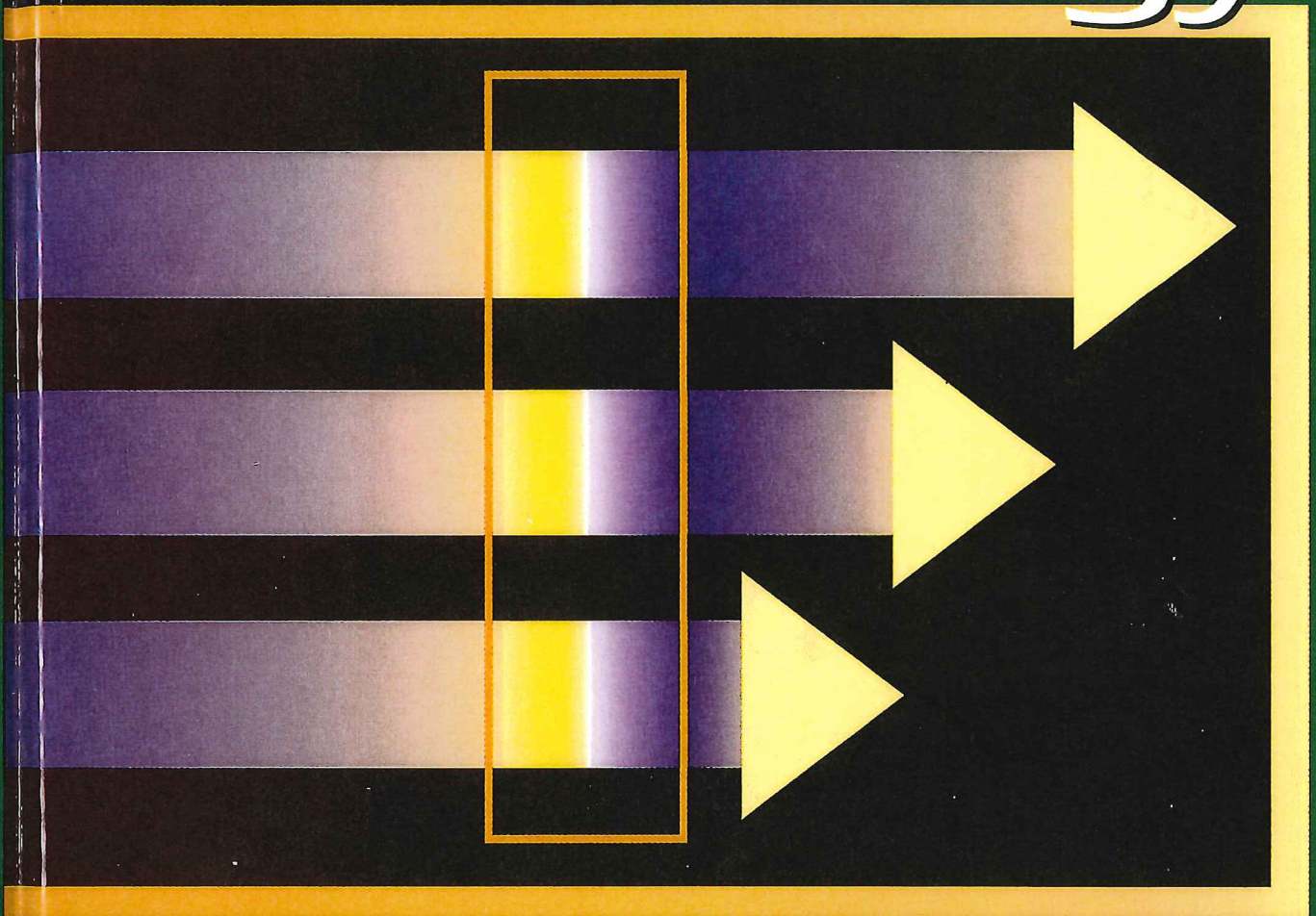


Second Edition  
*In Situ*  
Treatment  
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 **ARCADIS**  
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**Environmental Science  
and Engineering Series**



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## CHAPTER 8

# Reactive Zone Remediation

Frank Lenzo

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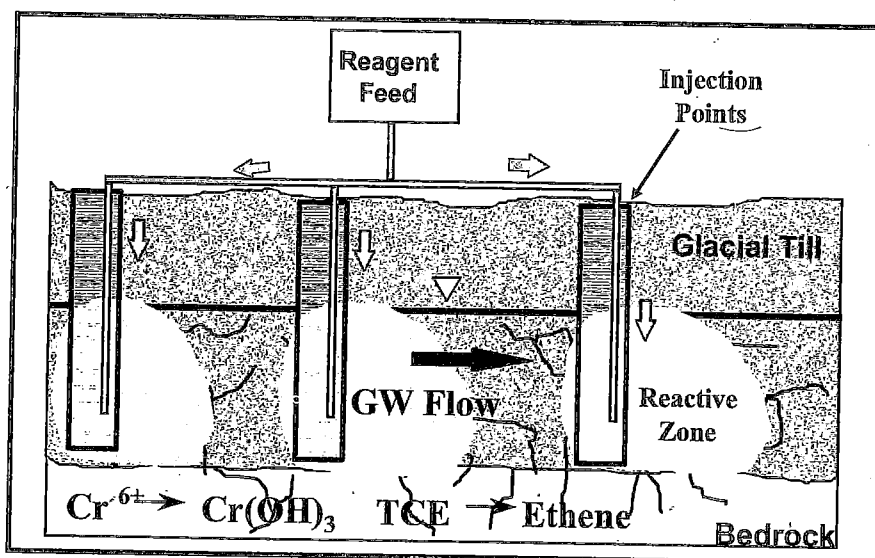
## INTRODUCTION

One of the most important advances in the remediation of aquifers during the last few years has been reactive zone technologies. Before the development of these techniques we were limited to treatment methods that relied on advective movement of air and water. Once these processes removed the mass of contaminants that the carrier came into contact with, we had to rely on natural attenuation to remove the remaining contaminants. (This is the diffusion controlled portion of the project that we discussed in Chapter 2, Lifecycle Design.) While we could design mass removal techniques that would perform their function in several years, the natural attenuation would then take 25 to 100 years to complete the remediation. Even though we did not have any remediation equipment on the site, the project was not over, and we still had to monitor and report to the state. Reactive zone technologies increase the rate of remediation during the diffusion-controlled portion of the project. These techniques will finally allow us to remediate sites in a reasonable time frame.

The creation of subsurface (*in situ*) reactive zones was considered an innovative approach to remediation as late as 1997 (Suthersan 1997). As of the writing of this text, a handful of sites have been closed, dozens of sites have full-scale systems in place, and dozens more are in the midst of pilot demonstrations. The elegance of the approach and the focus on manipulating chemistry and microbiology *in situ* to achieve remedial goals make the technology appealing on many levels:

- Aesthetics
- Ease of implementation—less invasive and more natural
- Environmental compatibility—complements the natural environment
- Enhances and takes advantage of nature's capacity to remediate
- Regulatory acceptance
- Based on sound scientific principles
- Cost—capital and operating
- Holistic, environmentally, and economically sound solution

Reactive zones are simply treatment zones, developed *in situ*, using selected reagents that enhance, or modify, subsurface conditions in order to fix or degrade target contaminants (Figure 1). These zones are typically created to intercept and treat mobile groundwater impacts, but are now being applied to less mobile soil impacts as well. Ideally, reactive zones enhance natural conditions in order to speed up naturally occurring remedial processes (for example, enhancing an already reducing *in situ* environment can accelerate the natural attenuation of chlorinated compounds).



**Figure 1** Reactive zones. Reprinted with permission from Power magazine, copyright McGraw-Hill, Inc., 1966.

*In situ* reactive zones are applicable to a wide range of target contaminants. They have been applied or are being tested on heavy metals (chromium, zinc, mercury, copper, arsenic, lead, and cadmium), chlorinated aliphatic hydrocarbons (CAHs) (trichloroethene, tetrachloroethene, 1,1,1-trichloroethane, carbon tetrachloride, and daughter products of these compounds), pentachlorophenol, and halogenated organic pesticides (1,2-dichloropropane [DCP] and 1,2-dibromo-3-chloropropane [DBCP]). Table 1 is a list of contaminants that have been treated using reactive zone technology, as well as several presently being tested.



Table 1 Compound and Representative Site List for *In Situ* Reductive Reactive Zone Technology

Location	Site Name/Description	Regulatory Authority	Target COCs	Status
Williamsport, PA	Textron/Manufacturing	CERCLA	Cd, Cr <sup>6+</sup> , TCE, DCE, VC	Pilot 1995; Full-Scale 1997; closure proposed 1999
Saegertown, PA	Lord/Chemical	CERCLA	Chlorinated VOCs	Pilot 1998; FFS/Full-Scale Design
Reading, PA	Manufacturer/Textile Equipment	PA Act 2	TCE, Cr <sup>6+</sup> , Pb, Cd	Pilot/Full-Scale 1997-1998 100% reduction in Cr <sup>6+</sup> , 95% VOCs
Amble, PA	Chemical Manufacturer	PA Act 2	TCE, TCA, Ni	Pilot ongoing
Central New Jersey	Pharmaceutical Manufacturer	NJDEP ISRA	PCE	Pilot 1998, Full-Scale 2000
Raritan, NJ	Pharmaceutical Manufacturer	RCRA	TCE	Site Screening, Pilot 1999
Utica, NY	Defense Contractor	CERCLA	TCE, DCE	Pilot 1999, ongoing
Jamestown, NY	Manufacturer	NYDEC	TCE, DCE	Pilot 1998, ongoing
Long Island, NY	Manufacturer	CERCLA	Cr <sup>6+</sup> , TCE	Pilot 1998-1999
Binghamton, NY	Landfill	CERCLA	TCA, TCE, BTEX, chlorinated propanes	Pilot 1998-1999, Full-Scale Design, ongoing
Wooster, Ohio	Sand and Gravel Distributor	Ohio EPA	TCE, DCE, VC	Pilot ongoing 1999
Greenville, SC	Manufacturer	SC DHEC	CT, CF, TCE	Pilot complete 1998, Full-Scale implementation ongoing
Oxford, NC	Manufacturer	CERCLA	TCE	Pilot 1999 ongoing
Myrtle Beach, SC	Chemical Manufacturer	SC DEQ	TCE	Site Screening, Pilot 1999
Blairsville, GA	Former Laboratory	GA DEP	PCE, TCE	Pilot 1998; Full-Scale Design ongoing
Crawfordsville, IN	Manufacturer	IN DEP	TCE, DCE	Pilot 1998, ongoing
Dallas, TX	Chemical Manufacturer	TNRCC	PCP, Cr <sup>6+</sup>	Site Screening, Pilot 1999
Texas	Pharmaceutical Manufacturer	TNRCC	PCE, TCE, ketones, BTEX	Site Screening
Houston, TX	Drycleaner	TNRCC	PCE, TCE, DCE	Full-Scale 1997, 60% reduction in VOC mass
Houston, TX	Drycleaner	TNRCC	PCE, TCE, DCE	Full-Scale 1997, ongoing
Houston, TX	Shopping Mall	TNRCC	PCE, TCE	Pilot 1996; Full-Scale 1997 ongoing
Jasper, TN	Former Manufacturing Facility	TN DSWM/SRP	PCE	Site Screening, Pilot 1999
Oak Ridge, TN	Electronic Manufacturer	TN DSF/VOAP	TCE, radionuclides	Site Screening, Pilot 2000
Lansing, MI	Landfill	MI DEQ	PCE, TCE, TCA	Pilot 1998, ongoing
Grand Rapids, MI	Railcar Spill Site	MI DEQ	1,1 DCE, TCE, TCA	Site Screening, Pilot 1999

Reactive zones can take the form of a reducing zone or an oxidizing zone. The choice is driven by two factors: the natural environment and the nature of the contaminant being targeted. In addition, reactive zones can be created by taking advantage of the activity of indigenous microbial populations (through the injection of degradable organic substrates, other electron donors, or electron acceptors) or through the addition of chemical reagents (sodium sulfide, sodium bicarbonate, or sodium dithionite, for example).

This chapter will review the state-of-the-art of *in situ* reactive zones, by first covering the theory and basis of the processes applied for both metals and organics. The chapter will then present the application of the technology:

- Design considerations including hydrogeology, groundwater chemistry, subsurface microbiology, and reactive zone reagents
- Design criteria for wells, reagent feeds, system configurations
- Pilot testing including selection, set up and monitoring

Full-scale application of the technology will be covered using case studies from three sites in various stages of remediation. Finally, a section summarizing the limitations of the technology will close the chapter.

## THEORY

Reactive zones can take a variety of forms, based on the target contaminants and the environment in which they are found. There are two basic types commonly applied: oxidizing and reducing. Both of these types can be applied by either changing the environment to produce the desired chemical and biochemical reactions or through a direct chemical reaction. Reactive zones can be created using two basic pathways: chemically induced and microbially mediated. These types of reactive zones, and the methods employed to create them, can be combined to suit the contaminant suite and the variability of site conditions as required. The next sections describe each individually and later sections describe how they can be combined to achieve the necessary remedial goals.

Before reading about the details of these treatment zones it is important to understand some basic elements of the chemical and microbial reactions that are taking place in the subsurface. It would be beneficial to the reader to review Chapter 7 for discussions related to chemical oxidation, microbial degradation processes and pathways, natural attenuation, and biogeochemical monitoring and sampling protocols. The following sections will review the more critical elements of each of these subjects, as they relate to reactive zones; however, a thorough understanding of the specific topics will be invaluable to the reader.

### Oxidizing Reactive Zones

Oxidizing reactive zones can be simply defined as artificially enhanced subsurface treatment zones, in which the environment is maintained as strongly oxidizing

(i.e., the redox conditions are maintained well above 0.0 mV and dissolved oxygen is maintained above 2.0 mg/l). This environment is created using the addition of air or oxygen—as in an air sparge system—or through the injection of chemical oxidants. The most common chemical oxidants include hydrogen peroxide, potassium permanganate, and ozone.

In an oxidizing reactive zone contaminants of concern (COCs) are specifically targeted to be chemically, or microbially, oxidized. The oxidant can be mild—for example,  $\text{ORC}_{\text{TM}}$ , air, or oxygen—and can be added to enhance the naturally aerobic environment in order to promote the biological oxidation of readily degradable compounds such as petroleum hydrocarbons, benzene, toluene, ethylbenzene, xylene, and vinyl chloride. This type of reactive zone application creates an aerobic environment that enhances bacterial growth that was limited in the original environment. These bacteria will degrade the COCs faster, and/or degrade certain organic compounds that only degrade under aerobic conditions. The oxidant can also take the form of a strong oxidant (peroxide, permanganate, or ozone, for example) that is injected specifically to chemically oxidize the COCs. The use of strong oxidants in reactive zones has the additional benefit of creating a down-gradient aerobic environment that can enhance aerobic microbial degradation of certain organic compounds. Both processes are discussed in more detail below.

Oxidizing reactive zones can be applied to the treatment of both organic compounds as well as metals. The suite of metals that can be treated using oxidizing reactive zones is small—primarily iron, manganese, and arsenic. It is important to keep the potential presence of metals in mind when evaluating the use of oxidizing reactive zones, particularly when chemical oxidants are applied. The concern revolves around the potential of releasing reduced forms of heavy metals such as chromium. One example involves the common historical use of TCE and chromium in plating operations, the release of which has led to the coincidental presence of both COCs in groundwater. As will be described in later sections of this chapter, chromium is naturally reduced from hexavalent to trivalent chrome. In the presence of a strong oxidant targeted at TCE, the trivalent chrome may be oxidized to reform the more toxic and mobile hexavalent form. Some forms of geological material (pyrite, for example) will release large amounts of iron and acid when exposed to oxidants. These potential negative results must be anticipated before application of aerobic reactive zones.

### Reducing Reactive Zones

Reducing reactive zones can be simply defined as artificially enhanced subsurface treatment zones, in which the environment is maintained as strongly reducing (i.e., the redox conditions are maintained well below 0.0 mV and dissolved oxygen below 1.0 mg/l). This environment is maintained using the addition of chemical reductants or naturally degradable organic mass. In the case of the former, reductants such as sodium sulfide, sodium dithionite, L-ascorbic acid, and hydroxylamine are used to chemically reduce target metals in the subsurface (Suthersan 1997, and Khan and Puls 1999). As with the aerobic zones, the chemical addition can be used to change the environment to enhance new types of biochemical reactions, or the reductant

can be used for direct chemical reduction of the metal. Both processes are discussed in more detail below.

In the latter case, degradable organic carbon—in the form of labile organic substrates such as sugars, lactate, or toluene—is added to the subsurface. The indigenous heterotrophic microorganisms present in the aquifer readily degrade the organic carbon resulting in the utilization of available electron acceptors present in the groundwater. Starting with dissolved oxygen, the microbial population then uses nitrate, manganese, ferric iron, sulfate, and finally carbon dioxide as electron acceptors. Depletion of these electron acceptors leads to successively more reducing conditions as the reduction-oxidation (redox) potential is lowered. Figure 2 summarizes the microbial respiration processes listed above.

Redox *	Respiration	e <sup>-</sup> Acceptor	By-Products
+ 200 mv	Aerobic	O <sub>2</sub>	CO <sub>2</sub>
	Denitrification	NO <sub>3</sub> <sup>2-</sup>	NO <sub>2</sub> <sup>-</sup> , N <sub>2</sub> , NH <sub>3</sub>
	Manganese Reduction	Mn <sup>4+</sup>	Mn <sup>2+</sup>
	Iron Reduction	Fe <sup>3+</sup>	Fe <sup>2+</sup>
	Sulfanogenesis	SO <sub>4</sub> <sup>2-</sup>	H <sub>2</sub> S
- 400 mv	Methanogenesis	CO <sub>2</sub>	CH <sub>4</sub>

\* The redox values are for guideline purposes only. These values can vary by 2 to 3 times based on other factors.

Figure 2 Respiration processes/redox regimes.

Microbially mediated reducing reactive zones are being applied to treat both metals and organics in the subsurface. A variety of CAHs and heavy metals have been treated using reactive zones; recently, halogenated organic pesticides (HOPs) (ARCADIS Geraghty & Miller 1999) and pentachlorophenol (Jacobs et al. 2000) have been targeted for treatment using reducing reactive zones.

### Chemically Created Reactive Zones

Reactive zones can be created using chemical reagents that impact the redox conditions in the subsurface or directly react with COCs present in the groundwater or soil matrix. Examples of oxidizing reactive zones that use chemical reagents to directly oxidize organic compounds were described earlier in this chapter.

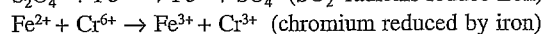
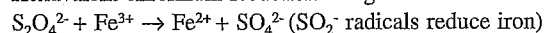
Oxidizing chemical reagents can also be used to modify subsurface conditions to create conditions favorable to the aerobic degradation of organic compounds. As



described earlier in this chapter, as well as in Chapter 5, biosparging is a form of reactive zone that uses the injection of air or oxygen to enhance aerobic degradation of organic compounds. ORC<sub>TM</sub> is magnesium peroxide, a solid that hydrolyses to release oxygen. The resultant increase in dissolved oxygen in the groundwater provides a long-term source of oxygen to serve as an electron acceptor for indigenous aerobic and facultative aerobic bacteria present in the subsurface. These bacteria can then more rapidly metabolize aerobically degradable COCs.

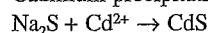
Examples of reducing reactive zones that use chemical reagents are numerous. Several examples are listed below:

Hexavalent chromium reduction using sodium dithionite (Fruchter et al. 1999)

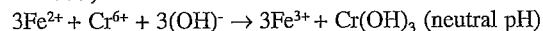


Fruchter, et al. have demonstrated that in the presence of heat (>25 C) sodium dithionite can be used to reductively dechlorinate TCE and field demonstrations for TCE and TNT are planned for 2000 (Fruchter et al. 1999).

Cadmium precipitation using sodium sulfide (Suthersan 1997):



Hexavalent chromium reduction using ferrous sulfate (Walker and Pucik-Erickson 1999):



Zinc precipitation using sodium bicarbonate (Suthersan 1997):



In each of these reactions the target COC metal is dissolved in groundwater. In the reaction that takes place with the reagent, the metal is reduced and precipitates out as a solid that is subsequently immobilized in the soil matrix. The solubility constant for the precipitated form is orders of magnitude lower than that of the dissolved form leading to much lower concentrations of the metal in groundwater.

### Microbially Mediated Reactive Zones

As discussed in previous sections microbial populations can be used to create reactive zones *in situ*. The favored approach is to use indigenous microbial populations. The bacterial population may be stressed due to the COC impacts, or the ability of the microbial population to degrade the COC mass may be limited by a lack of electron acceptors (dissolved oxygen, nitrates, manganese, iron, sulfates, or carbon dioxide), or a lack of degradable organic carbon (electron donors). In order to take full advantage of the microbial population's ability to degrade organic mass, or to create the necessary conditions for the precipitation of metals, electron acceptors and electron donors can be added to the subsurface. In so doing, the microbial population is allowed to complete the remediation process *in situ*.

Both aerobic and anaerobic conditions can be enhanced and engineered to bring about the remedial goals for a site. Aerobic processes typically involve the addition of oxygen in the form of ambient air, pure oxygen gas, or chemical reagents with oxygen releasing compounds such as hydrogen peroxide. Nitrate addition can also be used to provide an alternate electron acceptor for the bacterial population to use in order to degrade organic compounds. Anaerobic conditions are favored when the target COC is a metal that must be reduced, in order to precipitate, or an organic compound that is in an oxidized state and can therefore be readily reduced under the right biogeochemical conditions.

As will be discussed later the microbial processes that enhance the degradation of organic compounds involve four potential pathways:

1. The COC may be used as a primary source of carbon for the bacterial population
2. The target COC can be used as an electron acceptor
3. The target COC may be fortuitously degraded in the presence of other readily degraded organic carbon sources
4. The COC may be degraded as a result of a strongly reducing condition caused by the anaerobic environment created by the bacterial population

Examples of this will be discussed in the following sections of this chapter and have been covered to some extent in Chapter 7.

### Process Considerations

There are a number of specific process issues that must be considered when evaluating the use of, or applying, a reactive zone. These include the biogeochemical environment, COC chemistry, and microbiological degradation processes.

### Biogeochemistry

The biogeochemical environment that has naturally evolved at a site impacted by COCs should always be understood before attempts are made to manipulate it using reactive zones. Since this environment is impacted by the COCs released as well as the geochemistry of the soil and groundwater in and around the area of concern, understanding the biogeochemical state of the environment is always the first step before implementing a reactive zone.

The biogeochemical environment was discussed in detail in Chapter 7, *In Situ* Bioremediation, in the discussions on natural bioremediation. Reactive zones, by definition, are applied *in situ*. Therefore, by their very nature they require a manipulation of the natural environment. In order to better understand that environment it is necessary to collect relevant analytical data related to the biogeochemical reactions taking place. These data will also be used as part of the reactive zone design. For example, the amount of electron donor needed to enhance and maintain a strongly anaerobic environment would be based upon the level of natural organic carbon and the extent to which the environment has already been reduced. The groundwater flow rate is also needed in order to calculate the mass of electron donor

required. Specifically, it is necessary to collect the data summarized in Table 2 from three zones:

- Zone up-gradient of the impacted area—this provides a definition of the natural (i.e., unimpacted) environment that exists (or existed) when there are no COCs present in the subsurface
- Zone within the impacted area—this provides a definition of the state of the groundwater environment where COCs have become part of that environment. By comparing this zone to the up-gradient area, a measure of how much the COCs have influenced natural conditions can be made
- Zone down-gradient of the impacted area—this provides a definition of the residual impacts of COCs, COC degradation products and the byproducts of the biotic and abiotic reactions that have taken place within the impacted zone

The biogeochemical analyte list can be broken down into five major process related subsets:

1. Electron Acceptors: This includes dissolved oxygen, nitrate, manganese, ferric iron, sulfate and carbon dioxide. The microbial metabolic process is an oxidation-reduction process in which electrons are exchanged—electron acceptors being reduced and electron donors being oxidized. The electron acceptors listed above represent the most common electron acceptors utilized by the heterotrophic bacterial population in this metabolic process. Bacteria that use oxygen as an electron acceptor are considered aerobic, those utilizing the remaining electron acceptors are anaerobic. It should be noted that some COCs might also serve as electron acceptors for specific microbial populations (chlorinated aliphatic hydrocarbons for dehalorespirators have been reported) (Smailak et al. 1996 and Yager et al. 1997).
2. Electron Donors: This includes total and dissolved organic carbon, some COCs, and methane. These are the microbial populations' source of nutrition, their food. This group is oxidized in the microbial metabolic process. A lack of electron donors will typically slow down the natural microbial populations' utilization of electron acceptors sometimes resulting in less reducing conditions. Also, electron donors may be plentiful in the source area but limited in the zone down-gradient of the source area. This will create different environments for the two areas. Dechlorination stalling at 1,2 cis DCE is one example of the type of impact that this situation can create.
3. Metabolic Byproducts: This subset includes carbon dioxide, nitrite, nitrogen, ammonia, dissolved manganese, dissolved iron, sulfide, and methane. These are all by-products of the natural respiration processes listed in Figure 2. The presence, or lack thereof, of each helps to define the metabolic processes that are taking place in the subsurface environment. For example, if the levels of nitrates and sulfates are depressed and the level of sulfide is elevated in the heart of a xylene plume when compared to the up-gradient zone, there is a strong indication that there is sulfanogenic bacterial activity and strongly reduced conditions within the plume. These conditions are likely the result of the degradation of xylene by the native bacterial consortia. As discussed in Chapter 7, these values can also be used to calculate the mass rate of destruction.

Table 2 Analyses, Methods, and Data Types for Monitoring Associated with Enhanced Bioremediation

Parameter	Method/ Reference	Technical Protocol	Method Detection Limit	Analytical Level	Holding Time	Data Use
Alkalinity	USEPA 310.1	HACH Test Kit Model ALAPMG-L	50 mg/l	III	14 days	General water quality parameter used (1) to measure the buffering capacity of groundwater, and (2) as a marker to verify that all site samples are obtained from the same groundwater system.
Nitrate (NO <sub>3</sub> )	USEPA 353.1	Method E300	0.2 mg/l	III	28 days	Substrate for microbial respiration if oxygen is depleted.
Nitrite (NO <sub>2</sub> )	USEPA 354.1	None	0.1 mg/l	III	48 hours	May indicate anaerobic degradation process of nitrate reduction.
Sulfate (SO <sub>4</sub> )	USEPA 375.4	Method E300	5 mg/l	III	28 days	Substrate for anaerobic microbial respiration.
Chloride (Cl <sup>-</sup> )	USEPA 325.3	Method A4500	2 mg/l	III	28 days	General water quality parameter used as a marker to verify that site samples are obtained from the same groundwater system. Final product of chlorinated solvent reduction.
Methane (CH <sub>4</sub> )	AM-15.01	SW3810	5 to 15 ng/l*	III	14 days	The presence of methane suggests hydrocarbon degradation via methanogenesis.
Ethane & Ethene	AM-18	SW3810	5 ng/l*	III	14 days	Ethane and ethene are potential byproducts of chlorinated solvents suspected of undergoing biological transformation.
Nitrogen	AM-15.01	SW3810	0.4 mg/l*	III	14 days	May indicate anaerobic process of nitrate reduction.
Carbon Dioxide (CO <sub>2</sub> )	AM-15.01	SW3810	0.4 mg/l*	III	14 days	Indicator of anaerobic degradation processes and aerobic respiration of organics.
COD	USEPA 410.4	None	10 mg/l	III	28 days	General indicator of organic substrates (electron donors).
Ammonia (NH <sub>4</sub> )	USEPA 350.3	None	0.1 mg/l	III	28 days	General indicator of landfill leachate. May indicate reducing conditions.
Sulfide	USEPA 376.1	HACH Test Kit Model HS-WR	1 mg/l	I	7 days	May indicate anaerobic degradation process of sulfate reduction.
BOD	USEPA 405.1	None	2 mg/l	III	48 hrs	General indicator of organic substrates (electron donors).
TOC (dissolved)	USEPA 415.1	SW9060	1 mg/l	III	28 days	Used to evaluate the role of TOC and determine if cometabolism is possible in the absence of anthropogenic carbon.
Iron (total and dissolved)	USEPA 6010A	HACH Method DR/2000 10-phenanthroline	0.05 mg/l	I	6 months	May indicate an anaerobic degradation process due to depletion of oxygen, nitrate, and manganese.
Manganese (total and dissolved)	USEPA 6010A	None	0.01 mg/l	III	6 months	May indicate an anaerobic degradation process due to depletion of oxygen and nitrate.
Conductivity **			Manufacturers Range: 0 to 20 mS/cm	I		General water quality parameter used as a marker to verify that all site samples are obtained from the same groundwater system.



