CHAPTER 7

Permeable Reactive Barriers (PRBs) for Environmental Site Remediation

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7.1 Introduction

7.1.1 General Considerations

For the last 25 years, permeable reactive barriers (PRBs) have proved their practical applicability for the *in situ* remediation of contaminated groundwater. PRBs represent a green and sustainable remediation technology that has become a cost-effective alternative to *ex situ* methods, such as pump-and-treat systems. The installation of a PRB involves the emplacement of a reactive medium perpendicular to the direction of groundwater flow in order to intercept the contaminant plume (Figure 7.1). As contaminated groundwater migrates passively through the reactive medium under the control of natural hydraulic gradients, the contaminants in the plume can be either immobilized or chemically transformed into environmentally acceptable forms downgradient of the barrier (*i.e.* less toxic, more biodegradable).

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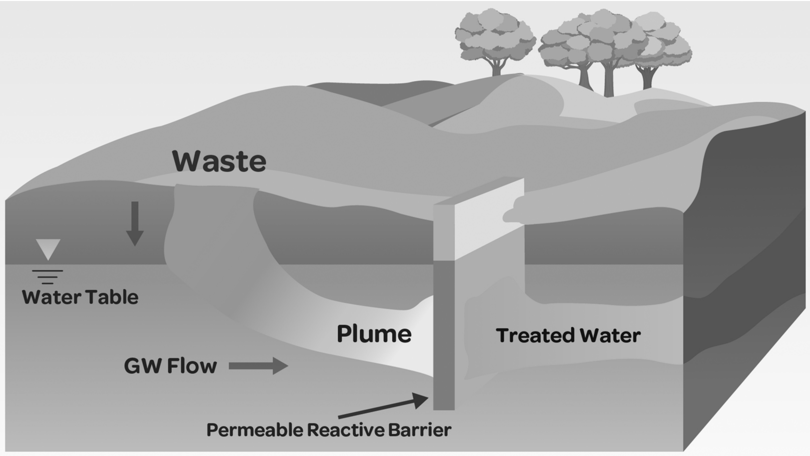

Figure 7.1 Diagram of a permeable reactive barrier (PRB).

7.1.2 Sustainability of PRBs Compared with Other Cleanup Technologies

One of the concerns that arise when selecting a clean-up strategy is how to determine whether a remediation technology is green and/or sustainable. New policies, analytical tools and standards of practice for identifying, assessing and managing collateral impacts of remediation projects have been developed and implemented by various regulators, governmental agencies and private organizations.[1]

PRBs emerged in the 1990s from the need for environmentally sustainable and more cost-effective techniques to remediate contaminated groundwater. PRBs are considered to be a passive remediation technology that is considered particularly sustainable when used for 10 years of more. Figure 7.2 illustrates a continuum of remediation technologies ranging from ‘‘least green’’ (excavation) to ‘‘most green’’ [monitored natural attenuation (MNA)]. PRBs lie next to MNA in terms of their green characteristics.[2]

This remediation technology has attracted considerable attention owing to the increasing interest in climate change issues as the footprint of PRBs is significantly lower than that in most remediation strategies. The term ‘‘remedy footprint’’ can be defined as ‘‘the overall environmental, social and economic impact of a remedial technology’’.[1]

The remedy footprint of installing PRBs can be calculated by using public domain tools such as the GSR Tool[3] or SiteWise.[4] These tools estimate the amount of energy saved by the use of PRBs compared with conventional methods, such as pump-and-treat systems. For this remediation technology, performed estimations show larger energy savings if the PRB lifetime exceeds 10 years.

