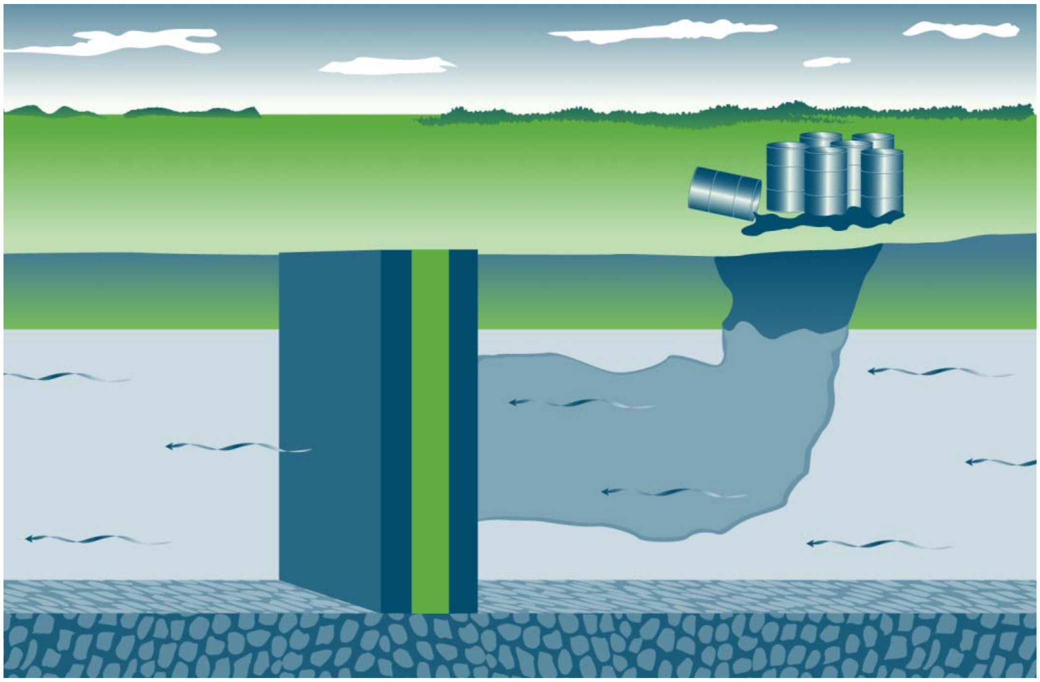
Technical/Regulatory Guidelines

Permeable Reactive Barriers: Lessons Learned/New Directions



February 2005

Prepared by
The Interstate Technology & Regulatory Council
Permeable Reactive Barriers Team

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EXECUTIVE SUMMARY

Lessons Learned/New Directions was prepared by the ITRC Permeable Reactive Barriers Team to update previous guidance written by the team. The goal for this document was to compile the information and data on permeable reactive barriers (PRBs) that have been generated over the last 10 years of technology development and research, as well as to provide information on non-iron-based reactive media that can be used in PRBs. This document also provides an update on a developing technology somewhat related to PRBs in which source zone contamination is treated with iron-based reactive media.

A PRB is defined as an in situ permeable treatment zone designed to intercept and remediate a contaminant plume. Zero-valent iron is the most common media used in PRBs to treat a variety of chlorinated organics, metals, and radionuclides. Reactive media such as carbon sources (compost), limestone, granular activated carbon, zeolites, and others had also been deployed in recent years to treat metals and some organic compounds.

The proper design of a PRB is highly dependent on a complete and accurate site characterization. A conceptual site framework is discussed as a means to perform a detailed characterization for PRB deployment. Collection of hydrogeologic, geochemical, microbial, and geotechnical data along with the complete vertical and horizontal plume delineation are necessary to characterize a PRB site. The Triad concept is also introduced as a means to gather site data.

The design of a PRB can be enhanced using probabilistic modeling to incorporate the variability of the input design parameters. Construction advancements include the use of biopolymer for trench stabilization or the use of vertical hydraulic fracturing for reactive media emplacement. Several other factors that can affect the construction and performance of the PRB, such as variability in the reactive media or permeability contrasts between the reactive media and the aquifer must be considered in the system design.

Hydraulic, geochemical, and microbial assessment of the PRB is all part of the performance assessment of the PRB system. Evaluation of the longevity of a PRB system has been examined using long-term column tests. The two systems studied resulted in predictions of decades before the PRBs will lose reactivity. Depending on several site-specific conditions, PRBs are now expected to last 10–30 years before reactivity or hydraulic issues will result in the need for maintenance.

Monitoring is discussed in terms of performance and compliance objectives. Details are offered on monitoring well placement, frequency of sampling, sampling parameters and methods. Passive sampling techniques such as low-flow sampling or the use of permeable diffusion bags are recommended for PRBs to obtain the most representative samples. All regulatory permits necessary for the installation of a PRB are identified, and some state specific permit information is provided. The need for institutional controls, evaluation of downgradient water chemistry, identification of reactive media impurities, and information on biostat addition as well as the development of contingency and closure plans are highlighted as other regulatory concerns.

An offshoot of the technology involves the use of iron media to treat source zones. This remedial measure is not considered a PRB but is presented since the reactive media and treatment mechanism are related. A detailed discussion and site-specific examples are presented of this developing technology.

Health and safety issues are addressed with emphasis on concerns related to PRB installation as well as the typical construction concerns that are part of this remedy. Stakeholders, defined as any nonregulatory interested party, also have some outlined concerns with this technology that should be addressed as part of the PRB deployment.

The costs of PRB systems are compared to those of other technologies. While not as cost-effective as groundwater remedies like monitored natural attenuation or bioremediation, PRBs can compare favorably to groundwater pump-and-treat systems. Since PRBs provide a mostly passive remediation technology, cost reductions can be found in the operation and maintenance of the system. The document provides site-specific examples of PRB system costs.

Since the 1994 introduction of the first zero-valent iron PRB in the United States, this technology has developed from innovative to accepted standard practice. Several issues surrounding the use of PRBs—such as accurately predicting the longevity of a system—have yet to be conclusively answered, but as the technology continues to mature and some of the early PRB installations age, these challenging issues will become the main focus for additional research and development.

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PERMEABLE REACTIVE BARRIERS: LESSONS LEARNED/NEW DIRECTIONS

1. INTRODUCTION AND DOCUMENT SCOPE

To date, granular iron has been the most widely used reactive media in full-scale permeable reactive barriers (PRBs). The prevalent use of granular iron, or zero-valent iron (ZVI), stems mainly from its documented ability to degrade a variety of contaminant types, the most common of which are the chlorinated solvent compounds such as perchloroethylene (PCE) and trichloroethylene (TCE) (Wilkin and Puls 2003). Lessons learned from the deployment of iron-based PRB systems have garnered much attention in the past few years primarily due to concerns about PRB longevity (i.e., long-term reactivity and permeability). Specific questions such as “How long will an iron wall remain reactive?” and “How does permeability change over time?” have been the focus of recent studies. Most PRBs are less than 10 years old, and it is not known whether they will remain effective over the lifetime of the contaminant plume, which could be on the order of decades or more. Therefore, much research has focused on changes in PRB reaction rates over time. Additionally, some PRBs have had problems with permeability and hydraulics, most of which seem to be an artifact of the construction techniques for PRB installation or inadequate predesign site characterization rather than chemical precipitation and clogging of the reactive media. As with any technology used to treat contaminants in the subsurface, successful implementation is contingent on effective site characterization, design, and construction. This document highlights many of the lessons learned over the successful 10-year history of iron-based PRB systems.

In the past few years, alternative PRB designs using non-iron-based reactive materials to treat additional contaminants have also gained attention. For example, reactive materials such as compost, zeolites, activated carbon, apatite, limestone, etc., are now being used to control pH, metals, and radionuclides. Use of various non-iron reactive media in PRB systems is discussed primarily in Section 2 of this document and in the case studies provided in Appendix E. Most lessons learned discussed in this document, however, are derived from iron PRB systems due to their longer deployment history.

Research and deployment of bio-barrier systems are also growing in recent years, particularly for treatment of chlorinated solvents and petroleum hydrocarbon constituents such as benzene, toluene, ethylbenzene, and xylenes (BTEX) and methyl *tert*-butyl ether (MTBE). Bio-barriers are often described as in situ bioremediation deployed with the PRB design concept (i.e., a continuous, linear, flow-through zone where treatment occurs). These systems may use solid, liquid, or gaseous amendments such as wood chips, compost, lactate, molasses, etc. to create an enhanced zone of biological activity where contaminant degradation occurs. In this way, the reactive treatment zone within a bio-barrier is created indirectly through the addition of amendments. This document provides a brief introduction to bio-barrier systems but does not address these systems in detail.

Additionally, advances in iron technology have lead to the use of powdered, catalyzed, emulsified, and other reactive iron materials while advances in construction techniques have lead to the emplacement of longer, deeper, thinner, and more targeted PRBs. An interesting offshoot of advances in PRB technology is the growing use of iron-based materials for direct source-zone treatment through injection or mixing. Although not defined as a true PRB, the use of iron-based materials for source-zone treatment is included in this document (Section 7) because the reaction chemistry is essentially the same as for iron-based PRBs.

1.1 Permeable Reactive Barrier Team

The Permeable Reactive Barrier Team of the Interstate Technology & Regulatory Council (ITRC) currently comprises representatives from four state regulatory agencies (New Jersey, California, Virginia, and Louisiana), federal agencies, private consulting and vendor companies, and academia. Several team members also participate in the Remediation Technology Development Forum (RTDF) sponsored by the U.S. Environmental Protection Agency (USEPA). Since 1996, the PRB Team has investigated the development of permeable reactive barriers as an emerging remediation technology.

This is the fourth PRB-related document produced or co-produced by the PRB Team. Previous documents focused on implementation of PRBs for treating inorganics, radionuclides, and dissolved chlorinated solvents. The team has also collaborated with the triagency group (U.S. Department of Defense [DoD], U.S. Department of Energy [DOE], and USEPA) on long-term monitoring of PRBs. This three-year project concluded in 2002 and culminated in the publication of a case studies report addressing the longevity and hydraulic performance of several PRBs.

Additionally, the team also conducts classroom and Internet-based training related to PRB design and deployment. In 2002, the team introduced its second Internet-based training on PRBs, an advanced course on installing iron- and non-iron-based PRBs.

1.2 PRB Definition and Application

In the broadest sense, a PRB is a continuous, in situ permeable treatment zone designed to intercept and remediate a contaminant plume. The treatment zone may be created directly using reactive materials such as iron or indirectly using materials designed to stimulate secondary processes, such as by adding carbon substrate and nutrients to enhance microbial activity. In this way, contaminant treatment may occur through physical, chemical, or biological processes. With most PRBs, the reactive material is in direct contact with the surrounding aquifer material.

The term “barrier” is intended to convey the idea of a barrier to contaminants, but not to groundwater flow. PRBs are designed to be more permeable than the surrounding aquifer materials so that contaminants are treated as groundwater readily flows through without significantly altering groundwater hydrogeology. Some of the words used in this document to describe the dimensions of a PRB are illustrated in Figure 1-1.

PRBs are often intended as a source-term management remedy or as an on-site containment remedy. Therefore, PRBs may be designed with different site-specific objectives in mind. For example, a PRB installed near the downgradient site boundary may be designed to protect downgradient properties or receptors such as surface waters or potable wells, and meet specific numerical objectives. Alternatively, a PRB installed near the source term may be designed to reduce mass flux by a given percent with the idea that natural attenuation or some other remedy will address the downgradient residual contamination. Figure 1-2 illustrates examples of PRB configurations in use today.

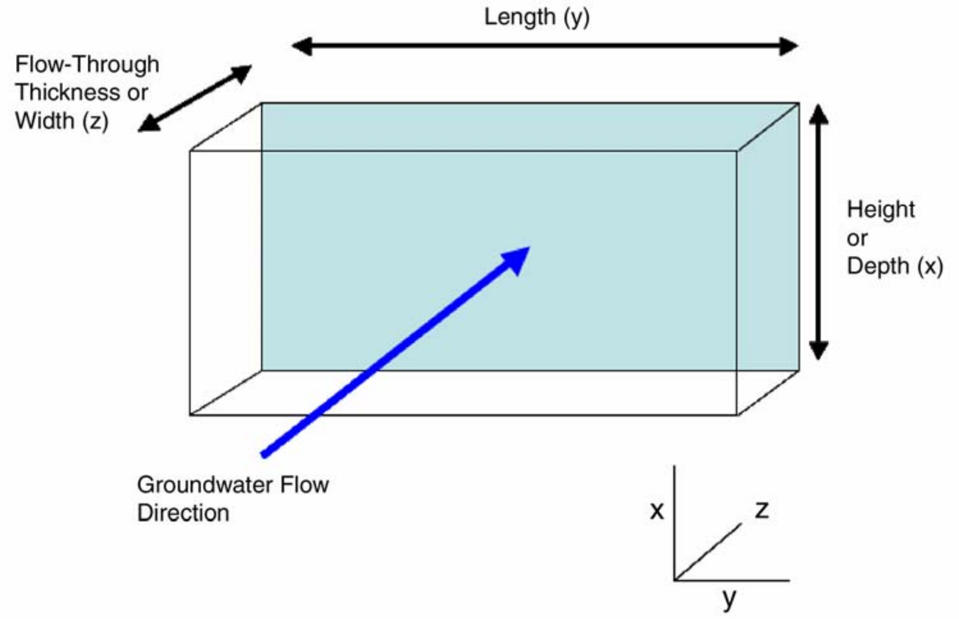
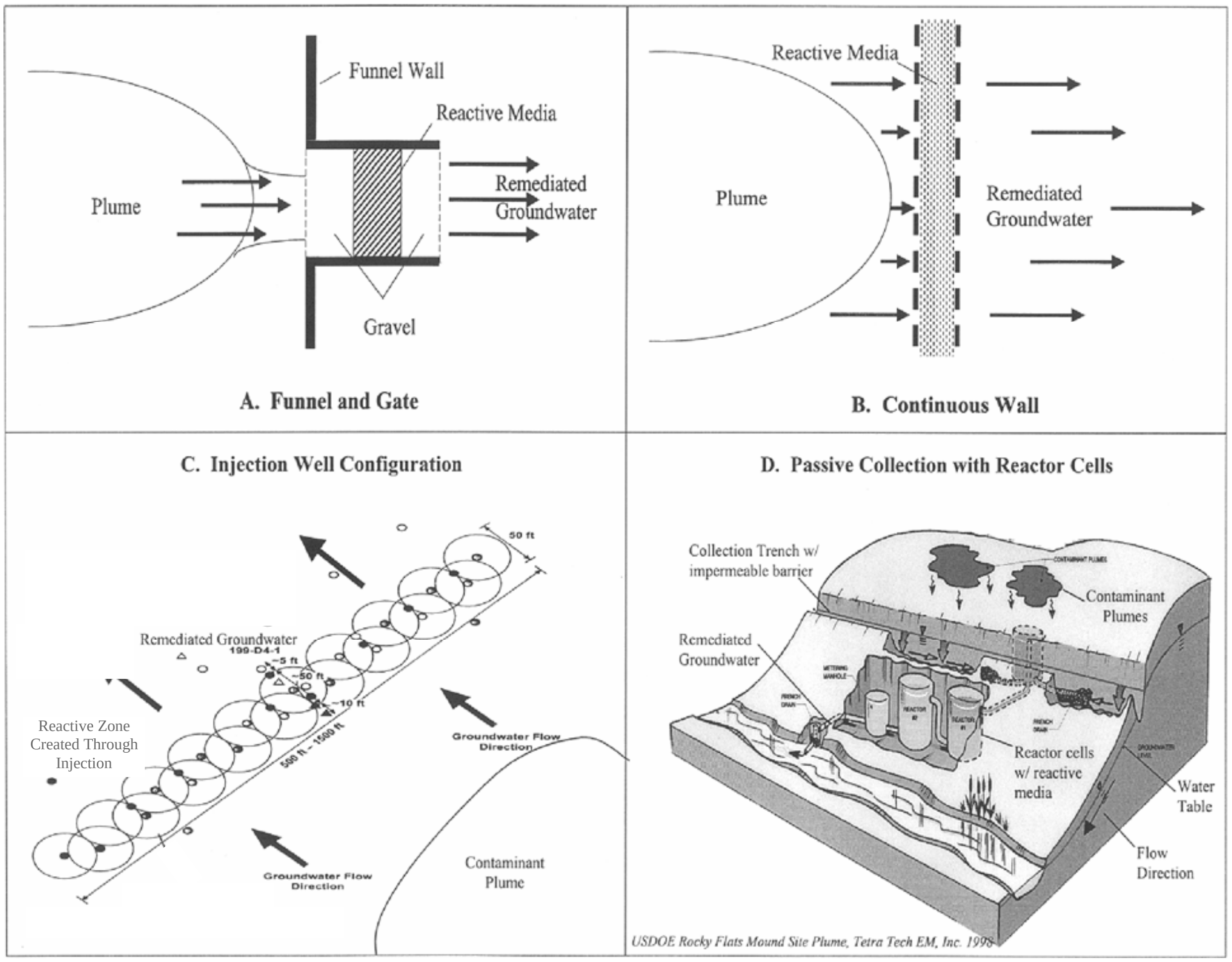


Figure 1-1. Dimensions of a PRB.



USDOE Rocky Flats Mound Site Plume, Tetra Tech EM, Inc. 1998

Figure 1-2. Examples of permeable reactive barriers.

Over the past 10 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. Worldwide, there have been nearly 120 applications of iron-based PRBs, 83 of which are considered full scale (see Table 2-3). In the United States, there have been more than 90 applications of iron-based PRBs, 67 of which are full scale (Figure 1-3). Based on this successful 10-year history, alternative non-iron-based reactive materials are now being researched and deployed in the United States and abroad. Considering all types of reactive media, there may currently be as many as 200 PRB applications worldwide.

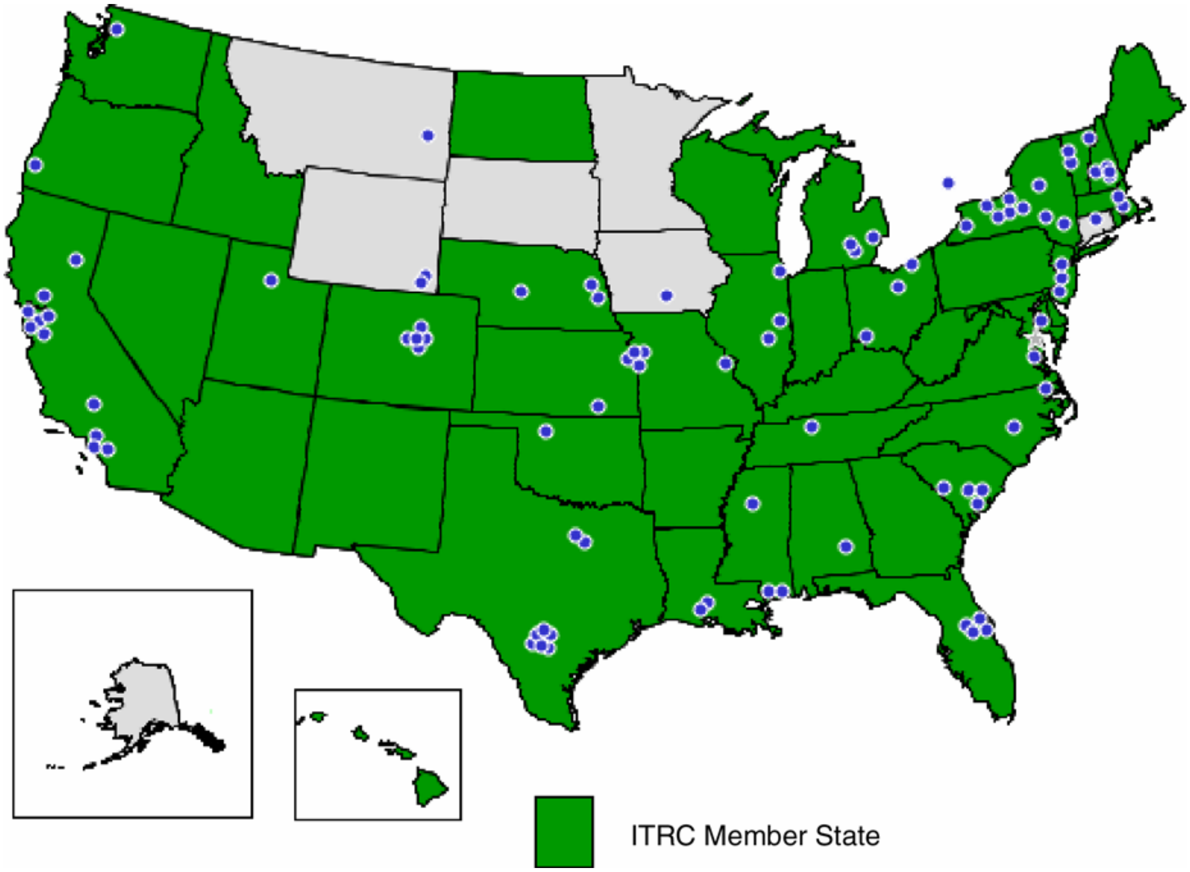


Figure 1-3. Location of iron-based PRBs for VOC treatment in the United States.

The economic benefits of PRBs drive the application of this technology. The passive functioning of a PRB means that relatively little energy or labor input (except for site monitoring) is necessary; thus, the technology has a potential advantage over conventional groundwater treatment systems such as pump and treat. Regardless, a cost-benefit approach should be used to evaluate the economic feasibility of a PRB at a given site.

PRB technology also has limitations and should not be considered as the only remedy for a site. For example, a PRB may be used in conjunction with one or more other remedies, such as monitored natural attenuation (MNA) for the downgradient portion of a contaminant plume and/or source removal technologies for dense, nonaqueous-phase liquid (DNAPL) or other contaminant residual. Additionally, since most PRBs operate passively, site remediation may take several years or even decades, requiring the use of long-term institutional controls for site management. Therefore, a PRB should be considered within the context of overall and long-term site remediation goals.

Although additional details about bio-barrier design and deployment are not addressed in this document, bio-barriers are considered a unique type of PRB. It is worth noting that some bio-barrier designs, particularly those that require deep delivery and circulation of liquid amendments, can challenge the passive operation concept of PRBs. For example, although many bio-barriers are designed to deliver amendments into the subsurface using relatively passive techniques (i.e., slow injection or diffusion of oxygen or air), some bio-barriers require substantial energy input to deliver amendments to the proper aquifer depth and then circulate and mix the amendments within the subsurface. Such designs function less passively than traditional PRBs and may incur greater operation and maintenance (O&M) costs.

It should also be recognized that bio-barriers are considered an innovative design extension of in situ bioremediation technology. Numerous documents provide guidance on in situ bioremediation (ITRC 1998, USEPA 2000a, USEPA 2004c); however, few have focused specifically on bio-barrier designs. Johnson, Miller, and Bruce (2004) and McGrath, Yang, and O’Reilly (2005) provide guidance on the use of aerobic bio-barriers for treatment of MTBE and other contaminants. Johnson, Miller, and Bruce (2004) also highlight a successful passive bio-barrier system at Port Hueneme, California. Additionally, USEPA’s *Engineered Approaches to In Situ Bioremediation of Chlorinated Solvents* (USEPA 2000a) and *Technologies For Treating MtBE and Other Fuel Oxygenates* (USEPA 2004c) provide brief summaries of the application of PRBs to in situ bioremediation for chlorinated aliphatic hydrocarbons and fuel oxygenates such as MTBE, respectively.

1.3 Purpose

The purpose of this document is to **provide updated information regarding new developments and innovative approaches in the application of PRBs to treat a variety of groundwater contaminants.** A major focus of this document is to summarize lessons learned from previous PRB deployments that can affect PRB longevity and long-term performance. Some of the information presented in this document was gathered through a survey of the ITRC states coordinated by the network of ITRC state points of contact. The survey helped to identify PRB sites as well as answer questions regarding the regulatory framework for PRBs.

This document also serves as an introduction to the use of iron-based reactive materials for source zone treatment. Additional guidance should be referenced for complete information.

This document is intended to serve as technical and regulatory guidance for state and federal regulators, consultants, project managers, and other stakeholders and technology implementers when a PRB is the selected remedy for a contaminant plume in groundwater. Where possible, this document identifies important regulatory issues to consider during site characterization, design, construction, monitoring, and closure. Case studies from around the country are also included to show various designs, contaminants, reactive media, and cost data for implementing PRB technologies.

Because PRBs are an evolving technology, this document is intended as a guide and should be updated periodically. In addition, current research should always be reviewed when considering the guidelines outlined in this document. Users of this document are encouraged to consult the references (Section 12) for further background and technical information on this technology.

1.4 Report Organization

In this report, lessons learned from previous deployments, improved site characterization methods, alternative construction and installation techniques, and costs are discussed throughout the document within each relevant section.

Section 2 begins with a summary of historic PRB applications using iron-based materials, primarily for the treatment of chlorinated ethenes and ethanes. This section also summarizes recent developments in the use of alternative, non-iron-based treatment media.

Section 3 discusses lessons learned regarding site characterization, as well as applicable state-of-the-art characterization methods and techniques useful for PRB sites.

Section 4 covers installation techniques and describes recent advances in trenching construction methods and vertical hydrofracturing for iron-based PRBs. Section 4 also discusses concerns when considering sequenced treatment systems (i.e., treatment trains), which generally couple one or more downgradient remedies, such as MNA or enhanced biological treatment, with the PRB.

Section 5 provides an overview of lessons learned from previous PRB deployments and detailed evaluations of iron-based PRB systems regarding long-term performance assessment. The section also summarizes key evaluation methods and findings regarding assessment of PRB hydraulic performance and longevity (i.e., long-term changes in reactivity and permeability).

Section 6 discusses regulatory permitting considerations associated with PRB design, construction, and closure. It also describes sampling and monitoring requirements for purposes of compliance with regulatory standards, PRB performance (hydraulic capture and contaminant residence time), and PRB longevity (long-term changes in reactivity).

Section 7 summarizes alternative uses of iron-based reactive media to treat source zones. This alternative “source zone” approach represents a shift away from the traditional definition of a PRB, although at its most basic level, this new approach still relies on direct, passive contact between contaminants and the reactive material.

Sections 8–10 discuss health and safety concerns associated with PRB deployments, construction methods, and chemical agents, as well as methods for assessing costs (capital and O&M) and issues of concern affecting these costs.

Sections 11 and 12 contain conclusions, recommendations, and references.

1.5 Previous PRB Documents

Several governmental agencies and organizations have been involved in PRB technology since the middle to late 1990s. Key among these groups are USEPA; DoD, including the Departments of the Navy, Army, and Air Force; DOE; the Federal Remediation Technologies Roundtable; and ITRC. In the past few years, these groups have sponsored the development of several guidance documents focusing on deployment of PRB technology, regulatory issues of concern, and performance and longevity of PRB systems. These key technical and regulatory documents are listed below and in Section 12. Readers are encouraged to refer to the ITRC Web site (www.itrcweb.org) or Appendix H to order copies of this or previous PRB Team documents.

- *Regulatory Guidance for Permeable Barrier Walls Designed to Remediate Chlorinated Solvents,* 2nd ed., PBW-1, Interstate Technology & Regulatory Council (ITRC 1999a).

- *Design Guidance for Application of Permeable Reactive Barriers for Groundwater Remediation*, PRB-2, Interstate Technology & Regulatory Council with the Air Force Research Laboratory (ITRC 2000).

- *Regulatory Guidance for Permeable Barrier Designed to Remediate Inorganic and Radionuclide Contamination*, PRB-3, Interstate Technology & Regulatory Council (ITRC 1999b).

- *Evaluation of Permeable Reactive Barrier Performance*, Revised, EPA/542/R/04/004, Federal Remediation Technologies Roundtable (Tri-Agency Permeable Barrier Initiative 2002).

- *Permeable Reactive Barrier Technologies for Contaminant Remediation*, EPA/600/R-98/125, Remedial Technology Development Forum (USEPA 1998).

- *Capstone Report on the Application, Monitoring, and Performance of Permeable Reactive Barriers for Ground-Water Remediation: Volume 1—Performance Evaluation at Two Sites*, EPA/600/R-03/045a, U.S. Environmental Protection Agency, Office of Research and Development (Wilkin and 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 Groundwater Sampling*, EPA/600/R-03/045b, U.S. Environmental Protection Agency, Office of Research and Development (Paul et al. 2003).

- *Final Design Guidance for Application of Permeable Reactive Barriers for Groundwater Remediation*, Battelle for Air Force Research Laboratory (Gavaskar et al. 2000a).

2. TREATMENT PROCESSES AND REACTIVE MEDIA

To date, zero-valent iron is the most widely used reactive material in PRBs owing to its success in treating common organic and inorganic contaminants in groundwater, such as chlorinated volatile organic compounds (VOCs), petroleum hydrocarbons, chromium, and arsenic. Other iron- and non-iron-based materials are also being used in pilot-scale and full-scale PRB applications or are being evaluated in laboratory or bench-scale demonstration projects because of their ability to treat additional contaminants, such as radionuclides, heavy metals, and impacts from acid mine drainage (AMD). The variety of treatment materials available for use in PRB applications is an important advancement because it allows for customization of PRB designs based on site-specific conditions. Examples include the use of a unique treatment material to target a specific contaminant or the use of multiple treatment materials in a sequenced-PRB design to target several different types of contaminants. This section summarizes the current state of the most common iron- and non-iron-based reactive media being used or demonstrated for use in PRB applications.

2.1 Treatment Processes

The process of treating contaminants with reactive media in a PRB generally can be described by one or more processes. Basic process categories include the following:

- chemical dehalogenation,
- pH control,
- reduction-oxidation,
- sorption, and
- biological enhancements.

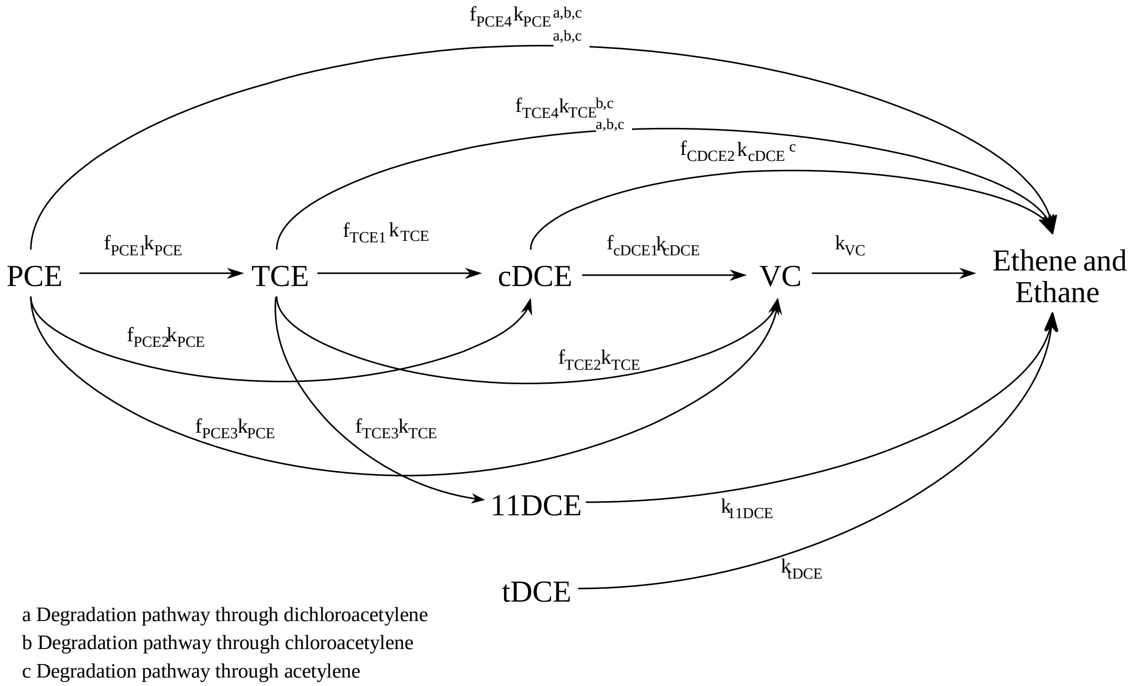
Brief descriptions of these processes are provided in the following paragraphs. As mentioned, the treatment of contaminants with many reactive materials involves a combination of processes.

2.1.1 Chemical Dehalogenation

In the presence of granular iron, dissolved chlorinated hydrocarbons (chlorinated solvents) degrade to nontoxic end products. This abiotic process involves corrosion (oxidation) of ZVI and reduction of dissolved chlorinated hydrocarbons. The process induces highly reducing conditions that cause substitution of chlorine atoms by hydrogen in the structure of chlorinated hydrocarbons. Two primary pathways have been reported for dechlorination of chlorinated ethenes in iron systems (Figure 2-1): β-elimination and hydrogenolysis (Eykholt 1998, Arnold and Roberts 1999). 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). The hydrogenolysis pathway is a slower reaction in which lesser-chlorinated intermediates are

There have been over 600 publications on the chemistry of contaminant reduction with zero-valent metal. The Center for Groundwater Research at the OGI School of Science and Engineering maintains a searchable database of these publications that can be accessed at http://cgr.ese.ogi.edu/iron/. This database contains information on reaction pathways for a variety of chlorinated ethenes, methanes, and ethanes.

produced and subsequently degraded. For example, during degradation of TCE, the intermediate products, *cis*-dichloroethene (cDCE) and vinyl chloride (VC), are produced in the hydrogenolysis pathway and are slower to degrade than TCE itself. Chlorinated hydrocarbon degradation observed in groundwater in contact with granular iron is typically described using first-order kinetics. The products of the dechlorination reaction that occur when in contact with granular iron are chloride (Cl^-), iron (Fe^{2+}), nonchlorinated (or less-chlorinated) hydrocarbons, and hydrogen. When measurable, chloride mass balances close to 100% are typically obtained in column experiments with granular iron and contaminated groundwaters.



a Degradation pathway through dichloroacetylene
b Degradation pathway through chloroacetylene
c Degradation pathway through acetylene

where
f = mole fraction,
k = first-order rate constant.

Figure 2-1. Reaction pathways for degradation of chlorinated ethenes with granular iron (adapted from Arnold and Roberts 1999).

Table 2-1 lists the more common chlorinated compounds that can be treated with iron. It is important to note that relatively common contaminants—such as 1,2-dichloroethane (1,2-DCA, also known as “ethylene dichloride” [EDC]), dichloromethane (DCM, also known as “methylene chloride”), and certain chlorinated aromatics—may not be degraded by most conventional iron materials.

2.1.2 pH Control

The effect of pH (or the log of hydrogen ion activity) on the mobility of many organic and inorganic constituents demonstrates that a strategy involving pH control can be an effective groundwater remediation remedy. Long applied with respect to certain critical water contamination projects (e.g., acid mine drainage), pH control processes can be applied through the PRB concept. The solubility of metals is dependent on pH, reduction potential, aqueous concentrations of reacting species, and reaction kinetics. The creation of stability diagrams (such as the Pourbaix diagram, Figure 2-2) is an excellent example of our reliance and understanding of the effect of pH on the fate of many constituents. It is well known that 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 (Figure 2-3). Organic constituents also may be less stable under various degrees of pH conditioning of the aqueous solution although this effect is highly dependent on the reduction-oxidation character of the aqueous system.

Table 2-1. Chlorinated compounds abiotically reduced by iron

Common name	Common abbreviation	Other pseudonyms	CAS number
Ethenes			
Tetrachloroethene	PCE	Perchloroethylene	127-18-4
Trichloroethene	TCE	Ethylene trichloride	79-01-6
cis-1,2-Dichloroethene	*cis*-1,2-DCE	*cis*-1,2-Dichloroethylene	540-59-0
trans-1,2-Dichloroethene	*trans*-1,2-DCE		540-59-0
1,1-Dichloroethene	1,1-DCE	Vinylidene chloride	75-35-4
Vinyl chloride	VC	Chloroethene	75-01-4
Ethanes			
Hexachloroethane	HCA	Carbon hexachloride	67-72-1
1,1,1,2-Tetrachloroethane	1,1,1,2-TeCA		630-20-6
1,1,2,2-Tetrachloroethane	1,1,2,2-TeCA	Acetylene tetrachloride	79-34-5
1,1,1-Trichloroethane	1,1,1-TCA	Methyl chloroform	71-55-6
1,1,2-Trichloroethane	1,1,2-TCA	Vinyl trichloride	79-00-5
1,1-Dichloroethane	1,1-DCA		75-34-3
1,2-Dibromoethane	1,2-DBA	Ethylene dibromide	106-93-4
Methanes			
Tetrachloromethane	CT, PCM	Carbon tetrachloride	56-23-5
Trichloromethane	TCM	Chloroform	67-66-3
Tribromomethane	TBM	Bromoform	75-25-2
Propanes			
1,2,3-Trichloropropane	1,2,3-TCP	Allyl trichloride	96-18-4
1,2-Dichloropropane	1,2-DCP	Propylene dichloride	78-87-5
Other Chlorinated			
N-Nitrosodimethylamine	NDMA	Dimethylnitrosamine	62-75-9
Dibromochloropropane	DBCP		96-12-8
Lindane		Benzene hexachloride	58-89-9
1,1,2-Trichlorotrifluoroethane		Freon 113	76-13-1
Trichlorofluoromethane		Freon 11	75-69-4

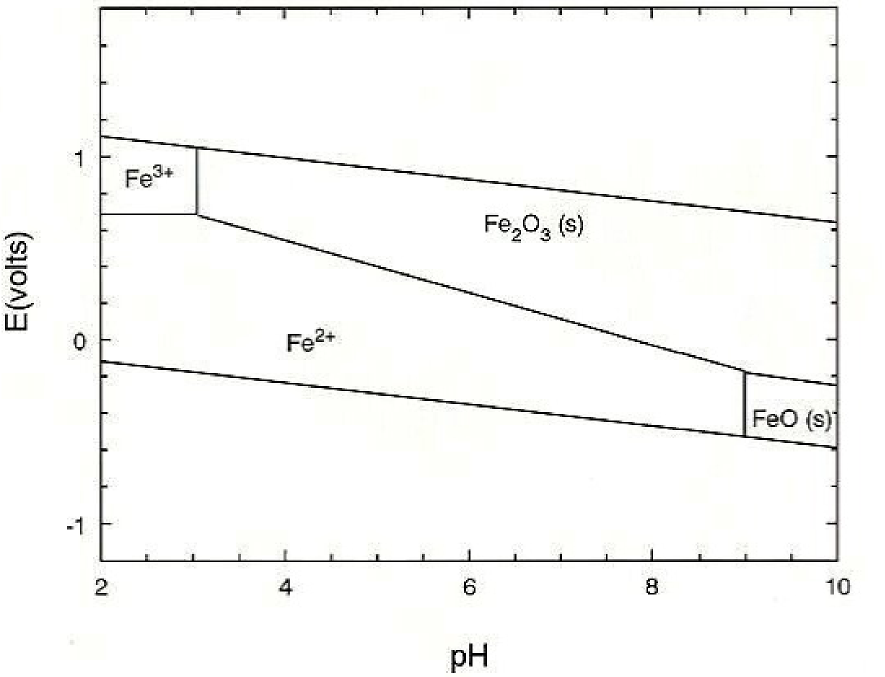


Figure 2-2. Simplified Pourbaix diagram for some naturally occurring forms of iron.

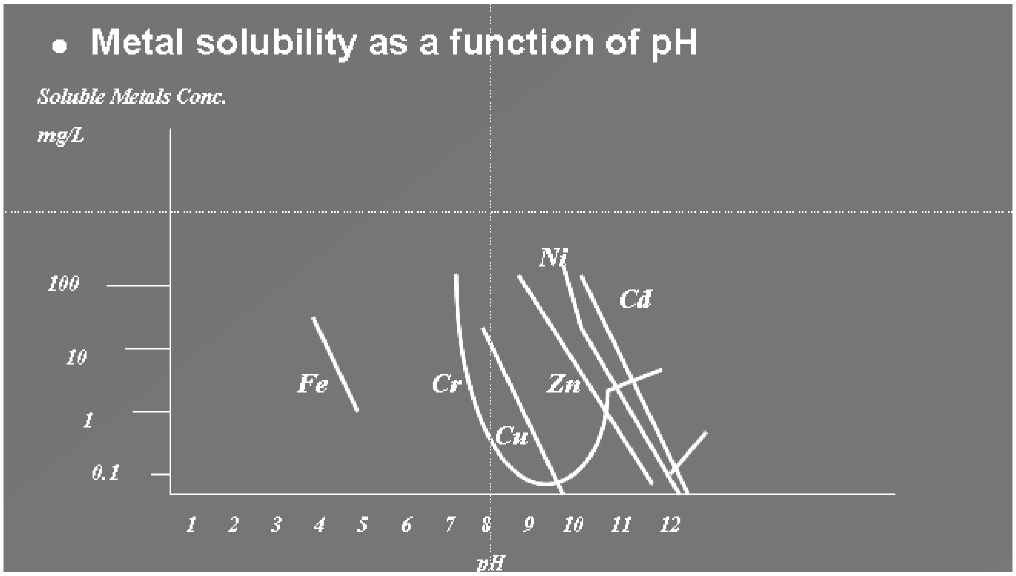


Figure 2-3. Generalized solubility relationship of common metals as a function of pH.

The direct and dramatic effect of a pH shift on carbonate equilibria has been well documented with respect to the use of granular iron for PRBs. As described earlier, the production of the hydroxyl radical that leads to higher pH conditions during the corrosion reaction between iron and water results in the precipitation of certain carbonate and other compounds within the iron system and thus can lead to porosity loss. However, for a non-iron-based material, the inclusion of small amounts of iron also can lead to pH conditioning and some mineralization due to the carbonate equilibria effects. For certain PRB designs, such as the inclusion of small amounts of iron in an upgradient pea gravel or pretreatment zone to a PRB, the effect can be to protect the primary iron-based treatment core from intense mineralization. Examples of materials that have been applied in PRBs to control contaminant migration through direct pH control include limestone or lime-based materials, compost, and various organic carbon materials.

2.1.3 Reduction-Oxidation

Several elements, including carbon, nitrogen, oxygen, sulfur, iron, and manganese (Stumm and Morgan 1996) are key constituents involved in reduction-oxidation (redox, or Eh) reactions. Presence of these elements in a given chemical or at sufficient quantities in an aqueous system ensures that redox-sensitive reactions will influence the fate of a target contaminant. Microbiologically mediated redox reactions, which predominate in natural waters, are key to the fate of common industrial organic contaminants, as well as to the fate of many inorganic contaminants of concern (COCs). Modifying redox reactions, through the modification of the state of the redox-sensitive elements and in conjunction with modifications to pH conditions, can be effective goals for PRB-based treatment technologies. Use of tools such as Pourbaix diagrams, or Eh-pH diagrams, to evaluate groundwater systems for the anticipated concentration of various aqueous species under certain geochemical conditions is important in assessing which treatment materials might be effective for a given suite of chemicals.

> Note that the use of Eh (which represents the redox potential on the hydrogen scale) should not be interchanged with ORP (oxidation-reduction potential) with respect to the numerical value associated with each. ORP represents values of redox potential measurements for aqueous solutions using nonhydrogen electrodes (e.g., the silver-silver chloride electrode). Measured values of ORP should be adjusted to equivalent Eh values by the numerical value (typically in millivolts) equal to the difference in the two scales. For additional discussion on the use and measurement of redox parameters for natural waters and in conjunction with assessing remediation systems, see USEPA 2002.

Redox reactions govern the carbon cycle and thus the state of many organic compounds (many of which are initially synthesized through microbial catalysis). Thermodynamic stability does not exist in natural waters, although the rate of decomposition (or reduction and precipitation) of certain groundwater contaminants through instability can be enhanced by the inclusion of various treatment materials in the aqueous system.

A relatively new class of redox-enhanced PRBs is based on the ability to manipulate the redox condition of natural waters. This so-called “in situ redox manipulation” process has gained some ground in that, by directing a strong reductant (or oxidant) into a natural groundwater system, the redox condition of, for example, iron-based species can be modified to create persistent reactions that cause instability of target contaminants. A better known use of this concept has been described in several publications (e.g., Fruchter et al. 1997) as involving the injection of sodium dithionite ($Na_2S_4O_2$) to reduce hexavalent chromium (chromate) to trivalent chromium and to reduce “structural” Fe(III) to reduced Fe(II) for electron-reduction reactions of organic compounds such as chlorinated ethenes.

Examples of materials that have been applied as PRB materials to promote remediation and control contaminant migration through reduction-oxidation control (in addition to iron) include compost, sodium dithionite, hydrogen sulfide, acetate, and various carbohydrates.

2.1.4 Sorption

Materials that promote sorption-type reactions (including ion exchange) are perhaps the best known in the groundwater remediation industry. Though not always associated with PRBs, sorption control has been used to limit the migration of contaminants or remove target chemicals from a groundwater system (in situ or ex situ). Materials such as granular activated carbon (GAC) have chiefly been used for aboveground treatment systems; however, GAC has found limited use in a PRB setting either as the sole treatment material or in combination with a second material such as iron (Kober et al. 2001). The use of zeolites to promote ion-exchange reactions also has received attention and has successfully been implemented to reduce the concentration of radioactive strontium-90 from groundwater systems (Lee 2002, Warner et al. 2004b). Surfactant-modified zeolites had been used also to promote reduction of certain metals as well as organic compounds (Bowman 1996). Various clay minerals and oxyhydroxides may also be effective as PRB materials. The spent material from bauxite milling, as a clay-type material, has been tested as a treatment for metal-impacted surface and groundwater. In addition, waste green sands have been shown in laboratory tests to be an effective reactive media for groundwater contaminated with TCE (Lee, Benson, and Eykholt 2004).

Keys to the use of effective sorption techniques in PRBs include selecting materials that are relatively hydrophobic, insoluble, and easy to apply. Materials that readily biodegrade are not likely to have great longevity, and those that absorb water may not promote the surface-based reactions important to binding the target compounds to the reactive surface sites on the treatment material. Also, the effects of potential desorption, or reversed ion-exchange, should be considered for all potential uses of these materials. Thus, frequent replacement of the material may be required, and easy access for such work must be considered in the engineered design of the sorption-based PRB.

Examples of materials that have been applied as PRB materials to control contaminant migration through direct sorption control, include the following:

- granular activated carbon,
- bone char,
- phosphatic compounds (including apatite and enhanced apatite),
- zeolites,
- coal,
- peat,
- synthetic resins,
- solid carbon sources (e.g., compost, peat, sawdust, wood chips, wheat straw, and cheese whey),
- recycled carbon-rich materials (e.g., foundry byproducts, tire chips, and paper sludges), and
- waste green sands.

2.1.5 Biological Enhancements

Many of the primary chemicals of concern, including VOCs, inorganic constituents, and radioactive constituents, can be addressed through biological reactions promoted via a PRB. The use of the PRB concept for promoting bioremediation or biologically enhanced treatment of target compounds was described in the 1998 RTDF document on PRB technologies (Remedial Technology Development Forum and USEPA Office of Research and Development 1998) and continues to be a recognized method for treatment of a plume of chemically affected groundwater. Biological processes, while generally considered to involve multiple steps to reduce or destroy a target compound (as compared to “one-step” direct chemical oxidation or reduction), can be an effective treatment strategy within the PRB environment. As with the abiotic PRB methods, biological reactions within a “constructed” treatment zone can be relatively well established, monitored, and evaluated for performance. Sustained conditioning of the aqueous system generally is important for biological processes to take effect to the level that the intended treatment of a given suite of chemicals can be promoted. A benefit of biological PRB systems over most abiotic systems is that the treatment process might extend beyond (upgradient and downgradient of) the constructed treatment zone. Another benefit is the ability of a single system to treat multiple contaminants with different chemical characteristics (i.e., inorganics, organics, metals, and radionuclides). Several examples of bioremediation through the PRB concept include early studies by Robertson and Cherry (1995) for denitrification and Benner, Blowes, and Ptacek (1997) for sulfate reduction. More recently, Wilson, Mackay, and Scow (2002); Mackay et al. (2001, 2004); and Johnson, Bruce, and Miller (2003) have published documents discussing the aerobic remediation of MTBE, and Craig (2004) presents the biological treatment of a perchlorate plume.

Examples of materials that have been applied as PRB materials to promote bioremediation enhancement (but not including bioaugmentation or direct application of microbes) include the following:

- solid oxygen-releasing and hydrogen-releasing compounds,
- oxygen source and hydrogen source in gas emitters,
- solid and liquid carbon sources (e.g., sawdust, wheat straw, cheese whey, vanilla, sucrose, and various other carbohydrates),
- compost (various compositions), and
- pecan shells, granular organic carbon (as an organic substrate).

2.2 Treatment Materials

The basic objective of any PRB-treatment material is to either directly destroy or immobilize the target chemical(s) in groundwater or to condition the groundwater system to promote the destruction or immobilization of the target chemical(s). This simple concept can be expanded to the realization that any material placed in the groundwater environment influences the geochemical and biological characteristics of the aqueous system. A number of different solid materials may be used as effective PRB treatment media.

Table 2-2 is a partial list of materials that have been used as components within PRB systems. Each of the materials, including iron, which is shown for reference, conditions the aqueous system to either directly reduce the presence or mobility of the target chemical or promote its destruction or immobilization by other chemical or biological changes to the aqueous system. The observation that most of the materials listed are natural materials (e.g., not manufactured or enhanced by human intervention) is encouraging as PRBs can be promoted as remedies that take advantage of natural conditioning processes. The fact that most of the materials are well known to both the scientific community and the regulatory and public stakeholder community is also beneficial for receiving public approval for their use.

