Technical/Regulatory Guidance

Permeable Reactive Barrier: Technology Update

June 2011

Prepared by
The Interstate Technology & Regulatory Council
PRB: Technology Update Team

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EXECUTIVE SUMMARY

The Permeable Reactive Barrier (PRB): Technology Update Team of the Interstate Technology & Regulatory Council (ITRC) produced this document to provide an update on information pertinent to the design and use of PRBs for treating contaminants in groundwater. *Permeable Reactive Barrier: Technology Update* is the fifth document published by ITRC, since 1999, to investigate the development of PRBs as an emerging remediation technology. It is a comprehensive resource that incorporates elements from previous documents and provides updates on additional types of reactive media, contaminants that can be treated, PRB longevity issues, and new construction/installation approaches and technologies.

The definition of the PRB as an in situ permeable treatment zone designed to intercept and remediate a contaminant plume is now standard in the remediation industry and is not changed in this document. PRBs have become an important component among the various technologies available to remediate groundwater contamination. Since the first implementation in the early 1990s, more than 200 PRB systems have been installed.

Since inception, the PRB has remained an evolving technology with new and innovative reactive materials introduced to treat different contaminants as well as innovative construction methods. “New” reactive materials include mulch for treating chlorinated solvents, metals, and energetic and munitions compounds, zeolites for treating radionuclides and heavy metals, and “transformed redmud” (a waste material formed from bauxite ore during the production of alumina that has been used to treat acid-rock drainage), but other materials such as carbon/zero-valent iron (ZVI) combinations also are being tested and used. Installation innovations include the use of single-pass trenchers, large-diameter boring installations, and injection methods.

The PRB system is typically intended to perform using hydraulically passive means; that is, the PRB is designed to allow groundwater and the target chemicals to flow through the PRB without mechanical assistance. After construction, PRB technology fits the concept of green and sustainable technology. In keeping with the green concept, effects from construction of a PRB also can be minimized. Reactive materials frequently are waste products (e.g., mulch, some iron ore slags) or are recycled (e.g., iron scrap). The actual installation of a PRB is the largest energy expenditure, but even this can be minimized if the work is completed in one mobilization and local equipment and contractors are used.

New developments have shown that ZVI also is effective in treating other contaminants, including dissolved metals and energetic compounds, such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and 2,4,6-trinitrotoluene (TNT). Biowalls using solid organic materials (mulch) also have been applied to treat energetic and munitions compounds as well as for treating nitrate-impacted groundwater. PRBs have evolved with respect to arsenic treatment, and new media, including carbon-rich organic/iron combinations, emulsified ZVI, and organophilic clays, have been applied as reactive treatment media.

We have learned that inadequate performance of a PRB typically stems from incomplete site characterization and inadequate hydraulic design. The nature and extent of the contaminant plume(s) must be well characterized to design an effective PRB and should consider the nature and anticipated persistence of the contaminant source. The vertical extent of contamination is particularly important. The contaminant discharge (mass flux) through the PRB should be sufficiently characterized so that the upgradient concentrations can be accommodated by the PRB design. It is also imperative to understand the contaminant plume shape and variability in the direction of groundwater flow over time.

ZVI PRBs have been installed and performing in place for 15 years in a variety of geochemical environments. Data gathered have shown that the major effect of inorganic constituents on the technology involves the formation of mineral precipitates on the iron surface; this can passivate reactive sites and clog the PRB. Calcium carbonate, iron carbonate, iron hydroxide, and iron sulfide precipitates may form in the media as the pH of the groundwater increases in response to corrosion of the iron metal. Geochemical changes to ZVI from the presence of sulfate, nitrate, and oxygen also are widely observed, and more research into prevention of performance loss is an ongoing area of research.

This document provides the basics for understanding what a PRB is and what it can—and can't—do, but it also provides updates on the technology. Section 2 covers regulatory considerations; Section 3 covers remediation considerations, including setting performance objectives. Section 4 looks at the various reactive media now in use, while Sections 5 and 6 cover design and construction of PRB systems. Section 7 discusses monitoring and how to design a monitoring program that will allow the system to work optimally so remediation goals can be met. Section 8 introduces the concept of longevity and discusses the useful life of PRB systems while also looking at how and when to rejuvenate PRBs already in use. Section 9 discusses the green and sustainable concept as related to PRBs.

While many important lessons have been mastered, it is obvious that continued research and practical applications will yield a much greater understanding of the technology. Site characterization must continue to improve so that as much data as reasonably possible for a given site can be collected and worked into a PRB design. Construction methods must continue to expand if PRBs are to be deployed in more and different conditions. Also, cost and performance data must be collected from a greater number of sites, in particular those involving novel reactive media, to better confirm the long-term efficacy of PRB technology for treating groundwater plumes.

The PRB: Technology Update Team believes that the reader will, through the use of this guidance, be better equipped to evaluate PRB technology as a remedial alternative at contaminated sites. The document provides readers a better understanding of the advantages and limitations of PRBs and helps them navigate the associated regulatory, hydraulic, and engineering challenges. This guidance ultimately allows users to optimize and more closely match the needs of the site to the selected remedy, whether or not it includes a PRB.

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1. INTRODUCTION AND DOCUMENT SCOPE

1.1 PRB: Technology Update Team

The Permeable Reactive Barrier (PRB): Technology Update Team of the Interstate Technology & Regulatory Council (ITRC) comprises representatives from six state regulatory agencies (South Carolina, New Jersey, Alabama, California [Department of Toxic Substances Control and State Water Quality Control Board, San Francisco Bay Region], and Oklahoma), the U.S. Department of Defense (DOD), the U.S. Environmental Protection Agency (USEPA), Atomic Energy Canada Limited, private consulting and vendor companies, and academia. Since 1996, various ITRC PRB teams have investigated the development of PRBs as an emerging remediation technology. This is the fifth PRB-related document produced and/or coproduced by ITRC. Previous ITRC guidance focused on implementation of PRBs for treating dissolved chlorinated solvents (ITRC 1999a) and inorganic and radionuclide contamination (ITRC 1999b), design guidance (ITRC 2000), and a lessons-learned document (ITRC 2005b). This fifth document—*Permeable Reactive Barrier: Technology Update* (PRB-5)—is a comprehensive resource that incorporates elements from previous documents and provides updates on additional types of reactive media, contaminants that can be treated, PRB longevity issues, and new construction/ installation approaches and technologies.

1.2 Purpose and Organization of the Document

This document is intended to serve as a comprehensive technical and regulatory resource when a PRB is being considered as an in situ remedy for contaminated groundwater. Readers who will benefit include state and federal regulators, consultants, project managers, and other stakeholders and technology implementers.

This document provides updated information regarding innovative approaches in applying PRB technology to treat a variety of groundwater contaminants; it provides fresh ways to evaluate the site-specific applicability of a PRB and provides some basic information for readers new to PRBs. Section 2 discusses regulatory considerations; Sections 3, 4, 5, and 6 look at how to determine whether a PRB is suitable for a site and how to design/construct the "right" PRB to get the job done. Section 7 covers monitoring network design; evaluating remedial performance; and monitoring the effects of the PRB on hydraulics, geochemistry, and microbiology of the groundwater system. In addition, monitoring approaches for concentration-based and mass flux performance standards are covered, and downgradient water quality issues and advanced monitoring tools also are discussed in Section 7. Section 8 discusses sustainability issues related to PRBs, while the PRB as a green and sustainable remedial technology is discussed in Section 9.

Where possible, this document identifies important regulatory issues to consider at each stage of the remedial process. Case summaries are included (Appendix A) to illustrate various PRB designs, contaminants treated, reactive media used, and cost data for implementing PRB technologies. Appendix D is a glossary of terms.

Because the PRB is an evolving technology, this document is intended as a guide only. Recent peer-reviewed literature from research studies and field demonstrations, as well as current regulatory requirements, should always be reviewed when considering the guidelines outlined in this document. Users of this document are encouraged to consult the reference list (Section 12) for further background and technical information on this technology.

1.3 PRB Definition and Application

In the broadest sense, and for the purposes of this document, a PRB is an in situ, permeable treatment zone designed to intercept and remediate a contaminant plume. The term "barrier" is intended to convey the idea that contaminant migration is impeded; however, the PRB is designed to be more permeable than the surrounding aquifer media so that groundwater can easily flow through the structure without significantly altering groundwater hydrology. The treatment zone may be created directly using reactive materials such as zero-valent iron (ZVI), or indirectly using materials designed to stimulate secondary processes (e.g., adding carbon substrate and nutrients to enhance microbial activity). In this way, contaminant treatment may occur through physical, chemical, or biological processes.

PRBs are a multipurpose remedial technology. They can be installed anywhere along the plume and designed to address different site-specific objectives. For example, a PRB installed near the source area may be designed to reduce mass flux and act as a source term management remedy, whereas a PRB installed farther downgradient may be designed to protect downgradient receptors.

1.4 Treatment Train

Like many technologies implemented today, a PRB is not a stand-alone, one-size-fits-all remedy but is generally part of a "treatment train." Remediation strategies are site specific and by necessity are quite diverse. A PRB may act as a polishing technology after active source removal (physical removal, thermal treatment, surfactant flushing, soil vapor extraction, or even bioremediation), or a PRB may be installed near the source, in the middle of the plume, or at the toe of the plume to protect human health or nearby ecological receptors. In some cases, phytoremediation and monitored natural attenuation (MNA) can become a part of the "treatment train" to address residual downgradient contamination.

1.5 What's New

Reactive Media and Treatment Process (Section 4)

Over the past 15 years, the use of iron-based PRBs has evolved from innovative to accepted standard practice for the containment and treatment of a variety of groundwater contaminants. This success has encouraged other innovative ideas, including the use of mulch biowalls to degrade chlorinated solvents or immobilize metals and of zeolite and apatite to control radionuclide plumes. A new type of reactive media being used today is the nonaqueous-phase liquid (NAPL)–absorbing organophilic clay used to control creosote and coal tar contaminants at wood-treating sites and former manufactured gas plant sites. Additional data have been obtained from systems using some of the more novel reactive media, such as mulch and other organic materials used in biowalls. In addition, there have been data collected on the use of apatite, whereas there were previously little to no data on the performance of these systems. Additional information on these reactive media is provided in Section 4.

Design Considerations (Section 5)

Previous ITRC PRB documents have discussed mulch biowalls, but design considerations for these systems are new to this document. Additionally, updated inorganic geochemical considerations for ZVI PRBs are discussed in Section 5.

Construction and Cost (Section 6)

Section 6 of the document discusses the major cost drivers for PRBs, as well as cost factors for large sites vs. small sites and active vs. passive PRBs. Example costs for biowalls and injected media are provided, and advances in construction techniques are discussed, such as continuous trenching, increased depths (35–40 feet), the use of larger equipment and improved techniques for trenched PRBs, and improved delivery methods for fluid or slurry forms of reactive media in injected PRBs.

Performance Assessments (Section 7)

Alternative compliance monitoring metrics such as mass discharge and toxicity reduction are new ideas discussed in Section 7. Additionally, information regarding improved analytical monitoring tools such as compound-specific isotope analysis (CSIA) and molecular biological tools (MBTs) is provided, along with analysis of iron and sulfide mineralogy to evaluate biogeochemical transformation processes. Operations and maintenance (O&M) plans are discussed with emphasis on monitoring protocols to evaluate when a PRB should be optimized or replenished.

Longevity (Section 8)

Evaluations of the long-term performance of PRB technologies are provided in Section 8 of the document. Long-term case studies are included, and issues such as hydraulic capture, residence time, and reactivity are discussed.

Sustainability (Section 9)

Discussions regarding the evaluation of PRB technologies from the perspective of how green and sustainable the systems are or can be and what should be considered when evaluating a technology with regard to how sustainable it is are discussed in Section 9.

Document Road Map

Figure 1-1 demonstrates how this technical and regulatory guidance document can be used to determine whether a PRB is an appropriate technology for a site. The roadmap also provides links to the appropriate section of the document.

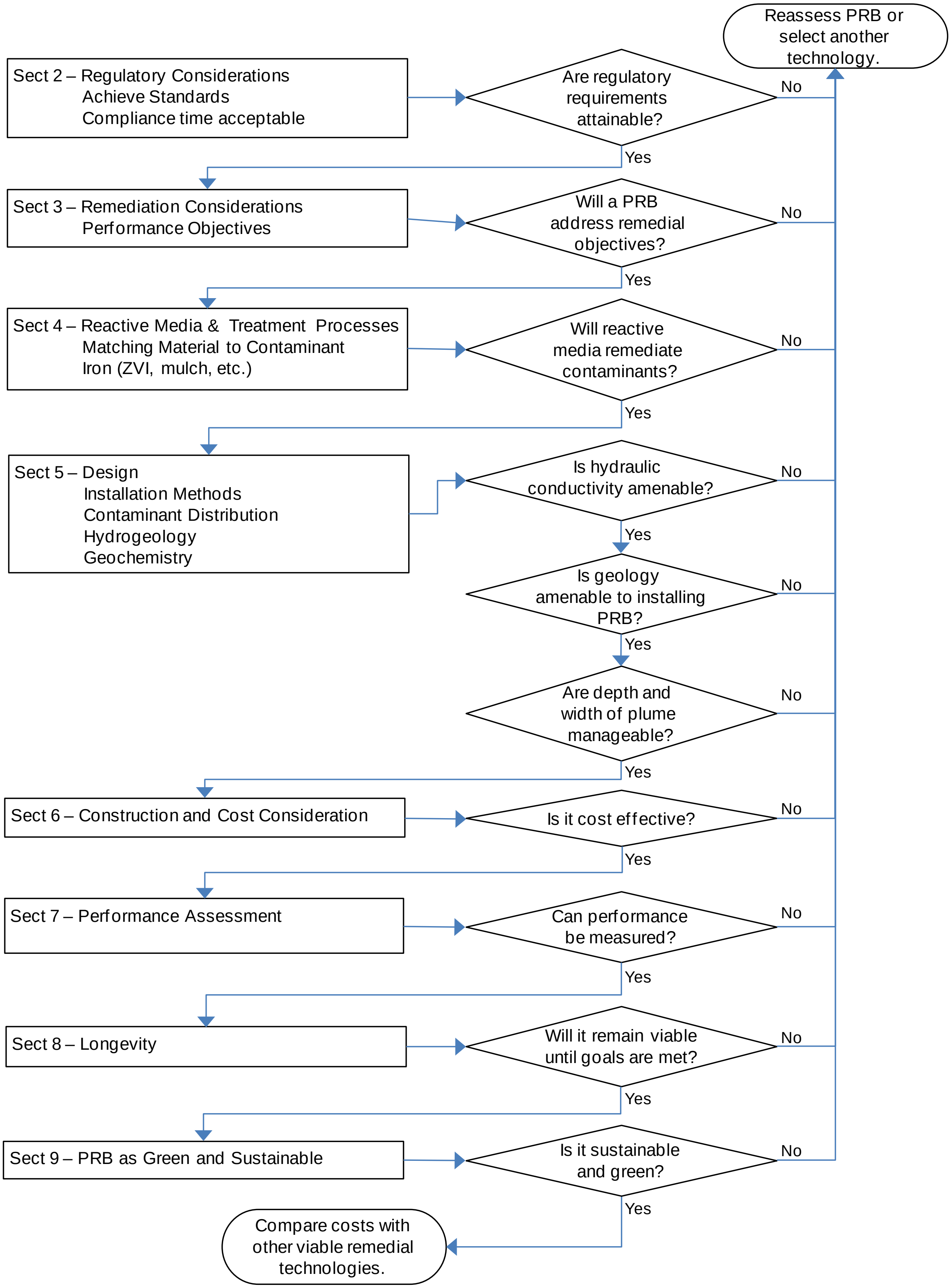

Figure 1-1. Document road map.

2. REGULATORY CONSIDERATIONS

This section describes regulatory permitting considerations associated with PRB design, construction, and closure. This section also discusses sampling and monitoring requirements for purposes of compliance with regulatory standards. The topic of performance assessment is covered more fully in Section 7.

What's New?

- PRBs are a widely used and accepted technology
- Performance monitoring information
- Secondary water-quality information
- Downgradient attenuation issues

In most cases, regulatory permits are not required for the operation of a PRB. However, one or more permits may be necessary for the design, construction, monitoring, or closure of a PRB to the extent that the activity affects surface water, air, or groundwater quality or involves the management of hazardous waste. A thorough review of all permitting issues and state and local regulations should be conducted on a site-specific basis.

In addition to regulatory permits, PRB approval may occur through different regulatory mechanisms. The approval mechanism (e.g., approval letter or cleanup order) often depends on the regulatory program/process under which the site cleanup is managed (e.g., Resource Conservation and Recovery Act [RCRA], state Superfund, or voluntary cleanup programs). Various regulatory programs may require submittal of a work plan, corrective action plan, remedial action plan, feasibility study (FS), or similar regulatory planning document. Following are brief explanations of key potential regulatory permits that may be required for a PRB.

2.1 Underground Injection Control

Underground injection control (UIC) is a federal program administered by USEPA; however, regulatory approval may be delegated to authorized states. The UIC program is responsible for regulating the construction, operation, permitting, and closure of injection wells that place fluids underground for storage or disposal.

UIC permits are not typically required for PRBs; however, this requirement varies from state to state; therefore, a review of the pertinent regulations should be conducted during initial design stages of the project, especially if the reactive media is installed by a high-pressure jetting technique or by vertical hydraulic fracturing. If USEPA has not delegated the UIC program to the state, the regional USEPA office makes the determination.

2.2 National Pollution Discharge Elimination System

National Pollution Discharge Elimination System (NPDES) permit authority resides within the federal Clean Water Act (CWA). The NPDES permit program controls water pollution by regulating point sources that discharge pollutants into waters of the United States. An NPDES permit may be required during construction if excess fluid (e.g., displaced groundwater or excess slurry) is generated. If it is necessary to dispose of the liquid or if there is potential that storm water generated during construction could carry pollutants or sediment into surface water bodies, then an NPDES permit from the state may be required. Additionally, many states now require storm-water pollution prevention plans, which require use of best management practices (BMPs) to manage storm-water discharges at construction sites 1 acre or larger.

2.3 RCRA and State Superfund Programs

In most cases, PRBs treat groundwater contaminated by listed (i.e., RCRA) hazardous wastes. Since PRBs are considered an in situ treatment technology, their deployment does not trigger RCRA management requirements for the treated groundwater. However, contaminated soil, groundwater, or reactive material that is brought to the surface, such as during PRB construction or closure, must be managed as a RCRA hazardous waste if the contaminants were initially considered RCRA hazardous waste. Closure plans, similar to the closure plan requirements for RCRA facilities, should be developed to consider and address these issues.

A number of states do not require permits for remedial activities when performed under state Superfund or corrective action programs (e.g., RCRA). In lieu of permits, these remedial activities are required to meet the technically substantive requirements (e.g., discharge limitations, monitoring requirements, design specifications, performance criteria) of the applicable regulations. In these cases, a work plan/remedial design is required for state review and approval. The need for a permit versus meeting the technical substantive requirements should be clarified with the state agency overseeing the project.

2.4 Air Quality Control

Air quality permits are not typically required for PRBs designed to treat volatile compounds such as chlorinated solvents. However, if the PRB installation requires excavation and stockpiling of highly contaminated soil (such as near the source area), a permit could be required. In such cases, monitoring or modeling data may be required by the air quality permitting authority to demonstrate that air releases are below the appropriate threshold. An evaluation should also be made to determine the need for health and safety monitoring and to ensure that there are no off-site excursions of fugitive emissions.

2.5 Other Discharge/Construction Permits

Individual states may require other permits for PRB construction. The emplacement of a foreign material—the reactive media in a PRB—into the subsurface which may affect groundwater or surface-water quality may require a state permit. Additionally, the land application of wastes generated from PRB construction (i.e., displaced groundwater or excess slurry) could require a permit. In these cases, a state permit might be required to ensure the land discharge is appropriate and not harmful to human health or the environment.

When the construction of a PRB is near a building or other structure, in a traffic corridor, or simply in an urban area where nuisance issues may arise during PRB construction, other state or local permits may be required. If the PRB is to be constructed near a wetland or surface water body, U.S. Army Corps of Engineers regulations must be followed, and a federal permit may be required. In such cases, mitigation measures and a corresponding certification by state regulatory agencies also may be necessary. Well construction permits also may be required by local agencies such as county environmental health departments and local water and utility districts.

2.6 Trenching and Excavation Permits

Trenching and excavation permits are typically required by local agencies (city and county governments), primarily for compliance with local, state, and federal occupational health and safety laws and regulations.

2.7 Operations and Maintenance and Abandonment Permits

O&M and abandonment permits may be required by oversight regulatory agencies and municipal governments that issue site cleanup orders or permits. These permits are issued to ensure PRBs are properly operated, maintained, and abandoned.

2.8 Institutional Controls

Deployment of a PRB can require the enactment of institutional controls (ICs). These administrative and/or legal controls and tools are typically implemented to restrict land use to limit human exposure—especially exposure of sensitive populations—to contaminants that may remain at the site. For example, an IC could act to protect the remedial measure from excavation activities, the installation of wells, local groundwater pumping, or any other intrusive actions that could affect the performance of the remedial system. When a PRB is the chosen remedy, the site should be evaluated to determine whether one or more ICs are needed to protect the operation of the remedial system and any contamination remaining on site that would require site restrictions should be noted. The use of ICs is not a way around treatment but rather part of a balanced, practical approach to site cleanup that relies on both engineered and nonengineered remedies.

In general, ICs do not involve construction or physically changing the site and are generally divided into the following three categories:

- **Government controls** include state and local laws or permits (e.g., zoning restrictions, building permits, ordinances, statutes, well-drilling prohibitions and Base Master Plans at military facilities) that restrict land or resource (e.g., surface water and groundwater) use at a site.
- **Property controls** include property use restrictions based on private property law (e.g., easements and covenants). Environmental covenants, also known as environmental deed restrictions, are commonly used property controls for contaminated site cleanup and redevelopment.
- **Informational devices** include state registries of contaminated properties, deed notices, hazard notices, public advisories, and fact sheets that alert and educate people about contamination remaining on a site above levels that permit unlimited use and unrestricted exposure.

2.9 Future Responsibility of O&M

The following are some of the tools and instruments used to ensure that the responsible party and the owners and operators of PRBs remain responsible for the O&M and abandonment of PRBs at their sites.

2.9.1 Site Management Plans

The purpose of a site management plan is to provide a plan to prevent or minimize human exposure to contaminated soil and groundwater at hazardous waste sites prior to meeting the cleanup standards. Site management plans govern all future intrusive work at the PRB site, such as drilling, soil excavation, contaminated soil and groundwater disposal, trenching, dewatering, backfilling, and capping activities.

2.9.2 O&M Requirements

Monitoring of both the reactivity of the media being used to remediate the contaminant and the hydraulic performance of the PRB system should be incorporated into a long-term performance monitoring and maintenance plan for the system. Performance assessment is discussed in greater detail in Section 7. O&M issues that involve the regeneration of the reactive media and the restoration of the hydraulic performance of the PRB are typically of concern to the state and federal environmental agencies. If the barrier is being repaired or reconstructed, contaminated reactive media or soil may be generated. Any material generated should be properly classified and disposed of in accordance with state and federal hazardous waste regulations. In addition, many states require that the monitoring or performance assessment requirements be incorporated into O&M requirements.

2.10 Contingency Plan

In many cases, a contingency plan is required in the event that the PRB fails to meet the compliance criteria. The need for a contingency plan should be evaluated during the design of the PRB system. Contingency plans may range from modification of the PRB system to the use of an alternative technology. In evaluating applications for a PRB remedy, regulators often require that one or more contingency measures be incorporated in the design to prevent contaminant migration in case of PRB failure. Some examples of contingency measures include the following:

- extending the PRB to capture more of the plume if monitoring shows that the capture zone is inadequate
- blocking the end(s) of the PRB with an impermeable barrier (slurry wall or sheet piling)
- modifying/amending the PRB if sufficient treatment is not being provided
- installing a second PRB downgradient from or adjacent to the first one
- pumping the PRB as an interceptor trench (a variation of the pump-and-treat measure)
- recirculating groundwater through the PRB or provide other active hydraulic control
- operating a pump-and-treat system if monitoring shows contaminant breakthrough or bypass for the PRB

In a survey (Gavaskar et al. 2002), regulators noted that the actual contingency measure adopted would depend on the mechanism of failure. Means of measuring hydraulic performance and identifying appropriate contingency measures to deal with any future loss of hydraulic performance were key issues that regulators thought would benefit from more research.

2.10.1 Monitoring Programs and Objectives

Monitoring of conditions in and around PRBs should begin once installation is complete. Typically, monitoring in one form or another is necessary as long as the groundwater contaminants pose a significant concern. The key lines of evidence targeted by most monitoring programs include contaminants of concern (COCs) and their breakdown products, hydraulic flow characteristics through and around the PRB, and groundwater geochemistry. Together, these lines of evidence are considered indicators of PRB performance and longevity. A monitoring plan is generally prepared along with the design report, and both documents are required to obtain regulatory approval.

A PRB monitoring program typically consists of both compliance and performance monitoring programs. The objective of compliance monitoring is to demonstrate achievement of cleanup standards at designated "compliance points," while the goal of performance monitoring is to verify proper PRB operation and effective contaminant treatment within the barrier. Further discussion regarding performance objectives can be found in Section 3 of this document. Further discussion on monitoring can be found in Section 7 along with the ITRC PRB lessons learned document (2005b).

2.10.2 Methods for Establishing When Contingency Should Be Initiated—Evaluating Changes in Barrier Reactivity and Permeability

A contingency sampling plan should also be developed whenever a PRB is the chosen remedial alternative. A contingency sampling plan addresses alternative sampling and investigative techniques useful in addressing a situation where the PRB fails to meet compliance or performance criteria. Techniques or methods that should be considered as part of the contingency sampling plan include changes in monitoring frequency, tracer testing, and coring, followed by analysis of the reactive media from the PRB.

One of the first sampling options that can be employed in the event the PRB fails to perform as designed is to increase the sampling frequency. The site sampling plan typically includes field parameters, COCs, and any breakdown or by-products, along with groundwater chemistry parameters. Increasing the frequency of the sampling helps to confirm any problems and can help isolate problem locations or areas within the PRB for further evaluation.

Tracer testing of the PRB can be conducted to evaluate the flow patterns and velocity through the system. These tests are typically resource-intensive and complex in nature and therefore have not been conducted on a routine basis at PRB sites. The tests have been conducted at both the Moffett Field Site in Mountain View, California, and the U.S. Coast Guard Site in Elizabeth City, North Carolina (see Appendix A case summaries) (Wilkin and Puls 2003). If conducted correctly, the tests can provide valuable information on the hydraulics of a PRB system.

2.10.3 Compliance Issues

The implications for the post-installation monitoring system design include the following examples.

A major compliance challenge at many PRB installations is the long time (several years) it may take for a perceptible improvement in downgradient groundwater quality to appear when the PRB is placed within the groundwater plume. Possible factors contributing to the long cleanup times in the downgradient aquifer are naturally slow groundwater flow at many sites, slow diffusion of contaminants from less accessible pores in the downgradient aquifer, smearing of low-permeability materials across the face of the PRB during construction, and development of vertical gradients and stagnant zones in the PRB and in the downgradient aquifer.

At many sites, regulators have dealt with this issue by allowing a temporary compliance point inside the PRB where cleanup levels are measured. Subsequently, as a clean front shows signs of emerging on the downgradient side, the compliance point can be moved back to the property boundary or other downgradient locations.

Contaminant levels, field parameters (pH, oxidation-reduction potential [ORP], temperature, and conductivity), native inorganic constituents (e.g., calcium, magnesium, alkalinity), dissolved organic carbon (DOC), and water levels are all good parameters to use in monitoring the long-term performance of a PRB. Contaminant levels at most sites need to be monitored on a quarterly basis per regulatory guidelines. The other parameters can be monitored on a schedule based on site-specific conditions (e.g., groundwater flow velocity). Not all monitoring parameters may be necessary at all sites.

If the PRB is designed or performs in such a way that natural attenuation processes on the downgradient side become important, monitoring the microbiology of the downgradient aquifer may be important.

If hydrologic problems (inadequate plume capture, inadequate residence time, unusual delay in water quality improvement on the downgradient side) are encountered after installing a PRB, contingency measures, starting with problem identification (monitoring), need to be initiated. Water-level measurements can sometimes be effectively supplemented with tracer tests to uncover flow problems. Groundwater flow and solute transport modeling can be used to evaluate prospective PRB modifications.

2.11 System Closure Perspectives

Currently, no sites have attained closure status using PRB as the primary remedial technology, so it is difficult to specify appropriate closure options for PRBs. However, closure will most likely be linked to the type of treatment mechanism the PRB is providing. In general, the mechanism involves one of two processes: to either degrade the contaminant or concentrate the contaminant within the reactive media. A PRB installed to treat chlorinated solvents typically degrades the contaminants, while one designed for metals and/or radionuclides retains the contaminants in a modified chemical/physical state.

Closure of a PRB will typically not occur until the upgradient and downgradient aquifer meets the applicable groundwater quality standards or cleanup goals. Consequently, PRBs will often remain active for an extended period. Upon closure, there will usually be no need to remove the PRB that was designed to degrade contaminants such as chlorinated organics.

In cases where the PRB will remain in place after closure, concern may arise regarding the long-term dissolution of the reactive media and its effect on downgradient water quality. The PRB will most likely impact downgradient secondary water quality. The need for post-closure downgradient monitoring should be based on the data collected during operation of the PRB. Depending on the concentration of parameters detected during operation of the PRB, consideration may be given to reducing or eliminating future monitoring. Any reduction should be based on a thorough understanding of the dynamics of the system.

The second treatment type of PRB is a system designed for metals and/or radionuclides that retain the contaminants in a modified chemical/physical state (e.g., alteration of oxidation state, formation of insoluble precipitates, absorption of contaminants or precipitates, etc.). Treatment mechanisms may involve a change in the oxidation state of the metals and/or radionuclides under specific groundwater oxidation-reduction (redox) conditions. Any change in redox conditions over a period has the potential to alter the contaminants' oxidation state, causing them to remobilize. The PRB designed to retain contaminants within the reactive media may have to be removed following treatment. However, if it can be proven that the contaminants will not be mobilized after treatment is complete, then the PRB could remain in place. If the PRB remains in place, monitoring should be determined based on the closure method and data collected during operation of the PRB.

A number of site-specific factors may influence the decision to remove an aged PRB, including the following:

- loss of permeability through the reactive media
- potential for contaminant desorption from reactive media
- potential for spent reactive material to provide a future contaminant source
- concentrations of contaminants in reactive media affecting disposal options
- substantial deterioration of reactive media effectiveness
- future use of property
- cost of removal vs. long-term O&M
- regulatory requirements for closure
- noncontaminant changes in downgradient water quality
- potential need for ICs

Upon completion of treatment, all monitoring wells not needed for follow-up or future groundwater monitoring should be plugged and abandoned in accord with state-specific regulations and requirements. If the PRBs are removed, the PRB treatment materials should be transported to an appropriate disposal facility, which may depend on the contaminants involved. Concentration of contaminants in the reactive barrier might influence appropriate disposal. Dewatering may be necessary prior to backfilling the PRB area with clean soil. Once backfilled, the area should be brought to elevation and revegetated in a manner similar to its surrounding area.

3. REMEDIATION CONSIDERATIONS

3.1 Remedial Action Objectives

The performance objectives (POs) for any PRB must be consistent with the remedial action objectives (RAOs) established for the site. RAOs are those goals established to protect human health and the environment and are applicable to the entire site. POs are goals the PRB must meet for the site to meet RAOs.

What's New?

- Performance objectives based on functional requirements
- Site management strategies
- Site screening technical considerations

Previous documents for PRBs (ITRC 1999a, 1999b, 2005b) have addressed various PRB monitoring objectives with respect to both technical performance and regulatory considerations. The reader is directed to these documents (and references cited therein) for specific methods by which monitoring can be implemented. However, little guidance has been provided on how to establish PRB POs, likely because PRB designs are site-specific and PRB POs are likewise unique for each site.

RAOs determine POs, which in turn define the PRB functional requirements (FRs). It is very important to define these FRs because they determine the appropriate design for a PRB. Within the FRs, objectives for hydraulic performance, contaminant treatment performance, and sustainability are defined. Figure 3-1 graphically represents the POs and FRs for site-specific RAOs.

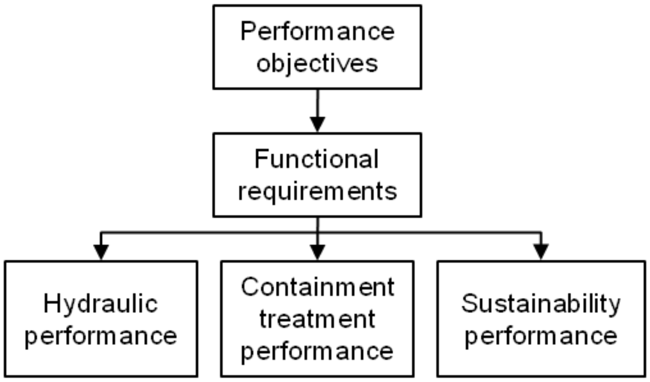

Figure 3-1. Relationship between RAOs and functional requirements for PRBs.

3.1.1 Performance Objectives

Any evaluation of PRB performance must be based on site RAOs. When establishing POs, the appropriate use of the PRB concept must be considered. The primary use of a PRB is to eliminate or substantially reduce the mass discharge of the contaminant(s) downgradient of the PRB. The PRB is not typically used as a source remediation technology; however, it may be used as a source control technology depending on the placement of the PRB relative to the location of the contaminant source. The PRB may also be used as a receptor protection technology if a primary RAO is to protect sensitive receptors located downgradient from a potential contaminant source. The treatment of contaminated groundwater occurs within the PRB or within a relatively short distance from the downgradient edge of the PRB, depending on the specific PRB design. For example, the release of hydrogen from an iron-based PRB may enhance biodegradation processes a short distance downgradient from the PRB. Figure 3-2 illustrates examples of these uses.

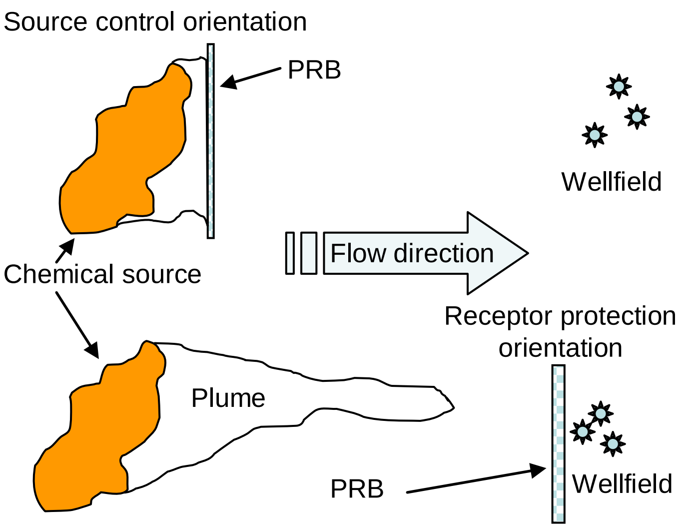

Figure 3-2. Examples of PRB receptor protection configurations.

POs should be identified working closely with site regulators and based on the intended function of the PRB in terms of the site remediation strategy. For example, a PRB located near a high-strength source zone may not be required to reduce the mass discharge of the chemical mass to zero. Rather, the PRB may fit into the overall RAO by having a PO of reducing the mass discharge by a percentage sufficient to allow a secondary treatment such as natural attenuation to effectively treat the dissolved phase plume. Similarly, a PRB located immediately upgradient from a sensitive receptor (such as a drinking water source) may be considered successfully meeting its PO only if it reduces groundwater contaminant concentrations to drinking water standards.

These concepts are explored further in the discussion regarding PRB FRs.

3.1.2 Functional Requirements

The FRs are technical objectives defined by the POs of PRB system. These requirements comprise the specific technical goals of the PRB that will allow the system to meet the POs and ultimately the RAOs for the project. FRs may include a number of specific technical demands for the system but principally fall into three basic areas: hydraulic objectives, contaminant treatment objectives, and sustainability. The third technical area—sustainability—is a newly defined category of performance intended to ensure that the PRB system considers resource conservation in its development and implementation.

Since the first PRB pilot test (Gillham and O’Hannesin 1994) and first PRB commercial installation (Yamane et al. 1995), it has been recognized that the success or failure of a PRB system depends on the ability of the PRB to accomplish the following:

- promote hydraulic performance whereby target contaminants are (1) routed through the reactive materials within the PRB with an appropriate residence time and (2) not deflected around, over, or under the PRB without being treated

- promote contaminant treatment in situ whereby target contaminants are reduced to intended concentrations in groundwater flowing through the PRB

These two areas are the key FRs for a PRB. Every PRB design should ensure that the intended hydraulic and contaminant treatment functions are defined clearly and that the design elements in each area are supported by well-organized and thorough scientific analysis. While the PRB is a relatively "simple" remedial system, it typically is employed in complex conditions. Therefore, establishing the FRs for a design provides backup for monitoring the performance of the PRB once installed and more importantly, if interpreted correctly, provides appropriate information for constructing the PRB system initially.

The following sections further discuss the three functional objective areas: hydraulics, contaminant treatment, and sustainability.

Hydraulic performance objectives

Establishing hydraulic POs begins with the development of a comprehensive and representative conceptual site model (CSM). From the CSM, specific details relating to the hydraulic characteristics of the subsurface system can be evaluated. This step is important because aquifer material heterogeneity and spatial and temporal variability of the groundwater flow field can have major influence on the hydraulic performance (and thus total performance) of the PRB system. A closely monitored PRB installation (Laase et al. 2000) and the results of modeling work by Elder, Benson, and Eykholt (2002) illustrate the problems, such as the potential for flow to bypass the PRB or for contaminant residence time in the PRB to be insufficient for completed treatment to occur.

Information useful in developing the site CSM (as listed in ITRC 1999a), and thus in establishing FRs for the PRB system, include the following:

- aquifer geometry and distribution of geologic materials (both laterally and vertically, including occurrence and details of confining units)
- hydraulic parameters (vertical and horizontal hydraulic gradients, transmissivity, and storativity)
- water budget information (recharge and discharge regimes)
- description of hydraulic boundaries (including rivers, wells, and low-flow and no-flow boundaries)
- contaminant occurrence and migration information (plume distribution, mass flux, and velocity information)

Similar data should be collected for the PRB system, including the hydraulic data specific to the treatment media (e.g., porosity and hydraulic conductivity [*K*] of the material) that might be used and its anticipated placement (e.g., geometry) within the aquifer system. Note that material properties may change following installation depending on settlement, other construction-related effects, mineral precipitation, or loss of reactive media over time.

Numerical modeling is a powerful tool for assessing the hydraulic conditions and uncertainties associated with the hydraulic system. Models—both hydraulic and geochemical—can point to areas where additional information is required or where conservative design steps must be implemented to ensure proper function of the PRB system (see Laase et al. 2000). Because PRBs are typically intended to operate under passive hydraulic conditions, their ability to handle spatial and temporal fluctuations in flow conditions must be evaluated and designed into the system. The numerical (or analytical, if appropriate) analysis is an important step. The results can also be used to develop performance-monitoring approaches for the specific PRB system. Aging of the PRB system—that is, geochemical changes that may occur over time—also should be considered.

Using the CSM information as well as key data from the conceptual PRB design (including contaminant treatment objectives), FRs specific to the hydraulic performance may be developed, including the following:

- sustaining certain flow rates
- ensuring that targeted groundwater flows through the PRB (i.e., preventing flow bypass around, under, or over the PRB)
- maintaining desired water-level requirements (e.g., preventing deleterious hydraulic mounding upgradient from or within the PRB)

Specific FRs also may be established that focus on the construction of the PRB to ensure that the nature and placement of PRB components are able to perform to meet the FRs for the hydraulic system (Benson and Dwyer 2006). These FRs may focus on the durability of PRB materials over time or their competence for supporting the PRB structure. The permeability of hydraulic barrier components (e.g., within a funnel-and-gate design) can have a large influence on the ability of the PRB to meet its hydraulic objectives. Similarly, the stability of the treatment media itself may lead to a specific FR. For example, the assurance that certain porosity will be maintained over a given life of the PRB, or that the material remains structurally sound over time, may be expressed as an FR. For injected PRBs, the effects of the injected media on the hydraulic characteristics of the native materials must also be considered, especially if the injected materials are dispersed within the native sediments.

A PRB system typically is intended to perform using hydraulically passive means; that is, the PRB is designed to allow groundwater and target chemicals to flow through the PRB without mechanical assistance. Modern sustainable hydraulic enhancements may include the use of solar or wind-driven, low-rate groundwater pumps or passive-siphon action to further control and route affected groundwater through a PRB. However, to date, use of these approaches has not been commonplace. If hydraulic enhancements are included in the PRB design, specific FRs may be established to address their operation (e.g., pumping rates and duration of pumping or specification of conditions that warrant pumping). Table 3-1 summarizes a variety of the hydraulic POs and the evaluation approach of a PRB design.

Table 3-1. Typical hydraulic performance objectives and evaluation approaches

Performance objective	Description	Evaluation approach
Maintain appropriate hydraulic gradient conditions as defined by the PRB design	The hydraulic gradient—vertical and lateral direction and magnitude—must be maintained within a specified range to ensure that velocity or mass flux is appropriate for (1) contaminant treatment processes and (2) targeted chemicals flowing through the PRB. This includes not redirecting targeted groundwater under, over, or around the PRB and avoiding a sustained hydraulic mound within or immediately upgradient of the PRB.	Regularly monitor water-level conditions and evaluate gradient information to determine most probable chemical migration direction and rate.
Maintain appropriate surface-water recharge controls	Excess or high-impact surface-water recharge within the PRB or adjacent (upgradient or downgradient) of the PRB may negatively impact the hydraulic performance by influencing hydraulic gradients and chemical migration conditions.	Establish engineering controls, and monitor the effectiveness of these controls during times of potential surface-water recharge conditions (such as during precipitation events).
Maintain appropriate flow conditions within the PRB	Plugging, secondary mineralization, settling, and compaction may all negatively affect the flow conditions within the PRB. Some changes will occur over time; construction defects should be avoided.	Perform a combination of routine-to-frequent water-level monitoring and single-hole borehole dilution tests within the PRB at regular intervals (3–5 years) after construction.
Ensure the PRB is placed as intended within the subsurface	This is a design objective but is key to proper performance and thus is listed here. This objective covers placement of the PRB, as well as physical parameters (e.g., media density, porosity, quality, and volume).	Assess as-built conditions and compare to design specifications; evaluation techniques may include post-construction hydraulic tests, borings to assess placement of the PRB, geophysics, water-level monitoring, and water-quality parameter monitoring. This process is particularly important for injected systems.

Contaminant treatment performance objectives

The contaminant treatment process is the second major component, and perhaps the most straightforward to evaluate, of the PRB system. The PRB is intended to treat via a chemical (or biological) reaction specific targeted dissolved contaminants within (or in close proximity to) its treatment matrix. From a pragmatic perspective, potential treatment materials for which many years of performance assessment exist (e.g., ZVI) typically have a substantial amount of performance data for a wide variety of contaminants. In most cases these data provide substantial information for developing an appropriate design to meet site-specific objectives.

The treatment process itself is complex and can increase in complexity as the system "ages" through exposure to the natural groundwater system. Complexities also occur due to heterogeneities in the chemical and biological makeup of the native aquifer, as well as the heterogeneities in the constructed PRB. Spatial and temporal hydraulic characteristics also affect the geochemical conditions of the aquifer and PRB (for example, levels of dissolved oxygen [DO] in the groundwater can be influenced by the timing and magnitude of recharge events near the PRB). For these and other reasons, the CSM is a key instrument in developing appropriate design and contaminant treatment POs (in concert with the regulatory objectives for a given site). The CSM should be comprehensive and, at a minimum, provide the following information on a site:

- plume occurrence and distribution in three dimensions for key aquifer horizons
- transient information on plume growth over time
- transient information on the fate of key chemical constituents (including both the target contaminants and other parameters, including inorganic compounds that may be important in the treatment process and PRB performance)
- occurrence and distribution of water-quality parameters such as pH, DO, temperature, ORP, specific electrical conductance, total dissolved solids (TDS), and other parameters deemed important

Additionally, laboratory treatability studies or the results of previous case studies for similar PRB installations can provide valuable information regarding future performance, including contaminant treatment performance. Laboratory studies including batch and column studies can be used to estimate longevity of the treatment system, provide information on potential secondary reactions, and establish benchmarks for the behavior of certain water-quality parameters (such as pH, dissolved gases, or inorganic constituents) as the treatment system ages.

Numerical modeling of the laboratory results also should be considered to establish the potential behavior of the contaminant treatment system over long periods of time. Typically, laboratory studies can be performed only long enough to provide direct data useful for understanding the early lifetime of a treatment system because most PRB design projects are time dependent; that is, a system usually has only a short time (1–2 years) from initial concept to installation for which design studies may be performed. Within this time, the laboratory studies can simulate only a relatively small to modest number of years (as pore volumes through a laboratory column, for example). Numerical modeling using such codes as those described by Jeen et al. (2007b), the PHREEQC computer program,[1] or the MOUSER software (Rabideau et al. 2005) may be useful in predicting the long-term system life of a PRB.

Using the CSM information, the results of laboratory studies, and key data from the conceptual PRB (including hydraulic treatment objectives), FRs specific to the contaminant treatment performance may be developed, including the following:

- maintaining certain chemical concentration goals for groundwater samples collected from the PRB (These concentration goals may have a certain time objective associated with them.)

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[1] http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc.

- ensuring that the plume is not diverted by the PRB, thus resulting in increased concentrations of target constituents in aquifer horizons downgradient of the PRB beyond the end of the PRB (i.e., plume expansion) or in aquifer horizons below (and sometimes above) the target aquifer
- maintaining certain water-quality criteria important for PRB performance (such as DO levels, redox levels, pH levels, etc.)
- maintaining certain water-quality objectives in groundwater and/or surface water downgradient of the PRB (i.e., dissolved iron, pH, and DO conditions continue to meet water-quality and/or ecological objectives)

Additionally, the FRs can lead to long-term assessment of other performance parameters including pH and certain dissolved gases to evaluate the performance of the PRB system.

Table 3-2 summarizes a variety of FRs, or contaminant treatment POs, and the general evaluation approach that may be applied for a given PRB design.

Table 3-2. Typical contaminant performance objectives and evaluation approaches

Performance objective	Description	Approach
Meet specific water-quality objectives for target chemicals, including secondary targets	Concentration goals are typically set for compliance or performance wells.	Regularly monitor performance (and compliance) wells per regulatory requirements (typically quarterly to annually).
Evaluate water-quality and chemical analyte data for trends in treatment efficacy	Long-term or statistical evaluation of the data to develop a more comprehensive understanding of the treatment process, including how the system is aging. Graphical and statistical analysis is recommended.	Trend analysis performed after each sampling event.
Maintain secondary analytes, such as inorganic parameters or dissolved gases, if appropriate at a certain level	Treatment progress media plugging or mineral precipitation and aging status may be assessed by evaluating the trends in secondary, or process-related, analytes. For example, dissolved hydrogen and reduction potential (Eh) are evaluation parameters for assessing efficacy of ZVI or organic carbon–based treatment processes.	Analyze parameters using a combination of regular (for water-quality parameters such as pH, DO, and redox) and occasional (non-COC parameters, including dissolved gases and inorganic compounds) timed monitoring events (quarterly to every 2–3 years depending on the parameter). Track trends over time. Use specialized nomographs or other statistical methods to evaluate performance.

Sustainability performance objectives

As represented by Kresic (2008), Roehl et al. (2005), and others, most PRBs are designed to operate in situ for years with little or no maintenance. This concept led to the development of the PRB in the early 1990s and has been proven in that the earliest commercially installed PRB has operated since late 1994 with only regular compliance monitoring and periodic specialized performance monitoring having been performed (Warner et al. 2005; S. D. Warner, verbal communication, 2009).

When the first PRBs were being designed and installed, the concept of sustainability in groundwater remediation was not a principal design metric. Today, the concept of sustainability takes on greater meaning and can be requested by regulatory agencies as a key design element. Under the category of sustainable *construction*, key concepts include attempting to use “green,” recycled, or nonmanufactured treatment media (if there is a benefit for treatment in using such materials) and to construct the PRB using methods and materials that are as energy-efficient and material-efficient as possible. Under the category of sustainable *treatment*, the key performance metrics focus on the ability of the system to meet regulatory treatment goals under hydraulically passive means, that is, the ability to provide long-term treatment without the need to add energy or mechanical means to promote groundwater flow/contaminant flux through the PRB.

Generally, the key sustainability performance metrics for PRBs are not rigorously defined. However, designers can develop metrics that are intended to show resource conservation (i.e., volume of water conserved or amount of energy conserved by a PRB system when compared to hydraulically active systems such as pump and treat). Section 9 provides a more detailed discussion.

3.2 Site Management

PRB site management involves both short- and long-term activities, including routine maintenance of the property (mowing grass, maintaining fences in good repair, etc.) as well as ensuring that the physical and structural integrity of the PRB is maintained. Short-term activities include monitoring of hydraulic and chemical parameters. Measuring the static water level and collecting groundwater samples for chemical analysis from both upgradient and downgradient monitoring wells, analyzing the samples for a consistent list of parameters, and interpreting the data will help determine whether the PRB is performing as expected or there are problems that need to be addressed.

Long-term monitoring (LTM) involves more detailed assessment of the hydraulic and chemical components. In some cases, if the downgradient chemical results are not consistent with expectations, then core samples of the reactive material may be taken to evaluate the reactivity, consistency, and heterogeneity of the barrier. Likewise, if the difference in static water levels is not consistent with expectations or if there is a shift in hydraulic gradient or preferential pathways are noted, then additional assessment is required. LTM may also involve assessing the depletion of the reactive material and the need for its rejuvenation or the evaluation of residence time. Groundwater models can be used to compare field-gathered data to earlier long-term projections of PRB performance to assess whether the reactive material is performing as expected. This assessment may show that the reactive material may be depleted and needs to be rejuvenated and/or show that the residence time of the groundwater in the PRB needs to be reevaluated.

3.3 Site Conditions in Considering/Screening PRB Technologies

A PRB creates an in situ treatment zone that intercepts and treats a groundwater contaminant plume. PRBs can be an effective remedy in many environmental settings with varying hydrogeologic and geochemical conditions. Careful assessment of the site is essential since there are conditions that may limit the effectiveness of the technology. Inadequate site characterization has proven to be one of the key factors leading to inadequate PRB performance.

The physical setting and the site's regulatory constraints must be evaluated to determine whether the technology is feasible. Important features of the physical setting include topography, surface structures, underground utilities and structures, surface water features, and ecological resources. A well-researched CSM accurately represents the real-world natural system as well as possible. A CSM should be constructed to ensure that the PRB system is designed to be effective in reducing contaminant concentrations to RAOs. A good CSM also assists in determining whether consideration should be given to alternate installation methods, configurations, or even other in situ technologies.

The development of a CSM distills what is already known about the site and evaluates any uncertainty associated with the site. It can then be used to identify what additional data are needed. A good CSM allows sound decisions to be made as to proceeding with work or stopping to perform additional assessment. Once developed, the limits of the treatment area and system boundaries can be determined so the PRB can achieve project goals.

Guidance on developing CSMs and evaluating natural attenuation processes can be found in various publications, including USEPA (1998b) and AFCEE, NFESC, and ESTCP (2004). Additional details on data collection activities can be found in ASTM International’s (ASTM’s) *Standard Guide for Developing Conceptual Site Models for Contaminated Sites* (ASTM 1995, reapproved 2003).

Table 3-3 summarizes some common criteria used to determine the suitability of a site for implementing a PRB. These are general guidelines only; there may be notable exceptions to these criteria.

Table 3-3. Suitability of site characteristics common to PRBs

Site characteristic	Ideal case for PRBs	Suitability unclear—requires further evaluation
Infrastructure and land use	No infrastructure or utilities to interfere with trenching or excavation	Some utilities (e.g., sewer lines) or roadways may be moved or temporarily breached during construction. Buildings or utility lines that cannot be breached may leave gaps in the PRB. May lead to consideration of injection methods.
Contaminant distribution (depth)	<45 feet to base of contaminant plume	35–45 feet to base of contaminant plume, >45 feet to base of contamination, beyond practical depth of trenching or excavation. May lead to consideration of injection methods.

Site characteristic	Ideal case for PRBs	Suitability unclear—requires further evaluation
Contaminant peak concentrations (chlorinated aliphatic hydrocarbons [CAHs] only)	CAH concentrations <10,000 µg/L[a], depending on media (e.g., ZVI more robust than some carbon-based approaches)	Treat CAH concentrations >10,000 µg/L with caution. Mixed contaminant plumes require further evaluation to determine whether all contaminants can be degraded by one or more selected processes.
Evidence of anaerobic dechlorination (CAHs only)	Presence of dechlorination products	Limited evidence of anaerobic dechlorination. No evidence of any degradation of CAHs depending on the specific treatment media applied in the PRB.
Lithology	Cohesive silts and sands	Well consolidated or hard bedrock. Loose, flowing sands.
Stratigraphy	Optimal: PRB extends to a lower confining layer	Lack of a lower confining layer, but where the PRB may extend to the total depth of contamination. Lack of a lower confining layer and uncertainty about the total depth of contamination requires further evaluation.
Hydraulic conductivity (*K*)	<1.0 ft/day (<3.5×10^{-4} cm/sec)	1.0–10 ft/day (3.5×10^{-4} to 3.5×10^{-3} cm/sec)
Groundwater velocity	<1.0 ft/day (generally but not in all cases)	1.0–10 ft/day, >10 ft/day
pH	6.5–7.5 (neutral)	<6.0, >8.0
Dissolved oxygen	<4.0 mg/L	>4.0 mg/L combined with a high rate of groundwater flow (>1.0 ft/day).
Sulfate concentration (CAHs)	<1,000 mg/L	>1,000 mg/L with caution, may be suitable for abiotic degradation processes.

[a] Units: µg/L = micrograms per liter, cm/sec = centimeters per second, ft/day = feet per day, ft/yr = feet per year, mg/L = milligrams per liter.

4. REACTIVE MEDIA AND TREATMENT PROCESSES

Since its conception in the late 1980s, PRB technology has become an accepted practice for groundwater remediation. Several key agencies in addition to ITRC have participated in the development of PRB technology, including USEPA's Remediation Technologies Development Forum (RTDF), DOD, and the U.S. Department of Energy (DOE). Most of the initial PRB applications involved ZVI. This section describes the properties and uses of ZVI and several other reactive materials that have been used or have the potential for use in PRBs.

What's New?

- Improved understanding of treatment mechanisms for metals with ZVI
- ZVI treatment of energetic compounds (RDX, HMX, and TNT)
- Arsenic treatment using ZVI field applications
- Biowalls using solid organic materials (mulch) to stimulate anaerobic degradation of chlorinated solvents, energetic, and explosive compounds
- Improved understanding of biogeochemical transformation processes resulting in abiotic dechlorination of chlorinated solvents
- Long-term monitoring data for mineral media (zeolite, slag, apatite) PRBs
- Combined media: organic carbon/iron combinations and emulsified ZVI
- Organophilic clay as a reactive medium

4.1 Matching PRB Materials to Contaminants

Table 4-1 provides a list of common COCs treated by different types of reactive materials used in PRBs. The properties and degradation processes of these materials are described in the following sections. While early PRBs tended to use singular reactive media (for example ZVI or mulch), there are an increasing number of applications using combined media to treat multiple contaminants within a groundwater plume.

Table 4-1. Examples of COCs treated by types of reactive materials used in PRBs

COCs	ZVI	Biobarriers	Apatite	Zeolite	Slag	ZVI-carbon combinations	Organophilic clay
Chlorinated ethenes, ethanes	F[a]	F			L	F	
Chlorinated methanes, propanes						F	
Chlorinated pesticides						P	
Freons						L	
Nitrobenzene	P						
Benzene, toluene, ethylbenzene, and xylenes (BTEX)		F					
Polycyclic aromatic hydrocarbons (PAHs)							L
Energetics	P	F				P	
Perchlorate		F	F	L		L	
NAPL							F
Creosote							F
Cationic metals (e.g., Cu, Ni, Zn)	L	F	F		L	F	
Arsenic	F			L	F	F	
Chromium(VI)	F			L	L	F	
Uranium	F	P	F			T	
Strontium-90			F	F			
Selenium	L					L	
Phosphate					P		
Nitrate		F	F			F	
Ammonium				L			
Sulfate		F				L	
Methyl tertiary butyl ether (MTBE)		F					

[a] F = full-scale application, L = laboratory evaluation, P = pilot-scale application.

Another approach is to use sequenced PRBs. A multicomponent, sequenced PRB may be applied at sites where the mixture of contaminants necessitates use of distinctly different processes to achieve overall remedial goals. For example, a mixture of BTEX compounds and chlorinated organic compounds could involve the use of oxygen addition coupled with an anaerobic abiotic (ZVI) or bioremediation (biowall) process. This concept was the subject of a monograph entitled *Sequenced Reactive Barriers for Groundwater Remediation* (Fiorenza, Oubre, and Ward 1999).

Although the number and form of candidate types of reactive media have expanded since its publication, the general guidance concerning the application of coupled technologies provided in this document remains valid.

4.2 Iron-Based Reactive Media

Researchers involved in the initial field trials of ZVI PRB technology struggled to find a suitable source and quantity of ZVI for their relatively small applications. Currently, multiple vendors can supply large quantities of ZVI. The general characteristics of ZVI used in PRB technology applications are described below.

4.2.1 Characteristics and Types of ZVI

ZVI used in PRB applications should have a high fraction of iron metal (>90%), low carbon content (<3%), and nonhazardous levels of leachable trace metal impurities. It must be free of any surface coatings (oils or grease) that inhibit its reactivity. The ZVI used for PRB applications comes from two primary sources. The more common is recycled scrap iron from the manufacture of automotive parts (e.g., engine motors, brake drums, etc.). The iron particles are fired in a kiln to remove residual cutting fluids, oils, and greases, then milled and sorted to a specified grain size range. Another source of ZVI is molten iron, which is then granulated with high-pressure water jets. The granulated iron is then sieved to a specified grain size. Figure 4-1 shows different ZVI types and sizes.

The surface area of ZVI particles is very important because reactions occur at the iron/water interface. On a per-weight basis, reaction rates generally increase as the surface area of the ZVI particles increases. For PRBs constructed using excavation-based methods, the grain size range typically used is 2.0–0.25 mm (–8/+50 mesh U.S. standard sieve size), which provides an average hydraulic conductivity of about 5×10^{-2} cm/sec (142 ft/day). Typically, the surface area of this coarse ZVI has a range of 0.5–1.5 m^2/g. Finer-grained fractions of 1.0 mm or less (microscale ZVI) are emplaced using injection-based techniques and have a higher surface area.

Since the concept of nanoscale metallic particles for in situ environmental remediation was introduced by Dr. Wei-Xian Zhang and his colleagues in the late 1990s (Wang and Zhang 1997), these highly reactive particles have been the subject of considerable laboratory and field testing. Nanoscale iron particles have a high reactivity but relatively short life. They are best suited to remediation of source zones, where they can degrade a relatively large quantity of volatile organic compounds (VOCs) in a short period of time.

4.2.2 Treatment Processes with Zero-Valent Iron

Dehalogenation of chlorinated solvents

Most granular PRBs to date have been applied for the remediation of dissolved chlorinated VOC plumes. During contact with ZVI, chlorinated VOCs (CVOCs) degrade to nontoxic end products (Gillham and O’Hannesin 1994). This abiotic process oxidizes (corrodes) the ZVI and reduces the dissolved CVOCs. The process induces highly reducing conditions that promote substitution of a chloride atom with a hydrogen atom in the CVOC molecule.

Figure 4-1. Examples of ZVI and ZVI emplacement: (a) fine-grained ZVI, (b) coarse-grained ZVI being placed in a trenched PRB, (c) microscale ZVI in an injectable EHC® slurry, and (d) installation of ZVI PRB at a U.S. Coast Guard facility using a one-pass trencher.

CVOCs are in an oxidized state because of the presence of chloride. Iron, a strong reducing agent, reacts with the chlorinated organic compounds through electron transfer, in which ethane and chloride are the primary products, as shown below for the degradation of trichloroethene (TCE) (C_2HCl_3):

$$\begin{array}{c} 3Fe^0 \rightarrow 3Fe^{2+} + 6e^- \\ C_2HCl_3 + 3H^+ + 6e^- \rightarrow C_2H_4 + 3Cl^- \\ \hline 3Fe^0 + C_2HCl_3 + 3H^+ \rightarrow C_2H_4 + 3Fe^{2+} + 3Cl^- \end{array} \tag{4-1}$$

The products of the dechlorination reaction are chloride (Cl^-), ferrous iron (Fe^{2+}), nonchlorinated (or less chlorinated) hydrocarbons, and hydrogen. The process is well documented and reliable. Chloride mass balances approaching 100% are typically obtained during passage of contaminated groundwater through columns filled with granular iron. Dechlorination is complete with ethene and ethane as the final carbon-containing compounds (Sivavec and Horney 1995, Orth and Gillham 1996, Fennelly and Roberts 1998). Ethene/ethane mass balances of 80% and higher have been reported from closed-system tests with chlorinated ethenes and ethanes (Sivavec and Horney 1995, Fennelly and Roberts 1998, Roberts et al. 1996).

Figure 4-2 shows two pathways for the dechlorination of chlorinated ethenes in iron systems: β-elimination and hydrogenolysis (Eykholt 1998, Arnold and Roberts 2000). The β-elimination pathway dominates the reaction and produces chloroacetylene intermediates, which are unstable and rapidly reduced to ethene (Roberts et al. 1996, Sivavec et al. 1997).

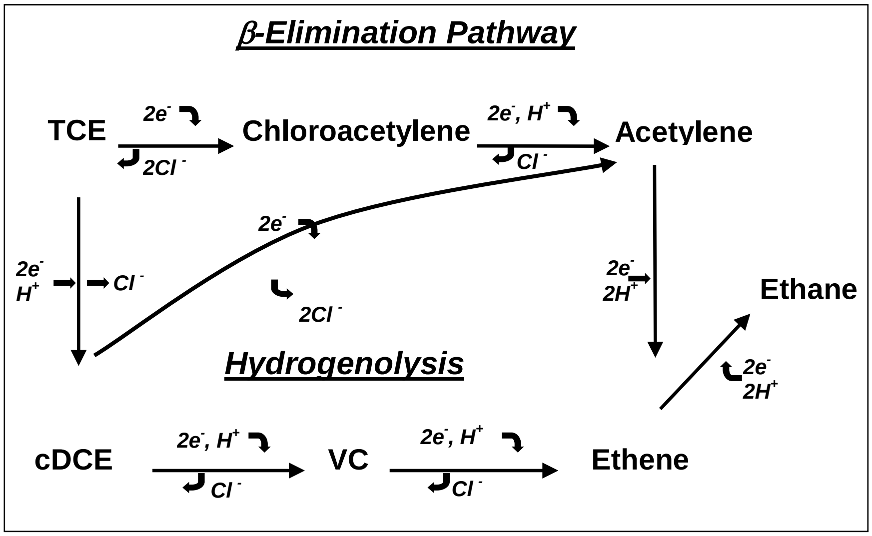

Figure 4-2. Iron degradation process for TCE. *Source:* Arnold and Roberts 2000.