The footprint of PRBs can be reduced during the construction phase by using recycled materials and hiring locally based suppliers of materials and

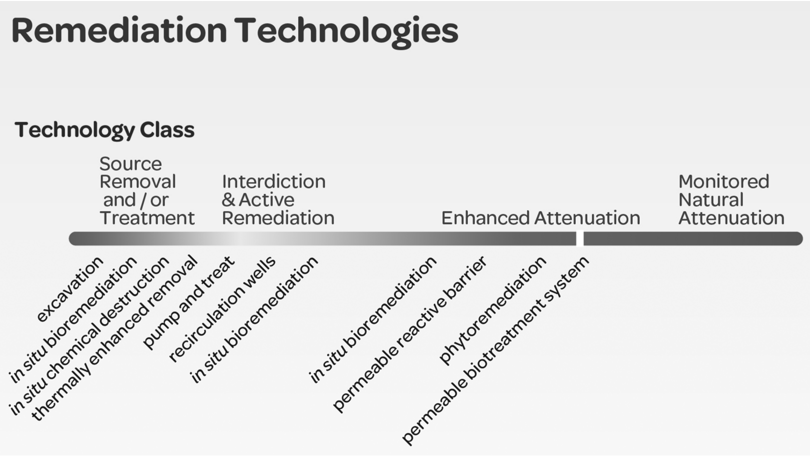

Figure 7.2 A continuum of remediation technologies ranging from least green (excavation) to most green (MNA).[2]

equipment. During operation, for performance monitoring, telemetric monitoring methods and passive or automatic samplers can be applied in order to reduce gas emissions from sampling vehicles. These actions together with savings from recycling and water conservation could contribute to a zero-sum carbon balance.

7.1.3 Advantages of PRB Technology

PRBs represent a green and sustainable groundwater remediation technology, able to treat a wide range of pollutants (organics, inorganics, radionuclides). The installation of PRBs reduces the exposure to pollutants since remediation takes place in the subsurface directly inside the contaminated aquifer and, therefore, no contaminated groundwater is pumped to the surface. Hence the contaminated site can be exploited while groundwater remediation is ongoing, as there are no above-ground installations except for the monitoring wells.

Among the advantages over conventional technologies are relatively low operational and maintenance costs. PRBs are more cost-effective than *ex situ* remediation alternatives, such as pump-and-treat systems. Although the installation costs are generally higher than those of other groundwater remediation technologies, operational and maintenance (O&M) costs are significantly lower. They present little or no energy cost and also low or no disposal costs for the by-products of the remediation process. In the case of PRBs, the O&M costs are mostly due to monitoring measures, which are required for any remediation approach.

The use of waste products and/or recycled materials as reactive media (agricultural wastes, iron slags, *etc.*) contributes to the reduction of the carbon footprint of the PRB system and favours the implementation of this technology in economically disadvantaged areas.

One of the main features of this technology is the longevity of reactive barriers, having operational lifetimes ranging from 10 to 30 years.[1]

An issue that will attract increasing interest in the coming years is the application of multiple PRB systems for the remediation of complex contaminated sites. The design of serial barrier systems or the use of mixed reactive media will allow the treatment of large multi-contaminant plumes.

7.1.4 Limitations of PRB Technology

The performance of PRBs is highly dependent on several parameters, such as site hydrogeology, type of contaminant and the nature of the reactive media used. Bypassing and the existence of preferential pathways may result in the hydraulic failure of the barrier, as only contaminants flowing in the direction of the barrier can be treated. Hence an exhaustive site characterization is essential for the success of a PRB.

These systems age owing to the exhaustion of the reactive media and the occurrence of undesirable processes that may hinder the performance of the barrier (*i.e.* clogging due to mineral precipitation, biofouling, *etc.*). Although only limited information about the long-term performance of PRBs is available, existing studies on real-scale PRBs have acknowledged problems related to the design of the systems and the difficulties in monitoring. Owing to the passive nature of this technology, long times may be required for meeting regulatory limits and long-term monitoring may therefore be needed.

Conventional construction methods impose depth restrictions. PRBs cannot be applied to plumes deeper than 20 m. In addition to these limitations, the existence of above-ground structures or buried rocks may also interfere during the installation of the barrier.