Table 2-2. Examples of reactive materials used in PRBs

Treatment material categories	Example materials	Constituents treated (examples, not comprehensive)
Metal-enhanced reductive dechlorination for organic compounds	Zero-valent metals (Fe)	Chlorinated ethenes, ethanes, methanes, and propanes; chlorinated pesticides, Freons, nitrobenzene
Metal-enhanced reduction for metal contaminants	Zero-valent metals (Fe), basic oxygen furnace slag, ferric oxides	Cr, U, As, Tc, Pb, Cd, Mo, U, Hg, P, Se, Ni
Sorption and ion-exchange	Zero-valent iron, granular activated carbon, apatite (and related materials), bone char, zeolites, peat, humate	Chlorinated solvents (some), BTEX, Sr-90, Tc-99, U, Mo
pH control	Limestone, zero-valent iron	Cr, Mo, U, acidic water
In situ redox manipulation	Sodium dithionite, calcium polysulfide	Cr, chlorinated ethenes
Enhancements for bioremediation (including carbon, oxygen, and hydrogen sources)	(Includes solid, liquid, and gaseous sources) Oxygen-release compounds, hydrogen-release compounds, carbohydrates, lactate, zero-valent iron, compost, peat, sawdust, acetate, humate	Chlorinated ethenes and ethanes, nitrate, sulfate, perchlorate, Cr, MTBE, polyaromatic hydrocarbons

2.3 Iron-Based PRBs for Chlorinated Solvents

To date, granular iron is the most frequently used reactive media for the in situ remediation of groundwater plumes containing chlorinated organic compounds in a PRB. Currently, there have been 83 full-scale and 37 pilot-scale installations of PRBs worldwide using granular iron to treat chlorinated organic compounds.

The granular iron used in most PRB applications to date comprises a mixture of ductile and cast iron cuttings and borings that are obtained by manufacturers from a number of primary industries that use iron in the production of automotive and related industrial parts. To create the end product used in PRB applications, a number of these “feedstocks” are mixed together, put through a rotary kiln at several hundred degrees Fahrenheit in proprietary gas mixtures, cooled by a variety of methods, milled, and sorted to a specific grain size range (Landis et al. 2001).

For PRBs constructed using excavation-based methods where the iron is placed directly into an excavation, the grain size range that is typically used is 2.0–0.25 mm (–8 to +50 mesh U.S. standard sieve size), which has a hydraulic conductivity of about 5×10^{-2} cm/sec (142 feet/day). A grain size range of 1.0–0.17 mm (–18 to +84 mesh U.S. standard sieve size) is used with the azimuth-controlled vertical hydraulic fracturing technology, where the iron is suspended in a biodegradable gel and injected into the subsurface. Iron with a grain size of 0.59–0.21 mm (–30 to +70 U.S. standard sieve size) and less has been used in pilot-scale trials involving high-pressure jetting. Liquid atomized injection and pneumatic fracturing typically uses a fine iron powder, where the grain size range is 0.04–0.08 mm (+140 to –325 mesh U.S. standard sieve size).

A number of other types of metallic iron materials have been used in PRBs, including the following:

- iron prepared by high-temperature direct reduction of iron ore, including material referred to as “sponge iron”;
- iron foams and pellets prepared through a high-temperature process combining aluminosilicates and iron;
- iron particulates and powders prepared using water-atomized, remelted iron scrap materials; and
- granular combinations of iron and solid degradable carbon materials.

These materials exhibit varying degrees of reactivity relative to the standard cast iron particles, although none have the multiyear track record of performance. However, because of their particular physical characteristics and their ability to degrade compounds that cannot be degraded by iron alone, they may be appropriate for use in some situations. Some of these materials can be produced with a codex (food-grade) certification.

2.3.1 Chemical Considerations

Recent research has highlighted the particular importance of the following geochemical parameters specifically related to the use of iron for treatment of chlorinated solvents:

- *Nitrate*—Nitrate has been shown to negatively impact reaction rates by progressively passivating iron surfaces. Ritter, Odziemkowski, and Gillham (2002) found that redox potentials were more positive in the presence of nitrate than in similar water containing no nitrate. This positive shift in potential resulted in a system on the thermodynamic equilibrium line between hematite and maghemite (Fe_2O_3) and magnetite (Fe_3O_4). Thus, all the maghemite was removed, but a thin layer of hematite persisted over a majority of the iron surface. Furthermore, any Fe^{2+} produced would result in the formation of maghemite and/or goethite (α-FeOOH), which is also stable at these redox potentials and pH values. Goethite and maghemite are known to inhibit iron corrosion by their protective properties (i.e., passivation of the iron surface). Thus, it is believed that, as these minerals form, they reduce the surface area available for nitrate and VOC reduction, resulting in advancing nitrate and VOC profiles with time.

- *Dissolved organic carbon*—Certain types of dissolved organic carbon (DOC) have been shown to coat reactive sites on the iron, rendering it unreactive.

- *Metals*—High concentrations of certain dissolved metals, many of which will be COCs, will also be reduced and compete for the reactive sites on the iron. These metals include chromium, uranium, arsenic, technetium, lead, and cadmium.

- *Silica*—Although the results are not conclusive, research suggests that silica may have an effect on PRB reaction rates similar to that of nitrate.

The presence of these constituents does not mean a PRB is infeasible at a site. However, if a high mass flux of these constituents is anticipated through the PRB (i.e., if they are present at high concentrations in relatively high groundwater velocity environment), they could significantly affect the PRB's long-term performance. VOC reaction rates in granular iron have shown to be relatively robust in the presence of elevated carbonate and sulfate concentrations, but if the concentrations of these constituents are in the 100s–1000s-mg/L range, the long-term performance of the PRB could be significantly affected due to the precipitation of carbonate and sulfide minerals.

2.3.2 Use

The first pilot-scale iron PRB for treatment of chlorinated compounds with iron was installed in 1991 at Canadian Forces Base, Borden, Ontario. The first commercial application was installed in Sunnyvale, California in November 1994. Since that time, the technology has been accepted in the marketplace and has a greater than 10-year track record of successful field performance. In June 2002, USEPA stated, "PRBs are no longer perceived as an innovative remediation technology but are rapidly maturing and may be considered as a standard remediation technology" (Powell, Powell, and Puls 2002).

2.4 Iron-Based PRBs for Treatment of Metals in Groundwater

The strong geochemical reduction promoted by zero-valent iron in an aqueous solution removes metals and metalloids in the system primarily through reductive precipitation on the ZVI surfaces, or as coprecipitates with the iron oxyhydroxides that form on the ZVI surfaces. Reducible metals including chromium and uranium can be treated with a PRB. For example, Powell et al. (1995); Pratt, Blowes, and Ptacek (1997); Blowes, Ptacek, and Jambor (1997); Blowes and Mayer (1999); and Blowes et al. (1999a, b) investigated the reduction of Cr(VI), precipitation of Cr(III) hydroxide, and the coprecipitation of Cr(III) with iron oxyhydroxides by ZVI in the laboratory and in a full-scale field application of PRB technology in Elizabeth City, North Carolina in 1996. Sorption on the iron oxyhydroxide material could also provide attenuation of the metals and metalloids (including arsenic) in groundwater. The grain-surface removal mechanisms do suggest that ZVI has a finite treatment capacity for metals and metalloids.

A PRB system was installed in June 1999 to treat the groundwater at a site in Monticello Canyon, Utah, where groundwater has been contaminated by seepage from uranium mill tailings. Although the mill wastes were removed from the site in 1999, elevated concentrations of uranium, arsenic, selenium, molybdenum, vanadium, manganese, and nitrate continue to migrate through an alluvial valley (Morrison et al. 2002, Morrison 2003). Infiltration of precipitation was responsible for leaching the metals, metalloids, and nitrate from the mill wastes. The valley is underlain by a shale aquitard at a depth of 4.5–6 m below ground surface (bgs). The PRB is a funnel-and-gate system that includes two low-permeability slurry walls to direct the flow of contaminated groundwater through a central permeable treatment zone or gate. The treatment gate is 30 m long and 2.4 m thick in the direction of groundwater flow and extends to the base of the aquifer. The treatment gate has three components: an upgradient gravel pack 0.6 m thick containing 13% ZVI, a central zone of ZVI 1.2 m thick, and a downgradient gravel pack containing 10% ZVI 0.6 m thick. The treatment gate was installed in temporary trench excavation supported by steel sheet piling. Groundwater velocity in the treatment gate was estimated to be 5.7 m/day using flow sensors and tracers (Morrison et al. 2002). Thus, residence time of groundwater in the 100% zero-valent iron portion of the PRB is approximately 5 hours. On the basis of solid-phase mineral accumulations in the PRB, Morrison (2003) suggested that groundwater flux may actually be about 10% of that determined by flow sensors and tracer tests.

Using influent data from five wells 1 m upgradient of the treatment zone, and effluent data from five wells in the downgradient portion of the treatment zone, Morrison et al. (2002) demonstrated excellent treatment of all contaminants except manganese within the PRB. Uranium decreased from 396 mg/L in the influent to less than 0.24 mg/L in the effluent from the PRB; arsenic decreased from 10.3 mg/L to less than 0.2 mg/L; selenium decreased from 18.2 mg/L to 0.1 mg/L; molybdenum decreased from 62.8 mg/L to 17.5 mg/L; vanadium decreased from 395 mg/L to 1.2 mg/L; nitrate decreased from 60.7 mg/L to less than 0.065 mg/L; and manganese decreased from 308 mg/L to 177 mg/L. Consistent with observations of other ZVI PRB systems, the pH of the groundwater within the ZVI increased from a maximum of 6.8 in the influent to 10. Although nitrate concentrations were observed to decrease, the form of treatment was not clear. It is possible that the nitrate was reduced to ammonia abiotically or that some microbially mediated denitrification within the ZVI may have occurred.

Morrison (2003) indicated that the concentration of uranium exiting the upgradient gravel and ZVI zone increased from less than 0.2 mg/L at early time to 185 mg/L after 2.7 years. This increase reflects consumption of available contaminant removal sites on the ZVI but may also reflect loss of reactivity as a consequence of the precipitation of secondary carbonate minerals on the grain surface. Additional precipitation of carbonate material had occurred within the ZVI zone after 2.7 years of operation, but the evidence suggests excellent treatment of uranium and vanadium continued to occur. Furthermore, Morrison (2003) could not detect any decrease in the hydraulic conductivity of the PRB as a consequence of the formation of the precipitates. This work is consistent with evaluations of the 100% ZVI PRB in Elizabeth City.

An example of arsenic removal by ZVI includes a gold mine in northern Ontario, for which column tests were performed. The columns operated for more than 30 months and continued to function very effectively. In the column containing the mixture, arsenic was detected in the pore water within 10 cm of the influent end only and was nondetectable beyond this distance. The flow rate in this column was less than 0.5 pore volumes per day, so the water resided in the 40-cm column for more than two days. The influent concentration of arsenic exceeded 10 mg/L. The reactive materials in the columns exhibited excellent capacity for removal of arsenic. The field-scale evaluation of an in situ PRB was initiated in 2002 in a test cell through which flow of tailings-impacted groundwater could be controlled (Bain et al. 2002).

Blowes and Mayer (1999), on the basis of monitoring and numerical modeling, evaluated the potential influence of secondary precipitates on long-term PRB performance. They suggested that the precipitation of secondary carbonate and sulfide minerals could result in the reduction of the porosity from the initial 0.5 to approximately 0.4 after 20 years of operation, but that hydraulic performance of the PRB will not be compromised with the loss of porosity. Wilkin, Puls, and Sewell (2002) noted some evolution of Eh (slightly less reducing) and pH (slightly lower) conditions as a consequence of secondary carbonate precipitation within the ZVI PRB after five years of operation. No loss of hydraulic function was measurable, and treatment of Cr(VI) was excellent. After five years, with influent concentrations of Cr(VI) 5–10 mg/L and a groundwater velocity of approximately 0.1 m/day, Cr(VI) remained nondetectable 0.1 m into the ZVI zone. As indicated by the investigations at Monticello and Elizabeth City, secondary precipitate formation may limit long-term performance of ZVI PRBs in groundwater with high total dissolved solids (TDS) or alkalinity.

2.5 Non-Iron-Based PRBs

There are numerous types of materials that may provide treatment for contaminated groundwater. Materials that provide sorption, direct reduction, biological enhancements, ion exchange, and other beneficial processes are all worth consideration. Reasons why materials other than iron may be more appropriate for use within the PRB include the following:

- greater ability of the non-iron treatment material to treat the target chemical(s) to water quality objectives and
- lower cost of the alternative treatment material relative to iron for the specific use.

All potential treatment materials must be fully assessed for their ability to provide the intended treatment including longevity and constructability as well as for their potential to negatively impact the groundwater system. For example, some treatment materials can cause geochemical changes in groundwater that lead to changes in the concentration and mobility of naturally occurring metals and other chemical compounds. One such change can occur with the use of ZVI, which has been demonstrated to cause an increase in pH and chloride concentration and a decrease in Eh, TDS, alkalinity, dissolved oxygen (DO), calcium, sulfate, and other naturally occurring inorganics. Other treatment materials, particularly those used to enhance aerobic/anaerobic biological activity or to directly manipulate redox conditions (e.g., calcium polysulfide, sodium dithionite, etc.) can affect the prevalence and/or mobility of nitrate and sulfate compounds and/or metals such as iron, manganese, chromium, copper, and arsenic. Furthermore, in biological treatment remedies it is these changes in nitrate, sulfate, iron, or manganese compounds that provide a line of evidence for the breakdown process. Although these changes in groundwater geochemistry are typically buffered by natural aquifer conditions further downgradient, this will occur to varying degrees with different reactive materials and different site conditions. Additionally, sufficient aquifer buffering capacity may not exist between the PRB and a downgradient receptor. Therefore, geochemical changes and their effects on chemical and contaminant occurrence and mobilization should be evaluated whenever alternative reactive materials are proposed for use in a PRB application.

The following paragraphs provide examples of the use of non-iron-based materials for various PRB-based remedies.

2.5.1 Organic Media for Solvents

The use of several types of organic materials for treatment of groundwater affected by various solvent-related contaminants also have been investigated, and in some cases, have been applied as PRB treatment materials. These materials include activated charcoal (GAC), cottonseed meal, peat moss, lignite, humite, and compost, for example (see Benner et al. 1999; Blowes, Ptacek, and Jambor 1997). Several field deployments have resulted from these studies as well (for example, Goldstein et al. 2000; Naftz et al. 2000; Wickramanayake, Gavaskar, and Chen 2000).

The use of organic material in PRBs to treat groundwater affected by solvent-related compounds primarily is to promote or enhance biologically mediated destruction of the target analytes. The use of bioremediation to promote in situ treatment is an established method using a variety of solutions and materials placed in the subsurface. An implementation concept for bioremediation includes placing the treatment material within a PRB-type of system, whereby the treatment can be controlled in an engineered type of structure or design and the monitoring can be focused.

An attempt to remediate perchlorate-affected groundwater using a PRB approach also has been attempted (Craig 2004). The U.S. Navy has been evaluating a PRB composed of a mixture of gravel and carbon material (wood chips) in an approximately 7:1 ratio at the Naval Weapons Industrial Reserve Plant McGregor near Waco, Texas, where groundwater is contaminated by perchlorate at concentrations greater than 10 mg/L. Various forms of wood chips were tested along with the addition of acetate and soaking with soybean oil or a soybean oil/mushroom compost mixture. The addition of carbon sources acting as electron donors changed groundwater conditions from aerobic to anaerobic. Through this process, indigenous bacteria were enabled to use perchlorate (ion) as respiratory oxygen until it was depleted and only (nontoxic) chloride remained.

2.5.2 Limestone for Metals

Limestone, lime, or other calcium carbonate or hydroxide materials can be an effective material for use within a PRB system, if the goal of the PRB is to modify pH conditions for the purpose of reducing the solubility of certain metals or for conditioning the hydrochemical system to assist with other treatment processes, including bioremediation. The use of a limestone-type material for reducing the effects of AMD, for example, has been applied for decades, though mostly for aboveground treatment through channels, wetlands, or other holding basins for AMD-impacted water.

Highly acidic and metal-rich water from mine drainage conditions typically occurs from the weathering of iron- and sulfur-rich minerals such as pyrite, FeS_2. The overall reaction leading to the production of sulfuric acid and acidity generally are indicated as

$$4FeS_2 + 15O_2 + 14H_20 \rightarrow 4Fe(OH_3) + 8H_2SO_4 \text{ , or}$$

$$2FeS_2(s) + 7O_2 + 2H_2O \rightarrow 2Fe_2^{+} + 4SO_4^{2-} + 4H^{+} \text{ .}$$

Inherent in this reaction are several weathering reactions where the oxidation of pyrite by oxygen at the surface leads to the creation of sulfate and ferrous iron and the generation of acidity. Belowground, this oxidation generally does not occur. However, where pyrite-affected groundwater does discharge, the oxidation of the iron does lead to further acid production and the generation of iron hydroxides:

$$Fe^{2+} + 1/4O_2 + 5/2H_2O \rightarrow Fe(OH)_3(s) + 2H^{+} \text{ .}$$

These reactions continue until pyrite is depleted; however, the subsequent weathering solutions are extremely acidic. Acidic conditions lead to the increased solubility of several metals, which can create difficult environmental conditions for aqueous systems.

The reduction of pH to control the acid levels and thus reduce metal solubility can be created by passing mine drainage effluent through a limestone-based channel or system. Dissolution of the limestone ($CaCO_3$) increased the solution alkalinity to raise pH. The longevity of the limestone material may be lessened by the creation of ferric carbonate or hydroxide minerals during the process; thus, the design of the system must consider longevity and potential replacement of the treatment material. A type of limestone-based PRB for AMD effluent is referred to as an “anoxic limestone drain” (ALD). The Pennsylvania Department of Environmental Protection (www.dep.state.pa.us/dep), as well as Hedin and Watzlaf (1994), describes the use of ALDs and provides a general method to calculate the mass of limestone necessary to treat a given flow of AMD effluent.

Mixtures of limestone with other materials, including compost to stimulate microbial action and inert material such as sand to provide appropriate permeability, have been used in PRBs specifically for treating metal-enriched water. Such a system uses readily available and inexpensive materials that can be prepared into a treatment mixture with conventional construction equipment. Several metals, including iron, manganese, aluminum, nickel, chromium can be treated through microbial processes, with the limestone providing the appropriate geochemical conditioning and media to promote microbial growth.

A well-studied use of a limestone mixture with compost and sand is the Nickel Rim, Ontario, Canada site, which has been well published. See www.rtdf.org/public/permbarr for a complete description of the site.

2.5.3 Oxygen for Fuel Sites

The in situ remediation of dissolved constituents that have migrated to groundwater from the release of refined petroleum products has been implemented in the field at numerous sites. Most attempts involve methods to enhance aerobic microbiological processes that can degrade typical constituents from a fuel release, such as benzene, and somewhat more recalcitrant compounds, including MTBE. Many implementations rely on placing or injecting a substrate into the ground that promotes sustained aerobic conditions. The locations where these substrates are injected are typically based on the spatial occurrence of a plume and often are intended to cover all or most of the source area and plume core. Recent examples of this remedial process, however, have relied on the PRB concept to create a zone of aerobic biological activity across an existing or future flow path of the affected groundwater to limit further migration of the target constituents. The application of in situ bioremediation using a PRB design is commonly referred to as a "bio-barrier." Introduction of solid oxygen-releasing materials or direct delivery of oxygen gas into the subsurface is the preferred method for promoting sustainable aerobic conditions and treatment of fuel constituents such as BTEX and MTBE.

As with other PRB treatment materials, this concept also must be matched to the geochemical and hydrochemical conditions of the site. For example, the presence of great amounts of organic carbon in the subsurface (such as in near-shore or bog environments) likely result in zones of high oxygen consumption rates that render such a technology impractical as most of the oxygen would be consumed from natural conditions. Also, certain oxygen-containing treatment materials may be expended of their available oxygen prior to remedial goals' being met and thus would require replacement at frequent intervals. Such conditions are to be considered during the alternative selection and design phases.

The aerobic bio-barrier concept may be a good choice for reducing the migration of more recalcitrant compounds such as MTBE, which tend to produce longer plumes than those resulting from less recalcitrant compounds such as benzene. Examples of aerobic bio-barrier projects where the release of oxygen in a PRB-like design has been implemented include the Vandenburg Air Force Base (AFB) (Wilson, Mackay, and Scow 2002) and Port Hueneme (Johnson, Miller, and Bruce 2004), both located in California. Port Hueneme used an aerobic bio-barrier where 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 of MTBE. Results of the pilot indicate that MTBE concentrations are reduced by at least two orders of magnitude (from up to 400 μg/L upgradient of the barrier to <5 μg/L downgradient of the barrier). The transient production and subsequent destruction of *tert*-butyl alcohol (TBA) within the bio-barrier is further evidence of the success of the pilot implementation.

The key to the success of bio-barrier at Port Hueneme is the presence of microbes capable of degrading MTBE. Without the MTBE microbes in the subsurface, addition of oxygen alone would not create the biological conditions necessary to degrade the MTBE. Whether such microbes are naturally present at a site must be considered prior to engaging this technology at fuel release sites.

2.5.4 Amorphous Mineralogic Compounds

Several types of amorphous mineralogic compounds have been developed and applied for use as a PRB treatment media. These compounds, which are developed from natural sources but may be modified by surfactants or other surface enhancement, include amorphous ferric oxides and phosphatic compounds, primarily.

For example, the apatite mineral group (e.g., calcium phosphate minerals) has been shown to be effective both in removing dissolved metals from an aqueous solution and in transforming soil-bound metals to less soluble phases (Conca et al. 2002, Conca 1997). The effectiveness of apatite-type minerals as a reactive media for removing radioactive constituents from groundwater also has been demonstrated. An example is the treatment of a shallow multicontaminant plume of Pu-239, -240; Am-241, Sr-90, nitrate, and perchlorate in Mortandad Canyon, Los Alamos, New Mexico (Conca et al. 2002, Taylor et al. 2002). For this case nitrate, perchlorate, Pu, Am, and Sr-90 concentrations were reduced to below their maximum concentration limits (MCLs) and usually to below detection limits in these laboratory studies. The specific treatment material for this case was composed of a primarily amorphous form of a carbonated hydroxy-apatite embedded with nanocrystals of apatite; the reaction in the aqueous system allows for the precipitation of various phosphate phases of metals and radionuclides. The material is reported to exhibit large sorption coefficients for several radioactive metals, which makes it highly valuable for sequestering these constituents from an aqueous solution (e.g., K_d values of almost 100,000 for U and over 1,000,000 for Pu have been reported).

Amorophous ferric oxide (AFO) has been pilot-tested as a potential reactive treatment material at DOE’s Fry Canyon, Utah site. Though considered to be a potentially effective material, the AFO showed less effective performance than other materials, including ZVI and bone char (phosphatic constituent) for the treatment of dissolved uranium (Naftz et al. 2000, USEPA 2000b, see also http://ut.water.usgs.gov/fry/fry.html).

2.5.5 Zeolites for Radionuclides

Zeolites are natural aluminosilicate minerals that can have very high ion-exchange capacities and thus certain characteristics that make them potentially useful as treatment materials for use in a PRB. The typical mineral is a framework of stacked tetrahedra that form pores or channels where the ion exchange can occur. Because the mineral is anionic (negatively charged), it can be used to remove cations from an aqueous solution.

Several hundred zeolitic minerals exist; synthetic zeolitic minerals also have been produced for various industrial needs. For consideration in a PRB design, the zeolitic mineral clinoptilolite (solid solution composition $[(Ca, Mg, Na_2, K_2)(Al_2Si_{10}O_{24} \bullet 8H_2O)]$) has been researched by several groups (including those at Brookhaven National Laboratory and the State University of New York at Buffalo) and has been applied in pilot-test programs to assess the ability of the material to remove radioactive strontium (Sr-90) from a groundwater system (e.g., Lee et al. 1998, Warner et al. 2004b). Surface-modified zeolites also have been evaluated for their potential use as PRB materials in removing anionic constituents from groundwater (e.g., Bowman 1996).

An example pilot program evaluating the use of the zeolite clinoptilolite to remove Sr-90 from groundwater was initiated in 1999 at the West Valley Demonstration Project site in West Valley, New York. This was the first site in the United States that was intended to assess the use of the zeolite to promote ion exchange reactions capable of treating groundwater affected by Sr-90.

The pilot system was constructed using cofferdam-type methods (i.e., sheet piles, excavation, and backfilling) within the shallow (bottom depth of approximately 20–25 feet bgs) groundwater system that exists in lacustrine and outwash sediments lying above a low-permeability till. The geometry of the pilot permeable treatment wall was approximately 30 feet long by 7 feet wide by 25 feet deep; the upgradient face of the pilot PRB was composed of an approximately 1-foot-thick pea gravel section where a lateral drain assembly was installed for potential use as a development tool. Evaluation of hydrogeologic conditions in and around the pilot PRB indicated a complex hydrostratigraphy that likely controlled the migration of Sr-90 groundwater to specific depth intervals that may have become affected along portions the face of the pilot permeable treatment walls during construction.

Assessment of hydrochemical conditions in and around the pilot system appeared to indicate that the exchange of potassium for strontium is taking place within the PRB, suggesting that the ion exchange process was occurring. Assessment of hydraulic conditions using the results of field hydraulic testing and groundwater modeling also suggested that groundwater flow was occurring through enough of the pilot PRB to provide sufficient information for assessing the efficacy of the treatment method. The pilot test thus provided valuable information regarding design considerations and construction lessons learned, including the following:

- Most intrusive PRB construction methods alter subsurface hydraulic and chemical migration conditions; this disruption to the natural system should be considered during the PRB design phase, and performance expectations should consider this influence to the subsurface system.
- Because the installation of the PRB creates disequilibrium in the hydraulic and chemical migration systems, sufficient time should be allowed for the system to reequilibrate before performing a comprehensive performance evaluation.
- Chemical migration may be controlled by discrete zones or pathways in an aquifer system; the PRB design (pilot or full scale) should consider such pathways.
- The scale (i.e., size) of a PRB pilot test can influence the interpretation of results (e.g., smaller-scale or short-length PRBs can be strongly influenced by regional changes to hydraulic conditions). The data quality objectives of the test should thus consider the potential effect of scale on the test results.

2.5.6 Organic Carbon for Denitrification, Sulfate Reduction, and Perchlorate Destruction

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 permeable organic carbon materials to stimulate biologically mediated denitrification and sulfate reduction in contaminated groundwater in PRB systems. 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. Using a general form of a carbohydrate for organic carbon, denitrification can be represented by the reaction

$$4NO_3^- + 5CH_2O \rightarrow 2N_2 + 5CO_2 + 3H_2O + 4OH^- \,.$$

Sulfate reduction and the generation of hydrogen sulfide and bicarbonate ion can be represented by the reaction (Berner 1971)

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^- \,.$$

In the presence of hydrogen sulfide, soluble metals or metalloids may precipitate as low-solubility sulfide minerals, consistent with the reaction

$$Me^{2+} + H_2S \rightarrow MeS + 2H^+ \,.$$

In this reaction Me represents a variety of monovalent and divalent metals or metalloids such as Fe, Cd, Cu, Co, Ni, Zn, Mo, Sn, As, or Se. In combination, the sulfate reduction and sulfide precipitation reactions have the potential effect of decreasing concentrations of sulfate, iron, and other metals and metalloids and increasing alkalinity and pH. The Air Force successfully treated a perchlorate-contaminated groundwater plume by applying a carbon-based mixture of gravel and wood chips in a 7:1 ratio, along with the addition of acetate and a soybean oil/mushroom compost mixture (Craig 2004). Laboratory and field applications have investigated the potential application of range of solid-phase organic carbon materials for inclusion in PRBs, such as straw, newspaper, raw cotton, alfalfa, wheat straw, jute pellets, cattle slurry screenings, vegetable oil, compost, leaf mulch, wood mulch, sawdust, and pulp wastes (Boussaid, Martin, and Mowan 1988; Wakatsuki, Esumi, and Omura 1993; Blowes and Ptacek 1994; Vogan 1993; Volokita et al. 1996a, b; Hunter, Follett, and Cary 1997; Benner, Blowes, and Ptacek 1997; Benner et al. 1999, 2002; Schipper and Vojvodic-Vukovic 1998; Stuart et al. 1999; Taylor et al. 2002; Thombre, Thomson, and Barton 1997; Waybrant, Blowes, and Ptacek 1998; Waybrant, Ptacek, and Blowes 2002; Robertson and Anderson 1999; Robertson et al. 2000; Hulshof et al. 2003).

Benner, Blowes, and Ptacek (1997) and Benner et al. (1999, 2002) applied an organic-carbon PRB in an aquifer affected by acid-mine drainage derived from a sulfidic mine tailings impoundment in the Sudbury area, Ontario. A plume of AMD-impacted groundwater extended from a mine tailings area several hundred meters through a fine sand to silt aquifer and discharged to a small lake. The surficial aquifer was bounded by a bedrock valley. Active disposal of mine tailings had ceased, but the effects of AMD within the aquifer tended to increase with time. The pH of the groundwater at the location of the PRB was less than 6, the alkalinity was 50 mg/L as $CaCO_3$, the concentration of sulfate was 2400–3600 mg/L, and the concentration of iron was 250–1300 mg/L. The groundwater velocity was approximately 16 m per year. The reactive materials were selected on the basis of preliminary laboratory batch and column testing, which evaluated sulfate-reduction and metal removal characteristics of various permeable organic-carbon mixtures (Waybrant, Blowes, and Ptacek 1998; Waybrant, Ptacek, and Blowes 2002). The testing indicated that a mixture of plant-based materials provided gradual release of labile organic compounds over a sufficiently prolonged period. For the full-scale PRB, the reactive materials consisted of three organic carbon sources (40% plant-based compost, 40%

leaf mulch, and 19% wood chips) and 1% limestone by volume. The materials were combined in a 1:1 mixture with carbonate-rich gravel. The reactive zone was 4 m thick in the direction of groundwater flow and was bounded on the upgradient and downgradient faces of the wall by zones of coarse sand 2 m in thickness. The PRB was installed in August 1995 in an excavated trench with no shoring. The PRB extended across the small bedrock valley and was 15 m in length and 3.6 m in depth on average.

The wall has been successful in promoting microbially mediated sulfate reduction and the subsequent precipitation of iron and other metal sulfides. In groundwater within the wall, sulfate concentrations decreased by as much as 3000 mg/L, iron concentrations decreased by as much as 1250 mg/L, pH increased from less than 6 to 7.0, and alkalinity increased from <50 mg/L to 600–2000 mg/L as $CaCO_3$. The groundwater became net acid consuming, and the ability of the groundwater to generate acidity upon discharge to surface water or ground surface was significantly decreased (Benner, Blowes, and Ptacek 1997; Benner et al. 1999, 2002). Residence time of water within the PRB ranged from 60 to 180 days. Evidence for sulfate reduction has included the following:

- the decrease of sulfate concentrations within the reactive materials,
- the proliferation of sulfate-reducing bacteria within the PRB,
- the presence of dissolved sulfide (as much as 17 mg/L) in groundwater within the PRB,
- the isotopic enrichment of ^{34}S in remnant sulfate (Benner et al. 1999), and
- the identification of iron mono-sulfide solids including mackinawite on cores from within the PRB using scanning electron microscopy with energy-dispersive X-ray analysis (Herbert, Benner, and Blowes 2000).

Benner et al. (2002) suggest the most active sulfate-reduction occurred during the three-month period immediately following installation of the PRB and that reactivity gradually decreased with time thereafter. Monitoring in 2001 suggested that the overall performance of, and rate of metal sulfide accumulation within, the PRB have not decreased significantly since the initial years of operation (Daignault, Blowes, and Jambor 2003). It is anticipated that effective treatment of AMD-impacted groundwater will occur for at least a decade.

A similar approach to treatment was also employed at a field-scale demonstration in Vancouver, Canada. The groundwater contains high concentrations of sulphate, iron, and other heavy metals, including cadmium, copper, nickel, lead, and zinc. The compost-based reactive media was installed in a guar-gum slurry trench. The trench dimensions were 10 m in length, 6.7 m in depth, and approximately 2.5 m in thickness in the general direction of groundwater flow. Zinc concentrations decreased from in excess of 2 mg/L in the influent to <0.1 mg/L, and typically <0.05 mg/L within the 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). Groundwater velocity estimates were as high as 1 m/day, and the input concentration of sulphate was approximately 1000 mg/L. A full-scale PRB was constructed at this site between November 2000 and February 2001. It was approximately 400 m in length, as much as 15 m in depth, and 2.5–5 m in thickness. The barrier was thicker in the vicinity of the central part of the plume where copper concentrations were highest. Guar gum slurry trenching was used for the full-scale installation. The PRB was constructed over a period of more than two months (Mountjoy and Blowes 2002).

If the water table conditions in the vicinity of PRBs are maintained, metal sulfide minerals will not be released. Even in the presence of oxygenated water, the release of Fe by oxidation of sulfide precipitates in the reactive materials will be limited by the low solubility of oxygen in water (~10 mg/L O_2 solubility at 15^oC). Furthermore, sulfide oxidation by O_2 is slow at pH values above 4 (Stumm and Morgan 1996). The concentration of released metals will be much lower than the original plume conditions. Additionally, laboratory evidence from sulfate reduction columns set up to treat simulated mine drainage indicates that the sulfide minerals form in close proximity to the organic solids (Waybrant, Ptacek, and Blowes 2002). The organic carbon has a high capacity to consume oxygen and protects sulfide minerals from the influx of oxidizing groundwater.

2.5.7 Combinations of Solid Carbon and Iron for Organic Contaminants

Various forms of liquid carbon amendments as well as solid carbon sources have been recognized for their ability to promote the degradation of organic contaminants. In particular, materials combining controlled-release solid carbon and microscale granular iron have been developed to take advantage of the integration of abiotic and biotic degradation pathways for the dechlorination of VOCs (Mueller et al. 2004). These materials are enhancements of materials used successfully for the remediation of polynuclear aromatic hydrocarbon (PAH)- and pentachlorophenol-contaminated soils (USEPA 1996). Direct reduction of contaminants may occur through the oxidation with the iron. Microbial growth is promoted through the controlled release of dissolved organic carbon from the solid. Extremely low redox values can be obtained through the combined action of microbial oxygen consumption and chemical reduction of electron acceptors by the iron. Together these processes create an environment under which many contaminants can be degraded. The corrosion of the iron increases the pH while the microbial metabolism of the slow-release carbon component results in biological generation of organic acids, meaning proper conditions for microbial growth (i.e., near neutral pH) can be maintained. Particles combining iron and solid carbon have been proposed for treatment of carbon tetrachloride at an active grain storage facility in Kansas (Mueller et al. 2004). A primary factor in their selection was the particles’ ability to promote degradation not only of carbon tetrachloride and trichloromethane, which can be degraded by iron alone, but also of dichloromethane, which cannot be degraded by iron.

This combination of materials may also create extremely low redox conditions, which reduce many metals and result in precipitation of the metal from solution. Arsenic, for example, is precipitated through the production of iron arsenic sulfide minerals that are practically insoluble in groundwater.

2.5.8 Basic Oxygen Furnace Slag

Baker, Blowes, and Ptacek (1998); Blowes et al. (2000); and McRae, Blowes, and Ptacek (1999) recognized the potential for basic oxygen furnace (BOF) slag to remove contaminants such as phosphate and arsenic and waterborne bacteria and viruses from groundwater. BOF slag is a poorly sorted mixture of material ranging in grain size from silt to fine gravel and is a nonmetallic waste by-product of steel production generated at several steel plants throughout North America. BOF slag contains various oxides and silicates of iron, calcium, magnesium, and aluminum but in particular is rich in iron and calcium oxyhydroxides. Typically, the interaction between BOF slag and water results in elevated pH conditions of as high as 12. Proctor et al. (2000) identified antimony, cadmium, total chromium, manganese, molybdenum, selenium, silver, thallium, tin, and vanadium at concentrations in excess of background soil in the United States in samples of BOF slag as part of a review of 58 active steel mills. Toxicity Characteristic Leaching Procedure (TCLP) tests using leach solution at pH 2.8 for their samples generated leachate from BOF slag of nonhazardous characteristics. BOF slag is inexpensive, and shipping and transport have a strong influence on its overall cost. BOF slag is commonly used as aggregate in roadbed and other construction projects.

Baker, Blowes, and Ptacek (1998) initiated testing with laboratory columns containing BOF oxide and slag mixtures to remove phosphorus from water in the mid-1990s. With influent phosphorus concentrations of approximately 3 mg/L PO_4-P, the effluent from columns, one of which has operated continuously since 1993, contains phosphorus at concentrations of less than 0.05 mg/L. Phosphorus is removed by sorption, but subsequent mineral precipitation reactions also occur (hydroxyapatite). Baker, Blowes, and Ptacek (1997) applied BOF slag in a PRB to treat phosphorus in groundwater emanating from a septic system and removed phosphorus from a stream of effluent from a municipal wastewater treatment plant using columns.

In a project implemented and administered by the provincial and municipal governments, phosphorus removal from septic system effluent has been achieved in a BOF slag chamber at a single-family residence near North Bay, Ontario since 1999 (Smyth et al. 2002). Phosphorus concentrations of approximately 5 mg/L PO_4-P in the septic system effluent are decreased to less than 0.01 mg/L PO_4-P in discharge from the BOF slag treatment chamber. The chamber also effectively removes *E. coli* from the wastewater. The pH within the treatment chamber is approximately 12, but neutralization of the pH has been observed in groundwater adjacent to the subsurface discharge gallery. Maintenance of the influent and effluent lines of the BOF chamber was not required until the end of the fourth year of operation.

McRae, Blowes, and Ptacek (1999) investigated the removal of arsenic from groundwater in laboratory columns containing BOF slag. A sorptive removal mechanism for arsenic was suggested. Subsequent laboratory testing confirmed the capability to remove arsenic to concentrations of <0.005 mg/L from groundwater from an industrial site. The results of the laboratory testing indicated that excellent treatment of arsenic-contaminated groundwater could be achieved by BOF slag. Under conditions present at many sites, the testing also suggested that in situ treatment systems could be designed to function for periods of at least several years before the reactive capacity of the BOF slag might be exceeded.

BOF slag from the Chicago area was used in a PRB to treat arsenic-impacted groundwater at an industrial site in Chicago in 2002. The PRB was installed using a continuous trencher and was approximately 2000 feet (600 m) long, 30 feet (~10 m) deep, and 2 feet (0.6 m) thick. The initial two years of monitoring confirm excellent removal of arsenic from influent concentrations of >1 mg/L to <0.001 mg/L in groundwater within the PRB (Wilkens et al. 2003).

2.5.9 In Situ Redox Manipulation

To date, probably the most successful reductant for the treatment of metals has been calcium polysulfide (Rouse et al. 2001). Calcium polysulfide is widely used as an agricultural soil-conditioning agent and hence is relatively inexpensive. It has been authorized for use by the National Sanitation Foundation for use in potable water systems, which means that it has certain advantages with respect to regulatory approval. Calcium polysulfide has proven to be highly useful for in situ remediation systems by having sufficient migration ability to allow transport from the point of injection to the point of reaction and yet sufficiently reactive to reduce hexavalent chromium upon contact (Rouse et al. 2001). When mixed with water, polysulfide dissociates to form bisulfide (HS^-) and aqueous hydrogen sulfide [H_2S (aq)] with the relative percentage a function of the solution pH. The sulfide can react directly with the Cr(VI) to form Cr(III). Alternatively, the sulfide can reduce Fe(III) present in the aquifer to Fe(II). Fe(II) then reduces Cr(VI) entering the reduced zone. A large-scale injection of calcium polysulfide solution was conducted at a former chemical manufacturing site in northern California (Zawislanski, Beatty, and Carson 2002).

Another in situ redox manipulation technology creates a treatment zone within the aquifer by injection of sodium dithionite, a strong reducing agent that scavenges DO from the aquifer and reduces ferric iron [Fe(III)], related metals, and oxy-ions. One contaminant for which this technology has been used is chromium. Sodium dithionite reduces hexavalent chromium Cr(VI) through an indirect reaction that requires the presence of reactive iron in the aquifer to be released as ferrous iron, which in turn, reduces the Cr(VI) to the less mobile trivalent chromium Cr(III). The sustainability of reducing conditions using the dithionite lixiviant relies on the presence of sufficient reactive iron in the subsurface. This technology was deployed at the Hanford Site in Richland, Washington for the treatment of a chromium plume. From 1999 to 2003, a 680-m-long barrier was installed (DOE 2000). The treatment included 70 injection wells along the barrier. Several years after treatment, groundwater in approximately 17 wells has been found to contain elevated Cr concentrations (DOE 2004b). A solution to the breakthrough of Cr is currently under investigation (DOE 2004a).

2.6 Sequenced Treatment

Many groundwater plumes contain a mixture of contaminants that are best treated with a sequence of treatment methods. Examples of sequenced reactive barriers that have been proposed and/or tested in the field include the following:

- granular iron to treat chlorinated hydrocarbons (e.g., TCE) followed by aerobic bioremediation to treat aromatic hydrocarbons (e.g., BTEX);
- granular iron to treat carbon tetrachloride and chloroform followed by MNA to treat dichloromethane;
- granular iron to treat chlorinated hydrocarbons followed by nutrient addition or solid carbon sources to promote anaerobic biodegradation of VOCs that cannot be degraded by granular iron;
- solid carbon sources to treat nitrate followed by granular iron to treat VOCs; and

- a series of four treatment cells consisting of scoria to remove colloids, apatite to remove radionuclides such as Sr-90; Am-241; and Pu-238, -239, -240 and metals using apatite, followed by a bio-barrier to treat nitrate and perchlorate and a final limestone "polishing" barrier to increase pH and remove any remaining soluble radionuclides by precipitation.

A very important aspect of the design of sequenced PRBs is the evaluation of the interactions between the multiple treatment technologies. Depending on the treatment technologies, the geochemical influence of the upgradient technology on the downgradient treatment process can be positive or negative. For example, using granular iron to treat chlorinated hydrocarbons followed by aerobic biodegradation to treat aromatic hydrocarbons requires a change from a reducing environment to an oxidizing environment. A transition zone must be incorporated into the treatment system.

2.6.1 Granular Iron and Aerobic Bioremediation

The use of sequenced treatment involving granular iron and biodegradation processes is the subject of a book titled *Sequenced Reactive Barriers for Groundwater Remediation* (Fiorenza, Oubre, and Ward 2000) This book is an excellent reference for design of this type of treatment system.

2.6.2 Granular Iron Followed by Monitored Natural Attenuation

A PRB can enhance downgradient biodegradation processes in a number of ways, including the creation of geochemical conditions conducive to anaerobic biodegradation, the reduction in overall contaminant loading, the production of hydrogen and simple hydrocarbon electron donors, the creation of partially dechlorinated breakdown compounds that can act as electron donors, and direct addition of DOC (Vidumsky 2003). This enhanced biodegradation downgradient of an iron PRB may allow the PRB to be designed primarily for VOC mass reduction, thereby reducing the installation cost. Natural attenuation may also be suitable for treatment of compounds that cannot be treated by the reactive media or are produced during treatment in the reactive media. For example, carbon tetrachloride can be rapidly degraded by iron, but a portion of the carbon tetrachloride degrades to DCM, which is not degraded by granular iron. As DCM can be effectively treated through natural biological degradation processes, a sequenced treatment approach for carbon tetrachloride plumes could involve the installation of a granular-iron PRB followed by a natural attenuation zone to treat the DCM (e.g., Vidumsky and Landis 2001).

2.6.3 Granular Iron Followed by Enhanced Anaerobic Biodegradation

Treatment with granular iron followed by enhanced anaerobic biodegradation may be applicable for groundwater plumes containing a mix of compounds degradable by either of these two processes. Configurations that have been proposed include a typical, continuous iron PRB along with a bio-barrier. The bio-barrier could contain a solid electron donor such as a solid carbon source or a liquid electron donor injected into a permeable trench. The sequencing of the granular iron and bio-barriers must consider the potential interaction between the treatment technologies. For example, if nitrate is to be used as the electron donor for the bio-barrier, the bio-barrier must not be placed upgradient of the granular-iron PRB, as any nitrate not consumed in the bio-barrier will cause passivation of the granular iron. In addition, there is also the distinct possibility that DOC leached from the bio-barrier could also cause passivation of the iron.

2.6.4 Carbon Sources Followed by Granular Iron

Waste cellulose solids have been used as a carbon source to promote denitrification in horizontal PRBs beneath septic plumes at several sites. Granular iron will also reduce nitrate; however, precipitates that form on the iron surface during nitrate reduction negatively affect VOC degradation rates. Thus, for nitrate and VOC plumes, removal of nitrate prior to entering an iron treatment zone will facilitate complete treatment of both nitrate and VOCs.

Laboratory investigations (Vogan, Duchene, and Robertson 2003) have shown this form of sequenced treatment could be used to treat relatively high (10s of milligrams per liter) nitrate and TCE plumes; however, the dissolved organic carbon leached from the upgradient cellulose solids caused slightly lower TCE degradation rates. Based on these and other results, site-specific laboratory studies are necessary or the design of this type of sequenced treatment system.

2.6.5 Four-Component PRB

A four-component PRB for treating multiple contaminants was installed for demonstration of the technology in Mortandad Canyon, located at Los Alamos National Laboratory (Kaszuba et al. 2003). The major COCs in the alluvial system include perchlorate, nitrate, plutonium (Pu-238, -239, -240), americium (Am-241) and strontium (Sr-90). The PRB uses a funnel-and-gate system with a series of four reactive media cells to immobilize or destroy the contaminants. The cells, ordered by sequence of contact with groundwater, consist of gravel-sized scoria (for colloid removal); phosphate rock containing apatite (for metals and radionuclides); a “bio-barrier” of pecan shells and cottonseed admixed with gravel (to deplete dissolved oxygen, and destroy any Resource Conservation and Recovery Act [RCRA] compounds present, plus nitrate and perchlorate); and limestone (for pH buffering and anion adsorption). The PRB was designed with the following criteria: one-day residence time within the bio-barrier, 10-year lifetime, minimal surface water infiltration and erosion, optimal hydraulic capture, and minimization of excavated material requiring disposal. The PRB was installed in January–February 2003 to a depth of 27 feet. The PRB is continuously monitored through a series of wells that were part of the design. The levels of nitrate and perchlorate have been reduced to below detection in the apatite and bio-barrier cells, and Sr-90 levels also have been reduced by an order of magnitude in the apatite cell. More information is available in the case study section.

2.7 Deployment Tables

While iron PRBs are treating groundwater in several countries, most installations have occurred in the United States, where 67 full-scale PRBs have been installed in 29 states. Table 2-3 lists the full-scale installation of iron PRBs for VOC treatment within the United States and abroad. Table 2-4 contains information on PRB installations worldwide that use alternative reactive media.