The hydrogenolysis pathway is a slower reaction during which less-chlorinated intermediates are produced and subsequently degraded. For example, during degradation of TCE by ZVI, <10% by mole of the initial TCE concentration appears as the intermediate products *cis*-dichloroethene (cDCE) and vinyl chloride (VC) via the hydrogenolysis pathway (Gillham et al. 2010). These intermediate products also degrade, albeit at a slower rate than TCE. Figure 4-3 shows an example of the typical degradation of 10 mg/L TCE and 100 µg/L cDCE in groundwater. In this example, the cDCE concentration increases to 110 µg/L, followed by an increase in VC to about 10 µg/L, followed by the degradation of both compounds to below their maximum contaminant levels (MCLs).

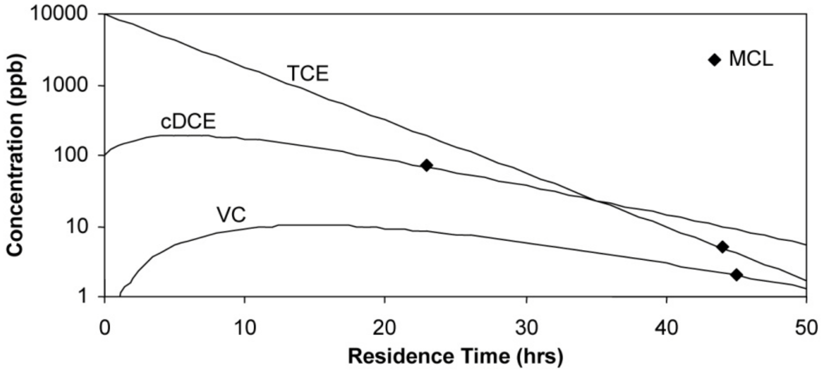

Figure 4-3. Typical trends in TCE and breakdown product concentrations in the presence of coarse ZVI. *Source:* Gillham et al. 2010.

The VOC degradation trends observed in groundwater in contact with ZVI are typically described using first-order kinetics:

$$C = C_o e^{-k_{obs} t}, \text{ or } \ln(C/C_o) = -k_{obs}\, t \qquad (4\text{-}2)$$

where

C = VOC concentration in solution at time t
C_o = VOC concentration of the influent solution
k_{obs} = pseudo-first-order rate constant
t = time

The reaction rates for CVOCs in contact with ZVI can be affected by the presence of a variety of inorganic species in groundwater and precipitates that build up on iron surfaces over time. These effects are discussed in Section 8.

Reductive precipitation of hexavalent chromium

Treatment of hexavalent chromium [Cr(VI)] using granular iron has been extensively tested and demonstrated at several sites. For example, a continuous PRB installed at a U.S. Coast Guard facility to remediate a plume of 10 mg/L TCE and 10 mg/L Cr(VI) has been operating since June 1996 (Puls, Paul, and Powell 1999).

The key mechanisms for Cr(VI) removal using granular iron involve reduction to trivalent chromium [Cr(III)], followed by the precipitation of sparingly soluble chromium hydroxides and oxides, such as $Cr(OH)_3$ and Cr_2O_3, respectively. Cr(III) can also be removed from solution by coprecipitation with iron phases, such as FeOOH or Fe_2O_3 (Yang et al. 2007). The reaction sequence that leads to the precipitation of a mixed Cr(III)-Fe(III) oxyhydroxide (Blowes et al. 2000) can be described as follows:

$$CrO_4{}^{2-}{}_{(aq)} + Fe^0 + 8H^+{}_{(aq)} \rightarrow Fe^{3+} + Cr^{3+}{}_{(aq)} + 4H_2O \qquad (4\text{-}3)$$

$$(x)Cr^{3+}{}_{(aq)} + (1-x)Fe^{3+}{}_{(aq)} + 2H_2O \rightarrow Cr_xFe_{(1-x)}OOH_{(s)} + 3H^+{}_{(aq)} \qquad (4\text{-}4)$$

The net reaction results in the removal of Cr(VI), the formation of $Cr_xFe_{(1-x)}OOH$, and an increase in pH.

During the Cr(VI) removal process, the chromium mineral precipitation occurs on the iron surface, progressively blocking reaction sites over time and eventually leading to chromium breakthrough. An iron PRB for Cr(VI) treatment must be sized to allow for operation over a specified lifetime based on Cr(VI) flux and/or replacement of some or all of the iron at specified time intervals. Furthermore, for remediation of mixed plumes containing Cr(VI) and VOCs, the design iron PRB thickness should provide sufficient residence time to treat all VOCs downgradient of the Cr(VI) migration front throughout the projected lifetime of the PRB.

The amount of iron required for Cr(VI) removal depends on the Cr(VI) removal capacity of the iron. This removal capacity varies, depending on granular iron source and site conditions. Based on previous laboratory and field results for U.S. commercial iron sources, a removal capacity of 2.5–5 mg of Cr(VI) per cubic centimeter of iron is typically used in preliminary design calculations for iron PRBs (provided by EnviroMetal Technologies, Inc.). Treatability tests with site groundwater are recommended to obtain site-specific Cr(VI) removal rates before design finalization and technology implementation.

Reduction, sorption, and precipitation of redox-sensitive oxyanions

Laboratory bench-scale studies and field demonstrations have evaluated the potential of elemental iron for remediation of redox-sensitive oxyanions, such as selenium, technetium, and uranium. The treatment mechanisms for these contaminants take advantage of their lower solubility in their more reduced state with removal through sorption and/or precipitation.

Selenium is much more soluble in its most oxidized state, Se(VI), than in its less slightly reduced state, Se(IV), which is strongly sorbed onto iron oxyhydroxide surfaces (Zhang, Amrhein, and Frankenberger 2005). Spectroscopic evidence indicates that in the presence of sulfate, Se(VI) can also be reduced by elemental iron to selenide and precipitated as iron selenide (Sasaki et al. 2008). Batch test results have shown removal of up to 40 mg/L of Se(VI) from solution by elemental iron (Sasaki et al. 2008). Column testing has demonstrated removal of Se(VI) from 1.0 to <0.1 mg/L for more than 250 pore volumes (Blowes et al. 2000).

Several mechanisms have been proposed for the treatment of uranium and specifically U(VI), by elemental iron, including reductive precipitation (Gu et al. 1998; Morrison, Metzler, and Carpenter 2001), sorption onto hydrous ferric oxide (Fiedor et al. 1998), and coprecipitation with iron oxides (Noubactep, Meinrath, and Merkel 2005). A ZVI PRB designed to treat U(VI) has been in continuous operation since 1997 at the Fry Canyon demonstration site in southeastern Utah (Naftz et al. 2006). After 10 years of operation, the PRB was removing nearly 100% of the influent U(VI) with no decrease in efficiency over time (Figure 4-4), although decreases in groundwater velocity of approximately threefold indicate partial clogging due to the formation of mineral precipitates.

Monitoring results from a large-scale treatment system at the DOE Oak Ridge National Laboratory site indicate that Tc(VIII) and U(VI) were completely removed by ZVI (Gu et al.

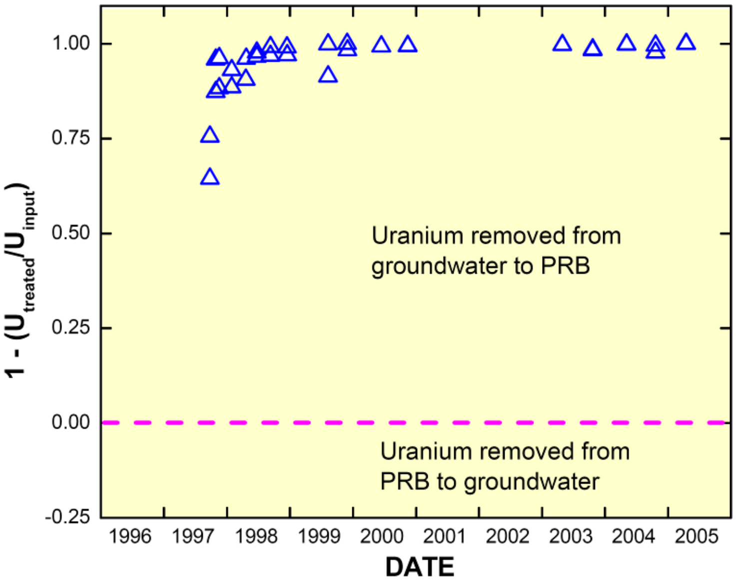

Figure 4-4. Uranium removal efficiency measured at 0.15 m into the ZVI PRB at Fry Canyon, Utah.
Source: Naftz et al. 2006.

1998). Bostick et al. (1996) suggested a mechanism of reduction of soluble Tc(VII) and binding of Tc(IV) oxyhydroxide product to iron surfaces.

Sorption and coprecipitation of arsenic

ZVI has been used to treat arsenic in soil and groundwater (Su and Puls 2001a, 2001b; Wilkin et al. 2008; Ludwig et al. 2009). Unlike other metals and metalloids that occur predominantly as oxyanions in groundwater, such as selenium and uranium, arsenic solubility is lowest in its most oxidized state [As(V)], and increases in its slightly reduced state [As(III)]. However, several mechanisms for arsenic treatment by ZVI have been identified. Adsorption of both As(III) and As(V) appears to be the key treatment mechanism with ZVI (Manning et al. 2002; Melitas et al. 2002). Arsenic forms inner-sphere complexes with ZVI corrosion products, including ferrous hydroxide, mixed-valence iron oxides and hydroxides, and ferric oxyhydroxides (Manning et al. 2002). As(III) and As(V) that are adsorbed onto ZVI surfaces are consequently occluded by successive layers of corrosion products (Kanel, Greneche, and Choi 2006). The observed correlation between immobilized arsenic and sulfur on ZVI (Nikolaidis, Dobbs, and Lackovic 2003; Przepiora, Hill, and Seech 2008) suggests the potential precipitation or coprecipitation of arsenic with iron phases, such as arsenopyrite. Spectroscopic data from the ZVI PRB installed in Helena, Montana, showed As(III) and As(V) sorbed to iron (oxy)hydroxides and As(III) sorbed to iron sulfide (FeS) phases (Wilkin et al. 2008).

A pilot-scale granular-iron PRB was installed in June 2005 at a former metal-smelting facility, near Helena, Montana, to treat groundwater contaminated with arsenite and arsenate (Wilkin et al. 2009). Influent arsenic concentrations of >25 mg/L were reduced to <0.01 to 2 mg/L. Significant decreases in arsenic concentrations were observed in wells downgradient of the PRB after 2 years of operation.

A pilot-scale mixed-media PRB containing granular iron, compost, limestone, and pea gravel was installed at a former phosphate fertilizer manufacturing facility in Charleston, South Carolina, to treat a plume containing arsenic, heavy metals, and acidity (Ludwig et al. 2009). The granular iron was used chiefly to treat arsenic, while compost and limestone were used to treat metals and acidity, respectively. Data collected after 30 and 42 months of operation showed successful arsenic treatment, with influent concentrations of up to 206 mg/L being reduced to below 0.05 mg/L in the PRB.

Removal of cationic metals

The applicability of ZVI for the treatment of cationic metals in groundwater has been investigated (Wilkin and McNeil 2003; Rangsivek and Jekel 2005; Li and Zhang 2007; Fiore and Zanetti 2009). Studies have focused on the use of ZVI for treatment of metals associated with acid rock drainage, i.e., in a low-pH matrix. Several mechanisms for the treatment of metals by ZVI have been postulated, including sorption, reduction, and precipitation. There are conflicting reports in the literature on mechanisms for individual metals; these may reflect differences in the composition of the aqueous matrix and the impact of competing species in similar aqueous-phase and surface complexation reactions. Concurrent biological reactions may also affect metal immobilization mechanisms (Wilkin and McNeil 2003).

Under low-pH conditions, metals removal by ZVI appears to be controlled by sorption processes onto the iron surface or onto iron corrosion products (Wilkin and McNeil 2003). Under neutral to alkaline pH conditions, the precipitation of carbonate species will provide different types of sorption surfaces and potential for metals coprecipitation. As the pH of groundwater passing through a ZVI PRB substantially increases due to the hydrolysis of water and production of hydrogen gas, the precipitation of metal hydroxides may play an important role in metals immobilization (Li and Zhang 2007).

Reductive precipitation of metals is a potential treatment mechanism for metals with a standard potential much higher than that of ZVI. For example, ZVI has been shown to reduce divalent copper [Cu(II)] to zero-valent copper, resulting in the precipitation of Cu(0) and Cu_2O (Rangsivek and Jekel 2005). Li and Zhang (2007) presented a model summarizing the potential mechanisms for metals removal using nanoscale ZVI (NZVI) (Figure 4-5).

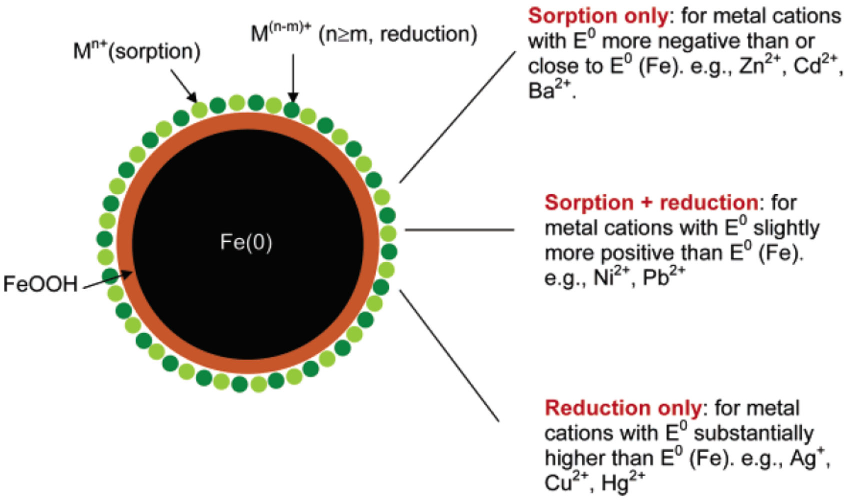

Figure 4-5. Conceptual model for metals removal from water using NZVI.

High metal removal efficiencies and rapid kinetics are often observed in ZVI systems (Fiore and Zanetti 2009, Li and Zhang 2007). To date, ZVI has not been applied in a field-scale PRB for the targeted sole purpose of removing cationic metals.

Reductive degradation of energetic compounds

Granular iron has been shown to effectively treat energetic compounds, such as trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (Royal Demolition Explosive, or RDX).

Groundwater contaminated with TNT and RDX is difficult to treat because of the resistance of these compounds to aerobic biodegradation (Oh et al. 2002). Current approaches to treating explosives include incineration, composting, in situ bioremediation, alkaline hydrolysis/oxidation, and aqueous thermal decomposition (Wildman et al. 2000).

Recent research results have indicated that granular iron can chemically reduce TNT and RDX in soil and water environments. In a batch study by Oh et al. (2002) of TNT degradation pathways, four major reduction intermediates were detected (2-amino-4,6-dinitrotoluene [2-ADNT], 4-amino-2,6-dinitrotoluene [4-ADNT], 2,4-diamino-6-nitrotoluene [2,4-DANT], and 2,6-diamino-4-nitrotoluene [2,6-DANT]) and one end product, 2,4,6-triaminotoluene (TAT), during reduction with a laboratory-grade and a construction-grade iron. Miehr et al. (2003) conducted a column test using a commercial granular iron that showed complete conversion of TNT to dissolved TAT. However, after about 500 pore volumes had passed through the column, a breakthrough of TNT and other intermediate reduction products was observed. This breakthrough was attributed to gradual passivation of the iron, likely due to the accumulation of adsorbed amines or growth and oxidation of a passive film, both driven by reduction of TNT.

Reduction of RDX by granular iron has been demonstrated in batch experiments by Hundal et al. (1997) and Singh, Comfort, and Shea (1998, 1999). The mechanism of RDX removal by ZVI included adsorption onto iron and chemical transformation, with about 60% of the degraded RDX adsorbed onto iron based on the carbon balance. Singh et al. (1998) identified RDX degradation products as 1-nitroso-3,5-trizacyclohexane (MNX), 1,3-dinitroso-5-nitro-1,3,5-trizacyclohexane (DNX), and 1,3,5-trinitroso-1,3,5-trizacyclohexane (TNX).

In 2003, a pilot-scale iron PRB for treatment of TNT and RDX was installed at the Cornhusker Army Ammunition Plant (CAAP), Nebraska (Johnson 2003). This system has effectively treated TNT and RDX for 2 years (Johnson and Tratnyek 2008). Contrary to laboratory findings, breakdown products like TAT from TNT have not been observed under field conditions.

4.3 Organic Substrates (Biowalls)

PRBs that promote biological treatment of groundwater contaminants were described in the 1998 RTDF document on PRB technologies (RTDF and USEPA 1998), but their use as a recognized method for treatment of dissolved contaminant plumes has greatly increased since *Permeable Reactive Barriers: Lessons Learned/New Directions* (ITRC 2005b) was published. Contaminants in groundwater that can be remediated by biological reactions in a PRB include chlorinated solvents, energetics and explosives (perchlorate, TNT, RDX), inorganic constituents [nitrate and Cr(VI)], and radioactive constituents. The Air Force biowall protocol (AFCEE 2008) provides guidance for the use of permeable mulch biowalls for remediation of chlorinated solvents, perchlorate, and energetics. Sustaining the anaerobic reaction zone is essential for biological treatment systems. A benefit of biological PRB systems over purely abiotic systems is that the treatment processes may extend downgradient of the constructed treatment zone due to migration of soluble organic carbon, enabling the effects of anaerobic degradation beyond the biowall. Another benefit is the ability of a single system to treat multiple contaminants with different chemical characteristics, including both organic compounds (e.g., CVOCs, energetic compounds) and inorganic compounds (e.g., nitrate, sulfate, perchlorate, and metals). However, the longevity of biowalls is anticipated to be shorter than that of ZVI walls, and replenishment of organic substrate may be required.

4.3.1 Types of Organic Substrates

Examples of organic materials that have been applied in PRBs to promote bioremediation include the following:

- solid carbon sources, such as mulch, compost, sawdust, wheat straw, and similar commercial materials specifically processed for environmental purposes
- dissolved and suspended carbon sources, such as cheese whey, sodium lactate, molasses, emulsified vegetable oils (EVOs), and various other carbohydrates and alcohols
- solid or viscous fluid hydrogen-releasing compounds

Protocols have been developed to provide guidance for the use of soluble carbohydrates (Suthersan et al. 2002), vegetable (edible) oils (AFCEE 2007), and permeable mulch biowalls and bioreactors (AFCEE 2008). Consistent with the definition of PRB presented in Section 1, the following discussion focuses on solid substrates for application in a PRB.

Mulch and compost

The long-term effectiveness of mulch and compost substrates varies depending on ambient groundwater conditions and the contaminants being treated. Determining the mulch and compost requirements necessary to sustain anaerobic degradation processes over periods of 5–10 years or more is a critical design and operational objective.

Early laboratory and field trials investigated a variety of solid-phase organic carbon materials for treating nitrate and other inorganics (e.g., acid mine drainage). The materials included straw, newspaper, raw cotton, alfalfa, wheat straw, jute pellets, vegetable oil, compost, leaf mulch, wood mulch, sawdust, and pulp wastes (Boussaid, Martin, and Mowan 1988; Wakatsuki, Esumi, Omura 1993; Benner et al. 1999, 2002; Schipper and Vojvodic-Vukovic 1998; Taylor et al. 2002; Waybrant, Blowes, and Ptacek 1998; Robertson, Vogan, and Lombardo 2008; Hulshof et al. 2003).

Solid substrates used in PRBs are intended to be long-term sources of organic carbon, with anticipated life spans exceeding 5–10 years. Investigators have installed trenches and backfilled excavations with sawdust and mulch for the treatment of nitrate-contaminated water since the mid-1990s and have found little reduction in performance after 15 years of operation (Robertson et al. 2000; Robertson, Vogan, and Lombardo 2008).

Materials used in biowall PRBs generally include tree mulch as a long-term carbon source, materials that supply nutrients (e.g., compost), and coarse sand or pea gravel to maintain permeability and to prevent compaction (Figure 4-6, AFCEE 2008). Other agricultural or waste products may be suitable as biowall materials, such as cotton gin trash, mushroom compost, rice hulls, and blended corn cobs.

Figure 4-6. Materials used in construction of the OU-1 biowall, Altus Air Force Base, Oklahoma.

Mulch and compost are usually mixed with coarse-grained sand or pea gravel at a ratio of 40%–60% by volume. Wood mulch is composed of approximately 40%–50% cellulose, 20%–30% hemicellulose, and 25%–30% lignin; with lignin being the component of plant cell material most recalcitrant to biodegradation (Duryea, English, and Hermansen 1999; Richard 1996). The leaves and soft tissue of the mulch are more amenable to biodegradation; thus, the mulch should contain a high percentage of fresh "green" or "soft" material. Alternatively, partial composting of the mulch breaks down the plant cell walls and produces more readily degradable material. Composted plant material, or alternative organic amendments, should be added to mulch that contains a high percentage of dry woody material.

Other organic substrates in PRBs

The use of vegetable oil for in situ bioremediation is described in *Protocol for In Situ Bioremediation of Chlorinated Solvents Using Edible Oil* (AFCEE 2007). Vegetable oils are a long-lasting carbon source due to their low solubility in water and typically sustain an anaerobic reaction zone for 2 years or more. A few biowall applications (Naval Weapons Industrial Reserve Plant [NWIRP] McGregor, Texas, and Seneca Army Depot, New York) have coated the wood mulch with soybean oil prior to installation. Another application of vegetable oil is the use of EVO to replenish a biowall after several years of operation. Biowalls at NWIRP and Altus Air Force Base (AFB), Oklahoma, have been replenished using this technique.

Other slow-release substrates used for PRBs include EHC® and HRC®. Ideally, stable reactive zones are created by sustaining elevated concentrations of DOC at levels sufficient to stimulate anaerobic degradation processes over long periods of time. The plumes of DOC generated from vegetable oil, EHC, and HRC are readily biodegraded, although the reaction zone generally does not extend more than a short distance from the point of injection. Because of the cellulose and hemicellulose carbon source in mulch and EHC, these materials are typically longer lived (Section 8.4). Figure 4-7 is photographs of EHC mixing and injection.

4.3.2 Anaerobic Degradation Process with Organic Substrates

AFCEE (2008) describes the use of permeable mulch biowalls for the biological treatment of chlorinated solvents and perchlorate. Appendix A contains an example of a biowall PRB for the treatment of RDX and HMX at the Army Pueblo Chemical Depot (PCD), Colorado (GSI 2008). Other examples of biological PRBs include applications for denitrification (Robertson and Cherry 1995; Robertson and Andersen 1999; Robertson et al. 2000; Robertson, Vogan, and Lombardo 2008) and for sulfate reduction (Benner, Blowes, and Ptacek 1997). Biological PRBs are not limited to anaerobic degradation processes. Wilson, Mackay, and Scow (2002); Mackay et al. (2001); Johnson, Bruce, and Miller (2003); and Johnson, Miller, and Bruce (2004) have published documents discussing the aerobic remediation of MTBE.

Figure 4-7. EHC mixing and injection equipment.

Anaerobic degradation pathways for chlorinated solvents

There are several potential aerobic and anaerobic reactions that may degrade chlorinated solvents in the subsurface. CVOCs are amenable to degradation under both aerobic and anaerobic conditions. However, anaerobic degradation processes may potentially degrade all of the common chloroethenes, chloroethanes, and chloromethanes.

There are three general reactions that can degrade chlorinated solvents under anaerobic conditions:

- **metabolic anaerobic reductive dechlorination** (halorespiration), a biologically mediated process illustrated in Pathway 1 of Figure 4-8
- **cometabolic anaerobic reductive dechlorination**, in which an enzyme released by bacteria during metabolism of an unrelated compound serendipitously degrades a CVOC or another contaminant
- **abiotic reductive dechlorination**, in which a CVOC compound is reduced by contact with a reactive mineral such as iron monosulfide (Pathway 2 in Figure 4-8 illustrates this reaction, which is similar to the β-elimination pathway in Figure 4-2.)

In practice, it may be difficult to distinguish among these different reactions at the field scale, and several or all these reactions likely occur simultaneously to some degree.

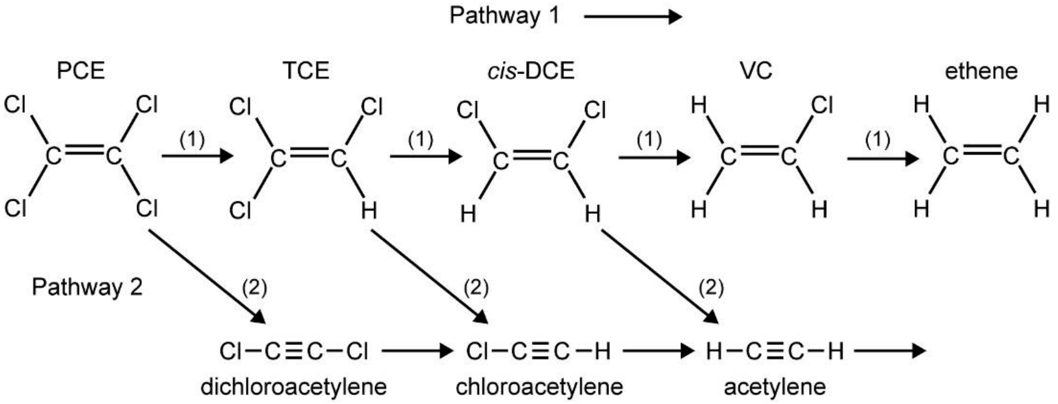

Figure 4-8. Pathways for (1) biotic transformation of chlorinated ethenes and (2) abiotic transformation by iron monosulfide. *Source:* AFCEE 2008, modified from Butler and Hayes 2001.

The primary causes of incomplete dechlorination of CVOCs include (1) insufficient redox conditions due to a limited supply of electron donors or an excess of electron acceptors such as sulfate, iron [Fe(III)], and manganese [Mn(IV)] and (2) the absence or low activity of microorganisms capable of dechlorinating cDCE and VC. Other potential causes may include interspecies competition for molecular hydrogen (e.g., the use of hydrogen for CH_4 production, limiting its availability for dechlorination) or high concentrations of inhibitory substances such as sulfide or tetrachloroethene (PCE) (in the case of VC). Careful monitoring of substrate distribution, geochemistry, and redox conditions and use of MBTs to determine microbial sufficiency can help determine an appropriate course of action when cDCE and/or VC accumulates to unacceptable levels.

Another alternative may be to stimulate degradation processes that typically do not produce cDCE or VC. Abiotic transformation of CVOCs by metal sulfides formed in biowalls has been investigated using pyrite (FeS_2) (Weerasooriya and Dharmasena 2001; Kriegman-King and Reinhard 1994; Lee and Batchelor 2002a, 2002b), troilite (Sivavec and Horney 1997), and mackinawite (FeS) (Butler and Hayes 1999, 2000). Pathway 2 in Figure 4-8 illustrates the abiotic reduction of chlorinated ethenes by reaction with FeS. This reaction typically occurs by reductive dihaloelimination (removal of two chlorine atoms), similar to the reaction of chlorinated ethenes with ZVI (e.g., Arnold and Roberts 2000). The overall degradation pathway is referred to as biogeochemical transformation (Becvar et al. 2008) because the reactive mineral may be formed due to both biological and chemical processes (USEPA 2009a). CVOC degradation using iron oxides, such as magnetite (Ferrey et al. 2004) and green rusts (Lee and Batchelor 2002b), have also been studied.

Reduction of perchlorate

Perchlorate (ClO_4) is an anion consisting of a Cl atom bonded to four oxygen atoms. Perchlorate is highly soluble and adsorbs poorly to soil (Urbansky 1998). It is usually produced commercially as the anion of a salt such as ammonium perchlorate (NH_4ClO_4). The physical and chemical properties of perchlorate and its degradation products are listed in Appendix C of AFCEE (2008).

Perchlorate is known to degrade anaerobically in the presence of perchlorate-reducing microorganisms (ITRC 2002, 2005a). Perchlorate is used as an electron acceptor and reduced to chlorate, which is further reduced to chlorite and finally to chloride as follows:

$$ClO_4^- \text{ (perchlorate)} \rightarrow ClO_3^- \text{ (chlorate)} \rightarrow ClO_2^- \text{ (chlorite)} \rightarrow Cl^- \text{ (chloride)} + O_2 \quad (4\text{-}5)$$

Microorganisms capable of using perchlorate as an electron acceptor appear to be ubiquitous in the environment (Xu et al. 2003, Coates et al. 1999, Wu et al. 2001).

Microbial degradation of perchlorate is an anaerobic process suitable for a biological PRB. The reducing equivalents of mulch and compost substrates must be sufficient to overcome the native electron acceptor demand from DO and nitrate, which may inhibit perchlorate reduction. Parameters such as DO, nitrate, and total organic carbon (TOC) are typically monitored to ensure that geochemical conditions are sufficiently reducing for perchlorate reduction.

Reduction of nitrate and sulfate

The role of organic carbon as an energy source for microbes in denitrification and sulfate-reduction reactions has been recognized for several decades (e.g., Tuttle, Dugan, and Randles 1969; Grienko and Ivanhoff 1983). Robertson and Cherry (1995) adapted the use of organic materials to stimulate biologically mediated denitrification and sulfate reduction for contaminated groundwater in PRB configurations. Denitrifying and sulfate-reducing bacteria are ubiquitous in the environment. These are heterotrophic bacteria that reduce nitrate to nitrogen gas and sulfate to sulfide in the absence of oxygen.

Benner, Blowes, and Ptacek (1997) and Benner et al. (1999, 2002) installed an organic-carbon PRB in an aquifer affected by acid-mine drainage derived from a sulfidic mine tailings impoundment in the Sudbury, Ontario, area. For the full-scale PRB, the reactive materials consisted of 40% plant-based compost, 40% leaf mulch, 19% woodchips, and 1% limestone by volume. The materials were combined in a 1:1 mixture with carbonate-rich gravel. The PRB was successful in promoting microbially mediated sulfate reduction and the subsequent precipitation of iron and other metal sulfides. In groundwater within the PRB, sulfate concentrations decreased by as much as 3,000 mg/L, iron concentrations decreased by as much as 1,250 mg/L, pH increased from <6 to 7.0, and alkalinity increased from <50 mg/L to 600–2,000 mg/L as calcite ($CaCO_3$). Monitoring in 2001 suggested that the overall performance and rate of metal sulfide accumulation within the PRB had not decreased significantly since the initial years of operation (Daignault 2002).

Transformation/immobilization of metals

The solubility of metals depends on pH, reduction potential, aqueous concentrations of reacting species, availability of sorption sites, and reaction kinetics. The solubility, and thus mobility, of many inorganic compounds, such as chromium, copper, zinc, and nickel, are reduced in a range of neutral to slightly basic pH, while the solubility and mobility can increase in either very acidic or very basic pH solutions. The solubility of divalent metals generally increases under reducing conditions, unless sufficient sulfides are present to remove the metals as metal sulfide minerals. Stability diagrams (such as the Eh-pH diagram, Figure 4-9, modified from Suthersan and Payne [2005]), can be useful for engineering geochemical conditions that are conducive to the immobilization of metals.

Metals can be immobilized by biowalls through four processes (Neculita, Zagury, and Bussière 2007):

- precipitation of metal sulfides resulting from sulfate reduction
- precipitation of metal hydroxides due to increased pH
- precipitation of metal carbonates due to the production of bicarbonate resulting from microbial activity
- sorption onto organic matter and precipitated inorganic minerals

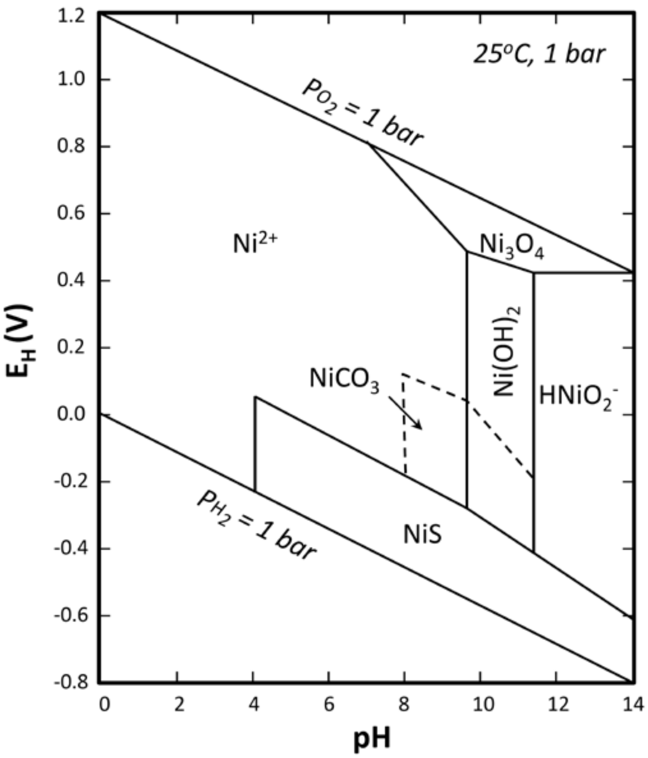

Figure 4-9. Eh-pH diagram for the Ni-O-H-S-C system.

Precipitation of metals in biowalls can be enhanced by the addition of limestone to increase pH.

An approach similar to that described above by Benner et al. (2002) for acid mine drainage was employed at a site in Vancouver, Canada. The groundwater contains high concentrations of sulfate, iron, and other heavy metals, including cadmium, copper, nickel, lead, and zinc. Groundwater velocity estimates were as high as 1 m/day, and the input concentration of sulfate was approximately 1,000 mg/L. A full-scale PRB was constructed at this site between November 2000 and February 2001. The compost-based reactive media were installed in a guar-gum slurry trench. In a pilot study preceding installation of a full-scale PRB, zinc concentrations decreased from >2 mg/L in the influent to <0.1 mg/L, and typically <0.05 mg/L, within the pilot PRB. Copper decreased from as much as 3.6 mg/L to <0.01 mg/L, and cadmium concentrations decreased from 0.015 mg/L to <0.0001 mg/L within the PRB (Ludwig et al. 2002).

Anaerobic degradation of TNT, RDX, and HMX

Potential contaminants in soil and groundwater from the use of military munitions include 2,4,6-TNT, RDX, and HMX. HMX is a by-product of the synthesis of RDX and is also used in RDX formulations (McCormick, Cornell, and Kaplan 1981). The physical and chemical properties of TNT, RDX, HMX, and some of their intermediate degradation products are listed in Appendix C of AFCEE (2008). The following is a brief description of the anaerobic degradation pathways for TNT, RDX, and HMX that are thought to occur in groundwater. A more thorough summary may be found in GSI (2008).

Anaerobic biodegradation of TNT has been observed to occur in the laboratory (e.g., Lewis et al. 1997; Preuss, Fimpel, and Diekert 1993; Khan and Hughes 1997). The anaerobic transformation of TNT led to the initial formation of reduced amino derivatives, which were ultimately transformed to 2,4,6-TAT. Hawari et al. (1998) similarly described the anaerobic transformation of TNT to TAT, observing a near stoichiometric transformation of TNT to TAT in a mixed culture incubated under methanogenic conditions.

Anaerobic biodegradation of RDX has been reported by McCormick, Cornell, and Kaplan (1981), with intermediate products observed that included TNX, DNX, and MNX. Concentrations of these products were observed to increase and decrease sequentially as they were sequentially reduced to the corresponding nitroso- (MNX), dinitroso- (DNX), and trinitroso- (TNX) analogs of RDX. Hawari (2000) postulated two pathways for anaerobic degradation of RDX in liquid cultures mixed with municipal anaerobic sludge. In addition to the pathway demonstrated by McCormick, Cornell, and Kaplan (1981), Hawari (2000) observed a second degradation pathway with the production of the intermediate metabolites methylenedinitramine and bis(hydroxymethyl)nitramine. The two metabolites did not accumulate in the cultures but were further transformed to innocuous end products such as nitrous oxide and carbon dioxide.

The role of extracellular electron shuttling compounds and ferric iron (Fe^{3+}) reduction has recently been shown to be important in microbially mediated biodegradation of RDX. Finneran, Kwon, and Drew (2007) were able to demonstrate that electron shuttles mediated biodegradation of RDX more rapidly than previously described microbial or chemical processes and that biodegradation was more complete with less formation of nitroso or ring-cleavage metabolites.

HMX appears to be more recalcitrant to biodegradation than RDX, as the chemical structure of HMX is reported to be more stable (Hawari 2000). However, Finneran, Kwon, and Drew (2007) found that the electron-shuttling and ferric iron–reducing processes for biodegradation of RDX were also applicable to HMX, suggesting that HMX may be amenable to anaerobic biodegradation.

Microorganisms capable of degrading RDX and TNT include those of the *Clostridia* genus and other microorganisms that display nitroreductase activity (Ederer, Lewis, and Crawford 1997; Regan and Crawford 1994; Zang and Hughes 2002; Ahmad and Hughes 2000, 2002). These microorganisms are thought to be ubiquitous in the environment.

A bench-scale study was performed using pine mulch to degrade RDX and HMX as part of a technology demonstration for the Environmental Security Technology Certification Program (ESTCP) (Ahmad, Schnitker, and Newell 2007). Results of the column study included complete removal of RDX and HMX at a pseudo first-order, steady-state rate constant for RDX of 0.20–0.27/hr. Based on these results, a field demonstration of a permeable mulch biowall has been conducted at the Army PCD, Colorado (GSI 2008).

4.3.3 Amendments to Organic PRBs

Amendments to organic PRBs may include materials to promote the formation of reactive iron sulfide minerals to stimulate biogeochemical transformation processes, materials to buffer pH, and bioaugmentation cultures to initiate or accelerate breakdown of hazardous intermediates.

Materials for pH control (crushed limestone)

Sand and gravel are added to the backfill for biowalls to provide a weighting material for emplacement, reduce the amount of compaction after installation, and enhance and maintain the permeability of the mixture. Limestone gravel may also be used as a weighting material and has the added benefit of providing calcium carbonate as a buffer for stabilizing pH. A lowering of pH may occur due to formation of metabolic acids, which may inhibit degradation processes in some cases. Calcium carbonate from the limestone is slowly dissolved by acids generated by degradation of the organic substrate; hence, the limestone provides a long-term buffering agent. Sites with high concentrations of sulfate in groundwater typically have sufficient natural buffering capacity that the use of limestone to buffer pH is usually not required. If the addition of limestone gravel is considered at a high sulfate site, then caution is advised that the calcium sulfate may precipitate on the limestone surfaces as calcium carbonate (gypsum).

Iron and sulfate for biogeochemical transformation

Inorganic amendments may be added to stimulate biogeochemical transformation (abiotic) processes, including sulfate and iron reduction. Both sulfate and iron are found naturally in aquifer systems, but concentrations are highly variable. Sulfate in groundwater at concentrations above 500–1,000 mg/L may be a sufficient source for stimulating biogeochemical transformation with reduced iron sulfides such as iron monosulfide (e.g., mackinawite) or iron disulfide (e.g., pyrite, see Figure 4-10) (Lebrón et al. 2010). If additional sulfate is required, it may be added to the biowall PRB in the form of crushed gypsum or gypsum pellets commonly used as an agricultural soil amendment.

Ferric iron has two purposes: it is reduced and precipitates with sulfide to form FeS as an abiotic reactant, and it also reduces the concentration of hydrogen sulfide (H_2S), which can inhibit the reductive dechlorination process (Maillacheruvu and Parkin 1996). The easiest and most cost-effective way to increase the amount of available iron is to choose a sand backfill material that is naturally

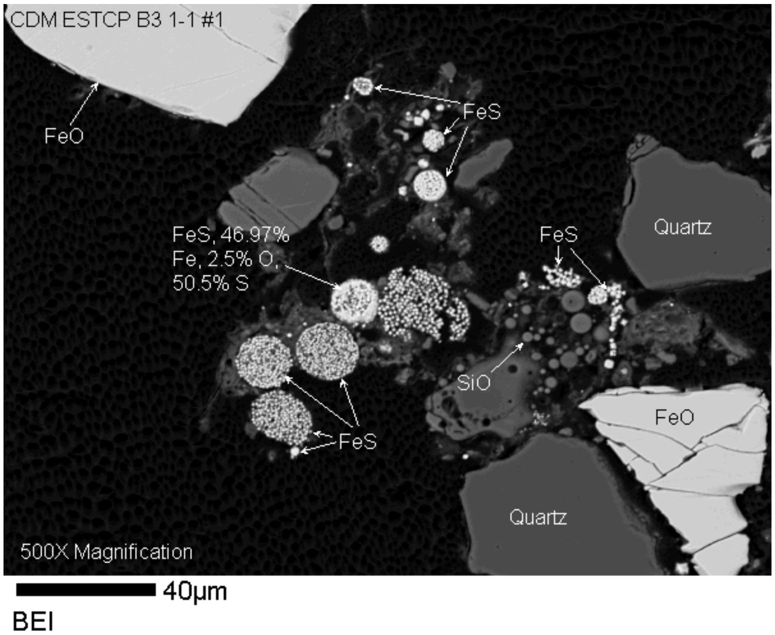

Figure 4-10. Photomicrograph of framboidal iron sulfide pyrite. *Source:* Lebrón et al. 2010.

high in iron. Attempts have been made to increase the mass of Fe^{3+} in biowall PRBs by blending magnetite ore with the backfill material on an experimental basis, as done at Altus AFB, Oklahoma, and at Ellsworth AFB, South Dakota (AFCEE 2008).

Methods for determining how much iron or sulfate should be added to stimulate biogeochemical transformation of chlorinated solvents have not been established. Appendix D of AFCEE (2008) describes the stoichiometry and mass calculations that may be used to evaluate the potential for FeS to form and simple calculations to evaluate whether a sulfate or iron amendment should be added. These are theoretical calculations only. Research into biogeochemical transformation of chlorinated solvents and field validation of this approach is in the early stages of demonstration (Becvar et al. 2008).

Bioaugmentation

Bioaugmentation is an option for PRBs that rely on specific microbial species to degrade the COCs. Bioaugmentation is most commonly considered for bioremediation of chlorinated solvents, either from initiation or as a contingency when degradation stalls at intermediate dechlorination products (e.g., Stroo, Major, and Gossett 2010; Steffan, Schaefer, and Lippencott 2010). Bioaugmentation should be considered when native dechlorinating species capable of complete dechlorination of the CVOCs are not present, are poorly distributed, or are present at low population densities. Additional information on bioaugmentation for CVOCs can be found in GeoSyntec Consultants (2005) and Stroo, Major, and Gossett (2010). The effectiveness of bioaugmentation for chlorinated solvents using mixed cultures with *Dehalococcoides* species may be limited if pH is below 6.0 or above 8.0 (Zhuang and Pavlostathis 1995; Middeldorp et al. 1999; Steffan, Schaefer, and Lippencott 2010).

Aerobic biodegradation in PRBs

Addition of oxygen has been used in PRBs to promote aerobic microbiological processes to degrade fuel-related constituents such as benzene or MTBE. Applications include rows of air- or oxygen-sparging wells to increase the oxygen content of passing groundwater and sparging within gravel-filled trenches to improve the contact between fuel contaminants and oxygen. In addition to direct delivery of oxygen gas into the subsurface via oxygen diffusers or by air sparging, solid oxygen-release compounds (e.g., ORC®, EHC-O™), may also be used.

As with other PRB materials, this concept must be matched to the geochemical and hydrogeological conditions of the site. For example, the presence of high concentrations of native organic carbon in the subsurface (such as in near-shore or bog environments) may result in zones of high rates of oxygen consumption that render the technology impractical as most of the oxygen is consumed by natural processes. High levels of reduced dissolved iron may increase the opportunity for iron precipitation and fouling.

Examples of aerobic biobarriers include applications at Vandenburg AFB (Wilson, Mackay, and Scow 2002) and Port Hueneme (Johnson, Bruce, and Miller 2003; Johnson, Miller, and Bruce 2004). At Port Hueneme, oxygen was released through a constructed panel of oxygen emitters that were installed across a portion of an MTBE plume. The goal of this PRB was to create an aerobic biologically active zone capable of reducing the mass discharge of MTBE. Results of the field test indicate that MTBE concentrations were reduced by at least two orders of magnitude (from up to 400 µg/L upgradient of the biobarrier to <5 µg/L downgradient of the biowall). The transient production and subsequent destruction of tertiary butyl alcohol within the biowall provided further evidence of the effectiveness of the pilot test.

One key to the success of the biobarrier at Port Hueneme was the presence of microbes capable of degrading MTBE under aerobic conditions. Without these microbes, the addition of oxygen would create the conditions necessary to degrade the MTBE, but none would occur. Whether such microbes are naturally present at a site must be considered prior to engaging this technology at fuel release sites.

4.4 Combined Media

Combined media can be considered as having two or more reactive components in one treatment material. Combined media are distinguished from amendments designed to enhance a treatment process or the addition of inert components (e.g., gravel) to improve geotechnical properties and hydraulic conductivity.

4.4.1 Biowalls Combined with ZVI

The combination of organic media with ZVI has been evaluated for the concurrent treatment of divalent metals and arsenic (Ludwig et al. 2009) and sulfate, nitrate, and selenium (Sasaki et al. 2008). As discussed in Section 4.2.2, biowalls are effective in promoting denitrification, reducing sulfate to sulfide, and precipitating cationic metals as low-solubility sulfides. As discussed in Section 4.1.2, ZVI effectively promotes selenium reduction and sorption, as well as multiple treatment mechanisms for arsenic. Consequently, the combination of biowall (organic) materials and ZVI facilitates both reduction and sorption mechanisms that are effective in treating a wider range of contaminants than either medium alone.

Sasaki et al. (2008) conducted column experiments with mine drainage water and PRB materials consisting of ZVI, municipal leaf compost, sawdust, and wood chips. This combination of media treated an influent selenate concentration of 40 mg/L down to <0.014 mg/L and an influent sulfate concentration of 620 mg/L down to 200 mg/L after one month of treatment. Geochemical modeling indicated the formation of metallic selenium and selenite and the reduction of sulfate to sulfide.

Ludwig et al. (2009) performed a 30-month evaluation of a pilot-scale PRB consisting of a mixture of leaf compost, ZVI, limestone, and pea gravel, designed to treat divalent metals and arsenic (Figure 4-11). Arsenic, lead, cadmium, zinc, and nickel were treated from concentrations of 206 mg/L, 2.02 mg/L, 0.324 mg/L, 1060 mg/L, and 2.12 mg/L, respectively, to below analytical reporting limits. X-ray spectroscopic data indicated that arsenic [present in both As(III) and As(V)] forms) was removed from solution through sorption onto and coprecipitation with iron (hydr)oxides present on the corroded surfaces of the ZVI, direct precipitation with sulfides, and/or coprecipitation with iron sulfides.

4.4.2 Emulsified ZVI

Emulsified ZVI (EZVI) is created by adding microscale or NZVI particles into a surfactant-stabilized biodegradable water-oil emulsion. This emulsion is injected into dense, nonaqueous-phase liquid (DNAPL) zones in the subsurface. The DNAPL is solubilized within the oil emulsion and then reacts with the ZVI. Though designed for treating DNAPL, EZVI is also effective at treating dissolved-phase contaminants (NASA 2009).

Figure 4-11. Components for a biowall-ZVI PRB bench test. Clockwise from top left: limestone, granular ZVI, leafy compost, gravel.

4.4.3 Other Iron-Organic Combinations (e.g., EHC, ABC+)

There are several types of reactive media that combine iron and organic carbon, which can be used in PRBs. EHC (from the Adventus Group) is a combination of plant-derived, controlled-release carbon and ZVI particles. It stimulates both biotic reductive dechlorination and direct chemical dechlorination of CVOCs in groundwater. EHC is normally injected into the subsurface under high pressure using direct-push technology but can also be applied using direct mixing, hydraulic fracturing, and pneumatic fracturing and in trenches. The organic component of EHC (fibrous organic material) is nutrient-rich and hydrophilic and has high surface area. The organic material is fermented and a variety of volatile fatty acids (VFAs) are released, which diffuse into the groundwater plume and serve as electron donors for other bacteria, including halorespiring species. Microscale ZVI particles provide substantial reactive surface area that stimulates direct chemical dechlorination and an additional drop in the ORP of the groundwater via chemical oxygen scavenging and produces hydrogen gas. Additional nutrients and buffers are also added to the formulation.

The product Anaerobic Biochem (ABC+®, from Redox Tech) is a mixture of lactates, fatty acids, and a phosphate buffer, together with ZVI. The organic component of this product contains soluble lactic acid as well as slow- and long-term releasing components. A phosphate buffer provides phosphates, which are a micronutrient for microorganisms. In addition, the buffer helps to maintain the pH in a range that is best suited for microbial growth.

In addition to the above, several small pilot studies have investigated the combined use of soluble carbon sources such as molasses and EVO with ZVI (e.g., Martin, Horst, and Lenzo 2005). The goal in these applications was the same: to take advantage of the synergistic abiotic and biotic reduction reactions available with these combinations.

Note that the reducing environment established in these carbon ZVI systems is also conducive to promoting the precipitation of trace metals, including chromium and arsenic (Przepiora, Hill, and

Seech 2008). For example, nickel, copper, and cobalt were removed at a small industrial facility in Ontario, Canada, using these combined media (Mueller et al. 2009).

4.5 Apatite Media

Phosphate media—in particular apatite and enhanced apatite—have removed dissolved metals from an aqueous solution and transformed soil-bound metals to less soluble phases (Conca 1997, Conca et al. 2002). The ability of phosphate minerals to remove radioactive constituents from groundwater has also been demonstrated (Conca et al. 2002). Of the phosphate minerals, apatites are most suitable for PRB applications because of their relatively low solubility and long-term stability. A thorough review of apatite chemistry and use in environmental remediation has been presented by Magalhaes and Williams (2007).

Several field-scale, apatite-based PRBs have been installed in the United States for the treatment of metals and radionuclides, including at Success Mine in Idaho (Conca and Wright 2006); Nevada Stewart Mine in Idaho (McCloskey 2007); Oak Ridge, Tennessee (Wright and Conca 2002); Fry Canyon, Utah (Naftz et al. 2002); and Mortandad Canyon, New Mexico (LANL 2004).

4.5.1 Types of Apatite Media

Natural phosphate materials include phosphate rock and a number of different natural sources of apatite, including bone meal, bone charcoal (“bone char”), and pelletized bone charcoal (Figure 4-12). Natural apatite minerals are composed mainly of calcium and phosphorus, with varying fractions of hydroxide (hydroxyapatite [$Ca_5(PO_4)_3OH$]), fluoride (fluorapatite [$Ca_5(PO_4)_3F$]), and chloride (chlorapatite [$Ca_5(PO_4)_3Cl$]). Apatite minerals can be both geogenic and biogenic and are a key component of bones and teeth. Properties of natural phosphate materials from different sources vary substantially, with surface area from 0.3 m^2/g to 64 m^2/g and grain size from 3 microns to >1 mm (Fuller et al. 2002).

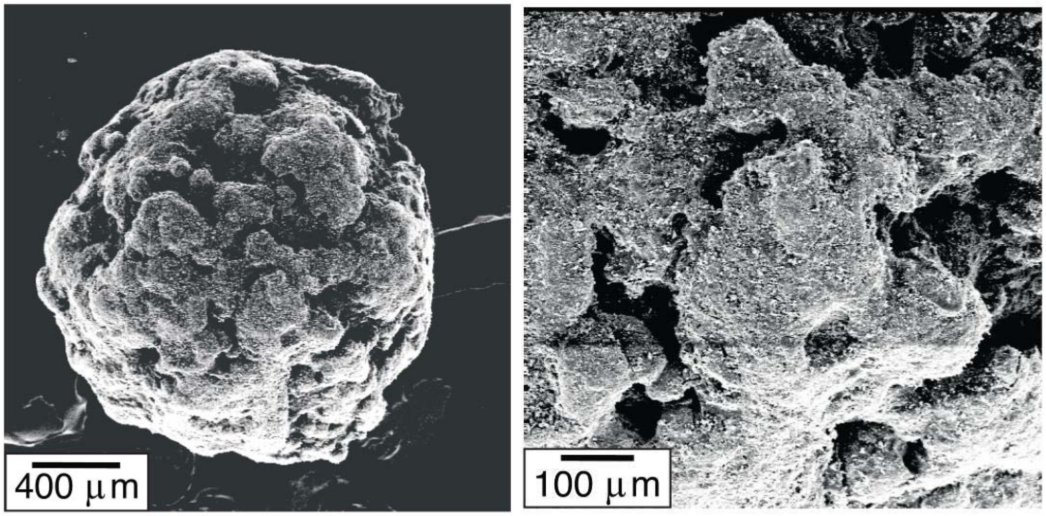

Figure 4-12. Electron micrograph of bone-char phosphate pellets illustrating morphology and microporosity of apatite materials.
Adapted from USEPA 2000b.

Apatite II™ is a biogenically precipitated apatite material derived from fish-bone wastes, with the general composition Ca_{10}-$xNa_x(PO_4)_6$-$x(CO_3)_x(OH)_2$, where x<1, and 30%–40% by weight of organic materials trapped in the internal porosity of the inorganic structure (Conca and Wright 2006). Apatite II was developed to have increased reactivity due to its high degree of substituted carbonate ion, absence of substituted fluorine, amorphous structure, and high microporosity (Wright and Conca 2003).

The use of liquid reagents to form apatite in situ was field-tested at the Hanford N-100 Area, with successful injection of both a Ca-citrate-PO_4 solution and high-pressure injection of sodium phosphate and/or fish-bone apatite (Szecsody et al. 2010).

4.5.2 Apatite Treatment Mechanisms

Apatite minerals usually carry a net negative surface charge at neutral and alkaline pH (Somasundaran and Wang 1984) and therefore are effective for the adsorption of cationic metals over a wide range of environmental conditions. The physical characteristics of apatites vary widely. Modifications to apatites have been made to improve treatment performance or to change surface properties of the apatite to promote effective treatment of COCs other than cationic metals. For instance, treatment of apatite with a highly concentrated iron solution has produced a positive surface charge, which attracts anions, such as arsenic (Fisher, Talley, and Hanson 2008).

The key treatment mechanisms for metal removal by apatite include cation exchange, precipitation of metal phosphates, and incorporation into the apatite structure (Fuller et al. 2002). Due to the presence of associated organic materials, apatites may also promote the precipitation of low-solubility, metal-sulfide phases due to chemical changes induced by biological activity (Conca and Wright 2006).

Precipitation of lead

Immobilization of lead in the form of pyromorphite is a well-recognized and important apatite treatment mechanism. Nriagu (1974) recognized the potential for lead immobilization using phosphatic compounds. The removal of lead with apatite is rapid and produces a very stable, low-solubility product (Magalhaes and Williams 2007).

Precipitation and surface complexation of radionuclides

Radionuclides—in particular uranium and strontium-90—have been treated using apatites. Uranium is removed from solution through the precipitation of uranyl phosphate and uranium-phosphate surface complexation (Naftz et al. 2002). In addition to surface complexation and coprecipitation, strontium-90 is also substituted for calcium (Szecsody et al. 2008). Fuller et al. (2002) and Fuller, Bargar, and Davis (2003) evaluated the speciation of uranium on several types of apatite and found that most of the uranium uptake occurred by surface complexation and not uranyl phosphate precipitation. These findings have implications for the long-term stability of immobilized uranium.

Potential performance challenges for apatite PRBs include loss of reactivity due to the dissolution of apatite, precipitation of sphalerite, loss of organic content, and potential reversibility of reactions (Conca and Wright 2006). Reductions in hydraulic conductivity have been noted in field applications (Naftz et al. 2002). Dissolution of apatite can lead to increased phosphate concentrations downgradient of the PRB.

4.6 Zeolites

Zeolites have been widely used for a number of water treatment applications, from removing heavy metals in wastewater treatment plants to the treatment of ammonium in animal waste (Cyrus, Reddy, and Forbes 2008). Zeolites are natural aluminosilicate minerals that have very high ion-exchange capacities (in the 200–400 milliequivalent weight [meq] per 100 g range) and large surface areas (up to 145 m^2/g). The typical zeolite mineral is a framework of stacked tetrahedra that form pores or channels where ion exchange can occur. Because zeolites are anionic (negatively charged), they can be used to remove cations from an aqueous solution. The negative charge is considered permanent because it is not affected by the concentration and types of ions in the soil solution over a wide range of pH.

Field-scale zeolite PRBs have been installed at two locations in the North America: Chalk River, Ontario (Figure 4-13) and West Valley, New York. Both of these PRBs use clinoptilolite to treat strontium-90. Appendix A includes a case summary for the West Valley site.

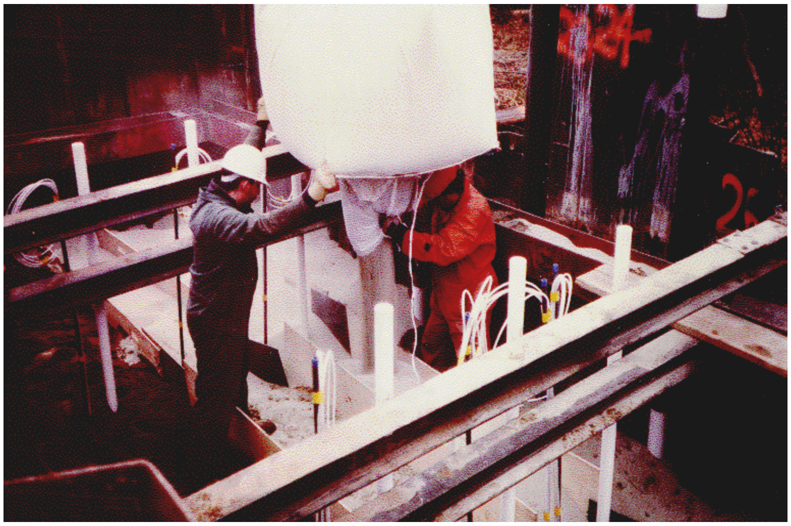

Figure 4-13. Granular zeolite (clinoptilolite, 14 × 50 mesh) being emplaced in an instrumented PRB trench, Chalk River, Ontario.

4.6.1 Types of Zeolite Media

Several hundred zeolitic minerals exist; synthetic zeolitic minerals also have been produced for various industrial needs. Clinoptilolite, with a solid solution composition ($[Ca, Mg, Na_2, K_2][Al_2Si_{10}O_{24} \bullet 8H_2O]$) is the zeolite most commonly researched with respect to potential PRB applications.

4.6.2 Zeolite Treatment Mechanisms

The key treatment mechanisms for metal removal by zeolites are cation exchange and adsorption. Zeolites are "molecular sieves," meaning they can selectively adsorb molecules on the basis of their size, shape, or electrical charge (Van Bekkum, Flannigen, and Janmsen 1991). Natural zeolites have cation exchange capacities superior to most other inorganic cation exchange materials (Mohan and Pittman 2007).

Surface-modified zeolites (SMZs) also have been evaluated for their potential use as PRB materials in removing anionic constituents from groundwater (Bowman 1996).

Treatment of radionuclides and ammonium by cation exchange

Certain zeolites exhibit strong selectivity for the radionuclides cesium and strontium-90 (Robinson, Arnold, and Byers 1991). Clinoptilolite has been applied in pilot test programs to assess the ability of the material to remove radioactive strontium (strontium-90) from a groundwater system (Lee et al. 1998, Lee and Hartwig 2005, Warner et al. 2004). Rabideau et al. (2005) conducted laboratory column tests and performed cation-exchange modeling for the removal of strontium-90 from groundwater using clinoptilolite. The results indicated excellent immobilization of strontium-90 after approximately 160 pore volumes, with the majority of the strontium-90 mass being sorbed in the first 2 cm of a 15-cm-long clinoptilolite column.

Van Nooten, Diels, and Bastiaens (2008) tested the potential for the removal of ammonium from landfill leachate using a clinoptilolite laboratory column. Ammonium was removed very effectively for the first 20 days, from over 250 mg/L to below 8 mg/L. However, ammonium started leaching from the clinoptilolite column after 20 days. The removal capacity was calculated to be 46.7 mg nitrogen/g of clinoptilolite.

Sorption of oxyanions by surface-modified zeolites

Zeolites can be modified by ion exchange to acquire a net-positive surface charge, which can then be used for adsorption of anions. Immobilization of chromate (Bowman et al. 2001), arsenic (Sullivan, Bowman, and Legiec 2003), and perchlorate (Zhang, Avudzega, and Bowman 2007) by SMZ for potential use in a PRB has been investigated. Zhang, Avudzega, and Bowman (2007) found that perchlorate was effectively removed by SMZ in batch and column systems, even in the presence of competing anions, such as nitrate, sulfate, and chloride. The maximum perchlorate loading on the SMZ was 47 mmol/kg.

4.7 Iron and Steel Furnace Slag

Slag is a nonmetallic by-product of iron and steel production, widely used for road base construction and other aggregate products. Being an industrial by-product, slag has the advantage of being very inexpensive, especially when a local source is available.

Slag's potential to remove contaminants from water was first documented by Yamada et al. (1986) in the treatment of phosphorus. Subsequently, Baker, Blowes, and Ptacek (1998) and McRae, Blowes, and Ptacek (1999) evaluated the potential for using slag in a PRB.

Slag has been applied in two pilot-scale PRB applications for the removal of phosphate from wastewater (Smyth et al. 2002) and one pilot-scale PRB application for the treatment of arsenic in groundwater (Bain et al. 2006). A full-scale slag PRB was installed in 2002 in East Chicago, Indiana, to treat arsenic-impacted groundwater (Wilkens et al. 2003; Bain, Blowes, and Wilkens 2007). Appendix A includes a case summary for the East Chicago site.

4.7.1 Types of Slag Media

The physical and chemical composition of slag varies substantially depending on the smelting process, cooling process, and composition of the fluxing agents (Proctor et al. 2000, Metz and Benson 2007). Iron slag (or blast furnace slag [BFS]) products include air-cooled slag, expanded or foamed slag, pelletized slag, and granulated slag (Turner-Fairbank Highway Research Center[2]). Basic oxygen furnace slag (BOFS) and electric arc furnace slag (EAFS) are the by-products of steel production. The cooling process controls the degree of crystallization, the bulk density, and the texture of slag. Due to the varying cooling methods, the specific surface area of slag can vary widely from 0.089 to 5.7 m^2/g (Sasaki et al. 2008, Metz and Benson 2007). The wide range of treatment performance among slag material makes bench-scale testing compulsory prior to field implementation. Furthermore, the variability in material properties within a single slag source may affect not only the treatment of COCs but also hydraulic gradients across the PRB due to heterogeneity in grain size and porosity (Metz and Benson 2007). Differences in iron content may be particularly important in slag PRB performance for certain COCs.

Slag composition is dominated by calcium, magnesium, and aluminum oxides and silicates, which derive from impurities in the iron source and from fluxing agents (Proctor et al. 2000). Slag also contains iron and magnesium oxides, sulfur, and trace elements. Typical BFS comprises 31%–48% calcium oxide and 27–45% silicon dioxide (based on data from 99 slag sources, Emery 1992). Iron content of slag is highly variable, depending on the smelting process, with BOFS and EAFS generally containing more iron than BFS (Proctor et al. 2000). Cope and Benson (2009) evaluated the characteristics of iron slag from six foundries and found the total iron content ranged 7.5%–57%. Although slag usually contains trace elements at concentrations in excess of background soil values, it generally does not exceed the toxicity characteristic leaching procedure (Proctor et al. 2000). Due to the high lime content, slag usually buffers the pH of groundwater to between 12 and 13.

4.7.2 Slag Treatment Mechanisms

Surface sorption is considered to be the primary treatment mechanism in slag, although the wide variety of minerals and mineral surfaces present in slag provide several potential treatment mechanisms, such as precipitation of calcium minerals (Ahn et al. 2003, Bain et al. 2006), precipitation of metal hydroxides at high pH (Sasaki et al. 2008), and complexation with iron oxides in slag containing significant amounts of iron (Zhang and Itoh 2005). In groundwater applications, slag has been most commonly used for the treatment of phosphorus and arsenic. The treatment mechanisms are complex and not completely understood. Additional research is needed to identify the relative importance of treatment mechanisms for each COC; modeling and field studies are necessary to evaluate long-term performance of slag PRBs.