Table 2 Analyses, Methods, and Data Types for Monitoring Associated with Enhanced Bioremediation (continued)

Parameter	Method/ Reference	Technical Protocol	Method Detection Limit	Analytical Level	Holding Time	Data Use
Temperature **			Range: -5 to +45°C	I		Well development
Dissolved Oxygen (DO) **			Mant's Range: 0 to 20 mg/l	I		Concentration less than 1 mg/l generally indicate an anaerobic pathway.
Oxidation- Reduction Potential (ORP) **			Range: -999 to +999 mV	I		The ORP of groundwater influences and is influenced by the nature of the biologically mediated degradation of contaminants; the ORP of groundwater may range from more than 800mV to less than -400mV.
pH **			Range: 0 to 14 units	I		Aerobic and anaerobic processes are pH sensitive.

Notes:

Level III. Analyses are performed in an off-site analytical laboratory. Level III analyses do not use CLP procedures, but does utilize the validation or documentation procedures required of CLP analyses.

Level I. Field screening and analyses using portable instruments. Results are available in real time and the method is cost effective.

Technical protocols and data use from Wiedemeier et al (14).

\* Method quantitation limit reported by Microseeps, Inc., Pittsburgh, Pennsylvania.

\*\* Field parameters will be measured with a Yellow Springs (YSI) Model 600xl probe Method detection limits reports by YSI.  
Source: (courtesy ARCADIS Geraghty & Miller, Inc.)

4. Indicator Parameters: This subset includes temperature, pH, conductivity, alkalinity, and oxidation-reduction potential (ORP)—also commonly referred to as redox potential. Natural changes to these analytes are an indication of microbial activity. Elevated temperature and conductivity, and depressed pH and ORP are typically seen in the presence of anaerobic bacterial activity. Alkalinity provides an indication of the buffering capacity of the ground water. Properly collected ORP (using the low-flow purge sampling technique [McCarty and Semprini 1994]) is a powerful tool for defining the anaerobic zones critical to the reductive dechlorination of CAHs. However, it should be noted that due to the complex geochemistry that results in the ORP value, it is difficult to compare ORP readings between sites.
5. Degradation Products: The last subset includes COC daughter products (such as TCE, cis-1,2-dichloroethene, and vinyl chloride for PCE; and chloroform, methylene chloride and chloroethane for carbon tetrachloride) and COC degradation end products (such as ethene, ethane, methane, and carbon dioxide). These are critical to understanding how far along the degradation pathway that the natural environment has carried the target COCs. These are also critical to the demonstration that degradation is in fact a component of the attenuation process and not that simply dilution, dispersion, and volatilization are taking place.

With a baseline snapshot of the biogeochemical environment available, it is possible to begin the reactive zone selection process and answer, to some extent, critical design questions:

- Is natural degradation taking place? If so, in what type of environment, aerobic or anaerobic?
- Is the natural degradation process stalled due to a lack of electron acceptors? Electron donors?
- Is there evidence that the necessary microbial population is present to degrade the target COCs?
- Are biotic or abiotic processes taking place? Or both?
- Should an oxidative or reducing zone be used?

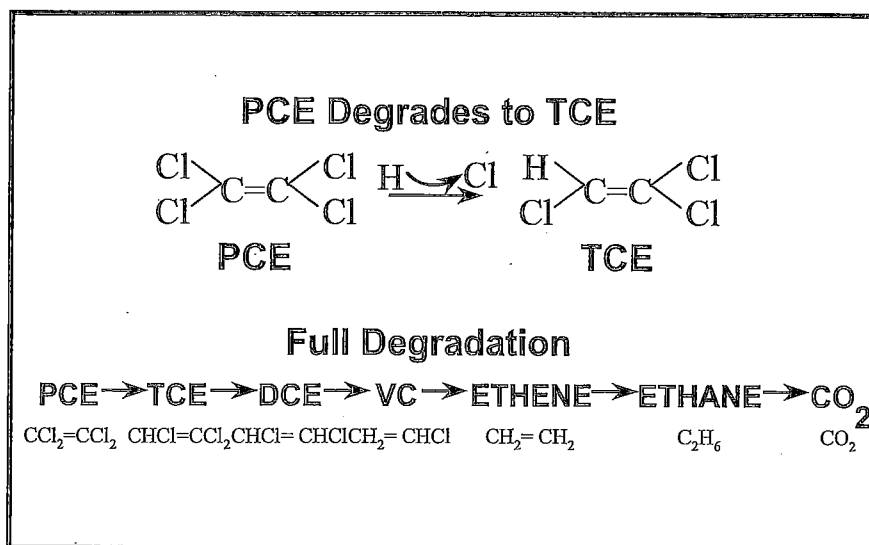
Before more than a basic answer can be given for each of these questions it is necessary to consider two other elements in the reactive zone equation: COC chemistry and microbiological degradation processes.

### ***COC Chemistry: Halogenated Aliphatic Hydrocarbons***

One of the most common applications of the reactive zone technology is for the enhanced degradation of CAHs and other halogenated aliphatic hydrocarbons (HAHs). This is in part due to the widespread occurrence of CAHs in groundwater, but also as a result of the efficacy of the technology in handling CAHs. It was recognized in the middle to late 1980s that both aerobic and anaerobic bacterial populations naturally degraded petroleum hydrocarbons and BTEX, with aerobic populations providing the most rapid degradation rates. It wasn't until the early 1990s that the anaerobic degradation of CAHs was considered a viable mechanism in the remedial tool kit, this primarily due to the work of McCarty (1994), Wilson (1995), and Weidemeier (1996).

Enhancing an anaerobic environment using reactive zones in order to accelerate the degradation of CAHs has only become an accepted practice in the last two to three years (refer to Nyer et al. 1998, Suthersan 1997, Burdick and Jacobs 1998, Cirpka et al. 1999, and Lenzo 1999). In Chapter 7 the biological pathways available for several common CAHs are summarized (refer to Figure 7 in Chapter 7 for PCE, TCE, 1,1,1 TCA, and carbon tetrachloride). There are also potential abiotic pathways that can occur for these compounds; however, except for 1,1,1 TCA, the abiotic pathway is not practical unless chemical reagents are applied (refer to Chapter 7). The degradation pathways that are the focus of this discussion of reactive zones are biotic.

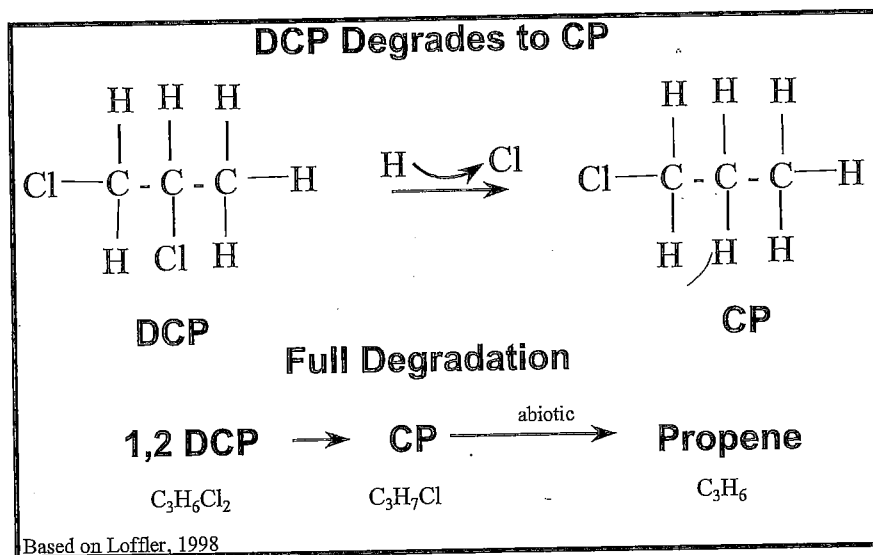
The primary pathways described in Chapter 7 for the CAHs are anaerobic pathways. For many of the more common COCs (such as TCE, 1,1,1TCA, and PCE) the anaerobic pathways are particularly efficient due to the fact that these compounds are relatively oxidized and are thus susceptible to reductive dechlorination in a reducing environment. As the chlorine atoms are stripped from the parent CAH, and there are fewer chlorine atoms attached to the base alkene or alkane molecule, the resultant chlorinated aliphatic is more reduced—less oxidized—and thus less susceptible to reductive dechlorination. Conversely, the more reduced forms (less chlorinated) are more easily oxidized than reduced and thus can be degraded under more highly oxidized conditions. An excellent example of this is the degradation sequence for PCE (Figure 3). PCE and TCE are readily reduced under anaerobic and reducing conditions; however, it takes more and more aggressively reducing conditions to achieve the degradation of TCE to DCE, DCE to VC, and finally vinyl chloride to ethene. The necessary reducing conditions for VC degradation may not be achieved naturally in the environment and thus a buildup of VC may be expected in a reducing environment. In an aerobic environment, however, VC, which is highly reduced,



**Figure 3** Reductive dechlorination of tetrachloroethylene.

can be readily degraded. In fact, VC can serve as a primary carbon source to aerobic bacteria (Guest, Benson, and Rainsberger 1995).

As the state-of-the-art of reactive zones for the CAH treatment has advanced, new compounds that can be remediated with this technology have been added to the list. Recently, work has begun in California to address HAH pesticides, specifically DBCP and DCP, using anaerobic reactive zones, and pentachlorophenol (PCP) has been targeted for treatment using *in situ* anaerobic reactive zones (Mueller et al. 2000, Jacobs et al. 2000). The most common degradation pathway for DCP is presented in Figure 4.



**Figure 4** Reductive dechlorination of DCP.

### Microbiology of Reactive Zones

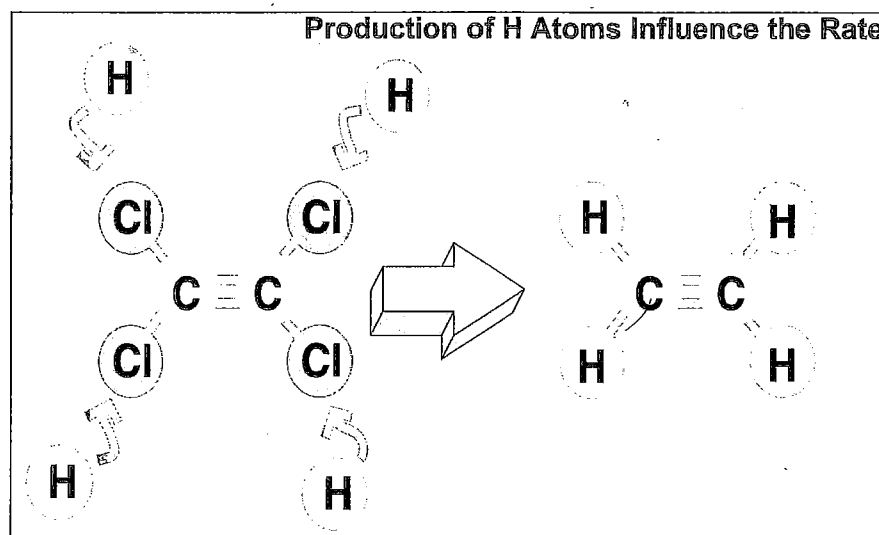
The last consideration in the understanding of the reactive zone process is the role that microbiology plays. There are a number of microbial mechanisms that are naturally occurring in the environment that lead to the conditions necessary for the degradation of organic compounds or the precipitation of metals. Natural metabolic respiration processes are responsible for creating the reducing conditions necessary to reduce the valence state of chromium from +6 to +3 and in the process convert a soluble, toxic, and mobile form of chromium to a non-toxic form that can readily precipitate under typical groundwater conditions. These respiration processes have been covered in previous sections.

The key to the success of a reactive zone is the ability to manipulate the existing natural conditions in order to bring about the remedial ends sought. Thus if it is necessary to maintain a strongly reducing environment in order to reduce cadmium and form sulfide for the precipitation of cadmium sulfide, the natural conditions must be manipulated to allow the sulfanogenic bacterial population to flourish. Since

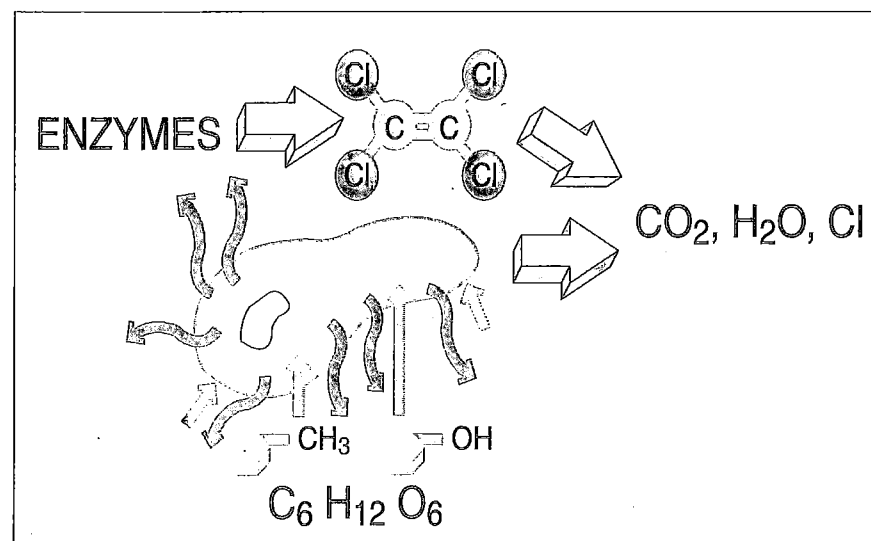


sulfanogenesis takes place under reducing conditions near a neutral pH (Norris et al. 1994), the necessary conditions are created when applying the reactive zone. This assumes that there is an adequate supply of sulfate to produce sulfide and that the alkalinity is adequate to balance the pH of the ground water system.

The application of reactive zones for the treatment of HAHs involves several different microbial mechanisms. Each of the three major mechanisms is depicted in Figures 5, 6, and 7.



**Figure 5** Hydrogenolysis.



**Figure 6** Cometabolic degradation.

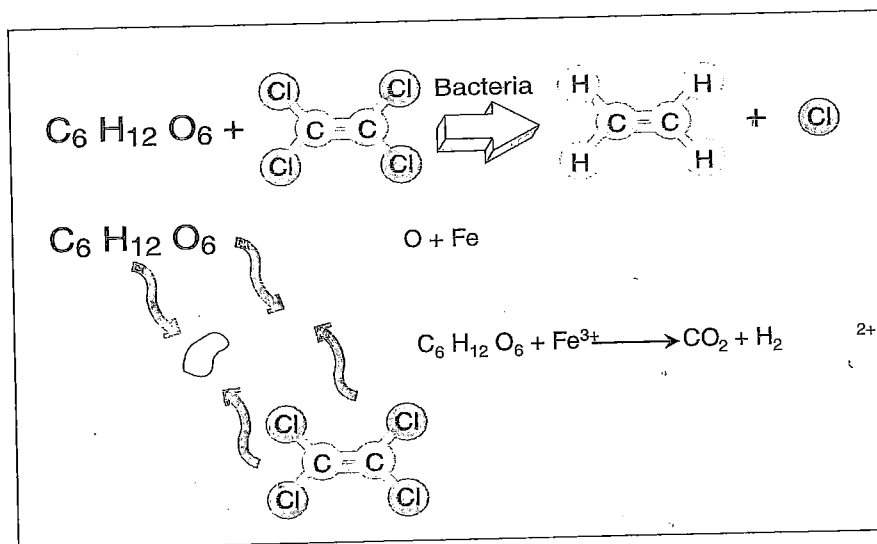


Figure 7 Dehalorespiration.

As with most microbially mediated processes in the subsurface, the microbial processes that take place in a reactive zone are a collection of processes that result from the natural selection of microbial populations that can survive and thrive in the conditions that exist at the site. As a result there is not any one mechanism, nor is there one bacteria that is responsible for the degradation process. It is in fact a consortia of microorganisms and a variety of mechanisms that bring about the results.

Figure 5 is a representation of the reductive dehalogenation of a HAH under reducing conditions. In this environment, an overabundance of hydrogen ions provides the opportunity for the dehalogenation process to take place. In the process, chlorine atoms are sequentially replaced by hydrogen ions, until finally the double-bond of the ethene molecule is broken and ethane is formed. The strongly reducing conditions created by the microbial population provides adequate hydrogen ions to bring about a rapid sequential dehalogenation of the HAH. Even the more reduced forms (fewer halogens on the base aliphatic molecule) are reductively dehalogenated. In this case the microbial population needs a readily degradable source of organic carbon in order to survive. This organic carbon can take the form of natural organic matter, anthropogenic forms (like BTEX or phenol), or injected labile sources such as sugars or other easily degradable compounds. The bacterial population is living in an anaerobic environment.

Figure 6 is a representation of a cometabolic degradation process. In this mechanism the target COC does not serve as a primary source of organic carbon. Instead, the microbial population utilizes another source of organic carbon in order to survive. This carbon source could be natural, man-made, or a supplemental source. In the process of metabolizing the organic carbon, cofactors and enzymes are produced that are used by the bacterial population to degrade the organic carbon that is serving as the food for the bacteria. These enzymes fortuitously degrade the target COC, although the microbial population receives no direct benefit from the degradation

of the COC. This mechanism can take place under both anaerobic and aerobic conditions. An example of an aerobic process is the cometabolic degradation of TCE in the presence of methanotrophic bacteria. The methanotrophs are provided with methane as a source of organic carbon. As the bacteria degrade the methane they cometabolically degrade the TCE. A similar process can take place in an anaerobic environment in which DCE is cometabolically degraded in the presence of xylene.

Figure 7 represents the degradation of a HAH by a dehalorespirator. The concept of a dehalorespiration process was introduced by McCarty (1997). In the process, certain microbial populations utilize the target HAHs as electron acceptors and in the process degrade the target compounds. The bacteria still require a source of electron donors in order to complete the metabolic redox reaction.

### **COC Chemistry: Metals**

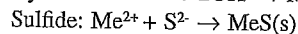
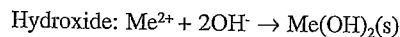
Reactive zones have been applied to the *in situ* treatment of metals in the groundwater for decades. One of the oldest applications of this process is related to the treatment of iron and manganese for drinking water supplies using the Finnish treatment process Vyredox<sub>TM</sub> (Zienkiewicz 1984). The Vyredox<sub>TM</sub> process utilizes an *in situ* oxidizing zone surrounding a groundwater production well to treat iron and manganese. The iron and manganese is oxidized *in situ* by creating an oxidizing environment through the introduction of aerated water in a series of injection wells surrounding the production well.

The *in situ* coprecipitation of arsenic and iron has been reported by Suthersan (1997), Whang (1997) and others, as a means of removing arsenic from groundwater via *in situ* oxidizing reactive zones. In the process an oxidant such as Fenton's reagent, peroxide, permanganate, or oxygen is used to oxidize arsenite (valence state 3+) to arsenate (valence state 5+) and to precipitate iron. In the process, iron and arsenic co-precipitate as an iron hydroxide arsenate complex and are removed from the groundwater (Figure 8). The efficacy of this process has yet to be tested in the field, however it holds a great deal of promise.

Some of the newest work in metals treatment using reactive zones is taking place in the arena of environmental cleanup and the application of reducing reactive zones for the treatment of heavy metals. The application of reducing reactive zones for metals will be examined through reference to a case study for a Superfund site in Pennsylvania (Lenzo 1999).

A Superfund site located in central Pennsylvania is impacted with chromium, cadmium, and CAHs. In the summer of 1996, an *in situ* reactive zone process was tested to demonstrate the ability to treat the heavy metals *in situ*. Molasses was used as an electron donor to create the necessary reducing conditions to bring about the reduction and precipitation of chromium and cadmium.

The goal of the reactive zone was to create the necessary reducing conditions to achieve precipitation of the target heavy metals as hydroxides, sulfides, or carbonates:



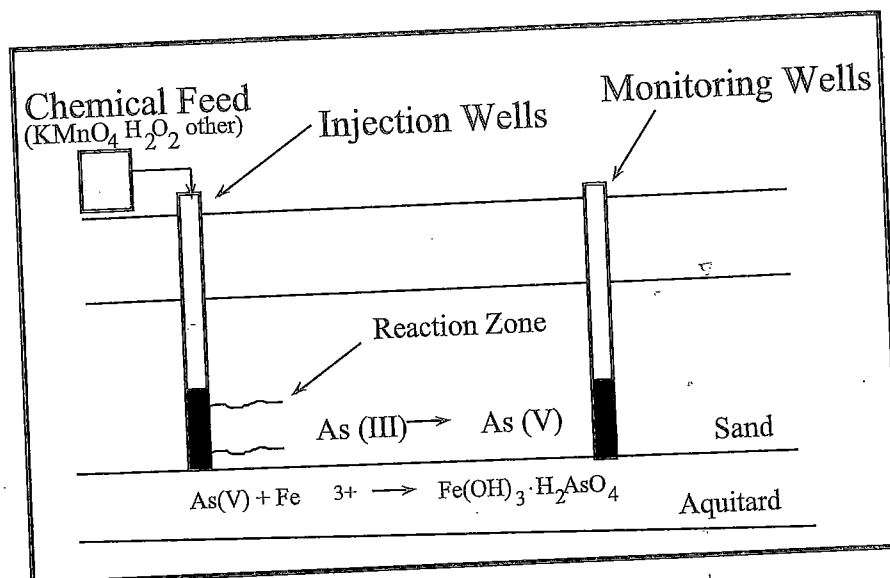


Figure 8 Arsenic oxidative IRZ.

Carbonate:  $\text{Me}^{2+} + \text{CO}_3^{2-} \rightarrow \text{MeCO}_3(\text{s})$   
 (Other metals that can be targeted using this approach include Fe, Hg, Mn, Zn, Ni, Cu, Ag, and Pb.)

The insoluble compounds that precipitate are immobilized in the soil matrix. This precipitation process is essentially irreversible.

The creation of the desired reducing conditions in the groundwater were promoted by injecting a source of easily biodegradable carbohydrates, in the form of dilute molasses solution, into the impacted saturated zone through a network of injection wells. The carbohydrates (primarily sugars) present in the molasses were degraded by the indigenous heterotrophic microorganisms present in the aquifer. The biological degradation of the injected carbohydrates resulted in the utilization of available electron acceptors present in the groundwater. Starting with dissolved oxygen, the microbial population then used nitrate, manganese, ferric iron, sulfate (sulfanogenesis), and finally carbon dioxide (methanogenesis) as electron acceptors. Depletion of these electron acceptors leads to successively more reducing conditions as the reduction-oxidation (redox) potential was lowered.

Following creation of the necessary reducing conditions in the groundwater, dissolved cadmium in the groundwater reacted with available sulfide, and to a lesser extent carbonate, in the aquifer to form the very stable cadmium sulfide and cadmium carbonate precipitates. Sulfide was present in the groundwater as a result of the microbial reduction of sulfate; sulfate was present naturally in the groundwater and was also a component of the injected molasses solution. The precipitation of cadmium sulfide was also influenced by the presence of sulfate-reducing bacteria in the subsurface which provided a biologically mediated pathway for the reduction of sulfate to sulfide. Carbonate was naturally present in the groundwater.

Creation of the reducing conditions also led to the reduction of hexavalent chromium to trivalent chromium. This reduction process yielded significant remedial benefits because trivalent chromium is less toxic, less mobile, and precipitates more readily than hexavalent chromium. The trivalent chromium created by hexavalent chromium reduction reacted with naturally occurring hydroxides to form chromium hydroxide precipitates.

Both the cadmium and chromium precipitates that formed in the reactive zone have extremely low aqueous solubilities. As a result, the concentrations of cadmium and chromium dissolved in groundwater exiting the reactive zone were less than, or equal to, the target standards of 0.003 and 0.032 milligrams per liter (mg/l), respectively.

Figure 9 is a summary of the chromium pilot test data gathered during the 6 month demonstration test. The test was conducted in two areas of the site. Concentrations of hexavalent chromium were reduced from 7 mg/l to nondetectable during the first 2 months of testing. Based on this pilot test data a full-scale system was designed and installed. Figure 10 is a simple process diagram for the treatment system, and Figure 11 is a photo of the inside of the 10 foot square treatment building.

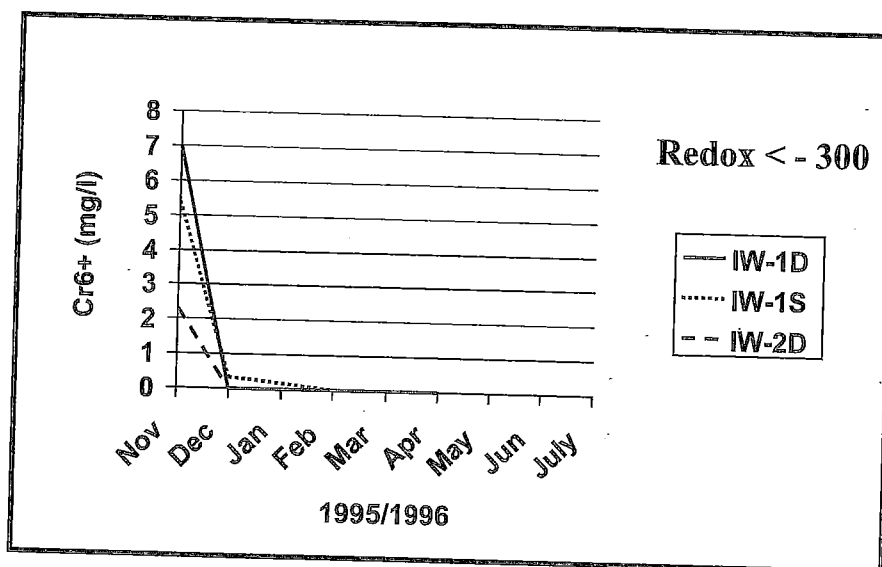


Figure 9 Chromium pilot data superfund site.

The full-scale system consisted of 20 injection wells and 16 monitoring wells. A solution of molasses and water, varying in strength from 1:20 to 1:200, was injected twice a day into each injection well. The system went on line in January 1997. Data was collected on a quarterly basis for select biogeochemical parameters, chromium, cadmium, and CAHs.

