Final

Design Guidance for Application of Permeable Reactive Barriers for Groundwater Remediation

Prepared for

Project Officer: Alison Lightner
Air Force Research Laboratory
Tyndall Air Force Base, Florida

Contract No. F08637-95-D-6004
Delivery Order No. 5503

By

Arun Gavaskar, Neeraj Gupta, Bruce Sass,
Robert Janosy, and James Hicks

BATTELLE
Columbus, Ohio

March 31, 2000

Study sponsored by

DoD EPA DOE SERDP
Strategic Environmental Research
and Development Program
Improving Mission Readiness through
Environmental Research

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (*Leave blank*)

2. REPORT DATE
March 2000

3. REPORT TYPE AND DATES COVERED
Final, April 1997 through March 2000

4. TITLE AND SUBTITLE
Design Guidance for Application of Permeable Reactive Barriers for Groundwater Remediation

5. FUNDING NUMBERS
F08637-95-D-6004
DO 5503

6. AUTHOR(S)
Arun Gavaskar, Neeraj Gupta, Bruce Sass, Robert Janosy, and James Hicks

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Battelle
505 King Avenue
Columbus, OH 43201

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Air Force, Air Force Research Laboratory (AFRL)
139 Barnes Drive, Suite 2
Tyndall AFB, FL 32403

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
A012

11. SUPPLEMENTARY NOTES
Task was performed by Battelle under contract to AFRL, U.S. Air Force

12a. DISTRIBUTION/AVAILABILITY STATEMENT
May not be released by other than sponsoring organization without approval of AFRL, U.S. Air Force

12b. DISTRIBUTION CODE

13. ABSTRACT (*Maximum 200 words*)

Battelle, under contract to the Air Force, has prepared a comprehensive update to the February 1997 version of a design guidance document for the proposed use of site managers, contractors, and regulators. The design guidance covers permeable barrier application to sites with contaminated groundwater. The document does not purport to replace the scientific judgment of the on-site engineer or hydrogeologist, but provides guidance on the issues and options that need to be considered based on the current understanding of the technology. The guidance addresses design, construction, and monitoring of permeable barriers in various hydrogeologic settings.

This update includes the lessons learned during the design, construction, and monitoring of a permeable reactive barrier at Dover AFB, DE, as well as progress made at other sites. It also includes the advances in the technology since the completion of the previous version of the report.

14. SUBJECT TERMS
permeable barrier, groundwater, reactive medium, funnel-and-gate, chlorinated solvent

15. NUMBER OF PAGES
167 + Appendices

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT

18. SECURITY CLASSIFICATION OF THIS PAGE

19. SECURITY CLASSIFICATION OF ABSTRACT

20. LIMITATION OF ABSTRACT

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. 239-18
298-102

Preface

This document was prepared by Battelle Memorial Institute, 505 King Avenue, Columbus, OH 43201, under Contract No. F08637-95-D-6004 (Delivery Order No. 5503) for the Air Force Research Laboratory (AFRL), 139 Barnes Drive, Tyndall Air Force Base (AFB), FL 32403. The United States Department of Defense's (DoD's) Strategic Environmental Research and Development Program (SERDP) provided the funds for this project. The AFRL Project Officer for this document was Alison Lightner. Previous versions of this document were supervised by Project Officers Maj. Mark Smith, Cpt. Jeff Stinson, 1st Lt. Dennis O'Sullivan, and Cpt. Gus Fadel. This document is an updated version of the *Design Guidance for Application of Permeable Barriers to Remediate Dissolved Chlorinated Solvents* prepared by Battelle in 1997.

The objective of this report is to provide site managers with a guidance document for designing, constructing, and monitoring a permeable reactive barrier (PRB) for remediation of dissolved groundwater contaminants. Another objective of this document is to bring together the existing knowledge base (published and unpublished) on this technology. This is intended to be a stand-alone document that provides guidance to site managers, contractors, and regulators. Supporting material for the main document is provided in the Appendices.

Battelle would like to acknowledge the advice and reviews provided by several members of the Remediation Technologies Development Forum's (RTDF's) Permeable Barriers Working Group (PBWG) and the members of the Interstate Technology and Regulatory Cooperation's (ITRC's) Permeable Barriers Subgroup. We appreciate the support provided by John Vogan of EnviroMetal Technologies, Inc. (ETI) in providing updates on several new PRB sites and on the other information in the guidance document. Timothy Sivavec from General Electric Co. and Kirk Cantrell from Pacific Northwest National Laboratory are acknowledged for their contributions to the 1997 version of this document.

The information relating to the PRB at Dover AFB was based on a demonstration conducted by Battelle for AFRL, with Alison Lightner as the project officer and Greg Jackson at Dover AFB as the Base contact. The information relating to the PRB at former Naval Air Station (NAS) Moffett Field was based on a study conducted by Battelle for the Naval Facilities Engineering Service Center (NFESC), with Charles Reeter as the project officer and Steve Chao from Engineering Field Activity West as the Base contact. Catherine Vogel, at the DoD SERDP, provided guidance and review support during the project.

Executive Summary

A. Objective

The Air Force Research Laboratory (AFRL) at Tyndall Air Force Base (AFB), FL contracted Battelle in Columbus, OH to prepare a design guidance document for the application of permeable barriers. The first version of this document was issued in February 1997, after being widely reviewed by several members of the Remedial Technologies Development Forum's (RTDF's) Permeable Barriers Working Group (PBWG) and the Interstate Technology and Regulatory Cooperation's (ITRC's) Permeable Barriers Subgroup. The current document is an effort to update the previous design guidance after reviewing the performance of previously installed permeable reactive barriers (PRBs) and evaluating the design and construction of newer PRB applications, such as the one at Dover AFB. The United States Department of Defense's (DoD's) Strategic Environmental Research and Development Program (SERDP) provided the funds for this project.

The objective of this document is to guide site managers, contractors, and state and federal regulators through the process of:

(a) Determining the technical and economic suitability of a PRB for a given site, and
(b) Designing, constructing, and monitoring the PRB.

Unlike conventional ex situ technologies, such as pump-and-treat (P&T) systems, in situ technologies are more dependent on site-specific parameters. Therefore, this document does not purport to replace the scientific judgment of the site hydrologist or site engineer. Instead, this document highlights various chemical, biological, and hydrologic issues that affect the application of PRBs to various sites and the options available for resolving these issues.

B. Background

At many sites, groundwater remediation is proving to be a much more difficult and persistent problem than originally thought. One of the more common and difficult groundwater problems prevalent at DoD sites and other government and industrial properties is the presence of chlorinated solvent-contaminated soil and groundwater. Chlorinated solvents or chlorinated volatile organic compounds (CVOCs), such as trichloroethylene (TCE) and perchloroethylene (PCE), were commonly used at these sites and properties for aircraft maintenance, dry cleaning, electronics manufacturing, metal finishing, and other operations. These solvents have entered the ground through leaks, spills, or past disposal practices, and there may be more than 600 such sites at Air Force bases across the country. The United States Environmental Protection Agency (U.S. EPA) estimates that there are 5,000 DoD, United States Department of Energy (DOE), and Superfund sites contaminated with chlorinated solvents.

Because chlorinated solvents often tend to persist in soil and groundwater for several years or decades, their remediation is usually a technically and economically challenging undertaking. The conventional method for addressing groundwater contamination at most sites has been P&T

systems, which extract groundwater from the aquifer, treat it above ground, and discharge it to a sewer or back to the environment. The energy and labor inputs required to keep these systems operational for many years is a severe economic burden for site owners. PRBs are an innovative technology that offer a passive alternative to conventional P&T systems for addressing long-term groundwater contamination problems. Although PRBs initially were applied to treat CVOC plumes, they also have been applied to treat or capture other contaminants, such as hexavalent chromium and uranium.

C. Scope

The overall methodology for the application of a PRB at a given site is discussed in this document and involves the following steps:

- Preliminary assessment
- Site characterization
- Reactive media selection
- Treatability testing
- Modeling and engineering design
- Selection of a suitable construction method
- Monitoring plan preparation
- Economic evaluation.

The guidance in this document is organized in accordance with these design steps.

D. Conclusions

The preliminary assessment is conducted to evaluate the technical and economic suitability of a given site for PRB application. Once a site is determined to be suitable, additional design steps are initiated as shown above. For common contaminants, such as TCE, that are to be treated with common reactive media, namely iron, it may be possible, if regulators agree, to forego treatability testing in favor of published contaminant half-lives and a design that includes appropriate safety factors.

At several existing sites, PRB construction generally has involved installation of reactive media in an excavated space. Excavation using backhoes, continuous trenchers, augers, or caissons is a conventional way of ensuring that the desired thickness and continuity of the reactive cell is achieved. The increasing use of a biodegradable slurry, instead of sheet piles or cross-bracing, to stabilize the excavation has increased the convenience and safety of installing the reactive media in the ground. However, these excavation methods have varying depth limitations (generally between 30 to 50 ft below ground surface). Innovative installation methods, such as jetting, hydraulic fracturing, vibrating beam, deep soil mixing, and the use of mandrels, have been tested at some sites and offer potentially lower-cost alternatives for installing reactive media at greater depths. As published data from various field sites become available on the ability of these techniques to install the reactive media at the desired thickness and continuity, it is likely that deeper aquifers can be accessed in a cost-effective manner.

Ensuring and verifying hydraulic performance are the main design and monitoring challenges during application of PRBs. Aquifer heterogeneities, plume heterogeneities, and seasonal fluctuations in flow are the factors that make the design and monitoring of a PRB's hydraulic performance difficult. Groundwater flow bypass and/or inadequate residence time in the reactive medium have been the main causes of the inability to meet treatment targets reported at some sites. Adequate site characterization, simulation of multiple flow scenarios, and incorporation of adequate safety factors during design are the main ways of achieving satisfactory hydraulic performance.

The economics of a PRB application depend largely on the useful life (longevity) of the reactive media, especially when treating plumes that are expected to persist for several years or decades. Most current geochemical evaluation techniques (e.g., groundwater monitoring, reactive medium coring, and geochemical modeling) have not been able to predict the life of common reactive media, and empirical evidence is lacking given the relatively short history of PRB applications. In the absence of reliable longevity predictions, this document suggests that multiple longevity scenarios be evaluated to place long-term PRB application costs (and benefits) in the context of varying life expectancies of the reactive medium.

Table of Contents

Table of Contents
(Continued)

Table of Contents
(Continued)

Table of Contents
(Continued)

List of Figures

List of Tables

List of Abbreviations, Acronyms, and Symbols

2-D	two-dimensional
3-D	three-dimensional
AFB	Air Force Base
AFRL	Air Force Research Laboratory
ATR	attenuated total internal reflection
B	bulk density
BET	Brunauer-Emmett-Teller Adsorption Isotherm Equation
bgs	below ground surface
BTEX	benzene, toluene, ethylbenzene, and xylenes
CCD	charge coupled device
CPT	cone penetrometer testing
CQC	construction quality control
CRB	continuous reactive barrier
CVOC	chlorinated volatile organic compound
DCE	dichloroethene
DDT	dichlorodiphenyltrichloroethane
DI	deoinized
DNAPL	dense, nonaqueous-phase liquid
DO	dissolved oxygen
DOC	dissolved organic carbon
DoD	United States Department of Defense
DOE	United States Department of Energy
ECD	electron capture detector
EDS	energy dispersive spectroscopy
Eh	redox potential
EPA	Environmental Protection Agency
EQL	estimated quantitation limit
ESTCP	Environmental Security Technology Certification Program
ETI	EnviroMetal Technologies, Inc.
FID	flame ionization detector
FTIR	Fourier transform infrared spectroscopy
GC	gas chromatography
GC/MS	gas chromatography/mass spectrometry
GC-FID	gas chromatograph-flame ionization detector

HDPE	high-density polyethylene
HSU	hydrostratigraphic units
IAP	ion activity product
IC	ion chromatography
ICP	inductively coupled plasma
ISRM	in situ redox manipulation
ITRC	Interstate Technology and Regulatory Cooperation
JAG	jet-assisted grouting
K	hydraulic conductivity
$K_{aquifer}$	aquifer hydraulic conductivity
K_{cell}	reactive cell hydraulic conductivity
MCL	maximum contaminant level
meq	milliequivalent(s)
MS	matrix spike
MSDS	Material Safety Data Sheet
mV	millivolts
n	porosity
NA	not available
NAS	Naval Air Station
NASA	National Aeronautics and Space Administration
NDMA	*n*-nitrosodimethylamine
NERL	National Exposure Research Laboratory
NFESC	Naval Facilities Engineering Service Center
O&M	operating and maintenance
OMB	(U.S. EPA) Office of Management and Budget
ORC®	oxygen-release compound
ORNL	Oak Ridge National Laboratory
ORP	oxidation-reduction potential
OSHA	Occupational Safety and Health Administration
PAH	polycyclic aromatic hydrocarbon
PBWG	Permeable Barriers Working Group
PCB	polychlorinated biphenyl
PCE	perchloroethylene
PFLA	phospholipid fatty acid
PPE	personal protective equipment
ppmv	parts per million by volume
PRB	permeable reactive barrier
PRC	PRC Environmental Management
PRP	potentially responsible party

P&T	pump-and-treat
PV	present value
PVC	polyvinyl chloride
QA	quality assurance
QA/QC	quality assurance/quality control
QC	quality control
RACER	Remedial Action Cost Engineering and Requirements (System)
RCRA	Resource Conservation and Recovery Act
RFI	RCRA Facility Investigation
RI/FS	Remedial Investigation/Feasibility Study
ROD	Record of Decision
RTDF	Remediation Technologies Development Forum
SEI	secondary electron image(s)
SEM	scanning electron microscopy
SERDP	Strategic Environmental Research and Development Program
SHE	standard hydrogen electrode
SI	saturation index
SPH	smooth particle hydrodynamics
T	temperature
TCA	trichloroethane
TCE	trichloroethylene
TDS	total dissolved solids
TOC	total organic carbon
TSS	total suspended solids
USAF	United States Air Force
U.S. EPA	United States Environmental Protection Agency
USGS	United States Geological Survey
V	volts
VC	vinyl chloride
VOC	volatile organic compound
WSRC	Westinghouse Savannah River Company
XRD	x-ray diffraction

1.0 Introduction

1.1 Project Background

At many sites, groundwater remediation is proving to be a much more difficult and persistent problem than originally thought. One of the more common and difficult groundwater problems presented by United States Department of Defense (DoD) sites and other government and industrial properties is the presence of chlorinated solvent-contaminated soil and groundwater. Chlorinated solvents or chlorinated volatile organic compounds (CVOCs), such as trichloroethylene (TCE) and perchloroethylene (PCE), were commonly used at these sites and properties for aircraft maintenance, dry cleaning, electronics manufacturing, metal finishing, and other operations. These solvents have entered the ground through leaks, spills, or past disposal practices, and there may be more than 600 such sites at Air Force bases across the country. The United States Environmental Protection Agency (U.S. EPA) (1995) estimates that there are 5,000 DoD, United States Department of Energy (DOE), and Superfund sites contaminated with chlorinated solvents.

Because chlorinated solvents often tend to persist in soil and groundwater for several years or decades, their remediation is usually a technically and economically challenging undertaking. The conventional method for addressing groundwater contamination at most sites has been pump-and-treat (P&T) systems. P&T systems extract groundwater from an aquifer, treat it aboveground, and discharge it to a sewer or back to the environment. The energy and labor inputs required to keep these systems operational for many years is a severe economic burden for site owners. Permeable reactive barriers (PRBs) are an innovative technology that offer a passive alternative to conventional P&T systems for addressing long-term groundwater contamination problems. Although PRBs initially were applied to treat CVOC plumes, they also have been applied to treat or capture other contaminants, such as hexavalent chromium and uranium.

The Air Force Research Laboratory (AFRL) at Tyndall Air Force Base (AFB), FL contracted Battelle in Columbus, OH to prepare a design guidance document for the application of permeable barriers (Battelle, 1997a). The first version of this document was issued in February 1997, after being widely reviewed by several members of the Remedial Technologies Development Forum's (RTDF's) Permeable Barriers Working Group (PBWG) and the Interstate Technology and Regulatory Cooperation's (ITRC's) Permeable Barriers Subgroup. The current document is an effort to update the previous design guidance after reviewing the performance of previously installed PRBs and evaluating the design and construction of newer PRB applications, such as the one at Dover AFB. Funding for this project was provided by DoD's Strategic Environmental Research and Development Program (SERDP). A list of relevant points of contact is included as Appendix A.

The objective of this document is to guide site managers, contractors, and state and federal regulators through the process of:

(a) Determining the technical and economic suitability of a PRB for a given site, and
(b) Designing, constructing, and monitoring a PRB.

Unlike conventional ex situ technologies, such as P&T systems, in situ technologies are more dependent on site-specific parameters. Therefore, this document does not purport to replace the scientific judgment of the site hydrologist or site engineer. Instead, this document highlights various chemical, biological, and hydrologic issues that affect the application of PRBs to various sites and the options available for resolving these issues.

1.2 Groundwater Remediation Difficulties

One class of groundwater contaminants that has proved to be particuluarly difficult to remediate is chlorinated solvents. Chlorinated solvents have been used extensively in the past by industry and government for a variety of operations, such as degreasing, maintenance, and dry cleaning. Leaks, spills, and historical disposal practices have led to widespread contamination of the soil and groundwater. Ten of the 25 most common groundwater contaminants at hazardous waste sites are chlorinated solvents, with TCE being the most prevalent (National Research Council, 1994).

Most chlorinated solvents belong to a class of compounds which, when present in sufficient quantity, may form dense, nonaqueous-phase liquids (DNAPLs). DNAPLs are denser than water and therefore move downward in the subsurface until they encounter a low-permeability zone or aquitard. On their way down, solvents typically leave a trail of free-phase residual DNAPL that is virtually immobile and is resistant to pumping. The DNAPLs present in pools or in residually saturated zones provide a long-term source for contaminant releases into groundwater, which often result in large dissolved-phase plumes. Although most chlorinated solvents are sparingly soluble in water, their solubilities are several times higher than the U.S. EPA's maximum contaminant level (MCL) standards for drinking water. Table 1-1 shows the properties of common chlorinated solvents. Because of their low solubilities and mass transfer limitations, chlorinated solvent source zones can persist in the aquifer for several years, decades, or centuries. The dissolved contaminant plume resulting from the source zone can persist for similar lengths of time and has been known to travel large distances because chlorinated solvents are relatively recalcitrant to biodegradation processes at many sites.

Table 1-1. Properties of Common CVOCs

Compound	MCL (mg/L)	Water Solubility (mg/L at 25°C)	Density (g/cm^3 at 20°C)	Vapor Pressure (Pascals at 25°C)
Carbon tetrachloride	0.005	800	1.59	15,097
1,1,1-Trichloroethane	0.2	1,250	1.34	13,300
1,2-Dichloroethane	0.005	8,600	1.26	9,000
Methylene chloride	0.005	20,000	1.33	46,522 (20°C)
Perchloroethylene	0.005	150	1.63	2,415
Trichloroethylene	0.005	1,100	1.46	9,910
cis-1,2-Dichloroethene	0.07	3,500	1.28	26,700
trans-1,2-Dichloroethene	0.1	6,300	1.26	45,300
Vinyl chloride	0.002	2,000	0.91	350,000

Although one apparent approach to cleaning up these sites is to remediate the DNAPL source zone, in practice this often proves difficult. First, DNAPL source zones are difficult to locate; second, when found, these zones generally are difficult to remediate. Therefore, at many sites, a more viable option is to treat the plume. Conventional P&T systems can be used to capture and treat the plume. However, past experiences at contaminated groundwater sites and recent studies (National Research Council, 1994) have shown the inadequacies of this approach. Also, a P&T system would have to be operated for many years or decades or as long as the source zone and plume persist, and the associated operational costs over several decades can be enormous. The recent development of PRBs has presented a potentially viable alternative to conventional P&T systems.

1.3 The Innovative PRB Technology

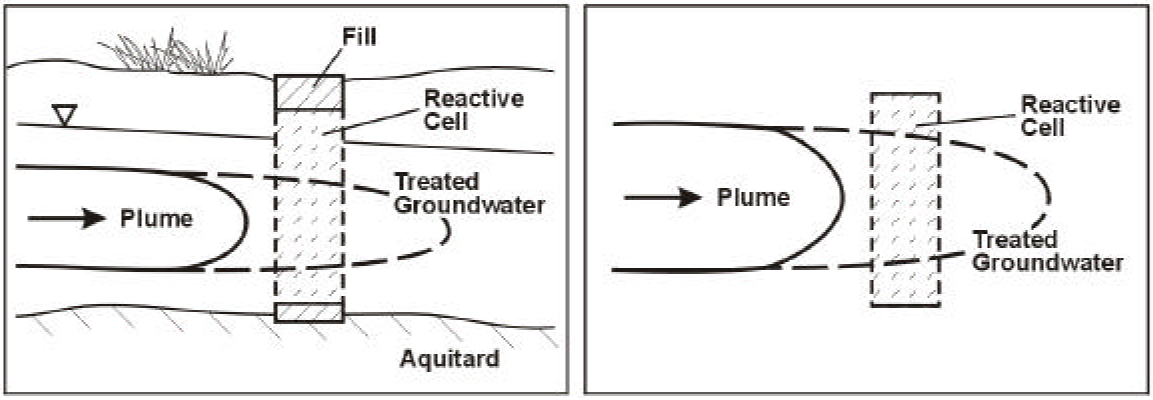
Figure 1-1 shows some possible configurations of PRB systems. In its simplest form, a PRB consists of a zone of reactive material, such as granular iron, installed in the path of a dissolved chlorinated solvent plume (Figure 1-1a). As the groundwater flows through the reactive zone, the CVOCs come in contact with the reactive medium and are degraded to potentially nontoxic dehalogenated organic compounds and inorganic chloride. The main advantage of a PRB is that, generally, no pumping or aboveground treatment is required; the barrier acts passively after installation. Because there are no aboveground installed structures, the affected property can be put to productive use while it is being cleaned up. Also, initial evidence indicates that the reactive medium is used up very slowly and, therefore, PRBs have the potential to passively treat the plume over several years or decades, which would result in hardly any annual operating costs other than site monitoring. Depending on the longevity of the reactive medium, the barrier may have to be rejuvenated or replaced periodically; however, it is expected that such maintenance would be required infrequently if at all.

A PRB typically may be installed either as a continuous reactive barrier or as a funnel-and-gate system. A continuous reactive barrier (Figure 1-1b) consists of a reactive cell containing the reactive medium. A funnel-and-gate system (Figure 1-1d) has an impermeable section (or funnel) that directs the captured groundwater flow toward the permeable section (or gate). This configuration may sometimes allow better control over reactive cell placement. However, most recent PRB applications have been continuous reactive barriers. Continuous reactive barriers are easier to install and generate less complex flow patterns compared to funnel-and-gate systems.

1.4 Mechanism of Abiotic Degradation with Metals

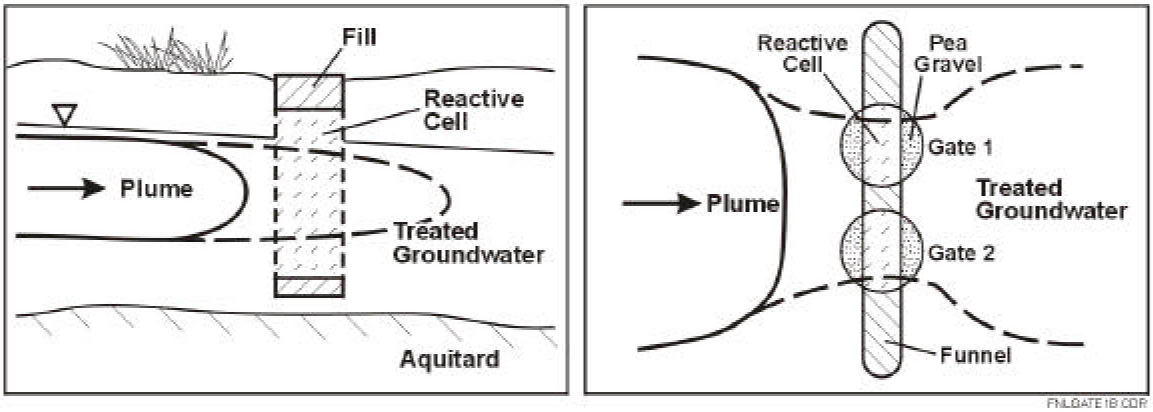
Although a variety of reactive media (see Section 4.0) can be used to treat groundwater contaminants, the most commonly used media are zero-valent metals, particularly granular iron. As the zero-valent metal in the reactive cell corrodes, the resulting electron activity is believed to reduce the chlorinated compounds to potentially nontoxic products. Because the reaction mechanism of CVOC degradation with zero-valent iron has been the most widely studied and reported to date, this document focuses on the chemistry of CVOC-iron interactions and groundwater-iron interactions.

The first reported use of the degradation potential of metals for treating chlorinated organic compounds in the environment was by Sweeny and Fischer (1972), who acquired a patent for the



(a) PRB (elevation view)

(b) Continuous reactive barrier configuration (plan view)



(c) Hanging barrier configuration for shallow plumes (elevation view)

(d) Funnel-and-gate system with two gates (plan view)

Figure 1-1. Schematic Illustration of Some PRB Configurations

degradation of chlorinated pesticides by metallic zinc under acidic conditions. These researchers found that *p,p¢*-dichlorodiphenyltrichloroethane (*p,p¢*-DDT) was degraded by zinc at ambient temperatures at a satisfactory rate with ethane as the major product. In two later papers, Sweeny (1981a and 1981b) described how catalytically active powders of iron, zinc, or aluminum could be used to destroy a variety of contaminants, including TCE, PCE, trichloroethane (TCA), trihalomethanes, chlorobenzene, polychlorinated biphenyls (PCBs), and chlordane. The process could be carried out by trickling wastewater through a bed of iron and sand to give suitable retention and flow properties, or by fluidizing a bed of iron powder with the aqueous influent. Sweeny suggested that the reduction proceeds primarily by the removal of the halogen atom and its replacement by hydrogen (Equation 1-1), although other mechanisms probably play a role. Another important reaction suggested was the replacement of a halogen by a hydroxyl group (Equation 1-2). The iron metal also was believed to be consumed by water (Equation 1-3), although this reaction proceeds much more slowly than the other two.

$$\mathrm{Fe} + \mathrm{H_2O} + \mathrm{RCl} \rightarrow \mathrm{RH} + \mathrm{Fe}^{2+} + \mathrm{OH}^{-} + \mathrm{Cl}^{-} \tag{1-1}$$

$$\mathrm{Fe} + 2\ \mathrm{H_2O} + 2\ \mathrm{RCl} \rightarrow 2\ \mathrm{ROH} + \mathrm{Fe}^{2+}\ 2\ \mathrm{Cl}^{-} + \mathrm{H_2} \tag{1-2}$$

$$\mathrm{Fe} + 2\ \mathrm{H_2O} \rightarrow \mathrm{Fe}^{2+} + 2\ \mathrm{OH}^{-} + \mathrm{H_2} \tag{1-3}$$

Other researchers such as Senzaki and Kumagai (1988a and 1988b) and Senzaki (1988) also suggested the use of iron powder for removal of TCE and TCA from wastewater. More recently, researchers at the University of Waterloo (Reynolds et al., 1990; Gillham and O'Hannesin, 1992) conducted focused efforts in this area, and were issued a patent for the use of zero-valent metals for in situ groundwater treatment (Gillham, 1993).