Phosphorus treatment: Sorption and precipitation of hydroxyapatite

Phosphorous has been effectively removed from water using all slag types: BFS, BOFS, and EAFS. A thorough summary of phosphorus treatment using slag is presented by Drizo et al.

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[2] www.tfhrc.gov/hnr20/recycle/waste/bfs1.htm.

(2008). Chemical fractionation showed that phosphorus in EAFS was primarily bound to calcium and iron, whereas in BFS it was primarily bound to calcium and aluminum (Drizo et al. 2008). The predominant association with calcium phases in both BFS and EAFS is consistent with previous findings that showed the formation of hydroxyapatite on EAFS surfaces (Drizo et al. 2006) and suggests long-term stability of the immobilized phosphorus phase. Phosphorus sorption capacity varies with slag type and source. Bowden et al. (2009) cite eight experiments in which slag materials adsorbed 0.1–15.7 mg of phosphorus/g of slag, while Mann (1997) found adsorption capacity of phosphorus on slag of >380 mg/g.

Sorption and precipitation of arsenic

Mechanisms considered to be responsible for arsenic removal by slag include sorption to metal oxides, precipitation of calcium arsenate minerals (McRae, Blowes, and Ptacek 1999; Ahn et al. 2003, Bain et al. 2006), precipitation of arsenic-bearing iron hydroxides (Bain et al. 2006), and the oxidation of arsenic to arsenate by BOFS, which is subsequently adsorbed to the BOFS surface (Smyth et al. 2001). Studies have shown that in batch experiments, slag can remove both arsenite and arsenate (McRae, Blowes, and Ptacek 1999; Ahn et al. 2003). Oxidation of arsenite to arsenate and its adsorption/precipitation onto BFS has been observed during arsenite removal (Kanew et al. 2006).

Most studies have shown slag to be less effective than ZVI in treating arsenic (Metz and Benson 2007, Sasaki et al. 2008). However, batch tests performed by Metz and Benson (2007) with four slag materials with widely varying iron contents showed that arsenic removal was not correlated with iron content, indicating that precipitation of low-solubility calcium minerals [e.g., arsenate apatite, $Ca_5(AsO_4)_3OH$] and other mechanisms may be more important in slag than sorption to iron (Metz and Benson 2007, Sasaki et al. 2008).

Sorption and precipitation of metals

The removal of metals by slag is likely to occur through sorption and precipitation of metal hydroxides and carbonates under high-pH conditions (see Section 4.7).

Batch tests have been performed to evaluate the potential use of atomized steel slag for the treatment of dissolved metals in landfill leachate (Chung et al. 2007). The slag contained 22%–45% iron oxides by weight. Lead, copper, cadmium, and Cr(VI) concentrations of 25–50 mg/L were reduced by up to 93% after 96 hours of mixing. It is important to note that these batch tests were buffered to pH of 5, 7, and 9, with optimal results observed at neutral pH.

In column studies of acid mine drainage treatment using granulated BFS, concentrations of certain metals (iron, manganese, lead, and zinc) decreased from 0.5–35 mg/L to below reporting limits and remained below reporting limits for about 17 pore volumes (Sasaki et al. 2008). The formation of metal hydroxides, oxides, and carbonates at high pH was the presumed removal mechanism (Sasaki et al. 2008).

Abiotic reductive dechlorination of TCE

Cope and Benson (2009) compared the potential of BFS (specifically, six grey-iron foundry slags) to ZVI for treating TCE in groundwater. Reactivity of the slag was proportional to iron content, indicating that reduction by iron present in the BFS was the key TCE treatment mechanism. Based on the absence of *trans*-1,2-dichloroethene (tDCE) and the predominance of cDCE, beta-elimination may be the pathway for TCE reduction with slag as it is for ZVI; however, no direct confirmation of this pathway was made, and additional research is needed to determine the degradation pathways for TCE on slag (Cope and Benson 2009).

4.8 Organophilic Clays

Organophilic clays are widely used for removal of organics in a number of wastewater treatment applications. Organophilic clays exhibit a synergistic effect when used as pretreatment to remove oil and grease prior to other water treatment processes, including granular-activated carbon, reverse osmosis, and air strippers (Patel et al. 2006). Thus, organophilic clays appear to have potential for use in PRBs in certain applications.

A field-scale PRB containing organophilic clay manufactured with quaternary amine compound was installed at a former railroad tie treating facility in Escanaba, Michigan, in November 2005 (see case summary in Appendix A). A standard soil filter was used to size the active media to the adjacent soil. The PRB was designed as an interim action to control migration of a creosote DNAPL plume to surface water.

4.8.1 Physical and Chemical Characteristics

Organophilic clays are a chemically modified form of granular or powdered clay. Numerous methods can be employed to modify clays and clay minerals. Native clay is converted from hydrophilic to hydrophobic and oleophilic in nature. Organophilic clay has a high sorption capacity for oil and creosote, typically >50% by weight. Organophilic clay does not hydrate and swell with water like sodium bentonite does and has a hydraulic conductivity similar to that of sand. When oil, creosote, or similar NAPL is sorbed onto the organophilic clay, the hydraulic conductivity decreases. Higher hydraulic conductivity in the presence of such NAPL can be maintained by mixing organophilic clay with inert media, such as sand or gravel (Benson, Lee, and Ören 2008; Lu and Reible 2007).

4.8.2 Treatment Mechanisms

Nonaqueous-phase liquids

Sorption of oil, creosote, and similar NAPLs is completed through a partitioning mechanism. The driving force is the hydrophobic interaction between the organophilic clay long alkyl chains and the organic contaminants. Hydrogen bonding can also occur when the contaminant molecule has oxygen or nitrogen groups since the clay layer edges have abundant hydroxyl groups.

Polycyclic aromatic hydrocarbons

Low-solubility PAHs are sorbed through a partition mechanism. Batch isotherm studies have shown a correlation between the partition coefficients of certain organophilic clays and the PAH octanol-water partition coefficient (Benson, Lee, and Ören 2008; Reible et al. 2008).

4.9 Other Mineral Media

4.9.1 Transformed Red Mud

Red mud is a waste material formed during the leaching of bauxite ore for the production of alumina. It is a mixture of compounds originally present in bauxite and compounds formed or introduced during ore processing. Transformed red mud (TRM) is created by mixing red mud with calcium chloride and magnesium chloride brine from solar salt plants (De Gioannis et al. 2008). TRM products are marketed under the Bauxsol™ trade name. TRM has been used to treat wastewater, amend agricultural soils, and as an alternative to lime for treating acid sulfate soils (Lin et al. 2002).

A TRM PRB was field-tested for the treatment of acid-rock drainage, which included copper, lead, zinc, and mangenese, with encouraging results (Munro, Clark, and McConchie 2004). No full-scale applications of TRM in PRBs have been implemented to date.

Physical and chemical characteristics

Red mud is a slurry with high ionic strength and a pH near 13. It consists primarily of iron oxides, aluminum oxides, and silica, with lesser fractions of sodium and calcium oxides. Due to its very high pH and fine texture, red mud by itself is not suitable for PRB applications. TRM consists mainly of hydrated iron oxides (hematite and ferrihydrite) and hydrated alumina. These are impregnated with alkaline minerals, mainly sodalite, calcium hydroxides, hydroxycarbonates and calcium aluminosilicates, magnesium hydroxides, and magnesium aluminosilicates (De Gioannis et al. 2008). TRM has a pH of 8–10.5 (McConchie et al. 1999). Physically, TRM is a fine powder (<10 microns) and needs to be mixed with sand for PRB applications (Munro, Clark, and McConchie 2004).

Treatment mechanisms

TRM has an acid-neutralizing capacity of about 4 mol of hydrogen ions/kg of dry solid down to pH 5.5 and can bind up to 1,000 meq/kg of metals by adsorption and/or precipitation (De Gioannis et al. 2008). Metals can be immobilized on TRM by adsorption and precipitation as hydroxides due to high acid-neutralization capacity (Munro Clark, and McConchie 2004), making TRM well suited for the treatment of acid-rock drainage.

High metal-removal efficiency has been shown for TRM in column studies, with up to 99% removal of iron, copper, zinc, nickel, and lead from acid-rock drainage (Lapointe, Fytas, and McConchie 2006). TRM has shown high sorption capacity for arsenate, with column retention of up to 95% after 400 bed volumes (Genc-Fuhrman, Bregnhøj, and McConchie 2005). TRM (in the proprietary form of Virobind™) was effective in removing up to 96% of arsenic from groundwater with an initial pH of 7.2, from an initial arsenic concentration of 33 mg/L down to 1.5 mg/L after 24 hours of batch equilibration (LFR 2009).

4.9.2 Green Sand

Green sand is a waste product from grey-iron foundries, where it is used for molds for metal casting (Lee and Benson 2004). Batch and column tests have indicated potential for the use of green sand in the treatment of TCE, pesticides, arsenic, mercury, and chromium. The key treatment mechanisms for green sand are adsorption onto mineral phases, reduction by residual iron, and adsorption by organic carbon (Benson, Lee, and Eykholt 2003).

Green sand is a blend of sand, bentonite binder, organic additive, and water, which after use also acquires 2%–12% residual iron (Benson, Lee, and Eykholt 2003). It is physically well suited for flow-through applications because it consists of 85%–98% uniform fine sand and has a relatively high hydraulic conductivity (Benson, Lee, and Eykholt 2003).

Nye and Keefer (2004) evaluated the use of green sand for the treatment of arsenic, chromate, and mercury. Results indicated effective removal of arsenic and mercury, but only partial treatment of chromate. Only minor decreases in ORP were observed, suggesting that sorption and not reduction was the key treatment mechanism and that chromium likely remained present as chromate.

No pilot-scale or full-scale applications of green sand in PRBs have been implemented to date (C. H. Benson, personal communication, 9/11/2009).

5. DESIGN

What's New?

- Updated inorganic geochemical considerations for ZVI PRBs
- Design considerations for mulch biowalls

The design and construction of a PRB requires careful consideration of RAOs and site conditions. The primary goal of any PRB design is to ensure the targeted portion of the contaminant plume is intercepted for treatment and that contaminant flow beneath, around, or above the treatment system does not occur. The second goal is ensure that the dimensions of a PRB are adequate to achieve the contact time between contaminants and reactive media needed for reduction of contaminant concentrations to acceptable levels. Therefore, understanding the site-specific hydrogeology, contaminant properties, and properties of the reactive media are critical to the design and construction of a PRB. This section describes design considerations; PRB construction is covered in Section 6.

5.1 Hydrogeology and Contaminant Distribution

The first design consideration that most people think of is the physical size of the PRB. The following discussion defines PRB dimensions that are referred to in subsequent sections on design considerations.

5.1.1 PRB Dimensions

The PRB must be able to intercept the contaminant plume without unacceptable contaminant bypass either below or around the barrier. Biowall dimensions used in this document are shown in Figure 5-1 and include length (y) perpendicular to groundwater, flow-through thickness, or width (z), and depth (x).

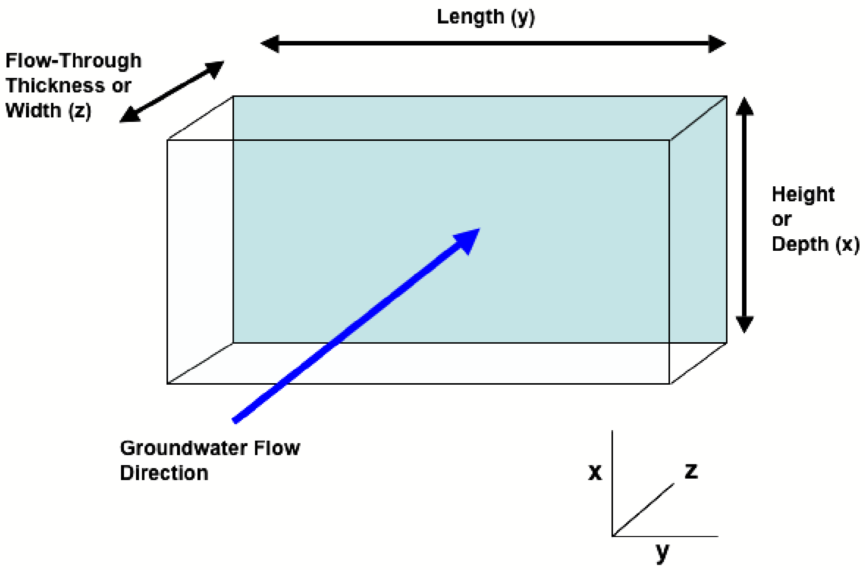

Figure 5-1. Dimensions of a PRB.

5.1.2 Length

The PRB must be long enough to treat the entire width of the plume (dimension perpendicular to groundwater flow). If a funnel-and-gate design is used, the PRB must extend beyond the lateral extent of the plume (perpendicular to the flow direction) to ensure that all contaminated groundwater is captured and treated. If multiple barriers are installed, the adjoining sections should be overlapped to reduce the chance of treatment gaps.

5.1.3 Thickness (Width)

Effective remediation using PRBs depends on appropriate quantities of reactive media and the geochemical and redox conditions to allow constituent degradation. The reactive zone must be large (thick, wide) enough to allow the degradation. The thickness of the PRB is designed based on the required residence time of the contaminants and the groundwater flow velocity. The residence time is the contaminant contact time with the reactive media, which depends on the constituent degradation rate, maximum contaminant concentrations, and groundwater flow rate. The residence time must be sufficient to allow contaminant remediation. Insufficient residence times can result in the breakthrough of parent contaminants and/or accumulation of regulated intermediate products.

Simply stated, the required PRB flow-through thickness, z, can be determined as (V)*(t), where V is the groundwater flow velocity and t is the residence time. Hydrologic modeling and direct measurements (velocity meters, dye tracers, etc.) can be used to determine the anticipated groundwater velocity, V, through the PRB. Safety factors should be applied to the result obtained to account for seasonal groundwater flow variations, field uncertainties, and potential loss of media reactivity.

5.1.4 Depth

If at all possible, the PRB should extend to and be keyed into a competent bedrock layer or aquitard. Keying into a competent, less permeable layer reduces the chance that contaminated groundwater flows under the barrier. If a sufficient aquitard does not exist, the PRB should extend to below the depth of contamination. Groundwater monitoring below the PRB should be conducted to document that contaminant bypass has not occurred.

5.1.5 Safety Factors

Factors that can affect the performance of the PRB include changes in the influent contaminant concentrations, the hydraulic gradient, flow direction and velocity, and hydraulic conductivity. Any changes in the groundwater chemistry and subsurface permeability also have an impact on the effectiveness of the PRB. The uncertainties associated with these factors may result in the need for wider and thicker PRBs to make certain that residence time and capture zone requirements are met.

Detailed and careful site characterization can reduce the magnitude of these uncertainties, and ensure that the PRB placement, width, depth, and thickness are suitable to meet performance objectives. In some cases, an arbitrary safety factor between two and three times the calculated flow-through thickness may be deemed appropriate. The safety factor can be lowered by realistically assessing the downgradient risks of partial treatment (i.e., less than design) and by careful modeling of the full range of groundwater velocity, flow direction, and contaminant concentrations expected at the site. Consideration should also be given to whether a probabilistic design approach is most suitable for a given set of site conditions. Multiple PRBs can be installed to ensure that a sufficient reactive zone is in place. Additionally, the geometry of the PRB based on site conditions may not be a straight wall, and other geometric alignment may be appropriate.

5.1.6 Hydrogeology

Subsurface hydrogeological heterogeneities complicate all in situ treatment technologies and must be identified and considered during the method selection and design process. Inadequate site characterization can cause the remedy to fail to meet performance and regulatory objectives. Difficult hydrogeologic conditions that may preclude cost-effective application of PRBs include high rates of groundwater flow, preferential flow paths, either very high or very low permeability, a high degree of aquifer heterogeneity, or excessive depth to groundwater.

Subsurface geology and geotechnical characteristics

Installation of PRB trenches or excavations may be limited by (1) subsurface formations that are too hard or consolidated (e.g., competent bedrock) for excavation, (2) sediments that are too unconsolidated to remain open while the PRB media is being emplaced (flowing sands), or (3) large cobbles, which can limit the success of continuous trenching tools. Some weathered, poorly cemented, or poorly indurated bedrock formations may be cut by trenchers with special rock-cutting teeth. A trenching contractor should be consulted to determine the feasibility of trenching into bedrock materials. In addition, the placement of reactive materials with components of significantly different densities may separate when passed through a standing column of water.

Geotechnical testing may be appropriate to support characterization of earth materials prior to and during trenching excavations. Geotechnical laboratory studies identify site-specific factors to consider during trenching and/or excavation of PRBs, such as the shear strength and cohesion properties of the earth materials, sieve/grain size analysis, moisture content, consolidation, and density. For deeper PRB systems installed through jetting, fracturing, or similar injection methods, consideration of soil properties that affect the propagation of the reactive materials should be assessed to ensure proper placement and geometry of the PRB. Geotechnical testing should apply ASTM or equivalent methods. An exploration program to define the soil and groundwater conditions over the full extent of the PRB alignment is recommended for full-scale applications so that the design of the stable, open-trench system (e.g., shoring, slurry, and guar gum) can be adjusted to satisfy varying site conditions.

Groundwater hydraulics

Groundwater velocity and flow direction impact the effectiveness of a PRB. Groundwater seepage velocity and flow direction are determined by measuring both horizontal and vertical hydraulic gradients, as well as hydraulic conductivity and permeability. Horizontal groundwater flow rates impact the residence time of the contaminants within the PRB. High rates of groundwater flow reduce contaminant residence time in the PRB, while low rates of groundwater flow increase the residence time. Where the PRB is keyed into a low-permeability confining layer, vertical gradients and flow are generally not an issue.

The highest potential seepage velocity or specific discharge (i.e., Darcy velocity resulting from the highest K and gradient) that may be encountered at a site should be used for site screening and system design. While it may not be practical to determine the absolute highest rate of groundwater flow that may occur within high-permeability sediments at the site, an estimate of an upper bound for K can be made based on aquifer test results for high-permeability zones. Literature values for similar sediments should be consulted to check that the measured values of K are realistic. A reasonable upper bound to hydraulic conductivity can be used to estimate conservative groundwater flow rates for screening and design purposes.

Groundwater seepage velocities of <1 ft/d, or 360 ft/yr, are generally suitable for most PRB systems. Depending on the contaminant flux and reactivity of the media, higher velocities may be accommodated. The magnitude of the groundwater seepage velocity or specific discharge dictates how robust the system should be. In certain situations, multiple sets of PRBs spaced along the axis of the plume could be used to provide greater net residence time for the contaminants in the reactive treatment zone. Contaminants that have a relatively high degradation rate without production of persistent regulated intermediate products (e.g., perchlorate) will require significantly less residence time than chlorinated solvents.

5.1.7 Contaminant Distribution

The nature and extent of the contaminant plume(s) should be well characterized to design an effective PRB, including the nature and anticipated persistence of the contaminant source. The vertical extent of contamination is particularly important and varies based on the type of contaminant and its proximity to the upgradient source (e.g., petroleum hydrocarbons at the water table vs. a chlorinated solvent plume at depth). The contaminant mass flux through the PRB should be sufficiently characterized so that this flux can be accommodated by the PRB design to achieve the desired reduction in mass discharge. The peak concentrations of contaminants may vary both spatially (preferential flow paths) and temporally (seasonal changes in groundwater table and flow rate).

It is also important to understand that plumes change direction and location over time and may change shape due to attenuation, degradation, mixing with other plumes, dilution, recharge, and other natural and anthropogenic disturbances. An annual cycle of quarterly groundwater elevation measurements is recommended for sites where low-flow or seasonally fluctuating water tables must be accounted for in the PRB design. The vertical extent of contamination is a primary consideration for PRB design. The PRB must be able to intercept the plume without unacceptable contaminant bypass either over, below, or around the PRB treatment system. Contaminants that may be treated by PRBs and the reactive media used to treat them are discussed in Section 4. Each contaminant has different properties (e.g., solubility and tendency to adsorb to the aquifer matrix) that impact its distribution and migration. More importantly, contaminants degrade by different processes and at different rates depending on the reactive media used. These characteristics should be evaluated during PRB design.

5.2 Geochemistry and Microbiology Considerations

5.2.1 Geochemical Consideration for ZVI

ZVI PRBs have proven to be a relatively robust technology and have functioned for years in a variety of geochemical environments. The major effect of inorganic constituents on the technology involves the formation of mineral precipitates on the iron surface. Calcium carbonate, iron carbonate, iron hydroxide, and iron sulfide precipitates may form in the media as the pH of the groundwater increases in response to corrosion of the iron metal. The potential effects of certain specific groundwater constituents on reactivity and the long-term performance of iron PRBs are described below. Section 8.2, which describes the field scale longevity of iron PRBs, will assist the reader in placing these considerations in context of actual field experience.

Sulfate

At high Eh, the stable form of sulfur is sulfate (SO_4^{2-}), while at low Eh, sulfide (H_2S or HS^-) is the stable form with HS^- being predominant at pH>7:

$$HS^- + 4H_2O \leftrightarrow SO_4^{2-} + 9H^+ + 8e^- \qquad (5\text{-}1)$$

Given the corrosion of iron, high pH, and low Eh established in a ZVI PRB and the low solubility of FeS, the HS^- produced likely precipitates out of solution:

$$Fe^{2+} + HS^- \rightarrow FeS_{(s)} + H^+ \qquad (5\text{-}2)$$

Over time, iron sulfides transform to pyrite (FeS_2) and/or marcasite, a polymorph of pyrite. Since sulfate reduction is predominantly mediated by biological activity, it is typically not observed in bench-scale (short-term) column tests. However, declines in sulfate concentrations have been observed at most field sites as groundwater passes through the iron treatment zones. Although a small portion of the disappearance of sulfate from groundwater in ZVI barriers can be attributed to formation of iron-sulfate-hydroxide complexes (sulfate green rust), most of the sulfate precipitates as some form of iron sulfide. Recent research (He, Wilson, and Wilkin 2008) has shown that much of the sulfate entering a ZVI or mulch biobarrier forms FeS, at least under the moderately reducing conditions prevalent in mulch biowalls or near the entrance of ZVI barriers. Much of this iron sulfide precipitates and forms a coating on the reactive ZVI media.

Evidence for the formation of marcasite in cores from several PRB field sites has been reported (Battelle 2002; Yabusaki et al. 2001; Wilkin, Puls, and Sewell 2003). However, the resulting sulfide formed has not resulted in any observable loss of performance during study periods ranging 5–8 years (e.g., the former Naval Air Station [NAS] Moffett Field, California).

Although not well documented in the field, the presence of aqueous sulfide has been shown to negatively affect the degradation rate of cDCE in ZVI column studies (Pinder 2007), while TCE degradation rates remained unaffected. The preponderance of evidence from field sites operating for several years indicates that the presence of a few 100s of mg/L of sulfate does not significantly impact PRB performance. However, at sites with a few 1,000s of mg/L of sulfate, especially those where cDCE is present as a primary contaminant requiring treatment, the impact on PRB performance should be considered.

Nitrate

Nitrate reduction on granular iron results in the production of ammonia/ammonium with nitrogen balances typically >80% (Ritter 2000, Schlicker et al. 2000), as shown by equation (5-3).

$$NO_3^- + 9\,H^+ + 4Fe^0 \rightarrow NH_3 + 3H_2O + 4Fe^{2+} \qquad (5\text{-}3)$$

Nitrate affects iron reactivity and therefore PRB longevity. The reduced reactivity is brought about through the precipitation of a passivating layer of hydrous ferric oxide. Commercial granular iron is composed of ZVI (Fe^0) with a surface coating consisting of an inner layer of magnetite (Fe_3O_4) and an outer layer of hematite (α-Fe_2O_3) and maghemite (γ-Fe_2O_3) (Odziemkowski and Gillham 1997). When granular iron is exposed to water without nitrate, the Fe_2O_3 layer is almost completely removed (Ritter, Odziemkowski, and Gillham 2002), and the only remaining coating is magnetite (Fe_3O_4), which is considered to be a good electron conductor and does not prevent VOC reduction from occurring. Given the redox potential and pH conditions normally occurring in granular iron treatment zones, magnetite is the thermodynamically stable form of iron oxide. However, when nitrate is present, the formation of nonconducting maghemite and goethite occurs, and the iron is passivated and does not degrade CVOCs. The extent to which nitrate passivates ZVI depends on nitrate flux. Short-term column studies may underestimate the effect of nitrate passivation (Ritter, Odziemkowski, and Gillham 2002; Mishra and Farrell 2005).

Test results (Lu 2005) have shown that the iron passivation due to nitrate may be reversible. These findings are important in the context of potential iron PRB applications at sites where nitrate concentrations vary seasonally. Also, the lifetime of iron PRBs at sites with high nitrate levels could be extended (theoretically) by periodic flushing of nitrate-free water through the iron zone. This has not been attempted in the field, however.

The effects of elevated nitrate can also be mitigated by using an upgradient denitrifying PRB as a pretreatment to remove the nitrate before the groundwater enters a granular iron treatment zone (Vogan, Duchene, and Robertson 2003). Such a sequenced PRB was installed in Perth, Australia, in early 2010 (Western Australia Department of Environmental Conservation 2009).

Oxygen

PRBs have functioned for several years in shallow water table settings although elevated DO has resulted in a significant loss in hydraulic conductivity in bench-scale column tests (Mackenzie, Sivavec, and Horney 1997; Fort 2000) and field-scale aboveground and in situ fixed-bed reactors.

Based on observed field results from in situ systems, there is little evidence of plugging due to DO consumption. Of the 10 sites where coring data have been reported, ferric oxide impacts have been noted at only one site. At this site, a PRB installed to treat radionuclides in groundwater with high levels of DO and nitrate (120 mg/L) suffered from significant cementation after 2 years (Gu et al. 2001). Like nitrate, DO is readily reduced by iron and forms goethite (α-FeOOH) (Ritter 2000), which can cause cementation and reductions in hydraulic conductivity. It is expected that nitrate, rather than DO, was responsible for the observed cementation at this site.

Mackenzie, Sivavec, and Horney (1997) and Fort (2000) both used iron-sand mixtures to overcome the loss in hydraulic conductivity. Fort recommended iron-sand mixtures containing 5%–20% iron to provide long-term DO reduction and reported only moderate hydraulic conductivity losses. If needed, these could be placed as sacrificial zones upgradient of the main iron treatment section in certain applications.

Based on the above research, it appears that loss of permeability due to DO reduction will be a larger issue in aboveground systems where groundwater may come into contact with air. If DO concentrations and groundwater flow velocities are high in situ, an iron-sand mixture should be used to minimize loss of permeability (Figure 5-2), but there is little field evidence to indicate such “sacrificial” iron-sand mixtures are necessary upgradient of the main treatment section of a PRB in most aquifer environments.

Carbonate

As discussed in Section 8, carbonate precipitates over time and can cause passivation of iron surfaces and loss of reactivity. Therefore, PRB longevity in groundwater exhibiting high carbonate content merits extra consideration during design.

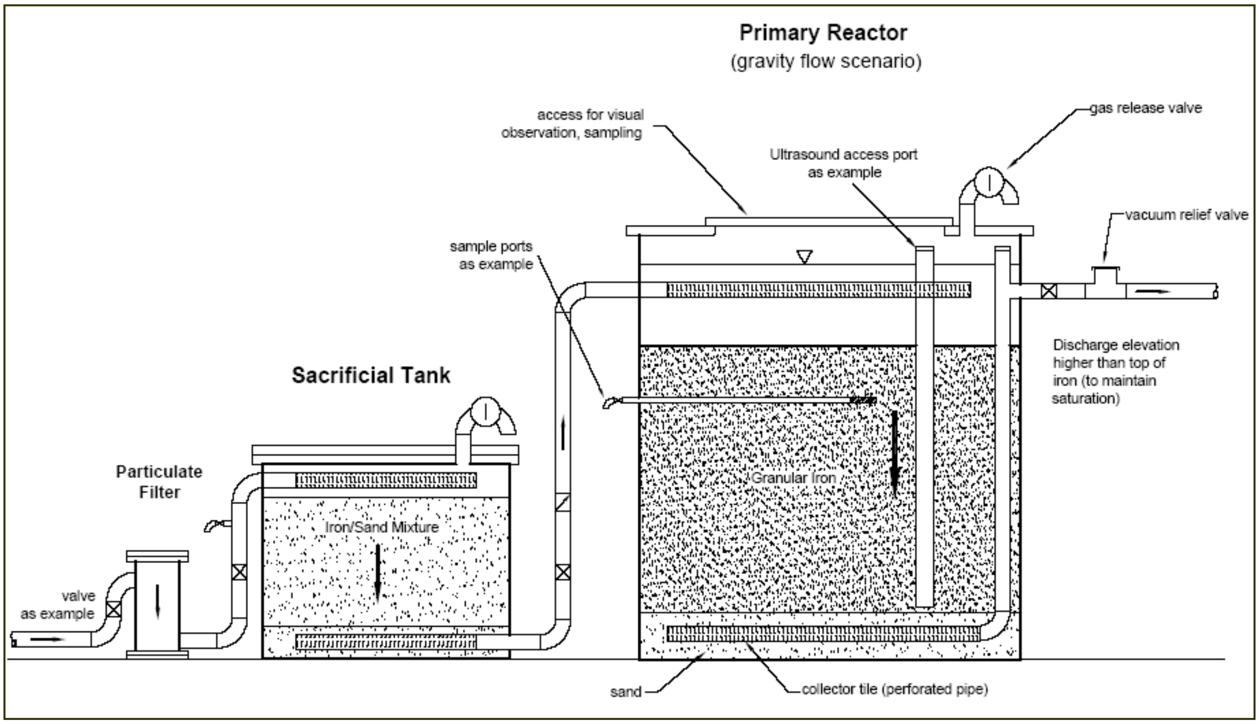

Figure 5-3. Schematic of aboveground ZVI reactor design with sacrificial tank to remove DO.

Silica and phosphate

Although the effect of silica on full-scale PRBs has not been evaluated to date, column studies have shown that silica has a detrimental effect on the reactivity of ZVI on TCE degradation (Kohn et al. 2005, Klausen et al. 2003). The loss of reactivity was seen throughout the column. It has been suggested that silica precipitates in the PRB as a hydrated silica gel/iron hydroxide that passivates ZVI.

Silicates can also negatively influence PRBs designed for trace metal removal. In column tests, As(V) reduction was severely affected in the presence of both silica and phosphate (Su and Puls 2001a, 2001b). Tests revealed that phosphate concentrations of 0.5–1 mg/L along with silica at concentrations of 10–20 mg/L greatly reduced removal of arsenic. The primary removal process for arsenic is through sorption to corrosion products. This reduced capacity for precipitation is thought to be caused by competition between As(V)/As(III) and the phosphate/silicate for sorption sites. This theory implies that an excess of PRB material may be required for the removal of arsenic in the presence of phosphate and silica.

Chromate

Using simulated groundwater, Dries et al. (2005) demonstrated that chloroethene degradation in the presence of Cr(VI) would be severely hindered. This reduction in degradation is twofold. First, the strong oxidant Cr(VI) inhibits dechlorination of TCE. Secondly, the precipitation of the newly formed Cr(III) generates a Fe (III)–Cr(III) oxide, which passivates ZVI. Dries et al. (2005) and Melitas, Chuffe-Moscoso, and Farrell (2001) also demonstrated that the extent of TCE dechlorination is dependent on the Cr(VI) mass flux. The efficiency to which a PRB can remove Cr(VI) may also depend on groundwater constituents. For example, Lai et al. (2006) demonstrated with column studies that the largest impact to Cr(VI) removal was a combination of both calcium and carbonate. However, the field experience in treating mixed TCE and chromium plumes has been more positive than these data would indicate, as described in Section 8.

Microbial activity

The occurrence of biodegradation processes in conjunction with abiotic ZVI-driven processes is discussed in Section 4.2.3. The following discussion focuses on field observations of microbial activity in ZVI PRBs.

Field tests to date from most ZVI PRB sites have confirmed the lack of biological fouling. Detailed studies at Moffett Field (Gavaskar et al. 1998), the Elizabeth City PRB, the Denver Federal Center (Wilkin and Puls 2003), and Oak Ridge National Laboratory (Gu et al. 2002) show that microbial activity does occur in granular-iron PRBs. The total biomass in the upgradient iron at many of these PRB sites was not significantly higher than that in the upgradient aquifer. However, phospholipid fatty acid (PLFA) analysis showed the proportion of anaerobic metal reducers and sulfate reducers in the biomass to be higher in the iron (Gavaskar et al. 2002, Wilkin and Puls 2003). PRBs in North Carolina and Colorado indicate that loss of porosity due to biomass buildup and mineral precipitation range only from 1%–5% of the original volume (Wilkin, Puls, and Sewell 2003).

There are usually site-specific reasons that contribute to high biomass numbers. For example, in Gate 2 at the Denver Federal Center PRB, biomass buildup was unusually higher than in the other iron gates at the same site, and higher than biomass buildup observed at other sites such as Elizabeth City. The biomass was attributed to low-flow conditions caused by a smear zone across the face of Gate 2 and to high sulfate concentrations in groundwater. Concentrations of iron sulfide precipitates were also higher in Gate 2. Gu et al. (2001) found biomass concentrations 1–3 orders of magnitude higher in an iron PRB treating radionuclides compared to background soil and groundwater. However, this water was unusual in that it contained 120 mg/L of nitrate. Abundant sulfate reducers and denitrifiers were identified in the PRB. However, after 2 years of operation, no evidence of biofouling was observed.

PRB construction techniques that involve the use of guar slurry may be a source of electron donor for anaerobic microbial growth (Crane et al. 2004; Johnson et al. 2008a, 2008b; Johnson and Tratnyek 2008) within and adjacent to the PRB reactive media. (Figure 5-3 provides a photograph of a guar slurry being installed.) A biopolymer slurry was used in the construction of a PRB at Carswell AFB, Texas, where enhanced microbial activity was observed along Transect 2 (Crane et al. 2004). Elevated levels of cDCE and VC were measured downgradient of the PRB during early sampling events, presumably due to sequential biotic reductive dechlorination rather than abiotic (iron-driven) degradation of TCE, the primary contaminant at this site. Thus, the overall efficiency of the PRB was reduced, at least temporarily. Elevated concentrations of cDCE and VC on the downgradient side of the PRB decreased over time, indicating less biotic dechlorination was occurring. Guar movement into the formation on both

Figure 5-3. Guar slurry used during biopolymer PRB construction.

sides of a PRB may have influenced observed sulfate reduction in the aquifer at the Cornhusker Army Ammunition Plant (Johnson and Tratnyek 2008).

Aside from the influence of guar, it is unclear how microbial activity in the adjacent aquifer is otherwise affected by ZVI. At the Elizabeth City and Moffett Field sites, for example, aquifer materials near the downgradient edge of the PRB were comparatively depleted in total biomass and in biomarkers indicative of metal-reducing and sulfate-reducing bacteria (Wilkin and Puls 2003, Gavaskar et al. 2002). Possible reasons for this effect could be depletion of organic substrate by the enhanced microbial activity at the upgradient edge of the PRB and/or creation of more inhibitory conditions downgradient when groundwater with higher pH emerges from the PRB.

For certain types of cocontaminants, microbial growth in ZVI PRBs may be beneficial. For example, Stening et al. (2008) indicated the establishment of microbial degradation of 1,2-dichloroethane in a ZVI PRB, whereas this contaminant is normally unaffected by ZVI. As described in Section 4, certain PRBs rely on microbial activity for dissolved metals removal via precipitation as sulfide minerals under sulfate-reducing conditions.

A few general conclusions can be reached upon review of the references discussed above:

- In most cases, total biomass numbers in the iron zone are usually no greater than in the upgradient aquifer.
- Within the iron zone, the greatest accumulation of biomass is at the upgradient aquifer/iron interface (Vogan et al. 1998, Wildman and Alvarez 2001).
- Microbial populations in the iron zone are likely to be dominated by anaerobic, often sulfate-reducing and/or metal-reducing bacteria.
- Biofouling has not been observed to be an issue at most ZVI PRB sites.

5.2.2 Geochemical Considerations for Biogeochemical Transformation (Biowalls and Other Biological-Based PRBs)

Groundwater

Geochemistry is an integral part of the design for a PRB based on biological processes because groundwater geochemistry can have an effect on the performance of the PRB. For biological PRBs, the addition of an organic substrate to an aquifer is intended to consume native electron acceptors and to maintain optimal redox conditions for high rates of anaerobic degradation to occur. Excessive levels of native electron acceptors (e.g., DO, nitrate, bioavailable iron, and sulfate) may limit the ability to achieve sufficient reducing conditions for effective and complete anaerobic degradation. Due to the large mass and the reducing capacity of mulch and compost substrates commonly placed in biowall PRBs, the native electron acceptor demand is easily overcome for many years. Some groundwater conditions are more favorable for efficient biowall PRB treatment than others. For example, groundwater with significant concentrations of dissolved sulfate and minimal DO or nitrate, combined with a source of ferric iron in the aquifer formation or in the PRB backfill, may induce biogeochemical transformation of chlorinated solvents through reaction with reduced iron sulfides.

Dissolved iron

Dissolved iron can exist in two oxidation states: +2 (ferrous iron) and +3 (ferric iron). Ferric iron has a very low aqueous solubility at pH values greater than about 3.5, while ferrous iron is more soluble. The direct reduction of chlorinated ethenes by dissolved ferrous iron is unlikely to be significant due to the very low electron density of the dissolved species compared to solid phases or iron adsorbed to mineral surfaces (Cui and Eriksen 1996, Hwang and Batchelor 2000). However, ferrous iron may precipitate with sulfide to form FeS, which is known to abiotically reduce chlorinated ethenes (e.g., Butler and Hayes 2001). The presence of dissolved ferrous iron in upgradient groundwater or produced by iron reduction in the PRB may be beneficial to the formation of FeS. Elevated concentrations of dissolved iron indicate that conditions within the aquifer are iron-reducing and that concentrations of oxidants such as nitrate and oxygen are likely to be low. However, the absence of detectable dissolved iron in the groundwater does not mean that a biowall PRB is not appropriate for the site. Iron mineral amendments may be added to the mulch mixture to provide an ongoing source of iron for removing sulfide from groundwater and for producing reactive iron sulfide minerals (see Section 4.2.1).

Dissolved sulfur species

Dissolved sulfur species (sulfate, persulfate, thiosulfate, etc.) can be reduced to sulfide within a biowall PRB. FeS may be formed when sulfide precipitates with soluble ferrous iron or directly reduces ferric iron in the PRB backfill material. Sulfate is the most abundant sulfur species in groundwater and is an electron acceptor for sulfate-reducing bacteria. Concentrations of sulfate up to 500–600 mg/L in groundwater are desirable for the intentional formation of reduced iron sulfide minerals. Sulfate amendments may also be added to the mulch backfill mixture. As the technology for engineering biogeochemical transformation processes is still developing, there is currently no established criterion for the minimum sulfate concentration required within the upgradient groundwater. A recent investigation (Lebrón et al. 2010) has shown that sulfate concentrations of <10 mg/L are clearly too low, while concentrations of a few hundred mg/L are sufficient. The most effective biowall system investigated in this study was located at Altus AFB, Oklahoma, with an influent sulfate concentration of 1,200 mg/L or higher. A biowall at Dover AFB, Delaware, showed a large difference in the production of iron sulfides between the portion of the biowall which contained a sulfate amendment (4.5 mmol/yr) and a portion which did not (0.67 mmol/yr).

Dissolved organic carbon

DOC in groundwater can provide a source of organic carbon for sulfate- and iron-reducing bacteria, which produce the reduced iron and sulfide phases required for the formation of reduced iron sulfide minerals. DOC is also used as an electron donor in the reduction of oxygen, nitrate, and other oxidants that can inhibit the growth and activity of sulfate-reducing bacteria.

Dissolved oxygen and nitrate

DO or nitrate at elevated concentrations in upgradient groundwater does not preclude the use of a biological PRB because the organic matter within the substrate is capable of consuming these oxidants. However, in such cases the upgradient portion of the wall where the groundwater first enters is generally not conducive to treatment of CVOCs because at this point the oxygen and nitrate are being removed from groundwater. The biowall PRB should be sufficiently thick to provide sufficient residence time for complete treatment of CVOCs, especially at sites with high rates of groundwater flow (refer to Table 3-3).

pH

The reaction rate constant for the abiotic dechlorination of TCE has been found to be pH-dependant for pyrite (Weerasooriya and Dharmasena 2001) and mackinawite (Butler and Hayes 2001). Weerasooriya and Dharmasena (2001) found that for pH values <6, the effect of pH was minor, but at pH >6 the rate constant for TCE reductive dechlorination increased dramatically. Butler and Hayes (2001) found a similar trend for TCE dechlorination by mackinawite. Based on their data, the reaction rate of TCE with mackinawite more than doubles when the pH is increased from pH 6 to pH 7, and the rate increases fivefold when the pH is increased from 6 to 8. Therefore, higher pH groundwater favors the rapid reaction between chlorinated ethenes and reactive iron sulfide minerals. Amendments to a biowall PRB such as limestone have the potential to buffer the pH of the water and increase reaction rates.

Aquifer matrix

The aquifer matrix is important to PRB systems in that some minerals may be present that provide an essentially unlimited supply of sulfate or iron. At the Altus AFB site, the lithology of the aquifer matrix includes lenses of gypsum ($CaSO_4 \cdot 2H_2O$), which provide 1,200–2,000 mg/L of sulfate in groundwater. Iron minerals (hematite, goethite, lepidocrosite, etc.) can be reduced to soluble ferrous iron, provided a supply of DOC is present and redox conditions are sufficiently reducing.

The pH of the groundwater is also largely determined by the aquifer matrix, which may contain carbonate minerals such as calcite or dolomite, which can buffer the pH to values >7. Sand and gravel aquifers generally have little buffering capacity, and pH values tend to be in the 6–7 range. Organic matter can contribute organic acids, which can result in pH values between 5 and 6 in the absence of carbonate minerals.

5.2.3 Microbiology for Biological PRBs

An assessment of biodegradation potential is primarily based on a review of site-specific data on electron donors, electron acceptors, metabolic by-products, geochemical indicators, contaminant trends, and hydrogeology. The success of biological PRBs largely depends on the presence of microbes capable of facilitating the requisite degradation reactions. In general, it can be assumed that microbes capable of aerobic respiration—nitrate, manganese, iron, and sulfate reduction—as well as methanogens are ubiquitous in the environment. Microorganisms used for reduction of perchlorate and explosive compounds also appear to be ubiquitous in the environment (e.g., Logan 1998; Logan et al. 1999; Xu et al. 2003; Ederer, Lewis, and Crawford 1997; Regan and Crawford 1994; Zang and Hughes 2002; Ahmad and Hughes 2000, 2002), and microbial characterization usually is not warranted.

The question of microbial sufficiency for CVOCs has been a subject of extensive research. Current literature suggests that halorespiration of CVOCs is carried out by relatively few metabolic classifications of bacteria and that in some cases a buffering agent may be useful to maintain pH within an optimal range for dechlorinating activity. In particular, cultures containing *Desulfitobacterium*, *Dehalobacter restrictus, Desulfuromonas*, *Dehalospirillum multivorans*, and *Dehalococcoides* are known to be capable of dechlorinating PCE and TCE to cDCE (Scholz-Muramatsu et al. 1995; Krumholz 1997; Maymo-Gatell et al. 1997; Holliger et al. 1993; Löffler et al. 2000). In practice, microorganisms capable of degrading PCE and TCE to cDCE should be considered ubiquitous in the subsurface environment. However, complete dechlorination of PCE to ethene by a single species has been demonstrated in the laboratory only for *Dehalococcoides* strains, which while appearing to be common, cannot be considered ubiquitous in the environment (Hendrickson et al. 2002; He et al. 2003).

Not only must the appropriate dechlorinating bacteria be present, but they must be stimulated to sufficient activity and growth to degrade the contaminants present to the extent and at a rate that meets the intended RAOs. Incomplete dechlorination may lead to accumulation of intermediate daughter products such as cDCE or VC due to insufficiently reducing conditions or lack of appropriate dechlorinating populations. Therefore, a microbial assessment of dechlorinating bacteria using MBTs is useful to assess native microbial activity and to confirm that the desired microbial population is present (Section 7.7). In the event that the native microbial population is not capable of complete dechlorination of CVOCs, bioaugmentation may be considered in the PRB design (Section 4.3.3).

5.3 Reaction Kinetics and Residence Time

Effective remediation of groundwater contaminants using PRBs depends primarily on achieving optimal conditions for the degradation reactions to occur and having a reaction zone (size/ thickness) that provides sufficient residence time for contaminants to degrade to POs. For biological PRBs treating CVOCs, insufficient residence time of the contaminants in the reaction zone may result in accumulation of regulated intermediate degradation products, such as cDCE or VC.

The primary parameters required to estimate the necessary residence time are the rate at which the contaminant(s) are degraded and the maximum contaminant concentrations. The dimensions of the PRB can then be determined from the rate of groundwater flow through the reaction zone. In practice, the flow-through thickness of a PRB is often a result of the trenching or excavation equipment used. For example, most continuous chain trenchers cut a width of 2 feet. Reasonable estimates of the rate of groundwater flow and degradation rate that can be achieved are therefore needed to determine whether one or more PRBs are required to meet performance objectives. The following subsections describe how this information is used to design PRB systems.

5.3.1 Reaction or Biodegradation Rates

The constituent degradation rate is needed to determine the length of time that the contaminant must stay in contact with the reactive media. Determining degradation rates that can be achieved using a PRB is challenging since each site is unique with widely variable conditions. For PRBs installed in trenches of fixed width where ZVI or mulch are the primary reactive media, bench-scale studies (Section 5.5.3) and field demonstrations have been used to determine appropriate degradation rates for design.

Analytical modeling may be used to estimate site-specific degradation coefficients using known site information and assumptions regarding the material properties. AFCEE (2008) describes using a steady-state analytical model based on the advection-dispersion equation developed by Van Genuchten and Alves (1982). For target contaminants that experience reactions in series with toxic intermediates, the first-order rate coefficients can be estimated using the BIOCHLOR screening model (Aziz, Newell, and Gonzales 2002). BIOCHLOR is a program that models the degradation of chlorinated solvents.[3]

The results of laboratory testing must be corrected for field application. Generally, the water temperature and the bulk density of the reactive media vary between the lab and the field. Studies have shown that the microbial reactions are slower at lower temperatures. Because the water temperature during laboratory column tests is generally higher than the in situ groundwater temperature, the PRB width generally must be increased to account for the temperature differences.

The effect of temperature on both biological and chemical reactions follows the Arrhenius equation. The Arrhenius equation relates the reaction rate, K, to the absolute temperature, T, as follows:

$$K = Ae^{-E_a/RT} \tag{5-4}$$

where

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[3] www.epa.gov/ada/csmos/models/biochlor.html.

A = a preexponential factor
E_a = the activation energy
R = the universal gas constant (8.314 Joules/mol Kelvin)

Degradation rates for many chemical or physical reactions are proportional to the available surface area of the reactive media. In many instances, the bulk density of the reactive media in the field is lower than that obtained in the laboratory. This lower bulk density in the field means that there will be less reactive media surface area available in the field. Thus, the PRB width must be increased relative to that based on laboratory results to account for the lower expected bulk density (i.e., to provide a sufficient amount of surface area).

5.3.2 Residence Time

The residence time required to meet POs may be estimated from reasonable first-order rate constants and the maximum contaminant concentration present. The solution to a first-order decay rate is as follows:

$$C_t = C_o e^{-(kt)} \tag{5-5}$$

where

C_t = the concentration (mass per unit volume or µg/L) at time t (days)
C_o = the initial concentration (µg/L)
k = the first-order degradation coefficient (per day)

Equation (5-5) can be rearranged to yield the time (t) to meet a target concentration as follows:

$$t = -\ln (C_t/C_o) / k \tag{5-6}$$

For example, to reduce the concentration of TCE from 1,000 µg/L (C_o) to 5 µg/L (C_t) at a first-order rate of 0.1/d (k) requires a residence time of approximately 53 days.

These equations have been adapted for use in several commercial software programs, which can be used to fit first-order equations to experimental data using the least-squares best fit or other methods. In some programs, the degradation rate and molar conversion are determined for each compound sequentially starting with the most chlorinated compound. The modeling results include half-lives and molar conversions for all CVOCs selected and statistical fit data, including coefficient of determination (r^2) values. The r^2 values indicate how well the degradation model represents the experimental data. Using the first-order kinetic equation and supplied initial CVOC concentrations and degradation rates, these programs may also simulate the change in CVOC concentrations over time.

The rate of migration of contaminant mass through a PRB may be calculated based on site-specific hydrogeology and the properties of the reactive media. A simplistic approach may follow the use of Darcy's law (AFCEE 2008). Darcy's law states that the volumetric flow rate (Q) through a pipe filled with sand can be calculated as follows:

$$Q = -KA(dh/dl) \quad (5\text{-}7)$$

where

K = proportionality constant (length divided by time [L/T])
A = the cross-sectional area of the pipe (L^2)
dh/d = the horizontal hydraulic gradient (unitless)

More simply stated, equation (5-7) can be solved to yield the Darcy velocity or specific discharge. As defined, the specific discharge (q) is a volumetric flow rate per unit surface area of porous media:

$$q = Q/A = -K(dh/dl) \quad (5\text{-}8)$$

This equation is useful because the water balance across a PRB of limited thickness can be assumed to be approximately the volumetric flow of water through the aquifer, where values for the proportionality constant are measured as K. Both K and the horizontal hydraulic gradient (dh/dl) are commonly known from site investigation activities.

The Darcy q represents the velocity at which water would flow if the aquifer were an open conduit but does not account for dispersion that causes water to flow through different pore spaces at different rates along individual flow paths that vary in length. The velocity of water through the aquifer pore spaces is termed the average linear velocity or seepage velocity:

$$v = -K(dh/dl) \,/\, n_e \quad (5\text{-}9)$$

where

v = pore water (seepage) velocity (L/T)
n_e = effective porosity of the aquifer matrix (unitless)

Typical groundwater seepage velocities range from about 30 to 1,000 ft/yr. To calculate the seepage velocity across a PRB, the effective porosity of the reactive media must be known or estimated.

Considerations for biowalls

Ahmad et al. (2007) conducted a study where the effective water-filled porosity of biowall mulch materials was evaluated in column studies. The results of this study indicate that the effective porosity of biowall backfill is about 40% where the mulch fraction is 40%–60% by volume. Another study by Shen and Wilson (2007) calculated an effective porosity of 25% for columns constructed of 50% mulch, 10% cotton gin ash, and 40% sand.

As an example, consider a TCE contaminant plume located in an aquifer with a seepage velocity of 0.17 ft/d and an effective porosity of 15%. The hydraulic gradient is 0.003 ft/ft, and the average hydraulic conductivity is 8.7 ft/d. Assuming that the specific discharge (q) is the same across the PRB and the aquifer and a reactive media effective porosity of 25%, the seepage velocity through the PRB can be estimated as 0.10 ft/d. Thus, if the barrier is 2 feet thick, the contaminant residence time would be approximately 20 days. Note that this estimate is conservative as it does not take into account the effects of sorption and retardation of organic compounds on the organic media.

Considerations for ZVI PRBs

Based on porosity measurements obtained gravimetrically from bench-scale column tests coupled with field observations, the porosity in a PRB containing 100% ZVI ranges from 45% to 55%, while the porosity of most aquifer materials is in the range of about 25% to 35%. Thus, from equation (5-9), the groundwater flow velocity in the PRB could be within the range of about 50%–75% of the aquifer velocity.

The use of the porosity ratio in PRB design depends on the overall design objective and economics of the application. In the most conservative approach, the aquifer velocity is used to determine iron thickness. This approach treats any differences in porosity as a form of safety factor in the design. However, this maximizes the amount of iron needed in the application. A less conservative approach uses the difference in porosity between the aquifer and 100% iron to reduce the velocity in the iron by a corresponding factor, thereby reducing the required iron flow-through thickness and volume of iron required.

Other parameters to consider when evaluating iron thickness and density during PRB design include the following:

- Lower porosities may occur in iron/sand mixtures used with some construction methods, relative to 100% iron.
- Depending on the carbonate flux through the system, carbonate precipitation may cause a 5%–15% decline in porosity over time.
- The accuracy of the hydraulic conductivity and hydraulic gradient of the aquifer and corresponding estimate of aquifer velocity.
- Whether a probabilistic design approach incorporating these uncertainties is most appropriate for the application being considered.

In summary, the decision as to the groundwater velocity to be used in PRB design is site specific, and a number of technical factors, as well as material iron costs and regulatory objectives, should to be considered when determining the most appropriate PRB velocity for design purposes.

Although the estimated residence time is conservative, these calculations should be used with caution as they assume average flow rates. If the PRB must be of fixed thickness due to construction equipment or other constraints, multiple barriers may be required to provide sufficient residence time to degrade the plume constituents to the required concentrations.

5.3.3 Bench-Scale Column Studies

Bench-scale studies may be useful to determine reaction kinetics or degradation rates. For ZVI PRBs, column studies are often conducted to determine the most suitable (reactive) ZVI type for particular groundwater chemistry and the required residence times in ZVI media. For biological PRBs, column studies are conducted to determine the characteristics of the media being considered (e.g., permeability), the ability to stimulate anaerobic degradation processes, and the rate and extent of biodegradation that may be achieved.

ZVI bench-scale tests

Because of the wide variety of ZVI materials currently available, batch screening tests may be undertaken to determine the material's suitability for a PRB application. A typical screening test consists of numerous samples prepared in 40 mL glass vials. Simulated groundwater is typically used in the test and is prepared using deionized water and COCs, typically at concentrations ranging 5–10 mg/L. Two types of samples are prepared: control vials, which contain only groundwater, and reactive vials containing 10 g of reactive material and groundwater.

At predetermined time intervals (sampling more frequently at early times), the vials are subjected to analysis of the target COCs, Eh, and pH measurements. Two vials are sacrificed per sampling interval: one control vial and a reactive material vial. For CVOCs, first-order rate equations can be applied to the resulting concentration vs. time curves to determine degradation rates for the chemicals of interest.

ZVI column tests for VOCs

Column tests establish the site-specific degradation rates for the CVOCs present in the site groundwater and their breakdown products under flowing conditions (Gillham and O'Hannesin 1994). These rates are used to determine the required residence time in the reactive material. Using the residence time and the flow rate, the size of the treatment zone can be determined. The column tests also include analysis of column influent and effluent samples for inorganic constituents. This provides information concerning potential mineral precipitation in the reactive material caused by changing Eh/pH conditions.

A typical column (Figure 5-4) is constructed of Plexiglas® with several sampling ports positioned along its length. To ensure a homogeneous mixture of reactive material while filling the columns, aliquots of iron material are packed vertically in lift sections. The bulk density, porosity, and pore volume are determined gravimetrically.

Groundwater should be collected from a well in the vicinity of the proposed PRB such that the

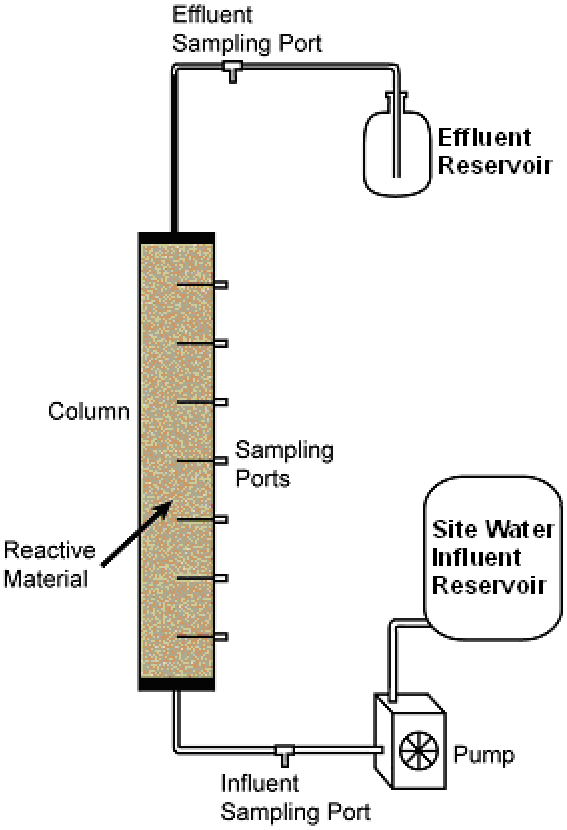

Figure 5-4. Schematic of the apparatus used in the treatability test.

groundwater is representative of groundwater expected to enter the treatment zone. Groundwater obtained from the site is supplied to the influent end of the column at a constant flow velocity using a laboratory pump. If concentrations in the groundwater as received are lower than those expected to enter the PRB, the groundwater may be spiked with laboratory reagents. The flow velocity is selected to approximate the velocity expected in a field-scale treatment zone. Ideally, column tests should be conducted at field groundwater temperatures.

CVOC concentrations are monitored at the inlet, outlet, and sampling ports of the column (i.e., "a profile" of the column) to determine when steady state has been reached. In these tests, steady state is normally defined as the time when CVOC concentration vs. distance profiles do not change significantly between sampling events, typically achieved after 40–50 pore volumes throughput. Eh and pH profiles are measured periodically during the test period. Inorganic parameters (major cations, anions, and alkalinity) are monitored to help predict possible mineral precipitation.

As in the batch tests, first-order equations can be applied to the experimental data for determination of CVOC degradation rates and then interpreted in the context of the site hydrogeologic data to provide basic conceptual residence time simulations for field-scale designs.

ZVI column tests for trace metals

Column tests for trace metal removal are operated in a similar fashion. In this case, observed breakthrough curves can be used to quantify the removal capacity of the reactive material. Trace metal removal capacity can be calculated by dividing the trace metal flux (influent concentration × pore volume × number of pore volumes of flow) by the mass of passivated material in a given column length (passivated column length × column cross-section area × material bulk density).

Biowall material column studies

Column studies may also be conducted to determine the geochemistry and hydrogeologic properties (e.g., effective porosity and hydraulic conductivity) of biowall mulch mixtures. Influent and effluent contaminant concentrations provide information on degradation rates and the residence time required for treatment. However, the column should be allowed to acclimate over a period of several weeks to months to obtain representative results. An example of a column study for chlorinated ethenes is described by Shen and Wilson (2007), an example for perchlorate is described by Perlmutter et al. (2000), and an example for RDX is described by Ahmad, Schnitker, and Newell (2007).

A bench-scale study was performed using pine mulch to degrade RDX and HMX as part of a technology demonstration for the ESTCP (GSI 2008; Ahmad, Schnitker, and Newell 2007). Steady-state flow-through column tests were run at average seepage velocity for the field demonstration site at the Army PCD, Colorado (GSI 2008). The columns were packed with a mixture of pine mulch and pea gravel at a 70/30 volume ratio. Results of the column study included (1) complete removal of RDX and HMX at influent concentrations of 90 µg/L and 8 µg/L, respectively; (2) a pseudo first-order, steady-state rate constant for RDX of 0.20–0.27/hr; (3) accumulation of RDX intermediates in the column effluent at <2% of the influent RDX mass; and (4) no apparent binding (sorption) of RDX to the column fill material. Based on these results, a field demonstration of a permeable mulch biowall has been conducted at PCD, Colorado (GSI 2008).

Because a number of biowall case studies have been reported, an alternative approach may be to extract relevant first-order decay constants for CVOCs or other contaminants from past case studies using the approach described in Ahmad et al. (2007). However, column studies may be warranted in situations where degradation pathways or kinetics are poorly understood or where cocontaminants are present. For example, suitable materials and the appropriate quantities required to stimulate biogeochemical transformation of CVOCs has not been fully explored. Shen and Wilson (2007) extracted data from a column study that implied an overall first-order rate constant for abiotic dechlorination of TCE by reaction with FeS on the order of 0.22–0.53/d using a mulch mixture derived from materials used for the SS-17 biowalls at Altus AFB, Oklahoma. After 383 and 793 days of operation, approximately 50% of the removal of TCE was attributed to abiotic reactions with FeS that had accumulated in the reactive matrix. Note that these rates may not be representative of sites where the potential for production of reduced iron sulfides is low.

5.4 Modeling

Even in relatively homogeneous aquifers, hydraulic conductivity can vary by an order of magnitude or more, and hydraulic gradients are often difficult to determine on a localized scale. Modeling of the aquifer and PRB system (e.g., using MODFLOW/MT3D) is one tool that may be used to evaluate the variability and uncertainty in subsurface conditions to complete a successful PRB design.

5.4.1 Hydrogeologic Modeling

Using average or maximum values for hydraulic conductivity or hydraulic gradient may lead to a limited understanding of the groundwater flow. Groundwater flow and solute transport modeling can provide understanding of the impacts of the flow variability. The effects of a range of conductivities and a range of gradients on the flow through a PRB can be modeled through multiple simulations that allow for the optimization of the PRB design. For example, if seasonal variations in hydraulic gradient cause flow directions to vary, the PRB can be oriented along a direction that is near perpendicular to the flow during most seasons.

After the site has been adequately characterized, different hydrogeologic and geochemical scenarios and engineering designs can be modeled to determine the best location of the barrier with respect to the plume distribution and site-specific features. The model results help determine the PRB orientation that will capture the maximum flow with the smallest reactive cell width and the most suitable barrier configuration and dimensions. Hydrogeologic modeling allows for an estimate of the capture zone for a given PRB design. The modeled capture zone then helps the designer to calculate the appropriate flow-through thickness and the required permeability of the reactive media. Modeling also allows for the evaluation of long-term scenarios and provides data to develop an appropriate monitoring plan. To some extent, the modeling and design process are iterative. Modeling results should be calibrated to the field monitoring results and continually validated using those results.

Two primary interdependent parameters in PRB design are the capture zone width and the residence time. Hydrogeologic modeling yields the observation that as the discharge through the reactive cell increases, capture zone width increases and residence time decreases. With an iterative modeling and design approach, the capture zone can be optimized by maximizing the discharge through the reactive media. The residence time can be maximized by either minimizing the discharge through the reactive media or increasing the reactive media width. Modeling will help determine the optimal discharge velocity through the PRB.

Particle tracking could also be performed. Studies cited by Battelle (1997) indicate that groundwater flow paths do not bend toward or away from the PRB until the particles are within a few feet of the barrier. Consequently, to determine the capture zone, hydrologic monitoring needs to be focused on the small transitional zones near the upgradient side of the PRB.

5.4.2 Modeling VOC Reaction Kinetics in ZVI

Commercial software programs are available to model first-order degradation behavior of CVOCs in ZVI. These can be used to simulate the time needed for CVOC degradation with known concentrations, half-lives, and molar conversions. This approach is used for preliminary estimates of residence time required in iron PRBs using typical degradation parameters. Secondly, these models can be used to obtain half-lives and molar conversions based on the laboratory column results (first-order model fit to CVOC column profiles). This approach is used for obtaining site-specific degradation parameters based on results of column tests conducted with contaminated site groundwater.

5.4.3 Inorganic Geochemical Modeling

Geochemical calculations and modeling can be used to evaluate rates of trace metal removal in reactive media designed for this purpose and to investigate potential precipitation impacts to the reactive media (Section 8). Inorganic results of column tests can be used as inputs into such modeling efforts. In the absence of geochemical modeling, arithmetic comparisons of calcium and magnesium concentrations before and after PRB installation can provide information on potential reactions. Geochemical modeling may also include an evaluation of the PRB materials regarding sorption, direct reduction, biological enhancements, ion exchange, etc.