The baseline biogeochemical, chromium and cadmium conditions are shown in Figures 12, 13, and 14, respectively. The conditions after implementation and oper-

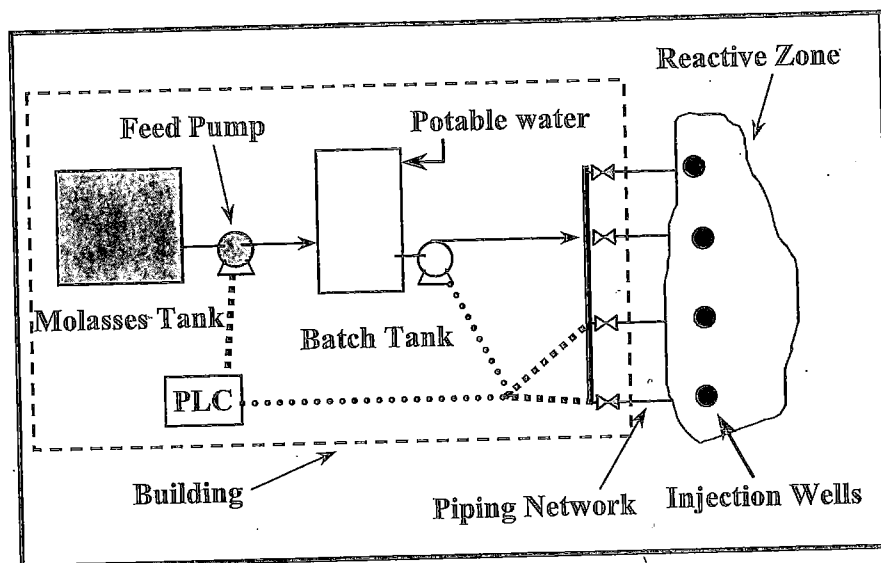


Figure 10 Molasses injection system: superfund site.

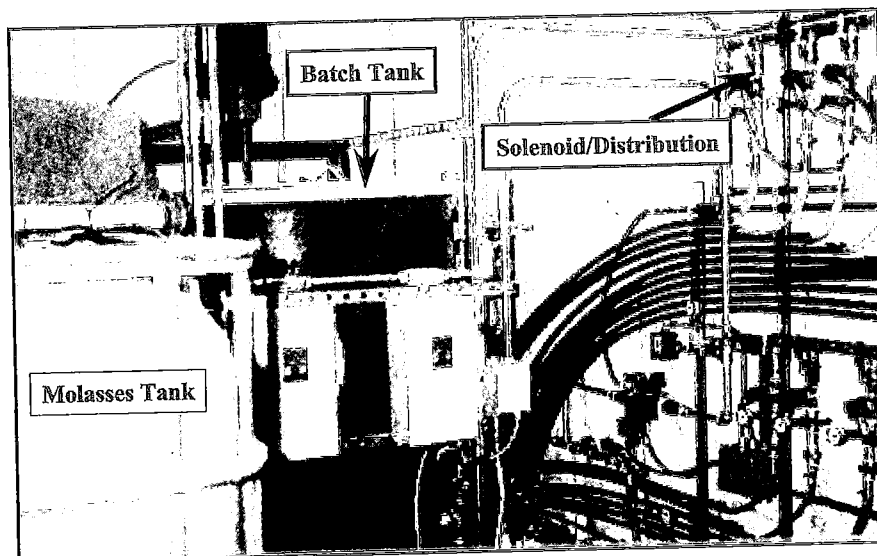
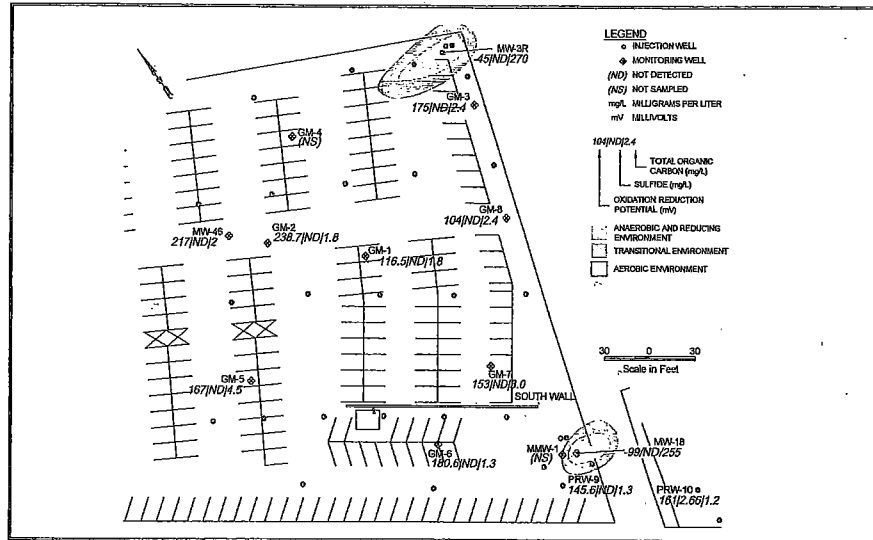


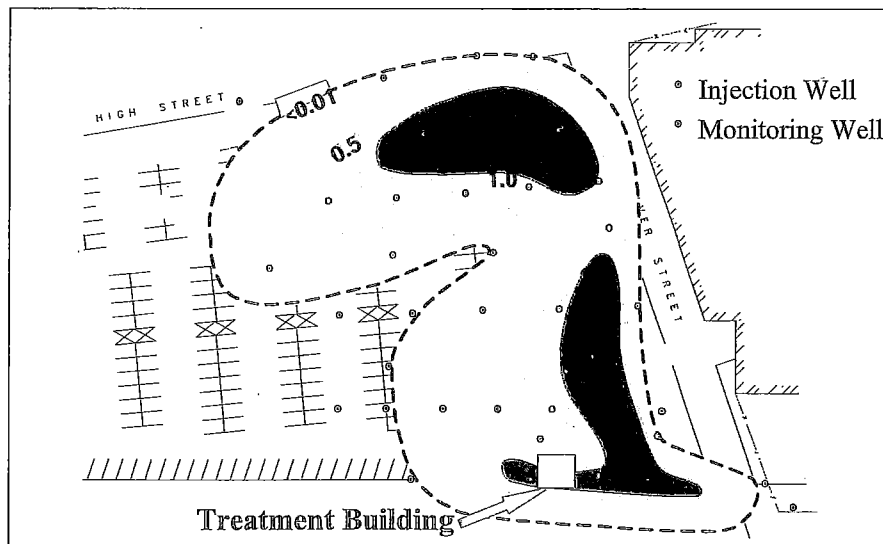
Figure 11 Molasses injection system: superfund site.

ation of the reactive zone system for 18 months are shown in Figures 15, 16, and 17 for the biogeochemical parameters, chromium and cadmium, respectively. The data was collected from monitoring wells located within and down-gradient of the injection well system.

As the data indicates (compare Figures 12 and 15), the establishment of a strongly reducing reactive zone led to the formation of sulfanogenic conditions and the



**Figure 12** Distribution of groundwater indicator parameters, baseline conditions, January 1997.



**Figure 13** Distribution of hexavalent chromium baseline conditions.

reduction of sulfate to sulfide. The chromium and cadmium plume maps (Figures 13, 14, 16, and 17) highlight the effectiveness of the reactive zone technology in treating metals in groundwater.

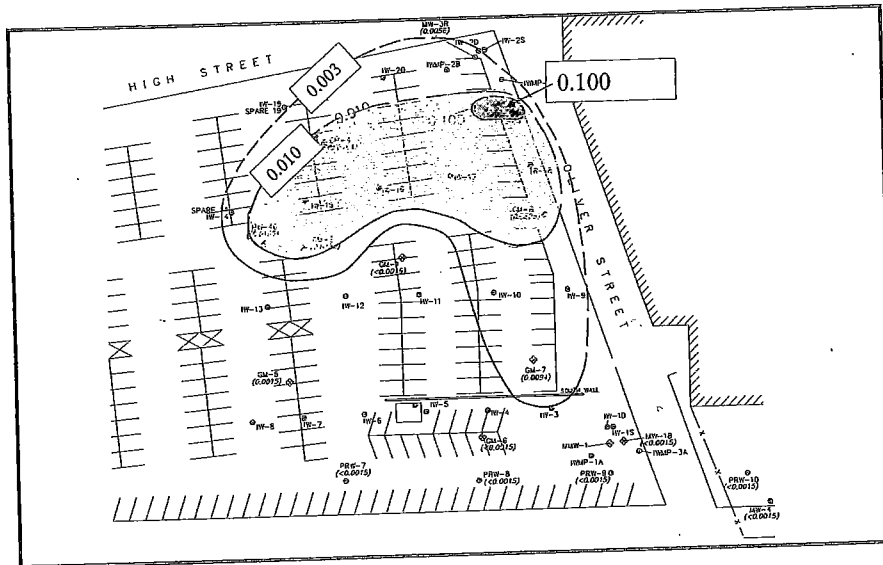


Figure 14 Distribution of cadmium: baseline conditions.

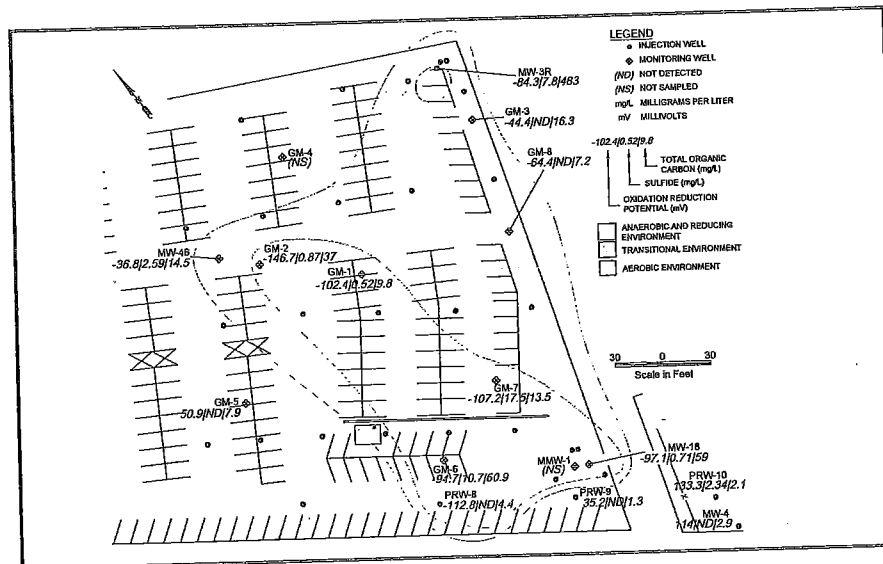


Figure 15 Distribution of groundwater indicator parameters, July 1998.

## APPLICATION

The application of *in situ* reactive zones to the remediation of groundwater and soils must take into account all of the issues discussed above, as well as many issues not specifically discussed. Many of the latter items are common issues encountered



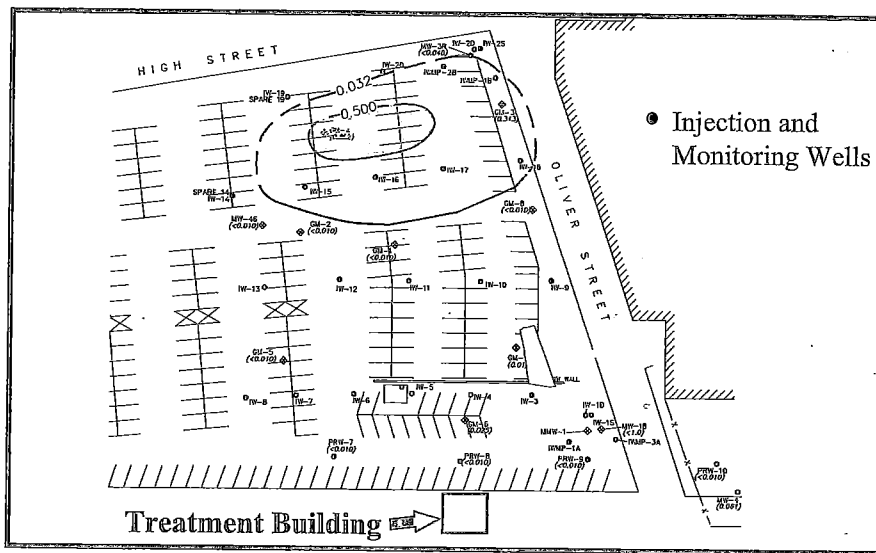


Figure 16 Distribution of hexavalent chromium, July 1998.

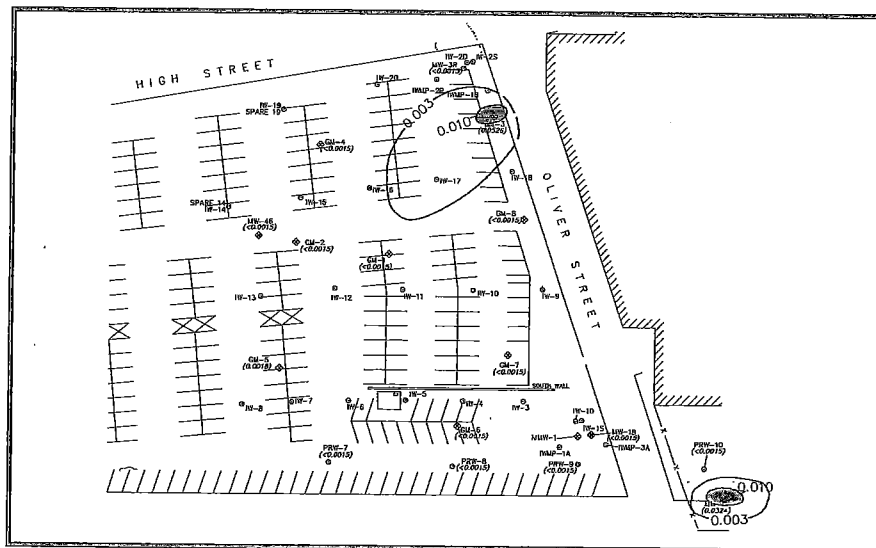


Figure 17 Distribution of cadmium, July 1998.

when applying any technology *in situ*. In this section particular attention will be paid to the following:

- Hydrogeologic Considerations: lithology, permeability, GW flow velocity, gradients, soil matrix conditions, saturated thickness, depth to groundwater, macro heterogeneities

- Groundwater Chemistry: biogeochemical parameters, TOC, pH, temperature, HAH daughters, toxicity
- COC Characteristics: degradability, DNAPL

In addition to these design considerations are the issues associated with the system implementation, including the well layout, type of injection points, reagents to be used, frequency of injections, solution strength, and the maintenance and monitoring of the process. The need for, duration, and type of pilot testing required is also critical in understanding the application of the technology.

This section will include a review of these issues as they relate to the application of *in situ* reactive zones and will serve as an introduction to the case studies that follow.

### Design Considerations

Any *in situ* technology is applied, de facto, out of sight. The understanding used to select, design, and apply the technology is projected based on limited data. The accuracy of the data we have describing the environment is a function of when, how, where, and often why it was collected. As a result, it is important to use layers of useful information to define the subsurface and the conditions in which we must apply an *in situ* technology. Equally as important is to collect relevant corroborating data after a specific technology is selected in order to ensure the proper application of that technology.

Among the critical design considerations for *in situ* reactive zones are hydrogeology, groundwater chemistry, microbiology, IRZ layout options, baseline definition, and reagents.

### Hydrogeology

It is important to obtain specific hydrogeologic data in order to properly select and apply *in situ* reactive zones. The type of geology and the lithology of the subsurface are critical to the selection and placement of the injection points. While a complicated lithology can place constraints to the use of reactive zones, in most cases it will not completely eliminate reactive zones as a remedial option. By properly placing injection well screen zones to target specific impacted groundwater bearing layers, the technology can be effectively applied in most environments. Understanding the complexity and defining the lithologic variability as it relates to the groundwater impacts is an important first step.

A formation's permeability is important in that it impacts the ability of a single well point to serve as an effective reagent delivery mechanism. The higher the permeability the easier it is to deliver the reagent into the subsurface and the more effective a single delivery point can be. As the permeability decreases—all other factors remaining equal—the lateral distribution of reagent from a single injection point decreases.

Groundwater flow characteristics are another important consideration in the design of reactive zones. The groundwater velocity, flow direction, and the horizontal

and vertical gradients impact the effectiveness of reagent injections and the speed with which the reagent will spread. Low velocity systems typically require lower reagent mass feed rates since the groundwater flux is reduced—all other conditions being equal. This is also an important criterion for the concentration and amount of additive that is needed to create the reactive zone.

Groundwater flow direction and gradients are also important to consider. They impact the groundwater velocity and also the direction in which groundwater flows. It is critical to understand the dynamics of groundwater flow to assure that the reagent injections will in fact form a reactive zone in the target area. Horizontal and vertical gradients are used to define the lateral (well point) and vertical (screen zone) location of the injection and monitoring wells. It is also important to understand the heterogeneity of the aquifer. The groundwater is the carrier that will take the additives throughout the aquifer. If there are areas where the groundwater does not flow, then the additives will not be able to reach those areas and the environment will not be changed. We will not be able to create the reactive zone in the no flow areas except through the slow process of diffusion.

The saturated thickness and depth to groundwater are also important characteristics to determine prior to applying reactive zones. The depth to groundwater will define well design and contribute significantly to determination of the cost of the full-scale system. The saturated thickness can also have a profound influence on cost, since there are practical limits on the maximum screened interval that can effectively be used in an injection well. Based on experience, a 25 foot screened interval represents a practical limit for an injection point. Of course, this limit will be impacted by the subsurface lithology, permeability, and groundwater flow characteristics. For example, if the lithology and resultant groundwater flow characteristics are such that there are variations in the flow characteristics that change within the target saturated interval, the use of multiple screened zones or multiple well points should be considered—even if the interval is less than 25 feet.

Finally the soil characteristics are important. The fraction of organic carbon ( $f_{oc}$ ) will impact the amount of available organic carbon dissolved in groundwater, as well as the adsorptive capacity of the soil matrix. High  $f_{oc}$  soils are more likely to result in high DOC groundwater and high adsorptive capacity. The pH of the soil can affect the pH of the groundwater, and while microbial populations can endure a wide range of pH, ideally a pH close to neutral is the most conducive to healthy, diverse microbial populations.

### ***Groundwater Chemistry***

Groundwater chemistry includes an understanding of the target COCs, their daughter products, and the biogeochemical parameters discussed in the section entitled Process Considerations.

Understanding the conditions present in the groundwater will make the selection and application of reactive zones more likely to succeed. As discussed previously, the enhancement of natural conditions allows the designer to take advantage of natural processes that are already contributing to the degradation of the target compounds. Lacking that understanding one may end up trying to undo

nature and find that it is necessary to spend twice the effort to bring about the desired result.

Of particular importance is the presence of degradation products, the presence and nature of electron acceptors, a definition of the redox conditions, and ORP in Figure 2, and the presence of electron donors. The presence of degradation products that indicate that a particular environment has established itself is typically easy to verify. For many sites historical COC data is available that may date back years—sometimes decades—and can be used to establish the presence of degradation products, as well as to evaluate trends in source and daughter products over time. This data can also provide information regarding historical impacts of variable organic species that may have served as electron donors. For example, at a site in central Pennsylvania, historical impacts of benzene provided a source of electron donors for indigenous microbial populations. This resulted in the degradation of TCE to ethene via the anaerobic reducing pathway described earlier (Figure 3). As the benzene source burned out the reductive dechlorination process stalled at DCE (Figure 18).

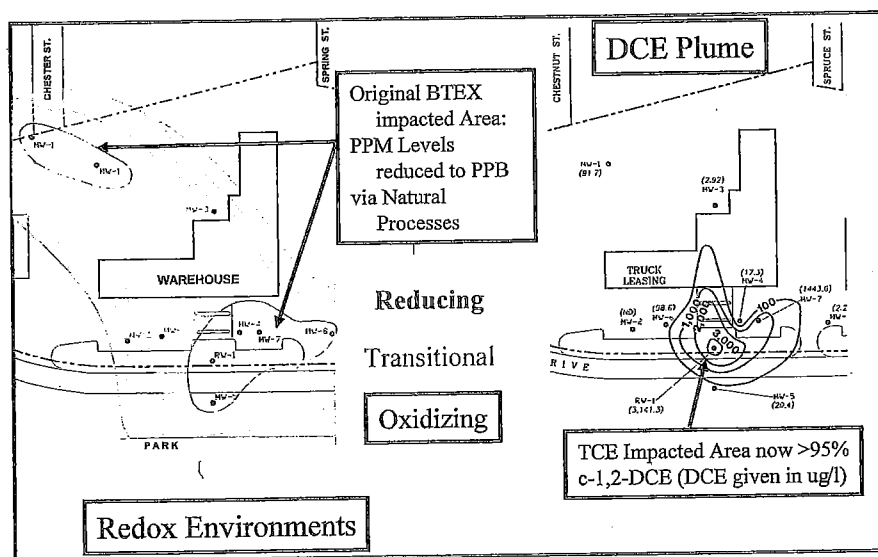


Figure 18 Mixed plume impacts.

Reducing reactive zones rely on the presence of an adequate source of electron donors (in the form of organic carbon) to establish and maintain a bacterial population that can maintain an anaerobic environment. The organic carbon may take the form of natural organic matter or anthropogenic carbon sources—other organic COCs, such as BTEX, PHCs, ketones, or alcohols. Many times, as in the example in Figure 18, the source of organic carbon is weak or absent, and as a result supplemental sources must be considered to enhance the naturally reducing environment.

### ***Microbiology***

The presence of an indigenous microbial population is vital to the success of a microbially-mediated reactive zone. As discussed in Chapter 7, *In Situ* Bioremediation, this microbial population is a consortia of microbes, naturally adapted to the environment and thus ideally suited to surviving, and even thriving, in the impacted environment.

There are seldom situations that require the addition of specialty microbes to the subsurface to enhance degradation. Most "designer bugs" are developed in a controlled environment, in which they are allowed to evolve to treat specific target compounds. Often the selection process leads to select species of bacteria. The difficulty in using these bacteria in the natural environment relates to two major issues: survivability and distribution.

A single species targeted at a specific COC, or class of compounds, provides a uniquely focused means of attacking the target compound. With respect to survivability, however, it also represents an entire population that is vulnerable to the same stresses, diseases, and natural enemies. Once invaded, the entire population is at risk, and in a single event can be eliminated. In addition, the "designer bug" was developed under controlled conditions, not those found in the target groundwater environment to which they will be applied. Naturally evolved populations, on the other hand, are composed of multiple species. These natural populations have survived the precise environment they need to in order to bring about the remedial goals envisioned.

The distribution of the bacterial population is also critical. Microbial species spread slowly in the subsurface, therefore to effectively introduce a new population to a targeted subsurface zone, numerous injection points are required, making the practicality of the process suspect. Once again, the water would have to act as a carrier to move the bacteria throughout the affected area. This would not be an efficient method of distribution for the new bacteria. The only viable subsurface bacterial population is the natural population. However, as has been shown in this chapter, there are methods to enhance certain portions of the natural population so that they dominate.

### ***Reactive Zone Layout***

Reactive zones are applied in a number of different configurations and using a variety of approaches. The variety and combinations used are limited only by the variety of potential scenarios that may be encountered in the field and the ingenuity of the practitioner. For the purposes of this text, three basic layouts will be discussed: cutoff/barrier, plume-wide, and hot spots. Cutoff/barriers consist of a series of reagent injection points established perpendicular to the groundwater flow direction along a line that represents a critical boundary for remediation. This layout is commonly employed along a property line, or other artificial boundary established for the purpose of remediation or regulatory closure. In most cases the cutoff layout is less expensive to deploy since the density of injection points is not effected, but the number of points is typically significantly lower than the other layout options available.

Plume-wide reactive zones target a large portion of the impacted groundwater. Typically the injection points will be evenly spaced throughout the target impacted groundwater (Figure 19). By applying the reactive zone across the entire selected target isopleth, the speed and completeness of the remediation is enhanced. Obviously, there are cost implications with such an application; higher capital costs are traded for shorter remedial timeframes and the potential commensurate reduction in total O&M costs.

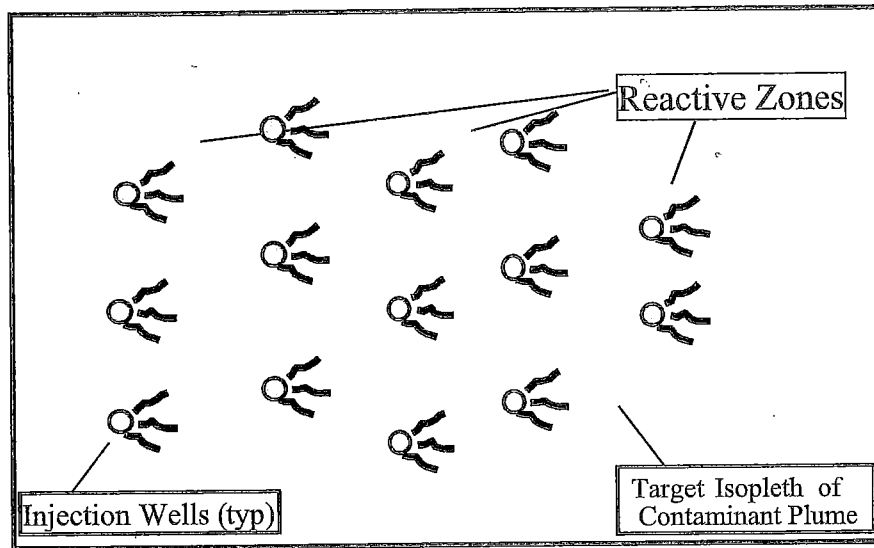


Figure 19 Plume-wide reactive zone.

Hot spot reactive zones target the source area. This layout is often employed in situations where the natural remediation process is successfully controlling the movement of the contaminant plume, but there is a need—regulatory or other—to speed up the overall remediation. In this case the source area is targeted with an area-wide reactive zone, in order to reduce contaminant mass quickly. Once the reactive zone has brought concentrations in the source area down to concentrations comparable with the remainder of the plume, the remediation can be allowed to progress at its natural pace.

These three basic layouts can be combined to suit the needs of the remediation. For example, if there is the potential for off-site movement of a plume in the short-term and a source area remains, it may prove most effective to establish a barrier reactive zone near the property line. At the same time a hot spot reactive zone can be established to reduce source mass and thus speed up the overall remediation.

### Baseline Definition

It is critical that baseline conditions be established prior to initiating an active treatment program. Baseline conditions help establish a scale against which success

can be measured. At a minimum, a complete suite of biogeochemical parameters and target COCs should be measured from wells in the up-gradient, impacted, and down-gradient areas of the site. During application of the reactive zone, field parameters such as ORP, DO, temperature, and pH should be monitored along with two or three electron acceptor species, TOC, DOC, two or three metabolic byproducts, and target COC end-products. Table 3 is a summary of the recommended analytical parameters for monitoring a reactive zone system.