The exact mechanism of degradation of chlorinated compounds by iron or other metals is not fully understood. In all probability, a *variety of pathways* are involved, although recent research seems to indicate that certain pathways predominate. If some dissolved oxygen (DO) is present in the groundwater as it enters the reactive iron cell, the iron is oxidized and hydroxyl ions are generated (Equation 1-4). This reaction proceeds quickly, as evidenced by the fact that both the DO and the oxidation-reduction potential (ORP) drop quickly as the groundwater enters the iron cell. The importance of this reaction is that DO can quickly corrode the first few inches of iron in the reactive cell. Under oxygenated conditions, the iron may precipitate out as ferric oxyhydroxide (FeOOH) or ferric hydroxide [$\mathrm{Fe(OH)_3}$], in which case the permeability could potentially become considerably lower in the first few inches of the reactive cell at the influent end. Therefore, the aerobic nature of the groundwater can be potentially detrimental to the technology. However, contaminated groundwater at many sites is not highly oxygenated. Also, engineering controls (see Section 6.0) possibly can be used to reduce or eliminate DO from the groundwater before it enters the reactive cell.

$$2\ \mathrm{Fe}^{0} + \mathrm{O_2} + 2\ \mathrm{H_2O} \rightarrow 2\ \mathrm{Fe}^{2+} + 4\ \mathrm{OH}^{-} \tag{1-4}$$

Once DO has been depleted, the created reducing conditions lead to a host of other reactions. Chlorinated organic compounds, such as TCE, are in an oxidized state because of the presence of chlorine. Iron, a strong reducing agent, reacts with the chlorinated organic compounds through electron transfers, in which ethene and chloride are the primary products (Equation 1-5).

$$\begin{array}{c} 3\,\mathrm{Fe}^{0} \rightarrow 3\,\mathrm{Fe}^{2+} + 6\,\mathrm{e}^{-} \\ \\ \mathrm{C_2HCl_3} + 3\,\mathrm{H}^{+}\ 6\,\mathrm{e}^{-} \rightarrow \mathrm{C_2H_4} + 3\,\mathrm{Cl}^{-} \\ \hline 3\,\mathrm{Fe}^{0} + \mathrm{C_2HCl_3} + 3\,\mathrm{H} \rightarrow 3\,\mathrm{Fe}^{2+} + \mathrm{C_2H_4} + 3\,\mathrm{Cl}^{-} \end{array} \tag{1-5}$$

In one study, Orth and Gillham (1996) found that ethene and ethane (in the ratio 2:1) constitute 80% of the original equivalent TCE mass. Partially dechlorinated byproducts of the degradation reaction such as *cis*-1,2-dichloroethene (DCE), *trans*-1,2-DCE, 1,1-DCE, and vinyl chloride (VC) were found to constitute only 3% of the original TCE mass. Additional byproducts included hydrocarbons (C1 to C4) such as methane, propene, propane, 1-butene, and butane. Virtually all the chlorine in the original TCE mass was accounted for as inorganic chloride in the effluent, or as chlorine remaining on the partially dechlorinated byproducts. Similar results were obtained by Sivavec and Horney (1995), who quantified both liquid and gas phases of the reaction to obtain a carbon balance greater than 90%.

It is unclear whether the reported production of ethane during TCE degradation represents a different pathway or whether it results from the iron-mediated catalytic transformation of ethene. Also unclear is whether the C1 to C4 hydrocarbons represent an alternative pathway for TCE degradation or are the result of some other reaction. One study (Hardy and Gillham, 1996) suggests that aqueous CO_2 is reduced on the iron surface to form these hydrocarbon chains. Another study (Deng et al., 1997) suggests that the source of these hydrocarbons is the acid dissolution of gray cast irons containing both carbide and graphite carbon.

A number of interesting issues are raised by the reaction mechanism as explained in Equation 1-5. For Equation 1-5 to take place in one step without the generation of larger amounts of partially dechlorinated products (e.g., DCE or VC), six electrons must be transferred almost instantaneously. Given the low probability of an instantaneous transfer of this magnitude, Orth and Gillham (1996) suggest that the TCE molecule must remain attached to the metal surface long enough for the six-electron transfer to occur. The TCE molecule remains attached to the metal surface either through the inherent hydrophobicity of TCE or, as Sivavec and Horney (1995) suggest, by the formation of a strong chloroethene-iron pi bond. This bonding prevents desorption until dechlorination is complete, although a few random chloroethene molecules may desorb early, leading to the presence of small amounts of DCE and VC. Overall, these explanations suggest that the degradation of chlorinated organics by metals is a surface phenomenon and that the rate is governed by the specific surface area of the reactive medium.

There is evidence that PCE and TCE in contact with iron may degrade at least partly through a different pathway from the hydrogenolysis pathway discussed above. Experiments by Roberts et al. (1996) indicate that PCE and TCE could be reduced through the β-elimination pathway shown in Figure 1-2 (for TCE only) to dichloroacetylene and chloroacetylene, respectively. Both of these byproducts are potentially toxic, but are likely to be short-lived. Hydrogenolysis could lead to their transformation to lesser chlorinated acetylenes, which could further be reduced to substituted ethenes. Hydrolysis of the chloroacetylenes to acetates is also a possible pathway. Overall, these experiments indicate that there may be multiple pathways (as shown in Figure 1-2) by which chlorinated ethenes, such as PCE and TCE, are transformed in the presence of iron into dehalogenated products such as ethene (Sivavec et al., 1997).

Iron also reacts with water itself under reducing (anaerobic) conditions, although this reaction is believed to be much slower than reactions of iron with halogenated compounds. The slow reaction with water (Equation 1-6) is advantageous to the technology because very little reactive medium (iron) is used up in this side reaction. Hydrogen gas and OH^- are formed as water is reduced, as shown in Equation 1-6.

$$\begin{array}{c} Fe^0 \rightarrow Fe^{2+} + 2\,e^- \\ 2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^- \\ \hline Fe^0 + 2\,H_2O \rightarrow Fe^{2+} + H_2 + 2\,OH^- \end{array} \qquad (1\text{-}6)$$

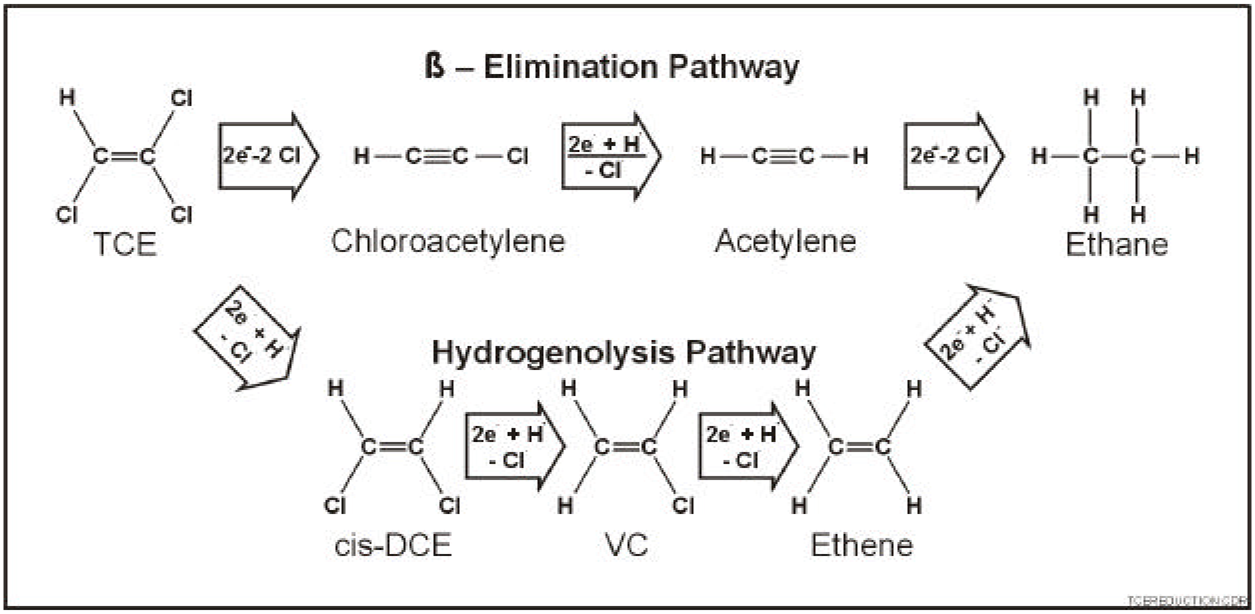


Figure 1-2. Currently Proposed Mechanism for TCE Degradation by Iron

Hydrogen generation could be a concern if hydrogen accumulates in the aquifer as it appears to do in some column tests (Mackenzie et al., 1999). Moreover, hydrogen evolution rates calculated by Reardon (1995) for Master Builder's iron (10-32 mesh) are not insignificant. Apart from the flammability issue, formation of hydrogen could potentially lead to porosity loss and decreased permeability. Column tests have shown porosity losses of 5 to 10% attributable to hydrogen gas buildup (Sivavec, 1999). Because the porosity losses were measured immediately after starting the column tests, it is unlikely that they were caused by mineral precipitation. However, in natural aquifers, hydrogen generated through the reaction shown in Equation 1-6 can degrade through biological transformations (Chiu and Cha, 2000). Therefore, hydrogen buildup has not been identified as a problem at field PRB sites. Hydrogen generation and its fate in natural aquifers is an area requiring further research.

Because several of the above reactions produce OH^-, the pH of the water in the reactive iron cell typically increases, often reaching values above 9.0. One effect of increased pH initially was thought to be a slowing down of the TCE degradation rate (O'Hannesin, 1993), because changes in pH were expected to cause changes in the degradation rate through direct involvement of H^+ (see Equation 1-5). However, subsequent research has raised questions about whether pH affects degradation rate (Agrawal and Tratnyek, 1996).

An indirect effect of increased pH is the potential for precipitates to form, which could coat the surface of the iron and potentially reduce the reactivity of the iron and the hydraulic conductivity of the reactive cell. The dissolved carbonic acid and bicarbonate (alkalinity) present in many natural groundwaters act as buffers limiting pH increase and precipitate formation (Equations 1-7 and 1-8):

$$H_2CO_3^0 + 2\,OH^- \rightarrow CO_3^{2-} + 2\,H_2O \qquad (1\text{-}7)$$

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \qquad (1\text{-}8)$$

Soluble carbonate ions are formed as the OH^- ions are consumed. If carbonate ions continue to build up, however, precipitation of carbonate solid species may occur. Depending on the composition of the groundwater, the precipitates formed could be calcite ($CaCO_3$), siderite ($FeCO_3$), or magnesium hydrocarbonates (Reardon, 1995). If groundwater carbonate is exhausted through the precipitation of carbonate minerals, the water may become saturated with respect to $Fe(OH)_2$ and $Fe(OH)_3$ as the iron continues to oxidize. $Fe(OH)_2$ is relatively insoluble and $Fe(OH)_3$ is extremely insoluble; therefore, both compounds may precipitate if the iron concentration exceeds saturation levels.

In summary, most groundwaters contain many different aqueous species that may play some role in affecting the performance of a PRB. In general, the course of chemical reactions taking place in multi-component systems cannot be predicted by considering each species individually, because most of these reactions are interdependent. To some extent, equilibrium behavior in complex systems can be predicted using geochemical modeling codes, which are described in Sections 6.0 and 8.0. However, many groundwater reactions in PRB systems may not reach equilibrium during the passage of groundwater through the reactive cell. Also, even if the type and mass of reaction products could be predicted, it is unclear how many of these products are actually retained in the reactive cell and how the products affect performance. For example, very fine precipitates that may be formed could be carried out of the reactive cell by colloidal transport with the groundwater flow. It also is unclear whether the precipitates retained in the reactive cell occupy the same reactive sites as those targeted by the contaminants (i.e., CVOCs). However, the reaction chemistry discussed above and the geochemical modeling codes described in Sections 6.0 and 8.0 do provide some basis for selecting appropriate reactive media and assessing the longevity of the media in the groundwater environment at a given site.

1.5 Potential Biologically Mediated Reactions In The Reactive Cell

Microbial growth in the reactive cell can help or hinder the degradation or removal of some types of contaminants. Some reactive media, such as iron, appear to degrade CVOC contaminants primarily through abiotic processes. Similar TCE degradation rates were observed with and without added biocide in column tests with granular iron (Gillham and O'Hannesin, 1994). However, there are indications that microbes could potentially populate the reactive cell and/or the downgradient aquifer under certain conditions.

In one laboratory study (Chiu and Cha, 2000), researchers found that lactate, iron, or hydrogen were able to serve as electron donors in order to sustain a microbial culture from a TCE-contaminated site. These researchers suggest that the microbes used the hydrogen generated during anaerobic iron corrosion for energy and for TCE dechlorination. In this case, microbial activity may be beneficial because it prevents the buildup of hydrogen in an iron reactive cell. However, microbes could potentially enter a field reactive cell through groundwater transport and then populate the reactive medium; if the growth of microbes is excessive, it could lead to biofouling of the reactive cell in the long term.

Microbes can potentially cause biofouling of iron reactive cells over the long term in several ways. For example, three different mechanisms have been identified by which microorganisms can promote Fe(III) precipitation from the groundwater (Tuhela et al., 1993). The first and most common mechanism for bacteria to produce Fe(III) is by directly using Fe(II) as an energy source. These bacteria include *Thiobacillus* ferrooxidans and *Leptospirillum* ferrooxidans. However, these bacteria are acidophiles, and although they may be present in acidic soils, they probably would not be expected to proliferate in alkaline environments produced by zero-valent iron. The second mechanism is one that relies on a process available to stalked and sheathed bacteria, which is to oxidize Fe(II) on sheath surfaces. *Gallionella* and *Leptothrix* spp. are two such bacteria that appear to be involved in Fe(II) oxidation (Tuhela et al., 1993), and sulfide- and thiosulfate-dependent forms also have been reported (Lütters-Czekalla, 1990). Extensive biofouling by stalked and sheathed bacteria has been detected in water wells (Tuhela et al., 1993) and accumulation of stalked iron bacteria in sand filters used for iron removal also have been reported (Czekalla et al., 1985). By this mechanism, growth of stalked and sheathed bacteria potentially can occur in the reactive cell iron or in the downgradient aquifer. The third mechanism involves heterotrophic bacteria that use carbon in organo-ferric complexes. Biodegradation of organo-ferric complexes would liberate Fe(III), resulting in rapid precipitation of ferric hydroxide. However, this third mechanism may not be a primary source of ferric hydroxide precipitation in DNAPL-contaminated groundwaters, unless a strong Fe(III) chelant is also present.

A concomitant occurrence is the oxidation of ferrous iron or Mn(II) by microbially mediated reactions and the subsequent precipitation of ferric or Mn(IV) hydroxides. Iron-related biofouling has been attributed to various types of clogging problems in groundwater treatment systems (Chapelle, 1993), and there has been speculation that such problems may be encountered in the reactive cell of a PRB or in the downgradient aquifer. Ferric hydroxides can precipitate as amorphous $Fe(OH)_3$, or they may develop a crystalline structure such as ferrihydrite ($5\ Fe_2O_3 \bullet 9\ H_2O$). Ferrihydrite has been identified as the solid phase in biofouled water wells (Carlson and Schwertmann, 1987; Tuhela et al., 1992). In general, ferric hydroxides have very low solubilities at neutral and alkaline pH; hence, oxidation of Fe(II) is accompanied by nearly complete removal of iron from the aqueous solution by precipitation.

Despite these possibilities, groundwater and iron/soil core samples collected from reactive cells and from downgradient aquifers at PRB sites show no signs of any significant PRB-induced microbial growth, after two to five years of operation at sites such as the former Naval Air Station (NAS) Moffett Field, Dover AFB, and the Intersil site in Sunnyvale, CA (Battelle, 1998; Battelle, 2000; EnviroMetal Technologies, Inc. [ETI], 1999). More research is needed on the potential role of microbial interactions in primarily abiotic media, such as iron. Interestingly, some reactive media may actually be selected for the beneficial role that microbial processes play in contaminant degradation/removal (see Section 4.1.4.5).

2.0 The Design Methodology

The overall methodology for the application of a PRB at a given site is shown in Figure 2-1. PRB design involves the following steps:

- Preliminary assessment
- Site characterization
- Reactive media selection
- Treatability testing
- Modeling and engineering design
- Selection of a suitable construction method
- Monitoring plan preparation
- Economic evaluation.

The preliminary assessment is conducted to evaluate the technical and economic suitability of a given site for PRB application. Once a site is determined to be suitable, additional design steps are initiated.

2.1 Preliminary Assessment

Typically, the first assessment that site managers must make is whether or not the site is suitable for a PRB application (see Figure 2-2).

2.1.1 Preliminary Technical Assessment

The factors that need to be considered to determine the suitability of a site for PRB application are listed below. Although an unfavorable response to any of the following factors does not necessarily rule out the use of a PRB, it can make the application more difficult or costly:

- **Contaminant Type.** Are the contaminants of a type reported in scientific and technical literature as amenable to degradation by suitable (i.e., commercially available, relatively inexpensive, and benign to the environment) reactive media? Table 2-1 lists the contaminants that are currently reported as either amenable or recalcitrant to abiotic degradation with iron. An economically feasible half-life is necessary to support the application. As alternative media or enhancements are discovered, more contaminants may come within the scope of this technology.

- **Plume Size and Distribution.** Is the plume very wide or very deep? Very wide or very deep plumes will increase the cost of the application. However, at least two sites currently have installed PRBs that are more than 1,000 ft wide (see Section 10.0). Depth of the plume or depth of the aquitard may be a more significant cost consideration.

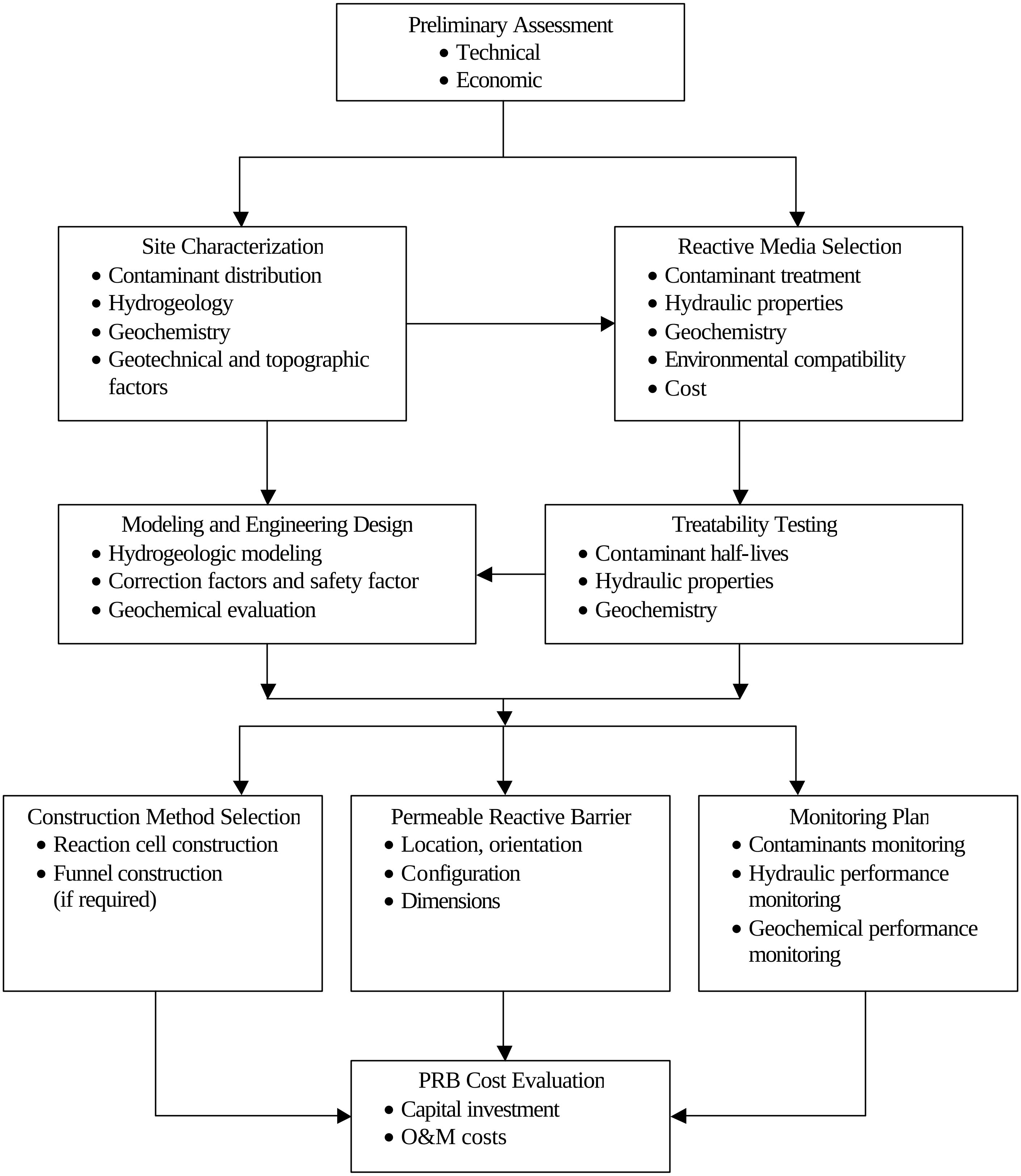


Figure 2-1. Design Methodology for a PRB Application

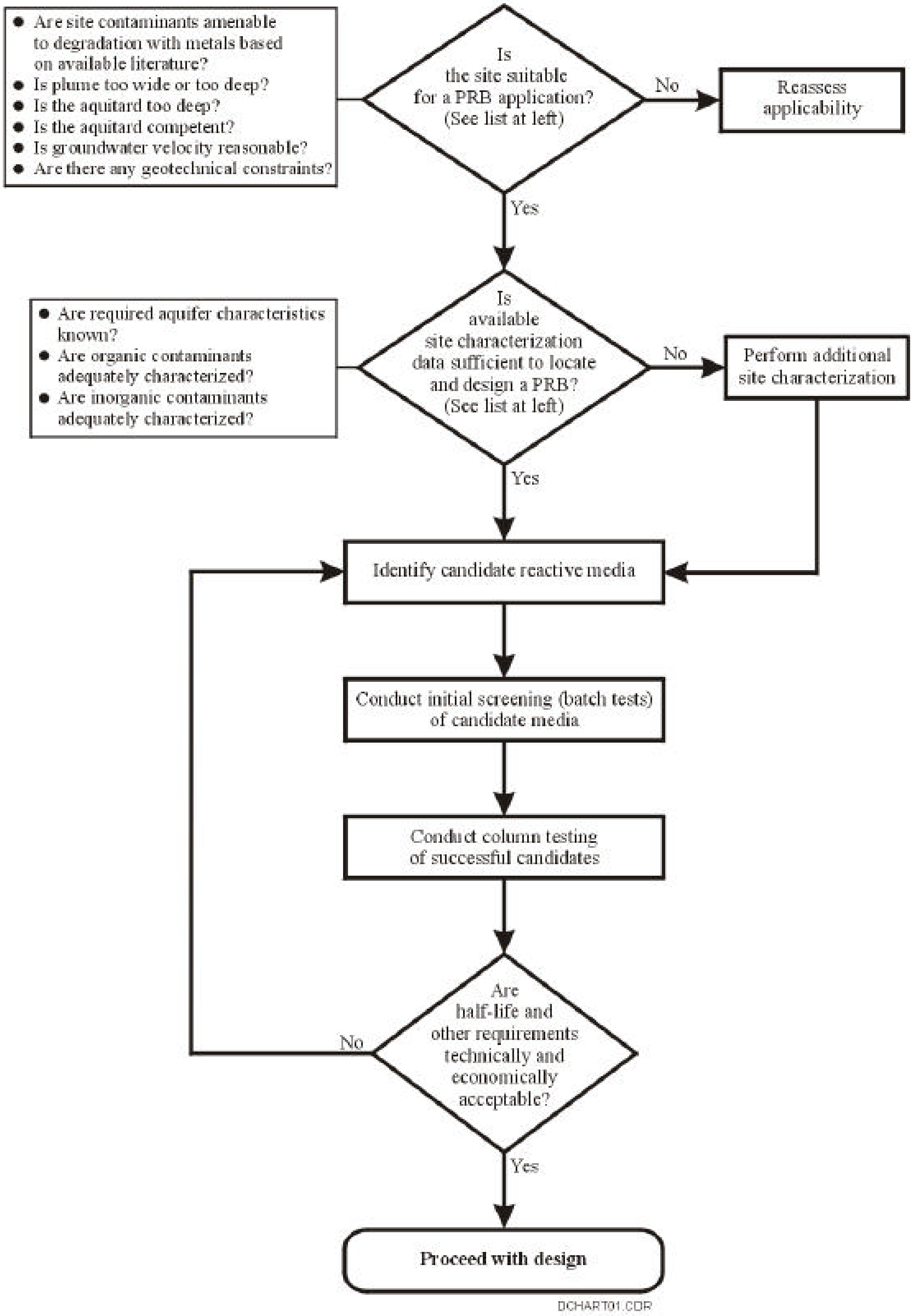


Figure 2-2. Preliminary Assessment of the Suitability of a Site for PRB Application

Table 2-1. Compounds Tested and Half-Lives Normalized to 1 m^2 Iron Surface per mL Solution (Adapted from Gillham, 1996 and other sources listed in the footnotes)

Organic Compounds	Pure Iron(m) $t_{1/2}$ (hr)	Commercial Iron(m) $t_{1/2}$ (hr)
Methanes		
Carbon tetrachloride	0.02(a), 0.003(g), 0.023(i)	0.31-0.85(b)
Chloroform	1.49(a), 0.73(g)	4.8(b)
Bromoform	0.041(a)	
Ethanes		
Hexachloroethane	0.013(a)	NA
1,1,2,2-Tetrachloroethane	0.053(a)	NA
1,1,1,2-Tetrachloroethane	0.049(a)	NA
1,1,1-Trichloroethane	0.065(a), 1.4(h)	1.7-4.1(b)
1,1-Dichloroethane	NA	NA
Ethenes		
Tetrachloroethene	0.28(a), 5.2(h)	2.1-10.8(b),3.2(e)
Trichloroethene	0.67(a), 7.3-9.7(g), 0.68(j)	1.1-4.6(b), 2.4(e), 2.8(f)
1,1-Dichloroethene	5.5(a), 2.8(h)	37.4(e), 15.2(f)
trans-1,2-Dichloroethene	6.4(a)	4.9(b), 6.9(e), 7.6(f)
cis-1,2-Dichloroethene	19.7(a)	10.8-33.9(b), 47.6(e)
Vinyl chloride	12.6(a)	10.8-12.3(b), 4.7(e)
Other Organics		
1,1,2-Trichlorotrifluoroethane (Freon 113)	1.02(b)	NA
1,2,3-Trichloropropane	NA	24.0(c)
1,2-Dichloropropane	NA	4.5(c)
1,3-Dichloropropane	NA	2.2(c)
1,2-Dibromo-3-chloropropane	NA	0.72(b)
1,2-Dibromoethane	NA	1.5-6.5(b)
n-Nitrosodimethylamine (NDMA)	1.83(b)	NA
Nitrobenzene	0.008(d)	NA
Inorganics		
Chromium(k)(l), nickel(l)	NA	NA
Uranium(l)	NA	NA
Nitrate (l)	NA	NA
No Apparent Degradation		
Dichloromethane(a)(g)(h)	NA	NA
1,4-Dichlorobenzene(h)	NA	NA
1,2-Dichloroethane(b)	NA	NA
Chloromethane(b)	NA	NA

(a) Gillham and O'Hannesin (1994)
(b) ETI (1997)
(c) Focht (1994)
(d) Agrawal and Tratnyek (1994)
(e) Sivavec and Horney (1995)
(f) Mackenzie et al. (1995)
(g) Matheson and Tratnyek (1994)
(h) Schreier and Reinhard (1994)
NA = Not available.