Table 2-3. Full-scale installations of iron PRBs for VOC treatment worldwide

Site name	Location	Construction and configuration	Installation date
Intersil Semiconductor site[a]	Sunnyvale, CA, USA	Sheet pile continuous wall	Nov 94
Industrial facility	Sunnyvale, CA, USA	Sheet pile continuous wall	Sep 95
Industrial facility[a]	Belfast, N. Ireland	Slurry wall funnel and in situ reactor vessel	Dec 95
Industrial facility[a]	Coffeyville, KS, USA	Slurry wall funnel and sheet pile gates (extension Nov 99)	Jan 96
U.S. Coast Guard facility[a]	Elizabeth City, NC, USA	Continuous trencher continuous wall	Jul 96
Federal Highway[a] Administration facility	Lakewood, CO, USA	Sheet pile funnel and gate	Oct 96
Industrial facility[a]	Manning, SC, USA	Continuous trencher continuous wall	Nov 97
Industrial facility	CO, USA	Gate and slurry funnel	Nov 97
Industrial facility	Upstate NY, USA	Continuous trencher continuous wall	Dec 97
Aircraft maintenance facility[a]	Southern OR, USA	Continuous trencher funnel and gate (soil bentonite funnel)	Mar 98
U.S. DOE facility, Kansas City Plant[a]	Kansas City, MO, USA	Sheet pile continuous wall	Apr 98
Caldwell Trucking Superfund site	Northern NJ, USA	Vertical hydrofracturing	Apr 98
Copenhagen freight yard[a]	Copenhagen, Denmark	Continuous wall	Jun 98
U.S. DOE facility[a]	Rocky Flats, CO, USA	In situ collection system and reactive vessel	Jul 98
Industrial facility	VT, USA	Continuous trencher funnel and gate (high-density polyethylene [HDPE] funnels)	Aug 98
Former manufacturing site[a]	Fairfield, NJ, USA	Sheet pile continuous wall	Sep 98
Industrial facility[b]	Tuebingen, Germany	Gate and slurry funnel	Oct 98
U.S. DoD facility, Watervliet Arsenal[a]	Watervliet, NY, USA	Shored excavation continuous wall	Oct 98
Industrial facility	Louisiana, USA	Continuous trencher continuous wall	Nov 98
U.S. DoD facility, Shaw AFB[a]	Sumter, SC, USA	Continuous trencher continuous wall	Nov 98
Haardkrom site[a]	Kolding, Denmark	Continuous wall and recirculation system	Nov 98
U.S. DoD facility, Seneca Army Depot[a]	Romulus, NY, USA	Continuous trencher continuous wall	Dec 98
U.S. DoD facility, Pease AFB, Site 73	Portsmouth, NH, USA	Biopolymer (BP) continuous wall	Aug 99
U.S. DOE facility[a]	Rocky Flats, CO, USA	In situ collection system and reactive vessel	Aug 99
Industrial facility[a]	Kinston, NC, USA	Jetting in panel configuration	Aug 99
Industrial facility	Sudbury, MA, USA	Sheet pile continuous wall	Aug 99
Vapokon Petrochemical Works[a]	Sonderso, Denmark	Sheet pile funnel and gate	Aug 99
U.S. DoD facility, Warren AFB	Cheyenne, WY, USA	Shored excavation continuous wall	Aug 99
Industrial facility[a]	Seattle, WA, USA	BP gates, slurry funnels	Oct 99
Industrial facility	Cleveland, OH, USA	Open-trench excavation continuous wall	Nov 99
McGraw-Edison Superfund	Centerville, IA, USA	Vertical hydrofracturing	Nov 99
U.S. DoD facility, Pease AFB	Portsmouth, NH, USA	BP continuous wall	Jun 00
Somersworth Landfill Superfund site[a]	Somersworth, NH, USA	BP continuous wall	Aug 00
U.S. DoD facility, Lake City AAP	Lake City, MO, USA	BP continuous wall	Aug 00
Industrial facility	Cincinnati, OH, USA	Open-trench excavation continuous wall	Sep 00
Former dry cleaning site	Geneva, NY, USA	Shored excavation continuous wall	Sep 00

Industrial facility	Los Angeles, CA, USA	BP continuous wall	Dec 00
Industrial facility[b]	Edenkoben, Germany	Funnel and gate—sheet piles	Dec 00
DuPont facility[a]	Oakley, CA, USA	Vertical hydrofracturing	Dec 00
City of Needham	Needham, MA, USA	BP continuous wall	Jul 01
Industrial facility	St. Louis, MO, USA	BP continuous wall	Sep 01
Former dry cleaning site	Burlington, VT, USA	Shored excavation continuous wall	Sep 01
Industrial facility	Bradford, UK	Trench box gates and HDPE funnel	Sep 01
Industrial facility	Florida, USA	Aboveground vessel	Mar 02
U.S. DoD facility, Carswell AFB	Forth Worth, TX, USA	BP continuous wall	Apr 02
NASA facility, Stennis Space Center	MS, USA	BP gates, slurry funnels	May 02
Arrowhead Superfund site	Montross, VA, USA	Vertical hydrofracturing	May 02
Industrial facility	Osaka, Japan	Sheet pile continuous wall	Jun 02
U.S. DoD facility, Kelly AFB	San Antonio, TX, USA	BP continuous wall	Jul 02
Industrial facility	Detroit, MI, USA	BP continuous wall	Jul 02
Industrial facility[b]	Oberursel, Germany	Funnel and gate	Jul 02
Industrial facility	Amersfoort, Netherlands	Sheet pile funnel and reactive vessels	Sep 02
U.S. DoD facility	Charleston, SC, USA	BP continuous wall	Dec 02
Industrial facility	Nashville, TN, USA	BP continuous wall	Dec 02
Industrial facility	Dallas, TX, USA	Aboveground vessel	Mar 03
U.S. DoD facility, Kelly AFB	San Antonio, TX, USA	BP continuous wall	Jun 03
U.S. DoD facility, Kelly AFB	San Antonio, TX, USA	BP continuous wall	Aug 03
Industrial facility	Sunnyvale, CA, USA	BP continuous wall	Aug 03
Industrial facility	Gardena, CA, USA	Vertical hydrofracturing	Aug 03
U.S. DoD facility, Offutt AFB	Omaha, NE, USA	BP continuous wall	Sep 03
U.S. DoD facility, Offutt AFB	Omaha, NE, USA	Continuous trencher continuous wall	Oct 03
Industrial facility	Michigan, USA	Continuous trencher continuous wall	Oct 03
Industrial facility	Belgium	Funnel and gate	Oct 03
Industrial facility	Missouri, USA	Continuous rock trencher continuous wall	Nov 03
Industrial facility	Illinois, USA	Continuous trencher continuous wall	Nov 03
Industrial facility	Veile County, Denmark	Bentonite funnel and caisson gates	Dec 03
U.S. Government facility	Louisiana, USA	Granular iron collection trench	Dec 03
Industrial facility	Connecticut, USA	Continuous wall	Dec 03
U.S. DoD facility, Kelly AFB	San Antonio, TX, USA	BP continuous wall	Apr 04
Industrial facility	Michigan, USA	BP continuous wall	May 04
Industrial facility	Montana, USA	Continuous trencher in bedrock	May 04
Industrial facility	Ontario, Canada	Shored excavation continuous wall	May 04
U.S. DoD facility, Tinker AFB	Oklahoma City, OK, USA	Vertical hydrofracturing	July 04
Industrial facility	Saitama, Japan	Soil mixing	Oct 04
Industrial facility	Yamagata, Japan	Soil mixing	Oct 04
U.S. DoD facility, Kelly AFB, Zone 2	San Antonio, TX, USA	BP continuous wall	Nov 04
Industrial facility	Italy	BP continuous wall	Nov 04
Industrial facility	Ohio, USA	Continuous trencher continuous wall	Nov 04
U.S. DoD facility, Hill AFB	Utah, USA	Continuous trencher continuous wall	Nov 04
Superfund site	Vermont, USA	BP continuous wall	Nov 04
U.S. DoD facility, Kelly AFB	San Antonio, TX, USA	Vertical hydrofracturing	Dec 04
Industrial facility	Mississippi, USA	BP continuous wall	Dec 04
Industrial facility	Illinois, USA	BP continuous wall	Dec 04

For detailed descriptions of applications, refer to

[a] www.rtdf.org/public/permbarr/PRBSUMMS

[b] www.rubin-online.de

Table 2-4. PRBs with alternative reactive media composition worldwide

Site name	Location	Reactive media	Contaminants	Construction, configuration and scale	Installation date	Reference/contact
Non-Iron Reactive Materials						
Chalk River Laboratories	Ontario, Canada	Clinoptilolite (Zeolite)	Strontium-90	Funnel and gate, full scale	1/1998	www.rtdf.org/public/permbarr/prbsumms/default.cfm
100 D Area Hanford site	Richland, Washington	Sodium dithionite	Chromium	Injection, full scale	1997	www.rtdf.org/public/permbarr/prbsumms/default.cfm
Tonolli Superfund site	Nesquehoning, Pennsylvania	Limestone	Lead, cadmium, arsenic, zinc and copper	Continuous trench, pilot scale	8/1998	www.rtdf.org/public/permbarr/prbsumms/default.cfm
Marzone Inc./ Chevron Chemical Co.	Tifton, Georgia	Activated carbon	BHC, DDT, xylene, ethylbenzene, methyl parathion	Funnel and gate, full scale	8/1998	www.rtdf.org/public/permbarr/prbsumms/default.cfm
Amax US Metals	Carteret, New Jersey	Limestone and sodium carbonate	Copper, nickel, zinc, arsenic, cadmium, lead, selenium	Continuous trench, full scale	1993	Matthew Turner, NJDEP, (609) 984-1742
West Valley Demonstration Project	West Valley, New York	Clinoptilolite (Zeolite)	Strontium-90	Continuous trench, pilot scale	1999	Robert Steiner, (716) 942-2870, steiner@wvnsco.com
Louisiana Pacific	Fort Bragg, California	Activated carbon	Chlorinated volatile organic compounds	Funnel and gate with 4″ carbon canisters and upgradient gravel collection trenches	Unknown	Craig Hunt, North Coast Water Board, chunt@waterboards.ca.gov, (707) 576-3767
Success site	Wallace, Idaho	Apatite II™	Zinc, lead, cadmium	Belowground vault, full scale	1/2001	James Conca, New Mexico State University, (505) 706-0214
Industrial site	East Chicago, Indiana	Basic oxygen furnace slag	Arsenic	Full-scale wall	2002	Wilkens et al. 2003
In-Situ Bioremediation Using a PRB Design (i.e. Bio-barrier)						
Industrial site	Vancouver, British Columbia	Organic carbon mixture	Dissolved metals, sulfate	Full-scale wall	2000	Mountjoy and Blowes 2002
Nickel Rim Mine site	Sudbury, Ontario	Organic carbon	Nickel, iron, sulfate	Excavation and backfill, full scale	8/1995	www.rtdf.org/public/permbarr/prbsumms/default.cfm
Zeneca/Campus Bay	Richmond, California	Compost (leaf material with soil/sand mix) and sulfate-reducing bacteria	Acid mine drainage (low pH, iron, mercury, copper, arsenic, zinc)	Continuous slurry trench, full scale	10/2002	Peter Zawislanski, LFR, peter.zawislanski@lfr.com, (510) 596-9685

Site name	Location	Reactive media	Contaminants	Construction, configuration and scale	Installation date	Reference/contact
Naval Base Ventura County	Port Hueneme, California	Microbes and oxygen	MTBE, BTEX	Continuous trench, full scale	9/2000	Johnson, Bruce, and Miller 2003
Vandenberg AFB	Lompoc, California	Dissolved oxygen	MTBE	Polyethylene tubing flow-through barrier	Unknown	Beatrice Kephart, (805) 605-7924
Dow Pittsburg	Pittsburg, California	Propylene glycol, sodium lactate, and nutrients	Chlorinated volatile organic compounds (PCE, TCE, DCE, carbon tetrachloride, chloroform)	Subsurface circulation system (39 circulation wells screened over two zones: 40–80 feet and 110–130 feet), full scale	Pilot 2000, full scale 2002	Alec Naugle, S.F. Bay Water Board, anaugle@waterboards.ca.gov, (510) 622-2510 www.bcilabs.com/monterey2.html www.bcilabs.com/monterey1.html
Altus AFB	Oklahoma	Cotton gin compost, sand, and shredded bark mulch	Chlorinated VOCs	Continuous trench, full scale	2002	www.afcee.brooks.af.mil/ms/msp/center/spring2003/6.asp www.afcee.brooks.af.mil/products/techtrans/bioremediation/downloads/AltusBiowallPaper-163PEHa.pdf
McGregor Naval Weapons Plant	Texas	Solid carbon substrate	Perchlorate	Interceptor trench, full-scale field demonstration	2002	www.afcee.brooks.af.mil/products/techtrans/perchloratetreatment/permeablereactivebarriers.pdf
Moss-American	Milwaukee, Wisconsin	Air and nutrients	PAHs, BTEX	Funnel and gate with air and nutrient injection at gates, full scale	2000	Federal Remediation Technologies Roundtable (2004)
Dover AFB	Delaware	Soybean oil	Chlorinated VOCs	Injection wells spaced over two 6-m lengths, pilot scale	2000	www.afcee.brooks.af.mil/products/techtrans/bioremediation/downloads/DoverAFBBattellePaper04.pdf
SAFIRA test site	Bitterfeld, Germany	Hydrogen with paladium catalyst	Benzene, chlorobenzene, dichlorobenzene, TCE, DCE	Vertical well shafts and horizontal wells, pilot scale	1999	www.rtdf.org/public/permbarr/prbsumms/default.cfm
East Garrington	Alberta, Canada	Oxygen	BTEX	Trench and gate, pilot scale	9/1995	www.rtdf.org/public/permbarr/prbsumms/default.cfm
Private Industrial site	Mountain View, California	Liquid carbon substrate including cheese whey	Chlorinated VOCs	Shallow injection points aligned in barrier formation, full scale	Unknown	Mark Johnson, S.F. Bay Water Board, mjohnson@waterboards.ca.gov, (510) 622-2493

Site name	Location	Reactive media	Contaminants	Construction, configuration and scale	Installation date	Reference/contact
ExxonMobil Bayway Refinery	Linden, New Jersey	Dissolved oxygen	BTEX and product collection	Cutoff wall with trench collection, pilot to full scale	Full scale 8/2002	Brent Archibald, Exxon Mobil, (908) 730-2404
Offutt AFB Building 301	Nebraska	Sand and wood mulch	TCE	Continuous trench, pilot scale, full scale	Pilot scale 1/1999, full scale 7/2001	Philip E. Cork, Chief, Environmental Restoration Element, (402) 297-7621
Combination or Sequenced PRB Designs						
Rocky Flats Environmental Technology Center	Golden, Colorado	Iron and wood chips	Nitrate, uranium	Reaction vessel, full scale	1999	www.rtdf.org/public/permbarr/prbsumms/default.cfm
Fry Canyon site	Fry Canyon Utah	Iron, amorphous ferric oxide and phosphate	Uranium	Funnel and gate, pilot scale	8/1997	www.rtdf.org/public/permbarr/prbsumms/default.cfm
Mortandad Canyon, Los Alamos National Laboratory	Los Alamos, New Mexico	Scoria, phosphate rock, pecan shells, limestone	Perchlorate, nitrate, plutonium, americium, strontium	Funnel and gate, pilot scale	2/2003	Betty A. Strietelmeier, Los Alamos National Laboratory, (505) 665-9986
Former phosphate fertilizer manufacturer	Charleston, South Carolina	Compost, iron and limestone	Arsenic, heavy metals, and acidity	Continuous trench, pilot scale	9/2002	Ralph Ludwig, USEPA, (580) 436-8603
Alameda Point	Alameda, California	Zero-valent iron followed by oxygen biosparging	DCE, VC, TCE BTEX	Funnel and gate, pilot scale	1997	www.rtdf.org/public/permbarr/prbsumms/default.cfm
Private site	Texas	Solid carbon and zero-valent iron	PCE, TCE, DCE	Continuous trench, full scale	2/2004	www.adventus.us/vocs_ehc.htm

3. SITE CHARACTERIZATION OF PRB SYSTEMS

A site must be thoroughly characterized to enable design and installation of a PRB. The physical setting and the site's regulatory constraints must be accounted for before this technology can be considered feasible. This step is particularly important for PRBs as the treatment system is immovable or passive, yet must intercept and capture the contaminant plume for effective treatment. Important features of the physical setting include topography, structures at the surface, underground utilities and structures, surface water features, and ecological resources. All sources of existing information should be researched, including permits and radiation licenses, operating records, waste disposal records, interviews, site reconnaissance maps and aerial photographs, and previous reports. This existing information may need to be enhanced by acquiring and properly analyzing additional site-specific data needed to develop an appropriate design. Sampling should be supported by a sampling and analysis plan that is based on specific data quality objectives (USEPA 1994).

3.1 Conceptual Site Framework

The conceptual site framework is a system of tasks that characterize sites by collecting and integrating site data. Typically, six basic activities are part of this work:

- identification of potential contaminants;
- identification and characterization of the source or sources of contaminants;
- delineation of potential migration pathways through environmental media, such as groundwater, surface water, soils, sediment, biota, and air;
- establishment of background areas of contaminants for each contaminated media;
- identification and characterization of potential environmental receptors (human and ecological); and
- determination of the limits of the study area or system boundaries.

Further details on these activities can be found in the American Society for Testing and Material's (ASTM) *Standard Guide for Developing Conceptual Site Models for Contaminated Sites* (ASTM 1995, reapproved 2003).

The complexity of this work should be consistent with the complexity of the site and available data and is usually iterative, as detailed in the discussion of the Triad approach (Section 3.10).

The emphasis of this data collection is on the requirements for PRBs and the determination of their success as a remedial alternative. A summary description of data needs and design approach is presented in Table 3-1.

Finally, chemical and biological parameters involved with reaction mechanisms affecting inorganic and organic contaminants are discussed in detail in Chapter 3 of the RTDF's *Permeable Reactive Barrier Technologies for Contaminant Remediation* (1998).

Table 3-1. PRB design approach

Primary objective	Detailed subobjective	Data analysis method	Timing of activity
Determine background and contaminants of concern	Characterize hydrogeologic, geochemical and microbiological conditions, and contaminant profile to determine whether the PRB installation is applicable at the site.	Analysis of borings, push technology, monitoring wells, and modeling.	During alternative analysis
Determine applicability of PRB at site		Analysis of borings, push technology, monitoring wells, and modeling.	During alternative analysis
Evaluate treatability of contaminants by reactive media	Evaluate reactivity and longevity of various media. Determine reaction rate, residence time, and compliance with state-specific cleanup standards. Identify the potential need for alternative cleanup standards or technologies if compounds cannot be treated to compliance levels.	Batch and column experiments with site groundwater and/or soils.	During design and during system operation
Identify contingencies	Identify the potential need for alternative cleanup standards or technologies if compounds cannot be treated to compliance levels.	Batch and column experiments with site groundwater and/or soils.	During design and during system operation
Define hydrogeologic characteristics	Evaluate impact of PRB on aquifer and ensure capture of contaminants.	Compare pre- and post-emplacement aquifer hydrologic tests and water quality data across PRB.	During design, emplacement and system operation
	Hydrologic performance evaluation including contaminant degradation capability, system longevity (i.e., compaction, plugging, precipitate formation and migration, by-product formation, etc.) and subsurface characteristics.	Compare post-emplacement and final aquifer hydrologic tests across the reactive media using site investigation techniques. Evaluate precipitate formation from geochemical data and modeling.	During bench scale longevity testing, feasibility study, design, and system operation
	Determine groundwater gradient.	Measure water levels.	Before construction and during system operation
Determine constructability of the PRB	Evaluate ability to achieve design depth and width.	Install boreholes, test pits, and/or conduct cone penetrometer testing.	Before construction
	Evaluate ability to emplace reactive media without abrading, crushing, or mixing with fines from excavated and surrounding materials.	Observe. Review proposed construction method.	Before and during construction
	Evaluate ability of the method to control and provide quality assurance of design parameters.	Review design package.	Before and during construction
	Determine performance and compliance monitoring requirements.	Review design package	Before and during construction
	Identify operational issues in the following categories: environmental impacts, public acceptance, health and safety.	Review proposed design package/construction method. Solicit public comment.	During feasibility study, design and construction
	Identify any other construction issues and ideas for improvement.	Observe.	During construction

Primary objective	Detailed subobjective	Data analysis method	Timing of activity
Evaluate costs	Determine design and installation costs.	Obtain quotes and cost estimates.	During procurement process, feasibility study and design
	Determine any operation/maintenance and monitoring costs.	Obtain quotes and cost estimation tools.	Feasibility study and design
	Develop information for cost comparisons with other remedies.	Obtain quotes and cost estimation tools, perform benefit/cost analysis, if necessary.	Feasibility study and design
	Obtain information to document final cost and performance.	Federal Remediation Technology Roundtable.	Throughout project

3.2 Hydrogeologic Data

All relevant hydrogeologic and aquifer characteristics should be identified so that the PRB can be designed to capture the entire targeted portion of the contaminant plume. These characteristics should include stratigraphy; vertical and horizontal lithologic continuity; fracturing; groundwater levels and gradient (horizontal and vertical gradient); flow velocity; hydraulic conductivity; temperatures; pH; porosity; aquifer heterogeneity; preferential pathways; depth to aquitard; and aquitard continuity, thickness, and competence. All major controlling influences on groundwater flow should be defined (e.g., bedrock, production wells, tidal and seasonal influences, surface features, and infiltration). Remedial investigation activities such as soil borings and aquifer testing may be necessary to enhance existing site information. Hydrogeologic data will typically include maps and cross sections to present three-dimensional aspects of the hydrogeology. For further detail see Chapter 3 of Battelle’s *Final Design Guidance for Application of Permeable Reactive Barriers for Groundwater Remediation* (Gavaskar et al. 2000a).

Detailed site characterization in the local vicinity of a prospective PRB site is an essential first step in a successful PRB application. Site characterization should be sufficient to provide a good understanding of the hydraulic flow system at the prospective PRB location.

Groundwater flow velocity is one of the most important parameters influencing the design and monitoring of a PRB. The residence time in a PRB is a product of the flow-through thickness of a PRB and the groundwater flow velocity. Hence, the thickness of the PRB is directly proportional to the groundwater flow velocity. An accurate determination of the groundwater flow velocity at a site is required for the successful application of the PRB technology and for the correct interpretation of performance data once the PRB is installed.

Three general methods are used to determine the groundwater flow velocity:

- Darcy’s law
- in situ flow measurement
    - HydroTechnics™ VECTOR® Probe
    - KVA GEOFLO® Groundwater Flowmeter
    - colloidal borescope
    - University of Waterloo Drive-Point Probe

- tracer tests
    - single-well tracer tests (borehole dilution test)
    - multiple-well test

The Darcy velocity provides an average flow velocity (assuming hydraulic conductivity estimates are representative), and the direct measurement methods provide localized flow velocities (i.e., at a specified location and/or vertical horizon). The application of Darcy's law is described below. and in situ flow measurement is described in Section 3.2.3.

3.2.1 Darcy's Law

The most common method used to determine the groundwater flow velocity involves Darcy's law. The groundwater flow velocity can be determined with Darcy's law in the form $v = Ki/n$, where v = average groundwater flow velocity, K = hydraulic conductivity, i = hydraulic gradient and n = porosity. Darcy's law provides reasonable estimates of the flow velocity provided the estimates of the parameters (K, n, and i) are representative. The most common methods used in PRB design to determine each of these parameters are briefly described below.

3.2.1.1 Hydraulic Conductivity (K)

The three common methods of determining the hydraulic conductivity are

- field measurements:
    - pump test
    - slug or bail test
    - hydraulic interference
- laboratory measurements:
    - falling-head permeameter
    - constant-head permeameter
- empirical determination based on grain size distribution.

A detailed description and application of these methods is beyond the scope of this report. The following briefly describes some of the advantages and disadvantages of each method specifically for PRB design.

Field measurements—The estimate of *K* determined from a pump test is an average over the measured area of aquifer (i.e., between the pumping well and the monitoring well[s]). Pump tests may not identify relatively small zones of contrasting (i.e., higher or lower) hydraulic conductivity, which may or may not be a concern for design purposes.

Slug tests provide *K* estimates that are representative of a small volume of porous media in the immediate vicinity of the well screen. Slug tests should be completed along the proposed line of installation. The frequency and test locations are dependent on the heterogeneity of the aquifer in relation to the length and depth of the proposed PRB.

Pump tests are generally considered more reliable than slug tests, but slug tests have several advantages over pumping tests: they can be conducted in small-diameter wells, they do not produce large volumes of contaminated water that may require treatment and/or disposal, a large number of tests can be conducted in the amount of time and for the same cost as for one pumping test, and slug tests can be used to estimate the spatial variations in K at heterogeneous sites.

One commonly cited limitation to slug testing is that the method generally gives K information for only the area immediately surrounding the test well. Another limitation on slug tests is that they are heavily dependent on the characteristics and construction of the monitoring well. The hydraulic conductivity estimated with a slug test or bail test could be highly influenced by the monitoring well (including the well screen and sand pack), resulting in the estimate's being more representative of the well than of the aquifer.

Hydraulic pulse interference tests involve a cyclic injection of fluid onto a source well, and by high-precision measurement of the pressure pulse in a neighboring well, detailed hydraulic characterization can be made. Hocking (2001) provides a detailed description of this method. The advantages of the test are the short duration of the test, the high resolution and directional characterization data obtained, and the fact that no contaminated groundwater is generated. A disadvantages are that the method requires high-precision equipment and there is limited documentation for conducting the test and interpreting the test data.

Laboratory measurements—Hydraulic conductivity can be determined in a laboratory with either a falling-head or constant-head permeameter test using an undisturbed sample of aquifer material. A number of samples would have to be analyzed to obtain a useful set of K values for PRB design.

Empirical determination—Hydraulic conductivity is related to the grain size distribution of granular porous media. There are several empirical equations available that use this relationship to estimate the hydraulic conductivity. One of the most common is the Hazen formula, an empirical relationship that relies on the effective grain size, d_{10}. This method is not recommended for design of a PRB, as there is typically too much uncertainty in the K estimate.

3.2.1.2 Porosity (n)

The porosity of the aquifer used in PRB design is typically obtained from standard tables using the soil description. Table 3-2 is one such standard table.

Table 3-2. Porosity ranges for sediments

Sediment type	Porosity range (%)
Well-sorted sand or gravel	25–50
Sand and gravel, mixed	20–35
Glacial till	10–20
Silt	35–50
Clay	33–60

Source: Fetter 1994.

The porosity can also be measured in laboratory with standard methods using an undisturbed sample of aquifer material.

3.2.1.3 Hydraulic Gradient (i)

The hydraulic gradient is determined using a water table or potentiometric surface maps. Sufficient measurements should be taken to delineate localized and seasonal variations in the flow field. At some sites, it may be necessary to evaluate both the lateral and vertical hydraulic gradients. If available, multiyear variations in the potentiometric surface should be evaluated. The hydraulic gradient over a section straddling the proposed location of the PRB is determined and used in the design. The groundwater flow direction can also be determined from these maps.

3.2.2 Localized Scale of the Application

Most "well-characterized" sites have good water level and contaminant plume maps on a moderately large scale (few tens or hundreds of feet). However, to ensure that a PRB is designed to capture the targeted volume of groundwater, data on a more localized scale (with monitoring points spaced within a few feet) often are required. Because most PRBs are built with a flow-through thickness of 6 feet or less, groundwater flow information along this scale is required. However, at many sites with low or moderate groundwater velocities, such as Dover AFB and Seneca Army Depot, water level differences on a localized scale are difficult to discern, even when a relatively large number of monitoring points are present in the area of interest. At such a small scale, local aquifer heterogeneities play a much larger role in determining flow. Because a PRB captures more of a targeted plume when the length of the PRB is oriented perpendicular to the flow, it is important that the local flow direction and magnitude at a prospective PRB location be well identified. At particularly difficult sites, where this feat has been a challenge, such as at DOE's Kansas City Plant (Laase et al. 2002) and Lake City Army Ammunitions Plant (Keller, Graff, and Buechler 2003), groundwater has been found to be flowing at a sharp angle to the length of the PRB, considerably reducing the capture of the targeted portion of the groundwater.

3.2.3 Limitations of Flow-Measurement Tools

Many different tools have been tested in the field to determine flow on a more localized scale. Water levels and slug tests/pump tests are the conventional tools and, despite their limitations, have been used in some way at almost every PRB site. Examples of some secondary tools that can be used include down-hole heat sensors and colloidal borescopes. Down-hole heat sensors that measure groundwater velocity in monitoring wells were used at former Naval Air Station (NAS) Moffett Field, in situ heat sensors installed permanently in the ground were used at Dover and Lowry AFBs, and the colloidal borescope (another down-hole instrument that measures groundwater velocity in wells) was used at Lowry and Dover AFBs (Gavaskar et al. 2002). Although many of the readings appeared to agree with the expected direction of the flow at these sites, enough readings appeared to be anomalous so that relying solely on these sensors would be unwise. This shortcoming may be a deficiency of the instrument itself or a consequence of measuring point flow instead of bulk flow. However, at particularly heterogeneous sites, these sensors could be useful in delineating local variations in flow. Another example of a secondary tool is tracer testing. At sites such as Moffett Field and Elizabeth City Coast Guard Station, tracer tests have proved to be a very useful tool for determining flow velocity, flow direction, and the extent of groundwater capture by PRBs. They can provide valuable information to aid in the design of a PRB or to evaluate a PRB that has already been installed. Consideration should be given to this investigative technique, especially when other techniques provide a wide range of data. However, successful tracer tests are relatively difficult to conduct and can be very resource-intensive.

3.2.4 Temporal and Seasonal Variations

Depending on the presence of tidal and/or seasonal influences at a site, groundwater flow magnitude and direction can change substantially. At Dover AFB, groundwater flow direction was found to vary by 30° on a seasonal basis. At other sites, the variability has been even higher. Tidal influences have been a factor in determining flow at the Elizabeth City site. Generally, it is advisable to obtain at least four quarters of water level data on the local scale of the PRB to account for seasonal variability. Where tidal influences are possible, monitoring frequency needs to be adjusted accordingly. With changing seasons, another factor that may change significantly is groundwater temperature. In the PRB at the Vapokon site, for example, it was observed that the reaction rate increased from January to March to August to September (Lo, Lai, and Kjeldsen 2004). As the groundwater temperature rose to a maximum in August and September, the reaction rate was highest. O'Hannesin, Przepiora, and Gillham (2004) have conducted laboratory tests with granular iron and reported that TCE half-lives decreased exponentially with temperature and, in general, conformed to the theoretical Arrhenius equation for temperature dependence. From a hydrologic perspective, the PRB must be designed to provide adequate residence time during the cold season, when groundwater temperature and, consequently, the contaminant half-lives are at their highest. Reaction rate (half-life) data obtained from laboratory treatability tests (at room temperature) must be carefully adjusted to field temperatures to determine residence time and PRB thickness.

3.2.5 Aquifer Heterogeneity

At most sites, aquifer properties in the region of interest often show significant heterogeneity. Even in the relatively homogeneous aquifer at Dover AFB, where a pilot-scale funnel-and-gate PRB was installed, hydraulic conductivity varied by more than an order of magnitude from well to well. In addition, there is the uncertainty in hydraulic gradient measurements that are collected on a very localized scale. At many sites, either average or maximum values of these aquifer properties have been used to determine an average or maximum groundwater velocity that was then used in the PRB design. Detailed soil coring and hydrogeologic testing to identify soil and rock stratigraphy and aquifer properties are essential. These should be conducted both vertically and horizontally along the PRB installation area. Groundwater and solute transport modeling can be used to simulate representative flow conditions for determining the orientation and dimensions of the PRB. At sites such as Dover AFB and Moffett Field, groundwater modeling has been used successfully in addressing the flow variability and inherent uncertainties in measurements (Gupta and Fox 1999). Other designs have employed a probabilistic approach when evaluating the range of groundwater velocities expected to occur in the PRB (see Section 4.1.3).

Several theoretical studies have examined the effect of aquifer and PRB heterogeneity on flow through PRBs and the monitoring network needed to identify and adequately characterize this heterogeneity (Benner, Blowes, and Molson 2001; Elder, Benson, and Eykholt 2002). The numerical simulations show that the spatial variations in the hydraulic conductivity of both the aquifer and PRB will result in preferential flow through the PRB. In general, the studies showed that all aquifer heterogeneities (e.g., hydraulic conductivity, porosity, etc.) can produce preferential flow in PRBs, and such preferential flow is be more pronounced in thinner barriers. While these efforts need to be tempered in the context of PRB sizes and the complexity of the geologic setting, consideration of possible heterogeneities intersected by the PRB is a critical step in a successful design.

At one site, the presence of a zone of high hydraulic conductivity at one end of the PRB was not identified in the predesign investigation. The zone of high conductivity influenced groundwater flow and resulted in groundwater flow around the end of the PRB (Laase et al. 2002). Lastly, often highly conductive nonnative fill materials, which are often heterogeneous by nature, have also been observed at several PRB sites.

3.3 Contaminant Plume(s)

Information regarding the contaminant plume(s), the existence of nonaqueous-phase liquid (NAPL), and contaminant source(s) should be generated. The nature and concentration of all contaminants, their vertical and lateral distributions, and all pertinent degradation characteristics should be accurately identified. The concentration of contaminants within soil should also be assessed to determine the effect on groundwater concentrations. The contaminant flux should be sufficiently characterized so that the upgradient concentrations can be accommodated by the PRB design. It is also imperative to understand variability in plume shape and direction over time. Plumes deviate in direction and location over time and may change shape due to attenuation, degradation, mixing with other plumes, dilution, recharge, and other natural and anthropogenically induced disturbances. Groundwater level measurements are particularly important in areas where low flows or seasonally fluctuating water tables must be accounted for in the PRB design. These fluctuations impact both the performance of the media and hydraulic capture.

3.4 Geochemical Data

The geochemistry of the groundwater must be evaluated as part of the design for a PRB. The groundwater geochemistry can have an effect on the efficacy of the treatment of the PRB and on the long-term performance of the PRB. Sufficient samples should be collected in the vicinity (along the proposed length and depth) of the PRB to characterize the geochemistry of the groundwater. Field measurements of specific conductance, pH, oxidation-reduction potential (ORP), temperature, and DO should be completed. For the design of a PRB, samples should be collected and analyzed for inorganic parameters listed in Table 3-3, including Ca, Fe, K, Mg, Na, Si, Cl, SO_4, NO_3, alkalinity, total organic carbon (TOC), and DOC. Characterization of additional constituents (e.g., high levels of dissolved metals) may be necessary on a site-specific basis.

3.5 Microbial Data

Microbial data may be needed on a site-specific basis and for the evaluation of specific reactive media. If the treatment process will be biological (bio-barrier), it is important to confirm that the microbial population required for treatment is present within the aquifer or can be introduced and sustained.

Microbial data are not typically collected for the design of PRBs using granular iron because the treatment media and the reaction mechanism are abiotic. Microbial data have been collected as part of the performance monitoring for iron PRBs. Microbial data that can be collected include the following:

- lipid analyses
    - Phospholipid fatty acid (PLFA) analysis provides a quantitative way to assess viable biomass, community structure, and metabolic activity.
    - Quinones provide an indication of aerobic/anaerobic conditions at a site.
- DNA analyses
    - To provide qualitative information about prominent organisms (e.g., bacteria or fungi) in a sample. Of particular interest may be the presence or absence of *Dehalococcoides* microorganisms in soil and groundwater samples. Currently, only microorganisms belonging to this group have demonstrated the capacity to biologically reduce cDCE and VC to ethene (e.g., Maymo-Gatell et al. 1997).
    - Depending on the type of PRB, the number of delta-Proteobacteria that are sulfate- or iron-reducers, the number of Geobacter bacteria, and the presence and number of aerobic hydrocarbon degraders and anaerobic hydrocarbon degraders may be useful.
    - Isolate identification determines the phylogenetic affiliation of pure cultures.
    - DNA-based fluorescent probes can be used to determine the presence of organisms (and identify species) in selected groups of bacteria that are expected to be present (i.e., denitrifiers when nitrate is present).
- culture analyses
    - Culture methods can be used for estimating the number of bacteria capable of degrading contaminants and can be used for other general purposes.
    - Most-probable number and other semiquantitative enumeration techniques can be used to give estimates of the numbers of various species involved in anaerobic respiration of contaminants (e.g., denitrifiers, perchlorate reducers, iron reducers, sulfate reducers).

3.6 Dissolved Gases

Dissolved gases can be produced by the treatment process promoted by a PRB installation. For example, the reaction of granular iron in a typical natural groundwater affected by chlorinated hydrocarbon compounds can generate several gas constituents, including hydrogen, methane, carbon dioxide, ethene, and other hydrocarbon gases related to either the iron corrosion reaction or the degradation of target chemical constituents. Dissolved gases related to the use of non-iron-based treatment materials may also be expected due to direct reaction of the treatment material in an aqueous environment or indirectly due to the reaction process on (e.g., due to enhanced biological processes).

Because the production of dissolved gases can be evidence that the reaction process intended by the PRB treatment is occurring, collecting background information on the presence, occurrence, and concentration of dissolved gases is recommended during the PRB design phase. For example, a typical dissolved hydrogen content of a natural groundwater under sulfate-reducing conditions may be very low (e.g., 1–4 nanomolar ([nM]; under typical conditions, the solubility of hydrogen approaches 800,000 nM) (Chapelle et al. 1996). The concentration of dissolved hydrogen in groundwater collected from within an iron-filled PRB has been measured at a concentration greater than 600,000 nM (Sorel et al. 2003).

A variety of methods can be used to both collect and analyze groundwater samples for dissolved gas occurrence and content. The designer should contact the laboratory to develop the appropriate protocol and analytical techniques after consulting with the regulatory agency. An example of analytical techniques used for dissolved gases include those listed in Table 3-3, which analyze groundwater samples collected in typical 40-mL volatile organic analyte (VOA) bottles.

Table 3-3. Analytical techniques used for dissolved gases

Carbon dioxide	SM 4500 or ASTM D1945
Methane	RSK 175M or ASTM D1945
Ethane	RSK 175M or ASTM D1945
Ethene	RSK 175M or ASTM D1945

For dissolved hydrogen, a typical collection protocol involves the bubble-strip method followed by analysis by gas chromatography using a mercury-reduction detector.

3.7 Geotechnical Characterization

The geotechnical design of a PRB is an integral component of the overall system design and is critical to ensuring a sustainable and effective subsurface remediation system. Most of the historical attention on PRB design and effectiveness has focused on the chemical and hydraulic systems; however, the geotechnical or geomechanical components are equally important. Soil properties and PRB material properties define the ability of the PRB system to maintain the structural integrity for its design lifetime. PRB material properties including specific gravity, grain size, shape, and moisture content affect the constructability of the system and its ability to be uniformly mixed with either support or multiple treatment materials in ways that maintains structure and permeability. Also, depending on land use, the installed PRB must not compromise surface conditions or structures. In all cases, it is recommended that a certified professional such as a geotechnical engineer and/or a certified engineering geologist provide oversight for the geotechnical characterization and design. Proper engineering of the installation can help eliminate schedule delays, cost overruns, and hazardous conditions, as well as other unexpected and unwanted circumstances. This section summarizes several basic tenets relevant to assessing the geotechnical aspects of a PRB design.

3.7.1 Geotechnical Considerations for PRB Systems

Geotechnical testing should be performed as a fundamental part of a comprehensive study at a PRB site (shallow or deep installation) to support characterization of earth materials prior to and during trenching excavations. Shallow excavations (e.g., <50 feet bgs) are likely to have greater potential impact to surface features and structures; thus, this geotechnical section focuses on those shallowly excavated PRB systems. Geotechnical laboratory studies used to support the project work will identify factors to consider during trenching and/or excavation of PRB, such as the shear strength and cohesion properties of the earth materials, sieve/grain-size analysis, moisture content, consolidation (placing a load on it), and density. For deeper PRB systems involving 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 the ASTM methods listed in Appendix D or equivalent methods.

Most shallow PRBs have been, and likely will continue to be, implemented by excavation with backfilling, single-pass trenching, and caisson installation. High-pressure injection (e.g., jetting) and fracturing methods are mostly used for deep installations. For shallow systems, two basic types of excavations include “open” excavations, where stability is achieved by providing stable side slopes, and “braced” excavations, where vertical or sloped sides are maintained with protective structural systems that can be restrained laterally by internal or external structural elements. Both excavation types may include a biopolymer slurry (e.g., guar gum) to stabilize the trench walls and maintain the open excavation. Important factors for selecting and designing the excavation system include soil type and soil strength parameters, groundwater conditions, slope protection, side and bottom stability, vertical and lateral movements of adjacent areas, and effects on existing structures. The depth of an excavation and groundwater conditions generally control the overall stability and potential movements of open excavations. During PRB construction operations, the stability of an open excavation must be evaluated and determined by the geotechnical field investigation and laboratory testing. In certain geologic formations (stiff clays, shales, sensitive clays, clay tills, etc.) stability is controlled by construction procedures, side effects during and after excavation, and inherent geologic planes of weaknesses. The U.S. Department of the Navy Design Manual DM-7.2 (1986a) provides a summary of the primary factors controlling stability in excavation slopes and for a variety of soil and rock types. U.S. Department of the Navy Design Manual DM-7.1 (1986b) describes methods for controlling bottom heave.

An exploration program to define the soil and groundwater conditions over the full extent of the PRB project is strongly recommended so that the design of the stable open-trench system (e.g., shoring, slurry, and guar gum) can be adjusted to satisfy the varying site conditions.

3.7.2 Geomechanical Considerations for PRB Treatment Materials

Since its modern inception in the early 1990s, the PRB has employed the use of nonnative materials, including granular iron metal, granular activated carbon, zeolitic minerals, compost, limestone, and other “solid” materials placed in the subsurface to promote the physical, chemical, and biological conditions necessary for treatment of chemically affected groundwater. Assessing the potential geomechanical and geohydraulic considerations for a PRB material should first consider the design and performance objectives of that material. The general geomechanical and geohydraulic purpose of the PRB is to encourage sustained groundwater flow through it, and provide a sustainable framework (i.e., maintain certain porosity and geometry) for the chemical reactions to occur. Contrast these with typical objectives for the conventional backfill material emplaced within any excavation (Table 3-4) (Warner 2002).

Table 3-4. Geotechnical intent of placed materials

Purpose of compaction	PRB material considerations
Reduce compressibility	Maintain pore space
Increase material strength	Maintain pore strength
Reduce permeability	Maintain (or increase) permeability
Control expansion	Affect chemistry of native soils
Control frost susceptibility	Promote hydraulic uniformity

Soil properties and PRB material properties contribute significantly to the ability of the PRB system to transmit groundwater through it and sustain the flow for its design lifetime. PRB material properties including specific gravity, grain size, shape, and moisture content affect the constructability of the system and its ability to be uniformly mixed with either support or multiple treatment materials in a way that maintains structure and permeability. The use of specific geotechnical tests, as described previously, or numerical modeling methods can assist with developing composition designs for a given application. It is recommended that the designer consider such methods, particularly if the PRB system is to be located where the potential for significant dynamic loading may occur within the design life of the PRB system. This step enables a more sustainable PRB composition to be developed and likely contributes to increasing the treatment efficacy of the PRB system.

Each potential PRB material has specific physical properties that affect both the constructability of a PRB and its long-term performance. Properties such as density or specific gravity, unit dry weight, shape, and moisture content affect compaction, effective porosity, permeability, geometry of the backfilled zone, and—when two or more materials are used in a PRB—ability to sustain a uniformity of mixing within the emplaced treatment cell.

3.7.3 Consideration of Unanticipated Events

PRBs are intended to remain in the subsurface for many years if not decades. Even if the chemical treatment efficacy is lost, the PRB may continue to remain in place. Changes in land use, adjacent subsurface excavations, nearby dewatering of the groundwater system (causing variable filling and drainage), are all considered "unanticipated events" that may reduce the competency of the PRB structure. Like conventional soil-bentonite slurry wall systems that are designed to reduce groundwater flow through them, typical PRB compositions are not designed to maintain high lateral or shear strength conditions. PRB systems can be composed of a mixture of both granular materials (such as iron particles) and finer-grained materials closer to silt in grain size. Unless there is sufficient granular material to maintain structure, nearby dynamic loads such as pile driving or earthquakes can result in geometrical changes in the PRB structure and the uniformity of its composition. These can lead to channeling and void spaces, which can reduce the treatment efficacy of the PRB. Also, exposure of the PRB system by removing its lateral support (such as excavating adjacent or in close proximity to the PRB) can lead to structural failure. Constructed and compacted systems such as PRBs would be expected also to have much less shear strength than undisturbed native soil material. While these events cannot necessarily be predicted, the lesson is that the design of the PRB system should consider the positioning of subsurface systems to areas that are less likely to be subject to controllable dynamic loading (such as excavation and dewatering) (Warner 2002).

3.8 Analytical/Sampling Methods

Inorganic analytes (e.g., nitrites, sulfates, and metals) and VOCs should be measured by USEPA-approved methods. Besides being contaminants at some sites, these inorganic analytes and VOCs can provide valuable information on the chemistry of the local groundwater and its effects on the performance of the reactive media. At sites where radiological contamination is suspected, radiological analysis such as isotopic analysis should be performed to determine the concentrations of site-specific radionuclides, gross alpha, and gross beta. Laboratory methods may include alpha or gamma spectroscopy or various mass spectrometry methods. Standardized methods for characterizing radiologically contaminated sites are described in the *Multi-Agency Radiation Survey and Site Investigation Manual* (USEPA et al. 1997).

Table 3-5 identifies suggested field and laboratory parameters that should be monitored within the groundwater. This table should be used as a guide to select site-specific parameters of concern but is not all-inclusive—other parameters may apply. State-specific protocols and regulatory agency requirements should be reviewed to determine whether filtered or unfiltered samples should be collected.

Table 3-5. 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°C	24 hours
Anions: SO_4, Cl, Br, F	40 CFR, Part 136, Method 300.0	100 mL	Polyethylene	4°C	28 days

Analyte or parameter	Analytical method	Sample volume	Sample container	Preservation	Holding time
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
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, ethene	RSK-175 (gas chromatograph–flame ionization detector)	None	None	None	None
Carbon dioxide	SM 4500	None	None	None	None
Hydrogen gas	Bubble strip method (gas chromatograph with mercury-reduction detector)	None	None	None	None
Radionuclides					
Field screening	HPGe gamma spectroscopy FIDLER	None	None	None	None
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 Gamma spectroscopy	4 L[d]	Polyethylene[d]	pH < 2, (HNO_3)[d]	6 months[d]

[a] If <1.0 mg/L, use photometric field kit for analysis.

[b] Gas chromatograph methods may be substituted once identity of compounds and breakdown products are verified.

[c] .Other metals analytes characteristic of the media should be included.

[d] General guidelines; the parameter is laboratory specific.

3.9 Data Management

During site characterization activities, careful field notes and field data forms should be kept and maintained for the project. During site characterization and monitoring, site-specific groundwater quality objectives should be identified and used to determine the appropriate analytical methods based on the goals and cleanup standards/criteria applicable to the site. Upon completion of these activities, all data should be recorded, including appropriate visual presentations such as maps, graphs, diagrams, etc. Many regulatory agencies now require electronic reporting of analytical data.

Quality assurance/quality control (QA/QC) requirements and reporting requirements should be determined by project-specific data quality objectives. All QA/QC measures required by the analytical method used should be completed. At a minimum, the lab should provide QA/QC summary documentation (including nonconformance summary report and chain of custody) with the analytical results. QA/QC deliverables, as specified by the analytical method, should be maintained and made available upon request for at least three years. Ultimate responsibility for QA/QC documentation belongs with the responsible party of a site, the contractor installing the PRB for a site, or a vender conducting a demonstration. However, the responsible party may contract with another entity, such as an analytical laboratory, to house the actual QA/QC data. In addition, all state-specific reporting requirements should be adhered to, as they tend to vary from state to state. QA/QC may also be applied to the construction of the permeable and impermeable barriers.

Additional considerations and guidance for various types of barriers can be found in *Design Guidance for Application of Permeable Barriers to Remediate Dissolved Chlorinated Solvents* (Battelle 1997).

3.10 Triad

Triad is a methodology developed by USEPA to update, unify, and form a logical approach to environmental investigation planning, execution, and evaluation. It relies on technological, scientific, and process advances to increase effectiveness, improve quantity, and save costs.

It recognizes the scientific and technical complexities of site characterization, risk estimation, and treatment design. In particular, the Triad approach acknowledges that environmental media are fundamentally heterogeneous at both larger and smaller scales. Heterogeneity can have important repercussions on sampling design, analytical method performance, spatial interpretation of data, toxicity and risk estimation, and remedy design and success. It is applicable across all types of environmental programs.

Triad emphasizes three components: better investigation preparation (systematic project planning), greater flexibility while performing fieldwork (dynamic work strategies), and advocacy of real-time measurement technologies, including field-generated data.

The central concept that joins all of these ideas is the need to understand and manage uncertainties that affect decision making. These are decision uncertainties (those unknowns that stand in the way of making confident decisions) and data uncertainties (sources of variation in data results when decisions are based on data).

In the systematic planning component of the Triad approach, the project goals and objectives are established. Once these goals and objectives are defined, a conceptual site model (CSM) is developed to incorporate existing knowledge about the site and to establish what additional information and data are needed to achieve the goals. The CSM is expanded and improved as additional knowledge is obtained. It serves as the organizing tool for communication among the project team, the decision makers, and the field personnel. The systematic planning process allows the CSM to evolve and mature as site work progresses and data gaps are filled. During the systematic planning phase of the project, the project team identifies the type, quality, and quantity of data needed to answer the questions raised in the conceptual site model. Those decisions guide the design of sampling procedures and the selection of analytical tools and methods for providing relevant information.

The dynamic work plan component of the Triad approach is centered on the activities in the field. The dynamic work plan is designed to allow the project team to update the CSM with real-time data and make decisions in the field on how subsequent site activities will progress. For this phase of the Triad approach to be successful, it is essential that the field personnel are experienced and are allowed to make decisions in the field based on decision logic developed during the systematic planning phase. They must, however, stay in close communication with regulators or others overseeing the project during implementation of the plan.

The third component of the Triad approach, real-time analysis, focuses on gathering and analyzing real-time data to support real-time decision making. This phase uses technologies that support data gathering, management, processing, and interpretation. The use of proper quality control protocols for field-generated data and data management tools is also extremely important and essential in managing uncertainty. The use of real-time measurement technologies facilitates faster decision making with fewer uncertainties and an improved CSM.

The advantages of the Triad approach are that it produces better investigation quality, faster investigations, and improved stakeholder communication, leading to faster and more effective cleanups and redevelopment and lower life-cycle costs. The disadvantages are higher up-front costs, a change in approach to data quality, a greater need for training about Triad, and negative bias towards field-generated data.

There are barriers to implementing the Triad approach. These are organizational barriers, concerns with real-time measurement technologies, conflicts with state law, lack of regulatory guidance, difficulties of establishing cleanup criteria during initial planning, and confusion in associating uncertainty to specific decisions. The methodology details ways to overcome these barriers.

Triad's emphasis on systematic planning to manage the full range of uncertainties, which clarify project goals and concerns through open discussion and documentation, creates an atmosphere conducive to trust and cooperative negotiations among all involved parties. If the technical issues are out in the open and stakeholders are assured that resource limitations and scientific uncertainties are being fairly balanced in relation with their concerns, then there is a stronger foundation for negotiating parties to work on more challenging social issues.

Further information on this concept is available in *Technical and Regulatory Guidance for the Triad Approach: A New Paradigm for Environmental Project Management* (ITRC 2003), prepared by the ITRC Sampling, Characterization and Monitoring Team.

4. DESIGN AND CONSTRUCTION

This section describes the design and construction of PRBs in general. The use of probabilistic design to incorporate the variability of the input parameters into the design process is discussed. Recently, biopolymer has been used extensively for the construction of PRBs. The use of biopolymer for support of excavations and as a carrier gel for injection of reactive media using vertical hydrofracturing is discussed. Lessons learned from the design and construction of PRBs over the last decade are presented in this section.

4.1 PRB Design

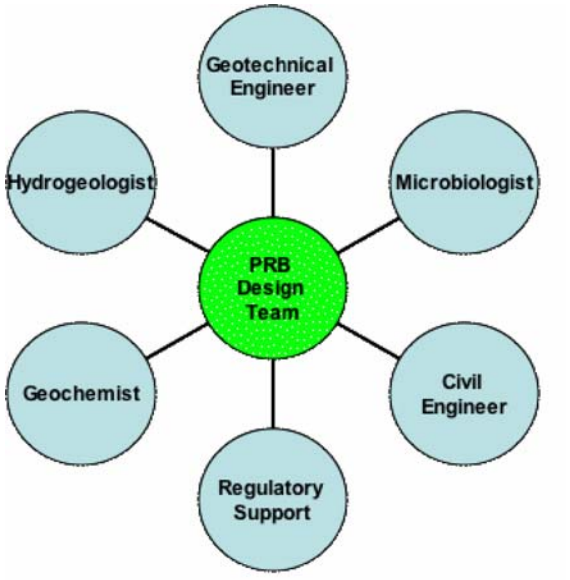


Figure 4-1. Conceptual PRB design and construction team.

