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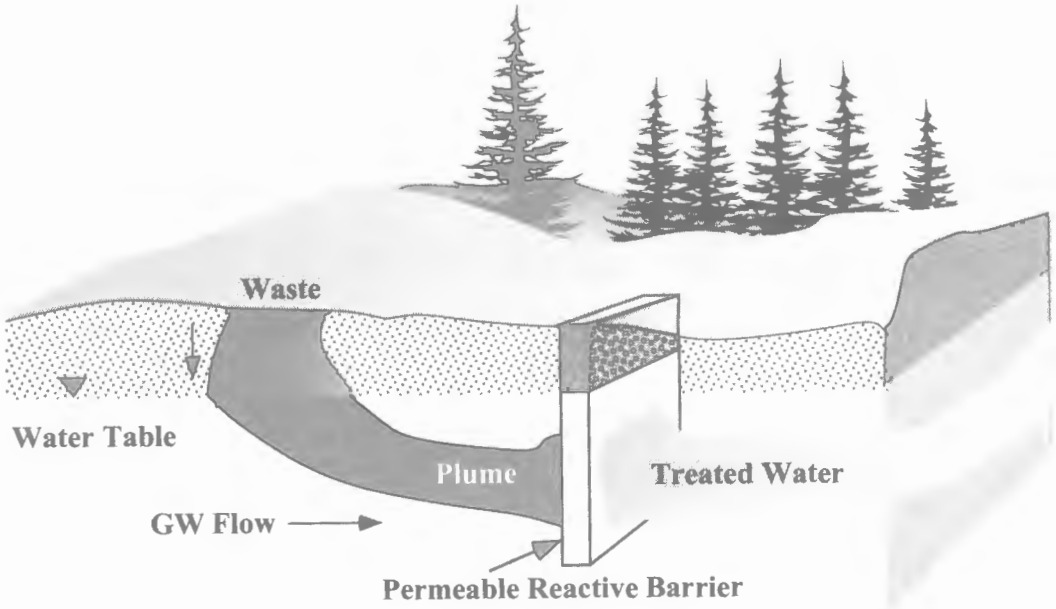
Permeable Reactive Barrier Technologies for Contaminant Remediation



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PERMEABLE REACTIVE BARRIER TECHNOLOGIES FOR CONTAMINANT REMEDIATION

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Notice

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FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet these mandates, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for reducing risks from threats to human health and the environment. The focus of the Laboratory's research program is on methods for the prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites and ground water; and prevention and control of indoor air pollution. The goal of this research effort is to catalyze development and implementation of innovative, cost-effective environmental technologies; develop scientific and engineering information needed by EPA to support regulatory and policy decisions; and provide technical support and information transfer to ensure effective implementation of environmental regulations and strategies.

Environmental scientists are generally familiar with the concept of barriers for restricting the movement of contaminant plumes in ground water. Such barriers are typically constructed of highly impermeable emplacements of materials such as grouts, slurries, or sheet pilings to form a subsurface "wall". The goal of such installations is to eliminate the possibility that a contaminant plume can move toward and endanger sensitive receptors such as drinking water wells or discharge into surface waters. Permeable reactive barrier walls reverse this concept of subsurface barriers. Rather than serving to constrain plume migration, permeable reactive barriers (PRB's) are designed as preferential conduits for the contaminated ground water flow. A permeable reactive subsurface barrier is an emplacement of reactive materials where a contaminant plume must move through it as it flows, typically under natural gradient, and treated water exits on the other side. The purpose of this document is to provide the most recent information on PRB technologies in a format that is useful to stakeholders such as implementors, state and federal regulators, Native American tribes, consultors, contractors, and all other interested parties. It includes information on treatable contaminants, design, feasibility studies, construction options, site characterization needs and monitoring, as well as summaries of several current installations. It is hoped that this will prove to be a very valuable technical resource for all parties with interest in the implementation of this innovative, passive, remedial technology.

Clinton W. Hall

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Subsurface Protection and Remediation Division

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Table of Contents

1.0 Executive Summary 1
2.0 Introduction 4
2.1 Defining Permeable Reactive Subsurface Barriers 4
2.2 Research Support and Application of The PRB Technology 5
2.3 Regulatory Acceptance of PRB Technology 6
3.0 Treatable Contaminants, Reactants and Reaction Mechanisms 8
3.1 Desirable Characteristics of Reactive Media 8
3.2 Treatable Contaminants 8
3.2.1 Halogenated Organic Compounds and Iron 8
3.2.2 Redox-sensitive Inorganic Anions and Iron 11
3.2.3 Biologically Mediated Reduction and Removal of Anions 13
3.2.4 Adsorption and Precipitation of Inorganic Anions 14
3.2.5 Reduction of Inorganic Cations 14
3.2.6 Biologically Mediated Reduction and Precipitation of Cations 15
3.3 Enhancing Iron Reaction Rates 15
4.0 Remediation Feasibility, Laboratory Treatability, and PRB Design Studies 16
4.1 Laboratory Treatability Studies 16
4.1.1 Batch Studies 16
4.1.2 Column Studies 18
4.1.2.1 Column Test Methodology 18
4.1.2.2 Interpretation of Column Data 18
4.1.2.3 Interpretation of Changes in Non-Contaminant Inorganic Constituents 20
4.2 Determination of Required Residence Time in PRBs 22
4.2.1 Chlorinated Volatile Organic Compounds (VOCs) 22
4.2.2 Inorganic Constituents 22
4.3 Ancillary Laboratory Studies 23
5.0 Site Characterization for Permeable Reactive Barriers 24
5.1 Hydrogeologic Characterization 24
5.2 Contaminant Characterization 25
5.3 Geochemical Characterization 25
5.4 Microbial Aspects 26
5.5 Implementing the Field Characterization 27
6.0 Permeable Reactive Barrier Design 28
6.1 The Continuous PRB and Funnel and Gate Designs 28
6.2 Emplacement Methods and Comparisons 30
6.2.1 Conventional Excavation 30
6.2.2 Trenching Machines 31
6.2.3 Tremie Tube/Mandrel 31
6.2.4 Deep Soil Mixing 31
6.2.5 High-Pressure Jetting 32
6.2.6 Vertical Hydraulic Fracturing and Reactant Sand-Fracturing 32
6.3 Emplacement Verification 32
7.0 Monitoring Permeable Reactive Barriers 33
7.1 Planning the Monitoring Effort 33
7.2 Compliance Monitoring 33
7.2.1 Objectives 33
7.2.2 Compliance Monitoring System Design 33
7.2.3 Compliance Sampling Methods 34
7.2.4 Compliance Sampling Frequency 35
7.2.5 Contaminant Breakthrough/Bypass and Formation of Undesirable Products 36
7.2.6 General Water Quality Parameters 36

7.3 Performance Monitoring 37
7.3.1 Objectives 37
7.3.2 Performance Monitoring System Design 37
7.3.3 Performance Sampling Methods 38
7.3.4 Performance Sampling Frequency 38
7.3.5 Contaminant Degradation/Transformation 39
7.3.6 Geochemical Indicator Parameters 39
7.3.7 Coring for Precipitate Buildup, Microbial Effects 39
7.3.8 Hydrologic Testing for Permeability Alteration 39
8.0 Field Installations 40
8.1 Chlorinated Hydrocarbon and Chromium Removal in Field Scale Systems 40
8.1.1 Industrial Site, Sunnyvale, California (January 1995) 40
8.1.2 Industrial Site, Mountainview, California (September 1995) 40
8.1.3 Industrial Site, Belfast, Northern Ireland (December 1995) 43
8.1.4 Industrial Site, Kansas (January 1996) 43
8.1.5 USCG Facility, Elizabeth City, North Carolina (June 1996) 43
8.1.6 FHA Facility, Lakewood, Colorado (October 1996) 46
8.2 Interpretation of VOC Monitoring Data from the Field-scale Systems 47
8.3 Inorganic Constituent Removal in Field-scale Systems 47
8.3.1 Nickel Rim Mine Site, Sudbury, Ontario (August, 1995) 47
8.3.2 Langton, Ontario On Site Wastewater Treatment (July, 1993) 49
8.4 Biological Effects on Field-scale PRBs 50
8.4.1 Microbial Effects on Iron PRBs 50
8.4.2 Microbial Effects in PRBs for Inorganic Constituents 50
8.5 Effects of Mineral Precipitation on Field-scale PRB Performance 51

Appendix A. Reference Table A-53

Appendix B. Explanation of Relevant Physical/Chemical Phenomena B-74

Appendix C. Scoping Calculations C-78

Appendix D. Acronyms D-83

Appendix E. Glossary E-86

References 89

List of Tables

Table 1. Full-Scale in situ Remediation Projects. 5
Table 2. States That Have Approved the Installation of Iron PRBs. 6
Table 3. Contaminants Treatable By Reactive Materials in PRBs. 9
Table 4. Contaminants Presently Not Treatable By Fe(0). 9
Table 5. Contaminants With Unknown Treatability. 10
Table 6. Typical Treatability Study Results, Elizabeth City Example. 17
Table 7. Construction Details of Six PRB Installations. 41
Table 8. VOC Degradation Rate Data. 49
Table 9. Required Weight-Per-Area (W/A) of Granular Iron. Calculated with n = 0.33, P_0/P = 1000, and F = 3.5). Information and Equations from Appendix C. C-79
Table 10. Summary Information on Full-Scale Permeable Reactive Barriers Using Fe(0). C-80
Table 11. Cost Elements of Funnel and Gate Systems: High Estimate (Gate @ \$1000/yd^3; Funnel @ \$25/ft^2) C-82
Table 12. Cost Elements of Funnel and Gate Systems: Low Estimate (Gate @ \$200/yd^3; Funnel @ \$10/ft^2) C-82

List of Figures

Figure 1. Example of plume being treated by a permeable reactive barrier wall. 1
Figure 2. Schematic of the column apparatus used in the bench-scale tests. 19
Figure 3. Conceptual residence tme calculation for VOC removal. 21
Figure 4. Correlation of TCE degradation rates with temperature. 21
Figure 5. Potential effects of ground water flow diversion on plume direction. 24
Figure 6. Effects of plume center-of-mass movement downgradient, and higher concentrations impacting the barrier. Incomplete remediation is now occurring. 25
Figure 7. Potential effects of precipitation buildup on the iron over time. 26
Figure 8a. Plume capture by a continuous PRB trenched system. The plume moves unimpeded through the reactive gate. 28
Figure 8b. Plume capture by a funnel-and-gate system. Sheet piling funnels direct the plume through the reactive gate. 28
Figure 9. Continuous trencher used at Elizabeth City, North Carolina. 34
Figure 10. Bundled tubes with short screens for performance monitoring. 38
Figure 11. PRB configuration, Sunnyvale, California. 40
Figure 12. PRB configuration, Mountainview, California. 42
Figure 13. PRB vessel configuration, Belfast, Northern Ireland. 44
Figure 14. PRB configuration, Kansas. 44
Figure 15. PRB configuration, USCG facility, Elizabeth City, North Carolina. 45
Figure 16. PRB configuration, FHA facility, Denver, Colorado. 46
Figure 17. Pilot scale PRB configuration, Colorado and New York. 48
Figure 18. Example of an electrochemical corrosion cell. B-75

1.0 Executive Summary

Perhaps no recent remedial technology has generated as much interest as the use of subsurface permeable reactive barriers (PRBs). This is due to the perceived PRB cost/benefit ratio and the potential of PRBs to mitigate the spread of contaminants that have proven difficult and expensive to manage with other cleanup methods. The concept of a PRB is relatively simple. Reactive material is placed in the subsurface where a plume of contaminated ground water must move through it as it flows, typically under its natural gradient (creating a passive treatment system) and treated water comes out the other side (Figure 1). The PRB is not a barrier to the water, but it is a barrier to the contaminant. When properly designed and implemented, PRBs are capable of remediating a number of contaminants to regulatory concentration goals. It is currently believed that these systems, once installed, will have extremely low, if any, maintenance costs for at least five to ten years. There should be no operational costs other than routine compliance and performance monitoring.

The majority of installed PRBs use iron metal, Fe(0), as the reactive media for converting contaminants to non-toxic or immobile species. Iron metal has the ability to reductively dehalogenate hydrocarbons, such as converting trichloroethene (TCE) to ethene. It can also reductively precipitate anions and oxyanions, such as converting soluble Cr(VI) oxides to insoluble Cr(III) hydroxides. Organic materials are being used as reactive media in some PRBs to biologically remediate certain other contaminants, such as nitrate and sulfate. Both laboratory and field results have shown that the rate of transformation of these and many other contaminants is sufficiently rapid for PRBs to be successfully used as full-scale remediation systems. Numerous other reactive materials are being investigated, as are means to enhance both the iron and biological reactions. Many of the references for these investigations are listed and described in Appendix A.

Commercial PRBs are currently built in two basic configurations (although others are being evaluated), the funnel-and-gate and the continuous PRB. Both have required some degree of excavation and been limited to fairly shallow depths of fifty to seventy feet or less. Newer techniques for emplacing reactive media, such as the injection of slurries, hydrofracturing, driving mandrels, etc., may serve to overcome some of these emplacement limitations. The funnel-and-gate design PRB uses impermeable walls (sheet pilings, slurry walls, etc.) as a "funnel" to direct the contaminant plume to a "gate(s)" containing the reactive media, whereas the continuous PRB completely transects the plume flow path with reactive media. Due to the funnels, the funnel-and-gate design has a greater impact on altering the ground-water flow than does the continuous PRB. In both designs it is necessary to keep the reactive zone permeability equal to or greater than the permeability of the aquifer to avoid diversion of the flowing waters around the reactive zone.

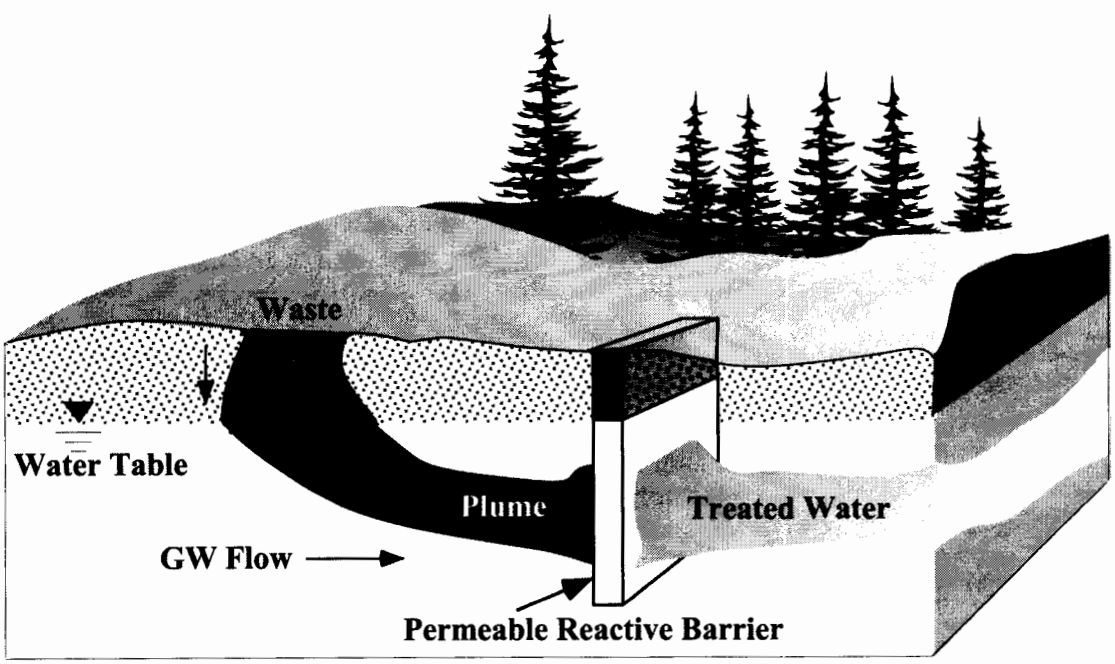


Figure 1. Example of plume being treated by a permeable reactive barrier wall.

Several important issues must be addressed when considering contaminant remediation through the use of PRB technology. These include the nature of the contaminant and the availability of reactive media that can transform the contaminant yet remain reactive, in situ, for relatively long time periods. For contaminants of unknown treatability or media of unknown reactivity, addressing these issues will require laboratory studies using both batch and column techniques. The mobility, toxicity and stability of the transformation products resulting from the contaminant and media interactions must also be assessed. If these transformation products are regulated compounds, they must not exit the reactive zone of the PRB without themselves being immobilized or transformed to innocuous compounds.

A thorough understanding of system hydrogeology and plume boundaries is needed prior to implementing a PRB, due to the need for the plume to passively flow through the reactive zone of the PRB. The hydrogeologic characterization must also yield information suitable for determining the rate of ground-water flow through the reactive zone of the PRB. This is necessary to establish the ground-water/contaminant residence time per unit thickness of reactive media which, when combined with the contaminant transformation rate as it passes through the media, determines the total thickness of reactive media that is required. During PRB installation the reactive media must be made accessible to the contaminant by some emplacement method and, as with most remedial technologies, this becomes increasingly difficult at greater contaminant depth or for contaminants in fractured rock. Once installed, the PRB should be carefully monitored for both compliance and performance; compliance to ascertain that regulatory contamination goals are being met, and performance to assess whether the PRB emplacement is meeting its design criteria and longevity expectations.

As for any remedial technology, it is important to fully understand the factors that can result in either successful implementation and remediation or failure to achieve the remedial design goals. This document addresses the factors, such as those mentioned above, that have been found to be relevant for successfully implementing PRBs for contaminant remediation. Additionally, it provides sufficient background in the science of PRB technology to allow a basic understanding of the chemical reactions proposed for the contaminant transformations that have been witnessed both in the laboratory and in field settings. It contains sections on PRB-treatable contaminants and the treatment reaction mechanisms, feasibility studies for PRB implementation, site characterization for PRBs, PRB design, PRB emplacement, monitoring for both compliance and performance, and summaries of several field installations. The appendices supplement this information with a detailed table of information available in the literature through 1997, summarizing the significant findings of PRB research and field studies (Appendix A), a further examination of the physical and chemical processes important to PRBs, such as corrosion, adsorption, and precipitation (Appendix B), and a set of scoping calculations that can be used to estimate the amount of reactive media required and facilitate choosing among the possible means of emplacing the required amount of media (Appendix C). Appendix D provides a list of acronyms and Appendix E a glossary of terms that are used within this document.

The goal of this Issue Paper is to provide the most recent information available on PRB technologies and to do so in a format that is useful to stakeholders such as implementors, state and federal regulators, Native American tribes, consultants, contractors, and all other interested parties. Other documents are also available which address PRB topics that are not discussed in detail in this report to avoid duplicative effort, such as regulatory issues related to PRB technology and cost information. For example, the Interstate Technology and Regulatory Cooperation (ITRC) Workgroup (Permeable Barrier Wall Subgroup) has prepared a document titled "Regulatory Guidance for Permeable Barrier Walls Designed to Remediate Chlorinated Solvents" (ITRC, 1997) and the Environics Directorate, U.S. Air Force, has published "Design Guidance for Application of Permeable Barriers to Remediate Dissolved Chlorinated Solvents" (Battelle, 1997). Documents on the costs of PRB technology are being prepared by U.S. EPA's Technology Innovation Office (TIO) and by its Office of Research and Development, National Risk Management Research Laboratory (ORD-NRMRL). Several web sites also provide information about PRB technology. Among these are:

RemedialTechnologies Development Forum

- http://www.rtdf.org

Ground-Water Remediation Technologies Analysis Center

- http://www.gwrtac.org

U.S. EPA's Robert S. Kerr Environmental Research Center of the National Risk Management Research Laboratory

- http://www.epa.gov/ada/eliz.html

EnviroMetal Technologies, Inc.

- http://www.beak.com/eti.html

Powell & Associates Science Services

- http://www.powellassociates.com

Oregon Graduate Institute of Science and Technology

- http://www.cgr.ese.ogi.edu/iron

2.0 Introduction

A great deal of money and effort has been spent on environmental restoration during the past 30 years. Significant progress has been made improving air quality, dumps and landfills, and surface water quality, although challenges still exist in these areas. Among the more difficult and expensive environmental problems, and often the primary factor limiting closure of contaminated sites following surface restoration, is contaminated ground water. The most common technology used for remediating ground water has been to pump the water and treat it at the surface. Although still useful for certain remedial scenarios, the limitations of pump-and-treat technologies have recently been recognized, along with the need for innovative solutions to ground-water contamination (Keely, 1989; National Research Council, 1994).

One of the most promising of these innovative solutions is the use of permeable reactive barriers (PRBs) filled with reactive material to intercept and decontaminate plumes in the subsurface. The concept of PRBs is relatively simple. Reactive material is placed in the subsurface to intercept a plume of contaminated ground water which must move through it as it flows, typically under its natural gradient, thereby creating a passive treatment system. As the contaminant moves through the material, reactions occur that transform it to less harmful (nontoxic) or immobile species.

Many reactive media combinations can be envisioned for use in PRBs and numerous media and mixtures of media are being investigated for a variety of contaminants (Appendix A). As of this writing, iron metal, variously designated as Fe^0, Fe(0), or zero-valent iron, is the most common reactive media in the majority of field-scale and commercial implementations. Scrap iron is not expensive and can be obtained in a granular form in the large quantities needed. It has the ability to reduce oxidized inorganic species and reductively dehalogenate hydrocarbon compounds. Reactive iron barriers depend upon corrosion to drive these reactions (Appendix B). For example, chromate plumes are reduced from Cr(VI) to Cr(III) and precipitated, in situ, as chromium (III) hydroxides or chromium-iron hydroxide solid solutions. An example from among the amenable halocarbon plumes are those resulting from the dense, nonaqueous phase liquid (DNAPL) halogenated hydrocarbons. These include chlorinated ethenes such as perchloroethylene (PCE), trichlorethylene (TCE), dichloroethylene (DCE), and vinyl chloride (VC). The reductive dehalogenation of these compounds occurs due to electron transfers from the iron to the halocarbon at the iron surface. This results in the halogen ions (e.g., Cl^-) being replaced by hydrogen species, ultimately yielding ethene or ethane that can be mineralized via biodegradation.

The ability to perform dehalogenation in a reactive barrier is significant since the sources of DNAPL contamination, such as residual saturation, often cannot be easily located and may continue to generate a continuous plume of dissolved halocarbons (National Research Council, 1994). Although these plumes can often be controlled by pump-and-treat, the systems require extensive maintenance and continual energy input. PRBs are also designed for plume control, but with significant differences from pump-and-treat systems. PRBs are in situ systems, are intended to operate in a totally passive manner, do not routinely bring the contaminant to the surface, and should operate for years with minimal, if any, maintenance.

Although simple in concept, there is a great breadth of science and technology involved in the selection of reactive materials for different contaminants and in the design, installation, and monitoring of these emplacements in the subsurface. The purpose of this document is to provide an introduction and a guide to the science and technology of PRBs.

2.1 Defining Permeable Reactive Subsurface Barriers

Environmental scientists are generally familiar with the concept of barriers for restricting the movement of contaminant plumes in soil and ground water. Such barriers are typically constructed of highly impermeable emplacements of materials such as grouts, slurries, or sheet pilings to form a subsurface "wall." The goal of such barriers is to minimize the possibility that a contaminant plume can move toward and endanger sensitive receptors, such as drinking water wells, or discharge into surface waters. Rather than serving to constrain plume migration, PRBs are designed as conduits for the contaminated ground-water flow. As contaminated water passes through the reactive zone of the PRB, the contaminants are either immobilized or chemically transformed to a more desirable (e.g., less toxic, more readily biodegradable, etc.) state. Therefore, a PRB is a barrier to contaminants, but not to ground-water flow. A permeable reactive subsurface barrier is defined as:

> *an emplacement of reactive materials in the subsurface designed to intercept a contaminant plume, provide a flow path through the reactive media, and transform the contaminant(s) into environmentally acceptable forms to attain remediation concentration goals downgradient of the barrier (Powell and Powell, 1998; Powell and Puls, 1997a).*

In addition to PRBs, research is being conducted on a similar class of subsurface remediation technologies which, in this document, will be referred to as reaction zone formation (RZF) technologies. These are somewhat different from PRBs because they do not necessarily emplace solid phase reactive media in the subsurface. One approach, for example, is the injection and withdrawal of a sodium dithionite solution into an aquifer matrix (Fruchter et al., 1996). The dithionite reduces Fe^{3+} that is naturally available on the mineral matrix surface to Fe^{2+}, thus increasing the reducing capacity of the aquifer material itself. This has been shown to be an effective means of removing chromate from ground water by reductive precipitation as the Cr(III) hydroxide, in much the same manner as was previously discussed for its precipitation by Fe(0). Another RZF technology is the use of in situ electrodes, not to directly move or remediate the contaminants, but rather to supply hydrogen as an electron donor to the subsurface microbes. The microbes can then potentially remediate the contaminant, e.g., a chlorinated hydrocarbon, by using it as the electron acceptor. This would reductively dehalogenate the compound, as was described above for the electron transfer between Fe(0) and PCE. Although these RZF technologies are not the subject of this document, it is important to realize that such processes are being investigated and implemented in the field.

2.2 Research Support and Application of the PRB Technology

The U.S. Environmental Protection Agency has supported the development of this innovative in-situ technology through active collaboration on research involving the National Risk Management Research Laboratory (NRMRL) and the National Exposure Research Laboratory (NERL) of USEPA's Office of Research and Development (ORD), through the Remediation Technologies Development Forum (RTDF) Permeable Barriers Action Team, and from support provided by USEPA's Technology Innovation Office (TIO). In addition, support has been provided from several regional offices where sites are testing the technology at pilot-scale. Both DOD and DOE have also actively supported research on PRB technology, financially supporting both laboratory and field trials.

As with any emerging technology, the field installation of this technology is limited relative to the research and laboratory testing that has been performed and the overall potential of the technology for contaminant remediation. Most full-scale PRBs are currently being used for the treatment of plumes of chlorinated hydrocarbons and chromate, using granular Fe as the reactant. Laboratory studies have shown, however, that many other contaminants can also be treated using PRB technology with the selection of the proper reactant (Appendix A). As of this writing (March 1998), at least thirteen full-scale reactive barriers have been installed in the field (Table 1).

Table 1. Full-Scale in situ Remediation Projects

Industrial facility	Sunnyvale, California	gate and slurry wall	December 1994
Mine Site,	Sudbury, Ontario	continuous wall	August 1995
Industrial facility	Mountainview, California	gate and HDPE liner	December 1995
Industrial facility	Belfast, Northern Ireland	in situ reactive vessel and slurry wall	December 1995
Industrial facility	Coffeyville, Kansas	gate and slurry wall	January 1996
USCG facility	Elizabeth City, North Carolina	continuous reactive wall	June 1996
Government facility	Lakewood, Colorado	sheet pile funnels and 4 gates	October 1996
Industrial facility	South Carolina	continuous iron/sand reactive wall	October 1997
Industrial facility	Colorado	gate and slurry funnel	November 1997
Industrial facility	Oregon	gates (2) and slurry funnel	November 1997
Industrial facility	Upstate New York	continuous wall	December 1997
Superfund site	New Jersey	continuous wall - hydrofracturing	April 1998
U.S. DOE facility	Kansas City, Missouri	continuous wall	April 1998

2.3 Regulatory Acceptance of PRB Technology

The USEPA recognizes this technology as having the potential to effectively remediate subsurface contamination at many types of sites with significant cost savings compared to more traditional approaches (e.g., pump-and-treat). The USEPA is actively involved in the evaluation and monitoring of this new technology to answer questions and provide guidance to various stakeholder groups.

The Interstate Technology and Regulatory Cooperation (ITRC) Workgroup (Permeable Barrier Wall Subgroup) is also actively involved in defining the regulatory implications associated with the installation of permeable reactive barriers in the subsurface and in providing guidance on regulatory issues where possible.

The first full-scale commercial PRB was approved for use in the State of California by the San Francisco Regional Water Quality Control Board (RWQCB) in 1994. Since that time, ten other full-scale systems have been installed in the U.S., along with one in Sudbury, Canada, and one in Belfast, Northern Ireland. Table 2 lists some of the states where permeable barriers have been approved for installation, either at pilot-scale or full-scale. The regulatory approach to the technology at several sites has been to treat the installations as "at risk" remedies. That is, the owner would be required to implement a more conventional remedy if the permeable barrier failed to meet performance criteria. In some cases, the lack of existing groundwater use, particularly in industrial areas, facilitated implementation of PRBs. At sites in California and Colorado, there was a consensus among the regulators, site owners and site consultants that existing pump and treat systems were not achieving the desired level of groundwater remediation, making PRBs a favorable alternative solution.

From a federal perspective, one of the more significant advances for PRB technology occurred when a "chemical treatment wall" was identified in June 1995 as the preferred alternative in the Record of Decision (ROD) at a Superfund site (the Somersworth Municipal Landfill in Somersworth, New Hampshire). This decision, coupled with the 1996 directive from the U.S. EPA Office of Solid Waste and Emergency Response (OSWER) to evaluate alternatives to pump and treat remedies has encouraged consideration of the technology at other Superfund sites. Active research programs at several U.S. EPA laboratories have also led to greater acceptance of the technology at the federal level. A pilot-scale PRB for removal of VOCs in groundwater was evaluated in 1995 under the Superfund Innovative Technologies Evaluation (SITE) program. The Technology Evaluation Report for this project

Table 2. Some States that have Approved the Installation of Iron PRBs.

State	Full-Scale Installations	Pilot-Scale Installations
California	2	2
Colorado	2	1
Delaware	0	1
Florida	0	3
Kansas	1	0
Illinois	0	1
Missouri	1	0
New Hampshire	0	1
New Jersey	1	0
New York	1	1
North Carolina	1	1
Oregon	1	0
South Carolina	1	1
Totals	11	11

remains to be published at the time of this writing (March 1998). The inclusion of PRBs in the SITE program and Vendor Information System for Innovative Treatment Technologies (VISITT) has also increased the awareness of the technology. Recent developments in interstate environmental technology verification programs may further expedite regulatory acceptance.

In summary, regulatory acceptance of PRBs is expected to increase as the number of site installations increases and more long-term performance data becomes available from existing installations.

3.0 Treatable Contaminants, Reactants and Reaction Mechanisms

3.1 Desirable Characteristics of Reactive Media

Reactive media used in permeable barriers should be compatible with the subsurface environment. That is, the media should cause no adverse chemical reactions or byproducts when reacting with constituents in the contaminant plume, and should not act as a possible source of contaminants itself. This requires that the material be well understood and characterized. To keep PRB costs to a minimum, the material should persist over long periods of time, i.e., it should not be readily soluble or depleted in reactivity, and the material should be readily available at a low to moderate cost. The material selected should minimize constraints on ground-water flow by not having excessively small particle size and it should not consist of a wide range of particle sizes that might result in blocked intergranular spaces (i.e., it should preferably be unimodal with respect to grain size). Worker safety, with regard to handling the material, should also be considered.

3.2 Treatable Contaminants

Table 3 lists contaminants that have been shown to be successfully treated by zero-valent iron or other media. Tables 4 and 5 list some contaminants that have been shown to be not affected by zero-valent iron or have not yet been fully evaluated, respectively.

3.2.1 Halogenated Organic Compounds and Iron

Considerable research during the past several years has focused on the degradation of chlorinated solvents, such as TCE and PCE, by reactions at the surfaces of Fe(0). Although met with initial skepticism, the degradation process is now widely accepted as abiotic reductive dehalogenation, involving corrosion of the Fe(0) by the chlorinated hydrocarbon.

Iron corrosion processes in aqueous systems have been studied extensively. Until recently, the fate of corrosion processes in dilute aqueous concentrations of chlorinated solvents acting as the oxidizing agents have not been investigated. The net reductive dechlorination reaction promoted by Fe(0) (Equation 3) may be viewed as the sum of anodic and cathodic reactions occurring at the iron metal surface (Equations 1 and 2, respectively), resulting in hydrocarbon products if the dechlorination proceeds to completion.

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \quad \text{Anodic Reaction} \quad (1)$$

$$RCl + 2e^- + H^+ \rightarrow RH + Cl^- \quad \text{Cathodic Reaction} \quad (2)$$

$$Fe^0 + RCl + H^+ \rightarrow Fe^{2+} + RH + Cl^- \quad \text{Net Reaction} \quad (3)$$

Under aerobic conditions, dissolved oxygen is usually the preferred electron acceptor and can compete with the chlorinated hydrocarbon as the favored oxidant (Equation 4). Indeed, chlorinated hydrocarbons such as PCE and carbon tetrachloride have oxidizing potentials very similar to that of O_2 (Archer and Harter, 1978). When sufficient oxygen is present, the Fe^{2+} generated in Equation 4 further oxidizes to Fe^{3+} (Equation 5) and can precipitate as ferric hydroxide or (oxy)hydroxides (Equation 6) at the elevated pH typical of corroding Fe systems. Corrosion of the iron can generate large amounts of iron oxides and (oxy)hydroxide precipitates that can exert significant additional chemical and physical effects within the reactive system (Powell et al., 1994; Powell et al., 1995a). The rapid consumption of dissolved oxygen at the entrance to an iron system (column or barrier) has been shown to result in these precipitates that might impact a system's hydraulic performance at its upgradient interface (MacKenzie et al., 1995; Mackenzie et al., 1997).

$$2Fe^0 + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^- \quad (4)$$

$$4Fe^{2+} + 4H^+ + O_2 \rightarrow 4Fe^{3+} + 2H_2O \quad (5)$$

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_{3(s)} \quad (6)$$

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \quad (7)$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_{2(s)} \quad (8)$$

Anaerobic corrosion of iron by water (Equation 7) proceeds slowly. Both reactions 4 and 7 result in an increased pH in weakly buffered systems, yielding ferric (oxy)hydroxides in aerobic systems (Equation 6) and ferrous (oxy)hydroxides in anaerobic systems (Equation8). The aqueous corrosion of iron is mediated by the layer of oxides, hydroxides and oxyhydroxides that are present at the iron-water interface. The formation of these precipitates might further occlude the iron surface and affect its reduction-oxidation properties. However, this

Table 3. Contaminants Treatable By Reactive Materials in PRBs.

Organic Compounds		**Inorganic Compounds**	
Methanes	tetrachloromethane trichloromethane dichloromethane	Trace Metals	Chromium Nickel Lead Uranium Technetium Iron Manganese Selenium Copper Cobalt Cadmium Zinc
Ethanes	hexachloroethane 1,1,1-trichloroethane 1,1,2-trichloroethane 1,1-dichloroethane	Anion Contaminants	Sulphate Nitrate Phosphate Arsenic
Ethenes	tetrachloroethene trichloroethene cis-1,2-dichloroethene trans-1,2-dichloroethene 1,1-dichloroethene vinyl chloride		
Propanes	1,2,3-trichloropropane 1,2-dichloropropane		
Aromatics	benzene toluene ethylbenzene		
Other	hexachlorobutadiene 1,2-dibromoethane freon 113 N-nitrosodimethylamine		

Table 4. Contaminants Presently not Treatable by Fe(0)

Organic Compounds	**Inorganic Compounds**
dichloromethane 1,2-dichloroethane chloroethane chloromethane	chloride perchlorate

Table 5. Contaminants with Unknown Treatability

Organic Compounds	Inorganic Compounds
chlorobenzenes chlorophenols certain pesticides PCBs	mercury

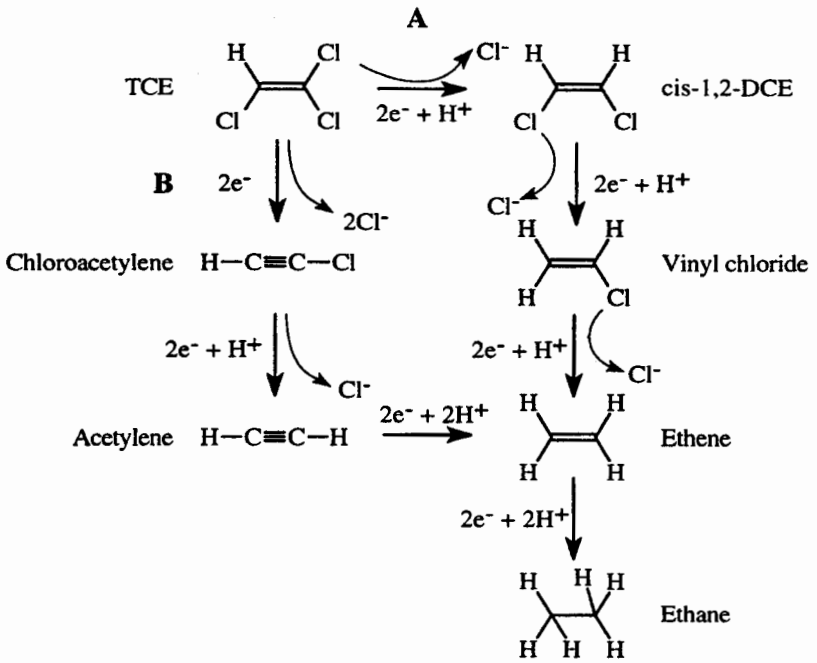
passive coating appears to be converted to magnetite (Odziemkowski et al. 1998), which is non-passivating, and seems to allow sufficient contaminant degradation rates that can be sustained over years of operation in the ground.

Zero-valent iron is a mild reductant, and consequently the dehalogenation rates vary for the various chlorinated solvents of environmental interest. A number of studies have shown that the primary determinant of degradation rate is the specific surface area, or the surface area of iron per unit volume of pore water (Matheson and Tratnyek, 1994; Sivavec et al., 1995). Degradation rates are typically pseudo-first-order with respect to the halogenated hydrocarbon, with the rate constant relatively insensitive to the initial hydrocarbon concentration. Studies of published degradation rate data for individual halogenated hydrocarbons show that transformation rates are proportional to iron surface area concentration (Johnson et al., 1996) and that observed rate constants can be normalized to iron surface area to yield a specific rate constant, or k_{sa}, for the halocarbon.

The reaction pathways by which Fe(0) reduces halogenated hydrocarbons have been determined for a few major classes of chlorinated hydrocarbons. Such information is significant to the optimal design of a permeable reactive barrier, as incomplete dechlorination of a highly chlorinated ethene, for example, could produce an intermediate product, such as VC, which is more hazardous and more persistent than the parent compounds. Even very low concentrations of undesirable by-products in the reactive barrier effluent must be avoided.

Typically, permeable reactive barriers are designed to provide adequate residence time in the treatment zone for the degradation of the parent compound and all toxic intermediate products that are generated. At sites where the ground-water contamination includes a mixture of chlorinated hydrocarbons, the design of the PRB is usually determined by the least reactive constituent. Perhalogenated hydrocarbons tend to be reduced more rapidly than their less halogenated congeners, and dechlorination is more rapid at saturated carbon centers (for example, carbon tetrachloride) than at unsaturated carbons (for example, TCE or VC).

Excellent product mass balances have been determined for the transformation of several chlorinated ethenes (Orth and Gillham, 1996) and methanes. These mass balance studies are best accomplished in a flow-through column design, as sorption effects can be minimized. TCE, a common ground-water contaminant, is largely converted to ethene and ethane. Generally less than 5%-10% of the initial TCE appears as chlorinated degradation products, including the three dichloroethene products (cDCE is dominant) and VC. As shown in Equation 9, zero-valent iron reduces TCE via two interconnected degradation pathways: (A) sequential hydrogenolysis and, (B) reductive ß-elimination (Roberts et al., 1996). The intermediate products, cDCE and VC, are produced in the sequential hydrogenolysis pathway, and are slower to degrade than is TCE itself. The chloroacetylene intermediate produced via the ß-elimination pathway, by contrast, is a very short-lived intermediate and is very rapidly reduced to ethene. The ß-elimination pathway accounts for the rapid conversion of TCE to ethene and ethane, with relatively minor intermediate product formation.



(9)

The degradation pathway for chlorinated methanes is a much simpler one than that for chlorinated ethenes, as the ß-elimination route is not available to the methane family. Carbon tetrachloride has been shown to undergo sequential hydrogenolysis to chloroform and dichloromethane (Equation 10) (Matheson and Tratnyek, 1994). The formation of chloroform accounted for about 70% of the carbon tetrachloride lost. Methylene chloride appeared, after carbon tetrachloride decreased to the detection limit, and typically accounted for about 50% of the chloroform lost. No further reaction of dichloromethane has been detected in an unamended zero-valent iron system.

$$CCl_4 \xrightarrow{2e^- + H^+} CHCl_3 + Cl^- \xrightarrow{2e^- + H^+} CH_2Cl_2 + 2Cl^- \qquad (10)$$

3.2.2 Redox-sensitive Inorganic Anions and Iron

Negatively charged anions and oxyanions, the dissociation products of Lewis acids formed by the hydrolysis of cations, are important ground-water contaminants. Elements which occur as anions or oxyanions under natural ground-water conditions include arsenic, selenium, chromium, technetium and antimony. In addition, the dissolved nutrient species nitrate and phosphate occur as anions, as does sulfate. Because of the negative charge, anionic species are not attracted to negatively charged mineral surfaces, which are usually predominant in aquifers under neutral pH conditions. This limited tendency for adsorption, and the high solubility of minerals containing oxyanions, result in the potential persistence of high concentrations of these elements in aquifers. Treatability studies, pilot-scale field trials and full-scale demonstration projects have been conducted for a series of anionic inorganic contaminants, including SO_4^{2}, NO_3^-, and those containing Cr(VI), Se(VI), As(III), As(V), Tc(VII).

Treatment of chromate, CrO_4^{2-} which contains Cr(VI), has been the most extensively tested and demonstrated of the anionic inorganic contaminants. Chromium commonly occurs in two oxidation states, Cr(III) and Cr(VI), in the environment. Trivalent Cr(III) is relatively non-toxic and a micronutrient. It forms sparingly soluble hydroxide precipitates under conditions prevalent in most surficial aquifers and is also readily adsorbed by some minerals. Cr(VI) is a known carcinogen, which forms relatively soluble precipitates, resulting in the persistence of relatively

high concentrations of dissolved Cr(VI) in affected aquifers (Palmer and Puls, 1994; Puls et al., 1995). Cr (VI) is usually speciated as chromate, CrO_4^{2-}, under typical ground-water pH and Eh conditions. This results in a high degree of mobility for the Cr(VI) because anions are not readily adsorbed to the predominantly negatively-charged aquifer materials. Treatments to remove Cr(VI) from ground water typically use reduction to Cr(III) and precipitation of insoluble Cr(III) hydroxide precipitates.