(i) Lipczynska-Kochany et al. (1994)
(j) Orth and Gillham (1995)
(k) Blowes et al. (1997)
(l) WSRC (1999)
(m) The half-lives reported in this table are for illustration purposes only. Contaminant half-lives may vary depending on the iron source and site-specific groundwater chemistry.

- **Aquifer Depth.** Is the aquifer very deep? If the aquitard is very deep and the barrier must be keyed into it, the construction costs could be high. For many chlorinated solvent applications, the PRB may have to be keyed in because of the potential for underflow of contaminants. If a hanging barrier configuration is used (that is, the PRB does not extend all the way down to the aquitard) for shallow plumes, detailed site characterization and hydrologic modeling will have to be conducted in order to demonstrate to stakeholders that plume underflow will not occur. Currently, PRBs can be installed to depths of 25 to 30 ft using relatively inexpensive excavation equipment, such as a standard backhoe. At greater depths, relatively more expensive commercial methods may have to be deployed, such as clamshell or caisson excavation. Some innovative construction techniques, such as jetting, have been tested at some sites to overcome depth and cost constraints (see Section 7.0). Individual construction contractors generally can provide site managers with guidance on whether the particular construction technique that they offer is feasible for the specific site characteristics involved.

- **Geotechnical Considerations.** Are there any geologic features at the site that may make installation more difficult? The presence of consolidated sediments or large gravel or rocks may make some types of construction more difficult. Caissons, for instance, may bend or get caught in such formations. Aboveground structures, such as buildings, that are in the vicinity of the installation may impede the maneuverability of construction equipment.

- **Competent Aquitard.** Is the aquitard very thin or discontinuous? If so, keying the PRB into the aquitard could be difficult. If there is a possibility that the aquitard could be breached during construction of the PRB, thus causing contamination to migrate into the lower aquifer zone, then the application should be reassessed.

- **Groundwater Velocity.** Is the groundwater velocity too high? If the velocity is high, the reactive cell thickness required to obtain the desired design residence time may also be high and the barrier could become costly. However, PRBs have been installed at sites with groundwater velocities as high as 3 ft/day. A site with very slow-moving or stationary groundwater may also not be particularly suitable because of the dependence of the PRB on achieving passive contact with the groundwater (plume) flow.

2.1.2 Preliminary Economic Assessment

Instead of going through the entire design process and then performing a detailed cost evaluation for the PRB application, it may be desirable to prepare a rough cost estimate during the preliminary assessment stage itself. The preliminary cost evaluation includes a rough cost estimate for a PRB and other competing remediation option(s), such as a P&T system or air sparging, for a given site. Section 9.0 contains the methodology for preparing and comparing the cost estimates for a PRB and a P&T system for plume control/treatment. Appendix B contains an example of a cost evaluation conducted for a PRB site.

A rough estimate can be obtained for most capital investment and operating and maintenance (O&M) cost components for comparison between PRB and a competing technology without preparing a detailed PRB design. The only two exceptions are the reactive medium and PRB construction costs; these two elements require some guesses as to the dimensions and construction method that will be used. However, if the preliminary economic assessment is viewed as an extension of the technical feasibility determination for the PRB application, it may be possible to arrive at a reasonably good cost estimate during preliminary discussions with reactive medium suppliers and construction contractors. Multiple design and construction scenarios may have to be prepared in order to obtain a cost range for the two technologies. As seen in Appendix B, although preconstruction costs constitute a significant portion of the total costs of a PRB, these costs tend to be fairly similar no matter what technology is used. The same is the case with post-construction monitoring costs, which tend to be approximately the same for most technologies. Therefore, preconstruction and monitoring costs could be ignored at the preliminary assessment stage and the focus should be on cost estimates for the reactive medium, construction, and O&M costs of the competing technologies. Significant differences are likely to show up between the O&M costs of active and passive technologies.

Although there may still be some uncertainty in the costs developed at this stage, a preliminary cost assessment performed at this stage would make site managers aware of the cost ramifications of various design scenarios pursued later during detailed design. If nothing else, a qualitative evaluation of the factors listed in Section 2.1.1 from a cost perspective will give site managers some idea about whether any of these factors are likely to make the costs of a PRB application relatively high or relatively low.

Section 10.0 summarizes the reactive medium and construction costs encountered at various PRB sites and could be used to obtain some idea of the costs involved. Note that most of the site-specific cost estimates mentioned in Section 10.0 do not include preconstruction costs (costs for site characterization, modeling and engineering design, and procurement process) or post-construction (i.e., O&M) costs.

2.2 Site Characterization

If a preliminary assessment shows that the site is suitable, the next issue is whether or not the available site characterization data are sufficient to locate and design the PRB. If the site information is inadequate for the purpose, additional site characterization may be required. Section 3.0, Site Characterization, describes the site information that is required and discusses the tools available to collect this information. The important site information required includes the following:

- **Aquifer Characteristics.** The aquifer characteristics that should be known include groundwater depth, depth to aquitard, aquitard thickness and continuity, groundwater velocity, lateral and vertical gradients, site stratigraphy/heterogeneities, hydraulic conductivities of the different layers, porosity, and dimensions and distribution of the plume. This information is required to assist in hydrogeologic modeling performed to locate and design the barrier.

- **Organic Composition of the Groundwater.** The types of chlorinated solvent compounds and the concentrations should be known. This information will be used to select appropriate reactive media, conduct treatability tests, and design the thickness of the wall.

- **Inorganic Composition of the Groundwater.** This information is required to evaluate the long-term performance of the PRB and select appropriate reactive media. Knowledge of the presence and concentrations of calcium, magnesium, iron, alkalinity (bicarbonate), chloride, nitrate, and sulfate can be used to evaluate the potential for precipitate formation that may affect the reactivity and hydraulic performance of the PRB. Field parameters such as pH, ORP, and DO also are good indicators of conditions conducive to formation of precipitates.

- **Geotechnical and Topographic Considerations.** Underground (e.g., utility lines or rocks) and aboveground (e.g., buildings or utility lines) structures that could impede the construction of the barrier need to be identified and evaluated.

2.3 Reactive Media Selection

Once the required site characterization data have been obtained, the next step is to identify and screen candidate reactive media. Section 4.0, Reactive Media Selection, discusses the various media available and the factors affecting their selection. The main considerations in identifying initial candidates are as follows:

- **Reactivity.** The candidate medium should be able to degrade the target contaminants within an acceptable residence time. Generally, the shorter the half-life of the contaminant with a given media, or higher the reaction rate constant, the better the media. Table 2-1 shows the ranges of half-lives of several contaminants that are degraded by iron. Any alternative medium selected should have comparable or better reactivity, unless other factors (such as the following five factors) dictate a trade-off.

- **Hydraulic Performance.** Selection of the particle size of the reactive medium should take into account the trade-off between reactivity and hydraulic conductivity. Generally, higher reactivity requires lower particle size (higher total surface area), whereas higher hydraulic conductivity requires larger particle size.

- **Stability.** The candidate medium should be able to retain its reactivity and hydraulic conductivity over time. This consideration is governed by the potential for precipitate formation and depends on how well the candidate medium is able to address the inorganic components of the site groundwater. One important characteristic of the groundwater that limits precipitate formation is alkalinity, which acts as a buffer. If natural buffers are absent from the groundwater, a reactive medium that provides the required buffering capacity could be incorporated.

- **Environmentally Compatible Byproducts.** The byproducts generated during degradation should not have deleterious effects of their own on the environment. For example, during degradation of TCE by iron, small amounts of potentially toxic byproducts (such as vinyl chloride) may be generated (see Section 1.0). However, given sufficient residence time for groundwater flow through the reactive cell, these byproducts are themselves degraded to potentially nontoxic compounds. Any alternative reactive medium selected should demonstrate similar environmental compatibility.

- ☐ **Construction Method.** Some innovative construction techniques, such as jetting, may require a finer particle size of the reactive medium.
- ☐ **Availability and Price.** The candidate medium should be easily available in large quantities at a reasonable price, although special site considerations may sometimes justify a higher price.

2.4 Treatability Testing

Section 5.0 describes the treatability tests that can be conducted to determine some of the design parameters for a PRB. Following identification of candidate reactive media, batch tests could be performed to quickly screen several candidate media. If only one or two candidates have been identified, screening by batch testing could be forgone in favor of column tests. Column tests are more representative of dynamic field conditions than batch tests and provide more accurate design information. Column tests are conducted to select the final reactive medium and determine half-lives and residence times. It is recommended that column tests be performed with groundwater obtained from the site to generate representative design data.

2.5 Modeling and Engineering Design

Once data is obtained from site characterization and laboratory testing, it can be used for conducting modeling of different hydrogeologic and geochemical scenarios and engineering designs to determine the location, orientation, configuration, and dimensions of the PRB. Section 6.0 describes the modeling and engineering design process involved. An iterative process is required to some extent between modeling/design and choice of construction method. For example, if caissons are used for installing the reactive medium in the ground, a funnel-and-gate type configuration may be designed to provide the required plume capture width. If backhoe excavation is used, a continuous reactive barrier configuration may be more suitable. Different PRB configurations will generate different flow velocities and therefore different reactive cell thickness requirements.

Hydrologic modeling (see Section 6.1) is an important tool that can be used to define many aspects of the design. Several hydrogeologic models are available for modeling a PRB flow and transport system. Appendix C describes the various flow and particle transport models available and their main features. Widely available and validated models such as MODFLOW and its enhancements are generally sufficient to achieve PRB design objectives. Hydrogeologic modeling, along with site characterization data, is used for the following purposes:

- ☐ **Location of Barrier.** Determine a suitable location for the PRB with respect to the plume distribution, site hydrogeology, and site-specific features, such as property boundaries and underground utilities.

- **PRB Orientation.** Design the best PRB orientation that will capture the maximum flow with the minimum reactive cell width, given the seasonal variations in flow direction.

- **Barrier Configuration.** Determine a suitable PRB configuration (e.g., continuous reactive barrier or funnel-and-gate system).

- **Barrier Dimensions.** Modeling can be used with the site characterization and laboratory testing data to determine a suitable width and thickness of the reactive cell and, for a funnel-and-gate configuration, the width of the funnel.

- **Hydraulic Capture Zone.** Estimate hydraulic the capture zone for a given PRB design.

- **Design Trade-Offs.** Identify a balance between hydraulic capture zone and flow-through thickness of the reactive cell (gate), which are interdependent parameters.

- **Media Selection.** Help in media selection and long-term performance evaluation by specifying required particle size (and hydraulic conductivity) of the reactive medium with respect to the hydraulic conductivity of the aquifer.

- **Longevity Scenarios.** Evaluate future scenarios whereby reduced porosity resulting from precipitate formation could potentially cause flow to bypass the reactive cell. This evaluation gives an indication of the safety factors needed in the design.

- **Monitoring Plan.** Assist in planning appropriate monitoring well locations and monitoring frequencies.

Geochemical evaluation (see Section 6.4) of the site also can commence while treatability tests are in progress, although knowledge of the inorganic composition of the influent and effluent from column tests is helpful to the evaluation. Geochemical evaluation may consist simply of a qualitative assessment of the potential for precipitate formation in the reactive cell based on site characterization and treatability test data. Numerical geochemical codes may or may not be used, depending on site objectives. Most available geochemical models are predictive and based on equilibrium codes, although inverse modeling codes can be used to back-calculate the mass of precipitating and dissolving compounds along a known flowpath.

2.6 Construction Method

Once the location, configuration, and dimensions of the PRB have been designed, the best way to install the barrier in the ground needs to be determined. Section 7.0, Construction Methods, describes the various techniques available for installing the reactive cell and funnel walls (in case the barrier is a funnel-and-gate design). Because the technical feasibility and cost of a construction method depends to a large extent on the depth below ground surface (bgs) that needs to be accessed, the depth of the aquitard is the primary parameter governing selection of the construction method at a given site. Geotechnical considerations, such as presence of rocks or highly consolidated sediments, also may affect the viability of the technique used. Section 7.0 discusses both conventional construction methods (such as backhoe excavation, sheet pile walls, and slurry walls) and innovative methods (such as caissons and jetting).

2.7 Monitoring the Performance of a PRB

Once the construction of the barrier is complete, the barrier will need to be monitored for as long as the plume is present. Section 8.0 discusses PRB monitoring requirements in terms of the locations, frequency, and type of monitoring. Target contaminants (and their byproducts), hydraulic flow characteristics, and geochemistry (PRB longevity indicators) are the main categories of parameters that are monitored. A monitoring plan generally is prepared along with the design report, and both documents play a significant role in obtaining regulatory approval for PRB application.

2.8 PRB Economics

Detailed estimates of the capital investment and O&M costs of a PRB can be prepared once the engineering design is complete. Section 9.0 discusses the methodology for estimating the costs of a PRB and a competing technology, such as P&T. For both PRB and P&T options, the capital investment is incurred immediately, but the O&M costs are spread over several years or decades of operation. To consolidate present and future costs into a total cost in today's dollars, a present value (PV) or discounted cashflow approach is used. In this approach, future costs are reduced to their PV by incorporating the time effects of inflation, productivity, and risk.

One significant unknown in the cost evaluation is the *longevity* of the reactive medium, a term that refers to the time during which the PRB retains the desired reactive and hydraulic performance. Because existing PRBs have been operational only for about five years, and because most geochemical assessment tools (e.g., modeling, inorganic analysis of groundwater, and analysis of field cores of reactive media) have been primarily qualitative rather than quantitative or predictive, it is unclear how long a PRB may be expected to retain its performance. In a PV analysis of costs, it is important to know not only how much the replacement/regeneration of the reactive medium will cost, but also when in the future it will have to be done. In the absence of a longevity prediction, the methodology outlined in Section 9.0 stresses development of multiple longevity scenarios. In other words, multiple PV cost estimates of a PRB application are obtained assuming different longevities. This multiple-estimate process allows site managers to assess their expectations of the longevity of the reactive medium in terms of the minimum longevity required for the PRB application to be more cost-effective than a competing technology.

Any economic benefits of the PRB application may be included in the evaluation as an offset, or reduction, to capital investment or O&M costs. Economic benefits may accrue, for example, from being able to put the property to more productive use (because of the absence of aboveground treatment structures and the need to operate those structures). Intangible benefits of the PRB, such as the long-term risk reduction achieved, also should be considered.

3.0 Site Characterization

In comparison with a P&T system, a PRB is a relatively permanent structure. For a P&T system, locations of pumping wells, pumping rates, and aboveground treatment methods can be changed or modified as understanding of the site grows. However, once installed, a PRB is difficult to relocate and change, so it is important to understand the site as well as possible before installing a PRB. The following aspects of the site are important to know:

- ☐ Hydrogeology of the site
- ☐ Contaminant distribution in the groundwater
- ☐ Geochemical composition of the groundwater
- ☐ Geotechnical and topographic features.

Seasonal variations in such factors as flow and rainfall events could affect some of these site features, so quarterly data collected over a period of one year are desirable. However, at many sites, site managers must work with the data that are available. It may be useful to note that many of the performance problems encountered at PRB sites have been due to hydraulic issues, such as inadequate plume capture or inadequate residence time.

Table 3-1 contains a list of parameters that are generally required to determine the suitability of a site for PRB treatment and to establish treatability testing and computer modeling parameters.

Table 3-1. Suggested Site Characterization Parmaeters for a Prospective PRB Site

Objective	Parameters	Comments
Contaminant Distribution	Target contaminants (e.g., TCE, PCE, DCE, VC, and Cr)	Horizontal and vertical distribution through multi-level or cluster wells for thicker aquifers; horizontal distribution through long-screen wells for thinner aquifers.
Site Hydrogeology	Site stratigraphy Hydraulic gradient Hydraulic conductivity (K) distribution Particle size distribution in aquifer Porosity of aquifer	In the plume, with special emphasis in the vicinity of prospective PRB location; may be conducted in two steps at some sites.
Site Geochemistry	Field parameters (ORP, DO, pH, and conductivity) Cations (e.g., Ca, Mg, Fe, and Mn) Anions (e.g., SO_4, Cl, NO_3/NO_2, and alkalinity) TOC and DOC	Horizontal and vertical distribution through multi-level or cluster wells for thicker aquifers; horizontal distribution through long-screen wells for thinner aquifers.
Geotechnical and Topographic Features	Consolidated sediments Overhead utility lines/other structures Underground utility lines/other structures	Evaluate accessibility of prospective PRB location to construction equipment; evaluate underground features that may cause difficulties for construction.

3.1 Hydrogeology of the Site

The requirements for groundwater flow system characterization include data on geologic and hydrologic parameters. A preliminary characterization of the site geology is necessary to identify formation characteristics that may affect groundwater flow, contaminant movement, and permeable wall design. A search for background geologic information should be completed as part of this characterization. In many cases, some of the needed information is available from previous site characterization studies. Remedial Investigation/Feasibility Study (RI/FS) reports, Record of Decision (ROD) reports, RCRA Facility Investigation (RFI) reports, and/or groundwater modeling reports are good sources of initial information. Sometimes, additional site-specific characterization may be needed to support the feasibility study, site selection, and design of the PRBs. Although the regional geology and groundwater flow regime generally is known on a property-wide scale, local information often must be obtained through additional characterization. (The term "local" implies that the information is required on the scale of the plume and in the immediate vicinity of the proposed barrier location. In fact, relatively smaller plumes generally require greater local detail than is available in most site reports.)

3.1.1 Local Hydrogeology

Any pre-existing geological background and site information should be assembled and a preliminary conceptualization of the subsurface geologic features should be completed. This model should have general information on the site-wide lithology, various aquifer layers and confining units, contaminant plume configuration, and factors such as precipitation. A conceptualization of the lithologic variations also should be developed. These variations have a significant impact on aquifer heterogeneity, which may be the most important control on the groundwater flow system and placement of the PRB. This preliminary assessment should be used as a basis for further delineation of the local geology for PRB installation.

At the local scale, the most significant data to be collected include variations in the depth, thickness, lithology, and water levels of different hydrogeologic units. Data collection is achieved by drilling and sampling several locations by conventional drilling or newer characterization techniques, such as cone penetrometer testing (CPT) or Geoprobe® sampling. The number and locations of boreholes and samples required for the site heterogeneity assessment should be based on the scientific judgment of the on-site hydrogeologist and on the availability of pre-existing data. At relatively homogeneous sites, only a few boreholes are needed to characterize the site adequately. However, at sites with heterogeneous sediments or channeling, a large number of boreholes are needed before a reliable picture of the subsurface features can be developed. Most of the information for geologic characterization can be collected from soil borings and observation of core samples. The physical properties of the sediments can be determined using borehole logging techniques. CPT rigs have been particularly useful for this. In addition, the CPT or Geoprobe® borings also can be used for collecting one-time groundwater samples from specific depth intervals. Some or all of the boreholes may be converted to permanent groundwater monitoring wells for periodic and/or continuous water-level measurements and groundwater sampling. Additionally, these wells also can be used for determination of hydraulic conductivity (K) and porosity (n) by pumping or slug tests. Some of the monitoring wells should be installed as clusters which are screened at different depths to evaluate vertical hydraulic gradients.

Some intact formation samples (e.g., cores, split-spoons, and/or thin-walled tubes) should be collected to provide a field description of the geological conditions and to identify or estimate hydrogeologic properties of the aquifer. Formation samples can be analyzed to measure physical properties (e.g., grain size, mineralogy, lithology, and texture) and hydrogeologic properties (e.g., porosity and permeability). Samples should be described and logged in the field and, if appropriate, submitted to a laboratory for analysis. Laboratory analysis of porosity can be used in the development of design requirements for the PRBs because the determinations of residence times, flow velocity, and discharge are based on these hydrogeologic properties. Other laboratory analyses can be completed to evaluate concentrations of adsorbed contaminants and to evaluate geochemical properties, such as organic carbon content of the aquifer material.

Once all of the field and laboratory data have been obtained, site-specific geologic cross sections should be prepared to evaluate the lithologic variations at the site. In addition, water-level measurements from shallow and deep hydrostratigraphic units (HSUs) should be plotted on the cross section to evaluate the vertical hydraulic gradients across the adjacent aquifers. An example of a detailed hydrogeologic cross section for PRB site characterization at Dover AFB is shown in Figure 3-1. This cross section shows the correlation for soil lithology based on CPT logging of soil properties, on water-level measurements, on depths to aquitard, and on concentrations of key contaminants in the boreholes. Several such cross sections were developed (Battelle, 1997b) for the site as part of the PRB design. Similarly, at former NAS Moffett Field, geologic data from several boreholes and numerous CPTs were used (Battelle, 1998) to delineate the location of the sand channel at the site (see Section 6.1.3). The local-scale lithologic cross sections at this site were also correlated with the Base-wide maps of subsurface sand channel deposits that act as preferential pathways for most of the groundwater flow and contaminant transport. The pilot-scale PRB was placed across one of these channels, and the funnel walls were placed across the finer-grained interchannel deposits.

3.1.2 Determination of Groundwater Velocity and Direction

Hydrologic or groundwater flow parameters are important in PRB design because these parameters determine the groundwater capture zone, and the location, orientation, configuration, and dimensions of the PRB. The objectives of taking hydrologic measurements are to estimate the groundwater flow velocity and direction in the prospective PRB location. These objectives can be achieved through measurement of aquifer properties and the use of Darcy's Law, through tracer testing, or through direct measurement with appropriate probes. Most available probes are in various stages of development and evaluation; therefore, at most sites, the most reliable method of estimating groundwater velocity and direction involves using water-level measurements along with Darcy's Law.

3.1.2.1 Groundwater Flow Direction

Groundwater flow directions are determined using a water-table or potentiometric surface map based on water-level measurements made at the site. Groundwater flow is perpendicular to the equipotential lines expressed on a map as contours of water-table or potentiometric surface elevation. For simple flow fields, groundwater flow directions may be determined using a three-point problem approach. At most sites, however, sufficient measurements should be taken to delineate localized variations in the flow field using contour maps. Maps should be constructed for several different measurement events to determine the range of seasonal hydraulic variations

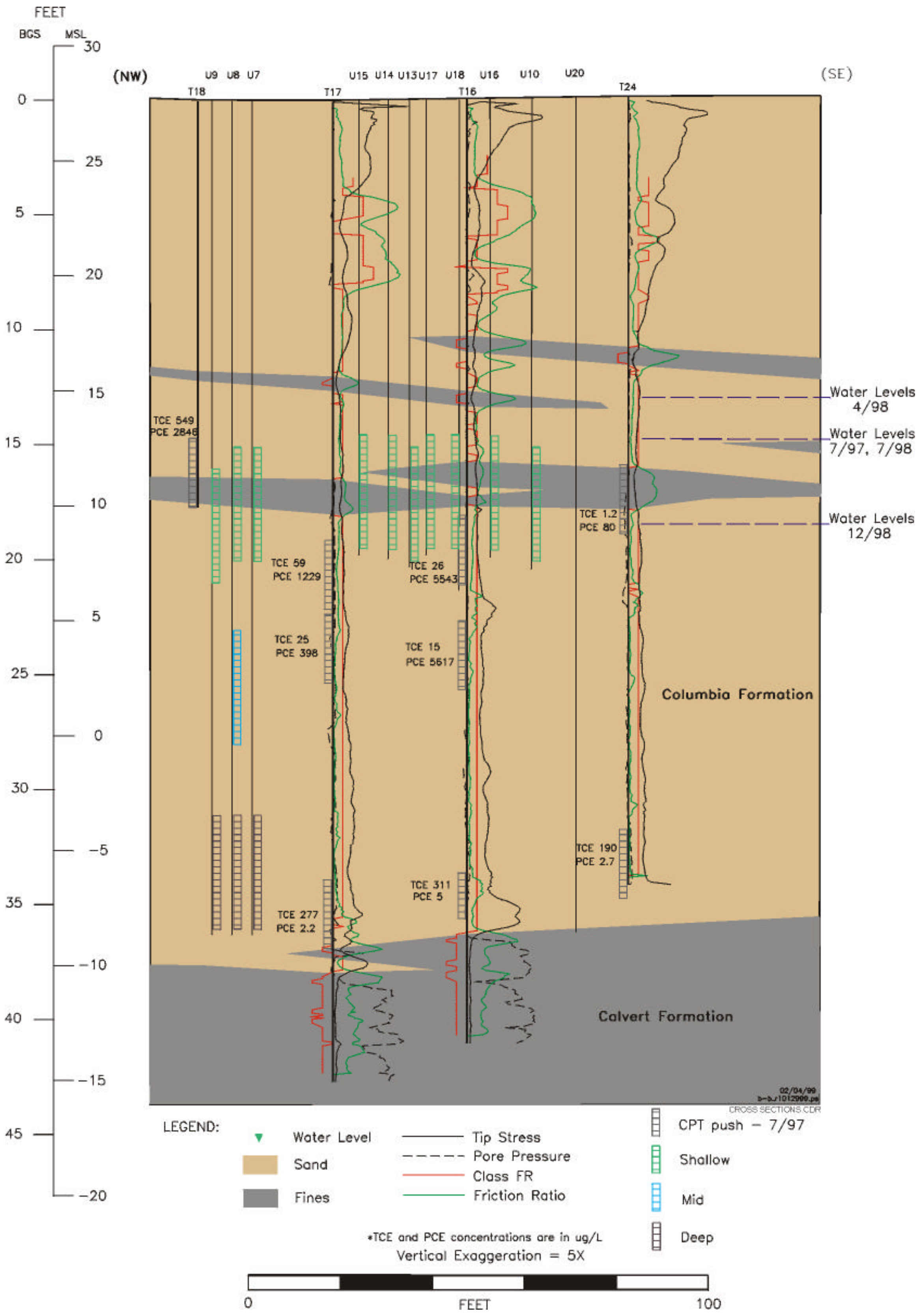


Figure 3-1. Hydrogeologic Cross Section based on CPT Site Characterization

at the site. The final design of the PRB should incorporate the effect of maximum variation in flow directions to avoid future situations where the plume may bypass the barrier.

3.1.2.2 Groundwater Velocity Estimate Using Darcy's Law

The use of the Darcy's Law equation is the most common approach for determining groundwater velocity in the aquifers. This approach requires measurement of hydraulic conductivity (K), effective porosity (n_e), and hydraulic gradient (dh/dl) distribution in the local vicinity of the proposed PRB. The average linear groundwater flow velocity can be calculated by the following equation:

$$V_x = \frac{K(dh/dl)}{n_e} \tag{3-1}$$

where V_x = the average linear groundwater flow velocity
K = the K of the aquifer material (L/t)
dh/dl = the hydraulic gradient
n_e = the effective porosity.

The parameters needed for hydraulic evaluation are discussed further in the following subsections.

3.1.2.2.1 Hydraulic Conductivity. K is the measure of an aquifer's ability to transmit water and is expressed as the rate at which water can move through a unit thickness permeable medium. K is perhaps the most critical aquifer parameter for the design of PRBs, because K can vary by an order of magnitude or more, even in relatively "homogeneous" sites (e.g., the Dover AFB site). The velocity of groundwater movement and dissolved contaminant migration is directly related to the K of the saturated zone. In addition, subsurface variations in K directly influence contaminant fate and transport by providing preferential pathways for contaminant migration. Estimates of K are used to determine flow velocities and travel times for contaminants and groundwater. At relatively more heterogeneous sites, most of the groundwater flow and contaminant transport in the aquifers may be restricted to high K zones (e.g., the former NAS Moffett Field site). It is important to delineate these preferential pathways by a combination of geologic and hydrologic characterizations so that the permeable barriers can be located across these zones. Ultimately, an accurate estimate of K (or K distribution) at the site will reduce the uncertainties in the velocity estimate and required flowthrough thickness for the PRB. At sites with significant vertical heterogeneities or anisotropy, it would be useful to estimate vertical K. These data can be important in estimating the potential for overflow, underflow, and cross-formational flow.