6. CONSTRUCTION AND COST CONSIDERATIONS

6.1 Technical Approach

This section describes PRB system configurations and construction or placement methods, with considerations for plume size, site infrastructure, and cost. Installation methods are being improved or modified, which is often necessary to emplace newer materials, such as EZVI or reactive materials in slurry form.

What's New?

- Cost drivers for PRBs
- Large sites vs. small sites
- Active vs. passive PRBs
- Example costs for biowalls and injected media
- Continuous trenching depth increased to 35–40 feet using larger equipment and improved techniques
- Improved injection methods to deliver reactive media in fluid or slurry forms

6.1.1 PRB System Configurations

The continuous PRB has been the most common configuration used to date. In a continuous PRB configuration, the reactive media is distributed across the width and vertical extent of the groundwater contaminant plume. Properly designed and constructed, continuous PRBs have minimal impact on natural groundwater flow. Unlike impermeable barrier walls, PRBs are not designed to prevent the flow of groundwater and, therefore, theoretically do not need to be keyed into a low-permeability layer. However, it is good practice to key the PRB into an underlying low-permeability layer if one is present, to ensure complete plume capture and as a safeguard in the event the permeability of the PRB is compromised.

A funnel-and-gate configuration uses low-permeability materials to direct (funnel) groundwater towards a permeable treatment zone (gate). Directing the groundwater towards a treatment gate may increase the natural groundwater flow velocity. Funnel-and-gate designs need to extend beyond the extent of the plume to ensure all contaminated groundwater is captured and treated.

Related to the funnel-and-gate design are in situ reactive vessels, which use funnels and/or collection trenches to capture the plume and pass the groundwater by gravity or hydraulic head through a buried vessel containing the reactive media. The treatment vessels can be located within the contained area, within the funnel, or some distance downgradient.

Note that an active reaction zone may extend downgradient of the PRB when using soluble reactive media that can migrate with groundwater flow, or when using viscous/solid media that release dissolved constituents. For some reactive materials, multiple PRBs may be required to ensure that a sufficient reactive zone (i.e., residence time) is created and maintained. A larger reaction zone may be established by spacing parallel PRBs close enough to each other so that any reactive material that migrates sustains the desired reaction conditions within the aquifer formation between the barriers.

Figure 6-1. Horizontal PRB for treatment of septic system nitrate.
(Courtesy of Septech, Inc., 2003)

Most PRBs are configured vertically to intercept and treat groundwater flowing horizontally. Although relatively uncommon, horizontal PRBs may also be constructed to treat groundwater flowing vertically. One such example is seepage moving vertically from beneath septic tile fields (see Figure 6-1). In this case the PRB is constructed as a horizontal layer of reactive media.

Horizontal PRBs also may be constructed in the base of a source area excavation to treat infiltrating groundwater as a secondary means of ensuring treatment of any residual contaminants or to treat percolating precipitation. Finally, some PRBs incorporate groundwater injection or recirculation to expand the volume of aquifer that is captured and treated or to expand the volume of aquifer affected by the reactive media. The injected or recirculated groundwater may be configured to flow horizontally or vertically.

6.1.2 Small Sites vs. Large Sites

Costs for remediation are proportional to the size of the site. This factor may favor using an innovative approach on a small site where the cost of implementing a more conventional remedy—should the innovative approach prove unsuccessful—would not be significant. Conversely, installation of a pilot-scale PRB may be an option on a large site to examine innovative PRB approaches before proceeding to full-scale installation. Mobilization and demobilization costs can be significant for some installation techniques, and these costs have a greater impact on a small site. For example, the mobilization for a continuous trencher is generally >$25,000, which is a fixed cost whether the PRB is 100 or 1,000 feet long.

Small contaminant plumes from a single, well-defined location (e.g., a dry cleaner) may lead to consideration of more innovative PRB remedies and construction approaches than large plumes several hundred feet in width. Costs for treating small plumes with injectable media may be significantly less than those using media that must be placed in an excavation, even if the media costs are more expensive. Often these small plumes occur in areas with numerous buried utilities and a relatively small working area, again leading to consideration of injection methods over excavation.

6.1.3 Land Use and Infrastructure

Selection of a PRB remedy and configuration must consider the impact or interference with site infrastructure. Installation of a trench or excavation is not feasible underneath or close to permanent structures or utilities, particularly when multiple utilities are perpendicular to the trench. Some utilities (e.g., storm sewer lines) may be temporarily breached during installation, but others (e.g., gas lines or fiber optic communication lines) may be impractical to breach and cost-prohibitive to reroute. Overhead electrical lines also must be avoided during construction for safety. In the event a utility cannot be breached or rerouted during construction, the continuity of the PRB trench may be maintained by hand excavation around the utility and injection of a reactive material in groundwater below the utility. Since many PRBs are less than 3 feet wide, the structural integrity of the utility may be preserved even when soil is removed from beneath it. But whenever possible, the installation of a trenched PRB should avoid congested utility areas and is best suited for open areas with few utilities.

PRBs are intended to remain in the subsurface for many years, and most remain in place even when the contaminant treatment efficacy is exhausted. Because the PRB will probably remain in place, a risk management plan, as described in ITRC's technical and regulatory guidance document *Project Risk Management for Site Remediation* (ITRC 2011b), should be developed.

Typical PRB compositions—in particular those containing organic carbonaceous-based materials—are not designed to maintain high lateral or shear strength conditions. Unless there is sufficient granular material to maintain structure, nearby dynamic loads, such as pile driving, can result in consolidation and/or geometrical changes in the PRB structure and the uniformity of its composition. While these events cannot necessarily be predicted, the design of the PRB system should consider its positioning in areas of the site that are less likely to be subject to controllable dynamic loading, such as excavation and dewatering. Other "unanticipated events" that may reduce the competency of the PRB structure but may not be considered during PRB design include changes in land use, adjacent subsurface excavations, and nearby dewatering of the groundwater (causing variable saturation and drainage).

6.2 Installation Methods

Several installation alternatives are available to construct PRBs. The method selected depends on several site-specific factors, including the depth and width of the PRB, the reactive media, the site geology, and the surface/subsurface obstructions present (e.g., buildings and utilities). The required flow-through thickness or volume of reactive media required also has a large influence on the selection of construction method as all construction methods have a minimum or maximum flow-through thickness that can be achieved. Below is a summary of the methods used to install PRBs, the depth range over which the method can be used, and, where appropriate, the flow-through thickness that can be achieved. The goal of this section is to provide commonly used installation methods; references are provided as specific case studies.

6.2.1 Excavation Methods

Conventional trenching techniques

Unsupported excavation. This is the simplest and least expensive installation. The soil must have sufficient cohesion to remain open until the trench is backfilled with the reactive material or mixture method (Figure 6-2, left). This method has been successfully used to install PRBs to depths of 25 feet (8 m) below ground surface (bgs) at numerous sites. At some sites, surface soils may be unstable and the trench must be benched to remove the upper layer of unstable soil that is prone to cave in.

Figure 6-2. Unsupported excavation (left) **and temporary trench box** (right)**.**

Supported excavation. Where the soil will not remain open without caving in, a form of trench support can be used to similar depths. Temporary support methods such as trench boxes (Figure 6-2, right) have been used. The permeability of the soil must be low enough to avoid the necessity of dewatering for these methods to be cost-effective. Prefabricated trench boxes commonly used during construction of sewers can be used to maintain trench integrity during excavation and backfilling operations. The trench box is slid along the trench with excavation occurring just ahead of the trench box and backfilling occurring in the back half of the trench box. Typical trench boxes are 4 feet (1.2 m) wide, but custom trench boxes can be fabricated. An alternative to using trench boxes is to use a system of temporary shoring. Typically, shores (large steel plates held apart by a hydraulic ram) are used to provide additional stability to the trench until it is backfilled. The temporary shores are placed in the excavation immediately after the trench is excavated to provide support between the excavation and backfilling operations. Advantages of the shored excavation method are that the trench width can be as narrow as 2 feet (0.6 m) and that two workers can place the shores without the use of heavy equipment.

Continuous trenching

Continuous-trenching machines allow simultaneous excavation and backfilling without an open trench. Excavation is performed by a cutting chain immediately in front of a trench box (boot) that extends the width and depth of the treatment zone. Both the cutting chain and boot are attached to the trenching machine. As the trencher moves forward, reactive material or a material/sand mixture is added to the boot creating a continuous treatment zone. Trenchers are available to install treatment zones from 1.5 to 3 feet (0.5–0.9 m) in width and to depths of 35 feet (11 m). A wide bench may be excavated using conventional equipment through the upper 5–10 feet of unsaturated surface, and by operating within the excavation, the continuous trencher can reach depths of 40–45 feet bgs. Some continuous trenchers have the ability to install a continuous, slotted, HDPE pipe within the PRB (Figure 6-3). This design has been useful for future recharging of biowalls with liquid organic substrates.

Figure 6-3. Continuous chain trencher at Ellsworth AFB, South Dakota. (Courtesy of the U.S. Air Force)

Biopolymer trenching (hydraulic shoring)

Installation of a treatment zone using biopolymer (biodegradable) trenching is similar to constructing a conventional, impermeable slurry wall. As the trench is excavated, the biopolymer is added as liquid shoring to provide stability to the excavated trench walls (Figure 6-4). The biopolymer used is typically guar gum based. Excavation continues through the biopolymer without the need for dewatering. The reactive material (or material-sand mixture) is typically placed into the trench by injecting from the bottom up using a long (tremie) pipe. Recirculation wells are spaced along the length of the trench. Residual biopolymer in the PRB after it is constructed is broken down by circulation of an enzymatic breaker fluid and through natural biological degradation, which allows groundwater to flow through the PRB. Depths of up to 70 feet (21 m) bgs and a width of 2 feet (0.6 m) or greater can be achieved using this method.

Figure 6-4. Biopolymer trench construction.

6.2.2 Alternative Excavation Methods

Cofferdam/sheet piling

With the cofferdam/sheet piling method, sheet pile is driven around the perimeter of the treatment zone and the soil within the sheet pile is excavated. Internal bracing is typically required with greater depths. Practical depths achievable with this method are in the order of 30 feet (9 m). The sheet pile maintains the dimensions of the treatment zone during excavation and backfilling of the reactive media. After backfilling is complete, the sheet piling is removed and groundwater is allowed to flow through the treatment zone. The main advantages of this method are the high degree of control in placing materials and the well-defined boundaries of the treatment zone. However, smearing of the media/aquifer interface (creation of a low-permeability skin) may be a concern at some sites.

Augured boreholes or caissons

Treatment zones can be constructed by an array of augured boreholes or caissons. A hollow-stem auger may be used to install borings up to 30 inches (76 cm) in diameter to the total depth of the PRB. Reactive media is placed into the auger stem as the auger is withdrawn from the ground. Alternatively, the reactive media can be mixed with biodegradable slurry and pumped through the hollow stem as the auger is withdrawn. A continuous PRB is constructed by drilling a series of overlapping rows of borings.

As an example, 200 bioborings were installed at NWIRP, McGregor, Texas, in 2000 to treat perchlorate in groundwater (Perlmutter et al. 2000). The bioborings were installed in row to create a biobarrier. Additional bioborings were subsequently installed in areas where trenching was not feasible or was opposed to by off-site land owners. The bioborings were backfilled with cottonseed meal (30% by volume) and gravel, and the mixture was “spiked” with sodium acetate (acetic acid) and a microbial culture capable of degrading perchlorate. The borings were then capped above the water table.

Caisson installation involves driving a large, circular steel caisson into the ground and auguring out the native material. Depths in excess of 60 feet (20 m) are achievable. The caisson is then backfilled with iron and removed. Some contractors are capable of installing caissons as large as 15 feet (4.6 m) in diameter; however, smaller caissons are more common. Overlapping or tangential caisson-emplaced treatment zones can be used to create a larger permeable treatment zone. As the caisson is removed, the reactive media moves into the annular space left by the caisson walls. Reactive media densification due to the caisson vibrations can cause the surface of the reactive media to subside.

Depending on local lithology, smearing of the interface between the aquifer materials and reactive media may be an issue with auger and caisson methods.

Clamshell excavators

In general, clamshell buckets can be used to excavate to about 200 feet (61 m) bgs; however, this technique has been deployed only at shallower depths (45 feet [15 m]) for PRB application. Mechanical clamshells are cable-suspended, crane-operated grabbing tools that depend on gravity for accurate excavation and grab closure. Hydraulic clamshells use Kelly bars to help guide and control the vertical line. Mechanical clamshells are generally preferred over the hydraulic ones as they are more flexible in soils with boulders, can reach greater depths, and have lower maintenance costs. Clamshells are efficient for bulk excavation of most subsurface materials except highly consolidated sediments and bedrock. Clamshells are often used in combination with biopolymer slurries, which support the walls of the excavation.

6.2.3 Injection Methods

Injected PRBs are configured to establish a continuous zone of reactive media across a contaminant plume over a specific vertical interval. The configuration consists of a number of injection points arrayed perpendicular to the plume. Generally, injection consists of drilling a series of boreholes and then injecting the reactive media under pressure, often using a carrier fluid (e.g., high-pressure gas, water, or other solution) to carry the media into the subsurface.

Ideally, sufficient material is added at each injection point to obtain a uniform distribution of reactive material radially from the injection point, with the number of injection points arrayed so as to obtain “complete” spatial coverage of the plume. However, complete uniformity is rarely achieved, a fact the design process should take into account when determining the density and location of injection points. The spacing and/or overlap of adjacent injection points becomes key to obtaining as much of a continuous reactive zone as possible. The disadvantage of injected PRBs is the lack of control over the thickness and uniformity of the treatment zone, which may significantly reduce the remedial performance.

Accepting that injection methods generally provide a less uniform treatment zone than trenched PRBs, there are instances when injection of reactive media through boreholes is preferable to conventional trenching techniques. These include when surface or near-surface obstacles (e.g., existing buildings or utilities) make trenching impractical, where contaminant depth requires deeper depths than can be cost-effectively achieved with trenching, when a grid injection pattern is preferable to a single line, or simply when costs for injection are less than for trenching. Advantages of injection borings include the following:

- flexibility in their placement, including a single line of injection wells (similar to a traditional passive reactive barrier), multiple treatment lines, or a grid pattern

- the ability to install borings deeper than 100 feet, which is much deeper than possible using conventional trenching techniques
- the ability to address specific vertical contaminated intervals without excavation of overlying materials
- suitability for emplacement in urban settings, where surface structures and underground utilities may make surface trenching impractical
- less soil spoils generated—generally <0.5% of the volume of spoils generated during trenching construction

Depending on the estimated radius of influence (ROI), borings are typically installed 5–20 feet apart; however, in some cases pilot testing may be appropriate. Spacing depends on the following:

- injection method (e.g., direct injection, hydraulic fracturing, pneumatic fracturing)
- lithology (hydraulic conductivity, porosity, degree of heterogeneity, etc.)
- volume of reactive material to be added
- properties of the reactive material (viscosity, proportion of solids in slurry, etc.)
- experience of injection contractor

In Situ Bioremediation of Chlorinated Ethene: DNAPL Source Zones (ITRC 2008) provides an overview of PRB injection methods. With any technique, care must be taken to seal and grout the injection well and nearby well points in place to withstand the designed injection pressure and to prevent escape of the substrate to the vadose zone or ground surface.

Direct injection

Direct injection refers to the emplacement of reactive media through injection wells or borings. Viscous substrates such as HRC are injected directly, while soluble or emulsified substrates (e.g., lactate, molasses, EVO) are mixed with water and injected as a low-viscosity fluid. Reactive media containing solids (e.g., ZVI, EZVI, EHC) are commonly mixed with water and injected as a slurry (Figure 6-5). These methods use a direct-push drill rig to advance injection rods with a specialized injection tip or disposable tip to the target depth. The reactive media is pumped through the injection rods and tip into the formation. Many design parameters must be evaluated, including the following:

Figure 6-5. Iron guar mixture prepared for direct injection.

- injection spacing—the horizontal distance between injection boreholes
- injection interval—the vertical distance between injections over the injection thickness
- injection pressure—whether to use a lower pressure to permeate the aquifer with the reactive media or a higher pressure to fracture the aquifer solids
- injection volume—using a low volume of injection slurry to minimize the potential displacement of the plume or a high volume to maximize coverage and contact

- whether to inject “chase water” to enhance the distribution of reactive media but risk the potential negative effect of dispersing and displacing the plume

Temporary direct-push probes are used to advance specially designed injection tools to create generally vertical zones 1–5 feet high. Numerous vendors have modified drilling equipment to allow low-cost direct injection of reactive media as aqueous solutions. Therefore, multiple injections are typically used to cover the specific targeted vertical depth.

Pressurized injection is commonly used because the pressure speeds injection of a viscous solution, overcomes the hydrostatic back pressure, and promotes even and wider distribution of reactive media within the subsurface. Pumping may be performed using low-pressure air diaphragm pumps (generally 0–120 psi), moderate-pressure progressive cavity pumps (0–400 psi), or high-pressure piston pumps (0–1,500 psi).

Pneumatic fracturing and injection

Pneumatic fracturing technology was originally developed as a permeability enhancement technique. Injection of high-pressure gas (typically nitrogen) creates fractures or fissures in soil or rock formations. The process is completed in two sequential steps: pneumatic fracturing and pneumatic injection. Pneumatic fracturing and injection have been applied in many types of geologic media, including sands, silts, silty clays, and highly weathered fractured bedrock at depths to 160 feet (50 m). It is important to maintain a dilute concentration of the injected media with respect to the carrier gas to prevent clogging and achieve maximum penetration of the soil formation).

Pneumatic injection can also involve liquid or dry media and pressurized gas as a carrier. To date, pneumatic fracturing has been implemented at over 100 sites, particularly in low-permeability and bedrock sites. When injecting media intended to enhance reducing conditions (e.g., ZVI, EHC, EZVI, EVO), nitrogen is frequently used as the fracturing and transport gas because it is both readily available from local gas suppliers and maintains anaerobic conditions. Injection radii of over 15 feet have been documented (Camino et al. 1998).

The ROIs of the gas and media are typically different, with the gas extending farther than the injected media. Several monitoring techniques are applied to distinguish the two ROI. Typically, the fracturing area is monitored for surface heave using tilt meter alarms, graduated heave rods, and engineering levels. Surrounding monitoring points in the expected ROI are measured for gas pressure influence throughout the injection activities and inspected for evidence of day-lighting. This real-time monitoring typically assists in recognizing and preventing excessive structural movement or damage during injection.

Hydraulic fracturing and injection

Hydraulic fracturing is the injection of a slurry solution at a pressure that exceeds the combined lithostatic pressure and cohesive strength of the formation. This creates fractures or openings within the subsurface to promote greater distribution of the reactive media. The method uses high initial pumping pressures to initiate fracturing of the contaminated strata, followed by subsequent injection at pressures as low as 1 psi for the reactive media solution to fill the induced fractures. Once emplaced, the reactive media may form horizontal and/or vertical zones near the targeted contaminants, depending on the hydraulic fracturing techniques used and the media characteristics (see Figure 6-6).

Figure 6-6. Hydraulically placed sand fracture emplaced in clay till. (Courtesy Frac-Rite Environmental, Ltd.)

Rods with a specialized injection nozzle are pushed into the subsurface to the required depth. The reactive media is typically suspended in biopolymer slurry and pumped into the formation at a rate that exceeds the ability of the formation to accept the fluid. As a result, the pressure rises until fractures are created. The injection pressure drops dramatically at the onset of fracturing. After fracturing occurs, slurry injection is continued to keep the fractures open. Enzymes added to the biopolymer slurry during injection degrade the slurry after the injection is complete.

6.2.4 Alternative Construction Techniques

Several methods other than trenching/excavation and injection methods have been used to construct PRBs. See ITRC’s PRB lessons learned/new directions document (2005b) for a more detailed discussion of these methods, which are not in widespread use but may have some utility under certain site-specific conditions. The following paragraphs briefly discuss each method.

Vertical hydrofracturing

This is a term used specifically for injection of iron in vertical planes using a biodegradable gel and an enzyme to biodegrade the gel. Continuous PRB treatment walls deeper than 100 feet and up to 9 inches thick can be created using vertical hydrofracturing. This installation method requires the drilling of 6-inch boreholes approximately every 15 feet on the planned placement line (azimuth) of the PRB. After the boreholes are drilled, a special split-winged casing is inserted into the borehole to the required depth with the wings oriented to control the direction and fracture pathway for what will become the PRB wall. A fine-grained iron is suspended in biodegradable slurry and pumped under low pressure (25 psi) into the formation. The fracturing fluid pumped through the split-wing casing causes the soil to separate creating an iron treatment zone a few inches in width with a controlled vertical thickness. Fractures propagated from boreholes located along the line of installation coalesce to create a continuous PRB (i.e., a thin vertical plane of iron). Parallel vertical planes can be installed to increase the flow-through thickness of the iron system. This method is best suited to depths >30 feet due to the confining pressures needed to keep the fracture planes vertical.

Deep soil mixing

Large in situ soil mixing augers with diameters of 10 feet (3 m) are capable of adding reactive media such as ZVI in reactive columns to a depth of over 50 feet (15 m) bgs. Deep soil mixing also can be used to install permeable funnels in funnel-and-gate configurations. This technique uses one to three large augers (3–8 feet [1–2.5 m] in diameter) with mixing paddles along the treatment zone. Fine iron is added as the augers penetrate the ground and mix the iron with the subsurface materials. The iron can also be introduced in biodegradable slurry. This method generates minimal spoils and reduces costs associated with the removal of contaminated soils. However, equipment mobilization costs may make this method cost-prohibitive, especially at small sites. ZVI-clay technology for DNAPL source areas often makes use of this technology (see Figure 6-7).

Figure 6-7. ZVI-clay application using soil mixing.

High-pressure jetting

Like deep soil mixing, high-pressure jetting can be used to construct the reactive cell or a containment/funnel wall. During jetting or jet grouting, grout or slurry is injected into the subsurface at high pressures. A triple-rod injection system delivers a high-pressure mixture of granular iron, guar gum, air, and/or water. The rods are advanced to the design depth of the PRB, and the injection begins. The grout and slurry are continually injected as the rods are pulled toward the surface, creating a column or panel of reactive media. If the jetting nozzles are rotated during drill extraction, the jetted material will be approximately columnar, about 3–7 feet in diameter. If the jetting nozzles are not rotated during extraction, the process creates a thin diaphragm wall. Rows of columns or panels create the PRB. This procedure was used to create a panel wall PRB at a private site in North Carolina (Jensen et al. 2000). Another common use of this application is to add clay to ZVI to treat source areas and to reduce outward migration of contaminants.

Vibrating beam/mandrel/tremie tube

In this method, an H-beam or mandrel (hollow steel shaft) with a special shoe at its base is driven into the subsurface, creating a void space. As the beam/mandrel is pulled out of the ground, reactive media or a slurry/grout-containing reactive media is injected into the created void through a nozzle (tremie tube) connected to the bottom of the beam. The beams/mandrels are driven in overlapping panels to create a continuous treatment wall. Using this technique, the wall can be installed on an angle of up to 45 degrees, avoiding utilities and subsurface structures. This technology was used to install a wall at an industrial facility in Tifton, Georgia, and at Hangar K at Cape Canaveral Air Force Station (AFS), Florida (ITRC 2000).

Generally, mandrels have cross-sections of only 2 × 5 in (5 × 13 cm), so a series of mandrel-installed voids is needed to construct the reactive cell. H-beams tend to have larger cross-sectional areas. No spoils are generated using vibrating beams/mandrels, thus reducing construction costs by removing the necessity of hauling contaminated soils from the site. As with caisson installations, a negative impact can be smearing of soils and loss of permeability.

Pressure pulse injection

Fractures can be created using high-pressure pulses of fluid, called pressure pulse technology (PPT). PPT involves the use of regular pulses of air pressure to remove NAPLs or to advance an NZVI slurry. The pulses cause the pores of the subsurface formation to expand, forcing the slurry to move through the formation in a wave-like motion. The pressure pulse method was applied in 2004 at Launch Complex 34 at Cape Canaveral AFS, Florida (Quinn et al. 2005).

6.3 PRB Cost Drivers

There has been a marked increase in the variety of reactive media used in PRBs and in the variety of approaches used to emplace these materials. The purpose of this section is to provide the reader with some appreciation of the factors affecting the cost of these applications. This section also provides a current (2011) "snapshot" of media costs using publicly available data and examples of costs involved in recent field applications, with a particular focus on injection methods that have become more commonplace since the publication of the last ITRC PRB guidance.

6.3.1 Common Factors

The cost of PRB construction depends on several site-specific factors, including the design of the PRB, the depth of installation, the nature of the geologic materials present, and surface/subsurface obstructions (e.g., buildings and utilities). The choice between trenched methods of construction (continuous PRBs, funnel-and-gate systems), injected PRBs, in situ reactive vessels, and more innovative configurations such as the Geosiphon™ (Figure 6-8) often drive PRB capital costs.

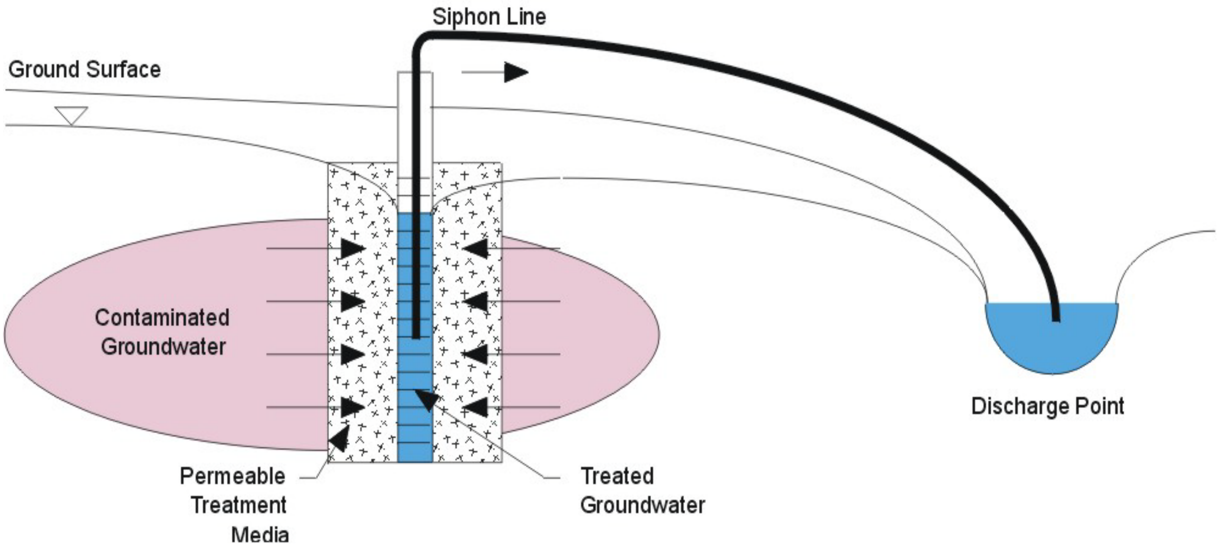

Figure 6-8. Conceptual Geosiphon design.
(Modified from Phifer, Nichols, and Sappington 2000)

Intuitively, construction costs increase with depth of application. In general, in addition to some of the technical advantages of injection methods over trenching (see Section 6.2.3), costs for reactive media injection are normally less than that for trenching, especially when the cost of excavated soils removal is taken into account. This differential normally increases with increasing depth.

Lithologic characteristics of a site also influence the cost of PRB construction. Injection methods may allow targeting a specific vertical horizon containing most of the contamination. However, small vertical variations in permeability or grain size may negatively impact the ability of injection approaches to achieve uniform vertical distribution of reactive materials and/or require additional injection points. Cobbles and other granular aquifer sediments may prevent the cost-effective advancement of injection tooling but can also influence the cost of supported excavation and/or limit the use of continuous trenching methods.

6.3.2 Small vs. Large Sites

As discussed in Section 6.1.2, as PRB application technology matures, it may well be that injected PRBs become the norm for small site (e.g., "dry cleaner"–type) applications, except in cases where the plume is narrow and shallow and can be reached with simple, readily available excavating equipment (e.g., backhoes and/or temporary shoring). However, for larger (longer) systems where numerous overlapping injections would otherwise be required to install a high-integrity system (along a property boundary, for example), excavation-based methods still merit serious consideration.

6.3.3 Media Requirements vs. Regulatory Goals

The required reactive media volume and/or flow-through thickness has a large influence on project cost, particularly for trenched ZVI PRBs and for manufactured zeolite. The cost of the media itself is significant, and thus the media volume may also influence the overall cost of construction. One important consideration is whether available injection methods can achieve placement of the amount of material required. Moreover, the variety of trenching-based construction methods each have a minimum or maximum flow-through thickness that can be achieved, so depending on the thickness required, a more expensive trench method may be needed.

In this context, the goal of the PRB application merits consideration. If relatively low concentrations (MCLs or less) must be met at every point along the line of installation, PRB application costs will be considerably more than if the technology is being used as a mass reduction tool. This principle is particularly true for treatment processes governed by first-order reactions, where it can take the same residence time or volume of material to lower concentrations from 500 to 1 ppm as to lower concentrations from 500 to 1 ppb. The concept of PRBs as a mass reduction tool has been suggested for several years. For example, Vidumsky and Landis (2001) suggested using an iron PRB as a form of "step function" to reduce contaminant mass, coupled with natural attenuation downgradient.

However, designs of most trenched iron PRBs to date have employed U.S. federal or state MCLs as design criteria. The principle of mass reduction has been employed more often with injected iron treatment applications (Figure 6-9), especially in source areas where reduction of high contaminant concentrations is desired. This change in approach is perhaps in part due to recognition of the inability to achieve "100% coverage" of the plume with injection approaches but also due to increasing documentation of the ability of reactive materials to promote contaminant degradation outside the injected area itself over time due to the establishment of requisite redox conditions (Stening et al. 2008). The development of materials designed to release amendments outside the zone of emplacement (iron-carbon combinations or various carbon sources, see Section 4.4) also has contributed to the increasing popularity of injected methods.


Figure 6-9. Fine-grained iron injected in a guar suspension.

6.3.4 Persistence of Upgradient Source

The persistence and potentially changing nature of the upgradient source may have a significant impact on the selection, design, and monitoring cost of the PRB application. If there is confidence that the source may be effectively removed over a short period of time, then a shorter-lived but less expensive material may be suitable for use in a downgradient PRB. However, if the source term cannot be removed due to physical constraints (e.g., its location underneath a building) or if costs of removing the source are prohibitively expensive, then a more expensive but longer-lasting material in the PRB may be the most cost-effective approach for long-term site remediation. The monitoring program for the PRB application should also reflect the nature of the source term in relation to its anticipated longevity, monitoring frequency, etc.

6.3.5 Need for Treatment of Plume Downgradient of PRB

Most PRBs are installed within existing plumes and therefore some level of contamination exists both upgradient and downgradient of the PRB. Monitoring results from most completed PRB applications indicate that the monitoring wells installed within and closely downgradient of the PRB show the expected contaminant degradation within months of the PRB being installed. Monitoring wells placed in the aquifer downgradient of the PRB continue to exhibit VOC concentrations for some time following PRB installation due to desorption or back diffusion of VOCs from the downgradient aquifer sediments and the time required for flushing the downgradient aquifer. Thus, groundwater flow velocity, the presence of fine-grained zones, and the fraction of organic carbon content within the aquifer sediments, which may represent an ongoing source of desorbing VOCs downgradient, all play key roles in influencing VOC concentrations downgradient. Recent research by Sale, Zimbron, and Dandy (2008) has focused on quantifying these effects.

Therefore, costs of technology application may need to include the costs to treat the residual plume downgradient of the PRB, especially if the reactive material is ZVI and not designed to release amendments into the downgradient aquifer. Some form of risk assessment may be needed to assess the impact of the persistent downgradient concentrations on the local environment.

6.4 Capital Costs of PRB Construction

6.4.1 Media Costs

Media costs cannot be compared directly on a per mass basis, as different mass of each specific reactive media may be required to treat a certain mass of contaminant (an "apples and oranges" comparison). There are two primary factors that must be assessed to determine how much mass of reactive media is required: the effectiveness of the media at treating the contaminants and the effective lifespan for the media. Once the time frame for treatment and the effective life of the media are determined, the number of applications of the media and/or the number of media replacements, the overall thickness of the PRB, and the overall cost of the media can be determined.

Table 6-1 provides examples of some of the commercially available reactive media that can be used in PRB applications along with the relative cost and expected longevity (where data are available). Ideally, the mass of reactive media per mass of contaminant degraded would be included in this table, but this varies significantly with site-specific factors and must be evaluated on a site-by-site basis.

Table 6-1. Examples of reactive media costs and longevity information (2009)

Reactive media	**Range in unit cost**	**Approach to application**	**General range in longevity**[a]
ZVI—coarse (-8–+50 U.S. mesh, (300–2,360 microns)	\$0.30–\$0.45/lb	Several inches of 100% ZVI (or equivalent mixed with sand)	>15 years
ZVI—fine/micro (<300 microns)	\$0.40–\$0.75/lb	Using a low (<2.5%) weight percentage of aquifer mass treated	5 to more than 10 years
ZVI—carbon combination	\$1.50–\$2.50/lb[4]	Estimate electron acceptor demand or use a low (<2%) weight percentage of aquifer mass treated	3–5 years
Biowall materials[b]	\$10–\$12/yd^3	Minimum 1-foot thick	4–6 years before replenishment
Emulsified vegetable oil (for biowall replenishment)	\$1.25–\$2.00/lb	Estimate electron acceptor demand or calculate desired DOC level	1.5–3 years
Emulsified ZVI[c]		Estimate electron acceptor demand or use a low (<2%) weight percentage of aquifer mass treated	Not available
Organophilic clay	\$1.10–\$1.25/lb	Mix 25% by volume with sand or pea gravel	>4 years

[a] Additional information on longevity is provided in Section 8.
[b] Mulch may often be found for the cost of shipping and handling alone (e.g., municipal sources).
[c] While several licenses have been issued for EZVI, a commercial product is currently not readily available.

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[4] These costs indicate prices for EHC as an example. ZVI-carbon combination mixtures that are manually created by mixing at the site or from other vendors may have different costs but were either not readily available or are too site specific, but these should be evaluated when this combination is being considered.

6.4.2 Emplacement Costs

Emplacement methods and costs for excavated PRBs are covered in PRB-4 (ITRC 2005b), and costs for several excavated PRBs are also presented in Powell, Powell, and Puls (2002). While somewhat dated, these reports do provide a good general guideline for trenched PRBs. Recent (2009–2010) costs for PRB installations using continuous trenching have ranged \$200–500/ linear foot, depending on depth, while costs for biopolymer trenching in the order of \$15–30/ft^2 of PRB constructed are common. These unit costs do not include mobilization. It is still possible to construct shallow PRBs (Figure 6-10) using temporary shoring for about \$10–15/ft^2, depending on site conditions. Costs for injected PRBs vary depending on the depth injection method, injection spacing, and other site-specific factors. As conditions can vary significantly from site to site, qualified contractors should always be contacted to obtain budget quotes. Example costs of more recent PRB applications are described in Section 6.6 and in the case summaries presented in Appendix A.

Figure 6-10. PRB installation in an unsupported excavation.

6.4.3 Capital Costs for Passive vs. Active PRBs

Truly passive systems involve materials like ZVI, where material change-out or rejuvenation is expected to occur only after several years of operation. The longevity of such systems is discussed in Section 8. On the other end of the spectrum, frequent soluble substrate addition constitutes a type of "active" PRB, which is more reliant on aquifer hydraulics or recirculation methods for its operation. Component costs (see Table 6-2) need to be considered in the design of a passive vs. an active system (note not all costs are applicable to every project).

Table 6-2. Project components for passive vs. active PRBs

Passive PRB	Active PRB (substrate addition)
Phase 1: Preconstruction activities	
Preliminary site assessment	Preliminary site assessment
Site characterization	Site characterization
Laboratory treatability tests (if necessary)	Laboratory treatability tests (if necessary)
Design, contract, and regulatory review	Design, contract, and regulatory review
Phase 2: Construction	
Mobilization/demobilization	Mobilization/demobilization
Site preparation	Site preparation
Supply and delivery of granular iron Supply and delivery of sand (certain methods)	Supply and delivery of substrate and amendments
PRB construction	Install and develop injection wells Piping/electrical/injection equipment
Excavated soil disposal	Disposal of soil cuttings
Monitoring well installation	Monitoring well installation
Site restoration	Site restoration

The following explains the specific costs associated with construction of a PRB and provides a guideline to costing these items.

Site characterization

Due to the passive in situ nature of PRBs, the performance of the PRB cannot be easily modified once it is installed. For this reason, the level of site characterization for the design of a passive PRB may be greater than for an active system, where additional substrate can be added at a relatively small incremental cost to reflect refinements in contaminant flux estimates, for example. The additional site characterization involves determining the groundwater velocity in the vicinity of the PRB, determining the degree of variation in groundwater flow direction, and determining the horizontal and vertical variation of VOC concentrations along the PRB alignment. Depending on the level of site characterization already completed, this information may be available from existing site data.

Laboratory treatability tests

Laboratory column tests are sometimes required to determine site-specific degradation rates for both passive and active systems. Column studies may be appropriate for solid media such as granular ZVI and mulch mixtures, while microcosms are often conducted for biological PRBs using fluid organic substrates.

Site preparation

Site preparation typically involves clearing the area where the barrier is to be constructed and installing controls (silt fences, berms) around the construction area. For certain construction methods, additional site preparation is required (e.g., for bioslurry construction where the groundwater table is located near the ground surface, a working pad may be required to allow an additional head of bioslurry in the trench). More site preparation will likely be involved for trenched passive systems.

Excavated soil disposal

The cost for disposal of excavated soils depends on the construction method, contamination levels in the soil relative to regulatory levels, and disposal options. The volume of excavated soil to be handled varies with the construction method. For example, excavation using conventional excavation equipment typically produces the largest volume of soil, whereas placement of granular iron with an injection method minimizes soil generation. Depending on the location of the PRB relative to the source, the concentration of contaminants in the excavated soils may not be above regulatory guidelines, resulting in lower disposal costs. Lastly, there may be disposal options on site (e.g., a landfill) that would reduce the disposal costs. The minimization of excavated soils represents one of the key cost savings associated with injectable PRBs.

Monitoring well installation

Monitoring wells are typically placed upgradient, within, downgradient, and, in some circumstances, sidegradient of the PRB. Some construction methods enable the monitoring wells within the PRB to be placed during construction. In most cases, the number of wells would be similar for both passive and active systems.

Site restoration

Site restoration involves regrading the construction area and restoring the preconstruction site conditions (e.g., paving, landscaping). No special surface treatments (markings, restrictions to traffic, etc.) are required with the exception of access to monitoring wells. As with site preparation costs, restoration costs will likely be higher for trenched systems.

Permitting

No special permits for trench-type PRB installations have been required to date, other than routine site construction permits that accompany any remedial activity. Some form of underground injection permit or regulatory approval may be required for injected PRBs (see Section 2 for more information).

6.5 Life-Cycle Costs

6.5.1 Passive vs. Active PRB Systems (e.g., Soluble Substrate Biobarriers)

The choice between a passive PRB (e.g., using ZVI) vs. an active system (e.g., frequent and ongoing injection of soluble substrate) is driven by several factors. If feasible, truly passive systems may offer the biggest long-term cost savings, but the difference in cost of the two types may in large part be driven by the frequency of change-out or replenishment of the reactive media.

6.5.2 Longevity of Reactive Materials/Frequency of Replacement

The longevity and associated costs of reactive media change-out/replenishment must be assessed in the context of the overall remedial goals of the project. Laboratory studies have shown that coarse-grained ZVI can persist for several decades in the subsurface environment (Reardon 2005). Precipitates may necessitate replacement and/or rejuvenation of the ZVI in a PRB, but this will not likely be needed for several years in most environments (see Section 8). Finer-grained nanoscale iron materials have much shorter lifetimes, on the order of 1–2 years in many instances. Therefore, the need for reinjection of these materials should be considered, depending on the expected persistence of the source term.

Solid carbon-based materials used in biowalls for CVOCs and perchlorate and in denitrification barriers have shown longevity in the order of 5–15 years. Similar injectable materials derived from solid carbon have also shown a 3–5-year time frame. More labile, soluble carbon substrates may have a shorter lifetime, depending on their composition and the demands of the local environment. Slow release substrates such as EVO and HRC typically have lasted 1.5–3 years. Soluble substrates such as molasses and lactate formulations may require injection on a frequency of every few weeks to months. A product such as dissolved whey powder has an intermediate longevity of perhaps 2–6 months. The injection frequency of fluid organic substrates varies depending on the rate of groundwater flow and native electron acceptor flux. Additional information on longevity of carbon-based materials is provided in Sections 8.2 and 8.3.

6.5.3 Cost to Replenish or Rejuvenate Reactive Media

Probably one of the most difficult aspects of predicting the long-term costs of a PRB is the estimation of the frequency and cost of replacement or rejuvenation of reactive media.

ZVI PRBs

The objective of rejuvenation of granular iron would be to restore the permeability loss due to precipitate formation and possibly to remove the precipitate from the iron to restore its reactivity. Using sophisticated flow and transport models (Jeen et al. 2007a), a theoretical estimate of the operational time before implementing rejuvenation methods can be calculated. Conceptual rejuvenation methods may include the following:

- using ultrasound to break up the precipitate
- using PPT to break up the precipitate
- using solid-stem augers to agitate the PRB
- periodic flushing with nitrate free water to remove nitrates

No full-scale test to rejuvenate mineralized ZVI has been performed to date. One developing method, ultrasound, has been subjected to limited field-scale tests to determine its effectiveness, with mixed results (NASA 2009). At this point, one can state only that these methods may prove to be successful in rejuvenating a ZVI PRB. For ZVI PRBs—in particular with injected PRBs—the cost-effectiveness of injecting new ZVI rather than attempting to rejuvenate mineralized ZVI is likely greater even though material cost of ZVI may vary greatly year to year.

Mulch biowalls

The need for, or frequency of, replenishing biowalls may vary significantly from site to site depending on the contaminant properties and the site-specific hydrogeology. Biowalls at NWIRP McGregor, Texas, are being replenished every 3–5 years based on experience with perchlorate degradation (EnSafe 2008). Other biowalls, such as the Building 301 biowall system at Offutt AFB, Nebraska, have remained effective after 6 or more years of monitoring without replenishment (Parsons 2010a). For costing purposes, it may be assumed that biowalls will require replenishment every 4–6 years. It is not known whether repeated rejuvenation of a biowall will lead to biofouling or an unacceptable loss in hydraulic conductivity. Biowall applications to date have not considered physical replacement of the biowall matrix.

EVO is the substrate most commonly considered for biowall replenishment. EVO is a suitable substrate based on the ability to distribute the substrate throughout the biowall matrix, the duration it will last and low frequency of injection required, and lower product cost relative to other slow-release substrate types. There is an economy of scale in large replenishment applications due to a single mobilization of equipment and procurement of large quantities of bulk materials. While site-specific cost data for biowall replenishment are not available, the cost to replenish a 300-foot-long biowall to a depth of 25 feet is anticipated to range $20,000–$30,000.

PRBs requiring periodic substrate addition

Fortunately, the price variation in various injectable materials is expected to be less variable than that of ZVI, so estimating future costs with a price increase roughly based on inflation rates is a reasonable approach for these materials. However, frequency of application is more difficult to estimate. Moreover, some attention should be paid to whether repeated injections may cause aquifer plugging (biofouling) over time, perhaps necessitating installation of new injection wells.

6.5.4 Monitoring and Maintenance Costs

The degree of groundwater level monitoring, sampling, and analysis typically required is similar for both passive and active types of PRBs. Table 6-3 summarizes the typical monitoring and maintenance activities for passive PRB and active PRBs.

Table 6-3. Passive vs. active PRB monitoring and maintenance activities

Passive PRB	Active PRB (substrate addition)
Phase 1: Monitoring activities	
Groundwater sampling and analysis	Groundwater sampling and analysis
Groundwater water level survey	Groundwater water level survey
Hydraulic conductivity (slug) tests	Hydraulic conductivity (pump) tests
Reporting	Reporting
Phase 2: Maintenance activities	
Reactive media rejuvenation (if required)	Periodic media addition
Operating labor	Operating labor
Parts repair and replacement	Parts repair and replacement
Electricity for pumps	Electricity for pumps

The hydraulic testing of a passive trenched PRB may be focused on the reactive media itself and performed periodically to provide an indication of possible reduction of hydraulic conductivity of a PRB due to precipitate formation in the PRB. These tests would normally be completed only if other data indicated a decline in PRB performance. Hydraulic testing typically involves performing slug tests on monitoring wells installed in the PRB. For systems involving injected substrates, larger-scale testing might focus on the aquifer materials within the injected zone to gauge whether reactive media addition had indirectly caused loss of aquifer permeability due to biofouling.

6.5.5 Economic Factors Pertaining to "Green" Remediation

There is an increasing awareness of assessing the overall impact of remediation projects in terms of "green" (sustainable) remediation. Economic indicators identified by USEPA as critical for green remediation projects include the following:

- direct cost of product

- life-cycle cost
- economic benefit from reuse of site
- economic benefit to local economy
- cost savings resulting from efficiency, reductions in materials use, or materials reuse
- reduced greenhouse gas (GHG) emissions

These economic indicators may also need to be assessed on a site-specific basis. Section 9 contains additional information.

6.6 Example PRB Application Costs

6.6.1 Example Biowall Costs

To illustrate the cost of a typical biowall application,
Table **6-** presents costs for the BG05 biowall at Ellsworth AFB, South Dakota. A 580-foot-long, by 32-foot-deep, by 2-foot-thick biowall was installed using a continuous one-pass trencher in June 2005. Total cost for system design and installation was <$300,000, with the trenching subcontract accounting for over half of that amount.

Table 6-4. Biowall technology costs, BG05, Ellsworth AFB, South Dakota (AFCEE 2008)

Element	**Cost ($)**
Capital costs	
Work plan and procurement	19,300
Mobilization/demobilization/permitting	9,600
Site labor	38,000
Equipment and appurtenances	
• Monitoring wells	16,800
• Biowall materials	30,100
• Monitoring equipment and supplies	3,200
Trenching subcontractor	154,600
Baseline laboratory analysis	7,800
Surveying	1,200
Reporting	12,600
Total capital cost	**293,200**
Annual operating costs (performance monitoring)	
Mobilization/demobilization	3,000
Site labor (sampling)	15,000
Sampling equipment and supplies	4,000
Laboratory analyses	14,000
Project management/reporting	6,000
Total annual operating cost (per year, semiannual sampling events)	**42,000**

Approximately $30,000 was spent on biowall materials, although approximately $7,200 of this cost was for iron ore and sulfate pellets added on a demonstration basis to a 60-foot segment of the biowall trench. The total cost reported here also includes work plan development, permitting, mobilization, installation of the monitoring network, baseline sampling, site restoration (grading and seeding), and a construction completion report.

The annual monitoring (two semiannual events) and reporting cost is approximately $42,000 for this demonstration. This amount includes mobilization of a field crew, sampling three well transects of four to five wells each, and an extensive analyte list. Annual monitoring by a base contractor using an optimized and more streamlined monitoring approach would be closer to $30,000/year for two semiannual sampling events. Either way, the cost of monitoring is of consequence and may exceed capital construction cost over a period of 10 years or more.

As another example, cost information for a 455-foot-long, 1.5-foot-thick biowall to a depth of 24 feet at Operable Unit (OU)-1, Altus AFB, Oklahoma, is included in the case summary in Appendix A and summarized in Table 6-5. Capitol cost to procure materials and install the biowall was $165,000, or approximately $360/linear foot. Of this cost, $115,000 was for the trenching subcontractor ($250/linear foot). Capital cost also included grinding and transporting the mulch to the base, installation of the monitoring system, and surveying. The monitoring cost was approximately $17,000/event in 2002/2003. The estimated cost of annual monitoring is estimated to be approximately $27,000/year, consisting of one annual monitoring event, reporting, and project management.

Table 6-5. Biowall technology costs, OU-1, Altus AFB, Oklahoma

Item	Cost ($)
System design and work plan	12,000
System installation (trenching, materials, and well installation)	165,000
Process monitoring (three events)	51,000
Reporting, meetings, and administration	37,000
Total cost	**265,000**
Estimated annual monitoring	**27,000**

The age of these biowalls should be accounted for when evaluating current costs for biowall construction. The BG05 biowall was installed in 2005, and the OU-1 biowall was installed in 2002. The most significant cost is the trenching subcontractor, with mobilization costing $20,000–$60,000 depending on the size of the trencher and the distance the machinery must be transported. In general, the cost for the mulch and sand materials is a very small percentage of the overall cost. The costs of design, monitoring well construction, and monitoring are similar to other PRB configurations. Additional cost analysis of biowall design and construction compared to other bioremediation configurations for treatment of perchlorate can be found in Krug et al. (2009).

6.6.2 Trenched Iron PRB Application at the Cornhusker Army Ammunition Plant, Nebraska

A demonstration project at CAAP involved installation of a mixed iron/sand PRB (30% by weight iron). The PRB was approximately 50-feet long by 15-feet in vertical thickness by 3-feet thick, installed to a depth of about 30 feet. A biopolymer guar trenching method was used. The

PRB was located within a large groundwater plume from a diffuse source resulting from production of munitions. The cost of the iron used was $17,600, and the construction cost was $121,000 (excluding design, well construction, and project administration) (Johnson and Tratnyek 2008). The project investigators noted that the greatest uncertainty in long-term costs for this application relates to the longevity of the PRB.

6.6.3 Denitrification Barrier, Logan County, Oklahoma

Denitrification barriers are relatively inexpensive to install because of the use of inexpensive reactive materials. Because of the shallow nature of most nitrate plumes, temporary shoring/ trench boxes can be used for small systems, while continuous trenching methods may be suitable for larger systems. For example, a 260-m-long, 1.2-m-wide, 6-m-deep PRB was built using hay straw as a reactive material to denitrify a plume emanating from a swine concentrated animal feeding operation lagoon in Logan County, Oklahoma (Wilkin et al. 2006).

7. PERFORMANCE MONITORING DESIGN AND ASSESSMENT

Monitoring is used to assess the performance of a PRB, both in terms of the system functional objectives (also known as performance objectives) and overall compliance with regulatory agency requirements set to protect the public and environment. This section discusses monitoring to assess hydraulic performance, contaminant treatment, changing geochemical and microbiological conditions, and downgradient water quality.

What's New?

- Alternative compliance monitoring metrics (mass discharge and toxicity reduction)
- Improved analytical monitoring tools, including compound-specific isotope analysis and molecular biological tools
- Analysis of iron and sulfide mineralogy to evaluate biogeochemical transformation processes
- O&M plans with monitoring protocols to evaluate when a PRB should be optimized

7.1 Monitoring to Evaluate Performance Objectives

Section 3 discussed the selection of POs. Site monitoring is generally performed to achieve one of three purposes:

- **Baseline characterization** is used as a basis for design of the system and for later performance comparison.
- **Process monitoring** is used to optimize system operation and performance and to evaluate the need for system modifications. This monitoring is more specific to the PRB treatment zone.
- **Performance (compliance) monitoring** is used to evaluate and validate the effectiveness of the system with regard to meeting RAOs. This monitoring is more specific to downgradient water quality. Process monitoring and performance monitoring may require different analytical protocols, monitoring locations, and monitoring frequencies. The following sections describe monitoring network design and the monitoring parameters and tools that can be used for evaluation of the above monitoring purposes.

7.2 Monitoring Network Design

A PRB design includes development of a monitoring network to document that performance and compliance objectives are attained. Baseline conditions should be established for comparison to performance monitoring results. The configuration of the monitoring network and frequency of monitoring should be adequate to document POs and to assess long-term O&M requirements.

7.2.1 Monitoring Locations

Monitoring locations for PRBs should be installed upgradient, within, downgradient, and side-gradient of the reaction zone, parallel to the direction of groundwater flow. These locations are used to monitor changing groundwater chemistry over time and distance along path of groundwater flow. Figure 7-1 (from AFCEE 2008) illustrates an example of a monitoring network for a biowall PRB. Side-gradient wells may be used to document that contaminant bypass around the ends of the PRB is not occurring. Downgradient locations are sampled to determine the effectiveness of the PRB in reducing contaminant concentrations.

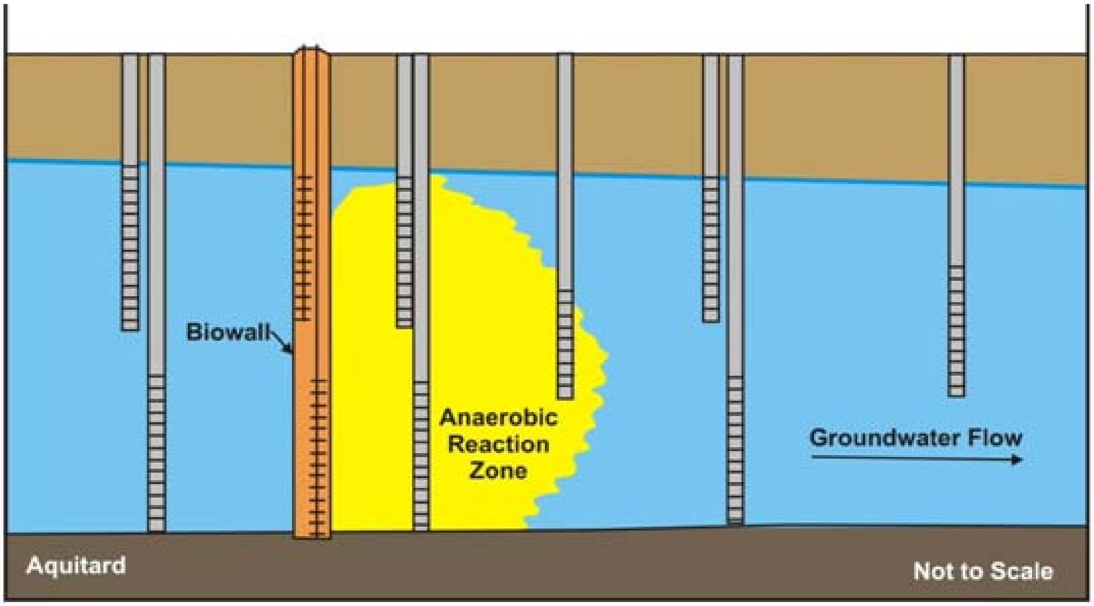

Figure 7-1. Cross-section of a monitoring well transect for a permeable mulch biowall.

Consideration should be given to the groundwater velocity and the desired frequency of performance monitoring when determining monitoring locations and spacing. Closer well spacing and/or less frequent monitoring may be warranted for sites with low groundwater velocity relative to sites with higher groundwater velocity. Rationale for well placement and examples of effective monitoring networks are described in AFCEE (2000) and Wiedemeier and Haas (2003).

Well screen intervals should be adequate to monitor the saturated zone treated by the PRB. Focused (sometimes referred to as "surgical") monitoring networks that target high-flow zones or areas of highest contaminant concentrations may be required to monitor contaminant treatment along preferential pathways. The presence of vertical hydraulic gradients, particularly where a lower confining layer is not present, may require monitoring wells screened at deeper depths to ensure there is no contaminant bypass beneath the PRB. For saturated zones of significant vertical thickness, it is useful to have wells screened at multiple depths to determine vertical hydraulic gradients to evaluate the potential for vertical groundwater flow and contaminant bypass over or under the PRB.

It is useful to have monitoring locations within the PRB (see Figure 7-2), as samples collected from within the PRB reactive media may be most representative of the processes occurring within the barrier. Depending on the width of the reactive zone and the reactive media employed, substantial changes in groundwater chemistry may occur from the upgradient to downgradient edges of the reaction zone.

Figure 7-2. Photo of a pilot-scale monitoring system, New York (prior to sheet pile removal to create a flow-through gate section).

As noted previously in this document, it is not uncommon to see higher reductions in contaminant concentrations within the PRB relative to downgradient locations due to desorption of contaminant mass from the native formation and back-diffusion of contaminants from low-permeability sediments downgradient of the PRB. While concentrations in downgradient locations should be used to determine the overall impact of the remedy on groundwater quality, samples from downgradient locations may not accurately reflect the rate and extent of degradation processes that are occurring within the treatment zone.

7.2.2 Monitoring Frequency and Duration

Most PRBs are operated as passive or low-maintenance systems, with performance monitoring typically conducted on a quarterly to annual basis. For biological PRBs, microbial growth and acclimation within the PRB may take 6–12 months or more for the system to achieve optimal performance. Frequent sampling at periods of less than a few months may yield unsatisfactory early results and result in an unjustified lack of confidence in the effectiveness of the system (AFCEE 2008).

Long-term sampling protocols and monitoring frequency should be optimized based on the more extensive and more frequent monitoring that is initially performed. For example, long-term performance monitoring of passive systems may be tied to annual sitewide monitoring programs for the duration of the PRB remedy.

7.3 Monitoring Hydraulic Performance

Monitoring hydraulic performance is intended to verify that the PRB is intercepting the contaminant plume without contaminant bypass. Conventional methods include measuring the groundwater potentiometric surface to evaluate changes in hydraulic gradient and direction of groundwater flow and measuring vertical hydraulic gradients as an indication of upwelling over the PRB or downward flow beneath the PRB. Potentiometric surfaces have the most value for assessing the impact of the PRB on both local and regional flow patterns, for example delineating features such as groundwater mounding. Tracer tests provide definitive results on a more local scale, but the scale of the measurement needs to be considered when interpreting or extrapolating trends to adjacent regions of the PRB and/or aquifer.

More advanced tools include borehole flow meters. A description of tools used to measure flow may be found on the U.S. Geological Survey (USGS) website.[5] These methods use a tool that is placed in an open borehole or within the screened interval of an existing monitoring well. Tools used to measure vertical flow include heat-pulse, electromagnetic, and mechanical (spinner) sensors.

Another method uses a tool permanently installed in a borehole that measures flow in three dimensions.[6] The tool is heated and measures changes in the three-dimensional direction of groundwater flow (vector flow) due to temperature variations induced by differing rates and directions of groundwater flow. A datalogger measures the changes in groundwater flow that occur over time. For example, this tool was used to evaluate a groundwater circulation well at an Air Force site at Cape Canaveral AFS, Florida (Parsons 2001).

Tracer studies may also be used to evaluate the permeability of the PRB and whether any groundwater bypass may be occurring. Tracer studies typically involve the addition of a conservative inorganic compound (e.g., sodium bromide or sodium iodide) to groundwater upgradient of the PRB, which is then measured in downgradient monitoring locations over time. For example, USEPA conducted a tracer study using sodium bromide to evaluate the direction and rate of groundwater flow across the OU-1 biowall PRB at Altus AFB, Oklahoma (Lu et al. 2008).

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[5] http://water.usgs.gov/ogw/bgas/flowmeter.

[6] www.hydrotechnics.com.

7.4 Concentration-Based Performance Monitoring Approaches

The primary performance measure for a PRB is a reduction in contaminant concentrations in groundwater to a specified remedial standard, including any regulated intermediate degradation products. Groundwater geochemical and microbial data also may be evaluated to determine whether redox and geochemical conditions have been modified as desired and to detect changes in environmental conditions that may reduce the efficiency of the PRB system.

7.4.1 Parameters for Groundwater Performance Monitoring

Groundwater is analyzed to evaluate performance and to guide O&M activities for PRB systems. Table lists typical groundwater analytes and parameters and the rationale for their use. Analytical methods and sampling requirements for most of these analytes can be found in AFCEE (2008) and ITRC (2005b). Analyses may also be performed on surface water samples if the contaminant plume discharges to a surface water body. Evaluation of these parameters is most useful after equilibrium conditions are attained.

Table 7-1. Parameters and rationale for groundwater performance monitoring

Parameter	Rationale
Primary contaminants	Reductions in contaminant concentrations are the primary measure of performance. Many compounds have regulated intermediate products that should also be analyzed.
Dissolved oxygen	Determine whether aerobic or anaerobic conditions exist. DO values <0.5 mg/L generally indicate an anaerobic pathway is possible.
Oxidation-reduction potential (ORP or Eh)	The ORP of groundwater reflects the relative oxidizing or reducing nature of the aquifer and the treatment zone.
pH	Aerobic and anaerobic processes are pH sensitive. Also a well-purging and secondary water-quality parameter.
Temperature and conductivity	Primarily used as well-purging parameters. The rates of both biological and chemical reactions are temperature dependent, and high conductivity may be an indication of high salinity, which may impact chemical precipitation or inhibit biological processes.
Terminal electron-accepting processes (TEAPs) • Nitrate • Manganese • Ferrous iron (Fe^{2+}) • Sulfate • Methane (CH_4)	Primarily for biological PRBs, as indicators of the predominant microbial processes that are occurring. Measures either the production of reduced species (Mn[II] and Fe^{2+}), the reduction of oxidized species (nitrate, sulfate), or the production of CH_4.
Major cations (Fe, Mn, Ca, Mg, Na, K)	Some metals may be more mobile under highly reducing conditions. May be required for compliance with secondary water-quality standards. May be used for geochemical modeling. Persistence of Fe^{2+} downgradient may be a concern for ZVI PRBs in settings close to surface water discharge.
Major anions (HS^-, Cl^-, NO_2^-, NO_3^-, SO_4^{-2}, PO_4^{-3}, CO_3^{-2})	May be used for geochemical modeling or to evaluate the potential for precipitation of minerals that may inhibit the reactivity of ZVI media.
Sulfide	By-product of sulfate reduction. Elevated concentrations of sulfide may inhibit dechlorinating microorganisms and may pose taste and odor problems.

Parameter	Rationale
Alkalinity	For biowalls, an indicator of biodegradation and buffering capacity of the aquifer, and an indicator of the precipitation of carbonate minerals in ZVI PRBs.
Carbon dioxide	By-product of both aerobic and anaerobic biodegradation processes.
Nitrite (NO_2^-)	By-product of denitrification of nitrate.
Chloride (Cl^-)	General water-quality parameter in high CVOC concentration settings may be used to evaluate mass balance.
Hardness and total dissolved solids	General water-quality parameter; used as an indication of secondary water quality.
Turbidity	Secondary water-quality parameter. Low turbidity is desirable to reduce analytical method interferences.
Dissolved organic carbon or total organic carbon	Indication of organic substrate available for biological metabolism. For biological PRBs, declining TOC levels in conjunction with elevated levels of contaminants may indicate additional substrate is required to sustain the treatment zone. May indicate the persistence of guar residuals if these methods used or ZVI PRB construction.
Total inorganic carbon (TIC)	TIC includes aqueous CO_2, carbonic acid, and total carbonate alkalinity. The distribution is a function of pH and an increase in TIC relative to background concentrations indicates zones with increased microbial activity.
Biological and chemical oxygen demand	Secondary water-quality parameters that may also be used as an indication of substrate demand. Alternate to TOC/DOC analyses.
Volatile fatty acids	Biodegradation breakdown products and fermentation substrates. Indicator of substrate distribution.
Phospholipid fatty acids	Indicator of bioactivity, measure of biomass, and characterization of the microbial community.
Dissolved hydrogen	Specialized analysis used to determine primary TEAPs. Hydrogen is the primary electron donor used in anaerobic dechlorination.
Nitrogen, phosphate, and potassium	Nutrients needed for microbial growth. May be needed as a substrate amendment for biological PRBs.
Ethane and ethane	The presence of ethane and ethene are indicative of reductive dechlorination of chlorinated solvents.
Sodium bromide or sodium iodide	Conservative groundwater tracers.