A range of solid-phases containing reduced iron have been observed to promote the reduction and precipitation of Cr(VI), including elemental iron (Gould, 1982; Bowers et al., 1986; Bostick et al., 1990; Blowes and Ptacek, 1992; Powell et al., 1994; Powell et al., 1995a), iron-bearing oxyhydroxides (Eary and Rai, 1989) and iron-bearing aluminosilicate minerals (Eary and Rai, 1989; Kent et al., 1994). Iron bearing reductants have been evaluated as potential candidate materials to promote Cr(VI) reduction in reactive barriers. Comparison of reaction rates observed using Fe(0), pyrite (FeS_2), and siderite ($FeCO_3$), indicate that more rapid Cr(VI) reduction is attained using Fe(0) (Blowes and Ptacek, 1992; Blowes et al., 1997). It has also been shown that the rates of Cr(VI) reduction are dependent on the Fe(0) itself (i.e., how it was refined and manufactured, its level of impurities, etc.) and whether certain aluminosilicate-containing aquifer materials are present and mixed with the iron (Powell et al., 1995a; Powell et al., 1995b; Powell and Puls, 1997).

The overall reactions for the reduction of Cr(VI) by Fe(0) and the subsequent precipitation of Cr(III) and Fe(III) oxyhydroxides are:

$$CrO_4^{2-} + Fe^0 + 8H^+ \rightarrow Fe^{3+} + Cr^{3+} + 4H_2O \quad (11)$$

$$(1-x)Fe^{3+} + (x)Cr^{3+} + 2H_2O \rightarrow Fe_{(1-x)}Cr_xOOH_{(s)} + 3H^+ \quad (12)$$

The extent and rate of Cr(VI) removal by elemental iron has been evaluated in laboratory batch tests and stirred batch reactors (Blowes and Ptacek, 1992; Powell et al., 1995a), column tests (Blowes and Ptacek, 1992; Powell et al., 1994; Blowes et al., 1997a), pilot-scale field trials (Puls et al., 1995) and a full-scale field demonstration (Blowes et al., 1997b). The results of these experiments indicate that the rate of Cr(VI) reduction and precipitation is sufficient for use in ground-water remediation systems. The removal of Cr(VI) from solution is accompanied by a sharp decrease in the Eh, from initially oxidized conditions (Eh > 100 mV) to very reduced conditions (Eh < -300 mV), and a sharp increase in the pH from initially near neutral conditions (6.5 < pH < 8.5) to more basic conditions (pH > 9.5). Details of these reactions and the mechanisms of CrO_4^{2-} reduction by Fe(0) have been described (Powell et al., 1995a; Powell and Puls, 1997a).

Scanning probe microscopy of the reaction precipitates has indicated a one-to-one correspondence of the locations of Cr(III) and Fe(III) hydroxide phases on the surface of reacted iron filings, indicating coprecipitation and the likelihood of the formation of a solid solution phase of the general formula $(Cr_x, Fe_{1-x})(OH)_3$ (Powell et al., 1994; Powell et al., 1995a). More detailed mineralogical studies indicate that the dominant reaction product derived from the laboratory experiments is a mixed Fe-Cr oxyhydroxide phase with the mineral structure of goethite (FeOOH) as shown in Equation 12. The distribution of Cr throughout the structure of this phase is variable, suggesting incorporation through solid-solution substitution (Blowes et al., 1997b). X-ray Photoelectron Spectroscopy (XPS) indicates that the Cr within the precipitate is exclusively in the Cr(III) oxidation state, and that Fe present in the precipitate is in the Fe(III) oxidation state (Pratt et al., 1997). Auger Electron Spectroscopy indicates that the Fe(III) and Cr(III) of the precipitate surface occur in the hematite (Fe_2O_3) structure, that is distinct from the goethite structure of the bulk phase, suggesting Cr(III) exolution and formation of a chromite-like (Cr_2O_3) phase at the precipitate surface (Pratt et al., 1997).

Reduction and precipitation of other anion-forming elements by elemental iron have also been investigated at the laboratory scale. Laboratory experiments conducted to evaluate the treatability of Tc indicate rapid reduction using elemental iron (Bostick et al., 1990; Del Cul et al., 1993; Clausen et al., 1995). Reduction of Se(VI) by elemental iron, and precipitation of elemental selenium (Se^0) is favored thermodynamically. McRae et al. (1997) observed removal of 1000 μg/L of Se(VI) from solution in laboratory batch experiments using elemental iron, and proposed the reaction:

$$HSeO_4^- + 3Fe^0 + 7H^+ \rightarrow 3Fe^{2+} + Se^0_{(s)} + 4H_2O \quad (13)$$

Although removal of Se(VI) was observed, the secondary reaction product was not isolated or identified.

Arsenic commonly occurs as a dissolved species in two oxidation states, As(V) and As(III), and less commonly in other oxidation states, including As(0), As(-I) and As(-II). The As(V) oxidation state occurs as H_3AsO_4 and its dissociation products. The As(III) oxidation state occurs as H_3AsO_3 and its dissociation products. Although As(III), which has greater health effects, is considered to be potentially more mobile in ground-water systems, As(V) is also

observed to be mobile in natural systems. In addition, the rate of arsenic transformation between the As(III) and As(V) oxidation states occurs rapidly in response to changing environmental conditions. Arsenic reduction to the As(0) oxidation state and precipitation of native arsenic, or incorporation into a secondary arsenic sulfide, has been proposed as a potential treatment technique (McRae et al., 1997). In batch tests conducted using elemental iron, McRae et al. (1997) observed rapid removal of As(V) from concentrations of 1000 μg/L to < 3 μg/L over a two-hour period. Similar experiments using As(III) and mixtures of As(III) and As(V) indicated equally rapid removal rates. The mechanisms resulting in arsenic attenuation, and the potential duration of treatment are being evaluated by continuing experiments (McRae et al., 1997). The applicability of Fe(0) in PRBs for permanent As removal and retention requires further investigation.

Reduction of NO_3^- by Fe(0) has been observed to proceed rapidly, resulting in production of NO_2^-, and subsequently ammonium ion (Cheng et al., 1997; Rahman and Agrawal, 1997; Till et al., 1998). The proposed pathway for the overall reaction is:

$$4Fe(0) + NO^{3-} + 10H^+ \rightarrow 4Fe^{2+} + NH_4^+ + 3H_2O \quad (14)$$

During laboratory studies, NO_3^- reduction was observed to proceed through NO_2^- to NH_4^+ formation. The rate of reduction was observed to be first order with respect to the Fe^0 substrate. In addition the rate was observed to decline with increasing duration, particularly in the presence of chloride (Rahman and Agrawal, 1997). However, NH_4^+ formation is not desirable since its MCL is lower than that of NO_3^-. Less NH_4^+ is formed when Fe^0 is used in conjunction with microbial consortia (Till et al., 1998). [See section on Biologically Mediated Reduction and Removal]

3.2.3 Biologically Mediated Reduction and Removal of Anions

Biological processes affect the cycling of numerous elements, including nitrogen, sulfur, iron and manganese. Treatment strategies employing these biologically mediated reactions have been proposed for direct treatment of nitrate (Robertson and Cherry, 1995; Vogan, 1993; Till et al., 1998), sulfate (Blowes et al., 1994; Waybrant et al., 1995), and for indirect removal of other anions through precipitation as sulfide phases.

A denitrification system for removal of nitrate from ground water affected by discharge from site wastewater disposal systems has been developed (Robertson and Cherry, 1995). This system intercepts a plume of nitrate-bearing ground water with a reactive barrier containing solid phase organic carbon. In the presence of organic carbon, under anaerobic conditions maintained below a water cover in the subsurface, reduction of NO_3^- to N_2 gas is thermodynamically favored. The proposed reaction is:

$$5CH_2O_{(s)} + 4NO_3^- \rightarrow 2N_2 + 5HCO_3^- + 2H_2O + H^+ \quad (15)$$

CH_2O represents a simple form of organic carbon which is catalyzed by bacteria of the Pseudomonas group. These bacteria use NO_3^- as an electron acceptor in the oxidation of organic carbon. In a laboratory study a series of inexpensive organic carbon sources were evaluated to assess their potential use in reactive barriers for treatment of NO_3^- (Vogan, 1993). Results to date indicate that readily available materials, including sawdust and wood waste, are suitable materials for a reactive barrier system. Robertson and Cherry (1995) evaluated permeable reactive barriers for treating NO_3^- at several domestic and institutional septic systems. The results of these studies indicate that sufficient denitrification occurs rapidly and reduces NO_3^- from concentrations typically observed in the effluent of onsite wastewater disposal systems (5 - 90 mg/L NO_3^- - N) to below the World Health Organization drinking water standard (10 mg/L NO_3^- - N). Reactive barriers using a variety of design configurations have been implemented. No evidence of assimilatory NO_3^- reduction and NH_4^+ formation has been observed.

A combined system of Fe(0) and the denitrifying bacteria *Paracoccus denitrificans* to reduce NO_3^- has been investigated (Till et al., 1998). The hydrogen produced by the corrosion of the iron was used as the electron donor for nitrate-based respiration. Using steel wool as the Fe^0 they found that the combination increased nitrate removal rates, relative to steel wool alone, and transformed a greater portion of the added NO_3^- to innocuous gases rather than to NH_4^+ .

Biologically mediated reduction of sulfate to sulfide, accompanied by the formation of metal sulfides occurs through the reaction sequence

$$2CH_2O_{(s)} + SO_4^{2-} + 2H^+ \rightarrow H_2S_{(aq)} + 2CO_{2(aq)} + 2H_2O \quad (16)$$

$$Me^{2+} + H_2S_{(aq)} \rightarrow MeS_{(s)} + 2H^+ \quad (17)$$

where CH_2O represents organic carbon and Me^{2+} represents a divalent metal cation in solution. Biologically mediated sulfate reduction has been proposed to treat metal cations derived from mine sites in wetlands (McIntire

et al., 1990; Kleinmann et al., 1991; Eger and Wagner, 1995), bioreactors (Dvorak et al., 1992) and permeable reactive barriers (Blowes et al., 1995; Waybrant et al., 1995; Benner et al., 1997; Blowes et al., 1997b). Although these systems are designed to promote the removal of dissolved metals, metal removal is accompanied by removal of sulfate. In laboratory studies, (Waybrant et al., 1995, 1997a) sulfate removal was observed at rates of 0.14 to 4.23 mg L^{-1} day^{-1} g^{-1} of media.

3.2.4 Adsorption and Precipitation of Inorganic Anions

Inorganic anions which are not susceptible to reductive or oxidative processes must be removed from solution by other means. These anions, as well as redox-sensitive species, may be removed by precipitation, adsorption or coprecipitation on mineral surfaces.

Artiole and Fuller (1979) proposed the use of barriers containing crushed agricultural limestone to neutralize the pH of landfill leachate and precipitate Cr. Laboratory tests indicated successful removal of the cation form, Cr^{3+}, and less successful treatment of the anionic form of Cr(VI), CrO_4^{2-}. Thomson et al. (1991) and Longmire et al. (1991) described the potential use of sphagnum peat, crushed limestone, and hydrated lime, to remove U, As, Mo, and Se in laboratory batch tests. Morrison and Spangler (1992, 1993) proposed the use of a series of industrial byproducts as reactants to remove U, As and Mo in precipitation or sorption barriers. Phases evaluated included bases, reductants, and sorbents, including hydrated lime, ferrous sulfate, hydrous ferric oxides, peat, and phosphate-bearing phases to remove both anionic and cationic species from solution. The system described by Morrison and Spangler (1992; 1993) is potentially suitable for a wide range of anionic contaminants.

Phosphate (PO_4^{3-}) derived from anthropogenic sources is a limiting nutrient in many aquatic ecosystems. Release of excess phosphate results in accelerated biological activity, and ultimately in eutrophication of the aquatic ecosystem. In many regions, phosphate released from onsite wastewater disposal systems, such as septic systems or sewage lagoons, results in excess phosphorus. Baker et al. (1996, 1997) used a mixture of iron oxide, calcium oxide and limestone to promote adsorption and coprecipitation of phosphorus. Phosphate was removed rapidly in batch experiments. In column experiments extending over 3 years and 1200 pore volumes, influent PO_4^{3-}, at a concentration of 4 mg/L PO_4^{3-} - P, was removed to <0.3 mg/L PO_4^{3-} - P, indicating more than 90% removal of the phosphate over a prolonged period. Field-scale demonstration at an institutional septic system resulted in removal of phosphate from influent concentrations of 1 to 2 mg/L PO_4^{3-} - P to less than 0.1 mg/L PO_4^{3-} - P. Test systems, established at onsite wastewater treatment systems, indicate potential for removal of PO_4^{3-} from wastewater under continuous flow conditions. The effluent concentrations achieved by this technique are sufficiently low to prevent eutrophication of surface water flow systems in which PO_4^{3-} is the limiting nutrient (Baker et al., 1996).

The mixture used by Baker et al. (1996) was evaluated for the potential treatment of arsenic (McRae, 1997). Batch experiments indicated a decrease in As(III) from 1000 μg/L to < 3 μg/L in less than 2 hours. Experiments showed decreases in As(V) concentrations, and in mixtures of As(III) and As(V) from 1000 μg/L to <3 μg/L over a similar period. A column test conducted using this material indicated decreases in mixed As(III) and As(V) concentrations from a total of 1000 μg/L to <3 μg/L for more than 120 pore volumes (McRae et al., 1997). Research on this system is continuing.

3.2.5 Reduction of Inorganic Cations

Positively charged inorganic cations, including the metals Cd, Co, Cu, Mn, Ni, Pb, Zn, and complex cations such as UO_2^{2+} are important ground-water contaminants. High concentrations of these metals are associated with industrial wastes, mine wastes and nuclear waste disposal sites. Ground water within mine waste piles, and leachate derived from mine wastes commonly contains high concentrations of dissolved metals (Dubrovsky et al., 1984; Morin et al., 1988). Leachate derived from waste disposal areas, containing high concentrations of dissolved uranium and technetium, has been reported from the Oak Ridge National Laboratory (Olsen et al., 1986).

Reduction and precipitation of sparingly soluble solids has been proposed for inorganic cations, as well as anions. Treatment of cation-forming electroactive metals, including mercury, uranium, copper and technetium by reduction with elemental iron and coprecipitation within secondary precipitates has been investigated at the laboratory scale. Laboratory batch experiments indicate rapid removal of U(VI) and Tc(VII) from solutions in contact with elemental iron (Bostick et al., 1990; Liang et al., 1996). The reaction between U(VI) and Fe(0) can be expressed as

$$Fe^0 + UO_2^{2+}{}_{(aq)} \rightarrow Fe^{2+} + UO_{2(s)} \qquad (18)$$

where $UO_{2(s)}$ is an amorphous or crystalline uranium oxide precipitate. Strongly reducing conditions must be attained for uranium reduction and precipitation to proceed. In addition, if oxidizing conditions recur, the reduced uranium may become reoxidized and remobilized. Other metal cations potentially treatable by reduction with Fe(0) include Cu and Hg.

3.2.6 Biologically Mediated Reduction and Precipitation of Cations

Biologically mediated reduction reactions can promote the attenuation of inorganic cations. These reactions include direct reduction of the cation and precipitation of a sparingly soluble solid, and indirect precipitation resulting from the oxidation or reduction of an inorganic anion. An example of direct reduction is the reduction of U(VI) through a bacterially mediated reaction. Bacteria have been isolated that are capable of reducing U(VI) to U(IV), and sustaining metabolism based on this reaction (Lovely et al., 1991; Lovely and Phillips, 1992a; Lovely and Phillips, 1992b). It was found that U(VI) reduction by organic matter or H_2 was insignificant without microbes present. The proposed reaction for catalysis of U(VI) reduction by acetate, using the microbe *G. matallireducens* is:

$$CH_3COO^- + 4UO_2(CO_3)_2^{2-} + 4H_2O \rightarrow 4UO_2 + 10HCO_3^- + H^+ \quad (19)$$

It was also proposed that the *A. putrefaciens* could oxidize hydrogen to reduce U(VI) by the reaction:

$$H_2 + UO_2(CO_3)_2^{2-} \rightarrow UO_2 + 2HCO_3^- \quad (20)$$

Indirect precipitation of inorganic cations results from the reduction of an anion-forming species, usually sulfate. Sulfate reduction generates hydrogen sulfide, which combines with metals to form relatively insoluble metal sulfide precipitates, described in Equations 16 and 17. Laboratory studies indicate that many metals are treatable using this approach, including Ag, Cd, Co, Cu, Fe, Ni, Pb, and Zn (Waybrant et al., 1995; Waybrant et al., 1997a). Column experiments, conducted using a range of organic substrates demonstrated the potential to remove a range of dissolved metals at ground-water velocities similar to those observed at sites of ground-water contamination. A field-scale reactive barrier for the treatment of acid mine drainage and removal of dissolved Ni was installed in 1995, at the Nickel Rim mine site near Sudbury, Ontario. It was composed of municipal compost, leaf compost and wood chips. Monitoring of the reactive barrier indicates continued removal of the acid generating capacity of the ground water flowing through the PRB and decreases in dissolved Ni concentrations from up to 10 mg/L to <0.1 mg/L within the PRB. Monitoring is continuing at this site.

3.3 Enhancing Iron Reaction Rates

The range of reactivity of halogenated hydrocarbons and other contaminants with zero-valent iron illustrates the value of achieving faster degradation rates and more complete degradation of less reactive products. Research into increasing these rates has investigated metals that are stronger reducing agents than iron, the addition of aluminosilicate minerals, and metal couples. Metals that are stronger reducing agents than iron have higher oxidation potentials; i.e., yield their electrons more readily to an oxidized substance, hence they corrode faster. Aluminosilicate mineral addition and metal couples result in increased corrosion rates for the iron that is present.

Many aluminosilicate minerals seem to enhance corrosion of Fe(0) by buffering reaction pH to lower values (pH=7-8 rather than > 9). This buffering comes from dissolution of the aluminosilicate minerals (Powell et al., 1995a; Powell and Puls, 1997b) with the generation of hydrogen as protons. These protons can coordinate with the cathodic regions of the iron surfaces, accepting electrons and thereby increasing corrosion rates. In laboratory batch tests using Fe(0) with an aluminosilicate-containing aquifer material from Elizabeth City, North Carolina, the half-life of Cr(VI) in solution was decreased by an order of magnitude relative to a system with Fe(0) and silica sand. The Cr(VI) half-life was about two orders of magnitude shorter than tests where only Fe(0) was present (Powell and Puls, 1997). The protons (H^+) or their reduced species, surface coordinated monoatomic hydrogen atoms (H•), may also serve as replacement moieties for the halogen atoms on the hydrocarbons that are being reductively dehalogenated at the cathodic surfaces (Powell and Puls, 1997b).

Bimetallic systems (metal couples) prepared by plating a second metal onto a zero-valent iron surface, including Fe/Cu, Fe/Ni (Sivavec et al., 1997; Gillham et al., 1997) and Fe/Pd (Muftikian et al., 1995), have been shown to accelerate solvent degradation rates relative to untreated iron metal. Palladized iron has been shown to be effective in dechlorinating halogenated aromatic compounds such as polychlorinated biphenyls (PCBs) in addition to chlorinated aliphatic compounds (Grittini et al., 1995). The rate enhancement observed in bimetallic systems may be attributed to corrosion-inducing effects promoted by the second, higher reduction potential metal and possibly some catalytic effects. However, some investigators have found the enhanced reactivity of these systems to diminish relatively quickly, whereas others have found no apparent loss of reactivity (Gillham et al, 1997). These differences may be related to ground-water chemistry or the method used for plating the iron, but further investigation is needed. It is important to note that zero-valent iron systems have not shown similar losses in reactivity in long-term laboratory, pilot and field investigations.

4.0 Remediation Feasibility, Laboratory Treatability, and PRB Design Studies

Most, if not all, PRB installations have been designed and implemented based on the results of laboratory batch and column studies used to test reactant materials and the kinetics of contaminant removal. These data are used in combination with site-specific information (such as ground-water velocity, contaminant type and concentration, and the total mass flux of the contaminant requiring treatment). The following sections present information on these laboratory studies and how the information is used in the development of a PRB as a remedial solution. However, there will often be a need to develop some approximate design configurations and cost estimations prior to carrying out extensive laboratory studies, to determine whether PRB technology is more suitable for a site than other options. Appendix C provides some scoping calculations that have been proposed to allow such cost estimation. These can also provide some insight into the PRB emplacement methods and designs that could provide iron in thicknesses sufficient to meet the regulatory requirements of the site.

4.1 Laboratory Treatability Studies

The need for laboratory treatability studies for PRB design is primarily dependent on the contaminants present, their concentration and the geochemical conditions at the site. For contaminants where an extensive database of removal rates exists (TCE or chromate in granular iron, for example), these rate data can be used for design purposes and the treatability tests can potentially be omitted. When there are mixtures of contaminants, the geochemical conditions are significantly different from sites previously tested, or where reactive mixtures or sequential zones of reactive materials are proposed, treatability tests can be highly instructive and are strongly recommended. Laboratory treatability studies can be used to compare the reactivity and longevity of reactive materials under uniform and controlled conditions, as well as to estimate half-life ($t_{1/2}$) information useful for PRB design. In addition, performing studies at differing experimental temperatures allows determination of the temperature dependence of the reaction rates. This temperature dependence might be described by an Arrhenius expression, allowing prediction of rate constants for various types of reactions (i.e., abiotic reductive dechlorination or biologically mediated contaminant removal) over a range of temperature.

Laboratory treatability studies should be conducted using ground water from the subject plume. Although VOC degradation rates in granular iron are not greatly influenced by the inorganic chemistry of ground water, information on inorganic geochemical changes has proven to be very useful. Removal of inorganic contaminants may be strongly influenced by the background geochemistry of the plume. Every effort should be made to maintain the oxidation-reduction (redox) state of the ground water used in the studies. This requires both proper sampling and storage in the field and as the water is transferred from the field sample bottles to the influent reservoir. The possible effects of sample storage on redox state can be evaluated by comparing pre-batch and column laboratory results to field pH, DO, and Eh measurements.

4.1.1 Batch Studies

Batch treatability studies are most suitable for screening candidate reactive barrier materials. Results obtained using various types of materials give relative rates that can be useful in selecting the most appropriate material(s) for subsequent testing and/or field application. Batch tests are usually faster, cheaper, and simpler to set up than columns, and allow rapid comparison of varied parameters on the experimental results (Powell et al., 1995a).

Laboratory batch treatability tests should include blanks, which contain only site water, and reactive samples containing the candidate reactive materials along with the site water. It is simple, for example, to determine which of two types of reactive media is most effective for remediating a contaminant using batch tests. Three or more replicates for each of the two media types can be set up in capped tubes or bottles using a constant aqueous volume, contaminant concentration, and media mass (or surface area). After shaking for some interval, the concentration of the contaminant can be analyzed in each of the replicates and a determination made whether a difference exists in the effectiveness of the two types of media.

Increasing the experimental complexity somewhat by adding multiple sampling intervals allows the determination of the rate of contaminant removal using the equations of classical kinetics. Batch systems are somewhat limited in this regard, however, since shaking of the tubes or bottles negates many of the mass transport and diffusive effects that would limit reactions in unshaken systems. Also, batch tests usually have very low ratios of reactive material to solution relative to column tests and actual field implementations. Although Johnson et al. (1996) found that batch and column studies did not give distinguishable distributions of results when rate data for VOCs was normalized to iron surface area (k_{SA}), they did observe that experimental conditions determined whether the degradation rates were reaction or diffusion limited. To develop a table of representative kinetic data for dehalogenation by iron metal, they averaged reaction rates for a given halocarbon from column studies, batch tests,

and regression analyses of observed rates (k_{obs}) versus iron surface area concentration (i.e., $m^2 L^{-1}$). This resulted in average k_{SA} values with relatively large standard deviations for each halogenated organic compound. For example, TCE had an average k_{SA} value of (3.9±3.6) x 10^{-4}. Therefore, some caution is warranted when results from laboratory experiments are extrapolated to field-scale systems.

The test procedures can vary significantly depending upon contaminants of interest and characteristics of the reactive material. For a site at the U.S. Coast Guard Air Support Center, Elizabeth City, North Carolina, a series of batch experiments were conducted to evaluate the effectiveness of various commercial iron sources for the simultaneous removal of both hexavalent chromium, Cr(VI), and trichloroethene (TCE) from the site water. The results are shown in Table 6, together with the column test results using the same site water. From Table 6, it is apparent that using TCE batch test half-lives would result in an overdesign of the field treatment system. However,

Table 6. Typical Treatability Study Results, Elizabeth City Example.

6.1 Trichloroethene Half-Lives from Batch Tests.

Iron Source (1, 2, or 3)	$t_{1/2}$ (hr)
1 plus silica sand	32
2 plus silica sand	73
3 plus silica sand	31
1 plus aquifer material	22

6.2 Time to Non-Detectable Chromium Levels in Batch Tests.

Iron Source (1, 2, or 3)	time to non-detect (hr)
1 plus silica sand	0.6
2 plus silica sand	1.2
3 plus silica sand	0.4
1 plus aquifer material	0.72

6.3 Trichloroethene Half-Lives from Column Tests (v = + 2 ft/day).

Reactive Mixture	$t_{1/2}$ (hr)
100% Source 1 Iron	0.61
100% Source 3 Iron	0.80
50% Source 1 Iron, 50% Silica sand	0.97
50% Source 1 Iron, 25% sand, 25% aquifer material	0.48
50% Source 2 Iron, 25% sand, 25% aquifer material	0.99

Note: chromium removal to detection limits was obtained within 0.1 ft of travel distance in all columns (i.e., within ± 1.2 hrs)

the data does indicate which of the commercial mixtures tested (in this case iron sources 1 and 3) were the best candidates for further testing using columns.

A second use of batch tests involves the evaluation of new PRB emplacement methods. Several existing construction techniques, used historically to build low permeability (containment) walls, are being modified to facilitate the construction of permeable iron barriers at greater depths. Several of these involve the use of a finer grained fraction of iron in a biodegradable slurry mixture to allow injection or placement of this mixture in the subsurface. Laboratory-scale and limited field-scale testing has shown that the reactivity of the iron is maintained following contact of the material with guar based slurry; however, this should still be confirmed on a site-specific basis. If an enzymatic or acid-based breaker is used to promote slurry breakdown, then batch tests can also be used to confirm that the breaker used will function in the high pH, low Eh conditions established in the Fe(0).

4.1.2 Column Studies

Laboratory column tests are useful in determining contaminant removal rates under conditions that more closely approximate the operating conditions anticipated in the field, such as flow velocity. These rates are the basis for the design parameters used to determine the required residence time for the contaminant in the reactive material. Using the residence time and the flow rate, the thickness of the treatment zone can be determined. The laboratory column tests may also include sampling of the column profile and/or influent and effluent, in addition to the contaminant, to assess changes in the major ion composition of the water. These data provide information concerning potential mineral precipitation in the reactive material caused by changing redox potential (Eh) and pH conditions, which are also important parameters affecting the removal of inorganic contaminants in PRBs. Mineral precipitation rates may also impact the operation and maintenance requirements for VOC removal systems.

Though column tests are more costly and time consuming than batch tests, they typically yield more realistic field performance rates, provide a better opportunity to examine products of the reactions and can provide useful information concerning long-term performance.

4.1.2.1 Column Test Methodology

Columns are typically 10 to 100 cm long, and 2.5 to 3.8 cm inside diameter, with sampling ports at the influent and effluent ends and preferably, also along the length (Figure 2). The sampling ports are designed to allow water samples to be collected along the central axis. Details concerning column test methodology can be found in several publications (see Appendix A).

Ground water obtained from the site is supplied to the influent end of the column at a constant flow velocity using a laboratory pump. The flow velocity is selected to approximate the velocity expected in the field-scale treatment zone. Contaminant concentrations are measured at the inlet, outlet, and sampling ports along the column every 5 to 10 pore volumes (one pore volume is equal to the total volume of liquid within the column) until a steady-state concentration profile is achieved (i.e., concentrations at a point remain relatively constant over time). For example, this generally occurs after 40 to 100 pore volumes of flow for VOCs in granular iron. Eh and pH profiles are also measured periodically during the test period. Concentrations of the major cations, anions, and alkalinity are usually monitored at less frequent intervals to help predict the potential for mineral precipitation within the reactive material. If necessary, other chemical parameters relevant to a particular site can also be measured.

4.1.2.2 Interpretation of Column Data

For each test column at each velocity, contaminant concentrations are plotted as a function of distance along the column. The flow rate is used to calculate the residence time at each sampling position (relative to the influent) for each profile. The contaminant degradation or disappearance rate constants are calculated for each contaminant in the influent solution ground water, using kinetic models. For VOCs and/or chromate a first-order model is used:

$$C = C_0 e^{-kt} \tag{21}$$

where:

C = contaminant concentration in solution at time t,

C_0 = initial contaminant concentration of the influent solution,

k = first order rate constant, and

t = time.

By rearranging and taking the natural log, Equation (21) becomes:

$$\ln (C/C_0) = -kt \tag{22}$$

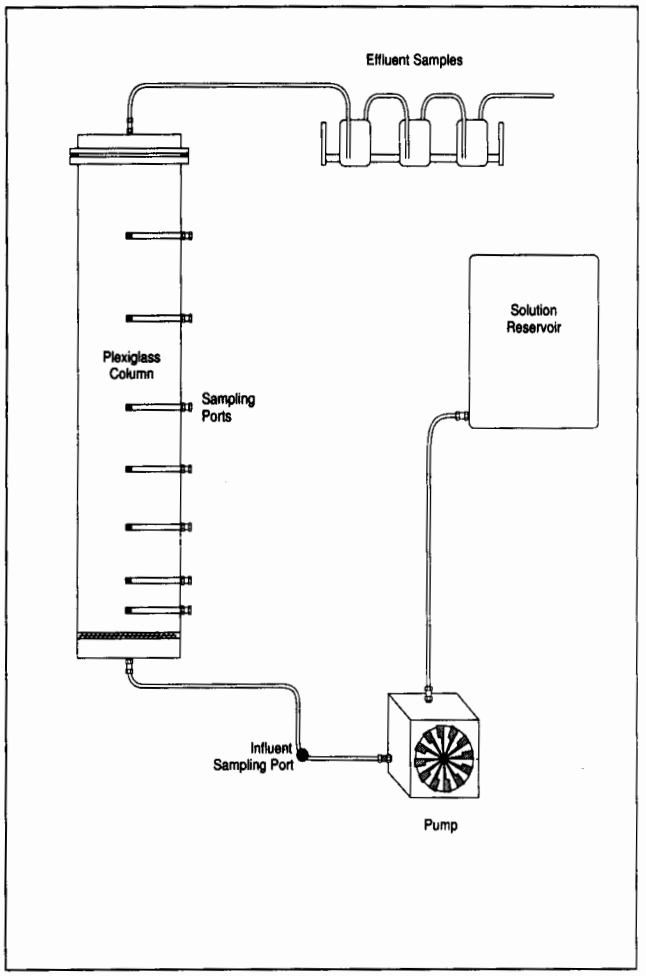


Figure 2. Schematic of the column appartus used in the bench-scale tests.

The time at which the initial concentration declines by one-half, ($C/C_0 = 0.5$), is the half life, which, by rearranging equation (22), is given by:

$$t_{1/2} = 0.693/k \tag{23}$$

The first-order rate constant, k, has the units of time^{-1} (e.g., sec^{-1}, hr^{-1}) and is computed from the slope of the first-order model obtained by fitting equation (22) to the experimental data. Half lives, along with corresponding standard error of estimate ($s_{y/x}$)values can then be calculated.

When the contaminant is a VOC, breakdown products from the VOCs in the influent solution (e.g., dichloroethene isomers from TCE) may reach maximum concentrations at an interior sampling port. In this case, an approximate degradation rate for the breakdown product can be calculated using the maximum concentration at this port, rather than the influent concentration, as C_0. Ideally, both parent and intermediate concentration data should be fitted using a first-order kinetic model to determine degradation rates and conversion factors.

A variety of mechanisms are potentially suitable for the removal of inorganic contaminants. Many of the mechanisms employed in treatment of inorganic species rely on the precipitation or adsorption of a chemical constituent. Laboratory batch and column data should be combined with geochemical modeling to assess the stability of potential precipitates, adsorbates, and to assess the potential utility of reactive mixtures for remediation of inorganics. Altering the concentrations of potential nutrients (e.g., NH_4^+, PO_4^{3-}) in biologically mediated systems permits an assessment of potential nutrient limitations on the rate of contaminant removal.

A comprehensive characterization of the water chemistry within a batch test permits the use of geochemical speciation calculations. Geochemical models commonly used to perform these calculations include MINTEQA2

(USEPA, 1993) and PHREEQC (USGS, 1998). These models contain large and comprehensive databases that can be used to evaluate the tendency for mineral phases to precipitate or dissolve based on the saturation state of anticipated minerals. MINTEQA2 also includes a variety of surface ionization/complexation models, which can be used to evaluate the potential for contaminant adsorption onto mineral surfaces.

The results from laboratory experiments can be augmented by the application of mineralogical characterization techniques and surface analytical procedures. These techniques allow the isolation and identification of reaction products, identification of the oxidation state of adsorbed or precipitated elements, and characterization of the mineral structure of secondary precipitates. Mineralogical techniques can also be used to verify the identity of secondary phases that are inferred from geochemical modeling. Accumulations of secondary minerals and the occurrence of coatings can be used to infer reaction progress and to assess potential transport limitations arising from reaction products blocking reactive surfaces.

When used in conjunction with geochemical speciation/mass transfer calculation, kinetics and column flow data can also be used to assess the rate-determining steps within an overall reaction sequence. The results of long-term column experiments can be used to assess variations in the reaction rates resulting from consumption of substrate materials, growth of bacterial species, and the formation of potentially deleterious reaction products (Waybrant et al., 1997a). These data can also be used to assess changes in the dominant reaction mechanisms.

The effectiveness of treatment of contaminant species may be limited by changes in the accessibility of the reactive material due to the formation of coatings by secondary phases. The degree and duration of treatment may also be limited by depletion of the mass of reactive material, or in the case of adsorbent barriers, by the availability of reaction sites on the substrate surface. Continuing controlled column experiments for prolonged periods of time provides an opportunity to drive the treatment system to failure, to evaluate the potential limitations of proposed field installations (Blowes et al., 1997a).

4.1.2.3 Interpretation of Changes in Non-Contaminant Inorganic Constituents

The carbonate equilibrium present in the contaminant plume may be significantly affected as the ground water passes through the reactive barrier. In Fe(0) columns, calcium and alkalinity concentrations normally decrease as ground water passes through the iron in response to increasing pH caused by the corrosion of iron. Corrosion also causes the Eh of the ground water to decrease (see Appendix B). As the pH of the solution increases, bicarbonate (HCO_3^-) ions are converted to carbonate ions (CO_3^{2-}). The CO_3^{2-} ion formed can then combine with the cations present in solution (Ca^{2+}, Fe^{2+}) to form carbonate mineral precipitates such as calcite ($CaCO_3$) and siderite ($FeCO_3$). At some sites, Mg^{2+} may precipitate in solid solution with $CaCO_3$.

Independent corrosion rate measurements of metallic iron (Reardon, 1995) indicate that several mmol/L Fe^{2+} would be introduced to ground water in these columns due to iron corrosion. In many instances, iron precipitates including siderite ($FeCO_3$), iron hydroxides and oxyhydroxides, and "green rusts" will form in the column. Observed higher carbonate alkalinity loss relative to the amount of calcium loss can be used to indicate that siderite formed in addition to calcium carbonate. Iron (oxy)hydroxides which form in the column are converted over time to magnetite (Odziemkowski and Gillham, 1997). Concentrations of iron are often observed to increase in the upgradient portion of a column due to metal corrosion, followed by decreases in iron concentrations in the downgradient part of the column as iron precipitates are formed.

Results of the influent and effluent inorganic chemical analyses can be input to a geochemical speciation model such as MINTEQA2. In MINTEQA2, aqueous concentrations are used to calculate the saturation indices (SIs) of various mineral species. These SIs can be used to gauge the potential for these minerals to precipitate. A negative SI indicates undersaturation with respect to the particular mineral phase, while a positive SI indicates oversaturation. Some caution must be used in interpreting these results, especially since such models assume equilibrium conditions and often do not take into account the potential surface reactions involving the solid phases. Kinetic controls on the reaction rates could, in some circumstances, result in lower rates of precipitate formation than predicted by the speciation models.

The reliability of the column data to gauge the potential effect of precipitates on performance of field-scale PRBs is dependent on the location of precipitation sites in-situ, and on the extent and kinetics of precipitation under field conditions. From the calcium and alkalinity profiles collected during column tests, and the data from other field trials, it appears that most of the carbonate precipitation occurs in the upgradient section of the reactive zones.

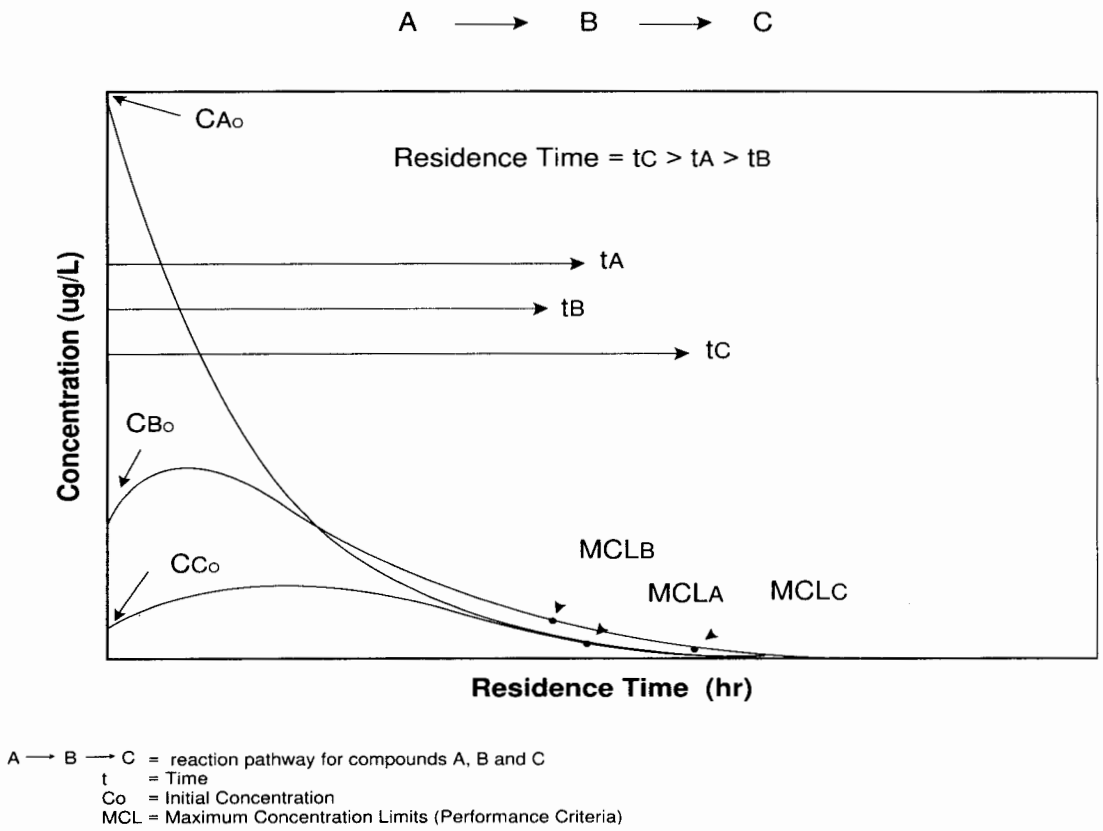


Figure 3. Conceptual residence time calulation for VOC removal.

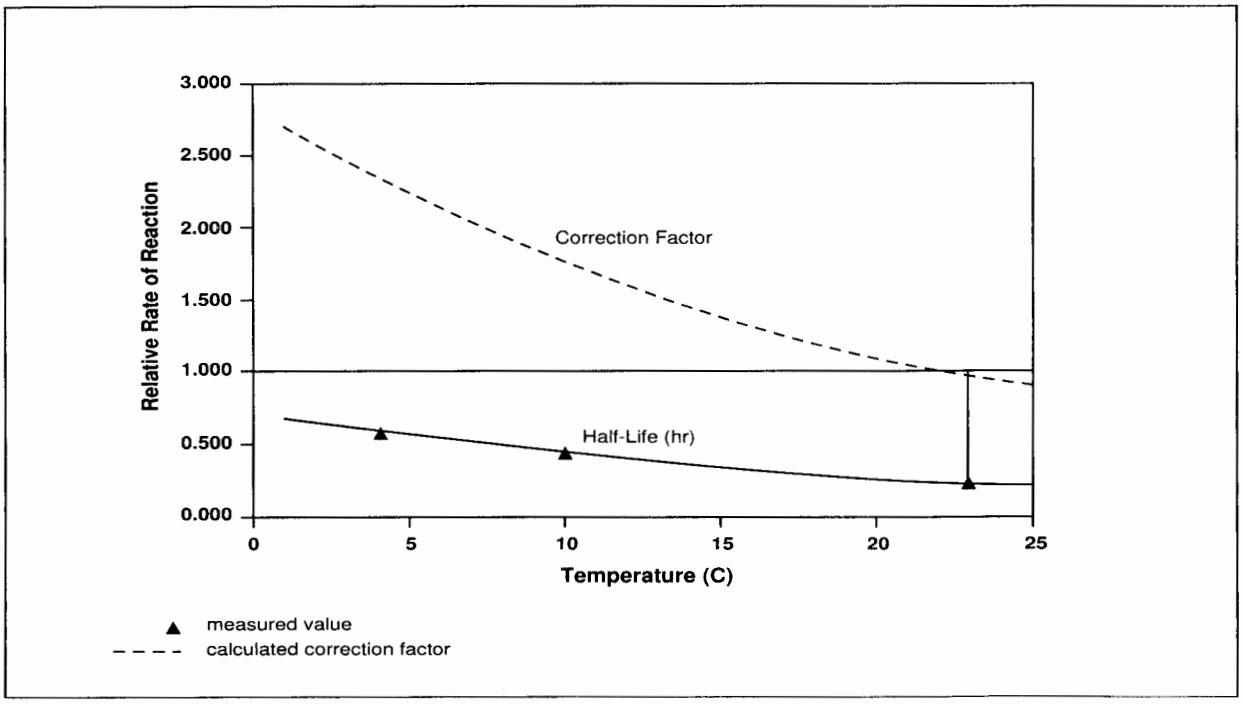


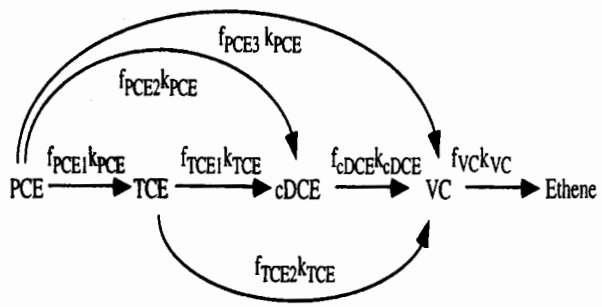
Figure 4. Correlation of TCE degradation rates with temperature.