The most common methods used to quantify K are single- and multiple-well pumping tests and slug tests. Horizontal and vertical K also can be determined from laboratory testing of sediment cores. Pumping tests involve the pumping of a test well and measurement of drawdown in the surrounding wells. Greater details on these tests can be found in Domenico and Schwartz (1990), Fetter (1994), and Kruseman and de Ridder (1991). Pumping tests generally give the most reliable information on K, but they may be difficult to conduct in contaminated areas because the water produced during the test generally must be contained and treated. One of the disadvantages of pumping tests is that they are relatively expensive and time consuming to conduct, and may cause temporary displacement of the plume if conducted in the contaminated region of interest. Therefore, at highly heterogeneous sites, it generally is impractical to conduct a sufficient number of tests to estimate the K variations in all the hydrostratigraphic units of interest.

Slug withdrawal or injection tests are the most commonly used alternative to pumping tests. A slug test consists of the insertion or removal of a “slug” or known volume of water, or the displacement of water by a solid object. The displaced water causes a stress on the aquifer that is monitored through the change and recovery of hydraulic head or water level. One commonly cited limitation to slug testing is that the method generally gives K information only for the area immediately surrounding the test well. Slug tests do, however, have two distinct advantages over pumping tests: they can be conducted in small-diameter wells, and they do not produce contaminated water that may require treatment and/or disposal. If slug tests are used as part of a site characterization effort to determine the K distribution in an aquifer, it is important that multiple slug tests be performed. The tests should be performed with replicates and in as many wells as feasible. Another big advantage of slug tests over pumping tests is that a large number of tests can be conducted in the amount of time and cost it takes for one pumping test. Therefore, slug tests can be used to estimate the spatial variations in K at heterogeneous sites. A description of the theory and application of slug testing is provided in Fetter (1994), and a complete description of the analysis of slug test data is provided in Kruseman and de Ridder (1991).

K also can be determined from laboratory testing of the soil cores collected in the field. However, this method may not generate representative results because the samples are invariably disturbed during collection, which may impact the accuracy of the tests. CPT pressure dissipation tests also have been used for K determination. For the PRB at Dover AFB, this method resulted in reasonable estimates of K for the lower-K clayey zones. However, for the high-K sandy zones, the pressure dissipation was too fast and the results were not reliable (Battelle, 2000).

3.1.2.2.2 Porosity. The porosity (n) of an aquifer material is the percentage of the rock or soil/sediment that consists of void space. The porosity of a sample of aquifer material is normally determined in the laboratory by submerging a dried sample in a known volume of water until it is saturated. The volume of voids is equal to the original water volume less the volume in the chamber after the saturated sample is removed. This method excludes very small and non-interconnected pores, thus providing the effective porosity of the sample. Table 3-2 lists general ranges of porosity that can be expected for typical sediments. For the purpose of PRB design, the range of porosity for all sediment types at the proposed site should be determined by collecting soil samples from the aquifer and the underlying confining layers.

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).

3.1.2.2.3 Hydraulic Gradient. The hydraulic gradient is the change in hydraulic head (dh) over a unit distance (dl) along the direction of the steepest head decline. Like groundwater flow direction (see Section 3.1.2.1), the hydraulic gradient is determined using a water-table or potentiometric surface map constructed using water-level measurements taken at the site during a specific time. It is generally important to estimate values of both the lateral and vertical hydraulic gradients at the site. The vertical gradients are useful in evaluating potential for underflow or overflow and flow between adjacent aquifers. The vertical hydraulic gradients may be determined by comparing water levels in multiple well clusters with individual points screened at different vertical depths. It is critical to take water-level measurements at several times during the year and over several years so seasonal and long-term variations in groundwater flow velocity and direction can be evaluated. These variations should be incorporated into the safety factor for PRB design to prevent future bypass of the system by the plume or insufficient residence times.

3.1.2.3 In Situ Groundwater Velocity Sensors

Recently, the in situ groundwater velocity sensors developed at Sandia National Laboratory (Ballard, 1996) have been used at several PRB sites, including former NAS Alameda, Dover AFB, and former Lowry AFB, for evaluation of groundwater velocity and flow direction mainly during the performance assessment phase. The sensors and associated data acquisition system are marketed by HydroTechnics, Inc., of Albuquerque, NM. The sensors have been deployed both in the PRB media and in the surrounding aquifers. So far these sensors have not been used for site characterization during the PRB design phase; however, their use can provide valuable information on the local-scale and seasonal variations in groundwater velocity. If used for site characterization purposes, several sensors should be installed across the investigation area. This may include installation in different lithologic zones, in recharge and discharge zones, or at different depths in the aquifer.

The HydroTechnics sensor uses a thermal perturbation technique to directly measure the three-dimensional (3-D) groundwater flow velocity vector in unconsolidated, saturated, porous media. The technology allows for long-term and continuous monitoring of the groundwater flow regime in the immediate vicinity of the probe. The instrument consists of a cylindrical heater 30 inches long and 2.37 inches in diameter which has an array of 30 calibrated temperature sensors on its surface. The velocity sensor is installed directly in contact with the aquifer media at the depth of interest. Only a data transmission wire connects the sensor to the surface. A heater activated with 70 W of continuous power supply heats the sediments and groundwater surrounding the sensor to about 20 to 30°C above background. The temperature distribution at the surface to the sensor is affected by the groundwater movement resulting from advective flow of heated groundwater. The measured temperature distribution is converted into flow velocity (3-D magnitude and direction) by a computer program.

The manufacturer's specifications indicate that Darcy velocity range of 0.01 to 1.0 ft/d can be measured with the probe with a resolution of 0.001 ft/d and an accuracy of 0.01 ft/d. The life span of the sensor is 1 to 2 years and it can be installed up to a depth of 400 ft. The data can be retrieved remotely with a telephone and modem connection.

3.1.2.4 Downhole Velocity Measurement Probe

A possible alternative to the HydroTechnics velocity sensor is the Geoflo Groundwater Flowmeter System manufactured by KVA Analytical Systems, Inc. This probe can be used in

2-inch-diameter monitoring wells for direct downhole measurement of groundwater velocity and direction. The system is a portable self-contained instrument consisting of a 2-inch-diameter flowmeter probe and associated packer assembly attached to 80 ft of electronic cable, aluminum suspension rods, and a control unit with battery packs. The submersible probe consists of a central heating element surrounded by four pairs of opposed thermistors. The heating element and thermistors are contained within a packer assembly that is filled with 2-mm-diameter glass beads. The measurement of groundwater velocity and direction by the flowmeter is based on initiating a short-term heat pulse at the center of the probe. The distribution of the resulting heat in the glass beads is measured by the thermistors, and the relative difference between opposed thermistors is displayed. The values read from the display are resolved into the rate and direction of flow in the well through (1) a process of vector resolution, and (2) computation with a flow velocity calibration equation. The quality of the tests can be evaluated by use of a cosine test as described in the user's manual.

Proper calibration of the flowmeter instrument is required to ensure accurate results. Factors potentially affecting the instrument response include aquifer matrix type, well screen type and orientation, type and amount of the fill in the annular space of the well, adherence of uniform and horizontal groundwater flow through the well screen, and operator techniques. The calibration is based on measuring the instrument response in a laboratory tank with flow velocity, probe screen, and glass beads similar to that expected at the site. The flow velocity calculated for several flowrates in the tank is plotted against the instrument reading, and the slope of the resulting calibration curve is used to calculate field velocity in the wells. Thus a site-specific calibration equation is obtained for each site. The stated range of velocity for KVA probe use is 0.02 to 100 ft/day. However, at low end of this range, the results may not be very good for the screen types and monitoring well construction at many contaminated sites. An illustration of KVA probe use at the former NAS Moffett Field PRB site is presented in Battelle (1998). The velocity measurements proved to be a mixed success at this site in part because the flow velocities encountered at the site turned out to be lower than the instrument calibration range. However, the results still provide a qualitative indication of groundwater flow directions at the site. At higher flow velocities and in properly screened and completed monitoring wells, the results are expected to be more reliable.

3.1.2.5 Colloidal Borescope

The colloidal borescope is an in situ device that provides direct visual means for observing colloids in monitoring wells. Colloidal size, density, and flow patterns can be assessed, and an evaluation of sampling effects on the natural groundwater flow system can be made. This device has been used previously to evaluate micropurge sampling techniques (Kearl et al., 1994), and currently is being used to determine the flow velocity and directions in monitoring wells by direct observation of colloidal particle movement (Korte, 1999). The colloidal borescope was developed at Oak Ridge National Laboratory (ORNL) as part of the Exploratory Studies Program. The borescope also is marketed by AquaVISION Environmental, LLC.

The instrument consists of a charge coupled device (CCD) camera, optical magnification lens, illumination source, and stainless steel housing. The device is about 60 cm (2 ft) long and has a diameter of less than 5 cm (2 inches), making its use possible for the 2-inch-diameter monitoring wells present at most PRB sites. The electronic image from the well can be seen at the surface on a monitor and recorded on a VHS tape. The magnified image corresponds to a field of view of approximately 1.0 mm × 1.4 mm × 0.1 mm. The colloidal borescope is inserted into the monitoring well by a set of rigid quick-connect tubes. These tubes maintain the alignment of the borescope in the well so that the flow directions can be determined. The flow velocity and direction can be measured after a waiting period during which the flow changes from turbulent (due to probe insertion) to laminar (due to natural groundwater flow).

A recent study (Kearl, 1997) presents in detail the various aspects of groundwater velocity measurement using the borescope and its comparison with traditional (i.e., Darcy equation-based) approaches to velocity estimation. Kearl evaluates the performance of the borescope in different geologic settings and in laboratory tanks. In most cases flow magnitude and direction appear to be stable within an acceptable standard deviation range. However, large fluctuations and standard deviation due to swirling were observed in a low conductivity setting. It was concluded that the laminar flow establishes more easily in the relatively high-flow zones of the aquifers. In comparison, swirling flow conditions develop as the groundwater enters from the lower-flow zones into the well bore. As a result of this effect, the borescope tends to be more reliable in the higher-flow zones, and the results are biased toward preferential flow zone velocity rather than bulk flow velocity. Essentially, the borescope provides an estimate of maximum velocity rather than the average velocity in the borehole. According to Kearl (1997), field borescope measurements should be reduced by a factor of 1 to 4 for velocity magnitude to account for higher than actual velocities. Within this range, higher multiples are needed for wells with filter pack than those without filter pack, based on laboratory tank studies. A field study of the applicability of the borescope and HydroTechnics sensors at multiple PRB sites is currently being conducted through a joint DoD-DOE effort (Battelle, 1999).

3.1.2.6 Tracer Testing

Tracer testing is a relatively difficult, more expensive way of determining the flow properties of the targeted portion of an aquifer. However, if successfully applied, tracer tests can provide the most direct measurement of flow. Tracer tests can be used to estimate the average groundwater velocity and determine flowpath variations. In general, tracer tests involve injecting a known concentration and volume of a chemical tracer in the upgradient locations and then monitoring for the arrival and concentration distribution in one or more downgradient wells. The plots of concentration versus time are used to calculate travel velocities through the medium. The spread in the concentration distribution is an indicator of the dispersion caused by heterogeneities. The most significant aspects of conducting the tracer tests include the selection of tracers, the location of monitoring points, and the determination of appropriate sampling frequencies.

Conservative tracers usually are used to determine flow velocity in order to prevent the tracer from being retarded significantly by chemical reactions with the aquifer medium. The monitoring point locations must be based on a reasonable understanding of the flow patterns so that the wells are placed directly downgradient of the injection points and so most of the injected tracer can be accounted for during mass-balance calculations. The sampling frequency is based on a pre-estimate of the expected flow velocity and should be sufficient to obtain a relatively large number of samples during the time the tracer passes through the monitoring locations. The mass of tracer should be small enough that the injected volume does not have a large impact on the flow field (i.e., the natural hydraulic gradients should not be disturbed). However, the mass of tracer should be large enough to obtain detectable concentrations in the monitoring wells. Monitoring for tracer movement may be based on a combination of laboratory analyses of samples and the use of specific ion electrodes. It is better to install specific ion electrodes with data loggers for continuous monitoring of tracer concentrations in several wells. The only disadvantage of using the specific ion electrodes may be the need to calibrate them often. Generally, tracer tests are time-consuming, cumbersome, and expensive. However, when conducted properly, they provide the most direct evidence of the flow patterns in the subsurface.

3.2 Contaminant Distribution in the Groundwater

The distribution of the target contaminants needs to be mapped out so that a suitable location which meets regulatory/administrative objectives can be determined. Many of the design features of the PRB are also dependent on the contaminant distribution, as described in Section 6.0.

3.2.1 Spatial Distribution of Contaminants

In general, the 3-D distribution of each contaminant plume at the site needs to be delineated so that the PRB can be appropriately located and sized to capture it. This delineation includes the identification of the contaminated aquifer(s), the depth and width of the plume(s), the average and maximum concentration, and the rate of plume movement. In addition, it is important to characterize the significant processes that may affect the spread of contamination in the subsurface at the site. These processes may include the effects of adsorption/retardation, chemical reactions, dispersion, and vertical plume movement due to fluid density effects.

In many cases, some of the required data already would be available from the RI/FS, ROD, RFI, or routine monitoring reports from the site. Therefore, no new data may need to be acquired for plume characterization at these sites. Instead, a careful review of existing reports should be conducted and new data should be collected only if significant data gaps are found or if the preexisting data are out of date or inadequate. If needed, groundwater samples can be collected to fill data gaps or to improve sampling density in areas of particular interest or for specific analytes. Generally, discrete-depth samples of groundwater from several locations are recommended for proper delineation of the plume. Even at sites (e.g., Dover AFB) with relatively homogeneous geology, contaminant concentrations may be heterogeneously distributed both in lateral and vertical planes (Battelle, 2000), either due to preferential flow channels or due to the existence of multiple DNAPL sources. At former NAS Alameda, for example, the plume was found to contain a very thin core of high contamination that was stretching the treatment capacity of the installed PRB (Einarson et al., 2000). Multi-level samples or clusters of short-screen wells should be used to better delineate the plume.

The width of the contaminant plume can be determined from the isopleth maps of concentration. If sufficient data are available, the maps also may reveal the potential source zones for the contaminants and the existence of preferential pathways for contaminant migration along which the contaminants have advanced. The plume maps also can be used to identify a potential location and design for the PRB installation. In most cases, the barrier is installed near the downgradient end of the plume. However, several factors may lead to the installation of barriers within the plumes. For example, site access to the edge of the plume may be difficult, or barriers may have to be installed at the edge of the property boundary even if a portion of the plume already has moved past the property boundary. Sometimes the barrier may be located in the proximity of the highest concentration parts of the plume to expedite the remediation of the most contaminated areas. Such a location may be required for slow moving plumes. Other measures may be required in such cases to address the remaining portion of the plume.

3.2.2 Temporal Changes in Contaminant Concentration

Although much of the site characterization effort is directed toward mapping the current contaminant distribution, an effort should be made to anticipate the changes in the contaminant distribution over time. The objective is to anticipate the way that the shape of the plume and concentration of the contaminants near the PRB may change with time. If concentrations change significantly over time, the amount of reactive medium installed in the PRB may become insufficient to treat the plume to target cleanup levels. If the shape of the plume changes significantly over time, it may find its way around the PRB. In addition, if the PRB is being designed to replace an existing P&T system, it may be difficult to predict the future shape and movement of the plume once the P&T system is shut down.

Predicting changes in shape and concentration of the plume over time is very difficult. This issue may need to be addressed by evaluating different design scenarios and by incorporating suitable safety factors in the design, rather than through predictions from site characterization. However, characterizing more of the upgradient plume and source area may provide a preliminary indication of how the plume may develop in the future. At the very least, the maximum contaminant concentration upgradient from the prospective PRB location should be determined. Historical plume maps or contaminant data taken at different points in time may be helpful.

3.2.3 Groundwater Sampling for Volatile Organic Compounds

Groundwater sampling for volatile organic compounds (VOCs) provides essential information on water movement, contaminant levels, and inorganic chemistry and geochemistry needed to understand and model the performance of a PRB. Proper quality assurance (QA) procedures, as described in EPA SW-846, should be followed during sampling to ensure that the data are valid. Zero headspace should be ensured prior to sealing the sample containers. Sample containers should be labeled, logged, and stored at approximately 4°C while they are being transferred under chain-of-custody protocol to an analytical laboratory for analysis. Analysis must be completed prior to expiration of recommended holding times. Field duplicates, field blanks, and trip blanks are commonly used quality control (QC) samples that aid data quality evaluation.

At some field sites, monitoring wells already will be installed at a distance from the PRB suitable enough to enable water sample collection that will meet the objectives of the project. The locations of existing groundwater wells may be adequate, particularly if the goal is compliance monitoring. However, questions concerning plume capture or plume migration may arise after the project has begun which could render the number and distribution of existing wells inadequate. To cover a wider sampling area or to enlarge the dataset collected at important points, it is often practical, fast, and economical to install temporary monitoring points, as opposed to installing additional permanent wells. Also, the need for certain types of information may be immediate and there may be no need for follow-up sampling. All of these goals can be met by installing temporary monitoring points.

Temporary points can be installed using several types of available direct push equipment, such as a CPT rig and Geoprobe®. Usually, a narrow diameter (typically ¾-inch) polyvinyl chloride (PVC) tube with slotted well screen is installed through the bore of the drive casing. After the casing is removed, native soil begins to collapse around the PVC tube while adjacent groundwater flows inside. Screen sections can be obtained in various lengths to accommodate discrete level (typically 6-inch to 3-ft) or continuous (long-screen) sampling. Also, narrow slot sizes should be used if the soil texture is fine. The aboveground length can be shortened to a convenient height if desired to accommodate the sampling method.

Sampling can begin immediately after temporary well installation. If water levels are relatively shallow (generally no deeper than 25 ft), samples can be collected by pumping with a peristaltic pump. This is done by first inserting a thin (e.g. ¼-inch outside diameter) flexible or semi-rigid tube (a grade of Teflon™ is recommended) into the middle of the screened section of the PVC tube. The sample tubing then should be connected to a section of flexible Viton® tubing which is inserted into the pump mechanism. If water levels are too deep for sampling using a peristaltic pump, water samples can be recovered by using a narrow-diameter bailer. An alternative method for collecting moderately deep groundwater is to use a collection device built into the drive tip of a direct-push sampler. One drawback to this kind of device is that only a small volume (up to 100 mL) of sample can be collected. Additionally, a narrow-diameter bailer can recover only a small sample volume and the water will likely remain turbid due to disturbances in the aquifer caused by its use. The peristaltic pump method allows continuous collection of water, as long as the pumping rate is lower than the recharge rate. Slow recharge can be a limitation of temporary wells, because of the small diameter of the hole and absence of an annular sand pack.

When groundwater sampling is done within or nearby the PRB, it should be done in a manner that causes the least disturbance to the inside of the PRB. This is true no matter whether temporary or permanent wells are used. Even relatively low rates of water removal can lead to increased flow and reduced residence time of groundwater in contact with the reactive medium. If a peristaltic pump is used, water samples should be extracted at low flowrates to prevent artificial gradients. In addition, to minimize disruption of normal flow through the barrier, successive samples should be collected in different parts of the barrier, rather than being sampled progressively in nearby wells.

If pumping is used, the flowrate should be set to minimize water-level drawdown. As a rule of thumb, drawdown in the sampling well should be no greater than 0.05 ft. Water levels in nearby wells also may be monitored to check for drawdown until a suitable withdrawal rate is determined for the site. At PRB sites, a typical range of sampling rates is 50 to 500 mL/min. Purging of the wells before sample collection should be kept to a minimum to restrict the sample to the water immediately surrounding the well. One method to assure that water samples are representative is to purge at least three volumes of the sample collection tubing. For a typical $^{3}/_{16}$-inch-inside diameter, 25-ft-long tubing segment, three tubing volumes are equivalent to about 400 mL. After sample collection, all tubing should be decontaminated as described below. In addition, all downhole sampling equipment (e.g., water-level tape and water quality sensors) should be similarly decontaminated prior to reuse.

The possibility for cross-contamination during sampling should be minimized by taking certain precautions. The favored approach is to use dedicated sample tubing for specific rows of wells (i.e., rows cross-gradient to the flow direction). For example, different sets of tubing could be used to sample the upgradient aquifer, downgradient aquifer, pretreatment zone, exit zone, and different portions of the reactive cell. Also, if more than one plume will be encountered within the aquifer, different sets of tubing can be used for each plume type. All of the tubing should be thoroughly decontaminated by sequentially flushing with detergent, tap water, and deionized (DI) water, prior to collecting the next investigative sample. Rinsate blanks should be collected after the DI water rinse. If free-phase petroleum hydrocarbons will be encountered, it may be desirable to include a methanol rinse prior to the detergent washing step.

3.2.4 Analytical Methods for Volatile Organic Compounds

This section briefly describes the methods used for analysis of groundwater to meet the essential requirements of a site characterization study. VOCs in groundwater samples can be analyzed using EPA Method 8240 *(Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry [GC/MS]*, EPA SW-846, Update II, September 1994) or EPA Method 8260 (similar to Method 8240, but uses capillary column) in conjunction with EPA Method 624 (*Purgeables*, EPA SW-846, July 1991). Method 624 is a sample preparation and extraction procedure for analysis of VOCs using a purge-and-trap apparatus. This technique can be used for most VOCs that have boiling points below 200°C and are insoluble or slightly soluble in water. Volatile, water-soluble compounds can be included in this analytical technique; however, quantitation limits by gas chromatography (GC) are generally higher because of poor purging efficiency.

QA involves the use of blanks, duplicates, and matrix spikes (MSs) to ensure laboratory data quality. The accuracy and precision of either EPA Method 8240 or EPA Method 8260 are related to the concentration of the analyte in the investigative sample and are essentially independent of the sample matrix. Linear equations pertaining to accuracy and precision for a few compounds are discussed in the method descriptions. The estimated quantitation limit (EQL) for individual compounds is approximately 5 μg/L in groundwater samples. EQLs are proportionally higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

3.3 Geochemical Composition of the Groundwater

Monitoring of field parameters such as pH, DO, or ORP (i.e., redox-potential [Eh]) in the groundwater during site characterization is very important because they can be used to determine whether conditions at the site are conducive to formation of inorganic precipitates in the presence of a reactive medium (see Section 1.4 for a discussion of inorganic reactions that occur in reactive cells containing iron). These three groundwater field parameters should be monitored on a quarterly basis, if possible, to evaluate seasonal fluctuations. Unless the aquifer is relatively thin, these parameters may vary by depth. Although mapping local geochemical heterogeneities is not as important as mapping the local contaminant distribution, depth profiles of these parameters in the aquifer may provide important information that might limit the longevity of the reactive medium over several years. Some geochemical parameters, such as DO, may vary by depth in the aquifer, leading to different degrees of iron corrosion in the reactive cell. Section 8.3 contains additional discussion on the use of inorganic geochemical parameters for evaluating the longevity of PRBs.

Geochemical species that may potentially react with the reductive media considered for PRBs include Ca, Fe, Mg, Mn, Ba, Cl, F, SO_4^{2-}, NO_3^-, silica, and carbonate species (alkalinity); significant redox-sensitive elements include Fe, C, S, and N. For example, iron in solution may be in the ferrous (Fe^{2+}) state or ferric (Fe^{3+}) state, and organic carbon as humic or fulvic substances may be reduced to methane in the reactive cell. Sulfate (S^{6+}) may be reduced to bisulfide (HS^-) and nitrate may be reduced to nitrogen gas or ammonia if conditions are sufficiently reducing. Geochemical modeling codes can be used to determine the types of reactions and products that may be expected when groundwater contacts the reactive medium. Geochemical modeling is discussed in Sections 6.4.3 and 8.3.2.

3.3.1 Sampling and Analysis of Field Parameters

The primary purpose of taking field parameter measurements is to monitor aquifer conditions that can affect the performance of the reactive wall. Therefore, the water level, temperature (T), pH, Eh, and DO should be measured at designated monitoring wells. To obtain accurate readings, T, pH, Eh, and DO should be measured using the most appropriate method available to provide representative values. Typical devices include downhole sensors or flowthrough cells with multiple sensors. Other parameters, such as specific conductivity, turbidity, and salinity of a groundwater sample, can be measured ex situ, if required, using appropriate field instruments. Table 3-3 lists the field parameters and corresponding analysis methods.

3.3.2 Sampling and Analysis of Inorganic Chemical Parameters

Inorganic analytes should be measured because they provide useful information about the corrosion byproducts that may be produced during operation of the PRB. Samples should be collected from selected monitoring points for laboratory analysis as indicated in Table 3-1.

Samples for cations should be filtered and preserved immediately after collection. Filtering is especially critical for transition metal cations such as iron and manganese. Without filtering, adsorbed metals on colloidal particles would bias the solution analysis toward higher concentrations. The typical filter pore size for cation analysis is 0.45 µm; however, filters of smaller pore size may be used from time to time for comparison. Samples for anion analysis usually do not require filtering.

In addition, several samples should be collected and preserved without filtering to determine the content in the suspended matter. TDS and TSS should be determined from filtered and unfiltered samples, respectively. QA procedures include the use of blanks, duplicates, and MSs to ensure data quality.

3.4 Geotechnical and Topographic Considerations

Aboveground factors that could impede the access of construction equipment to the site, such as the presence of buildings or overhead utility lines, should be identified while choosing prospective locations for the PRB. Underground factors that could impede the construction of the PRB, such as the presence of consolidated sediments or rocks, need to be identified. This process could start during the preliminary assessment to evaluate whether the site lends itself to PRB application. These issues may have to be revisited when selecting construction methods for the PRB.

Table 3-3. Requirements for Field Parameters and Inorganic Analytes (based on EPA SW-846)

Analytes/Parameters	Analysis Method	Sample Volume	Storage Container	Preservation	Sample Holding Time
Field Parameters					
Water level	Probe	None	None	None	None
pH	Probe	None	None	None	None
Groundwater temperature	Probe	None	None	None	None
Redox potential	Probe	None	None	None	None
Dissolved oxygen	Probe	None	None	None	None
Specific conductivity	Field instrument	None	None	None	None
Turbidity	Field instrument	None	None	None	None
Salinity	Field instrument	None	None	None	None
Inorganic Analytes					
Metals (K, Na, Ca, Mg, Fe, Mn, and Ba)	EPA 200.7	100 mL (all)	Polyethylene	Filter[(a)], 4°C, pH<2 (HNO_3)	180 days
Anions (NO_3, SO_4, Cl, Br, and F)	EPA 300.0	100 mL (all)	Polyethylene (all)	4°C (all)	28 days (48 hours for NO_3)
Alkalinity	EPA 310.1	100 mL	Polyethylene	None	14 days
Other					
TDS, TSS	EPA 160.2, 160.1	100 mL	Polyethylene	4°C	7 days
TOC, DOC	EPA 415.1	40 mL	Glass	4°C, pH <2 (H_2SO_4)	7 days
Dissolved silica	EPA 6010	250 mL	Polyethylene	None	28 days

(a) 0.45-µm pore size.

DOC = Dissolved organic carbon.

TOC = Total organic carbon.

TDS = Total dissolved solids.

TSS = Total suspended solids.