7.2 Design and Configuration of PRBs

The engineering design of PRBs comprises the selection of the most suitable barrier configuration, an appropriate reactive medium, the size of the barrier, barrier construction technology, quality control of the barrier and groundwater installation performance monitoring.[5]

A proper design of PRBs requires consideration of groundwater hydraulics, geochemical processes and reaction kinetics, and also the interaction between these processes.

In general, the design of a PRB follows some consecutive steps that include a preliminary technical and economic assessment, characterization of the site where the barrier is to be constructed, selection of the reactive medium, treatability studies (batch and column tests), engineering design, choice of the construction method, formulation of the monitoring plan and economic analysis.[6,7]

A detailed site characterization will help to determine the suitability of a PRB for a particular site, minimizing the risk of PRB failure by identifying construction and performance issues that may arise during the lifetime of the barrier.

The design needs to be tailored to provide a site-specific solution to meet the groundwater remediation objectives. A key aspect of the PRB design is a good understanding of the site and aquifer characteristics, which includes the site geology, hydrology, geochemistry, microbial activity and the contaminated plume 3D geometry. Directions and rates of groundwater flow (including variations over time and depth) and preferential flow paths are important. To avoid bypassing or overflow of the contaminant, temporal and depth variations in flow velocity and direction need to be understood.[7–9]

Once the site has been fully characterized, the selection of the reactive medium and the engineering design should be carried out on the basis of treatability studies at the laboratory scale (batch and column tests) and pilot scale. Laboratory-based trials are a prerequisite whereas field-based pilot-scale trials are recommended but not obligatory. Nevertheless, it is recommended that both laboratory and field-scale trials be conducted prior to full-scale installation, as these are considered the best ways of optimizing the design and minimizing the risk of failure of an PRB.[8]

After the reactive material has been selected, the dimensions, location and orientation of the barrier have to be defined. The ''capture zone'' refers to the width of the barrier necessary to capture the entire plume and ''residence time'' is defined as the time required for the contaminated groundwater to flow through the reactive material within the PRB to achieve the treatment goals.[7,8]

The hydraulic conductivity of the filling material is usually selected as a value one order of magnitude higher than that of the aquifer hydraulic. In order to obtain this condition, the reactive material is typically mixed with sand to achieve a suitable permeability.[10] However, the PRB interior changes its hydraulic properties during operation, as chemical reactions and/or bacterial growth may cause clogging/fouling.[11–14]

There is an increasing need to incorporate contingency plans. The development of contingency plans requires the specification of design criteria and performance objectives and the determination of what constitutes a failure in order to trigger clearly the activation of the contingency plan.

7.2.1 Elements and Configuration of PRB Systems

The treatment matrix and the hydraulic control system are the two main design components of PRBs. The treatment matrix can be composed of a single or a combination of several reactive materials able to enhance natural attenuation processes and degrade or immobilize target contaminants.

The hydraulic control system is designed to conduct groundwater and the target contaminants towards the reactive zone. In order to improve the hydraulic performance of the PRB, sustainable hydraulic enhancements may be applied, including the use of solar or wind-driven, low-rate groundwater pumps or passive siphons, to control and route the plume through a PRB.

7.2.2 Configuration of PRB Systems

Two geometric configurations are the most frequently used in field applications: continuous and funnel-and-gate PRBs. The continuous PRB configuration consists of a single reactive zone installed across the contaminant plume whereas the funnel-and-gate system consists of a permeable gate (reactive zone) placed between two impermeable walls that redirect the contaminated plume towards the reactive zone (Figure 7.3).