4.2 Determination of Required Residence Time in PRBs

4.2.1 Chlorinated Volatile Organic Compounds (VOCs)

In the presence of granular iron, chlorinated organic contaminants degrade with first order kinetics. Thus required residence times can be determined from the degradation half-life. Using half-lives and influent concentrations as input, models are available that will calculate the time required to reach the desired treatment level. The most useful of these models will accommodate simultaneous degradation of several compounds and will also accommodate the simultaneous formation and degradation of breakdown products. As an example, the residence time calculation is shown conceptually in Figure 3 for PCE degradation.

In the model, potential breakdown products are concurrently produced and degraded as described by first-order kinetic equations. The model is an expression of the chemistry that is observed in the solution phase. For PCE, TCE, cDCE and VC, the model takes the form



(24)

where:

f	=	mole fraction
k	=	first-order rate constant

In order to determine the VOC concentrations at a given time, first-order equations are used either directly in commercially available software, or in their integrated form.

The residence times determined from VOC degradation rates measured in laboratory column studies of iron materials need to be adjusted due to the effects of lower ground-water temperatures. Laboratory column studies are normally performed at a temperature of about 20° to 25° C. Rate constants determined during laboratory studies can be adjusted for temperature effects using the Arrhenius equation. As an example, experimental data from controlled temperature column tests at the University of Waterloo were used to generate the linear plot of TCE degradation rate constant vs temperature (Figure 4, Stephanie O'Hannesin, personal communication). The plot indicates that at 15° C, TCE rates could be expected to decline by a factor of 1.4 from those measured at 23° C.

There has been little published to date concerning similar relationships for other VOCs such as PCE, TCA, cisDCE, and vinyl chloride. Limited testing at the University of Waterloo has shown little dependence of cDCE and vinyl chloride rates on temperature. Field observations at some sites with ground-water temperatures in the order of 8°-12° C have shown apparent decreases in TCE degradation rates by factors of 2 to 2.5, but often uncertainties in flow rates, etc., affect the interpretation of results.

4.2.2 Inorganic Constituents

Reaction rates for inorganic species vary widely, and depend on the site specific characteristics of the aquifer, the ground water and the reactive material. Laboratory tests using site ground water, or pilot-scale field tests may be required to accurately estimate reaction rates representative of field conditions. Estimates of reaction rates can be drawn from batch tests, however, the accumulation of secondary reaction products may not be accurately represented by the short-term tests. The results of column experiments may provide more accurate estimates of reaction rates under dynamic flow conditions, but again are limited by the duration of the test.

Reaction rates drawn from laboratory experiments can be incorporated into reactive solute transport models for estimating anticipated reaction progress within a reactive barrier. Direct application of laboratory rates may be possible for reactions that show little temperature dependence, or dependence on site specific parameters. Reaction rates for Cr(VI) reduction using Fe(0) shows only slight temperature dependence, allowing direct application of laboratory rates to predict field-scale performance. Biologically-mediated systems are anticipated to be more susceptible to variations in temperature and in nutrient concentrations. Direct transfer of laboratory-measured rates to these systems is less certain. Use of field-scale pilot tests is warranted until a greater understanding of the limiting factors in biologically-mediated systems is obtained.

Estimates of field reaction rates and determinations of residence time requirements must also include an assessment of the potential variability of the constructed barrier. Reasonable factors of safety need to be included in design parameters to account for construction defects and site characteristics. Ground-water flow velocities frequently vary over small spatial intervals, resulting in sharp changes in residence times within a barrier system. In addition, variability in the material reactivity and emplacement density may substantially influence the performance of a barrier system (Bennett et al., 1997).

To assess residence requirements for the Elizabeth City project, five columns containing 100% granular iron and various mixtures of iron and aquifer materials were tested using ground water from the site which contained both TCE and Cr (VI). The column flow rates (about 2 ft/day) were similar to the flow rates predicted by a ground-water transport model of the installed system. TCE half-lives obtained from the column tests are shown in Table 6. Similar to other sites, TCE degraded at relatively high rates and chromium was removed quite rapidly in all columns. The column data also indicated that VOC degradation rates rather than chromium removal rates, had the greatest influence on the required residence time in the PRB. TCE half-lives (and the half-lives determined for breakdown products cis-1,2-dichloroethene and vinyl chloride) were subsequently used in the field design (Bennett et al., 1997).

4.3 Ancillary Laboratory Studies

A variety of more specialized laboratory studies may be conducted to provide additional information which can be used in PRB design. These studies could include:

(i) laboratory hydraulic measurements (falling head tests, etc.) along with field data to provide input data for system modeling;

(ii) surface area measurements of various candidate reactive materials. (For some contaminants, these can be used to predict the relative performance of the respective materials);

(iii) breakdown product and reaction pathway analysis. (This could be accomplished either in batch or column tests and may be useful in examining compounds not previously tested);

(iv) microbial analyses of solid phase or water samples from batch/column testing. (These tests may be of particular value in evaluating PRB materials that rely on the stimulation of biological activity);

(v) tracer studies can be conducted on core samples of PRB materials to assist in evaluating the effects of precipitate formation on system performance (Mackenzie et al., 1997; Sivavec et al., 1997).

Mineralogical study could include X-ray diffraction (XRD), to determine the presence and nature of the reaction products, and Scanning Electron Microscopy (SEM) to determine the morphology of secondary precipitates. When SEM is coupled with Energy Dispersive X-ray Analysis (EDX), the qualitative distribution of elements within the reactive materials and the secondary precipitates can also be evaluated.

Other studies could incorporate surface chemical analyses, including Auger electron analyses to determine elemental composition, X-ray photoelectron spectroscopy to determine elemental concentration and oxidation state, and secondary ion mass spectroscopy (SIMS) to assess elemental composition and perform depth profiling of oxidation layers.

5.0 Site Characterization for Permeable Reactive Barriers

A complete site characterization is of critical importance for the design and installation of a reactive barrier. This characterization should include an evaluation of the surface features, structures and buried services to determine whether the site is amenable to PRB installation and, if so, what types of PRB emplacement technologies are feasible within these limitations.

The plume location and extent, ground-water flow direction and velocity, and contaminant concentrations must be accurately known to achieve the required performance. In addition, information on stratigraphic variations in permeability, fracturing, and aqueous geochemistry is needed for the PRB design. The plume must not pass over, under, or around the PRB and the reactive zone must reduce the contaminant to concentration goals without rapidly plugging with precipitates or becoming passivated. The PRB design, location, emplacement methodology, and estimated life expectancy are based on the site characterization information, therefore insufficient or faulty information could jeopardize the remediation effort.

In general, four aspects of site characterization should be evaluated before implementing a PRB:

- hydrogeology
- contaminant loading
- geochemistry, and when possible
- microbiology.

5.1 Hydrogeologic Characterization

As with any ground-water remediation technique, adequate hydrogeologic characterization must be done to understand the ground-water flow patterns and the distribution of the contaminant plume. This is especially important for the installation of a PRB since the entire plume must be directed through the reactive zone of the barrier. To attain a "passive" remediation system, the PRB must be placed in a location that allows the plume to move through the reactive zone under the natural ground-water gradient; i.e., the gradient must do all the work.

Information that must be obtained includes advective velocity parameters such as the piezometric surfaces (if a confined aquifer) or gradient, the hydraulic conductivity, porosity, and the usual hydrologic parameters typical of a careful and complete subsurface characterization. It is also important to understand seasonal changes in flow direction and flux due to processes such as recharge, since the PRB should be designed to accommodate these changes. An awareness of the effects of large pumping systems at the site, such as water supply wells or pump-and-treat remediation technologies, should also be known. These types of effects on flow velocity and direction can be intermittent and have unforeseen influences on the flow entering the PRB. Figure 5 conceptually depicts how changes in ground-water flow can reduce the effectiveness of a reactive barrier system due to incomplete plume capture.

Beyond general hydrologic factors, the stratigraphy and lithology of the site will often dictate the type of PRB design chosen. It is desirable to "key" the bottom of the barrier into a low-permeability clay layer to prevent contaminant underflow, for example. If such a layer is not available at a reasonable depth, then a "hanging" design

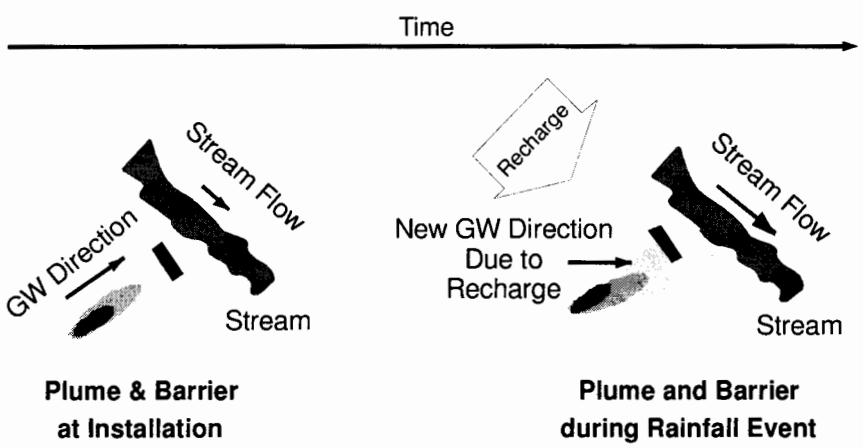


Figure 5. Potential effects of ground water flow diversion on plume direction.

might be necessary. This type of system should be engineered to prevent contaminant underflow. In addition, stratigraphic and lithologic features might limit the ability to perform certain installation procedures. Buried rock might interfere with the driving of sheet piling, for example.

Understanding the vertical variation in stratigraphy is also important for choosing the stratigraphic zone(s) that the PRB will intersect. If the contaminant plume is moving through a highly permeable layer amidst less permeable layers, the PRB should be placed vertically to encompass this high permeability layer. It is also important that impermeable materials, such as clays, not be "smeared" by the installation techniques across the permeable aquifer zone that is expected to provide flow into the PRB. Therefore, a careful evaluation of the stratigraphic variability at the location of the PRB, and the continuity of the stratigraphy with respect to the upgradient plume, will provide confidence in the design and installation.

Stratigraphic features such as fractured rock are also important. If the plume-carrying flow zone is contacted by zones of fractured rock, allowing some flow diversion into the fractures, then it is possible that some fraction of the contaminant could be short-circuited around the PRB. This could give the appearance that the remediation within the PRB is incomplete when, in fact, the PRB simply fails to intersect all the potential flow paths of the contaminant. Reactive media emplacement into bedrock fractures may be necessary to intercept contaminant migration pathways and achieve performance goals.

5.2 Contaminant Characterization

Information on contaminant concentrations is necessary for any successful remedial operation, whether pump-and-treat or in situ technologies are used. The remediation technique must be effective up to the maximum concentrations and the total mass of contaminant that will be encountered at the treatment point. This is especially important for PRBs because, once emplaced, it is difficult to change the thickness of the reactive zone. The PRB must also be designed to eliminate the possibility that portions of the plume could flow around the barrier in any direction. This requires a complete understanding of the extent of the plume, its width, depth, length, contaminant concentrations within these spatial dimensions, and how these can be expected to change over time.

Because PRBs are generally placed downgradient of the plume center-of-mass, it is important that the barrier be designed to accommodate the higher upgradient concentrations, should they arrive at the barrier unattenuated. This requires sufficient contaminant characterization to accurately determine this high concentration zone. It is also desirable to know whether this zone is moving downgradient over time or whether a pseudo-steady-state has been achieved that would suggest natural attenuation is occurring. If steady-state plume boundaries have been achieved, the PRB could be designed to transect and attenuate only the lower downgradient concentration(s) for the protection of nearby receptors or to eliminate contaminant migration beyond site boundaries. Figure 6 illustrates the potential result if a reactive barrier is not designed to fully handle the contaminant concentrations that reach it over time.

5.3 Geochemical Characterization

Site/plume geochemical information is needed for PRB design and implementation and to further our understanding of the expected lifetime of these systems. It has been shown, for example, that water passing through a reactive

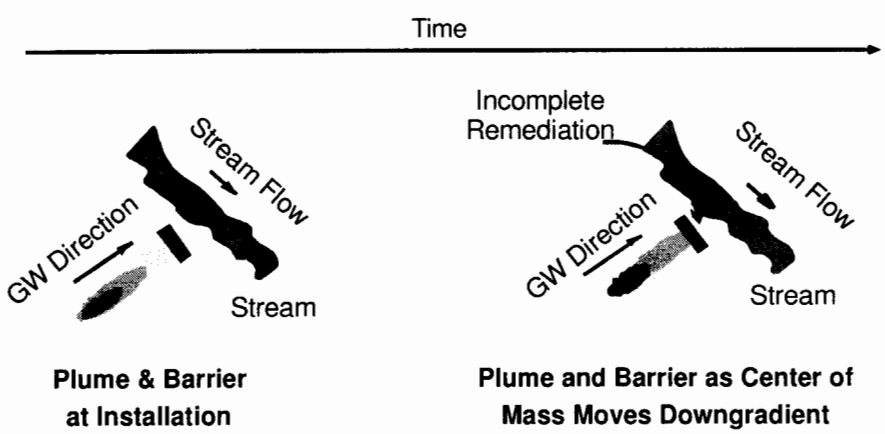


Figure 6. Effects of plume center-of-mass downgradient, and higher concentrations impacting the barrier. Incomplete remediation is now occurring.

barrier of Fe(0) undergoes radical geochemical changes, including an increase in pH up to 9 or 10, elimination of oxygen with Eh reduction to minus several hundred millivolts, and a reduction in carbonate alkalinity. Often, sulfate is reduced to sulfide and dissolved iron appears. Other changes might also be observed, dependant upon the contaminants being reacted and the overall ground-water geochemistry. Some of the geochemical changes can result in precipitation onto the reactant surfaces, potentially reducing the reactivity and permeability of the reactive zone over time. Therefore, waters high in carbonate might result in significant buildup of calcite ($CaCO_3$) or siderite ($FeCO_3$). In addition, (oxy)hydroxides can also be expected to precipitate. Of particular potential importance is the precipitation of ferric hydroxide, $Fe(OH)_3$, at the upgradient reactive zone interface due to the reaction of dissolved oxygen with the iron. At this time, the significance of these reactions over the lifetime of a field installation is not fully understood. However, column plugging in lab studies, particularly at the influent end where dissolved O_2 contacts the Fe(0), has been observed. Laboratory research is under way to identify methods of "refreshing" the reactivity of the Fe(0) surfaces should this become necessary.

To illustrate these possible effects, the upper graphic in Figure 7 depicts the flow of TCE-contaminated water through a portion of a PRB of Fe(0) shortly after installation. TCE enters and ethylene exits, with a velocity of 1 and a residence time of 1, exactly as the wall was designed. In the middle graphic precipitates have begun to significantly coat the iron particles, limiting access of the TCE to the surface for dechlorination reactions. The velocity is still about one, as is the residence time; however, in this system a residence time of one does not provide sufficient contact with the reactive surfaces due to the coatings. This results in the intermediate products of incomplete dechlorination appearing downgradient of the PRB. The bottom graphic shows that further precipitation has blocked the pore spaces between some iron particles. As a result, the entire ground-water flux must pass through the remaining open channels, making the velocity greater than one, the residence time less than one, and dechlorination incomplete. This type of plugging could also result in upgradient head increase and flow around the barrier rather than through it. It should be noted that significant plugging problems have not been observed in field scale applications using iron to degrade TCE.

5.4 Microbial Aspects

One area of site characterization for PRBs that needs further study is microbial activity. The interactions of native microbial populations, contaminants, and reactive barrier materials are likely to be quite complex, and have the potential for either beneficial or detrimental effects on the remediation. Native microbial consortia are often responsible for natural plume attenuation processes. Other beneficial effects could include enhanced contaminant degradation within or downgradient from the PRB; for example, the further reduction in Eh due to the presence of

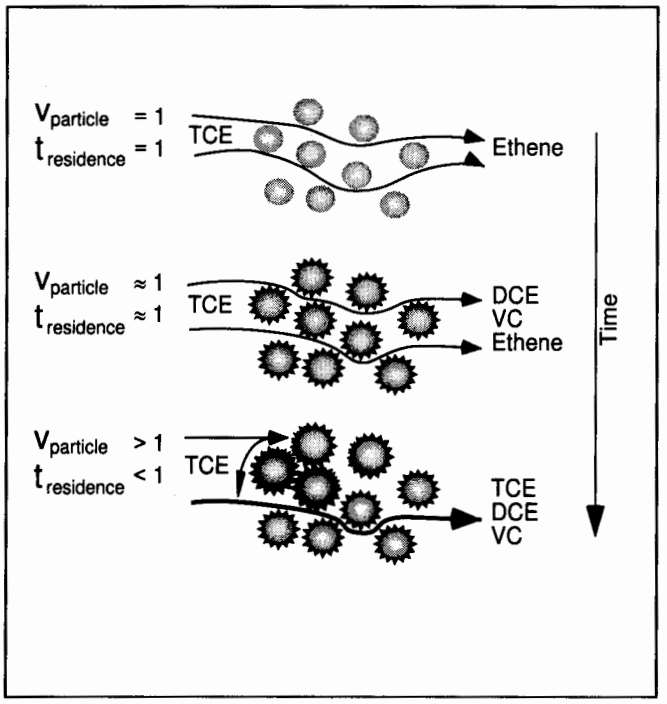


Figure 7. Potential effects of precipitation buildup on the iron over time.

sulfate-reducing bacteria might increase the rates of contaminant reduction. Adverse effects could include the potential loss of permeability of the reactive zone due to biofouling. Additional laboratory and field studies are being conducted to understand these interactions and learn how to enhance the potential positive effects and reduce the potential negative effects of native microorganisms.

5.5 Implementing the Field Characterization

All known information about the site should be assessed prior to mobilizing the field characterization. Usually some information has been obtained in the process of discovering that there is a contamination problem. Due to regulatory concerns and reporting requirements, monitoring wells may have been installed shortly after this discovery to evaluate the contaminant(s) and its concentration. This information can be combined with historical records, the memories of current or former workers, and surface features to obtain at least a general idea of the location of the source term(s) and its nature. General information on topics such as aquifer locations, yields and water table depths, water quality, stratigraphy, recharge areas, drainage basins, etc., can often be obtained from local, state and federal agencies. Although this information might not be sufficient at the (usually) smaller scale of the contaminated site for effecting a complete remedial design, it can be very helpful in designing the site characterization effort.

When this information has been compiled, the choice of locations and screen depths for a few, select aquifer testing/monitoring wells can be made, primarily to obtain general hydrologic information. Historically, plume dimensions and site characteristics have also been determined during the installation and use of such monitoring wells. However, these are expensive, time-consuming to install and sample, and require special multi-level installations to provide adequate delineation in the vertical dimension. A better approach might be to begin with surface geophysical techniques such as electromagnetic surveys, ground-penetrating radar (GPR) and seismic studies. These techniques are of particular use when a site is completely unknown with regard to subsurface features. Geophysical techniques can locate buried drums, pipes, and power lines in addition to providing information on water table and bedrock depth, fractured zones, and strata thickness. Once this information is compiled, push-tool technologies can be used for further characterization, when possible, otherwise conventional drilling techniques may be necessary. If conventional drilling is necessary, careful consideration should be given to the surface locations of the wells and the location of the screens with depth.

Push technologies, such as Geoprobe®, Hydropunch®, and cone penetrometers are rapidly becoming the tools of choice for evaluating shallow plume locations in fine- to medium-grained soils of low to moderate density. Direct push samplers can be driven rapidly and relatively inexpensively, allowing more points to be sampled than could be accomplished with monitoring wells for the same amount of time and money. They can be used to collect soil cores, water, and soil gas samples. Additionally, they can be used to collect these samples over very thin vertical intervals, allowing better delineation of the contaminant concentrations in the plume and better stratigraphic characterization than could normally be acquired with conventional exploratory drilling techniques.

6.0 Permeable Reactive Barrier Design

6.1 The Continuous PRB and Funnel-and-Gate Designs

The residence time required and the anticipated ground-water velocity through the PRB are used to determine the size of PRB needed to achieve the desired treatment level. Two basic configurations are currently being used for full-scale field application, continuous PRBs or "funnel-and-gate" designs. The effect of system configurations on flow patterns and system dimensions can be evaluated as part of the modeling effort. Factors which may affect the choice of configuration are discussed below.

Properly designed and constructed continuous PRBs (Figure 8a) have relatively minimal impact on the natural ground-water flow conditions at a site. The type of continuous PRB most commonly being installed is simply a trench that has been excavated and backfilled with granular Fe. Several other emplacement methods are possible such as hydraulic fracturing and jetting. The continuous design incorporates no funnels and, therefore, allows the water to pass through the barrier under its natural gradient and at its natural flow velocity. As a result, a continuous PRB only needs to cover an area comparable to the cross-sectional area of the plume. The ground-water flow velocity through the PRB will be very similar to the velocity in the aquifer. As long as the hydraulic conductivity of the aquifer is less than that of the PRB, underflow of contaminated ground water should not occur.

Ideally the continuous PRB is built to a depth that somewhat over-encompasses the vertical and horizontal dimensions of the contaminant plume, as a safety factor, and is filled with granular iron or some other reactive material. The PRB thickness must be sufficient to remediate the contaminant of concern to the established concentration goals. As with the funnel-and-gate design, it is desirable to place the bottom of the continuous PRB into an impermeable zone; i.e., "key" it into impermeable strata to mitigate the potential for contaminant underflow. The upgradient and downgradient surface areas of the aquifer material contacting the PRB will be approximately the same, minimizing disruption in the natural ground-water flow relative to current funnel-and-gate designs (Figure 8b).

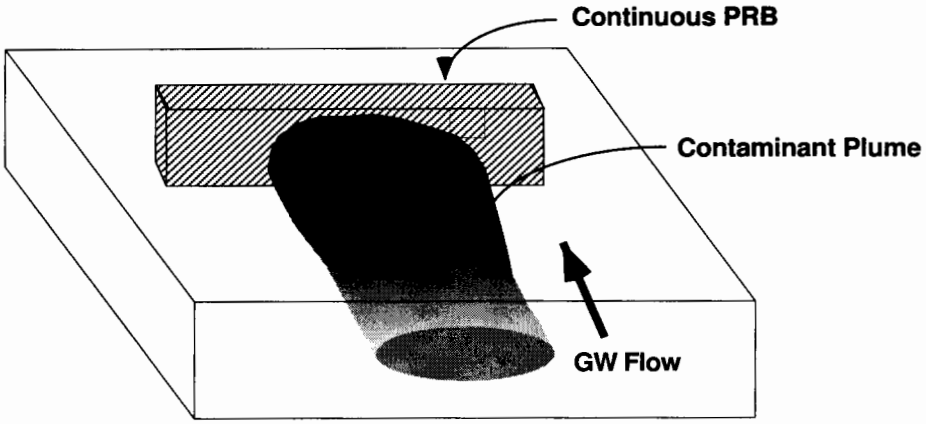


Figure 8a. Plume capture by a continuous PRB trenched system. The plume moves unimpeded through the reactive zone.

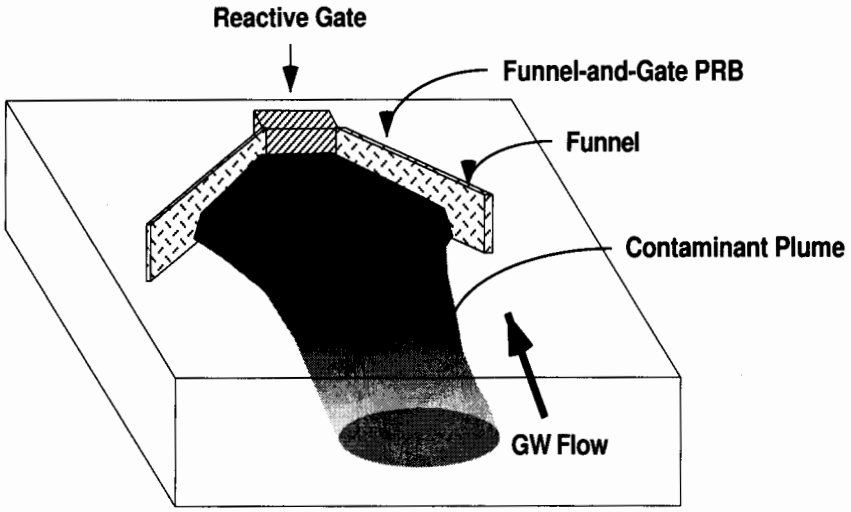


Figure 8b. Plume capture by a funnel-and-gate system. Sheet piling funnels direct the plume through the reactive gate.

A difficulty with the trench emplacement involves trenching and filling in the fully saturated zone due to the problems of immediate water intrusion and potential collapse of the trench walls. This problem requires that the aquifer materials be removed and the reactive media emplaced nearly simultaneously unless subsurface constructions (sheet pile walls, trench filling with biodegradable slurries such as guar, etc.) are used. This rapid aquifer material removal/reactive media emplacement is possible using continuous trenching devices such as the one shown in Figure 9. During June 1996 a 150 foot long, 2 foot wide, 24 foot deep continuous trench PRB of iron was installed at the U. S. Coast Guard Air Support Center near Elizabeth City, North Carolina, to intercept a mixed plume of chromate and TCE, following the success of a small-scale field test (Puls et al., 1996). This marked the first time that a continuous trenching technique had been used to emplace iron in a subsurface reactive barrier. A drawback of this type of PRB installation is the difficulty tracking the volume of reactive material actually emplaced during the construction.

In a funnel-and-gate configuration, low permeability funnels direct ground water toward permeable treatment zones or gates.The basic design of a funnel-and-gate system is shown in Figure 8b. The "funnel" typically consists of sheet pilings, slurry walls, or some other material and is preferably "keyed" into an impermeable layer (clay, bedrock) to prevent contaminant underflow. This funnel is emplaced to encompass and direct the flow of contaminated water to a "gate" or "gates" containing a permeable zone of granular Fe(0) or other reactive material.

Due to directing a large cross-sectional area of water through the much smaller cross-sectional area of the gate, ground-water velocities within the gate will be higher than those resulting from the natural gradient. The funnel portion of the design is engineered to completely encompass the path of the contaminant plume and the overall design must prevent the contaminant plume from flowing around the barrier in any direction. The gate shape may be controlled by construction techniques, but have most commonly been rectangular. Recent variations include the use of backfilled caissons, media filled hollow vibrating beams, or emplaced reaction vessels. For the emplaced reaction vessels, contaminated upgradient waters are directed into the subsurface vessel which contains reactive media, and the treated water is discharged through a pipe that extends downgradient through the impermeable wall.

The more typical rectangular, or box-shaped gate can be built by driving temporary sheet pilings and/or building removable subsurface walls within which the reactive materials are emplaced. Sheet pilings can be driven to delineate the sides and ends of the media gate. The interior of this construction can then be dewatered and excavated to make room for the reactive material (Gillham and Burris, 1992). Water intrusion is reduced by the impermeable pilings and any seepage can be pumped away. This construction approach also allows the incorporation of other features, such as additional treatment zones or monitoring zones.

The permeability of the reactive material in the gated zone must be equal to or greater than the aquifer permeability to minimize flow restrictions. At the same time, it is necessary for the flowpath length through the gate to be long enough for complete contaminant remediation; i.e., sufficient contact, or residence time, must be allowed between the reactive material and the contaminant. Overall system length depends on the number, location and size of treatment gates and should be determined through ground-water flow modeling. Particular care is required in designing and constructing the connection between the impermeable "funnel" section and the permeable "gate" section in order to avoid bypass of contaminated ground water.

Some problems can accompany the funnel-and-gate design that should be addressed, prior to installation, with a careful site characterization. Foremost among these is the potential for diversion of ground water around the funnel-and-gate. Even if the permeability of the gate section is tremendously enhanced relative to the aquifer permeability, the gate again contacts the same aquifer material on the downgradient side and permeability is immediately reduced to the initial aquifer value. It is important that the gated zone and the downgradient gate/aquifer interface be able to pass the flux of contaminated ground water intercepted by the funnels, if not the entire flux of intercepted water (both contaminated and uncontaminated). It would seem unlikely that the total volume of water in a high flux system, directed by a high surface area funnel, could be infiltrated through the much smaller surface area of the gate and aquifer material interface that contacts the downgradient side of the gate. This constriction of flow could result in a significant head difference across the reactive barrier. In fact, a seven to ten foot head difference reportedly developed across the funnel and multiple-gate system that was installed at the Denver Federal Facility, Denver, CO (Cushing et al., 1996) and has continued to persist (McMahon, 1997). The important point when designing a funnel-and-gate system, however, is not that some water is diverted around the barrier, but that none of the contaminated water is diverted and it passes through the reactive zone for treatment.

Several combinations or "treatment trains" of different types of reactive materials might be considered at specific sites containing a combination of contaminants (e.g., metals and VOCs, or VOCs and petroleum hydrocarbons). The funnel-and-gate PRB configuration may be more appropriate for these systems, providing a "focused"

treatment area. This may be of particular value if the materials need to be replaced or replenished periodically over the life of the system. These "focused" treatment areas will also facilitate performance monitoring of the system. However, research needs to be done on how to integrate differing reaction technologies into a subsurface "treatment train," so that the reactions do not interfere or limit one another.

Many of the reaction mechanisms associated with PRB materials are surface area dependent. The amount of reactive material needed is, therefore, proportional to the mass flux of contaminant requiring treatment. Therefore, both the funnel-and-gate and continuous PRB configurations should theoretically require the same amount of soil excavation and disposal since the PRB should contain the same volume of reactive material. However, in an actual field implementation, it is possible that more iron will be required by a continuous PRB using current commercial-scale installation techniques (trenching), particularly if the plume is very broad and requires a relatively long PRB. The reason for this is the need to be certain that the PRB has no unreactive gaps or flowpaths throughout its length. There will be some limiting thickness that has to be maintained to assure PRB integrity throughout its volume. The use of jetting, as an emplacement method rather than trenching, could potentially mitigate this problem for thin continuous PRBs.

Given the above, the selection of an appropriate configuration should be made on a site-specific basis. The cost of construction of either configuration will ultimately be dependent on the depth, width and saturated thickness of the plume, which controls the overall dimension of the system. Costs for reactive materials, "funnel" materials (if required), and construction will be the major capital cost components of these systems.

When considering emplacement methods and system configuration, several other factors common to subsurface construction procedures need to be considered, including:

- the need for dewatering during excavation;
- the means and costs of ground water and soil disposal;
- health and safety. The only "hazard" associated with granular iron used to date has been nuisance dust. However, the entry of construction personnel into gate excavations does create a health and safety issue;
- disruption to site activities

These factors will also influence the cost of the system.

6.2 Emplacement Methods and Comparisons

The installation methods used thus far for PRBs are few in number. Most systems have relied on standard means of excavating and backfilling to place reactive material in the path of a plume, as was discussed for the continuous PRB and the funnel-and-gate designs. Likewise, the impermeable walls of funnel-and-gate systems have used sheet pile driving or slurry wall constructions. Among the other methods being developed, tested, and implemented are the use of trenching machines, mandrel or tremie tubes, deep soil mixing, high-pressure jetting and vertical hydraulic fracturing. It is unlikely that any single approach will be found to be feasible and cost-effective for all types of applications. Rather, the value of having a variety of methods from which to choose will be the ability to select the best method for each application, with its particular combination of depth requirement, reactive media thickness requirements, stratigraphy, sensitivity to spoils generation, and other factors. Calculations based on the equations in AppendixC can be used to estimate whether a given emplacement method can provide sufficient iron thickness to accomplish site-specific remediation goals, provided the method also achieves the other emplacement requirements.

6.2.1 Conventional Excavation

Conventional excavation is a basic construction practice using equipment such as backhoes, excavators, and cranes. Standard excavators can reach depths of about 35 feet, and modified excavators can reach depths of about 70 feet. Cranes fitted with clamshells can attain greater depths.

Shallow trenches may not require any support to remain open before backfilling, but most PRB applications must be deep enough that they will need to be supported prior to being backfilled with either permeable or impermeable materials. There are two means of supporting trenches: structural walls (e.g., trench boxes) and slurries.

The trench box approach has been used to install the gate portions for most PRBs thus far. Often the final stages of excavation involve time-consuming confined entry procedures, making gate installation the most expensive component of a PRB project. As a result, some recent projects have tested other means of supporting trenches,

namely caissons (used for the Somersworth, NH, and Dover Air Force Base projects), continuous trenching machines (used at Elizabeth City, NC, Oregon, New York and California) and biodegradable slurries (Vancouver, Canada).

The use of slurries to support trenches prior to backfilling may provide significant cost savings. Bentonite slurries are commonly used for this purpose in constructing slurry walls. Bentonite slurries cannot be used to construct permeable zones, but using a biodegradable polymer solution such as guar gum may be feasible and cost-effective. A biodegradable slurry was used to install a small-scale test PRB (30ft x 6ft x 30ft) in Vancouver, Canada. Tests are ongoing to evaluate the effects (if any) of the biodegradable slurries on iron and other reactive materials.

6.2.2 Trenching Machines

Trenching machines are an effective means of installing relatively shallow trenches. The type most applicable to installing PRBs are of the "chain saw" design, which cuts a trench between 12 and 36 inches wide. During installation, the trench is held open by a trench box attached to the chain saw cutting belt mechanism. The trench box is pulled along after the cutter chain. A hopper attached to the top of the trench box can be filled with reactive material and feeds the material into the trench. Typical trenchers are limited to depths of about 20 to 30 feet, but larger equipment is expected to be more widely available in the future. Based on calculations presented in Appendix C, for a trench width of 36 inches and a granular iron bulk density of 160 lb/ft^2, the maximum weight-per-area achievable by this method is 480 lb/ft^2.

6.2.3 Tremie Tube/Mandrel

A tremie tube approach is a modification of the means of installing wick drains. A hollow rectangular tube with expendable drive shoe on the bottom is driven to depth with hydrostatic force or a vibratory hammer. The tube can then be filled with dry granular material or a slurry containing the reactive media. The tube then is extracted, leaving the drive shoe and added materials in the ground. Then the process is repeated along the desired path, each emplacement overlapping the previous one by an amount necessary to provide continuity.

This method was used to install iron-containing zones for the Phase IIA Lasagna™ project at the DOE gaseous diffusion plant in Paducah, Kentucky. In that case, mixtures of iron/coke or iron/clay were installed to a depth of 45 feet. At a bulk density of 160 lb/ft^3, the use of 100% granular iron in a 4-inch zone would give a weight-per-area of slightly more than 50 lb/ft^2 (see Appendix C).

6.2.4 Deep Soil Mixing

Deep soil mixing utilizes large augers (e.g., 3 ft to 8 ft diameter) suspended by cranes and driven by large motors. Once a zone is mixed, the auger and crane are indexed to the next location. Applications carried out to date include injecting cement or other grouting agents to build containment walls or to stabilize an area. In addition, deep soil mixing has been used with air or steam injection to volatilize contaminants.

It is thought that relatively large amounts of iron can be emplaced by deep soil mixing, but little data is available. Assuming that the resulting zone is 50% iron, 3-foot augers could be used to apply about 180 lb/ft^2, and 8-foot augers could apply up to about 480 lb/ft^2 (see Appendix C).

An important aspect of deep soil mixing is the relatively high mobilization costs associated with transporting and setting up the large equipment involved. For small projects, this may be prohibitive.

6.2.5 High-Pressure Jetting

High-pressure jetting is an established practice to inject grouting agents to improve the structural characteristics of soil for construction purposes. More recently, it has been used to inject grouts to make impermeable walls. Jetting is an attractive concept for many reasons. An important advantage in certain settings will be the ability to install a wall around obstructions such as boulders and utility lines. Also, the equipment is small and the mobilization costs are relatively low.

This approach uses jetting nozzles incorporated into a specialized section of the drill string located above the drill bit. Once the drill string reaches the desired depth, the pump increases its output (up to 90 gpm and 6,000 psi). As the slurry is injected into the formation, the drill string is extracted from the borehole at the desired rate. Due to the jetting process, most of the finer soil fractions are forced to the surface, but a significant portion of the coarser fractions remain.

If the jetting nozzle is rotated during extraction, a column of injected material forms which is approximately three to seven feet in diameter. Depending on the pumping and extraction rates, it is anticipated that the columnar zone

will contain up to 75% of the injected reactive material. Therefore, a 3-foot diameter permeable reactive zone might contain up to 360 lb/ft^2 granular iron (see Appendix C).

If the jetting nozzle is not rotated during extraction, it creates an injected zone known as a thin diaphragm wall. If such a wall averages five inches thick and contains 75% iron, then the resulting weight-per-area is 50 lb/ft^2 (see Appendix C).

A pilot test to inject granular iron was conducted recently by DuPont. Guar gum (a natural food thickener) was used as the viscosifying agent for making slurries of 50-mesh iron particles. Both columnar and thin diaphragm wall injections were successfully demonstrated. The depth of injection was only fifteen feet in this case, but the principle of using high pressure jetting was established, and it appears to be ready for use at greater depths.

6.2.6 Vertical Hydraulic Fracturing and Reactant Sand-Fracturing

In vertical hydraulic fracturing (VHF), holes are bored to initiate a fracture in permeable sands. A Fe(0)-containing fracturing fluid gel is then pumped into the fractures, forming a continuous wall of reactive material. The gel can be guar gum, which dissolves and leaves a PRB of Fe(0). The fracturing fluid used at the Caldwell trucking site, New Jersey, consisted of potable water, guar gum, a borax cross-linker (to link iron to the gel), pH buffer, an enzyme breaker (to break down starch in the guar after injection), and a fine-sand propant (Hocking, 1998). Cross-linking was necessary to prevent the iron from falling from the gel before permeating the fracture. Because many undesired reactions can occur between gel ingredients, potentially reducing the reactivity of the iron, proposed fracture fluid ingredients should be extensively tested prior to using this installation method.

Reactant sand-fracturing (RSF) uses high-pressure fracturing with a sand propant, taking advantage of the fractures that exist in bedrock, and providing a means of creating reactive fracture zones of Fe(0) within contaminated bedrock. As with VHF, a reactive fracturing fluid is needed for RSF since granular iron and iron filings do not have the needed hydraulic properties. An iron foam propant was chosen for a pilot test at a California facility as a method for placing reactive Fe(0) media into a fractured bedrock aquifer contaminated with chlorinated solvents and metals (Marcus, 1998). The pilot test consisted of boring holes, with chemical and physical testing to identify fractures containing contamination, pretreatment hydraulic fracturing (to ascertain that the injection equipment could fracture the bedrock), injection of the foamed iron propants, and post-treatment confirmation of emplacement with down-hole geophysical and geochemical testing. Cross-linkers in the propant were not necessary due to the low density of the iron foam relative to some other Fe(0) forms. The low-density foam also allowed the use of standard hydraulic fracturing equipment.

6.3 Emplacement Verification

As part of the quality assurance program for the installed system, certain measures should be used to verify emplacement of the PRB system as designed. This is most critical for continuous barrier configurations, but also required for funnel-and-gate and other emplacement designs. Whether the PRB is installed with excavation and fill, continuous trenching, hydrofracturing, or jetting, its emplacement and integrity should be confirmed. This will entail additional analyses beyond contaminant disappearance in downgradient monitoring wells. Geophysical methods have been used to a limited extent in this regard. These methods include natural gamma, conductivity, electrical resistivity, cross borehole tomography and surface radar. Tracer tests and standard hydrologic characterization methods can also provide useful information, especially when the data are combined with and compared to the data from the geophysical studies.

7.0 Monitoring Permeable Reactive Barriers

7.1 Planning the Monitoring Effort

A Quality Assurance Project Plan (QAPP) must be developed prior to any ground-water sampling, including baseline water quality data collection efforts. The QAPP must address the data quality requirements established for the project. U.S EPA's Pocket Guide for the Preparation of a Quality Assurance Plan (EPA/600/9-89/087) is a useful resource in this regard. A monitoring plan is an integral part of the QAPP for the project and emphasis should be placed on data collection methods and monitoring network design equal to that traditionally placed on analytical methods and sample handling.

All procedures and techniques used for site characterization, ground-water monitoring well installation and development, sample collection, sample preservation and shipment, analytical procedures, and chain-of-custody control should be specified in a QAPP. At a minimum, the QAPP should address

- sampling objectives
- pre-sampling activities
- sample collection
- in-situ or field analyses and equipment calibration
- sample preservation and handling
- equipment decontamination
- chain-of-custody control and records management
- analytical procedures and quantification limits for both laboratory and field methods
- field and laboratory quality assurance/quality control
- evaluation of data quality, and
- health and safety.

Other sources of useful information on the topics of QA procedures and ground-water monitoring include the following: Chapter Eleven "Ground Water Monitoring" of EPA's manual titled Test Methods for Evaluating Solid Waste (U.S. EPA 1986c, commonly known as "SW-846"); Ground Water Sampling - A Workshop Summary (EPA/600/R-94/205, 1995); Subsurface Characterization and Monitoring Techniques - A Desk Reference Guide, Vol. 1: Solids and Ground Water and Vol. 2: The Vadose Zone, Field Screening and Analytical Methods (EPA/R-93/003b, 1993).

7.2 Compliance Monitoring

7.2.1 Objectives

Compliance monitoring typically involves the monitoring of the contaminants of interest at a particular hazardous waste site where dissolved concentrations have been detected that exceed regulatory limits. The focus is on the site and its compliance points with the monitoring program driven by regulatory requirements. General water quality monitoring is also often included, such as determinations of major cations and anions and other water quality indicator parameters such as pH, alkalinity, specific conductance, etc. For permeable reactive barriers, similar compliance monitoring requirements are necessary; however, the placement and design of monitoring wells or points and the methods used to sample ground water may be different. In addition, monitoring of degradation products from reductive dehalogenation reactions or other contaminant transformation products may be required.

7.2.2 Compliance Monitoring System Design

Well placement and design are important to ensure adequate assessment of system performance. In addition to upgradient and downgradient wells, wells should be located to ensure that contaminated water is not flowing around, under, or over the barrier wall. The number of wells used will depend on system design and size. Figure 8 shows two examples for a funnel-and-gate design and a continuous wall design. Use of two inch diameter wells is usually sufficient and appropriate for compliance monitoring purposes. Smaller diameter wells or piezometers can be used if the selected sampling devices permit it. Selection of screen length should be compatible with sampling program objectives and site conditions, particularly with respect to plume location as it exists in three dimensions within the aquifer (Powell & Puls, 1997c) and the depth of the reactive zone. Compliance wells located near the permeable reaction zone should be located far enough away to avoid mixing of water from distinct geochemical

zones during purging and sampling of the wells. For example, a well located immediately downgradient of the PRB should be located such that water is not extracted from the reaction zone itself during well sampling. However, the well should not be located so far downgradient that it takes a long time to determine the effectiveness of the PRB. Similarly, wells located upgradient should not be too close to the PRB, such that water is inadvertently pulled from the reaction zone during purging and sampling operations. Wells located beneath the PRB should also be carefully located with respect to the target sampling zone. The sampling device and sampling methods employed will dictate how close wells can be located to the PRB and some thought must be given to the zone of influence during the sample collection process.