Groundwater samples are collected from locations upgradient of the PRB to establish pretreatment concentrations and from within and downgradient of the PRB to evaluate changes in contaminant concentrations and geochemistry. Groundwater analysis is conducted for the following reasons:

- **Reductions in contaminant concentrations.** Reductions in contaminant concentrations within and downgradient of a PRB are the primary performance metric.
- **Groundwater redox state.** Degradation processes require appropriate redox conditions. Groundwater ORP/Eh and relative changes in concentrations of inorganic compounds, native electron acceptors, and/or metabolic by-products may be used to determine the redox state and the abiotic and/or terminal electron-accepting processes (TEAPs) that are occurring.
- **Substrate availability (biological PRBs).** Soluble organic carbon is often measured to indicate the amount of organic substrate available for biological processes. TOC (unfiltered

samples) or DOC (filtered samples) are usually the most cost-effective measurement. DOC may be measured for ZVI PRBs to evaluate the potential for impacts from biological processes on the reactive media, for example from the degradation of guar gum.

- **Diagnostic tools.** When additional diagnostic information is needed to evaluate the performance of a PRB, molecular screening techniques and isotope fractionation can be used to supplement the data obtained from conventional groundwater analyses (Section 7.7).
- **Secondary water quality.** Secondary water-quality parameters may be analyzed if the aquifer is a potable drinking water supply (Section 7.8). In many cases it may be sufficient to document that secondary water quality is not adversely impacted at an appropriate location downgradient of the treatment area.

Many groundwater analyses are performed only by specialized laboratories (e.g., isotope fractionation and molecular screening). These analyses are based on standard operating procedures (SOPs) specific to the analytical laboratory.

7.4.2 Interpretation of Contaminant Data

Reductions in contaminant concentrations are the primary line of evidence used to demonstrate that degradation is occurring. Methods to assess the effectiveness of a PRB include evaluations of changing contaminant concentration over time or with distance through the reactive zone and an evaluation of the efficiency (rate) and extent of degradation. The use of vertical cross-section contour plots oriented along the path of groundwater flow is recommended to understand the vertical distribution and reduction of contaminants. In addition to evaluating contaminant concentrations in units of weight per unit volume (for example µg/L), other units of measure may be used to show that transformation is occurring, particularly for contaminants such as CVOCs or explosive/energetic compounds that degrade sequentially with regulated intermediate degradation products. These include the use of molar concentrations, chlorine numbers (for CVOCs), and calculating toxicity factors.

Evaluation of monitoring data should include assessment of whether contaminant mass loss may be due to degradation processes or due to nondestructive processes such as sorption, dilution, or dispersion. Data from upgradient wells and historical data trends may be used to account for the effects of natural attenuation over time.

Changes in contaminant concentrations

Reductions in post-installation contaminant concentrations relative to preinstallation baseline conditions or to concentrations upgradient of the PRB are used to show that the PRB is operating as expected. For chlorinated solvents or other contaminants that may degrade to regulated intermediate products, the evaluation may also include changes in concentrations of parent and intermediate products over time or distance through the reaction zone.

Evaluating trends and ratios of molar concentrations for CVOCs can often be more informative than evaluating changes in the parent/dechlorination product concentrations alone. The molecular weights of the various parent compounds and dechlorination products vary, with the dechlorination products having progressively lower molecular weights. As a result, the reductive transformation of a given mass of TCE, for example, does not produce the same mass of dichloroethene (DCE) (e.g., anaerobic dechlorination of 100 µg/L of TCE produces 74 µg/L of DCE).

Conversion of conventional concentrations (e.g., µg/L) to molar concentrations (mol/L) facilitates assessment of the degree to which sequential transformations occur. Decreases in the molar concentration of total chlorinated ethenes, for example, indicate that chlorinated ethene mass is being lost and that transformation of these compounds to nontoxic end products is occurring. The steps required to calculate molar concentrations and ratios to determine trends over time can be found in Section 6 of AFCEE, NFESC, and ESTCP (2004).

Concentration vs. time or distance

Plots of concentrations of parent compounds and dechlorination products over time or distance within the reaction zone are useful in evaluating the effectiveness of a PRB. Figure 7-3 (AFCEE 2008) depicts concentrations of individual compounds and the total molar concentration of chlorinated ethenes over distance along a flow path through a dual biowall PRB pilot test at the Ash Landfill, Seneca Army Depot Activity, New York, approximately 27 weeks after biowall installation (AFCEE 2008). Within the biowalls, the concentrations of TCE, cDCE, and VC are all reduced. However, the intermediate dechlorination products cDCE and VC are produced between the biowalls, perhaps due to desorption or back-diffusion of contaminant mass in native sediments between the two biowalls, with dechlorination limited to producing cDCE and VC.

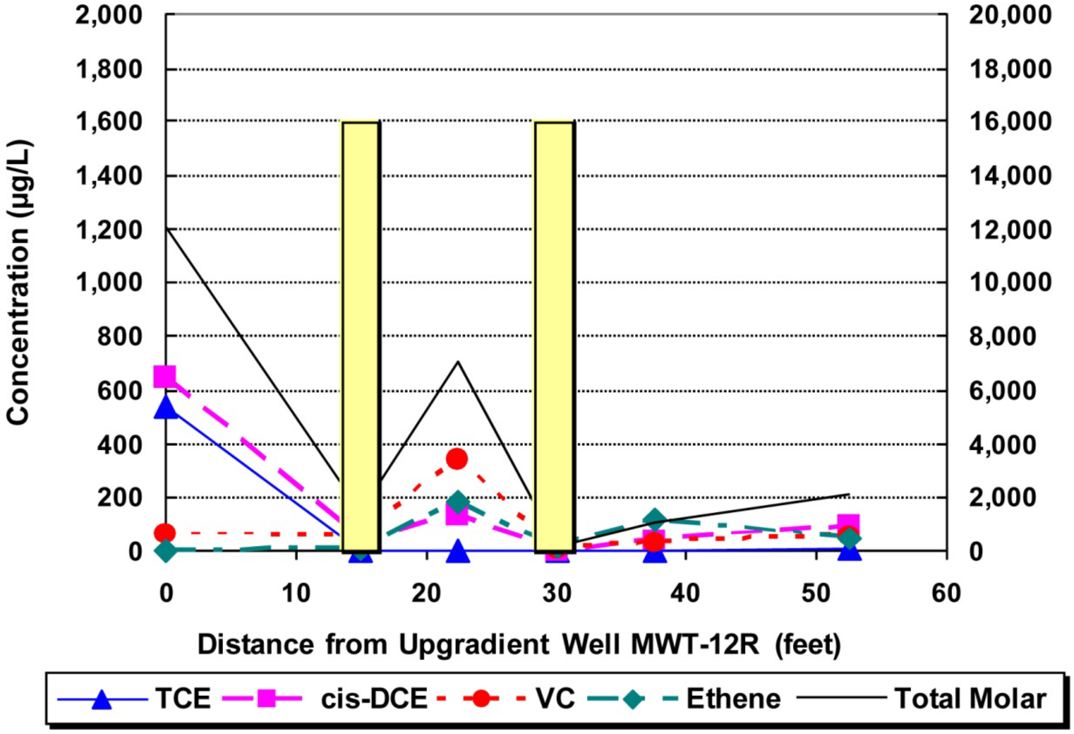

Figure 7-3. Concentrations of chloroethenes and total molar chloroethenes along the northern flowpath at 27 weeks.

The overall reduction in total molar concentrations of chlorinated ethenes between the upgradient location and the second biowall is apparent. The spike in total molar concentration between the two biowalls is predominately composed of VC. Increases in ethene/ethane are apparent, indicating that the biowall system has acclimated to highly reducing conditions and that sequential dechlorination is occurring. Total molar concentrations of chlorinated ethenes within the biowalls at the Ash Landfill site were much lower relative to locations outside of the biowalls. If TCE were being degraded by sequential reductive dechlorination to cDCE and VC alone, then the total molar concentration would be expected to remain steady across the biowall treatment zone. Because molar conservation of TCE and cDCE to VC and ethene was not observed within the biowalls for this site, it is possible that alternative anaerobic degradation processes (e.g., biogeochemical transformation) of chlorinated ethenes also may be occurring within the biowalls.

Changes in total molar concentration and molar fractions

A plot of the molar fraction or ratio of chlorinated compounds over time is another method used to determine whether degradation has been stimulated. This method is often employed when there is a constant or continuing source of contaminant mass entering a treatment system, such as a PRB. In this case, the total molar concentration may remain elevated due to a continuing mass influx, but an increase in the molar ratio of dechlorination products demonstrates that sequential anaerobic dechlorination is occurring.

Figure 7-4 (AFCEE 2008) is a plot of molar fractions of individual chlorinated ethenes and ethene/ethane for the same monitoring transect as shown in Figure 7-3. TCE and DCE are predominant contaminants upgradient of the first biowall, where they are dechlorinated to DCE and VC. Following the path of groundwater flow along the monitoring transect, the majority of the DCE and VC is converted to ethene between the first and second biowall. Within the second biowall, ethene/ethane accounts for over 80% of the total molar concentration of chlorinated ethenes plus ethene/ethane. Downgradient of the second biowall the relative percentage of DCE and VC rebound to over 20% of the total molar concentration, perhaps due to a residual source of contaminant mass in the sorbed phase mixing with untreated groundwater or a less robust reaction zone downgradient of the biowall trench.

Chlorine number plots

Chlorine number plots are another approach for evaluating the effect of anaerobic biodegradation processes, particularly the extent to which sequential degradation of PCE or TCE is occurring (AFCEE 2007). Similar to evaluating changes in the ratio of molar concentrations, calculating the chlorine number of the total chlorinated solvent concentration may indicate that transformation is occurring even if there is not a readily apparent reduction in overall concentration due to a continuing source.

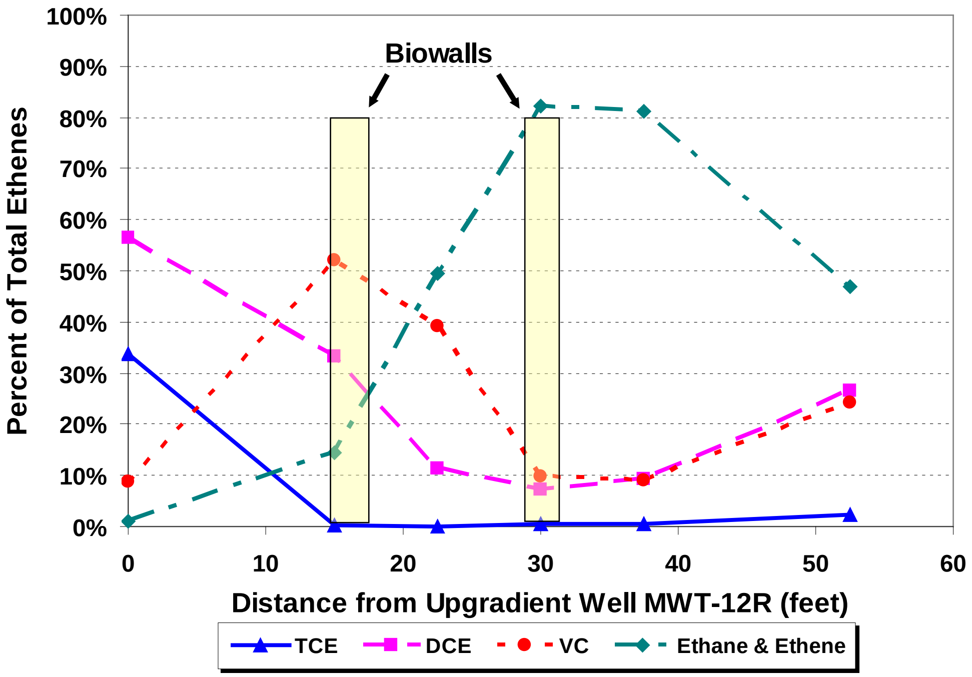

Figure 7-4. Molar fractions of chloroethenes and ethene/ethane for the northern transect at 27 weeks.

Toxicity reduction

Sequential reductive dechlorination of chlorinated solvents can produce regulated intermediate dechlorination products that may persist in groundwater for extended periods. A common concern is that these intermediate dechlorination products—specifically VC—may pose an equal or greater risk to human health and the environment than the parent compounds. However, the potential for production of VC often overshadows the overall reduction of toxicity that may be achieved. The remediation selection processes specified by USEPA requires that each candidate technology or approach be evaluated against nine criteria, including long-term effectiveness and the reduction of contaminant toxicity, mobility, and volume over time (USEPA 1988). Even when DCE and VC are present, large reductions in toxicity can be achieved without expansion of the contaminant plume. Accordingly, toxicity reduction is an important metric for evaluating site remedies (Downey et al. 2006).

An example of calculating toxicity requirements can be found in Downey et al. (2006) and AFCEE (2008) for two bioremediation applications at Altus AFB, Oklahoma. Even though concentrations of VC increased by over an order of magnitude, reductions in total toxicity after 2 years ranged from 93%–95%. Although VC was produced at these sites, the footprint of the VC plume has been confined to well within the footprint of the initial contaminant plume.

Degradation rate calculations

Calculation of degradation rate constants prior to and after PRB installation may be useful to demonstrate the effectiveness of the application and to compare to rates used in the PRB design (Section 5.5.1). Estimates of degradation rate constants can be calculated by many methods;

USEPA (1998b) and Newell et al. (2002) provide examples and discussion for estimating biological degradation rate constants. As an example, Ahmad et al. (2007) describe the use of a steady-state analytical model based on the advection-dispersion equation developed by Van Genuchten and Alves (1982) to calculate first-order degradation rates from biowall case studies.

Most methods to calculate degradation rates assume that steady-state conditions (hydraulic, geochemical, biological, and contaminant) exist (e.g., the method of Buscheck and Alcantar 1995). This may not be a valid assumption, particularly for biological PRBs where microbial populations are continually acclimating and evolving. However, a reasonable approximation of degradation rates may be calculated if geochemical and microbiological conditions stabilize to a moderate degree.

7.5 Mass Discharge Approach

Another approach to evaluating the ability of PRB to reduce contaminant mass is that of calculating mass flux and mass discharge of the plume as groundwater migrates through the PRB. As defined by ITRC (2010), mass flux is a rate measurement specific to a defined area, expressed as mass/time/area (e.g., $g/d/m^2$). Mass discharge is an integrated mass flux estimate (the sum of all mass flux measurements across an entire plume) and represents the total mass of any solute conveyed by groundwater through a defined plume. Mass discharge is therefore expressed as mass/time (e.g., g/d).

Benefits of a mass discharge approach for monitoring PRBs includes improved evaluation of preferential flow paths and potential areas of contaminant bypass. A typical approach is to use multiple well transects to measure mass flux at different planes oriented perpendicular to groundwater flow along a contaminant plume (i.e., both upgradient and downgradient of a PRB). Mass discharge is calculated by combining concentration data with the Darcy velocity of groundwater. Measuring mass flux is monitoring intensive due to the density of monitoring locations required and the quantity of data that must be collected. The most difficult aspect of this monitoring is determining the Darcy velocity at each sample point. Therefore, careful consideration should be given to the relative benefit of a mass discharge approach compared to the increase in cost of monitoring.

Several mass flux/mass discharge field demonstrations have been conducted by ESTCP. See ITRC (2010) for a summary of the ESTCP demonstrations and the methods used to measure mass flux and calculate mass discharge.

7.6 Monitoring PRB Geochemistry and Microbiology

The geochemical conditions that are produced within a PRB are important in evaluating performance and may be useful in predicting the long-term performance of a PRB system. Analysis of the reactive media or soil (for injected PRBs) may also be conducted to evaluate PRB performance although these evaluations are conducted much less frequently.

Assessment of the microbial processes that occur within biological PRBs is commonly conducted to evaluate how the organic substrate is being used and the potential for complete dechlorination of CVOCs. Microbial assessments of ZVI PRBs may be conducted to evaluate the impact of biological activity on the reactivity of the iron media or, conversely, the effect of ZVI-induced changes in groundwater chemistry on the microbial community. Microbial activity also has a role in the performance of PRBs using combination organic/iron materials (e.g., EZVI or EHC). The following sections describe the parameter and analytes most useful for monitoring ZVI and biological PRB performance. Other reactive media (e.g., apatite or zeolites) may have their own unique monitoring parameters.

Field studies (Wilkin and Puls 2003; Sass et al. 2002; Phillips et al. 2003) have shown that the strongly reducing and high pH conditions within ZVI PRBs cause several inorganic constituents to precipitate onto the iron. This effect can lead to formation of coatings on the iron surfaces that may reduce reactivity (Section 5.3.1 and Section 8). Therefore, monitoring of anion and cations within a ZVI PRB is often performed in addition to measurement of the concentrations of target contaminants, degradation products, and measurement of the groundwater redox state. For ZVI PRBs designed to treat CVOCs, major cations typically include iron, manganese, calcium, magnesium, sodium, potassium, and silicon. Major anions typically include HS^-, Cl^-, NO_2^-, NO_3^-, SO_4^{-2}, PO_4^{-3}, and CO_3^{-2} (Table 7-1). When ZVI or other media are used for trace metals, obviously any metals of concern (arsenic, chromium, etc.) should be monitored. For any PRB, metals that could possibly be remobilized in the pH-Eh conditions established by the reactive media (e.g., naturally occurring arsenic) should also be monitored.

Microbial monitoring of a ZVI PRB is typically performed to evaluate microbial communities in the iron media. Analytical parameters that may be monitored to determine the impact of microbial growth may include PLFA analysis to measure total biomass and the primary types of bacteria present (particularly sulfate-reducing and/or metal-reducing bacteria) and DOC as an indication of the substrate available for microbial activity (Table 7-1). pH and Eh conditions should also be measured, as high pH and low Eh within the ZVI media may inhibit microbial activity and reduce the potential for biofouling. If guar is used during PRB construction (Section 6), then microbial assessments in the aquifer both upgradient and downgradient of the PRB may be worthwhile to help gauge the effect of guar residuals on microbial activity and resultant aquifer geochemistry.

7.6.2 Field Measurements of ORP and Eh Values

The ORP of groundwater is a measure of electron activity and is an indicator of the relative tendency of a solution to accept or transfer electrons. Therefore, measurement of the ORP of natural groundwater reflects the electron transfer activity of the prevailing TEAPs that are occurring. Figure 7-5 illustrates the redox potentials at which common reduction half reactions for native electron acceptors occur, measured as Eh, the voltage measured relative to a standard hydrogen electrode (SHE).

The ORP of a groundwater sample can change significantly within a short time following sample acquisition and exposure to atmospheric oxygen; therefore, this parameter is measured in the field using a flow-through cell during purging of a monitoring well. The standard reference for ORP is set at 0.0 mV for a SHE. However, the use of hydrogen electrodes in the field is not practical, and field meter readings for ORP are typically measured against a silver/silver chloride

(Ag/AgCl) reference electrode. Redox potentials for reactions listed in the literature (e.g., Thauer, Jungermann, and Decker 1977; Bouwer 1992) involving common groundwater electron acceptors are usually reported as Eh, which is defined as a voltage reading against a SHE.

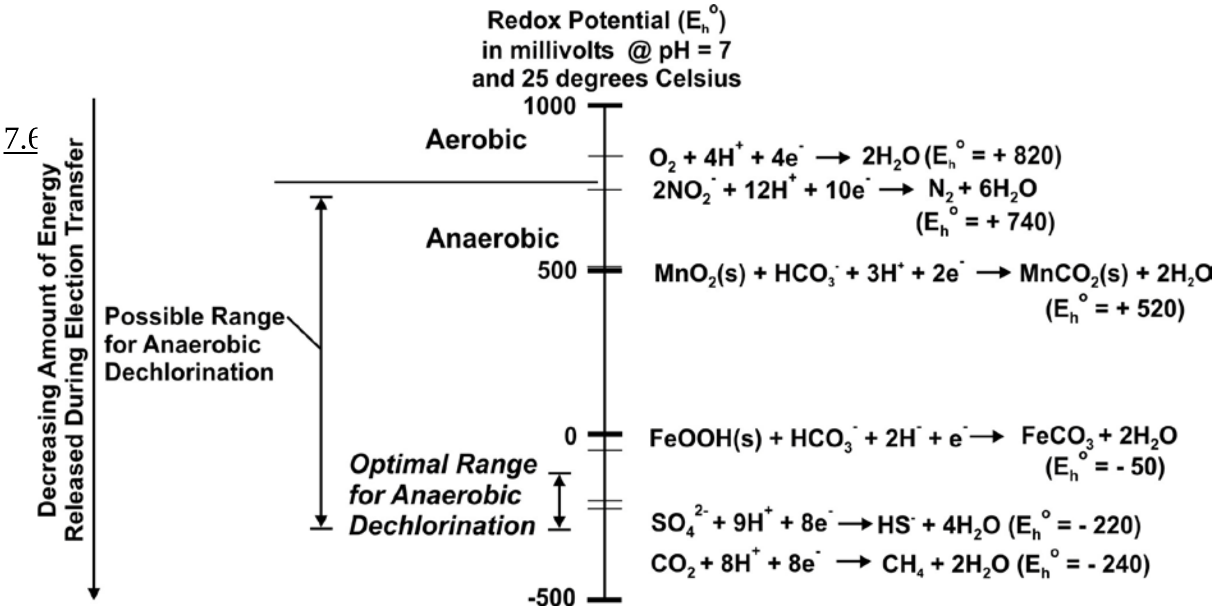

Figure 7-5. Oxidation-reduction potentials for various electron-accepting processes.
(Modified from Bouwer 1992)

The practitioner should be aware of the reference electrode used to measure ORP in the field when comparing field ORP measurements to redox potentials listed in the literature. Redox potentials measured with an Ag/AgCl electrode are approximately 200 mV less than the Eh value, depending on the fluid used to fill the Ag/AgCl electrode.

As an example, the potential of Zobell solution used for calibration versus an Ag/AgCl electrode is +228 mV, which is the value typically used to calibrate the field meter. However, Zobell solution measured versus a SHE yields +448 mV (Eh). Some field meters using an Ag/AgCl electrode allow the user to specify +448 mV as the calibration value, in which case the meter automatically compensates the Ag/AgCl reading to yield Eh measurements. ORP is also temperature dependent, which is usually not compensated for with field meters. Therefore, documentation of the type of field meter, electrode, calibration solution, and calibration procedure used, as well as the temperature of the groundwater during measurement, are essential to provide useful ORP readings. Manufacturer's equipment manuals and tech notes are available to provide additional information (e.g., see https://www.ysi.com/portal/page/portal/YSI_Environmental/Support).

Measurement of ORP is further complicated in that ORP is a nonspecific measurement, which means that the measured potential is reflective of the combination of all the effects of the dissolved species in groundwater. Therefore, ORP is useful only when combined with additional lines of evidence (i.e., changes in concentrations of native electron acceptors between background conditions and the anaerobic treatment zone) to determine the predominant TEAPs that are occurring.

7.6.3 Monitoring of Biowall PRB Biogeochemistry

Biowall PRBs require specific biogeochemical conditions to operate efficiently. For biological reductive dechlorination to take place efficiently, the groundwater conditions should be favorable to sulfate-reducing or methanogenic bacteria. These favorable conditions include the following:

- depleted concentrations of DO, nitrate, and sulfate
- elevated concentrations of Fe^{2+}, Mn^{2+}, CH_4, ethene, ethane, hydrogen, CO_2, Cl^-, and alkalinity
- reduced Eh (<–0 mV)

Other areas of interest include the following:

- degradation products
- microbe type and concentration
- substrate (DOC or VFAs) and nutrient availability

These parameters are most useful for determining when a biowall PRB may need to be optimized by replenishment of additional organic substrate or other amendments (Section 8.3.3).

7.6.4 Analysis of Reactive Media and Soil for Iron and Biowall PRBs

Sampling and analysis of the reactive media or soil are conducted to evaluate impacts on reactivity or precipitation of reactive or passivating mineral phases. Table 7-2 lists examples of analytes and parameters for reactive media or soil. Normally, this monitoring is conducted only when contaminant removal efficiency within the PRB begins to decrease and the cause of the reduced efficiency must be determined. Analytical methods and sampling requirements for most of the analytes listed in Table 7-2 can be found in AFCEE 2008.

Table 7-2. Possible analytical protocols and rationale for reactive media

Parameter	Rationale
Primary contaminants	Screen soil and reactive media for disposal or for potential buildup of contaminants on material surfaces.
Fraction organic carbon	Used to calculate sorption of contaminants to the soil matrix.
Total iron and manganese	For biowalls, evaluate competing electron acceptor mass and potential for formation of metal sulfides under anaerobic conditions.
Acid volatile sulfide	Measures the amount of sulfide present in the form of reactive metal monosulfides, predominately as iron monosulfide (FeS).
Chromium extractable sulfide	Measure the total amount of sulfide. Measured after acid volatile sulfide extraction, it is a measure of how much elemental sulfur and metal disulfides (Fe_2S) are in the aquifer matrix.
Bioavailable iron and manganese	Measures the amounts of ferric iron(III) and Mn(IV) in the solid phase that are bioavailable as competing electron acceptors.
Strong acid solution Fe(II) and Fe(III)	Measures the total amount of ferric and ferrous iron in the solid phase. A relative measure of the amount of reduced iron in the aquifer matrix.

Parameter	Rationale
Total carbonate	Determine the carbonate content in ZVI as a measure of porosity loss and mineral coating
Nitrogen, phosphorous, and potassium	Determine presence of essential nutrients for microbial growth.
X-ray diffraction	Determine mineral crystalline phases.
Scanning electron microprobe	Help identify minerals and crystalline forms of precipitates and corrosion products.

Coring of the reactive media can be employed to better understand compliance or performance problems with the PRB system. Coring of the media is not a technique that should be employed on a regular basis. It could, however, play a role in determining the source and extent of precipitate formation, clogging of the reactive media, short-circuiting, loss of reactive sites, or other related problems. Core samples can be collected both from a vertical profile and from an angled profile. The vertical profile can provide information on the characteristics of the in-place reactive media at a specific location in the PRB, while angled cores can provide a profile of the changes in the reactive media in the horizontal flow direction in the direction of flow. When evaluating iron media, the initial precipitate formation occurs at the upgradient interface, so angled cores have the ability to collect iron from this interval. A direct-push device can be used for core collection. When coring iron media, a conductivity probe can be used to identify the location of the highly conductive iron media prior to sample collection.

The use of an inner plastic sleeve to collect media allows collection of intact cores that can be preserved until sample analysis. Once collected, the cores should be protected from exposure to oxygen that could result in further degradation of the core. Upon retrieval, the inner plastic sleeve can be capped and sealed. Preservation methods include storage of cores in nitrogen purged bags, the use of oxygen-scavenging material, along with icing to 4°C, or freezing the cores until analysis. Boreholes should be backfilled with fresh reactive media.

Various techniques, including the use of scanning electron microscopy, are available to determine the presence of precipitates or biomass. Such techniques can be useful in providing high-resolution visual characterization of mineral precipitates on the ZVI particles. The spatial relationship between the precipitates can be evaluated, and estimates of the percent loss of pore space can be made. Scanning electron microscopy equipped with energy-dispersive X-ray spectroscopy can also be used to determine the composition of the surface precipitates on a semiquantitative basis. X-ray diffraction (XRD) can be used to determine the crystalline phases of the precipitates on the iron surface. Inorganic carbon analysis and sulfur analysis can also be conducted on the cores to determine the composition of these two elements in the precipitate formation.

Microbiological analyses can also be conducted on the iron cores. This information can provide data on total microbial biomass as well as the presence or absence of dechlorinating, iron-oxidizing, or sulfate-reducing bacteria.

Iron cores collected after a few years of field operation are typically analyzed by specialized methods. At Moffett Field, Elizabeth City, and several other sites where detailed examination of the iron medium has been conducted (see Appendix A case summaries), the types of precipitates identified have been similar and consist primarily of carbonates, hydroxides, sulfides, oxides, and silicates of calcium, iron, and, to some extent, magnesium. In addition to “bulk” analyses for carbonate content, XRD can be used to determine crystalline mineral phases, and scanning electron microscopy to identify specific compounds on the iron grains.

Sand and mulch biowall mixtures have been analyzed for bulk iron and sulfide/sulfur content (AFCEE 2008), and one study has been conducted using a scanning electron microprobe to identify the reactive iron sulfide species that have formed for biowalls at Altus AFB, Oklahoma; Seneca Army Depot, New York; and Dover AFB, Delaware (Lebrón et al. 2010). Figure 7-6 is a photomicrograph showing framboidal forms of iron sulfide (pyrite) that have formed in a biowall at Altus AFB, Oklahoma (Lebrón et al. 2010).

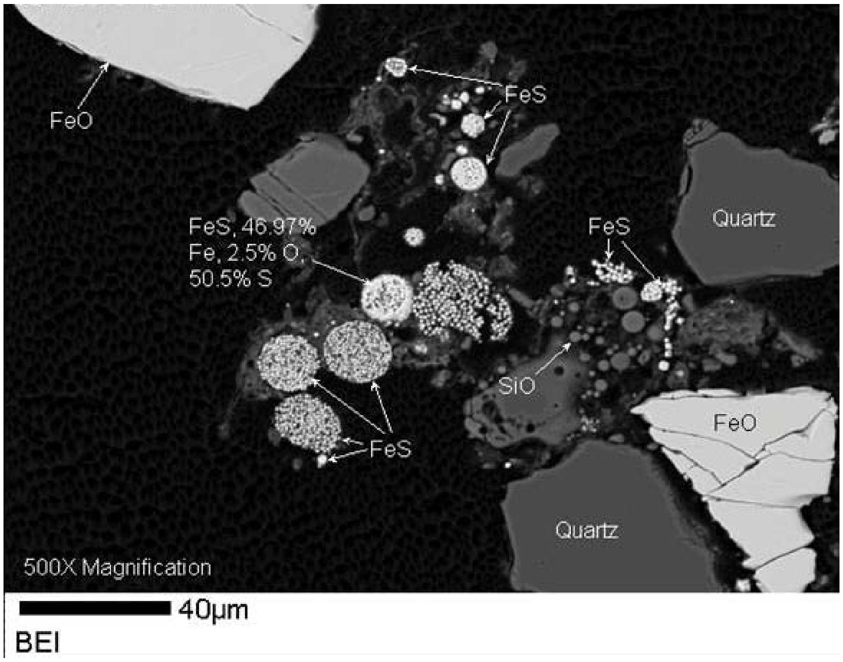

Figure 7-6. SS-17 column study sample showing framboidal forms of iron sulfide (pyrite), Altus AFB, Oklahoma.

7.6.5 Assessment of Biogeochemical Transformation in Biowall PRBs

Biogeochemical transformation processes within a PRB rely on the production of biogenically formed minerals that react with the contaminants as they flow through the PRB. Biogenically formed minerals are created in response to reactions such as biological iron and sulfate reduction and are particularly important, as these minerals are continuously replenished. Some of the minerals that can be biogenically formed and have been found to degrade CVOCs such as TCE at the laboratory-scale include the following: FeS (Butler and Hayes 1999, 2001; Jeong and Hayes 2007), troilite (Sivavec, Horney, and Baghel 1995), pyrite (Weerasooriya and Dharmasena 2001, Lee and Batchelor 2002a), magnetite (Lee and Batchelor 2002a, Ferrey et al. 2004), and green rust phases (Lee and Batchelor 2002b, Christianson and Stipp 2003, Maithreepala and Doong 2005).

The evaluation of the occurrence of biogeochemical transformation processes focuses on the mineralogy and surface area of the reactive minerals using the following techniques:

- extraction tests to measure the total concentration of differing valance states of iron and sulfur minerals
- saturation state assessment using a geochemical model or Eh-pH diagrams
- microscopy techniques to evaluate the mineral forms present

- XRD to measure concentrations of individual iron and sulfur minerals

The identity of the biogenically formed minerals within a mulch wall is important because some minerals react with the contaminants much faster than others. The generally accepted order is as follows (Lebrón et al. 2010):

Siderite ($FeCO_3$) < magnetite (Fe_3O_4) < green rust (ferrous/ferric iron oxyhydroxide) < pyrite (FeS_2) < mackinawite (FeS)

A PRB system targeting biogeochemical transformation processes should be optimized for sulfate and iron reduction under optimal Eh and pH conditions to produce iron monosulfides. Such conditions include sufficient organic carbon, influent sulfate, and a supply of easily reduced iron minerals within the wall, such as iron oxyhydroxides, hematite, or magnetite (e.g., present within the river sand used in most mulch formulations). In addition, the pH should be >6.0, as shown in Figure 7-7.

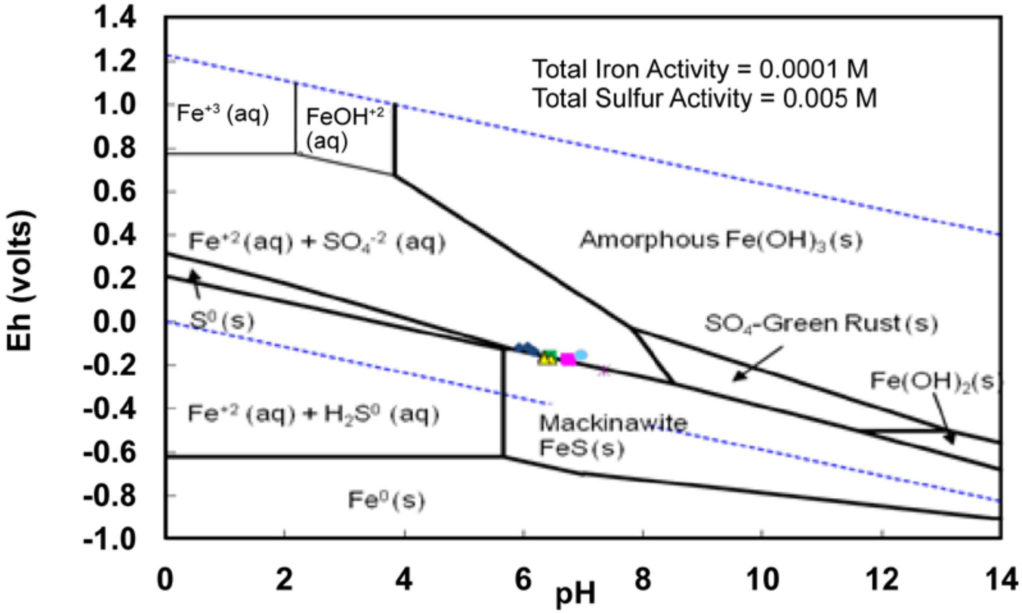

Figure 7-7. Eh-pH diagram of the iron sulfur system at 25°C and 1 atmosphere pressure. Symbols represent data from the systems evaluated in Lebrón et al. (2010) and indicate equilibrium with respect to mackinawite.

The evaluation of the saturation state is determined either using an equilibrium geochemical model such as PHREEQC (Parkhurst and Apello 1999), which requires a complete inorganic chemical analysis of the pore water within the wall or plotting the Eh and pH of the pore solutions on an Eh-pH diagram such as Figure 7-7. Dissolved iron and total dissolved sulfur concentrations are also required to construct the diagram.

Iron sulfides can be determined using acid volatile sulfide (AVS) and chromium-reducible sulfide (CrRS) extractions (Table 7-2). The AVS analysis is useful for discriminating between iron monosulfides (mackinawite, pyrrhotite, and troilite) and greigite (Fe_3S_4), which dissolve at low pH, and the iron disulfides (pyrite and marcasite), which are stable at low pH (Morse et al. 1987, Schoonen and Barnes 1991, Anderko and Shuler 1997). The iron disulfides are quantified using the CrRS test on the residual material remaining following the AVS test. However, the results of the sulfur extractions should be viewed with caution as fine-grained pyrite can dissolve during the AVS test and greigite dissolution has been found to be incomplete (Cornwell and Morse 1987). In addition, dissolved sulfides or aqueous FeS clusters can account for the majority of the AVS analysis (Morse and Rickard 2004).

Other analyses, such as XRD, can be used if the phases are crystalline and if the concentrations are high enough. Generally, iron phases must be present at concentrations of a few percent (~2%–5% for an XRD with a copper source) to be reliably identified using XRD. As biogenically formed minerals are often amorphous and are present at relatively low concentrations, XRD may not be an appropriate technology for this purpose. The grain size of the biogenically formed minerals is important because finer-grained materials have higher specific surface areas (surface area per mass) compared to coarser materials. Microscopy techniques are generally required to determine the grain size and may be impractical for routine performance assessments given the cost and expertise required. However, in cases where the performance is poor despite the presence of iron sulfides (as determined via AVS and CrRS analyses), microscopy techniques may be the only option for troubleshooting the system (Lebrón et al. 2010).

7.7 Advanced Monitoring Tools

Monitoring tools have been developed to assess the presence of microbes capable of facilitating the degradation of specific contaminants (e.g., *Dehalococcoides* sp.) and other evidence that degradation is being enhanced (e.g., isotope fractionization due to degradation by both abiotic and biological processes). This section describes the use of MBTs and CSIA and how they are used in evaluating the performance of PRBs.

7.7.1 Molecular Biological Tools

MBTs are generally used to evaluate whether the desired microorganisms that facilitate contaminant degradation are present and active. MBTs that analyze for *Dehalococcoides* species (or other dechlorinating microorganisms such as *Dehalobactor*) are useful to indicate whether complete dechlorination of chlorinated ethenes (PCE, TCE, DCE, and VC) to ethene is likely to occur (Stroo et al. 2006). MBTs are most likely to produce useful results after the growth of anaerobic microorganisms has been stimulated. Several MBTs are commercially available for *Dehalococcoides* and other dechlorinating organisms. A USEPA method for assessing *Dehalococcoides* organisms is not currently available, but efforts to standardize the techniques are being funded by the Strategic Environmental Research and Development Program (SERDP). ITRC is also developing a technical and regulatory guidance document on the use of molecular diagnostic tools.

Other MBTs can be used to examine the total microbial community in the aquifer and/or test for multiple dechlorinating bacterial populations. Note that the detection of specific populations such as *Dehalococcoides* may be subject to false negatives if the population of interest is not predominant in the overall community. In subsurface environments amended with organic substrates, high concentrations of iron-reducing, sulfate-reducing, and fermentative populations may mask the detection of relatively low concentrations of dechlorinating organisms.

7.7.2 Compound-Specific Isotope Analysis

CSIA may help determine whether a compound has undergone a chemical or biological transformation rather than a nondestructive physical process such as dilution or sorption. Recent USEPA guidance (USEPA 2008b) describes the use of CSIA in evaluating degradation of chlorinated solvents, aromatic petroleum hydrocarbons, and fuel oxygenates (e.g., MTBE). Because the use of CSIA for groundwater remediation is a relatively new approach, there are no widely accepted standards for accuracy, precision, sensitivity, and representativeness. The USEPA guidance document is an important first step in addressing best practices for sampling and analytical quality assurance.

CSIA may also help to elucidate the degradation pathways that are occurring. The degree of isotopic enrichment between biotic and abiotic processes may be sufficient in some cases to differentiate the processes. As an example, CSIA may provide valuable data at sites where multiple chlorinated solvents are degrading to VC or other compounds of concern (e.g., Hunkeler, Aravena, and Cox 2002; Hunkeler et al. 2005). CSIA data can be used in conjunction with chemical concentration data or may provide an additional line of evidence supporting results from other studies. For example, CSIA was used to evaluate the effects of a guar-based construction method on observed geochemistry in and around a ZVI PRB in California (Lima et al. 2009).

North American providers of CSIA services for aquifer samples include several leading universities (e.g., University of Oklahoma, University of Toronto, University of Waterloo), national government laboratories (e.g., Argonne and Livermore), and commercial laboratories (e.g., Microseeps, Inc.).

7.8 Downgradient Water Quality

The objective of a PRB is to restore groundwater quality downgradient of the PRB to compliance levels and to beneficial use. These objectives are not always realized, even though the primary contaminant(s) may be reduced to compliance levels within the PRB. Two common concerns of PRB systems are the production and persistence of toxic intermediate degradation products and impacts to secondary water quality.

7.8.1 Downgradient Persistence of Contaminants

Many compounds such as PCE and TCE adsorb into organic matter within the aquifer matrix or diffuse into low-permeability sediments. It is not uncommon for up to 80% or more of the mass of chlorinated solvents to be sorbed to the aquifer matrix (Cohen and Mercer 1993). PRBs may degrade contaminants in the aqueous phase as they pass through the PRB, but a significant amount of mass may remain within the downgradient aquifer.

Enhanced desorption has been observed to occur in the presence of elevated levels of soluble organic carbon in groundwater (Payne et al. 2001). For biological PRBs, soluble organic carbon is often released to the downgradient aquifer. The anaerobic conditions that are produced often result in the dechlorination of desorbed PCE and TCE to cDCE and VC. Less chlorinated compounds are more soluble and less hydrophobic. The organic carbon partition coefficient (K_{oc}), which defines the distribution of CAH mass between the sorbed and aqueous phases, also decreases as the level of chlorination decreases. As anaerobic dechlorination proceeds, each successive dechlorination product is more soluble and less susceptible to adsorption than the previous compounds in the sequence. This tendency may result in an increase in aqueous-phase concentrations of less-chlorinated dechlorination products (Sorenson 2003).

Back-diffusion of groundwater contaminants from low-permeability sediments may also occur due to the concentration gradient created between clean groundwater migrating out of the PRB and contaminated groundwater within low-permeability sediments or dead-end pore spaces. The time frame for contaminants to diffuse from these low-permeability sediments may be years to decades, particularly for older plumes (Sale and Illangasekare 2003). This condition is often the cause for the "tailing" effect seen with many groundwater remediation technologies where concentrations may decrease only to levels close to or above remedial targets such as MCLs.

The effects of desorption and back-diffusion often mask (e.g., cause underestimation of) the amount of degradation that has occurred within the upgradient PRB. Because contaminant mass is being removed from the aquifer system, a reduction in concentrations downgradient of the PRB should ultimately (albeit gradually) be observed over time. However, the time frame for these reductions to occur may make achieving performance or compliance objectives downgradient of the PRB problematic.

7.8.2 Secondary Water Quality

The term "secondary water quality" is used here to refer to water quality issues or concerns apart from the primary contaminants being treated that result from addition of reactive media and organic substrates to the subsurface. Table 7-3 (Parsons 2010b) lists some of the common parameters monitored during in situ remediation and associated federal water quality standards. This list is not inclusive, as many USEPA regions and state agencies enforce additional water quality standards. Several USEPA Region 9 Regional Screening Levels (RSLs) are included in Table 7-3 as examples.

Practices to mitigate secondary water-quality issues include the following:

- Site screening to identify site-specific potential for secondary water issues. Examples may include characterizing the iron, manganese, and heavy-metal content of aquifer sediments and evaluating the buffering capacity of the aquifer (pH and alkalinity).
- Determining the background concentrations of secondary water-quality parameters and the potential use of the impacted groundwater. Groundwater at many sites is not classified as a drinking water aquifer, and in these cases secondary water-quality criteria may not apply.
- For biological PRBs, it is beneficial to provide a more uniform distribution of substrate without "spikes" of highly concentrated substrate solutions. Adding a buffering amendment to control pH may also be beneficial; however, care must be taken as buffering may cause fouling especially at sites with metals contamination.
- Providing for an adequate redox recovery zone downgradient of the PRB treatment zone.

Table 7-3. Secondary water-quality parameters subject to regulatory compliance

Compound or element	Molecular formula	USEPA MCL (mg/L)[a]	USEPA secondary standard[b] (mg/L)	USEPA Region 9 RSLs for tap water (mg/L)
Volatile organic compounds				
Acetone	C_3H_6O	--	--	5.5
Carbon disulfide	CS_2	--	--	1.0
Isobutanol	$C_4H_{10}O$	--	--	1.8
Methyl ethyl ketone (2-butanone)	C_4H_8O	--	--	7.0
Total trihalomethanes (includes chloroform)	--	0.080	--	
General water-quality parameters				
Nitrate (as nitrogen)	NO_3^-	10	--	10
Nitrite (as nitrogen)	NO_2^-	1.0	--	1.0
Sulfate	SO_4^-	--	250	--
Chloride	Cl^-	--	250	--
pH	--	--	6.5–8.5	--
Total dissolved solids	--	--	500	--
Odor (e.g., sulfide)	--	--	3 threshold odor number	--
Metals/inorganics				
Arsenic	As	0.01	--	0.045
Selenium	Se	0.05	--	0.18
Iron	Fe	--	0.3	11
Manganese	Mn	--	0.05	0.88

[a] USEPA MCL = USEPA maximum contaminant level.

[b] National secondary drinking water regulations are nonenforceable guidelines; however, states may choose to adopt them as enforceable standards.

In many cases, providing a downgradient redox recovery zone is sufficient. This is readily accomplished at many large DOD/DOE facilities but may be more difficult to incorporate at small industrial or commercial sites.

8. LONGEVITY

What's New?

All of it is new!

The goal of a PRB is to intercept a groundwater contaminant plume and prevent it from migrating to downgradient receptors. The interception generally involves the capture of a targeted portion of the groundwater and transformation of dissolved contaminants to less toxic or less mobile products [e.g., conversion of TCE to ethene or conversion of Cr(VI) to Cr (III)]. The PRB, therefore, has both hydraulic capture and reactivity functions. Implicit in the hydraulic capture function is the need to provide the contaminants with sufficient residence time for the desired reactions to occur. Longevity refers to the ability of a PRB to sustain these functions (hydraulic capture, residence time, and reactivity) in the years and decades following installation. Because PRBs passively address plumes that may persist for years or decades, there is interest among past and future users of the technology and regulators in determining how long PRBs will continue to retain the designed (or at least, a desirable minimum) level of hydraulic capture and reactivity without requiring major maintenance or replacement of the reactive media.

8.1 Introduction

For ZVI PRBs there is 15 years of laboratory and field experience to draw upon; mulch biowalls have a field history of 8 years. Since 2005, when the previous ITRC guidance was issued, a fair amount of progress has been made on these two media (ZVI and mulch) in understanding the performance, limiting events, or processes that limit the longevity of PRBs. For other emerging reactive media with a shorter history, longevity projections may have to be made when long-term data is available based on scientific judgment and understanding of the media and contaminants involved.

Inevitably, all long-term treatment systems age over time, and PRBs are no exception. With pump-and-treat systems, for example, pumps may wear out, and chemical and/or biological fouling may reduce extraction well performance over time. On a periodic basis, pumps may have to be repaired or replaced, and wells may have to be redeveloped or replaced; this periodic maintenance is usually anticipated and factored into the economic expectations of the technology. With PRBs, on the other hand, the economic case for the required capital investment depends on sustained passive performance over a number of years. Modification and/or replacement of a PRB or the PRB media can be relatively expensive.

Failure of a PRB is said to occur if it fails to meet some minimum performance requirements in terms of hydraulic capture, residence time, and reactivity. A certain inevitable loss of performance over time may be acceptable, even after the designed performance of a new PRB starts declining. In an ideal situation, the aging process of a PRB moves in tandem with the declining strength of the plume (or declining strength of the source feeding the plume). However, field evidence from many ZVI and mulch PRBs indicates that this may not be the case. Therefore, it is important that on a site-specific basis, site owners and regulators determine the design and minimum expectations of a PRB.

This section focuses on laboratory and field experience that sheds some light on the factors that contribute to the loss of hydraulic and reactive performance of PRBs over time and what (if anything) can be done to mitigate some of these factors. Key findings for ZVI and mulch PRBs are summarized in Boxes A and B, respectively. Evidence continues to be gathered on other media that are relatively new.

8.2 Longevity of ZVI Barriers

The first full-scale PRB application occurred in 1994 to treat a TCE plume at the Intersil Site in Sunnyvale, California. Since then, more than 200 PRBs have been installed in different parts of the world. Many are reported to be performing acceptably although problems have been reported at a few sites. Despite this vast collection of sites, longer-term performance aspects of PRBs are still a source of some uncertainty in planning future applications.

There is an uneven set of information available for studying the longevity of ZVI PRBs. In the early years of the PRB technology (1994–2004), many laboratory-scale investigations reported on the various reactions that potentially affect the aging process of the ZVI in a PRB. Since the previous ITRC guidance was published in 2005, many newer laboratory studies have continued to study the types of reactions and reaction products that occur in ZVI PRBs and that may affect their longevity. However, field data that could potentially shed more light on how laboratory findings play out in the practice are relatively sparse in recent years for a variety of reasons.

In the early years of the technology, many field PRBs were installed as pilot applications; many of these pilots were at government sites and were intensively monitored, so detailed field data were easily available. Many of the early field-pilot scale PRBs (e.g., former Lowry AFB and former NAS Moffett Field) have since been decommissioned and are no longer being monitored. The older, full-scale PRBs (those installed 1994–1998) continue to be monitored in a limited way, sufficient to comply with applicable regulations and within the limitations of available funding. Some of these PRBs were installed at private sites from which data are not as easily available. In particular, field information from recent PRBs that were installed by injecting (rather than trenching) the ZVI into the subsurface is still emerging. On the other hand, some newer, full-scale installations (e.g., CAAP) are conducting and reporting more detailed monitoring. The two oldest sites with the most field data from a longevity perspective are U.S. Coast Guard Elizabeth City, North Carolina (installed 1996), and Nortel Networks, Monkstown, Ireland (1995) (see Appendix A). Based on this mixed bag of information, certain cautious observations can be made about the longevity of ZVI PRBs that are useful in managing past PRBs and designing future applications.

Box A. Key Findings on the Longevity of ZVI PRBs

- A number of native dissolved constituents in groundwater have the potential to reduce the hydraulic and reactive performance of PRBs over time through a variety of processes that may include corrosion, precipitation, gas production, and microbial metabolism. The resulting surface passivation and/or pore-space reduction in the ZVI media leads to the gradual loss of performance seen in some laboratory and field PRB systems. The degree and speed with which these processes have affected the long-term field performance of ZVI PRBs are varied.
- At some field sites, ZVI PRBs have retained the desired hydraulic and reactive performance for 10 or more years. Confirmation of this sustained performance was obtained through a significant and sustained improvement in downgradient contaminant levels. At some sites, the decline in field performance has been relatively faster, with hydraulic and/or reactive performance declining significantly within 1–5 years.
- Calcium, carbonate, sulfate, and silicate are common groundwater constituents that precipitate out on ZVI surfaces, while nitrate and DO oxidize the reactive iron surface. Both processes lead to gradual loss of performance.
- A flow blockage (or preferential flow) that develops as a result of PRB construction has the potential to accelerate the loss of performance of a ZVI PRB beyond the normal aging process involved in sulfate and carbonate precipitation.
- Conversely, an inordinate amount of precipitation, especially in the highly active zone near the inlet of the ZVI, has the potential to generate flow blockage and preferential flow.
- Following BMPs during PRB construction and early monitoring of the hydraulic performance of a PRB may help identify any precipitation related problems so that mitigation can be conducted.
- When ZVI is injected into the subsurface for plume interception, insufficient ZVI mass and/or nonuniform distribution can limit both short- and long-term plume treatment performance. Field experience with ZVI injection is growing.

Box B. Key Findings on the Longevity of Mulch Biowalls

- The effectiveness and longevity of biowall PRBs depends primarily on (a) sustaining appropriate levels of bioavailable organic substrate in the biowall reactive zone and (b) maintaining the permeability of the biowall trench to prevent bypass of contaminated groundwater.
- Even though biowalls are intended as passive, long-term remedies, an O&M plan may be necessary to evaluate when bioavailable substrate may decrease to levels that cannot support effective degradation and when (and how) the substrate should be replenished.
- For biowalls that are designed to stimulate biogeochemical transformation processes, the availability of sulfate and the availability and redox state of iron over time are also important considerations for biowall longevity.
- Loss of hydraulic conductivity is difficult to reverse without removal and replacement of the biowall media. It is important to use sufficient amounts of sand or gravel during construction to prevent compaction and settling.
- The economic impact of replenishing substrate should be considered when selecting a mulch biowall as a remedy. In general, the cost to replenish substrate at periods of 4–5 years (or more) is a relatively low percentage of the total life-cycle cost (i.e., compared to capital construction and monitoring cost). However, certain factors may increase the potential for more frequent replenishment (e.g., high rates of groundwater flow), which can have a significant impact on life-cycle cost.

As noted above, longevity of a ZVI PRB refers to its ability to sustain its reactivity and hydrologic performance over several years of passive operation. Longevity can be viewed from several practical perspectives:

- Will the PRB continue to capture the plume at the design level or at some minimum level required to protect potential downgradient receptors?
- Will the PRB continue to provide sufficient residence time for contaminants passing through the ZVI?
- Will the PRB outlast the plume without requiring major modifications or complete replacement?
- Can the hydraulic and reactive performance of the PRB be sustained long enough to generate a significant improvement in downgradient plume concentrations?
- Can the relatively higher capital investment in a PRB be recovered through savings realized from many years of passive operation?

8.2.1 Factors Influencing Longevity of ZVI PRBs

In general, there is good agreement among many laboratory studies regarding changes that occur in the geochemistry of the groundwater as it flows through a ZVI barrier. Reduction in redox potential and increase in pH within the ZVI, often aided by some degree of microbial activity at the ZVI-aquifer interface, lead to precipitation of several native inorganic dissolved species, such as calcium, carbonates, sulfate, and silicates. These precipitates may coat the ZVI, potentially reducing its reactivity. If formed in suitable quantity, these precipitates can affect the permeability or the flow through the PRB. The changes in dissolved groundwater species upon contact with ZVI are described in detail in Section 5.2. The major mineral phases that may form include iron oxides/hydroxides, iron and calcium carbonates, iron sulfides, and green rusts.

Equilibrium geochemical models and microscopic evaluation of ZVI samples from active PRBs show that compounds likely to precipitate in the ZVI include magnetite (Fe_3O_4), maghemite

(Fe_2O_3), iron carbonate hydroxide, calcite ($CaCO_3$), carbonate green rust $\{[Fe^{2+}{}_4Fe^{3+}{}_2(OH)_{12}]^{2+}[CO_3\ 2H_2O]^{2-}\}$, magnesite ($MgCO_3$), siderite ($FeCO_3$), mackinawite (FeS), goethite (α-FeOOH), and pyrite (FeS_2) (Yabusaki et al. 2001, Kohn et al. 2005, Johnson et al. 2008b, Wilkin and Puls 2003, Sass et al. 2002, Phillips et al. 2003). In some cases, such as the PRBs at Cotter's Canon City, Colorado, site and Monkstown, Ireland, calcium carbonate and other minerals were found deposited not just on the ZVI surfaces but also intergrown between ZVI particles, leading to some degree of cementation (Morrison, Mushovic, and Niesen 2006; Phillips et al. 2010).

Over time, precipitates occupy space in the PRB, potentially reducing its porosity and hydraulic conductivity. However, field observations and modeling have shown that in many cases this loss of porosity and permeability occurs at relatively low rates. It helps that the initial porosity of many field PRBs tends to be relatively high (50%–70%) because of the higher granular size of ZVI used and because of some variability in the distribution of the ZVI during construction. At the Vapokon PRB site in Denmark, site representatives estimated that a porosity loss of 0.88%/yr was occurring due to the precipitate formation evidenced by loss of 90% of carbonates (alkalinity), 82% of calcium, and 69% of sulfate from the groundwater passing through the field PRB (Lai et al. 2006).

Box C1. The Chemistry of Precipitation on ZVI Surfaces

- The level and mass flux of native inorganic species in groundwater are the primary cause of passivation and buildup on ZVI surfaces.
- Some precipitates (e.g., bivalent iron oxides/hydroxides/carbonates) are conductive and allow electron transfer between the ZVI and contaminants. Some precipitates (e.g., calcium carbonate and trivalent iron oxides/hydroxides) are more insulating and cause passivation or loss of reactivity of ZVI surfaces. In many laboratory studies and field applications, bivalent precipitates have been found to dominate in a PRB.
- Iron monosulfide formed when sulfide precipitation occurs is itself highly reactive with many contaminants. When the iron sulfide is in the form of pyrite, the compound is much less reactive.
- High levels of nitrate in the groundwater have a more immediate passivating effect on ZVI because the nitrate prevents the autoreduction of trivalent iron oxide films that are present on most manufactured ZVI used in PRBs.
- Organic species in groundwater by themselves or in conjunction with inorganic species may have some impact on the reactivity of the iron in the long-term, but these impacts have not been as closely studied.
- In addition to affecting reactivity of the ZVI, precipitation can affect PRB performance simply by occupying pore space and blocking flow.

There is empirical evidence from longer-term column tests that the mass flux of dissolved species through the PRB is more important than their absolute concentration in the groundwater (Gavaskar et al. 2002; Parbs, Ebert, and Dahmke 2007). In other words, a site with higher TDS in the groundwater but lower groundwater flow velocity could present the same potential for precipitation (and loss of performance) as a site with low TDS and higher groundwater velocity. Therefore, both the level of TDS in the groundwater and the groundwater velocity at a site are factors in determining expected level of precipitation in a PRB. Key laboratory studies since 2005 (see Boxes C2 and C3) have indicated that the issue of precipitation and loss of performance is more complex than these two factors.

One key finding is that not all precipitates are detrimental to continued good performance. For example, not all iron compounds that precipitate on the ZVI surface block the reactions between the ZVI and the contaminants. Bivalent iron precipitates, such as magnetite (Fe_3O_4), iron carbonate hydroxide, and green rust, are conductive of electrons and, therefore, allow continued electron activity and reduction of target pollutants. On the other hand, trivalent iron precipitates, such as maghemite or goethite, are more insulating and can prevent ZVI-contaminant reactions that depend on electron transfers. Therefore, the degree to which ZVI ages (loses reactivity) over time depends on which of these species (bivalent or trivalent iron) is dominant under the conditions encountered at the given site. Both laboratory and field evidence indicates that at many sites, the bivalent iron precipitates are the dominant species (Kohn et al. 2005, Phillips et al. 2010).

Carbonate and sulfide precipitation has been studied the most and have complex implications for long-term performance of PRBs. Boxes C2 and C3 summarize the key findings from recent studies on these two types of precipitates.

Box C2. Carbonate Precipitation

Calcium carbonate precipitates are thought to be more insulating and, therefore, inhibitory of long-term PRB performance. However, this cause-effect relationship between formation of insulating or noninsulating precipitate compounds and continued ZVI performance is not absolute. Some researchers (Kohn et al. 2005) have noted that beyond a certain thickness, even conductive layers of iron carbonate hydroxide could become insulating, simply due to the distance over which efficient electron transfer would have to occur. These researchers also showed that in column tests, conductive iron carbonate hydroxide would oxidize to magnetite and eventually to the more insulating maghemite (Fe_2O_3) over very long periods of time.

Translating time measured in column tests into PRB time in the field has always been a challenge. Much of the uncertainty in predicting field performance has often revolved around translating thermodynamic possibilities from equilibrium geochemical models and laboratory studies into kinetic realities in the field. Complex reactive transport models have been developed to represent the chemical changes occurring within a PRB due to carbonate precipitation (Li, Benson, and Lawson 2005). Jeen, Gillham, and Blowes (2006) and Jeen et al. (2007b) incorporated an empirical relationship between iron reactivity and the amount of precipitate present into a multicomponent reactive transport model; however, it has yet to be extensively field-tested.

Box C3. Sulfide Precipitation

There is some evidence that sulfate entering a ZVI or mulch biobarrier forms FeS, especially under the moderately reducing conditions prevalent in mulch biowalls or near the entrance of ZVI barriers (He, Wilson, and Wilkin 2008; Nooten, Springael, and Bastiaens 2008). Much of this transformation (of sulfate to sulfide) is thought to occur through microbial reduction, and hence there may be greater likelihood of these sulfides forming at locations where microbial activity is likely (e.g., at the ZVI-aquifer interface). Deeper in the ZVI, stronger reducing conditions and higher pH are more restrictive of microbial growth. Gu et al. (2002) noted the presence of microbes in a ZVI barrier, but the biomass in the ZVI was much less than the biomass in either the upgradient or downgradient aquifers adjacent to the PRB.

Laboratory column studies involving ZVI (Nooten et al. 2007) and mulch (He, Wilson, and Wilkin 2008) reactive media have reported that FeS minerals are formed from sulfate reduction and react efficiently with TCE through the highly desirable reductive elimination (abiotic) pathway, producing acetylene as a transient by-product, thus avoiding hydrogenolysis by-products (i.e., cDCE and VC). However, both in the laboratory study and in the associated field application at Altus AFB (Oklahoma), He, Wilson, and Wilkin (2008) found that over time, some of the FeS is transformed to FeS_2 (pyrite), which is a more stable mineral. Pyrite is more than three orders of magnitude less reactive than FeS and could therefore lead to a longer-term decline in the performance of the PRB. In both the Nooten et al. (2007) and He, Wilson, and

Wilkin (2008) studies, the availability of organic substrates and microbial communities were artificially facilitated. However, the higher concentration of the biomass at the ZVI-aquifer interface and the formation of iron sulfides have also been noted in several field applications (Puls 2007, Phillips et al. 2010).

There are other constituents found in groundwater that can adversely affect PRB performance and can compromise longevity, two of which are silica and phosphate. Column studies have been performed by several researchers demonstrating that silica has a detrimental effect on the reactivity of ZVI with TCE (Kohn et al. 2005, Klausen et al. 2003). However, field evidence of these two precipitates (silicate and phosphate) on the ZVI has only been sporadic thus far.

Nitrates are also an important groundwater constituent affecting longevity. Recent studies (Ritter, Odziemkowski, and Gillham 2002; Mishra and Farrell 2005) point out that many older, shorter-term column studies with little turnover in reactive sites may have underestimated the effect of nitrate passivation. In the absence (or at low levels) of nitrate, passivating ferric compounds appear to transform by autoreduction to lower-valence ferrous compounds that allow electron transfer between the ZVI and the contaminants. However, after at a certain nitrate threshold, ferric oxides are resistant to further (auto) reduction. It is also possible that nitrates allow new iron oxide/hydroxide films to be formed on the ZVI. The extent to which nitrate passivates ZVI depends on nitrate flux. Mishra and Farrell (2005) indicate that concentrations of nitrate <1 mmol were not enough to form a passivating layer although field experience may indicate the threshold is much lower.

Enhanced microbial growth is another factor that influences longevity. Enhanced microbial growth in and around ZVI PRBs has been noted both in laboratory and field studies (Gu et al. 2002; Lai et al. 2006; Da Silva, Johnson, and Alverez 2007). PRB construction techniques that involve the use of guar slurry may be a strong source of electron donor for anaerobic microbial growth (Crane et al. 2004, Johnson et al. 2008a). Microbial growth appears to be concentrated in regions more conducive to microbes, such as at the influent and effluent interfaces of a ZVI PRB. Formation of sulfide precipitates near the PRB inlet is a sign of microbial activity. Microbial activity can be advantageous when it leads to the formation of reactive species, such as FeS. The PRB continues to perform well in this case. Deeper in the interior of the ZVI, extremely low Eh and higher pH conditions are not conducive to microbial growth.

8.2.2 Field Experience

Two of the older ZVI PRBs that have sufficiently detailed data suitable for evaluating longevity are the PRBs at Elizabeth City (installed 1996) and Monkstown (installed 1995) (see Appendix A). From a longevity perspective, these two sites share some common features:

- Both have been monitored for at least 10 years.
- Both have collected detailed information on groundwater contamination, precipitate formation, and hydraulic performance over their operating durations.
- Both have consistently monitored contaminant levels in the downgradient groundwater.

The last point is important because improvement in downgradient contaminant levels is the ultimate goal of a PRB. A PRB is usually installed to protect potential downgradient receptors. PRBs are often located along the property boundary to prevent further migration of upgradient contamination and allow the downgradient contamination to attenuate through natural processes, such as flushing with treated water and/or biodegradation. However, this longevity indicator has been one of the more difficult ones to monitor in the field.

For the first few years after PRB installation, downgradient contaminant levels may persist for a variety of possible reasons, including slow groundwater flow in the aquifer, continued desorption and diffusion of contaminants from lower-permeability strata, or interference from neighboring plumes. However, over longer periods of time (5–10 years or more) continued flux of treated water emerging from the PRB should cause a noticeable improvement in downgradient contaminant levels. This expectation is similar to that of pump-and-treat systems often installed along property boundaries that seek to halt the progress of a plume and allow the downgradient (or off-site) portion of the plume to attenuate naturally.