The choice between these two configurations will depend on the site characteristics and the cost of the reactive material. The funnel-and-gate configuration is preferred when expensive reactive materials are used, since the reactive zone requires less material. However, the construction costs of continuous-type barriers are lower than those of the funnel-and-gate system. Hence a balance must be struck between the cost of the reactive material and the construction cost of the barrier. For the treatment of complex

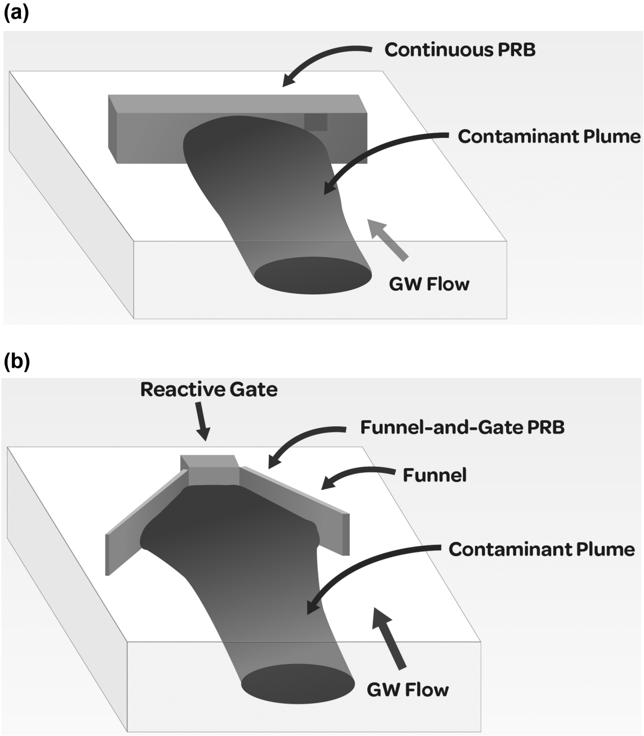

Figure 7.3 PRB configurations: (a) continuous barrier and (b) funnel-and-gate barrier.[15]

contaminant plumes, consecutive multiple reactive media can be installed in the funnel-and-gate setup[7] (Figure 7.4).

For any site where the groundwater flow and plume geometry are well understood and there are no construction constraints, the continuous barrier is the best design choice.[6] Continuous PRBs are the most common configuration. Their construction is easier and cheaper, minimizing the impact on the natural groundwater flow site conditions at a site. However, the barrier covers the full width of the plume, so the continuous barrier design generally requires a larger amount of reactive material than the funnel-and-gate system.

In the funnel-and-gate PRB configuration, the groundwater is routed towards the reactive medium (the gate) by using low-permeability funnels. It is recommended that the funnels be installed in an impermeable layer (aquitard) to prevent contaminant underflow.[6] In an extremely large contaminant

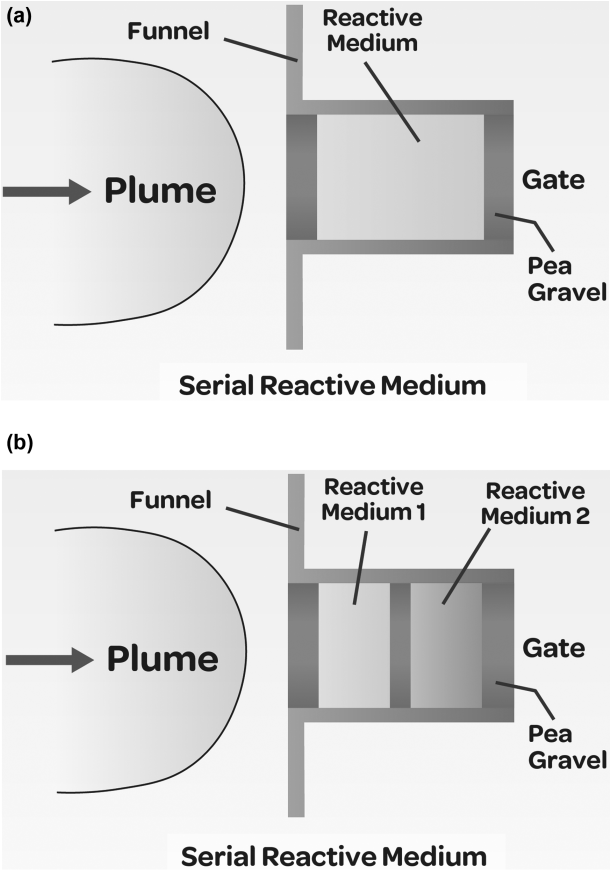

Figure 7.4 Funnel-and-gate PRB: (a) single and (b) consecutive multiple reactive media.[16]

