Chapter 12
Physical and Chemical Groundwater Remediation Technologies

Krishna R. Reddy[*]

Abstract Groundwater is the main source of drinking water as well as agricultural and industrial usage. Unfortunately, groundwater quality has been degraded due to improper waste disposal practices and accidental spillage of hazardous chemicals. Therefore, it is critical that the groundwater contamination be prevented and the contaminated groundwater at numerous sites worldwide be remediated in order to protect public health and the environment. This chapter provides an overview of relevant regulations, general remedial approach, and most commonly used physical and chemical groundwater remediation technologies. The remediation technologies include pump-and-treat, in-situ air sparging, in-situ flushing, and permeable reactive barriers. The process description, applicability, limitations and a case study for each of these technologies are also presented.

Keywords Groundwater, contamination, remediation, pump-and-treat, air sparging, flushing, permeable reactive barriers

12.1 Introduction

About 40% of the drinking water comes from groundwater, about 97% of the rural population drinks groundwater, and about 30–40% of the water used for agriculture comes from groundwater (Sharma and Reddy, 2004). Therefore, groundwater is a valuable resource and it must be protected from any pollution. The United States Environmental Protection Agency (USEPA) estimated that there are thousands of sites that have been contaminated in the United States and over 217,000 these sites require urgent remedial action. These sites include:

Krishna R. Reddy
Department of Civil and Materials Engineering, University of Illinois at Chicago,
842 West Taylor Street, Chicago, IL 60607, U.S.A.

[*] To whom correspondence should be addressed. E-mail: kreddy@uic.edu

C.J.G. Darnault (ed.), *Overexploitation and Contamination of Shared Groundwater Resources.*

- National Priorities List (Superfund) sites;
- Resource Conservation and Recovery Act (RCRA) Corrective Action sites;
- Underground Storage Tanks (USTs) sites;
- Department of Energy (DOE) sites;
- Department of Defense (DOD) sites;
- Various Civilian Federal Agencies sites;
- State and private parties (including brownfields) sites.

Contamination of groundwater has been a major concern at these sites. The contaminants encountered at these sites include organic compounds, heavy metals, and radionuclides. DOE sites contain mixed wastes, including radioactive wastes, while DOD sites contain explosives and unexploded ordnance. The cost to cleanup these sites is estimated to exceed US $270 billion. This chapter provides an overview of regulatory framework, general remedial approach, and different common physical and chemical remediation technologies for cleanup of polluted groundwater.

12.2 Relevant Regulations

The assessment and remediation of previously contaminated sites and the proper management of newly created hazardous wastes have been regulated through the passage of major environmental laws and regulations (Sharma and Reddy, 2004). In 1980, the United States Congress established the Superfund program, also known as the Comprehensive Environmental Response, Compensation and Liabilities Act (CERCLA), to provide the financial assistance needed for the remediation of abandoned hazardous waste sites that pose serious risk to the health and safety of the public as well as the welfare of the environment. The Superfund program is administered by the USEPA in cooperation with regional governmental agencies. In order to determine which sites are eligible to receive federal aid under the Superfund program, a ranking system has been established to allow for a quantitative rating of sites across the United States. Sites that score high enough on the USEPA's hazard ranking system are placed on the National Priorities List (NPL). The National Priorities List is a published list of hazardous sites that require extensive and long-term remediation, and that are deemed eligible to receive funding from the Superfund program. Superfund sites must comply with the stringent remediation codes, liability standards, and documentation required by the Superfund program. According to this program, purchasers of contaminated sites may be held responsible for damage caused by previous owners even if these sites were contaminated by legal activities at the time of occurrence. Additionally, Superfund regulations require that a contaminated site be remediated to very low contaminant levels such that risk to public health is minimized. Such an approach is often inflexible and does not take into account the intended use of the rehabilitated site.

In 1980, the United States Congress also promulgated the Resource Conservation and Recovery Act (RCRA) to control newly created hazardous waste from the “cradle-to-grave”. These regulations provide criteria for defining hazardous waste, generator responsibilities, transporter’s requirements, manifest systems, and treatment, storage and disposal facility (TSDF) requirements. The regulations also address problems that could result from underground tanks storing petroleum and other hazardous substances.

Many state governments are also assisting in cleanup of contaminated sites. Nearly half of the states in the United States offer some type of voluntary remediation program. The purpose of such programs is to encourage remediation of sites with possible contamination while preventing any increased liability for participating parties. When a remediation project is completed, many states will issue a statement releasing the participants from state liability for any contamination that may exist at the site. Often state agencies will offer assistance to project participants if they are subject to federal liability.

12.3 General Remedial Approach

A systematic approach for the assessment and remediation of contaminated sites is necessary in order to facilitate the remediation process and avoid undue delays. The most important aspects of the approach include site characterization, risk assessment, and selection of an effective remedial action (Sharma and Reddy, 2004). Innovative integration of various tasks can often lead to a faster, cost-effective remedial program.

12.3.1 Site Characterization

Site characterization is often the first step in a contaminated site remediation strategy. It consists of the collection and assessment of data representing contaminant type and distribution at a site under investigation. The results of a site characterization form the basis for decisions concerning the requirements of remedial action. Additionally, the results serve as a guide for design, implementation, and monitoring of the remedial system. Each site is unique; therefore, site characterization must be tailored to meet site-specific requirements. An inadequate site characterization may lead to the collection of unnecessary or misleading data, technical misjudgment affecting the cost and duration of possible remedial action, or extensive contamination problems resulting from inadequate or inappropriate remedial action. Site characterization is often an expensive and lengthy process; therefore, it is advantageous to follow an effective characterization strategy to optimize efficiency and cost.