Anticipating the long periods of time often involved in achieving a decline in downgradient contaminant concentrations, many PRBs incorporate monitoring wells inside the ZVI near the downgradient edge of the PRB to represent effluent contaminant concentrations. These ZVI wells have been a valuable tool for monitoring PRB performance in the first few years after installation. However, the field experience at the Monkstown and Canon City sites described below (Boxes F and G, respectively) shows the limitations of monitoring wells located inside the PRB in monitoring sustained plume capture and treatment in the longer term.

Box D. Field Experience in ZVI Longevity

- Laboratory studies are useful in understanding the mechanisms and products of precipitation and ZVI surface passivation but have limitations in predicting field experience for a variety of reasons, for example, accelerated flow rates used in column tests and variables that need to be kept constant to study other variables. Therefore, detailed longer-term monitoring of PRBs as they age is essential for assessing sustained reactive and hydraulic performance over time.
- Among the older PRBs (ones installed 10+ years ago), sustained longer-term performance can be verified in some PRBs. Sustained improvement in contaminant levels in the downgradient aquifer is the clearest sign of long-term PRB performance.
- Interference from neighboring plumes and/or diffusion from lower-permeability soils may delay the emergence of this treated water front on the downgradient side.
- Groundwater chemistry monitored within the ZVI is a useful tool in the short term but needs to be supplemented by hydraulic and chemical measurements both inside and outside the PRB over the long term.
- Flow blockages that may be a relic of PRB construction can accelerate inordinate precipitation, leading to early loss of hydraulic and/or reactive performance of the ZVI.
- Conversely, inordinate precipitation, especially near the ZVI inlet, can create preferential flow or flow blockage and lead to early loss of PRB performance.
- Chemical monitoring of PRB performance should be supplemented by hydraulic performance monitoring early in the life of a PRB and should be continued at periodic intervals afterwards to verify (and perhaps address loss of) long-term performance.
- Longevity depends on a PRB’s ability to maintain a certain acceptable level of reactive and hydraulic performance, especially as design performance inevitably starts to deteriorate over time. This minimum acceptable level of performance is a site-specific decision among the site representatives and regulatory agencies involved.

Long-term performance of some older and more recent PRBs

Among the older PRBs, the one at Elizabeth City (installed in 1996) has shown substantial and sustained removal of contaminants [TCE and Cr(VI)] and decline in downgradient contaminant concentrations over measurements conducted during 13 years of operation. Box E provides a more detailed description of the longer-term performance of the PRB at Elizabeth City. The experience at Elizabeth City shows that a decline in contaminant levels downgradient of the PRB is achievable after a period of time in which groundwater flows relatively unhindered through the PRB.

Box E. Elizabeth City

Installed in 1996, this PRB site started showing a noticeable decline in downgradient chromium concentrations 2–3 years after installation (Puls 2007). TCE also started to show a noticeable decline 6–7 years after installation. Downgradient concentrations of both chromium and TCE declined below target cleanup levels (100 and 5 µg/L, respectively).

This PRB is approximately 140 feet long, 2 feet thick, and 22 feet deep and was constructed by continuously trenching (dry) and backfilling with 100% ZVI. The aquifer consists of sandy fill material underlain by finer sand and silt deposits. The PRB is relatively close to a river and may be in an area of tidal influence. Much of the contaminant flow appeared to be occurring through a highly conductive layer 5–7 feet bgs. A tracer test indicated that the average groundwater velocity in the aquifer was 0.3–0.6 ft/d.

Periodic coring of the PRB shows that precipitates on the ZVI surfaces consist primarily of calcium carbonates, iron hydroxyl-carbonate, carbonate green rust, hydrous ferric hydroxide, ferric oxyhydroxide, and iron monosulfides. Much of the precipitate buildup appears to be occurring near the upgradient aquifer-ZVI interface, but so is the chromium buildup. Microscopy results indicate that chromium is, in part, associated with iron sulfide grains, formed as a consequence of microbially mediated sulfate reduction. Chromium is predominantly in the less-soluble trivalent oxidation state in the PRB.

There was no evidence of a decline in PRB performance in groundwater sampling conducted 13 years after installation, and downgradient TCE and chromium concentrations continue to remain low compared to preinstallation and upgradient levels.

The PRB at Monkstown (Ireland) is another well-monitored older system (installed in 1995) and was monitored consistently for the first 10 years (Phillips et al. 2010). The detailed and sustained data collection provides a rare glimpse of the longer-term evolution of a field PRB. Box F describes this funnel-and-gate type PRB with an innovative design and its performance. In summary, the PRB experienced a loss in hydraulic performance and a decrease in plume capture within the first 5 years of operation. The loss in hydraulic performance was due to precipitation buildup within the first several inches of the PRB. This cemented iron material was removed, and again the PRB was put into service; however, within 5 years there was additional loss in hydraulic performance and reactivity due to precipitation. The loss of reactivity and hydraulic conductivity was confirmed by high TCE concentrations downgradient of the PRB during the 10 years of operation.

Box F. Monkstown, Ireland

The PRB at Monkstown is a funnel-and-gate system with long funnel walls that channel flow through a central gate. The interesting feature of this PRB is that the gate consists of a 7-foot-diameter outer cylinder and a 4-foot-diameter inner cylinder or reactive (ZVI) chamber through which groundwater is forced to flow vertically. This innovative design enables the groundwater to flow through a much longer path through the ZVI than would be possible with a conventional trench-type gate. The lower part of the reactive chamber is filled with ZVI to a height of 22 feet, through which groundwater flows vertically. The annular space between the two cylinders is filled with sand. An inlet pipe collects incoming groundwater and introduces it into the top of the ZVI in the reactive chamber. The groundwater moves vertically to the bottom of the chamber, where it is collected and discharged through an effluent pipe. The design ensures that anaerobic conditions are maintained in the reactive chamber. Monitoring wells were located inside the cylinder (in the annulus) near the influent and effluent ends of the reactive chamber, as well as at regular intervals along the flow path in the ZVI. Monitoring wells were also located in the upgradient and downgradient aquifers.

Core samples of the ZVI collected from the PRB after 10 years showed precipitate buildup occurring primarily in the top 1 foot of the ZVI (near the inlet). The precipitates consist of iron oxide (primarily magnetite), calcium carbonate, iron carbonate, carbonate green rust, iron sulfide (mackinawite and amorphous monosulfide), and greenalite (silicate). The ZVI grains were mainly loose except for a thin cemented section at the top near the ZVI inlet. This cemented section was approximately 2 inches thick in 2001 (approximately 5 years after installation) and was removed when the chamber was opened for coring, where there was a cemented crust. Another 1 inch of cemented crust was observed when the ZVI was cored again after 10 years of operation. Iron sulfide and calcium carbonate predominated in this cemented layer. Underlying this cemented layer, there was less continuous cementation for about 10 inches. A strong and diverse microbial community of denitrifying, iron-reducing, sulfate-reducing, and methanogenic bacteria was found in the first few inches of ZVI near the inlet. Microbial growth was much less in the rest of the ZVI.

A multi-tracer test conducted in 2006 (10 years after installation) indicated that flow had become quite constricted and effective porosity had diminished greatly in the uppermost 10 inches. The tracer test also indicated that flow through the uppermost 8 inches of ZVI (from inlet to the first monitoring point in the ZVI) was occurring at a very slow rate, with an average residence time of 180 days (compared to a design residence time of 6 days). The implied porosity of this cemented and semicemented upper zone was 0.29 vs. an estimated range of 0.45–0.6 at installation. This relatively stagnant flow condition occurred despite the fact that 2 inches of the most cemented material was broken up and removed from the top of the reactive chamber when the PRB was cored after 5 years of operation. Significant separation of the gas-phase and liquid-phase tracers indicated that gas bubbles at the inlet end may be playing a role in the flow reduction. Interestingly, considerable TCE removal occurs in these 8 inches of cemented and semicemented layers, as evidenced by sharply reduced concentrations at the monitoring point 8 inches from the inlet.

The rest of the ZVI (approximately 21 feet) along the flow path below this cemented layer appears to remove most of the remaining TCE, as indicated by the low to nondetect levels of TCE in the last monitoring point before the ZVI chamber outlet. However, pH measurements create uncertainty about how reactive the rest of the ZVI is. The pH in the ZVI dropped from a range of 9.2–9.5 to a range of 7.2–8.9 at the end of the first 5 years of operation (in 2001). When pH was next measured in 2003, it was around 8.4 and further declined to a range of 5.7–6.4 over time. Rebound of carbonate and TDS levels in the groundwater also indicate loss of reactivity. Therefore, in the Monkstown PRB, after significant precipitate buildup, the upstream portion of the ZVI appears to have lost much of its reactivity, but the very long residence time allows much of the TCE in the lower, uncemented sections to be degraded. The biggest impact is on hydraulic performance. As flow progressively slowed down in the PRB, less and less groundwater flowed through it, reducing groundwater and plume capture and increasing the probability of flow bypass. This is one reason why monitoring wells located inside the PRB provide only limited information on the longer-term performance of a PRB. Once the hydraulic performance and reactivity of a PRB decline, wells within the ZVI could continue to show low levels of target contaminants simply because very little water is flowing through the PRB. The little water that flows would have a long contact time with the ZVI, resulting in slow, but considerable, degradation and low contaminant concentrations in the ZVI.

TCE levels in downgradient wells have remained persistently high in the 10-year period, for a variety of possible reasons. The PRB was installed in the midst of very high concentrations of TCE (up to 390 mg/L upgradient and up to 12 mg/L downgradient prior to PRB installation). It is possible that source contamination is present on both sides of the PRB although soon after installation of the gate, when considerable source material was removed, a decline in upgradient TCE concentrations was tracked by a similar decline in downgradient concentrations. It is possible that the designed funnel-to-gate ratio was very high and that the groundwater and plume have continued to flow around the PRB since the time the PRB was first installed (a good reason why an early measurement of hydraulic performance of a PRB soon after installation is desirable). It is also possible that flow through the ZVI (gate) was progressively reduced over the years and that the plume increasingly bypassed the PRB. Contaminated groundwater from a downgradient well is pumped into an upgradient well to be treated by the PRB, and this may be helping maintain a positive gradient across the gate, despite the precipitation and flow blockage.

At Monkstown, precipitates appear to have progressively accumulated over 10 years of operation, primarily in the first 1 foot of ZVI near the inlet. Reactivity of the rest of the ZVI (in the remaining 21 feet) also declined over that time, as indicated by a decrease in pH from 9.3 at the time of installation to a range of 5.7–6.4 after 10 years. Cementation of the grains near the inlet also was observed. A tracer test at the end of 10 years indicated that groundwater was moving extremely slowly through the ZVI. Interestingly, monitoring wells near the outlet end of the ZVI continued to show low TCE levels because the sharply increased residence time afforded to the slower-moving groundwater offset the reduced reactivity of the ZVI. Therefore, the significantly less-reactive ZVI continued to treat the groundwater, but very little water was flowing through the PRB. TCE levels in the downgradient aquifer remained persistently high over the 10 years of operation, for a variety of possible reasons as described above.

Another PRB where longevity appeared to be limited is in Canon City, Colorado (see Box G). Within the first 2 years after installation in 2000, the PRB suffered sharp permeability losses due to precipitate buildup in the first few inches of ZVI near the inlet (Morrison, Mushovic, and Niesen 2006), as evidenced by groundwater mounding along the upgradient ZVI interface. A decrease in pH inside the PRB indicated that ZVI reactivity had declined. In addition, permeability losses and preferential pathways may have led to a shorter residence time for the groundwater and increased contaminant levels in the ZVI, particularly for molybdenum, which is more sensitive to a pH decrease than uranium, the other contaminant. In the third year, mounding grew sharper, and by the fourth year, groundwater was relatively stagnant in the ZVI and was mostly bypassing the PRB. Interestingly, under relatively stagnant conditions, most of the performance indicators in the ZVI turned positive. Groundwater pH, which had declined in the first 3 years, rebounded back to 10, contaminant levels in the ZVI dropped, and calcium and magnesium were almost completely absent in the groundwater. Declining reactivity of the ZVI was offset by the much higher residence time now available to the contaminated groundwater under relatively stagnant conditions.

Box G. Canon City

This funnel-and-gate PRB consists of a ZVI section (gate) that is 27-feet long, approximately 5-feet thick (in the direction of flow), and 6-feet deep. This PRB was installed to reduce molybdenum and uranium in groundwater (Morrison, Mushovic, and Niesen 2006). In the first year after installation, the PRB performed well with a residence time of 56 hours and uniform flow through the PRB. In the second year, mounding of the water table was observed at the upgradient ZVI interface as excessive precipitation started occurring in the first few inches of the ZVI. This development led to preferential pathways through the ZVI, a much reduced residence time, and increase in contaminant concentrations in the ZVI. A decrease in pH in the ZVI was another indicator of declining performance. In the third year, upgradient mounding grew sharper, pH declined to neutral, and contaminant levels in the ZVI increased. In the fourth year, precipitation had occurred to such an extent that groundwater was bypassing the PRB. Groundwater that remained in the PRB was mostly stagnant, leading to long residence times, almost complete loss of calcium and magnesium from the water, significantly lower sulfate concentrations in the water, and pH values that increased up to 10 in the ZVI. These conditions indicate that the ZVI in the bulk of the PRB remained reactive despite the precipitation and flow problems. Column tests conducted with a sample of the aged ZVI collected from the middle of the PRB confirmed that the iron remained reactive. Therefore, the physical/chemical changes and microbial activity in the first few inches of the ZVI near the PRB inlet were the cause of reduced longevity of the PRB. Interestingly, once flow through the PRB declined to a stop, residence time increased significantly, pH increased significantly, and these conditions caused both molybdenum and uranium to redissolve in the groundwater, leading to levels much higher than in the influent. Given that flow was almost stagnant by this time, it is unlikely that much of this contamination exited the PRB. The excessive precipitate buildup was attributed by site representatives (at least partly) to flow stagnation along its upgradient face.

At the Monticello, Utah, site (PRB installed in 1999) as well, the permeability of the PRB became progressively worse over 5 years to the point where groundwater was mostly bypassing the PRB (see Box H). Unlike the PRB in Canon City, however, periodic slug tests indicated that permeability losses were occurring throughout the ZVI, not just at the influent end (DOE 2005, Morrison 2003). A pretreatment zone of 13% ZVI mixed with pea gravel at the upgradient ZVI interface may have helped push precipitate formation further into the PRB.

Box H. Monticello, Utah Site

At the Monticello site, a ZVI PRB was installed in 1999 for treatment of arsenic, molybdenum, selenium, uranium, and vanadium in the groundwater (DOE 2005, Morrison 2003). The ZVI section (gate) is 105 feet long and 8 feet thick (in the direction of flow). The 8-foot thickness includes a 4-foot section of 100% ZVI, with 2-foot pea gravel sections upgradient and downgradient. Slurry walls that are 100 and 250 feet long flank the gate on either side. Soon after installation, water level measurements indicated steep hydraulic gradients near the influent and effluent edges of the PRB. Although mild gradients are expected along the edges of zones where groundwater migrates from higher-permeability to lower-permeability strata (Gavaskar et al. 2002), the gradients at these sites are reported as being high enough to be indicative of smearing of alluvium across the face of the PRB during construction (perhaps during the driving or extraction of sheet piles in the trench-box style construction). The gradient inside the PRB initially was flat, but water levels inside the PRB rose progressively over the next 4 years (with increasing mounding of the water table near the influent end of the PRB). Although the gradient across the upgradient face of the PRB declined to some extent in response to the mounding inside the PRB, the effluent end continued to display a steep gradient. Slug tests conducted in 2000, 2003, and 2004 (one, four, and 5 years after installation) indicated a progressive decrease in hydraulic conductivity over time in the middle of the ZVI section. At the time of the last reported event in 2004, slug tests indicated that the hydraulic conductivity of the PRB was then less than that of the surrounding aquifer, and water level measurements indicated that groundwater was mounding at the influent interface, indicating that groundwater was mostly bypassing the PRB.

Based on analysis of several core samples, the loss of hydraulic performance at Monticello was attributed primarily to calcium carbonate buildup. A tracer test indicated some preferential flow on a local scale, but the calcium carbonate buildup appeared to be relatively uniform across the flow path through the ZVI and across depth (unlike the PRBs at Monkstown and Canon City, where the majority of precipitation occurred in the first few inches of ZVI near the inlet end). At Monticello, 13% by volume of ZVI was mixed with the upgradient pea gravel, which may have helped to push the precipitation front farther along the flow path. Much of the contaminant metals removal occurred in the ZVI near the inlet end. There is no reported microbial evaluation from this site. Also, calcium carbonate levels from filtered and unfiltered samples from the same locations did not show much difference, indicating that the precipitates generated stayed within the PRB rather than migrating out.

At the CAAP, Nebraska, a continuous reactive barrier (no funnel walls) was installed in 2003 by trenching under a head of guar gum slurry (see Box I). In approximately 1 year, the permeability and reactivity of the ZVI PRB appeared to be considerably reduced. Site representatives reported two possible causes for the early loss of performance (Johnson et al. 2008a, 2008b): heightened microbial activity at the influent end that led to excessive sulfide precipitation or uneven degradation of guar gum slurry that may have penetrated the upgradient aquifer during construction and that promoted excessive microbial activity and sulfide precipitation. This is an example of a construction artifact affecting performance, rather than a gradual decline in reactivity or hydraulics. At the time of the last reported monitoring event after 2 years of operation, overall contaminant removal within the PRB remains adequate.

Box I. Cornhusker Army Ammunition Plant

At the CAAP site, a ZVI PRB was installed in 2003 by trenching under guar slurry (Johnson et al. 2008b). After the ZVI was placed in the trench, an enzyme was circulated to break down the guar. Approximately 1 year after installation, reactivity and hydraulic conductivity of the PRB appeared to be considerably reduced. A tracer test indicated that the groundwater velocity in the PRB was lower than in the surrounding aquifer. Much of the reduction in hydraulic conductivity seemed to occur in the first few inches of the influent end of the PRB. The hydraulic conductivity at the center of the Cornhusker PRB appeared to be relatively unchanged. Geochemistry data in monitoring wells upgradient and downgradient of the PRB indicate that the loss of conductivity in the PRB was causing groundwater flow to be diverted under and around the PRB. After 2 years of operation (the time of the last reported monitoring event), the PRB continued to remove most of the target contamination, which is low levels of the explosive compounds TNT (30–200 ppb), DNT (dinitrotoluene) (10–50 ppb), and HMX (1–2 ppb).

An analysis of aquifer and ZVI core samples from the upgradient end of the PRB showed a preponderance of iron carbonates and iron sulfides. These same compounds were present to a lesser extent in ZVI surfaces in the middle of the ZVI. Sulfate, nitrate, and calcium had been completely removed from the groundwater entering the PRB and carbonate levels were significantly reduced. Interestingly, the total sulfur content on the ZVI surfaces was five times higher than the AVS, indicating that much of the sulfide precipitate was the much less reactive FeS_2 instead of the more reactive FeS. As He, Wilson, and Wilkin (2008) noted, two of the factors that seem to govern transformation of FeS to FeS_2 are the presence of oxidized species and long residence times. Both factors are typically present at the upgradient interface of the PRB, in addition to the heightened microbial activity.

Site representatives report two possible causes for the flow impedances at the influent end (Johnson et al. 2008b): the heightened microbial activity and precipitate formation at the upgradient edge or the use of guar during installation of the PRB. Site representatives believe that guar entered the formation upgradient of the PRB and did not degrade uniformly at the completion of the installation. This guar could have directly caused early plugging of the upgradient interface, or more probably the guar led to strongly reducing conditions just upgradient of the PRB and the removal of sulfate as sulfide precipitates in the aquifer material, as observed in core samples.

A PRB installed at OU-12, Hill AFB, Utah, in 2005 demonstrates the deleterious effects of relatively higher nitrate flux in the groundwater. Native groundwater pH is neutral, and sulfate content is moderate at 70 mg/L. Nitrate levels in the influent groundwater have fluctuated 2–13 mg/L. Performance started to decline in less than 1 year after installation. Beginning in 2006, cDCE and *trans*-DCE levels downgradient started increasing (Battelle 2008). By 2007, TCE levels had progressively increased in wells inside the PRB and in downgradient aquifer. A geochemical study indicated that nitrate may have rapidly passivated the ZVI, as described in Section 4.5.1.

The field experience at these various sites indicates that PRBs are capable of sustained longer-term performance but can be affected by construction artifacts and site-specific geochemistry. Despite the multitude of laboratory and field studies on the longevity of PRBs, it is unclear which site-related and/or PRB construction-related factors determine the difference between sustained and limited longevity. In some instances, do flow impedances (e.g., caused by smearing or inadequate degradation of guar) cause excessive precipitation, which then leads to excessive reactivity and permeability losses and flow bypass? Or does excessive precipitation (say, due to excessive microbial activity) at some sites lead to flow impedances and permeability losses? Better understanding of these field drivers is required so that future PRBs can be designed to avoid or mitigate these factors.

There are some important implications from the Monkstown and Canon City experience for sites that are monitoring long-term performance or longevity of PRBs. Indicators of continued acceptable performance of a PRB are assumed to be contaminant levels, Eh, and pH. These indicators are monitored in the ZVI. All of these indicators can point to declining ZVI performance when mineral precipitation or flow blockages start developing in the PRB, leading to preferential pathways and reduced residence time. Consequently, TCE levels and Eh can rise, and pH can fall as the ZVI performance deteriorates. However, when precipitation and permeability losses increase to the point where the groundwater in the ZVI is relatively stagnant, these indicators actually reverse. Residence time increases (to infinity, when groundwater is stagnant), which leads to a decline again in TCE, as the reduced reactivity of the ZVI is offset by greatly increased residence time. A decline in Eh and an increase in pH (indicators of good performance) may follow in the wells inside the PRB, as at least some reactive surface area still remains. These effects highlight the need for monitoring of downgradient aquifer concentrations to verify sustained long-term performance or longevity of a ZVI PRB.

Contaminant degradation by-products may be a slightly better indicator of longer-term PRB performance, even when measured inside the PRB. Elevated DCE and VC levels persisted much farther into the ZVI (along the flow path) in the Monkstown PRB. This fact may indicate (a) that some of the ZVI is unable to generate the strong beta-elimination reactions necessary to degrade TCE to ethene without the generation of DCE and VC and/or (b) that the DCE and VC generated in the upgradient aquifer or at the upgradient interface due to heightened microbial activity is not being efficiently degraded in the aging ZVI.

Long-term performance of injected PRBs

The method of introducing the ZVI into the subsurface has some bearing on longevity. In the last few years, there have been many injections of ZVI into the subsurface to create a PRB for either plume or source containment. Injection allows deeper PRBs to be installed, as the depths of trench type PRBs are often limited to the reach of a backhoe or continuous trencher at approximately 35–40 feet bgs. However, injections have been conducted for shallower applications too, as this method is often more cost-effective than trenching. A review of available data from sites where ZVI has been injected with hydraulic and pneumatic fracturing shows that effectiveness and longevity of these applications depends greatly on the mass and uniformity of the ZVI injected. Unlike trench-type barriers, where all native soil in the target PRB space is removed and replaced with ZVI (or a ZVI/sand mix), injected PRBs introduce ZVI into existing soil pore spaces or fractures. Injectable ZVI tends to be smaller in particle size (micron- or nano-size) to facilitate its entry into soil pores. This smaller particle size tends to be more expensive (per unit mass) than the granular ZVI used in trench PRBs. Because of these injectability and cost concerns, typical field applications have involved injection of 0.4%–0.8% of ZVI by mass of soil.

Relatively detailed injection data are available from four case studies posted on vendor websites (ARS Technologies 2010). At all four sites, TCE levels were substantially reduced in several monitoring wells, indicating relatively good distribution of ZVI was achieved through injection. At two of the sites, cDCE levels increased substantially, and at the other two sites, VC levels increased substantially. Aquifer pH remained relatively unchanged after the injections. These results are similar to those reported in a 2005 study of several injected ZVI applications (Gavaskar et al. 2005) and have important implications for both short- and long-term performance of injected PRBs.

A substantial increase in DCE and/or VC indicates that hydrolysis reactions that favor DCE/VC production are predominant, instead of beta-elimination reactions that do not produce these less-chlorinated by-products. Gavaskar et al. (2005) reported that when enough ZVI mass is injected to reduce the aquifer ORP down to –400 mV or below, beta-elimination reactions appear to be predominant, and TCE degradation occurs without substantial DCE/VC production. When substantial DCE/VC production is encountered, it implies that the injected ZVI mass is sufficient to take the ORP down to, say, –200 mV and cause TCE to degrade by hydrolysis or biodegradation but not sufficient to trigger beta-elimination reactions.

The limited data available from these studies show that even when a redox state necessary to produce beta-elimination reactions (say, –400 mV) is reached in some locations, the aquifer often rebounds first to the –200 mV levels where hydrolysis reactions continue (with DCE and VC generation) and eventually to former mildly anaerobic or aerobic levels within weeks or months. This time period is sufficient if, for example, the ZVI is injected into a source area and much of the source contamination is reduced by the initial injection.

If the objective is longer-term containment of the source or plume (typical of a PRB), much more ZVI mass would need to be injected to get the target portion of the aquifer to a state that facilitates the desired beta-elimination reactions and to keep the redox state down long enough to contain and treat the oncoming plume. Therefore, from a longevity perspective, the two considerations at an injected PRB site are how much ZVI mass should be injected to adequately treat the plume passively for the desired length of time and how to ensure that the injected ZVI mass is distributed relatively uniformly. For example, at a site in the western United States, coring through an injected ZVI PRB indicated a very heterogeneous distribution of ZVI around the injection points rather than a uniform "wall" of iron (Fiorenza, Oubre, and Ward 1999). If a certain degree of heterogeneity is unavoidable, then additional ZVI mass may have to be injected to create the desired reductive zone and intercept the plume. Also, consideration should be given to some threshold amount of injected ZVI mass that would divert groundwater flow around the PRB rather than through it.

8.2.3 Operational and Economic Implications

Since the previous ITREC PRB guidance (ITRC 2005b) was issued, understanding of the longer-term performance of ZVI PRBs has increased through a combination of detailed laboratory studies and a few well-monitored field applications. Many field applications have achieved the 10-year mark that early economic studies (Gavaskar et al. 2002) had indicated would be required for recovery of the higher capital investment in a PRB (as compared to competing plume interception technologies, such as pump-and-treat systems). In the past, many of the economic comparisons determining the longer-term attractiveness of a PRB were based on a comparison with an equivalent pump-and-treat system.

However, few pump-and-treat systems have been installed since 2005. For future ZVI PRB applications, a more realistic economic comparison may be with biowall (mulch or other solid media) or biobarrier (injectable substrates) applications. The economics of both (ZVI and other types of permeable barriers) hinges on the expected longevity of the application. Therefore, there is a continuing need to more closely monitor the longer-term performance of field PRBs and to identify/address the factors that drive longevity.

In the mid- to late-1990s, there was some interest in researching ways to restore the performance of ZVI PRBs without excavating the entire PRB. Various methods were studied, such as acid injection or ultrasonic disruption of precipitates. There may be value in continuing to study these or other PRB rejuvenation methods. Also, a review of past PRB projects indicates that hydraulic performance is studied in earnest only after flow or reactivity problems arise and significantly affect performance. Early and periodic evaluation of the hydraulic performance of a PRB may be a possible way of identifying and addressing potential problems before the entire PRB needs to be replaced.

8.3 Longevity of Biowalls

The effectiveness and longevity of biowall PRBs primarily depend on sustaining appropriate levels of bioavailable organic substrate in the biowall reactive zone and maintaining the permeability of the biowall trench to prevent bypass of contaminated groundwater. Even though biowalls are intended as passive, long-term remedies, an O&M plan may be necessary to evaluate when bioavailable substrate may decrease to levels that cannot support effective degradation and when (and how) the substrate should be replenished. For biowalls that are designed to stimulate biogeochemical transformation processes, the availability of sulfate and the availability and redox state of iron over time are also important considerations for long-term performance.

A loss of hydraulic conductivity is difficult to reverse without removal and replacement of the biowall media. It is important to use sufficient amounts of sand or gravel during construction to prevent compaction and settling. To mitigate potential bypass, it is useful to extend the biowall a reasonable distance (both laterally and vertically) beyond the extent of contamination to be treated.

The economic impact of replenishing substrate should be considered when selecting a mulch biowall or other biological PRB. In general, the cost to replenish substrate in a biowall at periods of 4–5 years (or more) is a relatively low percentage of the total life-cycle cost (i.e., compared to capital construction and monitoring cost). However, certain factors may increase the potential for more frequent replenishment (e.g., high rates of groundwater flow), which can have a significant impact on life-cycle cost (Section 6).

8.3.1 Factors Influencing Longevity of Biowalls

The primary factors that appear to affect the longevity of a biowall application are as follows:

- the initial quantity and bioavailability of the organic material added to the biowall
- the rate of groundwater flow
- the native and anthropogenic electron acceptor demand that impacts the rate of substrate use
- the availability and use of iron and sulfate (for stimulation of biogeochemical transformation processes)

Adequacy of organic substrate

Maintaining sufficient bioavailable organic substrate is necessary to develop and sustain optimal biogeochemical and redox conditions for anaerobic degradation processes to occur. Insufficient substrate may result in areas of the treatment zone that are not sufficiently reducing for complete degradation to occur. These may result in contaminant bypass through the PRB or the accumulation of regulated intermediate degradation products such as cDCE and VC.

The minimum or threshold quantities or concentrations of organic substrate required to sustain the reaction zone may differ significantly from one site to another depending on the contaminant type and concentration and the hydrogeological and geochemical conditions at the site. The mass of bulk organic material used in construction of a mulch biowall typically lasts for periods of 10 years or more (e.g., Robertson, Vogan, and Lombardo 2008; Shen, Adair, and Wilson 2010). However, it is less well understood how long anaerobic degradation processes can be sustained at rates sufficient to meet POs.

Concentrations of soluble organic carbon alone may not be an adequate parameter for evaluating substrate availability or depletion when using mulch and compost substrates (Parsons 2010a). Besides being a source of organic carbon, mulch provides an excellent medium for microbial growth. As the mulch breaks down by enzymatic processes (hydrolysis), soluble organic matter may be used by the biomass before it can accumulate in groundwater. Measurement of DOC is not specific to the types of organic acids that may be present; measurement of humic and fulvic acids may be a more precise measurement of the availability of soluble organic carbon.

The rate of groundwater flow may also impact the ability to induce strongly anaerobic conditions. Mulch and compost are mostly cellulose, hemicellulose, and lignin, which are slowly degraded under anaerobic conditions in the subsurface. It may be difficult to maintain highly anaerobic conditions under high-flow conditions, where soluble substrate (i.e., humic and metabolic acids) are quickly dispersed and diluted with groundwater flow. For this reason, many biowalls include a secondary source of organic carbon (compost or vegetable oil), or multiple biowalls are installed. For example, the OU-1 biowall at Altus AFB, Oklahoma, included 10% by volume composted cotton gin trash as a secondary source of readily degraded organic matter. Other biowall applications have used mushroom compost and vegetable oil as secondary sources of organic carbon (AFCEE 2008). Alternatively, additional biowalls may be installed in series, where the first biowall reduces native electron acceptors so that highly reducing conditions can be maintained in successive downgradient biowalls. In any case, a conservative approach is to add more organic material and/or install additional biowall trenches to reduce the risk that bioavailable organic substrate is not a limiting factor to biowall PRB performance.

Iron and sulfate for biogeochemical transformation processes

Biogeochemical transformation processes include the formation of reactive iron sulfide minerals for the abiotic dechlorination of chlorinated solvents. A recent sampling effort was conducted by the Air Force, ESTCP, and the USEPA National Risk Management Research Laboratory Ground Water and Ecosystems Restoration Division to evaluate the process at several biowalls (Lebrón et al. 2010). The results of that study suggest that the flux of sulfate into the biowall must remain high and that fresh iron sulfides must be continually formed for the process to sustain its effectiveness. Therefore, each of the three key components that drive the process (organic substrate, sulfate, and reducible iron) must be present at concentrations that are sufficient to sustain a high degree of sulfate and iron reduction.

The threshold concentrations to sustain these processes are not known with certainty, and future research is needed to determine the minimum concentrations of each (substrate, sulfate, and reducible iron). For example, it appears that production of reduced iron sulfides in the BG05 biowall at Ellsworth AFB was limited by high rates of groundwater flow and low concentrations of organic substrate, which resulted in limited sulfate and iron reduction within the biowall. Conversely, biogeochemical transformation processes remained effective for several years at the OU-1 biowall where sulfate reduction was sustained (Parsons 2010a).

8.3.2 Field Experience

Data are now becoming available to determine the longevity or long-term effectiveness of biowall PRBs over periods of 8 years.

Biowall sustainability

The OU-1 biowall installed by the Air Force at Altus AFB shows little reduction in percent TCE removal through 2009, over 8 years after installation (Parsons 2010a). However, unpublished data collected by USEPA in 2010 do show increases in TCE within the biowall, and the Air Force has plans to replenish the biowall in 2011. The B301 biowall at Offutt AFB shows a similar effectiveness in reducing concentrations of TCE at 5 years after installation of the full-scale biowall. Figure 8-1 illustrates the reduction of TCE and cDCE along a monitoring well transect oriented along the path of groundwater flow through the B301 biowalls in August 2006, 5 years after construction of the full-scale biowall.

Pilot biowalls at NWIRP McGregor have been operating since 1999, with additional pilot and full-scale systems installed 2002–2005. The effectiveness of the full-scale biowall system is monitored on an annual basis to determine the need for replenishment (EnSafe 2005, 2008; EnSafe and DSE 2010). For Areas S, F, and M at NWIRP McGregor, the biowalls are operating as designed, meeting performance expectations, and requiring no replenishment as of 2007. The sampling ports for biowalls at Area S were mostly dry in 2008 due to drought, with perchlorate below detection in the few that were sampled. Several biowalls at Area S were replenished in June 2008, and several additional biowalls were replenished at Areas S and M in 2009. The replenished biowalls continued to operate properly and to achieve target reductions in perchlorate after replenishment (EnSafe and DSE 2010). Overall the biowalls continue to perform to expectation. Occasional injection of EVO substrate is required at select biowalls, but not all biowalls have required replenishment. Pilot mulch biowalls to treat chlorinated solvents and perchlorate were first installed in 1999. Over 8 years of monitoring is available to evaluate biowalls at Altus AFB, Oklahoma and at the former NWIRP Plant, McGregor, Texas (Parsons 2010a, EnSafe and DSE 2010).

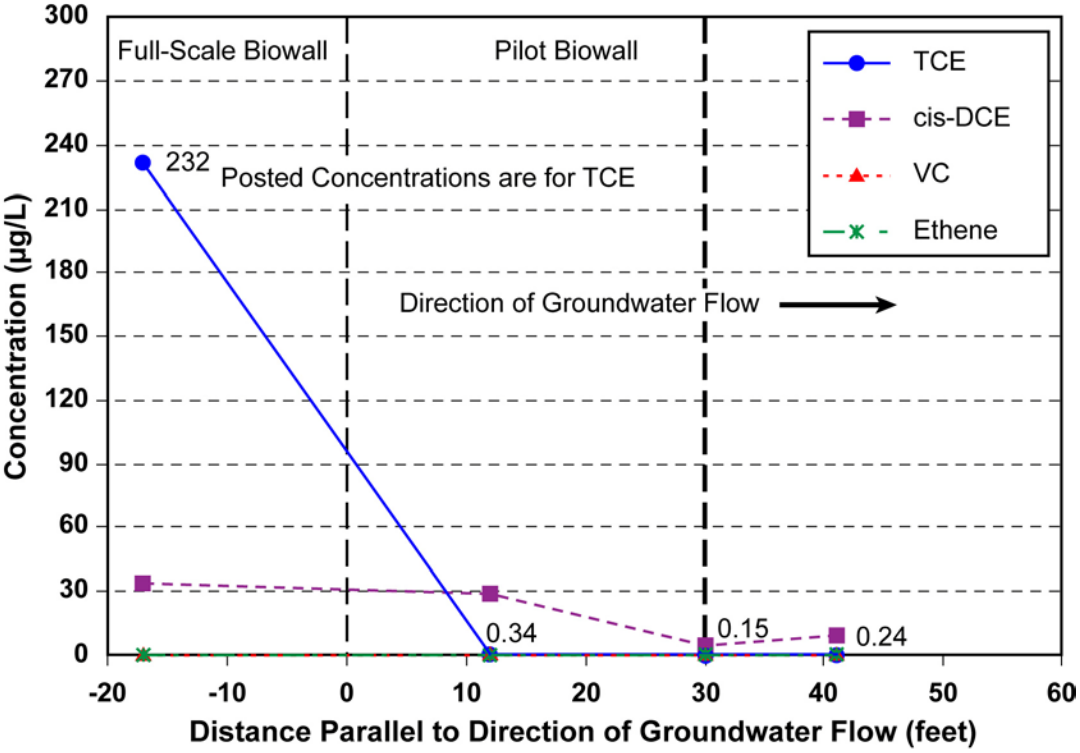

Figure 8-1. Concentration of chlorinated ethenes over distance along southern transect of B301 biowalls, August 2006. *Source:* Parsons 2010a.

Other investigators have installed biowalls filled with a variety of waste cellulose solids (e.g., sawdust and mulch) for the treatment of nitrate-contaminated water and have found little reduction in performance over periods of 7–15 years of operation (Robertson et al. 2000; Robertson, Vogan, and Lombardo 2008). Data from these sites indicate that concentrations of TOC or VFAs alone do not appear to be suitable parameters to measure substrate sustainability. Rather, they should be combined with other geochemical parameters and contaminant data to provide a "multiple lines of evidence" approach as to when the mulch substrate needs to be replenished. Based on evaluation of several biowall sites (AFCEE 2008, Parsons 2010a), the most useful geochemical parameters to determine when a biowall may need to be replenished are as follows:

- contaminant concentrations (e.g., chlorinated solvents or perchlorate)
- bioavailable organic carbon or electron donor supply (TOC or DOC, dissolved hydrogen, or humic and fulvic acids)
- indicators of predominant TEAPs (ferrous iron, sulfate, and methane)
- indicators of redox state and chemical equilibrium (ORP/Eh and pH)

In general, biowalls operate most efficiently when sulfate reduction and methanogenesis are predominant TEAPs. An evaluation of TOC or DOC alone may not indicate a shift from highly to less reducing geochemical conditions. A combination of a shift in decreasing ORP/Eh combined with an increase in sulfate and decrease in methanogenesis in the biowall are better indicators that a biowall may begin to lose efficiency in removal of chlorinated solvents.

Each biowall and groundwater environmental setting is unique, and the geochemical conditions under which the biowall loses efficiency may be very different. For example, the B301 biowall system at Offutt AFB, Nebraska, continues to be very effective under geochemical conditions that are only moderately reducing (ORP near 0 mV). AFCEE (2008) describes the development of an O&M plan recommended for biowalls that are designed to meet specific RAOs over period of 5 years or more.

Removal efficiency over time

The efficiency in removal of TCE and chlorinated ethenes (total molar concentrations) for the B301 biowalls continue to be effective with TOC <5 mg/L, where cDCE and VC have not accumulated. Similarly, the OU-1 biowall showed little reduction in percent TCE removal over the first 7 years of monitoring, indicating that conditions suitable for degradation of TCE have been sustained. However, after approximately 2–3 years of operation, TCE began to be transformed primarily to DCE and VC without further transformation to innocuous end products.

Complete transformation of chlorinated ethenes to innocuous by-products within the OU-1 biowall appears to be limited by the loss of reactivity of iron sulfides due to oxidation and insufficient reducible ferric iron for continuous production of fresh iron sulfides and by a lack of microorganisms capable of the biotic dechlorination of DCE and VC to ethene (Parsons 2010a). Because highly reducing conditions have been sustained, the long-term effectiveness of the biowall does not appear to be limited by depletion of the mulch and compost substrate. Rather, the long-term effectiveness appears to be limited by a persistent source of reducible iron and a deficient microbial population.

8.3.3 Operational and Economic Implications

Because biowalls are passive systems and require no energy to operate, they are a highly sustainable remediation technology. Biowalls may need to be replenished with a fluid substrate such as EVO, but this need is not anticipated to arise more frequently than every 4–5 years. Therefore, biowalls offer a promising long-term alternative to remediation of persistent groundwater contaminant plumes. The following sections describe recommendations for biowall construction, operation, and monitoring that can be used to improve biowall performance and longevity.

Biowall construction and materials

Many biowalls installed to date have been single trenches, and many have been constructed with just tree mulch and sand. As a result, the degradation of chlorinated ethenes may be limited by insufficient residence time or insufficient amounts of bioavailable organic substrate. More conservative biowall designs (e.g., multiple trenches in parallel) and more robust biowall construction (e.g., wider trenches, additional substrate, or biogeochemical amendments) may be needed to consistently achieve remedial goals.

A significant cost of biowall construction is the mobilization cost for large trenching equipment. But once the equipment is mobilized, there is an economy of scale for biowall construction. Practitioners should consider the improved performance that can be achieved by installing a second or third biowall in parallel. By spacing a second or third biowall within a few weeks of groundwater travel time, an anaerobic reaction zone can be maintained between the biowalls that greatly increases the effective residence time of contaminant(s) in the reactive zone. For sites with a relatively high flux of native electron acceptors, an upgradient biowall may be used to reduce concentrations of native electron acceptors so that highly reducing conditions can be sustained in successive downgradient biowalls.

Alternatively, or in addition to multiple biowalls, the organic content of the biowall matrix can be optimized by the addition of secondary amendments. Common amendments include compost (e.g., mushroom compost or composted cotton gin trash) and vegetable oil (typically sprayed onto the mulch). Other sources of organic amendments may be derived from local waste streams. Examples might include composted leaf and grass clippings, hay or other silage, feed corn, off-specification grains, poultry litter, stable bedding materials, composted manure, spent grain from breweries, rice hulls, or bulk chitin from seafood processing.

Design criteria for biogeochemical amendments are still in the developmental stage. AFCEE (2008) provides design guidance for biowall construction in terms of promoting both biological and biogeochemical transformation processes. While the document provides theoretical guidance for balancing sources of iron and sulfur to promote biogeochemical transformation of chlorinated solvents through iron sulfide formation, the theory has not been demonstrated, and there is significant uncertainty regarding the materials and groundwater geochemical conditions required to stimulate the process. Additional research in this area is being conducted by the Air Force with the objective of providing practical guidance in the future on biowall construction for stimulating biogeochemical transformation processes.

Operations and maintenance

While older biowalls, such as the B301 and OU-1 biowalls, continue to be effective after more than 5 years of operation, there are indications that the reducing conditions within the biowalls are gradually diminishing over time. Therefore, it is beneficial to have an O&M plan that periodically evaluates the need to replenish the biowall and provides a plan to replenish the biowall to sustain its effectiveness. Development of an O&M plan is highly site specific in regards to the hydrogeology, geochemistry, contaminants, and biowall system configuration. Development of an O&M plan is described in Section 8 of AFCEE (2008).

One objective of an O&M plan is to determine when replenishment is required prior to contaminant breakthrough. Therefore, the monitoring protocol for O&M should focus on critical geochemical thresholds and not simply on monitoring for breakthrough of the COCs. The frequency of monitoring should be adequate to provide sufficient time to implement a substrate replenishment event prior to unacceptable contaminant breakthrough. Thus, the frequency of monitoring is a function of how accurate geochemical indicators are in determining when replenishment will be required. An iterative approach may be necessary, and monitoring protocols should be evaluated periodically as additional data are collected and experience is gained with the treatment system.

Biowall O&M analytical protocols

In addition to analytical protocols used to document contaminant reductions, biowall analytical protocols are also needed to evaluate the geochemical conditions required to sustain long-term effectiveness of the biowall and also to evaluate the occurrence of biogeochemical transformation where the potential for this process to occur is high. A typical groundwater protocol for long-term operations may include some combination of the analytical protocol listed in Section 7.6.3. Most of these analytes are monitored during the initial performance monitoring period, and multiple lines of evidence should be used to determine when replenishment is necessary.

Analytical protocols that are useful in determining the potential for biogeochemical transformation of chlorinated solvents may include the following:

- bioavailable ferric iron of native sediment and biowall material
- strong acid–extractable ferric and ferrous iron of native sediment and biowall material
- AVS and CrRS of native sediment and biowall material
- sulfate, sulfide, and ferrous iron in groundwater
- pH and Eh (ORP) of groundwater

These analyses may be performed on a less frequent basis than groundwater sampling. For example, it may be useful to perform the analyses at 6–12 months after installation to determine whether conditions are optimal for production of reduced iron sulfides, and again at 3–4 years to determine whether the process has been sustained.

Biowall replenishment

Replenishment of a biowall PRB typically involves the injection of a supplemental organic substrate in the biowall trench. EVO is the substrate most commonly considered for biowall replenishment. EVO is a suitable substrate based on the ability to uniformly distribute the substrate throughout the biowall matrix, the duration it will last and low frequency of injection required, and lower product cost relative to other slow-release substrate types.

Biowalls that have been replenished with EVO include NWIRP McGregor, Texas; SS-17 at Altus AFB, Oklahoma; and the BG05 biowall at Ellsworth AFB, South Dakota. Methods to determine how much substrate to apply may be based on mass discharge of contaminants and native electron acceptors, a ratio of substrate to the mass of solid media in the biowall, or an empirical concentration of substrate based on past experience. Because biowalls are typically constructed perpendicular to groundwater flow and are typically only 2–3 feet wide, there is little transverse dispersion within the biowall itself. For this reason the substrate should be physically distributed throughout the entire biowall volume, requiring injection volumes equal to or greater than the effective pore volume of the biowall trench.

Three methods were used to determine substrate requirements for biowall replenishment at NWIRP McGregor, Texas (EnSafe 2005). The first method was based on a recommendation from the EVO vendor (EOS Remediation) to use a ratio of 0.1%–0.4% of EOS product by weight of the mass of solid media in the biowall. As an example, 2,090 pounds of EOS product was calculated to be required for biowall segment S-1B of 380 feet in length, 2.5 feet in width, and a saturated thickness of 10 feet; an assumed "soil" mass of 110 pounds/ft^3; and an oil-to-soil mass ratio of 0.2%. This is equivalent to 2,090 pounds of EVO product or 1,254 pounds of soybean oil, assuming the product is 60% oil by weight.

The second method used the EOS Remediation design spreadsheet and was based on electron acceptor demand and groundwater-specific discharge through the biowall. For the S-1B biowall example above, the design spreadsheet yielded a substrate requirement of approximately 3,780 pounds of EOS product (2,268 pounds of oil) assuming a 2-year design life and an average perchlorate concentration of 1,000 µg/L.

The third method used an assumption initially used when the biowalls were installed. The assumption was that 10 pounds of oil per cubic yard of biowall material was needed. For the S-1B biowall, this calculation yielded a requirement of 5,870 pounds of EOS product (3,522 pounds of oil, assuming the product is 60% oil by weight). The first method yielded the lowest of the three calculated substrate requirements and was selected based on economic considerations.

To ensure that substrate is uniformly distributed throughout the biowall, the injection volume should be sufficient to displace at least one pore volume of the section of biowall being treated. Although some substrate will flow into the surrounding formation, the total pore volume of the biowall section is a first approximation of the volume of the substrate mixture to inject. The total volume to inject in each biowall section can be calculated by multiplying the biowall dimensions to obtain a total trench volume, then multiplying by the matrix porosity to estimate the trench section pore volume. Example calculations are provided in AFCEE (2008).

8.4 Longevity of Combination ZVI and Carbon Substrates

PRBs that incorporate both ZVI and a carbon source in the reactive zone have become more common in the past decade with the advent of commercially available materials, such as EHC (Adventus 2009) and ABC+ (Redox Tech LLC Products, Inc.), and the development of EZVI (NASA 2009). While these materials may be used in a traditional PRB configuration to treat a dissolved plume, in many cases these combination materials have been applied in DNAPL and suspected source areas to both capture and treat chlorinated solvents. In these combined materials, particles are generally in the microscale range, and the ZVI contained within them may be micro- or nanoscale. Where source areas have been treated, a reduction in chlorinated solvent mass flux as well as degradation has occurred. However, because these materials have not been in widespread or field-scale use for longer than about 5 years, longevity data have been developed using bench studies.

8.4.1 Factors Influencing Longevity of ZVI and Carbon Substrates

In combined ZVI-carbon source PRBs, declining performance may be attributed to consumption of the carbon materials and, for ZVI, the precipitation of metals or other materials onto the reactive iron surface. Iron consumption can be attributed to the following general mechanisms (in no particular order) of iron consumption rate:

- complete reductive dechlorination of TCE
- water corrosion (iron oxidation)
- DO demand
- nitrate reduction
- sulfate reduction

These competing processes, along with precipitation of materials onto the iron surface, would impact any ZVI PRB (not only the combined materials considered here) and emphasize the need for comprehensive site characterization prior to PRB design.

Carbon consumption rates depend in part on the composition of the carbon material. The more insoluble forms of carbon—cellulose and hemicellulose—such as found in commercial products like EHC, degrade much more slowly than more soluble forms, such as lactate, oil, and glucose-based amendments (Vogan 1993).

The in situ longevity of these materials is then a consequence of the interaction of groundwater conditions, contaminant concentrations, and the amount and nature of the combined ZVI-carbon treatment materials. Based on bench-scale evaluations of EHC where it is assumed that nitrate and sulfate electron acceptor reduction and VOC degradation do not compete with water corrosion of ZVI, ZVI may last for several years (Reardon 2005).

In the case of EZVI, the iron inside the emulsion droplet is protected for a period of time from several of the iron-consuming and precipitation processes that exposure to natural groundwater may initiate. However, the iron is still consumed through the reductive dechlorination and water corrosion processes. The integrity of the emulsion droplet is compromised by both biological degradation of the oil membrane and iron consumption and eventually the droplet destabilizes. Because oil and surfactant, by weight, may constitute some 39% of typically formulated EZVI, or approximately 3.4 pounds per gallon EZVI (USEPA 2009b), longevity of oil products may provide insight into the potential longevity of EZVI injections. The ZVI component may be expected to have a lifespan similar to nonemulsified irons, perhaps a decade or longer, depending on site conditions.

8.4.2 Field Experience

Combined ZVI-carbon materials have been used for less than 10 years; therefore, not a lot of long-term field information exists. For example, the earliest EZVI injection occurred in 2002, and EHC has been on the market only since 2004. Also, with new materials, many initial injections/emplacements that were at pilot scale have been subsequently overwhelmed when a full-scale remedy was installed. Another potential complication in determining longevity is the use of these materials concurrently or in series with a bioaugmentation culture. While the currently available field data seem promising, further evaluation is needed and will be available as more and longer-lived projects are constructed.

Select EHC field data

Currently, several field installations of EHC are being monitored for long-term performance. One PRB designed to intercept a chloroethene plume demonstrated a notable reduction in PCE over a 21-month observation period. The reduction likely reflects both biotic and abiotic degradation processes (Molin et al. 2010). A second, pilot-scale injected PRB constructed to treat carbon tetrachloride (CT) exhibited an approximate 90% decrease in CT concentration 42 months post-construction with no significant accumulation of chlorinated intermediates. Data gathered at other sites appear to indicate that sequential dehalogenation occurs, followed by abiotic degradation processes (Molin et al. 2009a, 2010; Peale, Mueller, and Molin 2010).

Select EZVI field data

Because of the significant oil-surfactant component of EZVI, evaluating emulsified oil remediation technology may be useful in projecting EZVI longevity. Based on a pilot-scale injection, emulsified oil continued to effectively treat both chlorinated solvents and perchlorate 2.5–3.5 years post-injection with no observed adverse affect on aquifer hydraulic conductivity. Over this 3.5-year monitoring period, 76% of the injected substrate had been consumed, indicating very efficient substrate use. Although not quantified, the continued slow dissolution of the remaining carbon that was initially sorbed to the aquifer sediments is expected to provide a continuing source for an even longer period of time (Solutions IES 2002).

A 2004 full-scale EZVI-bioaugmentation remediation of a Florida DNAPL site project exhibited significant reduction in source area concentrations after 16 months and is slated for a 5-year evaluation (Faircloth et al. 2006). A 2006 pilot-scale injection of EZVI continues to be monitored for long-term performance. Substantial increases in ethane production have been noted, and stable isotope analyses indicate EZVI promoted degradation of PCE and its daughter products after 2½ years (USEPA 2009b).

8.4.3 Operational and Economic Implications

As has been discussed in previous sections, the smaller the scale of ZVI used, the faster the rate of degradation that can be expected, but at a greater cost. While nanoscale iron yields significantly faster reaction rates due to tremendous surface area, microscale iron seems to be gaining in usage because of the acceptable reaction rates at significantly lower costs than NZVI. Some of the combined materials such as EHC and EZVI have the option of using and/or adding either nanoscale or microscale iron, allowing the user to evaluate site-specific cost-benefits.

8.5 Longevity of Mineral Media PRBs

8.5.1 Factors Influencing Longevity of Mineral Media PRBs

Mineral media PRBs include those systems constructed of slag, apatite, zeolite, TRM, and green sand and organophilic clay. Similar to ZVI- and mulch-based PRBs, the longevity of PRBs constructed of mineral media is a function of sustaining media reactivity and permeability. Factors specific to mineral media PRBs are discussed in the following sections.

Reactivity of mineral media

Adsorption, ion exchange, and precipitation in low-solubility phases are the key mechanisms for contaminant treatment by mineral media. Therefore, long-term performance of mineral media in a PRB depends on the ability to maintain these mechanisms. Due to the variability in the composition within each type of mineral media, such as slag (Metz and Benson 2007), apatites (Magalhaes and Williams 2007), and zeolites (Van Bekkum, Flannigen, and Janmsen 1991), batch and column testing is necessary to establish the required type and amount of the reactive components of the reactive medium with respect to site-specific COCs. For instance, the effectiveness of TCE treatment by slag was found to be proportional to iron content (Cope and Benson 2009), indicating that the iron content of the slag needs to be evaluated prior to implementation for TCE treatment. Precipitation and adsorption have been identified as the key mechanisms for slag treatment of metals, and therefore the specific surface and solubility of reactive phases need to be understood with respect to metals immobilization. Table 8-1 summarizes the key mechanisms and reactivity factors that need to be considered for each of the mineral media.

Table 8-1. Key mechanisms and reactivity factors for mineral media

Mineral media	Key mechanisms	Reactivity factors
Slag	• Adsorption	• Specific surface, surface charge, particle size, pH
	• Precipitation of calcium minerals	• Calcium content and solubility, pH
	• Precipitation of hydroxide minerals	• Alkalinity, pH
	• Complexation with iron oxides	• Iron content, partition coefficient
	• Reduction by iron	• Iron content
Apatite	• Precipitation of phosphate minerals	• pH, mineral solubility
	• Cation exchange	• Specific surface, competing cations
Zeolite	• Cation exchange	• Specific surface, competing cations
	• Adsorption	• Specific surface, surface charge, particle size, pH
	• Anion exchange (on SMZ)	• Specific surface, competing anions
	• Solid-phase substitution	• Strontium-calcium ratio
TRM	• Precipitation of hydroxide minerals	• Alkalinity, pH
	• Adsorption	• Specific surface, surface charge, particle size, pH
Organophilic clay	• Adsorption	• pH
		• Organic treat compound

Mineral media	**Key mechanisms**	**Reactivity factors**
Green sand	• Adsorption onto mineral phases • Reduction by iron • Adsorption onto organic carbon	• Specific surface, surface charge, particle size, pH • Iron content • TOC

The reactivity of slag materials varies substantially among and within slag sources (Metz and Benson 2007). The long-term reactivity of slag is likely to be less affected by the precipitation of minerals than is the reactivity of ZVI, which is dependent on the direct contact of COCs with iron. Furthermore, the wide range of key treatment mechanisms for slag may help maintain long-term reactivity. The treatment of anion COCs may be affected in the long-term by the presence of competing anions.

The long-term stability of uranium on apatite has been found to be dependent on the chemical speciation of uranium, the surface speciation of apatite, and the mechanism of retention (Wellman et al. 2008). If surface sorption is the dominant uranium sequestration mechanism, as was found by Fuller, Bargar, and Davis (2003), then the efficiency of uranium removal is expected to decrease with time as the concentration of uranium exceeds the number of available sorption sites. The distribution coefficient for U(VI) sorption on apatite was found to vary by an order of magnitude over a modest pH range (7.0–8.0) (Wellman et al. 2008). The removal of uranium by uranyl phosphate precipitation may result in the long-term reduction in removal efficiency due to the passivation of the phosphate surfaces (Morrison et al. 2002).

Calcium competes with strontium-90 for cation-exchange sites on zeolites, and therefore strontium-90 treatment efficiency is dependent on the strontium-90/calcium ratio (Lee et al. 1998, Lee and Hartwig 2005). Generally, the concentration of calcium in groundwater is much greater than that of strontium-90 and affects reactivity over time. Similarly, the sorption of target anions on SMZ may be limited over the long term due to competing anions (Zhang, Avudzega, and Bowman 2007).

Precipitation of metal hydroxides due to the alkaline conditions created by TRM may lead to passivation of TRM surfaces. Similar to other media for which adsorption is a key mechanism, the number of available TRM sorption sites is expected to decrease with time. Genç-Fuhrman, Bregnhøj, and McConchie (2005) observed decreases in arsenic sorption on TRM over time and accelerated arsenic breakthrough in the presence of sulfate, phosphate, and bicarbonate anions.

The long-term reactivity of green sand is likely to be limited by the availability of surface sorption sites, passivation of iron mineral surfaces, and the availability of organic carbon. The long-term reactivity of green sands with respect to TCE was found to be comparable to that of ZVI (Benson, Lee, and Eykholt 2003).

The long-term reactivity of organophilic clay may be limited by the biodegradability of the organic compound used in the manufacture of the organophilic clay and whether highly aerobic conditions exist. Under oxygen limited conditions, quaternary amine compounds show no or very poor primary biodegradation and no evidence of significant ultimate biodegradation was found (Ying 2005).

Due to the complexity of potential treatment mechanisms in mineral media, batch and column tests need to be performed to determine COC-specific partitioning coefficients and maximum removal capacity.

Long-term hydraulic conductivity

Precipitation of mineral phases on slag, apatite, and TRM is likely to lead to reduced PRB porosity and hydraulic conductivity, thereby reducing the flux of groundwater and potentially leading to groundwater mounding and flow around the PRB. Clogging is less likely to occur on zeolites because cation exchange processes and adsorption are the key treatment mechanisms (Morrison et al. 2002). The presence of organic material in green sand may contribute to long-term biological fouling.

8.5.2 Field Experience with Mineral Media PRBs

Long-term field data on the performance of mineral media PRBs are available for slag, apatite, zeolite, and organophilic clay. To date, TRM and green sand have not been used in full-scale PRBs.

Slag PRB—East Chicago, Indiana

Data from the BOFS PRB installed in East Chicago, Indiana, have been collected since 2002. Two parallel 1,800-foot (550-m) PRBs were installed 9 feet (3 m) apart to treat arsenic at influent concentrations up to 3 mg/L. Data collected in 2007 indicated that the PRBs were effectively removing arsenic to below 0.01 mg/L 5 years after installation and that a “clean zone” was developing up to 6 feet (2 m) downgradient of the second PRB (Bain, Blowes, and Wilkens 2007). The available data did not indicate a reduction in the arsenic treatment efficiency over the 5-year period. A high pH plume had developed downgradient of the first PRB and as of 2007 extended to approximately 15 feet (5 m) downgradient of the second PRB.

Apatite PRBs

The performance of apatite PRBs has been variable (see Section 4.5). The available data for the Success Mine Apatite II PRB show no reduction in the treatment efficiency for pH, cadmium, lead, and zinc from January 2001 to June 2004. The PRB consists of two cells, each of which contains five 10-foot-long Apatite II chambers installed in series (Conca and Wright 2006). Data collected in July 2003, or 2 years after PRB installation, indicated that cadmium and lead were being sequestered in the first 10 feet of the PRB, whereas zinc migrated to 20–30 feet in the PRB. Visual observations made after 5 years of operation indicated that approximately 30% of the apatite “appeared to be spent” (Conca and Wright 2006).

Data from the Fry Canyon bone char apatite PRB show mixed treatment of uranium over time (Naftz et al. 2002). During the first year of operation (1997–1998), the bone char apatite PRB was removing up to 99.9% of uranium within the first 1.5 feet of the PRB (Naftz et al. 1999).

However, the uranium removal efficiency decreased substantially thereafter in one of the PRB flow paths, to where the effluent uranium concentration exceeded the influent concentration, indicating that back-diffusion was taking place (Naftz et al. 2002). The uranium removal efficiency in the other flow path remained high. The differences in performance may be due to hydraulic issues, with groundwater entering the PRB at less than a 90° angle (Naftz et al. 2002).

The Mortandad apatite PRB was successful in treating strontium-90, nitrate, and perchlorate, but did not reduce concentrations of plutonium-239 and -240, americium-241, and uranium-235 and -238. The long-term performance of this PRB cannot be assessed because the groundwater level declined due to drought and monitoring was terminated after approximately 1 year of operation.

Zeolite PRBs

The Chalk River zeolite PRB, which treats about 4 million gallons of groundwater per year, has effectively removed strontium-90 from groundwater for over 11 years. The removal rate is approximately 99%, with an influent of 85 Bq/L and an effluent of <0.6 Bq/L (Lee and Hartwig 2005). There has been no apparent decrease in removal efficiency over the 11-year treatment period (David Lee, e-mail communication, 10/26/2009).

Organophilic Clay

The Escanaba, Michigan, organophilic clay PRB has been monitored since 2005. In the first 2 years, there was no breakthrough of creosote DNAPL (Leece 2007).

8.5.3 Operational and Economic Implications

In general, guidance specific to mineral media PRBs is limited. The number of PRBs installed to date is small, and none of the mineral media PRBs have been replaced or rejuvenated. However, most of the points that were raised in discussions pertaining to ZVI and biological PRBs in Sections 8.2 and 8.3 are likely to be equally pertinent to the installation, operation, and monitoring of mineral media PRBs. Factors unique to each of the mineral media are summarized in the following sections.

Slag

The design, installation, and operation of slag PRBs need to take into account the wide range of the chemical and physical composition of slag. Slag texture varies depending on the method used for cooling molten slag. The flow-through properties of slag and the option of adding gravel to improve hydraulic conductivity need to be considered.

Predicting the long-term reactivity of slag is more challenging than that of ZVI PRBs due to the large number of potential treatment mechanisms in slag. As seen at the East Chicago PRB (noted above), slag is likely to maintain high pH for a number of years, providing conditions conducive to the precipitation of metal hydroxides. The potential passivation of reactive iron surfaces and a decrease in the number of available sorption sites should be evaluated by monitoring trends in target COC concentrations over time. Periodic sampling and analysis of PRB solids can be used to determine the loading rate of target COCs and help predict the PRB longevity and potential need for replacement.

There are no viable means for slag PRB rejuvenation. Replacement of the slag material or the installation of a second slag PRB in parallel is a viable option. The cost of slag is very low compared with ZVI; therefore, the costs of a replacement slag PRB is driven primarily by installation costs.

LTM of slag PRBs must include measurements of pH and alkalinity downgradient of the PRB. Field experience has shown that slag can substantially affect groundwater geochemistry; the ability of the native soil to buffer the high-pH groundwater leaving the PRB should be established.

Apatite

The kinetics of COC uptake by apatite are controlled by the dissolution of phosphate and are relatively slow (Manecki, Maurice, and Traina 2000). Similarly, the sorption mechanisms on apatite appear to be kinetically controlled (Xu, Schwartz, and Traina 1994). Reactivity and kinetics need to be considered with respect to groundwater flow velocity through the PRB (Wellman et al. 2008). Apatite PRBs installed to date have generally been substantially thicker than most ZVI and biological PRBs, ranging 3–46 feet in thickness. As discussed in Section 8.5.2, zinc migrated to between 20 and 30 feet after 2 years in the Success Mine Apatite II PRB.

