other metals from groundwater. Life cycle costs compared to pump and treat are lower due to very low PRB operation and maintenance costs. While these factors make PRBs look very attractive, there is still need for additional data on long-term operation issues of PRBs such as barrier plugging, material disposal, and need for periodic renewal or replacement of reactive material. Once these issues can be better understood, the use of PRBs will become a valuable tool for the remediation professional.
REFERENCES


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