An effective site characterization includes the collection of data pertaining to site geology, including site stratigraphy and important geologic formations; site hydrogeology, including major water-bearing formations and their hydraulic properties; and site contamination, including type, concentration, and distribution. Additionally, surface conditions both at and around the site must be taken into consideration. Because little information regarding a particular site is often known at the beginning of an investigation, it is often advantageous to follow a phased approach for the site characterization. A phased approach may also minimize financial impact by improving the planning of the investigation and ensuring the collection of relevant data. Phase I consists of the definition of investigation purpose and the performance of a preliminary site assessment. A preliminary assessment provides the geographical location, background information, regional hydrogeologic information, and potential sources of contamination pertaining to the site. The preliminary site assessment consists of two tasks, a literature review and a site visit.

Based on the results of the Phase I activities, the purpose and scope of the Phase II exploratory site investigation need to be developed. If contamination was detected at the site during the course of the preliminary investigation, the exploratory site investigation must be used to confirm such findings as well as obtain further data necessary for the design of a detailed site investigation program. A detailed work plan should be prepared for the site investigations describing the scope of related field and laboratory testing. The work plan should provide details about sampling and testing procedures, sampling locations and frequency, a quality assurance/quality control (QA/QC) plan, a health and safety (S&H) plan, a work schedule, and a cost assessment. Phase III includes a detailed site investigation in order to define the site geology and hydrogeology as well as the contamination profile. The data obtained from the detailed investigation must be adequate to properly assess the risk posed at the site as well as to allow for effective designs of possible remedial systems. As with the exploratory investigations, a detailed work plan including field and laboratory testing programs as well as QA/QC and S&H plans should be outlined. Depending on the size, accessibility, and proposed future purpose of the site, this investigation may last anywhere from a few weeks to a few years. Because of the time and the effort required, this phase of the investigation is very costly. If data collected after the first three phases is determined to be inadequate, Phase IV should be developed and implemented to gain additional information. Additional phases of site characterization must be performed until all pertinent data has been collected.

Depending on the logistics of the project, site characterization may require regulatory compliance and/or approval at different stages of the investigation. Thus, it is important to review the applicable regulations during the preliminary site assessment (Phase I). Meetings with regulatory officials may also be beneficial to insure that investigation procedures and results conform to regulatory standards. This proactive approach may prevent delays in obtaining the required regulatory permits and/or approvals. Innovative site characterization techniques are increasingly being used to collect relevant data in an efficient and cost-effective manner. Recent advances in cone penetrometer and sensor technology have enabled contaminated sites to be rapidly characterized using vehicle-mounted direct push probes. Probes are available for directly measuring contaminant concentrations in-situ, in addition to measuring standard stratigraphic data, to provide flexible, real-time analysis. The probes can also be reconfigured to expedite the collection of soil, groundwater, and soil gas samples for subsequent laboratory analysis. Noninvasive, geophysical techniques such as ground-penetrating radar, cross-well radar, electrical resistance tomography, vertical induction profiling, and high-resolution seismic reflection, produce computer-generated images of subsurface geological conditions and are qualitative at best. Other approaches such as chemical tracers are used to identify and quantify contaminated zones, based on their affinity for a particular contaminant and the measured change in tracer concentration between wells employing a combination of conservative and partitioning tracers.

12.3.2 Risk Assessment

Once site contamination has been confirmed through the course of a thorough site characterization, a risk assessment is performed. A risk assessment is a systematic evaluation used to determine the potential risk posed by the detected contamination to human health and the environment under present and possible future conditions. If the risk assessment reveals that an unacceptable risk exists due to the contamination, a remedial strategy is developed to assess the problem. If corrective action is deemed necessary, the risk assessment will assist in the development of remedial strategies and goals necessary to reduce the potential risks posed at the site.

The USEPA and the American Society for Testing and Materials (ASTM) have developed comprehensive risk assessment procedures. The USEPA procedure was originally developed by the United States Academy of Sciences in 1983. It was adopted with modifications by the USEPA for use in Superfund feasibility studies and RCRA corrective measure studies (USEPA, 1989). This procedure provides a general, comprehensive approach for performing risk assessments at contaminated sites. It consists of four steps:

1. Hazard identification.
2. Exposure assessment.
3. Toxicity assessment.
4. Risk characterization.

The ASTM Standard E 1739-95, known as the Guide for Risk-Based Corrective Action (RBCA), is a tiered assessment originally developed to help assess sites that contained leaking underground storage tanks containing petroleum (ASTM, 2002).

Although the Standard is geared toward such sites, many regulatory agencies use a slightly modified version for non-UST sites. This approach integrates risk and exposure assessment practices with site assessment activities and remedial measure selection. The RBCA process allows corrective action activities to be tailored for site-specific conditions and risks and assures that the chosen course of action will protect both human health and the environment.

12.3.3 Remedial Action

When the results of a risk assessment reveal that a site does not pose risks to human health or the environment, no remedial action is required. In some cases, however, monitoring of a site may be required to validate the results of the risk assessment. Corrective action is required when risks posed by the site are deemed unacceptable. When action is required, remedial strategy must be developed to insure that the intended remedial method complies with all technological, economic, and regulatory considerations. The costs and benefits of various remedial alternatives are often weighed by comparing the flexibility, compatibility, speed, and cost of each method. A remedial method must be flexible in its application to ensure that it is adaptable to site-specific soil and groundwater characteristics. The selected method must be able to address site contamination while offering compatibility with the geology and hydrogeology of the site.