The concentration of phosphate and competing cations should be measured to help evaluate the longevity of apatite PRBs with respect to phosphate mineral precipitation and surface sorption. In addition, LTM of phosphate concentrations should be performed downgradient of apatite PRBs, as phosphate can have a significant negative impact on groundwater quality.

In situ rejuvenation of apatite is theoretically possible through the injection of calcium-citrate-phosphate solution (Szecsody et al. 2008) but has not been performed to date. Depending on the type of apatite used, the costs of a replacement apatite PRB may be driven by material or labor costs.

Zeolite

Cation exchange and anion exchange (in SMZ) are the key treatment mechanisms in zeolite PRBs. Therefore, the concentration of competing cations (or anions) should be measured to help evaluate the longevity of zeolite PRBs. For the treatment of strontium-90, the ratio of strontium to calcium concentrations should be measured.

There are no viable means for zeolite PRB rejuvenation. Replacement of the zeolite material or the installation of a second zeolite PRB in parallel is a viable option. Depending on the type of zeolite used, the costs of a replacement zeolite PRB may be driven by material or labor costs.

9. PRB AS GREEN AND SUSTAINABLE TECHNOLOGY

What's New?

- Evaluation of PRB technologies from a green and sustainable perspective
- Designing PRBs to minimize the net environmental impact by selecting recycled or natural materials and using renewable energy sources during installation
- Resources and tools for evaluating the sustainability of PRBs

The primary goal of contaminated site remediation is to mitigate the contamination to a level that results in an acceptable health risk to humans and is protective of the environment. Remedies traditionally have focused specifically on contaminant reduction or minimization of exposure but have not explicitly considered the net environmental impact, including the potential of transferring impacts to other media. For instance, many decisions on remediation technologies typically do not assess the impacts of GHG emissions, natural resource consumption (e.g., water, land), adaptability to climate change, or energy use. The intent of considering these factors during remedy selection is to improve overall environmental performance and ensure the implementation of sustainable processes while ensuring the remedy remains protective of human health and the environment.

The ITRC Green and Sustainable Remediation (GSR) Team is addressing the environmental impact of remedies. As of May 2011, the ITRC GSR Team consensus-derived definition of GSR is as follows:

> Green and sustainable remediation is the site-specific employment of products, processes, technologies, and procedures that mitigate contaminant risk to receptors while making decisions that are cognizant of balancing community goals, economic impacts, and net environmental effects.

This section examines the use of PRBs in the context of GSR and how PRBs likely compare with other, more traditional remedial technologies. For a more general overview of this concept, please reference the GSR Team's technology overview (ITRC 2011a).

9.1 Introduction

The "invention" of the PRB came about because of the need to develop groundwater remediation methods that were less resource intensive, more cost-effective, and more durable than conventional methods such as groundwater pump and treat. Due to recent attention on climate change issues and the negativity surrounding resource-intensive remediation programs, PRBs are again in the spotlight as a sustainable remediation method.

PRB technology is widely considered a sustainable groundwater remediation method for the following reasons:

- The general intent of a PRB system is to perform under hydraulically passive means (i.e., no energy or mechanical input for routing chemically impacted groundwater through the PRB).
- Groundwater is not removed from the subsurface nor degraded through discharge with lower quality surface or waste water.

- The ZVI technology has a track record for long-term performance (>15 years) without the need for substantial maintenance; biowalls, while having a shorter performance history, are developing newer methods for rapidly recharging mulch material with liquid organic substrates.
- The treatment media often consists of recycled or "waste" material such as mulch/compost.

Through its Best Management Practices Program, USEPA states that green remediation "results in effective cleanups minimizing the environmental and energy footprints of site remediation and revitalization" (USEPA 2008a). This is an attempt to look at a whole site approach and focuses on the following:

- energy requirements
- air emissions
- water requirements and impacts on water resources
- impacts to land and ecosystems
- material consumption and waste generation
- impacts on long-term stewardship of a site

Because USEPA practices for promoting green remediation focus on reducing energy consumption, air emissions, and water impacts, the PRB may be considered a cornerstone of green remediation BMPs. However, the PRB does have its limitations and uses resources to a certain extent, particularly during system installation. The objective of this section is to highlight these areas and provide guidance on how the PRB concept should be viewed in terms of GSR practices. The purpose of this section is not to provide an exhaustive study of the sustainable features of the PRB but instead to shed light and provide guidance on design and implementation areas relevant to assessing the benefits and adverse effects of PRB technology with respect to sustainable practices. Additionally, the section suggests other resources and tools to predict and reduce sustainability impacts of PRBs.

9.2 PRB Sustainability Impacts

The intent of the PRB is to operate as a hydraulically passive in situ groundwater remedy. Once the system is constructed, advective groundwater flow is the primary driver moving groundwater contaminants through the PRB for chemical and/or biological treatment. This section evaluates PRBs in light of the sustainability metrics outlined by USEPA and also suggests approaches to further enhance sustainability.

9.2.1 Energy Requirements

While it is acknowledged that energy consumption during PRB operation is low to negligible, energy consumption during PRB deployment can be moderate to high, depending on the PRB design and the site location. The following paragraphs discuss PRB implementation and operation in light of sustainability metrics with a focus on energy consumption.

Construction process

The construction of the PRB itself is a resource-intensive process that requires the use of heavy equipment (and thus fuel) to install the system. For standard designs, installation activities include monitoring well installation; trenching and/or drilling; material loading, transport, and installation; and soil disposal. Drill rigs, continuous trenchers, backhoes, delivery trucks, and other large equipment are usually required. Fracturing and injections require pumping and/or pressurized injection, often using substantial amounts of water and/or gases. Drilling and trenching activities usually result in investigation-derived waste, including soil cuttings, unless direct-push drilling techniques are used, which generate little to no waste soils. Certain specialized installation techniques, such as the use of single-pass trenchers, require support from specialized contractors; therefore, the equipment and crew may need to mobilize from substantial distances, thereby increasing the energy consumption when using specialized equipment unless other sustainable transportation method or installation techniques can be implemented (e.g., biofuels).

PRB materials

A PRB is constructed of two primary components: the hydraulic routing system and the contaminant treatment system. The hydraulic routing system is intended to route affected groundwater through the treatment matrix. If the PRB is a continuous wall with no hydraulic-control wing walls or funnels, the hydraulic system may be no more than a mixture of the treatment media designed with sufficient permeability to allow affected groundwater to pass through. The wing walls or low-permeability zones, if needed, as well as the primary reactive zone require the use of energy to produce the raw materials used in the wall (e.g., cement, bentonite, reworked soil, sheet piles).

The reactive media selected has the greatest impact on the sustainability of the overall PRB. Reactive media can range from very sustainable (e.g., mulch obtained from a local source) to less sustainable (e.g., manufactured iron or a highly processed chemical product shipped long distances). One project at Hill AFB is planning to recycle cast iron practice bombs available locally (Roginske, Stewart, and Olsen 2009). Other materials used in PRBs, such as sand, gravel, zeolites, and limestone, are mined materials that would be considered less sustainable media, particularly when they must be transported great distances.

The overall environmental impact of the type and source of the reactive media should be taken into consideration when selecting the appropriate material for the barrier:

- **ZVI ore vs. recycled iron:** ZVI typically is manufactured from recycled material rather than being created directly from a mining and iron mill operation. The source of ZVI (recycled or mined) should be confirmed, and recycled iron should be specified as part of the description of a ZVI PRB application.

- **Organic media:** The mulch or compost material for a PRB should be obtained from a source or supplier within the local community, if possible, as a highly sustainable and green benefit of the specific technology application. Local municipalities often have piles of tree mulch that are derived from storm cleanup that they give away or sell for a nominal price to the public.

Transportation

The transportation of the PRB media, materials, and construction equipment to the project site can increase the energy footprint and accident risk of the PRB implementation. This consideration is mostly based on the distance material and equipment must travel from their origin to the project site and the means of transport. Some examples follow:

- **ZVI media:** Currently, manufacturers of the material in North America are located in Detroit; Cleveland; southern California; and Ontario, Canada. Depending on the specific type of ZVI needed and the location, a site in Florida requiring ZVI from Detroit will have higher transportation energy consumption than will a site located in the Midwest (for the same given volume of iron needed by the PRB).

- **Zeolite media:** For an ion-exchange PRB requiring a specialized zeolite, two sources of zeolite—one in Idaho and one in Oregon—are typically considered. The energy required to mine and transport the material to a site on the East Coast would be higher than for a site located on the West Coast.

- **Biowall rejuvenation media:** Biowalls may require periodic recharging with liquid organic substrates. Transportation of these substrates generally requires tanker trucks to transport substrates from soybean or lactate production facilities located in Midwest states.

- **Equipment:** Equipment mobilization considerations include whether mobilizations can be combined to reduce the distance heavy equipment must be transported and whether renewable energy such as biodiesel can be used to power the equipment.

While these may be obvious considerations, the energy usage from media and equipment transport typically does not enter into formal BMP feasibility discussions. Whenever possible, local sources should be used. In addition, transporting media and equipment via rail rather than truck reduces the energy and accident risk footprints.

PRB operation

Because of the intended passive design of PRBs, energy and water consumption is intended to be low or negligible. Passive means are generally used to treat groundwater in situ. Low-permeability funnel walls or routing barriers may be used to assist with routing water through the PRB. Occasionally, a hydraulically active mechanism such as a siphon or low-rate pump may be used to direct the flow through the PRB. Biowalls may require periodic recharging with liquid organic substrates, which requires transportation to the site.

The typical consumption of energy once the PRB is implemented occurs through vehicle and generator use during monitoring events. However, this consumption typically is low and can be made more sustainable by using energy-efficient vehicles and low energy-intensive sampling methods, such as passive diffusion bags (PDBs), reduced interval monitoring schedules, and telemetric methods (a developing technology).

9.2.2 Air Emissions

Air emissions result from the activities discussed above. These air emissions include criteria priority pollutants (e.g., sulfur oxides, oxides of nitrogen, and particulate matter) and GHG emissions emitted primarily as a result of energy consumption. Typically, the PRB is not considered a remedial method that promotes substantial air emissions to the atmosphere. The system operates passively, and if no energy is input to the system via mechanical or power processes, no energy-related air emissions occur. As discussed above, emissions can be limited during implementation by using local sources for material and equipment (if feasible), using alternative means of transportation or fuel, and through design of the PRB system itself. Air emissions during monitoring are negligible and can be minimized further by implementing sustainable monitoring methods discussed previously.

The treatment process applied in a PRB can produce certain gases; however, the levels are very low compared to construction activities and typically are dissolved in groundwater where they are utilized microbially. Some examples follow:

- **Gases from ZVI PRB:** This is the production of dissolved hydrogen gas from the corrosion of ZVI in a ZVI PRB. The production of hydrogen is not expected to be greater than its solubility level in water (approximately 0.0009 mol/L), although it has been reported that "bubbles" can form. Previous pilot-testing also notes the production of C1–C5 hydrocarbons from the reaction of iron in water. However, these again are in low amounts and are typically consumed by natural processes (Warner et al. 2005). In fact, one area of developing technology is the use of ZVI to promote bioremedial processes that rely on excess hydrogen and other gases for metabolism. Because of the very low production of these gases, contribution toward GHG production may be considered negligible.

- **Gases from biowall PRB:** A biowall PRB produces CH_4, CO_2, hydrogen, and H_2S. These gases were measured for a biowall PRB treating acid mine drainage at the Nickel Rim site, Ontario, Canada. On average, over 90% of the CO_2 is produced by sulfate reduction; the remainder is produced by methanogenesis. Over the life of the barrier, it is possible to model and thus estimate the total amount of these gases that will be produced (Amos et al. 2004). However, given that the concentrations of groundwater contaminants are generally in the ppm range, the total quantity of these gases produced by PRB remediation is negligible compared to operation of a single internal combustion engine.

Generally, air emissions, including GHGs, are not a major concern for the PRB because of the passive operation.

9.2.3 Impact on Water Resources

The PRB is a water resource conservation method. No water is removed, and all water that passes through the PRB is returned to the native aquifer in a cleaner condition. Therefore, with respect to water use footprint, the PRB should be considered 100% green. Indeed, the PRB is intended to remove contaminants and clean the water passively. PRB materials can employ methods that also are commonly used for above groundwater filtration, such as natural ion exchange zeolites, and are thus safe for potential beneficial water use by ecosystem receptors. On occasion, secondary mineralization can occur depending on the treatment media used. Monitoring for secondary water-quality impacts (e.g., excess TOC, pH, arsenic, or iron) should be performed as outlined in Section 7.8.

The area upgradient of a PRB remain impacted by contaminated groundwater until all water and contaminants either flow through the PRB or are attenuated naturally. Therefore, deed restrictions for domestic groundwater use in these areas may be required.

9.2.4 Impacts to Land and Ecosystems

While land use is impacted during the construction period, this effect is typically of short duration (months) with few long-term implications. The PRB structure is built and maintained belowground. A key advantage is that the PRB can be used to "restore" the economic use of a property by allowing it to be fully used, as was the case of the first commercial PRB built in 1994 (Warner et al. 2005). Except for limitations on digging and groundwater extraction, the PRB generally does not limit typical land use. PRBs can be designed to exist in highly trafficked areas and do not impact vehicular or other heavy industrial use, provided that the at-grade design is built appropriately for the intended ground surface land use. Special designs are required for mulch-filled biowalls, as organic materials tend to degrade and consolidate over time, creating settlement issues. The primary impact to ecosystems occurs during PRB implementation. In the long term, PRBs enhance the quality of the local ecosystems through improved water quality.

9.2.5 Waste Minimization

The PRB is built as a typical remediation construction project. All PRBs involve the use of construction equipment and often require the removal and management of impacted soil and groundwater located along the construction alignment. These materials typically are removed and treated or managed using conventional methods. Soil should be sorted and reused, where regulatory and technical assessment will allow. In addition, waste generation may be minimized through certain construction techniques, including direct-push injection or soil mixing techniques. Furthermore, PRBs can often use recycled material as the treatment media. Green waste that forms mulch, recycled iron that is processed into ZVI, and excess food-grade bone (chiton, apatite, calcium phosphate) can all be applied in PRBs.

9.2.6 Impacts on Long-Term Stewardship

Another issue that must be addressed is that of stewardship. PRBs generally are considered semipermanent to permanent emplacements that require little to no O&M. Therefore, the long-term permanence in protecting human health and the environment is viewed favorably.

Replenishment of the reactive media, removal, or isolation (i.e., clean closure) may be required in some circumstances. Certain types of barriers (e.g., mulch barriers) may require recharging via injections of organic carbon substrate; a ZVI PRB may require that the wall be excavated and replaced. For sorption PRBs where contaminants are retained and not degraded (except very slowly if the contaminant is radioactive), the barrier may require additional special consideration to prevent desorption of the contaminant once the remedial life of the PRB is exhausted. That said, to date PRBs have generally proved to be good stewards of the environment.

9.3 Sustainability Assessment Resources and Tools

Few resources or tools currently are available and proven to accurately measure or represent "greenness" or the "sustainability" of a particular technology. However, as the concept of GSR becomes more broadly used, reliable tools for measuring these concepts should be developed and refined over time. Available resources regarding sustainable remediation include the following:

- ITRC GSR Team (www.itrcweb.org)
- USEPA (www.clu-in.org/greenremediation/tab_d.cfm)
- U.S. Air Force/AFCEE (www.afcee.af.mil/resources)
- Naval Facilities Engineering Command (NAVFAC) (www.ert2.org/t2gsrportal/default.aspx)
- The Sustainable Remediation Forum (an industry-led group that is developing various guidance and discussion white papers regarding the footprint of various remediation strategies, including PRBs)

Some tools currently accessible for this purpose generally fall under the banners of the following:

- life-cycle analysis (LCA) (see USEPA National Risk Management Research Laboratory's LCA website: www.epa.gov/nrmrl/lcaccess)
- net environmental benefit analysis
- sustainable remediation tools

DOD has recently developed two tools to facilitate evaluation of remediation technologies based on key sustainability factors:

- The Sustainable Remediation Tool (SRT) was developed to aid those selecting remedies to incorporate sustainable concepts into the FS technology screening and decision-making process. This tool allows for the comparison of different remedial technologies based on sustainability metrics. Two PRB technologies that can currently be evaluated using this tool are ZVI walls and biowalls.[7]

- The SiteWise™ tool consists of a series of spreadsheets allowing the user to specify the major components of remediation technology construction and operation. This tool is flexible and can be used to support an evaluation of the environmental footprint of any technology. The tool currently provides an assessment of several quantifiable sustainability metrics, including GHG emissions, energy usage, criteria air pollutant emissions, water usage, and accident risk.[8]

9.4 PRBs Compared to Other Treatment Technologies

Figure 9-1 illustrates a continuum of remediation technologies ranging from "least green" (excavation) to "most green" (MNA). PRBs lie next to MNA in terms of their green

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[7] www.afcee.af.mil/resources.

[8] www.ert2.org/t2gsrportal/SiteWise.aspx.

characteristics (ITRC 2008). PRBs are considered to be a passive remediation approach, which is considered particularly sustainable when used for 10 years or more.

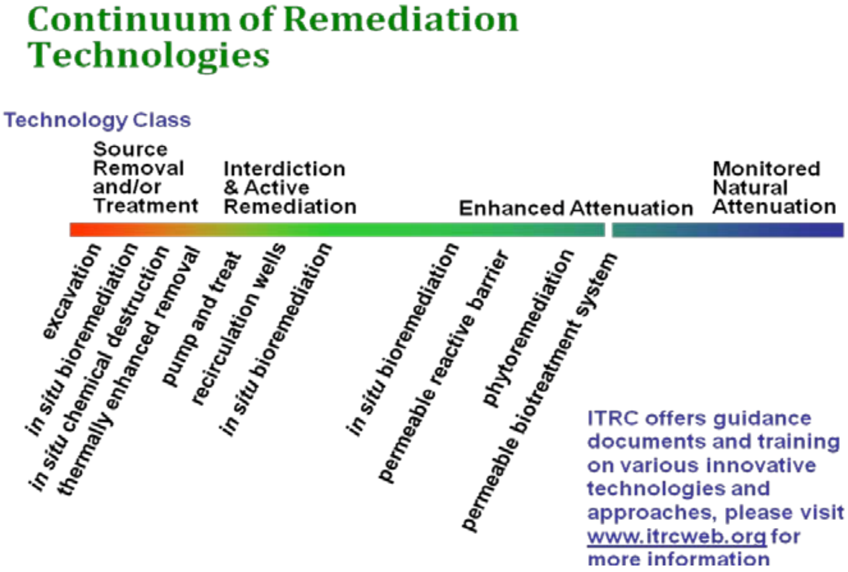

Figure 9-1. A continuum of remediation technologies ranging from least green (excavation) to most green (MNA).

The key consideration with regard to PRB materials is that the energy and water consumption to produce and transport the various construction components are considered one-time energy consumers. That is, these are not ongoing or long-term highly intensive energy sinks compared to an active remediation system such as pump and treat or steam injection, for example. The volume of materials used compared to the volume of affected aquifer being treated is considered very low compared to other more traditional technologies.

The amount of energy saved by using a PRB compared to a conventional method, such as pump and treat, can be calculated with tools such as SRT or SiteWise as described in the previous section. The energy benefits are greater as the life cycle of the PRB is extended beyond 10 years. While significant energy is consumed during PRB construction, minimal energy is used during operation, thereby creating a low life-cycle energy impact.

If recycled materials can be used, it may be possible to further reduce the “footprint” and possibly show a zero-sum carbon use when comparing both the construction infusion of energy with the savings from recycling and water conservation.

10. STAKEHOLDER INPUT

The people who live, work, study, and recreate on or near contamination sites tend to support PRBs as cleanup strategies. In particular, they prefer PRBs to the various forms of impermeable barriers historically used in remedies. However, they are likely to ask the same site-specific questions as responsible parties and regulators before endorsing the technology.

Stakeholders like PRBs because in most cases they degrade contaminants, rather than transferring them to other media such as the air or carbon filters. They also appreciate that most PRBs are passive, requiring no energy and generating no noise during their operational phase. In most cases, they are invisible once they are installed. At the Navy's Moffett Field, California, the Restoration Advisory Board endorsed a PRB demonstration in the 1990s—though they were amused by its nickname, the "iron curtain." More recently, the same stakeholders endorsed the National Aeronautics and Space Administration (NASA)–proposed iron PRB along the boundary between the Moffett military housing site, now owned by the Army, and NASA's Ames Research Center. Ironically, NASA switched to another PRB technology when the price of iron skyrocketed.

Stakeholders are often skeptical about impermeable barriers, the predecessors of PRBs. At the Middlefield-Ellis-Whisman Superfund site, Mountain View, California, stakeholders viewed slurry walls installed in the 1980s to prevent the migration of VOCs as a legal strategy to limit the liability of responsible parties. Not only did the slurry walls not treat the contamination, but some of them appear to be leaking. More recently, stakeholders at New York City school system's new Mott Haven Campus in the south Bronx questioned the installation of a jointed metal Waterloo Barrier along the edge of the school property. They expressed concern that the barrier would cause mounding of VOCs on the adjacent property. Stakeholders at another New York school, the Manhattan Center for Science and Mathematics, were concerned that a concrete wall on that property might cause the mounding of migrating coal tar. In this case, the responsible party, Consolidated Edison, plans to extract contaminants from behind the wall, but it has also agreed to evaluate the installation of a partial PRB. (Note: PRBs remain experimental for coal tar and other manufactured-gas plant wastes.)

PRBs are viewed as an effective way to prevent contaminants from migrating from a property that is the source of a groundwater plume, but stakeholders may reject them as a stand-alone strategy. For example, the neighbors of the former Kelly AFB in San Antonio, Texas, do not oppose the PRBs the Air Force installed to halt plume migration, but they also want off-site remediation—cleanup of the TCE and PCE plumes that underlie their homes.

Stakeholders with access to technical expertise may also question PRBs where there is a broad mix of contaminants. Members of the Astra-Zeneca Community Advisory Group, in Richmond, California, criticized a biologically active permeable barrier because there were too many COCs. For example, they say it did not treat the high levels of arsenic at the site. They also observed that tidal flows may have undermined the barrier's effectiveness.

In general, at sites where PRBs are considered as remedies, stakeholders ask many of the same questions as other parties. Does the technology fit the RAOs? Will it address the particular contaminants? Is it suited for the particular subsurface environment? Will it outperform other remedial alternatives? Is it cost-effective? Will the PRB last long enough to be considered passive, or will it need to be regenerated frequently? How will the PRB be monitored in the long run?

Stakeholders may be particularly sensitive to the location of barriers, to ensure that they do not interfere with property use. The 1995 placement of a PRB along the median strip of Central Expressway in Sunnyvale, California, resolved this problem at the Intersil groundwater plume.

As with other remedies, the traffic, noise, and dust of construction often cause concern. Obviously, trenching and piling dirt at the site of known contamination requires control measures as well as clear communications with neighbors. Furthermore, noise and traffic can be mitigated by working with site occupants or neighbors to develop less disruptive schedules and by organizing the project to ensure prompt completion.

Finally, the number one factor in determining public support for PRBs or any other proposed remedy is trust. If the community does not trust the parties leading the cleanup, then stakeholders will express skepticism and may even prevent cleanup progress. Mistrust may derive from local history such as territorial conquest or factory closures. It may be caused by a past failure to disclose the contaminant release in a timely fashion or by claims that the plume was smaller than it turned out to be after full investigation. It may result from all-too-common long delays in actual cleanup.

In many cases, building trust is extremely difficult, but the best way to develop community support is to offer stakeholders the chance to evaluate remedial alternatives at the same time as the other parties and to listen to and respond to their concerns. Cleanup is in the interest of community stakeholders, so they should be viewed as constructive participants in the cleanup decision-making process. Where PRBs are suitable, stakeholders can be expected to be some of the strongest proponents.

11. CONCLUSIONS (WHAT’S NEXT?)

Section 1 of this document began with the concept that at a development age of greater than 15 years, “PRBs are now a widely accepted technology.” This simple phrase demonstrates the success of the PRB remediation concept that less than 10 years ago was considered a new and “emerging” technology (Naftz et al. 2002). The acceptance of the PRB concept is not that surprising, however. Consider the opening statement from the 1998 RTDF Technical Document on PRBs (USEPA 1998a):

> Perhaps no recent remedial technology has generated as much interest as the use of subsurface permeable reactive barrier.

Contrast that statement to one from Dr. Robert Gillham, one of the key researchers in PRB technology, in 2004:

> The initial submission [regarding treatment of VOCs by a PRB composed of granular iron] to a refereed journal was rejected and the proposed approach was generally greeted with a high degree of suspicion and skepticism.

The detailed research described herein has significantly counteracted the skepticism the technology faced in the early 1990s as an innovative, uncertain, though conceptually simple, remediation approach. The project examples provided throughout this guidance document are indicative of its growing acceptance. More importantly and perhaps less acknowledged is that that the PRB concept continues to evolve, though perhaps with less direct industry attention than in previous years, and must continue to develop innovatively for the concept to be even more beneficial in efforts to remediate contaminated groundwater sustainably and effectively with respect to cost and technical success.

Following the pragmatic approach of the first ITRC guidance document on PRBs (ITRC 1999a) that correctly defined the PRB as an "evolving technology," this section is intended to provide the reader a synopsis of how the future of the PRB technology could evolve over the next 5 years to continue enhancing the beneficial attributes of this remediation approach. Topic items are presented herein as categories of ongoing and future PRB development. The categories are prioritized in order of importance of greatest potential benefit (as selected by the ITRC PRB: Technology Update Team); however, each category has merit and is considered of high value in increasing the utility of the PRB technology as a component of a groundwater site remedy.

11.1 Construction Methods

PRB construction and implementation methods have advanced over the past 15 years—from conventional trench-and-fill to single-pass trenching, and from pneumatic injection to large-diameter borehole filled completions. However, there remain relatively few deep installations compared to shallow (e.g., <50 feet bgs) completions due principally to the greater likely cost and greater complexity involved in proper placement and completion at depth compared to the installation of shallow systems. This is not to say that there are no successful deep completions. However, it is anticipated that over the next 5+ years, the construction methods for deep emplacements will advance substantially, primarily in terms of the ability to install thicker barriers or barriers with fast-reacting media. Verification methods for these deeper barriers will be one of the more important advancements as comprehensive ensurance of emplacement currently is a cost and technical limitation. Other advancements may also involve the development of longer length-emplacements using advances in horizontal drilling capabilities and emplacements under existing surface structures and buildings.

11.2 Reaction Rates

Research to develop treatment media with greater reaction rates has been ongoing for the past 15 years, and the expectation is that reliable, fast-acting, sustainable materials will continue to be a primary goal of work in PRB development. Advances in ZVI preparation include combinations of metals to provide catalytic reactions without reaction poisoning of the reactive surface (e.g., from sulfur species). Once the use of these new media becomes established, it is expected that PRBs will become much more versatile and allow for deeper, thinner designs. The key issues will be whether these more reactive materials will be sustainable over a long period, allow for comprehensive monitoring of treatment, and be economic and will not create secondary by-products or other conditions environmentally unacceptable.

11.3 Hydraulic Design Improvements

The lack of PRB performance is generally due to poor hydraulic performance rather than directly due to inadequate chemical or biological reactivity. While treatability of a reactive media can be tested under laboratory conditions, hydraulic efficacy must rely on numerical calculations that are often based on limited, incomplete, or inadequate site characterization and field hydraulic information. Also, field hydraulic conditions can vary greatly over short distances and typically are not uniform. Vertical disparity, anisotropy, and mineralized pore spaces that decrease permeability are all issues that can impact hydraulic performance. Add the structural changes to an aquifer system that occur during PRB construction, and the ability to predict and ensure appropriate hydraulic performance becomes substantially more complex. Yet, research and development that place focus on hydraulic design have been limited over the past 15 years. Essentially, there have been few major reported works regarding hydraulic improvements since the Starr and Cherry (1994) work on funnel-and-gate design, even though the funnel-and-gate—sometimes referred to as wall-and-curtain—could be considered an improvement for hydraulic control under specific site conditions.

For PRBs to become more reliable, usable, and sustainable, hydraulic design improvements must take center stage. Much of the enhancements in reliability will come from the use of more efficient and effective site characterization methods that can collect a greater amount of relevant data (i.e., lithology, hydraulic conductivity, etc.) less expensively and with greater accuracy. This might also include advances in combined geophysical/hydrophysical methods that can be used to better interpret and analyze the impacts on groundwater flow from lithologic changes in the subsurface. Finally, quantification of these data in reliable and easy-to-build three-dimensional transient models will greatly improve PRB design development.

11.4 Monitoring Improvements

PRB monitoring approaches generally have remained essentially unchanged in 15 years. Conventional monitoring devices (wells and multilevel sampling points) are placed within, upgradient, and downgradient of the PRB and with some reasonable and regulatory-acceptable spacing to provide a representative indication of the PRB performance. The only widespread advancement has been the use of PDBs placed in monitoring wells to collect samples rather than using direct extraction of groundwater. In situ flow devices for PRBs may be the greatest future advancement in PRB monitoring systems. In situ sensors and telemetric devices would increase the ease at which PRBs are monitored and perhaps allow for greater three-dimensional analysis of groundwater conditions. Also, greater use of optimized monitoring designs that combine hydraulic flow expectations with monitoring well placement would increase the effectiveness of monitoring systems. Understanding as-constructed PRB hydraulic conditions is a needed advance in assessing PRB performance. In this context, eliminating the need to use tracer tests and related methods that can be overly complex and expensive to perform would be of great benefit.

11.5 Specialized Systems for Treating Mixed Plumes and Emerging Contaminants

The ITRC PRB: Technology Update Team identified the need for developing reactive media and PRB systems that can reliably treat mixed plumes and emerging compounds. Early designs considered treatment for mixed VOC and aromatic (e.g., petroleum) compounds, and some field tests were implemented (e.g., the field test at Alameda Naval Air Station, California, for a mixed TCE and benzene plume [Fiorenza, Oubre, and Ward 1999]). Results have been limited, and few full-scale, mixed-plume systems have been deployed. One long-term pilot test for a mixed TCE and perchlorate plume at the Aerojet site in Sacramento does show promise, and injected composite iron-carbon media have been used to treat mixed TCE-chromium plumes (Frain et al. 2008).

Keys to the success of this approach will be sufficient laboratory and pilot tests to ensure complete treatment of chemicals that may have different geochemical stability signatures (oxidizing vs. reducing) and thus require different treatment mechanisms. Biological reactions in PRB systems that use facultative bacteria or cometabolic processes may be particularly promising in this context.

Newer designs based on existing reaction chemistry, such as the development of sustainable PRBs for nitrates and pesticides, may become more important as time goes on, particularly as characterization by regulatory groups and the USGS indicate greater occurrence of these contaminants in more and more water bodies (surface and groundwater).

11.6 Longevity Enhancements

Ensuring that PRBs provide long-term reliable treatment will be of even greater focus than has been seen over the past 15 years. At the outset, little information was available by which to design a PRB to perform successfully for more than five years; however, PRBs have now performed successfully for more than 15 years. With expectations that PRBs—at least ZVI systems—can function for at least 15 years, the ability to double the useful lifetime of a PRB may be the most important next advancement in PRB utility. Non-ZVI-based PRBs have not yet been proven to function for 15 years; however, several biowalls have a multiyear track record, and some injectable materials have shown successful performance in the 3–5 year time frame (e.g., Molin et al. 2009b).

Greater longevity will rely on the results of current and future research that determines what geochemical phases become important, or become inactive, as a PRB ages. This will allow the designer to anticipate various performance issues relating to treatment chemistry, secondary issues that may lead to reduced permeability, and unintended geochemical reactions that negatively impact groundwater migrating through a PRB regardless of the reactive media used in its construction. This work will also lead to advances in monitoring, as noted above, that should lead to a greater ability to predict long-term PRB performance over time.

11.7 Cost Performance Assessments

A fair criticism of several publications on PRBs (and indeed other new technologies in general) is the relative lack of cost-performance information. Even with 15 years of performance, there is little representative cost information (both capital installation and long-term operation costs) in the public record. There are explanations for this situation; however, for the PRB technology to be examined accurately with respect to actual cost-benefit values, the cost data should be more available. Over the next few years, particularly with a greater emphasis on implementing green and sustainable remediation methods, we likely will see less reluctance in providing cost data.

11.8 Closure and Decommissioning Plans

Since the first PRBs were installed, regulators, users, and the public have asked what the process would be for closing or decommissioning a PRB. Many ideas were postulated, including clean closure (i.e., excavating a spent PRB), cementing up grouting in a spent PRB, or otherwise isolating the system. However, these remain hypothetical approaches due to the relatively long time most PRBs have operated and to the degradative nature of several of the processes involved in most PRBs designed for chlorinated solvents, where the PRB does not become a reservoir of stored contaminants. Few, if any, PRBs have been closed. Aside from one of the original PRBs constructed at the Elizabeth City Coast Guard Station, the ITRC PRB: Technology Update Team is not aware of any other PRBs that have formally been closed. For the Elizabeth City site, closure simply involved no further monitoring (after the treatment for the entire contaminant plume was ended by regulatory completion of the overall project). For the future, given possible greater use of PRBs for metals including radioactive constituents and as PRBs continue to age, it should be anticipated that closure plans are requested more often by regulatory groups.

11.9 What Have We Learned after 15 Years—Were Expectations Met?

When the first commercial PRB was installed in 1994, there were few expectations that the system would last more than 5 years, even though all indications—through laboratory tests, comprehensive evaluations of the reaction system, site characterization information, and engineering—did not suggest that the system would *not* last at least that long. Now, 15 years later, hundreds of applications of PRBs composed of many different reactive media for many different contaminants have been successfully deployed.

In general, technology expectations have been met. However, there have been many lessons learned, reevaluations of how PRBs can best be used in the context of overall site goals, and continued development of the PRB deployment and design elements. These trends continue today as new research provides additional information.

The topics discussed in this closing section summarize the basic building blocks for continued successful use of the PRB in mitigating contaminant plume migration. Perhaps the most important lesson learned is that it is much easier to test the functionality of PRB treatment media under laboratory conditions than it is under field conditions—that is, uncertainty and heterogeneity in field settings cannot be completely represented in the laboratory, so field designs must incorporate potential uncertainty in the design so that the treatment remains sustainable and functional through a project's life. Hydraulic failure likely will be the Achilles' heel of any deployment, more often than poor chemical treatment performance (which typically is well established by laboratory studies or past performance of other systems). Site characterization must continue to improve so that as much data as reasonably possible for a given site can be collected and worked into a PRB design. Construction methods must continue to expand so that PRBs can be deployed in more and more complex conditions. Finally, cost performance data must be collected from a greater number of sites—in particular those involving novel reactive media—to better confirm the long-term efficacy of PRB technology for treating groundwater plumes.

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Appendix A

Case Summaries

CASE SUMMARIES

Site name	State	Contaminants of concern	Reactive media	Type of construction	Year installed	Page
Monkstown	Ireland	cVOCs	ZVI	Funnel and gate	1995	A-3
Elizabeth City	North Carolina	Cr(VI), TCE	ZVI	Continuous trenching	1996	A-5
Chalk River	Ontario	Strontium-90	Cliniptilolite	Sheet pile/curtain	1998	A-7
Port Hueneme	California	MTBE	Air, oxygen, cultures	Direct push	2000	A-9
Altus	Oklahoma	cVOCs	Mulch	One-pass trencher	2002	A-11
Pork facility	Oklahoma	Nitrates	Wheat straw	Trench	2002	A-13
Sunnyvale	California	cVOCs	ZVI and EHC®	Trench	2003	A-15
Cornhusker	Nebraska	TNT, RDX	ZVI	Biopolymer slurry trench	2003	A-17
Pueblo	Colorado	RDX, HMX	Mulch	One-pass trencher	2005	A-19
Escanaba	Michigan	Creosote, DNAPL	Organophilic clay	Continuous trenching	2005	A-21
Grain silo	Midwest	Carbon tetrachloride, chloroform, chloromethane, methylene chloride	ZVI and EHC®	Injection	2005	A-23
East Helena	Montana	Arsenic	ZVI	Biopolymer slurry trench	2005	A-25
Vandenberg	California	cVOCs	BOS100®	Deep soil mixing	2009	A-27

CASE SUMMARY - Monkstown

Site Location: Belfast, Northern Ireland

Target Contaminants: TCE and *cis*-1,2-DCE

Installation Method: vessel with funnel

Media Used: zero valent iron (ZVI)

Installation Date: November 1995

Years of Performance Monitoring: 10

Geology/Hydrogeology

The geology consists of more than 60 ft of superficial deposits overlying fine to coarse-grained Sherwood Sandstone bedrock. The drift is charaterized by a complex succession of stiff, red-brown clayey till, with intercalated, discontinuous lenses of silts, sands, gravels, and peat overlain by approximatley 0.3-3.5 ft thickness of made ground.

Shallow water tables occur at depths ranging from 1.5-25.5 ft below ground surface (bgs). Shallow horizontal groundwater flows to the east-northeast in the vicinity of the site. Calculated hydraulic conductivities range from 9×10^{-7} ft/sec in a coarse, silty sand to 1.52×10^{-9} in a clay.

Remedial Objectives

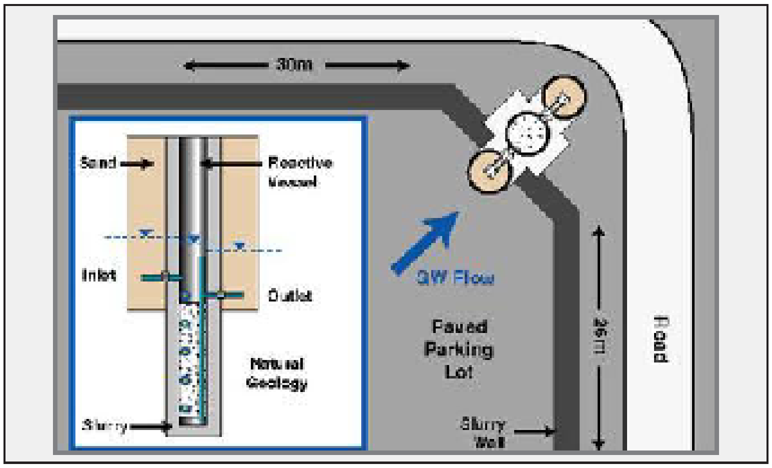
10 ppb TCE at design flow rate

Remediation Standards

500 μg/L TCE, which is standard for groundwater beneath industrial land slated for redevelopment

Selection Criteria

Primary considerations were that the remediation would not worsen environmental conditions, that the system would have zero external energy impact, and that no one would be put at avoidable risk during installation or operation of the system.



Technology Description

Design and Installation

An *in situ* steel reaction vessel filled with ZVI was installed to a depth of 40 ft. Two 100-ft bentonite cement slurry walls were constructed to direct groundwater to the inlet of the reaction vessell. The vessel is 4 ft in diameter and contained 16 ft vertical of ZVI. Groundwater flowed by gravity through the iron zone and discharged through a piped outlet on the downgradient side of the slurry wall. The vessel was accessed through a manhole at the top of the iron zone to allow periodic scarification of the iron surface (if necessary).

The system was designed for a flow rate of 176.6 ft^3/day (m^3/day) with a minimum residence time of 12 hrs.

Type of Installation

In situ steel reaction vessel with slurry wall funnel to direct groundwater

Reactive Media

ZVI

Technology Performance

Hydraulic Performance

Estimates of groundwater flow through the reactive cell, based on potential capture by the cut-off wall, are estimated at 35-210 ft^3/day, with the residence time between 17.4-105 hrs.

Monitoring System

Monitor wells were installed within the ZVI and downgradient of the reaction vessel.

Contaminant Concentration (data v time)

Not available

Performance Data

Concentrations of TCE and *cis*-1,2-DCE in groundwater have decreased by 97.5%. No evidence of biological fouling has been observed over a ten-year monitoring period. Consistent with other studies, the greatest variety of microbial populations was found in the upgradient portion of the ZVI. In cores obtained after ten years, mineralogical observation showed some precipitate formation concentrated in a slightly cemented 1-2 cm section at the upgradient interface. After ten years, flow was restricted in the upper 25 cm of the ZVI, which was predicted to have a usable lifetime of two to five more years. In the downstream section where less precipitate occurred, another ten-plus years of life was predicted.

Contact Information

Not available

Technology Cost

Total system cost including slurry walls, granular iron, reaction vessel, and engineering was approximately $375,000.

References

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Phillips, D.H., T. Van Nooten, L. Bastiens, M.I. Russel, K. Dickson, S. Plant, J.M.E. Ahad, T. Newton, T. Elliot, and R.M. Kalin. 2010. "Ten Year Performance Evaluation of a Field-Scale Zero Valent Iron Permeable Reactive Barrier Installed to Remediate Trichloroethene Contaminated Groundwater." *Environmental Science and Technology*. **44**: 3861-69.

Remediation Technologies Development Forum. 1999. PRB Summaries: Industrial Site, Belfast, Northern Ireland.

CASE SUMMARY - US Coast Guard Support Center

Site Location: Elizabeth City, North Carolina

Target Contaminants: hexavalent chromium and TCE

Installation Method: continuous trenching

Media Used: zero valent iron (ZVI)

Installation Date: 1996

Years of Performance Monitoring:

Geology/Hydrogeology

Site geology is characterized by variable sequences of surficial sands, silts and clays which are typical of Atlantic coastal plain sediments. The site is underlain by a shallow unconfined aquifer. The top two meters of the aquifer consists of sandy- to silty-clays that pinch out toward the north, near the Pasquotank River, where sandy-fill predominates. The remaining depth of the aquifer consists of fine-sands, with varying amounts of silt and clay, and silty-clay lenses. Groundwater begins approximately 1.5 – 2 m below ground surface (bgs). Groundwater velocity is variable with a highly conductive zone is located 4.5 – 6.5 m below the surface. This layer coincides with the highest aqueous concentrations of chromium and chlorinated organic compounds found on the site. A low-conductivity layer of clayey, fine sand to silty clay is located at a depth of about 22 ft. This layer acts as an aquitard to the contaminants located immediately above. The horizontal hydraulic gradient ranges from 0.0011 to 0.0033. Hydraulic conductivity calculated from slug tests on an interval 3 – 6 m bgs ranges from 0.3 – 8.6 m/day. Measured groundwater velocities range from 0.13 to 0.18 m/d at 3.9 - 5.9 m bgs. An average hydraulic conductivity of 26 m/day was calculated based on an average hydraulic gradient of 0.0023 and effective porosity of 0.38.

Remedial Objectives

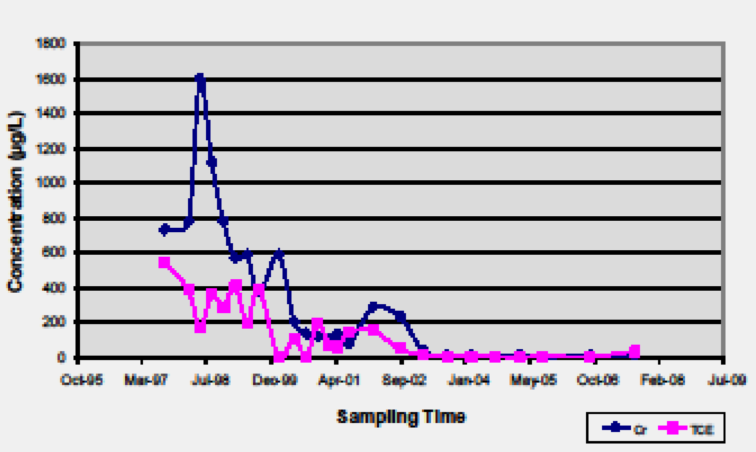
To remove hexavalent chromium and TCE from groundwater.

Remediation Standards

0.05 mg/L of hexavalent chromium and 5 µg/L of TCE

Selection Criteria

Not available



Technology Description

Design and Installation

A continuous wall composed of 100% ZVI was installed 30 m from the Pasquotank River in June 1996 using a trencher that was capable of installing the granular iron to a depth of 7.3 m. The continuous trenching equipment used for the installation has a large cutting chain excavator system to remove native soil combined with a trench box and loading hopper to emplace the iron.

The trenched wall is approximately 2 ft thick and about 46 m long adn 7.3 m deep. The wall begins about 1 m bgs and consists of about 450 tons of granular iron.

The reactive wall was designed to remediate hexavalent chromium-contaminated ground water and portions of the larger overlapping plume of volatile chlorinated organic compounds.

Type of Installation

Continuous trench

Reactive Media

granular zero valent iron (ZVI)

Technology Performance

Hydraulic Performance

Soil cores obtained from within both barriers show some geochemical changes at the upgradient interface. Resultant precipitation of secondary minerals may alter reactivity of the iron barrier by reducing surface area and/or reducing PRB permeability. This may adversely affect ground-water flow direction and velocity, resulting in ground water flowing around or beneath the reactive barrier and reduced effectiveness of the barrier.

Monitoring System

A monitoring network of over 130 subsurface multilevel well bundles was installed in November of 1996. These sample points were sampled annualy.

In addition, ten compliance wells were sampled on a quarterly basis from February 1997 to August 2001. Two wells are located upgradient of the PRB within the plume to monitor contaminant concentrations entering the barrier. Two wells are located upgradient and outside of the plume to monitor background conditions. The other 6 wells are located downgradient of the barrier to montior its effectiveness. Beginning in August 2001, sampling of these 10 wells was switched to a biannual schedule.

Contaminant Concentration (data v time)

Chromium and VOC concentrations were reduced to below regulatory limits. The concentration of chromium entering the PRB is greatest near ML21 (average concentration 0.82 mg/L) and least near ML31 on the west side of the PRB (average concentration 0.032 mg/L). Taking an average chromium concentration of 0.5 mg/L over the depth interval from 3 m to 6 m below ground surface and an average flow velocity of 0.16 m/d, it is estimated that the reactive wall removes about 4.1 kg Cr per year. Over the first five years of operation an estimated 21 kg of chromium has been removed from the ground-water plume and sequestered into immobile forms in the solid phase.

Performance Data

Results of geochemical sampling indicate that iron corrosion is proceeding within the iron barrier. Reduced concentrations below regulatory limits for contaminants of concern indicate the PRB is an effective treatment technology.

Contact Information

Robert Puls
Ground Water and Ecosystems Restoration Division
United States Environmental Protection Agency
580-436-8543
puls.robert@epa.gov

Technology Cost

$500,000 ($175,000 of which was for design, construction, materials, and iron)

References

http://www.rtdf.org/public/permbarr/prbsumms/profile.cfm?mid=64

Wilkin, R.T. and R.W. Puls. 2003. *Capstone Report on the Application, Monitoring, and Performance of Permeable Reactive Barriers for Ground-Water Remediation: Volume 1 – Performance Evaluations at Two Sites*. Ground Water and Ecosystems Restoration Division National Risk Management Research Laboratory U.S. Environmental Protection Agency. EPA/600/R-03/045a. August.

Paul, C.J., McNeil, M.S., Beck, F.P. Jr. Clark, P.J., Wilkin, R.T. and R.W. Puls. 2003. *Capstone Report on the Application, Monitoring, and Performance of Permeable Reactive Barriers for Ground-Water Remediation: Volume 2 - Long-Term Monitoring of PRBs: Soil and Ground Water Sampling*. National Risk Management Research Laboratory Office of Research and DevelopmentU.S. Environmental Protection Agency. EPA/600/R-03/045b. August.

CASE SUMMARY - Chalk River, Ontario

Site Location: Chalk River, Ontario, Canada

Target Contaminants: strontium-90 (^{90}Sr)

Installation Method: sheet pile and curtain

Media Used: clinoptilolite

Installation Date: Oct-Dec 1998

Years of Performance Monitoring: 11.5

Geology/Hydrogeology

The aquifer is sandy and has a 12 m saturated thickness. Hydraulic conductivity ranges from 1.2 X 10^{-4} m/s to 4 X 10^{-6} m/s The width of advancing front of the ^{90}Sr plume is 7 m and depth to contamination is 10 m.

Groundwater moves at approximately 150 m per year. The speed of the leading edge of ^{90}Sr contamination plume is 9 m per year.

Remedial Objectives

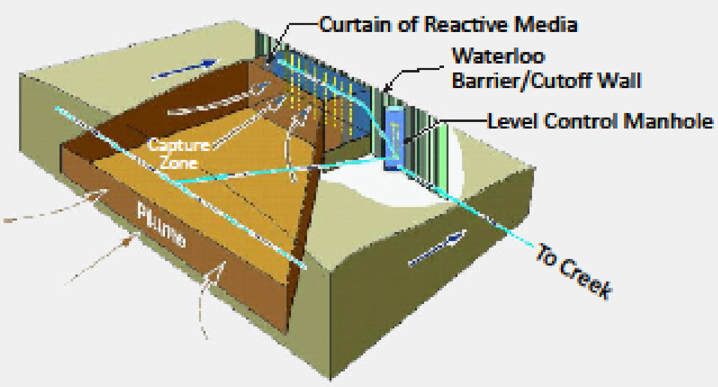
Prevent the accumulation of ^{90}Sr in groundwater discharge to wetlands and receiving water bodies.

Remediation Standards

Drinking water level of 5 Bq/L.

Selection Criteria

1) The system must allow for effluent monitoring. 2) The system must be able to control the capture zone because the position and width of the plume may change over time. 3) The system must allow for close monitoring to document its effectiveness.



Technology Description

Design and Installation

The PRB is a wall and curtain installation. It is installed as a sealed-joint, steel-sheet pile, cut-off wall located downgradient of a granular zeolite curtain or barrier. The cut-off wall extends 9.5 - 12 meter into bedrock to prevent groundwater backflow. The entire installation is 30 meter long. The reactive media is 130 cubic meters of 14 x 50 mesh clinoptilolite, which is a mineral in the zeolite group. The reactive barrier section is 2 m long x 11 m wide and extends about 6 m below ground surface.

Two drainage systems hydraulicly control the flow through the treatment zone and allow for performance monitoring at a single discharge pipe. One consists of ten vertical, continuously slotted well screens located in the curtain in front of the wall. The wells are linked to a drain that terminates with a flexible outflow hose to allow for adjustments in outflow elevation and performance measurement at a single pipe. The other consists of a drainage pipe located across the path of the groundwater 60 m upgradent of the wall and curtain to divert shallow, uncontaminated groundwater from the treatment system in order to extend its lifespan.

The installation type is well suited to situations where a pilot demonstration of reactive media is desired, where plume dimensions or directions may change over time and where detailed analyses on output quality are required.

Type of Installation

Wall and curtain

Reactive Media

14 X 50 mesh granular clinoptilolite - a natural zeolite mineral.

Technology Performance

Hydraulic Performance

There was no change in hydraulic conductivity over a period of 11.5 yrs. There is some leakage underneath the PRB (2.7 L/min) because the sheet-steel pilings were not grouted to the bedrock.

Monitoring System

An outlet pipe from the drainage systems provides access for timed-bucket flow measurements performed manually on a monthly basis. At the same time samples are taken to determine effluent concentration. Occassionally samples are taken from an array of close-interval multi-level samplers up gradient and lateral to the PRB to test for any plume by-pass.

Contaminant Concentration (data v time)

Gross beta measurements of the water from the dishcarge pipe were intially approximately 7 Bq/L in Dec 1998 just after installation. Gross beta dropped to below 1 Bq/L by June 1999 and has remained near the detection limit.

Performance Data

The influent water has a gross beta measurement of 85 Bq/L which is reduced to 0.6 Bq/L in the effluent from the barrier. 99.5% of the ^{90}Sr passing through the system has been captured. In a two year period from 2003 - 2005, the system prevented discharge of 1.7 x 10^{-9} Bq of ^{90}Sr into the adjacent wetland.

Contact Information

David R. Lee
Atomic Energy of Canada Ltd,
Chalk River, Ontario

Technology Cost

Installation cost $360,000 in 1998. Operation and maintenance costs are minimal.

References

Killey, R. W. D. and J. H.Munch. 1987. *Radiostrontium migration from a 1953-54 liquid release to a sand aquifer*. Water Poll. Res. Canada, Vol. 22, No. 1, pp. 107-128.

Lee, D.R., D.J.A. Smyth, S.G. Shikaze, R. Jowett, D.S. Hartwig and C. Milloy. 1998. *Wall-and-curtain for passive collection/treatment of contaminant plumes*. In: Designing and Applying Treatment Technologies (Eds. G.B. Wickramanayake & R.E. Hinchee), 1st Int Conf on Remediation of Chlorinated and Recalcitrant Compounds, 1998 May 18-21, Monterey, CA, pp. 77-84 (1998)

Lee. D. R. 2000. *Wall-and-Curtain for subsurface treatment of contaminated Ground Water*. In: Proceedings of Action Team Meeting, Remediation Technologies Development Forum, U.S. Environmental Protection Agency, Melbourne, Florida, February 16-17, 2000. (www.rtdf.org/public/permbarr/minutes/021600.htm)

Lee, D. R. and D. S. Hartwig. 2005. *Zeolite prevents discharge of strontium-90-contaminated groundwater*. In: Proceedings of Canadian Nuclear Society, Waste Management, Decommissioning and Environmental Restoration for Canada's Nuclear Activities: Current Practices and Future Needs. Ottawa, Ontario, Canada May 8-11, 2005

CASE SUMMARY - MTBE Biobarrier

Site Location: Port Hueneme, California

Target Contaminants: Methyl tert-butyl ether (MTBE)

Installation Method: direct push

Media Used: air, oxygen, cultures

Installation Date: 2000 (pilot), 2003

Years of Performance Monitoring: 10

Geology/Hydrogeology

Site consists of medium-to-fine-grain sand with a maximum hydraulic conductivity of approximately 0.3 ft/day. The hydraulic gradient is nearly flat and ranges from approximately 0.0001-0.0003 ft per foot (ft/ft).

Remedial Objectives

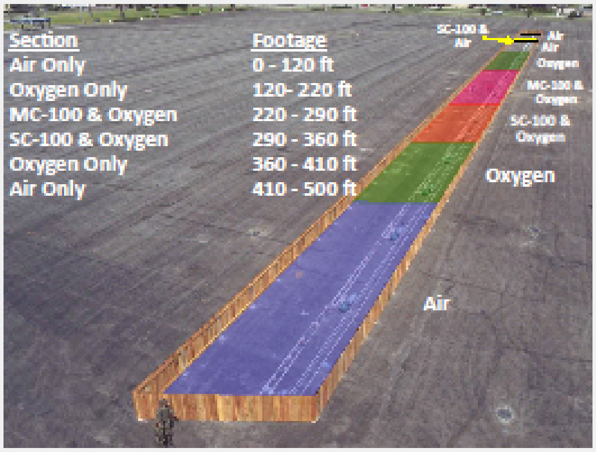
Contain MTBE plume from leaking from underground storage tank (UST). Reduce MTBE below California secondary standard of 5 µg/L. Demonstrate that aerobic biodegradation of MTBE is not impaired by BTEX.

Remediation Standards

California state primary standard for MTBE is 13 µg/L; secondary standard is 5 µg/L.

Selection Criteria

Pilot project constructed under Environmental Strategic Technology Certification Program (ESTCP).



Section	Footage
Air Only	0 - 120 ft
Oxygen Only	120- 220 ft
MC-100 & Oxygen	220 - 290 ft
SC-100 & Oxygen	290 - 360 ft
Oxygen Only	360 - 410 ft
Air Only	410 - 500 ft

Technology Description

Design and Installation

The site consists of a 5,000-ft mixed BTEX/MTBE plume with a 9-acre source area. Average groundwater volume through barrier is 11,000 gal/day. In general, the system is made up of up- and downgradient groundwater monitoring wells (MW), gas injection wells, an oxygen generator, and a piping manifold.

In 2000, a 500-ft-wide pilot barrier was installed, consisting of 252 air/oxygen injection wells and 174 MWs. In 2003, based on approval by stakeholders, two additional barriers were installed: a 500-ft-wide barrier at mid-plume (~2,000 ft from pilot barrier) and a 400-ft-wide barrier at leading edge of plume (~1,800 ft from mid-plume), with 96 wells on 8 ft spacing, multi-level injection depths.

All groundwater MWs were installed as multi-level pairs that sample the upper and lower five feet of the aquifer (approximately 10-15 ft below ground surface [bgs] and 15-20 ft bgs screened intervals). All were constructed from 3/4-in diameter threaded PVC using 0.010 slot well screen, and are spaced 50 ft apart laterally and at two or three distances up- and downgradient of the barrier.

The gas injection wells were installed at two depths: 18-20 ft bgs and 14-15 ft bgs. Gas injection wells were placed roughly every two feet along the barrier. All are constructed from 3/4-in diameter threaded PVC using 0.010 slot well screen.

Oxygen (or air) is not injected at any specific flow rate, but as a very short duration pulse approximately every 6 hrs. A satellite 20-gal oxygen storage tank is charged to approximately 45 psi by the oxygen generator or compressor, and then its contents are discharged to two wells at once. In these tests, complete discharge occurred within about 30 secs, which corresponds to a short-term flow rate of about 10 ft^3/min per well. There is a satellite gas storage tank placed every 20 ft, and each satellite gas storage tank provides gas to a total of six pairs of wells (but only to one pair at a time).

Type of Installation

Direct push (Geoprobe) - all monitoring and gas injection wells

Reactive Media

The initial (pilot) barrier was seeded with proprietary bioaugmentation cultures along 165 ft of its 500 ft length. Air and oxygen are also injected along its length. The mid-plume and leading edge barriers are injected with air only.

Technology Performance

Hydraulic Performance

No degradation of hydraulic conductivity has been noted.

Monitoring System

The pilot barrier has 174 groundwater MWs (3/4-in PVC).

Contaminant Concentration (data v time)

Influent MTBE concentrations ranged from 0.001 µg/L to approximately 20,000 µg/L.

Performance Data

The pilot barrier significantly reduced downgradient MTBE concentrations, but not to 5 µg/L. To reduce operational costs, oxygen injections were discontinued and only air was injected. Based on performance of the pilot, two additional biostimulation barriers (air injection, no bioaugmentation cultures) were installed in 2003 at mid-plume (500-ft wide, ~2,000 ft downgradient from pilot barrier) and at the leading edge of the plume (400-ft wide, ~1,800 ft downgradient from the mid-plume barrier). The three-barrier system continues to operate as of 2010.

Contact Information

NAVFAC ESC Environmental Restoration Technology Transfer Program
PRTH_NFESCT2@navy.mil

Technology Cost

Initial 500-ft barrier cost $808,000 for construction and demonstration and requires $75,000/yr for operations and maintenance (O&M). The two additional barriers (900 ft total length) cost $500,000 to install and require $125,000/yr for O&M.

References

ESTCP. 2008. "In Situ Bioremediation of MTBE in Groundwater." CU-0013, June.

http://serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Emerging-Issues/ER-200013/ER-200013/(language)/eng-US
This link provides information on the ESTCP project which demonstrated this technology and the documents produced from the project.

CASE SUMMARY - Altus Air Force Base, OU-1

Site Location: Altus AFB, Oklahoma

Target Contaminants: TCE, *cis*-1,2-DCE

Installation Method: continuous one-pass trenching

Media Used: mulch

Installation Date: June 2002

Years of Performance Monitoring: 8

Geology/Hydrogeology

Surface soils at the site consist of approximately 5 ft of clayey silt and a weathered and fractured stiff silty clay that extends to a depth of approximately 25-35 ft below ground surface (bgs). These sediments are underlain by cemented silt and shale of the Hennessey Group of Permian age. Shallow groundwater occurs under unconfined conditions and generally flows towards the east-southeast and Stinking Creek. Shallow groundwater at the site occurs at a seasonally variable depth of approximately 6-12 ft bgs.

The groundwater surface slopes toward the southeast with an average horizontal hydraulic gradient of approximately 0.003 ft per foot (ft/ft). Average hydraulic conductivity is approximately 8.7 ft/day in the overburden silty clay. Advective groundwater flow velocity in the overburden silty clay is approximately 0.174 ft/day, or 64 ft/yr. These are only average flow rates; actual flow rates may vary due to aquifer heterogeneity.

Remedial Objectives

Contain and attenuate a shallow groundwater plume contaminated with TCE and *cis*-1,2-DCE to prevent surface water discharge or offbase migration

Remediation Standards

Reductions in concentrations of TCE and *cis*-DCE are compared to USEPA drinking water MCLs

Selection Criteria

This demonstration site was selected based on groundwater at shallow depth, elevated concentrations of TCE and *cis*-DCE, and an open area readily accessible to trenching equipment.

Technology Description

Design and Installation

A 455-ft-long, by 24-ft-deep, by 1.5-ft-wide mulch biowall was installed using a continuous one-pass trenching machine. Final biowall composition consisted of approximately 300 cubic yards (cy) of shredded mulch, 60 cy of cotton gin compost, and 265 cy of sand. The mulch consisted of shredded deciduous and evergreen trees and shrubs generated by the city of Altus after a winter storm event and during seasonal landscaping operations.

Type of Installation

The 455-foot long by 2-foot thick trench to 24 feet deep was installed and backfilled with the mulch mixture in one continuous operation by a one-pass trencher.

Reactive Media

Shredded tree mulch, cotton gin compost and sand mixture

Technology Performance

Hydraulic Performance

Depth to groundwater within the biowall ranges from approximately 5 to 8 ft bgs, with a saturated thickness within the biowall ranging from 16 to 19 ft. Aquifer slug tests were conducted immediately after installation and repeated at three months after installation. These data indicated that the hydraulic conductivity of the biowall backfill material was only minimally impacted by settling and compaction, with the hydraulic conductivity in the biowall averaging 10.8 ft/day (or 3.8E-03 cm/sec). Visual examination of sediments from borehole cores indicates the presence of secondary permeability due to dissolution features and soil fractures. Groundwater flow through these high permeability zones may be an order of magnitude or more higher than the average estimated rate of groundwater flow.

Monitoring System

Ten groundwater monitoring wells were installed along two transects oriented perpendicular to the biowall. Monitoring wells were located upgradient, within, and at distances of 5, 10, 30, and 100 ft downgradient of the biowall. In addition, the USEPA National Risk Management Research Laboratory/Ground Water and Ecosystems Restoration Division (NRMRL/GWERD) installed 33 monitoring points in 2007 to supplement the existing monitoring well network. Analytical data from April 2007 through October 2010 were provided courtesy of the USEPA NRMRL/GWERD under the direction of Dr. John Wilson.

Contaminant Concentration (data v time)

Data over a period of 98 months (over 8 years) after biowall installation are available to determine the long-term performance of the OU1 biowall. An average decrease in the concentration of TCE of over 99 percent was observed within the biowall relative to upgradient monitoring locations over the first 24 to 34 months following installation, with little evidence of an accumulation of *cis*-DCE or VC. At approximately 34 months post biowall installation, concentrations of cis-DCE and VC began to increase within and downgradient of the biowall. Mean concentrations of TCE in October 2009 were still reduced by 93 percent within the biowall, although for the first time an increase in the mean total molar concentration of chloroethenes was observed for the biowall wells. In addition, concentrations of TCE within the biowall from 2007 to 2010 increased relative to the period from 2002 to 2007, indicating that that the biowall has become less effective in degrading TCE as well.

Performance Data

The transformation of TCE within the biowall over the first 24 to 34 months is associated with a reduction in total molar concentrations and a general lack of DCE, VC and ethene. This suggests that the predominant degradation process over this period was biogeochemical transformation in the presence of reactive iron-sulfide minerals produced under anaerobic conditions (Earth Science Services and Rowan University, 2003). After April 2005 the biowall continued to degrade TCE, but TCE was primarily transformed to DCE and VC. Therefore, the primary degradation process from April 2005 to October 2010 appears to be sequential biotic reductive dechlorination to DCE and VC, without further dechlorination to ethene.