4.0 Reactive Media Selection

Once site characterization information has been obtained, a suitable reactive medium must be selected for use in the reactive cell. The choice among reactive metal media for the reactive cell is governed by the following considerations:

- **Reactivity.** A medium that affords lower half-lives (faster degradation rates) is preferred.
- **Stability.** Length of time that a reactive medium or that mixed media will maintain reactivity is an important concern. No full- or pilot-scale barrier has been operating for a sufficient length of time to make a direct determination of stability. However, an understanding of the reaction mechanism can provide some indication of the future behavior of the medium.
- **Availability and Cost.** A cheaper medium is preferred over a more expensive medium, especially if any differences in performance are reported to be slight.
- **Hydraulic Performance.** The particle size of the reactive medium should be sufficient to ensure required hydraulic capture by the barrier.
- **Environmental Compatibility.** The reactive medium should not introduce harmful byproducts into the downgradient environment.
- **Construction Method.** Some innovative construction methods, such as jetting, may require a finer particle size of the reactive medium.

There may be a trade-off between these factors, and final selection may have to be based on the importance of each factor for a given site.

4.1 Types Of Reactive Media Available

Several different types of reactive metal media are available for use in PRBs and are discussed below.

4.1.1 Granular Zero-Valent Metal

Granular zero-valent metal, particularly iron, is the most common medium used so far in bench-, pilot-, and full-scale installations.

4.1.1.1 Granular Iron

The use of zero-valent iron medium for in situ groundwater treatment was investigated and patented by the University of Waterloo (Gillham, 1993). The technology is marketed under an exclusive license by ETI, of Waterloo, Ontario. Both reagent- and commercial-grade iron have proved effective for dissolved chlorinated solvent treatment. Sivavec and Horney (1995) studied the degradation rates for chlorinated compounds with commercial iron from 25 different sources. They and other researchers (Agrawal and Tratnyek, 1996; Matheson and Tratnyek, 1994) have found that the primary determinant of degradation rate in different irons is the available reactive surface area. The parameter generally used to discriminate between different irons is the specific surface area, or the surface area per unit mass (m^2/g) of iron.

Sivavec and Horney (1995) found that pseudo first-order degradation kinetics (with respect to chlorinated ethene concentrations) were applicable when the ratio of iron surface area to volume of aqueous phase ranged from 0.1 to 1,325 m^2/L. The surface area of the metal was measured by Brunauer-Emmett-Teller Adsorption Isotherm Equation (BET) Kr or N_2 adsorption. Specific surface areas of untreated iron from the 25 different sources varied by more than four orders of magnitude. Acid pretreatment was found to increase the degradation rate of iron (Agrawal and Tratnyek, 1996; Sivavec and Horney, 1995), probably due to removal of any passivating oxide layer on the iron or due to an increase in the surface area by etching or pitting corrosion. Therefore, commercial irons with higher surface area are preferred. However, the higher surface area requirement for reactivity should be balanced with the hydrogeologic necessity to select a particle size that affords a reactive cell K that is at least five times (or more) higher than that of the surrounding aquifer (see Section 6.1). Generally, sand-sized particles of iron are selected for use in reactive cells. The hydraulic conductivity of the reactive cell also can be improved by mixing sand (or coarser concrete sand) with finer iron particles. Adding sections of pea gravel along the upgradient and downgradient edges of the reactive cell also improves the distribution of flow through the reactive cell, and this feature has been used in several field installations to date.

One variation of granular iron medium that was applied at Dover AFB is the use of a pretreatment zone containing a coarse medium (sand or pea gravel) mixed with a small percentage (10%) of iron (Battelle, 2000). This pretreatment zone removed DO from aerobic groundwater before it entered the 100% iron reactive cell. The advantage of using this pretreatment zone was that the front-end precipitate formation (by the reaction between iron and DO) was spread over a greater flowthrough thickness of the reactive cell, which reduced the potential for clogging of the influent end of the reactive cell.

The general requirements for the iron media that have been used at existing PRB sites are:

- Iron ideally should be more than 90% Fe^0 by weight, with minor amounts of carbon, a minimal oxide coating, and no hazardous levels of trace metal impurities. Many suppliers perform environmental quality testing on their materials to determine the concentration of impurities.

- The desired grain-size range is between -8 to 50 mesh. Presence of fines (-50 mesh) should be minimized as much as possible by sieving.

- Because the iron may be generated from cutting or grinding operations, it should be ensured that there are no residual cutting oils or grease on the iron.

- A material safety data sheet (MSDS) that identifies health and safety hazards of the material should be provided by the supplier.

4.1.1.2 Other Zero-Valent Metals

A number of other zero-valent metals have been investigated for their potential to reduce chlorinated hydrocarbons. Experiments were conducted to determine the relative rates of reduction of various hydrocarbons by stainless steel, Cu^0, brass, Al^0, mild steel, and galvanized metal (Zn^0) (Reynolds et al., 1990; Gillham and O'Hannesin, 1992). Mild steel and galvanized metal had the fastest reduction rates, followed by Al^0. Little reduction occurred with stainless steel, Cu^0, and brass. These results indicate that there is no significant advantage to using any of these metals over Fe^0. Boronina et al. (1995) investigated the reactivity of Mg^0, Sn^0, and Zn^0 with CCl_4. Rapid oxidation of Mg^0 by water effectively prevented it from reducing CCl_4. Sn^0 and Zn^0 were capable of degrading CCl_4; however, the cost, the incomplete degradation of chlorinated reaction products, and the dissolution of these toxic metals must be considered before the use of these metals can be considered as a viable alternative to Fe^0. Schreier and Reinhard (1994) have investigated the ability of Fe^0 and Mn^0 powders to reduce several chlorinated hydrocarbons. Experiments conducted with manganese followed zero-order kinetics. The rates determined appeared to be fairly slow; the zero-order rate constants were determined to range from 0.07 to 0.13 molar units/day, depending on the aqueous-phase solution composition.

4.1.2 Granular Iron with an Amendment

Oxidation of Fe^0 to Fe^{2+} results in an increase in pH. Depending on a variety of physical and chemical factors (e.g., flowrate through the barrier and groundwater geochemistry), this increase in pH can result in the precipitation of a number of minerals, including $Fe(OH)_2$, $FeCO_3$, and $CaCO_3$. Various amendments can be added to the granular iron in order to moderate the pH. Pyrite has been used successfully in laboratory experiments for moderating the pH (Burris et al., 1995; Holser et al., 1995). The oxidation of the pyrite produces acid, which offsets the acid consumed during the oxidation of Fe^0:

$$Fe^0 + 2\,H^+ + \tfrac{1}{2}\,O_2 \rightarrow Fe^{2+} + H_2O \qquad (4\text{-}1)$$

The net reaction for pyrite oxidation is as follows:

$$FeS_2 + {}^{7}\!/_{2}\,O_2 + H_2O \rightarrow Fe^{2+} + 2\,H^+ + 2\,SO_4^{2-} \qquad (4\text{-}2)$$

In addition to lowering the pH, the addition of pyrite and iron sulfide to Fe^0 has been shown in the laboratory to reduce the half-life of carbon tetrachloride (Lipczynska-Kochany et al., 1994). At a FeS_2/Fe^0 ratio of 0.03, the half-life of carbon tetrachloride was reduced by 6% over that of iron alone. At a FeS_2/Fe^0 ratio of 0.11, the half-life was reduced by 45%. Ferrous sulfide also reduced the half-life of carbon tetrachloride degradation by Fe^0. When added at a FeS/Fe^0 ratio of 0.04, the half-life of carbon tetrachloride was reduced by 18%. In addition to the materials discussed above, other materials have been proposed for moderating the pH, including troilite, chalcopyrite, and sulfur. One potential side effect of adding pH-controlling amendments could be the presence of higher levels of dissolved iron in the downgradient water from the reactive cell.

In the PRB at Dover AFB, a mixture of 10% pyrite and sand was used as a pretreatment zone before the 100% iron reactive cell (Battelle, 2000; U.S. EPA, 1997). Just as with 10% iron and sand (see Section 4.1.1.1), front-end precipitation caused by DO was reduced with the use of this pretreatment zone. The pH reduction achieved in the pretreatment zone, however, did not persist in the 100% iron reactive medium, and pH rose to 11 in the reactive cell.

4.1.3 Bimetallic Media

A number of bimetallic systems in which various metals are plated onto zero-valent iron have been shown to be capable of reducing chlorinated organic compounds at rates that are significantly more rapid than zero-valent iron itself (Sweeny and Fisher, 1972; Sweeny, 1983; Muftikian et al., 1995; Korte et al., 1995; Orth and McKenzie, 1995). Some bimetals, such as iron-copper (Fe-Cu), act as galvanic couples. Other bimetals, such as iron-palladium (Fe-Pd), enhance the degradation rate because the metals (in this example, Pd) acts as a catalyst. Some publications (Appleton, 1996) have mentioned that the Fe-Ni bimetallic system has the potential to considerably enhance reaction rates. There may be a cost trade-off between the construction of a smaller reactive cell (because of the faster reaction rate) and the higher cost (relative to granular iron) of the new highly reactive medium.

Of the bimetallic systems studied so far, the Fe-Pd bimetal appears to have the fastest reaction kinetics. Laboratory studies with palladized iron have demonstrated that the reduction of TCE can be increased by up to two orders of magnitude over that of iron alone (Hayes and Marcus, 1997; Muftikian et al., 1995; Korte et al., 1995; Orth and McKenzie, 1995). In addition, palladized iron allows for the reduction of some of the more recalcitrant compounds, such as dichloromethane. However, due to the high cost of palladium, the economic viability of this medium is unclear.

One caution that should be exercised while examining bimetallic media in particular, and all media in general, is to ensure that the enhanced reactivity can be maintained over long periods of time. There is some preliminary indication from long-term column tests that the reactivity of bimetallic systems initially may be high, but may decline gradually after several pore volumes of groundwater have flowed through (Sivavec, 1997). Also, the metals used in bimetallic systems (e.g., Fe-Ni) should not introduce environmentally undesirable levels of dissolved metals into the downgradient aquifer.

4.1.4 Other Innovative Reactive Media

4.1.4.1 Cercona™ Iron Foam

One group of materials that has been proposed for use in PRBs is ceramic foam and aggregate products made by Cercona, Inc., Dayton, OH (Bostick et al., 1996). As opposed to conventional granular forms of iron that exhibit a trade-off between surface area and porosity, the iron foam material is claimed to be able to provide both properties, a high surface area (high reactivity) and a high porosity, in the same material. This iron foam material is based on gelation of soluble silicates with soluble aluminates. These two solutions are combined with an aggregate or powdered material in a controlled and reproducible manner under specific conditions including the solution concentration, the temperature, and the ratio of materials to make the final product. The addition of the custom aggregate or powdered material to the silicate/aluminate slurry results in a final product with a composition that typically is 5-15% silicate and aluminate with the balance being the additive of choice. The additives are based on the desired properties of the product. For PRB applications, typical additives would include metallic iron, iron oxides, zeolites, clays, or specialty ceramic materials.

4.1.4.2 Colloidal Iron

Granular iron materials of sand size and larger have been the most common reactive media used in laboratory and field studies of PRBs so far. One alternative form of iron that has been suggested is colloidal-size iron material (1 to 3 µm in diameter). This material is considerably more expensive than granular iron materials; however, it may have some advantages over granular materials. Colloidal-size iron allows the formulation of slurries that can be injected into the aquifer, making it possible to install a PRB anywhere a well can be installed, including in deep sites and fractured media. Some studies have explored the viability of this innovative approach for construction of an in situ PRB composed of iron (Kaplan et al., 1996; Cantrell and Kaplan, 1996; Cantrell et al., 1997). In the proposed approach, colloidal-size iron particles would be injected as a suspension into the subsurface. As the suspension of particles moves through the aquifer material, the particles would be filtered out on the surfaces of the aquifer matrix. As a result of the high density of the iron particles (7.6 g/cm^3), it appears that the primary removal mechanism of iron colloids in aqueous solution passing through sand columns is gravitational settling. Because colloidal-size iron particles have higher surface areas, a lower total iron mass may be required in the treatment zone. Cantrell and Kaplan (1996) estimate that a chemically reactive barrier which is 1.0 m thick with a iron concentration of 0.4% by volume would last for approximately 30 years under typical groundwater conditions. Although laboratory column experiments have been promising, this technology has not been field-tested. The cost of manufacturing iron in a colloidal form has a significant bearing on the economics of this medium and needs to be assessed.

4.1.4.3 Ferrous Iron-Containing Compounds

In addition to zero-valent iron, several ferrous iron-containing compounds have been investigated for their potential as suitable reducing agents for chlorinated hydrocarbons. Lipczynska-Kochany et al. (1994) found that Na_2S, FeS, and FeS_2 all were capable of reducing carbon tetrachloride with half-lives that were nearly the same as Fe^0 (approximately 24 minutes). Kriegman-King and Reinhard (1991 and 1994) also investigated the reduction of carbon tetrachloride by pyrite. The reaction rates that they observed appear to be similar; however, it is difficult to make an objective comparison between their two studies because different experimental conditions were used in each study.

4.1.4.4 Reduction of Aquifer Materials by Dithionite

Another treatment technology that involves lowering aquifer redox conditions has become known as in situ redox manipulation, or ISRM. In ISRM, a reducing agent, usually sodium dithionite ($Na_2S_2O_4$), is injected into the subsurface to create a permeable treatment zone for remediation of redox-sensitive contaminants. Although only certain CVOCs can be treated by ISRM (e.g., carbon tetrachloride), the technology appears promising for immobilizing a number of redox-sensitive metals, such as chromium, uranium, and technetium (Fruchter et al., 1997). The treatment zone is created by reducing ferric iron to ferrous iron in aquifer materials, such as clay minerals.

Work to date on ISRM has taken place in Hanford, WA, where it was developed to treat hexavalent chromium in an unconfined aquifer at the 100-H area. The site had relatively low concentrations of hexavalent chromium, which ranged from 46 to 71 µg/L. Initial bench-scale testing determined that the half-life of dithionite is roughly 18 hours when in contact with Hanford area sediments (Fruchter et al., 1997). An intermediate-scale test was conducted at Oregon State University using a wedge-shape flow cell. Specifications for field experiments were determined by modeling and site characterization information. A field-scale experiment was conducted at a site near the Columbia River, WA in September 1997. Approximately 77,000 L of buffered sodium dithionite solution were injected into the aquifer through a well in the expectation of impacting a zone 15 meters in diameter. After 18.5 hours, the spent reagent was withdrawn from the aquifer and monitored for unreacted reagent, buffer, reaction products (sulfate and sulfite), mobilized metals, and tracer. Subsequent monitoring showed that hexavalent chromium decreased to less than 2 µg/L (as total Cr) and DO was below detection levels.

One key advantage of ISRM over other PRB technologies is that it can be implemented at much greater depths than can usually be attained by excavation methods. Another advantage is that injection can be done easily and economically in remote areas, whereas installation costs tend to increase significantly for traditional placement methods when a site is difficult to access by heavy equipment. One disadvantage of ISRM may be that it does not treat a wide a range of contaminants.

4.1.4.5 Media that Impart Adsorptive and Biological Capability

Werner (1998) has proposed the development of granular activated carbon (GAC) as an adsorbent surface for bacterial growth. In an enhanced GAC system, chlorinated aliphatic hydrocarbons, such as PCE, would be sequestered from the contaminant plume and treated by stimulated anaerobic biodegradation simultaneously. Other materials that have been tested for their ability to adsorb dissolved organic contaminants include polymer beads (polyalkastyrene) (Venhuis et al., 1999) and ground rubber (Kershaw and Pamukcu, 1997).

Another application of biologically mediated reactions has been demonstrated by a barrier at the Nickel Rim Mine near Sudbury, Ontario, Canada. This barrier is being used to treat acidic leachate plumes produced by oxidized mine drainage (Herbert et al., 1998; Benner et al., 1997). The Nickel Rim barrier consists primarily of organic compost and wood, with a small amount of limestone, and has been shown to promote bacterially-mediated reduction of sulfate, leading to precipitation of iron sulfide (Herbert et al., 1998). Also, geochemical modeling calculations have suggested that other soluble metals in addition to iron may become precipitated in the form of sulfides (zinc) and carbonates (manganese) (Waybrant et al., 1998). Other elements that form sulfides in reducing environments include arsenic, cadmium, copper, nickel, and lead. Precipitation of these elements in organic barriers has been explored in laboratory and pilot-scale field studies (Blowes et al., 1998). Immobilization of uranium was studied in laboratory experiments by Thombre et al. (1997). In these experiments, bacteria were shown to use cellulose-based substrates to achieve reduction of nitrate and sulfate and to promote reduction of soluble U^{6+} to insoluble U^{4+}.

Air sparging remains a proven method for stimulating aerobic biodegradation, and numerous studies have been performed on this rather mature technology. In a novel design that incorporates reductive and oxidative processes in sequence, researchers at Waterloo University designed a PRB at Alameda Point, CA, with zero-valent iron in an upgradient gate segment and an air sparge system in a downgradient segment (Morkin et al., 1998). The purpose of this design was to treat a mixture of dissolved contaminants (CVOCs and petroleum hydrocarbons) using a single integrated technology. A recent development in passive biological treatment systems is oxygen release compounds (ORC®). These compounds typically are prepared from peroxides of magnesium, calcium, and urea. Biowalls composed of ORC® have been used to remediate benzene, toluene, ethylbenzene, and xylenes (BTEX); polycyclic aromatic hydrocarbons (PAHs); and other hydrocarbon contaminants in groundwater plumes (Borden et al., 1997; Clark et al., 1997).

4.2 Screening and Selection of Reactive Media

In general, suitable reactive media should exhibit the following properties:

- ☐ Sufficient reactivity to degrade the contaminants with an economically viable flowthrough thickness (residence time) in the reactive cell.
- ☐ Ability to retain this reactivity under site-specific geochemical conditions for an economically viable period of time (several years or decades).
- ☐ Appropriate particle size to create a porosity and hydraulic conductivity that allows the creation of a reactive cell which captures the targeted plume width.
- ☐ Ability to retain the porosity and hydraulic conductivity at or above minimum specified levels over long periods of time, through the inhibition of precipitate formation under site geochemical conditions.
- ☐ Environmentally compatible reaction products (e.g., Fe^{2+}, Fe^{3+}, oxides, oxyhydroxides, and carbonates).
- ☐ Easy availability at a reasonable price.

Batch tests can be conducted to initially screen prospective media, but column tests should be performed as described in Section 5.0 to determine half-lives and select the final medium.

Geochemical models (see Section 6.0) also can help identify candidate media by examining potential reaction products in the reactive cell, especially if media other than common granular iron are being considered. This kind of geochemical modeling is referred to as *forward* or *predictive modeling*, in which a set of reactions and their stoichiometries are assumed and the final outcome of water composition and mineral assemblage is calculated using a computer program (see Appendix D.2). The initial state of the groundwater usually is taken as its composition prior to encountering the reactive medium. The final (equilibrium) composition of the water and the mass of mineral matter that is precipitated or dissolved depends somewhat on its initial chemical makeup. For example, groundwaters that are high in inorganic carbon as a result of contact with carbonate minerals or of plant respiration along a root zone may become oversaturated with minerals in the reactive cell due to an increase in dissolved iron and elevated pH. Such conditions can lead to precipitation of minerals and other solids within the reactive cell. Predictions based on this kind of modeling should be tested using batch or column experiments in a few cases, to verify that relevant system parameters are well understood and can be applied to a laboratory-scale design. If, based on predictive simulations or treatability testing, precipitation is likely to occur, a different medium or mixture of media may be tested experimentally or modeled using a forward geochemical code, and the results may be used to attempt to minimize the potential for precipitation.

Another application of geochemical modeling to media selection is *inverse modeling* (see Appendix D.3), which calculates the outcome of probable reactions based on chemical data at initial and final points along a flowpath. One key difference between inverse and forward modeling is that the former does not necessarily represent equilibrium. Rather, changes in groundwater composition are attributed to changes in solid precipitation or dissolution. Another important difference is that inverse modeling has the capability to predict the amount of mass change that must occur to satisfy the observed conditions, whereas in forward modeling only the tendency for such changes is determined. Inverse modeling as a tool for media selection is best used to predict mass changes in a column experiment based on analyses at different locations within the column. Rates of reactions and subsequent mass changes then may be calculated in conjunction with flow velocity, residence time, and other parameters that are specific to the column setup. This information permits the user to determine whether mineral precipitation is significant in terms of the long-term performance of the PRB.

5.0 Treatability Testing

Following site characterization and identification of prospective reactive media candidates, treatability testing is conducted to evaluate the performance of the reactive medium with groundwater from a specific site. Treatability testing serves the following purposes:

- Screening and selecting a suitable medium for the reactive cell
- Estimating the half-life of the degradation reaction
- Determining the hydraulic properties of the reactive medium
- Evaluating the longevity of the reactive medium.

As treatability testing and field data from several sites with common contaminants (e.g., TCE) and common reactive media (e.g., granular iron) become available, it may be possible, if regulators agree, to forgo treatability testing at some sites.

5.1 Batch Testing for Media Screening

Batch experiments generally are conducted by placing the media and contaminant-spiked water in septum-capped vials with no headspace. When samples are drawn from the vial for analysis, either the vial is sacrificed or nitrogen is added to fill up the headspace created (Sivavec, 1996). Nitrogen can be introduced into the vial by sampling with the dual-syringe technique. As the sample is drawn into one syringe, the other syringe (filled with nitrogen) slowly releases nitrogen into the headspace. Alternately, deionized water may be used to replace the liquid withdrawn for analysis. In this way, organics concentrations can be measured as a function of time over multiple sampling events.

Batch tests are useful screening tools because they can be run quickly and inexpensively. However, care should be taken in extrapolating the results to dynamic flow conditions. For example, O'Hannesin (1993) found that the column half-lives for TCE and PCE exceeded batch values by factors of 3 and 2, respectively, even though a higher iron-to-solution ratio was used in the columns than in the batch tests.

5.2 Column Testing for Media Selection and Contaminant Half-Life Estimation

Batch tests are useful mainly as an initial screening tool for evaluating different media or for assessing the degradability of contaminants already known to be recalcitrant. For most other purposes, column tests are the favored method of treatability testing for the following reasons:

- Design parameters are determined under dynamic flow conditions. As concentrations of contaminants and inorganics change with the distance traveled through the reactive cell, they can be measured by installing a number of intermediate sampling ports along the length of the column.

- ☐ Half-lives measured through column tests generally are more reliable than half-lives measured through batch tests.

- ☐ Nonlinear sorption to non-reactive sorption sites (Burris et al., 1995) is better simulated in columns.

- ☐ Any reaction products formed tend to accumulate in a batch system. Continuous flow through the columns may cause some reaction products to be transported out of the reactive medium, a condition more representative of field operation.

Various types of water may be used to run treatability tests:

- ☐ Deionized water spiked with the targeted contaminant(s)

- ☐ Uncontaminated groundwater from the site spiked with the desired concentration of target contaminant compounds

- ☐ Contaminated groundwater from the site.

Screening of new reactive media may be conducted with clean deionized water, whereas other treatability tests may be conducted with uncontaminated or contaminated groundwater from the site. When clean deionized water or uncontaminated groundwater from the site is used, known concentrations of the target contaminants need to be spiked into the groundwater. In this way, better control over feed concentrations is obtained. When target contaminants are spiked into the groundwater using laboratory grade compounds, it may be noted that the minor components (e.g., stabilizers) that may be present in industrial grade chemicals (in site groundwater) may be hard to replicate. However, there is no indication that these minor constituents affect half-lives of the target contaminants to any significant extent. It is important to run at least some tests with groundwater from the site (uncontaminated or contaminated) because of the important role played by native inorganic parameters in the site groundwater.

The main objective of column tests is to estimate the half-life of the degradation reaction. The half-lives of the organic contaminants and their byproducts then are used to either select the reactive medium or to design an appropriate flowthrough thickness for the reactive cell.

5.2.1 Column Test Setup

The design of a typical column setup is shown in Figure 5-1. A single column with multiple sampling ports along its length is used. The column may be made from glass, plexiglass, stainless steel, or other suitable material. Strictly speaking, glass should be expected to have the least adsorptive or reactive effect with chlorinated organic compounds; however, no significant loss of organics has been found using plexiglass columns. All fittings are Teflon™ or stainless steel. Tubing is either stainless steel or Teflon™. A small section of tubing through the peristaltic pump is made of Viton® for added flexibility.

The column is packed with the reactive medium in such a way as to ensure a homogeneous matrix. One way of doing this is to make small aliquots of well-mixed media (e.g., iron and sand) and fill the column in small batches with each aliquot. Optionally, a section of sand may be placed above and below the reactive medium in the column to ensure good flow distribution. Average bulk densities, porosities, and pore volumes in the column can be taken by measuring the weights of the reactive media in the column.

The feed water is placed in a collapsible bag made from Teflon™ (or other suitable material) to prevent headspace as the bag empties out. The bag is filled by gravity flow to avoid aeration of the water. Water is circulated in the column from bottom to top in order to better simulate lower flowrates and to minimize the interference of gas production in the column. Sampling ports are equipped with gastight and watertight fittings. A nylon swage lock fitting may be used or a septum may be crimped onto the sample port. It is best to leave the sampling syringe needles permanently inserted into the column, with the tip at the center of the column. Valves with luer lock adapters are attached to the protruding ends of the needles outside the column. A luer lock plug is used to seal the needle between samples. Figure 5-2 shows a typical column test in progress.

Sampling should begin only after the concentration distribution in the column has reached steady state; that is, the net contaminant mass entering the column should be equal to the mass degraded in the column. Several pore volumes of contaminated water generally are required to be run through the column before it reaches steady state (Burris et al., 1995). Also, the time (pore volumes) required to reach steady state varies with contaminant type (Burris et al., 1995). For example, water contaminated with PCE requires a longer time to reach steady state than does water contaminated with TCE. The column may be sampled every 5 to 10 pore volumes until steady state is indicated. Depending on the influent concentration, column length, and flowrate used, the contaminant levels in the effluent may not be below detection.

Whenever a sample is to be drawn, a syringe is attached to the luer lock adapter on the needle and the sample is collected after a small amount of water is purged from the needle. The sample is drawn very slowly to create minimum disturbance in the flow. Most researchers conduct column experiments at room temperature. It is important to note, however, that temperature may be an important factor influencing reaction rate.

The flowrate through the columns may be set to simulate site conditions, if field flow velocities are moderate. However, flowrate may not be a critical parameter for column testing. Gillham and O'Hannesin (1992) found that degradation rates were insensitive to flowrates in the range tested (59 to 242 cm/day). Once degradation rates have been determined through column tests, designing the flowthrough thickness of the reactive cell requires an accurate estimate of groundwater velocity from site characterization data.

Concentration profiles may be generated periodically for the chlorinated organics distribution in the column by collecting and analyzing samples from the influent, the effluent, and the intermediate sample ports after every 5 to 10 pore volumes. Eh and pH profiles of the column may be generated less frequently because of the higher sample volumes required for taking these measurements with typical probes. The column influent and effluent should be analyzed also for inorganics, such as major cations (Ca, Mg, Na, Fe, Mn, and K), major anions (Cl, SO_4, NO_3, NO_2, and silica), and alkalinity (bicarbonate).