It should also be realized that if the PRB has been located to transect the contaminant plume rather than being installed entirely downgradient of the plume, compliance wells downgradient of the PRB will probably not show immediate reductions in contaminants. This is because diffusion and desorption of the contaminant from the aquifer materials downgradient of the PRB will continue for some time before gradually diminishing. Well number 46 at the Elizabeth City, North Carolina, PRB site is a good example of this phenomenon. The PRB was installed in June, 1996, with Well 46 (Figure 9) at a distance of about 56 feet downgradient of the PRB. In November of 1996, five months after PRB installation, the TCE concentration at Well 46 was 256 $\mu g\ L^{-1}$. The following September (1997), the TCE concentration was approaching compliance for TCE (10.9 $\mu g\ L^{-1}$) and was in compliance for VC.

7.2.3 Compliance Sampling Methods

Low-flow sampling methods are recommended for compliance sampling purposes (Puls and Barcelona, 1996). Low-flow refers to the velocity with which water is withdrawn from the aquifer and is usually from 0.1 to 0.5 L/min, depending upon site-specific hydrogeologic conditions. The effectiveness of using low-flow purging is intimately linked with proper screen location, screen length, and well construction and development techniques. The objective is to pump in a manner that minimizes stress to the hydrogeologic system, to the extent practical, taking into account established program sampling objectives.

The reestablishment of natural flowpath equilibrium in both the vertical and horizontal directions following disturbance of the water in the well and prior to sampling are important for correct interpretation of the data (Powell and Puls, 1993). Much of the need for purging has been found to be due to passing the sampling device through the overlying casing water, which causes mixing of these stagnant waters and the dynamic waters within the screened interval. These disturbances and impacts can be avoided using dedicated sampling equipment set within the screened interval, which precludes the need to insert the sampling device prior to purging and sampling (Powell and Puls, 1997c).

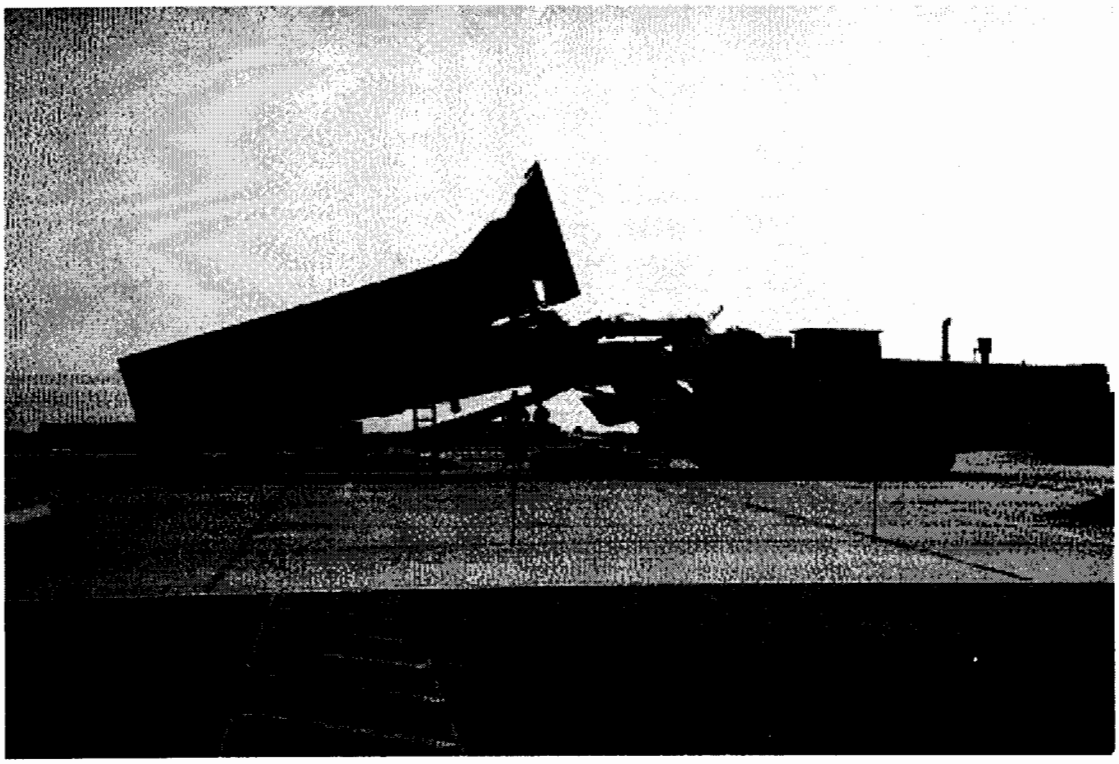


Figure 9. Continuous trencher used at Elizabeth City, North Carolina.

For high resolution sampling needs, screens less than 1 m in length should be used. Isolation of the screened interval water from the overlying stagnant casing water may be accomplished using low-flow minimal drawdown techniques. If the pump intake is located within the screened interval most, if not all, of the water pumped will be drawn directly from the formation with little mixing of casing water or disturbance to the sampling zone. However, if the wells are not constructed and developed properly, zones other than those intended may be sampled. At some sites where geologic heterogeneities are sufficiently different across the screened interval, higher conductivity zones may be preferentially sampled. This is another reason to use shorter screened intervals, especially where high vertical spatial resolution is a sampling objective.

It is recommended that water quality indicator parameters be used to determine purging needs prior to sample collection in each well. Stabilization of parameters such as pH, specific conductance, dissolved oxygen, oxidation-reduction potential, temperature and turbidity should be used to determine when formation water is accessed during purging. In general, pH stabilizes first, along with temperature and specific conductance, followed by oxidation-reduction potential (redox), dissolved oxygen and turbidity (Puls et al., 1992; Puls and Powell, 1992a). Temperature and pH, while commonly used as purging indicators, are actually quite insensitive in distinguishing between formation water and stagnant casing water; nevertheless, these are important parameters for data interpretation purposes and should also be measured. Instruments are available which utilize in-line flow cells to continuously measure the above parameters. Most of these same parameters are important performance measures for reactive barriers (e.g., for iron corrosion reactions occurring within the treatment zone).

It is important to establish specific well parameter stabilization criteria and then consistently follow the same methods thereafter. Generally, the time or purge volume required for parameter stabilization is independent of well depth or well volumes for low-flow sampling. Important variables are well diameter, sampling device, hydrogeochemistry, pump flow rate, and whether the devices are used in a portable or dedicated manner. If the sampling device is already in place (i.e., dedicated sampling systems), then the time and purge volume needed for stabilization is much shorter. Other advantages of dedicated equipment include less purge water for waste disposal, much less decontamination of equipment, less time spent in preparation for sampling as well as time in the field, and more consistency in the sampling approach which will probably translate into less variability between sampling results. The use of dedicated equipment is strongly recommended at wells which will undergo routine sampling over time, as will be the case with monitoring of permeable reactive barriers. The use of low-flow sampling techniques will also allow the placement of compliance wells closer to the treatment wall system, since the reduced purge volume will decrease the chance of mixing waters from unintended sources and zones.

Monitoring well sampling should always proceed from the well that is expected to be least contaminated to the well that is expected to be most contaminated, to minimize the potential for cross-contamination of samples that may result from inadequate decontamination of sampling equipment. Samples should be collected and containerized according to the volatility of the target analytes. The preferred collection order for some of the more common ground-water analytes is as follows (Barcelona et al., 1985):

1. Volatile organics (VOAs or VOCs);
2. Dissolved gases and total organic carbon (TOC);
3. Semivolatile organics (SMVs or SVOCs);
4. Metals and cyanide;
5. Major water quality cations and anions;
6. Radionuclides.

7.2.4 Compliance Sampling Frequency

The frequency with which compliance samples are collected should be based on the hydrogeologic character of the aquifer, the proximity of sensitive receptors such as water supply wells, and the risk posed by the contaminant(s). In general, if ground-water velocities are low, then samples can be collected less frequently than when velocities are high. As a general guideline, quarterly monitoring seems appropriate, at least initially, for most sites, with variations permitted for exceptionally slow or fast ground-water flow situations. In many cases, when the ground-water flow rate is very slow, semiannual sampling may be justifiable.

Due to the massive subsurface disturbance created during the construction and installation of a permeable reactive barrier, initial sampling results are often not representative of system performance. Re-equilibration of the ground-water flow field is required before sampling results can be properly interpreted. Based on field results thus far, this seems to take about 1-3 months. Water level measurements should be taken within the first few days, both

upgradient and downgradient of the PRB, and continued on a regular basis to ascertain that the system is functioning as designed with respect to plume capture, and the establishment and maintenance of designed flow parameters through the system and upgradient of the treatment zone. These data are relatively easy and inexpensive to obtain and the frequency of collection can therefore be increased compared to samples requiring expensive analysis.

The compliance sampling program should be reevaluated and potentially revised 1-2 years after the installation and initial data review. The sampling frequency may be reduced if quarterly sampling shows consistent results and other performance parameters indicate that the system continues to perform as designed.

7.2.5 Contaminant Breakthrough/Bypass and Formation of Undesirable Products

The primary objective of the compliance sampling program is to determine whether the treatment wall is meeting design goals for remediating the contaminated ground water. The presence of contaminants which exceed target cleanup goals in downgradient water samples is the first compliance measure most people, particularly regulators, will examine. It is equally important to examine other data with regard to meeting compliance goals. For example, hydraulic head data is arguably of equal importance to contaminant concentration data for compliance purposes. Changes in water flow patterns may lead to short circuiting of the PRB by the plume. The plume could dip below or move around the barrier due to changes in hydraulic head which could drastically alter previous flow paths. Underflow is a concern not only for hanging wall configurations (Figure 1), but also for designs keyed into low-permeability layers. Also, it should not be assumed that "impermeable" layers are perfectly flat, continuous, or even impermeable. There is typically never enough site characterization data to provide this assurance, so careful compliance monitoring is important.

It is also important to thoroughly understand the reactions which cause the transformation and destruction/ immobilization of the contaminants to be able to monitor for undesirable degradation or transformation products as part of the compliance sampling program. As was shown earlier for trichloroethylene (TCE) and Fe(0), there are two potential pathways for the reductive dechlorination to ethene and ethane to occur: sequential hydrogenolysis, and reductive ß- elimination, each leading to ethene and ethane as final products (Roberts et al., 1996). Possible intermediate products are cis- 1,2-DCE and vinyl chloride (VC). Monitoring for these intermediate constituents should be included as part of the compliance sampling program since they are also regulated toxic compounds.

In the case of chromium and Fe(0), the reaction product is an insoluble hydroxide mineral phase. This can only be confirmed using advanced surface analytical techniques, but can be inferred from non-detection of Cr(VI) and minute or non-detection of Cr(III) in aqueous samples together with ground-water quality data and geochemical modeling.

Evaluating trends in the data over time is important since this technology is new and many questions remain concerning long-term in situ performance, especially with regard to maintenance of reactivity and system permeability.

7.2.6 General Water Quality Parameters

Water quality parameters such as pH, specific conductance, alkalinity, major cations and anions and dissolved oxygen are routinely collected as part of many site assessments and remedial actions. These same data should be collected as part of the compliance sampling program for permeable reactive barriers. Also, parameters relevant to the reactive material used in the PRB should be considered for analysis. For example, when zero-valent iron is the reactive material, measurements such as redox (Eh) should be made and samples analyzed for dissolved ferrous iron. All of these parameters are important as either indicators of the corrosion process for iron-mediated transformation reactions, or for potentially undesirable secondary effects in downgradient water quality. Most of the effects due to the emplacement of a reactive iron barrier should disappear within a few meters downgradient of the reaction zone, due to the buffering of subsurface systems, but changes in downgradient water quality should be followed as part of the routine compliance monitoring program for this new and innovative remedial technology.

Physically or chemically unstable analytes should be measured in the field, rather than in the laboratory. Examples of unstable parameters include pH, redox potential, dissolved oxygen, alkalinity, temperature and dissolved iron. Dissolved oxygen (and other analyses that would be expected to vary significantly with dissolved oxygen or carbon dioxide concentration), turbidity, and specific conductance should be determined in the field as soon as practicable after purging. Most conductivity instruments require temperature compensation; therefore, the temperature of the samples should be measured at the time conductivity is determined unless the monitoring equipment automatically makes this compensation. Temperature data should also be collected as near the wellhead as possible. This reduces travel distance through the tubing and minimizes changes due to the atmospheric temperature.

Three methods generally are employed for measuring unstable field parameters: use of an in-line flow cell, collecting discrete samples and analyzing them at land surface, and using analytical equipment with probes that can be lowered into the well. The preferred method is use of an in-line flow cell. Although some investigators have experienced freezing of tubing in very cold weather, this method provides results that typically are more precise than those obtained using down-hole probes or collecting discrete samples and analyzing them at land surface. Analyzing discrete samples at the land surface involves collecting a sample in a clean bottle or beaker in the same manner that a sample for laboratory analysis would be collected, and then analyzing the sample using a field test kit or meter. Use of down-hole probes typically requires that investigators induce ground-water movement past the probe, either by physically moving the probe (potentially creating turbidity and potentially mixing casing water with screened interval water), or pumping (potentially producing inconsistent results from well to well). If down-hole probes (e.g., pH electrode, thermistor) are used to measure unstable parameters, the probes should be decontaminated in a manner that prevents them from contaminating the water in the well. In no case should field analyses be performed directly on samples that will be submitted for laboratory analysis.

7.3 Performance Monitoring

7.3.1 Objectives

Performance monitoring is focused on the PRB system itself (including impermeable funnels, if present), rather than the entire site or the compliance boundaries. Effective performance monitoring begins with adequate site characterization, to provide a baseline for later comparison, and its objective is to evaluate PRB performance relative to design. Performance monitoring of PRBs includes the evaluation of physical, chemical and mineralogic parameters over time. It should address verification of emplacement and be able to detect loss of reactivity, decrease in permeability, decrease in contaminant residence time in the reaction zone, and short circuiting or leakage in the funnel walls. In addition to monitoring the contaminants of concern and general water quality, the following are also recommended: contaminant degradation products, precipitates, hydrologic parameters and geochemical indicator parameters. Understanding the mechanisms controlling contaminant transformation, destruction or immobilization within the reaction zone is critical to interpretation of performance monitoring data as these data provide insight into barrier functionality.

7.3.2 Performance Monitoring System Design

Sample points to evaluate system performance are located within or immediately adjacent to the PRB system. Due to the relatively small zones within the aquifer where the reactive material is emplaced, these sampling points and the sampling methods can be somewhat different from the more traditional approaches employed for compliance monitoring purposes. Also, the volume of aquifer targeted for performance sample collection is usually significantly smaller than that targeted for compliance monitoring purposes.

Monitoring wells can be inserted into the reactive barrier zone easily and precisely if a shallow system is being constructed in a funnel-and-gate design. In some funnel-and-gate installations this has been accomplished by suspending the wells in a metal framework which is subsequently removed during backfilling of the treatment material. In a continuous wall design, where a trencher continuously excavates aquifer sediment and backfills with the reactive material in one step, this is not an option. Monitoring points in such designs must be installed later. This can be done using small drill rigs or by hydraulic push to place the well points. Precise placement of well points within the barrier can be problematic, particularly with increasing depth and with thin PRBs. Small vertical deviations can quickly result in screen placement into unintended zones. For example, in a 20 inch wide PRB where a well is positioned in the center of the barrier, a 3% deviation from vertical will cause the well point to exit the reactive media only 16 feet below ground surface. There are, however, rather simple and effective means to verify proper placement. Certain geochemical indicator parameters can confirm emplacement within zero-valent iron barriers. The use of a simple conductivity probe (commercially available for use in hydraulic push-type soil probes) can also verify iron placement because conductivity readings between the iron and the aquifer sediment can differ by as much as two orders of magnitude.

Smaller diameter wells (e.g., 3/4 inch i.d.) or even bundled tubes with short screens (< 1 ft screens) are often preferred for performance monitoring purposes (Figure 10). Proper location of the screened intervals in three dimensions is important for monitoring different vertical zones within the PRB as well as to provide coverage for different flow paths and allow estimation of degradation or transformation rates as the contaminants pass through the system. Similarly, these same monitoring points can be used for tracer tests to evaluate changes in permeability. The placement of monitoring points for flow path analysis requires prior detailed site characterization to determine flow path direction, flow velocities and system heterogeneities.

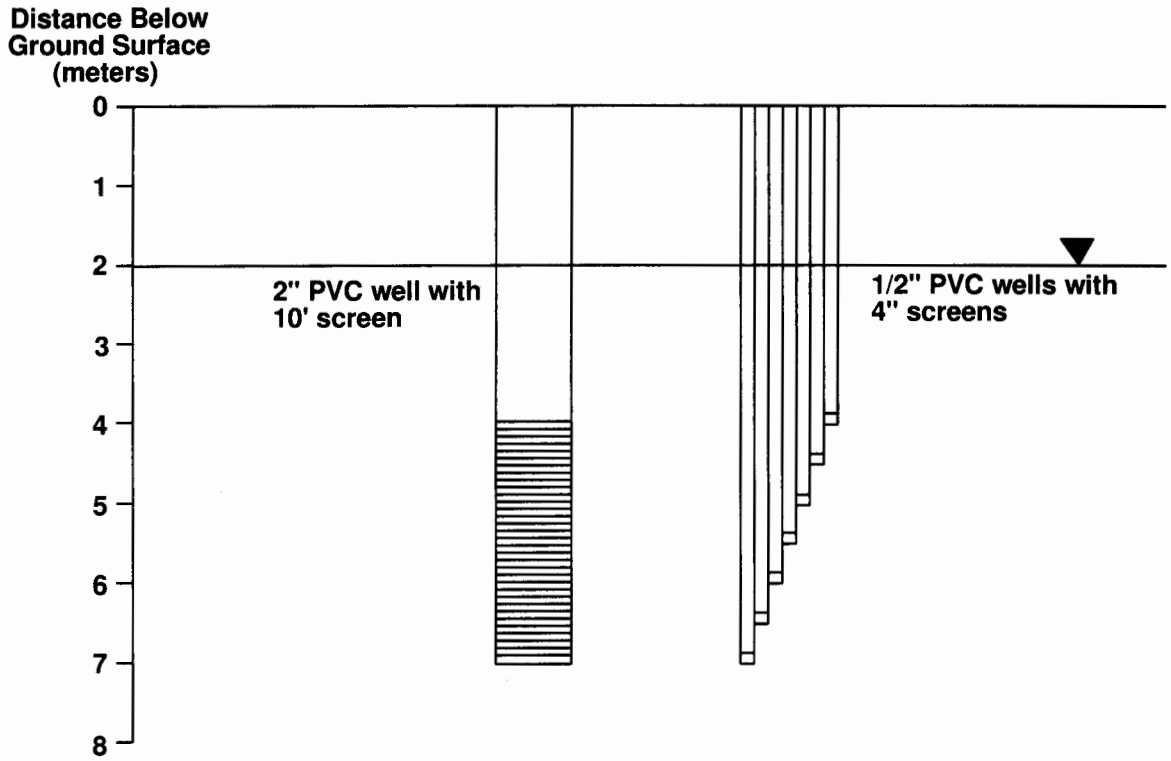


Figure 10. Bundled tubes with short screens for performance monitoring.

7.3.3 Performance Sampling Methods

Monitoring of permeable reactive barriers presents many unique challenges. Traditional sampling approaches are often inappropriate because the withdrawal of large water volumes might compromise PRB sampling objectives. Data is often sought to confirm not only contaminant reduction or removal but to provide data on contaminant transformation or degradation rates and changes in the wall reactivity. These rates and changes might need to be addressed over relatively small spatial intervals. To do this accurately, water from much smaller volumes of the aquifer or from within the PRB must be withdrawn.

The use of passive or semi-passive sampling approaches can provide the required samples for these objectives (Powell and Puls 1997c). Several researchers have demonstrated the effectiveness of using discrete-level sampling approaches (Robin and Gillham, 1987; Powell and Puls, 1993). Puls and Paul (1995) have shown the effectiveness of a discrete multi-level sampling device which can be used in traditional monitoring wells to provide no-purge samples representative of formation water. However, this work addressed only inorganic contaminants and inorganic constituents in ground water. Researchers at NRMRL-EPA are currently evaluating the use of this device for chlorinated organics and to understand the effects that highly reducing environments might have on sampling results.

7.3.4 Performance Sampling Frequency

The frequency for performance sampling will be dictated by site-specific hydrogeochemical conditions, system design, and performance sampling objectives, which should be specified prior to system installation. These objectives should be discussed among the responsible parties, the lead regulatory agency and those who will be tasked with implementing the sampling program and maintaining the remedial system. At current installations the scope of performance sampling activities ranges from almost no monitoring to extensive and detailed performance monitoring. Many of the heavily monitored installations are being used as research sites to resolve questions concerning effective implementation of the technology and long-term performance issues. As these questions are answered and issues are resolved, it is anticipated that subsequent performance sampling events will be greatly reduced over what is currently practiced. However, there will always be a need for some level of performance sampling (or at least the ability to perform such sampling on a contingency basis, should unexpected compliance results occur) to insure that the system continues to operate as designed, particularly with respect to reactivity and permeability.

7.3.5 Contaminant Degradation/Transformation

As with compliance monitoring, it is important to evaluate or confirm that the desired degradation or transformation of target contaminant species is occurring as the plume moves through the reaction zone. In addition to those degradation products which may also be regulated contaminants, it may be desirable to analyze for non-contaminant species which provide assurance of contaminant transformation.

7.3.6 Geochemical Indicator Parameters

Geochemical indicator parameters which provide some measure of system performance will vary based on the reactive barrier material and the contaminants present. For a reactive iron barrier these will include: pH, Eh, alkalinity, dissolved oxygen, total dissolved sulfide, ferrous iron and, potentially, dissolved hydrogen. These parameters can indicate that iron corrosion is proceeding and provide some indication of the extent of precipitate formation within the barrier that may eventually decrease wall performance over time. When included with general water quality monitoring and used in conjunction with geochemical modeling, these geochemical parameters can support modeling projections concerning potential precipitate formation.

For example, iron corrosion in subsurface PRB systems causes an increase in pH and can generate free Fe^{2+} and H_2 (Equations 4 and 7). Monitoring for increases in pH, the appearance of ferrous iron and increases in dissolved hydrogen can confirm that corrosion reactions are occurring. The redox status of the aqueous environment should decline significantly as the corrosion process proceeds. Levels to less than -400 mv versus the standard hydrogen electrode (S.H.E) have been observed in some installations.

Similarly, when chromate reduction by Fe(0) is occurring the key indicator parameters are pH increase and ferrous iron formation, but also include the loss of dissolved Cr from solution accompanied by the formation of a mixed Fe-Cr (oxy)hydroxide mineral phase solid solution (Equations 11 and 12). As pH increases, a shift occurs in dissolved carbonate equilibria with decreasing concentrations of carbonic acid and bicarbonate species in solution and increasing concentrations of carbonate ions. The potential for precipitation of calcite and siderite minerals can be evaluated by monitoring for changes in alkalinity, ferrous iron and calcium. By knowing which reactions govern contaminant transformation for a given system of contaminant and reactant, the monitoring program can be tailored to confirm that the system is performing as designed.

7.3.7 Coring for Precipitate Buildup, Microbial Effects

Laboratory column and field tests of Fe(0) have indicated the formation of iron (oxy)hydroxides, iron sulfide minerals, calcite and siderite as potential mineral phases which might impact iron reactivity and cause a decline in permeability within an iron treatment zone. More study is needed to evaluate the occurrence, rate of formation, and importance of these and other potential precipitates in existing emplaced iron systems. For PRBs comprised of other reactive materials, even less is known and more research is needed. Techniques that can be used to assess precipitate formation include scanning electron microscopy with energy dispersive x-ray analysis, auger spectroscopy, x-ray photoelectron spectroscopy, laser raman spectroscopy and conventional wet chemical extractions. Over time there will be less need for the collection of such core data, as the rate of precipitate formation and buildup become more predictable based on aqueous and solid phase site geochemistry and kinetics.

Microbial activity may also be important in terms of PRB performance, especially for systems dependent upon biologically-mediated contaminant remediation. Microbial characterization can utilize epifluorescence microscopy and scanning electron microscopy for microbial identification and enumeration along with fatty acid methyl ester (FAME) analyses to characterize the bacterial populations upgradient, downgradient and within the wall. In an iron PRB, the presence of a large reservoir of iron under conditions of suitable pH and substrate availability may promote the activity of iron and sulfate reducing bacteria and methanogens. Enhanced activity could influence zero-valent iron reductive dehalogenation reactions through favorable impacts on redox potential, the iron surfaces, or through direct microbial transformations of the target compounds. However, this activity enhancement may come at the expense of biofouling of the permeable treatment zone. Analysis of these effects under field conditions is under way.

7.3.8 Hydrologic Testing for Permeability Alteration

Hydrologic changes should also be closely monitored. Head measurements, tracer tests and in-situ flowmeters can be used to monitor changes in system permeability and alteration of flow paths over time. Flow heterogeneities of the natural subsurface system should be evaluated as part of site characterization and serve as the baseline for comparison to post-barrier installation. Significant changes in upgradient flow patterns or head measurements can result in hydrologic conditions which deviate from assumed design parameters and perhaps affect contaminant residence time in the reactive material or cause bypass around the reaction zone. Tracer tests performed in locations where prior tests have already been performed can be very helpful in this regard.

8.0 Field Installations

8.1 Chlorinated Hydrocarbon and Chromium Removal in Field Scale Systems

Six of the full-scale PRBs installed to date for ground-water remediation are described below. These six installations occurred from December 1994 through October 1996. From October 1997 to January 1998, six more full-scale installations have occurred. The configurations of the first six systems are shown in Figures 11 to 16, and construction details for these six are provided in Table 7. Summary information on these and other installations can be found on the internet at http://www.rtdf.org.

8.1.1 Industrial Site, Sunnyvale, California (January 1995)

In January of 1995, after being approved by the California Regional Water Quality Control Board, an iron PRB was installed at an industrial site in Sunnyvale, California (Szerdy et al., 1996). This in-situ system replaced an existing pump-and-treat system which was being maintained at a significant cost. The capital cost for the in-situ system, including the slurry walls used to direct ground water toward the permeable reactive wall, was $770,000. The reactive wall was 4 feet wide, 36 feet long and 20 feet deep (Figure 11). Since installation, VOC concentrations have been reported as non-detect from monitoring wells located within the iron wall.

The original pump-and-treat system at the site has been removed and the property has been restored to full economic use. The monitoring wells provide easy access to the in-situ system for periodic monitoring compliance.

8.1.2 Industrial Site, Mountainview, California (September 1995)

This continuous PRB was installed as a contingency measure for the remediation of residual cis 1,2-dichloroethene (cDCE) and vinyl chloride (VC) contamination found below the water table at an industrial facility in Mountainview, California. The water table at the site was 10 feet below ground surface.

A source area containing VOCs was dewatered and excavated to a depth of about 25 feet. As part of the backfilling procedure, a 44 foot long and 5 foot high zone of iron was placed at the downgradient base of the excavation (Figure 12). The iron zone was installed in order to treat any residual VOCs which were not removed during the excavation phase.

A low permeability HDPE liner was used to direct ground-water flow from the upgradient source area through the iron treatment zone. The HDPE liner was placed on top of the iron zone, and extended up to the high water table elevation on the upgradient side of the treatment zone. This ensured that any ground water contacting the HDPE

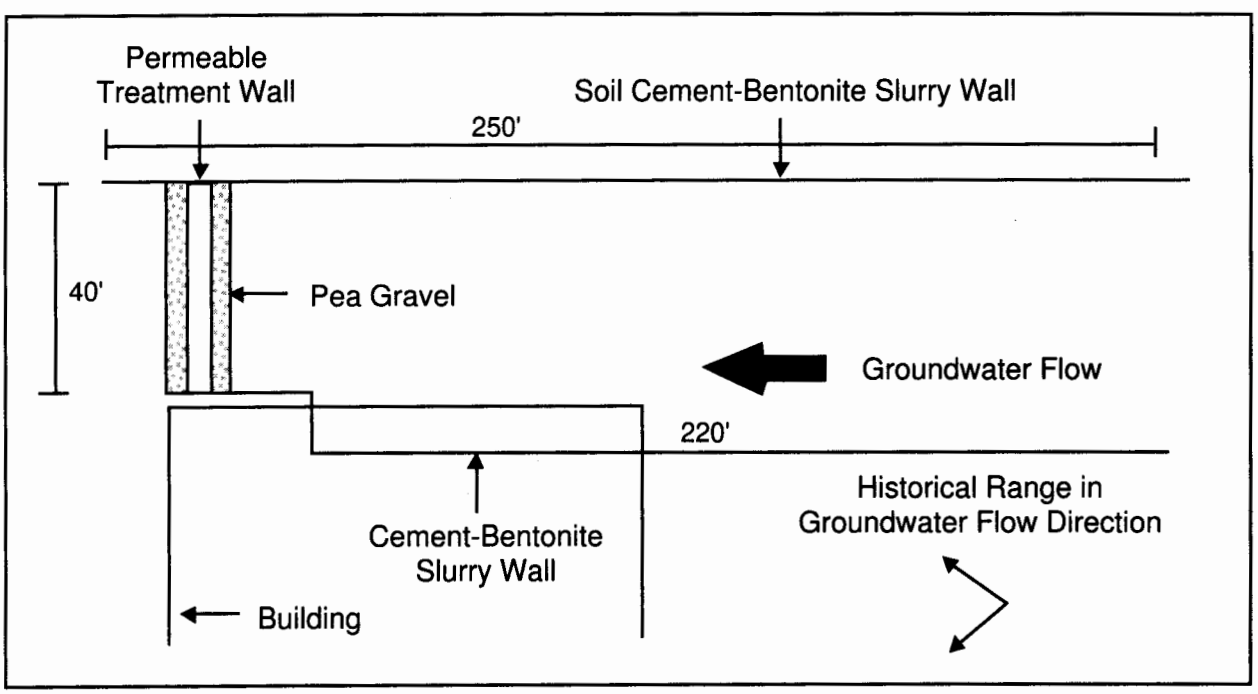


Figure 11. PRB configuration, Sunnyvale, California.

Table 7. Construction Details for Six Full-Scale Systems

Site	Industrial facility, Sunnyvale, California	Industrial facility, Mountainview, California	Industrial facility, Belfast, Northern Ireland	Industrial facility, Coffeyville, Kansas	USCG facility, Elizabeth City, North Carolina	Government facility, Lakewood, Colorado
Installation Date	Jan. 1995	Sept. 1995	Dec. 1995	Jan. 1996	June 1995	Oct. 1996
Contaminant & high conc. Design	0.5 mg L^{-1} VC 1.4 mg L^{-1} cDCE 0.2 mg L^{-1} TCE	2 mg L^{-1} cDCE	300 mg L^{-1} TCE	400 μg L^{-1} TCE	10 mg L^{-1} TCE 10 mgL^{-1} Cr(VI)	700 μg L^{-1} each TCE & DCE 15 μg L^{-1} VC
Reactive Wall Type	Funnel & Gate	Excavate & fill	Reaction Vessel	Funnel & Gate	Continuous Trench	Funnel & Multiple Gate
Funnel Material	Soil-Bentonite Slurry	Not Applicable	Slurry Walls	Soil-Bentonite Slurry	Not Applicable	Sealable Joint Sheet Pilings
Funnel Length	220 ft + 250 ft	Not Applicable	100 ft + 100 ft	490 ft + 490 ft	Not Applicable	1040 ft total
No. Of Gates	1	Not Applicable	1 Reaction vessel	1	Not Applicable	4
Reactive Material	Fe^0	Fe^0	Fe^0	Fe^0	Fe^0	Fe^0
Reactive Zone Height	10 ft	5 ft	16 ft in vessel	11 ft	Approx. 23 ft	10-15 ft
Reactive Zone Length	36 ft	44 ft	NA	20 ft	150 ft	40 ft each (4 x 40 = 160)
Reactive Zone Thickness	4 ft	4.5 ft	16 ft in vessel	3 ft	2 ft	Gates differed, low = 2 ft high = 6 ft
Total Mass of Reactant	220 tons	90 tons	15 tons	70 tons	450 tons	No Information
Treatment Wall Depth	20 ft	15 to 20 ft bgs	18 to 40 ft bgs	17 to 28 ft bgs	3 to 26 ft bgs	10-15 to 20-25 ft bgs
Total System Length	506 ft	44 ft	Approx. 200 ft	1000 ft	150 ft	1200 ft
Special Features & Misc.		HDPE atop Fe to surface upgradient directs H_2O through Fe	Walls direct H_2O to vessel inlet, gravity flow to outlet downgradient		Two contam. treated. Chain trencher with immediate Fe placement	Largest of its kind. Gates installed using sheet pile box.
Cost	$770 K	$100 K	$375 K	$400 K	$500 K	$1000 K

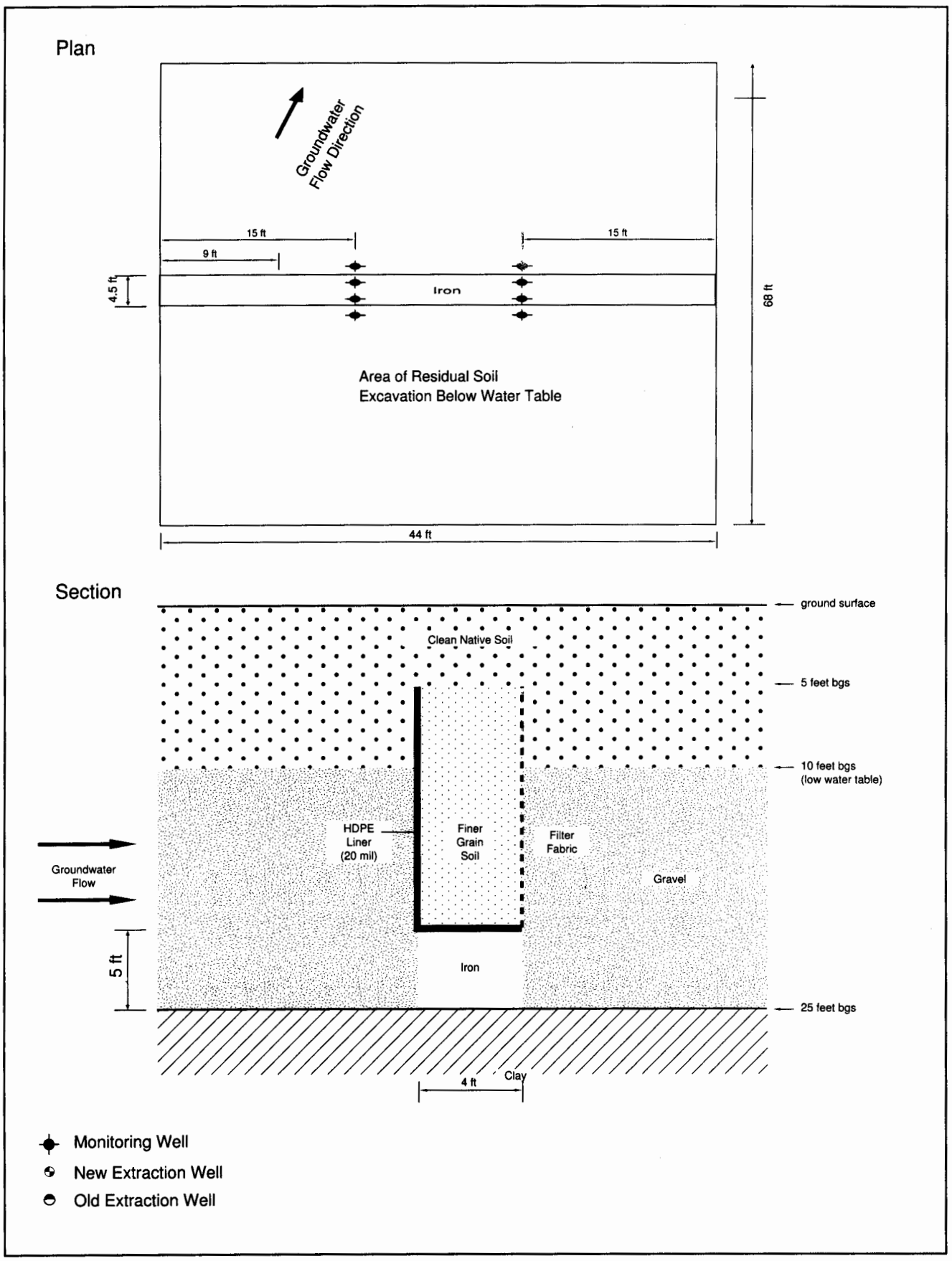


Figure 12. PRB configuration, Mountainview, California.

would be forced down and through the iron treatment zone. The entire excavation, including the iron treatment zone, was covered with clean backfill material.

The estimated construction cost of the iron treatment zone was $100,000 including $60,000 for 90 tons of iron. The 4.5 foot thick iron zone was designed to treat up to 2 ppm of cDCE and 100 ppb VC.

Monitoring at the site has been difficult because fluctuating water levels and pumpage in the area have resulted in uncertain flow patterns. It is clear, however, that VOC levels in the iron are significantly below those in the upgradient source area.

8.1.3 Industrial Site, Belfast, Northern Ireland (December 1995)

A circular in-situ reaction vessel was installed to a depth of about 40 feet at an industrial facility in Belfast to treat up to 300 ppm of trichloroethene (TCE) and related breakdown products. Two 100 foot long slurry walls direct water to the inlet of the steel reaction vessel, which is 4 feet in diameter and contains a 16 foot vertical thickness of iron (Figure 13). Ground water flows by gravity through the iron zone and discharges via a piped outlet on the downgradient side of the slurry wall. The vessel is equipped with a manhole to access the top of the iron zone, should periodic scarification of the iron surface prove necessary. The system was designed to provide about 5 days of residence time.

The total cost of the system, including slurry walls, granular iron, reaction vessel, and engineering was about $375,000 U.S.

The system was designed to meet ground-water quality criteria of 500 ppb for TCE. These criteria apply to ground water beneath industrial land slated for redevelopment. Flow rates through the reactor have varied substantially since its installation, but the TCE levels in the system have decreased to 10s of ppb in the effluent sample ports.

8.1.4 Industrial Site, Kansas (January 1996)

This treatment system was installed at the property boundary of an industrial site in Kansas in order to treat ground water containing up to 400 ppb of trichloroethene (TCE) and 100 ppb of 1,1,1-trichloroethane (TCA).

The system uses a funnel-and-gate configuration to direct ground water through a single, 20 foot long, 3 foot thick permeable treatment gate (Focht et al., 1996). The funnel section of the system consists of two 490 feet long soil-bentonite slurry walls on either side of the treatment gate (Figure 14). A low ground-water flow velocity of 0.2 ft/day permitted the use of this relatively high funnel-to-gate ratio. The system is installed to a depth of 30 feet in a basal alluvial aquifer. The treatment gate contains 70 tons of granular iron. The installation cost for the system, including slurry walls, treatment gate and granular iron, was approximately $400,000.

No determinations of ground-water velocity through the system have been made to date. Concentrations in the iron zone are below MCLs.

8.1.5 USCG Facility, Elizabeth City, North Carolina (June 1996)

A full-scale demonstration of a permeable reactive barrier (Figure 15) to remediate ground water contaminated with both chromate and chlorinated organic compounds was initiated at the USCG site by researchers from the U.S. EPA National Risk Management Research Laboratory (NRMRL) and the University of Waterloo in 1995. A continuous PRB composed of zero-valent iron was installed in June, 1996 using a trencher that was capable of installing the granular iron to a depth of 24 feet. The continuous trenching equipment used for the installation was similar to a large "Ditch Witch" (Figure 9).

This was the first application of the continuous PRB configuration in a full-scale system to treat a combined inorganic and organic plume. It was designed to meet cleanup goal concentrations of 0.05 mg/L Cr(VI), 5 μg/L TCE, 70 μg/L DCE and 2 μg/L VC. The trenched PRB was approximately 2 feet thick, 24 feet deep, and about 150 feet long. The PRB begins about 3 feet below the ground surface and consists of about 450 tons of granular iron. The total installation cost was $500,000, with the cost of iron representing approximately 35% of the total. It was installed with the trencher in less than 8 hours.

In addition to the compliance wells, the PRB is monitored using a series of multilevel sampling devices to monitor the geochemical mechanisms occurring in the barrier, and in the downgradient aquifer. To date there have been 2 years of post-installation performance monitoring performed. For all but one quarterly sampling event, 15 multi-level samplers (7 to 11 sample ports per sampler) and 9 to 10 compliance (2 in. PVC) wells have been sampled. In addition to on-site sampling of the full suite of geochemical indicator parameters listed in the site work plan, samples have been collected for laboratory analysis of the following constituents: TCE, cDCE, vinyl chloride, ethane, ethene, methane, major anions, and metals. In addition, numerous vertical and angle cores have been

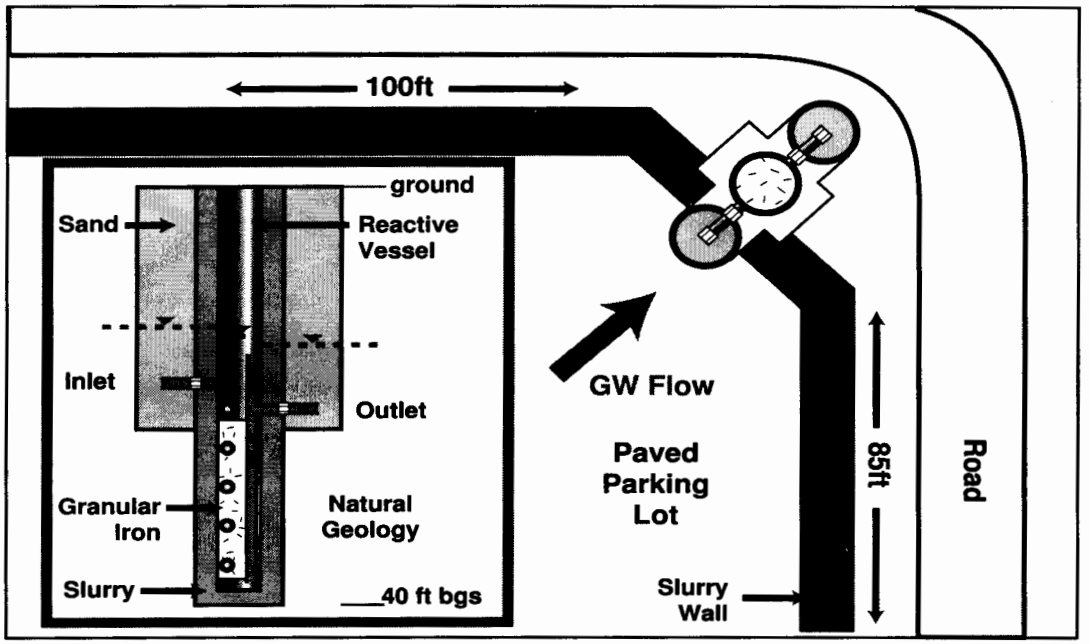


Figure 13. PRB vessel configuration, Belfast, Northern Ireland.