Generally, remediation methods are divided into two categories: in-situ remediation methods and ex-situ remediation methods. In-situ methods treat contaminated groundwater in-place, eliminating the need to extract groundwater. In-situ methods are advantageous because they often provide economic treatment, little site disruption, and increased safety due to lessened risk of accidental contamination exposure to both on-site workers and the general public within the vicinity of the remedial project. Successful implementation of in-situ methods, however, requires a thorough understanding of subsurface conditions. Ex-situ methods are used to treat extracted groundwater. Surface treatment may be performed either on-site or off-site, depending on site-specific conditions. Ex-situ treatment methods are attractive because consideration does not need to be given to subsurface conditions. Ex-situ treatment also offers easier control and monitoring during remedial activity implementation.

12.4 Remedial Technologies

If groundwater contamination is confirmed and remedial action is deemed necessary following a thorough site characterization and risk assessment, one of many remedial technologies may be utilized for corrective action. The most common physical and chemical remediation technologies are pump and treat, in-situ air sparging, in-situ flushing, and permeable reactive barriers. The most common biotechnologies include monitored natural attenuation, bioremediation, and phytoremediation, but these methods are not within the scope of this chapter. Containment methods such as slurry walls and grout curtains are also used to control contaminant plumes within groundwater but are not discussed within this chapter (USEPA, 1995). Containment methods such as these are often used as interim measures prior to the final selection and implementation of a remedial method. Actual remedial methods are varied in their applications and their limitations; thus, it is essential to evaluate the benefits, drawbacks, and economic impact of each method as well as the site-specific soil, hydrogeologic, and contaminant conditions.

12.4.1 Pump and Treat

Until recently, the most conventional method for groundwater remediation has been the pump and treat method. With pump and treat as shown in Figure 12.1, free-phase contaminants and/or contaminated groundwater are pumped directly out of the surface. Treatment occurs above ground, and the cleaned groundwater is either discharged into sewer systems or re-injected into the subsurface (Cohen et al., 1997). Pump and treat systems have been operated at numerous sites for many years. Unfortunately, data collected from these sites reveals that although pump and treat may be successful during the initial stages of implementation, performance drastically decreases at later times. As a result, significant amounts of residual contamination can remain unaffected by continued treatment. Due to these limitations, the pump and treat method is now primarily used for free product recovery and control of contaminant plume migration.

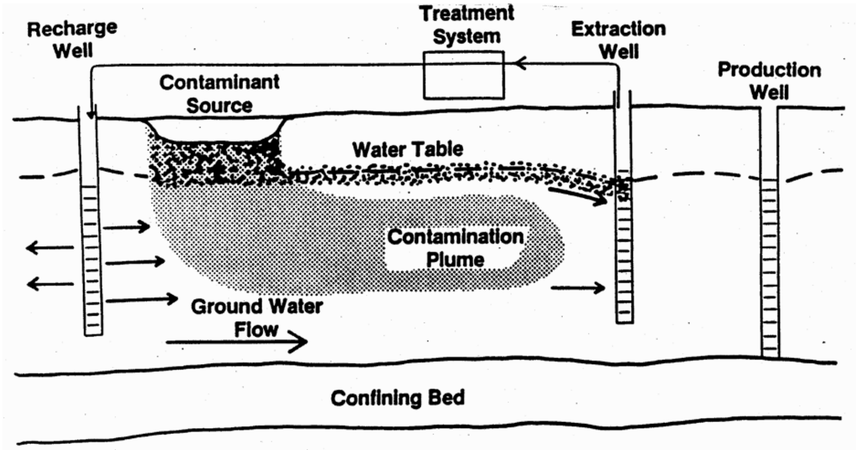

Fig. 12.1 Pump-and-treat system

Pump and treat requires simple equipment and it is effective for source zone removal where free-phase contamination is present. Some concerns with pump and treat include lingering residual contamination due to tailing and/or rebound, long time required to achieve remediation, biofouling of extraction wells and associated treatment stream that can severely affect system performance, high cost of treating large quantities of wastewater, and high operation and maintenance costs (USEPA, 1996). Tailing and rebound are attributed to presence of non-aqueous phase liquids (NAPLs), contaminant desorption, contaminant precipitation-dissolution, matrix diffusion, and groundwater velocity variation. The removal of NAPLs during pumping is attributed to dissolution of residual and pooled free-product, desorption and solubilization, and dissolution kinetics.

Numerous case studies are reported in the literature documenting the design and performance of pump-and-treat systems for groundwater remediation (FRTR, 1998a,b). For example, Fairchild Semiconductor Company in California manufactured chips, mother boards, and circuits for the emerging computer industry in the late 1960s. To maintain ultra clean conditions as a part of their manufacturing process, hundreds of gallons of solvent were used daily. Accidentally, hundreds of gallons of solvent have been spilled into the soil and underlying groundwater. The site soils consisted of alluvial deposits that are heterogeneous mixture of sand and gravel interbedded with silts and clays. The deposits are up to 1,500 ft thick. The upper aquifer zone occurs from the top of the saturated zone to the depth of approximately 165 ft below ground surface. Contaminants in the groundwater were TCE (trichloroethene), chloroform, 1, 1-dichloroethene, 1, 1, 1-trichloroethane, and vinyl chloride. The risk-based remedial objectives were:

- TCE: 5 μg/l for shallow aquifers;
- TCE: 0.8 μg/l for deep aquifers;
- Chloroform: 100 μg/l;
- 1,1- dichloroethene: 6 μg/l;
- 1,1,1-trichloroethane: 200 μg/l;
- Vinyl Chloride: 0.5 μg/l.