When designing a PRB system is it important to use experienced, well-trained professionals (see Figure 4-1). Selecting the PRB design team is an important step in the design and construction process. Note that there may be several variances to the mixture of professionals presented in Figure 4-1 and that the selection of team members is dependent on the scope and nature of the site.

The primary physical function of the PRB is to capture the targeted groundwater (and plume) and provide it with sufficient residence time in the reactive media to achieve the desired cleanup goals. Understanding the groundwater flow regime is key to the physical design of a PRB system.

Even the best site characterization effort has limitations, especially if the geology is complex. This is where a good design process can help. Even in a relatively homogeneous aquifer, hydraulic conductivity values tend to vary by an order of magnitude, and hydraulic gradients are often difficult to determine on a very localized scale. Seasonal variations in hydraulic gradient can cause flow direction to vary at many sites. Using average or maximum values for these site parameters (hydraulic conductivity and/or hydraulic gradient), as has been done in the past, may lead to a limited understanding of the flow. Groundwater flow and solute transport modeling can help understand the effects of this variability. The effects of an entire range of conductivities and a range of gradients on the flow through a PRB can be modeled through multiple simulations. Multiple simulations allow users to optimize the design of the PRB. For example, if the groundwater flow direction changes considerably on a seasonal basis, the PRB can be oriented along a direction that is not too far from perpendicular to the flow during most seasons. The design variables that often can be controlled to optimize the design of a PRB are orientation, dimensions, permeability of reactive media, and construction method.

Despite detailed site characterization and a thorough design process, flow problems may arise due to the uncertainties inherent in subsurface installations. If nothing else, aging PRBs could potentially develop flow problems as precipitation or microbial populations build up in the reactive media to the point where flow is impeded. Retroactive conceptual modifications, such as trench extensions, to improve groundwater/plume capture or increase residence time in the PRB have been modeled and described as part of an Environmental Security Technology Certification Program (ESTCP)–sponsored, ITRC-supported study (Gavaskar et al. 2002).

Underground utilities located beneath the groundwater table can have a significant influence on the groundwater hydraulics in the vicinity of a PRB. Utilities are typically bedded in a permeable material. If a PRB crosses a utility or even is installed in close proximity to a utility, flow paths along the PRB and into the utility line bedding can develop. The potential impact of utility lines on the groundwater flow patterns must be evaluated and incorporated into PRB design.

4.1.1 PRB Configurations

Various configurations of PRBs have been constructed, including continuous PRBs, funnel-and-gate systems, and in situ reactive vessels. In a continuous PRB configuration, the reactive media is distributed across the width of the contaminated groundwater plume. Properly designed and constructed continuous PRBs have minimal impact on the natural groundwater flow patterns. 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 to ensure complete capture and as a safeguard in the event the permeability of the PRB is reduced. The continuous PRB has been the most common configuration used to date. A funnel-and-gate configuration uses low-permeability materials (funnel) to direct groundwater towards a permeable treatment zone (gate). Directing or funneling the groundwater towards a treatment gate may increase the natural groundwater flow velocity several times. Funnel-and-gate designs need to extend beyond the extent of the plume to ensure that all the contaminated groundwater is captured and treated. The goal of a funnel-and-gate or continuous PRB is to ensure that contaminant flow beneath, around, or above the system does not occur.

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.

4.1.2 Geochemistry

Geochemistry refers to the native constituents of the groundwater that affect short- and long-term performance of a PRB. To a large extent, the type of reactive media used in a PRB determines the types of reactions that occur between the groundwater constituents and the PRB. ZVI, or granular iron, is the reactive media that has been most commonly used in PRBs so far, and most of the studies of PRB-groundwater geochemistry relate to this medium. However, the experience with iron medium serves as an illustration of the kinds of interactions that may impact the performance of reactive media, in general.

Geochemistry is important from the perspective that other groundwater constituents (constituents other than the target contaminants) may interfere with a PRB’s ability to perform its two main functions:

- capture groundwater from the targeted portion of the aquifer and provide it with sufficient residence time in the reactive media and
- react with the target contaminants and reduce their concentrations to target cleanup levels.

4.1.3 Probabilistic Design

Typically a deterministic approach has been used for the design of PRBs. Average or maximum values of groundwater flow velocity, contaminant concentrations, and reaction rates are used to calculate the thickness of reactive material required. Safety factors may be incorporated into the input parameters or applied to the design thickness. A probabilistic design incorporates the variability in the input design parameters into a probabilistic model to determine the PRB thickness required to achieve a certain confidence level. Probabilistic distributions are determined for the input parameters, including aquifer and PRB hydraulic properties, influent concentrations, and reaction rates and breakdown product yields. It is important for the input distributions to be realistic for the model to provide realistic results.

Advantages of this probabilistic approach include the following:

- The variability in input data is incorporated into the design.
- The degree of confidence in effluent concentrations is predicted.
- The need for arbitrary safety factors is eliminated.
- Sensitivity analyses can be completed to quantify the influence of the variability of specific parameters on the design.

For more information on this probabilistic approach to PRB design, see Vidumsky and Landis (2001) and Hocking, Wells, and Ospina (2001). Also see papers by Eykholt, Elder, and Benson (1999); Elder, Benson, and Eykholt (2002); and Bilbrey and Shafer (2001).

4.2 PRB Construction

Several construction methods are available to construct granular iron PRBs. Selecting the most suitable method depends on several site-specific factors, including the design of the PRB, depth of installation, the nature of the geologic materials present, and surface/subsurface obstructions (e.g., buildings and utilities). The flow-through thickness, which is governed by the residence time required for treatment, also has an influence on the selection of construction method. All construction methods have a minimum or maximum flow-through thickness that can be achieved. Where the minimum practical excavation or injection thickness is wider than the required flow-through thickness of certain reactive materials required for treatment, including granular iron, sand, or other inert material can be used as bulking material and mixed with the reactive material.

The more common methods of installing PRBs are excavation using a biodegradable slurry for support of the excavation, continuous trenching machines, and vertical hydrofracturing. The reactive material can be placed directly in an excavation if the excavation remains open. Trench supports like hydraulic shoring or trench boxes can be used for temporary support in shallower applications. The “traditional” method of using sheet piling to support the excavation, while effective, is relatively expensive and has mostly been replaced by the methods listed above.

4.2.1 Excavation with Biopolymer Trench Support

Installation of a PRB using biopolymer or biodegradable slurry is similar to constructing a conventional impermeable slurry wall. As the trench is excavated, biopolymer slurry is added as liquid shoring to provide stability to the trench walls. The biopolymer slurry used is typically guar gum based. Excavation continues through the biopolymer without the need for dewatering. The biopolymer slurry must be maintained to slow the microbial breakdown of the biopolymer during excavation. Microbial breakdown of the slurry can result in a decrease in the viscosity of the biopolymer and loss to the supporting properties of the slurry. The reactive media is placed through the slurry by tremie. Recirculation wells are spaced along the length of the trench. Any residual slurry in the PRB is broken down by circulation of an enzymatic breaker fluid and through natural biological degradation allowing groundwater to flow through the PRB. Depths of up to 90 feet (27 m) bgs and a thickness of 2 feet (0.6 m) or greater can be achieved using this method.

Using biopolymer as a liquid shoring is a specialized construction method, and it is recommended that an experienced and qualified contractor complete the construction. A well-prepared work plan prepared by the contractor can prevent potential problems arising during construction. One of the most significant problems that can occur is a collapse of the trench during excavation or backfill, which could present a health and safety issue. If a trench does collapse, a new trench must be excavated some distance away because the soils are disturbed and weaker.

The stability of trench/slurry walls also depends on the shear strength of soils and related factors, which can vary significantly based on site-specific conditions, e.g., soil type (percent sand, clay, silt and related properties), drained and undrained conditions, depth of trench, pore water pressure (a function of water table and variations due to any dewatering/flooding, etc), surcharge loadings from excavated/stockpiled materials or equipment, length of trench opened, etc. Section 3.7 provides recommended geotechnical characterizations that should be carried out along the alignment of the PRB. These characterizations need to be evaluated during preparation of the work plan for construction. Primary factors to address in a work plan are hydrostatic head required to maintain stability, maintenance of the biopolymer slurry, length of trench open, and control of surcharges on the edges of the trench. If required, additional hydrostatic head can be achieved by constructing a raised work platform. The biopolymer slurry is maintained against microbial degradation by increasing the pH of the slurry and the addition of a biostat (see Section 6.3.4 for more information on biostats).

4.2.2 Vertical Hydrofracturing

Vertical hydrofracturing enables placement of PRBs deeper than that possible by conventional construction methods of open trenching or biopolymer-supported trenching. Continuous PRB treatment walls deeper than 300 feet and up to 9 inches thick can be injected into the subsurface using vertical hydrofracturing. This installation method is minimally invasive (i.e., no trenching), requiring only the drilling of 6-inch boreholes approximately every 15 feet on the planned placement line (azimuth) of the PRB.

Due to minimal site disruption and depth capabilities, vertical hydrofracturing is ideally suited to treat deep contaminant plumes and/or emplace PRBs in urban settings where surface structures and underground utilities may make surface trenching impractical. The trenchless installation method of vertical hydrofracturing produces virtually no spoils, i.e., less than 0.5% of the volume of spoils generated by trenched placement methods. Because there are no swinging backhoe booms or heavy trucks to load and haul waste, trenchless construction of a PRB can be done along a two-lane street without having to close the road.

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. With proper alignment confirmed by a down-hole camera and compass, the borehole surrounding the casing is then filled with cement grout. After the grout has cured, the fracture injection process takes place. The vertical interval for fracturing and injection is isolated in the borehole by packers and the PRB is built from the bottom up. Iron filings of medium sand size are mixed with hydroxypropyl guar (HPG) biodegradable gel, and, immediately before injection, a special enzyme and cross-linker are mixed with the HPG gel and iron filings to form a highly viscous gel containing 10 pounds of iron filings per gallon. The gel and iron filings are then injected into the casing under low pressure, causing the casing to open and creating a fracture pathway for the gel and iron filings to follow. The enzyme breaks down the gel within a few hours, reducing it to water and harmless sugars, leaving a permeable wall of iron filings.

QA/QC tools and processes are employed to ensure and verify PRB placement according to all design specifications, i.e., height, depth, thickness, and length. In addition, a hydraulic pulse interference test (Hocking 2001) is conducted before and after placement of the PRB in to verify that the PRB is in fact permeable and that its placement has not impeded the permeability of the formation.

Vertical hydrofracturing has been used to complete nine iron PRBs up to 117 feet bgs and 1200 feet in length.

4.3 Lessons Learned from PRB Design and Construction

Several lessons have been learned from the design and construction of previous PRB applications. These lessons include reduced permeability due to construction, variability in the reactive media, aquifer heterogeneity, and permeability contrasts affecting groundwater flow. These lessons result in the need to use safety factors and more preferably probabilistic design to account for heterogeneity and uncertainty. These lessons are discussed below.

4.3.1 Reduced Permeability Resulting From Construction

Certain construction methods, when used at sites where the PRB has to be installed through low-permeability layers, have the potential for smearing and reducing the hydraulic conductivity at the face of a PRB. For example, if sheet piling has to be driven through low-permeability layers during construction of a PRB, there is potential for smearing and the consequent flow impedance.

In addition, sharp permeability contrasts between emplaced and native media should be avoided, whenever possible. For example, upgradient and downgradient pea gravel zones were incorporated into several of the early PRBs in an attempt to homogenize flow into the reactive media. To conserve iron medium, some PRBs have used mixtures of pea gravel and iron in portions of the PRB where the plume is not as strong. Mixtures of coarse sand and iron may be more desirable as permeability contrasts are more diminished. Actually, given the complexity of the flow system that develops even in the simplest (most homogeneous) of PRBs, there probably should be very strong reasons for choosing anything but the simplest PRB configuration, namely, a single trench (or space) filled with a uniformly sized reactive media.

A funnel-and-gate PRB was installed at the Denver Federal Center in Lakewood, Colorado in 1996. The PRB was completed as a 1200-foot-long sheet-pile funnel with four 40-foot-wide gates. The entire length of the system, including the gate sections, was preexcavated with a trackhoe, and the excavated material placed back in the trench and the sheet-piles installed. This method left a "smear zone" of backfilled material on the upgradient side of the gates that resulted in a 10-foot groundwater mound forming upgradient of Gate 2. Recently, a row of 2-foot-diameter auger borings filled with sand and granular iron was installed along the upgradient face of Gate 2 in the smear zone. Water level measurements indicated that the smear zone had been successfully removed by this modification (Hart and May 2004).

A PRB was installed at the Lake City Army Ammunition Plant in Lake City in Missouri in 2000. Biodegradable slurry was used to support the excavation. There were problems maintaining the viscosity of the biodegradable slurry and in placement of the sand and granular iron backfill. These issues have resulted in a significant reduction of permeability of the PRB (Moylan 2003).

At former NAS Moffett Field, there has been no significant mounding upgradient of the PRB, but detailed water level measurements have indicated that groundwater flows more easily from lower- to higher-permeability zones (e.g., from aquifer to pea gravel or from granular iron to pea gravel) than from higher- to lower-permeability zones (e.g., from pea gravel to granular iron or from pea gravel to aquifer), with slightly noticeable mounding upgradient of the high-to-low-permeability interfaces.

4.3.2 Preferential Flow Pathways in the Reactive Media

Although efforts are made during PRB construction to place the reactive media as uniformly as possible, packing variability may cause preferential pathways to develop. This may not be a pronounced problem in homogeneous material with a narrow grain size distribution placed in a PRB in a method that prevents the gradation of material or reduction of the permeability of the material. However, this problem may arise when mixtures of reactive material of differing grain sizes are used (e.g., a mixture of compost, granular iron, and pea gravel). A variation in the grain size of the reactive material may inadvertently occur as a result of construction (see Section 4.3.1). Tracer tests completed on a pilot-scale PRB installed at Moffett Field in California (Gavaskar et al. 2002), at the Vapokon site in Denmark (Lai, Lo, and Kjeldsen 2004), and at the Tubingen site in Germany (Parbs et al. 2004) have all indicated the presence of preferential pathways in the reactive media. It has been suggested that aquifer heterogeneity across the face of the PRB may have contributed, at least in part, to these results (Elder, Benson, and Eykholt 2002). Monitoring data from many PRB sites show no indication that variability in the reactive media is resulting in an impact on the PRB performance.

A PRB is typically designed to capture groundwater flow (and the plume) from the surrounding aquifer by ensuring that the particle size range (and the permeability) of the reactive media is significantly greater than that of the surrounding aquifer. Although this approach is widely practiced and has some obvious advantages, there may be some unintended consequences as noted at certain sites and in more sophisticated modeling exercises. At the Vapokon, Denmark site, a lithium tracer injected in the shallower portion of the upgradient aquifer emerged from the deeper portion of the aquifer on the downgradient side (Lai, Lo, and Kjeldsen 2004). Although the authors proposed precipitation and clogging in the upgradient section of the PRB as a possible explanation for the horizontal and vertical modifications in the flow path taken by the tracer, there could be other explanations.

In a detailed three-dimensional numerical modeling exercise, Thomson and Vidumsky (2004) found that the use of a significantly more permeable reactive media in a PRB leads to a vertical hydraulic conductivity that is orders of magnitude greater than that of the surrounding aquifer. In these simulations, the PRB was observed to be redistributing heads, with relatively reduced heads in the upper portion of the reactive media (near the top of the PRB) and relatively higher heads in the lower portion of the reactive media (near the base of the PRB). As a consequence, a stagnant zone occurred in the shallower portions of the aquifer, immediately downgradient of the PRB. This effect could explain the long time (several years) that it has often taken monitoring wells on the downgradient side of the PRB to show a significant decline in contaminant levels. A stagnant zone on the downgradient side would prevent the flushing of dissolved and adsorbed contaminants in that part of the aquifer. The authors also found that the deeper portion of the plume would bypass the PRB if such localized head differences appeared. Many earlier modeling efforts (e.g., Gupta and Fox 1999) used two-dimensional models in the horizontal plane to determine flow patterns through the PRB. These two-dimensional models were unable to identify vertical flow developments. More recent modeling in the vertical plane or in three dimensions is providing better delineation of the effects of introducing a high-permeability zone (PRB) in a relatively lower-permeability aquifer. Depending on the vertical saturated thickness of the PRB, the potential redistribution of heads may merit consideration during design.

In addition to the vertical flows described above, the existence of very low groundwater flow velocities at many sites is certainly a contributing factor in the time it takes for a clean front to emerge on the downgradient side. At many PRB sites, detailed characterization has shown the natural groundwater flow velocity to be less than 1 foot/day (Gavaskar et al. 2002). This situation can lead to slow flushing of preexisting contamination in the downgradient aquifer. Slow diffusion of contaminants from less accessible pores in low-permeability lenses and/or porous grains in the downgradient aquifer may also contribute to the long time it takes for perceptible changes to occur on the downgradient side.

4.4 Summary of Lessons Learned for PRB Design and Construction

The best time to incorporate lessons learned from previous applications is when a PRB is being designed. If the PRB is later found to be functioning inadequately, modifications are possible, but can be costly.

- Thorough site characterization is the best insurance against future PRB failure. The hydrogeology, chemistry, and microbiology of the site and the reactive media need to be well understood.
- Hydrologic properties of aquifers are highly variable even at relatively "homogeneous" sites. Using average values of aquifer properties can lead to inadequate performance. Modeling using a range of values for various hydrologic parameters, such as hydraulic conductivity and gradient, is the best way to optimize the design for a PRB.
- Seasonal variations in groundwater flow and temperatures can affect the performance of the PRB and need to be accounted for in the design.
- Despite their limitations, water level measurements are usually the best way to determine flow at prospective PRB sites. These measurements can be supplemented with the selective use of sensors at some highly heterogeneous sites.
- Tracer tests provide the best flow information but are somewhat more difficult and expensive.
- Even with the best characterization, performance of a PRB may sometimes turn out to be different from that expected. In many cases, performance problems can be corrected through appropriate modifications.
- Variability in packing of the reactive media or aquifer heterogeneity may lead to preferential pathways in the iron.
- When ZVI is used as the reactive media in a PRB, reactivity and hydraulic performance decline over long periods of time (probably several years or decades at many sites).
- Precipitation of native inorganic constituents such as calcium and carbonates in groundwater are the primary cause of loss of reactivity and porosity in an iron PRB.
- The level of total dissolved solids and magnitude of the groundwater flow through the PRB are the main determinants of the level of precipitation in iron PRBs. Consequently, a PRB at a site with high-TDS groundwater could have a longer life if the groundwater flow velocity at the site is low (mass flux of the dissolved solids through the iron is low).
- Indications from studies are that the reactivity of the iron starts declining before precipitates have built up to the level where the hydraulic performance of the PRB is affected.
- Preliminary estimates for the life of an iron PRB, based on field investigations and laboratory studies, range 10–30 years or more.
- PRB longevity has implications for cost projections used for comparison with conventional pump-and-treat systems. If a PRB can perform acceptably longer, regeneration and replacement costs get pushed into distant years, reducing the present value of the future cost of a PRB.
- Microbial communities have been found to exist in iron PRBs but appear to be concentrated near the upgradient edge, where pH and Eh conditions are more benign.
- Anaerobic microbial populations, especially metal reducers and sulfate reducers, have been identified in field iron PRBs.
- Farther along the flow path within the iron and in the downgradient aquifer, the microbial biomass may be different than the native material upgradient. The implications of this effect for downgradient natural attenuation of residual contamination are unclear. It is possible that groundwater emerging from the PRB may have to travel farther downgradient before natural biodegradation resumes. This topic is addressed further in Section 5.3.

5. PERFORMANCE ASSESSMENT

Performance assessment refers to evaluating a system to determine whether the design objectives are being met. The scope of this section includes an evaluation for iron PRBs focusing on the following components:

- hydraulic assessment
- geochemical assessment
- microbiological assessment

These criteria apply to both iron and non-iron PRBs. The assessment information for iron PRBs has a 10-year record of documentation. This section therefore focuses primarily on iron PRBs. Some additional information on the performance assessment of non-iron PRBs can be found at www.rtdf.org.

5.1 Hydraulic Assessment

The hydraulic performance of PRBs must be continually evaluated to monitor for any potential changes in the groundwater hydraulics that may affect the performance of a PRB. The hydraulics of a PRB can change over time due to several factors, including precipitation of minerals within the PRB and reduction of the hydraulic conductivity of the reactive media. Other external factors can affect the hydraulic performance of a PRB, including the addition or shutdown of groundwater extraction in the area of the PRB, changes in regional groundwater flow (excessive rainfall, drought, etc.), and changes in land use (e.g., development of a property which reduces or changes the infiltration and the groundwater flow). The hydraulic performance of a PRB must be monitored to identify any potential changes in plume capture and take corrective measures if required.

Tracer tests provide the most reliable flow information and have been conducted at many PRB sites, including former NAS Moffett Field (Gavaskar et al. 1998), Coast Guard Site Elizabeth City (Wilkin and Puls 2003), Vapokon Site in Denmark (Lai, Lo, and Kjeldsen 2004), and the Tubingen and Rheine sites in Germany (Parbs et al. 2004). However, successful tracer tests can be difficult and relatively resource-intensive to conduct. In general, water level measurements, with all their limitations, are the most cost-effective tool for characterizing the bulk flow at a prospective PRB site. Most in situ or down-hole flow sensors appear to be relatively accurate but provide point flow information. The magnitude and direction of flow from point to point, even at different depths in the same monitoring well, can be highly variable and can make interpretation difficult. At a site with significant heterogeneities, flow sensors can sometimes provide valuable information that supplements water level data.

5.2 Geochemical Assessment

For most types of PRBs, the geochemistry of the groundwater changes as the groundwater flows through the PRB due to reactions that occur in and adjacent to the PRB. The change in geochemistry may be part of the treatment (e.g., precipitation of metal sulfides for removal of trace metals) or a result of another treatment process (e.g., degradation of VOCs with granular iron, which results in a change in the geochemistry of the groundwater and precipitation of minerals). Assessment of the geochemistry can provide primary evidence that the treatment process is working (e.g., the removal of dissolved metals) or secondary evidence that the treatment process is working (e.g., a change in geochemistry indicates that the groundwater is flowing through the granular iron). Monitoring the geochemistry of the groundwater also provides data to assess the longevity of most PRBs.

5.2.1 Evidence from Changes in Groundwater Chemistry

The first evidence that granular-iron PRBs were affecting more than just the target contaminants came from groundwater monitoring of the influent and effluent water from iron PRBs, both in field applications and in treatability test columns. Table 5-1 illustrates the changes in common groundwater constituents during flow through the iron medium in a PRB installed at former NAS Moffett Field (Gavaskar et al. 2002). Further evidence of the changes to groundwater composition can be found in Li, Mergener, and Benson (2005). A number of sites are listed in table format within the paper indicating the changes that occur to groundwater as it moves through the PRB. These constituent losses between influent and effluent indicate that inorganic species are depositing on the iron surfaces.

Table 5-1. Groundwater sampling of influent to and effluent from the iron at the PRB

	Ca	**Mg**	**F**	**Alkalinity**	**Sulfate**	**Silicate**	**TDS**
Upgradient pea gravel, mg/L	170	66	0.11	370	410	20	810
Downgradient pea gravel, mg/L	6.2	0.18	<0.05	44	5	9	92
Change (reduction), %	96	>99	>55	88	99	55	89

For example, at the Vapokon site in Denmark, Lo, Lai, and Kjeldsen (2004) estimated that about 1% of the original porosity in the granular-iron PRB was being lost every year due to deposition of precipitates. A lithium tracer test conducted at this site appears to indicate that after four years of operation, mineral precipitation and the consequent changes in permeability were already causing groundwater to move through preferential pathways through the iron. At the Elizabeth City site, Wilkin and Puls (2003) estimated that iron medium porosity in the PRB was being lost at the rate of 1%–4% of the original porosity per year. At these sites, the porosity losses appeared to be unevenly distributed through the PRB. Whereas approximately 7% of the original porosity was lost near the upgradient edge of the iron in the Elizabeth City PRB after five years of operation, less than 1% of the original porosity was lost near the downgradient edge. At the Denver Federal Center site, the maximum porosity loss in the PRB was estimated at 17% of the original porosity, after five years of operation.

5.2.2 Evidence from Geochemical Modeling

Reaction path modeling has been used to simulate reactions between iron and groundwater to understand precipitation of mineral phases inside a PRB. The objective of the modeling exercise was to develop a better understanding of the overall process of precipitate formation. In reaction path modeling, a small amount of iron is allowed to dissolve, then equilibrium is calculated using thermodynamic constraints. The size of the increments can be made arbitrarily small so that the evolution of the system can be observed in small steps. For the reaction path approach to be valid, the aqueous species and solid phases (other than iron) must equilibrate quickly, relative to the time scale of process. In a real system, the appropriate time scale is the residence time of the water inside the reactive media, which is typically several hours or days, depending on thickness and flow rate. Reactions between common ions and ZVI need to be considered in the context of kinetics and the relative rates at which flow and reactions occur in PRBs. The operative time in these reactions is not necessarily equal to the average residence time (Li, Mergener, and Benson 2005).

For example, modeling runs were conducted to simulate stepwise equilibration of former NAS Moffett Field groundwater with ZVI (Sass et al. 2002). The geochemical modeling code PHREEQC was used to perform the simulations. ZVI was allowed to dissolve in increments of 1 mmole. After each increment, the model calculates whether the solution is oversaturated with respect to any solid phases in the thermodynamic database. Examples of compounds likely to precipitate from solution include carbonates and hydroxides such as calcite, brucite, $Fe(OH)_2$, and green rusts. Names and formulas of potential phases are listed in Table 5-2.

Table 5-2. Formulas for mineral phases with favorable precipitation kinetics when groundwater contacts iron

Mineral	Formula	Mineral	Formula
Aragonite	$CaCO_3$ (*ortho*)	Mackinawite	FeS
Brucite	$Mg(OH)_2$	Magnesite	$MgCO_3$
Calcite	$CaCO_3$ (*rhom*)	Magnetite	Fe_3O_4
Ferrous hydroxide	$Fe(OH)_2$	Marcasite	FeS_2
Ferric hydroxide	$Fe(OH)_3$	Siderite	$FeCO_3$
Green rust I	$3Fe(OH)_2 \cdot Fe(OH)_2Cl \cdot nH_2O$	Tobermorite-14Å	$Ca_5Si_6H_{21}O_{27.5}$
Green rust IIa	$4Fe(OH)_2 \cdot 2Fe(OH)_3 \cdot [SO_4 \cdot 2H_2O]$	Tobermorite-11Å	$Ca_5Si_6H_{11}O_{22.5}$
Green rust IIb	$4Fe(OH)_2 \cdot 2Fe(OH)_3 \cdot [CO_3 \cdot 2H_2O]$	Tobermorite-9Å	$Ca_5Si_6H_6O_{20}$

5.2.3 Evidence from Reactive Media Coring in Field PRBs

A number of field studies (Wilkin and Puls 2003, Sass et al. 2002, Phillips et al. 2003) have now shown that the strongly reducing (low-ORP) and high-pH conditions created when ZVI contacts groundwater cause several inorganic constituents to transfer from the solution phase onto the iron. This event can lead to formation of molecular or particulate films on the iron surfaces. Calcium carbonates, iron carbonates, and iron hydroxides are among the myriad of insoluble mineral species that form and deposit on the iron (see Table 5-2). Not only is iron mass consumed in these reactions, but the formation of potentially passivating films on the iron surfaces can reduce the reactivity of the remaining iron mass. The implication of this observation is that the reactivity of the PRB can potentially decline, even while considerable iron mass still remains in the PRB. Subsequent studies have shown that some of the corrosion films that form on the iron surface are themselves reactive and degrade certain contaminants (Wilkin and Puls 2003). Magnetite and carbonate green rust, for example, can conduct electrons and are not expected to hamper iron reactivity with groundwater constituents. Many other precipitates do not permit electron transfer and may be expected to inhibit iron reactivity. In the longer term (several years of exposure to groundwater), the reactivity of the iron medium does appear to decline (Gavaskar et al. 2002).

Typically, iron cores collected after a few years of field operation of the PRBs have been analyzed by specialized methods, such as X-ray diffraction to determine crystalline mineral phases and scanning electron microscopy to identify specific compounds on the iron grains. At Moffett Field, Elizabeth City, and several other sites where detailed examination of the used iron medium has been conducted, the types of precipitates identified have been relatively similar and have consisted primarily of carbonates, hydroxides, sulfides, oxides, and silicates of calcium, iron, and, to some extent, magnesium.

5.2.4 Assessment of Longevity

To date, no PRB has failed due to loss of permeability and reactivity as a result of mineral precipitations. However, it is recognized that all PRBs show a gradual decrease in performance from the time they are installed. Despite all the efforts in the field and in modeling studies to evaluate the geochemistry of iron-groundwater interactions, it is difficult to obtain more than just a qualitative estimate of the type and degree of precipitation and its effect on the reactivity and hydraulic performance of the iron medium. Even when the amount of precipitate formation can be deduced from detailed investigations at sites such as Denver Federal Center and Elizabeth City, by estimating the losses of inorganic constituents from groundwater flowing through the PRB at these sites, it is unclear how much precipitation would have to occur for the performance of the iron to be noticeably affected. Therefore, as part of an ESTCP-funded study, an accelerated laboratory simulation of the long-term operation of iron PRBs at Moffett Field and Lowry AFB was conducted in a one-year long effort (Gavaskar et al. 2002).

Accelerated long-term column tests were run to simulate several years of operation of the PRBs at former NAS Moffett Field and former Lowry AFB. The columns were filled with the same iron used in the field PRBs, and groundwater was obtained on a monthly basis from local site representatives. The objective was to observe the kind of aging of the iron that would not be visible in the field PRBs for many years in the future and get some idea about the change in performance of the iron over time (represented by pore volumes of flow).

About 1300 pore volumes of groundwater obtained from the site was run through the column that was packed with iron from Peerless Metal Products, Inc. (the same iron as that used in the field PRB). Exposure of the iron to 1300 pore volumes of water is equivalent to approximately 30 years of flow through the field PRB at former NAS Moffett Field, assuming a nine-day residence time in the field PRB. The column setup for the former Lowry AFB PRB simulation was conducted in exactly the same manner as the former NAS Moffett Field column simulation. Approximately 1300 pore volumes of groundwater obtained from former Lowry AFB was obtained and run through the column adequately containing Master Builder's iron. The 1300–pore volume of flow through the column simulates approximately 80 years of flow through the PRB, based on an estimated groundwater velocity of 0.2 feet/day. This velocity estimate is subject to considerable uncertainty, but the simulation provides a means of studying expected long-term trends.

The column tests show that, over the 1300 pore volumes of flow that the iron was exposed to, the half-life of TCE increased approximately by a factor of 2 in the former NAS Moffett Field column and by a factor of 4 in the former Lowry AFB column. In other words, iron reactivity declined by a factor of 2 in the Moffett Field column and by a factor of 4 in the Lowry AFB column. While some effects of aging may be intrinsic to the iron itself or to the manufacturing process, other differences may be due to the inorganic content of the water and the subsequent precipitation of dissolved solids. Former NAS Moffett Field has groundwater representative of a site with a moderate level of dissolved solids (500–1000 mg/L), and former Lowry AFB is representative of a site with relatively high levels of dissolved solids (>1000 mg/L). Consequently, former Lowry AFB showed a greater decline in reactivity over the same period of exposure to groundwater as the former NAS Moffett Field column. As a rough approximation, it was estimated that the two PRBs would lose about half their reactivity in 30 years. The effect of a higher level of dissolved solids in the groundwater at Lowry AFB, compared to that at Moffett Field, is offset by slower groundwater movement.

Several other researchers have studied the potential effects of precipitates on iron PRB performance. For example, Wilkin, Sewell, and Puls (2001) state that “upgradient groundwater chemistry and flow rate appear to be the main factors that control the rates (and type) of mineral precipitation.” In Korte 2001, sites with high levels of carbonate and sulfate are identified as being potentially more susceptible to clogging than groundwater with low TDS. Similar concerns with respect to high TDS sites are expressed by Benner, Blowes, and Molson (2001). Specifically, these concerns involve the potential for these precipitates to reduce the activity of the iron and/or to reduce the permeability through pore clogging. Zhang and Gillham (2005) showed in a long-term column study that calcium carbonate precipitation occurs as a moving front through the iron. The maximum loss in porosity was about 7% of the initial porosity, followed by no further accumulation. These general concerns should be viewed in the context of documented field performance.

The geochemical constituents of the groundwater appear to affect the reactivity of the iron on long-term exposure to groundwater. The rate of decline in iron reactivity over time is dependent on the native level of certain dissolved solids (e.g., alkalinity, sulfate, calcium, magnesium, and silica) in the groundwater. The rate of decline in iron reactivity over time also is dependent on the number of pore volumes of groundwater flowing through the PRB. Therefore, sites with a higher groundwater flow rates are likely to encounter higher rates of decline compared to similar sites (with similar levels of TDS) with lower groundwater flow rates. Over the long term, the PRB is likely to be passivated before the entire mass of ZVI is used up unless some way of regenerating or replacing the reactive media is developed and implemented.

The porosity and permeability of the iron (and hence the residence time) was not considerably affected over the duration of the test, as indicated by a bromide tracer test conducted in the column after 1300 pore volumes of flow. Therefore, the reactive performance of the iron is likely to decline much faster than any potential decline in long-term hydraulic performance. The progressive decline in iron reactivity over time indicates that the residence time required to meet groundwater cleanup targets also will be progressively higher in the long term. One way of ensuring that sufficient residence time is available in the future is to incorporate a higher safety factor in the designed flow-through thickness of the reactive media in the PRB. Therefore, there is a tradeoff between current capital investment (construction of a thicker PRB) and future costs (earlier regeneration or replacement of the PRB).

5.3 Microbiological Assessment

Field investigations, including examinations of iron cores after several months of PRB operation at the Moffett Field (Gavaskar et al. 1998), Elizabeth City, Denver Federal Center (Wilkin and Puls 2003), and Oak Ridge (Gu et al. 2002) sites, show that microbial activity does occur in granular-iron PRBs. Microbial growth appears to be stronger in the iron near the upgradient iron-aquifer interface, where anaerobic conditions have been established, but the pH is not as strongly alkaline as it is farther downgradient in the iron. Strongly alkaline pH (up to 10 or 11 log units) farther downgradient in the iron could be inhibiting for microbial growth. Although at many of these PRB sites the total biomass in the upgradient iron was not significantly higher than that in the upgradient aquifer, 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). 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 the buildup observed at other sites, such as Elizabeth City. The higher biomass buildup in this gate was attributed to low-flow conditions (caused by a smear zone across the face of Gate 2, see Section 4.3.1) and high sulfate concentrations in the groundwater. Concentration of iron sulfide precipitates was also higher in Gate 2.

The recent preference for using biopolymer slurry (guar gum) to support the trench during PRB construction may provide stimulus for microbial growth in the reactive media, or immediately downgradient, as the guar gum acts as an electron donor source for microbial growth. It is unclear yet whether microbial growth in the iron helps or hurts the operation of the PRB in the long term. Although uninhibited microbial growth in the iron could ultimately impact performance, as biofilms reduce the reactivity of the iron and impede flow, some microbial activity may aid in the transformation of contaminants. In the PRB at the Carswell site, where biopolymer slurry was used in the construction of a 1126-foot-long PRB, enhanced microbial activity was noticed along Transect 2 (Crane et al. 2004). Interestingly, neither the type of microbial community nor the level of microbial activity was consistent along the length of the PRB. In the transect where microbial activity was enhanced, elevated levels of cDCE and VC were found on the downgradient side during early sampling events. The accumulation of these by-products of anaerobic reductive dechlorination is indicative of biotic, rather than abiotic (iron-driven) degradation of TCE, the primary contaminant at this site. The microbially produced cDCE and VC (lower oxidation state compounds) are not as efficiently reduced by iron as is TCE. Thus, the overall efficiency of the PRB was reduced, at least temporarily. In later sampling events at Carswell, elevated cDCE and VC levels on the downgradient side appeared to subside.

On the other hand, for certain other types of contaminants, microbial growth in iron PRBs may actually help. For example, heavy-metal contaminants in groundwater could precipitate out as sulfide under the strongly anaerobic conditions that stimulate sulfate-reducing microbes. In fact, reactive media other than iron have been used in certain PRBs, primarily to stimulate microbial growth and biodegradation of target contaminants. For example, mulch was used in a PRB to stimulate microbial activity and degrade TCE in groundwater at Offutt AFB, Nebraska.

It is also unclear how microbial stimulation progresses or is suppressed in the downgradient aquifer. This fact has implications for downgradient natural attenuation that is claimed when the groundwater exiting the PRB does not meet target cleanup levels at a site. 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 electron donor 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. The groundwater may have to move farther away on the downgradient side before it mixes with more of the native groundwater and reverts to microbial activity comparable to that in the upgradient aquifer.

6. REGULATORY CONSIDERATIONS

This section describes regulatory permitting considerations associated with PRB design, construction, and closure and provides state highlights of specific permitting concerns and requirements. This section also describes sampling and monitoring requirements for purposes of compliance with regulatory standards, PRB performance (hydraulic capture and contaminant residence time), and PRB longevity (long-term changes in reactivity). Topics discussed include monitoring program objectives, monitoring locations, sampling methods, frequency, and parameters.

6.1 Permitting

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. For instance, many state or local agencies require permits for well installation and destruction. In some cases, a permit may be required for construction in a sensitive area, such as adjacent a wetland. Following is a list of key potential regulatory permits that may be required for a PRB and a brief explanation of each.

- underground injection control (UIC)
- National Pollution Discharge Elimination System (NPDES)
- RCRA
- air quality control
- other discharge/construction permits

In addition to regulatory permits, PRB approval may occur through different regulatory mechanisms. The approval mechanism (e.g., approval letter, cleanup order, etc.) often depends on the regulatory program/process under which the site cleanup is managed (e.g., RCRA, state Superfund, etc.). Various regulatory programs may require submittal of a work plan, corrective action plan, remedial action plan, feasibility study, etc.

6.1.1 Underground Injection Control

UIC is a federal program that may be delegated by USEPA to authorized states. The UIC program is intended to regulate the disposal (i.e., injection) of wastes into the subsurface via a well. Furthermore, the program defines various classes of wells, and permits the injection activity based on the well category.

UIC permits are not typically required for PRBs since most PRB emplacement methods do not meet the definition of a well under the UIC program. Furthermore, when the reactive media emplaced in the ground is in solid form, a UIC permit is not needed. However, if the reactive media is installed by a high-pressure jetting technique or by vertical hydraulic fracturing, a permit may, in some circumstances, be required. The need for a permit under these conditions will be a state-by-state determination. If USEPA has not delegated the UIC program to the state, the regional USEPA office makes the determination. A review of the pertinent regulations should be conducted during initial design stages of the project.

6.1.2 National Pollution Discharge Elimination System

NPDES permit authority resides within the federal Clean Water Act. NPDES permits are required whenever a potentially harmful discharge is made to a surface water body, such as a stream, river, lake, bay, or the ocean. The primary aspect of a PRB that could require an NPDES permit is when excess water or liquid from the installation method is generated or if storm water could carry pollutants or sediment into water bodies.

If it is necessary to dispose of the liquid (e.g., displaced groundwater, excess slurry, etc.) to a nearby creek or other water body, then an NPDES permit from the state is required. Additionally, many states now require storm water pollution prevention plans, which require use of best practices to manage storm water discharges at construction sites 1 acre or larger.

6.1.3 Resource Conservation and Recovery Act and State Superfund Programs

In some cases PRBs treat groundwater that is contaminated by listed (i.e., RCRA) hazardous wastes. Since PRBs are considered an in situ treatment technology, their deployment would 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, would have to 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.

It should be noted that 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, etc.) of the applicable regulations. In these cases a work plan/remedial design would be 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.

6.1.4 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.

6.1.5 Other Discharge/Construction Permits

In some cases, states may require a permit that focuses on the emplacement of a foreign material into the subsurface that can affect groundwater or surface water quality. For example, the land application of wastes generated from PRB construction or monitoring (i.e., displaced groundwater, excess slurry, monitoring well purge water, etc.) as well as the placement of iron reactive media into the subsurface could require a permit. In most cases, this activity would require a state permit to ensure the land discharge is appropriate and not harmful to human health or the environment.

In addition to these “discharge” type permits, the location of construction activities may itself trigger the need for a site-specific permit for building or construction, wetland/habitat encroachment, etc. Examples include construction of a PRB near a wetland or surface water body, near a building or other structure, in a traffic corridor, or simply in an urban area where nuisance issues may arise during PRB construction. If wetlands encroachment, destruction, or other impacts are involved, a federal permit is usually required from the U.S. Army Corps of Engineers. In such cases, mitigation measures and a corresponding certification by state regulatory agencies are also necessary.

6.1.6 State Highlights

Following are examples of state-specific permits that have been required for some PRB installations. These examples do not constitute all state permits that may be required in all instances, nor will these permits necessarily be required in every instance. The state regulatory agency should be contacted for permitting requirements prior to design and construction activities.

6.1.6.1 California

In California, some Regional Water Boards may issue Waste Discharge Requirements (WDRs) to ensure that the PRB material (solid or liquid) will not cause impairment of groundwater or surface water beneficial uses as it dissolves, reacts, or migrates. WDRs are more likely to be issued when liquid amendments are circulated in groundwater as with a bio-barrier–type deployment. Some Regional Water Boards may require WDRs to address potential effects caused by iron, iron corrosion products, and non-iron PRB materials, particularly those that do not have a similar demonstrated track record of full-scale use at other sites. For more information on permitting for PRBs, contact Alec Naugle at 510-622-2510 or anaugle@waterboards.ca.gov.

You can also find additional information on the San Francisco Bay Water Board Web site at www.waterboards.ca.gov/sanfranciscobay and the California State Water Board Web site at www.waterboards.ca.gov.

6.1.6.2 New Jersey

In New Jersey, the New Jersey Pollutant Discharge Elimination System regulations (N.J.A.C. 7:14A-1) govern discharges to groundwater of the state. The installation of a PRB and in particular the placement of reactive media into the subsurface may require a permit under these regulations to protect the groundwater from any potential discharge. For more information on New Jersey NJPDES discharge to groundwater permits, see the following Web site: www.nj.gov/dep/srp/regs/guidance.htm#dgwtechm.

6.1.6.3 Virginia

In Virginia, a PRB was built at a Superfund site, so the state followed the federal regulations for Superfund sites. Under these regulations, permits are not required, but sites must be in compliance with the applicable or relevant and appropriate requirements (ARARs) of all environmental laws.

ARARs include any standard, requirement, criterion, or limitation under any federal environmental law, such as the Toxic Substances Control Act, the Safe Drinking Water Act, the Clean Air Act, and RCRA. This would be in addition to the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), the federal Superfund law.

Also included is any promulgated standard, requirement, criterion, or limitation under a state environmental or facility-siting law, including those contained in USEPA-approved programs, that has been identified by the state to USEPA in a timely manner. Virginia has state laws equivalent to most of these federal laws. Finally, any local laws or regulations would apply. For more information, contact Thomas Modena at 804-698-4183 or tdmodena@deq.virgina.gov.

6.1.6.4 Louisiana

In Louisiana, the PRB work plan is usually reviewed and, if adequate, is approved by the Louisiana Department of Environmental Quality Remediation Services or Environmental Technology Division. An approvable work plan should include considerations for permitting requirements. Other agencies may be involved depending on the scope of the work plan. Local cities and municipalities may have requirements for construction permits. Discharges and waste generated by the PRB installation process must be avoided, but if they occur, they must be handled and disposed of appropriately in accordance with local and state regulations. Discharges to waters of the state, both surface and groundwater, must be avoided or, if unavoidable, permitted through the appropriate agency. Any wells installed must be constructed in accordance with Louisiana Department of Environmental Quality regulations and registered with the Louisiana Department of Transportation and Development. For more information, contact Douglas Bradford at 225-219-3420. The Louisiana Department of Environmental Quality Web site can be accessed at www.deq.louisiana.gov/.

6.1.6.5 Georgia

In Georgia, an underground injection permit is required unless the injection is part of a remediation plan approved in a permit or other enforceable agreement by the state Environmental Protection Division. In any event all requests for injection authorization are coordinated with the state's UIC program.

6.2 Monitoring

Monitoring of conditions in and around PRBs should begin once installation is complete. Typically, monitoring in one form or another will be necessary as long as the groundwater contaminants pose a significant concern. The key lines of evidence targeted by most monitoring programs include 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.

6.2.1 Monitoring Programs and Objectives

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.

6.2.1.1 Compliance Monitoring

Compliance monitoring is typically driven by regulatory requirements. Cleanup or compliance standards for contaminants in groundwater are usually established through a cleanup order or other regulatory mechanism. This may occur before, during, or after PRB installation, depending on the site maturity and goals of the PRB. Compliance points are usually established at the same time and describe where in the aquifer the cleanup standards apply. In some cases, this may be immediately downgradient from the PRB, while in others it may be some distance downgradient, such as at the property boundary.

At most sites, the PRB is placed within the contaminated plume rather than at the leading edge of the plume. In such cases it could take months to years for downgradient monitoring wells to show water quality improvements. Therefore, when a PRB is installed within a contaminant plume, additional wells should be installed within the PRB itself to monitor contaminant removal. If the PRB is too thin for this approach, monitoring wells should be located immediately adjacent to the downgradient edge of the PRB.

Lessons learned from previous PRB deployments have implications for post-construction monitoring of the PRB. One such implication is that it may take years before site owners can verify how well the PRB is working. Development of stagnant zones in the shallow portions of the reactive media and downgradient aquifer could slow the flushing of contamination (most PRBs are installed inside the plume boundaries and often have contamination present on the downgradient side). Therefore, even when residence time requirements in a PRB are being met for most of the water flowing through the PRB, it may be years before any obvious improvement in downgradient water quality becomes apparent during monitoring. This has been the experience at most PRB sites, including Elizabeth City (Wilkin and Puls 2003), Moffett Field (Gavaskar et al. 2002), and Sunnyvale (Warner and Sorel 2003), as well as in modeling studies undertaken by Simpkin and Schneider (2004) and Thomson and Vidumsky (2004). The challenge for regulators and site owners is how to interpret persistently elevated concentrations of contaminants in the downgradient aquifer. Are persistently elevated downgradient concentrations following PRB construction due to insufficient residence time (inadequate flow-through thickness of the PRB or presence of preferential pathways in the reactive media), or are they due to inadequate flushing of preexisting contamination in the downgradient aquifer? Slow diffusion of dissolved or adsorbed contaminants from more inaccessible pores in the downgradient aquifer could be another reason that it takes so long for water quality improvements to occur on the downgradient side.

Given the time lag in achieving downgradient water quality improvements, regulators and site owners should also consider establishing a temporary compliance point within the reactive media or near the downgradient edge of the PRB, for some period of time following installation. This approach would allow better evaluation of the PRB’s ability to treat groundwater contaminants to established regulatory standards. The location of the compliance points can be reevaluated as the downgradient residual contamination dissipates. One reason to establish compliance points farther downgradient is to accommodate a natural attenuation solution for residual groundwater contaminants in the downgradient area that predate installation of the PRB.

6.2.1.2 Performance Monitoring

Performance monitoring is generally focused on the PRB system itself rather than on the entire site or the compliance boundaries. The performance monitoring program should be designed to verify proper installation of the PRB and identify any changes in the system that would affect treatment effectiveness. In particular, performance monitoring should focus on evaluating PRB longevity (i.e., long-term reductions in permeability and reactivity due to factors such as precipitate deposition and loss of the reactive media) and hydraulic capture of the PRB system. The performance monitoring program should be designed to detect changes in reactivity, permeability, and contaminant residence time within the reactive zone; short-circuiting around, under, or over the PRB; or leakage through funnel walls, if present.

6.2.2 Monitoring Well Placement and Construction

The location of monitoring wells is a critical element in determining whether the PRB is meeting compliance and performance criteria. Although monitoring well locations must be evaluated on a site-by-site basis, in general, wells should be located upgradient and downgradient and, if possible, within the PRB. In addition, wells at each end of the PRB are necessary to verify hydraulic capture and evaluate potential plume by-pass, particularly if impermeable funnels are used to intercept and control groundwater flow. Figures 6-1 and 6-2 illustrate idealized monitoring networks for continuous and funnel-and-gate design PRBs, respectively. Note that site-specific conditions should always dictate the placement of monitoring wells.