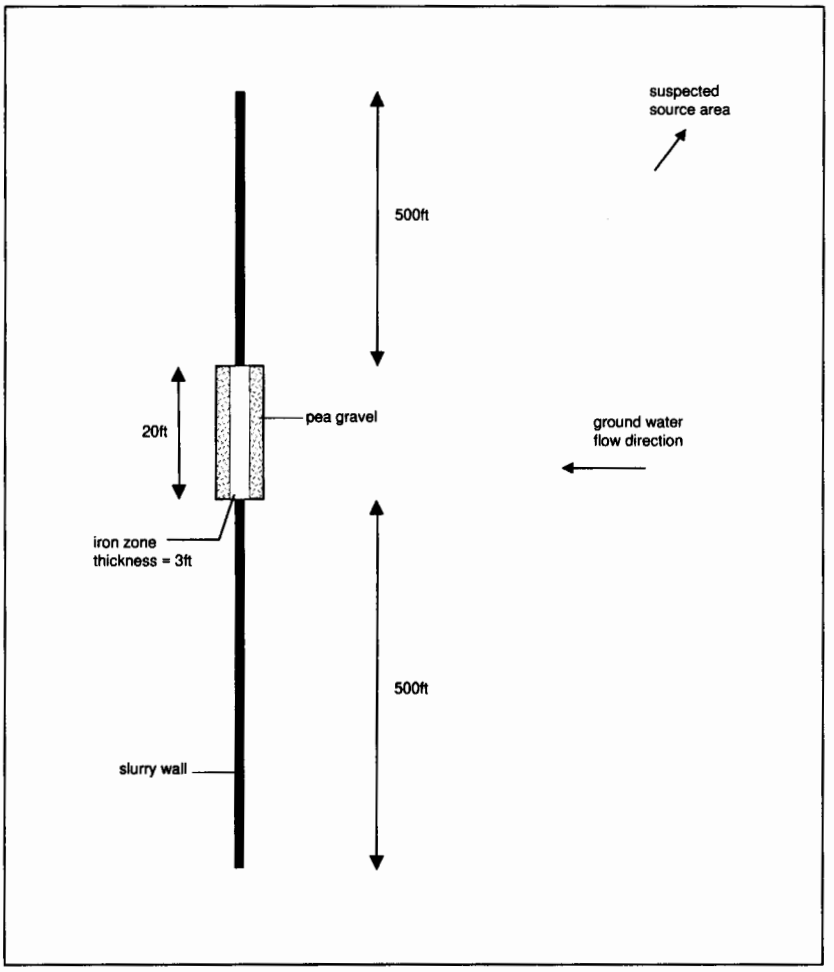


Figure 14. PRB configuration, Kansas.

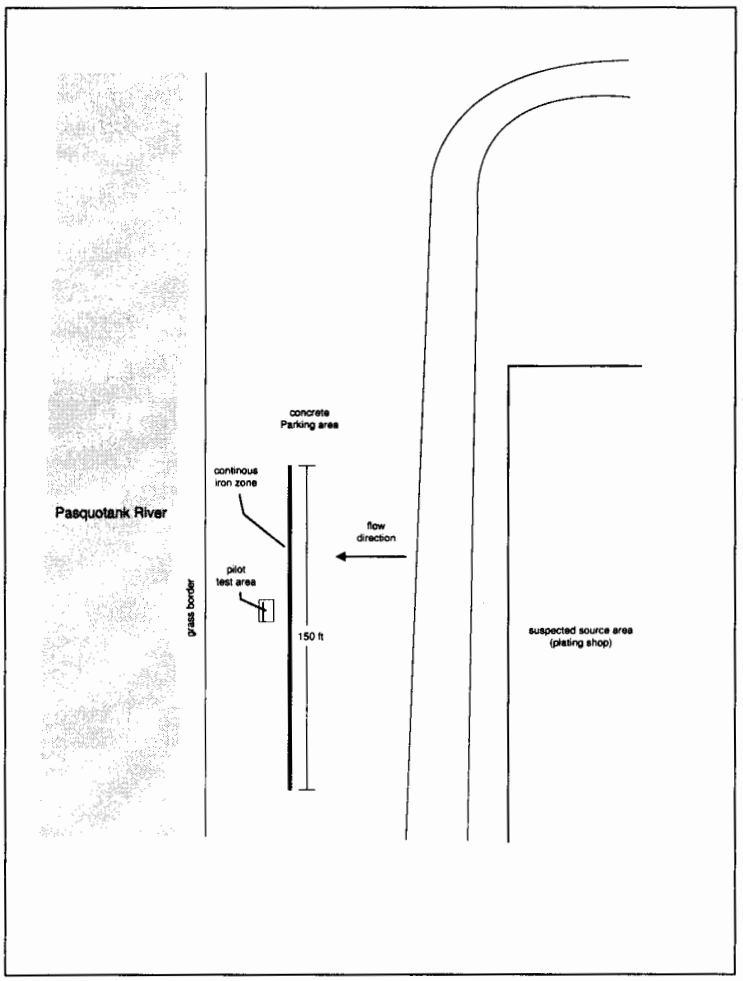


Figure 15. PRB configuration, USCG facility, Elizabeth City, North Carolina.

collected to examine changes to the iron surface over time and to evaluate the formation of secondary precipitates which may affect PRB performance over time. Coring was done vertically (perpendicular to ground surface) and on an angle (30°). The former method provided continuous vertical iron cores, while the latter provided a transverse core through the PRB with the aquifer-iron interfaces intact (front and back of the PRB). These cores continue to be under study. Inorganic carbon contents, in the form of carbonate minerals, increase dramatically at the upgradient aquifer sediment-iron interface and decrease within the PRB, reaching background levels within 4 inches downgradient from the upgradient iron-aquifer sediment interface. Total inorganic carbon content has increased over time within the PRB.

Results of geochemical sampling on site indicate that iron corrosion is proceeding within the PRB. There are significant reductions in Eh (to < -400 mv), increase in pH (to > 10), absence of DO, and decrease in alkalinity. Downgradient of the PRB (5 ft), pH returns to near neutral and Eh is quite variable with depth. Over time there have been indications that a redox front is slowly migrating downgradient within the first few meters from the PRB. Water levels indicate little difference (< 0.3 ft) between wells completed and screened at similar depths upgradient and downgradient of the PRB, indicating that it continues to effectively function as a "permeable" reactive barrier.

Sampling results for chromate indicate that all chromate was removed from the ground water within the first 6 inches of the PRB as expected. No chromate is detected downgradient of the PRB either in the multi layer samplers or in the 2 inches compliance wells located immediately behind the PRB.

The vast majority of the multilayer sampling ports show reduction of the chlorinated compound concentrations to less than regulatory target levels. Only one port (ML25-1) continues to show levels above target concentrations. This is the deepest port in the middle of the wall where the solvent concentrations are highest.

8.1.6 FHA Facility, Lakewood, Colorado (October 1996)

The first funnel-and multiple-gate system using granular iron was installed to a depth of about 25 feet below ground level at a site in Lakewood, Colorado. The system comprises about 1,040 feet of funnel section (sealable joint sheet piling) and four reactive gate sections, each 40 feet wide (Figure 16). The gates were constructed using a sheet pile "box." Native material was excavated from the box and the reactive material installed, separated from the aquifer materials by a layer of pea gravel. Capital cost of the system (iron plus construction) was about $1,000,000. A high degree of lateral geologic heterogeneity and variation in VOC concentrations exists in the unconsolidated sediments which led to varying iron thicknesses being placed in each gate. Ground water velocities through the gates were expected to range from 1 ft/day to 10 ft/day, depending upon the hydrogeologic conditions in the vicinity of the respective gates. Measurements in the PRB gates using a heat-pulse flowmeter have ranged from < 0.1 ft/day to about 1.5 ft/day (McMahon, 1997).

Design concentrations include up to 290 ppb of trichloroethane (TCA), 700 ppb of trichloroethene (TCE), 700 ppb of cis 1,2-dichloroethene (cDCE), and up to 15 ppb of vinyl chloride (VC). Half-lives of about 1 hour or less were measured for these compounds in bench-scale design studies. The only VOC exiting the gates above the 5 ppb reporting level is 1,1-dichloroethane, which has been measured at up to 8 ppb on the downgradient side of the gates. There is some evidence of the precipitation of calcite and siderite in the gates based on decreases in calcium and inorganic carbon in the treated ground water. This is estimated to result in a potential porosity loss of 0.5 percent of the porosity per year of operation.

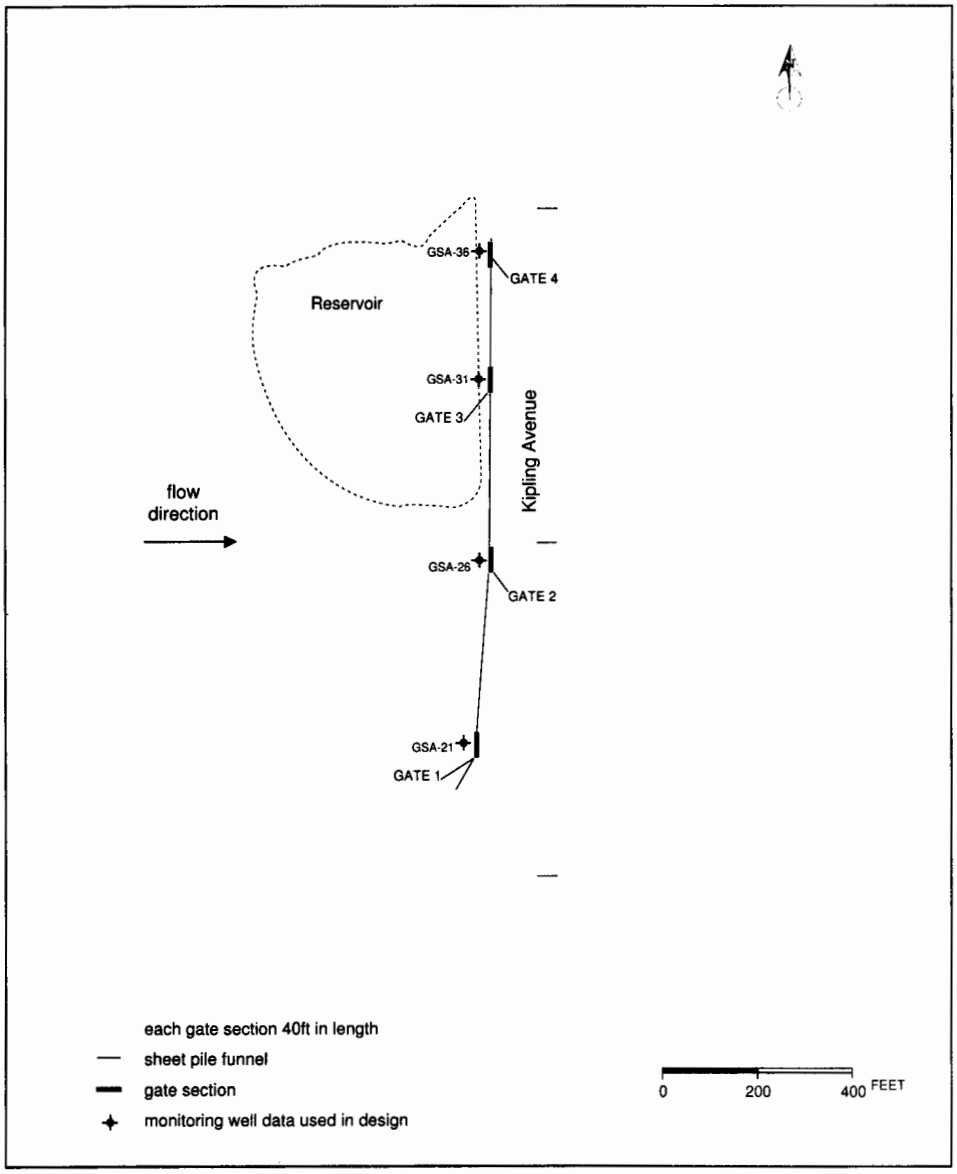


Figure 16. PRB configuration, FHA facility, Denver, Colorado.

Hydraulic head has increased upgradient of the funnel-and-gate system, with up to 10 feet of head difference measured across the barrier. This increases the possibility for contaminated water to move around the barrier. Indeed, VOC concentrations are increasing in ground waters moving around the south end of the barrier and there is some evidence of VOC moving under the barrier in one location.

8.2 Interpretation of VOC Monitoring Data from the Field-scale Systems

Although VOC concentrations from the six full-scale systems indicate compliance with regulatory criteria, the monitoring networks installed at most of these facilities do not generate sufficient field data to permit accurate evaluation of field VOC degradation rates. Pilot-scale systems at Lowry AFB and NAS Moffett Field (installed under the auspices of AFCEE and the U.S. Navy, respectively), at CFB Borden in Ontario, and at a private facility in New York state are much better suited to this purpose. Monitoring wells at these sites are located at various distances in the PRB, as well as on the upgradient and downgradient sides (Figure 17). This allows multiple point VOC concentrations vs. distance profiles to be obtained, which can be used to calculate field degradation rates.

However, there is significant uncertainty involved in these calculated rates as a consequence of uncertainty in the ground-water velocity through these systems. Three methods have been attempted to measure ground-water velocity:

- calculation using water level elevation data and Darcy's equation
- use of a conservative tracer
- use of an in-well heat pulse flow meter

Tracer tests, with bromide as a conservative tracer, may be very useful but the tests are time consuming. Calculations using water table elevations are limited by the accuracy of measurement (small gradients over short distances across the PRB) and the uncertainty in hydraulic parameters (porosity and hydraulic conductivity). The heat-pulse velocity meter has given magnitudes that are in the ranges anticipated but the directional vectors were, in some cases, suspect. Because of the ease of use, in-well velocity probes such as the K-V meter, or other in-situ probes (Ballard, 1996), appear to offer the greatest promise for velocity determinations in PRBs.

A second uncertainty in determining field reaction rates is a consequence of the rapid disappearance of the VOCs at several sites. This leads to the detection limit being used as the reported concentration at the first sample point in the reactive zone, with subsequent calculation of a degradation rate from a two point curve (i.e., the influent concentration and the detection limit). The use of detection limits in a two point curve causes an artificially long half-life to be calculated since, in reality, the detection limit would be reached at some unknown distance upgradient of the sampling point.

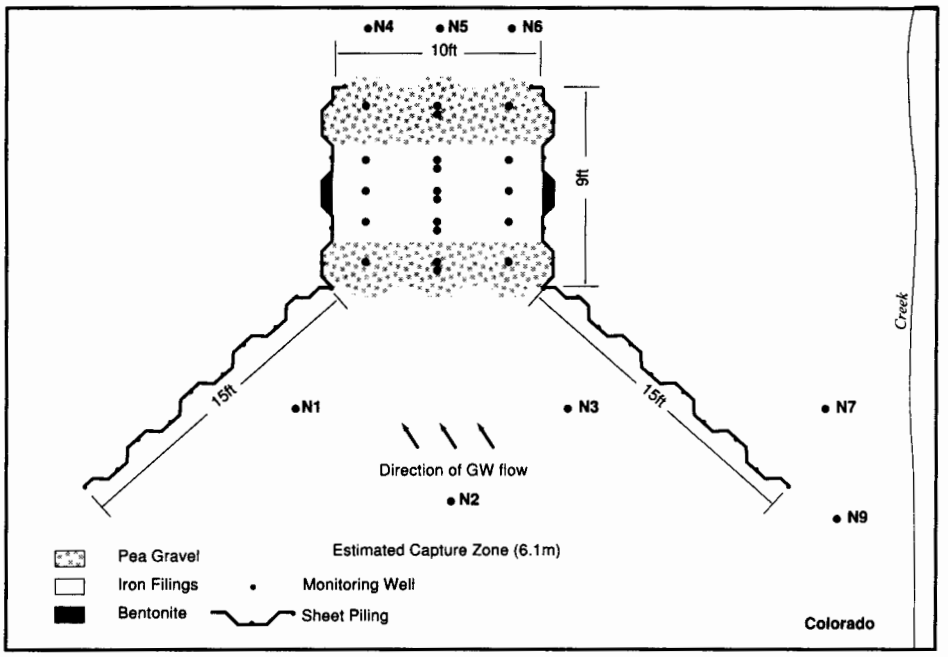
Degradation rate data from three pilot-scale PRBs are shown in Table 8. These data, when compared to the half-lives predicted from the results of bench-scale studies, compare reasonably well given the above uncertainties.

8.3 Inorganic Constituent Removal in Field-scale Systems

8.3.1 Nickel Rim Mine Site, Sudbury, Ontario (August 1995)

A full-scale continuous PRB was installed in an aquifer downgradient from an inactive mine tailings impoundment at the Nickel Rim mine site, Sudbury, Ontario, in August 1995. The PRB was installed by a cut-and-fill installation technique during which the reactive material was installed within a valley confined by bedrock. The PRB dimensions are 50 feet long, 14 feet deep and 12 feet wide. The PRB is composed of a reactive mixture containing municipal compost, leaf compost, and wood chips to promote bacterial sulfate reduction and metal sulfide precipitation reactions. These organic materials were mixed with pea gravel to attain a permeability greater than that of the aquifer. Three-foot wide buffer zones containing coarse sand were installed on the up*gradient* and downgradient sides of the reactive material.

After passing through the PRB, water quality shows a significant improvement (Benner et al., 1997). Concentrations of sulfate decrease from 2400 - 3800 mg/L to 110 - 1900 mg/L. Concentrations of Fe decrease from 740 - 1000 mg/L to < 1 - 91 mg/L. Alkalinity values increase from 60 - 220 mg/L as $CaCO_3$ to 850 - 2700 mg/L as $CaCO_3$. The acid producing potential of the water entering the wall is converted to an acid consuming potential. Concentrations of dissolved Ni up to 10 mg/L upgradient of the PRB are decreased to < 0.1 mg/L within and downgradient of the wall. Enumeration of sulfate-reducing bacteria indicates an abundance of these species within the wall, and elevated numbers in the downgradient aquifer (Benner et al., 1997).



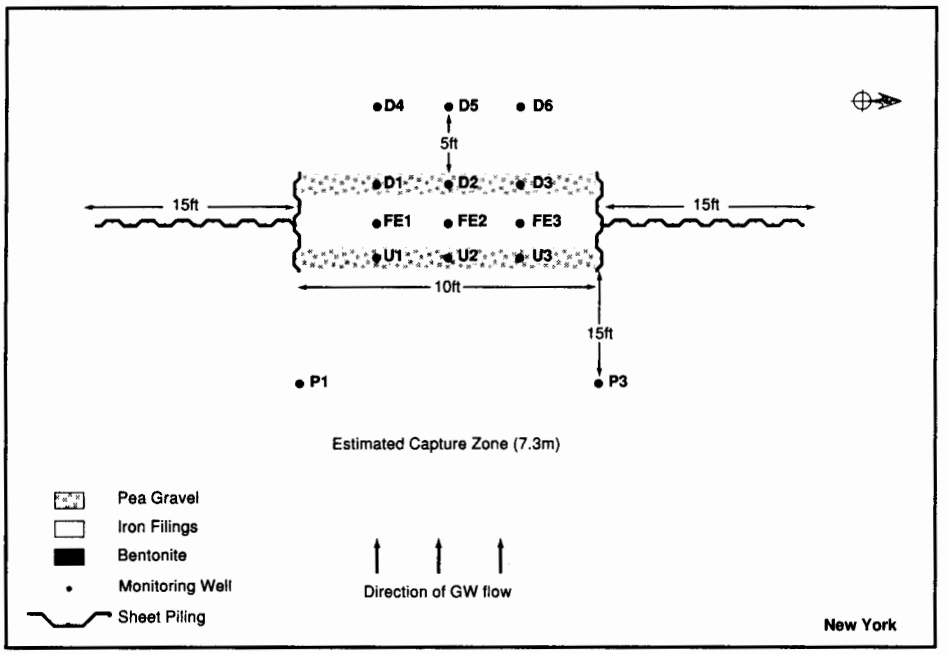


Figure 17. Pilot scale PRB configuration, Colorado and New York.

Table 8. Field Degradation Rates from Pilot-Scale Systems

(A) In-Situ Installation, New York (May 1995)

VOC	Predicted Half-Life[a] $t_{1/2}$, hr	Observed Half-Life[b] $t_{1/2}$, hr
TCE	0.4 to 1.1	< 4.0
cDCE	1.5 to 4.0	3.0 to 5.0
VC	2.0 to 6.0	5.0 to 10.0

(B) Pilot Installation Moffett Field

VOC	Predicted Half-Life[a,c] $t_{1/2}$, hr	Observed Half-Life[b,d] $t_{1/2}$, hr
PCE	0.6 to 1.2	< 2.5
TCE	1.2 to 1.8	< 0.84
cDCE	6.1 to 9.3	5.7

(C) Pilot-Scale, Lowry AFB, CO (December 1995)

VOC	Predicted Half-Life[a] $t_{1/2}$, hr	Observed Half-Life[a] $t_{1/2}$, hr
TCE	0.9 to 1.3	2.1 to 4.5
cDCE	4.4 to 6.6	2.6 to 9.3

a - rates at two velocities, temperature adjusted
b - two point curves using detection limit as second point
c - 50% iron
d - 100% iron

8.3.2 Langton, Ontario On Site Wastewater Treatment (July 1993)

A funnel-and-gate system designed to remove PO_4^{3-} and NO_3^- derived from a large-capacity septic system tile field was installed at a public school in Langton, Ontario, in July 1993 (Charmichael, 1994; Baker et al., 1997). The funnel consists of two sheet-piling walls extending 12 feet from the central gate area. The gate is 6 feet wide, 5 feet long and approximately 3 feet deep. It contains two treatment zones, a PO_4^{3-} treatment zone 2 feet thick, and a NO_3^- treatment zone 4 feet thick. The PO_4^{3-} zone contains a reactive mixture composed of 6% Fe/Ca oxide material, 9% high-Ca limestone, and 85% local aquifer sand. Phosphate is removed by adsorption onto Fe oxides and precipitation of Ca-PO_4 phases. The NO_3^- treatment zone contains organic carbon in the form of wood chips. Nitrate is removed by bacterial denitrification.

Monitoring of the performance of the barrier system for over two years indicates that influent PO_4^{3-} concentrations vary between 1.0 and 1.3 mg/L as P. Effluent concentrations within the treatment gate remained < 0.01 mg/L P for the first 221 days, then increased to a steady concentration of 0.19 ± 0.04 mg/L P (Baker et al., 1997). Nitrate

concentrations varied from 23 to 82 mg/L as N upgradient of the gate, and remained < 1 mg/L as N within the gate for a 292 day monitoring period (Charmichael, 1994). The very high organic carbon content of the nitrate treatment zone resulted in the release of high concentrations of dissolved organic carbon and other constituents from this portion of the gate. Current research focuses on optimizing the reactive mixtures for both PO_4^{3-} and NO_3^- treatment.

8.4 Biological Effects on Field-scale PRBs

8.4.1 Microbial Effects on Iron PRBs

The predominant concern expressed with respect to biological effects on iron PRBs has been the potential for loss of permeability due to biofouling. This in turn relates to iron-oxidizing bacterial populations that have been observed in aquifers at other sites and the related plugging of well screens and other treatment equipment. However, geochemical conditions and bacterial populations in an in-situ PRB of reactive iron are quite different from those encountered in normal ground-water pumping and monitoring wells. In a well screen, relatively reduced ground water containing dissolved iron enters an oxygenated environment in the well bore, creating conditions where iron-oxidizing bacteria can cause fouling problems. In an iron PRB, ground water becomes even more reducing as it moves through the iron. The pH within treatment zones of granular iron is generally close to 10, discouraging high levels of biological activity.

To date, no sliming or other visual evidence of microbial activity has been observed in over 50 laboratory-scale treatability studies, using ground waters exhibiting a wide range of inorganic and organic chemistry. Though encouraging, the applicability of these observations across a range of geochemical and microbiological in-situ conditions is subject to question.

The effects of microbial activity have also been examined at the field scale. Cores of the reactive wall at the Borden test site, collected two years after installation, showed no significant population of iron-oxidizing microbes, and only low numbers of sulfate-reducers (Matheson and Tratnyek, 1993; Matheson, 1994). No evidence of microbial fouling or decrease in performance was observed at the Borden site over a monitoring period of 5 years. Phospholipid-fatty acid analysis of ground water from an above-ground test reactor at an industrial facility in California showed no enhanced microbial populations in the reactive iron relative to background ground-water samples. An above ground reactor has been operating since October 1994 in New Jersey with no indications of biofouling.

The most detailed microbial ground-water sampling of an in-situ installation has been completed at a pilot-scale system in New York state. Data on microbial biomass and composition were collected from wells in the iron zone, in upgradient and downgradient pea gravel zones, and in upgradient and downgradient aquifer monitoring wells six months following installation. The background microbial community in the aquifer at this site appeared to be disrupted during construction, and then re-established itself in the new environment created by the gate. There was no evidence of significant microbial growth in the upgradient gravel and iron zones; the microbial populations in the upgradient, iron, and background zones appeared to be of similar size and composition. The microbial biomass in the downgradient gravel and aquifer zones was approximately 10 times greater than the microbial biomass in the background, upgradient gravel, and iron zones and was of different microbial composition. The difference in microbial population size and composition can largely be explained by the changes in the geochemistry created by the treatment wall on the downgradient side of the iron zone, notably the production of hydrogen gas from the iron which supports the activity of many obligate anaerobic bacteria such as sulphate reducing bacteria. Although the biomass increased on the downgradient side of the wall, it remained small relative to the microbial biomass commonly found in surficial soils and shallow aquifers.

Analysis of cores taken from the New York site two years after installation, and cores taken from the Lowry AFB pilot 18 months after installation, have confirmed the lack of significant microbial activity in iron PRBs. Plate counts on core samples showed only small numbers of microbial populations. No biofilms were observed on core samples examined by scanning electron microscopy.

In summary, assessment of microbial activity to date appears to show little effect on the performance of the reactive zero-valent iron materials at both the laboratory and field scale.

8.4.2 Microbial Effects in PRBs for Inorganic Constituents

Reactive barriers designed to promote biologically mediated reactions exploit the growth and respiration of anaerobic bacteria. Denitrification barriers are designed to promote biological denitrification by facultative anaerobic bacteria, such as *Pseudomonas sp.* These barriers are designed to provide the nutrients required for bacterial growth and sustained survival, with the exception of dissolved nitrate, which is provided by the plume of contaminated ground water. Observations of denitrification systems indicate active and sustained denitrification

over prolonged periods with no requirement for nutrient addition or mechanical modification (Robertson and Cherry, 1995). Although no efforts have been made to quantify the bacterial populations of these systems, continued denitrification indicates that conditions suitable for bacterial growth are sustained.

Barriers designed to promote sulfate reduction and metal precipitation as sparingly soluble precipitates require the growth and activity of sulfate reducing bacteria. Enumeration of sulfate reducing bacteria in the full-scale reactive barrier at the Nickel Rim site was conducted annually for the two years following barrier installation. The results of these studies indicate an abrupt increase in these bacteria within the barrier, increasing to more than five orders of magnitude greater than in the upgradient aquifer (S.G. Benner, personal communication). Because of changes in enumeration methods, bacterial numbers derived from the two sampling sessions are not directly comparable. These two enumerations, however, do show similar trends. In addition to sulfate reducing bacteria, the performance of the reactive barrier at the Nickel Rim site is affected by the activity of iron reducing bacteria and other heterotrophic bacteria. Enumerations of these bacteria, and estimates of bacterial activity are under way. In addition to direct enumeration of bacterial populations and measurements of bacterial activity, the activity of sulfate reducing bacteria in this system is indicated by measurements of the isotopic ratio of dissolved sulfate, the isolation of hydrogen sulfide and the identification of iron sulfide precipitates. All of these parameters indicate the occurrence and activity of sulfate reducing bacteria within the barrier.

8.5 Effects of Mineral Precipitation on Field-scale PRB Performance

Coring activity at pilot-scale PRBs in Canada, New York and Colorado have confirmed the formation of carbonate precipitates in the upgradient portion of these systems. Aragonite, calcite, iron oxyhydroxides and magnetite have been identified in core samples. Porosity losses in the range of 10% over the first foot of iron were measured at the Colorado and New York sites, after 18 months and two years of operation, respectively. Given that the original porosity of the media was on the order of 0.5, it is not expected that flow patterns have been significantly affected. The velocity measured at the New York site after two years (immediately prior to coring), was similar to that measured after six months.

To date, there is no evidence that precipitate formation in PRBs has adversely affected system performance. There was no discernible change in the performance of the CFB Borden trial over the 5-year period of monitoring. Cores taken after two years showed no measurable precipitate accumulation and only slight oxidation of the upgradient iron/aquifer interface was observed after four years (O'Hannesin and Gillham, 1998). Ground-water velocity and VOC removal rates were very similar at six months and 25 months at the New York installation. VOC removal rates appeared unchanged after 6 months and 18 months of operation of the pilot-scale PRB at Lowry AFB in Colorado.

Removal of precipitates could represent a significant operations and maintenance (O&M) cost for PRB technology. Though the evidence indicates that precipitates do not have a significantly adverse effect on reaction rates, they nevertheless form and one must assume that they will eventually cause an adverse reduction in permeability. Based on numerous laboratory evaluations of porosity loss, and fewer evaluations at field sites, it is estimated that in highly mineralized and/or oxygenated ground water some degree of maintenance could be required as frequently as every five years in order to manage potential problems caused by precipitate formation. In less mineralized waters, the frequency could be as low as every 10 to 15 years. The certainty in these estimates will increase as the period of experience grows.

To date, there has been no need for rejuvenation, thus methods have not been developed or tested. Methods that include techniques such as hydraulic or mechanical mixing are being considered. Hydraulic mixing with, for example, jetting equipment would provide the potential for adding chemical descalants. Though the need for maintenance to control the effects of precipitate formation remains uncertain, as does the most cost-effective methods for such maintenance, periodic O&M requirements should be included in long-term cost models for the technology.

Appendix A
Summary of Published Results Relevant to Subsurface Remediation Using Permeable Reactive Barriers

Appendix A. Summary of published results relevant to subsurface remediation using permeable reactive barriers

Metal (zero valent unless specified)	**Contaminant**	**Type test**	**Description/Conditions**	**Results**	**Reference**
Fe, Ultrasound (US)	TCE	Batch, Column	US is co-applied in batch/column to remove deposits from metal surface. Column 80:20 sand/iron with 50 mesh Fe, in N_2. Various concentrations of TCE used in studies. Steady flow conditions maintained throughout the columns with minimal channeling. HPLC pump used to sample from columns to provide accuracy at low flow rates and ensure minimal evaporation.	Batch: US removed inactive deposits and impurities thus extending activity of the metal surface. US also found to cleave Cl-H bond in TCE giving an added benefit. US probe in column did not extend deep enough but modifications in design show potential for application. Results w/o US in column: TCE $t_{1/2}$ = 260 min at 3mL/min; no less than 20 PV in the life of the column. $t_{1/2}$ = 360 min at 2 mL/min; samples taken after > 150 PV.	Afiouni, G.F., et al., *212th National ACS Meeting, Orlando, FL*, 36:22-29 (1996)
Fe	Nitrobenzene	Batch	Batch experiments to investigate nitro reduction by granular iron in model systems.	Nitrobenzene (disappears in few h) → nitrosobenzene → aniline Reduction by surface; dissolved Fe^{2+} & H^+ produced during corrosion.	Agrawal, A. & P.G. Tratnyek, *207th ACS Nat'l Meeting, San Diego, CA*, pp. 492 (1994)
Fe	Nitrobenzene and Carbonate	Batch	Adsorbed H_2CO_3 & HCO_3^- drives metal dissolution by: $Fe^0 + 2H_2CO_{3(ads)} \rightarrow Fe^{2+} + 2HCO_{3(ads)}^- + H_{2(g)}$ $Fe^0 + 2HCO_{3(ads)}^- \rightarrow Fe^{2+} + 2CO_{3(ads)}^{2-} + H_{2(g)}$ Corrosion rates decrease from carbonate precipitates.	Anaerobic bicarbonate buffer, Fluka Fe, and nitrobenzene as oxidant in batch exp. K_{obs} declined with increased carbonate and extended exposure of metal to carbonate buffer. $FeCO_3$ aggregates formed on metal surfaces when using bicarbonate medium but were not observed on surfaces exposed to DI water.	Agrawal, A., et al., *209th National ACS Meeting, Anaheim, CA, April 2-7*, 35:720 (1995)
Fe	Nitrobenzene	Batch	18-20 mesh Fluka Fe turnings, sonicated in 10% HCl, washed with buffer to remove acidity or Cl^-. Anaerobic batch in 60 mL serum bottles with 2 g dry, sieved Fe.	Rates for nitrobenzene (0.035) → nitrosobenzene (0.034) → aniline 0.008 /min. Rates controlled by mass transfer to metal surface. Precipitation of siderite on metal surface inhibited nitro reduction.	Agrawal, A., P.G. Tratnyek. *ES&T*, 30(1):153 (1996)
Fe	cDCE, tDCE	Batch	10 g Fisher pretreated 40-mesh filings; SA 1.0 m^2/g. 0.20 g powdered pyrite (buffer), DI water. cDCE & tDCE at two C, in ZHEs, anaerobic, at 12 rpm, 22-25°C.	Reductive dechlorination & sorption; Cl^- 80-85%; products: ethene, ethane; more VC found in cDCE. cDCE not 1st order reaction. Sorption is described by Freundlich isotherms (tDCE sorption > more soluble cDCE); quasi-equil. 1.1 h.	Allen-King, R.M., et al., *Environ. Toxicol. Chem.*, 16:424-429 (1997)
Fe	CCl_4	Batch	Aging & concentration effects of acetylene & CCl_4 in Ar-purged vials w/ 100 mL DI H_2O, 5 g HCl pretreated Fisher Fe & 0.10 g powder pyrite (buffer), 20°C, 6 rpm. Fresh systems: Fe/H_2O not mixed prior to compound exposure.	CCl_4 : initial rates in fresh systems were 2 to 4 X > in aged systems and faster at lower concentration. Acetylene initial rate (0.1 to 2.0 μmol) were > order of magnitude lower in systems aged as little as 1 d. For both compounds, pseudo-first-order rate constant independent of concentration in sufficiently aged systems (3 to 7 d). Fast reacting sites eliminated within few h due to precipitation, sorption, corrosion.	Allen-King, R.M., et al., *213th National ACS Meeting, San Francisco, CA*, 37:147-149 (1997)
Fe	Dithionite	Batch, Column	Batch and column with Hanford sediments to predict (1) longevity of dithionite, (2) efficiency as reductant of Fe (3) longevity and reactivity of the reduced Fe	Other than initial reaction with ferric iron, primary factor promoting loss of dithionite in system was disproportionation via heterogeneous catalysis at mineral surfaces.	Amonette, J., et al., *In Situ Remed.: Sci. Basis for Current & Future Technol. Sym.* Battelle Press, pp. 851 (1994)

Appendix A. continued...

Metal (zero valent unless specified)	Contaminant	Type test	Description/Conditions	Results	Reference
Fe(II) in aquifer material	Cr(IV)	Batch	Batch experiments using sand collected from a shallow sand and gravel aquifer to determine reduction of Cr(VI). C_i Cr(VI) varied 2 to 200 μM; Adjusted pH 4.5, 5.5, 6.5. *Note: Fine fraction Fe(II) minerals (≤64 μm dia.) dominated Cr(VI) reduction due to greater reactivity and SA. However, to provide consistent results fines and sands had to be separated and parallel experiments run on each.*	As pH decreased (6.4 to 4.5), Cr(VI) reduction increased 30 to 50 nmol/m^2 for the sand fraction (645 - 1000 μm) and 130 to 200 nmol/m^2 in fines. Amount reduced in both sand and fines increased from 35 to 80 and from 130 to 1000, respectively, for a 10-fold increase. Consistent rate descriptions achieve by assuming that intraparticle diffusion limited the observed rate of reduction.	Anderson, L.D., et al., ES&T, 28(1):178 (1994)
Ni-Fe Wall	Organics	In situ-Otis AFB, MA	Induce fracture to fill w/ Fe filings w/ slurry mixture moving down and outward, creating series of overlapping vertical planes thus becoming a "continuous" wall.	Plan 2 parallel 50' walls, 2' apart, perpendicular to flow path of 600' wide plume with 5 to 150 ppb TCE & PCE. Walls will begin 80' bgs to top of plume, extending to as deep as 150'.	Appleton, E.L., ES&T, 30(12):536A (1996)
Al, Fe, Zn	11 Chlorinated Solvents	Batch	Al coupon size 2 x 15 x 0.2 cm, Zn & Fe coupon 2.5 x 15 x 0.1 cm. 65 mL solvent and 5 mL DI water in 125-mL flask containing solvent and metal coupon.	Reactivity accelerated when water added. Problems with Al and Zn, but not Fe corrosion in dry systems. 1,1,2-trichloroethane only structure with appreciable oxidative breakdown.	Archer, W. & E. Simpson, Industrial Eng. Chem. Product R&D, 16(2):158 (1977)
Al, In, Cd, Bi, Sn, Ag, Ge, Sb, Cu, Hg, Pd, Th, Pb, Ti, Mn, Co	CCl_4	Batch	1 mL CCl_4 heated at 200° C, sealed tubes, for 14 d using twice the metal shot, powder, granules, or chips needed to complete reaction.	Hexachloroethane: end products perchloroethylene, hexachloro-butadiene. Most reactive Al (100%), Ti (100%), Cd (74%), antimony (58%), In (58%), Ge (47%), Sb (33%).	Archer, W.L. & M.K. Harter, Corrosion: Nat'l Assoc. of Corr. Eng. (NACE), 34(5):159 (1978)
Al	1,1,1-TCA	Batch	5 mL inhibitor-containing solvent refluxed with 0.5 g of 16-32 mesh pure Al pellets in open reaction tubes. Tubes in oil bath at 7° C. Upper portion extends through a water-cooled Al block that acts as a condenser.	Inhibitors compete with solvent for $AlCl_3$ produced at micro corrosion sites by complexing the chemisorbed $AlCl_3$ product. Resultant complex insoluble in solvent, acting as a plug covering original reaction site.	Archer, W.L., Industrial Eng. Chem. Product R&D, 21:670 (1982)
Zn	TCE, PCE rates; products	Batch	Deoxygenated water (buffered), Zn(0) PCE or TCE. Sampled for product formation. Early heterogeneous process, but initial rate does not increase linearly with increasing C_i (expected for pseudo-1st-order system), but levels off as C_i increased.	Reductive elimination (RE) important in Zn(0). ~ 15% PCE → dichloroacetylene (0.25 → acetylene bypass VC). TCE → acetylene (20% of original TCE); trace VC. Chloroacetylene intermed. → acetylene preferred over VC. Manipulating RE over initial hydrogenolysis would be beneficial goal.	Arnold, W.A. & A.L. Roberts, 213th National ACS Meeting, San Francisco, CA, 37:76-77 (1997)
Limestone	Cr	Column	Limestone or sand 2 cm over 10-cm depth of soil in PVC column. Leachate passed through columns at 1 PV/24 h until breakthrough. Unamended leachate diluted to 25% and pH 4.0 or 2.5 to keep Cr in solution. ~3,000 ppm TOC upon dilution and adjusting pH to 2.5.	Limestone delayed breakthrough of Cr. Retained Cr(III) more than Cr(VI). Retention>> Be, Cd, Fe, Ni, Zn. TOC & Fe(II) determine Cr(VI)/Cr(III) (Clay, Fe oxides better at retaining Cr). pH affects solubility of Cr and limestone. When Cr(VI) & Cr(III) in leachate, migration delayed several-fold by limestone barrier.	Artiole, J. & W.H. Fuller, Journal of Environmental Quality, 8:503-510 (1979)
Zn	CCl_4	Batch	Zinc powder ± B_{12} under N_2. Initial conc. 2.2 mM CCl_4.	Zn + B_{12} dechlorinated CCl_4 to CH_4 (50% recov). Rates slowed when B_{12} absent [CCl_4 → $CHCl_3$, DCM, CM, CH_4 (80% recov)].	Assaf-Anid, N. & L. Nies, 209th Nat'l ACS Meeting, April 2-7, Anaheim, CA, 35:09-811 (1995)
Zn	Hexachloro-benzene (HCB)	Batch	Zinc powder ± B_{12} under N_2. Initial concentration of 50 μM HCB.	Product pentachlorobenzene higher rates w/o B_{12} at 9.6 h^{-1} compared to 0.3 h^{-1} w/ B_{12}. B_{12} may compete w/ HCB for e^-.	

Appendix A. continued...