A network of extraction wells were designed to extract the groundwater. The groundwater was pumped to the surface and treated through an activated carbon process and re-injected into the ground to enhance hydraulic control and to flush the contamination zone. The extraction and treatment systems run continuously from January 1 through December 3, with the exception of brief shut downs for carbon change or routine maintenance. Monitoring the treatment included measuring groundwater elevations and collecting groundwater samples for analysis. Monitoring the pump system aims at maintaining a steady flow through extraction wells. The contaminant concentrations are steadily declining, but do not reached the remedial objectives. The remedial system is still in operation and the developments in Silicon Valley sparked the interest of Netscape Communications to lease 38.5 acres of the site.

12.4.2 In-situ Air Sparging

Air sparging, also known as biosparging, is an emerging remediation technology useful in the treatment of volatile organic contaminants. During the implementation of air sparging as shown in Figure 12.2, a gas, usually air, is injected into the saturated soil zone below the lowest known level of contamination. Due to the effect of buoyancy, the injected air will rise towards the surface. As the air comes into contact with the contamination, it will, through a variety of mechanisms, strip the contaminant away or assist in in-situ degradation. Eventually, the contaminant-laden air encounters the vadose zone, where it is often collected using a soil vapor extraction system and treated on-site (Reddy et al., 1995; Reddy and Adams, 2001).

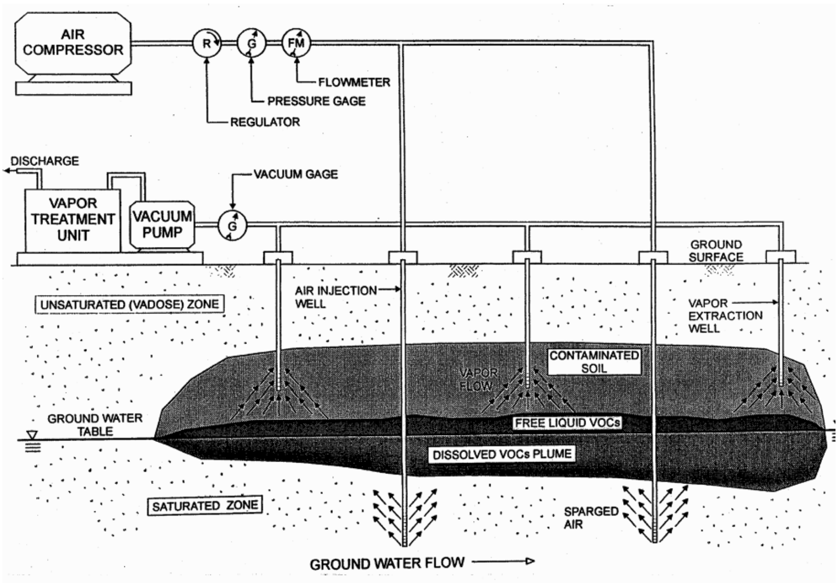

Fig. 12.2 In-situ air sparging system

This technology has been very popular because it causes minimal site disruption and reduces worker exposure to contaminants, it does not require removal, storage, or discharge consideration for groundwater, the equipment needed is simple and easy to install and operate, it requires short treatment time (1–3 years), and the overall cost is significantly lower than the conventional remediation methods such as pump and treat. However, there are several limitations of this technology. Contamination in low permeability and stratified soils poses a significant technical challenge to air sparging remediation efforts. Confined aquifers cannot be treated by this remediation technique. Air flow dynamics and contaminant removal or degradation processes are not well understood. If not properly designed, it could cause spreading of the contaminants into clean areas. It requires detailed data and pilot testing prior to its application.

Air sparging is based on the principles of air flow dynamics and contaminant transport, transfer and transformation processes (Reddy and Adams, 2001). Injected air moves through aquifer materials in the form of either bubbles or microchannels. In coarser soils such as fine gravels, air flow has been observed to be in the bubble form. In finer soils such as sands, the air flow has been observed to be in microchannel form. The density of bubbles or microchannels is found to be depended on the injected air flow rate. Soil heterogeneities are found to significantly affect the air flow patterns and the zone of influence. The transport mechanisms include advection, dispersion, and diffusion. The mass transfer mechanisms include volatilization, dissolution, and adsorption/desorption. Besides these, biodegradation is enhanced due to increased dissolved oxygen that can promote aerobic biodegradation.

Many sites have been successfully remediated using air sparging (Reddy and Adams, 2001). For example, Eaddy Brothers was a gasoline service station located in Hemingway, South Carolina. In September 1998, a release was reported from the station’s underground storage tanks. Soil and groundwater at the site were found to be contaminated with MTBE, BTEX, and naphthalene. Concentrations are: MTBE 5,110,000 μg/L; benzene 226,000 μg/L; toluene 301,000 μg/L; ethylbenzene 280,000 μg/L, xylene 278,000 μg/L; and naphthalene 2,700 μg/L. Subsurface soils at the site consists of silty clays with inter-fingered thin clayey-sand lenses, and no confining units have been identified. The average hydraulic gradient is 0.005 with a calculated seepage velocity of 0.138 ft/year. The depth to groundwater is 2.5–17.9 ft below ground surface. The risk-based remedial objectives were:

- MTBE: 646 μg/L;
- Benzene: 191 μg/L;
- Toluene: 11,938 μg/L;
- Ethylbenzene: 9,426 μg/L;
- Xylene: 78,496 μg/L;
- Naphthalene: 418 μg/L.