Analysis by scanning electron microprobe of biowall material collected in September 2007 (Lebron *et al.*, 2010) indicates that the iron sulfides are present primarily as partially oxidized pyrite and greigite, not as more reactive iron mono-sulfides. This suggests that the iron sulfide minerals in the biowall have been oxidized to less reactive forms and no longer support measurable abiotic dechlorination of TCE and DCE to acetylene. Furthermore, the presence of high concentrations of sulfide within the biowall after 2007 (60 to 300 mg/L) are likely inhibiting biotic dechlorination. Due to the observed decrease in the ability of the OU1 biowall to reduce concentrations of chlorinated ethenes and the highly elevated concentrations of sulfide present, AFCEE and the USEPA NRMRL/GWERD are conducting a demonstration in 2011 of engineered biogeochemical transformation by injection of ferric iron (hematite powder) and emulsified vegetable oil within a segment of the biowall to evaluate optimization measures for long-term operation.

Contact Information

Ms. Erica Becvar
HQ AFCEE/TDV
2261 Hughes Avenue, Suite 155
Lackland AFB, TX 78236-9853
PH: 210-395-8424
E-mail: Erica.Becvar.1@us.af.mil

Technology Cost

Approximate costs to install and monitor the biowall include $23,800 for design, work plan development, and procurement; $187,700 for mobilization, trench installation, monitoring well installation, and baseline sampling; and $28,500 for reporting and meetings. The trenching subcontract was approximately $120,000. Total cost for trenching subcontractor and biowall materials was approximately $138,800, or approximately $305/linear ft for biowall construction. (Cost is not available for efforts conducted by the USEPA NRMRL/GWERD.)

References

Earth Science Services and Rowan University. 2003. *Aqueous and Mineral Intrinsic Bioremediation Analysis (AMIBA) of the Pine Bark Mulch Permeable Reactive Barrier at Altus Air Force Base SMU-7 (OU1)*. Prepared for the AFCEE, Brooks City-Base, Texas.

Lebrón, C., P. Evans, K. Whiting, J. Wilson, E. Becvar, and B. Henry. 2010. *In situ Biogeochemical Transformation of Chlorinated Ethenes Using Engineered Treatment Systems*. Technical report prepared by CDM for NAVFAC ESC and ESTCP. February.

Parsons. 2010a. *Final Demonstration of In Situ Bioremediation of Chlorinated Solvents in Groundwater using a Permeable Mulch Biowall, Operable Unit 1, Altus Air Force Base, Oklahoma*. Prepared for AFCEE, Lackland Air Force Base, Texas. May.

Parsons. 2010b. *Demonstration of the Performance and Sustainability of Permeable Mulch Biowalls for Enhanced Bioremediation*. Prepared for AFCEE and the USEPA OSWER. Final, May.

CASE SUMMARY - Oklahoma Pork Facility

Site Location: Logan County, Oklahoma

Target Contaminants: nitrate (NO_3)

Installation Method: vertical trench

Media Used: wheat straw

Installation Date: 2002

Years of Performance Monitoring: 9

Geology/Hydrogeology

The facility, lagoon, and land application areas are located over the Garber-Wellington aquifer. The aquifer is unconfined. The vadose zone is a sequence of shale and silt with occasional sandstone. The Garber-Wellington itself is an extremely permeable lithified hard sandstone. The water table is generally less than 20 ft below grade and has a very low gradient, which results in groundwater velocity of about 1 ft/day.

Remedial Objectives

Removal of the waste products from the lagoon (source reduction), containment of the plume from impacting the waters of the state, meeting water quality criteria, and protecting the lake from seasonal algae growth.

Remediation Standards

Remediation standard for NO_3 was the USEPA Maximum Contaminant Level (MCL) for drinking water, 10 mg/L. For NH_4 a 15 mg/L discharge was deemed adequate due to expected dilution in the lake.

Selection Criteria

Not available.

Technology Description

Design and Installation

The dentrification of the plume passing through the PRB was achieved by heterotrophic bacteria, which uses organic compounds as electron donors and carbon source. The resulting products in this reaction are nitrogen gas and water as described in the following half reaction:

$$2NO_3 + 12\ H + 10\ e > N_2 + 6\ H_2O$$

A 10-ft-deep, by 12-ft-wide, by 800-ft-long bench was excavated using earth moving machinery. The remain depth was excavated using a track hoe with a 15 ft reach. The total depth of the trench was 25 ft. A 4-ft-wide bucket was used to break the hard sandstone. The trench was filled with the wheat straw up to and above the seasonal water table depth. The rest was back-filled with the excavated soil.

Several organic substances were screened in the lab in batches and the most promising carbon source was subjected to the column study. The locally available wheat straw was found to be the most appropriate carbon source to degrade the NO_3 in groundwater. The PRB became functional in December 2002.

Type of Installation

Trench - 10-ft-deep, by 12-ft-wide, by 800-ft-long

Reactive Media

Locally available wheat straw

Technology Performance

Hydraulic Performance

The gradient was not affected by the PRB. However, the permeability in the trench was greater than the sandstone matrix. No underflow was seen due to a thick shale layer at the bottom of the trench. However, in the southeast corner lateral bypass was seen as the NO_3 concentration did not decrease in MW 30.

Monitoring System

Performance of the PRB is being monitored using several upgradient and downgradient monitoring wells. Samples are collected quarterly. Additionally, the EPA Ada groundwater group has installed two transects at both ends of the 800-ft trench, which measure hydraulic properties and the geochemical environment.

Contaminant Concentration (data v time)

In all monitoring wells except one where bypass was seen, NO_3 was degraded below 10 mg/L. In some cases, NH_4 was seen generated due to the presence of excessive carbon.

Performance Data

Six downgradient wells in one transect showed significant reduction in NO_3 concentration within a year of installation. Five monitoring wells showed NO_3-N below 10 mg/L. In one well, the NO_3 concentration actually increased as a function of time probably due to local hydrogeological conditions resulting in preferential pathways and bypassing the trench. Overall, the trench is performing as expected. No monitored natural attenuation was proposed by the responsible party.

In 2005, the Oklahoma Deptartment of Agriculture joined hands with the EPA laboratory in Ada, Oklahoma, to conduct the long-term performance of this PRB. The EPA report is forthcoming.

Contact Information

Oklahoma Dept. of Agriculture Food
and Forestry
Agricultural Environmental Management
Services Division
2800 N. Lincoln Blvd.
Oklahoma City, OK 73105

Technology Cost

No cost data was submitted by the responsible party.

References

Not available.

CASE SUMMARY - Commercial Street Operable Unit

Site Location: Sunnyvale, California

Target Contaminants: *cis*-1,2-DCE, PCE, TCE, VC

Installation Method: trench

Media Used: zero valent iron (ZVI) and EHC®

Installation Date: 2003 (extended 2007)

Years of Performance Monitoring:

Geology/Hydrogeology

The subsurface stratigraphy of the Commercial Street Operable Unit (CSOU) is extremely heterogeneous and consists of higher permeability (sand/gravel) channels enveloped by lower permeability (clay/silt) soils and has been divided into A1-, A2-, and B-Zone aquifer units as follows: The A1-Zone extends from grade to approximately 25 ft below ground surface (bgs); the A2-Zone extends from approximately 25-35 ft bgs; the B-Zone extends from approximately 35 ft bgs to the depths explored (~100 ft bgs). The direction of groundwater flow and magnitude of the horizontal hydraulic gradient within the A-Zone aquifers beneath the CSOU have been consistent over the last ten years. Groundwater in the monitoring wells and piezometers within the CSOU is generally first observed between 6 and 12 ft bgs and flows to the north/northeast under a typical hydraulic gradient between 0.005 and 0.007 ft per foot (ft/ft). An upward vertical hydraulic gradient has been observed between the B-Zone and A-Zone aquifers.

Remedial Objectives

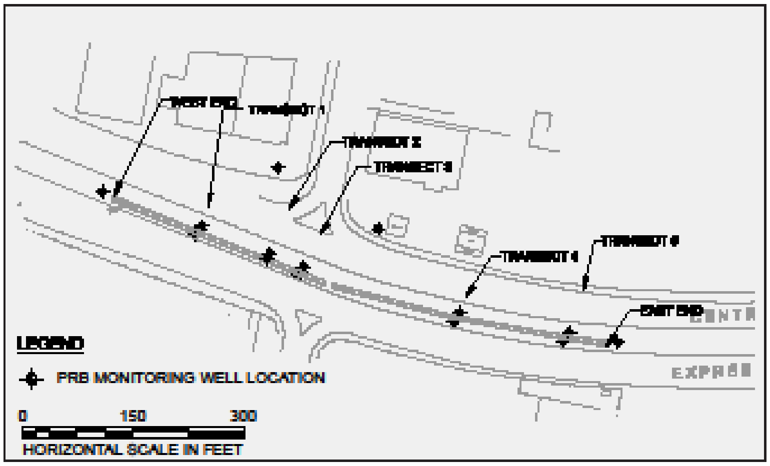
Prevent plume from migrating offsite

Remediation Standards

The PRB was designed to reduce total volatile organic compounds (VOCs) (predominantly PCE, TCE, and *cis*-1,2-DCE, and VC) concentrations to 600 µg/L.

Selection Criteria

The main advantage of the PRB is the passive and in situ method of the treatment. The other advantages of PRB are the long-life of the reactive media and the low operation and maintenance costs.



Technology Description

Design and Installation

The PRB was designed for significant reduction of dissolved VOCs concentrations rather than a complete reduction.

The PRB preliminary design was based on the following:

- Residence time calculations used to determine the thickness of PRB.
- Groundwater flow and contaminant fate and transport modeling MODFLOW and RT3D used as key design tool.

The PRB is located approximately 1,200 feet down-gradient of the source area and it is installed in the median of the Central Expressway, near its intersection with Commercial Street in Sunnyvale, California. An excavator was used to excavate the PRB trench. The consultant utilized a "panelized" approach for the PRB design and construction. The PRB consists of 14 approximately 50-ft long panels with overall dimensions of approximately 700 ft long, 2-4 ft wide, and approximately 24-33 ft deep. The barrier thickness and iron/sand content was customized according to the treatment requirements of each specific unit or zone. Each panel consists of ZVI with or without sand mixtures. Sheet pilings were used to support the trench during the trench excavation. Degradable biopolymer slurry was used to keep the trench open during the placement of ZVI and sand in the trench. Upon completion of the backfilling of the trench with the ZVI and sand mixtures, a non-woven geotextile fabric was placed along the length of the trench to preclude fines from migrating down into the reactive media. The trench was backfilled to final grade with native materials and clean fills.

The site owner completed an EHC® substrate injection in March 2007 as a remedial action to capture the VOC-impacted groundwater plume immediately on the west end of the existing Central Expressway PRP. EHC® substrate injections extended the PRB length by 50 feet. The EHC® substrate is composed of controlled-release carbon and ZVI and was injected to stimulate various chemical and microbiological reductive dechlorination processes.

Type of Installation

Trench with sheet pile supports

Reactive Media

ZVI and EHC®

Technology Performance

Hydraulic Performance

Not available

Monitoring System

To monitor the effectiveness of the PRB, the property owner installed a monitoring well network consisting of five transects of monitoring wells placed along the groundwater flow path within and immediately downgradient of the PRB. These wells were aligned with existing monitoring wells in the area to allow for comparison with historical data. In addition, two end wells were installed to the east and west of the PRB, and two downgradient wells were installed approximately 150 ft downgradient. Groundwater samples from wells upgradient, in situ, and downgradient of the PRB have been analyzed semiannually for VOCs and field parameters. Inorganic constituents have been analyzed annually.

Contaminant Concentration (data v time)

Total VOC mass flux estimates for the complete PRB length and depth indicate that the PRB is achieving an aggregate reduction of between 91% and 94% across the barrier-plume interface. In addition, a distinct reduction in PCE, TCE, and *cis*-1,2-DCE concentrations is noted north (downgradient side) of the PRB since installation.

Performance Data

Analytical results for the four transect wells upgradient of the PRB do not exceed short-term cleanup standards except for one well, which reported PCE at 600 µg/L. In the fourth quarter 2010, the total VOC concentrations immediately downgradient of the PRB were below the target level of 600 µg/L in three of the five transects indicating that, in general, the PRB is functioning as designed.

Groundwater samples were also collected from the two end wells located just east and west of the PRB. Analytical results from samples collected from the east end well continue to show low concentrations of dissolved VOCs. Analytical results from samples collected from the west end well (well No. PRB-E01) show considerable variations in both the blend and the concentrations of the VOCs. These variations may be attributed to the ZVI component of EHC® and/or mass flux contributions associated with upgradient ozone and/or enhanced anaerobic biodegradation (EAB) activities.

Contact Information

Max Shahbazian
State Water Resources
Control Board, California
510-622-4824
mshahbazian@waterboards.ca.gov

Technology Cost

Approximately $2.1 million

References

The Source Group, Inc. 2003. Permeable Reactive Barrier Completion Report. 932 Kifer Road, Sunnyvale, California, November 15.

The Source Group, Inc. 2010. Semi-Annual Self-Monitoring Report. 932 Kifer Road, Sunnyvale, California, January 29.

CASE SUMMARY - Cornhusker Army Ammunition Plant

Site Location: Grand Island, Nebraska

Target Contaminants: TNT, RDX

Installation Method: biopolymer slurry trench

Media Used: zero valent iron (ZVI)

Installation Date: November 2003

Years of Performance Monitoring: 20 mos

Geology/Hydrogeology

Medium sand with some silts. Water table is at 15-20 ft below ground surface (bgs). Groundwater velocity is approximately 1-2 ft/day.

Remedial Objectives

To reach USEPA Maximum Contaminant Levels (MCLs) and to evaluate barrier hydraulics.

Remediation Standards

Contaminant concentrations were compared to USEPA MCLs for TNT ad RDX.

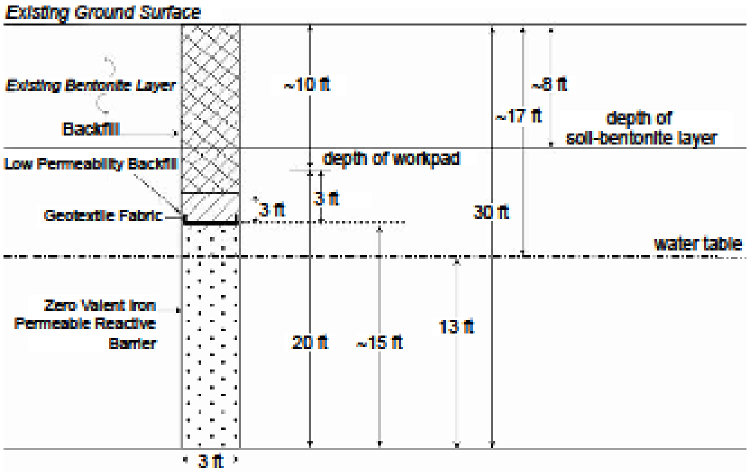
Selection Criteria

The criteria and requirements used in selecting the test site for an ESTCP demonstration of apassive ZVI PRB included 1) concentrations of TNT and/or RDX in groundwater greater than 100 ppb to demonstrate that the technology can reduce concentrations by >90%, 2) ready access to the site during the demonstration, and 3) a shallow, permeable aquifer suitable for installation of a PRB.

Technology Description

Design and Installation

The PRB was installed in a trench using a track hoe excavator and a biopolymer slurry. The trench was backfilled with a mixture of granular ZVI (30% by weight) and sand. The trench was 50 feet long by 3 feet thick by 15 feet deep. Development wells were installed within the trench to circulate an enzyme to break down the biopolymer guar used in the slurry.



Cross-section Drawing of the "as built" ZVI PRB.

Type of Installation

Biopolymer slurry trench

Reactive Media

Based on laboratory studies, ZVI has been shown to rapidly degrade TNT and RDX. For TNT, Tratnyek et al. (2001) showed that essentially all of the degradation products become completely sequestered on the iron, a process which can be sustained for thousands of pore volumes, even at very high flow rates and contaminant loadings. This demonstration was conducted to verify the process can be effectively applied in the field.

Technology Performance

Hydraulic Performance

There has been some diversion of upgradient groundwater beneath the PRB. One possible explanation is guar entering the upgradient formation and preventing flow. Alternatively guar residuals (high dissolved organic carbon [DOC]) may have facilitated the microbial reduction of sulphate and precipitation of sulphide minerals observed just upgradient of the PRB, causing this diversion of flow.

Monitoring System

Groundwater monitoring was conducted using a series of multi-level groundwater sampling wells. In addition to collecting groundwater samples, a bromide tracer test was conducted and soil cores were advanced at an angle through the ZVI PRB.

Contaminant Concentration (data v time)

The ZVI PRB reduced concentrations of TNT and RDX to below detection limits throughout the duration of the demonstration project.

Excavation of the trench

Performance Data

In addition to removal of the explosives, significant changes in groundwater chemistry occurred due to the PRB. Dissolved sulfate concentrations decreased substantially as groundwater flowed through the PRB. Groundwater concentration data and measured hydraulic conductivity data suggest that a portion of the water up-gradient of the PRB was diverted beneath the PRB. The reason for this is not entirely known; however, it is probably related to the use of guar during installation of the PRB. The investigators believe that guar entered the formation up-gradient of the PRB and was not fully removed at the completion of the installation. This may be the primary reason for flow reduction. However, it is also possible that the guar led to strongly reducing conditions just up-gradient of the PRB and the removal of sulfate resulted in sulfide precipitation just up-gradient of the PRB, as observed in core samples.

Contact Information

Dr. Rick Johnson
Oregon Health & Science University
Environmental and Biomolecular Systems
20000 NW Walker Road
Beaverton, OR 97006-8921
503-748-1193
(rjohnson@ebs.ogi.edu)

Technology Cost

Total demonstration cost of $603,600 including the following:

-Site Characterization, Becnh-scale Test, and Engineering Design = $195,000
-ZVI Product = $17,600
-PRB Construction = $121,000
-Monitoring Network Installation = $30,000
-Groundwater Monitoring and Reporting = $210,000
-PRB Core Collection and Analysis = $30,000

References

Johnson, R. and P. Tratnyek. 2008. *Remediation of Explosives in Groundwater Using a Zero-Valent Iron Permeable Reactive Barrier*. Prepared for the ESTCP. Arlington, Virginia. ESTCP Project ER-0223, Final Report, May.

Tratnyek, P.G., R.L. Johnson, T.L. Johnson, R. Miehr. 2001. *In Situ Remediation of Explosives Contaminated Ground-Water with Sequential Reactive Treatment Zones*. SERDP SEEDSON-00-02 SERDP Project Number ER-1176.

CASE SUMMARY - Pueblo Chemical Depot SWMU-17

Site Location: Pueblo Chemical Depot,
Pueblo, Colorado

Target Contaminants: RDX, HMX

Installation Method: continuous
one-pass trenching

Media Used: mulch

Installation Date: Nov 2005

Years of Performance Monitoring: 20 mo

Geology/Hydrogeology

RDX- and HMX-contaminated groundwater at SWMU-17 occurs in the unconsolidated alluvium that overlies the bottom-confining Pierre Shale bedrock. The geology of this area is known as the Southwest Terrace. The groundwater flows in a south-to-southwesterly direction from SWMU-17 in the Southwest Terrace, but is interrupted by unsaturated or dry areas resulting from subterranean outcrops of the Pierre Shale. In effect, the alluvial deposits at different locations on the shale bedrock form "paleochannels" that rapidly transmit groundwater.

Remedial Objectives

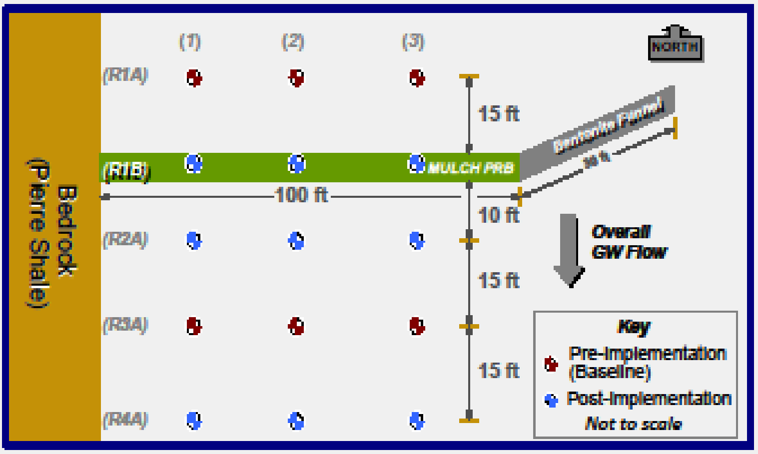
(1) >90% removal of RDX across the PRB and the treatment zone
(2) an RDX concentration of <0.55 ppb in the treatment zone
(3) cumulative toxic intermediate concentration (i.e., [MNX] + [DNX] + [TNX]) of <20% of the upgradient RDX concentration.

Remediation Standards

State-mandated, site-specific cleanup criteria: 0.55 ppb RDX and 602 ppb HMX

Selection Criteria

Selection was based on groundwater at shallow depth (<35 ft to bedrock), concentrations of RDX >50 ppb, and a groundwater flow velocity of 0.1 to <1.0 ft/day. Other considerations included the presence of competing electron acceptors, suitable soils for trenching (fine sand), and the presence of other remediation technologies in the immediate vicinity that could potentially interfere with the demonstration.



Technology Description

Design and Installation

A key design criterion for the mulch PRB was the thickness of the biowall trench. A preliminary biowall thickness was determined with a steady-state treatability test (column study) using a seepage velocity and hydraulic conductivity representative of site conditions. Based on the treatability study, a standard trench width of 2 feet using a mixture of 1 part pea gravel to 2 parts mulch by volume was deemed adequate to achieve performance objectives.

Prior to PRB installation, groundwater was collected from six monitoring wells installed during Phase 1 of the project. These samples established the baseline distribution of target contaminants in the field demonstration area. A mulch and gravel filled biowall trench and an adjacent soil bentonite impermeable wall were then installed using a continuous one-pass trencher. Both the biowall and the soil-bentonite wall were 2 feet thick. The completed length of the mulch biowall was approximately 105 feet. A mixture of 33%:67% (volume:volume) pea gravel to mulch was used for the biowall backfill. The soil-bentonite funnel/impermeable wall was approximately 30 feet long. Trenching depth varied between 14 feet below ground surface (bgs) and 24 feet bgs, following the bedrock topography along the length of the PRB, with the PRB keyed approximately 1 foot into bedrock. Trenching depth for the impermeable funnel was kept constant at 24 feet bgs to account for any drop in the bedrock elevation below the saturated alluvium. The impermeable funnel, as well as the impermeable bedrock formation to the west and at the bottom of the PRB, serve as hydraulic controls to limit any groundwater flow that may bypass the PRB.

Type of Installation

A 100-foot long by 2-foot thick trench up to 24 feet deep was installed and backfilled with the mulch mixture in one continuous operation by a one-pass trencher. Installation was completed within three days.

Reactive Media

A 33%:67% (volume:volume) pea gravel: tree mulch and sand mixture

Technology Performance

Hydraulic Performance

The potentiometric surface interpolated from hydraulic heads measured during the first post-implementation groundwater monitoring event on December 2, 2005, confirmed that groundwater flow continues to occur across the PRB in a south-to-southwesterly direction.

Monitoring System

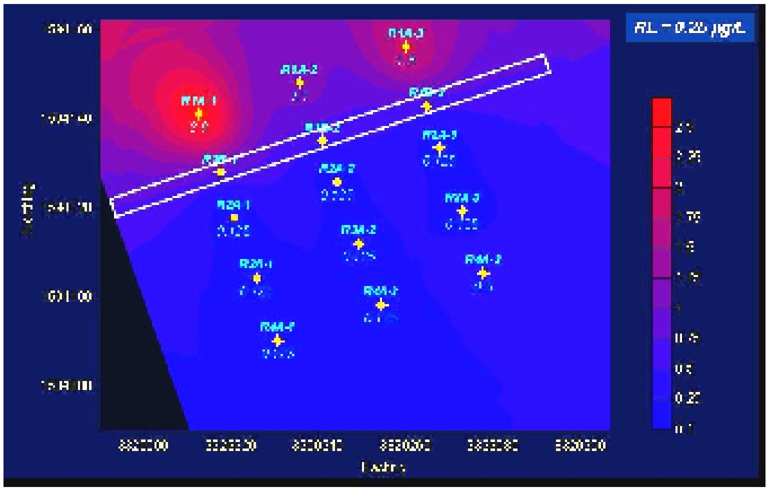
Two rows of three monitoring wells each were installed, developed, and sampled prior to PRB installation to establish the baseline distribution of target contaminants in the field demonstration area. After PRB installation, three more rows of monitoring wells were installed. The first row of three wells was installed into the mulch/gravel PRB itself. The location of the second row of wells was approximately 10 ft downgradient from the PRB. The final row of three wells was installed approximately 15 ft downgradient from the baseline wells installed in the first phase of the implementation. The screens of all wells extended to the base of the water-bearing alluvium.

Contaminant Concentration (data v time)

Concentrations of RDX upgradient of the mulch PRB ranged from 0.775 to 3.090 ppb over the four post-installation monitoring events. Concentrations immediately downgradient of the mulch PRB were reduced to below detection limit (typically 0.100 to 0.125 ppb) for each monitoring event. With few exceptions, concentrations of RDX were also reduced to below detection beginning with the second monitoring event at approximately 8 months after installation.

Performance Data

RDX was not detected in the treatment zone once the system approached steady state in the June 2006 monitoring event. Detections of RDX did occur in the furthest downgradient wells, but these were generally below the regulatory threshold of 0.55 ppb (with one exception). RDX removal rates averaged over 93% across the mulch PRB and in the other treatment zone monitoring wells. The mulch PRB continued to operate as expected during the last sampling event at 20 months post-installation.



RDX Concentrations Measured on 06/20/2006, 7 Months After Mulch PRB Installation.

Contact Information

Dr. Charles Newell, Ph.D., P.E.
GSI Environmental, Inc.
2211 Norfolk St. Suite 1000
Houston Texas 77098
713-522-6300

Technology Cost

Approximately $375,000 with a unit cost of $10.26/ft^3

References

Ahmad, F., S.P. Schnitker, and C.J. Newell. 2007a. Remediation of RDX- and HMX- Contaminated Groundwater Using Organic Mulch Biowalls. Journal of Contaminant Hydrology, Vol. 90(1-2):1-20.

Ahmad, F., T.M. McGuire, R.S. Lee, and E. Becvar. 2007b. Considerations for the Design of Organic Mulch Permeable Reactive Barriers. Remediation, Winter 2007, pp 59-72.

GSI Environmental, Inc. 2008a. Cost and Performance Report - Treatment of RDX and/or HMX Using Mulch Biowalls. Prepared for the Environmental Security Certification Program, Arlington, Virginia. April.

GSI Environmenal, Inc. 2008b. Final Report - Treatment of RDX and/or HMX Using Mulch Biowalls. Prepared for the Environmental Security Certification Program, Arlington, Virginia. July.

CASE SUMMARY - Railroad Tie Treatment Site

Site Location: Escanaba, Michigan

Target Contaminants: creosote DNAPL, dissolved PAHs

Installation Method: continuous trenching

Media Used: organophilic clay

Installation Date: November 2005

Years of Performance Monitoring: 5

Geology/Hydrogeology

Adjacent soils are primarily sands with some gravel. Groundwater flows toward nearby bay.

Remedial Objectives

Interim action to control migration of nonaqueous phase liquid (NAPL) to the surface water of the Little Bay De Noc in Lake Michigan

Remediation Standards

Eliminate sheen from NAPL seep.

Selection Criteria

Availability and cost of media

Technology Description

Design and Installation

To stop migration of creosote NAPL seep into neighboring bay, an organophilic clay PRB wall was designed. Based on monitoring well data at the time of installation, the dimensions of the PRB were 18 in wide, by 11 ft deep, by 270 ft long. One part organophilic clay was mixed with three parts by volume pea gravel. Standard "soil filter design" was used to determine particle size distribution to minimize intrusion and clogging of reactive media and backfill by adjacent native soils.

The organophilic clay and pea gravel were mixed by a backhoe on a plastic-lined pad. A DeWind continuous trenching machine was used to install the PRB. A geotextile separator fabric and topsoil layer were deployed over the PRB. The operation was completed in one day.

Type of Installation

Trenching with continuous trenching device

Reactive Media

25% by volume organophilic clay - sodium bentonite modified with quaternary amine compound
75% by volume pea gravel

Organophilic clay-pea gravel mix pile

11 07 2005

Technology Performance

Hydraulic Performance

There was no hyrdaulic mounding upgradient of the PRB.

Monitoring System

Monitoring wells were installed upgradient and downgradient of the PRB.

Contaminant Concentration (data v time)

Not available

Performance Data

No NAPL was observed migrating through PRB after two years. No mounding of groundwater.

Contact Information

Jeff Gentry
CH2M Hill
503-736-4390
jgentry@ch2m.com

Technology Cost

Total installed cost - $220,000 including mobilization, demobilization, PRB installation, reactive mat installation, site restoration and waste disposal.

References

Benson, C.H., S. Lee, and A. Ören. 2008. *Evaluation of Three Organoclays for an Adsorptive Barrier to Manage DNAPL and Dissolved Phase Polycyclic Aromatic Hydrocarbons (PAHs) in Ground Water – Final Report (Redacted).* University of Wisconsin, *Madison Geo Engineering Report*. 08-24.

Lee, S., A. Oren, C. Benson and K. Dovantzis. in press 2011. *Organoclay as Variably Permeable Reactive Barrier Media to Manage NAPLs in Ground Water*, Journal of Geotechnical and Geoenvironmental Engineering, American Society of Civil Engineers.

Leece, M. 2007. *Application of Permeable Adsorptive Barriers for In-situ Remediation of Petroleum Hydrocarbons.* Presented at the Railroad Environmental Conference at University of Illinois at Champaign-Urbana.

CASE SUMMARY - Grain Silo

Site Location: Midwest USA

Target Contaminants: carbon tetrachloride (CT), chloroform (CF), chloromethane (CM), methylene chloride (MC)

Installation Method: injection

Media Used: zero valent iron (ZVI)/ carbon mix (EHC)

Installation Date: April 2005

Years of Performance Monitoring: 5+

Geology/Hydrogeology

Geology consists of unconsolidated deposits overlying a regional shale. The unconsolidated deposits are typically fluvial (stream or river) deposits and, to a lesser extent, loess (wind-blown silt). The aquifer in the study area is composed of saturated sand units interbedded with clay. The shale aquitard rises to an elevation approximately 10 ft (3.0 m) above the present day water table in the northwest (upgradient) portion of the study area. Thus, an aquifer has not been identified in the presumed source area. The water table in the study area ranges from approximately 4-33 ft below ground surface (bgs). The groundwater flow direction is to the southeast, or from the elevator property towards the creek. The thickness of the saturated aquifer varies from approximately 15-ft (4.6 m)-thick to approximately 25-ft (7.6 m)-thick across the study area. Horizontal hydraulic gradients range from 0.002-0.004 ft per foot (ft/ft). Groundwater velocity ranges from 1.0-2.2 ft/day.

Remedial Objectives

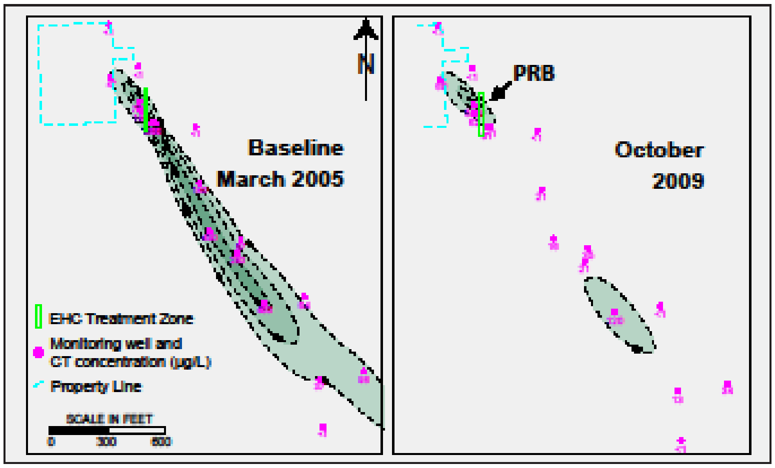
To reach State Maximum Contaminant Levels (MCLs).

Remediation Standards

State MCLs: CT < 5 PPB, CF < 100 ppb, CM < 20 ppb, MC < 5 ppb

Selection Criteria

ZVI alone would have produced MC; lab studies showed EHC degraded both CT and MC. Also wanted a remedy that would minimize local properties (injection versus trenching).



Technology Description

Design and Installation

Bench-scale testing was conducted using soil and groundwater collected from the study area to identify the preferred pilot test remedial technology– injection of EHC across the plume width near the source area to form the TZ. As part of a pilot-scale evaluation of the ISCR technology, 24 tons of EHC were injected as aqueous slurry into two saturated sand units across the 270-ft-wide CT plume along a road right-of-way in April 2005. Twenty-seven injection groups, comprising 126 injection borings of each targeting a discrete depth between 22-44 ft bgs, were installed. The EHC was emplaced at an average application of 1% weight-to-weight ratio. To identify the optimum locations and depths in which to install the EHC TZ, seven soil borings were installed prior to injections of EHC in the location of the TZ to gain geologic and analytical data needed to determine the appropriate EHC emplacement zone(s). Following injections of EHC, five soil borings were used to verify physical placement of the EHC.

Type of Installation

Aqueous slurry injection

Reactive Media

Adventus EHC™ - combination of controlled-release, fibrous organic carbon, and micro-scale ZVI

Technology Performance

Hydraulic Performance

There has been no evidence of mounding or deflection of contaminated groundwater around the edge of this system. A well at the edge of the plume remains non-detect (100% removal) for all analytes since August 2005.

Monitoring System

As well as an upgradient well, downgradient monitoring wells are located 70 ft (21 m), 140 ft (43 m), and 600 ft (183 m) downgradient of the PRB, which equals approximately 39, 78, and 333 days in terms of groundwater travel time. Groundwater samples have been collected every 4-8 months for five-and-a-half years following installation.

Contaminant Concentration (data v time)

Groundwater sampling results as early as four months after installation of the TZ showed a 76% and 88% decline in CT concentration at monitoring wells located 70 and 140 ft (21 and 43 m) downgradient of the TZ, respectively. Groundwater sampling results 13-22 months after installation of the TZ have shown a 97% decline in CT concentration 70 ft (21 m) downgradient of the TZ. Groundwater sampling results 22 months after installation of the TZ have shown a 88% decline in CT concentration 600 ft (183 m) downgradient of the TZ.

Performance Data

Upgradient inflowing concentrations have fluctuated with a high of 2,700 ppb measured in February 2007. Groundwater sampling results four months after installation of the PRB showed a 76% and 88% decline in CT concentration at monitoring wells located 70 and 140 ft (21 and 43 m) downgradient of the PRB, respectively. CT removal rates peaked 16 months after installation with >99% removal observed 70 ft (21 m) downgradient of the PRB (from a baseline of 1,000 ppb to <5 ppb). Two years after installation, these rates decreased slightly to approximately 95% removal, and have stabilized there. CF concentrations initially increased as a result of the CT degradation. However, by February 2007, CF had decreased to 8.4 ppb, which is below background and initial concentrations. DCM and CM have remained below the detection limits in both the upgradient and downgradient wells since the May 2006 monitoring event. In the six most recent sampling events (22-54 months after the EHC injections), effects of the PRB were observed 600 ft (183 m) downgradient from the PRB, with a 91% decline in CT concentration measured in April 2008 (from an initial concentration of 140 to 13 ppb) and no TCM or DCM.

Contact Information

John Valkenburg
Adventus Americas Inc.
517-669-5400
john.valkenburg@adventusgroup.com

Technology Cost

\$37/ft² of PRB

References

Biteman S., G. Foote, S. MacFabe, J. Mueller, and J. Molin. 2008. "Pilot-Scale Reductive Dechlorination of Carbon Tetrachloride in Groundwater." Presented at the 2008 Battelle Conference.

CASE SUMMARY - East Helena Smelter

Site Location: East Helena, Montana

Target Contaminants: arsenic

Installation Method: trench and biopolymer slurry

Media Used: zero valent iron (ZVI)

Installation Date: June 2005

Years of Performance Monitoring: 2

Geology/Hydrogeology

Surface deposits over much of the area surrounding the site consist of smelter tailings. Native geologic deposits in the region consist primarily of Holocene-age stream-channel deposits that are moderately sorted, fine-to-coarse sandy pebble to cobble gravel, and Holocene terrace and alluvial fan deposits consisting of moderately sorted pebble to cobble gravel in a silty, sandy matrix.

The shallow aquifer at the site consists of relatively coarse-grained but highly variable, unconsolidated alluvial deposits containing mixtures of cobbles, gravel, and sand with some silt. A confining layer consisting of volcanic ash deposits underlies the aquifer in the area of the site.

The hydraulic gradient in the location of the PRB ranges from 0.005 to 0.008 averaging 0.006. Groundwater flows to the northwest.

Remedial Objectives

Not available

Remediation Standards

USEPA Maximum Contaminant Level for arsenic - 0.01 mg/L

Selection Criteria

Not available

Technology Description

Design and Installation

This is a pilot scale installation. The reactive barrier was installed using biopolymer slurry methods and modified excavating equipment for deep trenching. A trench was dug 9.1 m long, by 13.7 m deep, by 2.4 m wide and located 280 m downgradient of the source area. The biopolymer slurry was added to the trench at this point to stabilize the trench walls. The slurry-filled trench was then backfilled with a 7.6 m thick layer of granular iron using tremie equipment. The iron was moisture conditioned and mixed with slurry before placement in the trench. The iron was tremied into the slurry starting at 13.7 m depth. The iron/slurry mixture was then overlain with 6.1 m of sand using a loader bucket. The top of the granular iron zone is located >1 m above the maximum groundwater level observed during site charactization. The base of the granular iron is located approximately 1 m above the confining ash tuff deposit making the PRB a "hanging wall." This was to ensure the confining layer was not breached, minimize costs, and examine potential bypass processes. Approximately 174 tons of granular iron was used with an initial porosity of 50%.

After the trench was backfilled, the bioslurry had to be broken down to free up the pore space in the granular iron. This was accomplished by (1) breaking down the biopolymer slurry to simple carbohydrates and (2) encouraging native soil microbes to consume the carbohydrates. The slurry was circulated via air lift pumps through eight temporary wells and discharged back onto the surface of the back-filled trench where it would travel thorugh the reactive media and back to the temporary wells. Liquid enzyme breaker was placed into the temporary wells. The "breaking" of the slurry was accomplished over three days.

Type of Installation

Trench and slurry

Reactive Media

ZVI

Technology Performance

Hydraulic Performance

Based on groundwater elevation measurements, there is no evidence of groundwater mounding upgradient of the PRB that would indicate the PRB is acting as a significant impediment to groundwater flow.

Monitoring System

A monitoring network of approximately 40 groundwater monitor wells was installed in July 2005. Wells are located upgradient, within, and downgradient of the wall. Sampling was conducted 1, 4, 12, 15, and 25 months after installation. Several wells were screened across the entire saturated zone and sampled using discrete multilevel samplers in order to create detailed concentration and geochemical profiles.

Contaminant Concentration (data v time)

Monitoring results indicate arsenic concentrations >25 mg/L in wells located hydraulically upgradient of the PRB. Within the PRB, arsenic concentrations are reduced to 2 - <0.01 mg/L. After two years of operation, monitoring points located within 1 m of the downgradient edge of the PRB showed significant decreases in arsenic concentrations at depths intervals impacted by the emplaced ZVI.

Performance Data

Solid phase test indicates that <10% of the arsenic uptake capacity of the reactive media was used after about one year of operation.

Contact Information

Not available

Technology Cost

Not available

References

Beak, D.G. and R.T. Wilkin. 2009. "Performance of a Zero Valent Iron Reactive Barrier for Treatment of Arsenic in Groundwater: Part 2." Geochemical Modeling and Solid Phase Studies. *Journal of Contaminant Hydrology*. **106**: 15-28.

USEPA. 2008. *Field Application of a Permeable Reactive Barrier for Treatment of Arsenic in Ground Water.* EPA 600/R-08/093, September.

Wilkin, R.T., S.D. Acree, R.R. Ross, D.G. Beak, and T.R. Lee. 2009. "Performance of a Zero Valent Iron Reactive Barrier for Treatment of Arsenic in Groundwater: Part 1." Hydrogeochemical studies. *Journal of Contaminant Hydrology*. **106**: 1-14.

CASE SUMMARY - Vandenberg AFB, Site 15

Site Location: Vandenberg AFB, California

Target Contaminants: trichloroethene (TCE), *cis*-1,2-dichloroethene (cis-DCE), and vinyl chloride (VC)

Installation Method: Deep Soil Mixing

Media Used: BOS100® (granular activated carbon impregnated with zero-valent iron)

Installation Date: Sep 2009 (Deep Soil Mixing Treatability Study)

Years of Performance Monitoring: ~1 yr.

Geology/Hydrogeology

Fine to medium grained sands overlying organic rich clay and bedrock. Depth to water approximately 25 feet below ground surface (bgs), with 25 to 45 feet of saturated thickness. Hydraulic conductivity ranges from 123 to 160 ft/day with an estimated groundwater velocity of 3 ft/day.

Remedial Objectives

Limit plume migration and prevent discharge of chlorinated ethenes to local creek, including any negative byproducts of treatment.

Remediation Standards

USEPA MCLs and State of California Toxicity Reference Values (TRVs)

Selection Criteria

Surface water sampling confirmed that groundwater was discharging to San Antonio Creek. BOS100® was selected at the treatment media to reduce the potential for production of VC. Site constraints included limited access to previously disturbed areas due to sensitive habitat and potential for unexploded ordnance.

Technology Description

Design and Installation

Heaving sands and depth to bedrock prevented the use of conventional trenching techniques. Two phases of direct injection were conducted using traditional and high pressure injection techniques. Confirmation soil cores indicated that the product was not evenly distributed in the subsurface, likely due to the product being filtered out by the sandy sediments close to the point of injection. Deep soil mixing was selected at the best alternative to evenly distribute the product in the PRB treatment zone.

Two PRBs were installed. PRB 1 was 50 feet in length, 5 feet wide (the size of the augers), and 14,648 pounds of BOS100® was mixed in at a depth of 28 to as deep as 71 feet bgs. PRB 2 was 50 feet in length, 5 feet wide, and 7,613 pounds of BOS100® was mixed in at a depth of 28 to as deep as 50 feet bgs. The auger borings were installed approximately 6 inches into clay. The BOS100® product was mixed with guar and added as a slurry during mixing. Laboratory bench-scale column test and field test columns were conducted to determine optimal BOS100® loading parameters and number of auger strokes necessary for emplacement. Results determined a loading rate of 1.7 pounds BOS100® per gallon and 5 strokes would achieve homogeneous mixture of 6% by volume. The bench test also confirmed that dechlorination products such as VC would not be produced.

Type of Installation

Deep Soil Mixing

Reactive Media

BOS100® is a granular activated carbon impregnated with zero-valent iron. The carbon adsorbs contaminants such as chlorinated ethenes, which is subsequently abiotically dechlorinated by reaction with the zero valent iron. Dechlorination products such as vinyl chloride are typically not produced.

Technology Performance

Hydraulic Performance

Significant decreases in ORP in the downgradient monitoring wells indicated flow through the barrier.

Monitoring System

Wells screened at different depths and multi-level samplers were installed up- and down-gradient of the PRBs to monitor groundwater.

Contaminant Concentration (data v time)

Performance Data

Concentrations of chlorinated ethenes prior to PRB installation ranged up to 274 ppb of TCE, 381 ppb of cis-DCE, and 4 ppb of VC. The presence and slow degradation of guar used in construction temporarily delayed treatment for a minimum of 2 to 3 months. Significant reductions have been observed at 5 months in approximately one-third of the downgradient wells, with no generation of VC. Treatment in the deeper zone has yet to be observed. The 11 month samples show similar results. Additional monitoring is being conducted to further evaluate treatment effectiveness and to determine whether the technology is suitable for full-scale application. An enzyme breaker was not used during installation due to concern that guar would breakdown prematurely causing the granular BOS100® to settle in the injection lines or the fine sand to collapse during installations. However, the presence and slow degradation of the guar temporally delayed treatment several months and in one of the barriers stimulated biological reduction of TCE to cis-1,2-DCE which is not the purpose of the project. Therefore, in future applications an enzyme breaker would be recommended for expansion of this type of barrier.

Contact Information

Kathleen Gerber, PG
IRP Project Manager, 30 CES/CEANR
1028 Iceland Avenue
Vandenberg AFB, CA 93437-6010
(805) 606-9834

Technology Cost

Not available.

References

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Appendix B

Field and Laboratory Parameters

FIELD AND LABORATORY PARAMETERS

Analyte or parameter	Analytical method	Sample volume	Sample container	Preservation	Holding time
Field parameters					
Water level	In-hole probe	None	None	None	None
pH	In-hole probe or flow-through cell	None	None	None	None
Groundwater temperature	In-hole probe	None	None	None	None
Redox potential	Flow-through cell	None	None	None	None
Dissolved oxygen	Flow-through cell[a]	None	None	None	None
Specific conductance	Field instrument	None	None	None	None
Turbidity	Field instrument	None	None	None	None
Salinity	Field instrument	None	None	None	None
Organic analytes					
Volatile organic compounds[b]	USEPA SW846, Method 8240	40 mL	Glass VOA vial	4°C, pH <2	14 days
				No pH adjustment	7 days
	USEPA SW846, Method 8260a or b	40 mL	Glass VOA vial	4°C, pH <2	14 days
				No pH adjustment	7 days
	40 CFR, Part 136, Method 624	40 mL	Glass VOA vial	4°C, pH <2	14 days
				No pH adjustment	7 days
Inorganic analytes					
Metals[c]: K, Na, Ca, Mg, Fe, Al, Mn, Ba, V, Cr^{+3}, Ni, SiO_2	40 CFR, Part 136, Method 200.7	100 mL	Polyethylene	4°C, pH <2, (HNO_3)	180 days
Metals: Cr^{+6}	40 CFR, Part 136, or Hach method	200 ml	Glass, plastic	4^{o}C	24 hours
Anions: SO_4, Cl, Br, F	40 CFR, Part 136, Method 300.0	100 mL	Polyethylene	4°C	28 days
NO_3	40 CFR, Part 136, Method 300.0	100 mL	Polyethylene	4°C	48 hours
Alkalinity	40 CFR. Part 136, Method 310.1	100 mL	Polyethylene	4°C	14 days
Other					
Total dissolved solids	40 CFR, Part 136, Method 160.2	100 mL	Glass, plastic	4°C	7 days
Total suspended solids	40 CFR, Part 136, Method 160.1	100 mL	Glass, plastic	4°C	7 days
Total organic carbon	40 CFR, Part 136, Method 415.1	40 mL	Glass	4°C, pH <2, (H_2SO_4)	28 days

Analyte or parameter	Analytical method	Sample volume	Sample container	Preservation	Holding time
Dissolved organic carbon	40 CFR, Part 136, Method 415.1	40 mL	Glass	4°C, pH <2, (H_2SO_4)	28 days
Dissolved gases					
Methane, ethane, ethane	RSK-175 (GC-FID)	None	None	None	None
Carbon dioxide	SM 4500	None	None	None	None
Hydrogen gas	Bubble strip method (GC with mercury-reduction detector)	None	None	None	None
Radionuclides					
Field screening	HPGe gamma spectroscopy	None	None	None	None
	FIDLER				
Gross α/gross β activities (screening)	Gas proportional counting	125 mL[d]	Polyethylene[d]	pH <2, (HNO_3)[d]	N/A[d]
Specific isotopes (Am, Cs, Pu, Tc, U)	Alpha spectroscopy	4 L[d]	Polyethylene[d]	pH <2, (HNO_3)[d]	6 months[d]
	Gamma spectroscopy				

Abbreviations: CFR = Code of Federal Regulations, FID = flame ionization detector, GC = gas chromatograph, HPGe = high-purity germanium, VOA = volatile organic analysis.

[a] If <1.0 mg/L, use photometric field kit for analysis.

[b] GC methods may be substituted once identity of compounds and breakdown products are verified.

[c] Other metals analytes which are characteristic of the media should be included.

[d] General guidelines; the parameter is laboratory specific.

Appendix C

PRB: Technology Update Team Contacts

PRB: TECHNOLOGY UPDATE TEAM CONTACTS

John Doyon, Team Co-Leader
NJ Dept. of Environmental Protection
609-633-0713
jdoyon@dep.state.nj.us

Kimberly A. Wilson, Team Co-Leader
SC Dept. of Health & Environmental Control
803-896-4087
wilsonka@dhec.sc.gov

Jeanne Barnes
AL Dept. of Environmental Management
334-271-7752
jmbarnes@adem.state.al.us

Erica Becvar
Air FCEE/TDN
210-395-8424
erica.becvar.1@us.af.mil

Kenneth Bowers
NAVFAC Atlantic
757-322-8341
kenneth.a.bowers@navy.mil

Kathleen Bradley
Noblis
210-408-5554
kathleen.bradley@noblis.org

Doug Downey
CH2M HILL
303-674-6547
doug.downey@ch2m.com

Arun Gavaskar
NAVFAC Atlantic
757-322-4730
arun.gavaskar@navy.mil

Bruce Henry
AFCEE
303-831-8100
bruce.henry@parsons.com

David Lee
Atomic Energy of Canada Limited
613-584-8811, ext. 44710
leed@aecl.ca

John Muegge
CA Dept. of Toxic Substances Control
916-322-0712
jmuegge@dtsc.ca.gov

Eric Nuttall
University of New Mexico
505-269-7840
nuttall@unm.edu

Jim Olsta
CETCO
847-851-1835
jim.olsta@cetco.com

Andrzej Przepiora
EnviroMetal Technologies, Inc.
519-746-2204
aprzepiora@eti.ca

Robert Puls
USEPA Office of Research & Development
580-436-8543
puls.robert@epa.gov

Nancy Ruiz
NAVFAC Engineering Service Center
805-982-1155
nancy.ruiz@navy.mil

Max Shahbazian
CA Water Quality Control Board, San Francisco Bay Region
510-622-4824
mshahbazian@waterboards.ca.gov

Lenny Siegel
Center for Public Environmental Oversight
650-961-8918
lsiegel@cpeo.org

Cannon Silver
Battelle
614-424-7406
silverc@battelle.org

Scott Warner
AMEC Earth and Environmental
510-663-4269
scott.warner@amec.com

Kent Whiting
Camp, Dresser, & McKee, Inc.
406-441-1400
whitingks@cdm.com

Peter Zawislanski
Terraphase
510-645-1850
peter.zawislanski@terraphase.com

APPENDIX D

Glossary

GLOSSARY

abiotic – Chemical and physical processes occurring without the involvement of living organisms. In some cases, such attenuation processes do not involve microorganisms or plants at all, while in other cases, biological and abiotic processes occur simultaneously and/or serve to enhance each other.

abiotic reductive dechlorination – A chlorinated compound is reduced by contact with a reactive mineral such as iron monosulfide.

advection – Transport of a solute by the bulk motion of flowing groundwater.

aerobic – Conditions for growth or metabolism in which the organism is sufficiently supplied with molecular oxygen.

aerobic respiration – Process whereby microorganisms use oxygen as an electron acceptor to generate energy.

aliphatic compounds – Acyclic or cyclic, saturated or unsaturated carbon compounds, excluding aromatic compounds.

amendment – Substrate introduced to stimulate the in situ microbial processes (vegetable oils, sugars, alcohols, etc.).

anaerobic – Environmental conditions requiring the absence of molecular oxygen.

anaerobic respiration – Process whereby microorganisms use a chemical other than oxygen as an electron acceptor. Common "substitutes" for oxygen are nitrate, sulfate, iron, carbon dioxide, and other organic compounds.

anisotropy – The property of being directionally dependent, as opposed to "isotropy," which means homogeneity in all directions.

attenuation – The reduction of contaminant concentrations. The term applies to both destructive and nondestructive contaminant removal.

attenuation rate – The rate at which a contaminant is removed. This is not a rate constant but a rate with typical units of micrograms per liter (µg/L) per year.

bacteria – Any of a group of prokaryotic unicellular round, spiral, or rod-shaped single-celled microorganisms that are often aggregated into colonies or motile by means of flagella that live in soil, water, organic matter, or the bodies of plants and animals and that are autotrophic, saprophytic, or parasitic in nutrition and important because of their biochemical effects and pathogenicity.

beta elimination – A mechanism whereby two atoms—one each from adjacent carbon atoms—are removed, usually resulting in formation of a carbon-carbon bond. Beta-eliminations are also called 1,2-eliminations. An example is dehydrohalogenation whereby a hydrogen and halogen, each on adjacent carbons, are removed to form a carbon-carbon double bond.

bioaugmentation – The addition of beneficial microorganisms into groundwater to increase the rate and extent of anaerobic or aerobic degradation processes.

biodegradation – Breakdown of a contaminant directly or indirectly by microorganisms in the subsurface.

biofouling – Biofouling occurs when bacteria attach, grow, and block the well screen, filter pack, or formation surrounding a nutrient delivery well, thereby limiting or preventing the proper function of the well.

biomass – Material produced by the growth of living material.

bioremediation – Use of microorganisms to biodegrade contaminants in soil and groundwater.

biotransformation – Microbiologically catalyzed transformation of a chemical to some other product.

chlorinated ethene – Chemical substances, such as trichloroethene and tetrachloroethene that have been used in industry as solvents.

chlorinated solvent – Organic compounds with chlorine substituents that commonly are used for industrial degreasing and cleaning, dry cleaning, and other processes.

chloromethanes – Chemical substances, such as carbon tetrachloride and chloroform, that have been used in industry as solvents.

cometabolic anaerobic reductive dechlorination – A process in which an enzyme released by bacteria during metabolism of an unrelated compound serendipitously degrades a chlorinated compound or another contaminant.

cometabolism – A reaction in which microorganisms transform a contaminant even though the contaminant cannot serve as an energy source for growth. The microorganisms require the presence of other compounds (primary substrates) to support growth.

compliance monitoring – The collection of data which, when analyzed, can evaluate the condition of the contaminated media against standards such as soil and or water quality regulatory standards, risk-based standards, or remedial action objectives.

conceptual site model (CSM) – A summary of all available site-specific information related to contaminant sources and release mechanisms, affected media, contaminant transport and environmental fate, and receptor exposure.

dense, nonaqueous-phase liquid (DNAPL) – A water-immiscible organic liquid that is denser than water.

desorption – The converse of “sorption,” either adsorption or absorption. The release of a solute from a solid.

diffusion – The process of net transport of solute molecules from a region of high concentration to a region of low concentration, caused by molecular motion and in the absence of turbulent mixing.

dilution – A reduction in solute concentration caused by mixing with water at a lower solute concentration.

dispersion – The spreading of a solute from the expected groundwater flow path as a result of mixing of groundwater.

electron – A negatively charged subatomic particle that may be transferred between chemical species in chemical reactions.

electron acceptor – A compound to which an electron may be transferred (and is thereby reduced). Common electron acceptors are oxygen, nitrate, sulfate, ferric iron, carbon dioxide, manganese, and chlorinated solvents, such as tetrachloroethene and its daughter products trichloroethene; *cis*-1,2-dichloroethene; and vinyl chloride.

electron donor – Chemical substances, such as molecular hydrogen or organic substrate, that yield an electron as they are oxidized, producing energy to sustain life and for the subsequent degradation of other chemicals, in this case, chlorinated solvents.

enhanced attenuation – Any type of intervention that might be implemented in a source-plume system to increase the magnitude of attenuation by natural processes beyond that which occurs without intervention. Enhanced attenuation is the result of applying an enhancement that sustainably manipulates a natural attenuation process, leading to an increased reduction in mass discharge of contaminants.

enhanced bioremediation – An engineered approach to increasing biodegradation rates in the subsurface.

flux – Rate of flow of fluid, particles, or energy through a given surface.

green – A process or material that uses minimal natural resources and energy, and whose life cycle releases minimal emissions or waste to the natural environment.

growth substrate – An organic compound upon which a bacteria can grow, usually as a sole carbon and energy source.

halorespiration – The use of halogenated compounds as sources of energy. The halogen serves as terminal electron acceptor.

hydraulic conductivity – The capability of a geologic medium to transmit water. A medium has a hydraulic conductivity of unit length per unit time if it will transmit in unit time a unit volume of groundwater at the prevailing viscosity through a cross section of unit area, measured at right angles to the direction of flow, under a hydraulic gradient of unit change in head through unit length of flow.

hydraulic gradient – The change in hydraulic head (per unit distance) in a given direction, typically in the principal flow direction.

hydrolysis – Decomposition of a chemical compound by reaction with water, such as the dissociation of a dissolved salt or the catalytic conversion of starch to glucose.

inorganic compound – A compound that is not based on covalent carbon bonds, including most minerals, nitrate, phosphate, sulfate, and carbon dioxide.

in situ – “In place,” refers to treating a compound where it is rather than first mechanically removing it (by excavation, pumping, venting, etc.) and then treating it.

mass flux – Contaminant load (per unit area per time), a general term where mass flux and/or mass discharge type calculations are performed

metabolic anaerobic reductive dechlorination (halorespiration) – A biologically mediated process.

metabolism – The chemical reactions in living cells that convert food sources to energy and new cell mass.

methanogen – Strictly anaerobic archaeabacteria able to use only a very limited substrate spectrum (e.g., molecular hydrogen, formate, methanol, carbon monoxide, or acetate) as substrates for the reduction of carbon dioxide to methane.

microcosm – A batch reactor used in a bench-scale experiment designed to replicate the microbial conditions present in the groundwater environment.

microorganism – An organism of microscopic or submicroscopic size, including bacteria.

mineralization – The complete degradation of an organic compound to carbon dioxide.

monitored natural attenuation (MNA) – A remediation strategy that relies on naturally occurring processes in soil and groundwater environments that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in those media.

natural attenuation – Naturally occurring processes in soil and groundwater environments that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in those media.

nanoscale zero valent iron (NZVI) – Nanoscale ZVI particles that are finer and more reactive than granular ZVI.

oxidation – Loss of electrons from a compound.

passivation – To make inactive or less reactive, passivate the surface of steel by chemical treatment, usually by the deposition of a layer of oxide on its surface.

performance monitoring – The collection of information which, when analyzed, allows for the evaluation of the performance of a system on environmental contamination.

permeable reactive barrier – An in situ permeable treatment zone designed to intercept and remediate a contaminant plume.

plume – A zone of dissolved contaminants. A plume usually originates from a source and extends in the direction of groundwater flow.

process monitoring – The collection of information documenting the operation of a system’s engineered components.

rebound – After contaminant concentrations in groundwater have been reduced through in situ treatment and the treatment is terminated or reduced, the return of concentrations to elevated levels due to the continued release of mass from a source zone beyond the natural attenuation capacity of the groundwater system.

reduction – Gain of electrons from a compound.

reductive dechlorination – The removal of chlorine from an organic compound and its replacement with hydrogen.

saturated zone – Subsurface environments in which the pore spaces are filled with water.

sorption – The uptake of a solute by a solid.

source zone – The subsurface zone containing a contaminant reservoir sustaining a plume in groundwater.

stakeholder – A person other than regulators, owners, or technical personnel involved in the environmental activity of concern, who has a vested interest in decisions related to those particular activities.

substrate – A molecule that can transfer an electron to another molecule and/or provide carbon to the microorganism. Organic compounds, such as lactate, ethanol, or glucose, are commonly used as substrates for bioremediation of chlorinated ethenes.

sulfate reducer – A microorganism that exists in anaerobic environments and reduces sulfate to sulfide.

volatilization – The transfer of a chemical from its liquid phase to the gas phase.

zero-valent iron – Elemental iron, which is a strong reducing agent.

Appendix E

Abbreviations, Acronyms, and Symbols

ABBREVIATIONS, ACRONYMS, AND SYMBOLS

AFB	Air Force Base
AFCEE	Air Force Center for Engineering and the Environment
AFS	Air Force Station
ASTM	ASTM International (formerly the American Society for Testing and Materials)
atm	atmosphere
AVS	acid volatile sulfide
BFS	blast furnace slag
bgs	below ground surface
BMP	best management practice
BOFS	basic oxygen furnace slag
BTEX	benzene, toluene, ethylbenzene, and xylenes
CAAP	Cornhusker Army Ammunition Plant
CAH	chlorinated aliphatic hydrocarbon
cDCE	*cis*-dichloroethene
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
COC	contaminant of concern
CrRS	chromium-reducible sulfide
CSIA	compound-specific isotope analysis
CSM	conceptual site model
CT	carbon tetrachloride
CVOC	chlorinated volatile organic compound
CWA	Clean Water Act
DCE	dichloroethene
DNAPL	dense, nonaqueous-phase liquid
DNT	dinitrotoluene
DNX	1,3-dinitroso-5-nitro-1,3,5-trizacyclohexane, or hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine
DO	dissolved oxygen
DOC	dissolved organic carbon
DOD	U.S. Department of Defense
DOE	U.S. Department of Energy
EAFS	electric arc furnace slag
Eh	reduction potential (mV)
ESTCP	Environmental Security Technology Certification Program
EVO	emulsified vegetable oil
EZVI	emulsified zero-valent iron
FR	functional requirement
FS	feasibility study
GHG	greenhouse gas
GSR	green and sustainable remediation
HMX	high-melting-point explosive (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine)
IC	institutional control
ITRC	Interstate Technology & Regulatory Council

K	hydraulic conductivity
K_{oc}	organic carbon partition coefficient
LCA	life-cycle analysis
LTM	long-term monitoring
MBT	molecular biological tool
MCL	maximum contaminant level
meq	milliequivalent weight
MNA	monitored natural attenuation
MNX	1-nitroso-3,5-trizacyclohexane, or hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine
MTBE	methyl tertiary butyl ether
NAPL	nonaqueous-phase liquid
NAS	Naval Air Station
NASA	National Aeronautics and Space Administration
NAVFAC	Naval Facilities Engineering Command
NFESC	Naval Facilities Engineering Service Center
NPDES	National Pollution Discharge Elimination System
NWIRP	Naval Weapons Industrial Reserve Plant
NZVI	nanoscale zero-valent iron
O&M	operations and maintenance
ORP	oxidation-reduction potential
OU	operable unit
PAH	polycyclic aromatic hydrocarbon
PCD	Pueblo Chemical Depot
PCE	perchloroethene, or tetrachloroethene
PDB	passive diffusion bag
PLFA	phospholipid fatty acid
PO	performance objective
PPT	pressure pulse technology
PRB	permeable reactive barrier
RAO	remedial action objective
RCRA	Resource Conservation and Recovery Act
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine (Royal Demolition Explosive)
redox	oxidation-reduction
ROI	radius of influence
RSL	Regional Screening Level
RTDF	Remediation Technologies Development Forum
SERDP	Strategic Environmental Research and Development Program
SHE	standard hydrogen electrode
SMZ	surface-modified zeolite
SOP	standard operating procedure
SRT	Sustainable Remediation Tool
TAT	triaminotoluene
TCE	trichloroethene
tDCE	*trans*-1,2-dichloroethene
TDS	total dissolved solids
TEAP	terminal electron-accepting process

TIC	total inorganic carbon
TNT	trinitrotoluene
TNX	1,3,5-trinitroso-1,3,5-trizacyclohexane, or hexahydro-1,3,5-trinitroso-1,3,5-triazine
TOC	total organic carbon
TRM	transformed red mud
UIC	underground injection control
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VC	vinyl chloride
VFA	volatile fatty acid
VOC	volatile organic compound
XRD	X-ray diffraction
ZVI	zero-valent iron