Metal (zero valent unless specified)	**Contaminant**	**Type test**	**Description/Conditions**	**Results**	**Reference**
Metal oxide from steel manufac., Limestone	Phosphorus	Column, Cylinder, Reactive Wall	Permeable mix 50% sand, 45% crushed limestone, 5% metal oxide in acrylic column w/ 3.3 mg/L PO_4-P over 3 y (1250 PV). Biofilter effluent in 0.5 x 0.5 m cylinder 2 L/d over 133 d (101 PV). Funnel-&-gate in septic plume. 7 m long funnel, 1.8 long; 2 wide; 10 deep (m) gate for 779 d.	>90% efficiency in column & cylinder. PO_4-P 0 to 0.3 mg/L in column effluent. Phosphate accumulated on oxide surfaces & precipitated as microcrystalline hydroxyapatite. Cylinder: 3.93 to 0.14 mg/L-P; 2.50 to 0.05 mg/L-*ortho* P. F&G: 4 m above 2 to 3 mg/L; 0.4 m above gate 1.5 to 0.4 mg/L. Average phosphate in wall ~ 0.19 mg P/L.	Baker, M.J., et al., Internat'l Contain. Technol. Conf. & Exhib., St. Petersburg, FL, Feb 9-12, pp. 697 (1997)
Fe	TCE; DCE, VC, dichloro-methane	Batch, Column	Site ground water (GW) from DOE Pinellas Plant. VWR coarse iron filings used for high reactivity and low cost.	Batch: fast rates for TCE, DCE , VC in site GW. Dichloro-methane rates very slow. Column: $t_{1/2}$ TCE = 36-103 min; DCE = 150-200 min. However, rapid plugging of iron by Pinellas GW.	Baghel, S., et al., G. E. Corp. R&D Center for USDOE, Sandia (1995)
Zeolite, 3 media types	Sr, Cs, TCE	Containers, TN & OH	55-gal drums of Na-chabazite zeolite (remove Sr, Cs. at seep, Oak Ridge National Lab, TN) and using 3 media types (reduce TCE, Portsmouth Gas.Diff. Plant, OH).	>99.9% Sr, Cs removal ORNL (25% red. total radioactive discharge). TCE reduced at PORTS X-120 site. Drums predict flow and allow easy media replacement and monitoring.	Barton, W., et al., Internat'l Contain. Technol. Conf. & Exhib., St. Petersburg, FL, Feb 9-12, pp. 827 (1997)
Mixture organics, sulphate-reducing bacteria	Acid Mine Drainage	Reactive Wall, Ontario	Wall installed at the Nickel Rim mine site near Sudbury, Ontario on 8/95. 15 m long perpendicular to GW flow, 3.6 m deep, 4 m thick. Used municipal & leaf compost, wood chips, and pea gravel (for permeability). Sand buffer, clay cap. Mon. wells parallel to GW flow.	After 9 mo sulfate reduction and metal sulfide precipitation. Sulfate: 2400 to 4600 mg/L to 200 to 3600 mg/L, Fe:250 to 1300 mg/L to 1 and 40 mg/L; pH 5.8 to 7.0. Alkalinity rose 60-220 to 850-2700 mg/L as $CaCO_3$. Fe mono-sulfide precipitate. Cost ~ $30,000.00 (half materials/half installation) potential life 15 y.	Benner, S.G., et al., 1 ACS Meeting, San Fran., CA, April 13-17, 140 (1997) 2 Internat'l Contain. Technol. Conf. & Exhib, St. Petersburg, FL, 835 (1997) 3 GWMR, Fall, 99-107 (1997)
Fe	Cr	Reac. Wall Eliz. City, NC	Models indicate reactive barrier most efficient/cost effective. 46 long x 0.6 wide x 7.3 deep (m) barrier installed < 6 h using continuous trencher 6/22/96.	11/9 sampling indicated 2.5 mg/L Cr(VI) declined to < MCL within barrier. Further sampling under way determining ground-water chemistry and organic concentrations.	Bennett, T.A., et al., 213th National ACS Meeting, San Francisco, CA, April 13-17, pp. 243-245 (1997)
Fe	Solubilized PCE Hydroxypropyl-β-cyclodextrin (HP-β-CD)	Batch, Column	Batch: 100 mesh Fisher Fe powder & -8 to 50 mesh Peer-less mix. 40 mL sealed vials, 10 g Fe, PCE, 40 mg/L $CaCO_3$; 0, 45, 70 g/L HP-β-CD. Column: 0.47 m x 5 cm, 15 cm 70/100 mesh sand below (30-cm head) 10 cm 30/40 mesh sand. 25 mL PCE to form pool. RT 25.3 h.	HP-β-CD enhances solubility w/o decreasing interfacial tension of PCE and water. Smaller % PCE degraded at higher HP-β-CD conc. PCE decreased in both non-recycling and recycling of post-treatment effluent. Greater degradation at higher iron SA. Plan to use higher Fe SA and longer RTs to increase degradation.	Bizzigotti, G.O., et al., ES&T, 31:472-478 (1997)
Fe	Cr	Batch, Column	Batch: Compare 100 g siderite, pyrite, Fe(0) (~ 0.5 -1mm), chips (~ 1-5mm). Use 500 g Cr in $CaCO_3$ DI water agitated at room temp. Column: 15 x 6.5 cm, pump tracer base upward to determine void v & dispersivity of column.	Batch: Fe(0) > pyrite. Column: Fe chips (remove 50% Cr < 2 h) > pyrite (w/ calcite 50% 0.5 h; no calcite 50% 1 h) > coarse Fe (50% 28 h). Chips: Coating (r_f 5.2). No Cr 4.5 PV. Filings: No Cr > 15 PV. Remain active, little coating.	Blowes, D.W. & C.J. Ptacek, Subsurface Restor. Conf., 3rd Interna'l Conf. on Ground Water Quality Res., June 21-24, Dallas, TX, 214-216 (1992)
Pyrite or Fe	Cr(VI), U, etc	Trench	Excavate trench, fill with active material such as pyrite or elemental iron to transform & precipitate contaminant.	This patent relates to the treatment of GW for the purpose of removing water-borne contaminants.	Blowes, D.W. & C.J. Ptacek, Patent 5,362,394 (1994)
Mixed organics, bacteria	Nitrate - Tile Drainage	In-Line Bioreactor	Two 200-L fixed-bed bioreactors, with coarse sand and organic carbon (tree bark, wood chips and leaf compost), to treat 3-6 mg L NO_3-N from farm-field drainage tile.	Reduced NO_3-N < 0.02 mg/L at 10-60 L/d over a 1-y period by anaerobic denitrification promoted organic carbon. Design is simple, economical and maintenance free.	Blowes, D.W., et al., Journal of Contaminant Hydrology 15:207-221 (1994)

Appendix A. continued...

Metal (zero valent unless specified)	Contaminant	Type test	Description/Conditions	Results	Reference
Fe	Cr(VI)	Batch, Column	Batch: 100 g (50% fine Fe filings, 49% sand, 1% calcite), Cr(VI). 2nd mix 50:50 Fe, quartz. Column: 50% Fe(0), 50% sand, top 5 cm 1% calcite. 20 mg/L Cr(VI) in simulated GW.	Cr(VI) 25 to <0.05 mg/L 3 h batch. Column: No breakthrough Cr after 140 PV. Dissolved & total Cr < 0.05 mg/L. Fe(III) oxyhydroxides form but not sufficient to inhibit Cr(VI) reduction at experimental velocity.	Blowes, D.W., et al., 209th National ACS Meeting, Anaheim, CA, April 2-7, 35:780 (1995)
Fe	Acid Mine Drainage	Test Reactive Wall	Test cell 1.5 long x 1 wide x 1 deep (m) installed 10/93 in sand aquifer ~ 75 m downgradient tailings impoundment. Organics (leaf, pine mulch, bark), creek sediment (sulfate-red. bacteria), limestone, coarse sand and gravel.	1 m on flow path, SO_4 3500 to 7 mg/L, Fe 1000 to < 5 mg/L, pH & alkalinity increased from sulfate-reduction. Sulfate-reducing reactive walls are potentially effective and economical solution to many acid mine drainage problems.	Blowes, D.W., et al., Mining & Environ. Conf., CANMET. Sudbury, Ontario, May 28 to June 1, 3:979 (1995)
Fe	Cr(VI), TCE	Fe Reactive Wall	Wall of 100% Fe filings 46 m long, 0.6 m wide, 7.3 m deep installed in < 6 h using a continuous trenching technique at Elizabeth City, NC on 6/96. Bench lab studies, and flow and transport models used in wall design.	Site GW, reactive materials: Cr(VI) 11 to <0.01 mg/L and TCE 1700 μg/L to < 1 μg/L. Decrease of Cr(VI) from influent 6 mg/L to < 0.01 mg/L and TCE from 5600 μg/L to 5.3 μg/L within wall. TCE approaches or attains the MCL within the barrier.	Blowes, D.W., et al., Internat'l Contain. Tech. Conf. & Exhib. St. Petersburg, FL, Feb 9-12, pp. 851 (1997)
Fe	Cr(VI)	Batch, Column	Batch: 500 g Cr(VI) to 100 g solid mixes (siderite, pyrite, coarse & fine Fe(0)) in open flasks, agitated, room temp. Settle 5 min; 10 mL sampled. Column: 6-6.5 cm dia acrylic, 5-15 cm long, 1-20 cm long with layers reactive mix. Void volume & dispersivity determined. Cr(VI) solution introduced.	Batch: Rate of Cr(VI): fine Fe(0) > pyrite & coarse Fe(0). Column: partial reduction of Cr(VI) by pyrite & coarse Fe(0); quantitative reduction of Cr(VI) by fine Fe(0) at rapid velocities. Fe(0) reduces Cr(VI) to Cr(III) with oxidation of Fe(0) to Fe(II) & Fe(III), and precipitation of sparingly soluble (oxy)hydroxide. Cr(III) forms a solid solution or adsorbs on goethite.	Blowes, D.W., et al., ES&T, 31:3348-3357 (1997)
Fe	CCl_4 or CT, CH_2Cl_2 or DCM	Batch	Open circuit potential time measurements using Fe with CT & DCM in borate buffer and simulated GW of KBr & $CaCO_3$. Polarization of Fe electrode in borate solution to which 0.2 mL of CT added. CT acts as an oxidizer of Fe electrode, while DCM does not.	Injection of CT shows faster and larger potential shifts in Fe than in freshly cleaned Fe electrode. Potential decay in all GW studies. Magnitude depended on pH and solution. Borate and KBr decay mainly from chemical dissolution of films. In $CaCO_3$, autoreduction/chemical dissolution may be responsible.	Bonin, P.M.L., et al., 213th National ACS Meeting, San Francisco, CA, 37:86-88 (1997)
Sn, Zn & Mg	CCl_4	Batch	Vaporization procedure (SMAD or cyro method) to compare metal powders.	H_2O oxidation overwhelmed Mg-CCl_4 reaction. Sn, Zn degrade CCl_4 but differ in carbon product (Zn $\rightarrow$ CH_4; Sn $\rightarrow$ CO_2. Intermediate Cl_3CMCl may be protonated by H_2O to give $CHCl_3$ or eliminate CCl_2 which subsequently reacts with H_2O to form CO_2 and HCl.	Boronina, T., et al., ES&T, 29:1511 (1995)
Steel wool	Tc^{99}	Column	Simulated process & GW from DOE uranium enrichment plants. Packed column of steel wool, Dowex TM 1-X8.	Use of iron economical but may be more difficult to accurately predict its sorptive capacity or functional "lifetime"	Bostick, W., et al., Oak Ridge K-25 Site Rep. Martin Marietta. DOE K/TCD-1141 (1995)
Fe	Cd, Mg, Ni, TcO_4^-, UO_2^{2+}	Batch	Shake solid w/ soln 16-24 h in sealed container. Exp 2: 0.01, 0.03, or 1.0-g iron to 10mL w/ 8 mg/L U, shake 18 h, sample day 1 & 30. Exp 3: 1.43 x 0.15-cm iron coupons in 500-mL bottle w/ 927-mg/L U. N_2 purge.	Iron surfaces passivate at elevated pH (little activity at >9.5). Sorption to iron corrosion products predominant removal process for uranyl (Cd, Mn and Ni also). Sorbed products need to be controlled. Columns needed to determine long-term capacity.	Bostick, W., et al., Oak Ridge & Martin Marietta Energy Systems, Inc. for U.S. DOE. K/TSO-35P (1996)

Appendix A. continued...

Metal (zero valent unless specified)	Contaminant	Type test	Description/Conditions	Results	Reference
Iron oxide aggregate	U	Batch	Continued from previous reference.	Fe(0) w/ sand or pelletized Fe oxide most effective. Reduces cementation from rust; enhances dilution of hydroxyl ion reaction product; enhances sorption of cationic contaminant to pelletized Fe.	Bostick, W., et al., Oak Ridge & Martin Marietta Energy Systems, Inc. for U.S. DOE. K/TSO-35P (1996)
Fe	U	Batch	Batch: ~1.4 x 0.16 cm Fe coupons, simulated GW, soluble U as uranyl nitrate. Gas glove box. Pure O_2 added to yield equivalent to solution purged with lab air.	Under oxic conditions, U(VI) rapidly and strongly sorbed to hydrous ferric oxide particulate ("rust"), whereas U slowly and incompletely reduced to U(IV) under anoxic conditions.	Bostick, W.D., et al., Internat'l Contain. Technol. Conf. & Exhib, St. Petersburg, FL, Feb 9-12, pp. 767 (1997)
Iron filings/pyrite	TCE, PCE	Batch	4-15 mL vials, anaerobic: 2 controls/2 Fe+pyrite (5 g pre-treated Fe filings, 0.1 g ground pyrite [buffer]).	Reaction orders 2.7 TCE & 1.3 PCE total system conc. Nonlinear sorption fit generalized Langmuir isotherm. 1st order rates.	Burris, D.R., et al., ES&T, 29:2850 (1995)
Fe	PCE	Batch	15 mL serum vials, 5 g iron, 0.1 g pyrite (ground). Pyrite added to stabilize the pH to 6.5 - 7.0. Anaerobic	Rapid initial rate followed by a slower rate. Sorption of PCE to Fe(0) follows Langmuir-type isotherm.	Campbell, T.J. & D.R. Burris. 209th Nat'l ACS Meeting, Anaheim, CA, 35:775 (1995)
Fe	UO_2^{2+}, MoO_4^{2-}, TcO_4^-, CrO_4^{2-}	Batch	Kinetic studies in 50 mL redox-sensitive-metal solutions added to polystyrene centrifuge tubes containing 1-g 40 mesh metallic iron with SA of 2.43 m^2/g.	Particulate Fe(0) effectively removed each of the contaminants from solution by reductive precipitation. Removal rates decreased by $CrO_4$2- > TcO_4^- > UO_2^{2+} >> MoO_4^{2-}.	Cantrell, K.J., et al., J. of Haz. Mat., 42:201 (1995)
Fe Colloid Barrier	Various	Batch	0.2% Fe colloids, surfactant. Polymers (vinyl (VP), vio (GX), cellulose (CMC)) tested to increased colloidal Fe(0) mobility in porous media. Turbidimeter meas. Fe colloids.	VP is superior to GX and CMC because VP suspension produced the lowest back pressure, resulting in the highest hydraulic conductivities.	Cantrell, K.J., et al., J. of Environ. Eng.-ASCE, 23:786 (1997)
Fe Colloids Barrier	Various	Column	1 m columns, 4.4 cm dia. 20-30 mesh sand avg η = 0.32. Fe(0) colloid dia. = 2 μm, bulk density = 2.25 $g \cdot cm^{-3}$, particle density = 7.6 $g \cdot cm^{-3}$. V = 0.154, 0.307, 0.614 cm/s. 0.01*M* $CaCl_2$ at 0.2 cm/min (~2 PV) to simulate GW.	Colloidal-size Fe(0) injected into porous media forming chemical reactive barriers. Relatively even distributions of Fe(0) in sand column at low conc.; high injection rates. As V increased, distribution of Fe(0) colloids became increasingly even.	Cantrell, K.J. & D.I. Kaplan, J. of Environ. Engineering-ASCE 123:499-505 (1997)
Pd/C	4-chlorophenol	Batch	Palladized graphite and carbon cloth electrode in 3-neck round-bottom flask (50 mL). Cu wire threaded through 5 mm glass tubing. Central portal used for pH & cathode potential. Anodic compartment vented for O_2 escape.	Rapid dechlorination of 4-chlorophenol on palladized carbon cloth or palladized graphite electrodes. Hypothesize H_2 gas interlaced in Pd lattice powerful reducing agent dechlorinating compounds adsorbed on palladized electrode surfaces.	Cheng, I.F., et al., ES&T, 31:1074-1078 (1997)
Fe	Nitrate	Batch	4 g untreated 325 mesh iron to 50 mL of 12.5 mM nitrate buffered at pH 5. No effort made to exclude O_2. Vigorously stirred.	Nitrate < 0.2 mM in 74 min. Ammonia 103%. Pseudo-1st order rate constant 0.0530/min. Buffer is key in nitrate reduction.	Cheng, I.F., et al., 213th ACS, San Fran., CA, 37:165 (1997)
Fe	PCBs (Aroclor 1221, 1254)	Batch	Iron powder (0.5 g), 1.5 μmol PCBs in 10 mL flame-sealed glass ampule.	PCBs undergo dechlor. & other reactions at > 300°C in presence of Fe powder. Virtually complete loss of chlorinated congeners.	Chuang, F.-W. & R.A. Larson, ES&T, 29:2460 (1995)

Appendix A. continued...

Metal (zero valent unless specified)	Contaminant	Type test	Description/Conditions	Results	Reference
Fe	DCE, TCE, PCE	Batch	Solutions incubated with lab grade iron under static conditions. Concentrations monitored as a function of time. Pyrite with Fe to counterbalance pH increases.	Oxidation reactions of Fe increased pH. Halocarbons convert slower at high pH. High grade pyrite more reactive. SA important consideration.	Cipollone, M.G., et al., 209th National ACS Meeting, Anaheim, CA, April 2-7, 35:812 (1995)
Fe	TCE	Column	Long-term (~30 d, >300 PV) & fast velocities (5-30 cm/h) w/ 4-600 mL Fe mix columns. Rates varied by medium, SA, mixture, time. Influent 50 μM TCE at 3.15 mL/min.	Fe oxidation increases pH, pyrite decreases pH. Pyrite is placed at column head because precipitation slower at lower pH w/ wider dispersion of precipitation zone throughout column and lessens plugging at head of column.	Cipollone, M.G., et al., 213th ACS Nat'l Meeting, San Fran., CA, 37:151-152 (1997)
Fe(II)	TcO_4^-	Batch	Fe(II), in slightly acid to base solution, in 500-cm^3 bottle w/ hydrophobic inner surface, ambient temperature, and under anaerobic conditions. 0.1 $FeCl_2$ (pH 4) added, sampled by syringe through septum.	3 *e*- reduction process, although thermodynamically feasible, slow if at all. Fe(II) [sorbed to wall or precipitate as $Fe(OH)_2(s)$ or $FeCO_3(s)$] reduced TcO_4^-. Rates proportional to sorbed or precipitated Fe(II). Discuss redox/paths TcO_4^- to $TcO_2 \cdot nH_2O$.	Cui, D. & T.E. Eriksen, ES&T 30:2263-2269 (1996)
Fe	Background hydrocarbon formation	Batch	15.0-mL sealed vial. 5.00 g Fe with low CO_2 water, anaerobic, 8 rpm in dark at 20° C. pH increased 5-7 when Fe added. $^{13}CO_2$ to determine if CO_2 is being reduced by iron to form the hydrocarbons. *Note: Non-Cl-hydrocarbons form during ethene reduction and when there is no ethene. Fischer-Tropsch type synthesis of hydrocarbons, proposed for hydrocarbon production.*	$^{13}CO_2$ was not incorporated into hydrocarbons produced. Acid dissolution of gray cast irons containing both carbide and graphite carbon yielded hydrocarbons and a substantial amount of graphite residual. The dissolution of metallic irons containing only carbide carbon yielded total carbon conversion to hydrocarbons. Carbide carbon in the iron most likely carbon source for the production of the background hydrocarbons.	Deng, B. & A.T. Stone, ES&T 30:463-472 (1996)
Fe	VC	Batch	40 mesh HCl pretreated Fisher Fe filings, SA 1.18 m^2/g (0.2 to 10 g) using 15 mL borosilicate in ZHE filled by VC solution, anaerobic, 8 rpm, 20° C. Also at 4, 20, 32, 45° C.	5.0 g Fe/15.0 mL: VC $\rightarrow$ ethylene (Partial absorb. to Fe). Rates increase as Fe & temperature increases. Activ. E 40 KJ/mole indicate surface reaction. H_2 also produced, but, Fe^{2+} not directly involved in reduction.	Deng, B., et al., 213th National ACS Meeting, San Francisco, CA. 37:81-83 (1997)
Fe	U	Pilot barrier in CO	Pilot barrier using Fe to remove U from tailings effluent. at UMTRA site scheduled 5/96 to 1999. Fe foam SA 0.1 & 5 m^2/g; Fe(0) SA 5.6E^{-3} m^2/g. During 3 years U, Se, Mo, other elements monitored as well as costs and benefits.	Field coincides with experimental findings. In Fe foam batch U removed to <DL in 10 h. Metallic hydraulic conductivity maintained. Initially conduc. 6.4 x 10^{-3} cm/s; Fe foam was 0.53 cm/s. Capacity maintained after > 700 PV oxygenated water.	Dwyer, B.P. & D.C. Marozas, Internat'l Contain. Tech. Conf. & Exhib. St. Petersburg, FL, Feb 9-12, pp. 844-850 (1997)
Fe	Tracers, D_2O	Column	Glass column with wet Ottawa sand or VWR coarse iron filings. 2.65 g/cm^3 for sand and 6.5-7.6 g/cm^3 for iron.	2 tracers (D_2O, KBF_4) for Fe column. D_2O more conservative and KBF_4 easier on-line detection. Both inert with respect to Fe.	Eykholt, G., et al., 209th Nat'l ACS Meeting, Anaheim, CA, April 2-7, 35:818 (1995)
Fe	Alachlor, Metalochlor	Batch Kinetics	100 mL ZHEs, ~ 40 g coarse Fe filings (40 mesh, SA 13.5 m^2/g), 10 mg/L or 100 mg/L alachlor and/or metalochlor, room temp, 3 rpm. Sampled over even intervals for 5 d.	Rapid dechlorination by Fe(0) shown by Cl^- and GC/MS analyses. Apparent 1st-order kinetics, but indication of rate limited and instant sorption. 2-site batch kinetic model fitted to results.	Eykholt, G.R.& D.T. Davenport, 213th Nat'l ACS Meeting, San Francisco, CA, 37:79-81 (1997)
Fe	CCl_4	Elemental Fe cathode	Experimental reactors using a two-part glass vessel with a Nafion-117 proton permeable membrane.	Reduction of CCl_4 $\rightarrow$ chloroform in hrs at .0005 to .005 / min. Suggest H_2 serves as intermediate for CCl_4 hydrogenolysis.	Festa, K.D., et al., 209th Nat'l ACS Meeting, Anaheim, CA, April 2-7, 35:711-715 (1995)

Appendix A. continued...

Metal (zero valent unless specified)	Contaminant	Type test	Description/Conditions	Results	Reference
Fe	1,2,3-trichloro-propane	Column	50 & 93 mg/L 1,2,3-TCP was passed through 6 flow-through reactive columns containing Fe(0)· silica sand & simulated GW.	End-product propene. Fe(0) enhanced dechlorination. Rate increased in proportion to iron SA to solution volume ratio. Ratios of 1.16, 3.7, 8 m^2/mL gave $t_{1/2}$ 17.6, 6.6, 3 h, respectively.	Focht, R.M. & R.W. Gillham. 209th National ACS Meeting, Anaheim, CA, April 2-7, 35:741 (1995)
Fe	Review	Reactive Walls	Gillham founded EnviroMetal Technologies in 1992 to commercialize the reactive wall technology.	To Date 5 full-scale in situ treatment zones installed: 2 in commercial sites in CA, 1 in KS, 1 in N Ireland and 1 at Elizabeth City, NC	Focht, R.M., et al., Remediation, Summer:81 (1996)
Fe	TCE	Funnel-and-Gate	In Sunnyvale CA site, 100% pure granular iron filing wall is 4' thick, 40' wide and 20' deep.	TCE levels of 30-68 ppb entering wall reduced to < 0.5 ppb; cDCE of 393-1916 ppb to < 0.5 ppb	
Fe	TCE	Funnel-and-Gate	1000 foot funnel- and-gate system installed at industrial facility in Kansas in January 1996 to treat 100 to 400 ppb TCE. Reactive zone 30' to 17' bgs and 3' thick.	Under optimum conditions, the soil-bentonite slurry wall could be built in 1 or 2 weeks and gate section in one week. Slurry wall, gate, 7900 ton of granular iron = ~$400,000	
Fe	TCE, cDCE, VC	Funnel-and-Gate	NY facility (1995) treats up to 300 TCE, 500 cDCE, 80 VC (ppb). 12' x 3.5' reactive section flanked by 15' sheet piling on either side.	Installed in 10 d. VOC reduced to MCLs within 1.5 feet of travel through reactive media. Cost $250,000 including $30,000 for 45 tons of iron.	
PRB	CCl_4, TCE, $CHCl_3$, Cr(VI), Tc, U	In situ	Used abiotic reagent sodium dithionite at the Hanford site. Biotic reagent/nutrient either citrate or glucose.	Compared abiotic & biotic methods for controlling redox potential to reduce solids in unconfined aquifer.	Fruchter, J.S., Pacific NW Lab & U. S. DOE. PNL-SA-21731 (1993)
PRB	Velocity measurements	Tracer	Bromide considered most appropriate tracer. Pilot system (3 long x 3 wide x 5.5 deep (m)) installed 11/95 gov. facility in CO. Models indicate ~ 60 cm/d (2'/d) in reactive zone.	Small tracer not detected. Large targets could disrupt flow; time consuming. Water table calculations are not accurate. Heat-pulse velocity meter give suspect directional vectors. In situ velocity probes are most promising/easy to use.	Focht, R.M., et al., Internat'l Contain. Tech. Conf. & Exhib. St. Petersburg, FL, Feb 9-12, pp. 975 (1997)
Fe Foam	As, Se, Mo, U, sulfate, nitrate	Batch, Column	Batch (1 wk) & column (70 d) using Fe foam and steel wool to compare removal of As, Se, Mo, U, sulfate, and nitrate. Precipitation and removal mechanisms also studied.	Batch Fe foam removed 100% Se, 86% nitrate, 100% U, 83% As. Steel wool ~ 80% U, 20% As, 70% nitrate. Neither remove sulfate or Mo. Column conductivity decreased slightly (0.08 steel wool; 0.09 cm/s foam). Reduction/ precip. Se; adsorption As, U.	Gallegos, T.J., et al., HSRC/ WERC Joint Conf. on the Environment, May 20, Paper 75 (1997)
Fe, Mg, Ultrasound (US)	TCE	Batch	TCE (20 ppmv) in 3 neck-1 L round bottom reactors, with US probe inserted in center neck and tip just above 1.0 g Fe or Mg, or 50:50 mix, w/ & w/o US. Controls only US, no metal or US.	Higher pH from dechlorination reactions increases deactivation by precipitating metal compounds on active surface. US can strip away corrosion keeping metals active longer. Another benefit is sonication produces H^+ ion to stabilize pH.	Geiger, C., et al., 211th ACS Meeting, New Orleans, LA, March 24-28, 36:17-18 (1996)
Fe	Halogenated compounds	Batch	10 g 100 mesh iron filings in 40 mL ZHE hypovials, at 2 rpm. C_o for CCl_4, HCE, PCE were 1630, 3620, 2250 μg/L, respectively.	$t_{1/2}$ CCl_4, PCE, HCE = 20, 1100, 13 min., respectively. Chloroform, produced by CCl_4 was the only breakdown product accumulating in significant quantities.	Gillham, R.W. & S.F. O'Hannesin, IAH Conf., Hamilton, Ontario, May 10-13 (1992)

Appendix A. continued...

Metal (zero valent unless specified)	Contaminant	Type test	Description/Conditions	Results	Reference
Fe, Zn, stainless steel, Cu, brass, Al	Chlorinated hydrocarbons	Batch, Column, Reac. Wall Borden, Ontario	Batch: 10 g stainless steel, Cu, brass, Al, Fe, & Zn in 40 mL hypovials w/ 1,1,1-TCA. Next, Fe w/ halo-aliphatics. Batch/columns used wall material. Constructed Borden wall by driving sheet piling to form 1.6 m x 5.5 m cell. Reactive material 22% Fe grindings and 78% concrete sand with 348 sampling points installed within wall.	Batch: 1st order TCA rates, Steel, brass, Cu low rates; Al better; Zn, Fe rapid ($t_{1/2}$ 100 min.). Fe(0) batch: Highly Cl-organics most rapid. $t_{1/2}$ 0.22 h HCA to 432 h cDCE. Fe mass to solution volume ratio important. Rates decline at pH ~ 9. Batch/column: $t_{1/2}$ 15 h TCE, PCE. In situ wall: Avg. max. conc. downstream of wall ~10% of influent conc. Performance constant over 14-months.	Gillham, R.W., et al., HazMat Central Conference. Chicago, Illinois, March 9-11, pp. 440-453 (1993)
Fe	Chlorinated hydrocarbons	Batch, Column	10 g 100 mesh iron powder, silica sand, 40 mg/L $CaCO_3$ added to 40 mL hypovials	All 14 chlorohydrocarbons except dichloromethane degraded. Rates in column independent of velocity and consistent with batch tests. When normalized to 1 m^2 Fe surface/mL solution: $t_{1/2}$ 0.013–20 h. 5 to 15 X > natural abiotic degradation.	Gillham, R.W. & S.F. O'Hannesin, Ground Water, 32(6):958 (1994)
Fe, Ni/Fe	PCE, cDCE, TCE	Canister, NJ	Fe canister, NJ site treating up to 15 PCE, 1 cDCE, 0.5 mg/L TCE since 11/94. Initial column used Ni plated Fe, site water. Reactor used commercially plated Ni-Fe 7/96. SA 3.1 m^2/g (before plating 1.1 m^2/g). 2nd column commercial Ni-Fe.	$t_{1/2}$ in initial column 10 X (30 to 3 min, TCE) lower than Fe alone (1 to 1.5 versus 24 h RT). Enhanced reactor $t_{1/2}$ 4X > initial column test, but 4X lower than Fe reactor. Longer $t_{1/2}$ may result from inadequacies in commercial plating process.	Gillham, R.W., et al., Internat'l Contain. Tech. Conf. & Exhib. St. Petersburg, FL, Feb 9-12, pp. 85 (1997)
Fe	TCE	Batch	Batch 150 μm, 370 μm mesh Fe & Fe powder in 40 mL ZHEs, TCE in DI water, shaken 150 rpm then analyzed for pH, dissolved Fe and Cl^- removal.	Amount TCE degraded directly proportional to dissolved Fe in solution. 2-fold increase in pseudo first order rate constant when metal particle size decreased from 370 μm by factor of 2.5. For iron SA/V of solution <1000 m^{-1} TCE degradation rate constant increased linearly with SA/V ratio.	Gotpagar, J., et al., Environmental Progress, 16:137 (1997)
Fe	Cr(VI)	Batch	Varied Cr(VI), H^+, and SA of iron as well as ionic strength and mixing rate.	Rate constant 5.45 x 10^{-5} cm^{-2} min^{-1} over wide range of conditions. 1.33 mol diss. iron for each mole Cr(VI) reduced.	Gould, J. P., Water Res., 16:871 (1982)
Fe, Pd/Fe	PCB	Batch	HCl treated Fe particles (<10 μm). K_2PdCl_6 w/ Fe powder (0.05% w/w Pd). 20 ppm PCB (1 mL Aroclor 1260 or 1254), methanol/water/acetone (1:3:1) w/ 0.05% w/w Pd/Fe in vial, amb. temp., capped, shaken. 1 μL samples.	Rapid (few minutes) dechlorination on Pd/Fe surface. Rate dependant on amount Pd/Fe, % w/w Pd(0) on Fe, & % v/v water. Pd/Fe surface can be used repeatedly if acid-washed after 3 to 4 uses.	Grittini, C., et al., EST, 29:2898-2900 (1995)
Fe, surfactant	TCE, PCB	Batch, Column	TCE batch ZHEs: 20 g of 40-mesh Fe & Pd (0.05%)-Fe, 100 mL TCE (2 mg/L), surfactant (2%, 4%), cosolvent (2%), 30 rpm. PCBs in 5-mL vials, 2 g of 100-200-mesh Fe-Pd(0.1%). Columns wet-packed w/ Fe or Fe-Pd, sampled after >10 PV at various levels, times, rates.	Batch Pd-Fe: $t_{1/2}$ TCE ~27.4 min.; PCB ~100 to ~500 min (as surfactant increased). Columns: TCE and PCBs degrade at enhanced rate $t_{1/2}$ ~1.5 and 6 min due to increased solid to solution ratio. Fe-Pd filings applicable for ex-situ treatment of TCE and PCBs in surfactant solutions generated during surfactant flushing.	Gu, B., et al., Internat'l Contain. Tech. Conf. & Exhib. St. Petersburg, FL, Feb 9-12, pp. 760-766 (1997)
Cu	Dioxin, Furans	Batch	Heat mixtures with Cu to enhance catalyzing reactions to degrade dioxins and other compounds.	Cu catalyzed degradation of PCDD, PCDF, 7 other chlorinated aromatics at low temp. similar to first observation using fly ash.	Hagenmaier, H., et al., ES&T, 21:1085 (1987)
Fe	TCE	Batch	1.5-2.0 g of elemental iron per 100 mL aqueous sample containing 0.02 mmoles TCE (25ppm); maintained pH.	With and without citric acid, pH 5.8: rate 5.37 h^{-1} & 0.85 h^{-1}; $t_{1/2}$ 7.74 & 48.9 min., resp. Citric acid chelating ligand for Fe^{2+}.	Haitko, D.A.& S.S. Baghel, 209th National ACS Meeting, Anaheim, CA, 35:807 (1995)

Appendix A. continued...

Metal (zero valent unless specified)	Contaminant	Type test	Description/Conditions	Results	Reference
Fe	CO_2	Batch, Column	Determined that C1 to C5 hydrocarbons are formed by the reduction of aqueous CO_2 by Fe(0) and product, have ASF distribution.	Pretreat iron with H_2 increased hydrocarbon conc. 140 h untreated Fe 3.8 ±1.2 μg/L vs. 7.9±2.4 μg/L using hydrogenation Indicate absorbed H is a reactant in reduction of aqueous CO_2.	Hardy, L.I. & R.W. Gillham. 209th National ACS Meeting Anaheim, CA, April 2-7, 35:724 (1995)
Fe	Hydrocarbon (HC) formation	Batch	Reduction of aqueous CO_2 by Fe(0). Reaction mechanism proposed for electroreduction of aqueous CO_2 with Ni electrodes, Fe. Anderson-Schultz-Flory (ASF) distrib.	10 HCs ≤ C5 products ASF distrib. w/ hydrophobics sorbed to Fe. Fe supply e^- & catalyst promotes formation/ growth of HC chains. H_2O also reactant. HC desorption may be rate-limiting step.	Hardy, L.I. & R.W. Gillham, ES&T, 30:57-65 (1996)
Fe, Sulfur	CCl_4	Batch	Determine if adding sulfur enhances degradation of CCl_4 by iron.	Sulphur (sulfate, organosulphonic acid, sulfides & pyrite) accelerated Fe induced degradation of CCl_4 under aerobic conditions.	Harms, S., et al. 209th National ACS Meeting, Anaheim, CA, April 2-7, 35:825 (1995)
Fe, Sulfur	TCE, PCE	Batch	2 grades Fe, TCE and PCE. Lab grade Fe filings, 420 μm, sulfur >180 ppm. Extra pure Fe, at a particle size of 6 to 9 μm and S content of 22.1 ppb.	Lab grade Fe resulted in ethyne, ethene, ethane in 24 h. Extra pure unreactive after 1 mo. despite high SA, but fast production of ethyne, ethene, ethane after adding sodium hydrogen sulfide.	Hassan, S.M., et al., 209th National ACS Meeting, Anaheim, CA, April 2-7, 35:735 (1995)
Iron, Fe-reducing microbes	10 Nitrobenzenes	Column	Columns to assess abiotic/biotic processes in reactive Fe & Fe-reducing bacteria. Nitrobenzene to analines.	NAC reduction primarily by a reaction w/ surface-bound Fe species, which serve as mediators for the transfer of e- originating from microbial oxidation of organic material by Fe-reducing bacteria-Regeneration of reactive sites, (not e- transfer to the NAC) rate-limiting process. Presence of reducible organic pollutants may significantly enhance the activity of Fe-reducing bacteria, in that reduction of such compounds continuously regenerates easily available Fe(III) species.	Heijman, C.G., et al., ES&T, 29:775 (1995)
Fe	CCl_4	Batch	CCl_4 1.5-5.5 μM; Fe(0) powder: 1 to 10 g per 265 mL distilled water in anoxic and oxic batch reactors	Products: $CHCl_3$, CH_2Cl_2. Anoxic Rate: 0.290 h^{-1}, 1 g Fe(0); 1.723 h^{-1}, 10 g Fe(0); increases with SA (2.4 mg/g) & time. Slower oxic rates: 0.085 h^{-1}, 1 g Fe(0); DO, 7.4 mg/L. pH rapid increase after O_2 depleted.	Helland, B., et al., 209th National ACS Meeting, Anaheim, CA, April 2-7, 35:732 (1995)
Pd/C	2-chloro-2-propen-1-ol, CT, Chlorobenzene	Batch	2-chloro-2-propen-1-ol, CT, Chlorobenzene, both bare and palladized graphite electrodes in aqueous solution over 24 h. Chlorobenzene rate limiting step in dechlorination of compounds such as PCBs.	Pd reduces CT by factor of 5; Both C and Pd/C cathodes effect dechlorination, however Pd/C electrode has a greater selectivity for dechlorination more products dechlorinated and gives much higher yields of fully dechlorinated products. Favor acidic media at higher ionic strength, O_2 does not affect. 2-chloro-2-propen-1-ol dechlorinates rapidly with Pd/C but by different mechanism. Chlorobenzene $\longrightarrow$ benzene w/ Pd/C.	Helvenston, M.C., et al., 213th National ACS Meeting, San Francisco, CA. 37:294-297 (1997)
Fe/Pyrite mixture	TCE	Column	TCE pumped through stainless steel column w/ mixtures of granular iron & pyrite. Products not considered.	Interaction of GW & geochemical environ. using MINTEQA2. Pyrite in granulated Fe mixtures provided of pH control.	Holser, R.A., et al., 209th Nat'l ACS Meeting, Anaheim, CA, April 2-7, 35:778 (1995)

Appendix A. continued...

Metal (zero valent unless specified)	Contaminant	Type test	Description/Conditions	Results	Reference
Mn^{2+}, Fe^{2+}, steel wool(Fe)	Cr(VI)	Batch	Low hexavalent, high hexavalent soils had 105, 460 mg/kg Cr(VI); 1.8, 104 g total Cr; 8.5, 10.4 pH, respectively.	Mn^{2+} reduced 50 to 100% Cr(VI) in both soils (no pH adjust.). Fe^{2+}, steel wool reduced soluble & insol. Cr(VI) reduction dependent on pH, reducing agent and soil.	James, B.R., J. of Environ. Quality, 23:227 (1994)
Fe	TCE, PCE, TCA	Column, reactor, Belfast, Ireland	EnviroMetal provided a treatability study w/ Fe filing, site water. RT ~ 12 h to reach regulatory limits. Designed 12 m tall x 1.2 m dia. Fe reactor with 5 m flow path entry and exit zones to collect and disperse flow. Reactor in cut-off wall to funnel flow.	$t_{1/2}$ TCE ~ 1.2 h. Small amount cDCE, Cl^- increased, VC formed from dechlorination (Up to 700 μg/L) in treatability study. Solvents degraded rapidly. Site Installation: After 7 mo. TCE 5 μg/L but slightly higher at exit due to backflow from sampling. DCE formed but ND (not detected) at 3 mo. VC at 4 mo 0.4 μg/L and ND 7 mo. At 6 mo TCE 2μg/L and DCE is ND.	Jefferis, S.A., et al., Internat'l Contain. Tech. Conf. & Exhib. St. Petersburg, FL, Feb 9-12, pp. 817-826 (1997)
Fe	CCl_4	Column	15-cm-dia Plexiglass pipe 90 cm long. Holes every 2.5 cm first 40 cm, rest 5 cm. Up & downgradient sand zone w/ intermed. Fe zone to simulate permeable iron barrier.	CCl_4 (up to 1.6 mM) fully dehalogenated by first sample port in Fe zone. $CCl_4 \rightarrow CHCl_3 \rightarrow CH_2Cl_2$. CCl_4 $t_{1/2}$ occurred within 0.25 h at a rate of 2.5 cm/h. $CHCl_3$ $t_{1/2}$ is slower but increased 2-fold with a 5-fold increase in flow velocity.	Johnson, T.L. & P.G. Tratnyek. 33rd Hanford Symp. on Health & the Environ.—In Situ Remed., pp. 931 (1994)
Fe	CCl_4	Column, Batch	100-mesh untreated Fisher Fe powder (SA 0.057 m^2/g) <325 mesh in N_2 purged unbuffered water and 20-32 mesh Fluka Fe turnings SA 0.019 m^2 g^{-1} in carbonate buffer. Mixed in dark, 36 rpm, 23±1°C. Table of new and previous experimental conditions provided.	New/previous k_{obs} from batch and column varied widely. Normalization to Fe surface conc. yields specific rate constant k_{SA} (vary by only 1 order of mag.). Dechlorination more rapid in saturated carbon centers and high degrees of halogenation favor rapid reduction. Representative k_{SA} values provided for solvents.	Johnson, T.L., et al., ES&T, 30:2634 (1996)
Fe Colloids	Chemical Barrier	Batch, Column	Hanford Site: Column/batch studies looking at injection of micrometer-sized Fe(0) colloids into subsurface to form chemical barrier.	Surfactants in low ionic strength solutions increased length of time dense colloids (7.8 g cm^{-3}) remained in suspension by 250%. Removal effic. sand column partially controlled by injection rate.	Kaplan, D., et al., In Situ Remed., Battelle Press, pp. 821 (1994)
Fe Colloids	Chemical Barrier	Column	PVC column study evaluating Fe(0) colloid injection rate and concentration on colloid retention by a sand bed. $CaCl_2$ tracer studies to compare transport rates of colloids.	Colloids controlled by rate & influent conc. As colloids accum., efficiency decreased due to gravitational settling. Colloids were evenly distributed & high flow required to mobilize.	Kaplan, D., et al., J. of Environ. Qual., 25(5):1086 (1996)
Mineral oxides in presence of Fe(II)	10 monosub-stituted Nitrobenzenes	Batch	Suspensions of magnetite, goethite, lepidocrocite, aluminum oxide, amorphous silica, titanium dioxide in presence and absence of Fe^{2+} addition.	Fast nitroaromatic reduction in all Fe hydroxides at 6.5 pH. Mineral oxides (no Fe^{2+}) show slow reduction, but increased w/ Fe (hydr)oxide coatings. Rates pH-dependent, decreasing w/ increasing compound to solids concentration ratio.	Klausen, J., et al., 209th National ACS Meeting, Anaheim, CA, April 2-7, 35:716 (1995)
Palladized iron	Chlorinated contaminants	Batch	Bimetallic process evaluated as a means of increasing rates of reaction.	TCE dehalogenation increased 2X using Pd/Fe instead of Fe and extends process to less reactive dichloromethane.	Korte, N., et al., 209th Nat'l ACS Meeting, Anaheim, CA. April 2-7, 35:752 (1995)
Pyrite	CCl_4	Batch	1 μM CCl_4 reacted with 1.2-1.4 m^2/L pretreated pyrite at pH 6.5, 25°C except experiments conducted with sulfide at pH 7.75; aerobic & anaerobic. Pyrite 75-300 μm.	>90% CCl_4 transform in 12-36 d (all conditions). Aerobic >70% $CCl_4 \rightarrow CO_2$. Anaerobic 50% $CCl_4 \rightarrow CHCl_3$. FeOOH coat on pyrite (aerobic). Pyrite depleted of ferrous Fe in all reactions.	Kriegman-King, M.R. & M. Reinhard, ES&T, 28:692 (1994)

Appendix A. continued...