**Table 3** Typical Reactive Zone Monitoring Program

Event	Analytes	Schedule
Baseline	Biogeochemical, COCs (injection and monitoring wells)	Week 0
Monitoring Event 1	Abbreviated Biogeochemical (injection and monitoring wells)	Week 3
Monitoring Event 2	Abbreviated Biogeochemical (injection and select monitoring wells)	Week 8
Monitoring Event 3	Abbreviated Biogeochemical, COCs (monitoring wells)	Week 13
Monitoring Event 4	Abbreviated Biogeochemical (injection and select monitoring wells)	Week 19
Monitoring Event 5	Abbreviated Biogeochemical, COCs (monitoring wells)	Week 26
Monitoring Event 6	Abbreviated Biogeochemical (injection and select monitoring wells)	Week 33
Monitoring Event 7	Abbreviated Biogeochemical, COCs (monitoring wells)	Week 39
Monitoring Event 8	Abbreviated Biogeochemical, COCs (monitoring wells)	Week 52
Future Monitoring Events	Abbreviated Biogeochemical, COCs (monitoring wells)	Every 3 to 6 months

Notes: Biogeochemical Analytes includes complete suite listed in Table 2.  
 Abbreviated biogeochemical list includes DO, ORP, pH, T, TOC, light hydrocarbons, ferrous iron, sulfide.  
 COCs include the target organic compounds and daughter products.  
 All monitoring events should include monitoring of injection wells for TOC, pH, and ORP.

### Reagents

There are a variety of reagents that are being used in reactive zone applications. Table 4 summarizes several of the available reagents reported in the literature, along with a brief description of the methods used to place the reagent and the means by which the reagent creates the reactive zone.

The most common reagents applied in the field today are molasses, Fenton's reagent/hydrogen peroxide, potassium permanganate, ORC<sub>TM</sub>, and HRC<sub>TM</sub>. Molasses and polylactate ester are used to create and maintain an anaerobic reducing zone for the reductive dechlorination of CAHs and for the precipitation of heavy metals. Magnesium peroxide is a slow release oxygen enhancement commonly applied to promote aerobic degradation of BTEX, petroleum hydrocarbons, and other aerobi-

Table 4 Selective Reactive Zone Reagents

Reagent	Type of Reactive Zone	Method of Delivery	Common Form of Reagent <sup>a</sup>	Mechanism	Comments <sup>b</sup>
Molasses	Anaerobic & reducing	Injection wells	Material is dissolved in water and then delivered via injection wells	Indigenous bacteria use as electron donor to create strongly reducing conditions	Numerous applications reported by ARCADIS Geraghty & Miller. (1, 15, 16, 26, 27) Applied under Patent #5,554,290 Cost: \$0.30/lb molasses Reported applications by DiStefano (27) PCE reduced (27) Cost: \$0.18/lb Reported applications in Europe Regulatory reluctance due to nature of reagent
Lactose	Anaerobic & reducing	Injection wells	Dissolved in water	Indigenous bacteria use as electron donor to create strongly reducing conditions	Reported applications by McCarty (28) Regulatory reluctance due to nature of reagent
Phenol	Anaerobic & reducing	Injection wells	Dissolved in water	Indigenous bacteria use as electron donor to create strongly reducing conditions	Reported applications by McCarty (28) Regulatory reluctance due to nature of reagent
Toluene	Anaerobic & reducing	Injection wells	Dissolved in water	Indigenous bacteria use as electron donor to create strongly reducing conditions	Reported applications by McCarty (28) Regulatory reluctance due to nature of reagent
Poly(lactate Ester)	Anaerobic & reducing	Injection wells, direct-push points	Semi-solid, gel-like material placed in canisters in wells or directly delivered.	Lactic acid released upon hydration of material is metabolized by bacteria to release hydrogen.(29)	Slow-release material \$12/lb Supplied by Regenesis under trademark HRC™ Injected in a number of proprietary and non-proprietary formulas (30, 31, 32).
Fenton's reagent	Oxidizing and/or aerobic	Injection wells, direct-push points	Ferrous iron solution and variable strength hydrogen peroxide (10% to 50% soln)	Ferrous iron and peroxide injected as a means of oxidizing target compounds	Requires pH to be in the 4 to 5.5 range



Table 4 Selective Reactive Zone Reagents (continued)

Reagent	Type of Reactive Zone	Method of Delivery	Common Form of Reagent <sup>a</sup>	Mechanism	Comments <sup>b</sup>
Permanganate	Oxidizing	Injection wells, direct-push points, recirculation systems	Potassium permanganate dissolved in water (0.1% to 3% bw)	Reagent injected to oxidize target compounds	Wide range of practitioners report success (33, 34, 35). Raw material cost: \$2/lb
Hydrogen Peroxide	Oxidizing and/or aerobic	Injection wells, direct-push points	Hydrogen peroxide injected at 1% to 35% solution strength	Reagent directly oxidizes target compounds or is a means to deliver oxygen	Wide range of practitioners report varying success (1, 13, 36). Most common use today is for direct oxidation
Dithionite	Reducing	Injection wells, direct-push points	Sodium dithionite directly injected into groundwater.	Reagent reacts with iron and hexavalent chrome to form tri-valent chrome	35% solution cost: \$0.42/lb Field demonstrations for chromium have been reported (6, 4) In the presence of heat, TCE reduction has been reported (6)
Sodium bicarbonate	pH adjustment	Wells or injection points	Mixed with water and injected.	Used to adjust pH as supplement to other reagents or stand-alone.	Used to maintain pH above 4.5 for chromium precipitation.
Magnesium Peroxide	Aerobic	Wells or injection points	Bulk powder, slurry or "socks"	Magnesium Peroxide is hydrolyzed, releasing oxygen into groundwater	Slow-release \$10/lb Supplied by Regeneration under trademark: ORC <sup>TM</sup>

<sup>a</sup> This represents the most common form used for injection.

<sup>b</sup> Costs are presented where available.

cally degradable COCs (e.g. ketones). The remaining reagents have been applied for the oxidation of a variety of COCs including BTEX and CAHs.

As previously discussed the goal of applying the reagent is to create a reactive zone in the subsurface that is sustained, easily maintained, inexpensive, and appropriate to the target compounds. As such, molasses and HRC have been successfully applied for the treatment of CAHs in groundwater. Molasses has also been applied for the treatment of heavy metals such as chromium, cadmium, mercury, and zinc. Polylactate ester is a slow-release material and, due to its viscous gel-like consistency, is most appropriate in low velocity groundwater systems, where the slow-release characteristic is particularly beneficial and where the consistency of the material will not lead to excessive implementation costs. Molasses is injected in a water solution and moves readily with groundwater. As a result the reagent can be effectively delivered across a wide area from fewer injection points. Molasses is readily degraded, thus leading to the rapid formation of anaerobic conditions. Over-delivery of the molasses, however, can lead to fermentation and pH-depression. Both materials are food-grade and acceptable to most regulatory agencies. Molasses and polylactate ester have been used in a number of different states in the United States and in countries around the world (Brazil, Canada, United Kingdom, Netherlands, and others).

As the efficacy of *in situ* reducing reactive zones has been demonstrated by many in the field, the variety of substrates applied has grown. Table 4 lists only a few of the many reagents tested in the laboratory or in the field. Other substrates include methanol, ethanol, sucrose, cellulose, edible oils, and proprietary blends of these and other sources of soluble organic carbon. The selection of the substrate is driven by the unit cost of the available soluble organic matter and the ease with which the material can be delivered to the subsurface. Many reagents are being selected from the wide variety of food-grade organic carbon sources (molasses, sucrose, and oils for example). The reagent selection process is often driven by how comfortable the regulatory agency is with the material and the variety and depth of practical applications available for a particular substrate.

Reagents for oxidative reactive zones have gained increasing attention recently, as the field data that has been developed has shown the efficacy of the application of oxidative reactive zones for the treatment of a wide range of organic compounds. Recent applications have included the treatment of adsorbed phase CAHs, BTEX, ketones and other common organic compounds (Geo-Cleanse Int. 1998, Tarr et al. 2000, Mott-Smith et al. 2000, Nelson et al. 2000, and Schnarr et al. 1998).

Hydrogen peroxide has been used as an oxygen supplement to enhance aerobic conditions since the mid 1980s. However, the recent applications of hydrogen peroxide (and Fenton's reagent—ferrous iron and hydrogen peroxide) in reactive zones has focused on the formation of hydroxyl radicals. Hydroxyl radicals are a very strong oxidizing agent and represent the strongest oxidant available other than fluorine. The resultant reactive zone is an environment in which target organic compounds are chemically oxidized to carbon dioxide, water, and chloride ions.

Potassium permanganate has been injected as a solution typically varying in strength from 0.1 percent to 3 percent. This reagent is not as aggressive as hydrogen peroxide; however, what it lacks in kinetics it makes up for in longevity. As a result,

potassium permanganate can be as effective as hydrogen peroxide in an *in situ* reactive zone.

### **Regulatory Issues**

Many states regulate the injection of materials into the subsurface. While this text does not attempt to cover the range of regulatory environments and issues that exist, it is important to consider the regulatory arena in which the remedial work is being conducted during the reagent selection process. Thus characteristics such as food-grade, no chemical residuals, and historic applications approved by other state or federal agencies all contribute to the rapid acceptance of an alternative substrate.

### **Design Criteria**

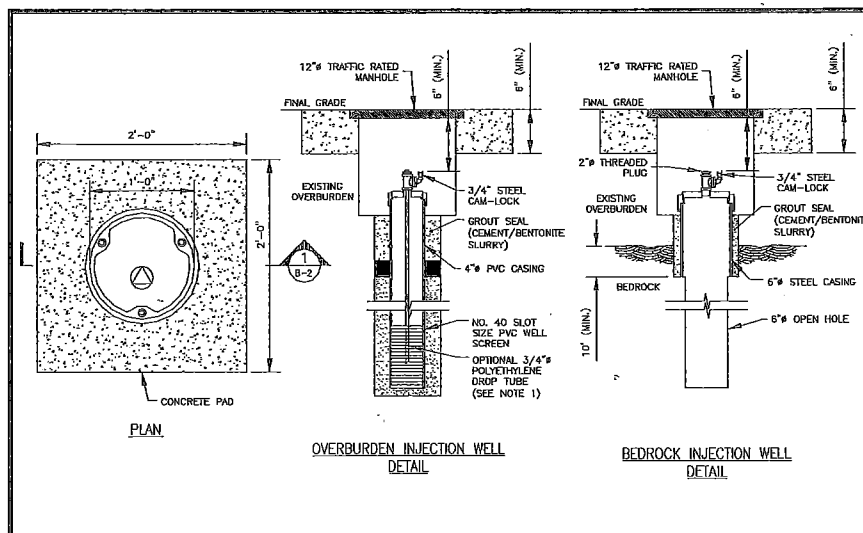
This section covers the design criteria that define the full-scale system, including:

- well design—type, number, depth, screen zone(s), layout
- reagent feed—feed rate, solution strength, frequency of injection
- monitoring—analytes, frequency

### **Well Design**

There are three basic types of wells (in reality delivery points) used in reactive zones: permanent wells, temporary well points, and direct-push delivery type well points. Permanent wells are constructed with materials appropriate for the geological formation, groundwater quality, and selected reagent. A typical injection well is shown in Figure 20. The wells in an unconsolidated formation are typically 2 to 4 inch diameter Schedule 40 or 80 PVC construction with slotted screens sized for the formation. In bedrock, an open bore hole in the target saturated zone is acceptable with a PVC or steel casing in the overburden. Wells constructed in this fashion provide a permanent means of delivering reagent to the subsurface. They are commonly applied in situations where readily soluble and degradable organic substrates—such as molasses—are applied. Permanent wells allow for multiple injections to establish and maintain the reactive zone. Permanent wells are also necessary in situations that involve impacts in bedrock geology, or where depths or soil strata make direct-push techniques impractical.

Direct-push techniques are also used for reactive zones in select applications. This type of well is limited to unconsolidated formations with impacts that are relatively shallow—depths can not exceed 50 to 75 feet. This technique is also constrained by the soil characteristics, particularly grain size. In some cases, where direct-push wells are used, a permanent well point is placed using a direct-push drilling rig such as a CPT (cone penetrometer type). This type of well is a small diameter point and is commonly applied where the number of injections will be limited and the need for well maintenance is minimal. This is a good design when the groundwater flow is shallow and slow. Under these conditions, a large number of injection points may be needed, and due to the slow groundwater flow few repeated



**Figure 20** Injection well construction detail.

injections will be required. Another practical constraint to the application of a CPT well is availability of drilling equipment; while these are common in Texas, California, and Oklahoma (oil country), they are somewhat rare in the northeastern United States.

Another type of direct-push wellpoint is a temporary geoprobe or hydro-punch well. In this case, the well drilling process is an injection process. Thus as the well point is placed, the reagent is injected. When the injection process is complete, no well points remain. This approach is applicable for slow-release materials such as polylactate ester, which will dissolve slowly and require well points on 2 to 5 foot centers to treat the target zone. As with CPT, this technique is limited by depth and geology.

All reactive zone wells must be designed to target the impacted groundwater. Thus the depth and screened interval will be determined by the vertical delineation of the groundwater impacts—with all the limitations this implies. In addition, the lithology can have a profound impact on the well design and screened interval since the injected reagent will flow with groundwater, following the path of least resistance, which MAY NOT be where the target impacts are located. As a result, it is important to understand both the geology and the contaminant distribution when designing the wells. As a practical limit, screened zones in excess of 50 feet are not recommended due to the difficulty in evenly distributing the reagent across more than a 50 foot interval. Where the saturated thickness exceeds this limit, multiple well points are recommended.

The number of injection points and the spatial distribution of these points are a function of the contaminant distribution, the hydrogeology of the impacted zone, the type of injection point selected, and the type of reagent being used. The injection wells need to cover the entire area targeted by the reactive zone. The geology and

groundwater velocity will control how wide an area a single point can impact. For example, in a tight geologic unit, groundwater is likely to move relatively slowly, and the ability to inject is limited by the permeability of the formation. As a result, the reactive zone developed from a single point will have a limited impact laterally from the injection point and in the direction of groundwater flow. Therefore more points will be needed on a tighter center to center spacing.

The type of reagent used can also effect the spatial distribution of the injection points. If a water soluble reagent, such as molasses, sucrose, or potassium permanganate is used, the reagent injectant will have flow characteristics, nearly identical to that of water and thus will move readily with the groundwater. As the reagent becomes more viscous, the ability to inject and achieve good lateral distribution will decline. As a result, in the latter case, more closely spaced well points will be required.

### ***Reagent Feed***

The feed rate, solution strength, and frequency of injection all relate to the target COC concentration. In Chapter 7, oxidant feed requirements were discussed, therefore in this chapter, comments will be limited to reducing reactive zones. For reducing reactive zones the reagent feed characteristics of rate, strength, and frequency tie back to the need to deliver adequate organic carbon, in the form of the selected reagent, in order to maintain reducing conditions in the subsurface. There are two criteria that must be met to create the reactive zone. First, enough organic must be added to ensure that the electron acceptors in the groundwater are utilized. This organic carbon feed rate can be derived based upon the total concentration of the various electron acceptors (primarily DO, nitrate, and sulfate) and the groundwater flow rate. The product of the electron acceptor concentration and the groundwater flow rate is the electron acceptor flux. The reactive zone design must supply enough substrate to overcome the electron acceptor flux.

Second, there must be enough substrate to drive the entire zone into highly reducing conditions. Typically the goal is to maintain between 50 and 100 times as much dissolved organic carbon in the reactive zone as there is COC in the target area (i.e., 100 ppm of DOC for every 1 ppm of COC). Based on experience, this translates to one or two orders of magnitude higher target DOC concentration in the injection wells. The reason higher concentrations must be fed in the injection wells relates to the fact that the organic carbon will be metabolized as it flows with groundwater, therefore it is necessary to establish a DOC gradient between the injection points and the rest of the reactive zone. It is important to keep in mind that the COC flux through a target zone is related to the groundwater flow velocity, the saturated thickness, and the COC concentration.

Both of these criteria are simply guidelines for a preliminary calculation of the donor feed rate. Experience has proven them to be adequate means to define a reasonable organic carbon feed rate to begin the reactive zone. Field data collected AFTER the reactive zone has been started is the true measure of the adequacy of the reagent feed. Field analytical data (in particular redox, pH, and TOC) from the injection wells and monitoring wells within the reactive zone should be used to

confirm that the reactive zone has been established and is expanding with groundwater flow. Pilot and full-scale data has shown that during the initial stages of some reactive zones the organic carbon load to the injection well needs to be maintained between 100 and 9000 mg/l of organic carbon. In the long-term, once the reactive zone is established, these concentrations can be reduced somewhat, with a sustainable target of 50 to 100 mg/l of organic carbon within the reactive zone.

The solution strength, while related to the target organic carbon feed rate, is also impacted by other factors such as the groundwater flux, the ease with which a solution can be injected, and the cost to perform the injection. In the example above involving a tight geology, the amount of reagent is reduced since the groundwater flow and the contaminant flux is low, thus less reagent is required to deliver the required DOC load. In this situation a slow dissolving substrate may be more applicable. Conversely, if the groundwater velocity is high, the COC flux will be proportionally higher and the need for organic carbon higher. In this situation a readily soluble, easily injected reagent is more applicable. It is worth noting that the lateral, advective dispersion in a high groundwater velocity environment is relatively low, thus the reactive zone formed will be narrow, but long. Therefore more injection points will be required across the plume (perpendicular to groundwater flow), but the lines of injection wells can be spaced further apart in the direction of groundwater flow.

### **Monitoring**

After the baseline biogeochemical environment has been defined and a reactive zone is being implemented, it is important to monitor the progress and health of the reactive zone. Early in the establishment of the reactive zone, possibly during a pilot, or demonstration phase, nearly the full suite of parameters (Table 2) should be monitored. After the zone has been established only the most critical analytes need to be monitored on a regular basis. In a reducing reactive zone the most important analytes include the redox (ORP), dissolved oxygen, pH, DOC, degradation end-products (ethene and ethane for CAHs), and COCs and their daughter products. In the case of reactive zones targeting metals, sulfides can also be important.

The frequency of monitoring is site specific, but generally the frequency should be adjusted over the lifecycle of the remediation. Initially, the sampling frequency will run between weekly and monthly—the former if no pilot test data is available to define feed rates. After the first two months of operation monthly or quarterly sampling will provide adequate data to monitor the reactive zone. Within the first 6 to 12 months of operation, quarterly monitoring should be sufficient. Long-term monitoring can be extended to semi-annual, however due to the short expected life of most reactive zones—less than 5 years—anything less frequent than semi-annual is unlikely to provide adequate data. Monitoring frequency should always remain flexible during the lifecycle of the reactive zone. This concept is critical to the health of the reactive zone and the success of the process. Disclosure of the need to be flexible is critical to the regulatory agency perceptions of the monitoring effort and the client's understanding of the budget and schedule.

## Pilot Testing

The design criteria are most often defined in a pilot or demonstration test. Such a test is used to gather critical design data—well spacing and reagent feed rate, strength, and frequency—as well as to demonstrate the efficacy of the technology and satisfy regulatory agency concerns regarding the technique. The pilot test should always focus on an area of concern within the plume. Thus a successful pilot test can also be used as an interim remedial measure.

This section covers a typical field test for a reducing reactive zone. Keep in mind that before testing it is important to answer questions regarding the biogeochemical environment, hydrogeology, regulatory arena, etc. as discussed earlier in this chapter. This basis is critical to the pilot test program set up, focus, and endpoint.

## Test Wells

To properly evaluate the *in situ* technology in the field, injection wells and a network of groundwater observation wells are required. The injection wells need to be located in an area of the site where sufficient impacts are present, and should be installed in a manner similar to wells that would be employed in a full-scale system. The groundwater observation wells for the field test should also be located within the impacted area. The observation wells should be located in a manner to evaluate both the performance of the degradation—or precipitation—process and the extent, both parallel and perpendicular to the direction of groundwater flow, of the *in situ* reactive zone.

The field test should employ at least one injection well, preferably two, that can be used to deliver reagent to the entire target zone. The screened interval should intercept the impacted zone, with consideration given to the lithology and groundwater flow conditions. The injection wells should be constructed as described above using appropriate drilling techniques. If there is little or poor quality geologic data available, consideration should be given to the need to gather supplemental geological data using split-spoon sampling techniques or other appropriate means. Following installation, the well should be developed to remove fine material and ensure hydraulic communication with the surrounding aquifer.

To provide the necessary level of performance monitoring for the field test, observation wells in the area down-gradient of the injection wells are required. A minimum of two and whenever possible as many as five observation wells can be included in the pilot program. The observation wells should be located at variable distances from the injection wells both parallel to the direction of groundwater flow and perpendicular to the direction of groundwater flow. This will allow the reactive zone to be defined in both directions relative to groundwater flow. Once again, consideration should be given to the variability of the site geology in locating screened intervals. It may be necessary to monitor multiple intervals if the geology dictates.

When possible, existing monitor or production wells may be used as injection or observation wells in order to speed up the pilot test program and control costs.

### ***Reagent Injection***

The composition of the reagent feed solution that will be used during the field testing, the solution injection rate, and the injection procedures are discussed in this section.

The composition of the reagent feed solution will need to be varied during the field test, based on field measurements made in the observation wells and the analytical results gathered during the groundwater monitoring program. The amount of reagent injected in the injection wells during the field testing will also be varied by increasing or decreasing the amount of solution injected, or by changing the frequency of injections.

An appropriate solution feed rate must be established and maintained in order to ensure that adequate electron donor solution is added and that the available electron acceptors are fully metabolized in the reactive zone in order to maintain a strongly reducing environment. At the same time, the feed rate needs to be controlled so as to minimize the amount of material that has to be injected into the subsurface. The proposed solution feed rate can be calculated based on achieving a sufficient DOC concentration in the groundwater that passes through the injection well area. For the field test, the volume of solution and solution strength should be calculated to achieve the DOC load discussed earlier using a reasonable number of injection events—in most cases pilot tests are conducted using a batch type injection program.

The frequency of injections will vary with the geologic, biogeochemical, and hydrogeologic conditions of each site. As a result the frequency of injections can vary from once a day to once every 6 months.

### ***Duration of Field Study***

Typical field tests last between 3 and 6 months. The rate of groundwater flow and the proposed observation well locations will determine the site-specific duration of the test—the closer the observation wells are to the injection wells and the faster groundwater moves, the sooner results can be expected and the shorter the pilot test needs to be. The testing is complete when the following criteria have been achieved:

- redox conditions down-gradient of the injection well are reduced (ORP less than -100 mV)
- the ratio of target COC to daughter products has declined—i.e., the source material is degrading
- the amount of end-product (ethene) has increased

These results may actually be achieved within 1 or 2 months of implementation of the pilot test program. Additional information may be necessary to satisfy regulators or clients and in order to optimize the full-scale design. For this reason the pilot is often extended beyond a simple demonstration. Additional criteria that are commonly applied include:

- reduction of target COC concentrations below a historical low baseline concentration



- a COC:daughter ratio less than 1
- definition of the lateral extent of the reactive zone based on a specified time frame
- rebound testing within the target zone (this applies to metals only) to demonstrate that precipitates do not remobilize after the reactive zone is terminated. This portion of the test will typically double the duration of testing

Many times the testing ends, but the injections continue. Once the reactive zone is established within the plume, maintenance dosages of the reagent will allow the zone to continue to serve as a remedial measure, until such time as the system is expanded or the cleanup goals are achieved.

### ***Field Test Performance Monitoring***

The most critical portion of the *in situ* field test is the performance monitoring. In this portion of the test, field monitoring of selected indicator parameters and groundwater sampling for field and laboratory analyses are conducted. The data collected from these performance monitoring activities are used to adjust reagent feed rates and, if necessary, the frequency of sample collection.

Performance monitoring takes the form of a baseline sampling event and periodic monitoring events during the period of field testing. The baseline monitoring event is used to establish the biogeochemical conditions and COC concentrations of pre-test groundwater and serves as the basis of comparison for all future data collected during the test.

To establish baseline conditions (i.e., groundwater conditions prior to the start of the field test), an initial round of groundwater samples should be collected from the injection and observation wells. These baseline samples should be analyzed for the following parameters:

- Metals: target metals (filtered and unfiltered), iron (total), iron (ferrous), manganese (total and dissolved)
- Biogeochemical Parameters: sulfate, sulfide, nitrate, total suspended solids (TSS), total and dissolved organic carbon (TOC/DOC)
- Dissolved gases and light hydrocarbons
- VOCs
- In some cases: bacteriological (total heterotrophic plate count, iron reducing bacteria, and/or sulfate reducing bacteria)

In addition, the levels of several indicator parameters should be collected in each of the wells. These indicator parameters include pH, redox, DO, and temperature.

In order to evaluate the extent of the *in situ* reactive zone, and the effectiveness of the *in situ* process, groundwater samples will also need to be collected as the field test progresses and at the end of the field test. The frequency will vary, but in most cases data should be collected within the first month of testing and then bi-weekly or monthly through the first 3 months of testing and bi-monthly to quarterly thereafter. The frequency is initially driven by the need to ensure that neither too much nor too little reagent is being added. After the first month or two of testing, sampling frequency will be driven by factors such as the groundwater flow velocity,

the natural baseline biogeochemical environment, and the extent of groundwater impacts. The data should be collected from the two injection wells and observation wells. Data from the injection wells should be limited to fewer analytes than from the observation wells. All samples should be collected using low-flow purge techniques to ensure the integrity of the analytical data generated.

Field analysis for ORP, DO, pH, temperature, and conductance provides the most rapid and inexpensive water quality data and reactive zone definition. These parameters should be monitored with the greatest frequency. Once the field parameters change, the performance monitoring can be extended to the more costly parameters analyzed in the laboratory.

### **Test Results**

The results from a pilot test can be used to:

- demonstrate the efficacy of the technology at a particular site by providing empirical, site-specific field data for the technology
- determine the reagent feed rate, the frequency of injections, and the solution strength required
- define the well spacing perpendicular and along the groundwater flow direction based on the extent to which the reactive zone was established during the test

The third case study reviews in detail a year-long pilot test program.

### **Full-Scale Application**

Once the pilot test program has defined the critical design criteria, the full-scale design can be completed and the full-scale system authorizations obtained. Regulatory approval will likely be required along with well construction permits, injection permits, and possibly construction permits.

In order to demonstrate the application of the technique, several case studies are presented in this section.

#### **Case Study 1: Federal Superfund Site, Pennsylvania**

In the section COC Chemistry: Metals an example of an *in situ* reactive zone was introduced to describe how chromium and cadmium can be reduced and precipitated as hydroxides, carbonates, or sulfides in the subsurface. In Case Study 1 additional details of this site are presented.