plume or highly heterogeneous aquifer, the funnel-and-gate system can be modified to have multiple gates.

An alternative to conventional configurations is the installation of multiple caisson gates (Figure 7.5). Caisson PRBs are also known as *in situ* reactive vessels. A caisson is a prefabricated vessel that can be pushed or vibrated down into the subsurface. After reaching the intended depth, the soil within the caisson can be augered out and replaced with the reactive medium. Upon emplacement of the reactive cell/medium, the caisson can be pulled straight out. It is not economical to drive a caisson with a diameter larger than 2.5 m into the subsurface.

This reactive vessel PRB design is similar to that of the funnel-and-gate barrier except that it replaces the gates with *in situ* reactive vessels. Reactive vessels can be pulled out of the ground for maintenance or replacement of the reactive medium.[17] This option facilitates maintenance operations without adding much cost compared with conventional funnel-and-gate systems. The reactive medium can be easily replaced when exhausted and its performance can be restored quickly. Furthermore, the reactive vessel design allows repairs in the barrier if performance failures occur. Despite the versatility of this design, a disadvantage is that the installation of reactive vessels requires permanent structures to be placed above ground.

A passive siphon can also be used in combination with a PRB in order to enhance the hydraulic performance.[18] A siphon system uses a natural hydraulic head to induce essentially passive groundwater flow for remediation (Figure 7.6). This method can significantly lower the operating and maintenance costs compared with traditional pump-and-treat methods. The passive operation of the siphon is similar to that of the funnel-and-gate and continuous permeable-wall treatment systems. This system can be used for

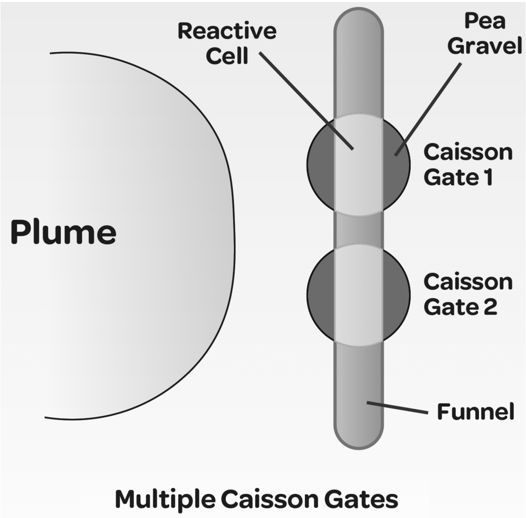

Figure 7.5 Reactive vessel PRB with multiple caisson gates.

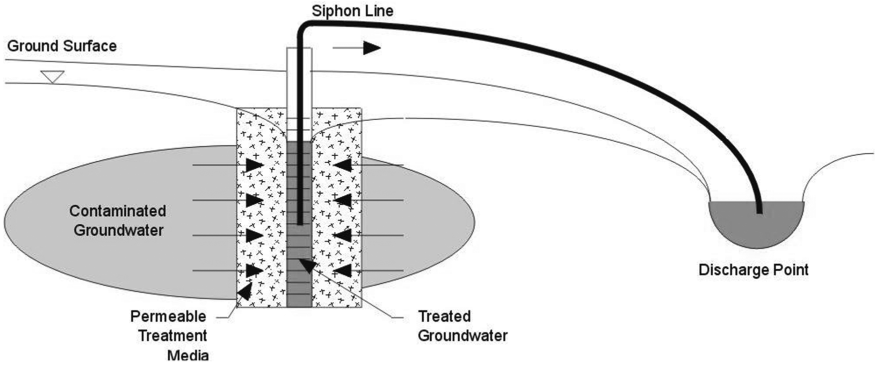

Figure 7.6 Conceptual geosiphon design.[2]

relatively shallow groundwater recovery, having a maximum practical lift of 7.5 m (25 ft) at standard temperature and pressure.