Metal (zero valent unless specified)	Contaminant	Type test	Description/Conditions	Results	Reference
Sulfide, Biotite, Vermiculite	CCl_4	Batch	Biotite, vermiculite, muscovite wet-ground to 200-50 mesh (73-300 μm). Ampules w/ 13.5 mL buffer, spiked with solution saturated with CCl_4 and flame sealed.	~ 80-85% $CCl_4 \rightarrow CO_2$ via intermed. CS_2. Chloroform 5-15%, 5% unidentified nonvolatile and CO. At 25° 1mM HS $t_{1/2}$ 2600, 160, 50 d for homogeneous, vermiculite, biotite system, respectively.	Kriegman-King, M.R. & M. Reinhard, ES&T, 26:2198 (1992)
Corrin, reductant	CCl_4	Batch	CCl_4 in vials w/ corrin (B_{12}, cobinamide dicyanide, or aquocobalamin), reductant (Ti(III), dithiothrietiol, or S^{2-}/cystenine), pH 8.2. Products in headspace and mixture determined by GC/MS, HPLC, NMR or TLC.	Proposed pathway: trichlromethyl radical forms adduct with reductant. In S^{2-}/cysteine produces CS_2 or thiazolidines by way of thiophosgene. Or radical further reduced to form $CHCl_3$ and CH_2Cl_2 or CO and formate by dichlorocarbene intermediation.	Lewis, T.A., et al., ES&T, 30:292 (1996)
Pd/Zn	TCE	Batch	TCE dechlorination by Zn(0) in aqueous solutions at room temp.	Bimetallics Ag, Ni, Pd to enhance Zn. Dechlorination few h to several d. Best rates w/ cryo-Zn (ultrafine Zn) & Pd. Ethylene, ethane, monochlorinated hydrocarbons products.	Li, W. & K.J. Klabunde, HSRC/WERC Joint Conf. on Environ., 5/20 Paper 35 (1997)
Fe	TCE	Batch	ZHEs w/ 3 Fe filings (Fisher, Columbus Chemical, MBS). TCE 0.5 to 20 ppm. Fisher Fe pretreated with HCl.	Rates varied by factor of 2 for 3 Fe's. TCE sorbed then reduced by MBS. Fisher Fe 7 to 5 h. TCE/Fe ratios changed rate as well.	Liang, L., et al., 209th Nat'l ACS Meeting, Anaheim, CA, April 2-7, 35:728 (1995)
Fe, Pd/Fe	TCE	Batch	25g of 40-mesh Fe filings added to ZHEs, containing 125 mL solution (nominally 2 mg/L of TCE) at 30 rpm. Pd/Fe prepared according to Muftikian et al. (1995).	When 5 ppm TCE reacts with Fe(0), ~ 140 ppb VC persists 73 d. VC (~ 10 ppb) remaining with Pd/Fe about an order of magnitude > w/ Fe(0). Volatile byproducts may be under-represented in other published data regarding reduction with Fe(0). Reduction of TCE w/ Pd/Fe (0.05 % Pd) > order of magnitude faster than with Fe(0). With a 5:1 solution-to-solid ratio TCE $t_{1/2}$ with Fe(0) =7.41 h, $t_{1/2}$ with Pd/Fe = 0.59 h.	Liang, L., et al., GWMR Winter, 122 (1997)
Fe and sulfur	CCl_4	Batch	Sodium sulfate, sodium sulfide, ferrous sulfide, pyrite, organic acid, electrolytic Fe(0) powder, Fe(0) degradation of CCl_4 under aerobic conditions.	Products: chloroform, potential for carbon disulphide (toxic). Sulphur significantly increased rates under aerobic conditions. Pyrite can regenerate ferrous ions, produce sulfate & control pH.	Lipczynska-Kochany, E., et al, Chemosphere, 29(7):1477 (1994)
Fe	Precipitation	Batch	Tracers, aqueous inorganic profiles, scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), and wavelength dispersive spectroscopy (WDS) to determine precipitates and porosity loss in Fe systems.	Precipitation changes color from black to gray. Loss of alkalinity and calcium, no signif. magnesium loss. Most loss (5-15%) early and levels off. SEM shows crystals form on the surface of Fe. Tracers indicate fairly uniform loss of porosity throughout.	MacKenzie, P.D., et al., Emerg. Technol. in Haz.Waste Manag. VII, Sept. 17-20, Atlanta, GA, pp. 59-62 (1995)
Fe	TCE, DCE	Column	148 lbs VWR coarse Fe filings in columns. Initially used buffered DI water (40 mg/L $CaCO_3$). pH 7-8.5. Later used GW, 400 mg/L $CaCO_3$ and pH 7-8. Flow velocities much higher than typical to accelerate effects of aging.	TCE $t_{1/2}$ 36 min at 40, 20, 12 mL/min. tDCE $t_{1/2}$ ~ 100 min., 1,1-DCE $t_{1/2}$ 200 min, although 1st order fit not as good as for TCE. cDCE particularly poor. Siderite formed at the top of column 1, throughout column 2 and at the bottom of column 3.	Mackenzie, P.D., et al., 209th National ACS Meeting, Anaheim, CA, April 2-7, 35:796 (1995)
Fe	Precipitation	Batch	Tracers, aqueous inorganic profiles, SEM, XPS, and WDS to determine precipitates and porosity loss in Fe systems.	GW forms precipitates ($Fe(OH)_2$, $FeCO_3$, $CaCO_3$) on Fe surfaces, which may affect reactivity. However, this effect, to date, small. Also, H_2 produced from anaerobic corrosion of Fe a factor controlling the measured porosity losses in iron systems.	Mackenzie, P.D., et al., National ACS Meeting, 37:154-157 (1997)

Appendix A. continued...

Metal (zero valent unless specified)	**Contaminant**	**Type test**	**Description/Conditions**	**Results**	**Reference**
Ferric Oxyhydroxide	Se	Batch, Site Samples	Three sediment samples from Kesterson, Merced County, CA with elevated levels of Se subjected to in situ Fe(II) amendment.	Both Se(IV) & Se(VI) occluded within FeOOH produced during Fe(II) oxidation & hydrolysis. Fe(II) salt amendment potential *in situ* remediation for trace Se.	Manning, B.A. & R.G. Burau, ES&T. 29(10):2639 (1995)
Fe	U	Column	Rocky Flats seep w/ Cl- organics, metals, radionuclides. Seep water in glass columns w/ steel wool (Fe(0)) at 5 (1st d); 10 (2nd d); 30 mL/min (next 4 d). Rates increased to determine effects on U removal. DO 5 to 6 mg/L, pH 8, and 13 to 21° C.	Fast removal of U by Fe(0). Chloro-organics determine RT in design. Studies also test various media on removal of plutonium and americium at site and excess Fe from barrier effluent. EnviroMetal Tech. Inc. to determine RT for barrier design.	Marozas, D.C., et al., Internat'l Contain. Tech. Conf. & Exhib. St. Petersburg, FL, Feb 9-12, pp. 1029-1035 (1997)
Fe	TCE, CCl_4	Batch	Evaluated core samples from actual field sites. Microbiology and geochemistry characterized.	Granular Fe dechlorinated CCl_4 & chloroform. Direct electrolytic process with metal surface may occur in combination with reactions involving hydrogen, ferrous iron, sulfur and microbes.	Matheson, L.J. & P.G. Tratnyek. 1993. 205th ACS Meeting, 33:3
Fe	TCE	Batch	Fe(0) participate by direct reduction, ferrous iron, and hydrogen produced during corrosion.	Surface reaction predominant in granular Fe. Investigating possible microbial activity that might affect dechlorination.	Matheson, L.J. & P.G Tratnyek, ES&T 28:2045-2053 (1994)
Fe	CCl_4, cDCE, tDCE	Batch	Temperature, steric, pH dependance of degradation and reactions of pollutants in response to untreated iron powder (finer than 100 mesh), under aerobic conditions.	Electronic (orbital) & conformational preference. Nature of reductant appeared to determine the stereochemical course of redox reaction. More investigation needed.	Milburn, R., et al., 209th National ACS Meeting, Anaheim, CA, April 2-7, 35:822 (1995)
Chemical Barriers	Mo, U	Column	10 cm dia acrylic pipe w/ ~1,250 mL sand mixed with test material. U and Mo measured. Used hydrated lime.	Chemical barriers low cost alternative. Site evaluation to determine type of chemical barrier (e.g., sorption or precipitation).	Morrison, S.J. & R.R. Spangler, Env. Progr., 12(3):175 (1993)
Amorphous ferric oxyhydroxide	Mo, U	Batch	Lab experiments to evaluate material for use in chemical barrier under a repository containing uranium mill tailings.	No additive extracted both U & Mo over pH range. Hydrated lime lowered U in pore fluid. Soluble ferrous materials extracted Mo.	Morrison, S.J. & R.R. Spangler, ES&T, 26(10):1922 (1992)
Palladized iron (Pd/Fe)	TCE, DCE, cis & trans-1,2-di-chloroethylene, PCE	Batch	Sealed 12 mL glass vial. Pd/Fe [3.6 g-10μm (Aldrich), or 3.6 g Fe filings (Baker & Adamson), or 10 g- 40 mesh Fe (Fisher)] with 10 mL of chlorinated compounds (20 ppm in H_2O), shaken. Sampled with a syringe for GC analysis.	Dechlorination 1,1,2-TCE, 1,1-DCE, *cis* & *trans*-1,2-DCE & PCE at 20 ppm to ethane in few min. No intermediate products detected at > 1 ppm. Chloromethanes, CCl_4, $CHCl_3$, CH_2Cl_2 also dechlorinated to methane. CCl_4 in a few minutes, $CHCl_3$ in < 1 h, CH_2Cl_2 in 4-5 h.	Muftikian, R., et al., Water Research, 29:2434-2439 (1995)
Palladized iron (Pd/Fe)	TCE	Batch	1x1-cm pure Fe foil, 0.254 mm thick welded to stainless steel stub etched w/ 8 keV argon ions. Potassium hexachloropalladate added and allowed to react.	Pd(IV) to Pd(II), protons on hydroxylated Fe oxide form Pd(II)-O-Fe bonds, collapsing to Pd/Fe. TCE forms hydroxylated Fe oxide film that deactivates Pd/Fe. Dilute acid removes film.	Muftikian, R., et al., ES&T, 30:3593-3596 (1996)
Fe-Pd	chlorophenols (CPs)	Batch	Batch Fe(0)-Pd(0) in unbuffered, DI water, room temp, dark, usually with [Fe(0)-Pd(0)]= 69.4 g/L and initial aqueous chlorophenols [CP] ~ 0.08 mM, 40 rpm.	Initial rapid loss CP ($t_{1/2} \leq$ 0.2 h) due to sorption to Fe(0)-Pd(0) surface. Rate constant, k_{obs}, proportional increase with Pd(0) used and SA of Fe(0)-Pd(0). Higher cosolvent corresponded to decrease in k_{obs}.	Neurath, S. K., et al., 213th ASC National Meeting, San Francisco, CA, 37:159-161 (1997)

Appendix A. continued...

Metal (zero valent unless specified)	Contaminant	Type test	Description/Conditions	Results	Reference
Fe	CCl_4, TCM, TCE, PCE	Batch	Fe catalyst and aquifer material collected from Canadian Forces Base, Borden, Ontario. C_i CCl_4-4050, TCM-4650, TCE-4080, & PCE-3970 μg/L at 12°C.	$t_{1/2}$ 2.2, 850, 1520 and 4000 minutes for CCl_4, TCM, TCE, and PCE, respectively. No Eh change in controls, reactive vials showed highly reducing conditions, but no significant pH change.	O'Hannesin, S.F. & R.W. Gillham, 45th Canadian Geotechnical Soc. Conf., Oct 25-28 (1992)
Fe	Halo-organic compounds	Wall, Borden	Reactive wall 22% Fe, 78% concrete sand; 5.5 m downgradient. Cell driven 9.7 m to bottom silty clay lens.	TCE reduced 95%, PCE 91%. No TCM downstream of wall. Cl^- increase consistent with quantity degraded. Traces DCE; no VC.	
Fe	TCE, PCE	Reac. Wall, Borden	Field demonstration in 1991 at Borden, Ontario. TCE 270 and PCE 43 mg/L. PRB 1.5m wide of 22% granular Fe and 78% sand placed in path of plume moving 19 cm/d.	90% TCE and 88% PCE removed from solution and Cl^- indicated dechlorination. Major product was cDCE with peak of 2200 μg/L followed by tDCE and 1,1-DCE, VC ND.	O'Hannesin, S.F., et al., Emerg. Technol. in Haz. Waste Mangmt VII, ACS, Sep 17-20, Atlanta, GA, pp. 55-58 (1995)
Fe	TCE	Column	Plexiglass columns packed with mixture 15% electrolytic iron and 85% silica sand. TCE pumped at 0.1 mL/min. C_i TCE = 1.3, 4.7, 10.2, 61 mg/L.	TCE C_i = 4.7 mg/L. Products: ethene 40%, ethane 18%, C1 to C4 10%. 3-DCE isomers & VC. c1,2-DCE primary product of degradation, though sum of all chlorinated was only 3 to 3.5%.	Orth, W.S. & R.W. Gillham, 209th National ACS Meeting Anaheim, CA, April 2-7, 35:815 (1995)
Fe	TCE	Column	Columns used simulated GW containing 1.3 to 61 mg/L TCE. Column packed with 15% iron powder mixed with sieved 35-mesh silica sand. SA of iron 0.287m^2/g, iron SA to solution volume ratio 0.21m^2/mL.	Pseudo-1st-order rates. Products :ethene > ethane >>> other C1—C4 hydrocarbons. 3.0-3.5% TCE appeared as chlorinated products. Most TCE probably sorbs to iron surface until complete dechlorination achieved.	Orth, W.S. & R.W. Gillham, ES&T, 30:66-71 (1996)
Fe	Cl_2	Batch	Chlorine solutions stirred in 250 mL reactor at 20°C. Granular Fe 0.2~.5 dia. added. 10 mL taken at 5, 10, 15, 20, 25 min and analyzed for chlorine & chloride contents. Experiments also carried out at pH 4, 5, 6, 7, 8, and 9.	Optimum conditions investigated for pH, particle size, and contact period. Species of OCl^- and HOCl removed by 100% between pH 4 and 7 within 25 min.	Özdemir, M. & M. Tüfekci, Water Research, 31:343-345 (1997)
Fe	Cr(VI)	Batch, Column	Geochemical effects and minerology on reduction CrO_4^{2-} by Fe(0) using stirred batch reactor (SBRs) and shaken batch bottles under N_2 to evaluate kinetics/mechanisms.	Chromate reduction rapid and complete in zero valent systems and natural aquifer material. $t_{1/2}$ = 11 h. When no aquifer material much slower and incomplete during 146 h.	Powell, R.M., M.S. Thesis, University of Oklahoma, Norman, OK (1994)
Fe	Cr(VI)	Batch, Column	SBRs: under N_2 w/ & w/o Elizabeth City aquifer material. C_0 of CrO_4^{2-} = 136 to 156 mg/L. 1st column portion of aquifer material. 2nd column mixture of Fe filings (7.5 g) & aquifer material (67.6 g). 6 mg/L chromate as K_2CrO_4 introduced at 0.05 mL/min.	Rapid changes in Eh from positive to highly negative upon introduction of Fe metal. Chromate reduction slow in system with no aquifer material but rapid in system containing the natural solid phase. Eh and pH changes less dramatic in effluent from column but influent chromate effectively removed.	Powell, R.M., et al., Water Environ. Fed. Conf., March, Miami, pp. 485 (1994)
Fe	Cr(VI)	Batch	Some types of iron and aquifer material more reactive than others. Ada Iron & Metal (AI&M) & Master Builders Supply (MBS); Eliz. City, NC & Otis AFB, MA aquifer material used along with commercial Si sand.	Data support conclusion that $CrO_4$2- can be reduced to Cr(III) in presence of elemental iron. AI&M and Eliz City aquifer material most reactive. Suitable e^- acceptors need to form appropriate couple. Mechanisms proposed.	Powell, R.M., et al., ES&T, 29(8):1913 (1995)
Fe	Cr(VI)	Batch	Aquifer materials from Elizabeth City, NC and Otis AFB, MA also kaolinite and montmorillonite using simulated GW. Scrap iron filings from AI&M and cast iron metal chips from MBS.	Coupled corrosion processes responsible for $CrO_4$2- reduction & precipitation, w/ AI&M Fe; much greater rates than MBS Fe. Aluminosilicate dissolution proposed to increase reaction rates.	Powell, R.M., et al., 209th National ACS Meeting, Anaheim, CA, April 2-7, 35:732 (1995)

Appendix A. continued...

Metal (zero valent unless specified)	Contaminant	Type test	Description/Conditions	Results	Reference
Fe	Cr(VI), TCE	Batch	Shaken batch bottle experiments were used to evaluate both the dissolution of 7 aluminosilicate minerals in the presence of Fe(0) and whether the dissolution affected the rates of chromate reduction by Fe(0).	Support previous hypotheses that aluminosilicate dissolution promoted Fe corrosion reactions, hence chromate reduction, due to generation of protons. Proposed mechanisms for chromate reduction and TCE dechlorination depicted in reaction diagrams.	Powell, R. M. & R. W. Puls, ES&T, 31:2244 (1997)
Fe	Cr(VI)	Column	Chromate reduction in Fe and quartz grains to determine fate of reduced Cr in wall material. Fe filings reacted with 20 mg/L Cr(VI), as K_2CrO_7 for more than 150 PV. Quartz grains flushed w/ $CaCO_3$ solution following Cr(VI) breakthrough in the column.	Reacted Fe developed coatings of goethite with Cr(III) concentrated on outermost edges. In regions of increased Cr, goethite acquired characteristics similar to Fe_2O_3 and Cr_2O_3. Complete reduction of Cr(VI) to Cr(III). Cr(III) incorporated into sparingly soluble solid species.	Pratt, A.R., et al., ES&T 31:2492-2498 (1997)
Fe	Atrazine	Batch	Thiocyanate reacts w/ Fe(III) giving red color (463 nm). 4.5×10^{-5} M Fe^{2+} (w/ light) accelerates atrazine decomposition.	Atrazine fully decomposed at pH 1.5 under sunlight within 2 h. Most important factors under light are surface area and nature of iron used. No degradation in dark.	Pulgarin, C., et al., 209th National ACS Meeting, Anaheim, CA, April 2-7, 35:767 (1995)
Fe	Cr(VI)	Char. Study, Eliz City NC	48 Cores at various depths. Assessed chemical speciation and distribution of Cr on contaminated soils and its leaching potential. Batch adsorption/reduction procedures used.	Adsorption and reduction capacity of soils were overwhelmed permitting passage of Cr(VI). Capacity differences related to clay content & pH; less to amorphous iron oxide coating.	Puls, R.W., C.J. Paul, D.A. Clark, J. Vardy.. J. of Soil Contam. 3(2):203 1994
Fe	Cr(VI), DCE, TCE, VC	Field Study, Eliz City NC	25% each by vol. EC aquifer material, sand, Fe-lathe turnings (0.1-2 mm) & MBS-Fe-chips (1-10 mm > sulphur, carbon) in field test. 21 augered boreholes, 3 to 8 m bgs, were filled with the mixture. 21 monitoring wells installed.	Disappearance of contaminants with appearance of ferrous Fe, decrease in oxidation-reduction potential and DO with slight pH increase. Sulfide also detected downgradient and within 30 cm of iron cylinders. Less reducing conditions downgradient.	Puls, R.W., et al, 209th National ACS Meeting, Anaheim, CA, April 2-7, 35:788 (1995)
Fe	Cr(VI)	Field Study, Eliz City NC	At Elizabeth City, 2 Fe sources (AI&M, MBS) mixed with native aquifer material and 10-mesh washed sand. 20-cm dia. cylinders installed in three rows 3 to 8 m bgs, 21 total.	Cr to < 0.01 mg/L Significant reductions in TCE. Siderite not detected, but Fe sulfides were. Full demonstration scheduled June 1996 of 50-long x 8-deep x 0.6-wide(m) trench of Fe(0).	Puls, R., et al., 4th Great Lakes Geotech. & Geoenviron. Conf., Univ. of Illinois, pp. 23 (1996)
Fe	Nitrate, Nitrite	Batch	Batch in unbuffered, anaerobic, DI water, 22°C, dark, HCl treated & untreated Fe(0) (>40 mesh) 69.4 g/L. Inject nitrate or nitrite[$C_o \sim 0.16$ mM), 40 rpm. IC for NO_3^- and NO_2^- quantification, estimated NH_4^- using a colormetric Hach kit.	1st-order nitrate rate constants, k_1, increased with HCl pretreated Fe(0). First 12 h following treatment, k_1 gradually declines in the presence of Cl-. High chloride in otherwise identical systems cause much smaller decline in k_1. Rate constant for nitrite reduction, k_2, small due to similar acid pretreatment of Fe. k_1 & k_2 for nitrate & nitrite reduction by untreated Fe(0) directly dependent on concentration of Fe(0), ranging 69.4 to 20.8 g L^{-1}.	Rahman, A. & A. Agrawal, 213th National ACS Meeting, 37:157-159 (1997)
Fe	PCP	Batch	Electrolytic Fe 5 g/20 mL used. Influenced by preparation of metal surface by treating with HCl, PCP concentration, pH, temperature, and presence of inorganic compounds.	Pretreated iron improved rates (6 h, 60-70% PCP [2.7×10^{-6} M] degraded). Keep pH near neutral. Some anions (e.g., Cl^-) retard degradation. Results indicated poor remedial choice for PCP.	Ravary, C. & E. Lipczynska-Kochany, 209th National ACS Meeting, Anaheim, CA, April 2-7, 35:738 (1995)

Appendix A. continued...

Metal (zero valent unless specified)	Contaminant	Type test	Description/Conditions	Results	Reference
Fe	Fe corrosion	Batch	Fe(0) anaerobic corrosion produce Fe^{2+}, OH^-, $H_2(g)$. Corrosion rates are measured by monitoring the H2 pressure increase in sealed cells containing iron granules and water. The principal interference is hydrogen entry and entrapment by the iron. The entry rate is described by Sievert's law ($R= kPH_2O_5$), and the rate constant, k, is evaluated by reducing the cell pressure once during a test.MBS Fe, Blend A, 50/50 mix of 10-18 & 18-32 mesh granules (C, 3.2%; Mn, 0.65%; S, 0.09%; SA, 1.5 m^2g^{-1}).	For the 10 - 32 mesh iron, k was 0.015 initially but decreased to 0.009 mmol kg^{-1} d^{-1} $kPa^{-0.5}$ in 150 d. Corrosion rate in saline GW 0.7 ~ 0.05 mmol of Fe $kg^{-1}d^{-1}$ at 25 °C—identical under saturated or fully-drained conditions. Rates decreased by 50% in 150 d due to alteration product buildup. First 40 - 200 h progressively increasing rates of pressure increase. Time before steady-state rates develop depends on the solution composition. Discarded this data in calculating corrosion rates. Tests on pure NaCl solutions at identical equivalent concentrations (0.02 equiv/L) show the following anion effect on corrosion rate: $HCO_3>SO_4^{2-}>Cl^-$. For NaCl solutions, corrosion rates decrease from 0.02 to 3.0 mmol kg^{-1} d^{-1} $kPa^{-0.5}$.	Reardon, E.J., ES&T, 29:2936-2945 (1995)
Fe	TCE, PCE	Site demo, Moffett, CA	Pilot field demo, Moffett Field, Mountain View, CA 1/96. 50' long x 10' wide x 22' thick funnel- &-gate installed across TCE and PCE plume 4/96.	Baseline sampling 6/96 & 9/96 positive. TCE > 1,000 μg/L upgradient reduced to ND w/in first 2' of cell (gate). Demo continue until 3/98; Report to be prepared for DOD.	Naval Facilities Eng. Service Center, Enviro. Restor. Div., www.Updated April 24, (1997)
Fe, US	TCE	Batch, column	5 to 20 mg/L TCE, 20-kHz US, 0.16 cm^2 in 0.5-L bag with 100-mesh Fe, anaerobic, 160 shakes/min. Column: 20% Fe, 80% sand. 4 Fe's: 50-mesh particles, Peerless acid-washed chips, unwashed Peerless, MBS washed chips. 43% 20-mesh; 40% 40-mesh, rest Fe dust. 15 mg/L TCE at 4.7 mL/min. US 15.9 mm-dia, auger drill bit, 15 cm long in 50-mesh Fe, 50% power.	US removes corrosion from Fe surface and prolongs reactive life Sonication for 0.5 h increased rates about 12%. But rates nearly tripled to 184% after 1 h treatment. Prior to US, lower half column (highest TCE conc.) $t_{1/2}$ 1.5 times upper section. After US $t_{1/2}$ dropped. Lower $t_{1/2}$ decrease 70%; upper $t_{1/2}$ 22%.	Reinhart, D.R., et al., Internat'l Contain. Tech. Conf. & Exhib. St. Petersburg, FL, Feb 9-12, pp. 806-813 (1997)
Fe	tDCE, cDCE	Batch	25-mL sealed bottles w/ 1.7 g Fe(0) & 34 mg ground pyrite in 1.7 mL Ar-sparged DI water. SA Fe(0) 0.7 m^2/g with either 6.7μL tDCE, 4.4 μL cDCE, 10 μL 1,1-DCE, 30μL VC in methanol,4 rpm. Volatiles partition into high headspace slowing further reaction and enhance accum.	2 categories of reductive dehalogenation: Hydrogenolysis (replace halogen by H^+) & reductive elimination (2 halide ions released), both net transfer of 2 e^-. Haloethylenes can undergo reductive, 0-elimination to alkynes under environmental conditions. Evidence of this is involved in reaction of chloroethylenes with Fe(0).	Roberts, A., et al., ES&T, 30:2654 (1996)
Fe	DDT, DDD	Batch	Sealed 40-mL vials. Fe powder (0.3-3 g) with 20 mL deoxygenated buffer, pH 7, DDT or DDD dissolved in acetone, and, with and without the presence of nonionic surfactant Triton X-114 at 250 mg/L. Uncapped reactors flushed with N_2, beads to improve mixing. Closed reactors shaken at 130 rpm at 20 ± 0.5 °C.	Rates of dechlorination of DDT and DDE were independent of the amount of iron, w/ or w/o surfactant. Rates w/ surfactant much higher than w/o. Initial 1st-order rate of DDT dechlorination was 1.7 ± 0.4 & 3.0 ± 0.8 d^{-1} or, normalized by the specific iron SA, 0.016 ± 0.004 and 0.029 ± 0.008 L m^{-2}/h^{-1}), w/ and w/o surfactant, respectively. Mechanistic model constructed that qualitatively fit the observed kinetic data, indicating that the rate of dechlorination of the solid-phase (crystalline) reactants was limited by the rate of dissolution into the aqueous phase.	Sayles, G.D., et al., ES&T, 31:3448-3454 (1997)

Appendix A. continued...

Metal (zero valent unless specified)	Contaminant	Type test	Description/Conditions	Results	Reference
Fe	CCl_4	Batch	System similar to that used by Matheson and Tratnyek (1994) except with the range of Fe(0) concentration extended from 5-31 m^2/L to 0.2 - 80 m^2/L.	Greater range of Fe(0) SA shows hyperbolic relationship. Concentration up to 80 m^2/L with sharp increase in rate indicating heterogeneous catalysis, electrical double layer or abrasion effects during mixing.	Scherer, M.M. & P.G. Tratnyek, 209th National ACS Meeting, Anaheim, CA, April 2-7, 35:805 (1995)
Fe	CCl_4	Reduction kinetics	Linear sweep voltammograms (LSV) of Fe(0) at 3000 rpm. Potentials set to avoid H^+ evolution at more (-). than -700 mV/SHE and O_2 evol. at more (+) than 800 mV/SHE. LSVs w/ & w/o CCl_4. Increased (-) current in CCl_4 attributed to reduction of CCl_4 to $CHCl_3$.	More reducing potential on Fe(0) increases rates of H_2O & CCl_4 reduction. However, H_2O becomes increasingly larger portion. At potentials more negative than -700 mV/NHE, water reduction larger portion than CCl_4 dechlorination, suggesting more reducing potential would not enhance CCl_4 dechlorination rate.	Scherer, M.M., et al., 214th National ACS Meeting, Las Vegas, NV, 37:247-248 (1997)
Fe	CCl_4	Reduction kinetics	Fe(0) from 99.5% pure Fe(0) rod 3.0 mm dia., SA 0.071 cm^2. Mass transport controlled by polished Fe(0) rotating disk electrode. Kinetics of CCl_4 dechlorination in pH 8.4 buffer at potential where oxide film would not form.	Cathodic current independent of electrode rotation rate, 1st-order rate constant ($k_{ct} = 2.3 \times 10^{-5}$ cm s^{-1}) < estimated rate constant for mass transfer to surface. Rate reduction of CCl_4 by oxide-free Fe(0) dominated by reaction at metal-water interface.	Scherer, M.M., et al., ES&T, 31:2385 (1997)
Fe, Mg	TCE	Batch	4.1 g/L Fe powder in oxygen-free, pH 7 water, 50° C.	TCE $t_{1/2}$ = 20 d using Fe. 1,1,1-trichloroethane, 1,1-dichloroethylene, tetrachloroethylene transformed using buffered water & landfill leachate.	Schreier, C.G. & M. Reinhard, Chemosphere, 29(8):1743 (1994)
Fe, Mg	TCE	Batch	0.5 g either 0.5% Pd alumina or 1% Pd on granular carbon (GAC) and 1% Pd PAC at 400 rpm. Total aqueous phase 60 mL, N_2 purged, capped, 5 mL H_2 added for 15 min to pre-reduce Pd. PCE = 1.1 μmoles in 3.5 μL of methanol.	5 chloroethylenes including PCE and VC reduced in 10 min by 0.5 g of 0.5% Pd on alumina and 0.1 atm H_2. Ethane 55-85%, ethene ≤ 5%. Pd on GAC yielded 55% ethane from PCE. PCE $t_{1/2}$ = 9 min for 0.055 μmole Pd (583 μg of 1% Pd on PAC). 10% nitrite decreased rate by 50%. O_2 greatly decreased all rates.	Schreier, C.G. & M. Reinhard, Chemosphere, 31(6):3475 (1995)
Fe	chlorinated ethylenes	Batch	Glovebox 90% N_2 / 10% H_2, bottles filled with iron and HEPES-buffered water (pH 7). Placed in 50° C waterbath, with or without shaking.	The more highly halogenated compounds most reactive (tDCE > TCE > PCE = cDCE = 1,1-DCE) with the exception of VC which is less reactive than PCE. Product: ethene, ethane. PCE:15-30%; VC: 50% reduction. Ethene/ethane ratio larger for VC. TCE intermediate of PCE. cDCE only intermediate of TCE.	Schreier, C.G. & M. Reinhard, 209th National ACS Meeting, Anaheim, CA, April 2-7, 35:833 (1995)
Pd, H_2	Chlorinated ethylenes (PCE, VC)	Batch	125 mL glass bottle, 60 mL N_2 purged water, 0.05-0.5 g catalyst [5 g either 0.5% Pd-alumina or 1% Pd on GAC and 1% Pd PAC or PCI-silica], w/ 1-1.1 μmoles PCE, 400 rpm. 5 mL H_2 added at stages; some initial H_2 = 0.1 atm. Sampled headspace for ethene, ethane, ethylenes.	Pd-PCI-silica PCE rate 0.034 min^{-1} ($t_{1/2}$ =20 min), 65% ethane; 2% ethene. Some PCE dehalogenated before double bond reduced. Al pellets, GAC or PAC, PCE 99.99% reduced in 10 min.; ethane 65-80%; ethene >5%. Sorption significant on carbon but did not hinder transformation using Pd-PAC.	Schreier, C.G. & M. Reinhard, 209th National ACS Meeting, Anaheim, CA, April 2-7, 35:749 (1995)

Appendix A. continued...

Metal (zero valent unless specified)	Contaminant	Type test	Description/Conditions	Results	Reference
Fe	Precipitates	Column	ID precipitates that form on iron surfaces w/ differing water chemistry. Two column tests performed using 100 mesh, 99% pure electrolytic iron. A 120 mg/L $CaCO_3$ solution passed through one column and a 40 mg/L KBr solution through other. Rate was at 0.23 mL/min. RT ~ 13.3 h. N_2 gas passed through 2nd column. Sampled after 158 and 166 PV.	$CaCO_3$ treated iron formed whitish gray coating on first centimeter of column but KBr treated iron did not display any visible precipitates. $CaCO_3$ and $FeCO_3$ phases were only present on the surface of the iron removed from the influent end of the column treated with a $CaCO_3$ solution. Fe surfaces analyzed from both influent and effluent end of the KBr treated iron and the effluent end of the $CaCO_3$ treated iron indicated presence of magnetite (Fe_3O_4) precipitates.	Schuhmacher, T., et al., 209th National ACS Meeting, Anaheim, CA, April 2-7, 35:801 (1997)
Fe	TCA, TCE	Batch, Column	Iron powder for removal of TCA and TCE from waste water.	50% TCA removal from 4 h to 1 h as temperature rose 20 to 50°C. Degradation rates highly sensitive to Fe SA, significant decline at pH values in excess of 8.0.	Senzaki, T. & Y. Kumagai, Kogyo Yosui, 357:2 (1988); Kogyo Yosui, 369:19 (1989); Senzaki, T., Kogyo Yosui, 391:21 (1991)
Fe	Al, Cd, Co, Cr, Fe, K, Mg, Mn, Ni, Pb, Zn	Electro-chemical Cell	Electrochemical cell of massive sulfide-graphite rock from mine site as cathode, scrap iron as the sacrificial anode and acidic leachate from mine site as electrolyte.	Cell raised pH of ~41 L leachate from 3.0 to 5.6 with decrease in redox potential from >650 to <300 mV. Iron sulfate precipitate formed with a concomitant lowering of Al, Cd, Co, Cu and Ni.	Shelp, G.S., et al., Applied Geochemistry, 10:705 (1996)
Fe & $H_2/Pd/Al_2O_3$	1,2-dibromo-3-chloro-propane (DBCP)	Batch	Iron powder and $H_2/Pd/Al_2O_3$. Palladium used as a catalyst with H_2 gas as the reductant. Looked at both sterile (abiotic) buffered and unbuffered conditions.	Fe(0) dehalogenated DBCP under sterile abiotic conditions buffered & unbuffered; also, Pd w/ H_2 gas as reductant in GW. pH had little effect, however, a solution with pH = 9 inhibited the reaction.	Siantar, D.P., et al., 209th National ACS Meeting, Anaheim, CA, April 2-7, 35:745 (1995)
Fe & $H_2/Pd/Al_2O_3$	1,2-dibromo-3-chloro-propane (DBCP)	Batch	Compared Fe(0) and H_2/Pd-alumina for DBCP $\rightarrow$ propane. 4 g of 100-200 mesh Fe powder in 125 mL glass bottle, 110 mL deox. solution, 10 μg/L DBCP, anaerobic, 400 rpm. MilliQ^m (DI) water (pH 7.0) or GW (pH 8.2-8.7), some amended w/ anions and/or buffer (pH 7.0).	Fe(0) in H_2O DBCP $t_{1/2}$ = 2.5 min; $t_{1/2}$ = 41-77 min in GW. O_2, NO_3- slow reaction. 60 mg/L nitrate removed in 14 min. DBCP trans. in min. w/ 75 mL GW, 22.5 mg 1% Pd-alumina. Rate in GW 30% slower compared to Milli-Q^m. Slight inhibition in Milli-Q^m by SO_4^-, NO^{3-}, Cl- or O_2. SO_3^{2-} >> inhibitory effect.	Siantar, D.P., et al., Wat. Res. 30:2315 (1996)
Fe	Atrazine	Batch, Soil	Fe(0) (10% w/w), 0.02 mg/L atrazine in batch. 20 mg ^{14}C-atrazine in Fe(0) (20% w/w) in batch. Fe(0) (2% w/w) in soil to determine mineralization and availability of the pesticide atrazine.	The batch test removed 93% atrazine in 48 h. 5% of that was adsorbed "readily available"; 33% "restricted"; 2% residues. 88% ^{14}C removed in 48 h of that 6% was available; 72% pool; the rest was bound. Fe in soil quadrupled mineralization in 120-d. 2% Fe(0) & 100 mg NO^{3-} kg^{-1} increased by a factor of 10; unextractable residue was greater than two times greater than the control (no Fe(0)).	Sinah, J., et al., HSRC/WERC Joint Conference on the Environment, May 20, Paper 36 (1997)
Fe	TCE, DCE, VC	Batch, Column	Anaerobic & mildly aerobic conditions; > 25 commercial iron metals in several forms; 0.1-1325 m^2/L iron metal; several groundwaters used.	No significant products from TCE batch or column. Strong Fe(0) π-bonds may prevent DCE & VC products from desorbing. Direct reduction of adsorbed chloroethene at metal/water interface. Reduction by iron oxide and oxyhydroxide not seen.	Sivavec, T.M. & D.P. Horney, 209th National ACS Meeting, Anaheim, CA, April 2-7, 35:695 (1995)
Fe and FeS	TCE	Batch, Column	Effect of FeS varying the FeS mass in batch. Columns with Fe filings, SA concentration avg. 6000 m^2/L.	TCE $t_{1/2}$ ~40 min. Rates constant over several hundred PV even though surface of iron filings coated with $FeCO_3$ precipitate.	Sivavec, T.M. et al. Emerg. Technol. in Haz. Waste Mngt. VII, Atlanta, pp. 42-45 (1995)

Appendix A. continued...

Metal (zero valent unless specified)	Contaminant	Type test	Description/Conditions	Results	Reference
Fe, Ni/Fe, Pd/Fe	TCE	Column	Bimetallics accelerate degradation relative to untreated Fe. Column of Ni-treated granular Fe with TCE-contaminated site GW (TCE 2.1-3.3 mg/L).	1st-order TCE rates and products in > 250 PV in Fe/Ni. In 76 PV rates accelerated above untreated Fe. Catalytic dehydrohalogenation to hydrogenation caused enhancement. But, decreased until rate similar to untreated iron. Gray precipitate after 100 PV GW (250 mg/L carbonate). Fe catalysts prone to deactivation. Similar losses not shown in granular Fe(0) systems.	Sivavec, T.M., et al. Internat'l Contain. Tech. Conf. & Exhib. St. Petersburg, FL, Feb 9-12 (1997) Sivavec, T.M., et al., 213th National ACS Meeting, 37:83-85 (1997)
Fe	Cd	Packed Bed	Packed bed of Fe sorbent supported on fine mesh stainless steel screen & Teflon® flakes at 0.12-0.70 cm/s.	Cd(II) 5 mg/L at pH 7, flow 1.6 mL/min. ~ 8,000 bed volume of synthetic waste treated before breakthrough of Cd(II).	Smith, E. H., Emerg. Technol. in Haz. Waste Mngmt. VII, Atlanta, GA, pp. 1205 (1995)
Fe and sulfur	Mo, U	Batch Column	Batch test of test material with synthetic U mill tailing pore fluid. The column consisted of a solids chamber and a water sampling chamber. 5 bottom chambers filled w/ $FeSO_4$ and sand, 5 top chambers w/ lime and sand.	Redox front coincided w/ precipitation of ferrous iron by contact w/ $Ca(OH)_2$. Mo & U successfully removed for 6 & 9 d, respec. U reduced to UO_2 & precipitated as $CaUO_4$ from elevated pH. Mo reduced to Mo_3O_8 or MoS_2, or precipitated as $FeMoO_4$.	Spangler, R.R. & S.J. Morrison, Pasco, WA, U.S. DOE Report (1991)
Funnel-and-gate	Configurations	Model	A variety of configurations simulated using FLOWNET ver. 2.0, a 2-D steady-state flow model based on dual formation of flow.	2-D model shows width of capture zone proportional to discharge through gate. Most efficient configuration is sides 180° apart, oriented perpendicular to the regional hydraulic gradient.	Starr, R.C.& J.A. Cherry, Ground Water, 32(2):465 (1994)
Fe	Halogenated organics	Batch	First environmental application for removal of chlorinated organic compounds from aqueous solution.	Catalyzed metallic iron powder was shown to degrade a wide range of halogenated organic contaminants.	Sweeny, K.& J. Fischer, Patent 3,640,821 (1972); Patent 3,737,384 (1973); Patent 4,382,865 (1983)
In Situ Fe Wall	VOCs	Field Site, CA	VOC degradation rates in GW through 7' Fe canister. 42.9 h RT determined 2.2' width wall. Steel plates divided ~220 tons granular Fe in center from outer pea gravel. 4 monitoring wells downgradient; 2 piezometers upgradient.	First commercial *in situ* iron wall treating VOCs at former semiconductor facility. Design & construction from 11/94 to 1/95. Operation and regulatory issues summarized. Monitoring shows water quality objectives being met.	Szerdy, F.S., et al, ASCE National Convention, Nov 12-14, Washington, D.C. pp. 245-256 (1996)
H_2O_2/Fe Powder	Azo Dyes	Batch	Open batch system of 1000 mL. H_2SO_4 or NaOH used to adjust pH. Optimal pH 2-3, well mixed, ratio H_2O_2 to iron 0.001 M:1 g/L	H_2O_2/iron powder is better than the Fenton's reagent due to continuous dissolution of iron powder and dye adsorption to powder even though Fenton's reaction major decolorizing agent.	Tang, W.Z. & R.Z. Chen, Chemosphere, 32(5):947-958 (1996)
Organics, inoculated w/ bacteria	U	Batch, Column	250 mL sealed bottles w/ organics, nutrients, pH 7.0, Shiprock bacteria. Columns w/ straw, alfalfa, sawdust, sand (25% f_{oc}). GW 15 mL/h (1 d RT), 1 PV bacteria.	Sulfate, nitrate, U(VI) monitored 90 d. Precipitated U(IV) crystalline UO_2(s). Batch and column results support use of cellulosic substrates as candidate barrier materials.	Thombre, M.S., et al., Internat'l Contain. Tech. Conf. & Exhib. St. Petersburg, FL, Feb 9-12, pp. 744 (1997)
Steel	Cr(VI)	Batch	Steel nuts put in barrel immersed in 2-L soln containing 90 ppm Cr(VI); at 16 rpm.	After 7.2 h, final Cr concentration < 0.5 μg/mL.	Thornton, R.F., Patent 5,380,441 (1995)
Zn	2,3-dibromo-pentane	Batch	Determine e^- transfer during reductive dehalogenation. Evidence from stereospecificity of reductive elimination of vicinal dihalide stereoisomers synthesized in lab.	*meso*-2,3-dibromopentene $\longrightarrow$ >95% *trans*-2-pentene; *D,L*-2,3-dibromopentane >95% *cis*-2-pentene. Reduction at metal surface where 2 e^- transferred w/ no free radical intermediate.	Totten, L.A.& A.L. Roberts, 209th National ACS Meeting, Anaheim, CA, April 2-7, 35:706 (1995)

Appendix A. continued...