Air sparging and soil vapor extraction units were installed. Ten vertical air sparging wells at a depth of 26 ft with 5 ft well screen were installed. Wells were connected to Kaeser SK-2 air sparge compressor operating at 70 psi. A total of 28 wells (on- and off-site) were used to monitor groundwater. Within a year, concentration dropped to 99% for MTBE, 99% for BTEX, and 96% for naphthalene. It took almost another year to drop the concentration of MTBE, benzene, and napthalene to the desired level. Air sparging was effective, fast, and easy to implement and monitor. The total cost for the cleanup of this site is US$ 197,515 which is relatively low compared to other means of remediation.

12.4.3 In-situ Flushing

Soil flushing involves pumping flushing solution into groundwater via injection wells as shown in Figure 12.3. The solution then flows down gradient through the region of contamination where it desorbs, solubilizes, and/or flushes the contaminants from the soil and/or groundwater. After the contaminants have been solubilized, the solution is pumped out via extraction wells located further down gradient. At the surface, the contaminated solution is treated using typical wastewater treatment methods, and then recycled by pumping it back to the injection wells (USEPA, 1991; Roote, 1997). Plain water or carefully developed solution (e.g., surfactant/cosolvent) are used as flushing solutions. However, one must select the type and concentration of flushing solution to optimize contaminant desorption and solubilzation.

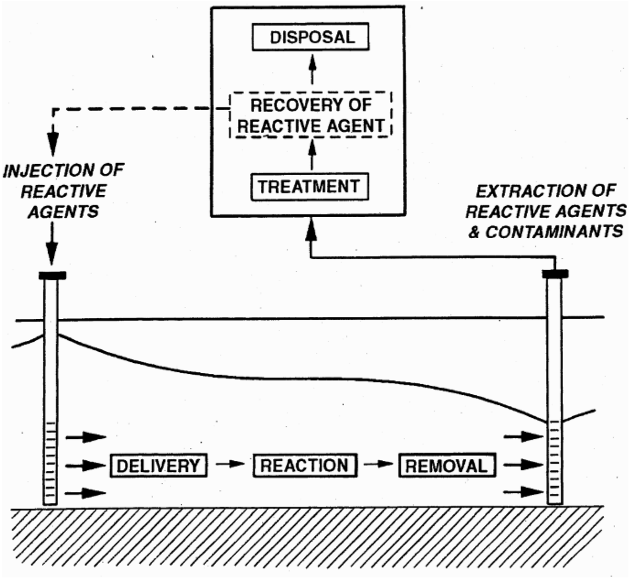

Fig. 12.3 In-situ flushing system

In-situ flushing causes less exposure of the contaminants to clean-up personnel and the environment. It is a simple and easy operation as compared to other technologies. It is applicable for a wide variety of contaminants, both organic and inorganic contaminants. It may be a slow process when heterogeneities such as soil layers or lenses of less permeable (less than 10^{-5} cm/s) or organic materials are located within the soil horizon. Since the contaminants are solubilized into the solution, they may be transported beyond the extraction well and unintentional spreading of the contamination may occur. Remediation times may be long and the effectiveness of the process largely depends on solution, contaminant, soil or groundwater interaction. Remediation depends strongly on the ability of the solution to desorb and solubilize the contaminant. The process may be costly with contamination located at large depths or with expensive solutions and long remediation times.

Marine Corps Base Camp LeJeune, Site 88, Building 25 was the location of a central dry cleaning facility. The site was contaminated with PCE and Varsol from storage and use during dry cleaning operations. PCE was present in groundwater at the site as DNAPL. Varsol—a petroleum distillate—was present as LNAPL. A demonstration of the surfactant-enhanced aquifer remediation system (SEAR) was performed under the U.S. Department of Defense Environmental Security Technology Certification Program (ESTCP). The target was to treat DNAPL in groundwater.

Shallow surficial aquifer existed at a depth of 16–20 ft. An order of magnitude difference existed in permeability between the shallower, more permeable zone (hydraulic conductivity of 10^{-4} cm/s) and the basal low permeability zone (hydraulic conductivity of 10^{-5} cm/s). The majority of DNAPL was present in a low permeability silty layer at base of the shallow aquifer, with about 105 gallons of DNAPL estimated to be present in the test zone. Contaminants found at the site include chlorinated solvents and total petroleum hydrocarbons (TPH); PCE was present as DNAPL, and Varsol was present as LNAPL. PCE concentrations in groundwater as high as 54 mg/L were monitored.

The test area was 20 ft wide by 30 ft long and 20 ft deep. Flushing solution consisted of surfactant, calcium chloride, and isopropyl alcohol. It was injected through three injection wells at a rate of 0.133 gallons per minute per well for 58 days. Six extraction wells removed subsurface liquids at a combined rate of 1 gpm. Above-ground treatment included gravity separation to remove separate phase DNAPLs. Evaporation to remove dissolved-phase contaminates, and ultra filtration (UF) to reconcentrate surfactant fluid prior to reinjection were implemented. Surfactant flush was followed by a 74 day water flush to remove injected chemicals and solubilized or mobilized contaminates. Partitioning interwell tracer test (PITT) was performed to demonstrate DNAPL removal and recovery of injected solution.