7.3 Reactive Media Used in PRBs

Contaminants in the plume can be removed by either degradation or immobilization as a function of the reactive medium used in the PRB.

Zerovalent iron (ZVI) has traditionally been used for the remediation of chlorinated solvents in groundwater. Halogenated compounds, including perchloroethylene (PCE) and trichloroethylene (TCE), and redox-sensitive metals (*e.g.* Cr, As) have often been treated by using granular ZVI. ZVI has also proven effective in treating energetic compounds, including nitrosamines and trinitrotoluene (TNT).

Although ZVI is the most commonly used reactive material, there is currently a wide range of other reactive materials available. Granular activated carbon (GAC), zeolites, peat, sawdust, oxygen-releasing compounds (ORCs), *etc.*, have been evaluated and/or used. Over the past 10 years, biowalls or biobarriers have been widely applied for the biologically enhanced degradation of chlorinated hydrocarbons.[19]

Table 7.1 summarizes frequently treated contaminants, reactive media and contaminant removal mechanisms.

7.3.1 Zerovalent Iron (ZVI)

ZVI is the most extensively used medium owing to its high reduction potential (*ca.* −440 mV). It has been applied to the removal of a wide range of contaminants, especially chlorinated hydrocarbons, *e.g.* TCE, PCE, vinyl chloride (VC) and dichloroethylene (DCE). Metals, metalloids and radionuclides have also been removed through processes including adsorption, surface complexation, reductive precipitation and coprecipitation. Currently, ZVI is being used in many commercially available products as a

Table 7.1 Summary of contaminants, reactive materials applied for their remediation and the mechanism of interaction. Reproduced from ref. 7 with permission from Elsevier, Copyright 2018.[a]

Contaminants	Reactive materials	Removal mechanism
Chlorinated hydrocarbons (PCE, TCE, DCE, TCA, VC)	ZVI, H_2/Pd, Zn^0	Reductive dechlorination
	GAC, SMZ, tyre rubber	Sorption/surface complexation
	Mulch, sand/wood chips	Anaerobic biodegradation
BTEX (benzene, toluene, ethylbenzene, xylene)	ZVI, H_2/Pd	Chemical reduction under anaerobic conditions
	GAC, ground rubber, SMZ, cyclophane I, II	Sorption/surface complexation/ion exchange
	Compost, peat, sawdust, leaf litter	Aerobic biodegradation
Phenol	GAC, SMZ	Sorption/surface complexation/ion exchange
Nitrobenzene	ZVI	Chemical reduction/surface complexation on corrosion products
PCBs, PAHs and pesticides (DDE, DDT, DDD)	ZVI	Chemical reduction/surface complexation onto corrosion products
	GAC	Sorption/surface complexation
Heavy metals (Ni, Cu, Zn, Pb, Cd, Fe, As, Cr, Hg, *etc.*)	ZVI	Reductive precipitation/surface complexation on corrosion products
	Sodium dithionite	Reductive precipitation
	Zeolites, OC, activated alumina, bentonite, ferric oxyhydroxides, chitosan	Sorption/surface complexation/ion exchange
	Limestones, bone char, apatite (clinoptilolite), TRM, fly ash	pH-induced precipitation (and/or sorption)
	Peat moss, compost	Surface complexation/sorption/bioprecipitation
Radionuclides (U, ^{99}Tc, Mo, Se, ^{137}Cs, ^{90}Sr, Pu, Am)	ZVI	Reductive precipitation/sorption or surface complexation onto corrosion products
	Zeolites, titanium dioxide, coal, pecan shells, lignite	Sorption/surface complexation/ion exchange
	Bone char phosphate, hydroxyapatite, limestone AFO, BOF, apatite II, ferric chloride, ferric nitrate	pH-induced precipitation/precipitation as nitrates
COD, AOX, NO_3^-, NH_4^+	ZVI	Reductive precipitation/surface complexation on corrosion products/precipitation of Fe phases
	Pecan shells, clinoptilolite, apatite II, polystyrene, zeolite	Sorption/surface complexation