#### **Background**

The site includes a 28-acre, operating aircraft manufacturing facility and the surrounding residential neighborhood, as well as down-gradient impacted groundwater (Figure 21). In the mid 1980s, the local water authority detected the presence of VOCs, specifically trichloroethene (TCE) and 1,2-dichloroethene (DCE), in the

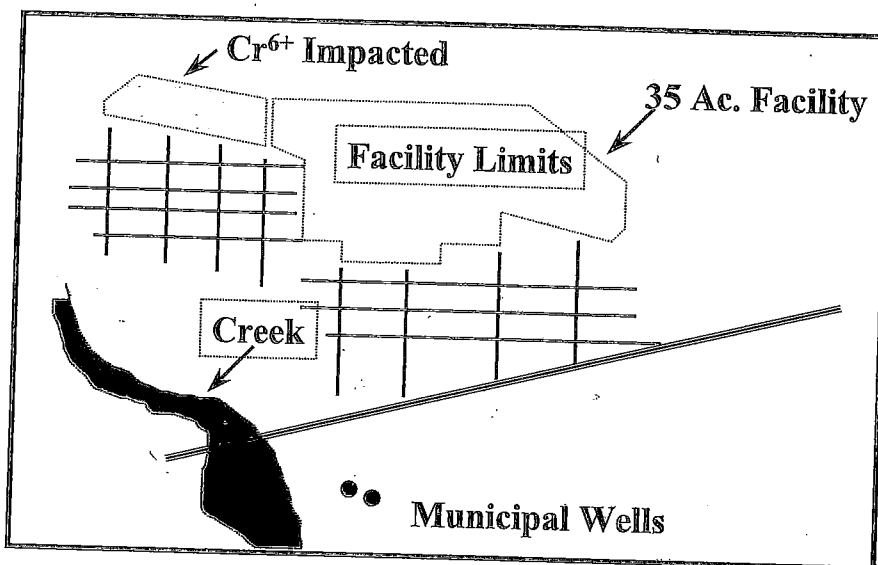


Figure 21 Case Study 1: Superfund site.

groundwater in the municipality's backup water supply well field, which is within 3,000 feet of the manufacturing facility. As a result, the facility owner entered into a Consent Order and Agreement (COA) with the state environmental agency to implement a remedial investigation and cleanup plan. The site was placed on the National Priorities List (NPL) in 1988; an Administrative Order of Consent (AOC) was signed for the purpose of conducting a Remedial Investigation (RI), Endangerment Assessment (EA), and Feasibility Study (FS) for the site. In 1991, a Record of Decision (ROD) was issued for the area of contamination within the plant boundaries. The ROD remedy consisted of:

1. A recovery and treatment system to contain and control off-site migration of groundwater
2. Institutional controls to limit future property use to those activities compatible with site conditions

In 1992 a Remedial Design Workplan (RDWP) was approved by the USEPA. The RDWP called for a line of pumping wells at the property boundary to contain and control off-site migration of the plume. The pumped water was to be treated for heavy metals (cadmium and chromium) and organic compounds (TCE, DCE, and vinyl chloride [VC]) using *ex situ* treatment; the treated water was to be discharged to a National Pollution Discharge Elimination System (NPDES) discharge point. In 1995, shortly after the NPDES permit was approved, the treatment system design and construction was bid. At that time an alternative treatment approach, which employed an *in situ* reactive zone, was proposed to the USEPA.

The primary target for the reactive zone at the time that the system was designed was a plume of hexavalent chromium and cadmium centered north and west of the

main plant area. Overlapping the heavy metals plume was the northwestern leg of the CAH plume. The CAHs consisted of TCE and its degradation daughter products, DCE and VC. A pilot test program was initiated in late fall 1995 to evaluate the efficacy of the reactive zone technology for chromium and cadmium reduction. Two pilot test areas (one in the northeast corner and one in the southeast corner of the target area) were selected. A single injection well (existing 4 inch monitoring wells) was used in each area. Within the first 2 months of testing, the hexavalent chromium concentrations were reduced from as high as 7 mg/l to less than 0.05 mg/l in the test zone (Figure 9). Following the 6 month pilot program, a series of geoprobe samples were collected radially away from the injection wells in order to define the lateral influence of the injection well. This data indicated that the injection well achieved at least a 10 foot radius of influence.

Coincidental with the pilot test program, the ongoing quarterly CAH sampling program continued. Quarterly data collected from wells located near the pilot test wells during this test program indicated that the reactive zone was not only creating the conditions necessary for precipitating cadmium and chromium, but also the conditions needed to reductively dechlorinate the CAHs.

### *Full-Scale System*

The full-scale remediation system was designed in the summer of 1996 and the ROD was rewritten to include the reactive zone for metals precipitation. The reactive zone system was constructed during the last four months of 1996 and went on line in January 1997. Based on the pilot study results that indicated enhanced reductive dechlorination of the CAH plume by the reactive zone system, the full-scale system design documents incorporated the use of the reactive zone as the technology to treat and contain the CAH contamination in the northwest corner of the property.

The geology at the site consists of a sandy-silt overburden overlying a weathered bedrock and a fractured limestone. The target area for the reactive zone is the shallow overburden to approximately 25 feet below land surface in an area covering approximately two acres. The maximum concentrations of hexavalent chromium, cadmium, and TCE were 3 mg/l, 0.8 mg/l and 0.7 mg/l, respectively, in the area being treated at the time that the treatment system was installed and went on line.

The use of the reactive zone to reduce chromium and cadmium is described in a previous section of this chapter. The reducing conditions created within the reactive zone are maintained to be strong enough to ensure that the enhanced reductive dechlorination of TCE and its daughter products results in the destruction of the CAHs of concern at the site to harmless end-products (carbon dioxide and water).

The full-scale system is summarized in schematic form in Figure 10. The system consists of twenty 2 inch diameter injection wells, completed in the unconsolidated sandy-silt overburden. A 2 inch diameter well was used to control capital costs and still insure ease of accessibility for well maintenance. The well spacing was based on the test data. Each well is connected to the reagent storage building via 1 inch diameter, buried, high density polyethylene piping. The reducing reagent (in this case molasses is applied under Patent #5,554,290) is added once or twice a day

(comparable to the pilot test feed rates) at variable rates and concentrations based on the results of the system monitoring program. A total of 16 additional wells are used for monitoring of the treatment system. (Most of these wells were installed in order to satisfy regulatory and client requirements, since at the time this was the first full-scale treatment system of its kind.) A programmable logic controller monitors and controls the feed rate and frequency of the molasses feed and solution feed pumps, as well as the timing of the solenoid valve network that controls the metered flow to the injection wells. The molasses storage tank, mixing tank, feed pumps, control panel, and solenoid valve nest are housed in a 10 foot square pre-engineered building (Figure 11).

### *System Performance*

The monitoring program was initiated when the treatment system went on line in January 1997. From that time, monthly to quarterly sampling has been conducted for redox, pH, chromium, cadmium, other metals, and CAHs. Quarterly sampling was dictated by the regulatory agency as part of the site-wide monitoring program; the initial monthly sampling was instituted to ensure that the process was properly controlled. The test results have closely matched or exceeded those collected during the pilot program:

- the concentrations of chromium have dropped in the hot spots from 2 to 3 mg/l to less than 0.05 mg/l (Figures 13 and 16)
- the overall chromium plume shrunk to approximately one-fourth its original area extent within 18 months of start up
- the peak chromium concentrations are isolated to one area at slightly above 0.5 mg/l
- the peak cadmium concentrations are isolated to two small areas at slightly more than 50 ug/l (Figures 14 and 17)
- TCE, DCE, and VC concentrations have steadily dropped in the majority of monitoring wells where CAH data is collected (Figure 22)

After 22 months of operation, the concentrations of TCE, DCE, and VC were near or below the regulatory limits of 5, 70, and 2 ug/l, respectively, indicating that the reactive zone technology can achieve concentrations in groundwater below mandated drinking water standards.

The operational efficiency of the reactive zone technology is also evidenced when the degradation rate is evaluated. Figure 23 summarizes the degradation rate for TCE and DCE before the reactive zone was implemented. Figure 24 presents the data at the site after the reactive zone was started. As the Figures illustrate, the rate of decline of TCE and DCE concentrations increased significantly once the reactive zone was implemented at the site.

The cost to implement the reactive zone and operate it for a little less than three years was approximately \$400,000 including capital, operations, maintenance, and monitoring. This system replaced a pump and treat system that had an estimated present worth cost of more than \$4,000,000. The cost for the pump and treat system included capital and operation and maintenance for a period of 20 years.

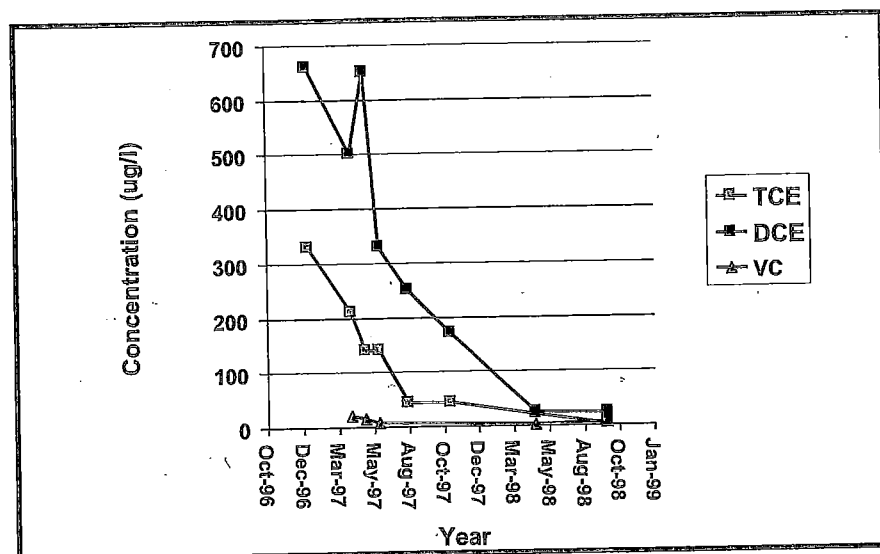


Figure 22 Case Study 1: chlorinated VOCs.

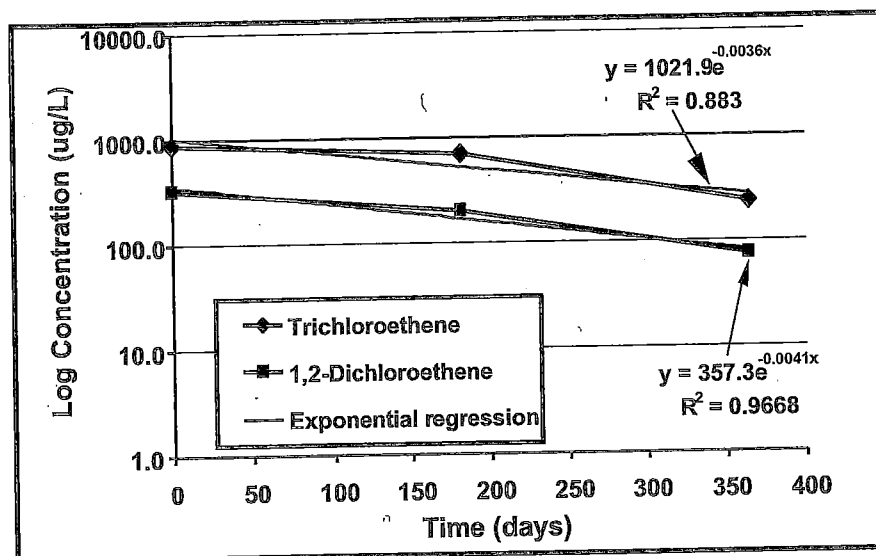
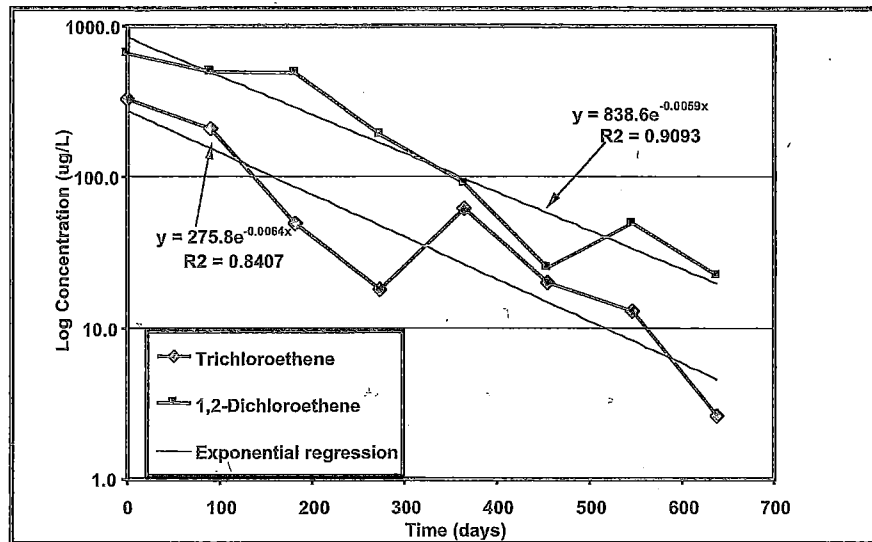


Figure 23 Case Study 1: historical concentration trends.

### Case Study 2: State Voluntary Cleanup

The second case study involves a manufacturing facility located on the west coast. Facility operations involved metal plating and degreasing that led to the release of hexavalent chromium and TCE into the site groundwater.



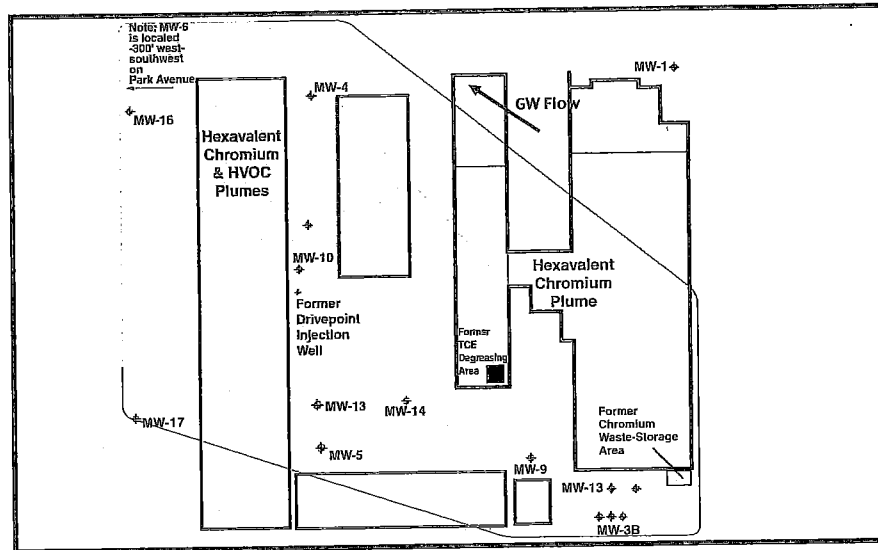
**Figure 24** Case Study 1: concentration trends following implementation of full-scale *in situ* reactive zone.

### Background

The site is slightly more than two acres in size (Figure 25). The geology is primarily silts and clays to 24 feet below land surface (bls), overlying an impermeable clay layer that serves as an aquitard. Groundwater flows from the area of MW-13 toward MW-10 at a relatively slow rate (less than 100 feet per year). The former chromium waste storage area is located near MW-13 and the former TCE degreasing area is located near the center of the plant.

Historic releases led to groundwater impacts in the forms of chromium and CAHs. As Figure 25 illustrates, the hexavalent chromium plume extends over most of the site. Initial peak hexavalent chromium concentrations in groundwater were more than 900 mg/l. The primary CAH was TCE, although degradation daughter products were also in evidence at the site, including DCE and VC. The initial maximum TCE concentrations in groundwater were approximately 24,000 ug/l, while DCE and VC concentrations were less than 500 and 100 ug/l, respectively.

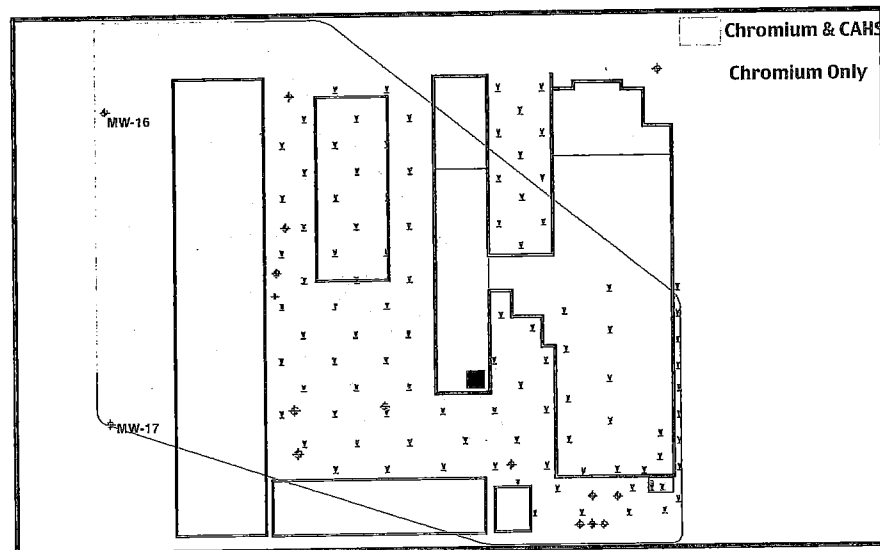
A pilot study was completed in a small up-gradient portion of the site in late 1995 and early 1996 in order to demonstrate the efficacy of molasses injection for the creation of a suitable reactive zone. Due to the high concentrations of hexavalent chromium, there was concern that the natural microbial population might be too stressed to adequately address the needs of creating the reactive zone necessary for groundwater treatment. In order to supplement the natural population at this site, sludge from an anaerobic sludge digester was added to the molasses/water reagent mixture used. The pilot test program successfully demonstrated that the reactive zone technology would be successful. Based on the data collected, the full-scale system was implemented.



**Figure 25** Case Study 2: site map, monitoring wells and plumes.

### *Full-Scale Implementation and Results*

Ninety-one injection points were installed (Figure 26) to 24 feet bls at the site. Each point was 1 inch diameter with a 10 foot long, 0.010-inch slot screen. Each injection point was installed rapidly and at a relatively low cost using a direct-push approach with a Geoprobe™ drilling technique. Existing monitoring wells were used to track the progress of the treatment process.



**Figure 26** Case Study 2: reagent injection points.



Each injection point received an injection of a mixture of molasses, water, and anaerobic sludge. Unlike the daily dilute molasses/water reagent injections used in Case Study 1, the injections for the full-scale reactive zone at the second site were more concentrated and less frequent. The injections were initiated in the spring of 1997. A single injection took place in May 1997; the next injection occurred approximately one year later.

The theoretical groundwater flow for the site is suspected to be artificially high. Due to the site's proximity to the Bay margin and the very dense lithology, it was suspected that, in spite of the calculated low groundwater flow rate of 100 feet per year, the actual groundwater flow rate may actually be an order of magnitude less. Transport of the reagent throughout the subsurface in an acceptable time frame using dosed injections into fewer points/wells would probably not result in an acceptable rate of remediation. In fact, monitoring wells approximately 100 feet down-gradient from the on-site remediation area do not yet indicate that remediated groundwater has reached the off-site wells (three years after remediation commenced). In addition, it was determined that the periodic, site-wide injection events were more cost effective for this site—a key consideration for the client.

The theoretical basis for selecting both the concentration and the volume of injection was based on the above referenced pilot study, in which dosage concentrations and volumes were changed over time until an effective remediation environment was established at monitoring wells near the pilot study injection areas. The spacing of the injection points was likewise established from the data acquired during the pilot study, which indicated, in this lithology, a maximum 17 foot radius of influence.

Figure 27 summarizes the average chromium concentrations collected from eight wells across the chromium plume. Hexavalent chromium concentrations have been reduced at the site from initial concentrations in the range of 66 to 140 mg/l, to concentrations of 0.14 mg/l, to nondetect. Hexavalent chromium concentrations declined at a steady rate during the period between the first and second injections and are now nondetect ( $<0.05$  mg/l) across the site. As the data in Figure 27 depicts, the majority of the chromium found in groundwater was hexavalent. In the reducing conditions created by the injection of the molasses/water/sludge mixture, the hexavalent chromium was reduced to tri-valent chromium and precipitated out of solution, most likely as chromium hydroxide. The precipitate was removed by the aquifer soils.

In the source area TCE concentrations were reduced from approximately 18 mg/l to 2 mg/l, while in the mid plume area, TCE concentrations were reduced from approximately 30 mg/l to nondetect. Figure 28 provides a summary of the data collected from MW-4 before the pilot test was initiated through March 2000. Prior to initiation of the reactive zone pilot the ratio of source CAH (i.e., TCE) to degradation product (i.e., DCE and VC) was approximately 9:1. After the first injection the concentrations of TCE initially dropped, while the concentrations of DCE and VC remained relatively unchanged. As a result, the ratio of source to daughter product declined to approximately 3:1.

Prior to the first full-scale injection the TCE concentrations increased again. This most likely occurred as a result of the release of microbial surfactants within the

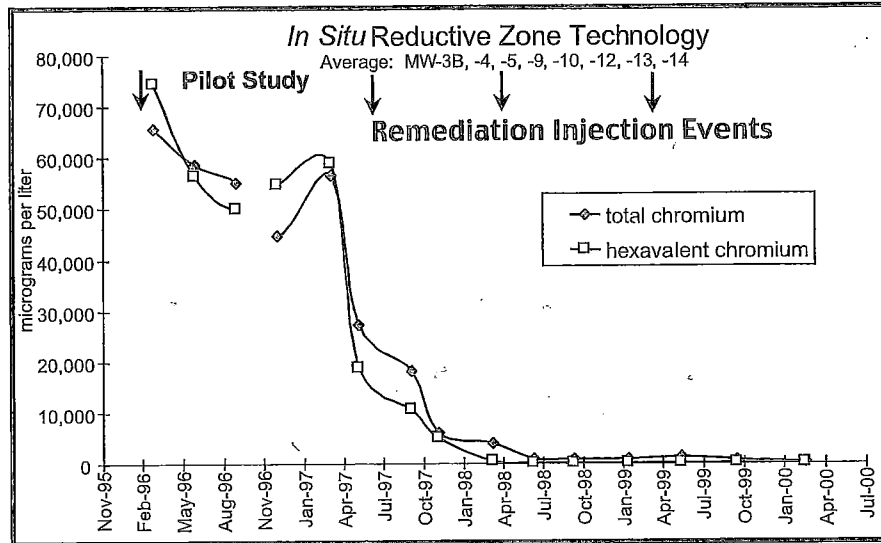


Figure 27 Case Study 2: chromium data.

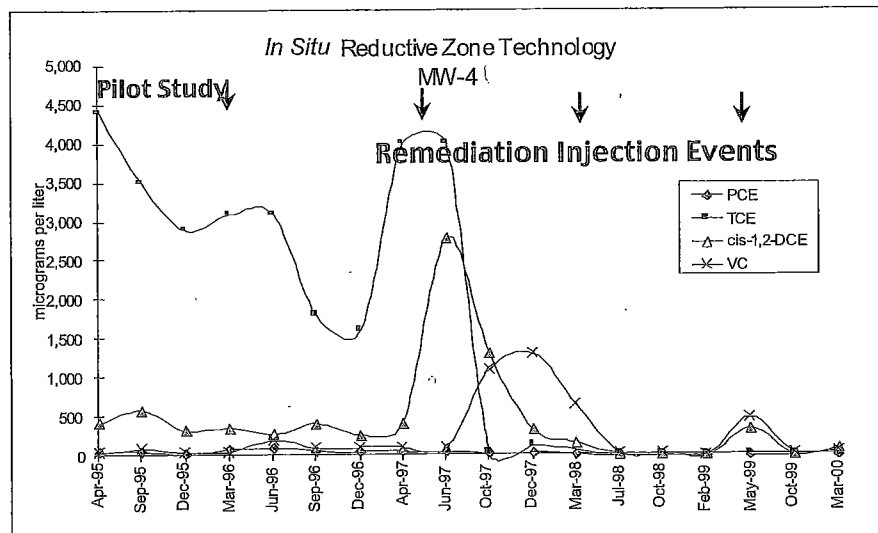


Figure 28 Case Study 2: CAH data.

reactive zone and/or transient increases in the groundwater elevation. Bacteria will generate surfactants in order to increase the amount of available organic carbon dissolved in the groundwater. The organic carbon must be in solution for the bacteria to metabolize the carbon. The surfactants are nondiscriminating, and thus aid in the desorption and dissolution of sorbed TCE. The resultant spike in TCE can be expected in some reactive zone sites.

Parallel to the TCE spike is an increase in daughter products, namely DCE and VC. As a result the ratio of source to daughter products continues to decline (less than 2:1 shortly after the first full-scale injection).

Another important observation that can be made using the data in Figure 28 is the lag between the peaks of the source and degradation products. The peak sequence follows the sequential dechlorination of the CAHs: the TCE peak is *followed* by the DCE peak; and the DCE peak is *followed* by the VC peak. It can also be concluded from the data that the reactive zone is reducing the concentrations of daughter products as well as the source product. Finally, the presence of daughter products of TCE also provides indication that the observed results are not a dilution phenomenon.

This site is presently being considered for the potential use of reactive zones to address vadose zone contamination at the site.

### ***Case Study 3: PCE-Impacted Bedrock Pilot Test***

This case study presents the results for a pilot test demonstrating the enhanced reductive dechlorination of tetrachloroethene (PCE) in bedrock groundwater. The pilot test was implemented in the mid-portion of an approximately 3000 foot long plume.

#### ***Background***

A tetrachloroethene (PCE) spill was discovered in 1985 at a northeastern United States manufacturing plant. A subsequent groundwater investigation resulted in the installation of approximately 40 wells to delineate the PCE plume. PCE has been delineated horizontally and vertically at the site, and a dissolved PCE plume has been defined. Low concentrations of PCE (1 µg/l) extend approximately 3,000 feet (914 meters) down-gradient of the spill area. Historical groundwater monitoring indicates that the plume is currently at equilibrium. Hydraulic control has been established at the site through pumping. Low concentrations of PCE breakdown products (such as TCE and 1,2-DCE) were detected in the former source area during the ongoing groundwater monitoring at the site, indicating that natural reductive dechlorination of PCE was taking place prior to initiating the bioremediation pilot test. The observed reductive dechlorination in the source area was a result of favorable geochemical conditions: anaerobic and reducing conditions and the presence of organic carbon (electron donor) in groundwater. Less favorable conditions that exist outside the former source area (more aerobic and oxygenated groundwater and a lack of electron donor) do not promote continued degradation of the PCE plume.

Soil vapor extraction (SVE) had been employed in the former source area at the site, but the mass recovery was low and had reached asymptotic levels. Pumping of groundwater in the former source area and up-gradient of a stream has been ongoing at the site since 1987. The pumping remedy has been effective in protecting the stream and containing any further migration of PCE from the site. However, due to the inefficiency of pump and treat, and the elevated long-term costs associated with this technique, an *in situ* reactive zone was tested.

A pilot test was initiated in October 1998 to evaluate if the rate of reductive dechlorination down-gradient of the source area could be enhanced via an anaerobic *in situ* reactive zone. Field and laboratory data were collected prior to initiating the pilot test to establish baseline conditions, and were collected periodically during the pilot test to adjust the rates of reagent feed and document the progress of the reactive zone.

### *Geology/Hydrogeology*

The overburden at the site consists of a thin layer of glacially deposited sands, silts, and clays and is approximately 10 to 20 feet (3 to 6 meters) thick. The overburden contains little groundwater and therefore the majority of the site wells were installed in bedrock, which consists of Triassic-aged, low permeability siltstones and shales. Results of several pumping tests completed at the site indicate that the bedrock at the site has a hydraulic conductivity (K) in the range of 0.14 to 1.78 feet per day (0.04 to 0.54 meter per day). The groundwater velocity for the site is within a range of approximately 10 to 70 feet per year (3.1 to 21.3 meters per year).

The bedrock is primarily fractured along horizontal bedding planes that strike to the northwest with a slight dip (9°) to the northeast. Minor vertical fractures are also present in the bedrock. Groundwater flow is believed to be primarily along the horizontal bedding plane partings that are coincident with the strike of the rock. Groundwater flow is generally south-southeast with the orientation of the plume being coincidental with strike. There is historical evidence supporting the interconnection of the bedding plane fractures through previous pumping and injection tests on the aquifer.

### *Baseline Biogeochemical Assessment*

A baseline biogeochemical sampling event was performed prior to initiating the pilot test to determine background conditions at the site, and to evaluate the biogeochemical environments present in various portions of the plume, including the pilot test area.