A total of 76 gallons of PCE was recovered during the demonstration with 32 gallons recovered as solubilized DNAPL and 44 gallons as free-phase DNAPL. DNAPL was effectively removed from the more permeable layer with DNAPL at a rate of 92–96%. DNAPL recovery from entire test zone (both layers) was 72%. Above-ground treatment system removed greater than 95% of extracted PCE, recovered 77% of surfactant and recovered 88% of isopropyl alcohol. The project reached an estimated 90% success level based on their initial goals. DNAPL was effectively removed from the more permeable layer with DNAPL remaining mostly in the lower permeable layer.

The results of the demonstration showed that aquifer heterogeneity has a strong influence on the performance of SEAR and that DNAPL source zone characterization is important because of the sensitivity of the technology to permeability contrasts. Total demonstration costs were US $3.1 million, including DNAPL source zone characterization, surfactant selection, well field installation, free-phase DNAPL removal equipment, pre-treatment PITT, technology application, surfactant regeneration, and indirect costs. Estimated total treatment cost for full-scale systems are US $12.8 million per acre.

12.4.4 Permeable Reactive Barriers

Permeable reactive barriers (PRBs) offer a passive approach for groundwater remediation. In general, a permeable wall containing an appropriate reactive material is placed across the path of a contaminant plume. As contaminated water passes through the wall, the contaminants are either removed or degraded (Figure 12.4). When designing a wall, not only must an appropriate reactive medium be chosen, but also wall dimensions must be designed to assure that the entire contaminant plume will be intercepted and enough residence time within the wall will be allowed for remediation to take place.

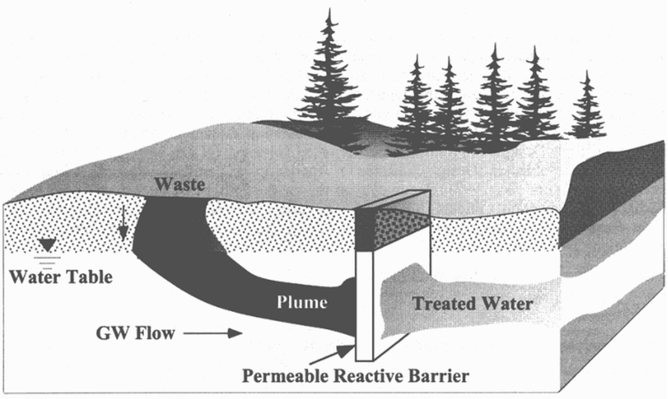

Fig. 12.4 Permeable reactive barrier

Typical reactant media contained in the barriers includes media designed for degrading volatile organics, chelators for immobilizing metals, or nutrients and oxygen to facilitate bioremediation (USEPA, 1998b). The media is often mixed with a porous material such as sand to enhance groundwater flow through the barrier. A permeable barrier may be installed as a continuous reactive barrier or as a funnel-and-gate system (Figures 12.5 and 12.6). A continuous reactive barrier consists of a reactive cell containing the permeable reactive medium (Figure 12.5). A funnel-and-gate system has an impermeable section, called the *funnel*, which directs the captured groundwater flow towards the permeable section, called the *gate*. The funnel walls may be aligned in a straight line with the gate, or other geometric arrangements of funnel-and-gate systems can be used depending on the site conditions (Figure 12.6). This funnel-and-gate configuration allows better control over reactive cell placement and plume capture. At sites where the groundwater flow is very heterogeneous, a funnel-and-gate system can allow the reactive cell to be placed in the more permeable portions of the aquifer. At sites where the contaminant distribution is very non-uniform, a funnel-and-gate system can better homogenize the concentrations of contaminants entering the reactive cell. A system with multiple gates can also be used to ensure sufficient residence times at sites with a relatively wide plume and high groundwater velocity (Figure 12.7). Figure 12.7a shows an example of a funnel-and-gate system with two gates emplaced with caissons, while Figure 12.7b shows an example of a funnel-and-gate system with two reactive media emplaced in series within the gate. PRBs are installed as permanent, semi-permanent, or replaceable units across the flow path of a contaminant plume.