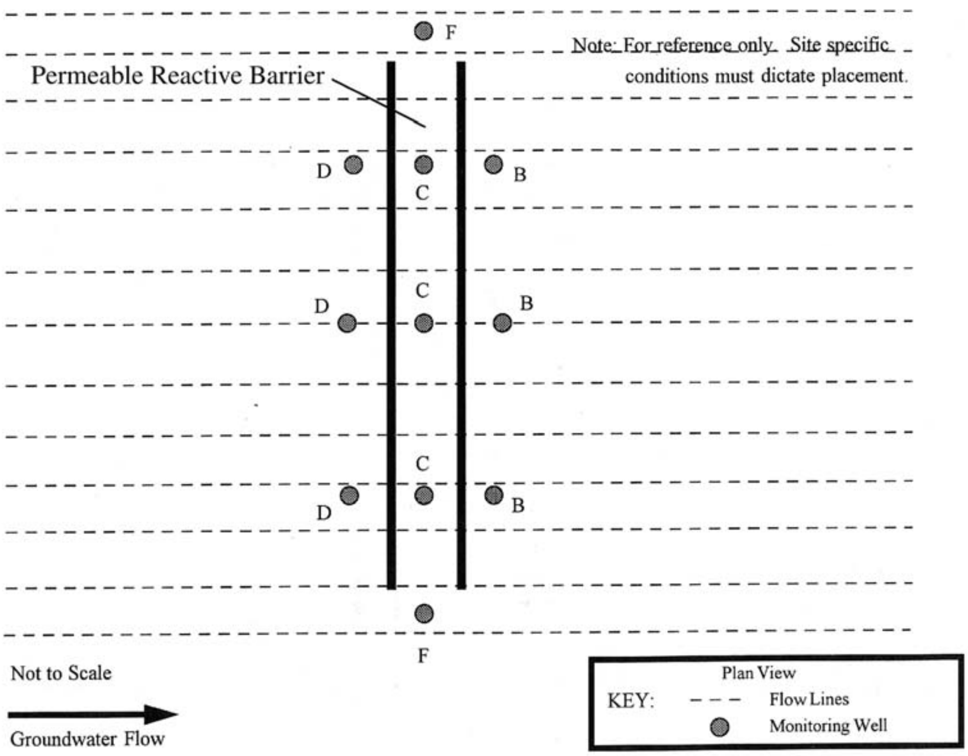


Figure 6-1. Continuous permeable reactive barrier monitoring diagram.

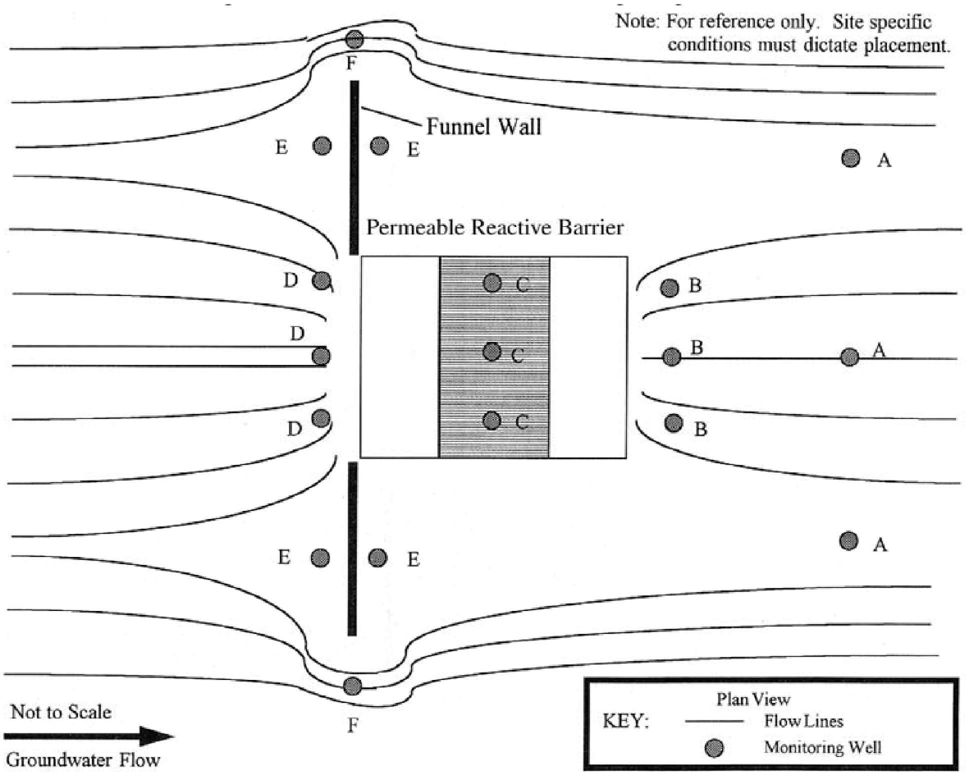


Figure 6-2. Funnel-and-gate monitoring diagram.

Key to Figures 6-1 and 6-2:

A. Determine downgradient groundwater quality.
B. Ensure treatment effectiveness and determine groundwater flow rate.
C. Determine treatment effectiveness, groundwater flow rate and reactive media fouling (Note: Wells B, C, D are located along lines through the reactive media to monitor flow paths. Monitoring wells are placed at both the sides and the middle of the reactive media to monitor differences in flow.
D. Determine upgradient concentration of contaminants, the potential for reactive media fouling, and groundwater flow rate.
E. Determine leakage, underflow, or overflow across the funnel wall.
F. Ensure plume capture and determine whether contaminant is migrating around the funnel wall.

Individual state requirements for monitoring wells vary and may limit alternatives for well design and construction. Therefore, state-specific monitoring well requirements should be considered during well design and construction.

6.2.2.1 Aquifer Monitoring Wells

When considering the number and location of wells, it is important that all aspects of the contaminant plume be well characterized. For example, contaminant type, distribution, groundwater gradient, groundwater velocity, geologic heterogeneities, etc. all play a role in determining the appropriate locations and number of monitoring wells. The number and location of wells must be sufficient to quantify reductions in contaminant levels, as well as changes in flow rates and direction over time, so as to provide a measure of performance of the PRB. Developing groundwater flow models (e.g., Elder, Benson, and Eykholt 2001) may be useful for evaluating monitoring well locations.

To ensure consistency of results and compliance with cleanup standards, monitoring wells should be screened to coincide with the highest level of contamination in the aquifer. Furthermore, in the vicinity of the PRB, wells should be screened at the same depth interval. In some instances, installation of multilevel monitoring wells may be appropriate. Selection of monitoring well screen intervals and lengths should consider the following:

- site geology,
- aquifer thickness,
- aquifer flow (horizontal and vertical) characteristics,
- presence of multiple aquifers,
- nature of contamination,
- construction details of the PRB, and
- conformance with state guidance and regulations.

Monitoring wells should be sized just large enough to accommodate the sampling equipment. Smaller wells, such as 1- or 2-inch-diameter wells, are preferred to minimize disruption of the flow field in and around the PRB during sample collection.

6.2.2.2 Wells Within the PRB

Monitoring wells installed within a PRB are usually designed differently from aquifer monitoring wells because they are designed to support a performance monitoring program rather than compliance monitoring. In general, PRB wells do not include a sand pack since it is preferable to have the well screen in direct contact with the reactive media. This feature tends to minimize disruption of the groundwater flow field within the PRB and alteration of groundwater geochemistry related to PRB functioning.

PRB monitoring wells should also be constructed using smaller diameter (1- or 2-inch) polyvinyl chloride casing to limit purge volume and disruption of the groundwater flow field within the PRB. Well diameter must be sufficient to accommodate sampling equipment. For funnel-and-gate configurations, wells can be suspended in the excavation prior to backfilling. For other configurations, wells may be pushed into the reactive media. Wells may be long-screened or may be nested or located in clusters with short screen intervals for sampling discrete areas and various depths. Installation of multilevel, nested, or cluster wells is generally recommended since there is the potential for heterogeneities to develop within the PRB due to compaction of the reactive media and development of corrosion products or precipitates that can reduce porosity and permeability. It is also important that some wells be screened below the bottom of the reactive media to monitor for potential contaminant migration beneath the wall.

6.2.3 Sampling Methods

Sampling within and around a PRB requires special techniques to collect representative samples. For groundwater sampling within the PRB, methods that ensure consistent groundwater residence times and flow rates and that minimize disruption of the groundwater flow field during sampling and between sampling events are recommended. Low-flow sampling and purging techniques (see Puls and Barcelona 1996) and passive sampling devices such as passive diffusion bag samplers (see discussion below) are recommended where appropriate to accomplish these goals. Since the concentration of compounds can change significantly in a PRB over a distance of a foot, the volume of water removed during purging and sampling must be assessed to ensure a representative sample is being collected (e.g., the water is collected from the PRB and not the upgradient or downgradient aquifer).

Other recommended sampling alternatives include use of dedicated submersible pumps, packers, or other specialized sampling devices that reduce the purge and sample volume and control flow rate. There are currently no guidelines on the amount or rate at which groundwater should be purged; therefore, these parameters should be determined on a case-by-case basis.

Conventional purging and sampling can be used on monitoring wells positioned away from the reactive media, provided the purging and sampling will not affect groundwater flow through the reactive media. In areas where the groundwater flow is tidally influenced, sampling events should be scheduled accordingly.

Field parameter measurements should be conducted with a flow-through cell and monitoring instruments for continuous measurement to minimize interferences associated with the introduction of oxygen into the sample. Field instruments can also be employed as down-hole probes inside wells for collection of field parameter data. Down-hole probes can be inserted during sampling, or they can be left in a well on a continuous basis (Sivavec et al. 2001).

Diffusion Bag Samplers

Increasingly, polyethylene diffusion bag (PDB) samplers are being used for site characterization and monitoring (see Vroblesky 2001). PDB samplers are low-density polyethylene bags containing deionized water, used to collect water samples in groundwater wells for laboratory analyses of VOCs. PDB samplers are passive devices, relying on the movement of groundwater from the aquifer or water-bearing zone through the screen or open interval of a well. VOCs in groundwater diffuse across the bag material until concentrations within the bag reach equilibrium with those in the surrounding groundwater.

PDB samplers cannot be used to sample for all contaminants; metals and other inorganic compounds will not diffuse across the membrane. However, many VOCs have shown good diffusion characteristics in laboratory tests and are recommended for sampling with PDBs. For these common contaminants, PDB sampling is as valid as low-flow and other conventional methodologies and is often substantially less expensive over the life of a long-term monitoring (LTM) program. Cost savings in the range of 40%–70% have been achieved by replacing other sampling methods with PDB sampling. PDB samplers can also be an effective tool to characterize vertical VOC stratification in the screened or open intervals of wells and have been used to identify and delineate groundwater flow into surface waters.

Groundwater sampling is performed to collect a sample that is representative of conditions in the aquifer. Therefore, it is essential that all parties involved in the implementation of PDBs for LTM at regulated sites identify and agree on data quality objectives, data evaluation techniques, and data end use and consider site characteristics before actual PDB deployment takes place.

For further information on PDB samplers see the U.S. Geological Survey publication *User's Guide for Polyethylene-Based Passive Diffusion Bag Samplers to Obtain Volatile Organic Compound Concentrations in Wells* (Vroblesky 2001). Also, see *Technical and Regulatory Guidance for Using Polyethylene Diffusion Bag Samplers to Monitor Volatile Organic Compounds in Groundwater* (ITRC 2004).

6.2.4 Sampling Parameters

Although sampling parameters may differ depending on monitoring objectives (i.e., compliance vs. performance), sampling parameters generally fall into four broad categories:

- field parameters,
- inorganic analytes,
- contaminants of concern, and
- groundwater levels.

Field parameters (see Table 3-3) typically include water level, pH, temperature, redox potential (ORP or Eh), dissolved oxygen, alkalinity, specific conductance, turbidity, and salinity. These parameters are necessary for both compliance and performance monitoring objectives and are usually measured during each sampling event.

Inorganic analytes (see Table 3-3) typically include metals, major cations and anions, total dissolved solids, total suspended solids, total organic carbon, and dissolved organic carbon. Inorganic analytes also include important geochemical indicator parameters necessary for PRB performance monitoring or for monitored natural attenuation that might be occurring downgradient of the PRB. For example, dissolved iron, sulfate, sulfide, nitrate, and hydrogen are key geochemical indicators for PRBs where iron is the reactive media. Table 6-1 compares the different use of the same parameter in evaluating the performance of an iron PRB and intrinsic bioremediation that may be occurring downgradient of the PRB (i.e., downgradient MNA). The downgradient MNA portion of the table, excerpted from ITRC's *Technical and Regulatory Requirements for Enhanced In Situ Bioremediation of Chlorinated Solvents in Groundwater* (ITRC 1998), summarizes key indicator parameters to assess intrinsic bioremediation, a key process of natural attenuation.

Table 6-1. Comparison of analytical parameters for evaluation of PRB performance and downgradient intrinsic bioremediation

Parameter	Iron PRB	Downgradient MNA[a]
Alkalinity	Declines as minerals precipitate in the PRB. Indicates that the groundwater is contacting the granular iron.	Provides an indication of the buffering capacity of the water and the amount of carbon dioxide dissolved in the water.
pH	Generally increases. Provides an indication that the groundwater is contacting the granular iron.	Microbial activity tends to be reduced outside of a pH range of 5–9, and many anaerobic bacteria are particularly sensitive to pH extremes.
Temperature	Affects rate of degradation of VOCs with granular iron. Degradation is slower at lower temperatures.	Affects rates of microbial metabolism. Slower biodegradation occurs at lower temperatures.
Dissolved oxygen	Dissolved oxygen is completely removed in the iron PRB.	Highest energy-yielding electron acceptor for biodegradation of organic constituents, <10 ppm.
Redox potential	A measure of the oxidation-reduction potential of the environment. Typically reduced to less than –200 mV as the groundwater flows through the PRB.	A measure of the oxidation-reduction potential of the environment. Ranges from +500 mV for aerobic conditions to –300 mV for methanogenic conditions.
Sulfate	Typically reduced through biological reactions as the groundwater flows through a PRB.	Used as an electron acceptor in biodegradation of organic constituents. Reduced to form sulfide. High sulfate concentrations may prevent methanogenic conditions from developing.
Sulfide	Typically occurs as a precipitate in the PRB (see above).	Microbially reduced form of sulfate. Indicates reduced conditions.
Methane	May be produced in the PRB.	Indicator of anaerobic conditions and of methanogenic bacteria. Produced by the microbial reduction carbon dioxide. Solubility limit 25–40 ppm.
Ethane/ Ethene	Metabolic end product of reductive dehalogenation of halogenated ethenes and ethanes.	Metabolic end product of reductive dehalogenation of halogenated ethenes and ethanes.

Parameter	Iron PRB	Downgradient MNA[a]
Total organic carbon	High background concentrations may affect degradation rate of VOCs with iron. Initially, there may be elevated levels of TOC for PRBs constructed with biopolymer.	A measure of the total concentration of organic material in water that may be available for biological degradation.
Chloride	Increases and may be useful as an indication of dechlorination.	May be useful as an indication of biological dechlorination and as a conservative tracer.
VOC/ daughter products	Persistence of daughter products may indicate insufficient residence time in the PRB.	Provides a measure of the type and quantity of parent and biogenic daughter products.
Iron (total, dissolved)	Produced in the PRB but typically precipitate within the PRB.	A product of bacterial iron reduction. Only the reduced form (ferrous) is soluble. The oxidized form (ferric) is used as an electron acceptor.
Nitrogen	See below.	An essential nutrient of microbial growth and biodegradation.
Nitrate	Reduced to ammonia/ammonium.	Used as an electron acceptor. Consumed next after oxygen.
Nitrite	Reduced to ammonia/ammonium.	Product of nitrate reduction. Produced only under anaerobic conditions. Rarely observed.

[a] *Source:* Remedial Technologies Development Forum and U.S. Environmental Protection Agency, Office of Research and Development (1998) and Wiedemeier et al. (1996).

COCs include the problem contaminants the PRB is designed to treat. They also include any associated toxic reaction/breakdown products. For example, iron PRBs designed to treat chlorinated solvents such as TCE should also include the daughter products *cis*-1,2-DCE and VC, among others. Monitoring these parameters is necessary for both compliance and PRB performance evaluation.

Measuring groundwater levels is also necessary for compliance and performance monitoring objectives. Accurate groundwater level measurements are critical to evaluate groundwater flow paths through and around the PRB as well as hydraulic capture and residence time within the treatment system. If the PRB is experiencing incomplete hydraulic capture, the system may not be performing as designed, and downgradient contaminant concentrations may remain elevated.

USEPA methodologies should be employed for all analyses. Table 3-5 summarizes the recommended sampling parameters, analytical methods, sample volumes, containers, holding times, and preservation methods.

6.2.5 Sampling Frequency

Sampling frequency depends primarily on the monitoring objectives (i.e., compliance vs. performance monitoring) and should be determined on a site-by-site basis. Additionally, sampling frequencies generally decrease over time as the system reaches equilibrium and more confidence in PRB performance is gained.

6.2.5.1 Effects from PRB Installation/Construction

Disturbances caused by the installation process can affect contaminant concentrations in groundwater surrounding the PRB. For example, in some cases, initial placement of a PRB has been reported to temporarily increase groundwater contaminant concentrations in close proximity to the PRB. Factors which may contribute to this effect include contaminant desorption due to installation disturbances or changes in groundwater flow velocity or direction due to groundwater mounding. In any case, the potential exists for the placement of a PRB to release a slug of groundwater contamination, which may affect noncontaminated wells. These phenomena are temporary effects of the installation process and should be monitored until stable.

To evaluate the effects of construction methods and the eventual return to equilibrium conditions, frequent monitoring may be required, particularly of water levels within and in close proximity to the PRB. In some cases this requirement may mean monthly or even weekly monitoring or more. In most cases the effects from construction subside within the first quarter following installation of the PRB. Determination of monitoring frequency and parameters during this period should be based on site-specific conditions and knowledge of the PRB construction method and associated disruptions.

6.2.5.2 Initial and Long-Term Monitoring

Once installation disturbances have subsided, monitoring frequency should be based on hydrogeologic conditions, the nature and extent of the contaminant plume, proximity to nearby receptors, and the risk posed to receptors. Additionally, selection of monitoring frequency should consider the degree to which the site was previously characterized and a baseline established, and the degree to which groundwater flow and contaminant concentrations are behaving as predicted.

As a general guide, compliance monitoring should be performed quarterly to allow for evaluation of seasonal changes. This should include monitoring of field parameters, inorganic analytes, and COCs from all wells. Adjustments in frequency can be made for sites with unusually fast- or slow-moving groundwater. After the first year or two, the PRB system should be evaluated based on compliance, performance, and stability. A reduction in the monitoring frequency may be appropriate where the system is consistently operating as originally designed.

Groundwater level measurements should be conducted monthly for the first quarter to verify that the groundwater flow direction, velocity, and hydraulic capture of the PRB system has stabilized or is approaching equilibrium. These data are necessary to justify future reductions in monitoring frequency or the number of monitoring locations. This period typically extends through the first year or two after PRB installation.

Long-term monitoring beyond the first two years of PRB operation is necessary to verify continued performance of the PRB and compliance with regulatory standards. Evaluation should occur on a yearly basis to determine the adequacy of monitoring frequencies and locations. After the first year or two, the PRB system should be evaluated based upon compliance, performance, and stability. A reduction in the monitoring frequency may be appropriate where the system is consistently operating as originally designed. The potential for clogging and channeling of the reactive media as well as desorption and leaching of COCs should be considered when modifying the long-term monitoring frequency.

Table 6-2 provides monitoring frequency guidance for PRBs. Site-specific considerations and professional judgment should be used to determine frequencies and parameters.

Table 6-2. Suggested permeable reactive barrier monitoring frequencies

Parameter	Frequency
A. Effects from PRB installation/construction	
Field parameters	To be determined (based on site-specific conditions, type of PRB, construction methods, etc.)
Inorganic analytes	
Contaminants of concern*	
Groundwater levels	
B. Initial monitoring program	
Field parameters	Quarterly
Inorganic analytes	
Contaminants of concern*	
Groundwater levels	Monthly, then to be determined
C. Long-term monitoring	
Field parameters	Quarterly (may be modified based on performance)
Inorganic analytes	
Contaminants of concern*	
Groundwater levels	
D. Post-closure monitoring	
Leachable constituents from reactive media	To be determined based on closure method and data collected during system operation
Contaminants of concern*	

*Contaminants of concern include all appropriate breakdown/daughter products.

6.2.6 Implications of Lessons Learned for Monitoring System Design

The implications for the post-PRB monitoring system design are as follows:

- The biggest monitoring 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 iron 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 location.

- Contaminant levels, field parameters (pH, Eh, temperature, and conductivity), native inorganic constituents (e.g., Ca, Mg, alkalinity, etc.), 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 the 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, the microbiology of the downgradient aquifer may be important to monitor. Cell biomass and PLFA are good measurements that have been used at some PRB sites to define the size and types of microbial populations in the PRB and in the surrounding aquifer.

- 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.

6.3 Other Regulatory Issues

6.3.1 Institutional Controls

Deployment of a PRB can require the enactment of institutional controls. These administrative and/or legal controls are typically installed to limit or protect land use. With the installation of a PRB, the institutional control could act to protect the remedial measure from excavation, the installation of wells, or any other intrusive actions that could affect the performance of the remedial system. The site may also require these controls to help minimize the potential for exposure to contamination. Sites where a PRB is the chosen remedy should evaluate the need for an institutional control to protect the operation of the remedy and note any contamination remaining on site that would require site restrictions.

6.3.2 Downgradient Effects

All potential treatment materials must be fully assessed for their ability to provide the intended treatment including longevity and constructability as well as for their potential to negatively impact the groundwater system. For example, some treatment materials can cause geochemical changes in groundwater that lead to changes in the concentration and mobility of naturally occurring metals and other chemical compounds. One such change can occur with the use of ZVI, which has been demonstrated to cause an increase in pH and chloride concentration and a decrease in Eh, total dissolved solids, alkalinity, dissolved oxygen, calcium, sulfate and other naturally occurring inorganics. Other treatment materials, particularly those used to enhance aerobic/anaerobic biological activity or to directly manipulate redox conditions (e.g., calcium polysulfide, sodium dithionite, etc.) can affect the prevalence and/or mobility of nitrate and sulfate compounds and/or metals such as iron, manganese, chromium, copper, and arsenic (Fruchter et al. 2000). Furthermore, in biological treatment remedies it is these changes in nitrate, sulfate, iron, or manganese compounds that provide a line of evidence for the breakdown process. Although these changes in groundwater geochemistry are typically buffered by natural aquifer conditions further downgradient, this phenomenon occurs to varying degrees with different reactive materials and different site conditions. Additionally, sufficient aquifer buffering capacity may not exist between the PRB and a downgradient receptor. Therefore, geochemical changes and their effects on chemical and contaminant occurrence and mobilization should be evaluated whenever alternative reactive materials are proposed for use in a PRB.

6.3.3 Reactive Material Impurities

The reactive material utilized for a PRB should be evaluated for impurities that could affect groundwater quality. A complete analysis of the material for any impurities that could be considered contaminants should be conducted before the material is placed in the subsurface. For example, the majority of the ZVI used in PRBs is derived from recycled cast iron borings. This material may have trace levels of other inorganic contaminants that could be considered groundwater pollutants. Typically, these impurities are at trace levels and not an issue in deploying a PRB. Other media such as zeolites or compost material may also contain impurities and should be analyzed and evaluated before installation in the PRB.

6.3.4 Use of Bioslurry and Biostat Agents

The use of guar gum (a natural food thickener) as a reactive media carrier or to support trench excavation has been used for the installation of several PRBs. Stabilizing the guar gum prior to installation typically includes the addition of a biostat to slow microbial breakdown of the mixture. The addition of the biostat into the aquifer has raised regulatory concerns. The biostat has the potential to contaminate groundwater, both from the biostat compound and any degradation products. It is important to understand the fate and transport of any biostat before it is used in these applications.

A biostat typically used during installations contains dazomet (tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione). Trade names include Troysan 142® and Busan 1059®. In surface soil application, this compound typically volatilizes or decomposes to other toxic compounds such as methyl isocyanate, formaldehyde, hydrogen sulfide, and others. While the fate, transport, and breakdown of the compound in subsurface soils, such as PRB installations, is not completely understood, recent laboratory studies (Marsden 2004) show that dazomet and related intermediates should degrade relatively rapidly in these environments.

Regulators in some states have voiced concerns about the use of a biostat that by the nature of its use is a toxic substance, in the aquifer. The use of biostat has been dealt with in different ways at installations. At one site, the use of a biostat was eliminated so that construction could proceed with the approval of the regulators. These concerns were directly related to a lack of data on the fate, transport, and breakdown of the biostat in the subsurface aquifer and potential ecological effects to the receptors in the wetland (Huber et al. 2002). At this particular site, shorter-than-usual portions of the trench were opened and immediately backfilled with iron to minimize the time for degradation of guar gum slurry to occur and to maintain trench stability, without the use of a biostat (Gavaskar et al. 2002, Tri-Agency Permeable Barrier Initiative 2002). This procedure requires the contractor to work on a smaller section of PRB installation at a time and can possibly increase the cost of the installation. Other sites have allowed the use of the biostat and required additional monitoring to address the fate and transport of the biostat compound. With or without the biostat, careful task and phasing of the construction is required to avoid early degradation of the slurry and collapse of portions of the trench (Gavaskar et al. 2002, Tri-Agency Permeable Barrier Initiative 2002).

Within U.S. borders, two manufacturers have been marketing biostats (Troy Corporation, Troysan 142 and Buckman Laboratories, Busan 1059) used for the construction and installation of PRBs. The manufacturer of Busan 1059 has an "active" registered status with the USEPA Office of Pesticide Programs. The manufacturer of biostat Troysan 142 is no longer registered for PRB use with the Office of Pesticide Programs, and therefore Troysan 142 cannot be sold, distributed, or used within U.S. borders for this application. Chemical registration was verified using the USEPA Web site (www.epa.gov/pesticides/regulating/registering/data_sources.htm).

Other biostats on the market could potentially be used for PRB construction. The petroleum industry (according to personal communication with U.S. Department of the Interior, U.S. Minerals Management Service, and Baker Petrolite) has documented many different uses and types of biocides. Of these types of chemicals, the class of tetrakishydroxymethyl phosphonium sulfate (THPS) biocides are deemed favorable and environmentally safe by USEPA and promoted by the Presidential 1997 Designing Safer Chemicals Award. When substituted for more toxic biocides, THPS biocides provide reduced risks to both human health and the environment. However, if an environmentally safe product is used, it may not have the capability or response (e.g., chemical half-life) to minimize the degradation process of guar gum slurry and to maintain trench/excavation stability potentially creating unsafe conditions. The use of these biocides should be further evaluated for their applicability during PRB construction and installation activities and to enhance good working practices for the site personnel and the environment (Penkala and Spalding 2001, USEPA 2004b). At this time, THPS biocides are not registered with the USEPA Office of Pesticide Programs for use in PRB installations.

6.3.5 Contingency Planning

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 of these contingency measures be incorporated in the design to prevent contamination migration in case of PRB failure:

- extension of 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);
- modification/amendment of the PRB if treatment is not being provided;
- ability to install a second PRB downgradient from or adjacent to the first one;
- ability to pump the PRB as an interceptor trench, a variation of the pump-and-treat measure;
- ability to recirculate groundwater through the PRB or provide other active hydraulic control; or

- ability to operate a pump-and-treat system if monitoring shows contaminant breakthrough or bypass for the PRB.

In a survey (Gavaskar et al. 2002), regulators have noted that the actual contingency measure adopted would depend on the mechanism of failure—that is, whether failure would occur because of loss of reactivity, inadequate residence time, inadequate groundwater capture, etc. 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.

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 dealing with 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 will help 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 Sunnyvale, California and the U.S. Coast Guard Site in Elizabeth City, South Carolina. If conducted correctly, they can provide valuable information on the hydraulics of a PRB system.

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 may, however, play a role in determining the source and extent of precipitate formation, clogging the reactive media, short-circuiting, loss of reactive site, or other related problems. Core samples can be collected from both vertical and angled profiles. The vertical profile can provide information on the reactive media at a specific location in the reactive media, while the angled cores can provide a profile of the changes in the reactive media from a horizontal perspective. The initial precipitate formation occurs at the upgradient interface, so, when evaluating iron media, angled cores can 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 the media allows collection of intact cores that can be preserved until sample analysis. Once collected, the cores should be protected from oxygen that could result in further degradation of the core. Upon retrieval the inner plastic sleeve can be capped and sealed. Preservation methods include storing cores in nitrogen-purged bags, using 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 are available to determine the presence of precipitates or biomass. Scanning electron microscopy is useful in providing high-resolution visual characterization of mineral precipitates on 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 can also use energy-dispersive X-ray spectroscopy to determine the composition of the surface participates on a semiquantitative basis. X-ray diffraction 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 analysis by PLFA, heterotropic plate count, or other suitable techniques can also be conducted on the iron cores. This information can provide data on total microbial biomass and the presence or absence of iron-oxidizing or sulfate-reducing bacteria.

6.3.6 System Closure

Currently, there is no history of PRB closure. Due to this lack of closure history, it is difficult to specify an appropriate closure option 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. PRB systems are designed to either degrade the contaminant or concentrate the contaminant within the reactive media. PRBs installed to treat chlorinated solvents typically degrade the contaminants, while those designed for metals and/or radionuclides retain 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 a PRB designed to degrade contaminants such as chlorinated organics.

In cases where a PRB will remain in place after closure, concern may arise regarding the long-term solubility of the reactive media and its effect on downgradient water quality. The PRB will most likely be impacting downgradient water quality. The need for post-closure downgradient monitoring should be based on the data collected during operation of the PRB (see Table 6-2, Section D). Depending on the concentration of parameters detected during operation of the permeable reactive barrier, 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. In addition, consideration should be given to the proper decommissioning of those monitoring wells that will no longer be needed.

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 involve a change in the oxidation state of the metals and/or radionuclides under specific groundwater redox conditions, and the contaminants form precipitates. 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 (see Table 6-2, Section D).

A number of site-specific factors can influence removal of reactive media, including the following:

- loss of permeability through the reactive media,
- 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,
- reaching capacity of the reactive media,
- future use of property,
- cost of removal vs. long-term O&M,
- regulatory requirements for closure,
- noncontaminant changes in downgradient water quality, and
- potential need for institutional controls.

Upon completion of treatment, all monitoring wells, if not needed for follow-up or future groundwater monitoring, should be plugged and abandoned in accordance with state-specific regulations and requirements. Removed PRBs 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.

7. USE OF IRON-BASED REACTIVE MEDIA FOR SOURCE TREATMENT

The objective of source treatment is to remove contaminant mass and reduce contaminant flux. An expansion of PRB technology is to use reductive reactive media (e.g., ZVI) to treat source zones. In the case of chlorinated solvents, materials that provide persistent releases to groundwater can include DNAPL, sorbed contaminants, and dissolved-phase constituents in stagnant zones (USEPA 2003). Use of reductive media for source treatment is an emerging technology that can stand alone or be coupled with PRBs. This document does not include peer-reviewed source treatment performance data because little is available. Case studies addressing source area treatment can be found in Appendix F. Table 7-1 is a summary of reactive media applications for source area treatment.

A complementary technology or approach may be implemented to address a downgradient plume in conjunction with ZVI application in the source area. These technologies may include, but are not limited to, MNA, a passive treatment barrier, engineered hydraulic control, and biostimulation or bioaugmentation. Actively addressing the contaminants in the source area may minimize the effort and cost in treating or containing a larger or dilute plume downgradient. An evaluation should be conducted to assess the compatibility, or potential enhancement, of the selected downgradient treatment with the ZVI source area treatment.

Table 7-1. Summary of reactive media applications to treat source areas and dissolved plumes

Site name	Location	Treatment type	Contaminants	Reference
Former manufacturing facility	Fairfield, NJ	Backfill with granular iron and sand	Chlorinated solvents	Tappert and Ishihara 1998
DuPont	Martinsville, VA	Soil mixing with granular iron and kaolinite clay	Carbon tetrachloride and other chlorinated compounds	Liberati 2003
Marshall Space Flight Center	Albany, GA	Ferox^{SM} process	TCE	Sprinkle 2004
Hunters Point Navy Shipyard	San Francisco, CA	Ferox process	TCE	McCall et al. 2004
NASA Marshall Space Flight Center	Huntsville, AL	Ferox process	TCE	McElroy et al. 2003
Memphis Army Depot, Dunn Field	Memphis, TN	Injection of ZVI	Chlorinated volatile organic compounds	Unknown
Cape Canaveral Air Force Station, NASA Launch Complex 34	Cape Canaveral, FL	Emulsified ZVI	TCE	O'Hara et al. 2004
Cape Canaveral Air Force Station, L-15	Cape Canaveral, FL	Large-diameter auger mixing (with iron injection)		Bogart, Fairloth, and LaMori 2004
Charleston, Naval Yard SWMU-70	Charleston, SC	Ferox process	Cr^{+6} source area	Favara, Williamson, and Liskowitz 2004
Jacksonville Naval Air Station, Hanger 1000 Area	Jacksonville, FL	Nanoscale-iron injection	Chlorinated volatile organic compounds	Tetra Tech NUS, Inc. 2004

The possibility of remobilizing source contamination is always a concern when investigating for and treating contamination, particularly when DNAPL is present. Provisions must be made and precautions should be exercised to anticipate and prevent the remobilization of DNAPL from taking place when the remobilization will result in more difficult attempts at remediation.

Source area treatment of high-concentration groundwater or DNAPLs using iron is different from PRB treatment. In the source area treatment of DNAPLs, an iron material is injected, mixed, or used as backfill to facilitate treatment. A remediation program employing iron source treatment of DNAPLs can also be complemented by a downgradient PRB. In addition, injection methods to treat DNAPLs with ZVI can be used at sites where intrusive digging methods are not possible (e.g., sites that have unexploded ordnance, buildings, or buried utilities). ZVI has been applied at field scale numerous times for the treatment of source areas using several emplacement methods, including the following:

- gas-atomized injection of iron slurry (Ferox^{SM} Process),
- mixing with a stabilizing agent,
- mixing with steam and iron injection,
- hydraulic-based injection of nanoscale iron,
- mixing with backfill material, and
- injection of emulsified ZVI.

Although the range of iron particle size varies relative to the emplacement method, the reaction chemistry with the ZVI is the same. The choice of iron grain size is dependent on a wide variety of design factors, including method of emplacement, the type of contaminant being treated, the site geologic and hydrogeologic conditions, contaminant concentration levels, and overall treatment objectives. Grain size ranges that have been used include the following:

- 0–0.59 mm (–8 to +70 mesh U.S. standard sieve size) for soil mixing, excavation backfill applications, and hydraulic injection;
- 40–150-µm (140 to –325 mesh U.S. standard sieve size) iron for slurry-based, gas-atomized injection (Ferox); and
- 50–500-nm iron particles either suspended in water or combined with emulsified oil and/or other substances including surfactant and polymers.

The contaminants listed in Table 2-1 can be treated with granular iron in a source area or dissolved plume.

Critical issues with this technology that likely need further investigation include the following:

- longevity of the iron as a function of iron amount and size;
- losses of iron to potentially unproductive reactions, including modifying the redox status of the soil and/or gas production;
- the potential for reactions to be biologically mediated;
- the ability to treat DNAPL;
- migration of DNAPL due to the injection technique;
- the ability to address contaminants in low-permeability layers; and
- performance data.

7.1 Gas Atomized Injection of Iron Slurry (Ferox^{SM} Process)

A ZVI source zone treatment process, called Ferox, consists of a food-grade sponge-iron microscale powder, which is suspended in water to create a uniform slurry. The iron-water mixture is fed into a nitrogen gas stream that is then injected into the subsurface. Nitrogen gas is used since it is readily available in bulk tankers and is low in cost. Depending on the depth and geology, the iron is distributed outward to distances of 25 feet. Figure 7-1 shows a schematic of the Ferox process.

Ferox injections are typically applied in open boreholes or using direct-push installed injection points. Injections are applied at discrete 2–3-foot intervals (lifts) starting from the deepest depth and moving upward.

The quantity of iron powder injected varies significantly depending on the concentration of target compound being treated, the mass flux of the contaminant within the treatment area, and the type of geologic material being treated. Typically, the amount of Ferox powder emplaced is equivalent to a ratio to soil mass range 0.25%–1%.

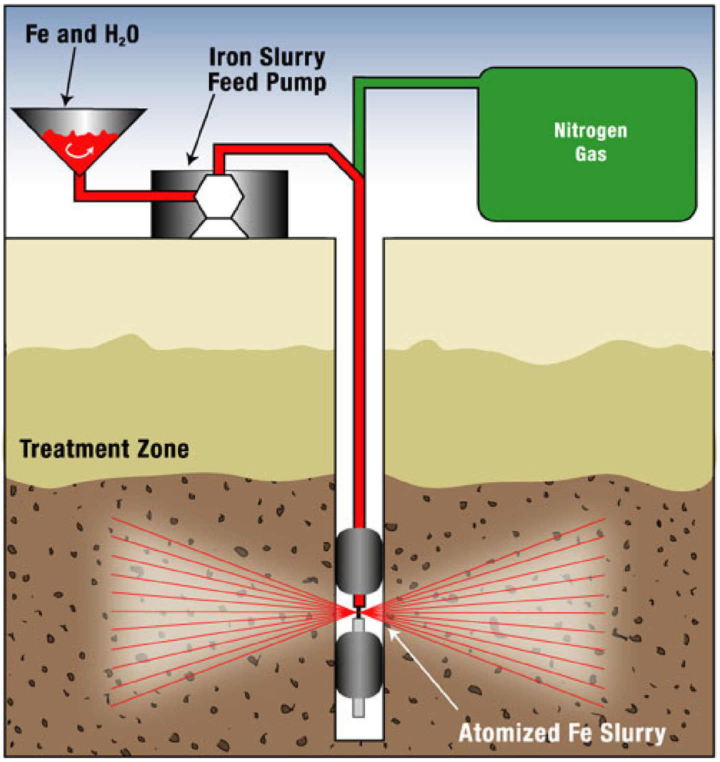


Figure 7-1. The Ferox^{SM} process.

Ferox applications include systems installed for the U.S. Navy at Hunters Point Shipyard (McCall et al. 2004) and NASA's Marshall Space Flight Center in Alabama (McElroy et al. 2003). Under the U.S. Navy program at Hunters Point, TCE source contamination located within a fractured bedrock aquifer contained TCE concentration as high as 88,000 ppb. Under the NASA project, a Ferox system was applied at Source Area 2, located at Marshall Space Flight Center in Huntsville. The remedial action was implemented under the CERCLA program targeting a former waste-holding pond. The project scope included the installation of two Ferox treatment zones: a 3000-square-foot source area treatment zone and a 450-foot-long by 60-foot-wide downgradient treatment zone. The primary contaminant, TCE, was detected at concentrations as high as 72,000 ppb in the groundwater within the source area treatment zone.

7.2 Mixing with a Stabilizing Agent

Soil mixing and injection techniques for the addition of granular iron and clay slurry for in situ containment and degradation of chlorinated source zones are being evaluated. Laboratory and field data indicate this technology is very effective in terms of efficacy and cost. The underlying principle of the technology is to use standard geotechnical equipment for soil mixing or injection to homogenize soils and contaminants in source zones and mix granular iron and clay uniformly into the source zones. The clay plays a number of roles, including improving the uniformity of iron emplacement via suspension, reducing flow through the source (allowing greater time for reactions to proceed and reducing contaminant flux), and reducing the mechanical energy needed to mix soils (Wadley, Gillham, and Gui 2005). A conceptual illustration of the process for this source zone technology is shown in Figure 7-2.

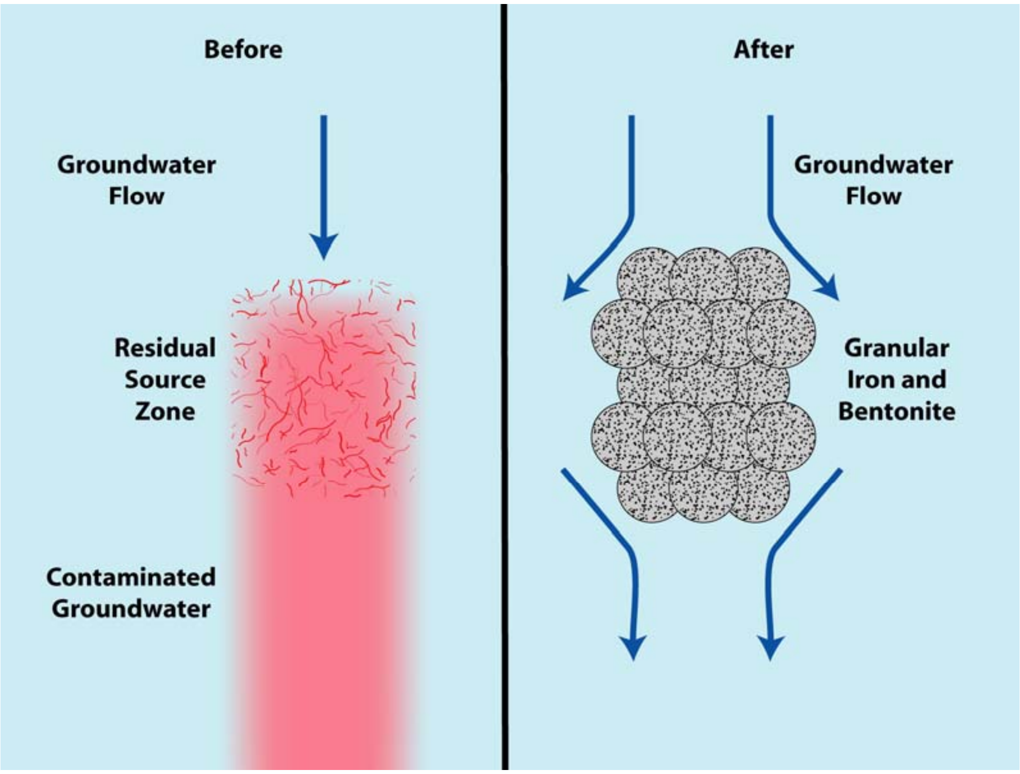


Figure 7-2. Soil mixing with stabilizing agents technology concept.

Current knowledge regarding iron-clay is focused on chlorinated ethenes (Batchelor et al. 2002; Wadley, Gillham, and Gui 2005; Shoemaker and Landis 2002) and chloromethanes (Batchelor et al. 2002, Liberati 2003). The most comprehensive effort to date has been DuPont's Martinsville, Virginia project (Liberati 2003).

7.3 Mixing with Steam and Iron Injection

This treatment approach consists of integrated mechanical mixing of source area soils, injection of hot air and steam (thermally enhanced), followed by ZVI injection as a polishing step. The process consists of a drill tower attached to a mobile platform. In most applications, the drill tower supports one or two drill blades or augers (5–10-foot diameter) designed to inject the hot air and steam into the subsurface soil as the drill blades or augers penetrate below the ground surface. The augers shear and mix the soil while the hot air and steam is being injected, causing volatilization of free product and dissolved contamination and thermal desorption of the organic contaminants from soil particles. The air, steam, and contaminant vapors are carried to the surface by the injected air and collected in a shroud placed over the treatment area. The shroud, operated under a slight vacuum, rests firmly on the soil so that the gases and vapors released during subsurface treatment are captured. The contaminant vapors collected in the shroud are rapidly removed by a suction blower and sent to an aboveground processing unit for treatment. Once the augers reach the bottom of the treatment zone, they are reversed out of the hole. Instead of hot air or steam being injected, ZVI slurry is injected as a polishing treatment for chlorinated volatile organic carbon (CVOCs) remaining after volatilization. The added use of ZVI makes the process more efficient and economical as the cost of the injected iron is much less than the cost of removal by additional steaming. This process was demonstrated at Argonne National Laboratory on approximately 8000 cubic yards of soil (Moos 1998) and confirmed at the Cape Canaveral Air Force Station in 2003 in the L15 Phase I Test.

7.4 Hydraulic Based Injection of Nanoscale Iron

Hydraulic injection methods have been used to emplace both granular and nanoscale iron to address source zones. Several field-scale pilot tests have documented processes whereby composite materials consisting of solid carbon source containing microscale iron and mixtures of bentonite and granular iron (Siegrist et al. 1999) were injected. More recently, colloidal iron slurries consisting of nanoscale iron particles have been used (Zhang 2003; Tetra Tech NUS, Inc. 2004). Hydraulic injection typically involves injecting the nanoscale iron in an aqueous solution. When using granular iron, a biodegradable slurry containing iron and guar is injected through a borehole into the subsurface. Depending on the geologic material present, fractures are created or the material is intermixed with the more permeable soils. When using the biodegradable method, an enzyme is added after the injections to degrade the slurry over a short time period, leaving a lens of granular iron in the subsurface.

7.5 Mixing with Backfill Material

Under a simpler configuration, granular iron has been incorporated into the backfill material where contaminated source zone soils have been excavated. The granular iron provides treatment for any residual contamination that flows back into the excavated area. The placement of the granular iron depends on the potential pathways for migration of residual contamination back into the excavated area. Granular iron can be placed as a layer along the base of the excavation, placed as a distinct zone on one or more walls of the excavation (analogous to a PRB), or mixed into a portion of the backfill material. Incorporation of granular iron into backfill material has been implemented at several sites.

7.6 Injection of Emulsified Zero-Valent Iron

NASA has developed a emulsified, nanoscale-iron process that directly targets DNAPL. The emulsified system consists of surfactant-stabilized, biodegradable water-in-oil emulsion with nanoscale-iron particles contained with the emulsion droplets (Figures 7-3 and 7-4). The surfactant serves two functions: it increases the stability of the emulsion for injection into the DNAPL zone, and the surfactant micelles within the oil membrane of the emulsion droplet aid in the delivery of TCE to the iron. The DNAPL diffuses through the hydrophobic oil membrane of the emulsion droplet, whereupon it reaches the surface of the iron particle and dehalogenation takes place (Geiger et al. 2003). This technology has demonstrated that DNAPLs such as TCE diffuse through the oil membrane of the emulsion droplet, whereupon they reach the surface of the iron particle and dehalogenation takes place. Recent field work at NASA's Launch Complex 34 on Cape Canaveral Air Force Station demonstrated the effectiveness of this process in treating DNAPL (O'Hara et al. 2004).

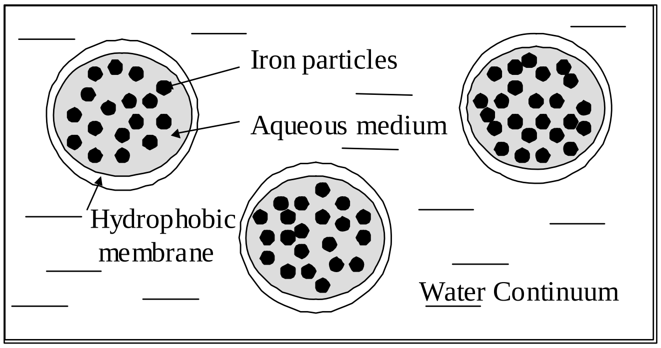


Figure 7-3. Rendition of emulsified zero-valent iron droplets.

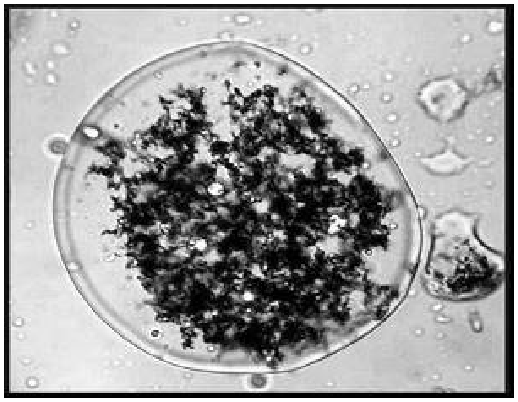


Figure 7-4. Micrograph of nanoscale iron particles (100–200 nm) contained within an emulsion droplet.

8. HEALTH AND SAFETY CONSIDERATIONS

As PRB technology continues to develop and become more sophisticated, designers and contractors have assessed new health and safety risks posed by new PRB installation technologies and considered appropriate working methods to avoid hazardous situations. Listed below are several elements that warrant an increased awareness level. These items should be considered in the development of site-specific health and safety field protocols.

- A company's health and safety program must continue to develop a plan and recognize new issues associated with maintaining deeper excavations, ensuring trench stability, and identification of all chemical and physical health and safety concerns.

- Air monitoring of areas containing COCs should be supported by real-time data provided by monitoring instruments. The air monitoring required at the site perimeter will provide immediate results. If monitoring results exceed predetermined action levels, measures must be taken to reduce the airborne contaminants or dust to acceptable limits.

- A company's industrial hygienist and/or site safety officer usually will direct company personnel involved in PRB construction and installation activities in the donning of appropriate personnel protective equipment (PPE).

- Most company personnel don Action Level D PPE for PRB construction and installation field efforts. After a period of time and monitoring the COCs and associated hazards, if appropriate, field efforts may be upgraded to Action Level C.

- When the trench is excavated, a biodegradable slurry consisting of guar gum, biostat, pH adjustment, and enzyme can be used. Biostat is considered a health and safety concern during PRB construction and installation activities. Comprehensive health and safety measures must be used to identify all associated hazards. This information should be effectively communicated to all parties.

Health and safety monitoring and controls must be maintained during PRB installation activities to protect construction workers and other participants. These PRB installation efforts need to consider health and safety elements in accordance with applicable federal, state, and local regulations at the site.

8.1 Applicable Health and Safety Regulatory Requirements

The U.S. Department of Labor Occupational Safety and Health Administration (OSHA) requires employers involved in hazardous waste activities to comply with OSHA's Title 29 of the Code of Federal Regulations (CFR). The major regulatory requirements applicable to employees during PRB construction and installation activities are Hazardous Waste Operations and Emergency Response (HAZWOPER, as found in 29 CFR 1910.120), Hazardous Communication (HAZCOM, as found in 29 CFR 1910.1200), and construction safety orders (as found in 29 CFR 1926.65). Supplemental health and safety information can be found in various OSHA and USEPA publications (U.S. Department of Labor 2002, 2003; USEPA 1992).

These HAZWOPER requirements and guidelines describe the donning of PPE for appropriate Action Levels. To date, mostly Level D has been used at PRB sites, with the option to upgrade to C if vapors or other hazards are encountered. The contaminants and construction activities driving an air monitoring and safety program are such that exposure over the OSHA Permissible Exposure Limits will require the appropriate PPE attire. The use of PPE attire is described in OSHA's 29 CFR 1910, American National Standards Institute, National Institute for Occupational Safety and Health (NIOSH), and Mine Safety and Health Administration.