Groundwater samples were collected utilizing low flow sampling procedures from a background well located up-gradient of the assumed source area and the pilot test area. Field parameters (DO, ORP, pH, temperature, and conductivity) were collected at the well head using a flowthrough cell and a multimeter, and samples were collected for a full suite of biogeochemical parameters. The laboratory parameters included VOCs, alkalinity, ammonia, biochemical oxygen demand, chemical oxygen demand, chloride, total and dissolved iron and manganese, nitrate/nitrite, sulfate/sulfide, DOC, and TOC. Samples were also analyzed in the field utilizing a spectrophotometer for ferrous iron and sulfide, and submitted to a specialty lab for analysis of permanent gases (carbon dioxide, oxygen, nitrogen, methane, and carbon dioxide) and light hydrocarbons (ethene and ethane). Select baseline sampling results from the background and pilot test areas are provided in Table 5.

The background biogeochemical environment flowing onto the site was fairly aerobic (DO = 7.09 mg/l) and oxidizing (ORP +42.7 millivolts [mV]). VOCs were

Table 5 Case Study 3 Performance Monitoring Data for Pilot Test Wells, MW-1 and MW-3

MW-1	DO mg/l	ORP mV	TOC mg/l	PCE µg/L	Ethene ng/l	MW-3	DO mg/l	ORP mV	TOC mg/l	PCE µg/L	Ethene ng/l
Apr-98	0.28	19.5	12	110	12	Apr-98	-	-	-	-	-
Dec-98	1.83	-73.3	27	-	-	Dec-98	-	-	-	-	-
Jan-99	3.33	-153.1	<1	-	-	Jan-99	-	-	-	-	-
Feb-99	0.35	-106.2	3.8	400	-	Feb-99	-	-	-	-	-
Mar-99	0.22	-90.4	4.4	-	-	Mar-99	-	-	-	-	-
Apr-99	0.19	-124.9	469	101	408	Apr-99	0.86	-41.2	1.9	17	92
May-99	0.08	-158.8	1,400	128	1,069	May-99	0.4	37.1	1.6	176	94
Aug-99	0.12	-167.4	1,110	250	2,115	Aug-99	0.52	-60.4	1.7	162	122
Sep-99	0.05	-309.2	814	134	3,651	Sep-99	1.11	-58.3	1.8	74.6	200
Oct-99	0.07	-194.8	1,180	156	2,937	Oct-99	0.29	129.3	1.6	39.6	122
Nov-99	0.25	-253.0	1,600	104	2,274	Nov-99	0.39	-14.9	<5	16.8	84
Dec-99	0.8	-198.6	1,430	56.6	2,332	Dec-99	0.27	134.5	2.6	104	189
Feb-00	0.29	-261.8		39.1	2,292	Feb-00	0.6	-76.1	1.6	20.9	157

not detected at this up-gradient location. Background groundwater contained low levels of some electron acceptors: non detectable levels of nitrate; < 1 mg/l of iron and manganese; and carbon dioxide concentrations of 9.7 mg/l. Ethene and ethane, the final products of reductive dechlorination of PCE were nondetect (< 5 nanograms per liter [ng/l]) in up-gradient groundwater.

The baseline biogeochemical environment in the pilot test area was transitional: DO levels indicated anaerobic conditions in two of the three pilot test wells, while ORP levels were in the +19 to +160 mV range. Total VOCs in this portion of the plume ranged from 1 to 813 µg/l. The only PCE degradation product detected was TCE in two of the three pilot test wells. Levels of ethene and ethane were low and not significantly above background, indicating that little natural reductive dechlorination was ongoing in this portion of the plume.

The pilot test wells showed a significant increase in the amount of nitrate in the groundwater during the baseline sampling event, which could also be a result of lawn watering (and fertilizer). Detectable concentrations of ammonia and the most elevated level of dissolved nitrogen detected during the initial baseline assessment at the site were also identified in this area, suggesting that some of the nitrate is being reduced in this area. ORP measurements suggest that the environment may be favorable for denitrification.

### *Pilot Study*

Wells associated with the pilot test are shown on Figure 29. Reagent injections were initiated in October 1998. Approximately 200 gallons of reagent was initially injected under pressure on a weekly basis and consisted of a 10:1 ratio of molasses to water. Molasses was used as the electron donor due to its relatively low cost (\$0.30/lb), high organic carbon content (approximately 60 percent by weight), and its ability to create a strong reducing environment in a short time period (as opposed to some other electron donors delivery techniques that rely on dissolution and diffusion). The frequency of injection was modified to biweekly in May 1999, and the ratio of molasses to water varied from a 10:1 to 20:1 ratio based on the performance monitoring performed during the pilot test. The reagent was injected under pressure (up to 30 psi) for a more thorough distribution into the bedrock aquifer system. Parameters associated with the performance monitoring focused on PCE and associated degradation products, DO, ORP, TOC, and ethene.

Performance monitoring was initiated in December 1998, approximately two months after commencement of the pilot test to monitor the development of the IRZ. Initial performance monitoring events focused on field parameters (primarily DO and ORP) and measuring TOC concentrations in groundwater. VOC monitoring was initiated after a TOC gradient had been established within groundwater in the pilot test area.

During the December 1998 performance monitoring event, anaerobic and reducing conditions had been established in the injection well and first down-gradient monitoring well (MW-1). TOC concentrations had significantly increased in the injection well, but little change in TOC concentrations were observed in the two

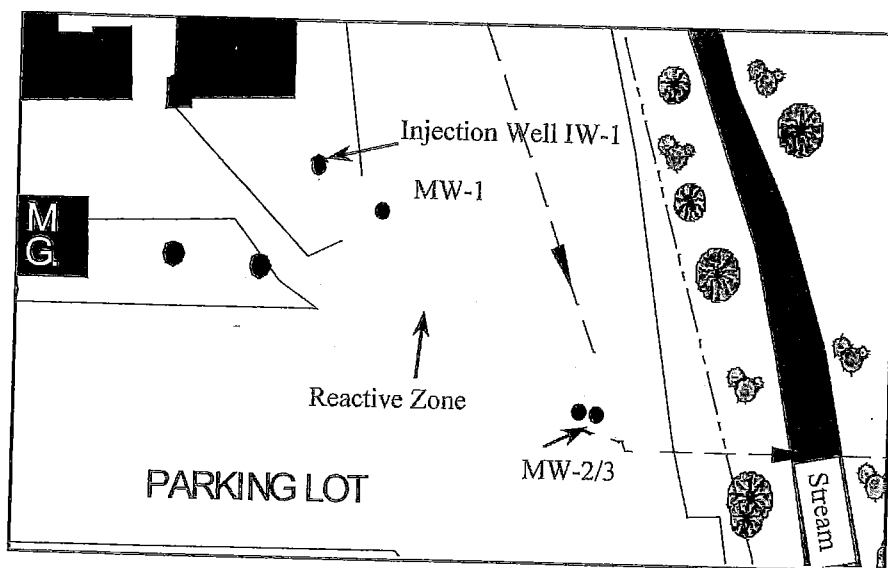


Figure 29 Case Study 3: pilot test area.

down-gradient wells. Little change was observed in the farthest down-gradient monitoring well (MW-2).

In January 1999, the injection well was deepened by 10 feet (3 meters) to encounter a more highly fractured bedrock zone, and increase the ability to deliver the reagent to the more impacted portion of the aquifer.

VOC concentrations in MW-1 significantly increased (PCE = 400  $\mu\text{g/l}$ , TCE = 40  $\mu\text{g/l}$ , and cis-1,2-DCE = 22  $\mu\text{g/l}$ ). This increase was due to a biological surfactant effect resulting from the increased microbial activity of the expanding microbial community. Reductive dechlorination was reducing an increased amount of TCE to cis-1,2-DCE, but increased rates of the reductive dechlorination of PCE to TCE were not occurring. The ratio of PCE to TCE during the background sampling event was 9:1; this ratio was 10:1 in February 1999, presumably due to natural surfactants. The ratio of PCE to TCE was 85:1 during the background sampling event, and this ratio was 18:1 during the initial surfactant effect. The increased degradation of TCE to DCE was due to the anaerobic and reducing conditions that had been established in the area of the well. However, significantly increased rates for the complete reductive dechlorination of PCE to ethene could not occur since the electron donor (carbon) injected in IW-1 had not reached this down-gradient location.

TOC concentrations continued to increase and the more strongly anaerobic and reducing conditions necessary for increased attenuation rates via reductive dechlorination were established in MW-1 through March 1999. Anaerobic and reducing conditions were present in IW-1, MW-1, and MW-3 during the April 1999 monitoring event, and aerobic and oxidizing conditions continued in MW-2. MW-3 is located adjacent to MW-2, and has a deeper open borehole interval. Monitoring was initiated in MW-3 since anaerobic and reducing conditions had not been observed in MW-2.

Elevated TOC concentrations continued to be present in the injection well (> 3,000 mg/l), and increased TOC concentrations (469 mg/l) were observed in down-gradient MW-1. PCE concentrations in MW-1 had been reduced from 400 µg/l to 101 µg/l. The reduced concentration was due to increased reductive dechlorination due to the availability of electron donor, and the ratio of PCE to TCE and DCE has also improved. The ratio of PCE to TCE was 4:1, and the ratio of DCE to PCE was 1.4:1. The most significant evidence for the increased rate of reductive dechlorination was the ethene data. Baseline concentrations in MW-1 for ethene were 12 nanograms per liter (ng/l). Ethene was detected at 408 ng/l during the April 1999 sampling event. Anaerobic and reducing conditions were present in MW-3 and ethene concentrations were also higher than background conditions (92 ng/l).

Subsequent monitoring events performed between May 1999 and February 2000 have indicated that the anaerobic and reducing conditions present in IW-1, MW-1, and MW-3 have been maintained, and TOC concentrations in MW-1 have continued to increase. PCE and associated degradation products have continued to decline in MW-1. These declines are due to reductive dechlorination since significant increases in the concentration of ethene have been observed throughout this same time period.

Increased TOC concentrations have not been observed in MW-3. This appears due to the increased rates of microbial activity up-gradient of these wells. However, PCE concentrations in MW-3 continue to decline after a slight biological surfactant effect was observed in May 1999, and ethene concentrations continue to be more elevated than background conditions. PCE, cis-1,2-DCE, and ethene concentrations for MW-1 and MW-3 are shown on Figures 30 and 31, respectively.

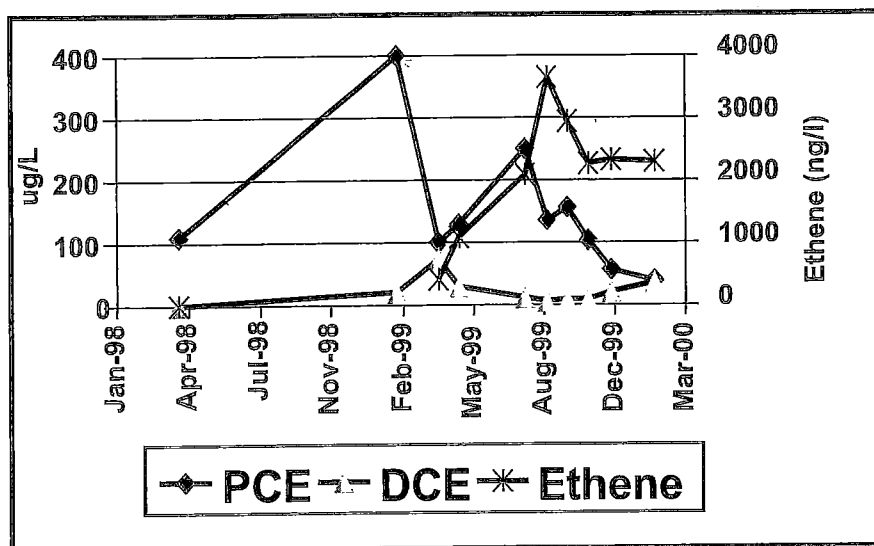


Figure 30 Case Study 3: MW-1 data.



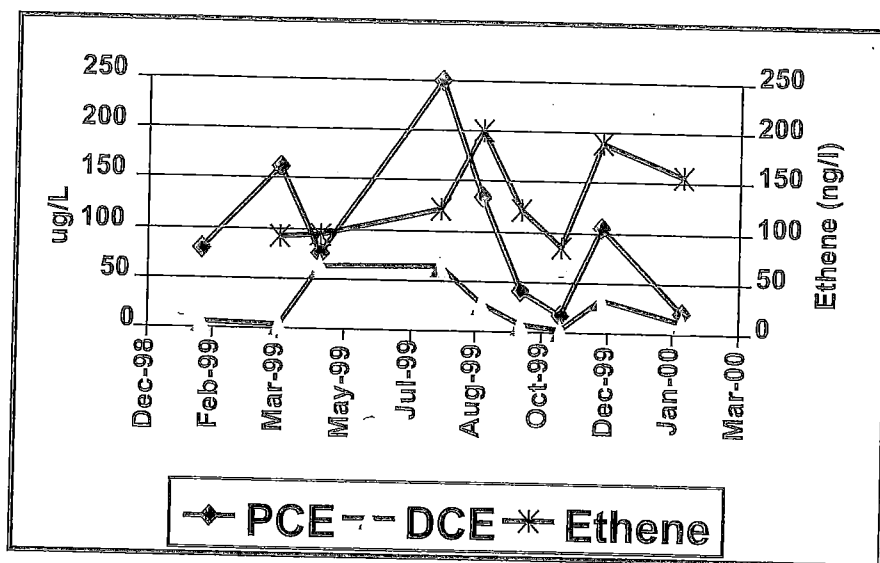


Figure 31 Case Study 3: MW-3 data.

### Bulk Attenuation Rates

The rate by which a dissolved constituent attenuates at a particular site can be estimated through first order kinetics. It is important to note that the calculation of attenuation rates are only approximations of the complex processes that are occurring in nature. It should further be noted that the attenuation rates presented in this section consist of the effects of both destructive (biotic attenuation) and nondestructive (dilution) mechanisms. Based on the minimal volume of reagent delivered to the aquifer, and the increases in degradation daughter products that have been observed at the site, the lowering of PCE mass that has been observed is believed to be affected minimally by dilution.

PCE concentrations versus time from August 1999 to February 2000 are plotted on Figure 32. A trendline for the exponential regression of PCE is also presented. The equation describing the exponential regression is posted on the plot. This is the equation describing the exponential regression, where the first order attenuation constant ( $k$ ) is  $-0.0099$  and  $x$  represents time in days. The correlation coefficient ( $R^2$ ) is also presented. Regressions with values of  $R^2$  at and above 0.8 are generally considered to be useful.

Based on an attenuation constant ( $k$ ) of  $-0.0099$ , the half-life for PCE is 70 days. This is significant due to the stable nature of the plume prior to the pilot test (little degradation) and in light of published half-lives for PCE in groundwater that range from 1 to 2 years (Howard et al. 1991).

The results of the pilot test demonstrate that the rate of reductive dechlorination in the bedrock aquifer was enhanced by the reagent injections associated with the reactive zone. The increased concentration of organic carbon quickly established the anaerobic and reducing conditions necessary for the complete degradation of PCE

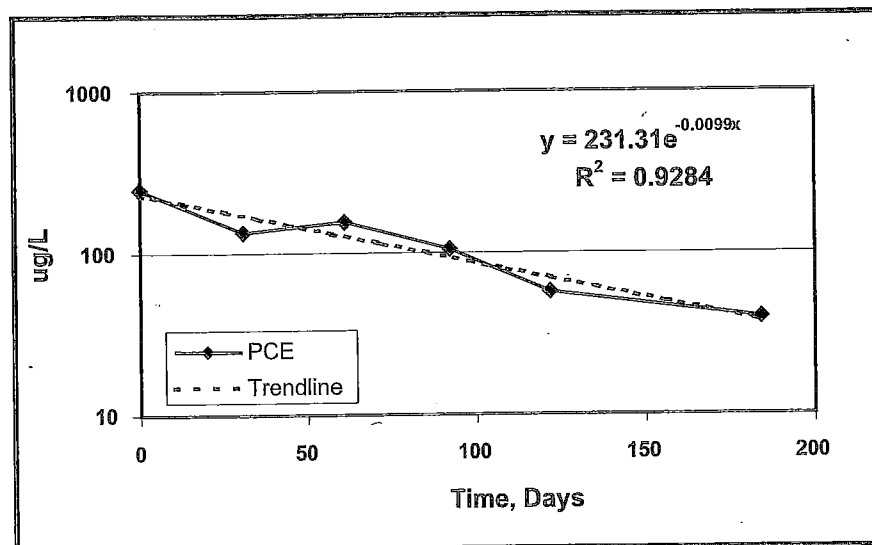


Figure 32 Case Study 3: reactive zone PCE degradation curve.

to ethene in the injection well. The anaerobic and reducing conditions migrated from the injection well to a well located approximately 240 feet down-gradient (MW-3). After initial desorption of PCE (presumably from a biological surfactant effect), PCE concentrations in the down-gradient wells have declined to concentrations significantly below the equilibrium conditions present prior to initiation of the pilot test. This is considered significant due to the elevated levels of ethene concurrently measured during the test.

The amount of time necessary to observe a significant reduction in overall source mass indicates some conditioning of the microbial population was necessary to enhance the natural degradation mechanisms. However, bioaugmentation was not necessary to provide the microbial populations to the bedrock groundwater environment, demonstrating that the microbial populations in bedrock at this site were ubiquitous.

A full-scale bioremediation treatment system was installed at the site during the first quarter of 2000. The reactive zone technology is also currently being evaluated in the source area (PCE concentration > 10,000 µg/l). The success of the bioremediation program has allowed for the discontinuation of groundwater extraction from some site wells, and will allow groundwater extraction to eventually be phased out for the site. This will result in a significantly more cost effective groundwater remedy for the treatment of chlorinated VOCs in bedrock groundwater at this site compared to traditional alternatives, limitations and lessons learned.

### Limitations

As with any technology there are limitations to reactive zones. Although this approach represents one of the most cost effective ways of addressing impacts in

*situ*, it still has limitations. The most important limitation is one suffered by all *in situ* technologies, the geologic conditions in which it must be applied. From the issue of variable lithologic units, to the difficulty in accurately defining the true variability in subsurface conditions, reactive zones are influenced by the nature of the geology in which it is implemented. For this reason, it is critical to define the geologic conditions as accurately as possible before applying a reactive zone. The most important issues were discussed in previous sections of this chapter, but three bear mentioning again.

1. Groundwater flow direction is so basic that sometimes its accurate definition can be overlooked, often to disastrous results. If the flow direction is not accurate, monitoring wells in a pilot study may be misplaced providing little or no data, or providing data that indicates that the process has failed, when in reality it has succeeded.
2. Groundwater flow velocity is critical to the selection and application of reagent feed rates, injection well locations, reagent selection, and monitoring frequency. Low groundwater velocity can lead to the development of uncontrolled fermentation, reduced pH, and the production of undesirable intermediates, such as alcohols, ketones, and mercaptans. High groundwater velocities can preclude the use of reducing reactive zones, by making the carbon demand so great to maintain the reactive zone that the injection rates and reagent requirements may no longer be cost effective.
3. The definition of the lithology and/or variability of permeability within the target zone impacts the well depths, screen locations, well design, and system capital costs. If the geology is not well defined, the reagent may be delivered to the wrong zone, or monitoring wells may be placed in zones where the reagent is not effectively being placed, leading to overfeeding of the reagent, based on poor data.

The variety of reagents available, the amount of testing conducted using any particular single reagent, and the regulatory hurdles associated with injecting foreign agents into groundwater are all issues that impact the applicability of this technique. These issues include public perception—a concern sometimes raised is the potential of creating a mutant super bug—which must be addressed anytime something is added to the environment.

Permitting requirements are another, often complicated, hurdle to clear. Most injection permits have been developed for waste disposal in deep injection wells, or for treated water being discharged to groundwater systems. These same permit programs are being applied to shallow injections of food-grade agents, many of which most people can find in their pantries at home. States have performed admirably in adjusting to the needs of reactive zones applications, by interpreting the existing permit programs to fit the needs of *in situ* reactive zones.

Coupling these issues with the typical issues of COC chemistry (degradability, solubility, volatility, DNAPL), groundwater chemistry (redox conditions, pH, buffering capacity) and microbiological factors (survivability, surfactant effects, nutrients, scavengers) makes reactive zones anything but a slam-dunk.

Listed below are several "lessons-learned rules" developed over the course of applying reducing reactive zones at more than three dozen sites. While they do not cover all the issues, they serve as a checklist of what to watch for:

- Rule #1.** Bacteria will utilize the easiest forms of carbon available to them; therefore, if they are successfully degrading BTEX and creating the necessary reducing conditions to co-metabolize CAHs, think twice before interrupting a good thing by giving the microbial population "candy" before they finish there "meal". By adding an easily degradable source of carbon (lactate, sucrose, etc.) the active degradation of COCs that are naturally serving as a primary substrate may be slowed. (Corollary to Rule #1: The best targets for reactive zones are plumes that have burned out their carbon source.)
- Rule #2.** Reactive zones should be used for VOCs when there are already indications of degradation. The remediation engineer should take cues from nature and enhance the natural processes whenever possible.
- Rule #3.** The microbial populations that are actively creating the reducing reactive zones are producing materials (surfactants) that can desorb mass from the soil matrix. This is necessary for the bacteria to metabolize the organics, but can result in some unwanted changes in plume character. In particular, COC concentration spikes should be anticipated and the disruption of plume equilibrium planned for. Surfactant effects can be detrimental without proper down-gradient control on the COC plume.
- Rule #4.** Plan for the byproducts of enhanced bacterial activity, namely the possibility of increases in methane, hydrogen sulfide, carbon dioxide, and COC vapors. Left unmonitored and uncontrolled these byproducts can lead to aesthetic nuisances (mercaptans, sulfide), explosive hazards (methane), and human health hazards (VC, hydrogen sulfide accumulation).

The treatment of DNAPL using reactive zones is a young and growing area of research and field application. The difficulty with using reducing reactive zones for DNAPL treatment is related to the need to make the target compound available to be impacted by the microbial population. In order to be degraded, the target COC must be dissolved in the groundwater. Thus it is necessary for the surfactants produced by the bacteria to dissolve the free-phase first. This is not a problem when the total mass of the DNAPL is small. This would be the case for DNAPL found in the form of residual DNAPL. However, when large pools of DNAPL are present, the process will be limited by the rate that the bacterial surfactants can interact with the DNAPL. Two problems can occur under these conditions. First, the CAH released from the DNAPL by the surfactants can cause a spike in the CAH concentration. Even though the process is removing mass from the site, the data shows an increase in concentration. This can be hard to explain to some regulators. Second, the process can take a long time. Due to the large mass of CAHs present in the form of the DNAPL, the reduction process will have to work a long time to eliminate all of the CAHs. Since we can only measure CAH concentration in the groundwater, progress will not be measurable. Once again, this can be hard to explain to a regulator, not to mention the client that provided the money for the IRZ effort.

## CLOSING

The fact remains that despite the hurdles listed above, reactive zones are rapidly becoming commonplace and, in many instances, replacing conventional remedial approaches. These applications are having the result of shortening the total time that it takes to complete a remediation project. Reactive zones are being applied in more varied environments—bedrock geology, high and low permeability unconsolidated geologic conditions—to treat a wider spectrum of compounds—CAHs, HOPs, PAHs, PCBs, perchlorates—and in multiple medias—groundwater, soil and sediments. Additional enhancements are also being investigated, such as the use of biodegradable surfactants, operating reactive zones in series, and the addition of reducing reagents in combination with other reductive processes such as zero-valent iron.

As stated in the beginning of this chapter, the elegance of reactive zones is embodied in the application of the technique to enhance natural conditions in order to speed up natural processes, thus taking advantage of nature's natural cleansing processes. The more the remedial engineer can enhance ongoing processes, the less the effort and time that will be needed to achieve the remedial goals.

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## CHAPTER 11

# Permeable Treatment Barriers

Peter L. Palmer

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## INTRODUCTION

Permeable treatment barriers are an innovative technology that show a lot of promise for remediating shallow groundwater plumes. In principle, a permeable treatment barrier (also referred to as permeable reactive barriers) containing the appropriate treatment material is placed across the path of a contaminant plume. As contaminated groundwater moves through the barrier, the contaminants are removed or degraded, allowing uncontaminated water to continue its natural course through the flow system. Much of the early work on permeable treatment barriers has been performed by the Waterloo Center for Groundwater Research, University of Waterloo. Their work focused primarily on the use of a reactive material, zero-valent granular iron, to degrade halogenated organic compounds in groundwater. Although much of the focus on permeable treatment barriers today is on the application of zero-valent iron, some of the concepts developed have been applied to permeable treatment barriers that use media other than zero-valent iron to remediate impacted groundwater. A summary of early developments using zero-valent iron as permeable treatment barriers has been compiled by Gillham and Burris (1994). More recent developments, including application of zero-valent iron for remediating chlorinated solvents as well as other constituents including metals, inorganics, nutrients, and radionuclides have been compiled by the Environmental Protection Agency (EPA 1999).

Permeable treatment barriers are gaining a lot of attention not necessarily because they speed up the remediation process, but because they recognize the limitations of groundwater cleanup programs and factor these limitations into minimizing the lifecycle costs of remedial programs. Permeable treatment barriers generally rely on the natural movement of water to carry the contaminants through the treatment barrier where they are removed or degraded. By doing so, permeable treatment barriers eliminate or at least minimize mechanical systems, thus minimizing long-term operation and maintenance costs that so often drive up the lifecycle costs of remedial projects. Long-term operation and maintenance costs are reduced because the site generally does not need a continuous input in energy and manpower. Failures due to mechanical breakdowns are also reduced. In addition, technical and regulatory issues concerning discharge of treated groundwater are avoided or minimized.

This chapter will focus on concepts, applications, and methodologies for installing and using permeable treatment barriers in remedial programs.

## DESIGN CONCEPTS

Permeable treatment barrier systems generally rely on groundwater to carry the contaminant to the barrier where it is removed or degraded. Since the vast majority of permeable treatment barriers rely on natural groundwater flow, the focus of this section on design concepts will be on these types of systems. Permeable treatment barriers can be constructed of a variety of materials or use natural geology. The system area can be used to create chemical or biochemical reactions or simply to facilitate a process to remove the contaminant. In its simplest form, the treatment

barrier is similar to that shown in plan view in Figure 1 and in cross section in Figure 2. As the reader can see in these figures, a plume is migrating down-gradient from a source and an *in situ* permeable barrier is present to remediate the plume constituents *in situ*. For example, if the plume contained VOCs, the treatment barrier could be a series of air sparging points, which would introduce air into the plume and rely on the air to carry the contaminants vertically for release to the atmosphere or for capture by a vapor extraction system. This design could be used for degradable

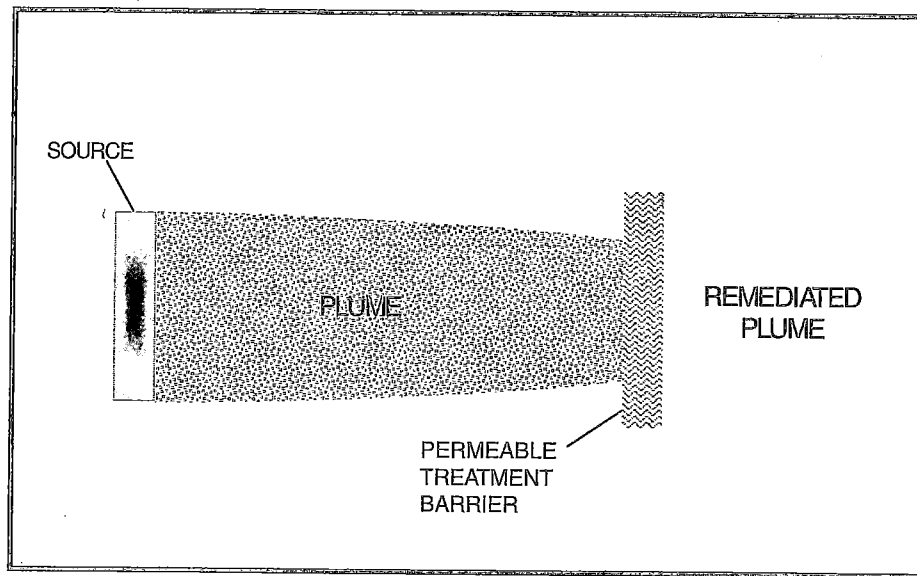


Figure 1 Plan view of permeable treatment barrier.