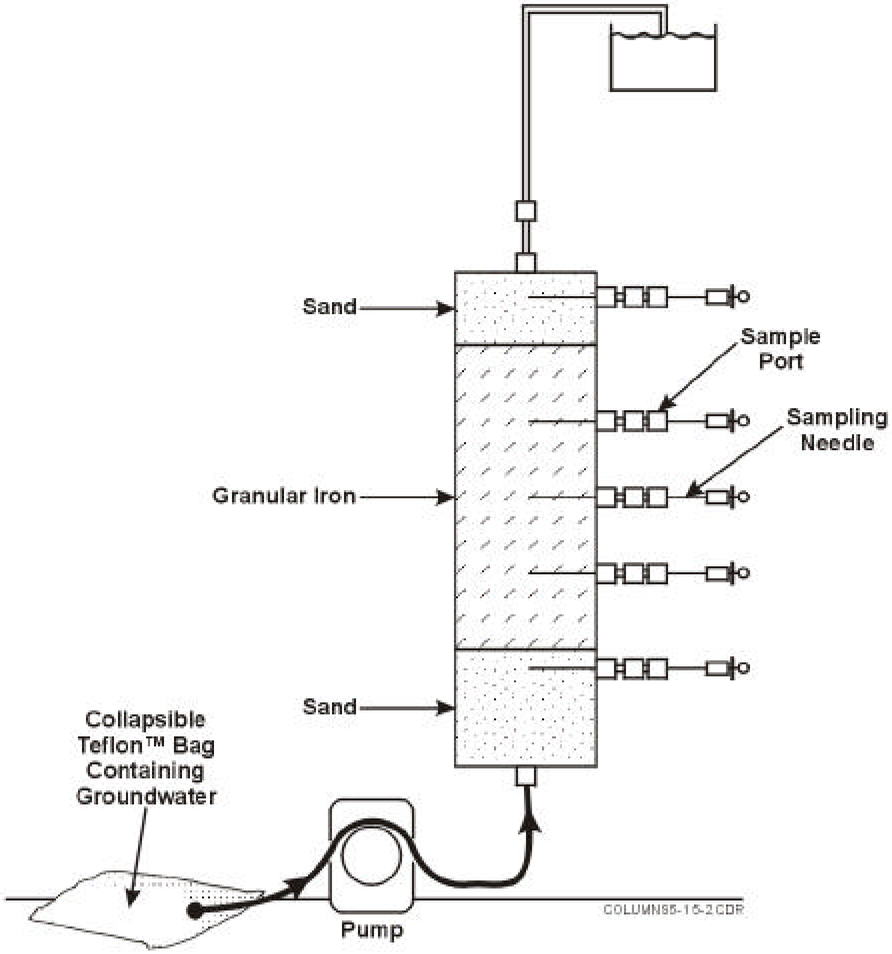


Figure 5-1. Typical Column Setup

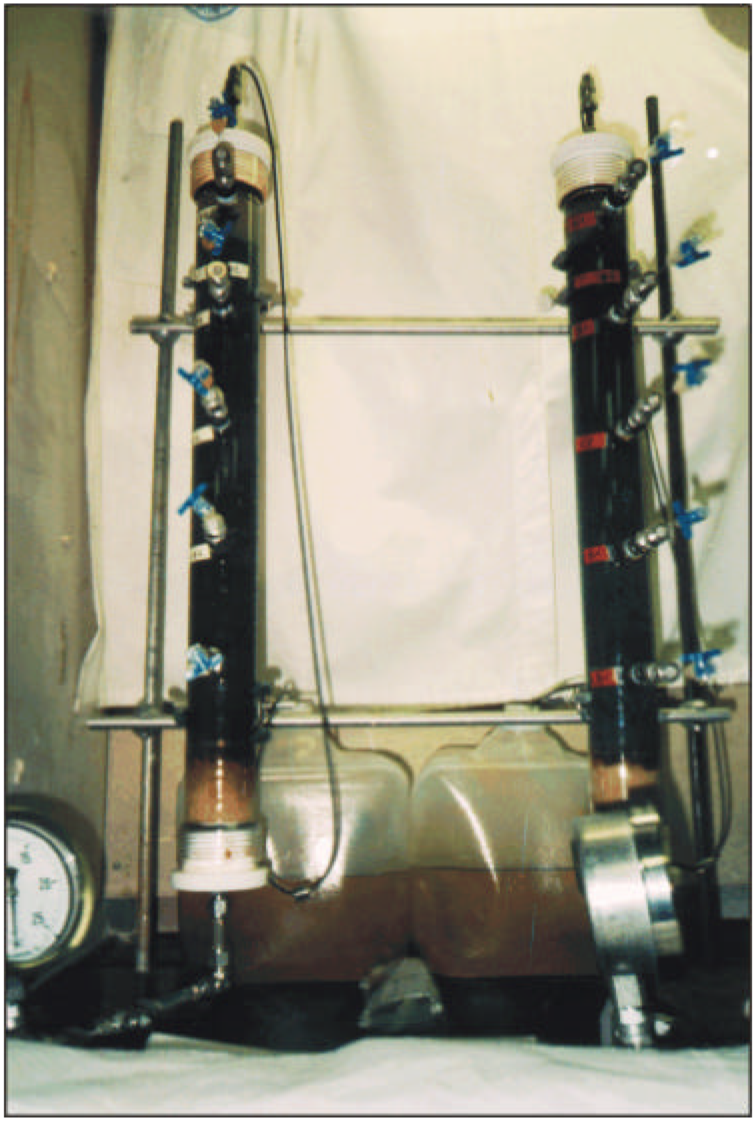


Figure 5-2. Column Test in Progress

Analysis of water samples collected from the column is done by the same general methods used for analyzing groundwater samples during site characterization (see Sections 3.2 and 3.3). Concentrations of CVOCs can be measured using a gas chromatograph-flame ionization detector (GC-FID) with purge-and-trap equipment. Water samples typically are drawn through sampling needles into a gastight syringe and are injected directly into the purge and trap through luer-lock adapters. Although chlorinated compounds can be detected using an electron capture detector (ECD), the GC-FID is suitable for general-purpose work because it can detect both a broad range of low-molecular-weight chlorinated compounds (e.g., TCE, DCE, and VC), as well as nonchlorinated hydrocarbon byproducts such as ethene or ethane. Normally, the instrument is calibrated to detect compounds at the lowest concentrations feasible. A typical detection limit for chlorinated hydrocarbons is 2 µg/L, provided that there is no strong matrix interference that requires dilution of the primary sample.

Anions typically are measured using ion chromatography (IC) and cations by inductively coupled plasma (ICP). Detection limits for inorganic constituents also can depend on the matrix. There should be very little problem with analyte interference when DI or low TDS water (synthetic or actual groundwater) is used; however, this may not be the case when high TDS water is used.

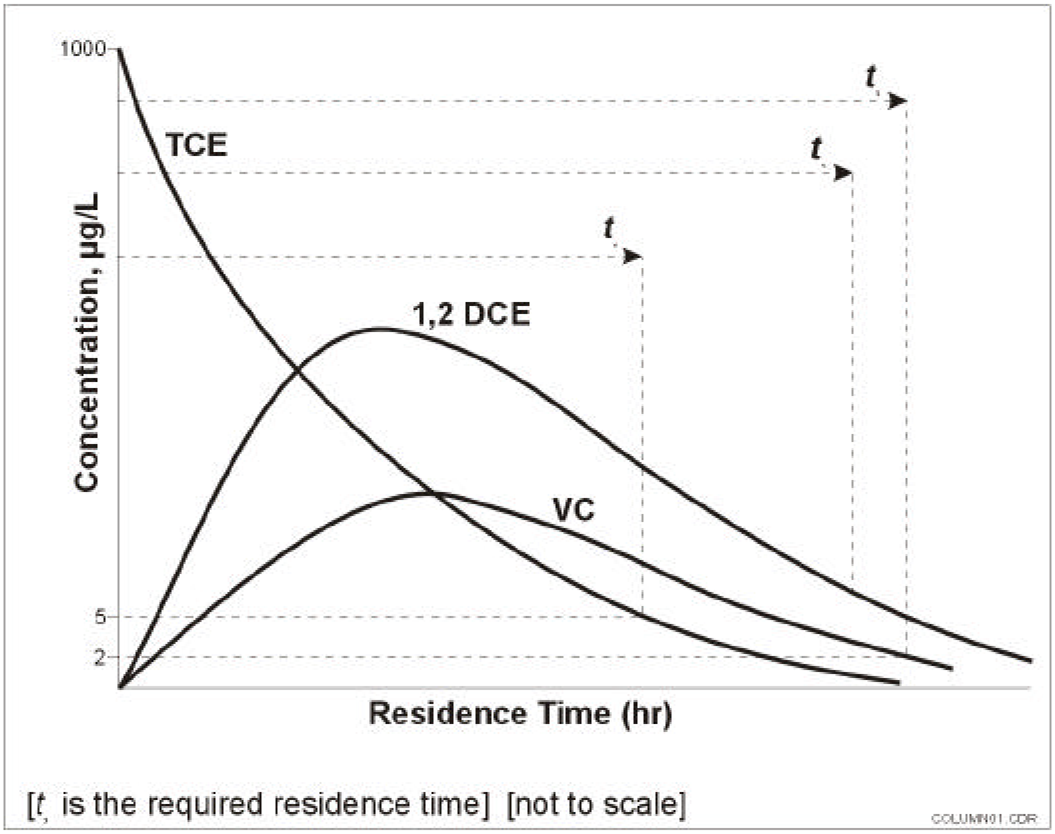
Eh and pH are measured using appropriate probes (usually combination electrodes). Eh and pH can be measured by electrodes inserted into the column at appropriate locations or they can be measured in water samples immediately after they are withdrawn from the column.

Accurate pH measurements can be taken in water samples withdrawn from the column only when the water is buffered or contains adequate concentrations of strong acid or strong base. Because most waters are near neutral to slightly alkaline and metallic compounds may raise the pH above 9, the pH range of 6 to 8 may be the most difficult to obtain accurate readings. This is particularly true when the water in the column contains no buffer, such as carbonate. Similarly, accurate Eh readings taken with a platinum electrode cannot be obtained in water withdrawn from the column unless the system is buffered with respect to electron transfer reactions; such a system is referred to as being “poised.” When a system is not well poised, Eh measurements do not reflect the abundance of electrons that result from the combinations of half-cell couples. Therefore, for accurate Eh and pH measurements, contact between air and the water withdrawn should be minimized as much as possible.

DO is difficult to measure offline, and may require an online flowthrough probe that excludes atmospheric oxygen from the sample. The DO concentration normally will be negligible when Eh is negative, as should be the case when highly reducing metals such as iron or zinc are in equilibrium with the water. Therefore, DO measurements potentially can be omitted during column tests, particularly if Eh can be measured with confidence.

5.2.2 Interpreting Column Data

For each water flow velocity and each column profile, CVOC concentrations can be plotted initially as a function of distance through the reactive column. When the flowrate and porosity are known, distances through the column can be converted easily to residence times. A graph of CVOC concentrations (µg/L) versus residence time (in hours) then can be generated. Several studies with iron and CVOCs in water have shown that the degradation of CVOCs follows pseudo first-order kinetics (Sivavec and Horney, 1995; Gavaskar, 1999). An example plot of TCE degradation is shown in Figure 5-3. This plot illustrates a series of first-order reactions leading to the formation, and subsequent degradation, of the reaction byproducts DCE and VC. A degradation rate constant, k, can be calculated for each concentration profile using first-order kinetics. Alternately, if the column used in the test is long enough and if the degradation kinetics are fast enough, the TCE, DCE, and VC curves in Figure 5-3 may progress to their respective MCLs. In this case, the required residence time is the longest time taken by any of these CVOCs to reach its MCL. In the illustration in Figure 5-3, the required residence time is determined by the VC degradation time.



[t is the required residence time] [not to scale]

Figure 5-3. Column Concentration Profiles of TCE and Its Degradation Byproducts

Alternately, the first-order kinetics equation (Equation 5-1) can be used to determine a reaction rate (k) or half-life ($t_{1/2}$) for each CVOC compound. When ln (C/C_o) is plotted against time in hours (see an example plot in Figure 5-4), the slope of the fitted line is the reaction rate, k (hr^{-1}). The degree of fit can be determined by calculating the correlation coefficient (r^2). The r^2 value indicates how well the pseudo first-order model fits the experimental data. Once the rate constant is known, a half-life can be estimated using Equation 5-2 for each organic contaminant of interest in the influent. A half-life is the time period required to reduce the concentration of a contaminant by half. Table 2-1 in Section 2.0 shows the estimated half-lives for various contaminants.

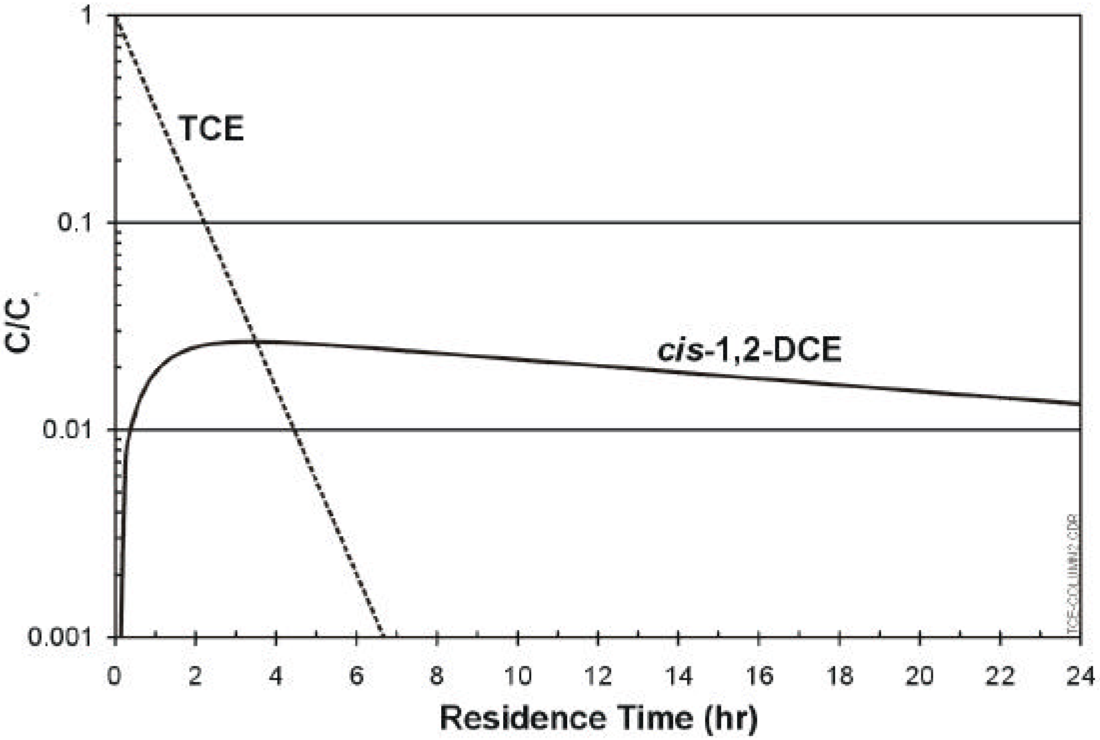


Figure 5-4. Psuedo First-Order Degradation Rate of TCE

$$C \; = \; C_o \, e^{-kt} \tag{5-1}$$

$$t_{1/2} = \frac{\ln(2)}{k} = \frac{0.693}{k} \tag{5-2}$$

When comparing the half-lives obtained for the same compound in columns with different reactive media, the reactive medium which provides the shortest half-life generally is selected. Costs, availability, environmental effects, and other factors also may be considered, as described in Section 4.0.

Residence time can be estimated from the half-life simply by counting the number of half-lives required to bring the concentration of the CVOC down to its MCL. For example, if TCE enters the reactive cell at 1,000 µg/L, eight half-lives are required to degrade TCE to an MCL of 5 µg/L. If the half-life of TCE from the column test was determined to be 2 hours, the required residence time in the reactive cell would be at least 16 hours. If there is more than one CVOC of interest in the influent, the residence time is determined from the CVOC with the longest half-life.

5.3 Measuring the Hydraulic Properties of the Reactive Medium

The hydraulic properties of the medium that are required for PRB design include:

- Hydraulic conductivity (K)
- Porosity (n)
- Bulk density (B).

The K value of the reactive medium is required to determine the flow velocity and residence time of groundwater in the reactive cell. Ideally, the K value for unconsolidated media is determined from constant head permeameter tests (Fetter, 1994). These tests are most reliably conducted in laboratories with conventional permeameter facilities. However, it may also be possible to use laboratory treatability test columns to estimate K by setting up the columns as constant head permeameters.

A constant head permeameter consists of an inlet tube with water level (head) maintained at a height slightly above the outlet level of the column. The water is allowed to flow through the reactive medium in the column until steady-state flow is obtained and the volume of water flowing out over a period of time is measured. K is determined from a variation of Darcy's law:

$$K = \frac{V \cdot L}{A \cdot t \cdot h} \tag{5-3}$$

where V = the volume of water discharging in time t
L = the length of the reactive medium sample
A = a cross-sectional area of the sample
h = the hydraulic head difference across the column.

It is important to prepare a uniformly packed column. For design purposes, K is often represented in units of ft/day.

When the flow velocity is known, a porosity (n) estimate of the reactive medium is required to estimate the volumetric flowrate through the reactive cell. The volumetric flowrate in turn is an indicator of the size of the capture zone of the PRB.

A bulk density estimate (B) for the medium is required to obtain initial estimates of the mass of reactive medium that will be required to fill up the specified dimensions of the reactive cell. Porosity and bulk density can be measured during column testing by pre-weighing the reactive medium before it is packed into the column.

Another way to determine K, n, and B is to send a small sample of the reactive medium obtained from a prospective supplier to a geotechnical laboratory for routine analysis for these three parameters. Because the same type of reactive medium (e.g., granular iron) may vary in particle shape and size distribution among different suppliers, sometimes (even for the same supplier) it is important to obtain a representative sample of the medium from the supplier and have it analyzed for K, n, and B during the design phase. It also should be noted that the actual values of these parameters in the field may differ somewhat from the laboratory-measured values because of differences in packing and settling in the field reactive cell. However, the laboratory measurements do provide a relatively good initial basis for design. Table 5-1 lists the hydraulic conductivities measured for granular iron media obtained from different commercial sources. A bulk density correction factor generally is applied to adjust this parameter for the design of the flowthrough thickness of the field reactive cell (see Section 6.2.2).

Table 5-1. Hydraulic Conductivities for Different Sources of Iron Measured in a Geotechnical Laboratory

Iron Source	Size Range U.S. Standard Sieve Mesh	Bulk Density (lb/ft^3)	Hydraulic Conductivity (K)[a] (cm/sec)	Hydraulic Conductivity (K)[a] (ft/day)
Peerless[b]	–8/+50	NA	7×10^{-2}	198
Peerless[b]	–8/+20	114	6.1×10^{-2}	173
Peerless[b]	–8/+20	150	6.1×10^{-2}	173
Peerless[b]	–8/+16	108	8.1×10^{-2}	230
Peerless[b]	–30/+76	NA	1.7×10^{-2}	48
Master Builders[b], Rancho Cucamonga, CA	–8/+50	NA	9.0×10^{-2}	255
Connelly[b]	–8/+20	110	8.3×10^{-2}	235
Connelly[b]	–8/+50	NA	5×10^{-2}	142
Connelly[c]	–8/+50	146	2.7×10^{-1}	765
Connelly[d]	–8/+50	122	5.5×10^{-2} to 1.9×10^{-1}	156 to 539

(a) Average value from four measurements.
(b) Data supplied by ETI from various PRB sites (ETI, 1999).
(c) Data obtained by Battelle for Dover AFB PRB (Battelle, 2000).
(d) Data obtained from slug tests in the field reactive cell at Dover AFB for comparison (Battelle, 2000).

5.4 Column Tests for Assessing the Longevity of the Reactive Medium

Column tests conducted for contaminant half-life determination also can be used to obtain some indication of the long-term performance potential of the reactive medium with groundwater from a specific site. Concentration profiles can be developed during the column test for inorganic parameters (e.g., plots of pH or Eh versus residence time in the column), just as for the target contaminants. In an iron medium, as conditions become more anaerobic in the column, Eh should decline and pH should increase with increasing distance. Concentrations of anions (nitrate, sulfate, and chloride), cations (Ca, Mg, and Mn), and alkalinity may be measured in the column influent and effluent. Loss of dissolved calcium or magnesium from the groundwater flowing through the column could indicate the potential for precipitate formation in the reactive medium. A comparison of the levels of inorganic constituents in the column influent and effluent can provide a good basis for reactive media selection and longevity assessment. Section 6.4 describes how chemical analysis of the influent and effluent from a laboratory column or a field reactive cell can be used to evaluate the geochemical processes affecting the longevity of the reactive medium.

A more resource-intensive method of evaluating the longevity of a reactive medium is the use of accelerated-flow column tests (Gavaskar et al., 1998; Sivavec, 1996). These tests are not directly required for designing the PRB; however, they provide a means of accelerating the aging of the iron by passing groundwater at a significantly faster rate through the column with reactive medium than would occur at the field site. The advantage is that many pore volumes of groundwater can be passed through the reactive medium in a short time to simulate several years of operation of the field PRB.

Before accelerating the column flow, degradation rates are measured in a column at the expected velocity in the reactive cell at a given site. The flow then is increased to "age" the iron by passing a large number of flow volumes. In the aging process, groundwater species (e.g., DO, cations, and anions) may precipitate out and coat the reactive and adsorptive sites on the medium. Periods of low and high flow are alternated. At each low flow step, as soon as steady state is reached, measurements may be conducted to estimate reaction rates, porosity losses (measured through tracer tests), inorganic profiles, and reaction products.

Caution should be exercised in interpreting the results of accelerated column tests. Aging the reactive medium with 100 pore volumes of flow at 20 ft/day in the laboratory may not exactly mimic the condition of the reactive medium after 1,000 pore volumes of flow at 2 ft/day in the field. Also, reactivity and porosity losses tend to be higher in the first part of the reactive medium. Therefore, extrapolation to the laboratory results to the field situation may not be easy. One precaution in such accelerated-flow tests is to ensure that the flowrate is not set so high that the target inorganic parameters (e.g., DO, pH, ORP, Ca, and Mg) have not leveled off by the time the water exits the column. If the inorganic parameters are leveling off, a fairly representative simulation of field behavior may be possible. Despite all these limitations, accelerated-flow column tests may be the only empirical means for evaluating the longevity of a reactive medium at a given site. Accelerated-flow tests may be considered more an area of investigation for PRB technology developers than for site owners considering routine PRB application.

6.0 Modeling and Engineering Design

Following preliminary assessment, site characterization, reactive media selection, and laboratory testing, the PRB design can proceed. As shown in Figure 2-1 in Section 2.0, designing a PRB involves the following steps:

- **Hydrologic Modeling.** Hydrologic modeling can be used to select and optimize the best PRB location, configuration, width, and orientation that provide sufficient groundwater capture in the targeted region of the aquifer (plume).

- **Reactive Cell Thickness Design.** Reactive cell thickness refers to the length of the groundwater flowpath in the reactive medium that provides sufficient residence (contact) time for the contaminants to degrade to target cleanup levels. This thickness is based on the half-lives of the contaminants and the groundwater flow velocity through the reactive cell. The groundwater velocity can be determined through hydrologic modeling of the selected PRB configuration, width, and orientation.

- **Geochemical Evaluation.** Interactions between the reactive medium and native groundwater constituents, such as DO, calcium, dissolved silica, and carbonate species, may lead to precipitate formation and deposition on the reactive medium surfaces. Over the long-term, precipitation may lead to loss of reactivity and/or hydraulic conductivity of the PRB. For both these reasons, an evaluation of site-specific geochemical parameters and their potential effect on the longevity of the reactive medium needs to be performed.

6.1 Hydrologic Modeling

Hydrologic modeling is an important component of PRB design. Hydrologic modeling analyzes the measured hydraulic characteristics of the aquifer and the reactive medium to:

- Determine a suitable location and configuration for the PRB with respect to the groundwater flow, plume movement, and site-specific features such as property boundaries, building foundations, and buried utilities.

- Determine the width of the reactive cell and, for a funnel-and-gate configuration, the width of the funnel that captures the targeted groundwater.

- Estimate the expected groundwater flow velocity through the reactive cell.

- Determine appropriate locations for monitoring points in the field PRB system and aquifer (discussed in Section 8.0).

- Evaluate and incorporate the effects of complications such as temporal fluctuations in groundwater flow direction and velocity; potential for groundwater or plume underflow, overflow, or bypass; and changes in hydraulic parameters over time.

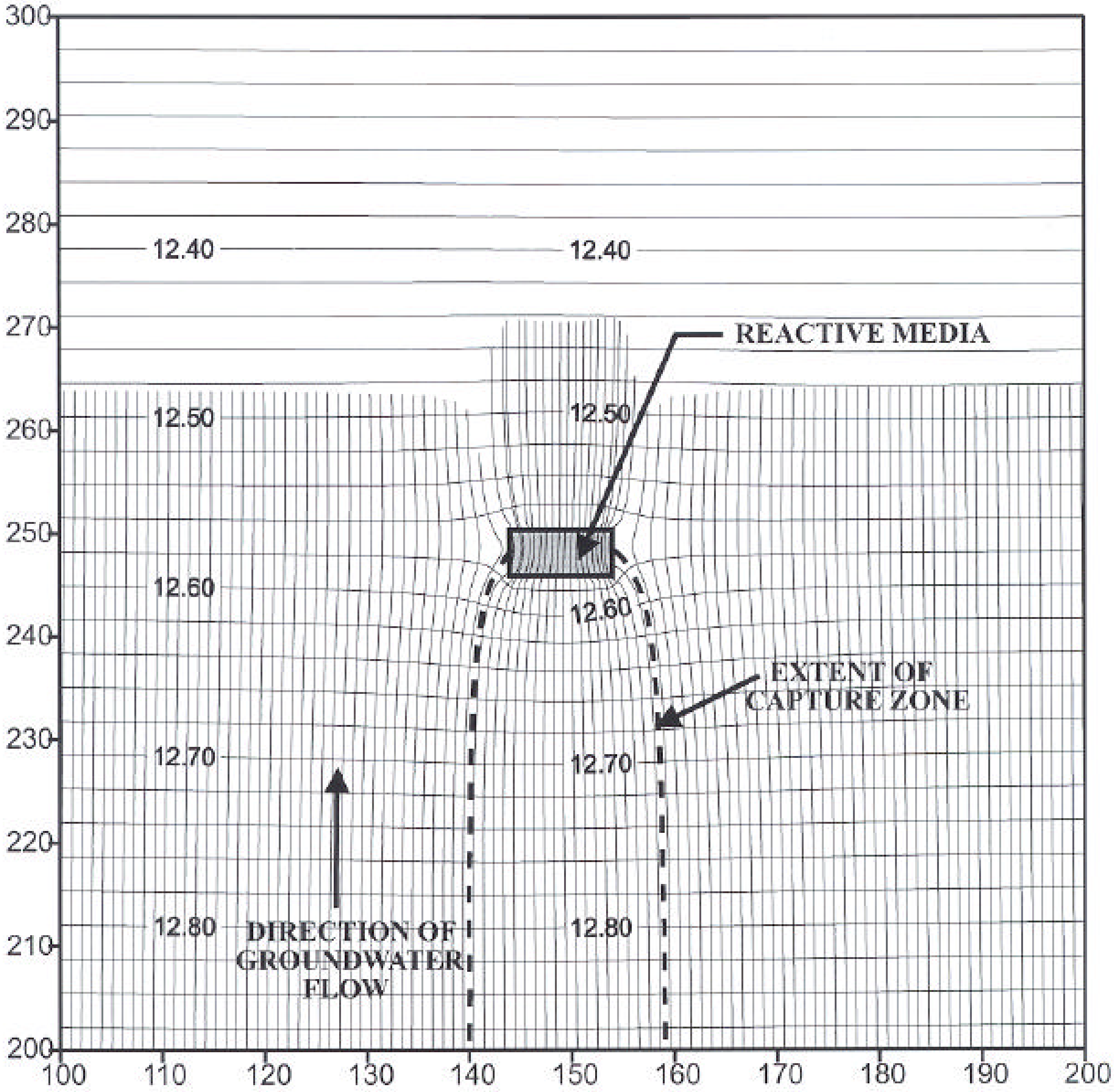
Although several different computer codes have been used for PRB design, the basic steps in hydrologic modeling are common. This section describes the use of models in the evaluation of PRB design and performance. The general requirements of the modeling codes useful for PRB application, a brief overview of the modeling methodology, descriptions of the available codes, and a review of previous modeling studies for PRB design are presented in Appendix C. For most practical purposes, commercially available models such as MODFLOW (flow model) coupled with a particle-tracking model (such as RWLK3D$^{©}$) have been sufficient for the design evaluation and optimization.