Prior to field efforts at a PRB site, the company's industrial hygienist and/or safety officer must adequately address the use of all toxic substances in a health and safety plan. The health and safety plan addresses chemical, biological, and radiological hazards of the site and generally addresses the physical hazards. Health and safety hazards posed to site personnel by subcontractor equipment and methods must be identified and brought to the attention of all field team members.

8.2 The Role of the Health and Safety Plan

Overall, the purpose of a health and safety plan is to provide the field team with a safe working environment during PRB construction and installation activities. Specifically, the health and safety plan should be developed to prevent and minimize personal injuries and illnesses and physical damage to equipment and property. It emphasizes management responsibilities, preplanning for all new jobs at the site, as well as consideration of the following elements:

- general health and safety policy statement
- an organizational structure
- safety and health training program
- medical surveillance program
- standard operating procedures for site tasks presented in an accompanying scope of work/ work plan
- safety and health risk or hazard analysis
- PPE to be used for the project

- frequency and types of air monitoring, personnel monitoring, and environmental sampling techniques and instrumentation to be used, including methods of maintenance and calibration
- site description and contaminant characterization
- personnel equipment and decontamination procedures
- emergency response procedures, including equipment and first aid
- permit-required confined-space entry procedures
- spill containment program
- contingency plan for severe weather, including heat and cold stress
- plans for maintaining a clean job site
- waste management and disposal
- site control measures
- logs, reports, and record keeping
- inspections and audits

8.3 Health and Safety Considerations at PRB Sites

Previous works by U.S. federal and state agencies, consulting companies, the ITRC PRB Team, and others have considered and discussed health and safety issues related to PRB installation technology. Two primary considerations of this technology include trench/excavation stability and the use of biostat.

During trench-type PRB installation and construction, various methods have been used at PRB sites to keep the trench open long enough for the placement reactive media. In many of the early PRB applications, sheet piling and cross bracing were used to support the trench. One challenge with this method was that it sometimes required the entry of personnel into the trench to clear out native soil from corners or to pack the reactive media into the excavation. This procedure would trigger safety issues associated with confined-space entry, and appropriate steps had to be taken to address the hazard. The use of a biodegradable slurry or bioslurry to shore up excavations is a relatively recent advance in trenching techniques and was first employed for the installation of a PRB at the Bear Creek Valley (Oak Ridge, Tennessee) site in 1997. The technique involves the use of a bioslurry, typically made of powdered guar gum bean, to exert hydraulic pressure and prevent the collapse of the trench as it is excavated.

Excavation of a PRB is generally done in large sections, and as each section is completed, the reactive media is backfilled, displacing the bioslurry. The guar gum itself is nonhazardous and environmentally benign. In fact, another use for guar gum is as a food additive for thickening. The hazard from this type of construction comes from the biostat added to the guar gum slurry to ensure that the guar gum does not degrade too soon and allow the trench to collapse before it has been filled with the reactive medium. The common biostats used in the past for PRB construction are Troysan 142 and Busan 1059, which contain dazomet (tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione). This biostat is used at levels which are adequate to provide biostatic effect (i.e., slow microbial growth but not kill all bacteria). The health and safety considerations when using these or similar biostats during PRB construction are to avoid eye, skin, and inhalation exposures (see Appendix C for Material Safety Data Sheets and Technical Data Sheets). The potential hazards of handling of biostats can be minimized by packaging the biostat in water-soluble, single-dose packages, thereby significantly reducing the potential contact of the biostat by workers.

In addition to trench stability and the use of biostat, several other health and safety considerations warrant further discussion:

- exposure to soil vapors or gases (e.g., VOCs, CH_4, H_2S) or dust (e.g., contaminated soil or reactive media) during excavation of the PRB
- exposure to soil vapors or gases (e.g., H_2, CO_2) after installation of the PRB
- dermal contact or ingestion of contaminated soils and groundwater
- risk of encountering underground utilities (e.g., electricity cables, gas mains, water pipes, sewers, telecommunications cables, etc.)
- fire/explosion risk due to the use of media (e.g., oxygen or hydrogen for biosparging)
- exposure to construction chemicals (e.g., fuel oil), including accidental spills of material(s) during transport and storage and potential employee injuries from handling and use of construction chemicals
- movement and use of large equipment and machinery; generation of gases (e.g., CO) emitted during excavation activities
- any specific health and safety issues related to the reactive media being used
- physical hazards related to injection of the reactive material into the subsurface

9. STAKEHOLDER INPUT

A stakeholder is any nonregulatory affiliated party with interest in a particular site or technology. Stakeholders within the community in which a PRB will be deployed should be properly informed, educated, and involved in the decision-making process and consulted regarding the use of the technology. This process may require holding public meetings or information sessions. An informative document entitled “A Guide to Tribal and Community Involvement in Innovative Technology Assessment,” developed by participants in the DOIT Tribal and Public Forum on Technology and Public Acceptance, explains the need for community involvement during site planning and implementation and should be used as a reference tool in forming a community outreach program. The USEPA has also developed a reference for PRBs entitled *A Citizen’s Guide to Permeable Reactive Barriers* (USEPA 2001).

Stakeholders have previously expressed the following concerns about proposed PRBs:

- There has been concern whether a PRB will treat the entire plume. In areas where there are preferential groundwater flow paths, ensuring total treatment must be demonstrated.

- Because this technology is passive (that is, it depends on the natural flow of the contaminant plume to pass through the PRB), complete breakdown or immobilization occurs only after the entire plume has passed through the PRB, which may take many years. A groundwater monitoring system should be put in place to monitor the performance. Local authorities should be informed of potential disruptions to landscaping and other activities during replacement of the media.

- When PRBs are used for precipitation of metals, it is not certain how long they will be effective. PRB permeability may decrease due to precipitation of metals, salts, and biological activity. PRBs may lose their reactive capacity over time, and the reactive media may have to be replaced periodically. As above, a groundwater monitoring system should be put in place to monitor performance. Local authorities should be informed of disruption in landscaping and other activities on site during replacement.

- There is insufficient information about what environmental conditions may influence remobilization of contaminants. For example, changes in pH, groundwater flow, or rainfall may create conditions that contribute to remobilization of contaminants. These factors should be identified prior to installation of this remedy and should be monitored over the long term.

- Potential leaching of reactive media or contaminants should be evaluated.

- When the PRB is used for precipitation of metals, the media may have to be removed and disposed of as a hazardous waste or contained in some other fashion. A plan similar to a closure and post-closure plan mandated by RCRA should be completed prior to installation. If it is known that the reactive media will have to be contained or disposed of due to its hazardous properties, RCRA-type financial assurances should also be made part of the closure and post-closure plans.

- A contingency plan should be incorporated into proposals for this remedy addressing alternative remedies in case the PRB fails to meet agreed-upon goals and actions that would be taken if potable water becomes contaminated.

- The remedial action work plan should address access restrictions during operations and deed restrictions if the PRB is left in place. Local authorities should be informed and be able to provide input at the time a decision is being made to keep a PRB in place.

- Special attention should be paid when the PRB is used for radionuclides. Communities are concerned about concentrating radionuclides in underground walls if they are long-lived or are gamma emitters. Periodic information sessions should be offered to the community and local government. Institutional controls (deed and access restrictions) may be considered. Communities may oppose leaving radionuclide-contaminated walls in the ground once remediation of groundwater has been completed.

10. COST

Estimating the cost of a PRB deployment can be a difficult task since a number of factors need to be evaluated, many of which are not well understood or documented. A number of different sources provide cost data for completed PRBs; however, these data are typically not broken down into the many tasks or cost categories which make up the project’s total cost. The *Guide to Documenting and Managing Cost and Performance Information for Remedial Projects* (Federal Remediation Technologies Roundtable 1998) should be consulted for tracking the cost of a PRB deployment. Its use will help to provide improved cost data at completed projects and aid in the estimation of proposed projects.

Another tool for estimating the cost of a PRB installation is the Remedial Action Cost Engineering and Requirements System ("RACER"), developed by DoD, which offers a database of costs for activities such as trenching or drilling.

10.1 Cost Factors

The site characterization data needed for placement of a PRB require much more detailed data gathering than that typically generated with an overall site characterization. Data gathering on a smaller scale is necessary for placement of a PRB, including the complete vertical and horizontal delineation of the groundwater plume and characterization of hydrogeologic, geochemical, geotechnical, and microbiological conditions.

Site characterization costs associated with a PRB system can be difficult to separate from the overall site characterization costs. The problem with documenting site characterization costs involves determining what cost is associated with PRB as compared to cost associated with the overall site investigation. For instance, if DNAPL is present on site, would the delineation of the DNAPL plume be part of the overall characterization or part of the costs associated with PRB installation? This type of data may be tracked differently at various sites. Site characterization costs can be substantial but are not the primary cost associated with PRB installation.

Design costs include all engineering and work plan development associated with PRB installation. They can include treatability studies, modeling, additional data collection, licensing fees, cost evaluation, cost comparisons, as well as work plan development and reporting. Designs costs can readily be tracked and reported since the costs are easily defined.

Construction is the largest cost factor for the remedial project, including the following costs: media, mobilization, emplacement, waste disposal, health and safety, and site restoration. Depending on the system design, the reactive media can be the most significant cost associated with construction, followed by the emplacement costs. Because there are numerous emplacement methods, the costs associated with emplacement can vary significantly from one installation to the next.

O&M costs can be difficult to estimate since the life cycle of the reactive media is typically hard to estimate. No ZVI PRB sites have reached the useful life of the media; therefore no data exist on which to base these estimates. Sites have estimated the replacement of the entire reactive media zone on varying schedules such as 5-, 10-, 20- and 30-year cycles. Other estimates are based upon the use of an innovative method to regenerate the iron. Some methods currently being evaluated include ultrasound, use of a pressure pulse technology, jetting, or agitation with a drilling auger to break up any precipitate formation. A reagent flush could also be employed to remove buildup on the iron surface. These techniques have not been employed full-scale, but all have been evaluated to some extent. Development of this type of rejuvenation technology will probably be driven by the need for action at some of the current deployments. It is difficult to determine the best means for estimating operation and monitoring costs associated with reactive media replacement or replenishment. For PRB systems employing iron as the reactive media, a general rule is to expect that some form of media maintenance will be required every 10 years and that the cost could run about 25%–30% of initial construction. However, as the technology matures and sites reach the useful life cycle for the reactive media, a better basis for estimating O&M costs will certainly emerge.

Some of the cost factors associated with O&M that can be readily estimated and documented are the annual monitoring costs, any institutional controls, reporting costs, and regulatory oversight costs. Another cost somewhat difficult to estimate is any savings associated with being able to return the property to its full economic potential. Because this technology is in situ and passive in nature, the property would have fewer restrictions than a more active remedy with aboveground structures. Cost savings could be associated with a property that has limited restrictions.

The cost factors that should be evaluated for a PRB installation include the following:

- site characterization costs
- design costs
- construction costs
    - purchase and installation of reactive media
    - licensing fees
    - reporting
    - monitoring costs
- O&M costs
    - annual monitoring and reporting costs
    - media replacement/rejuvenation
    - institutional controls
- unexpected and miscellaneous costs

10.2 Cost Evaluation

Several studies have looked at the cost of PRB installations. Originally, the cost of a PRB was compared to a pump-and-treat system. The cost information for a pump-and-treat system was well documented and readily available, providing a straightforward comparison to a conventional technology. Today, however, pump-and-treat systems are not being used at the same number of sites as in past years. This reduction is partially due to issues involving overall effectiveness and the high cost of O&M for pump-and-treat systems. The commercial availability of other in situ technologies requires a broader review of groundwater remedial technologies in a comparison to a PRB system.

A study comparing the cost of several groundwater remedial technologies was published by staff at DuPont (Quinton et al. 1997). The method to compare the technologies posited a generic, non-site-specific template site with a groundwater plume of dissolved PCE 400 feet wide, 1000 feet long, and 60 feet deep. Concentration of PCE averaged 1 mg/L. The study compared enhanced anaerobic bioremediation using both a bio-barrier and a recirculating groundwater system, intrinsic bioremediation, a PRB using ZVI, and a pump-and-treat system using an air stripper and liquid-phase/vapor-phase recovery. The PRB system consisted of emplacement using high-pressure jetting. The scenario assumed that the PRB would be replaced on a 10-year cycle. Costs of each of the four technologies were evaluated on a present-cost basis with a 30-year estimate for containment remedies. Costs evaluated include design, construction, operation, and monitoring. The comparison addressed the costs on a total system cost as well as per unit costs for both 1000 gallons treated and 1000 pounds of PCE treated. For total cost and unit costs, PRBs were more expensive than intrinsic bioremediation and anaerobic bioremediation but significantly less expensive than pump-and-treat systems.

Battelle prepared a report entitled *Final Cost and Performance Report Evaluating the Longevity and Hydraulic Performance of Permeable Reactive Barriers at Department of Defense Sites* (Battelle 2002) for the Naval Facilities Engineering Service Center. The cost section of the report evaluated PRB systems in comparison to pump-and-treat systems using present-value information. The report evaluated two sites, the Moffett Field site in California and Dover AFB in Delaware, both of which have demonstration pilot-scale PRB systems installed. From this information, an estimate was made for the installation of a full-scale PRB system. Replacement of the reactive media, iron, was included in the estimate on a 10-year cycle. This estimate was then compared to an equivalent full-scale pump-and-treat system. The equivalent pump-and-treat system was designed to capture the same amount of water that was flowing through the PRB system.

The cost of the PRB system was less expensive for both sites. The Moffett site cost estimate for the full-scale pump-and-treat system was $17,081,000, and the PRB system was $14,382,000, a cost saving of $2,699,000 (16%) over the 30-year analysis. The estimates for the two systems at the Dover Site were much closer. The pump-and-treat system was estimated at $4,857,000, and the PRB system at $4,618,000, a difference of only $239,000 (5%) in favor of the PRB system.

The economics of PRB systems are tied to the longevity of the media and long-term hydraulic capture in the system. Using the above estimates, if the reactive media functions for only five years before replacement or rejuvenation is necessary, then the cost of the PRB system may be greater than that of the pump-and-treat system. However, if the reactive media functions for greater than 10 years, the PRB system becomes much more cost-effective. The longevity of the media will dictate whether the PRB system will be cost-effective.

Overall, while the costs of PRB systems vary depending on the site-specific circumstances, the length and especially the depth tend to be the biggest factor that drives the cost of the installation. PRB systems typically require a higher cost for installation compared to the conventional pump-and-treat technology; however, O&M costs are lower and—depending on the useful life of the reactive media—offer costs savings over the project life. PRB systems offer several other advantages that are difficult to assign a monetary figure, such as passive treatment with no aboveground structures that could limit the reuse of the property.

USEPA conducted a study of PRB economics entitled *Economic Analysis of the Implementation of Permeable Reactive Barriers for Remediation of Contaminated Groundwater* (Powell, Powell, and Puls 2002). Cost data for 22 sites were gathered from a number of sources; however, the data were not always available for each site or broken down into the various identified cost categories. Comparisons were made to pump-and-treat systems, for which cost data were also gathered. This report took a different approach in comparing PRBs to pump-and-treat systems. Rather than compare the traditional unit of cost per volume per time, such as cost per 1000 gallons treated per year, the report compared cost per 1000 gallons of treated water. Using the cost per volume per time method skews the treatment toward the technology that treats the greatest amount of water rather than the amount of contaminated water. The cost per volume per time method results in the O&M costs being cheaper for the groundwater pump-and-treat system, a system that must pump much more water than the actual contaminated water volume to achieve hydraulic control. The cost per 1000 gallons of water treated method looks at the volume of contaminated water treated, making the PRB system much more cost-effective for O&M.

The report draws no absolute conclusions on the cost-effectiveness of PRB systems when compared to pump-and-treat systems. Concise conclusions on the comparison were complicated by the lack of accurately documented costs both for the overall PRB system and its many individual cost components. In addition, questions about the longevity of reactive media and the frequency, cost, and extent of media maintenance all complicate any cost comparisons. The results indicate PRB systems may be more cost-effective over the long term when O&M are included in the evaluation, especially if periodic reactive media maintenance is not necessary. The document also points out a number of advantages that PRB systems have over pump-and-treat systems that are not typically included in a financial comparison.

In conclusion, PRB systems appear to be cost-effective when compared to groundwater pump-and-treat systems if the useful life of the reactive media approaches 10 years. In many cases, it appears that this longevity may be obtainable. However, until there is a history on the useful life of reactive media and until techniques are developed for media rejuvenation. it will be difficult to accurately gauge the overall costs of PRB systems against a technology like groundwater pump and treat, where there is extensive knowledge and experience.

10.3 Site-Specific Costs

The first commercial PRB using ZVI for the treatment of chlorinated organic contaminants was installed at an industrial site in Sunnyvale, California. Initial construction of the site occurred in late 1994, so this site has been in operation for over 10 years. The cost data of the installation of this PRB have been documented (Warner et al. 2004a). The site had a groundwater pump-and-treat system in place prior to the installation of the PRB. With the placement of the PRB, the site no longer required aboveground structures and could again be used for commercial purposes, allowing the responsible party to stop paying a monthly lease on the property that was required for the aboveground pump-and treat system.

Figure 10-1 shows a comparison of the actual cost of the PRB versus the projected cost (Warner et al. 2004a). Also included is the estimated cost of maintaining the pump-and-treat system on the site. It can be noted that the actual and projected costs for the PRB system agree rather well with each other. The figure also shows that the cost for the pump-and-treat system begins to exceed the cost of the PRB after about two years of operation. The cost associated with the pump-and-treat system does not include the initial construction costs. This graph line included only O&M since the system was already installed before the PRB system was designed and installed.

Cost data was also evaluated for a site installed in Monkstown, Northern Ireland (Beck, Harris, and Sweeny 2001). The site cost data were reported in pounds, but for ease of review the cost data were converted to U.S. dollars using the exchange rate for the report date of November 1, 2001. The remediation costs for the PRB system installed at the Monkstown site was $1,075,000, as noted in Table 10-1. The amount includes site investigation costs, excavation costs, disposal costs, capitol costs, and 10-year monitoring costs. The longevity of the PRB system was estimated at 10–15 year before minor iron replacement would be necessary and 50 years before major iron replacement would be necessary. Alternative remedies for this site included landfilling with installation of a

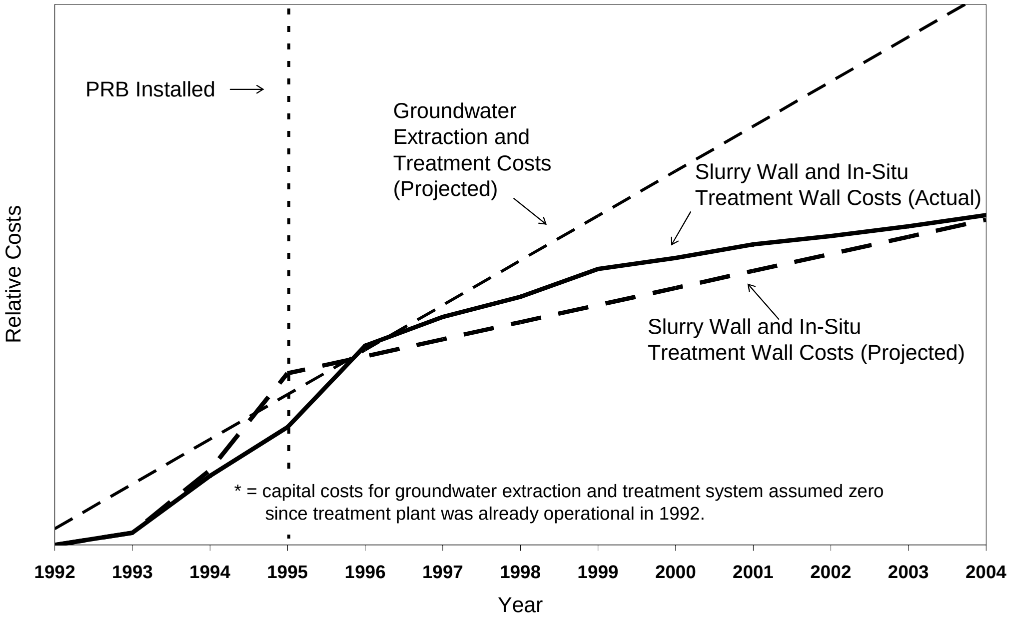


Figure 10-1. Costs for the PRB remedy compared to predicted costs and the former remedy (*Source*: Warner et al. 2004a).

pump-and-treat system that was estimated at $1,410,000, as well as containment with pump-and-treat installation at an estimated cost of $1,265,000. The cost-effectiveness of the PRB system was attributed to the lower installation, energy, and operational costs. Table 10-2 outlines the cost differential for the three site remedial alternative including the cost for the PRB system.

Table 10-1. Summary of costs of the permeable reactive barrier

Activity	Final cost ($)
Site investigation	
Main site investigation	281,470
Additional site investigation	54,117
Subtotal	335,587
Remediation	
Soil removal and disposal costs	109,650
Pilot-scale evaluation	26,316
Design preparation of contracts and working plan	23,392
Installation of cutoff wall and PRB	368,804
Supervision	55,615
Completion report	15,366
Subtotal	599,143
Groundwater monitoring	
Monitoring (10 years)	128,938
Tracer test	11,696
Consumables	292
Subtotal	140,926
Total	1,075,656

Source: Beck, Harris, and Sweeny 2001.

Table 10-2. Summary of costs for different remedial options

Activity	Landfilling with pump and treat	Containment wall with pump and treat	Permeable reactive barrier
Site investigation	$335,500	$335,500	$335,500
Excavation of soil and disposal	$438,600	$478,800	$109,700
Installation, O&M	$636,000	$450,300	$630,400
Totals	$1,410,000	$1,265,000	$1,075,600

Source: Beck, Harris, and Sweeny 2001.

11. CONCLUSIONS AND RECOMMENDATIONS

PRBs using zero-valent iron have been operating in the United States since 1994. Considerable information has been collected on the performance of PRBs in these 10 years. Although not all the design and performance issues are perfectly understood, the understanding of this technology has grown significantly since the early days. ZVI is the most common reactive media for PRBs and is used mainly to treat chlorinated solvents although it has application to other contaminants. Other reactive media, such as limestone, compost, zeolites, granular activated carbon, apatite, and others, have also been employed in PRBs in recent years and offer treatment options for additional contaminants. This technology has now been applied at more than 200 sites worldwide, including 72 full-scale installations to treat chlorinated solvent compounds. The vast majority of these PRBs are operating as intended. System hydraulics continues to be the main cause of inadequate performance. Ongoing refinements and improvements to construction methods are minimizing adverse impacts due to PRB construction.

Following are some of the key findings presented in this report:

- A thorough understanding of site characteristics is required for installation of PRBs.

- PRBs typically take advantage of ambient flow conditions. Promoting active flow through siphoning or limited pumping may be desirable in some cases.

- Once installed, this passive regime is difficult to modify or adjust, and therefore there is a greater stake in ensuring a successful PRB design, which is dependent on an accurate site characterization.

- Seasonal variations in groundwater flow and temperatures can affect the performance of the PRB and need to be accounted for in the design.

- In addition to recognizing the need for detailed hydrogeologic characterization, lessons learned from previous applications need to be incorporated into the design and construction of PRBs. These lessons include preventing zones of reduced permeability during construction and minimizing the variability in packing of the reactive material. Zones of reduced permeability or deflected flow can result from the use of sheet piling in incompatible geologic conditions, improper maintenance of biopolymer, and improper placement of reactive material through the biopolymer.

- Deployment of PRBs has been enhanced in recent years through the installation techniques using bioslurry and vertical hydraulic fracturing. This innovation has resulted in the installation of PRBs that are longer, thinner, and deeper. With biopolymer for trench support, PRBs can be installed to depths of 90 feet and thickness exceeding 10 feet. Vertical hydraulic fracturing has been used to install PRBs to depths as great as 117 feet.

- Research has shown that ZVI PRBs can be expected to last an estimated 10–30 years, depending on the rate of flow through the system and the levels of total dissolved solids.

- Use of low-flow and passive sampling methods to monitor the PRB is recommended to minimize disruption in the groundwater flow field.

- Despite its limitations, the most effective tool for monitoring the hydraulics of the PRB system is accurate groundwater head measurements.

- Tracer tests provide the best flow information but are difficult and expensive to conduct.

- When a PRB is located within the contaminant plume, it may be difficult to determine performance due to the residual downgradient contamination. Monitor wells should be installed within or close to the downgradient side of the reactive media to facilitate performance monitoring.

- Given the time lag in achieving downgradient water quality improvements, regulators and site owners should also consider establishing a temporary compliance point within the reactive media or near the downgradient edge of the PRB for some period of time following installation. This step would enable better evaluation of the PRB’s ability to treat groundwater contaminants to established regulatory standards. The location of the compliance points can be reevaluated as the downgradient residual contamination dissipates.

- The use of iron for source zone treatment is finding increased acceptance for site remediation.

- PRBs offer cost incentives due to the passive nature for the technology that adds to the reduced O&M costs. The one cost factor that is difficult to estimate is replacement or replenishment of the reactive media.

This technology has come a long way in the past 10 years, and it promises to provide effective and economical treatment of groundwater at many sites across the country. While PRBs have developed from an innovative technology to accepted standard practice, more research is still needed to understand several issues. Here are some areas where additional research or development is needed:

- Monitoring of the performance of the PRB is difficult where the downgradient plume is contaminated with residual contamination when the PRB is installed. Better monitoring techniques are necessary for monitoring performance in this situation. A better understanding of estimating the time necessary for desorption and flushing of the downgradient residual contamination is needed.

- Better means of identifying hydraulic performance of a PRB is needed due the current limitations with measuring groundwater head measurements over the short distance of a PRB system.

- Research on the regeneration or replenishment of reactive media is necessary. Replenishment of media has the potential to further reduce long-term O&M associated with this technology.

- Research and development is needed on source zone treatment using iron as a reactive media.

- The longevity of zero-valent iron and other reactive media used in PRBs is not fully understood and cannot be accurately predicted. Additional research could focus on how to predict longevity based on site-specific factors.

- Accurate documentation of the cost associated with deploying this technology is necessary. *Guide to Documenting and Managing Cost and Performance Information for Remedial Projects* (Federal Remediation Technologies Roundtable 1998) provides recommendations for documenting the cost and performance information for a technology deployment. Use of this guide will help to provide improved cost data at completed projects and aid in the estimation of proposed projects.

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APPENDIX A

Acronyms

ACRONYMS

α	alpha
αFeOOH	geothite
AFB	Air Force Base
AFO	amorphous ferric oxide
ALD	anoxic limestone drain
AMD	acid mine drainage
ARAR	applicable or relevant and appropriate requirement
ASTM	American Society for Testing and Materials
β	beta
bgs	below ground surface
BOF	basic oxygen furnace
BP	biopolymer
BTEX	benzene, toluene, ethylbenzene, and xylene
cDCE	*cis*-dichloroethene
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CFR	Code of Federal Regulations
Cl^-	chloride
CSM	conceptual site model
Cr^{+3}	trivalent chromium
Cr^{+6}	hexavalent chromium
$Cr(OH)_3$	chromium hydroxide
COC	contaminant of concern
CT	carbon tetrachloride
CVOC	chlorinated volatile organic carbon
CSM	conceptual site model
DBA	dibromoethane
DBCP	dibromochloropropane
DCA	dichloroethane
DCE	dichloroethene
DCM	dichloromethane
DCP	dicholorpropane
DNAPL	dense, nonaqueous-phase liquid
DO	dissolved oxygen
DOC	dissolved organic carbon
DoD	U.S. Department of Defense
DOE	U.S. Department of Energy
EDC	ethylene dichloride
Eh	reduction-oxidation, or redox, potential
ESTCP	Environmental Security Technology Certification Program
Fe^{+3}	ferric iron
Fe^{+2}	ferrous iron
$Fe(OH)_2$	brucite
Fe_2O_3	maghemite

Fe_3O_4	magnetite
GAC	granular activated carbon
HAZCOM	Hazardous Communication
HAZWOPER	Hazardous Waste Operations and Emergency Response
HCA	hexachloroethane
HDPE	high-density polyethylene
HPG	hydroxypropyl guar
HPGe	high-purity Germanium
HNO_3	nitric acid
H_2SO_4	sulfuric acid
ITRC	Interstate Technology & Regulatory Council
LTM	long-term monitoring
MCL	maximum concentration limit
MNA	monitored natural attenuation
MS	mass spectrometry
MSDS	material safety data sheet
MTBE	methyl *tert*-butyl ether
$Na_2S_4O_2$	sodium dithionite
NAPL	nonaqueous-phase liquid
NAS	Naval Air Station
NDMA	nitrosodimethylamine
NIOSH	National Institute for Occupational Safety and Health
NO_3	nitrate
NPDES	National Pollution Discharge Elimination System
OGI	Oregon Graduate Institute
O&M	operations and maintenance
ORP	oxidation-reduction potential
OSHA	Occupational Safety Health Administration
PAH	polynuclear aromatic hydrocarbon
PCE	perchloroethylene (perchloroethene, tetrachloroethene)
PCM	tetrachloromethane
PDB	polyethylene diffusion bag
PLFA	phospholipid fatty acid
PO_4	phosphate
ppb	parts per billion
PPE	personnel protective equipment
ppm	parts per million
PRB	permeable reactive barrier
QA	quality assurance
QC	quality control
RCRA	Resource Conservation and Recovery Act
RTDF	Remediation Technologies Development Forum
SO_4	sulfate
TBA	*tert*-butyl alcohol
TBM	tribromomethane
TCA	trichloroethane

TCE	trichloroethylene (trichloroethene)
TCLP	Toxicity Characteristic Leaching Procedure
TCM	trichloromethane
TCP	trichloropropane
TDS	total dissolved solid
TeCA	tetrachloroethane
THPS	tetrakishydroxymethyl phosphonium sulfate
TOC	total organic carbon
TSS	total suspended solids
UIC	underground injection control
USACE	U.S. Army Core of Engineers
USCG	U.S. Coast Guard
USEPA	U.S. Environmental Protection Agency
VC	vinyl chloride
VOA	volatile organic analyte
VOC	volatile organic compound
WDR	waste discharge requirement
ZVI	zero-valent iron

APPENDIX B

Additional Resources

ADDITIONAL RESOURCES

GENERAL RESEARCH WEB SITES

Ground-Water Remediation Technologies Analysis Center
www.gwrtac.org/html/tech_eval.html#PRB2001

Technology evaluation reports that provide reviews of selected remediation technologies, including PRBs.

Oregon Graduate Institute (OGI) School of Science & Engineering: Center For Groundwater Research (CGR)
http://cgr.ese.ogi.edu

Focuses on the development of new sampling and site characterization techniques, the development of new analytical techniques, and improved groundwater remediation techniques.

Remediation Technologies Development Forum (RTDF)
www.rtdf.org

A public-private partnership to undertake research, development, demonstration, and evaluation efforts focused on finding innovative solutions to high-priority problems.

Wiley InterScience
www3.interscience.wiley.com/cgi-bin/abstract/104520297/ABSTRACT

Remediation journal article: "The Use of Zero-Valent Iron Injection to Remediate Groundwater: Results of a Pilot Test at the Marshall Space Flight Center"

ONLINE DATABASES

Department of Energy
www.gjo.doe.gov/perm-barr/

DOE's Grand Junction Office PRB projects page.

Environmental Science and Technology Journal
http://pubs.acs.org/journals/esthag/

A journal published bimonthly that reports on aspects of the environment and its protection by scientific, engineering, and political means.

EPA Hazardous Waste Clean-Up Information Site (CLU-IN)
http://clu-in.org/conf/itrc/prb/resource.htm

List of PRB-related documents, Web sites, and other resources.

European Union

www.perebar.bam.de/PereOpen/PerebarFrameset-0.htm

Research project within the European Union: Long-Term Performance of Permeable Reactive Barriers Used for the Remediation of Contaminated Groundwater.

Federal Remediation Technologies Roundtable

http://costperformance.org/search.cfm

Case study database searchable by variables such as contaminant, technology, and location.

Oregon Graduate Institute (OGI) School of Science & Engineering: Center for Groundwater Research (CGR)

http://cgr.ese.ogi.edu/ironrefs/

Database of published information on contaminant remediation using zero-valent metals.

Remediation Technologies Development Forum (RTDF)

http://rtdf.org/public/permbarr/prbsumms/default.cfm#view

Profiles of ongoing and completed PRB demonstrations and installations.

U.S. FEDERAL/GOVERNMENT–SPONSORED WEB SITES

Department of Energy

- www.gjo.doe.gov/perm-barr/
  The Grand Junction Office PRB projects page.

- http://www-emtd.lanl.gov/Barrier/Mortendad.html
  Demonstration project with Los Alamos National Laboratory involving a multilayered PRB operating in Mortendad Canyon.

U. S. Environmental Protection Agency

- www.epa.gov/ORD/SITE/reports/r98501.html
  Superfund Innovative Technology Evaluation (SITE) Program: Technology evaluation report of a metal-enhanced in situ reactive iron wall designed to remediate volatile organic compounds.

- www.epa.gov/ada/pubs/reports.html
  Several interesting EPA reports related to groundwater and ecosystem restoration research.

- www.epa.gov/ada/pubs/reports.html
  Report describing the geochemical and microbiological processes within zero-valent iron PRBs. Two full-scale PRBs were evaluated: the U.S. Coast Guard Support Center PRB located near Elizabeth City, North Carolina and the Denver Federal Center PRB in Lakewood, Colorado.

Department of the Navy
www.efdsw.navfac.navy.mil/Environmental/pdf/hpnl1003.pdf
Newsletter describing the Navy's environmental cleanup program at the Hunters Point Shipyard using zero-valent iron injection.

NASA Kennedy Space Center: Groundwater Remediation Technologies
http://nasa.rti.org/ksc/remediation/
Information about environmental technologies developed at NASA's Kennedy Space Center.

INTERNATIONAL WEBSITES

Permeable Reactive Barrier Network (PRB-Net)
www.prb-net.org/
A network that promotes PRB technology funded by the Engineering and Physical Sciences Research Council, the U.K. government's leading funding agency for research and training in engineering and the physical sciences.

RUBIN
www.rubin-online.de/english/introduction/index.html
The German Permeable Reactive Barrier R&D network that covers more than 10 innovative PRB projects in Germany. The program is funded by the German Federal Ministry for Education and Research.

STATE-SPONSORED WEB SITES

Pennsylvania Department of Environmental Protection
www.dep.state.pa.us/dep/deputate/minres/bamr/amd/science_of_amd.htm
Report detailing the science of acid mine drainage and passive treatment.

TRAINING WEB SITES

Archive of ITRC PRB Training

- www.clu-in.org/conf/itrc/prb_031902/
  Permeable Reactive Barriers for Chlorinated Solvent, Inorganic, and Radionuclide Contamination.

- www.clu-in.org/conf/itrc/advprb_032102/
  Advanced Techniques on Installation of Iron-Based Permeable Reactive Barriers and Non-Iron-Based Barrier Treatment Material.

Environmental Restoration Technology Transfer (ERT2)
www.ert2.org/ert2portal/desktopdefault.aspx

List of Naval Facilities Engineering Command's (NAVFAC) environmental interactive Web training tools. NAVFAC manages the planning, design, and construction of shore facilities for U.S. Navy activities.

APPENDIX C

Material Safety and Technical Data Sheets for Busan 1059 and Troysan 142

BUSAN 1059 TECHNICAL DATA SHEET

Busan 1059: Broad-Spectrum Microbicide

Busan 1059 is a concentrated, flowable crystalline thione used in the control of microbiological fouling and spoilage in a variety of industrial applications. Busan 1059 is suitable for use in recirculating cooling water systems, oilfield water systems, preservation of a variety of slurries, adhesives and coatings, and in other EPA-approved applications.

Recirculating Cooling Water Systems

Busan 1059 can be used in the control of fouling related to the growth of bacteria, algae, and fungi in recirculating cooling water systems. Busan 1059 should be applied initially at a rate of 7.5–15 ppm (0.63–1.26 lb/10,000 gallons) every two to five days or until control is evident. Subsequent dosage should be 1.25–7.5 ppm (0.1–0.63 lb/10,000 gallons) every two to five days as needed to maintain control. This product is a crystalline solid and should be fed to an area of good flow to ensure adequate dissolution.

Oilfield Water Systems

Busan 1059 can be used to control fouling and corrosion caused by growth of microorganisms in oilfield water systems. Busan 1059 should be added to waterflood systems in an amount to provide up to 625 ppm (5.22 lb/1000 gal of water). The product should be fed as a slurry to the water leg of the manifold unit or the suction side of the triplex pumps, as often as needed to maintain control. In producing wells, Busan 1059 should be fed as a slurry and overflushed with an appropriate amount of water.

Oilfield Drilling Muds, Workover and Completion Fluids

Busan 1059 can be used to control growth of bacteria in drilling muds, frac fluids, and completion fluids. The product should be added to these fluids to maintain a concentration of 520 ppm (182 lb/1000 bbl of fluid). For best results, Busan 1059 should be added to the completion fluid or drilling mud mix tank or to the frac tank prior to gelling to ensure adequate dissolution. Busan 1059 can be used to control fouling and corrosion caused by growth of microorganisms in oilfield water systems and waterfloods.

General Preservation

Busan 1059 can be used as a preservative in adhesives, coatings, clay and calcium carbonate slurries, paper coatings, and other high viscosity suspensions. The level of Busan 1059 required will vary with the product to be preserved. Typically, Busan 1059 is added at levels between 0.01%–0.11% by weight of the formulation or product. To determine the amount needed for any given situation it is recommended that laboratory tests be conducted. For more information regarding the application of Busan 1059 , contact your Buckman representative.

Packaging and Handling

Busan 1059 is packaged in 40-lb Kraft-lined bags and 1000-lb Super Sacks. Improper handling of this product can be injurious to workers. Observe all safety precautions shown on the label and in the Material Safety Data Sheet. Busan® 1059 broad-spectrum microbicide.

Typical Product Characteristics

Active ingredient: Tetrahydro-3,5-dimethyl2H-1,3,5-thidiazine-2-thione	98.0%
Appearance	White crystalline solid
Density at 25°C (77°F)	0.53 cm^3
Solubility	Partially soluble in cold water; partially soluble in hot water
pH (100 ppm in water)	6–7

BUSAN 1059 MATERIAL DATA SAFETY SHEET

BUCKMAN LABORATORIES, INC.
SAFETY DATA SHEET

BUSAN 1059

Revision date: 2/5/2004 **Phone 1-800-BUCKMAN**

Buckman Laboratories, Inc.
1256 North McLean Boulevard
Memphis, TN 38108

24-Hour Emergency Phone: (901) 767-2722

SECTION 1 OSHA HAZARD CLASSIFICATIONS

Irritating to eyes, skin, and respiratory tract. Avoid inhalation of dust. Weak sensitizer.

SECTION 2 HAZARDOUS COMPONENTS

Chemical Name	***CAS Number***
Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione	533-74-4

% by Weight	***TLV***
98	Not available

The remainder of the components comprise proprietary information.

SECTION 3 FIRST AID INFORMATION

Eye Exposure: Flush immediately with copious amounts of tap water or normal saline (minimum of 15 minutes). Take exposed individual to a health care professional, preferably an ophthalmologist, for further evaluation.

Skin Exposure Wash exposed area with plenty of water. Repeat washing. Remove contaminated clothing and wash thoroughly before reuse. If irritation persists consult a health care professional.

Inhalation: If exposure by inhalation is suspected, immediately move exposed individual to fresh air. If individual experiences nausea, headache, dizziness, has difficulty in breathing or is cyanotic, seek a health care professional immediately**.**

***Ingestion*:** DO NOT INDUCE VOMITING. DO NOT INDUCE VOMITING. Rinse with copious amounts of water or milk, first. Irrigate the esophagus and dilute stomach contents by slowly giving one (1) to two (2) glasses of water or milk. Avoid giving alcohol or alcohol related products. In cases where the individual is semi-comatose, comatose or convulsing, DO NOT GIVE FLUIDS BY MOUTH. DO NOT GIVE FLUIDS BY MOUTH. In case of intentional ingestion of the product seek medical assistance immediately; take individual to nearest medical facility.

SECTION 4 PRIMARY ROUTES OF EXPOSURE

1. Effects from Acute Exposure:

Eye Exposure:
Hazardous in case of eye contact (irritant).

Skin Exposure:
Hazardous in case of skin contact (irritant, sensitizer). Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.

Inhalation:
May be harmful if inhaled. Do not breathe spray mists of the undiluted product. Effects will depend upon solution strength and length of time of exposure.

Ingestion:
Ingestion is not expected to be a primary route of exposure.

2. Effects from Chronic Exposure:
The effects from chronic exposure to this product have not been fully evaluated.

SECTION 5 Toxicological Information

Acute Effects:

Acute	Oral	(LD50)	=	363 mg/kg Rat
Acute	Dermal	(LD50)	=	>2000 mg/kg Rabbit
Acute	Inhalation	(LC50)	=	>1.7 mg/l (4 hours) Rat

Irritant/Sensitization Effects:

Hazardous in case of eye contact (irritant).

Hazardous in case of skin contact (irritant, sensitizer). Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering. May be harmful if inhaled. Do not breathe spray mists of the undiluted product. Effects will depend upon solution strength and length of time of exposure.

Carcinogenic Potential:

Not tested by Buckman Laboratories. Not shown as a carcinogen by OSHA, IARC, or NTP.

Target Organs Effects:

May cause damage to the following organs: upper respiratory tract, skin, eyes.

Other Health Effects:

None known.

SECTION 6 Environmental Toxicological Information

LC50 = 11.2 mg/l 48 hours Daphnia magna

LC50 = 16.2 mg/l 96 hours Rainbow trout

SECTION 7 Physical and Chemical Properties

Appearance	White crystalline solid
Odor	*Slight*
Density	0.53 g/cm^3 at 25˚C (77˚F)
Flash Point	Not available
Melting/Freezing Point	Not available

Boiling Point	Not available
Solubility	Partially soluble in cold water. Partially soluble in hot water.
pH (Neat)	Not available.
pH (100 ppm in water)	6–7
Vapor Pressure	Not applicable for solids
o/w Partition Coefficient	Not available
Oxidizing/Reducing Properties	Not available
Viscosity	Not available
Additional pH Information	Not available

NOTE: The physical data presented above are typical values and should not be construed as specifications.

SECTION 8 Fire and Explosion Information

Flammable Limits	Not available
Extinguishing Media	Water fog, carbon dioxide, foam, dry chemical.
Special Firefighting Procedures	Fire fighters should wear positive pressure self-contained breathing apparatus (SCBA) and full turnout gear.

SECTION 9 Reactivity Information

Stability	Stable under normal conditions of use and storage. Keep dry.
Incompatibility	Moisture.
Hazardous Decomposition Products	Carbon oxides (CO, CO_2), sulfur oxides (SO_2, SO_3).

SECTION 10 Handling Precautions

Rubber gloves, safety glasses or goggles, body protective clothing and shoes are required. Eye-wash fountains in the work place are recommended. Provide ventilation to control dust. If dusting can occur, a NIOSH approved respirator is recommended. The handling precautions for this product are based on the characteristics of the neat product unless otherwise specified.

SECTION 11 Satisfactory Materials of Construction

Not available.

SECTION 12 Spill, Leak, and Disposal Procedures

SPILL AND LEAK RESPONSE GUIDELINES:

Important: Before responding to a spill or leak of this product, review each section of this MSDS. Follow the recommendations given in the Handling Precautions sections. Check the Fire and Explosion Data section to determine if the use of nonsparking tools is merited. Insure that spilled or leaked product does not come into contact with materials listed as incompatible. If irritating fumes are present, consider evacuation of enclosed areas.

Emergency Response Assistance: Emergency technical assistance is available at any time from Buckman Laboratories, Inc., by calling (901) 767-2722.

Initially minimize area affected by the spill or leak. Block any potential routes to water systems (e.g., sewers, streams, lakes, etc.). Based on the product’s toxicological and chemical properties, and on the size and location of the spill or leak, assess the impact on contaminated environments (e.g., water systems, ground, air equipment, etc.). There are no methods available to completely eliminate any toxicity this product may have on aquatic environments. Minimize adverse effects on these environments. Buckman Laboratories, Inc. can be contacted for technical assistance. Determine if federal, state, and/or local release notification is required (see Regulatory Classifications section of this MSDS). Recover as much of the pure product as possible into appropriate containers. Later, determine if this recovered product can be used for its intended purpose. Address cleanup of contaminated environments. Spill or leak residuals may have to be collected and disposed of. Flushing residual material to an industrial sewer, if present at the site of a spill or leak incident, may be acceptable if authorized approval is obtained. If product and/or spill/leak residuals are flushed to an industrial sewer, insure that they do not come into contact with incompatible materials. Contact the person(s) responsible for the operation of your facility's industrial sewer system prior to intentionally flushing spills or leaks of this product to the industrial sewer.

DISPOSAL GUIDELINES:

Note: Follow federal, state, and local regulations governing the disposal of waste materials.

Neat Product: Contact your Buckman representative or Buckman Laboratories, Inc., at (901) 278-0330.

Contaminated Materials: Determine if waste containing this product can be handled by available industrial effluent system or other on-site waste management unit. If off-site management is required, contact a company experienced in industrial waste management. This product is not specifically listed in 40 CFR 261 as a Resource Conservation and Recovery Act (RCRA) hazardous waste. However, spill or leak residuals may meet the criteria of a characteristic hazardous waste under this Act. Check the characteristics of the material to be disposed of and/or the physical and reactivity data given in this MSDS for the neat product.

Container Disposal: Empty containers, as defined by appropriate sections of the RCRA, are not RCRA hazardous wastes. However, insure proper management of any residuals remaining in container.

DOT, IMO/IMDG, and IATA Shipping Information:
Not Regulated.

Unless otherwise stated, the shipping information provided above applies only to nonbulk containers of this product. Proper shipping name and general shipping information may vary depending on packaging and mode of shipment. All products shipped from Buckman locations have been properly packaged and labeled according to appropriate hazardous materials shipping regulations. If any alteration of packaging, product, or mode of transportation is further intended, different shipping information, including but not limited to proper shipping name, RQ designation, and labeling may apply. For further information pertaining to the shipping requirements for this product, contact Buckman's Transportation Department or DOT Coordinator.

SECTION 14 Regulatory Information

The following Regulations are known to apply to the use and disposal of this product. Additional Federal, State and Local regulations may also be applicable.

SARA (Superfund Amendments and Reauthorization Act)

SARA 302 Extremely Hazardous Substances List ...

No components of this product are listed.

SARA 312 Hazard Category ...

Immediate (Acute) Health Hazard

SARA 313 Toxic Chemicals List ...
This product contains the following toxic chemical(s) subject to the reporting requirements of section 313 of Title III of the Superfund Amendments and Reauthorization Act of 1986 and 40 CFR part 372: Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione

CERCLA (Comprehensive Environmental Response, Compensation and Liability Act) RCRA (Resource Conversation and Recovery Act) Listed Hazardous Waste CWA (Clean Water Act) Listed Substances FDA (Food and Drug Administration)

No components of this product are present above the *de minimus* levels.

No components of this product are listed.

This product is approved under the following FDA (21 CFR) sections: 1) 175.105 - Limitations: For use as a preservative only. 2) 178.3120 - Limitations: For use as a preservative only. 3) 176.230 - Limitations: For use as a preservative for substances added to the pulp suspension prior to the sheet forming operation, provided the preservative is volatilized by heat in the drying and finishing of the paper and paperboard. As a preservative for coatings, provided the preservative is volatilized by heat in the drying and finishing of the coated paper and paperboard. 4) 176.300 - No known limitations.

TSCA (Toxic Substances Control Act) Applicability FIFRA (Federal Insecticide, Fungicide, and Rodenticide Act)

All components are listed on the TSCA Inventory. Registered pesticides are exempt from the requirements of TSCA.

This product is a registered pesticide. EPA Reg. No. 1448-104

HMIS/NPCA Rating and NFPA Ratings
3 1 1 - Health Flammability Reactivity

State Regulations

Various State Right To Know Acts ...

Nonproprietary hazardous chemicals are listed in Section 2 of this MSDS. Should you require further information on specific proprietary or inert ingredients please contact Buckman Laboratories' Regulatory Affairs Department.

The information on this Material Safety Data Sheet reflects the latest information and data that we have on hazards, properties, and handling of this product under the recommended conditions of use. Any use of this product or method of application which is not described in the Data Sheet is the responsability of the user. This Material Data Safety Sheet was prepared to comply with the OSHA Hazard Communication regulations.

Buckman Laboratories, Inc. warrants that this product conforms to its chemical description and is reasonably fit for the purpose referred to in the directions for use when used in accordance with the directions under normal conditions. Buyer assumes the risk of any use contrary to such directions.

Seller makes no other warranty or representation of any kind, express or implied, concerning the product, including NO IMPLIED WARRANTY OF MERCHANTABILITY OR FITNESS OF THE GOODS FOR ANY OTHER PARTICULAR PURPOSE. No such warranties shall be implied by law and no agent of seller is authorized to alter this warranty in any way except in writing with a specific reference to this warranty.

The exclusive remedy against seller shall be in a claim for damages not to exceed the purchase price of the product, without regard to whether such a claim is based upon breach of warranty or tort.

Any controversy or claim arising out or relating to this contract, or breach thereof, shall be settle by arbitration in accordance with the commercial arbitration rules of the American Arbritation Association, and judgement upon the renderred by the Arbritrator(s) may be entered in any court having jurisdiction thereof.

TROYSAN 142 TECHNICAL DATA SHEET

Troysan 142:

- Powdered Organic Biocide
- FDA Certified Active Ingredient
- E.P.A. Registration No. 5383-7
- Product Code: 5065

Description

Troysan® 142 is a free-flowing powdered organic biocide. It has broad-spectrum efficacy in a variety of aqueous systems.