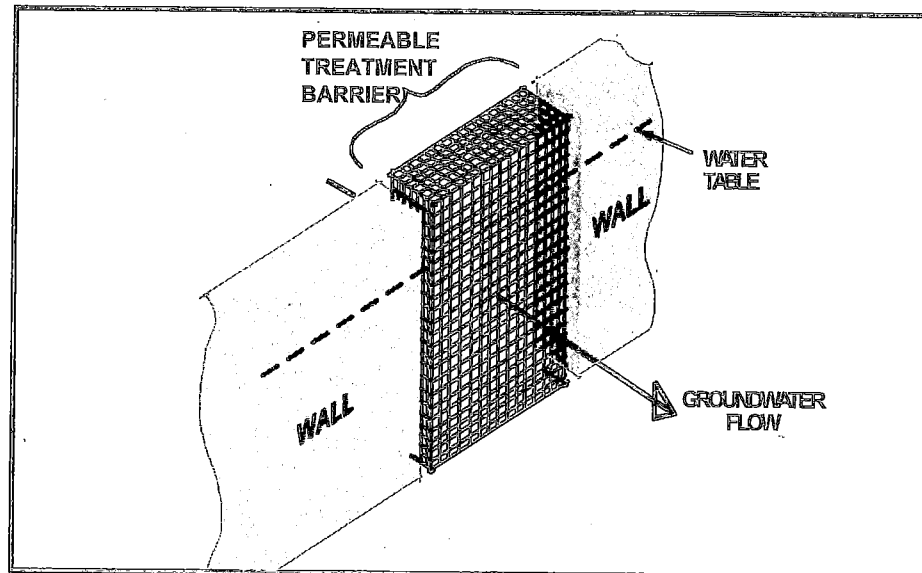
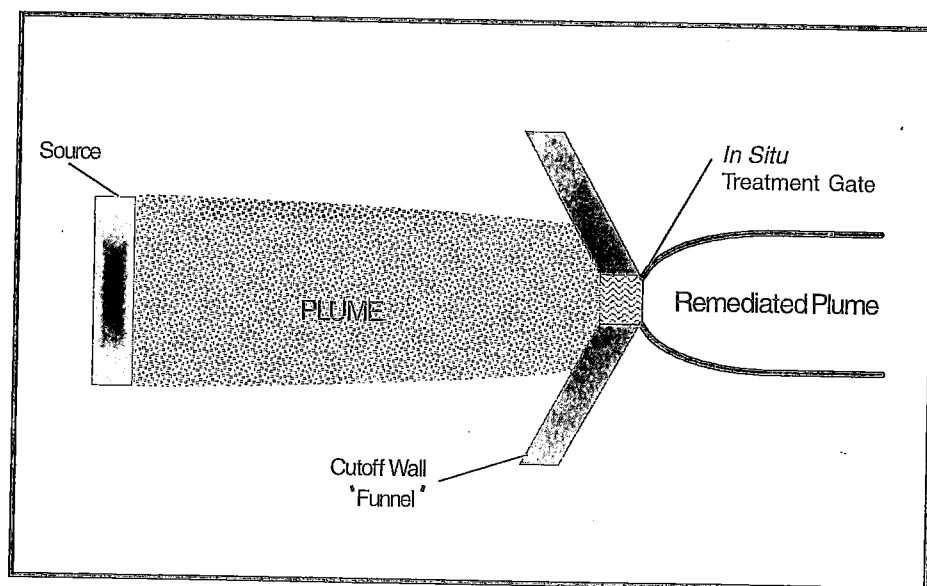


Figure 2 Cross section of permeable treatment barrier.

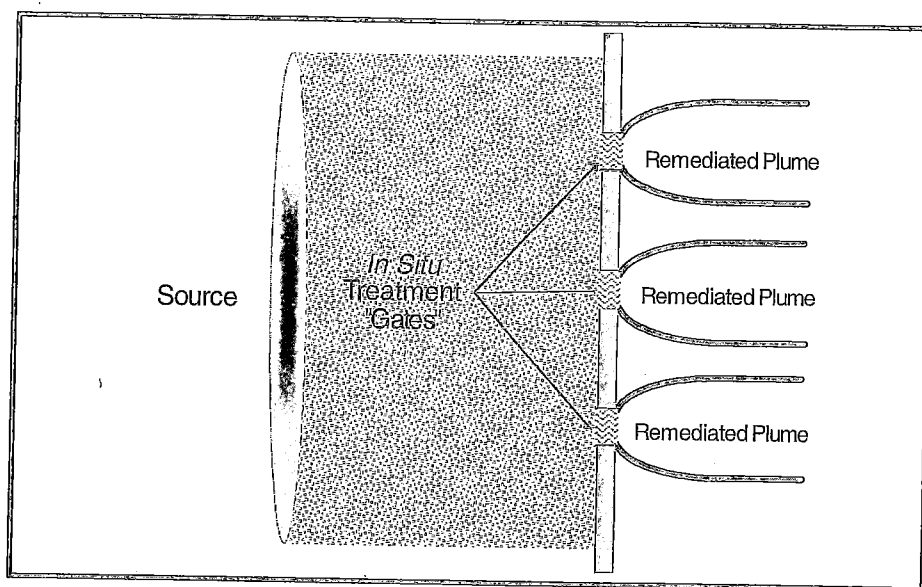
organics (oxygen transfer for the natural bacteria to degrade the compounds) or nondegradable volatile organics (air carrier to remove the compounds). This simple design would only be viable in geology that could facilitate air sparging.

Many times the geology prevents the application of a technology, or we need to add treatment material to the barrier. In these cases, we must remove the natural geology and create a permeable barrier out of the required material. To continue with the above example, if the native materials are low permeable sediments, then an additional purpose of the permeable barrier could be to change the geology by excavating the native material and back filling with more porous material which would be amenable to air sparging. Another method that is more widely applied for chlorinated hydrocarbons is the use of zero-valent iron to dehalogenate the compounds. In the above example, the natural geology would be removed so that zero-valent granular iron could be placed into the path of the groundwater. There are a number of ways that this could be achieved in order to minimize construction costs, and these are discussed later in this chapter.

To successfully remediate a plume, a permeable treatment barrier must be large enough to remediate the entire plume. For large or deep plumes this becomes impractical. To overcome this problem for large shallow plumes, a system can be installed consisting of low-permeability barriers, which funnel flow to a smaller permeable treatment barrier (referred to as a gate) to treat the plume (Figure 3). This concept was developed by the University of Waterloo and is referred to as the Funnel-and-Gate System™. There are a number of combinations/configurations that can be used to effectively control and remediate a plume (Starr and Cherry 1993). For instance, Figure 3 shows a single gate system, and Figure 4 shows a system consisting of three gates. When dealing with funnel and gate systems, in all cases, the sole purpose is to use the gate to pass contaminated groundwater through the treatment



**Figure 3** Funnel-and-Gate System™ using a single gate.

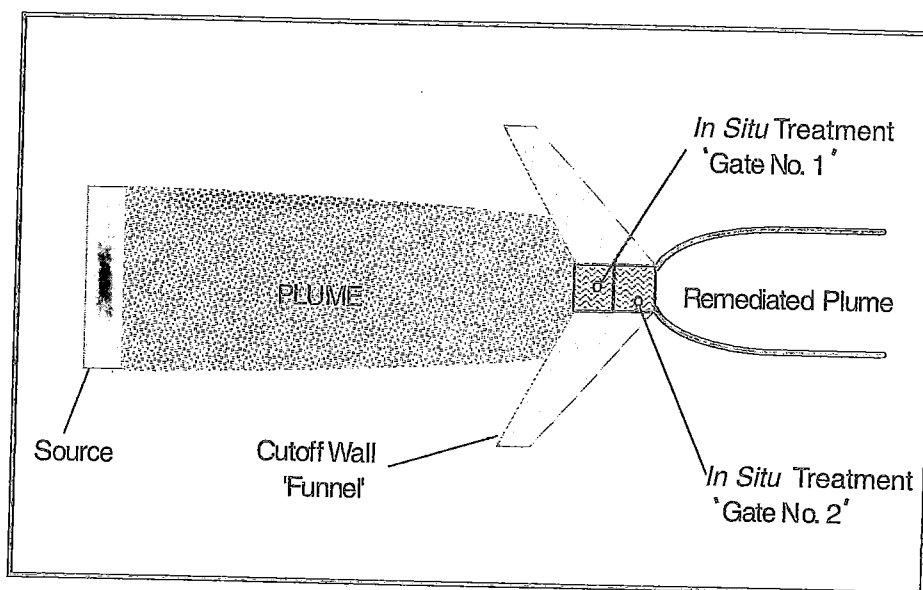


**Figure 4** Funnel-and-Gate System™ using multiple gates.

barrier that remediates the groundwater. The funnel is integrated into the system to force water through the gates and is used for practical and economic reasons. Slurry walls, sheet piling, and other materials which could form the funnel are often easier and/or more economical to install than the treatment barrier. Consequently, the design is focused on balancing the ratio of funnel to gate areas to achieve remedial objectives at the least cost. It must be remembered that groundwater travels at a relatively low speed. Therefore, the residence time in the reactive portion of the treatment barrier (gate) can be significant even when the treatment portion of the barrier is not continuous.

Conceptually, plumes with a mixture of contaminants can be funneled through a gate with multiple treatment barriers in series. For instance, one treatment barrier could be used for degrading hydrocarbons and a second treatment barrier in series could be used for precipitating metals. This concept is illustrated in Figure 5. In addition, if the gate needs to be removed at some point during or after remediation such as the case with sorption processes (activated carbon, ion exchange, etc.), then considerations should be given to installing a retrievable treatment barrier. These could take the form of different shapes, but they would each have sufficient permeability to allow migration of groundwater through the container holding the reactive material, and the container would have sufficient strength to maintain its shape and structural integrity during placement and removal.

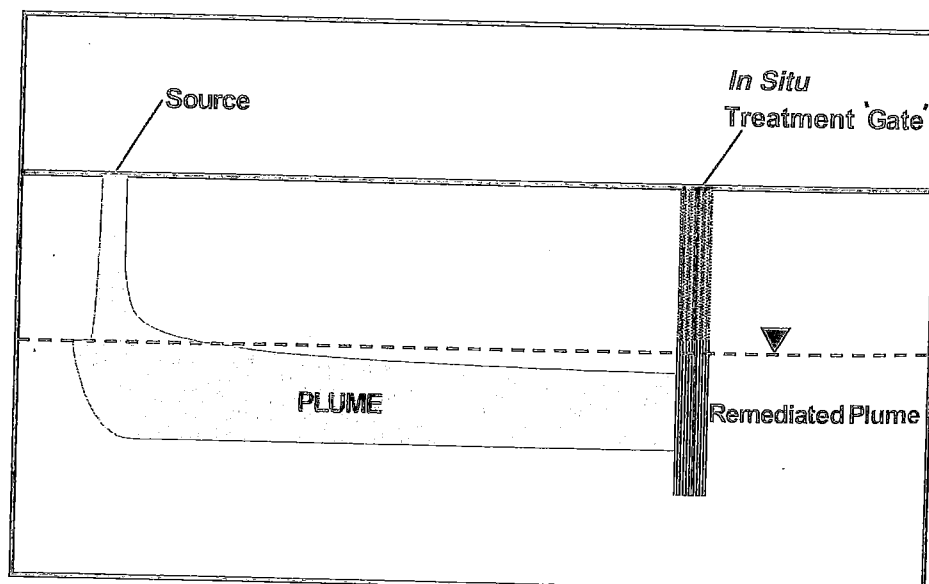
There are numerous nuances when installing a treatment barrier. For instance, Figure 6 shows a treatment barrier designed to remediate a shallow plume that is located in the uppermost portion of the aquifer. Since the plume remains shallow, the treatment barrier does not need to penetrate the entire thickness of the aquifer and is referred to as a hanging barrier (gate). In situations where a hanging barrier is under consideration, it is important to understand contaminant transport to ensure



**Figure 5** Funnel-and-Gate System™ using gates in series.

that the contaminants remain in the upper portion of the aquifer even after the subsurface is disturbed as a result of installation of the treatment barrier. If the barrier has a higher resistance to flow than the original geology, then the groundwater may flow around it and no treatment will occur.

In other cases where the saturated thickness is relatively thin compared to the overall aquifer thickness, a buried treatment barrier may be used. In these applica-



**Figure 6** A hanging gate system for remediating shallow plumes.

tions, the treatment barrier is limited in height to that portion of the zone in which groundwater is moving. A low permeable barrier, usually a synthetic liner, can be placed above the treatment barrier as a precaution to ensure that groundwater flow over the permeable treatment barrier does not occur.

Geosiphons are now being used to entice groundwater to move through a permeable treatment barrier. This is a relatively new application and is somewhat limited in that it requires that the hydraulic head between the contaminant plume and a discharge point be significantly different. The discharge point could be a surface water body at lower elevation, or it could be an underlying confined aquifer with a lower potentiometric surface. Geosiphon<sup>TM</sup> technology was developed at the DOE Savannah River Technology Center. This technology consists of a large diameter vertical well that is designed either with, (1) a gravel pack containing material that will degrade or absorb contaminants (for applications where treated groundwater is discharged above-ground), or (2) wells with removable, flow-through, permeable treatment barrier canisters (for discharges to underlying aquifers) that are positioned between the upper and lower well screens (Phifer et al. 1999).

### **Installation Methodologies**

There are a number of methodologies for installing permeable treatment barriers including continuous trenching, excavation and backfilling, overlapping caissons, soil mixing, and hydrofracturing. Each of these is discussed in more detail below.

#### ***Continuous Trenching***

Continuous trenching is generally used when placing a permeable treatment barrier across the entire length of a plume. Specialized equipment is used to remove the soil from the trench and replace it with the treatment material in one pass. This has some obvious advantages in that the equipment itself keeps the side walls of the trench open until the treatment material is in place. Continuous trenching is normally applied to depths of less than 20 feet.

#### ***Excavation and Backfilling***

Excavation and backfilling is normally used for installing funnel and gate configurations. The funnel is installed via one of two methods. The first method is to construct a slurry wall as the funnel. A slurry wall is constructed by using a backhoe to dig a trench down to the desired depth and to stabilize the side walls of the trench with a bentonite slurry mixture. As the trench is dug, the bentonite slurry is pumped in to maintain a positive head on the side walls and to act as a sealant to prevent groundwater from moving into the trench and undermining its stability. As trenching progresses, the soil removed from the trenching is mixed in with bentonite ( $\pm$  5 percent) at land surface and placed back into the trench. Care must be taken to ensure adequate mixing of the bentonite with the soils removed so that the desired hydraulic conductivity is achieved throughout the length of the slurry wall.

The other method used to construct the funnel is to use a traditional system of sheet piles driven along the length of the funnel. The sheet piles are installed using a vibratory or pneumatic hammer to the desired depth. For this type of application, special sheet piling with interlocking and sealable joints are available. This helps ensure that the funnel is leak proof and will effectively direct the flow of groundwater for treatment in the gate.

To construct the gate, several methods are also available. The most widely used method involves digging an open trench with a backhoe and stabilizing the side walls until after the trench has been backfilled with permeable and/or treatment material. Similar to the funnel installation methods, traditional methodologies such as steel sheet piling can be used. In this application, two rows of sheet piling are driven to the desired depth with a vibratory or pneumatic hammer, and the soil between them excavated. After placement of the treatment material, the sheet piling is removed. Biodegradable polymer slurry such as guar gum, which has been used in drilling water wells for decades, can also be used to stabilize the excavation. Similar to a slurry wall, during barrier construction the biodegraded slurry would provide physical support to stabilize the trench walls until the treatment material is in place. Where it differs from a slurry wall is that after barrier completion, the polymer is flushed out. Any material remaining should biodegrade over a short period of time. This method is generally applied to depths up to about 50 feet. It should be determined beforehand that the treatment material and polymer are compatible; otherwise, the polymer could degrade too quickly, which could cause the side walls to collapse prematurely.

### ***Steel Caissons***

Overlapping steel caissons are also used in some applications. Under the right conditions, steel caissons could be installed to depths up to 100 feet. Similar to steel sheet pilings, the caissons are driven or vibrated down to the desired depth, and the soil within them is removed with an auger and replaced with the treatment material. The caissons are then withdrawn. Steel caissons do not require the bracings that are needed between steel sheet pilings, and the selection of the preferred methods would probably be based upon site constraints (available space, proximity to structures whose foundations could be sensitive to displacement, etc.) and costs.

### ***Soil Mixing***

Soil mixing has been used in the environmental field primarily for *in situ* mixing of solidification/stabilization agents to physically or chemically bind the contaminants of concern (primarily metals) to minimize their mobility. For permeable treatment barriers, a similar process would be used whereby large diameter mixing augers are drilled into the subsurface and during the process, treatment barrier additives are injected through the hollow stem. This method is also good to depths of about 100 feet under the right conditions, and is desirable because soil management costs are minimized. The biggest concerns involve the ability to get complete mixing between the native soil and the treatment material. For this methodology to

be effective, the native material must have sufficient permeability and must be compatible with the treatment material. In addition, the treatment material generally must maintain its effectiveness throughout the duration of the remedial program.

### ***Hydraulic Fracturing and Permeation Infilling***

More recently, hydraulic fracturing and permeation infilling has been used. Both of these technologies are similar in that they rely on water or biodegradable polymer under pressure to place the treatment material across the path of groundwater flow. In the case of hydraulic fracturing, the technology is used to create a vertical barrier in unconsolidated sediments consisting of the treatment material, such as zero-valent granular iron. This is achieved by simultaneously creating a vertical fracture and placing the treatment material within that fracture. Orientation and depth of the fracturing is critical to ensure that a continuous treatment barrier is created. The hydraulic fracture is constructed using a series of PVC casings installed along the wall alignment and which are grouted in place and cut along the fracture orientation using a special down hole tool. A packer is then set and injection well heads attached to the packer assembly and injection hoses connected to the pumping unit. Hydraulic fracturing is then initiated using methods similar to that described in Chapter 10 (Hocking, Wells, and Ospina 1998).

Permeation infilling is used in fractured bedrock where most of the groundwater flow occurs within the fractures. The equipment that is used is similar to that used in hydraulic fracturing. In this situation the fracture already exists, so the objective is to use water and biodegradable polymer as a means to slurry the treatment material into the fractures.

## **PERMEABLE TREATMENT BARRIER PROCESSES**

There are a variety of processes that could be integrated into permeable treatment barriers including:

- Transformation processes
- Physical removal
- pH or Eh modification
- Metals precipitation
- Sorption processes
- Nutrient stimulation

Presented below is a brief description of each of these processes.

### **Transformation Processes**

Waterloo Center for Groundwater Research has conducted extensive research on the use of zero-valent metals to promote transformation of various chlorinated organic compounds. They have concentrated on using zero-valent iron to dehaloge-



nate chlorinated aliphatic organic compounds both in the laboratory and in field tests (Gillham, O'Hannesin, and Orth 1993). In the laboratory they studied various metals including stainless steel, copper, brass, aluminum, iron, and zinc using 1,1,1 TCA and found iron and zinc to be most effective. Because of lower costs and availability, they focused their follow-up tests on a range of chlorinated organic compounds using only iron.

The use of zero-valent iron to degrade chlorinated aliphatic organic compounds is an abiotic process. Studies performed by Matheson and Tratnyek (1994) suggested that direct electron transfer on the iron surface was the most probable degradation mechanism. This has since been confirmed and the reaction rates are generally considered to be directly proportional to the surface area of the iron. Studies performed by Matheson and Tratnyek (1994) and Gillham and O'Hannesin (1994) suggest that degradation is the result of two reactions. The first reaction is the corrosion of iron by water that produces ferrous iron ( $\text{Fe}^{2+}$ ), hydrogen gas ( $\text{H}_2$ ), and hydroxide ( $\text{OH}^-$ ). The second reaction is between the organic compound and the iron and again produces  $\text{Fe}^{2+}$ , along with halogen ions (such as chloride) and the nonchlorinated hydrocarbon. Two consequences of these reactions are, (1) dissolved iron is produced which can react with other compounds and precipitate on the zero-valent iron; and (2) hydroxide is formed which can cause a significant increase in pH. The effect of these by-products on the life of the zero-valent iron will be discussed later in this section.

Gillham (1996), Johnson, Sunita, and Tratnyek (1996), and Tratnyek et al. (1997) have published summary tables of reported degradation rates for common groundwater contaminants. The half-lives vary based on the compound, the source of iron, and the geochemistry of the groundwater (Gillham 1999). For chlorinated ethenes, Tratnyek et al. (1997) suggest the following half-lives: tetrachloroethylene (PCE)—20 minutes; trichloroethylene (TCE)—110 minutes; 1,1-dichloroethylene (1,1-DCE)—650 minutes; trans 1,2-dichloroethylene (t1,2-DCE)—350 minutes; cis 1,2-dichloroethylene (c1,2-DCE)—1000 minutes; and vinyl chloride (VC)—830 minutes. These rates were normalized to 1 m<sup>2</sup> of iron surface area per milliliter of solution. Gillham (1999) suggests that since surface area of commercially available iron materials varies, for design purposes for a specific site the half-lives of the contaminants present should be determined in the laboratory using the iron that will be used and the groundwater from the site.

Because the degradation process is first-order, Gillham (1999) provides a useful rule of thumb for designing zero-valent iron application: a decrease in concentration of three orders of magnitude requires 10 half-lives. For example, using the half-lives above, to reduce PCE from 1,000 ppb to 1 ppb would require a residence time of about 200 minutes. Thus if the groundwater velocity is 1 foot per day, then a wall thickness of about 2 inches would be required. Of course, factors of safety need to be considered in the design to account for the formation of degradation products, groundwater temperatures (compared to laboratory), and precipitation on the iron surface.

In 1992, the University of Waterloo commercialized using zero-valent iron in permeable treatment barrier applications by forming a company called EnvironMetal Technologies Inc., (ETI). ETI reports that more than 75 sites are in the design or

implementation stage using this technology. Since this is a new technology, long-term performance of this application is not available. Factors that would affect the long-term performance of this technology include, (1) consumption and replacement of the iron; (2) loss of activity of the iron surface; and (3) potential clogging of the pores. Clogging of the pores would increase the velocity through the wall, or even reduce the permeability such that contaminated groundwater can no longer pass through the permeable barrier. Gillham (1999) looked at each of these factors and concluded the following:

- Based on the expected rate of iron consumption, permeable barriers of only a few tens of centimeters in thickness should persist for many decades.
- Siderite ( $\text{FeCO}_3$ ), iron hydroxide ( $\text{FeOH}_2$ ), and/or magnetite ( $\text{Fe}_3\text{O}_4$ ) will likely precipitate on the iron. In addition, the increase in pH will likely cause calcium and bicarbonate dissolved in the groundwater to precipitate as calcium carbonate. For water high in calcium and with a high alkalinity, and considering the iron precipitation, annual porosity losses of as high as 2 to 5 percent could be expected. The loss in porosity would occur predominantly in the up-gradient end of the barrier.

Other constituents in the groundwater could interfere with the degradation kinetics. For instance, nitrate in solution can lower the degradation rate for TCE, most likely due to competition of reaction sites on the iron surface. Reduced degradation rates have also been observed for groundwater high in dissolved organic carbon.

The first field demonstration of this technology was at a test site at Canadian Forces Base Borden in Ontario that was initiated in 1991 and was terminated in 1996 (O'Hannesin and Gillham 1998). The treatment barrier was constructed into medium- to fine-grained sands by driving sheet piling to form a cell about 5 feet wide by 17 feet long. The barrier was formed using 22 percent iron grindings and 78 percent coarse sand by weight with a permeability greater than the native sands. The sheet piling was then removed and a plume of dissolved PCE and TCE was allowed to move through the barrier.

Over the five years that the study was conducted there was no evidence of a decline in the performance of the barrier in degrading PCE and TCE. Approximately 90 percent of the TCE and 86 percent of the PCE were removed from groundwater passing through the barrier. Figure 7 shows the maximum concentrations of TCE, PCE, and chlorides 299 days into the test. The barrier resulted in significant mass transformation of TCE and PCE, particularly within about the first 1.5 feet (5 days residence time) of the barrier. Although the barrier dehalogenated approximately 90 percent of the mass,  $\pm 10$  percent of the mass was not affected. It was concluded that had more reactive iron been used or had a greater percentage of iron been used in the iron/sand mixture, complete removal of TCE and PCE would have been achieved. The increase in pH (from 7.9 to 8.7) was less than what has been experienced at other sites (typically 9 to 10) which was believed to be due to the buffering effect of the sand. Core samples from the barrier were collected periodically during the study. These were taken at an angle such that a cross section of the barrier could be obtained. It was concluded that although precipitates were forming, only minor

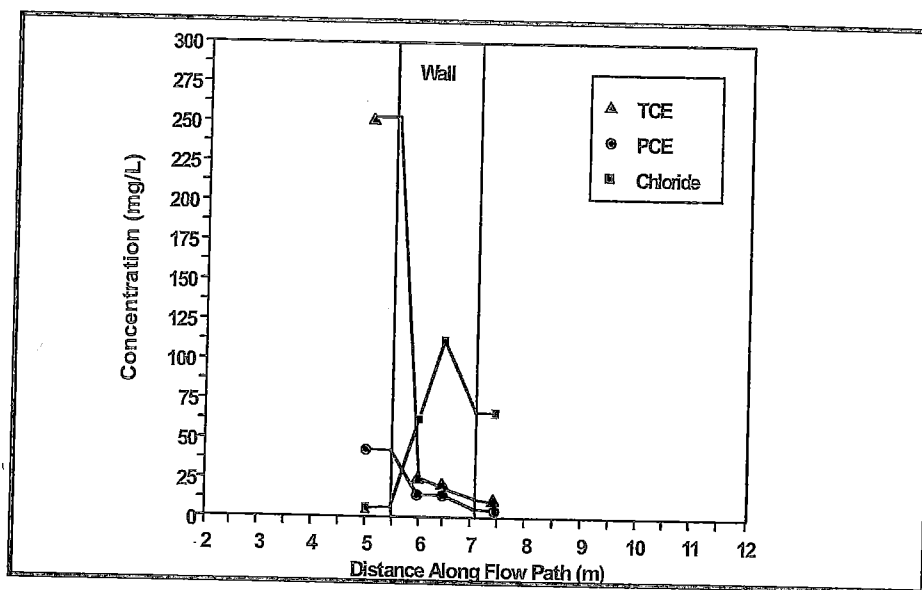


Figure 7 Concentrations of chlorinated compounds across the *in situ* treatment wall.

changes (believed to be iron oxide) in the up-gradient few millimeters of the barrier occurred.