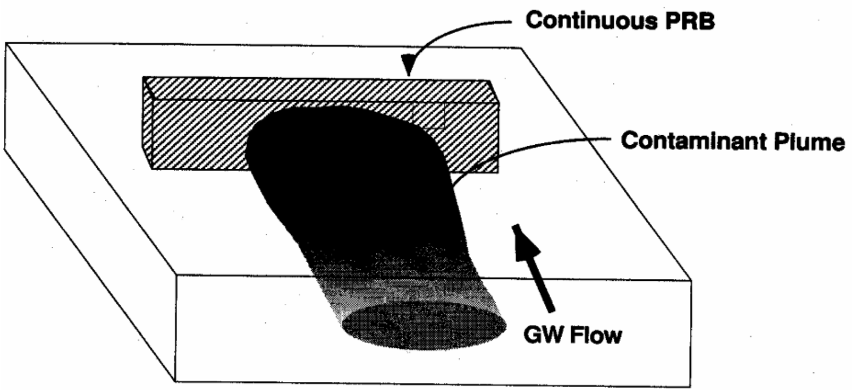

Fig. 12.5 Continuous permeable reactive barrier

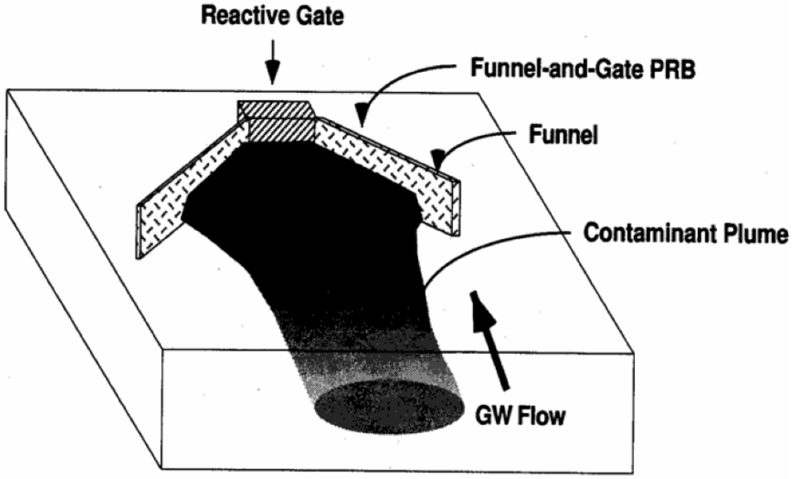

Fig. 12.6 Funnel-and-gate permeable reactive barrier

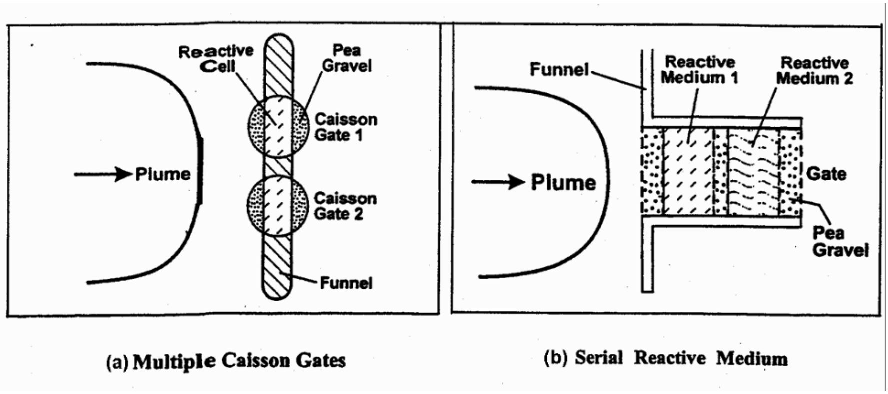

Fig. 12.7 Permeable reactive barrier configurations with multiple reactive cells

PRBs are often economically advantageous because:

- No pumping or above-ground treatment is required, the barrier acts passively after installation;
- No above-ground installed structures, so the affected property can possibly be put to productive use while it is being cleaned up;
- PRBs can be modified to treat several different types of contaminants;
- The reactive medium is often used up very slowly and has the potential to passively treat contaminated plumes for several years or decades;
- Very low operating costs other than site monitoring;
- No disposal costs or requirements for successfully treated wastes.

However, there are several limitations of PRBs which include:

- Lengthy treatment time relative to other active remediation methods (e.g., in-situ flushing, air sparging);
- Potential for loosing reactivity of the media, requiring replacement of the reactive medium;
- Potential for decrease in reactive media permeability due to biological clogging and/or chemical precipitation;
- Potential for plume bypassing the PRB as a result of seasonal changes in flow regime;
- Currently limited to shallow depths;
- Longevity of PRB performance is unknown.

General design approach includes site characterization, reactive media selection, treatability testing, PRB design using computer modeling, emplacement of PRB, and performance monitoring. Emplacement methods include conventional excavation, trenching machines, tremie tube/mandrel, deep soil mixing, high-pressure jetting, and vertical fracturing and reactant sand-fracturing. The monitoring parameters include contaminant concentration and distribution, by-products and reaction intermediates, groundwater velocity and pressure levels, permeability assessment of the reactive barrier, groundwater quality parameters (e.g., pH, redox potential, alkalinity), and dissolved gas concentrations (e.g., oxygen, hydrogen, and carbon dioxide).

Several studies have been reported where PRBs are used to treat contaminated groundwater (Sharma and Reddy, 2004). For example, the USCG facility Support Center included an electroplating shop which operated for more than 30 years, until 1984 (FRTR, 1997). In December 1988, a release was discovered during demolition of the former plating shop. Soil excavated beneath the floor of the shop was found to contain high levels of chromium. Subsequent investigation showed substantial groundwater contamination by chromium and chlorinated solvents. A full-scale PRB was constructed as part of an interim corrective measure. It was associated with a voluntary RCRA facility investigation where the electroplating shop was identified as a solid waste management unit under the facility's RCRA Part B permit. The barrier consisted of 450 tons of granular zero-valent iron placed into an underlying low conductivity layer at a depth of approximately 22 ft below ground surface. The required residence time in the treatment zone has been estimated as 21 h, based on a highest concentration scenario. The average velocity through the wall was reported as 0.2–0.4 ft/day. Analytical data from the first year of full-scale operation showed that the cleanup goal for Cr(VI) had been met but the goal for TCE had not. Cleanup goals for the site were based on primary drinking water standards: TCE (5μg/L) and Cr(VI) (0.1 μg/L). Cr(VI) concentrations were below cleanup goals in all down-gradient monitoring wells. However, TCE concentrations were above the cleanup goal in four of the six down-gradient wells. The reason for the elevated TCE concentrations in some of the down-gradient wells had not been identified. Estimated costs for the PRB were US $585,000, which corresponded to US $225 per 1,000 gallons of groundwater treated. By using a PRB rather than the typical pump and treat method, nearly US $4 million were saved in construction and long-term maintenance costs.