Use

Troysan® 142 is used in a variety of systems, including adhesives, pigment dispersions, resin emulsions, powder joint cements, protein colloids and other products where water is a primary component.

Further Troysan® 142 has the following FDA clearances:

- "CFR Title 21" Paragraph 176.300 Slimicides, Paragraph 175. 105, Adhesives, and Paragraph 176.170, Paper Paperboard, Paperboard Coatings.

Troysan® 142 should be added as early as possible in the manufacturing process to limit the potential of microbial attack. However, Troysan® 142 should not be exposed to elevated temperatures for extended periods of time.

Advantages

- Highly effective biocide
- Broad-spectrum (bactericide/fungicide) activity
- Long lasting
- 15 years of successful field experience
- Cost-effective protection
- FDA clearances

Packaging

Troysan® 142 is supplied in:

- 200 lb. fiber drums
- 50 lb. fiber drums
- 50 1 lb. water-soluble bags

Handling and Storage

Avoid storage at elevated temperatures for extended periods of time. Avoid contact with skin and eyes. If accidental contact should occur, wash affected area with large volumes of water. If irritation occurs, seek medical attention. Use in a well ventilated area. Avoid breathing dust for prolonged periods of time. May be harmful if ingested. Troysan® 142 should not be used in indoor spray application products.

Composition and Typical Physical Data

Active ingredient: 3,5-dimethyltetrahydro-1,3,5-2H-Thiadiazine-2-Thione	96–100% min.
Appearance:	White crystalline powder
Bulk density (g/cc):	1.39
Melting point:	103–107°C
Solubility:	
Water (30°C)	0.12%
Ethylene chloride (25°C)	21%
Acetone (30°C)	19.5%

NOTE: The above typical properties are not to be considered as purchase specifications.

TROYSAN 142 MATERIAL SAFETY DATA SHEET

TROY CHEMICAL CORP 1 Avenue L	**FOR MSDS INFORMATION: (973) 589-2500** **24 HOUR EMERGENCY PHONE NUMBER**	**Troysan 142** **Product Code:** 506X Effective Date: August 7, 2003 Replaces: October 22, 2001

1. PRODUCT & COMPANY IDENTIFICATION

PRODUCT NAME Troysan 142
CHEMICAL NAME Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione
CHEMICAL FAMILY Sulfur compounds
FORMULA Proprietary
SYNONYMS None

MANUFACTURER
Troy Chemical Corporation
1 Avenue L
Newark, N.J. 07105

2. COMPOSITION/INFORMATION ON INGREDIENTS

The listed components are considered to be hazardous based on OSHA's Hazard Communication Standard. For further regulatory information, see Section 15.

CHEMICAL NAME	**CAS#**	**%**	**AGENCY**	**EXPOSURE LIMITS**
Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione	533-74-4	>96	Not applicable	None established

OSHA Regulatory Status: This product is classified as hazardous under OSHA regulations.

3. HAZARDS IDENTIFICATION

EMERGENCY OVERVIEW

Troysan 142 is a white powder with a sulfur odor. May be toxic by ingestion. May cause skin sensitization. Toxic to fish and wildlife.

ROUTES OF ENTRY	Ingestion, skin contact, eyes, inhalation
INGESTION	May be toxic by ingestion. May cause convulsions and coma.
SKIN	May cause slight skin irritation and possible blisters. May cause sensitization in previously exposed individuals.
EYE CONTACT	May cause slight eye irritation.
INHALATION	May cause respiratory irritation.
CHRONIC EFFECTS	Repeated or prolonged skin contact may cause dermatitis due to irritation or sensitization. Prolonged or excessive inhalation may cause respiratory irritation.
TARGET ORGANS	Immune system (sensitizer)
CARCINOGENICITY	This product (or component) is not listed as a carcinogen according to OSHA, NTP, IARC, and ACGIH.

MEDICAL CONDITIONS AGGRAVATED BY EXPOSURE

May aggravate pre-existing respiratory and skin disorders.

4. FIRST AID MEASURES

INGESTION	Call poison control center or doctor immediately for treatment advice. Have person sip a glass of water if able to swallow. Do not induce vomiting unless told to do so by the poison control center or doctor. Do not give anything by mouth to an unconscious person.
SKIN CONTACT	Take off contaminated clothing. Rinse skin immediately with plenty of water for 15-20 minutes. Call a poison control center or doctor for treatment advice.
EYE CONTACT	Hold eye open and rinse slowly and gently with water for 15-20 minutes. Remove contact lenses, if present, after the first 5 minutes, then continue rinsing eye. Call a poison control center or doctor for treatment advice.
INHALATION	Move person to fresh air. If person is not breathing, call 911 or an ambulance, then give artificial respiration, preferably mouth-to-mouth, if possible. Call a poison control center or doctor for further treatment advice.
NOTES TO PHYSICIAN	None

Have the product container or label with you when calling a poison control center or doctor, or going for treatment.

5. FIRE FIGHTING MEASURES

FLASH POINT	Not applicable
FLAMMABLE LIMITS	Not applicable
AUTOIGNITION TEMPERATURE	Not applicable
FLAMMABILITY CLASS	Nonhazardous
HAZARDOUS PRODUCTS Of COMBUSTION	Carbon monoxide, carbon dioxide, nitrogen oxides, and sulfur oxides.
FIRE EXTINGUISHING MEDIA	Dry chemical, carbon dioxide, water spray, or regular foam.
FIRE FIGHTING INSTRUCTIONS	Move container from fire area if you can do it without risk. Do not scatter spilled material with high-pressure water streams. Avoid breathing vapors, keep upwind. Positive pressure self-contained breathing apparatus with full face piece and structural firefighters' protective clothing will provide limited protection.
UNUSUAL FIRE & EXPLOSION HAZARDS	This material may burn but does not ignite readily. Runoff from fire control or dilution water may cause pollution.

6. ACCIDENTAL RELEASE MEASURES

Keep unnecessary people away; isolate hazard area and deny entry. Wear protective equipment as specified in Section 8. Stop leak if you can do it without risk. For small dry spills, shovel material into clean, dry container and cover loosely; move containers from spill area. Wet residue with water, absorb with vermiculite or other noncombustible absorbent material and place into containers for later disposal. For large dry spill, cover spill with plastic sheet or tarp to minimize spreading. For large spills, dike far ahead of liquid spill for later disposal. If water pollution occurs, notify the appropriate authorities.

Observe all Federal, State, and Local regulations regarding notifications of accidental releases.

7. HANDLING & STORAGE

Avoid contact with eyes and skin. Avoid breathing dust. Wash thoroughly after handling. Keep container tightly closed. Use only with adequate ventilation. Do not permit dust to collect on walls, floors, sills, ledges, machinery, or equipment. Avoid breakage of bagged material or spills of bulk material. Store away from incompatible substances in a cool, dry, ventilated area. Keep containers closed until used. Avoid generating dust. Do not contaminate water, food, or feed by storage or disposal.

Observe all Federal, State, and Local regulations when storing or disposing of this substance.

8. PERSONAL PROTECTION/EXPOSURE CONTROLS

VENTILATION	Provide local exhaust or process enclosure ventilation to minimize exposure.
EYE/FACE PROTECTION	If potential for contact with material exists, use dust-resistant safety goggles or other approved eye protection.
SKIN PROTECTION	Wear impervious gloves and apron to prevent skin contact. Wear impermeable suit if exposure is possible to a large portion of the body.
RESPIRATORY PROTECTION	A respiratory protection program meeting OSHA 1910.134 must be followed whenever workplace conditions warrant the use of a respirator. If exposure may exceed recommended limits, a NIOSH/MSHA-approved respirator should be used based on exposure levels found in the workplace.
OTHER	Eyewash and safety shower should be available within the immediate work area for emergency use.

9. PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE	White powder
SPECIFIC GRAVITY AT 25˚C. (Water=1)	1.35–1.45
ODOR	Sulfur odor
WATER SOLUBILITY	Slight (decomposes)
INITIAL BOILING POINT	Not applicable
pH	Not applicable
MELTING POINT	105˚C (221˚F)(decomposes)
EVAPORATION RATE (Butyl acetate=1)	Not applicable
VAPOR PRESSURE AT 20˚C	Not applicable
% VOLATILES BY WEIGHT	Not applicable
VAPOR DENSITY (Air=1)	Not applicable

10. STABILITY & REACTIVITY

REACTIVITY	Stable under normal temperatures and pressures
CONDITIONS TO AVOID	Avoid excess heat and moisture
INCOMPATIBILITY	Avoid contact with acids and oxidizing agents.
HAZARDOUS DECOMPOSITION	Decomposition may release carbon monoxide, carbon dioxide, nitrogen oxides, and sulfur compounds.
HAZARDOUS POLYMERIZATION	Hazardous polymerization does not occur.

11. TOXICOLOGICAL INFORMATION

ACUTE ORAL EFFECTS

LD50 (oral, rat) - 519 mg/kg.

ACUTE SKIN EFFECTS

LD50 (dermal, rabbit) > 2000 mg/kg. Non-irritating. May cause skin sensitization in previously exposed individuals.

ACUTE EYE EFFECTS

Non-irritating.

ACUTE INHALATION EFFECTS

LC50 (rat, 4 hr) - 8400 mg/m3.

SUBCHRONIC EFFECTS AND OTHER STUDIES

A two-year feeding study and a one-year dog feeding study showed signs of liver and kidney damage. An 18-month mouse feeding study provided evidence of increased incidences of benign liver tumors.

12. ECOLOGICAL INFORMATION

ECOTOXICITY	This product is toxic to fish. Do not apply directly to water or wetlands. Do not contaminate water when disposing of equipment washwaters. Data on the active ingredient, Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione is as follows: LC50 (bluegill sunfish, 96 hr flow-through) - 0.30 mg/l LC50 (rainbow trout, 96 hr flow-through) - 0.16 mg/l
ENVIRONMENTAL FATE	This product is a pesticide and may cause adverse environmental impact. Do not discharge effluent containing this product directly into lakes, streams, ponds, estuaries, oceans, or public waters unless this product is specifically identified and addressed in a NPDES permit. Do not discharge effluent containing this product to sewer systems without previously notifying the sewage treatment plant authority. For guidance, contact your state Water Board or Regional Office of the Environmental Protection Agency. BOD - 85 mg O_2/g COD - 1270 mg O_2/g

13. DISPOSAL INFORMATION

RCRA HAZARDOUS WASTE	This product is not a RCRA hazardous waste by definition.
WASTE DISPOSAL PROCEDURE	The user of this material has the responsibility to dispose of unused material, residues, and containers in compliance with all Federal, State, and Local Regulations

14. TRANSPORTATION INFORMATION

DOT	**SHIPPING NAME**	Environmentally hazardous substance, solid n.o.s. (contains: Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione, marine pollutant)
	HAZARD CLASS	9 - Misc. dangerous goods
	UN/NA NUMBER	UN3077
	PACKING GROUP	PG III
	LABELS REQUIRED	Class 9, Marine pollutant
	ERG#	171
IATA	**SHIPPING NAME**	Environmentally hazardous substance, solid n.o.s. (contains: Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione, marine pollutant)
	HAZARD CLASS	9 - Misc. dangerous goods
	UN/NA NUMBER	UN3077
	PACKING GROUP	PG III
	LABELS REQUIRED	Class 9, Marine pollutant
	ERG#	9L

IMDG	**SHIPPING NAME**	Environmentally hazardous substance, solid n.o.s. (contains: Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione, marine pollutant)
	HAZARD CLASS	9 - Misc. dangerous goods
	UN NUMBER	UN3077
	PACKING GROUP	PG III
	LABELS REQUIRED	Class 9, Marine pollutant
	EMS#	F-A, S-F

15. REGULATORY INFORMATION

CERCLA SECTION 103 (40CFR302.4)

This product does not contain any chemicals that are reportable to the National Response Center under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA).

SARA SECTION 302 (40CFR355.30), SARA SECTION 304 (40CFR355.40)

This product does not contain any chemicals that require emergency planning based on Threshold Planning Quantities (TPQ) or release reporting based on Reportable Quantities (RQ).

SARA HAZARD CATEGORIES, SARA SECTIONS 311/312 (40CFR370.21)

ACUTE	CHRONIC	FIRE	REACTIVE	PRESSURE
X				

SARA SECTION 313 (40CFR372.65)

This product contains the following toxic chemicals subject to the reporting requirements of the Emergency Planning and Community Right-to-Know Act of 1986 . This information must be included in all MSDSs that are copied and distributed for this material.

CHEMICAL NAME	CAS#	%
Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione	533-74-	>96

CHEMICAL INVENTORIES

The ingredients of this product are all on the following Chemical Substance Inventories, are exempt from the Inventories, or are otherwise compliant with inventory requirements of the governing agency.

TSCA	EINECS	DSL/NDSL	AICS	ECL	MITI,ENCS	PICCS	IECSC
X	X	X	X	X	X	X	X
U.S.	Europe	Canada	Australia	Korea	Japan	Philippines	China

CALIFORNIA PROPOSITION 65

This product does not contain any substances that are currently on the list of Known Carcinogens and Reproductive Toxins, at levels which would require a warning under the statute.

STATE RIGHT-TO-KNOW

This product is regulated by the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) and is exempt from State Right-to-Know labeling requirements when labeled with an approved EPA label.

EPA Registration No. 9386-13-5383

16. OTHER

REVISIONS **Prepared by:** Environmental and Regulatory Affairs Dept.

This MSDS has been revised in the following sections: (revisions indicated in left border)

Sect. 3 (Revised Emergency Overview, Acute and Chronic Effects), Sect. 4 (Revised First Aid Measures), Sect. 9 (Revised Physical data), Sect. 10 (Revised Conditions to Avoid), Sect. 11 (Revised Toxicology Data), Sect. 12 (Added BOD, COD data), Sect. 14 (Revised Shipping name and labels - Marine pollutant, Revised IMDG EMS#), Sect. 15 (Updated Chemical Inventory Status)

ABBREVIATIONS

PNOC - Particulates not otherwise classified
PNOR - Particulates not otherwise regulated
STEL - Short-term exposure limit
TLV - Threshold limit value
TWA - Time-weighted average

HMIS RATING				**NFPA RATING**		
HEALTH	**FLAMMA-BILITY**	**REACTIVITY**	**PERSONAL PROTECTION**	**HEALTH**	**FLAMMA-BILITY**	**REACTIVITY**
2	1	0	C	2	1	0

APPENDIX D

American Society of Testing and Materials Geotechnical Testing Methods

AMERICAN SOCIETY OF TESTING AND MATERIALS
GEOTECHNICAL TESTING METHODS

ASTM D422-63 (2003), Standard Test Method for Particle-Size Analysis of Soils. Grain-size analysis or particle-size distribution utilizes sieves for segregation of coarse material (i.e., gravels and sands), and hydrometers and sedimentation cylinders for silts and clays. The basic objective of particle-size analysis is to determine relative proportions of each size range.

ASTM D698-00ae1, Standard Test Methods for Laboratory Compaction Characteristics of Soil Using Standard Effort (12,400 ft-lbf/ft^3 [600 kN-m/m^3]). These test methods cover laboratory compaction methods used to determine the relationship between water content and dry unit weight of soils (compaction curve) compacted in a 4- or 6-inch (101.6- or 152.4-mm) diameter mold with a 5.5-lbf (24.4-N) rammer dropped from a height of 12 inches (305 mm) producing a compactive effort of 12,400 ft-lbf/ft^3 (600 kN-m/m^3). Compaction tests provide the relationship between dry density and moisture content for a given degree of compaction effort. Compaction is achieved by mechanical means, thus increasing the soils dry density through reduction of air voids in the soil with little or no reduction in moisture content.

ASTM D854-02, Standard Test Methods for Specific Gravity of Soil Solids by Water Pycnometer. These test methods cover the determination of the specific gravity of soil solids that pass the 4.75-mm (No. 4) sieve, by means of a water pycnometer. When the soil contains particles larger than the 4.75-mm sieve, Test Method C 127 shall be used for the soil solids retained on the 4.75-mm sieve, and these test methods shall be used for the soil solids passing the 4.75-mm sieve. Specific gravity of a soil is used to calculate the phase relationships of soils or the relative volumes of solids to water and air in a given volume of soil.

ASTM D1140-00, Standard Test Methods for Amount of Material in Soils Finer Than the No. 200 (75-μm) Sieve. These test methods cover determination of the amount of material (silt and clay particles in a soil) finer than a 75-μm (No. 200) sieve by washing.

ASTM D2216-98, Standard Test Method for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass. Moisture content can provide an extremely useful method of classifying cohesive soils and of assessing their engineering properties.

ASTM D2434-68 (2000), Standard Test Method for Permeability of Granular Soils (Constant Head). This test method covers the determination of the coefficient of permeability by a constant-head method for the laminar flow of water through granular soils. The procedure is to establish representative values of the coefficient of permeability of granular soils that may occur in natural deposits as placed in embankments or when used as base courses under pavements. In order to limit consolidation influences during testing, this procedure is limited to disturbed granular soils containing not more than 10% soil passing the 75-μm (No. 200) sieve. Permeability of granular soils determines the coefficient of permeability by constant or falling head methods for the laminar flow of water through granular soils.

ASTM D2487-00, Standard Classification of Soils for Engineering Purposes (Unified Soil Classification System). This method is part of the unified classification system and often requires particle-size and Atterberg limits analysis. This method classifies natural soil including gravels, sands, silts, clays, organic silts and clays, and peat. The classification is based on the particle-size distribution from particle-size analysis, the percentage of organic matter for fine-grain soils (silts and clays), and the liquid limit and plasticity index from the Atterberg test.

ASTM D2488-00, Standard Practice for Description and Identification of Soils (Visual-Manual Procedure). This method provides a means for classifying soils by visual estimation and is used as an alternative to ASTM D2487. Based on the percentage of gravel, sand, silts, and clays, a group symbol and group name can be determined for the soil. This method established criteria for describing angularity of course-grain particles, particle shape, moisture condition, reaction with HCl, consistency, cementation, structure, dry strength, dilatancy, toughness, and plasticity.

ASTM D2937-04, In-Place Density or Bulk Density. This test method covers the determination of in-place density of soil by the drive-cylinder method. The test method involves obtaining a relatively undisturbed soil sample by driving a thin-walled cylinder and the subsequent activities for the determination of in-place density. When sampling or in-place density is required at depth, Test Method D 1587 should be used. In-place density is determined by the drive-cylinder method, which collects an undisturbed soil sample. The density is expressed by mass per unit volume. Modifications of this method can be used to determine bulk density and dry bulk density.

ASTM D2974-00, Standard Test Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils. These test methods cover the measurement of moisture content, ash content, and organic matter in peats and other organic soils, such as organic clays, silts, and mucks. This method is used to determine the organic content of organic soils and peat by combusting the sample and subtracting the ash content.

ASTM D4318-00, Standard Test Methods for Liquid Limit, Plastic Limit, and Plasticity Index of Soils. These test methods cover the determination of the liquid limit, plastic limit, and the plasticity index of soils. The objectives of "Atterberg limits" tests are to determine an estimate of a soil or sediment strength and settlement characteristics. It is the primary form of classification for cohesive soils.

ASTM D5084-03, Standard Test Methods for Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter. This test method covers laboratory measurement of the hydraulic conductivity of water-saturated porous materials with a flexible-wall permeameter. This test method may be used with undisturbed or compacted soil specimens that have a hydraulic conductivity $\leq 5 \times 102$ cm/s (fine soils/clays).

APPENDIX E

PRB Case Studies

PRB CASE STUDIES

This appendix contains case studies that use PRB technology, gathered from various sources and provided in a table or narrative format. The majority of case studies were obtained through an online case study survey developed by the ITRC PRB team and distributed among the ITRC state points of contact as well as several industry representatives and known site managers. Several case studies were also provided by individual PRB team members. The majority of case studies presented in this appendix are also summarized in Tables 2-3 and 2-4.

Case Study #1: ExxonMobil Bayway Refinery	
Site Location:	Linden, New Jersey
Installation Date:	August 2002
Type of Installation:	Full scale
Contaminants:	Product and BTEX
Reactive Media:	Dissolved-oxygen curtain wall
Site Contact:	Brent Archibald, brent.b.archibald@exxonmobile.com, 908-730-2404

Case Study #2: Alameda Point (Former Alameda Naval Air Station)	
Location:	Alameda, California
Installation Date:	1996/97
Type of Installation:	*Information not provided*
Contaminants:	cDCE, VC, TCE, BTEX
Reactive Media:	Zero-valent iron followed by oxygen biosparging
Type of Construction:	Sheet pile continuous wall, funnel and sequenced gate
Other Relevant Information:	• Former Naval Air Station • Leaks from on-site landfill • >100 mg/L CVOCs; 10 mg/L toluene • Gate is 10 feet wide and 15 feet long; 10-foot funnels perpendicular to groundwater flow • Pilot-scale demonstration; proposed for expansion
Contact:	Adriana Constantinescu, CA Regional Water Board, 510-622-2353

Case Study #3: Intersil Semiconductor	
Location:	Sunnyvale, California
Installation Date:	1995
Type of Installation:	*Information not provided*
Contaminants:	TCE, cDCE, VC, Freon 113
Reactive Media:	Zero-valent iron
Type of Construction:	Sheet pile continuous wall, funnel and gate

Case Study #3: Intersil Semiconductor	
Other Relevant Information:	• Semiconductor manufacturer • Leaks from wastewater neutralization holding tank • 200 μg/L TCE, 1000 μg/L *cis*-1,2-DCE, 500 μg/L VC • Barrier is 4 feet wide × 36 feet long × 11 feet deep with low-permeability wing to 20 feet deep • Installation cost: $1M
Contact:	Scott Warner, Geomatrix Consultants, 510-663-4269

Case Study #4: Fairchild/Applied Materials	
Location:	Sunnyvale, California
Installation Date:	1995
Type of Installation:	*Information not provided*
Contaminants:	Chlorinated VOCs
Reactive Media:	Zero-valent iron
Type of Construction:	Sheet pile continuous wall
Other Relevant Information:	*Information not provided*
Contact:	Keith Roberson, CA Regional Water Board, 510-622-2404

Case Study #5: Mohawk	
Location:	Sunnyvale, California
Installation Date:	2003
Type of Installation:	*Information not provided*
Contaminants:	Chlorinated VOCs
Reactive Media:	Zero-valent iron
Type of Construction:	Biopolymer slurry wall
Other Relevant Information:	~700-foot-long iron filing wall, 20 to 35 feet deep along Central Expressway median
Contact:	Keith Roberson, CA Regional Water Board, 510-622-2404

Case Study #6: Moffett Federal Airfield	
Location:	Mountain View, California
Installation Date:	1996
Type of Installation:	*Information not provided*
Contaminants:	TCE, 1,2-DCE, PCE
Reactive Media:	Zero-valent iron
Type of Construction:	Sheet pile continuous wall, funnel and gate

Case Study #6: Moffett Federal Airfield	
Other Relevant Information:	- Naval Air Station - Historic on-site and off-site sources - 13,000 μg/L TCE, 1118 μg/L 1,2-DCE, 130 μg/L PCE - Gate is 10 feet wide × 6 feet long with two 20-foot-long sheet pile funnels - Potential for long-term formation of precipitates; performance and longevity evaluations summarized in Tri-Agency report - Design and installation cost: $540,000
Contact:	Andrea Espinoza, BRAC Environmental Coordinator, Naval Facilities Engineering Service Center, 619-532-0911

Case Study #7: DuPont	
Location:	Oakley, California
Installation Date:	2001
Type of Installation:	*Information not provided*
Contaminants:	CCl_4, $CHCl_3$, Freon 11, Freon 113
Reactive Media:	Zero-valent iron
Type of Construction:	Continuous PRB; vertically oriented hydrofracturing
Other Relevant Information:	- Chemical manufacturer - Historic leaks and spills - 20–40 mg/L CCL_4, 3–10 mg/L Freon - PRB is 110 feet long × 6 inches thick; emplaced 65–120 feet deep - Problems due to sands at base, possible vertical conduit; proposal for alternative design - Installation cost: $1.15M
Contact:	Jim Vidumsky, DuPont, 704-362-6638, www.dupontoakley.com

Case Study #8: Sierra Army Depot	
Location:	Hertong, California
Installation Date:	2001, 2003
Type of Installation:	*Information not provided*
Contaminants:	TCE
Reactive Media:	Zero-valent iron
Type of Construction:	Injection with vertical hydrofracturing

Case Study #8: Sierra Army Depot	
Other Relevant Information:	• Two pilot studies • Injection of Ferox iron powder and iron filing slurry 95–115 feet bgs • 1000 μg/L TCE • Test 1: Nine injection points at 40-foot spacings in two rows • Test 2: Hydrofracturing and injection in five wells 25 feet apart
Contact:	James Brathovde, CA Regional Water Board, 530-542-5572

Case Study #9: Private Site	
Location:	Gardena, California
Installation Date:	2003
Type of Installation:	*Information not provided*
Contaminants:	Chlorinated VOCs
Reactive Media:	Zero-valent iron
Type of Construction:	Vertical hydrofracturing
Other Relevant Information:	*Information not provided*
Contact:	Jim Ortman, GeoSierra, 770-492-8214, jortman@geosierra.com

Case Study #10: Private Site	
Location:	Los Angeles, California
Installation Date:	2003
Type of Installation:	*Information not provided*
Contaminants:	Chlorinated VOCs
Reactive Media:	Zero-valent iron
Type of Construction:	Biopolymer slurry wall
Other Relevant Information:	Information not provided
Contact:	Pinaki Guha-Niyogi, CA Regional Water Board, 213-576-6072

Case Study #11: Zeneca Ag Products/Campus Bay	
Location:	Richmond, California
Installation Date:	2002
Type of Installation:	*Information not provided*
Contaminants:	Acid mine drainage (low pH, heavy metals)
Reactive Media:	Compost (leaf material w/soil-sand mix) sulfate-reducing bacteria added

Case Study #11: Zeneca Ag Products/Campus Bay	
Type of Construction:	Slurry trench
Other Relevant Information:	• ~1/4 mile long × 20 feet deep × 2 feet wide • Disposal of waste pyrite cinders from mining operations • Low pH and metals (Fe, Hg, As, Cu, Zn) • Wall creates reducing conditions, lowers pH, precipitates metals • Fortified with sulfate-reducing bacteria to stabilize iron
Contact:	Cecil Felix, CA Regional Water Board, 510-622-2343

Case Study #12: Louisiana Pacific	
Location:	Fort Bragg, California
Installation Date:	*Information not provided*
Type of Installation:	*Information not provided*
Contaminants:	Chlorinated VOCs
Reactive Media:	Activated carbon
Type of Construction:	Funnel and gate, 4-inch carbon canisters, upgradient gravel collection trenches
Other Relevant Information:	*Information not provided*
Contact:	Craig Hunt, CA Regional Water Board, 707-576-3767

Case Study #13: The Dow Chemical Company	
Location:	Pittsburg, California
Installation Date:	2000, 2002
Type of Installation:	*Information not provided*
Contaminants:	CCL_4, MeCL, TCE, PCE
Reactive Media:	Propylene glycol for enhanced anaerobic microbial destruction
Type of Construction:	39 subsurface circulation wells aligned in three distinct linear segments
Other Relevant Information:	• Three zones, ~1/4 mile long × 20 feet wide × 135 feet deep • Series of up and down pumping wells (36 total) aligned to create “bio-barrier” • Reinjection of “bio-augmentation” groundwater • Circulation between mid and deep transmissive zones to 135 feet bgs • Reductive dechlorination
Contact:	Alec Naugle, CA Regional Water Board, 510-622-2510

Case Study #14: Vandenberg Air Force Base	
Location:	Lompoc, California
Installation Date:	*Information not provided*
Type of Installation:	*Information not provided*
Contaminants:	MTBE
Reactive Media:	Oxygen
Type of Construction:	Permeable wall of polyethylene tubing to diffuse oxygen into groundwater
Other Relevant Information:	*Information not provided*
Contact:	Carol Kolb, CA Regional Water Board, 805-542-4625

Case Study #15: Cyprus AMAX Minerals Company/AMAX Realty Development, Inc.	
Site Location:	Carteret, New Jersey
Installation Date:	August 1993; extended in November 1999
Type of Installation:	Full scale
Site Characteristics:	The site was a copper-smelting facility that dissolved scrap copper in the tank house. Other metals in groundwater were the result of production in the precious metals plant. The site is underlain by fill material, glacial till, and clay, all of which overlie diabase bedrock. The depth to bedrock is approximately 50–60 feet bgs. The water table is approximately 10–15 feet bgs.
PRB Dimensions:	The barrier is approximately 685 feet long and was installed to a depth of approximately 45 feet. It was installed through the fill and upper till layers and into several feet of sand below. A 250-foot extension of the trench was installed downgradient of the nickel plant in 2000. The width of the trenches ranged 3–5 feet.
Contaminants:	Copper (154 mg/L), nickel (322 mg/L), selenium (0.15 mg/L) and zinc (8.9 mg/L); averages found in the tank house sumps in 1993 are noted in parentheses. Maximum concentrations were higher.
Permits Required:	None
Regulatory Issues:	Discharge of contaminated groundwater to surface water.
Cleanup Goals:	Reduce metals loading to the adjacent Arthur Kill, a saline estuary.
Reactive Media:	A total of 4700 tons of dolomitic limestone and 126,000 pounds of sodium carbonate were used in the construction of the tank house trench. Sodium carbonate (powder) was mixed with the ¾-inch dolomitic limestone at a rate of approximately 180 pounds per foot of trench. Flexible, perforated piping was installed at eight locations along the 685-foot trench to allow the future addition of sodium carbonate solution. Approximately 2600 tons of dolomitic limestone and 20 tons of sodium carbonate (at a rate of 150 pounds per foot of trench) were used in the construction of the barrier trench extension (adjacent to the former nickel plant) in November

Case Study #15: Cyprus AMAX Minerals Company/AMAX Realty Development, Inc.	
	and December 1999. Two rigid PVC pipes were installed to allow recirculation of groundwater in the trench and recharge of the trench with sodium carbonate solution. From May 4th to May 9th, 2000, approximately 2600 pounds of sodium carbonate was added to the trench as a slurry.
Type of Construction:	Continuous trench. Initially, groundwater was pumped from downgradient monitor wells and discharged into the trench in a closed loop. Thereafter, the barrier was allowed to act passively.
Advantages/ Disadvantages of Design and Installation Technique:	The flexible, perforated piping is very useful in allowing recharge of the trench.
Results Achieved:	Metals concentrations have generally decreased over time; however, long-term monitoring is still being performed to evaluate whether additional sodium carbonate will be needed to recharge the trench.
Problems Encountered:	The method causes the pH of the groundwater to rise and precipitation of metals onto soil solids, thus lowering the dissolved metals concentrations in groundwater. However, this has the potential to reduce the permeability of the aquifer materials over time.
Type & Frequency of Sampling:	Annual groundwater monitoring
Site Contact:	Jeff Story, jeff.story@dep.state.nj.us, 609-292-9964

Case Study #16: Lockheed Martin Space Systems Company	
Contaminants:	Trichloroethene and daughter products
Reactive Media:	Granular reactive iron
Construction:	Pilot project as corrective measures study—designed as a permeable chemical reactive wall configured as a manhole of permeable plastic with reactive iron in place to passively treat groundwater containing VOCs as the groundwater entered the storm drain system.
Results Achieved:	Preliminary results indicate that the reactive iron reduced VOCs in groundwater entering the storm drain during the time the system operated. PRB currently inactive pending corrective measures study results from other pilots.
Site Contact:	Carolyn Monteith (Lockheed Martin) 504-257-3189; Kristine Carter or Douglas Bradford (LDEQ) 225-219-3406

Case Study #17: Travis Air Force Base	
Site Location:	Fairfield, California
Date Installation Completed:	June 1999
Type of Installation:	Pilot scale
Target Contaminants:	TCE, DCE
Geologic Material	Clay, silt, and sand. Approximately 50 feet of alluvium (silt and sand) overly the semilithified lower permeable (silt/clay) Tehama Fm. Occasional thin (<2-foot) sand stringers.
Reactive Media:	Zero-valent iron. 303 tons of ZVI used, ~161 tons (53%) left in place.
PRB Configuration:	Continuous
PRB Construction Techniques:	Jetting
Dimensions:	The report dimensions are 91 feet long × 5 feet wide, depth 20–40 feet bgs. Four core samples were taken along the wall from within the jetted zones. Magnetic fractions ranged from 0.5% to 97% of the samples, with relative high variability of iron percentage within each core. Core lengths ranged 10–16 feet with magnetic fractions sampled at ~2-foot intervals.
Application:	Plume control
Was the PRB combined with another technology?	Yes. Placement via jet via both single-cut jetting using compressed air and double-cut jetting without compressed air. Double-cut without compressed air appears to have left more iron in place, but at a lower permeability.
Permits Required:	None
Initial Monitoring Frequency:	Quarterly; semiannually
Long-term Monitoring Frequency:	Semiannually
Target cleanup levels/ objectives:	MCLs
Are the target cleanup levels/ objectives being met?	No
Time required to meet target cleanup levels/ objectives:	Unknown
Performance Problems:	Hydraulic and site characterization problems. The jetting process was seriously flawed. Almost 50% of the ZVI was jetted out and never placed in the wall. After five years, the guar gum residuals are still present and groundwater flows around the “permeable barrier.”

Case Study #17: Travis Air Force Base	
Additional Information	The AF went forward with this pilot project without having a long-term program to address data gaps identified in the demonstration report. The data gaps include (1) lack of adequate monitoring wells for determining groundwater flow conditions, (2) lack of TOC and DOC data in the wall, and (3) distribution of ZVI within the wall. An enzymatic breaker should also be added to properly break the guar gum and residuals.
Site Contact:	Glenn Anderson; Glenn.anderson@travis.af.mil; 707-424-4359

Case Study #18: Pease Air Force Base, Site 73	
Site Location:	Portsmouth, New Hampshire
Date Installation Completed:	August 1999
Type of Installation:	Full-scale demonstration
Target Contaminants:	TCE, DCE, vinyl chloride
Geologic Material	Sand
Reactive Media:	Zero-valent iron
PRB Configuration:	Continuous
PRB Construction Techniques:	Biodegradable slurry
Dimensions:	Depth 32 feet (2–34 feet bgs), length 150 feet, thickness 2.5 feet
Application:	Plume control
Was the PRB combined with another technology?	No
Permits Required:	CERCLA Program site
Initial Monitoring Frequency:	Semiannually; annually
Long-term Monitoring Frequency:	Annually
Target cleanup levels/ objectives:	MCLs
Are the target cleanup levels/objectives being met?	No
Time required to meet target cleanup levels/ objectives:	Years
Performance Problems:	Hydraulic problems: small amount of underflow (through fractured bedrock)
Additional Information	Wall appears to be operating well, more time required to meet remedial goals. Difficult to estimate time. Site has been determined to be operating properly and successfully.
Site Contact:	Dave Strainge, dave.strainge@afrpa.pentagon.af.mil, 207-328-7109

Case Study #19: Has-Has Custom Cleaners	
Site Location:	Bensalem, Bucks County, Pennsylvania
Date Installation Completed:	June 2000
Type of Installation:	Full scale
Target Contaminants:	PCE; TCE; *cis*-1,2-, *trans*-1,2-, and 1,1-dichloroethene
Geologic Material	Clay, gravel, fill
Reactive Media:	Mixture of sand and industrial iron filings
PRB Configuration:	Other
PRB Construction Techniques:	Other
Dimensions:	PRB consisted of eight 1-inch-diameter borings drilled to a depth of 17 feet bgs in downgradient direction from the source
Application:	Plume control
Was the PRB combined with another technology?	No
Permits Required:	None
Initial Monitoring Frequency:	Quarterly
Long-term Monitoring Frequency:	*Information not provided*
Target cleanup levels/ objectives:	In worst monitoring well, concentration of PCE decreased from 48,300 ppb in April 1999 to <50 ppb in March 2002. A site-specific standard was attained by eliminating all open pathways, and the case was closed. Unfortunately, monitoring wells were destroyed so follow-up sampling is not possible.
Are the target cleanup levels/objectives being met?	*Information not provided*
Time required to meet target cleanup levels/ objectives:	Roughly two years
Performance Problems:	The PRB was shallow (justified by identifying a confining layer between overburden and the bedrock aquifer) and the 8 borings were somewhat widely spaced, so capture of the plume was probably not complete. However, the decrease in PCE concentration between 2000 and 2002 was impressive.
Additional Information	I would have been happier if there were more downgradient monitoring wells and more wells at the downgradient property boundary and if we could have required some post-closure sampling. But the minimum requirements for demonstrating attainment of a site-specific standard were met.
Site Contact:	Charlene R. Drake, Project Manager, React Environmental Services, 215-729-2777

Case Study #20: Offutt Air Force Base, Building 301 Iron Wall	
Site Location:	Offutt AFB, Nebraska
Date Installation Completed:	March 2004
Type of Installation:	Full scale
Target Contaminants:	TCE
Geologic Material	Clay, silt, sand
Reactive Media:	Zero-valent iron
PRB Configuration:	Continuous
PRB Construction Techniques:	Continuous trencher equipment
Dimensions:	Depth (extends to 35 feet bgs), 250 feet long, and 1.5 feet wide
Application:	Plume control
Was the PRB combined with another technology?	No
Permits Required:	None
Initial Monitoring Frequency:	Monthly
Long-term Monitoring Frequency:	Quarterly
Target cleanup levels/ objectives:	MCLs
Are the target cleanup levels/objectives being met?	Steady state not yet reached.
Time required to meet target cleanup levels/ objectives:	*Information not provided*
Performance Problems:	*Information not provided*
Additional Information	*Information not provided*
Site Contact:	Philip E. Cork, Chief, Environmental Restoration Element, philip.cork@offutt.af.mil , 402-294-7621

Case Study #21: Offutt Air Force Base, Building 301 Sand and Mulch Wall	
Site Location:	Offutt AFB, Nebraska
Date Installation Completed:	January 1999 (pilot) and July 2001 (full scale)
Type of Installation:	Pilot and full scale
Target Contaminants:	TCE
Geologic Material	Clay, silt, and sand
Reactive Media:	Sand and wood mulch
PRB Configuration:	Continuous

Case Study #21: Offutt Air Force Base, Building 301 Sand and Mulch Wall	
PRB Construction Techniques:	Continuous trencher equipment
Dimensions:	Depth (extends 4–25 feet bgs), 500 feet long, and 1.5 feet wide
Application:	Plume control
Was the PRB combined with another technology?	No
Permits Required:	None
Initial Monitoring Frequency:	Monthly
Long-term Monitoring Frequency:	Quarterly
Target cleanup levels/ objectives:	MCLs
Are the target cleanup levels/objectives being met?	Yes
Time required to meet target cleanup levels/ objectives:	*Information not provided*
Performance Problems:	*Information not provided*
Additional Information	*Information not provided*
Site Contact:	Philip E. Cork, Chief, Environmental Restoration Element, philip.cork@offutt.af.mil, 402-297-7621

Case Study #22: Arrowhead Plating	
Site Location:	Montross, Virginia
Date Installation Completed:	September 2002
Type of Installation:	Full scale
Target Contaminants:	TCE, PCE, DCE, vinyl chloride, TCA, DCA, cyanide, and heavy metals
Geologic Material	Clay and silt
Reactive Media:	Iron filings, 700 tons
PRB Configuration:	
PRB Construction Techniques:	Azimuth-controlled vertical hydraulic fracturing (82 frac injection wells)
Dimensions:	Depth 5–44 feet, length 1175 feet, thickness 3–9 inches
Application:	Plume control
Was the PRB combined with another technology?	Yes—cap to slow rate of groundwater flow through PRB
Permits Required:	None—Superfund site

Case Study #22: Arrowhead Plating	
Initial Monitoring Frequency:	Quarterly
Long-term Monitoring Frequency:	Quarterly
Target cleanup levels/ objectives:	MCLs
Are the target cleanup levels/objectives being met?	Steady state not yet reached.
Time required to meet target cleanup levels/ objectives:	No estimate
Performance Problems:	Site characterization problems. The groundwater flow reversed in some portions of the PRB.
Additional Information	*Information not provided*
Site Contact:	Nicholas B. Bauer, nick@bauerassociatesinc.com, 703-391-0888

Case Study #23: BFI Darrow	
Site Location:	On River Road between Geismar and Darrow, Louisiana
Date Installation Completed:	December 1998
Type of Installation:	Full scale
Target Contaminants:	TCE, PCE, DCE, vinyl chloride, hexachloro benzene, hexachloro butadiene, and numerous other chlorinated organics
Geologic Material	Clay, silt, and peat
Reactive Media:	Granular iron
PRB Configuration:	Funnel and gate
PRB Construction Techniques:	Continuous trencher equipment
Dimensions:	The reactive barrier is about 500 feet long. The top of the reactive material is at 12 feet with the depth at about 23 feet deep.
Application:	Plume control. It is actually a prophylactic measure. Natural dechlorination seems to be robust enough to stop the contaminants from getting this far. We sample a sump at the bottom of the trench on a regular basis to demonstrate that it is working. There are also a number of wells immediately downgradient of the wall.
Was the PRB combined with another technology?	Yes—a slurry wall
Permits Required:	None
Initial Monitoring Frequency:	Quarterly
Long-term Monitoring Frequency:	Semiannually

Case Study #23: BFI Darrow	
Target cleanup levels/ objectives:	No break-through
Are the target cleanup levels/objectives being met?	Yes
Time required to meet target cleanup levels/ objectives:	There is currently no end to the monitoring period.
Performance Problems:	Information not provided
Additional Information	Information not provided
Site Contact:	Thomas L. Stafford, 225-219-3222, thomas.stafford@la.gov

Case Study #24: Oak Ridge Reservation	
Site Location:	Oak Ridge, Tennessee
Date Installation Completed:	October 1994
Type of Installation:	Full scale
Target Contaminants:	Strontium
Geologic Material	Clay
Reactive Media:	Xeolite
PRB Configuration:	Funnel and gate
PRB Construction Techniques:	Other
Dimensions:	Contaminated groundwater was routed through six 55-gallon drums that contained the xeolite.
Application:	Source control
Was the PRB combined with another technology?	No
Permits Required:	None
Initial Monitoring Frequency:	Monthly
Long-term Monitoring Frequency:	Monthly
Target cleanup levels/ objectives:	90% mass reduction
Are the target cleanup levels/objectives being met?	No
Time required to meet target cleanup levels/ objectives:	*Information not provided*
Performance Problems:	Geochemistry/reactivity problems. Barrels became clogged with precipitation of iron oxide.

Case Study #24: Oak Ridge Reservation	
Additional Information	*Information not provided*
Site Contact:	Ralph Skinner, 865-576-7403

Case Study #25: Pease Air Force Base, Site 49	
Site Location:	Portsmouth, New Hampshire
Date Installation Completed:	August 2000
Type of Installation:	Full-scale demonstration
Target Contaminants:	TCE, DCE, and vinyl chloride
Geologic Material	Silt, sand, gravel, and rock. The material the PRB was installed into consisted of silty sand, glacial till, and fractured bedrock.
Reactive Media:	Zero-valent iron; overburden PRB Fe/sand mix; bedrock PRB 100% Fe
PRB Configuration:	Continuous
PRB Construction Techniques:	Biodegradable slurry
Dimensions:	Overburden PRB 150 feet long, 15 feet deep, 2.5 feet wide. Fractured-rock PRB 38 feet long, 6 feet wide, 15 feet deep.
Application:	Plume control
Was the PRB combined with another technology?	Yes—excavation of shallow contaminated soil.
Permits Required:	CERCLA Program Site
Initial Monitoring Frequency:	Quarterly
Long-term Monitoring Frequency:	Annually
Target cleanup levels/ objectives:	MCL
Are the target cleanup levels/objectives being met?	No
Time required to meet target cleanup levels/ objectives:	Years?
Performance Problems:	Hydraulic problems. Flat gradient, low groundwater velocity limits flushing through wall. Performance difficult to evaluate over short term.
Additional Information	Fractured-bedrock PRB was installed in 47 (6-inch) bore holes using tremie pipe.
Site Contact:	Dave Strainge, dave.strainge@afrpa.pentagon.af.mil, 207-328-7109

Case Study #26	
Site Location:	Vermont
Date Installation Completed:	September 2001
Type of Installation:	Full scale
Target Contaminants:	TCE, PCE, DCE
Geologic Material	Silt and sand
Reactive Media:	Iron mixed with sand
PRB Configuration:	Continuous
PRB Construction Techniques:	Excavation and backfill
Dimensions:	3–4 feet thick (could not keep the trench open another way, is approximately 250 feet long, 15 feet deep.
Application:	Plume control
Was the PRB combined with another technology?	No
Permits Required:	*Information not provided*
Initial Monitoring Frequency:	Monthly
Long-term Monitoring Frequency:	Quarterly
Target cleanup levels/ objectives:	Prevent contamination from crossing property boundary at concentrations above Vermont groundwater enforcement standards.
Are the target cleanup levels/objectives being met?	Yes
Time required to meet target cleanup levels/ objectives:	Immediate (not intended to remove source)
Performance Problems:	*Information not provided*
Additional Information	*Information not provided*
Site Contact:	Michael Smith, michael.smith@anr.state.vt.us

Case Study #27: Offutt Air Force Base, Building 301 Groundwater Contamination	
Site Location:	Offutt Air Force Base, Nebraska
Date Installation Completed:	January 1999
Type of Installation:	Pilot
Target Contaminants:	TCE
Geologic Material	Clay, silt, and sand
Reactive Media:	Sand and wood mulch
PRB Configuration:	Continuous
PRB Construction Techniques:	Continuous trencher equipment

Case Study #27: Offutt Air Force Base, Building 301 Groundwater Contamination	
Dimensions:	Depth extends 4–25 feet bgs, length is 100 feet, and thickness is 1 foot
Application:	Technology demonstration project
Was the PRB combined with another technology?	No
Permits Required:	None
Initial Monitoring Frequency:	Monthly
Long-term Monitoring Frequency:	Quarterly
Target cleanup levels/ objectives:	MCLs
Are the target cleanup levels/objectives being met?	Yes
Time required to meet target cleanup levels/ objectives:	*Information not provided*
Performance Problems:	*Information not provided*
Additional Information	*Information not provided*
Site Contact:	Philip E. Cork, Chief, Environmental Restoration Element, philip.cork@offutt.af.mil, 402-294-7621

Case Study #28: Offutt Air Force Base, Hardfill #2 Composite Groundwater Plume — PRB Wall	
Site Location:	Offutt Air Force Base, Nebraska
Date Installation Completed:	November 2003
Type of Installation:	Full scale
Target Contaminants:	TCE
Geologic Material	Clay, silt, sand, gravel, Pleistocene Terrace
Reactive Media:	Zero-valent iron and sand
PRB Configuration:	Continuous
PRB Construction Techniques:	Continuous trencher equipment
Dimensions:	Depth extends to 35 feet bgs, 350 feet long, and 1.5 feet wide
Application:	Source control
Was the PRB combined with another technology?	No
Permits Required:	None
Initial Monitoring Frequency:	Monthly

Case Study #28: Offutt Air Force Base, Hardfill #2 Composite Groundwater Plume — PRB Wall	
Long-term Monitoring Frequency:	Quarterly
Target cleanup levels/ objectives:	MCLs
Are the target cleanup levels/objectives being met?	Steady state not yet reached
Time required to meet target cleanup levels/ objectives:	*Information not provided*
Performance Problems:	*Information not provided*
Additional Information	*Information not provided*
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Case Study #30: Erickson Air-Crane	
Site Location:	Central Point, Oregon
Date Installation Completed:	February 1988
Type of Installation:	Full scale
Target Contaminants:	TCE, PCE, DCE, and chloro-benzene
Geologic Material	Silty sand and gravel over clay aquitard
Reactive Media:	Iron filings (50% w/sand)
PRB Configuration:	Funnel and gate
PRB Construction Techniques:	Excavation and backfill
Dimensions:	Funnel/slurry walls approximately 650 feet. Two “gates” approximately 50 feet long, 16 feet wide.
Application:	Plume control
Was the PRB combined with another technology?	Yes—monitored natural attenuation
Permits Required:	*Information not provided*
Initial Monitoring Frequency:	Monthly
Long-term Monitoring Frequency:	Quarterly
Target cleanup levels/ objectives:	Site-specific RBCs at property boundary, just downgradient of the treatment system
Are the target cleanup levels/objectives being met?	Yes

Case Study #30: Erickson Air-Crane	
Time required to meet target cleanup levels/ objectives:	Immediately following implementation
Performance Problems:	Hydraulic problems. Within about 6 months of installation, it was determined that contaminated water was migrating around one “wing wall” of the funnel-and-gate system, allowing untreated water to bypass the system. About 18 months after initial implementation, Erickson installed a linear array of 53 large-diameter borings backfilled with iron and sand to treat water flowing around the wall. The boring array is less effective in destroying the chlorinated solvents, reducing them from PCE and TCE to DCE and VC (VC is not typically a contaminant of concern at the site). However, RAOs are being met thus far at the property boundary, as the remediation by products are apparently being naturally degraded before the water reaches the property boundary monitoring well compliance points.
Additional Information	There has not been any apparent decrease in permeability of the “gates” after 6 years of operation. The lack of complete capture appears to be related to hydrogeology and not clogging of the gates because the problem arose soon after installation and has not been observed to worsen over time thus far.
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Case Study #31: Naval Base Ventura County, Port Hueneme, California

A full-scale cleanup has been ongoing using in situ bioremediation to treat MTBE and TBA in groundwater at the Naval Base Ventura County (NBVC), Port Hueneme, California. Geology at the site consists of shallow sand semiperched and unconfined aquifer bounded on the bottom by a clay aquitard, through which groundwater flows at a velocity of 1–3 feet/day. At a depth of 10–20 feet bgs lies the 5000- by 500-foot dissolved MTBE plume, which originated from a smaller BTEX plume that originates from sands contaminated with residual NAPL.