Metal (zero valent unless specified)	Contaminant	Type test	Description/Conditions	Results	Reference
Fe	CCl_4	Column	1st column: CCl_4 in air-sat. DI water. All O_2 consumed by Fe(0) giving anoxic downgradient region. 2nd similar but Fe zone longer and diluted by mixing with sand.	DO reacts with Fe(0) slowing dechlorination. But oxygen from air accelerated reactions, possibly due to pH effect from carbonate, changes in pathway, catalytic role of Fe^{2+}, or O_2 creating active corrosion sites.	Tratnyek, P.G., et al., Emerging Technol. in Haz. Waste Manag. VII. Atlanta, pp. 589 (1995)
Fe	Chlorinated organics	Reactive transport model, k_{SA}	Average estimates of rate constants. Assume reductive dechlorination. Deviations with longer exposure due to precipitates. 1st-order predictions vulnerable to changes in mechanism or rates for less reactive constituents.	Pseudo 1st-order rates normalized to Fe-SA(k_{SA}). Solvents compared over range of conditions. k_{SA} varies by concentration, Fe type, etc. Representative $k_{SA's}$ and reactive transport model calculate minimum barrier width for flow velocities and halocarbon.	Tratnyek, P. G. et al., GWMR, Fall, pp. 108 (1997)
Fe	PCE, TCE, cDCE, VC	Column	NJ site GW. Major VOCs- PCE ≤ 50 mg/L, TCE ≤ 3 mg/L. TDS 425-450 mg/L. 100% iron in column.	$t_{1/2}$ PCE, TCE, cDCE, VC = 0.5, 0.5, 1.5, 1.2 h, respectively. 2nd test similar for PCE, TCE but cDCE = 3.7 & VC 0.9 h. Corrosion increased pH & promoted precipitation of $CaCO_3$, $FeCO_3$, $FeOH_2$.	Vogan, J.L., et al., (1994)
	chlorinated solvents	Column	Column using site water and Single Layer Analytic Element Model to evaluate treatment zones, flow velocities, and residence times.	GW flow model & degradation rates to design and estimate cost for full-scale funnel-and-gate system at shallow sand aquifer (30-40 ft) at Army Ammunition Plant, MN.	Vogan, J.L. et al., 87th Ann. Mtg, Air & Waste Manag. Cincinatti, OH, (1994)
Fe	PCE, TCE, cDCE, VC	Pilot-scale Test	NJ site. Above-ground reactor influent PCE of 30 mg/L. RT 1.1 d. Flow rate 0.5 gpm for 3 mo.	Assumptions: Time for PCE degradation sufficient for any TCE to degrade; 10% cDCE, 1% VC from PCE & TCE degradation.	Vogan, J., et al. 209th National ACS Meeting, Anaheim, CA, April 2-7, 35:800 (1995)
Fe, Zn	CCl_4	Batch	Kinetics dependent on pH, SA of metal, CCl_4 conc., buffer and solvent composition (volume fraction 2-propanol).	Reduced CCl_4 to chloroform in few h. Rate was 1st-order with respect to CCl_4 at concentrations < 7.5 mM.	Warren, K., et al., J. of Haz. Mat., 41:217 (1995)
Fe	PCE	Surface chemistry	XPS identified surface elements, valence state. Alfa Aesar Fe (10 x 1mm) cleaned (H_2O_2, hydrofluric acid, H_2O). Vapor purified PCE, adsorbed to an Fe (100) single crystal (10 mm in diameter and 1 mm in thickness) purchased from Alfa Aesar by exposing 1 x 10^{-7} Torr 100 s or 5 x 10^{-7} Torr 200 s at room temp.	PCE adsorbed to metal surface, activated by chemisorption. Cl- from e^- transfer from Fe to adsorbed species. Adsorbed water can dissociate and provide H^+ for C surface species from PCE dissociation. Hydrocarbon can be produced from this reaction.	Wang, C.-B.& W.-X. Zhang, 213th ACS Meeting, San Francisco, CA, 37:163-164 (1997)
Organic mix, anaerobic bacteria	Mine Waste	Batch	Sealed, glass flasks simulated mine drainage, organic mixtures, measured permeability. Consortium of bacteria from creek facilitated reducing conditions & degradation. Limestone ensured optimum pH; anaerobic conditions.	Reactivity & permeability (> 10^{-3} cm/s) suitable. Higher sulphate reduction rates and longer effectiveness from organic mixture. Geochemical reactive and transport models will be used to assess effectiveness in treatment of mine drainage using reactive walls.	Waybrant, K. R., et al, Sudbury '95, Mining and the Environ. CANMET, Ottawa, Ontario, 3:945-953 (1995)
Methanogenic bacteria and Fe	$CHCl_3$	Batch	Anaerobic, 200 rpm, 20°C, 25 mL, methanogenic culture, iron powder, iron filings, steel wool. $CHCl_3$ tested in iron-cell, iron-supernatant and resting cell.	k = 0.11 (Fe-cell), 0.003 (Fe-supernatant) & 0.007 hr^{-1} (resting cell). Biodehalogenation to abiotic reactions 37:1. Biocorrosion of Fe & biodehalogenation of $CHCl_3$ via cometabolism using H^+ from H_2O.	Weathers, L.J., et al., 209th Nat'l ACS Meeting, April 2-7, Anaheim, CA, 35:829 (1995)
Fe Kinetics	dibromopentane	Batch	Synthesized stereoisomer to demonstrate *e*- transfer.	Experiments indicate reduction takes place at metal surface.	Weber, E.J., 209th Nat'l ACS Anaheim, CA, 35:702 (1995)

Appendix A. continued...

Metal (zero valent unless specified)	**Contaminant**	**Type test**	**Description/Conditions**	**Results**	**Reference**
Fe	4-amino-azo-benzene (4-AAB)	Batch	4-AAB has reactive amino group for attaching molecule to nonreactive surface. Reducing azo linkage suggests aqueous reductant, if not, then surface- mediated process.	Circumvented surface mediated contact to surface of Fe(0) by adding appropriate water soluble e^- mediators. Species that can function as e^- mediators were found present in the soil.	Weber, E.J., ES&T, 30:716 (1996)
Fe	1,2-DCE, TCE, Freon, VC	Treatment Wall	Granular Fe(0) & gravel at former semiconductor facility, San Francisco. GW flow 1'/d. 2 d RT required for VC.	Wall 40' long, 20 to 7' bgs, Fe 4' wide allow 2 d RT. Slurry walls east and west side for hydraulic control. 4 mon. wells in wall.	Yamane, C., et al., 209th Nat'l ACS Meeting, Anaheim, CA, April 2-7, 35:792 (1995)
Fe	Nitrate	Batch	150 mL flasks in air-dry & sat. (parafilm seal) 3 d. Samples extracted in 50 mL DI. Purged with N_2. "Artificial" soil contam. with nitrate (10 g clay + 10 g sand + 10 g Fe powder + 10 mL of 50 mg-NO_3^--N/L).	94.4% Nitrate removal using 0.01M HEPES & 6% (w/v) Fe(0). Treating 60 mg NO_3^--N/L w/ 6% Fe(0) at pH 1.0 transformed all in 24 h; nitrate transformation is inversely related to pH. Nitrate reduced to ammonium. Optimal removal at C_i NO_3^--N = 50-80 mg/L. In soil up to 97% transformation in air-dry samples, 99% in wet samples; 2% in controls.	Zawaideh, L.L., et al., HSRC/WERC Joint Conf. on the Environment, May 20 (1997)
Nano-Fe or Pd/Fe Particles	PCB, TCE	Batch	20 mg/L TCE, 1.0 g nano-Fe or Pd/Fe in 50-mL vial sealed, 30 rpm. PCBs, 50 μL 200 μg/mL Aroclor 1254 in methanol w/ 1 mL ethanol/water (1/9), 0.1 g wet Fe or Pd/Fe in 2-mL vial, 30 rpm, 17 h. Commercial Fe tested.	Synthesized sub-colloidal metals. Nanoscale Fe more reactive than commercial Fe powder, due to high SA, active Fe surface, less surface coverage by iron oxide layer. Nanoscale Pd/Fe more active than pure Fe but nano-Fe inactivated by Fe oxide formation.	Zhang, W.-X. & C.-B. Wang, 213th ACS Meeting, San Francisco, CA, 37:78-79 (1997)
Pyrite fines	Cr(VI)	Batch	Pyrite fines collected near mine area. Pyrite crushed to -45 μm. Used mixed batch reactors.	Pyrite found to act as efficient Cr(VI) reducing agent. The Cr(III) hydroxide precipitated onto pyrite particles.	Zouboulis, A., et al., Wat. Res. 29(7):1755 (1995)

Appendix B. Explanation of Relevant Physical/Chemical Phenomena

Corrosion

Corrosion processes are the required chemical underpinning of contaminant remediation by metallic iron. Until recently, the science of corrosion was concerned almost exclusively with studying the process in order to minimize, and if possible eliminate, corrosion reactions. Corrosion results in rusting of the iron and steel in cars, pipes, bridges, buildings, and other structures. It is perhaps the most expensive aspect of infrastructure deterioration in modern society. Although corrosion is familiar to everyone as rusting, few are aware of the extremely complex reactions occurring within the corroding metals, at their surfaces and, in the case of electrochemical corrosion, in the surrounding electrolyte solutions. To understand how these reactions can be used for remediating contaminants requires at least a fundamental awareness of the manner in which corrosion reactions proceed.

Zero-valence-state metals, such as metallic iron (Fe(0), can serve as electron donors for the reduction of oxidized species (Sculley, 1975). These metals are unstable in the natural environment and have to be created using high-temperature metal refining processes (Evans, 1960; Sculley, 1975; Snoeyink and Jenkins, 1980). Zero-valence-state metals tend to revert to a form that is more thermodynamically stable; for example, iron metal oxidizes to Fe_2O_3 in the earth's oxygen-rich atmosphere. At low temperatures the rate of simple atmospheric oxidation of iron and steel is negligible, however, due to the formation of oxide films that inhibit further surface exposure.

When a metal is immersed in an aqueous salt solution, as would be the case for a reactive barrier of iron chips or filings in an aquifer, an electrochemical corrosion mechanism will occur. Electrons are given up by the metal in one area (the anodic region) forming soluble cations of the metal, and taken up by oxidized species that become reduced, at another part of the metal surface (the cathodic region). The instability of the iron itself can provide the necessary energy for oxidation-reduction reactions without external energy input, provided suitable coupled electron-accepting reactions can occur with reducible species at the cathode.

Typically dissolved oxygen is the preferred oxidant, or electron acceptor, during aerobic corrosion processes. These systems can, however, become anoxic or anaerobic if oxygen is depleted by the reactions. When present, inorganic contaminants such as chromate (CrO_4^{2-}) or highly halogenated organic compounds such as PCE and TCE can serve as the oxidants, accept electrons, and become reduced. As long as electron acceptors are present, corrosion processes and electron transfer within the metal can continue.

An electrochemical corrosion cell (ECC) can form in a number of ways, including:

1) the simple contact of two different metals. One will become the anode, the other the cathode. The position of the metals in the galvanic series determines the direction of electron flow; i.e., which becomes the anode and which the cathode.
2) when anodic and cathodic regions develop on the same metal surface. This can result from compositional variations within the metal (i.e., other metal contaminants or inclusions with differing galvanic potentials), surface defects, differences in grain structure orientation, stress/strain differences, and chemical variations in the surrounding electrolyte solution (Evans, 1960; Sculley, 1975; Snoeyink and Jenkins, 1980; Adamson, 1990).

These electron transfer processes within a metal or between contacting metals are said to occur within the external circuit of the electrochemical cell. An internal circuit is also required to complete the cell. This requirement is fulfilled by the contacting electrolyte solution. This electrolyte can consist of water containing salts (such as ground water) and reducible, (i.e., electron-accepting), solute(s). In some cases the water itself can accept electrons via reductive dissociation. This is easily observed when the zero-valent metal is very low in the galvanic series, such as Mg. When Mg metal is added to even deionized water (i.e., no solutes present), bubbles of H_2 gas rapidly appear on the Mg surfaces. Mg is so low in the galvanic series that the water itself serves as the electron acceptor and is rapidly dissociated. As you proceed to metals higher in the galvanic series, the dissociation of water becomes less and less pronounced.

The ECC is basically a low-power version of the same type of circuit that is established in batteries. Figure 18 shows a simple ECC in a beaker of electrolyte solution with the external circuit resulting from the contact of two dissimilar metals, tin and iron. The electrons travel through the external circuit from the anode (Fe^0) to the cathode (Sn^0), where they can reduce oxidized species.

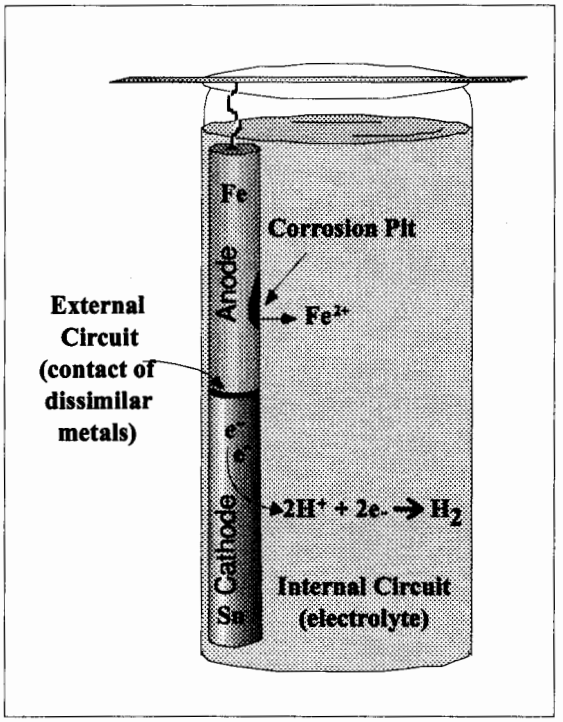


Figure 18. Example of an electrochemical corrosion cell.

Some of the potential corrosion and contaminant reduction reactions in zero-valent iron systems are:

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \quad \text{Anode} \quad (25)$$

$$2H^+ + 2e^- \rightarrow H_{2\,(gas)} \quad \text{Cathode} \quad (26)$$

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_{2\,(gas)} \quad \text{Net reaction} \quad (27)$$

and, when oxygen is present (aerobic system)

$$4Fe^0 \rightarrow 4Fe^{3+} + 12e^- \quad \text{Anode} \quad (28)$$

$$12H^+ + 3O_2 + 12e^- \rightarrow 6H_2O \quad \text{Cathode} \quad (29)$$

$$4Fe^0 + 3O_2 + 12H^+ \rightarrow 4Fe^{3+} + 6H_2O \quad \text{Net reaction} \quad (30)$$

where the increase in pH due to proton consumption (Equation 30) results in the precipitation of the Fe^{3+} as $Fe(OH)_3$. Should chromate be present as an oxidized species

$$Fe^0 \rightarrow Fe^{3+} + 3e^- \quad \text{Anode} \quad (31)$$

$$CrO_4^{2-} + 4H_2O + 3e^- \leftrightarrow Cr(OH)_3 + 5OH^- \quad \text{Cathode} \quad (32)$$

$$Fe^0 + CrO_4^{2-} + 4H_2O \rightarrow Fe(OH)_3 + Cr(OH)_3 + 2\,OH^- \quad \text{Net reaction} \quad (33)$$

Gillham and O'Hannesin (1994) have proposed that the reductive dechlorination of chlorinated organic compounds by iron metal corrosion may proceed as

$$2Fe^0 \rightarrow 2Fe^{2+} + 4e^- \quad (34)$$

$$3H_2O \leftrightarrow 3H^+ + 3OH^- \quad (35)$$

$$2H^+ + 2e^- \leftrightarrow H_{2\,(gas)} \quad (36)$$

$$X\text{-}Cl + H^+ + 2e^- \leftrightarrow X\text{-}H + Cl^- \quad (37)$$

$$2Fe^0 + 3H_2O + X\text{-}Cl \leftrightarrow 2Fe^{2+} + 3OH^- + H_{2\,(gas)} + X\text{-}H + Cl^- \quad (38)$$

Which of these reactions, or others, is dominant will depend on the conditions and contaminants present; for example, the presence or absence and the concentrations of other reactive species (including the partial pressures of gases such as O_2 and CO_2) and mineral surfaces, pH, etc. It should be noted that these reactions tend to increase the pH of the corrosion system. It is also important to note that although chromate is reduced and chlorinated hydrocarbons are reductively dechlorinated in the presence of Fe^0, current research indicates that the mechanisms of the reactions are different.

Sorption, Adsorption, Dissolution, and Precipitation Processes in Zero-Valent Iron Systems

As a contaminant plume moves through the subsurface, chemical processes occur that can affect both contaminant concentration and the overall hydrogeochemistry of the system. Three of the most important physical processes are sorption, dissolution, and precipitation. These processes also occur in iron PRBs, where the radical geochemical changes can exert profound effects on the ground water and contaminants.

Sorption and adsorption are loosely described as processes wherein chemicals partition from a solution phase into or onto, respectively, the surfaces of solid phase materials. Both sorption and adsorption at particle surfaces tend to retard contaminant movement in ground water. Retardation of the contaminant at the iron surface is a positive result, allowing increased time for reactions.

In the subsurface context, sorption usually implies movement, or dissolution, of a chemical into a surface coating on an aquifer material mineral grain. For example, hydrophobic organic compounds such as PCE tend to be sorbed into organic carbon coatings on mineral grains. In fact, evidence seems to indicate that graphitic inclusions/coatings on some granular iron surfaces might enhance reductive dechlorination relative to iron without such organic materials being present at its surfaces. It is possible that sorption of the chlorinated compounds to the graphitic constituents increases the contact time between the contaminant and the iron surface. This would allow increased reaction time and better proximity for the requisite electron transfers to occur.

Adsorption implies attachment of a chemical to reactive sites on mineral surfaces. These sites usually result from an excess or either positive or negative charge on the surfaces. These surface charges can be constant (fixed) due to ion substitutions in the mineral matrix (isomorphous substitution), variable with pH, or a mixture of both. In addition, the adsorption can result from either inner-sphere or outer-sphere complexation. Inner-sphere complexation is due to actual covalent and ionic chemical bond formation. In outer-sphere complexation adsorption results from ion-pair bonding due to electrostatic forces and hydration water separates the solvated ion from the surface.

Many metal oxides and some clay minerals have net surface charges that vary with pH due to the proportion of protonated versus deprotonated surface sites. Among these variably-charged materials are the iron oxyhydroxides (rusts) that result when zero-valent iron corrodes. These materials are very significant to adsorption of both inorganic and organic charged solution species (ionic species). The charges of both the surface and the solution ion control whether adsorption will occur or whether the surface and the ion will repulse one another. The pH_{zpc}, or pH of zero-point of charge, is the pH at which negatively and positively charged surface sites exist in approximately equal numbers on the mineral. Above pH_{zpc} the surface will have a net negative charge, enhancing cation adsorption; below pH_{zpc} the surface will have a net positive charge, enhancing anion adsorption. Research has shown that the reduction of the negatively-charged Cr(VI) chromate ion (CrO_4^{2-}) to Cr (III) by zero-valent iron occurs more rapidly when the system pH is below the $pH_{zpc} \approx 8.5$ of the iron oxyhydroxide rusts; i.e., the rusts have a net positive charge (Powell et al., 1995). This increase in reduction is probably partially due to the contaminant being maintained at the iron surface by adsorption.

Although flowing subsurface systems are not in true chemical equilibrium, they can establish a hydrogeochemical pseudo-steady state condition. This condition can be altered when a contaminant front/plume passes through (Puls and Powell, 1992). Contaminant fronts typically have pH, Eh, ionic strength, chemical species and complexants, and other features that differ from the intruded pseudo-steady state system. These differences can, among other things

- dissolve cementation between the mineral grains,
- change the adsorptive nature of the solid phase (potentially causing charge reversal and/or allowing desorption of previously immobilized species and/or adsorption of previously mobile species),
- alter mineral-bound and aqueous elemental oxidation states, or
- precipitate new phases onto the solid surfaces.

The implementation of a reactive iron barrier wall in the subsurface can be viewed as having effects on the aquifer in the vicinity of the wall that are analogous to a plume moving through the zone. Intra-wall and downgradient effects will include radically lowered Eh and loss of dissolved oxygen, higher pH, and increases in Fe^{2+} that will precipitate downgradient, possibly as iron oxyhydroxide colloids. Loss of cementation and precipitate formation can generate mobile colloidal particles, that can themselves transport adsorbed contaminants, or contain toxic materials that were naturally occurring in the geologic matrix. Additional research is needed on these disruptive effects to determine whether certain types of intercepted contaminants can be transported colloidally or, alternatively, whether naturally-occurring but immobilized metals in or on the aquifer minerals might be liberated and mobilized by the dramatic geochemical changes.

The dissolution and precipitation processes associated with the iron metal are, however, essential for contaminant remediation. The reduction of Cr(VI), for example, occurs primarily due to the anodic dissolution of Fe^{2+} during the corrosion process (Powell et al., 1995). The subsequent immobilization of the resulting Cr(III) is due to precipitation of the chromium as hydroxides or mixed iron/chromium oxyhydroxide solid solutions. Although the chlorinated hydrocarbons are not precipitated during remediation, dissolution of the iron still occurs as Fe(0) yields electrons to the hydrocarbon and the resultant Fe^{2+} is exposed to the solution. Understanding the dissolution/ precipitation geochemistry of these zero-valent iron systems and the contacting aquifer materials is an area of ongoing research.

Appendix C. Scoping Calculations

Cost-effective use of permeable reactive barriers for ground-water treatment requires proper estimation of the amount of reactive material required and choosing the best means of emplacing it in the ground. The weight of reactive material per unit cross-section of the plume may be estimated from laboratory reaction kinetics data and basic knowledge of the plume and the remediation goals. The value of this parameter has implications regarding the choice of permeable barrier design and emplacement method. The use of tremie tubes, trenching machines, high-pressure jetting, and deep soil mixing may be appropriate for different situations, depending on the amount of reactive material required, the dimensions of the plume, and other factors. The specific application considered here is granular iron to treat ground water contaminated with chlorinated solvents, but the principles are applicable to other types of media and contaminants.

Reaction rate parameters from laboratory studies of iron-mediated degradation of a variety of chlorinated solvents have appeared in the literature in the past several years (Johnson et al., 1996; Shoemaker and al., 1996). The work of Johnson et al. (1996) has been especially helpful in establishing the high degree of consistency between kinetics data obtained from batch and column studies. By expressing rate data in a way that accounts for the iron surface area concentration, it was demonstrated that results reported in the literature varied by less than had previously been thought. This makes it possible to obtain a fairly reliable estimate of the iron requirement for a potential application even before site specific laboratory feasibility tests are conducted. The bulk of the data reviewed by Johnson et al. suggest a surface-area-specific rate parameter (k_{SA}) of about 0.2 $cm^3\ h^{-1}\ m^{-2}$ for TCE and of about 0.04 $cm^3\ h^{-1}\ m^{-2}$ for cDCE. For the examples considered here, 1.0 m^2/g will be used for the specific surface area, a value typical of the granular irons which currently appear to be the most practical for permeable barrier applications. Further, the rate of reaction will be decreased by 50% to adjust for subsurface temperatures being lower than room temperature (Sivavec and Horney, 1995). Therefore, the effective rate parameter to be used is 0.1 $cm^3\ g^{-1}\ h^{-1}$ for TCE and 0.02 $cm^3\ g^{-1}\ h^{-1}$ for DCE.

Two example cases are considered below. The first and simplest involves degradation of a chlorinated compound (e.g., TCE) where the levels of intermediate products (e.g., DCE) are low enough that they do not influence the iron requirement. The second case involves significant generation of an intermediate product that degrades more slowly than the parent and thereby determines how much iron is required.

Case 1: Parent Products Only

The rate of reaction may be expressed as

$$\frac{dP}{dt} = -k_1 \rho_m P \tag{39}$$

where P is the concentration of dissolved chlorocarbon, t is the contact time between the dissolved chlorocarbon and iron particles, k_1 is the first-order rate parameter, and ρm is the mass of zero-valent iron particles per solution volume. This equation may be integrated to give

$$\ln\left(\frac{P_0}{P}\right) = -k_1 \rho_m t \tag{40}$$

where P_0 is the initial concentration of dissolved chlorocarbon. In a batch laboratory experiment, k_1 may be derived from the slope of a semi-log plot of P_0/P vs. time.

For the case of steady-state flow in a packed bed reactor, an expression analogous to Equation 40 may be derived by expressing the residence time (t) as the product of the bed void fraction (ε) and the reactor volume (V), divided by the liquid flowrate through the bed, yielding

$$\ln\left(\frac{P_0}{P}\right) = \frac{k_1 \rho_m \varepsilon V}{Q} \tag{41}$$

The term $\rho_m \varepsilon V$ is the mass of zero-valent iron, W, that the fluid encounters as it flows through the bed. With this substitution, and by representing the flowrate as the product of the cross-sectional plume area (A), the soil porosity (n), and the average flow velocity (u), the amount of iron required per unit cross-section of plume to effect a desired decrease in chlorocarbon concentration may be expressed as

$$\frac{W}{A} = \frac{un}{k_1} \ln\left(\frac{P_0}{P}\right) \tag{42}$$

This is a useful expression because it allows estimates to be made without assuming a particular design (such as funnel-and-gate) or calculating parameters such as residence time, but rather expresses a key aspect of the design (W/A) in the most fundamental terms. However, it does not reflect uncertainties and fluctuations in parameter values that must be considered in any design. These can be accounted for in terms of a factor of safety (F) which increases the amount of reactive material employed:

$$\frac{W}{A} = F\frac{un}{k_1} \ln\left(\frac{P_0}{P}\right) \tag{43}$$

A Monte-Carlo simulation has been developed to estimate appropriate factors of safety for permeable reactive barrier systems (Eykholt, 1997). With influent concentrations varying 10%, the reaction rate parameter varying 30%, and the ground-water velocity varying 100%, achieving a 1000-fold decrease in contaminant concentration with 95% confidence was found to require a safety factor of 3.5.

As shown in Table 9, calculations based on a safety factor of 3.5 and a range of practical values for reaction rate parameters and ground-water velocities suggest that W/A should be expected to vary from as little as about 20 lb/ft^2 to perhaps 1,000 lb/ft^2.

Case 2: Significant Intermediate Generation

If significant amounts of intermediate products are generated during the degradation of a parent chlorinated compound, the slower rate of degradation of the intermediate product may be the factor that determines how much iron is required (Focht et al., 1996). The kinetics of intermediate product generation and degradation may be expressed as

$$\frac{dP}{dt} = -k_1 \rho_m P \tag{44}$$

$$\frac{dD}{dt} = \alpha k_1 \rho_m P - k_2 \rho_m D \tag{45}$$

Table 9. Required Weight-per-Area (W/A) of Granular Iron. Calculated with n=0.33, P_0/P=1000, and F=3.5. Information and Equations from Appendix C.

k_1 ($cm^3\ g^{-1}\ h^{-1}$)	u (ft/day)	W/A (lb/ft^2)
0.1	0.1	21
	0.25	52
	0.5	100
	1	210
0.02	0.1	100
	0.25	260
	0.5	520
	1	1000

where D is the concentration of the intermediate product, is the fraction of parent compound which appears as the intermediate product, and k_2 is the rate parameter for intermediate product degradation. These equations can be solved to yield

$$D=\left(D_0+\frac{\alpha k_1 P_0}{k_1-k_2}\right)e^{-k_2\rho_m t}-\frac{\alpha k_1 P_0}{k_1-k_2}e^{-k_1\rho_m t} \tag{46}$$

where D_0 is the initial concentration of the intermediate product.

For most situations involving chlorinated compounds, k_2 is substantially less than k_1. For the time domain where net degradation of the intermediate product is occurring, the first term on the right side of Equation 46 dominates, therefore the concentration is approximated as

$$D\approx\left(D_0+\frac{\alpha k_1 P_0}{k_1-k_2}\right)e^{-k_2\rho_m t} \tag{47}$$

Making the same substitutions used in deriving Equation 42 yields

$$\frac{W}{A}\approx F\frac{nu}{k_2}\ln\left(\frac{D_0}{D}+\frac{\alpha k_1 \, {}^{P_0}\!/_{D}}{k_1-k_2}\right) \tag{48}$$

As TCE degrades, DCE and vinyl chloride often appear in solution at concentrations corresponding to a few percent of the TCE originally present (Focht et al., 1996). Depending on the actual amount of conversion (α) and the values of the other parameters, Equation 48 may indicate the need for more reactive material than would be suggested by Equation 42. For example, with no intermediate products initially present and with k_2/k_1 = 0.2, α= 0.03, and a remediation goal of P_0/D = 1,000, Equation 48 will indicate a weight-per-area that is 2.6 times the amount calculated with Equation 42.

Evaluation of Existing Iron Permeable Barriers Systems

The iron PRBs installed to date range in weight-per-area from 19 to 850 lb/ft^2 (Table 10), in good agreement with the calculations of the previous section.

Table 10. Summary Information on Full-Scale Permeable Reactive Barriers Using Fe(0).

Site	Iron (tons)	Capture Area (ft^2)	W/A (lb/ft^2)
Coffeyville, KS	70	7500	19
Belfast, N. Ireland	15	650	46
Denver, CO	580	11,700	99
Elizabeth City, NC	300	2900	210
Mountainview, CA	90	660	270
Lowry AFB, CO	45	270	330
Upstate NY	45	270	380
Moffett AFB, CA	96	475	400
Somersworth, NH	65	250	520
Sunnyvale, CA	220	520	850

Each of these W/A values can be understood in site-specific terms. Those sites with low W/A are examples of sites with low ground-water velocity and without significant concerns regarding slow-reacting intermediate products. The Sunnyvale, California, site has a high W/A value for several reasons. First, the reaction rate parameter (k) is low because the principal contaminants, DCE and VC, degrade much slower than TCE. Second, the ground-water velocity is relatively high, at approximately 0.8 ft/day. The safety factor applied in this case was 4 (Warner et al., 1995).

Cost Estimation

Characterizing a plume in terms of the weight-per-area of reactive material required lends itself to evaluating costs on a per-area basis. Installation costs for impermeable barriers are often expressed in this manner. For example, shallow impermeable barriers are often quoted to cost between $\$10/ft^2$ and $\$25/ft^2$ excluding mobilization. In this section, it is shown how this practice may be extended to permeable reactive barriers.

Many of the iron PRBs installed thus far are of the funnel-and-gate design, in which one or more discrete permeable trenches ("gates") is installed along with impermeable containment walls ("funnels") to direct ground water through the gate. The funnel-and-gate cost analysis presented here will focus on three elements: the iron itself, the creation of the gate, and the funnel. All incremental cost components will be expressed on a per-area basis. It is important to understand that these costs are on the basis of the total cross-sectional area of the plume being treated, not the area of the gate.

The cost of reactive material on a per-area basis is simply the product of its cost per weight and the weight-per-area (W/A) required:

$$\begin{pmatrix}\text{Reactive materials}\\ \text{cost per plume}\\ \text{cross-sectional}\\ \text{area}\end{pmatrix} = (Cost\ per\ weight)\times\left(\frac{W}{A}\right) \tag{49}$$

A typical price for the granular iron currently being used for PRBs is \$375/ton. This translates into incremental costs of $\$9/ft^2$ for a W/A of 50 lb/ft^2, $\$47/ft^2$ for a W/A of 250 lb/ft^2, and $\$188/ft^2$ for a W/A of 1,000 lb/ft^2.

The cost of installing a gate is most readily quoted on a per-volume basis. To obtain the gate cost on the basis of plume cross-sectional area, this value is multiplied by the required gate volume per plume area. The gate volume required per plume area is simply W/A divided by the bulk density of granular iron. So,

$$\begin{pmatrix}\text{Gate installation}\\ \text{cost per plume}\\ \text{cross-sectional area}\end{pmatrix} = \begin{pmatrix}\text{Installation cost}\\ \text{per volume}\end{pmatrix}\times\frac{W/A}{\rho_b} \tag{50}$$

where ρ_b is the bulk density of granular iron, typically about 160 lb/ft^3. In most funnel-and-gate systems installed thus far, gate installation has proved expensive. By using a trench box method and confined entry procedures for the final stages of installation, costs of $\$1,000/yd^3$ have not been unusual. This corresponds to a cost of $\$12/ft^2$ to install 50 lb/ft^2 of iron gate, $\$58/ft^2$ to install 250 lb/ft^2 and $\$231/ft^2$ to install 1,000 lb/ft^2.

Tables 11 and 12 present cost estimates for several scenarios. In each table, costs are estimated for three values of W/A: 50, 250, and 1,000 lb/ft^2. For Table 11, relatively high installation costs are used: $\$25/ft^2$ for funnels and $\$1,000/yd^3$ for gates. For Table 12, significantly lower costs were assumed: $\$10/ft^2$ for funnels and $\$200/yd^3$ for gates.

Comparing Tables 11 and 12 demonstrates that there is considerable incentive for employing less costly means of installing both the impermeable and permeable components of funnel-and-gate systems. Further cost savings may be realized in some cases by designing continuous PRBs, thereby eliminating the gate installation cost altogether, assuming that the costs of installing continuous permeable barriers are similar to the costs of installing impermeable barriers (funnels).

Table 11. Cost Elements of Funnel and Gate Systems: High Estimate (Gate @ $1000/yd^3; Funnel @ $15/ft^2)

		Incremental Costs ($/ft^2)	
Component	W/A = 50 lb/ft^2	W/A = 250 lb/ft^2	W/A = 1000 lb/ft^2
Iron	9	47	188
Install gate	12	58	231
Funnel	25	25	25
Sum	46	130	444

Table 12. Cost Elements of Funnel and Gate Systems: Low Estimate (Gate @ $200/yd^3; Funnel @ $10/ft^2)

		Incremental Costs ($/ft^2)	
Component	W/A = 50 lb/ft^2	W/A = 250 lb/ft^2	W/A = 1000 lb/ft^2
Iron	9	47	188
Install gate	2	12	46
Funnel	10	10	10
Sum	21	69	244

Appendix D. Acronyms

AFB	Air Force Base
AI&M	Ada Iron & Metal
ASF	Anderson-Schulz-Flory distribution
bgs	below ground surface
C_i	initial contaminant concentration of the influent solution
C_0	contaminant concentration in solution at time t = 0
CF	chloroform ($CHCl_3$)
CM	chloromethane (CH_3Cl)
CT	carbon tetrachloride (CCl_4)
DCE	dichloroethene ($C_2H_2Cl_2$)
tDCE	*trans*-dichloroethene ($C_2H_2Cl_2$)
cDCE	*cis*-dichloroethene ($C_2H_2Cl_2$)
DCM	dichloromethane (CH_2Cl_2)
DI	deionized
DO	dissolved oxygen
DOD	Department of Defense
DOE	Department of Energy
DNAPLs	dense nonaqueous phase liquids
DL	detection limit
e-	electron
ECC	electrochemical corrosion cell
EDX	Energy Dispersive X-ray Analysis
f_{oc}	fraction of organic carbon
F&G	funnel-and-gate
FAME	fatty acid methyl ester analyses
GAC	granular activated carbon
GC/MS	gas chromatography/mass spectrometry
GPR	ground-penetrating radar
GW	ground water
h	hour
HC	hydrocarbon
HCB	hexachlorobenzene
HPLC	high-performance liquid chromatography
ISTZ	in situ treatment zone
ITRC	Interstate Technology and Regulatory Cooperation Workgroup
k	rate constant
k_{obs}	observed rate constant
k_{SA}	surface-area-specific rate parameter
MBS	Master Builders Supply iron
MCL	maximum concentration limit
MW	monitoring well
NACE	National Association of Chemical Engineers
NAS	National Academy of Sciences
ND	nondetectable
NERL	National Exposure Research Laboratory
NMR	Nuclear Magnetic Resonance Spectroscopy
NRMRL	National Risk Management Research Laboratory
O&M	operations and maintenance

ORD	Office of Research and Development
ORNL	Oak Ridge National Laboratory
OSHA	Occupational Safety and Health Administration
OSWER	Office of Solid Waste and Emergency Response (U.S. EPA)
PAC	powdered activated carbon
PCE	tetrachloroethene (perchloroethene)
PEI-silica	polyethylenimine-coated silica beads
PRB	permeable reactive barrier
psi	per square inch
PV	pore volume
QAPP	Quality Assurance Project Plan
r_f	retardation factor
ROD	Record of Decision
rpm	revolutions per minute
RSF	reactant sand-fracturing
RT	residence or retention time
RTDF	Remediation Technologies Development Forum
RWQCB	Regional Water Quality Control Board (State of California)
rxn	reaction
RZF	reaction zone formation technologies
SA	surface area
SBR	stirred batch reactor
S.H.E	standard hydrogen electrode
SEM	scanning electron microscopy
SI	saturation index or indices
SIMS	secondary ion mass spectroscopy
SITE	Superfund Innovative Technologies Evaluation
SMAD cryoparticles	metal vapor–solvent codeposition method (in preparation of active metal surfaces)
SMVs or SVOCs	semivolatile organics
soln	solution
SPM	scanning probe microscopy
$t_{1/2}$	half life
TCA	trichloroethane
TCE	trichloroethene
TCM	trichloromethane
TCP	trichloropropane
TDS	total dissolved solids
TER	Technology Evaluation Report
TIO	Technology Innovation Office (U.S. EPA)
TLC	thin layer chromatography
TOC	total organic carbon
UMTRA	Uranium Mill Tailings Remedial Action Program
US	ultrasound
USCG	United States Coast Guard
vol or v	volume
VC	vinyl chloride
VISITT	Vendor Information System for Innovative Treatment Technologies
VOCs	volatile organic compounds
VOAs	volatile organic aromatics
W/A	weight per area
XRD	X-Ray Diffraction

XPS	X-Ray Photoelectron Spectroscopy
y	year
ZHE	zero head-space extractors
zpc	point of zero charge
ZVI	zero-valent iron

Appendix E. Glossary

anode — The electrode in an electrochemical cell toward which anions are drawn and where oxidation occurs.

Arrhenius equation — An equation that expresses the logarithmic relationship between the rate constant of a reaction and the reciprocal of the temperature (expressed in K).

bentonite — The term bentonite is used as a commercial name for clays that are predominantly sodium montmorillonite. Wyoming bentonite is the most common drilling fluid additive used in the water well industry.

biotite — An important mineral of many intrusive igneous rocks, pegmatites, lamprophyres, some lavas and metamorphic rocks.

calcite — $CaCO_3$. A sedimentary mineral formed by chemical precipitation. Specific Gravity ≈ 2.95 g/cm^3.

cell potential — The voltage of an electrochemical cell.

cation — A positively charged ion, attracted toward the cathode in an electrolytic cell.

cathode — The electrode in an electrochemical cell toward which cations are drawn and where reduction occurs.

Eh — or Nernst equation, expresses the relationship between the standard redox potential of a given redox couple, its observed potential, and the concentration ratio of its electron-donor and electron-acceptor species.

electrochemical cell — A system containing an oxidation-reduction reaction in which oxidation and reduction reactions are physically separated and the transferred electrons pass through an electrical circuit.

Fenton's Reagent — A way to generate OH• by Fenton reaction:

$$Fe^{2+}_{aq} + H_2O_2 \rightarrow Fe^{3+}_{aq} + OH^{\cdot} + OH^{-} \quad (1)$$

Irradiation with light λ<580nm effects photoreduction of Fe^{3+} to Fe^{2+} together with the production of OH• radicals

$$Fe^{3+}_{aq} + H_2O + h \rightarrow OH^{\cdot} + Fe^{2+}_{aq} + H^{+} \quad (2)$$

goethite — An iron mineral of the general formula FeOOH (alpha-FeOOH, see lepidocrocite). Specific Gravity 4.28 g/cm^3.

half-life — The time required for 50% of a material or compound to undergo transformation or decay.

hematite — An iron oxide mineral, Fe_2O_3, corresponding to an iron content of approximately 70%. Specific Gravity ≈ 5.26 g/cm^3.

iron metal — Variously designated as Fe^0, Fe(0), or zero-valent iron. The most common reactive media in the majority of field scale and commercial PRB implementations. Sources of Fe used in experiments and installations referenced in this document are: Ada Iron and Metal, Aldrich, Alfa Aesar, Peerless, Fluka, Fisher, VWR, MBS.

K_{obs}	This is the rate at which the contaminants are observed to degrade.
k_{SA}	Normalized k_{obs} to Fe surface concentration yields a specific rate constant, $k_{SA,}$ for a number of solvents.
Lewis acid	A species that accepts a pair of electrons to form a covalent bond.
Lewis acid-base theory	The idea that an acid is a species that accepts a pair of electrons to form a covalent bond and a base is a species that donates a pair of electrons to form a covalent bond.
lepidocrocite	gamma-FeOOH (see goethite)
MINTEQA2	A geochemical equilibrium speciation model for dilute aqueous systems. It is an update of MINTEQ, that was developed by combining the fundamental mathematical structure of MINEQL with the thermodynamic data base of WATEQ3. For more information see http://www.cee.odu.edu/cee/model/minteq.html
montmorillonite	An aluminosilicate clay mineral in the smectite group
muscovite	$[KAl_2[AlSi_3O_{10}](OH,F)_2]$. One of the more common minerals in rocks, especially plutonic igneous rocks rich in silica or aluminum and low or medium to high grade metamorphic rocks. Specific Gravity≈2.8 g/cm^3.
Nernst equation	An equation that expresses the exact electromotive force of a cell in terms of the activities of products and reactants of the cell.
oxidation	(1) a reaction in which there is an increase in valence resulting from a loss of electrons. Contrast with reduction. (2) A corrosion reaction in which the corroded metal forms an oxide; usually applied to reaction with a gas containing elemental oxygen, such as air.
passivation	(1) A reduction of the anodic reaction rate of an electrode involved in corrosion. (2) The process in metal corrosion by which metals become passive. (3) The changing of a chemically active surface of a metal to a much less reactive state.
PHREEQC	A program for aqueous geochemical calculations. For more information go to http://water.usgs.gov/software/phreeqc.html
potential-pH diagram	A plot of the redox potential of a system versus the pH of the system, compiled using thermodynamic data and the Nernst equation. The diagram shows regions within which the metal or mineral itself or some of its compounds are stable.
pyrite	An iron sulfide mineral with the general formula of (FeS_2). Specific Gravity≈5.0 g/cm3. Common in plutonic, volcanic, sedimentary and metamorphic rocks.
redox potential (Eh)	The subscript H is used to emphasize that the potential only has meaning in reference to the standard hydrogen electrode reaction.
saturation indices	Gauges the potential for minerals to precipitate. A negative SI indicates undersaturation with respect to the particular mineral phase, while a positive SI indicates oversaturation.
siderite	An iron oxide mineral with the general formula $FeCO_{3.}$ Specific Gravity≈3.95 g/cm^3.

surfactant A surface-active agent; usually an organic compound whose molecules contain a hydrophilic group at one end and a lipophilic group at the other.

vermiculite A mica-like silicate mineral of the general formula $(Mg,Fe^{2+},Al)_3(Si,Al)_4O_{10}(OH)_2$

zeolites Complex inorganic framework mineral structures made up from SiO_4 and AlO_4 tetrahedra joined together to form a series of interconnected channels and pores. Small molecules can diffuse through the zeolite and undergo chemical reactions catalyzed by active sites in the channel walls. The high acidity of their protonated form, coupled with the heterogeneous and controllable nature of the reactions which proceed within them has made them ideal choices for a wide range of catalytic processes.

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