12.4.5 Bio-based Technologies and Treatment Trains

Monitored natural attenuation (MNA) is the use of natural attenuation processes within the context of a carefully controlled and monitored site cleanup approach to reduce contaminant concentrations, within a reasonable time frame, to levels that are protective of human health and the environment (ASTM, 1998; USEPA, 1998a). Unlike MNA which occurs naturally, bioremediation requires human intervention to create conditions that stimulate the growth of microorganisms to degrade/immobilize contaminants (Cauwenberghe and Roote, 1998). Phytoremediation uses plants to uptake or stabilize the contaminants, which is applicable to shallow aquifers remediation (Sharma and Reddy, 2004).

Using just one technology may not be adequate to remediate some contaminated sites with different contaminants and complex site conditions. Under such situations, different technologies are used sequentially or concurrently along with the primary treatment technology to achieve the remedial goals. Such use of multiple remediation technologies is often referred to as "treatment trains". Typical treatment trains used in contaminated sites include soil flushing followed by bioremediation, and pump and treat along with soil flushing or air sparging.

12.5 Conclusion

Groundwater is a valuable source of drinking water. It is also used extensively for agricultural and industrial applications. Remediation of contaminated groundwater is critical in order to protect human health and the environment. It is of the utmost importance to properly characterize the site, and such a characterization includes defining the site's geology, hydrology, and contamination, potential releases to the environment, and locations and demographics of nearby populations. Once the site has been characterized, a risk assessment of hazards at the site is performed and a suitable remedial action may be selected. In order to perform these different tasks in a fiscally responsible manner, it is important that the entire remedial planning, from initial site characterization efforts until the completion of site cleanup, follows a rational strategy. If contamination has been detected and risk posed by the contamination is unacceptable, an appropriate remedial technology must be selected and properly implemented. This requires a thorough understanding of not only the conditions within the subsurface, but also the advantages and drawbacks of the available remedial options. Such an understanding is necessary because improper implementation can often exacerbate site contamination. By possessing knowledge of the available technologies, remediation professionals will be better equipped to utilize proper judgment for the decisions regarding the remediation of contaminated sites. Several technologies exist for the remediation of contaminated groundwater. These technologies include pump and treat, air sparging, in-situ flushing, permeable reactive barriers, monitored natural attenuation, and bioremediation. Many of these technologies are used in combination or other innovative technologies are being developed. Remediation technology for a particular site is selected based on the site specific hydrogeologic and contaminant conditions, desired cleanup levels, remedial time, and cost.

References

ASTM, 1998, *Standard Guide for Remediation of Groundwater by Natural Attenuation at Petroleum Release Sites*, E-1943-98, West Conshohocken, Pennsylvania.

ASTM, 2002, *Annual Book of ASTM Standards*, West Conshohocken, Pennsylvania.

Cauwenberghe, L. V., and Roote, D. S., 1998, In Situ Bioremediation, Technology Overview Report TO-98-01, Groundwater Remediation Technologies Analysis Center, Pittsburgh, PA.

Cohen, R. M., Mercer, J. W., Greenwald, R. M., and Beljin, M. S., 1997, *Design Guidelines for Conventional Pump-and-Treat Systems*, Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma.

Federal Remediation Technologies Roundtable (FRTR), 1997, In Situ Permeable Reactive Barrier for Treatment of Contaminated Groundwater at the US Coast Guard Support Center, Elizabeth City, North Carolina.

Federal Remediation Technologies Roundtable (FRTR), 1998a, *Remediation Case Studies: Groundwater Pump and Treat (Chlorinated Solvents)*, Volume 9, EPA 542-R-98-013, Washington, D.C.

Federal Remediation Technologies Roundtable (FRTR), 1998b, *Remediation Case Studies: Groundwater Pump and Treat (Nonchlorinated Contaminants)*, Volume 10, EPA 542-R-98-014, Washington, D.C.

Reddy, K. R., and Adams, J. A., 2001, Cleanup of chemical spills using air sparging, Chapter 14, in: *Hand Book of Chemical Spill Technologies*, M. Fingas, ed., Mc-Graw Hill Company, pp. 14.1–14.29.

Reddy, K. R., Kosgi, S., and Zhou, J., 1995, A Review of in situ air sparging for the remediation of VOC-contaminated saturated soils and groundwater, *Hazardous Waste and Hazardous Materials* 12(2): 97–118.

Roote, D. S., 1997, *In-situ Flushing*, Technology Overview Report, Ground-Water Remediation Technologies Analysis Center.

Sharma, H. D., and Reddy, K. R., 2004, *Geoenvironmental Engineering: Site Remediation, Waste Containment, and Emerging Waste Management Technologies*, John Wiley & Sons, Hoboken, New Jersey.

USEPA, 1989, Risk Assessment Guidance for Superfund, Washington, D.C.

USEPA, 1991, Engineering Bulletin: In Situ Soil Flushing, EPA/540/2-91/021, Washington, D.C.

USEPA, 1995, Assessment of Barrier Containment Technologies, International Containment Technology Workshop, Baltimore, Maryland, August 29–31.

USEPA, 1996, *Pump-and-Treat Ground-Water Remediation: A Guide for Decision Makers and Practitioners*, EPA/625/R-95/005, Office of Research and Development, Washington, D.C.

USEPA, 1998a, Monitored Natural Attenuation for Ground Water, EPA/625/K-98/001.

USEPA, 1998b, Permeable Reactive Barrier Technologies for Contaminant Remediation, EPA/600/R-98/125, Office of Research and Development, Washington, D.C.