The two primary interdependent parameters of concern when designing a PRB are *hydraulic capture zone width* and *residence time*. Capture zone width refers to the width of the zone of groundwater that will pass through the reactive cell or gate (in the case of funnel-and-gate configurations) rather than pass around the ends of the barrier or beneath it. Capture zone width can be maximized by maximizing the discharge (groundwater flow volume) through the reactive cell or gate. Residence time refers to the amount of time contaminated groundwater is in contact with the reactive medium within the gate. Residence times can be maximized either by minimizing the discharge through the reactive cell or by increasing the flowthrough thickness of the reactive cell. Thus, the design of PRBs must often balance the need to maximize capture zone width (and discharge) against the desire to increase the residence time. Contamination occurring outside the capture zone will not pass through the reactive cell. Similarly, if the residence time in the reactive cell is too short, contaminant levels may not be reduced sufficiently to meet regulatory requirements.

The major advantage of constructing a detailed groundwater flow model is that several design configurations, site parameters, and performance and longevity scenarios can be readily evaluated once the initial model has been set up. Thus, the combined effect of several critical parameters can be incorporated simultaneously into one model. Groundwater modeling has been used at most previous PRB installations. In most cases, groundwater flow models have been used in conjunction with particle tracking codes to construct maps showing travel paths and residence times through the reactive cell. The models are usually set up after laboratory column tests have shown the feasibility of the contaminant degradation, and the reaction half-lives and the resulting residence time requirements have been determined. The modeling illustrations for some of the PRB configurations and aquifer conditions are presented in the following sections.

6.1.1 Modeling Continuous Reactive Barriers

The simplest PRB design is a continuous reactive barrier installed in a surficial aquifer and keyed to a confining layer at the bottom. An example simulation for this scenario using MODFLOW followed by a particle-tracking model (RWLK3D$^{©}$) is shown in Figure 6-1. This simulation consists of a 10-ft-long section of reactive cell having a 6-ft thickness in the direction of flow. The aquifer is simulated as a single layer having uniform hydraulic properties with a conductivity of 10 ft/d. The reactive cell is simulated with a hydraulic conductivity of 283 ft/d (0.1 cm/sec). The flow field was simulated with an aquifer gradient of 0.005. Particle tracking techniques were used to delineate the capture zone of the reactive media by delineating flowpaths for 180 days. As indicated by the dashed lines, the capture zone has a width greater than the 10-ft length of the reactive cell. The width of the capture zone will increase or decrease as the ratio of the reactive media hydraulic conductivity to the aquifer hydraulic conductivity increases or decreases, respectively. Residence time through the reactive media can be estimated using particle-tracking methods to ensure sufficient residence time for the degradation reactions



Media: 10 feet long, 6 feet wide (parallel to flow)

K_{media} = 283 feet/day

$K_{aquifer}$ = 10 feet/day

Gradient = 0.005

Figure 6-1. Simulated Capture Zone for a Continuous Reactive Barrier Showing Flowpaths for 180 Days

to occur. In this case, where no funnel walls are used, several short flowpaths into and out of each end of the continuous reactive barrier can occur. Groundwater flowing along these paths does not pass through the entire thickness of the reactive media, and therefore, entrained contaminants may not be fully degraded in these zones unless appropriate safety factors are incorporated into the design. Variations on the straight continuous reactive barrier design mainly include the changes in shape to curvilinear or angled continuous reactive barriers based on site-specific conditions.

6.1.2 Modeling Funnel-and-Gate Systems in Homogeneous Aquifers

At many sites, funnel-and-gate systems may be more appropriate than continuous reactive barriers. The key step in modeling these systems is optimizing the dimensions of the funnel wall so that the capture zone and residence time requirements can be fulfilled. A detailed illustration of the modeling approach for a funnel-and-gate system in relatively homogenous aquifers is presented in Appendix C. This simulation incorporates common PRB features, such as the reactive cell, pea gravel, or funnel walls, into the baseline aquifer model as heterogeneities with the appropriate hydraulic conductivities. Figure 6-2 shows the simulated particle tracking result for this funnel-and-gate system. For the homogeneous aquifer, the hydraulic capture zone is symmetrical and extends beyond the width of the gate. The flow divide upgradient of the funnel walls is at the midpoint of the funnel walls on each side. Mixing of the water flowing through the gate and water flowing around the barrier takes place downgradient.

A more complex funnel-and-gate scenario was used for simulation of a funnel-and-gate system with two gates, one of which was installed at Dover AFB (Battelle, 1997b). The final design for this system is shown in Figure 6-3. Each gate consisted of an 8-ft-diameter caisson containing reactive media, and pre- and post-treatment zone sands. The reactive media section consisted of a 4-ft by 4-ft zone surrounded by a pretreatment and post-treatment zone up to 2 ft thick. Funnel walls were constructed using sheet piling up to a depth of about 40 ft. The funnel walls extended 30 ft between the two gate locations and 15 ft on each end of the installation. A single layer, two-dimensional (2-D) groundwater flow model was used with the aquifer assumed to have a uniform hydraulic conductivity. The calculated flow field was used to estimate the capture zones for the funnel-and-gate installation. At this site, several combinations of K values and temporal variations in groundwater flow conditions were simulated. Figure 6-3 shows the details of flowlines through one of the reactive gates. Based on the simulation, the estimated residence time in the gates ranged from 4 to 26 days and the capture zone ranged from 52 to 54 ft. The capture zone for the entire system and the effect of temporal variations in regional groundwater flow on the portion of the plume captured are shown in Figure 6-4. In this case, it appears that the effect of flow direction fluctuations on plume capture would be minimal and can be easily incorporated in the design. Another aspect at this site is the slow flow velocity of ambient groundwater (around 0.1 ft/d), which may result in very long cleanup times due to slow plume movement. Another observation from this and other flow system simulations presented here is that the flow lines retain their normal course until they reach very close to the funnel walls before turning toward or away from the funnel walls. Therefore, the groundwater flow monitoring efforts in the upgradient aquifer have to be concentrated on this very small zone to observe meaningful changes in flow directions.

6.1.3 Modeling PRBs in Heterogeneous Aquifers

Modeling studies and barrier designs at most existing PRB sites have been primarily based on the assumption that the aquifer sediments in the vicinity of the PRB are homogeneous.

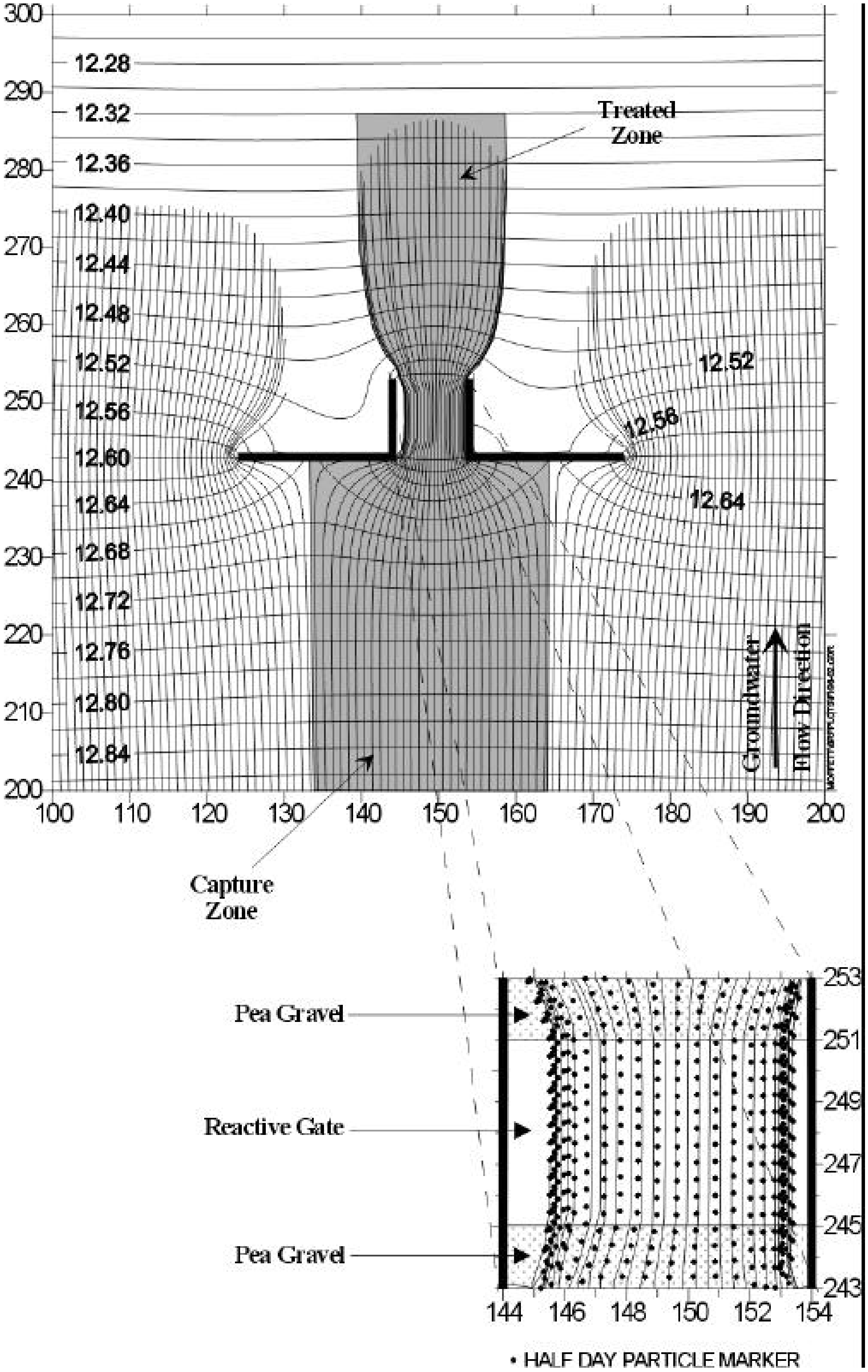


Figure 6-2. Simulated Particle Pathlines Showing Capture Zone for a Funnel-and-Gate System in a Homogeneous Aquifer

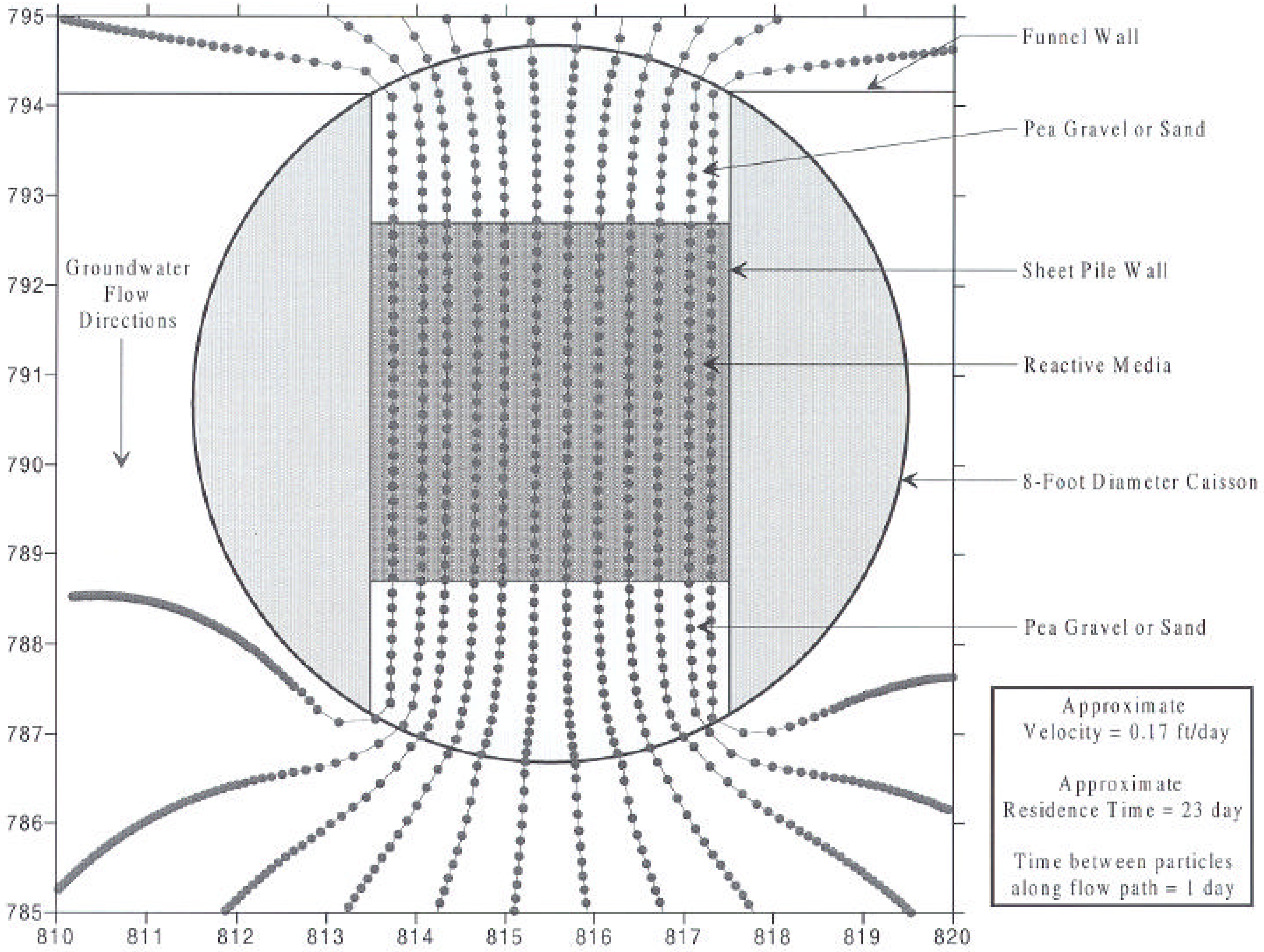
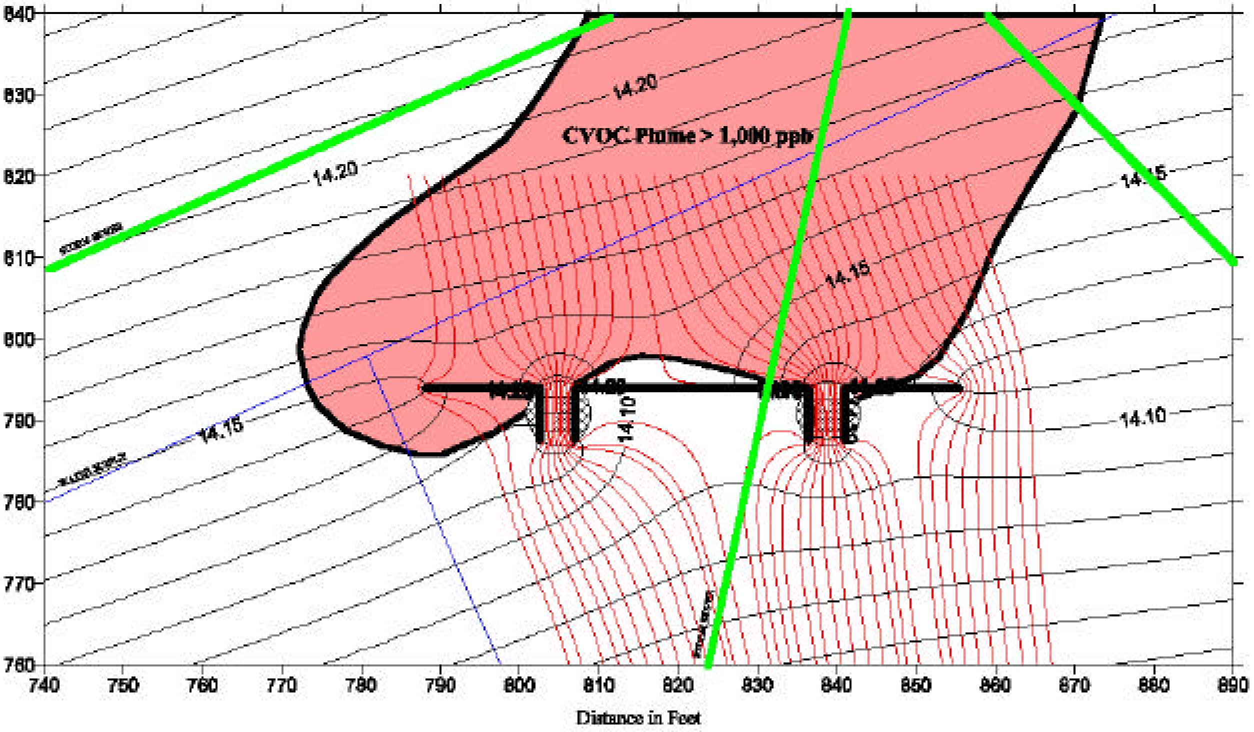


Figure 6-3. Details of Simulated Flowpaths in a Reactive Gate of the Funnel-and-Gate-Type PRB at Dover AFB

(a) May 1994



(b) July 1997

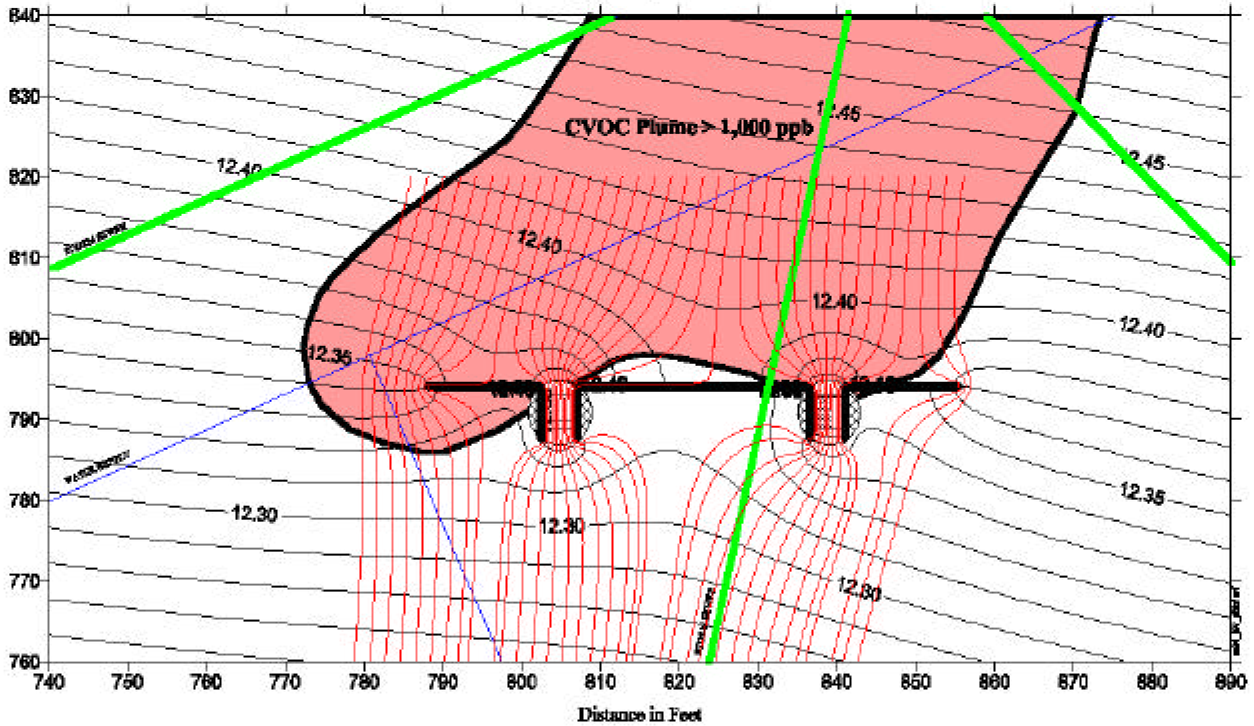


Figure 6-4. Capture Zones for the PRB at Dover AFB Showing the Effect of Fluctuating Flow Directions

However, at many sites, there may be strong heterogeneity in the sediments. This heterogeneity develops mainly due to the variations in depositional environments of the sediments. The general implications of heterogeneity are that more detailed site characterization is required and the models are more complex. The symmetrical capture zones seen in homogeneous sediments become asymmetrical and difficult to predict without detailed characterization and modeling.

Figure 6-5 shows the results of modeling conducted at former NAS Moffett Field (Battelle, 1998). The capture zones at this site, as seen from the particle tracking maps, are highly *asymmetrical*. In the less permeable shallow layers (Layers 1 and 2), there is hardly any movement of particles over 25 days. In the more permeable Layer 3, the particle movement is very fast upgradient of the gate but very slow upgradient of the funnel walls. In the more permeable Layer 4, the particle movement is very fast in front of the west funnel wall but somewhat slower on the eastern side. These irregularities exist because the lower part of the PRB (Layers 3 and 4) is located in a high-conductivity sand channel, whereas the upper part is located in lower-conductivity interchannel deposits. The location of the sand channels at the site was determined based on existing Base-wide site characterization maps and from localized CPT data generated during additional site characterization activities that were conducted to aid the design of the barrier. The irregularities in flow may result in vastly different residence times in the reactive cell. Pea gravel sections along the upgradient and downgradient edges of the reactive cell help to homogenize the vertical and horizontal flow to some extent.

A similar situation is reported by Puls et al. (1995) for the Elizabeth City, NC site. At this site, the geology is characterized by complex and variable sequences of surficial sands, silts, and clays. Groundwater flow velocity is extremely variable with depth, with a highly conductive layer at roughly 12 to 20 ft bgs. The reactive cell was installed in the sand channel to capture the contamination along the fastest flowpath.

These examples illustrate the benefit of placing the reactive cell in a zone of high conductivity that forms a preferential pathway for most of the flow and contaminant transport through the aquifer. Additionally, the dependence of capture zones on aquifer heterogeneities emphasizes the need for detailed site characterization and adequate hydrogeologic modeling prior to PRB design and construction. Particle tracking simulations, such as the one shown here along with a flow model based on good site characterization, also can help in optimizing monitoring well locations for evaluating the performance of the barrier.

6.1.4 Summary of Important Results from Modeling Studies

Several general observations regarding PRB design modeling can be made from the illustrations presented above, the detailed example provided in Appendix C, and from previous modeling studies. Most importantly, modeling can be used to evaluate and optimize different PRB configurations and dimensions for a given set of design parameters. Different widths of a continuous reactive barrier, gate, or funnel can be simulated to evaluate any trade-offs that may occur between various design parameters (e.g., increased hydraulic capture width versus longer residence time in the reactive cell). The illustrative modeling scenarios in Appendix C result in the following considerations for PRB design.

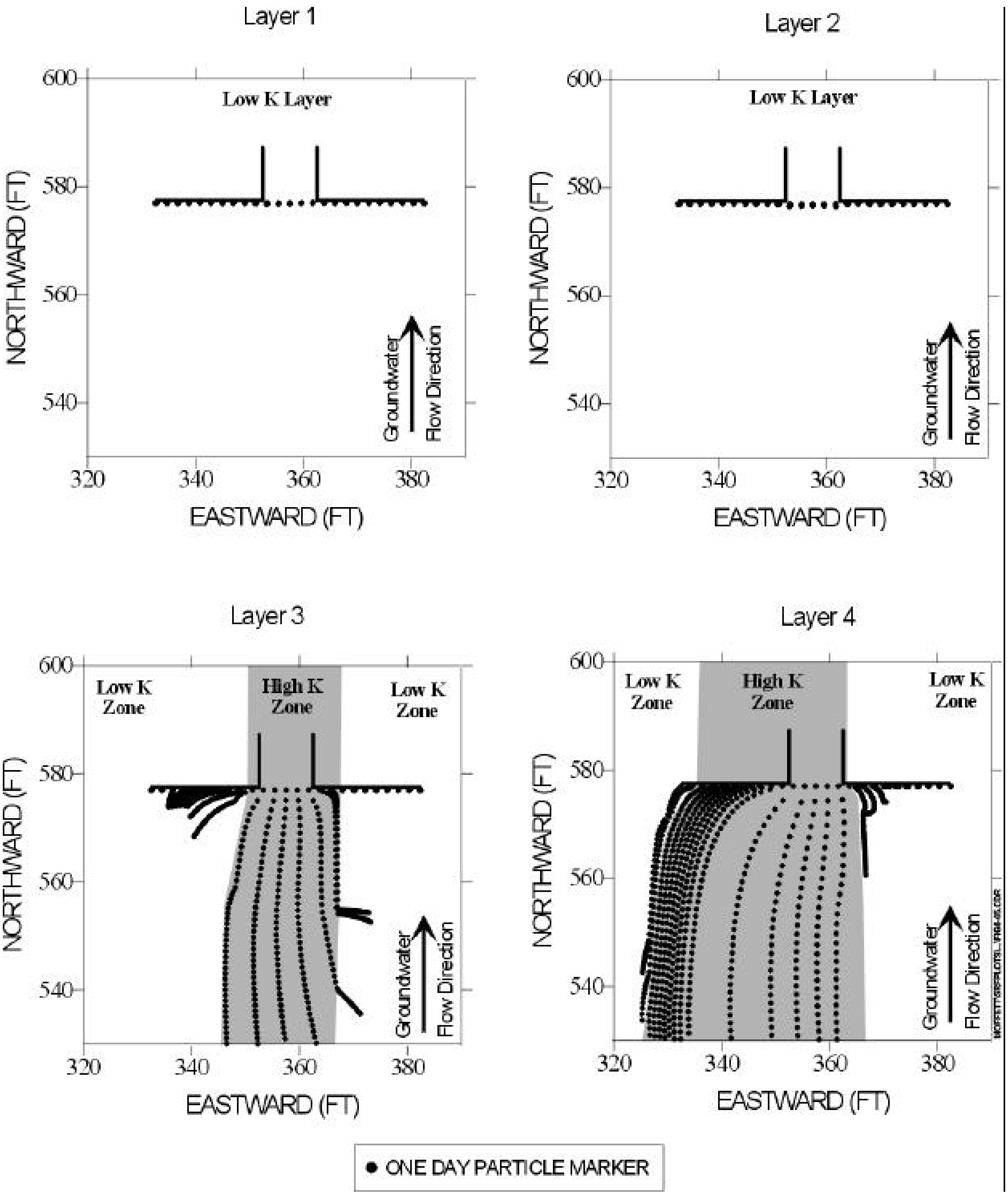


Figure 6-5. Funnel-and-Gate System at Former NAS Moffett Field Showing the Effect of Heterogeneity on Capture Zones (Battelle, 1998)

- While designing the dimensions of the reactive cell, it is important to note that $K_{aquifer}$ is the sensitive parameter for discharge and residence time through the reactive cell as long as the K_{cell} is several times (about 5) higher than $K_{aquifer}$. Reductions in K_{cell} do not significantly impact discharge and residence times through the gate until the ratio of K_{cell} to $K_{aquifer}$ drops below about 5:1, at which point K_{cell} becomes an increasingly sensitive parameter. This type of analysis can be used with site-specific models to evaluate the effect of decreasing reactive cell permeability over time on the performance of the permeable cell. Appropriate safety factors (in terms of additional reactive cell width or larger particle size reactive medium) then can be incorporated into the design for anticipated changes in capture zone and residence time.