Table 7.1 (*Continued*)

Contaminants	Reactive materials	Removal mechanism
	Sawdust, wood chips, wheat straw, softwood and sand, maize cobs, compost	Anaerobic biodegradation (and surface complexation/ sorption)
${PO_4}^{3-}$	ZVI, OC, iron oxides, peat/ sand	Sorption/surface complexation
	Limestone	pH-induced precipitation
${SO_4}^{2-}$	ZVI	Sorption onto corrosion products/chemical precipitation/chemical reduction by H_2 generated during corrosion
	SMZ	Sorption/surface complexation/ion exchange
	Limestone, TRM	pH-induced precipitation
	Mushroom compost	Anaerobic biodegradation
Cl^-	ZVI	Reductive precipitation/ surface complexation on corrosion products
	Zeolite, AC	Surface complexation/ sorption/ion exchange

[a] ZVI: zero valent iron; GAC: granulated activated carbon; SMZ: surfactant-modified zeolites; OC: organic carbon; TRM: transformed red mud; AFO: amorphous ferric oxides; BOF: basic oxygen furnace slag; TCA: trichloroacetic acid; PCBs: polychlorinated biphenyls; PAHs: polycyclic aromatic hydrocarbons; DDE: dichloro diphenyl dichloroethylene; DDT: dichloro diphenyl trichloroethane; DDD: dichloro diphenyl dichloroethane.

bioremediation-enhancing agent, since the ZVI corrosion reaction in water provides a sustained flux of dissolved hydrogen to the aqueous system.[20–22]

7.3.2 Activated Carbon

Activated carbon (AC) was one of the materials commonly used in the early stages of the PRB technology. It has been widely applied for the removal of organic contaminants such a as phenols, benzene, toluene, ethylbenzene and xylene (BTEX), PCE and TCE. Heavy metals, such as Cr, Cd and Pb, have also been removed using AC.[23] Removal of contaminants occurs mainly through sorption. Chemical parameters, such as pH and organic matter content, will reduce the sorption capacity by competitive reaction for binding sites.

7.3.3 Zeolites

Zeolites are aluminosilicate minerals that exhibit high cation-exchange capacities (200–400 meq per 100 g) and large surface areas (up to 145 $m^2\,g^{-1}$).[24] Natural zeolites, such as clinoptilolite, have been extensively used for the removal of ${NH_4}^+$ and heavy metals. In zeolites, the removal of cationic contaminants occurs *via* sorption onto negatively charged mineral surfaces and *via* ion exchange. Natural zeolites show poor performances for organic compounds. However, the surface chemistry of zeolites can be modified with surfactants such as cetyltrimethylammonium bromide (CTAB), to create hydrophobic and hydrophilic segments on the zeolite. Surface modification facilitates the removal of a wider range of contaminants including heavy metals, ammonium, nitrate, phosphate, radionuclides, PCE and BTEX, reaching efficiencies close to 90%.[24]

7.3.4 Alkaline Materials

Alkaline materials, (*e.g.* limestone, dolomite, quicklime) have frequently been used for the treatment of acid mine drainage.[25] The addition of these materials raises the groundwater pH, which favours the precipitation of the contaminants. These materials have mostly been applied to remove heavy metals, although they show good removal efficiencies with other contaminants, such as phosphates.[26] A major issue with alkaline media is that the precipitates formed can clog the barrier and affect its hydraulic performance. The application of materials such as limestone can also lead to environmental problems such as directly increasing the hardness of the groundwater and CO_2 content.