The original in situ bioremediation system consists of a 500-foot-wide bio-barrier, which acts as a passive flow-through system and was installed just downgradient of the NAPL plume. Contaminated groundwater containing dissolved MTBE and TBA travels through the bio-barrier, and biodegradation is enhanced by injection of various combinations of oxygen, air, and conditioned microorganisms. Oxygen gas and bioaugmented sections are located in the central core of the dissolved contaminant plume, and air injections are used on the edge of the plume. Operation of the system began in the fall of 2000. Initial MTBE and TBA concentrations in the groundwater plume were greater than 10,000 µg/L in the center of the plume.

After 18 months, contaminant concentrations were reduced to less than 5 µg/L in monitoring wells downgradient of the bio-barrier and extending across the width of the plume. No significant differences in performance were observed for the differently operated sections of the barrier. Dissolved oxygen increased from a preinjection concentration below 1 mg/L to 10–35 mg/L throughout the treatment zone, thereby increasing the potential for aerobic biodegradation to occur. In addition, increased dissolved oxygen levels upgradient of the treatment zone due to dispersion of the injected gas appear to cause upgradient reductions in MTBE concentrations. Peripheral monitoring wells have not shown an increase in contaminant concentrations, indicating that groundwater is flowing through and not around the bio-barrier.

The bio-barrier system includes 252 gas injection wells, 174 monitoring wells, 25 satellite gas storage tanks, 154 solenoid valves, a 240-feet^3/hour-capacity oxygen generator, automated timer circuits, and associated piping and electrical lines. The total installation cost of this equipment was $435,000; initial year (FY 01) O&M costs were $75,000 and are expected to continue for a service life of 40 years. A preliminary cost comparison with an existing pump-and-treat system at this site suggests savings of more than $34 million over the project life. The state regulatory agency recently approved continued use of this bio-barrier and installation of a bio-barrier approximately midway down the MTBE plume and at the toe of the plume as the final remedy for the MTBE plume.

Based on the success of the original bio-barrier project, the NBVC IRP Team together with Naval Facilities Engineering Service Center technical support awarded a contract for the installation and operation of the midplume and toe bio-barriers. The installation and operation was based on the original bio-barrier technology for the treatment of MTBE and related oxygenates in the groundwater. The combined length of the two new barriers was approximately 900 feet in length with oxygen injection points spaced every four feet. The construction of the midplume and toe barriers was completed summer 2003 and may reduce the overall remediation time by two thirds. Based on the original bio-barrier data, the project team decided to utilize oxygen injection in combination with the in situ bacterial colonies for both the midplume and toe bio-barriers. As demonstrated by sampling data, six months was required to build up sufficient microbial populations and since spring 2004 the midplume and toe bio-barriers have provided for the effective and comprehensive degradation of the MTBE contaminants in groundwater to below target concentration. The state regulators have been petitioned to cease the operations of the containment system. The full-scale operation of the three bio-barriers has demonstrated that effective destruction of the MTBE contaminants for incoming concentrations ranging from 20 μg/L to 1500 μg/L. It is anticipated that long-term operation of the three bio-barriers will continue and the frequency of the sampling regime will be reduced.

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Case Study #32: Los Alamos National Laboratory Mortandad Canyon PRB

The Mortandad Canyon PRB site is located on Los Alamos National Laboratory property on the Pajarito Plateau in a shallow alluvial canyon to which treated wastewater has been discharged for more than 40 years. The site geology is based on alluvium derived from weathering and erosion of the rocks that form the Sierra Los Valles and the Pajarito Plateau. This alluvium overlies the Bandelier Tuff in Mortandad Canyon, which serves as the bedrock or confining layer. The major contaminants of concern in the alluvial system include perchlorate, nitrate, plutonium (Pu-238, -239, -240), americium (Am-241) and strontium (Sr-90). There are many other chemical species present due to the nature of the research processes conducted at LANL, and the discharged waste water, but these are the only contaminants detectable at levels above regulatory limits.

A demonstration PRB was installed at a location in upper Mortandad Canyon where the canyon begins to widen. This location was chosen because of the narrow distance between the canyon walls and because of a reasonably shallow depth to bedrock, ~30 feet. The PRB uses a funnel-and-gate system with a series of four reactive media cells to immobilize or destroy the contaminants. The cells, ordered by sequence of contact with groundwater consist of gravel-sized scoria (for colloid removal); phosphate rock containing apatite (for metals and radionuclides); a "bio-barrier" of pecan shells and cottonseed admixed with gravel (to deplete dissolved oxygen, and destroy any RCRA compounds present, plus nitrate and perchlorate); and limestone (for pH buffering and anion adsorption). Design elements of the PRB are based on laboratory-scale treatability studies and on a field investigation of hydrologic, geochemical, and geotechnical parameters. The PRB was designed with the following criteria: 1-day residence time within the bio-barrier, 10-year lifetime for the PRB, minimal surface water infiltration and erosion, optimal hydraulic capture, and minimization of excavated material requiring disposal.

The PRB was installed in January–February 2003 to a depth of 27 feet, with a 17-foot width across the canyon. The length of the PRB totaled 24 feet. A suite of monitoring wells was installed across each section (three equally spaced wells at the trailing edge). In addition, wells for obtaining solid samples were included to study the reactions occurring in the media. The wing walls were extended out to the canyon walls and keyed into the walls and also into the bedrock interface at depth. Monitoring for a suite of field and analytical parameters has taken place since May 2003. The total cost of the laboratory work and installation was approximately $900,000.

The levels of nitrate and perchlorate have been reduced to below detection in the apatite and bio-barrier cells. This reduction has been consistent from the first sampling point throughout the past two years to the latest sampling event. Sr-90 levels are also reduced by an order of magnitude in the apatite cell. The hydraulic flow picture has been complicated, primarily due to the drought conditions that the area has experienced since well before the installation of the PRB. Flow from the wastewater treatment plant has been further reduced due to problems that have forced shutdown of many of the research activities that feed the plant; therefore, the flow dynamics have been further impeded. Plans for scientific studies of the PRB are being developed.

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Case Study #33: U.S. Department of Energy Hanford Site, Richland, Washington

A new method for creating permeable reactive groundwater treatment barriers has been developed at the Hanford Site in Washington State. Because the contaminant plumes at Hanford range 15–90 m bgs, an alternative to "trench and fill" permeable reactive barriers was developed.

This alternative, called in situ redox manipulation (ISRM), can be installed through conventional groundwater wells.

The permeable treatment zone is created by reducing the ferric iron [Fe(III)], present as surface oxides, to ferrous iron [Fe(II)] within the aquifer sediments. Some of the ferric iron in 2:1 smectite clays is also reduced. This is accomplished by injecting sodium dithionite ($Na_2S_2O_4$) into the aquifer. The sodium dithionite serves as a reducing agent for iron, changing the ferric iron to ferrous iron within the aquifer sediments. The reduced iron remains adsorbed to sediment surfaces or incorporated in the clay structure, thus producing a stationary barrier. In oxidizing aquifers such as the Hanford unconfined aquifer, the sulfite is rapidly oxidized to sulfate. The ISRM approach extends the permeable treatment zone concept to sites where the groundwater contaminant plumes are too deep (tens of meters below the ground surface) to be easily treated by excavation or by trench-emplaced permeable barriers.

Based on the success of laboratory and field treatability tests, DOE and the regulatory agencies decided to deploy the technology at the Hanford 100D Area. The site is underlain primarily by sands and gravels. The top of the unconfined aquifer is 85 feet bgs and is about 15 feet thick. The groundwater plume requiring treatment is about 700 m in width and has maximum concentrations of over 4000 ppb chromium(VI) as chromium. Therefore, a 700-m-long ISRM barrier has been installed parallel to the bank of the Columbia River, approximately 150 m from the river. Construction began in 1999 and was completed in 2003.

Chromium(VI) concentrations in most of the wells within the barrier (54 out of 66) are below or near the detection limit (<8 μg/L) of the analytical method used. Chromium(VI) concentrations in 3 out of 6 downgradient compliance wells have declined to below the target goal for compliance (<20 ppb Cr). Several issues that have impacted early installation of the barrier have been identified. Lessons learned are being applied to continuing deployment.

Costs for installation of the ISRM barrier at the Hanford 100-D Area were approximately $8.7 million.

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Case Study #34: Nickel Rim, Sudbury, Ontario

The Nickel Rim Mine site is an inactive mine near Sudbury, Ontario. Mining operations for copper and nickel began in 1953. When operations ceased in 1958, an impoundment of mine tailings was left at the site. Subsequent oxidation of the tailings has introduced acid-mine drainage to the groundwater, resulting in elevated concentrations of sulfate, iron, and nickel.

Groundwater moves from the tailings in a narrow bedrock valley. The aquifer in the valley consists of fine glacio-fluvial sand ranging 10–26 feet in thickness. Groundwater velocity in the aquifer is estimated to be approximately 50 feet/year. Groundwater contaminant concentrations ranged 2400–3800 mg/L sulfate; 740–1000 mg/L iron; and up to 10 mg/L nickel. Contaminant concentrations in the aquifer have tended to increase with time.

A full-scale continuous PRB was installed in an unsupported excavated trench in August 1995. The wall extends approximately 50 feet across the valley to a depth of approximately 14 feet. The zone of reactive material was approximately 12 feet thick in the direction of groundwater flow and was bounded by zones of coarse sand approximately 6 feet thick on both the upgradient and downgradient sides of the PRB. The reactive material consisted of a mixture of compost and wood chips, which were combined with pea gravel to increase the hydraulic conductivity of the media. To inhibit infiltration of surface water and oxygen into the reactive material, a clay cap was constructed over the wall. Total cost of the installation in 1995 was $30,000. This figure does not include post-installation monitoring.

Several series of multilevel monitoring wells were installed along the groundwater flow path perpendicular to the wall. Groundwater samples were collected one month after installation, after eight months, after one year, and generally annually since installation. The installation and treatment performance of the PRB are described in a series of papers (Benner, Blowes, and Ptacek 1997; Benner et al. 1999, 2002). During the initial year of operation sulfate concentrations ranged approximately 100–2000 mg/L, and iron concentrations ranged approximately 1–90 mg/L within the PRB. Dissolved nickel concentrations were reduced to less than 0.1 mg/L. Treatment has been achieved by sulfate reduction and the precipitation of metal sulfide minerals. The removal of iron and alkalinity generated by the sulfate-reduction process transformed acid-generating to acid-consuming characteristics in the groundwater. Herbert, Benner, and Blowes (2000) and Daignault, Blowes, and Jambor (2003) indicated that the rate of accumulation of solid-phase sulfide minerals in the initial two years and after seven years within the PRB were similar. Monitoring of the performance of the PRB will continue.

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APPENDIX F

Source Area Treatment Technology Case Studies

SOURCE AREA TREATMENT TECHNOLOGY CASE STUDIES

This appendix contains additional information about several of the sites discussed in Section 7 of the document. The case studies focus on source area treatment and were provided by individual PRB Team members.

Case Study #1: SA-2 NASA Marshall Space Flight Center, Huntsville, Alabama

The National Aeronautics and Space Administration (NASA) Marshall Space Flight Center (MSFC) is located in Huntsville, Alabama. The U.S. Army used MSFC area during World War II to manufacture chemical munitions and, in 1949, began conducting rocket and missile development until operations were transferred to NASA in 1960. The subsurface environment at the facility consists of low-permeability, clayey residuum that overlies fractured limestone bedrock. The contact between the residuum and bedrock is a transitional layer of heterogeneous aggregate of gravel, chert, clay, and sand commonly referred to as the "rubble zone." The rubble zone forms a main lateral groundwater flow pathway and is believed to contain a significant contaminant mass beneath many of the contaminant source areas at the facility. In August 2000, an in situ chemical reduction field pilot test using the Ferox^{sm} process was applied at Source Area (SA-2) located at the MSFC. At this site, TCE in the groundwater was detected at dissolved concentrations as high as 72,800 µg/L.

During the field application, 125 injections were completed in the rubble zone and selected vadose zone locations over approximately 3200 square yards. Approximately 11,000 pounds of ZVI was emplaced beneath the site. Nitrogen gas was used first to fracture the clayey residuum and (to some extent) rubble zones before introducing ZVI-water slurry into the formation.

Groundwater sampling was conducted for 24 months after the injections to assess technology treatment performance. The results of this sampling showed strong evidence of reductive dechlorination occurring within the treatment zone. Background levels of DO and ORP were reduced to approximately 2 mg/L and –400 mV, respectively. TCE concentrations declined by more than 89%. Increased levels of chloride and daughter product formation (mainly dichloroethene) were evident in treatment zone wells. Chloride mass balance calculations based on the observed monitoring data are within 89%, indicating that the monitoring data are reflecting the expected in situ reactions. Furthermore, groundwater monitoring data have also confirmed the production of ethene, ethane, methane, and carbon dioxide in the monitoring wells suggesting that biological degradation has been stimulated by the presence of ZVI as a side benefit of the Ferox^{sm} process.

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Case Study #2: Parcel C, Building 272, Hunter’s Point Navy Ship Yard, San Francisco, California

This project, completed in 2002, involved the demonstration of the Ferox^{SM} process integrated with pneumatic fracturing at Hunters Point Navy Yard adjacent to San Francisco Bay. The technology demonstration occurred under the U.S. Navy’s Alternative Restoration Technology Team program. This program evaluates innovative remediation technologies to expedite regulatory process and implementation at Navy and Marine Corps sites. The objective of the project was to evaluate the applicability of the zero-valent iron powder to address source contamination at this and other sites across this military facility, which is to be turned over for civilian use within the near future.

TCE, the target compound, was detected in the groundwater at concentrations as high as 88 mg/L. Other than the high levels of contamination, the site setting and geology also presented particular challenges to the implementation of the technology. The treatment zone resides beneath a warehouse building and extends vertically across a fill layer and the underlying weathered bedrock. The thickness of the fill material, depth to the bedrock, and the degree of weathering vary greatly within the treatment area. The field team had to adjust the injection parameters frequently in response to the geologic characteristics exhibited in the different injection zones. Approximately 16,000 pounds of ZVI powder was distributed across the treatment area via four injection points. Field observations and data showed significant coverage of the area by the injected iron.

Performance evaluation sampling consisted of monthly groundwater sampling for the initial three months after the injections followed by quarterly sampling for the next two years. The results of this sampling showed significant TCE destruction in the groundwater within three weeks after injection of the reactive iron powder. Greater than 99% reduction of TCE was observed in the three highest concentration monitoring wells within the treatment zone. Groundwater quality data in monitoring wells outside and beneath the treatment zone showed no increase in contaminant concentrations, thus demonstrating the injection process did not lead to the mobilization of TCE-laden groundwater below or outside the treatment zone. This was a common concern often voiced in considering injection of reactive materials into an aquifer with high contaminant concentrations or DNAPL. Through 18 months TCE concentrations within the treatment area remained depressed with no rebound observed. Groundwater geochemical parameters indicate the emplaced iron is still reactive.

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Case Study #3: Lakehurst Naval Air Station, Area I and J, Lakehurst, New Jersey

The Naval Air Engineering Station (NAES) is located in Lakehurst, New Jersey. In 2003, a bimetallic nanoscale iron (BNP) injection project was performed in two contaminated groundwater plumes at NAES.

The principal contaminants found in the groundwater at Areas I and J include tetrachloroethene (PCE), trichloroethene (TCE), 1,1,1-trichloroethane (TCA), and degradation products such as *cis*-dichloroethene (cDCE) and vinyl chloride. The contamination extends vertically 70 feet below the groundwater table with largest amount located 45–60 feet below the groundwater table in soil described as a fairly uniform, brown-yellow, fine to coarse sand.

A total of 300 pounds of BNP was injected using direct-push technology (DPT), at 15 specified locations in the northern and southern plumes of the site. For each 4-foot injection interval, 4 pounds of BNP was added to approximately 240 gallons of water, yielding a BNP concentration of approximately 2 g/L. A total number of five 4-foot intervals were injected at each location. The 240 gallons of solution was pumped through steel injection rods to the deepest interval first. After hydraulically pumping the iron water mixture into the ground, the drill rods were retracted up 4 feet, and another 240 gallons of BNP solution was injected at the next interval and so on.

In general, concentrations for total VOCs and the individual VOC compounds of interest (TCE, PCE, cDCE, and vinyl chloride) showed a decreasing trend throughout the six-month post-injection monitoring period. An apparent increase in VOC concentrations was observed in approximately 60% of the monitoring wells in the sampling round immediately following the BNP injections; however, subsequent sampling rounds showed a decrease in virtually all VOC compounds (and total VOCs), in all of the monitoring wells. It was hypothesized that the initial concentration increase was attributed to desorption of VOCs from the soil particles to the aqueous phase as a result of the BNP injection and treatment.

The percentage decrease from the baseline values collected prior to the injections were calculated for both the field parameters and laboratory analytical results. The two most prevalent VOC compounds detected show an average percentage decrease of 79% for TCE and 83% for cDCE. The average decrease in total VOCs concentration is 74%.

Although a strong correlation between field parameter and geochemistry results was not clearly demonstrated, the lack of substantial reduction in an upgradient well MW-LC (southern plume) well outside the treatment zone supports the assertion that BNP is responsible for VOC reduction in monitoring wells that were (presumably) downgradient of the BNP injection points.

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Reference: *Nanoscale Particle Treatment of Groundwater At Areas I and J. Naval Air Engineering Station, Lakehurst, New Jersey*, Draft Final Report, August 2004, N62472-02-D-0810.

Case Study #4: Hangar 1000, Naval Air Station, Jacksonville, Florida

A field demonstration project using nanoscale iron for source area treatment has been completed at Jacksonville Naval Air Station in early 2005. The demonstration was performed at a source area located at Hanger 1000 (H1K), which is located in the interior portion of the facility where two former underground waste storage tanks were located. The relatively small source area has an areal extent of approximately 1450 square feet and a thickness of 18 feet (saturated zone).

Geologic borings from the site indicates soil consisting of fairly uniform silty fine to medium-grained sand and sandy fill. Also within the saturated zone where the study took place, layers of ranging from clayey sand to amounts of silt and clay were present. The shallow aquifer at the site was present from a depth of 7–24 feet bgs. The highest VOC groundwater concentration measured at this site was 82,340 μg/L.

The nanoscale iron used for this demonstration project was a bimetallic iron material consisting of a trace coating of Pd. The nanoscale iron was engineered with a liquid food-grade polymer to enhance the iron transport through the subsurface. A total of 300 pounds of nanoscale iron was emplaced in the subsurface using two methods: direct injection via DPT and via a closed loop recirculation system.

Data from nine groundwater post injection sampling events were used to determine both short- and long-term performance data for the project. Two sample rounds are currently under review to complete the long-term field evaluation. Based upon changes in the potentiometric surface, changes in geochemistry parameters (e.g., DO and ORP), and visual observation of the iron in groundwater samples, it was determined that the iron migrated both within the recirculation array and at least 20 feet downgradient of the array into the contaminant plume. DO concentrations decreased from 1 mg/L to less than 0.5 mg/L, and ORP decreased from a range of 100 to –100 mV to values of –200 to –400 mV, indicating moderately to strongly reducing conditions were created within five days of the first injection event in all wells monitored. Daughter products such as *cis*-1,2-DCE and ethane (from TCE) and 1,1-DCA, 1,1-DCE and ethane (from TCA) were detected in all wells. In some wells, the intermediate concentrations increased and subsequently decreased followed by a rise in innocuous daughter products (ethene and ethane). Detections of innocuous compounds such as ethene/ethane and acetylene/C4-hydrocarbons were evidence of complete reductive dehalogenation and degradation via β-elimination, respectively, in all the wells. One well located approximately 20 feet downgradient of the recirculation array, achieved Florida Groundwater Cleanup Target Level (GCTL) for all compounds except for TCE. Despite a TCE reduction of 85% from the baseline levels, the 10-μg/L post-injection concentration marginally exceeded the GCTL for TCE (3 μg/L). The degradation in this well was coupled with the observation of daughter products and innocuous breakdown products such as ethene, ethane, and C4-hydrocarbons in the groundwater.

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Reference:

Tetra Tech NUS, Inc. 2004. “Interim Final Nanoscale Iron Injection Demonstration Cost and Performance Report at Hangar 1000, Naval Air Station Jacksonville.” NAVFAC, Contract Number N62467-94-D-0888.

APPENDIX G

Response to Review Comments

NOTE: Specific pages and line numbers mentioned in the comments refer to a review draft of this document. Page numbers are unlikely to correspond to those in this published version. Comments of a strictly editorial nature were gratefully considered but are not reproduced below.

PEER REVIEW COMMENTS

Tom Sale, Colorado State University
Overall—This is a solid document that makes strong contributions. Overall, it is well written and well organized. Many critical issues are addressed in a clear and complete fashion. I commend the authors for their effort. **Thank you!**
Line 89—Consider replacing “obvious” with “potential”; in all instances it may not be “obvious.” **Text was revised.**
Line 317—Perhaps “cannot be degraded” should be replaced with “may not be degraded.” There seems to be some uncertainty on this topic. **Text was revised.**
Pages 22 and 23—This text gets into the role of Eh (or pe) and pH in controlling solubility of metals. This is an excellent topic to bring up. Unfortunately, the presented discussion is a bit confusing. Here are some suggestions: a) The solubility of metals is dependent on 1) pH, 2) Eh, 3) aqueous concentrations of reacting species and 4) reaction kinetics. It might be better to say this than to say that pH is a master variable. b) I like Eh-pH stability diagrams. One of my favorites is for Fe presented Hem (19??). Its show regions in which various forms of iron are stable. I’m not sure what is being presented in Figure 2-2. Consider replacing Figure 2-2 or describing it further. Perhaps something is missing from the PDF version I’m looking at? c) Figure 2-3 doesn’t seem to clearly support the statement in the text. Consider describing what is going on in Figure 2-3 more carefully. It seems that Figure 2-3 needs to state the assumed Eh and concentration of reacting species (e.g., carbonate species). d) Overall the topic of chemical equilibria is fundamental to this text and is often not well understood by audiences. Perhaps in future documents this topic can be developed as a chapter. An excellent text on this topic is Lindsay, Willard (1979) Chemical Equilibria in Soils. **a, c, d) Text was revised.** **b) Figure was revised.**
Line 728—Paul Johnson at Arizona State University has recently won a number of awards for his reactive barrier work with MTBE. Perhaps you should mention his work. See Project (ESTCP)**:** In-Situ Bioremediation of MTBE in Groundwater (0013)**,** http://www.estcp.org/documents/techdocs/CU-0013.pdf. **Text was revised, and a reference was added.**
Line 1333—You may want to include the reference for the Triad Approach at the beginning, versus the end, of this section. **Text was revised.**
Line 1410—Consider replacing “capture” with “intercept.” This seems more consistent with the passive nature of PRBs. **The team feels that the word “capture” adequately represents the functionality of a PRB because PRBs are designed to have a capture zone.**

Tom Sale, Colorado State University

Line 2787—Consider replacing the first paragraph in this section with the following **-** It seems that source treatment can be described with more rigor and that the relative youth of this approach should be noted. “The objective of source treatment is to reduce contaminant flux and/or the longevity of release from subsurface zones that provide chronic releases of contaminants to groundwater. An expansion of PRB technology is to use reductive reactive media (e.g., ZVI) to treat chlorinated solvent source zones. In the case of chlorinated solvents, materials that provide persistent releases to groundwater can include DNAPL, sorbed contaminants, and dissolved phase constituents in stagnant zones (USEPA 2003). Use of reductive media for source treatment is an emerging technology that can stand alone or be coupled with PRBs. This chapter reviews current knowledge on this topic.” *EPA (2003) The DNAPL Remediation Challenge: Is There a Case for Source Depletion EPA/600/R-03/143 December*

Paragraph was revised. Thank you for the suggested text.

Line 2845—I’m not sure where these ideas belong, perhaps here, the end of the section introduction? Here are some critical issues that likely need further investigation:

a) Longevity of the iron as a function of iron amount and size
b) Losses of iron to potentially unproductive reactions including modifying the redox status of the soil and/or gas production.
c) The potential for reactions to be biologically mediated
d) The ability to treat DNAPL
e) The ability to address contaminants in low permeability layers.

These issues were added. Thank you for the suggestion.

Line 1065—Permeable barriers that cross connect hydrostratigraphic layers with different heads can cause problems. It seems this topic should be introduced here.

Topic was clarified in text.

Dawn Kaback, Concurrent Technologies Corporation

Thanks for giving me the opportunity to read the fine document on permeable barriers. My comments are below - most are very small. Overall the document is pretty well written, but in some places it rambles. The document spends a lot of time describing permeable barriers and I know there are other documents with that kind of information available....so I would recommend that you try to target new updata and long-term performance, etc. The in situ redox manipulation with dithionite and calcium polysulfide are not really discussed.

A new section discussing ISRM was added (2.5.10). Language was also added to Sections 2.5 and 6.3.2 to include mention of potential problems with geochemical changes that may cause increased mobility of certain chemicals.

2.3—There is no discussion here about nanoscale iron, yet later in the report it is discussed.

The use of nanoscale iron is still being developed, and it has a higher degree of applicability for source zone treatment. The use of nanoscale iron is discussed in the Source Zone Treatment section of the document.

2.3.1; Lines 552-562—The nitrate discussion doesn’t really explain why there is a problem. Isn’t this due to the oxidizing power of the nitrate?

Additional text was added to explain the effects of nitrate.

2.3.1; Line 573—The term “compounds” is not accurate for all of the described materials.

The word “compounds” was replaced with the word “constituents.”

2.3.1; Lines 573-580—The In Situ Redox Manipulation project at Hanford could be used as an example here, where the presence of nitrate may impact the longevity of the barrier.

A discussion about ISRM and the Hanford site was added as Section 2.5.10.

Dawn Kaback, Concurrent Technologies Corporation

2.3.1; Line 597—Respond well to PRB concept…..this is very awkward. Cr and U are good examples of metals that can be treated with this method.

Sentence was revised.

2.4; Line 628—What is the mixture referred to here?

The mixture was approximately 50%–100% ZVI. No changes were made to the text.

2.4—Should the Hanford In Situ Redox Manipulation example be discussed here? What about injection of calcium polysulfide to reduce metals. Many examples…..of deployments.

A discussion about ISRM and the Hanford site was added as Section 2.5.10.

2.5.3; Line 728—Attempted should be changed to implemented

Sentence was revised.

2.5.5; Line 795—Please describe the design and lessons learned here.

Additional text was added.

2.6—Could also use an example of a barrier designed at Los Alamos National Laboratory

A new section (2.6.5) discussing the LANL PRB was added.

3.1; Table 3-1—“Monitor” wells should be changed to “monitoring,” treatability testing should say it uses real groundwater and real core samples, contingencies should be lower case, must also consider cc-contaminants, the treatability testing should possible compare different media and test for longevity so that costs can be estimated, “constructability” should be lowercase.

The table was revised.

3.2—Primary tools…..seems too simple and there is no discussion. Flow meters are described in detail but other primary tools are not described at all.

The text was expanded and clarified.

3.2; Line 1112—Why is this described when lots of the basics are missing?

Additional text was added to Section 3.2.

3.2.3; Line 1132—Should use the Hanford In Situ Redox example in this section.

A discussion about ISRM and the Hanford site was added as Section 2.5.10.

3.2.4—May need detailed core data to determine if preferential pathways exist, such as at Hanford.

Additional text was added to this section.

3.10—This section is not well written. Right up front it needs to mention who developed and named this approach. It is not an initiative; it is an approach or methodology.

This section was revised.

3.10; Line 1335—First sentence talks about an ER process, but this is too general and arm wavy. It is a site characterization methodology.

This section was revised.

3.10; Line 1346—The Triad approach consists of ideas. This is too vague….whole section needs rewrite.

This section was revised.

4.1.1; Line 1471—Continuous barriers also need to be keyed in a low-permeability layer at the base or the groundwater may flow below.

Sentence was revised.

4.3.1; Line 1620—This example is already discussed earlier and so is repetitive.

Text in Section 4.1 was revised.

General—There is little discussion of the impact of reduction, the release of other contaminants such as arsenic, ammonia, etc.

Text was added to Section 6.3.2.

7.6; Line 2957—Are there any data or results?

Case studies containing data were added in Appendixes E and F.

Craig Benson, University of Wisconsin

Line 450—Foundry byproducts, tire chips, and some paper sludges have also been found to be good sorbents. I have included two of our papers on foundry byproducts (Lee et al. 04 in JHM, Lee and Benson 04 in JEQ) as examples. These materials are rich in organic carbon and also contain iron particles. Thus, foundry by-products can be sorbing and reactive. The papers I have included also have references to other papers describing by-products and sorbing materials that can be used for PRBs.

Additional bullet and text were added to Section 2.1.4.

Line 1164—The effects of heterogeneity on PRB performance cannot be emphasized enough. There is a good discussion of this issue in the attached paper by Elder et al. (2002, WRR). Variability in aquifer properties must be considered in design of the PRB as well as the monitoring system. Also, on line 1155, I believe the intent here is that *aquifer hydraulic conductivity* (rather than *aquifer properties*) can vary orders of magnitude. Other properties such as porosity and storage coefficient will not vary to such a degree.

Section 3.2.5 was renamed "Aquifer Heterogeneity," and a paragraph was added summarizing the results presented in Elder, Benson, and Eykholt 2002, as well as Benner, Blowes, and Molson 2001).

Line 1333—I did not follow how the "Triad" provides a better union of scientific and societal factors. The union of scientific factors is clear in the discussion, but I did not see any integration of social factors.

Comment noted. A reference is provided in Section 3.10 for further reading about Triad.

Line 1522—The reader should be referred to other works here as well on probabilistic design.
See the papers by Eykholt et al. 1999 and Elder et al. 2002, both of which are attached as well as Bilbrey and Shafer (*GWMR*, 21(2), 144–151, 2001).

Additional references were added.

Lines 1642-1655—I am not convinced that these effects are due to media variability. We studied the influence of media variability and found it to be insignificant (see Elder et al. 02, WRR, attached). The effects noted here are most likely due to aquifer heterogeneity, which manifests itself as heterogeneity in flow paths within the PRB (see a discussion of this issue in Elder et al. 02). I do agree that preferential flow occurs through PRBs, but do not believe it is due to media properties. Rather, preferential flow appears to be tied to the connection of permeable facies in the aquifer by the PRB. I also do not believe that the "use of closer particle sizes of the two media allows us to avoid sharp permeability" will be particularly beneficial in resolving this problem. My major concern here is the potential impact on regulators. You do not want regulators getting overly anxious about variability of the media within a PRB. The discussion here may set off some alarm bells, causing over-reaction to media variability, when the emphasis should be on aquifer heterogeneity.

A statement was added citing the work by Elder, Benson, and Eykholt 2002.

Line 1677—This effect is most likely due to hydraulics caused by aquifer heterogeneity, rather than clogging, as illustrated in Elder et al. 02 (WRR, attached). The explanation by Thomson and Vidumsky (2004) also seems reasonable. Indicate whether the modeling work by Thomson and Vidumsky (2004) was done in 3D. A 3D model is essential to capture these effects, and should be noted here.

The model was 3D, and the text has been modified.

Lines 1801-1807—There is a good discussion of the impacts on common ions in groundwater in the forthcoming paper by Li et al. (2005) in *Ground Water* (attached). This paper also contains a table of case histories showing the changes in common ion concentrations that occur within PRBs.

Additional text and the Li, Mergener, and Benson 2005 reference were added to Section 5.2.1.

Craig Benson, University of Wisconsin

Line 1811—When discussing porosity losses, a percentage should not be used because this representation leads to ambiguity in the actual change in porosity. For example, Line 1811 states that “0.88% of the porosity in the granular iron PRB was being lost every year due to deposition of precipitates.” Does this mean that the porosity (n) was decreasing by 0.0088 each year? Or does this statement mean that the change in porosity each year was 0.0088 x n? These remarks are better made explicitly by stating the change in porosity, e.g., “the annual reduction in porosity was 0.xxxx,” where 0.xxxx is the change in porosity in decimal form. Note also that porosity, defined as volume of voids per total volume, should not be reported as a percentage but rather as a ratio. While these may seem like picky issues, they are important so as to avoid ambiguity and confusion.

Text was revised to clarify data.

Section 5.2.2—I recommend that you review the papers by Yabusaki et al. 2000 (*Environmental Science & Technology*, 35(7):1493-1503), Mayer et al. 2001 (*Water Resources Research*, 37(12):3091-3103), and Li et al 2005 (*Ground Water*, attached) in this section. The statement “the aqueous species and solid phases (other than iron) must equilibrate quickly, relative to the time-scale of process. In a real system, the appropriate time-scale is the residence time of the water inside the reactive media, which is typically several hours or days, depending on thickness and flow rate” over-simplifies the problem. Reactions between common ions and ZVI need to be considered in the context of kinetics and the relative rates at which flow and reactions occur in PRBs. The operative time in these reactions is not necessarily equal to the average residence time. These issues are covered in some detail in Li et al. 2005.

Added text and reference.

Section 5.2.3—The table of case studies in Li et al. (2005) may be useful here.

This paper has been referenced elsewhere in document.

Section 5.2.4—There has been considerable interest in evaluating longevity through experiments and modeling. I know that Bob Gillham has recently completed some long-term testing that is to be published shortly in *Ground Water*. I recommend that Bob be contacted for a pre-print of his forthcoming paper. Also, the study by Li et al. focused on evaluating longevity in the context of hydraulics. I recommend that this section discuss the findings in both of these papers. Also, the results of the long-term column tests described in lines 1910-1923 are very similar to those reported by Lee and Benson (2004, JEQ, attached), which ran between 600-1500 pore volumes. The similarity is very encouraging, and may lend greater credibility to the conclusions presented in this section.

The work by Gillham is referenced in this section. The study by Li, Mergener, and Benson was not included as only theoretical geochemical modeling was presented, as opposed to laboratory data.

Section 7—This section describes some interesting new technologies. I am glad this material was included. Currently, the discussion indicates that these methods have been tried in the field, but there is no discussion of their effectiveness or other issues important to an evaluation of their suitability. This section would be stronger if each of the descriptions indicated how well the methods have worked.

Case studies have been added in an appendix.

Doug Mackay, University of California, Davis

All—This is an incredibly comprehensive and impressive document! I hope you find the following, mostly minor, comments of use.

Thank you!

Doug Mackay, University of California, Davis

1.0; whole paragraph—The scope of this document seems limited in that it does not really address passive (nonadvective) release of amendments such as oxygen, hydrogen, electron donors, etc., in a comprehensive way (such as you have ZVI, for example). I think you can't do that well with the current organization of the document, but you need to acknowledge that limitation. It also does not include mention nor evaluation of the potential for the between well recirculation methods tested by Stanford at various places and in simulations (see Christ et al., 1999. Journal of Contaminant Hydrology 37: 295-317, and McCarty et al. 1998. Env. Sci.& Tech., 32(1):88-100. Acknowledge that this document does not address passive release methods for creating PRBs (e.g., oxygen, hydrogen, electron donors from solid sources, etc.). Cite some works that do cover that topic (e.g., Mackay et al., in press*; and another API document in press prepared by Angus McGrath, Secor – ask Bruce Bauman of API bauman@api.org) *Mackay, D. M., R. D. Wilson, M. D. Einarson, and K. M. Scow. Migration and In Situ Remediation of MTBE. American Petroleum Institute report, in press. 60 pages. Final version expected for release by API in Fall 2004. Prepublication version available from D. Mackay since mid 2003. See other refs in column to the left.

The scope of this document was not intended to address this in detail but does present an introduction in Section 2.1.5. Text was added in Section 1.

1.2; Fig. 1.1—This figure does not include consideration of passive release methods. Figure was very faint in my review copy, something I assume can be resolved in final editing. Just note that limitation in the text that refers to the figure, and perhaps change the figure title to "Types of Permeable Reactive Barriers addressed in this report" or similar.

Title of Figure 1-2 was changed to "Examples of permeable reactive barriers." Text in the third paragraph in Section 1.2 was revised to state "examples of PRBs" instead of "the most common PRBs."

2.0; 250—Wording is odd. I would replace "typically under its own" with "in response to the natural or hydraulic induced gradients."

The sentence was revised.

2.1.1; 317—List may not be complete. Perhaps it would be wise to reword this sentence to more clearly indicate that there may be other "common" contaminants besides DCA and DCM that might also be untreated by ZVI (e.g., chlorinated aromatics? PCBs? Other pesticides? Aromatic compounds).

Text was revised.

2.1.2; 348-356—This paragraph may be too dense for most readers. Rewrite with some transition phrases or something.

Comment acknowledged. No changes were made.

2.1.3; 267-380—The first sentence is too long, and somewhat confusing. Second sentence will not likely mean much to most readers. End first sentence after "(redox) reactions." Reword the rest. "Inclusion" makes it sound like someone decided to put a C, N, O etc. in the chemical. Perhaps "presence" would be better.

The first sentence was divided into two sentences. The second sentence was deleted.

2.1.4; 426—Mention of clays as PRB materials may strike some readers as odd since earlier it is stated that PRBs have higher permeability than native formation. Clarify how clays could be used in thoughtful ways.

Text was revised.

Doug Mackay, University of California, Davis
2.1.5; 467—Incorrect citations for work on in situ bioremediation of MTBE. Use correct citations: Wilson, R. D., D. M. Mackay, and K. M. Scow. In Situ MTBE Degradation Supported By Diffusive Oxygen Release. Environmental Science and Technology, 36(2): 190-199, 2002. Mackay, D., R. Wilson, K. Scow, M. Einarson, B. Fowler and I. Wood. In Situ Remediation of MTBE at Vandenberg Air Force Base, CA. AEHS Special Issue of Contaminated Soil, Sediment & Water. Spring 2001, pp: 43-46. And the report cited previously in this column by Mackay et al. **References were updated.**
2.2; Table 2-4—Need citations. Need to add hydrogen release? I offered several for oxygen release above, but all from my own work. At a minimum, you should also refer to the Landmeyer paper in ES&T in 2001 on oxygen release using ORC. I don't have suggestions for citations for other topics. But isn't hydrogen addition being marketed by some consultants (e.g. Chuck Newell)? **Table was revised.**
2.4; 624—No mention of results of PRB application after all the discussion about its design. Shouldn't some comment be included about results? **The document is not intended to provide quantitative results on all PRBs. Additional references for Table 2-3 were added.**
2.4; 641—Nitrate numbers don't "decrease." Use correct numbers or reword. **The nitrate numbers were revised.**
2.5.3; 729—Incorrect citation. Use citations listed in this column above for Wilson et al., and one or both of the Mackay et al. pubs. **Reference was updated.**
2.5.9; 901—EHC source unknown. Should you add a citation so reader would know how to find more info? **Text was revised.**
3.1; Table 3-1—Table does not directly mention design of performance or other monitoring. Seems like that should be included in table somehow, but I have no specific suggestions other than to add a row. **Table was revised.**
3.2.1; 1099-1110—Length, width, and thickness are defined oddly. I know this has become a tradition, but it is an unfortunate consequence of engineering focus. Length should be in direction of flow, width cross flow, and thickness a vertical interval, just like all other discussions of groundwater issues. You should point out your terminology is just a convention, and different from general GW terminology. **Clarification text and diagram were added to Section 1.**
3.2.2; 1123 ff—Discussion of variability in point versus cross-section flow is confusing to me; isn't the variation over the cross section just a variation among point (local) flow directions? Reword. **Text was revised.**
3.2.4; 1160-1162—How is it known that modeling is a better approach? Seems to me it is important, but not "better." Wouldn't it be best to have the seasonal range of gradients, etc., from actual measurements and then conduct modeling to determine what the most robust design is? That may be what was intended here, but it doesn't sound like it. Reword. **Sentence was revised.**
3.10; 1365-67—Mentions that experienced field personnel are key; my experience with consultants is that as soon as field folks are experienced, they are often shifted away from field work and to the office – has this changed? Or should a comment be made on this paradigm shift (if it is one)? Reword if necessary. **Comment acknowledged. No changes were made.**
4.0; 1400-1485—Text seems to reiterate previous points, but in clearer ways. No revision required, I guess; probably inevitable in such a long and comprehensive document **Comment acknowledged. No changes made.**

Doug Mackay, University of California, Davis
4.2.2; 1587—May need citation for hydraulic pulse interference test. Add a citation or something so readers can find more information if they want. **Reference added.**
4.3.1; 1610-1614—Need to clarify that sharp permeability contrasts refers (presumably) with contrast between emplaced and native media. Reword. **Text was revised.**
4.3.3; 1701-3—Needs rewording a bit. Suggestion: “Slow diffusion of contaminants from less accessible pores in low permeability lenses and/or porous grains….” **Text was revised.**
4.4; 1750-4—This paragraph is a bit too terse to make the points clearly. Reword. Delete “indications are that,” replace “is diminished” with “may be lower and the community composition different than in the native media upgradient of the PRB.” Explain more clearly that the idea is that immediately downgradient of the PRB, the microbial community may be less capable of NA than in undisturbed zones. **Text was revised.**
5.1; 1771—“performance” missing after “hydraulic.” Add it. **The section title already includes the word “performance.”**
6.2.2.1; 1196-2300—Usefulness of modeling cannot be evaluated by readers since no modeling details are provided. Use more generalized summary of the results, not specifics. **Text was revised.**
6.2.2.2; 2338-9—I don’t understand how screening to the bottom of the reactive media will allow monitoring beneath it. This must be a typo or something, or perhaps I misunderstand the point. Reword to make the point more clearly. Presumably this refers to the need for well screens beneath the media. **Text was revised.**
6.2.5; 2659—This is one location where reference to the passive or between-well recirc methods alluded to in my first comment (this column, way above) might make sense as a “second” PRB. Consider expansion of this text. **Additional bullet was added.**
7.0; 2794—Text doesn’t really discuss the technologies in a complete way since there is no discussion of the success or failures. This limitation of the section should be stated up-front. **Text was added.**
7.1; Figure and text. Why is nitrogen used? Cheapest nonreactive gas? How did the process work? Add some text. **Text was added. Nitrogen gas is used since it is readily available in bulk tankers and is low in cost.**
7.2; All—This seems quite far afield of PRB focus; designed for impermeability, not permeability. Your call. **Comment acknowledged. No changes were made.**
10.2; 3300-5—Need perhaps to mention that there is higher uncertainty associated with the long-term success of the PRBs in controlling migration compared to P&T. **Text was revised. This idea is now captured more clearly.**
11.0; 4326—It is not clear that passive sampling methods are “necessary” though perhaps they are preferable, even to very low flow sampling (e.g. small diameter wells). Clarify. **Text was revised.**

Doug Mackay, University of California, Davis
11.0—Is there any consideration in this document (or should there be) to the possibility of creation of opportunities for lateral flow shifts caused by putting permeable things more or less cross-gradient to flow? In heterogeneous formations, that would seem of potential concern. Your call, but it seems it should be mentioned in this summary if not amplified elsewhere. Is this a research need? **Additional text was added to highlight this point.**
12.0; 3727—Citation is incorrect. See citations in first row of these comments. Delete this and add correct citations. **Citations and references were updated.**

STATE REVIEW COMMENTS

Nebraska Department of Environmental Quality (Wade Gregson)
1.2; Line 80—Unable to find Table 2-2. It's not included anywhere in document, including the Table of Contents. The Table should be placed immediately after the text referencing it, in Section 1.2 and it should then be labeled Table 1-1. Add the appropriate table and/or change the reference as applicable. **Text was revised.**
1.4; Lines 151-157—Repeated information about the purpose of document. The purpose is stated in the Executive Summary, in Section 1.0 of the Introduction, in Section 1.3 Purpose, and again in Section 1.4. Suggest removing some of the repetitive purpose and other general information throughout the document. **Comment acknowledged. No changes were made.**
4.3.1; Lines 1653-1640—The contents of that paragraph appear to need some clarification and may need to have a conclusion drawn. Edit/revise. **Comment acknowledged, but no changes were made.**
4.3.2; Line 1642—The Sub-heading "Variability in the Reactive Media" may be improved and changed to "Variability in the Flow Characteristics of the Reactive Media." Be more specific since the discussion is about permeability and preferential pathways. **Subheading was changed as suggested.**
5.2.1; Lines 1805-1807—The text "… indicate that certain groundwater constituents indicate …" is awkward. Revise. **Text was revised.**
7.1; Line 2852—The sentence used to introduce Figure 7-1 states: "… the Ferox$^{\mathbf{sm}}$ process is shown below" but the figure is on the following page. Suggest always introducing figures by referencing the Figure Number. **Text and figure placements have been revised.**
7.2; Lines 2896-2898—Figure 7-2 is unclear to this reader and may need modification/enhancement. Also the figure is not referenced or introduced in the text, as are others in the document. Consider revision/enhancing. Also, recommend always referencing/introducing figures in text. **The figure has been referenced in the text and a higher resolution figure has been inserted.**
8.0; Lines 2983-2986—The two bulleted sentences would work well together as a single bulleted discussion on level D versus level C PPE. Consider keeping both sentences together in the same bullet. **These two bullets were combined.**

Illinois EPA (Ted Dragovich)

The authors of the subject document have a good understanding of the regulatory issues/considerations associated with PRBs; the Illinois EPA agrees that one or more permits may be needed for design, construction, monitoring and operation, or closure of a PRB. In addition, the authors state that different regulatory mechanisms, such as an approval letter, may be needed to obtain PRB approval, which may require submittal of an assessment plan, corrective action plan, remedial action plan, workplan, etc. In summary, the Illinois EPA concurs that a thorough review of all permitting issues and state and local regulations should be conducted on a site-specific basis.

In regards to groundwater monitoring, the Illinois EPA is in agreement that groundwater monitoring or the development of a groundwater monitoring plan will be necessary based on chemicals of concern (COCs), site-specific cleanup objectives, and specific regulatory requirements. The discussion regarding techniques and procedures associated with well placement, well construction, sampling methods, parameters, frequency, and duration appear adequate; the methods and procedures are consistent with what is typically found in a RCRA groundwater monitoring program (RCRA permit, RCRA closure plan, approval letter, etc). As previously stated, it appears that the authors of the subject document have an exceptional understanding of the regulatory requirements.

The subject document provides a general discussion regarding compliance monitoring, performance monitoring, and cleanup standards established via regulatory mechanisms. Although a Compliance Monitoring Program, as found in 35 Ill. Adm. Code 724.199, may be appropriate under certain circumstances, the establishment of a groundwater Corrective Action Program, as found in 35 Ill. Adm. Code 724.200 may be required to ensure compliance with groundwater standards/objectives, when corrective action such as the operation of a PRB, is implemented. Such a program requires groundwater monitoring to not only demonstrate compliance with groundwater standards/objectives, but also to demonstrate the effectiveness of the correction action (PRB). Specific requirements of any groundwater monitoring/corrective action program are based on site-specific conditions.

The comment is acknowledged and appreciated. No changes were necessary.

Investigations of existing or potential groundwater contamination, including consideration of a PRB must initially include a thorough site characterization. Specifically, this would include: (1) defining/proposing technical objectives dictated by the regulatory program; (2) conducting a preliminary investigation based on exiting information; and (3) collecting site-specific data.

These points are covered in Section 3 (Site Characterization).

DOD REVIEW COMMENTS

Comments from Cliff Casey and Mike Singletary (EFDSOUTH): Some questions that may be useful in answering. There have been at least two failures (slurry wall collapse) of PRB’s built with polymer slurries that hold open the excavation. It would be useful to know what critical parameters might be useful to monitor during installation so that failure will be minimized. In other words hydrostatic pressure may need to be estimated and some indication of the polymer capacity to withstand that pressure needs to be addressed. Also potential for microbes native to the site that can break the polymer prior to completion of the wall needs to be more fully addressed or other reasons for the polymer to be insufficient such as viscosity or other.

Text was added to Sections 4.2.1 and 3.7.

Comments from Mike Maughon (EFDSOUTH): The stability of trench/slurry walls will also depend on the shear strength of soils and related factors, which can vary significantly based on site-specific conditions, e.g., soil type (percent sand, clay, silt and related properties), drained and undrained conditions, depth of trench, pore water pressure (a function of water table and variations due to any dewatering/flooding, etc.), surcharge loadings from excavated/stockpiled materials or equipment, length

of trench opened, etc.) To better ensure trench stability and related safety and PRB effectiveness, recommend the guidance clearly indicate trenching and slurry wall designs should be performed by a registered geotechnical engineer based on site specific conditions, including appropriate soil testing and analyses. **See above. Also, text and Figure 4-1 were added to the beginning of Section 4.**
Comments from Chuck Reeter (NFESC): I have 1 additional comment in relation to Mike’s suggestion that a registered GE be required for PRB slurry wall design. We have tried to not to make professional registration a specific requirement applied to all PRBs, particularly at the regulatory guidance level. We feel that this would be too restrictive and costly to be applied to all situations. We would certainly welcome professional registrations for site-specific situations, if the RPM feels it is necessary. In other words, this criterion should be left up to the individual site requirements. **See above.**
Comments from Joseph M. Saenz: I agree that a fully qualified and credential individual should perform and manage the design of PRBs in the field and office. Note that this draft guidance document is not policy nor regulations and should only simply provide guidance. However, as the guidance document should not be meant to dictate professional registration criteria, we can recommend language in the document to ensure that appropriate and qualified people are used during the design of PRB’s activities per federal, state, and local regulations. In addition, recommend adding language in the guidance document to include three DoD sites (listed below) write-ups listing them as “DoD CASE STUDIES” in the document: 1) Naval Air Engineering Station, Lakehurst 2) Naval Air Station, Jacksonville, Florida 3) Hunter’s Point Shipyard, San Francisco, California 4) Naval Base Ventura County, Port Hueneme, California (Non-PRB Site) **Text was clarified regarding using a qualified individual for the PRB design. All of the indicated case studies were added in Appendix E.**

APPENDIX H

PRB Team Contacts, ITRC Fact Sheet and Product List

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