- As discharge through the reactive cell increases, capture zone width increases, and travel time through the reactive cell (residence time) decreases. For the scenarios simulated in this illustration, residence times in the reactive cell ranged from more than 200 days for low-K (0.5 ft/day) aquifers to roughly one day for higher-conductivity aquifers (100 ft/day). The estimates of residence times based on particle tracking can be used to optimize the flowthrough thickness of the reactive cell required for achieving the desired reduction in contaminant levels.

- Particle tracking may be used to design a performance-monitoring network along specific flowpaths. As shown in the simulations, the flowpaths do not bend toward or away from the PRB until the particles are within a few feet of the PRB. Therefore, hydrologic monitoring efforts for capture zone determination need to be focused on these small transitional zones. Particle tracking also is useful if tracer tests are to be conducted in the reactive cell or its vicinity. Some particle tracking codes also can incorporate the solute transport processes, which can be used to evaluate the effects of dispersion within the reactive cell. The fastest travel times determined from the advective-dispersive simulations then would be used to determine the safety factor required in designing the reactive cell.

- For funnel-and-gate configurations, hydraulic capture zone width appears to be most sensitive to funnel length and aquifer heterogeneity. Capture zone width is generally greater for higher values of K_{cell} when $K_{aquifer}$ is held constant. At ratios greater than 5:1 between K_{cell} and $K_{aquifer}$, capture zone width does not change significantly when only the K_{cell} is varied. Higher conductivity aquifers have larger capture zones relative to less conductive aquifers for the same K_{cell}. Capture zone width is more sensitive to variability in $K_{aquifer}$ relative to changes in K_{cell}.

The following design results from previous modeling studies (Starr and Cherry, 1994; Shikaze, 1996) are also worth noting:

- In a funnel-and-gate configuration, the maximum absolute discharge (groundwater flow volume) through the gate occurs when the funnel walls are at an apex angle of 180 degrees (straight barrier).

- For all apex angles, the maximum discharge occurs when the funnel is perpendicular to the regional flow gradient.

- ☐ A balance between maximizing the hydraulic capture zone size of the gate and maximizing the residence time in the reactive cell should be achieved through modeling. In general, for a funnel-and-gate system, hydraulic capture zone size (or discharge through the gate) and residence time are inversely proportional. The residence time usually can be increased without affecting the size of the capture zone by increasing the width of the gate.

- ☐ For funnel walls at 180 degrees (straight barrier), the hydraulic capture zone size (or discharge) increases with increasing funnel width. However, the relative capture width decreases dramatically as the funnel width increases. The relative capture zone width is the ratio of the capture zone width to the total width of the funnel-and-gate system.

- ☐ For a constant funnel width, the absolute and relative capture zone width increase with gate width. Therefore, it is desirable to have a gate as wide as is economically possible.

- ☐ For a given funnel-and-gate design, the capture zone size increases with increase in K_{cell} relative to the aquifer. However, there is relatively little increase in capture zone size when the K_{cell} is more than 10 times higher than $K_{aquifer}$. Therefore, in selecting the particle size of the reactive medium, it is useful to note that the resulting K_{cell} value need not be more than about 10 times higher than the K of the surrounding aquifer.

6.2 Reactive Cell Thickness Design

The reactive cell thickness is determined by the half-life (residence time) requirements of the target contaminants for a given reactive medium and by the velocity of groundwater through the reactive cell.

6.2.1 Determining Flowthrough Thickness of the Reactive Cell

Based on the groundwater velocity expected in the field reactive cell and the required residence time, the flowthrough thickness (b) of the field reactive cell can now be determined as:

$$b = V \bullet t_w \qquad (6\text{-}1)$$

where V = velocity in the flow direction
t_w = residence time.

Hydrologic modeling (Section 6.1) may be used to determine the expected groundwater velocity through the reactive cell. Correction factors are required for temperature and bulk density (see Section 6.2.2). Safety factors may be incorporated into the calculated thickness to account for seasonal variations in the flow, potential loss of reactivity of the iron over time, and any other field uncertainties (Section 6.3).

6.2.2 Correction Factors for Field Application

Some corrections are required to adjust the degradation rate from laboratory data for field application. Temperature and bulk density are the two parameters that often differ between laboratory and field conditions. The temperature of the groundwater in the field application (typically 10°C) is generally lower than the room temperature of the laboratory column tests (typically 20 to 25°C). The empirical residence time may need to be increased to account for the lower temperature. For example, Senzaki and Kumagai (1988a and 1988b) found that the half-life of 1,1,2,2-TCA increased by 10% when temperature declined from 20 to 10°C. Jeffers et al. (1989) provide a discussion on the use of Arrhenius temperature dependence to adjust for the effects of temperature on degradation rate of organic compounds. The Arrhenius equation relates the reaction rate (k) to absolute temperature (T) as follows:

$$k \propto e^{-E/RT} \tag{6-2}$$

where E is the activation energy, and R is the universal gas constant (8.314 Joules/mol Kelvin). Equation 6-2 can be rearranged as:

$$1n\ k = (1n\ A) - (E/RT) \tag{6-3}$$

where k = first-order reaction rate constant
A = frequency factor for the reaction
E = activation energy
R = ideal gas constant
T = absolute temperature.

A plot of ln k versus 1/T should give a straight line with a slope of −E/R and an intercept on the l/T axis of (lnA)/(E/R). Experimental data from controlled-temperature column tests indicate that the effect of temperature follows the Arrhenius equation (ETI, 1997). Based on the fitted equation, at 15°C in the field, TCE degradation rates could be expected to decline by a factor of 1.4 from those measured in the laboratory at 23°C. Field observations at a test site in New Jersey have shown that the degradation rate declines by a factor of 2 to 2.5 at temperatures of 8 to 10°C compared with laboratory rates. Similar results have been observed at other field sites.

The applicability of the Arrhenius equation was demonstrated in another study (Su and Puls, 1998), in which batch tests were conducted to examine the effects of temperature (10 to 55°C) on TCE degradation by metals, including granular iron. In these batch tests, the normalized half-life for TCE with granular iron from Peerless Metal Powders and Abrasives, Inc., Detroit, MI fell from about 40 hrs to below 10 hrs when the temperature was increased from 10 to 25°C. From 25 to 40°C, and from 40°C to 50°C, the decrease in half-life was not as dramatic. For granular iron from Master Builders the normalized half-lives decreased from about 25 at 10°C to below 10 at 25°C, indicating that iron from different sources may behave differently with temperature. In this study, the activation energy (E) term in Equation 6-3 was estimated at 37.4 kilo-Joules/mole for Peerless iron and 32 kilo-Joules/mole for Master Builders iron.

Temperature versus reaction rate relationships have not yet been determined experimentally for PCE, DCE, or VC. Given PCE's similar behavior to TCE in dehalogenation reactions, it may be assumed that a similar temperature factor would apply.

The bulk density of the reactive cell in the field is generally lower than the bulk density measured in the laboratory because of different settling conditions for the medium. Therefore, the surface area of reactive medium per unit volume of groundwater in the field may be lower than the surface area measured during column testing. Also, degradation rates (or half-lives) are proportional to the specific surface area of the reactive medium (Gillham, 1996; Sivavec and Horney, 1995), so the field residence time must be increased to account for the lower expected ratio of reactive surface area to volume of solution. Currently, there is no clear indication of how large the bulk density correction factor should be. To some extent, this factor would depend on the efficiency of the construction and on how well the reactive medium consolidates after construction. Gillham et al. (1993) reported that an increase in the surface area of iron by a factor of 5 caused the half-life for TCE to decline by a factor of about 2.5. Reduced iron surface area per unit volume of groundwater is the reason why 100% iron degrades faster than iron-sand mixtures. Also, finer iron granules generally have larger surface areas and faster degradation rates.

6.3 Safety Factors for PRB Design Parameters

One of the major design issues in PRB construction is the incorporation of appropriate safety factors into the design. This is a tricky issue, because the estimates of input parameters used in the PRB design can vary by an order of magnitude or more. The parameters that can affect the performance due to variations include the influent contaminant concentrations, the hydraulic gradient, flow direction, and hydraulic conductivity. In addition, potential changes in groundwater geochemistry, porosity, and seasonal variations in temperature also should be considered.

The influent contaminant concentrations may change by several orders of magnitude either as higher-concentration parts of the plume reach the PRB or as a result of changes in recharge or flow patterns over time. The hydraulic gradient generally does not change more than an order of magnitude over time. On the other hand, the groundwater flow direction can change several tens of degrees over time, and hydraulic conductivity may vary by as much as a factor of 5 or 10 between estimated and actual field conditions, even with careful site characterization. These uncertainties may result in the need for wider and thicker PRBs to ensure that the residence time and capture zone requirements are fulfilled.

Detailed and careful site characterization generally can reduce the uncertainty in the parameters to a more acceptable range. It also can prevent future performance failures by ensuring that the minimum requirements for PRB location, width, depth, and thickness are met. However, it may not be possible to incorporate the full range of hydraulic parameter uncertainty into the PRB design, because such caution could lead to unacceptably high capital investment requirements. It is probably sufficient to use a reasonable safety factor, in the range of about 2 to 3 times the calculated flowthrough thickness at most sites. The exact value of this safety factor at a given site depends on the judgment of the design managers concerning the uncertainty in the input parameters (e.g., groundwater velocity) used in the design and in site-specific risk requirements. The safety factor can be reduced by modeling the PRB for a full range of input parameters (e.g., groundwater velocity, groundwater flow direction, and contaminant concentrations) expected at the site, rather than using average values.

A further safety factor can be incorporated into the final design width of the reactive cell, if any perceived uncertainty about groundwater flow velocity and direction exists as a result of either seasonal variations or limitations of site characterization measurements. Estimating very localized groundwater movement (within a few feet) can be difficult, especially with smaller plumes, and local flow characteristics may be different from regional flow characteristics. The more the actual flow direction deviates from the perpendicular (to the face of the reactive cell), the less likely it is that the targeted groundwater (plume) will be captured, even though the total capture volume may be the same. Such flow variations can be accounted for in the computerized modeling simulations and incorporated with a suitable safety factor into the width of the reactive cell to account for the reduced efficiency of capture. By simulating a wide range of hydraulic flow conditions (including flow direction), optimum orientation and dimensions of the PRB can be designed.

6.4 Geochemical Evaluation of the PRB

Concern over the longevity of permeable barriers arises for contaminant plumes that are expected to persist for the next several years or decades. However, no PRBs have been in operation for more than six years. During this time there have been no reported failures, nor is there a consensus on the factors that would cause them to lose their reactive or hydraulic performance.

Based on studies of geochemical processes in column tests and in existing field PRBs, there seem be two main reasons that PRB performance could decline. First, the reactivity of granular iron, or other reactive media, could diminish over time until it eventually allows breakthrough of the contaminants of concern. Granular iron, currently the most prevalent reactive medium in use, has not been studied for sufficiently long times in either laboratory or field PRB systems to define the performance lifetime of a barrier. In one accelerated column study (Gavaskar et al., 1998) with granular iron (Peerless Metal Powders and Abrasives, Detroit, MI), the half-life for TCE increased substantially after 1,200 pore volumes of groundwater flow. Samples of the iron were examined by scanning electron microscopy (SEM) and x-ray diffraction (XRD), which indicated the presence of iron oxyhydroxide and iron carbonate nearest the influent end. Carbonate precipitates (calcite and aragonite) were found in the bulk iron throughout the column. These precipitates, as well as the possibility of iron surface passivation by dissolved silica, have also been reported in studies involving groundwater analysis (inorganic parameters) and analysis of iron core samples from field PRBs at Dover AFB, former NAS Moffett Field, and former Lowry AFB. Trends in the distribution of inorganic parameters at other permeable barrier sites, including Alameda Point, U.S. Coast Guard Support Center at Elizabeth City, NC, and Denver Federal Center, have similarly been attributed to precipitate formation in the iron (Battelle, 1999). Additional research is required in this area to understand the relationship between geochemical processes and loss of reactivity.

Second, inorganic precipitates formed in the reactive medium could occupy the available pore space and eventually reduce the porosity and hydraulic conductivity of the PRB. In the highly reducing environment produced by zero-valent iron, dissolved species, including oxygen, carbonate, sulfate, calcium, magnesium, iron, and silica, can potentially interact to form precipitates that could deposit on the iron or within the pore spaces. Due to their irregular shape and broad size distribution (such as –8+40 or –8+50), the granular iron typically used in PRBs tends to have a large amount of void space; porosities typically range from 55 to 65% (Battelle, 1999). As shown from the modeling described in Section 6.1, this type of granular medium has considerable capacity to accept such precipitates before its hydraulic performance is significantly affected. On the other hand, even a thin or mono-molecular layer of precipitates on the iron surface may be enough to prevent access of contaminants to reactive sites on the iron. Additional research is needed in this area to understand the relationship between geochemical processes and loss of hydraulic performance.

The composition of the site groundwater has a strong bearing on the amount of precipitation encountered in a PRB system. Some column studies have shown that precipitation and clogging can be more severe in the entrance to the iron zone when influent DO content is high (Mackenzie et al., 1999). In these experiments a "solidified" zone of iron caused a rapid rise in pressure between a positive displacement pump and the entrance to the column. Clogging of this sort would have greatly reduced flow in a passively fed system, such as would be encountered in an in situ barrier. The researchers in the Mackenzie et al. (1999) study noted that short-term porosity losses are controlled by precipitation of $Fe(OH)_2$ and entrapment of a film of H_2 gas at the iron surface. $Fe(OH)_2$, $FeCO_3$, and $CaCO_3$ became important porosity controls at longer treatment intervals, and the appearance of calcium carbonate depended on the carbonate content of the groundwater.

Given these geochemical factors, and the uncertainties associated with their effects, it may be desirable during the PRB design process to evaluate the longevity of the PRB in terms of:

- Site characterization data (inorganic parameter levels in the site groundwater)
- Column test data (inorganic parameter levels in the groundwater influent and effluent to the column containing reactive medium)
- Geochemical modeling.

The sampling and analysis of field parameters (DO, pH, ORP, and conductivity) and other relevant inorganic parameters (including Ca, Mg, NO_3^-, SO_4^{-2}, and Cl^-) were discussed in Section 3.3. Use of these parameters in geochemical evaluation/modeling and their role in evaluating the longevity of the PRB are discussed in the following two subsections, and are followed by a brief review of further geochemical modeling options.

6.4.1 Geochemical Evaluation with Simple Inorganic Measurements

Inorganic parameters easily monitored during column tests are pH, ORP (Eh), DO, and conductivity. Inorganic parameter measurements should indicate that geochemical conditions inside the reactive medium are conducive to reductive dechlorination. For example, redox measurements should be low and pH should remain close to the steady-state value measured at the beginning of the column test.

DO measurements generally are taken in the field during groundwater collection to determine if the groundwater is aerobic or anaerobic. DO probes are useful for measuring oxygen levels in aquifer groundwater, but generally yield uncertain numbers inside a reactive cell, because iron scrubs oxygen to levels that are many orders of magnitude lower than can be measured by a DO probe.

Conductivity is useful for determining whether the concentration of dissolved ions in the groundwater are changing as water passes though the reactive medium. For example, groundwater entering the reactive medium may become diminished in dissolved ion content due to precipitation reactions brought about by the pH and redox changes. Although details about the precipitation process can only be found by analyzing the inorganic constituents in the water, conductivity measurements provide a quick method to determine if precipitation could be occurring.

6.4.2 Geochemical Evaluation with Other Inorganic Measurements

As water moves through the reactive medium, changes (losses) are often noted between the influent and effluent concentrations of native inorganic species. A change or loss could be an indication that precipitation is occurring within the reactive cell. Due to the large geochemical dissimilarity between a reactive medium (such as iron) and the native aquifer material, changes will be most notable at the influent end of the reactive cell. Although it is usually unclear how much of this precipitate mass stays in the reactive medium and how the mass affects reactivity, the amount of inorganic species (such as calcium and carbonate) lost as the groundwater moves through the reactive medium may be an important indicator of the type and degree of precipitation that is occurring.

Trends in groundwater geochemistry can be detected by routine analysis of some key inorganic species in native groundwater both before (influent) and after (effluent) it has passed through the reactive medium. The influent analysis can be obtained during site characterization. Both influent and effluent concentrations of the inorganic species can be obtained by sampling the influent and effluent to the columns during the laboratory testing stage. The influent and effluent concentrations of various inorganic species can be compared to determine losses that result from interactions with the reactive medium.

Indications that chemical precipitation reactions are taking place in a PRB can sometimes be determined by comparing inorganic parameters along the flowpath in a column test (or in the post-construction monitoring stage in the field PRB system). For example, Table 6-1 illustrates the analysis of groundwater along the flowpath through the reactive medium used at former NAS Moffett Field. The reactive medium samples represent intermediate points along the flowpath through the reactive medium where the speed of some of the reactions can be observed. It can be seen in Table 6-1 that concentrations of Ca, Mg, alkalinity, nitrate, and sulfate are significantly lower in the reactive medium than in the influent. Changes in magnesium are less pronounced compared to Ca and alkalinity, but are also apparent.

Comparing concentrations in the influent and effluent, it can be seen that there is significant decline in dissolved solids, which can be attributed to loss within the reactive cell. Table 6-2 shows the average changes in species concentrations between the influent and effluent sections (equivalent to the influent and effluent from a column test). It can be seen that losses of some species are quite high. For example, alkalinity and sulfate each decline by more than 300 mg/L. These losses also are substantial, relative to the respective influent concentrations; specifically, Mg, Ca, nitrate, and sulfate each decrease by more than 90% and alkalinity decreases by 85%. Some ions behave more conservatively, notably Cl (7%) and Na (18%), while K is intermediate at 34% decline.

Table 6-1. Illustrative Results of Inorganic Chemical Measurements for Groundwater Flow through a Column of Reactive Medium (Iron) Using Former NAS Moffett Field Data as an Example

Sample Location[a]	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Iron (mg/L)	Alkalinity[b] (mg/L)	Chloride (mg/L)	Nitrate (mg/L)	Sulfate (mg/L)
Influent to the Reactive Medium								
Influent	164E	65.7E	33.6E	U	215	45.2	1.5	329
	163E	63.7E	31.9E	U	289	45.7	U	335
	177	72.8	38.5	U	276	31.3	1.8	264
	164	63.9	35	0.118	310	46.1	2.8	342
Groundwater in the Iron Medium								
Upgradient iron	2.02B	30.4	36.1	U	U	38.3	U	56.7
	2.25B	17.5	34.3	U	89.2	37.8	U	21.8
	3.49B	32.8	32.6	U	70.8	39.5	U	94.4
	8.27	16.3	33	U	62.2	39	U	51
Down-gradient iron	0.921B	0.349B	36	0.029B	14.3	42.4	U	1
	1.48B	0.488B	35.7	0.044B	14.1	43.3	U	1.1
	0.486B	0.852B	34.7	U	16.6	41.2	U	4.2
	87.8E	1.16EB	41.6E	0.035B	134	39	U	111
Effluent from the Reactive Medium								
Effluent	1.41EB	0.593EB	26E	0.347	12.4	41.7	U	1
	5.21	1.13B	27.1	0.326	U	39.1	U	4.6
	7.51	2.31B	28.5	0.053B	13.6	37.1	U	11
	13.2	0.327B	32.1	U	19.4	36.5	U	29

(a) Multiple measurements.

(b) Alkalinity as $CaCO_3$.

U = The compound was analyzed but not detected at or above the specified reporting limit.

B = The compound was detected in the associated method blank.

E = The amount reported exceeded the linear range of the instrumentation calibration.

Table 6-2. Average Changes in Species Concentrations Between Influent and Effluent from the Reactive Medium Using Data from Former NAS Moffett Field as an Illustration

Section/Change	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	Alkalinity (mg/L)	Cl (mg/L)	Nitrate (mg/L)	Sulfate (mg/L)
Influent	35.5	2.1	66.9	165.4	412	42.2	2.0	333
Effluent	29.1	1.4	1.0	10.4	62	39.1	0.0	18.0
Change	6.4	0.7	65.9	155	350	3.1	2.0	315
% Change	18%	34%	98%	94%	85%	7%	100%	95%

As seen in Table 6-1, the decrease in calcium, nitrate, and sulfate concentrations appears to take place quickly in the iron. Concentrations of these ions decrease sharply as the water enters the upgradient portion of the reactive medium. However, following this initial decline, the concentrations of these ions remain steady as water moves through the rest of the reactive medium, which suggests that the kinetics of the controlling reactions for these ions take place on a similar time scale as the residence time of groundwater in the reactive cell. The appearance of steady-state conditions in the downgradient portion of the reactive medium suggest that reactions are completed by the time water reaches the downgradient end of the iron.

Such changes in inorganic constituents suggest that inorganic compounds are precipitating within the reactive medium as a result of changes in pH and Eh. For example, reductions in the concentrations of alkalinity, calcium, and magnesium are believed to be caused by precipitation of aragonite or calcite ($CaCO_3$) and magnesite ($MgCO_3$). The magnesium concentration also may be affected by precipitation of magnesium hydroxide (brucite). Sulfate concentrations are not sufficiently high to cause precipitation of minerals, such as gypsum ($CaSO_4 \cdot 2H_2O$). It is more likely that reducing conditions lead to reduction of sulfate to a lower oxidation state of sulfur, such as sulfide, which then precipitates as FeS or FeS_2. Other possible precipitates include ferrous carbonate (siderite), iron hydroxide, and "green rust," a compound of ferrous or ferric iron containing hydroxide, chloride, and sulfate.

A rough estimate of the amount of precipitation that may be expected to occur in the reactive medium in a field PRB can be obtained by measuring the losses (differences) of the inorganic species between the influent and effluent in a column test, without measuring intermediate concentrations. The reduced data set in Table 6-2 can be used to roughly estimate these losses, as shown in Table 6-3. The concentrations in Table 6-2 were multiplied by the estimated volumetric flowrate through the reactive cell designed at the former NAS Moffett Field site for a groundwater velocity range of 0.2 to 0.5 ft/day (310,000 L/yr at 0.2 ft/d and 775,000 L/yr at 0.5 ft/d). Table 6-3 shows that the total solids produced per year ranged from 279 to 697 kg. However, the distribution of inorganic matter may not be even throughout the reactive cell. For example, the bulk of the precipitation may take place in the upgradient portion of the reactive cell. The true difficulty lies in the inability to relate these groundwater inorganic parameter losses to the degree of loss of reactive sites on the reactive medium surfaces.

Table 6-3. Estimated Annual Loss of Inorganic Species Due to Precipitation at Former NAS Moffett Field

Flowrate[a] (ft/d)	Na (kg)	K (kg)	Mg (kg)	Ca (kg)	Alkalinity (kg)	Cl (kg)	Nitrate (kg)	Sulfate (kg)	Total (kg)
0.2	2.0	0.2	20	48	109	1.0	0.6	98	279
0.5	5.0	0.6	51	120	272	2.4	1.5	244	697

(a) Estimated from hydrogeologic modeling of the PRB-aquifer system.

Dissolved silica is another inorganic constituent present in groundwater that is of potential concern to the longevity of a barrier. Monomeric silicic acid, H_4SiO_4, is known to form polymers that may coat iron grains, producing a passivating film. It is unknown whether or to what extent dissolved silica acts as a corrosion inhibitor for granular iron. Figure 6-6 shows the distribution of dissolved silica (as SiO_2) in the PRB at former NAS Moffett Field. The trend line is for visual effect and is not based on modeling. Note that the overall behavior of silica is similar to that of other inorganic species, whose concentrations decrease due to precipitation.

At this stage of development of the PRB technology, there is no way of linking the mass of precipitates generated in the reactive cell to the depletion of reactive surface area in the reactive medium. Several studies currently are being conducted to address this issue.

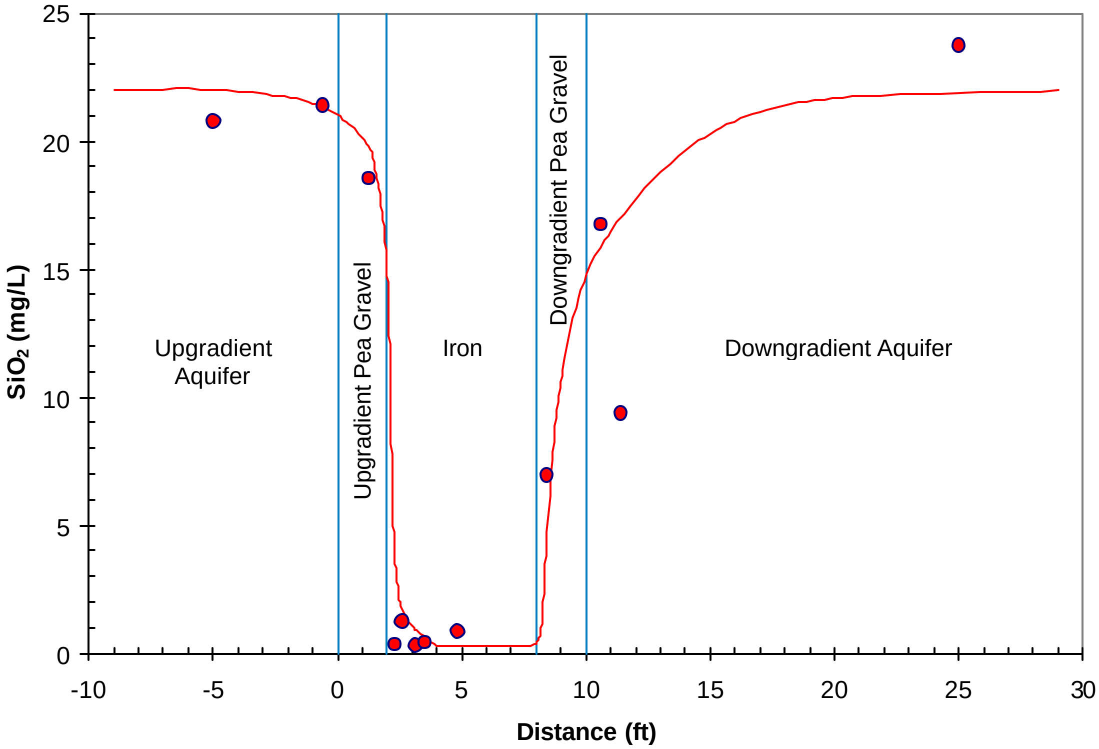


Figure 6-6. Distribution of Dissolved Silica in the PRB at Former NAS Moffett Field

6.4.3 Geochemical Modeling

The geochemical evaluation described in Sections 6.4.1 and 6.4.2 should be possible without significant resources being expended, and should be sufficient for most full-scale PRB applications. If more detailed evaluation is required, Appendix D describes the use of computerized geochemical modeling for evaluating precipitation reactions and the longevity of a PRB. In addition, core samples of the reactive medium can be analyzed after suitable intervals (after the field PRB is installed) for physical evidence of precipitates and confirm their existence (see Section 8.3.3). Geochemical modeling and core analysis are specialized analytical tools that are generally suitable for research work undertaken for technology development purposes. However, if reactivity or flow problems develop at PRB sites, these additional tools may be useful for further evaluation of geochemical processes affecting PRB performance. Geochemical modeling also is useful for evaluating new reactive media for PRB application.