EPA has compiled information on a number of sites using this technology (EPA 1999). Review of this document indicates that most if not all of the applications for the chlorinated aliphatic hydrocarbons are performing well with good contaminant degradation. Some problems have been encountered. At some sites the groundwater flow direction has varied or changed direction from that designed for. In other cases, an increase in groundwater levels up-gradient of the barrier has resulted in migration of contaminated groundwater around or beneath the barrier. As with any remedial technology, it is important to have a good understanding of the hydrogeologic and hydrogeochemical conditions in the contaminant zone so that these factors are well understood during the design phase. Some flexibility is also required in the design, in case the groundwater flow conditions change over the operational life of the treatment barrier.

At the Caldwell Trucking site in New Jersey, a permeable treatment barrier was installed in unconsolidated sands and a fractured basalt. The hydrofrac and infilling methodology was selected to form the treatment barrier, in part due to the depth of the plume (50 feet). The treatment barrier contains zero-valent iron and began at a depth of 15 feet. It consists of two 3 inch thick permeable barriers, 150 and 90 feet in length. The 150 foot barrier was constructed into the unconsolidated zone by using 15 hydrofrac/infilling wells at 15 foot intervals to emplace zero-valent iron using vertical hydrofracture technology. The barrier in the lower fractured bedrock was constructed by pumping guar gum containing zero-valent iron through an open borehole (referred to as infilling). Although there were some difficulties initially in the enzymatic degradation of the guar gum, the guar gum has not interfered with the barrier's permeability nor impacted the iron's reactivity (EPA 1999).

### Physical Removal

The best example of physical removal was discussed earlier, whereby air is used to physically remove VOCs from groundwater. This is an adaptation of air sparging; however, it differs in that in a treatment wall, the geology is changed to increase soil permeability, in order to make sparging applicable. Using the funnel and gate concept, a funnel would be constructed to direct groundwater flow to a gate and the gate would consist of materials more permeable than the native material with air sparging points placed within to remove the VOCs from the groundwater.

A pilot scale test using this type of application was performed at the East Garrington gas plant in Alberta, Canada. The target compounds were benzene, toluene, ethylbenzene, and xylene (BTEX). Air sparging was the preferred technology for remediation; however, the BTEX was located in a low hydraulic conductivity glacial till at shallow depth. To overcome the geology limitation, two 145 foot long trenches were dug and backfilled with pea gravel. Air sparging was then performed within these trenches with good results (EPA 1999).

### Modify pH or Eh Conditions

Modification of pH conditions occurs when the pH in the contaminant plume is raised or lowered. The main use of this application to date has been to precipitate dissolved metals in a plume. However, this technology could also be used as part of a multiple barrier application. The first barrier could be used to create the necessary environment for the reaction in the second barrier. A biological reaction zone may require a prebarrier to adjust the pH into a range in which the bacteria may grow. While organic destruction would be the main purpose of the design, the pH would have to be modified before the bacterial reaction could occur.

The main use of this application is for metal removal. For instance, at an abandoned mine site in the west, a plume of groundwater with a pH less than 3.0 was discharging elevated concentrations of copper and zinc to surface waters. To solve the problem, a permeable treatment barrier was installed adjacent to the seepage face of the plume. The barrier was designed to increase the pH of acidic groundwater by conveying the groundwater through a limestone bed. As a result of the increase in the pH, metal hydroxides precipitated, and the metals were removed from the groundwater. This was designed to have a contact time of one hour and has successfully operated for several years.

Similarly, a permeable treatment barrier was installed at the Tonolli Superfund Site in Pennsylvania. The barrier was designed to remediate lead, cadmium, arsenic, zinc, and copper. The barrier was constructed by using the continuous trench method. It was approximately 3 feet wide, 20 feet deep, and 1,100 feet long, and was backfilled with limestone (EPA 1999).

Modification of Eh involves the exchange of electrons between chemical species that effects a change in the valence state of the species involved. To be successful in permeable barriers, the redox (oxidation/reduction) reaction must occur readily under the natural temperature and chemical setting of the groundwater.

Blowes and Ptacek (1992) proposed to incorporate solid-phase additives as the reactive material in treatment walls to control redox conditions to promote removal of electro-active metals. Their work focused on using reduced iron (fine grained zero-valent) for removal of dissolved hexavalent chromium. Column studies in the lab demonstrated that highly reducing conditions generated by the reduced iron caused the chromium to change its state to the less soluble trivalent chromium that then precipitated (chromium hydroxide). Additional column studies were performed by Petrie and others (1993) on samples from the U.S. Coast Guard Station near Elizabeth City. Their work confirmed the findings of Blowes and Ptacek (1992). A pilot study was initiated at the facility in 1995 by constructing a treatment barrier 2 feet thick. The results indicate that dissolved chromium was reduced to acceptable levels within the first 6 inches of the barrier.

### Precipitation of Metals

Precipitation of metals could be accomplished by altering pH or Eh conditions as discussed above or by chemical additives to a treatment barrier. For instance, in a plume containing dissolved lead, hydroapatite added to a treatment barrier could serve as a source of phosphate to precipitate lead phosphate. Studies performed by Schwartz and Xu (1992) demonstrate its potential applicability to treatment barriers.

Other chemical reactions are possible to precipitate metals depending on the type of dissolved metal that is involved. The key to the design for precipitation of metals is to have the necessary chemical in a solid phase form so that it can be part of barrier construction. The chemical must still be able to interact with the dissolved metal in the plume. Another example would be to use sulfide to precipitate metals. Metal sulfides are generally less soluble than metal hydroxides. Sulfides will also transfer from one precipitate to another. The barrier could be constructed of calcium or iron sulfide. Metals that have lower solubility as sulfides (silver, mercury, etc.) would take the sulfide from the calcium or iron and precipitate. The calcium or iron would be released to the water.

In Fry Canyon, Utah, a field demonstration was initiated to determine the technological and economic feasibility of using a permeable treatment barrier to remediate uranium. The barrier was constructed in 1997 and comprised three different treatment materials including bone char phosphate ( $\text{PO}_4$ ), zero-valent iron, and amorphous ferric oxide (AFO). After one year of operation all three were removing uranium. Zero-valent iron has demonstrated the highest removal efficiencies at more than 99 percent. Both the AFO and the  $\text{PO}_2$  barriers removed about 90 percent of the dissolved uranium (EPA 1999).

### Contaminant Removal via Sorption or Ion Exchange

Contaminant removal via sorption also shows promise, but as with any developing technology a number of issues need to be resolved. Sorption could be accomplished using a number of commonly used above-ground sorptive material such as activated carbon, zeolites, or ion exchange resins.

Activated carbon, for instance, is used to physically absorb a variety of organic compounds in groundwater. The activated carbon physically absorbs the organics due to the attraction caused by surface tension of the activated carbon, and it has gained widespread use in above-ground applications for groundwater treatment because of the large internal surface area that activated carbon possesses. Since physical adsorption is a reversible process, its application in reactive walls requires that at some point, either after the carbon is spent or the plume is remediated, the carbon must be removed from the subsurface and managed accordingly. If the carbon is left below ground, it will release the absorbed organics to the clean water carrier. This requires that the activated carbon be installed in retrievable containers, discussed earlier in this chapter, or is installed so that a vacuum truck, or other extraction device, can easily remove it. Activated carbon treatment barriers require consideration of other factors that could interfere with their adsorptive abilities. For instance, dissolved iron could be present which could compete with organics for absorptive surfaces within the activated carbon. In addition, biological growth could also "blind" the carbon, significantly reducing its effectiveness to remove organics.

A permeable treatment barrier was installed at the Marzone Superfund site in Georgia using activated carbon to remediate groundwater contaminated with pesticides including BHC, beta-BHC, DDD, DDT, lindane, and methyl parathion. A modified funnel and gate system was constructed by installing a 400-foot barrier using vibrating beam technology. Up-gradient of and parallel to the barrier, a collection trench was installed using coarse-grained material. Collected groundwater was routed to treatment vaults containing 1,800 pounds of activated carbon. Treated groundwater was conveyed beyond the barrier wall by a pipe that terminated into a distribution trench constructed perpendicular to the wall. The results of preliminary testing indicate that contaminant concentrations are below detection levels (EPA 1999).

If the contaminants are inorganics, ion exchange may be applicable. Ion exchange is the exchange of an ion with high ion exchange selectivity for an ion with a lower selectivity. Solid phase materials that can exchange an ion dissolved in groundwater for one of its ions may be suitable for incorporation into a treatment barrier. Any divalent ion will usually have higher ion exchange selectivity than will a monovalent ion. Most metals present in groundwater are in the divalent or trivalent state and are amenable to ion exchange. However, ion exchange treatment can be expensive. As in the case of activated carbon it is a physical process which is reversible, so the spent material must eventually be removed and managed properly. Also, naturally occurring constituents such as dissolved iron and bacteriological growth can "blind" ion exchange material reducing its effectiveness.

A pilot-scale demonstration project using a surfactant-modified zeolite (SMZ) was performed by the Large Experimental Aquifer Program near Portland. The project was designed to demonstrate this technology for remediating hexavalent chromium. The results indicated that the barrier performed as designed with retardation factors on the order of 50 (EPA 1999).

## Biological Degradation

Biological degradation applications to permeable treatment barriers are generally aerobic and can be accomplished in many different ways. The two main criteria for an aerobic biological treatment barrier are surface area and oxygen. The bacteria need the proper amount of surface area in order to attach and interact with the plume. Too little surface area (i.e., large gravel) and an insufficient amount of bacteria will be in the treatment barrier. Too much surface area (i.e., silt and clay) and the water will not travel past and interact with all of the bacteria.

The oxygen can be supplied in many ways. An air sparging curtain can be installed in natural or geologically altered (to increase permeability) material to supply oxygen to enhance degradation of aerobically biodegradable compounds such as BETX. Early research was performed by Bianchi-Mosquera (1993) on using solid phase oxygen release compounds (ORC) to enhance degradation of BETX. ORCs are commonly in the form of concrete briquettes that slowly release oxygen to groundwater, although slurries are now being used that can be injected into an aquifer. Numerous full-scale applications of ORC have demonstrated their effectiveness in degrading BETX.

At a site in Alabama, a pilot study was conducted to remediate methyl isobutyl ketone (MIBK) using an *in situ* biological reactor. The reactor was designed with two sequential chambers. In the first chamber oxygen was added via a sparging system to raise the dissolved oxygen level and precipitate dissolved iron in groundwater passing through the chambers. The second chamber was filled with oyster shells, which have a high surface area, to promote biological growth of MIBK degrading bacteria. The results showed that after the initial start-up period, the *in situ* biological reactor achieved 95 percent reduction in MIBK levels.

## DESIGN CONSIDERATIONS

There are a number of considerations that must be carefully thought out in the design of permeable treatment barriers, particularly ones incorporated into funnel and gate configurations. Of utmost importance is that the system manages the entire plume. Since groundwater flow directions can vary, it is extremely important that these fluctuations are accounted for. Secondly, the residence time in the treatment barrier must be sufficient to achieve the desired reduction in contaminant concentration. Lastly, the ratio of cut off walls to treatment barrier in a funnel and gate system should be optimized to minimize costs. For funnel and gate systems, flow and transport modeling is almost always needed to evaluate these considerations and optimize the design.

One of the most critical factors in permeable treatment barrier design is the relationship between residence time of contaminated groundwater in the treatment zone (reactor) and the rate of contaminant degradation that occurs within the gate. On the one hand, the designer is trying to maximize discharge through the gate to maximize the width of the capture zone. On the other hand, the designer wants to maximize residence time in the gate to ensure adequate treatment. Since these are

inversely related, they must be properly balanced. Again, flow and transport modeling can be very useful in evaluating these relationships.

As one might expect, the discharge through the gate increases with increased hydraulic conductivity of the gate; however, relatively few increases occur with hydraulic conductivities greater than ten times the aquifer. This is important because high hydraulic conductivity porous media usually have large grain sizes and low surface area to mass ratios. Since reaction rates in most *in situ* media are proportional to surface area, high hydraulic conductivities would result in slower reaction rates.

The rate of contaminant degradation that occurs within the treatment barrier is an important factor. The actual retention time in the treatment zone is obtained by dividing the pore volume of the treatment zone by the discharge through it. For degradation processes that are first order reactions, the retention time necessary is given by the formula

$$N_{1/2} = [\ln (C_{\text{eff}}/C_{\text{inf}})]/\ln (1/2)$$

where,  $N_{1/2}$  = number of half lives required;  $C_{\text{eff}}$  = concentration of the desired effluent; and  $C_{\text{inf}}$  = concentration of the influent.

To put this in perspective, if the chlorinated compound TCE has a half life of 13.6 hours, to reduce a plume from 1000 ppb to 5 ppb would require 7.6 half lives or a residence time of 4.3 days. Of course this is a theoretical calculation and other factors need to be considered as discussed previously.

Since a key design consideration is to increase attenuation in the treatment zone, there are two ways to achieve this. The first way is to increase the reaction rates. This would most commonly be achieved by increasing the surface area of the treatment material (which goes back to the gate [reactor media] not needing to be more than 10 times more permeable than the aquifer) or by using a higher proportion of treatment material in the treatment zone. The second way is to increase the retention time within the reactor by decreasing the discharge through the gate (add more gates) or by increasing the gate's pore volume by making it longer or wider.

## CASE STUDY—REACTIVE WALL DESIGN

### Background

Pentachlorophenol (PCP) and tetrachlorophenol (TCP) were detected in on-site groundwater samples at a former wood treating facility in the western United States. The groundwater system consists of a shallow aquifer containing a heterogeneous mixture of marine deposits and artificial fill that is underlain by low permeability siltstones and mudstone. The shallow aquifer ranges in thickness from 10 to 20 feet and averages 15 feet; its saturated thickness averages seven feet. Based on the results of the site investigation, it was determined that impacted groundwater had the potential to move off-site and adversely affect downstream domestic users of the resource (Figure 8). Consequently, remedial action goals were developed to protect the quality and quantity of the resource.



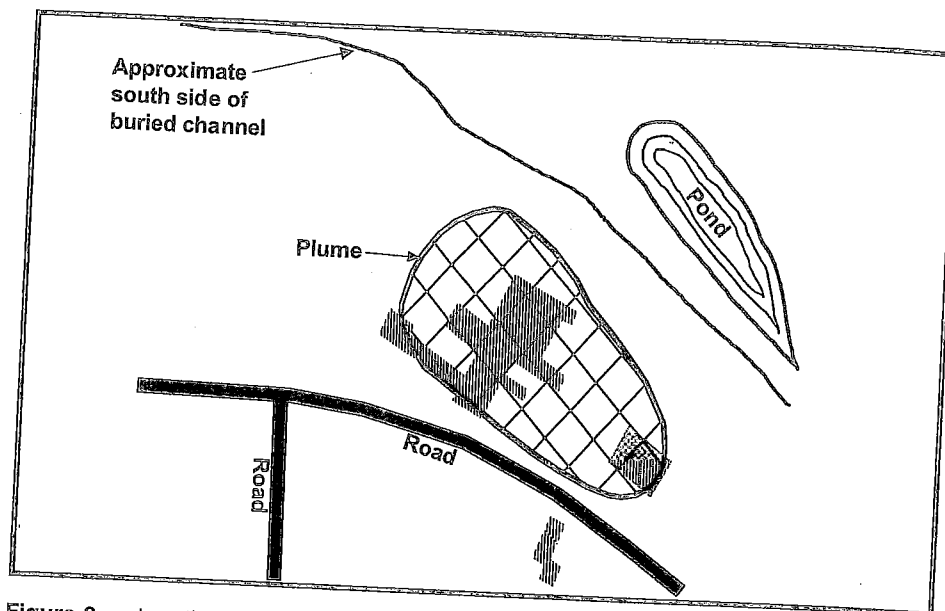


Figure 8 Location of groundwater plume.

A number of remedial alternatives were evaluated including pump and treat, containment, and *in situ* treatment. A permeable treatment barrier incorporating activated carbon was deemed the most attractive alternative and additional analyses were conducted to determine constraints on below-ground application of this technology and to evaluate its suitability for incorporation into a funnel and gate system with the funnel portion constructed using slurry wall technology. These studies focused on the following, (1) the potential for underflow beneath the funnel and gate system, (2) the spatial relationship between gates and funnels, (3) mass loadings on the gates, and (4) interferences with gate performance.

### Funnel and Gate Modeling Study

Since permeable treatment barriers are generally more expensive than impermeable barriers, groundwater flow modeling was conducted to optimize the design by minimizing the number and length of gates, while still accommodating flow from the entire plume and providing adequate residence time within the gate. Groundwater modeling and particle tracking were used to delineate flow paths through and around the funnel and gate system to demonstrate the efficacy of a given configuration. A conceptual model was developed based on varying hydrogeologic conditions and groundwater flow gradients found across the site. The background transmissivity for the site was modeled at 210 ft<sup>2</sup>/day with two imbedded permeability inhomogeneities of 28 ft<sup>2</sup>/day and 3.5 ft<sup>2</sup>/day.

Groundwater streamlines were generated for several combinations of gate lengths and spacings. After several alternatives were evaluated, an L-shaped configuration was selected which contains four gates, two of them installed adjacent to the buried stream channel where flow rates are expected to be higher (Figure 9). The modeling

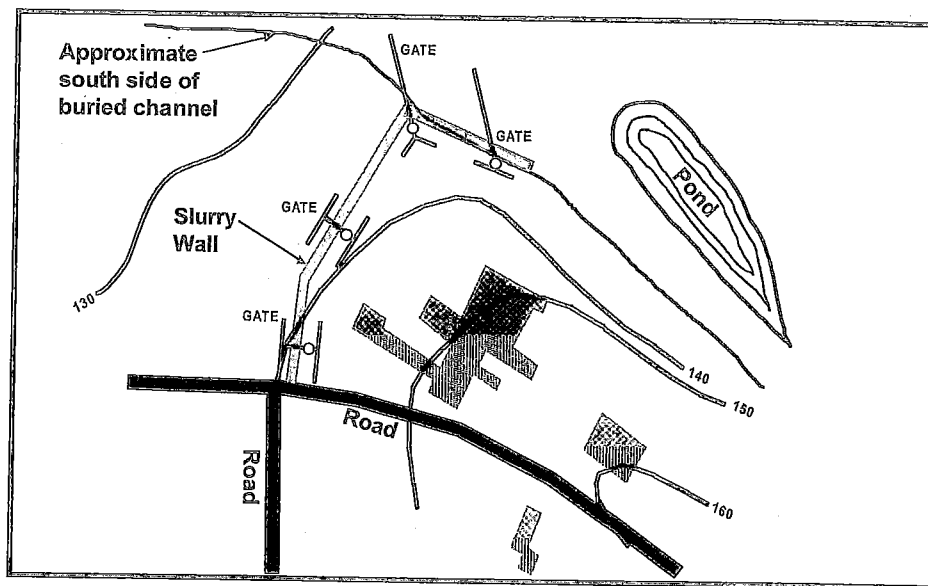


Figure 9 Water level contours and location of Funnel-and-Gate System™.

results showed that flow from a fairly broad area can readily be focused through a small number of small gates without causing groundwater seeps to occur at the surface and with minimal disruption of groundwater flow patterns.

The modeling results were also used to evaluate the volume of water expected to be captured for treatment. Based on the area encompassed within the flow lines and the hydraulic properties within this region, a flux of 22 gpm, or about 5.5 gpm per gate, was calculated.

### Gradient Control

Because of the nonuniform distribution of hydraulic transmissivities across the site, groundwater may be impeded in its lateral movement toward and away from the gates. In order to minimize this effect, gravel-filled collection and distribution galleries were installed at each gate to collect water from the up-gradient side of the gate, guide it through the gate, and then redistribute it uniformly after treatment (Figures 9 and 10). The collection and distribution galleries were trenched into the aquifer to expose a large cross-sectional area to groundwater flow. This minimized the pressure required to move water from the aquifer to the carbon treatment gates. Installation of these collection and distribution galleries helped ensure that the pressure drops across the funnel and gate system were minimal so as not to affect natural groundwater gradients and flow patterns.

### Underflow of Barrier

The potential for flow under the system was also evaluated by using data collected during aquifer tests conducted at the site along with results from the modeling study.

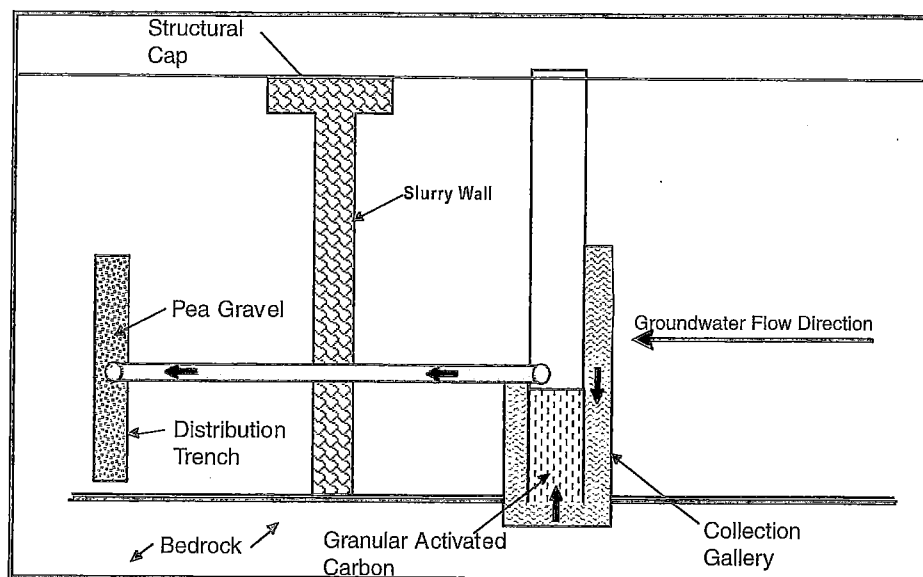


Figure 10 Profile view of treatment gate.

Aquifer tests of the upper marine terrace sediment yielded an estimated transmissivity of 210 ft<sup>2</sup>/day and the transmissivity of the lower Franciscan formation was estimated from slug tests conducted on wells completed solely within the underlying Franciscan formation. A comparison of these two values indicated that the hydraulic conductivity of the lower Franciscan formation is approximately 1/1,000 that of the overlying marine terrace sediment. The flows that are expected to travel through the treatment gates were compared with the flows that may flow under the barrier. The solution below for the flow beneath the barrier is similar to that for estimating flow under a dam, with a simplifying assumption that flow lines in the Franciscan are concentric semicircles when viewed in section from one end of the system.

k = 0.004	Hydraulic conductivity of Franciscan, in ft/day
i = 0.05	Hydraulic gradient
T = 210	Transmissivity of marine terrace, in ft <sup>2</sup> /day
w = 2	Width of barrier, in ft
h = 2.0	Average head difference across barrier, in ft
x = 400	Distance up-gradient from barrier, in ft, through which water permeates the Franciscan

Let  $q$  be the flow through a 1 foot thick slice under the slurry wall emanating from the shallow aquifer between the wall and a point  $x$  feet up-gradient of the wall

$$q = \frac{2kix}{\pi} + \frac{k(h-wi)}{\pi} \ln \frac{(\pi x + \pi x)}{2}$$

$$q = 0.07 \text{ ft}^3/\text{day}$$

Let  $Q$  be the flow through a 1 foot thick slice of the marine terrace deposits

$$Q = TI$$

For the parameters as defined above, the flow rate is

$$Q = 10.5 \text{ ft}^3/\text{day}$$

Since the  $K$  value for the Franciscan is a horizontal conductivity, the actual flow ( $q$ ) under the wall will be less than the computed value. This is because the effective conductivity is a weighted average of the horizontal and vertical  $K$ 's, and the vertical conductivity is likely much less than the horizontal conductivity. The maximum flow under the wall represents approximately 0.7 percent of the total flow through the system.

### Gate Design

The gate design incorporates several factors including contaminant concentration, flow rate, and time between carbon changeout. Using an estimated flow rate of 5.5 gpm, a carbon change-out of 3 years, a concentration of 200 ppb, and a 1 percent adsorptive capacity, approximately 48 ft<sup>3</sup> of carbon were required for each gate.

To minimize flow velocity and maximum residence time, each gate was designed using 4 foot diameter corrugated metal pipe filled with 4 feet of activated carbon. Figure 11 shows a photo of the installation of a gate. This configuration allows water to move easily through the gates with a design pressure loss of only 2 inches of water.

Groundwater samples are collected from the monitoring points located before each of the treatment gates to measure influent concentrations entering the gate. A sample is also collected from the monitoring point within the treatment gate to verify that the treatment gate is effective in removing these compounds prior to the water exiting the gate. This monitoring point is shown in Figure 11 and is the PVC pipe located in the middle of the corrugated metal pipe. A treatment buffer zone exists downstream of this mid-gate monitoring point to ensure that impacted water does not exit the gate prior to full removal of these compounds. Upon detection of a compound of concern at a concentration above water quality objectives at the mid-gate measuring point, the carbon will be removed and replaced. It is expected that biological activity will also be a part of the removal mechanism for the contaminants.

### System Performance

The system was installed in September 1995 and has been operated since that time. Flow rates through each of the gates were found to vary dependent on geology. The installation of the collection and distribution galleries which guide groundwater to and from the gates worked well. The spatial relationship between the gate, the slurry wall, and the distribution gallery is shown in Figure 12. In the photo the bulldozer is installing the distribution gallery. Figure 13 is a photo showing a close



**Figure 11** Photo showing gate installation.

up of installation of the slurry wall. A portion of the slurry wall was installed as shown in the photo between the gate and the distribution gallery. In addition, the



**Figure 12** Photo showing relationship between gate, slurry walls, and installation of distribution gallery.



**Figure 13** Photo showing slurry wall installation.

actual pressure drops across the gates have been only a couple of inches (the system was designed based on 1 foot) and have not changed during operation of the system. No changes in local groundwater flow patterns have occurred as a result of system installation, and the yields from shallow water supply wells immediately down-gradient of the barrier have not been impacted because of some unforeseen effect of the system.

The concentrations of TCP and PCP reaching the gates have been in the low parts per billion. Low levels of TCP and PCP were detected in samples collected from the middle of the carbon beds in the third quarter of 1998. These detections were sporadic and were only slightly above the detection limit. Detections, below action levels, have also occurred in a monitor well located down-gradient of Gate No. 2. No TCP or PCP has been detected in the middle sample point of the carbon bed within Gate No. 2. In addition, no TCP or PCP was detected in follow up sampling at the top of the carbon bed in Gate No. 2 prior to the water leaving the system. It was concluded that the detections in the down-gradient monitoring well were from residual contamination that was present prior to system installation.

The first carbon change out was successfully completed in September 1999. High groundwater levels due to heavy rains prevented draining the gates during an earlier attempt to change out the carbon. Change out was accomplished by excavating the soil above the gates with a backhoe and then dewatering the gates using a submersible pump. The pumped water was transferred to one of the other gates for processing so no water was hauled off-site. The carbon was then vacuumed out using standard vacuum equipment and hauled off-site as nonhazardous waste. As designed, the system minimized changes in dissolved oxygen levels and REDOX and minimal biofouling and iron precipitation occurred within the beds. While the gate was empty a visual inspection was made of the gate and no leaks or corrosion were identified in the seals and welds. New carbon was poured into the gates after the inspection.

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