7.3.5 Apatites

Apatites are calcium phosphate minerals whose structure allows both cationic and anionic solid solutions and substitutions. Naturally occurring apatite minerals include hydroxyapatite [$Ca_5(PO_4)_3OH$], fluorapatite [$Ca_5(PO_4)_3F$] and chlorapatite [HAp; $Ca_5(PO_4)_3Cl$]. HAp has been extensively used for environmental remediation purposes, especially for the removal of radionuclides (U and ^{90}Sr),[27] heavy metals[28] and anionic contaminants, such as AsO_4^{3-}.[2]

Apatites remove contaminants mostly *via* four mechanisms:

1. direct sorption of cationic contaminants on negatively charged surface sites;
2. ion exchange, mainly with Ca^{2+};
3. precipitation as phosphates, carbonates, oxides and hydroxides;
4. surface adsorption and immobilization by incorporation into the internal structure of the apatite.

7.3.6 Transformed Red Mud

Transformed red mud (TRM) is an alkaline solid whose pH ranges from 8 to 10.5, a by-product of the refinement of bauxite in alumina production. The mud is mostly composed of hydrated alumina and iron oxides. Accessory minerals such as calcium aluminosilicates, magnesium hydroxides, calcium hydroxides and hydroxycarbonates are also present. TRM has been applied as an alternative to lime for treating acidic sulfate soils and acidic mine drainage.[29] Removal of heavy metals by TRM has also been reported.[30,31] Red mud-based adsorbents have also been tried in laboratory trials for the removal of phosphates[32] and other frequent contaminants such as As and phenolic compounds.[33]

7.3.7 Alumina and Iron Oxides

Alumina (Al_2O_3), ferric phases such as amorphous ferric oxide [AFO; ($Fe(OH)_3$)], goethite (α-FeOOH), magnetite (Fe_3O_4) and haematite (Fe_2O_3), and hydrous titanium oxide [$Ti(OH)_4$] have attracted considerable attention owing to their high sorption capacity. Currently, the use of iron oxide nanoparticles enhances the removal efficiency and has proven to be a good option for groundwater cleanup, especially in the case of deep aquifers.[34]

The contaminant removal by these materials occurs *via* electrostatic attraction due to the development of surfaces charges on the oxides or by surface complexation mechanisms. At low pH, there is increased surface protonation, which tends to favour the sorption of anions.

Contaminants treated with oxides include As(III) and As(V),[35] UO_2^{2+},[36] PO_4^{3-},[37] and heavy metals.[38] Surface charge is generally dependent on geochemical conditions such as pH, redox potential E_h and the groundwater constituents such as sulfates and carbonates, which compete for surface sites.[39,40]

7.3.8 Biowalls

Biobarriers or biowalls can be defined as "PRBs that promote biological treatment of groundwater contaminants".[2] In *in situ* biowalls, solid inexpensive organic materials, such as mulch, compost or agricultural wastes, are generally used to stimulate the microbiological degradation of carbon-based compounds.[1] The performance of biowalls relies on the existing microbial populations able to degrade target contaminants. Therefore, it is important that the right microbial populations are present. When this method is used, the microbes needed to initiate such processes are often ubiquitous, particularly in the upper layers of the aquifer.

Biowalls have been widely applied over the last 10 years to enhance the anaerobic degradation of chlorinated hydrocarbons (*e.g.* PCE, TCE) and also energetic and munitions compounds. To a lesser extent, biological PRB systems have also been used for the removal of radionuclides, heavy metals and inorganic anions (*e.g.* sulfates, nitrates).[41]

These PRB systems allow the treatment of complex plumes, even beyond the biowall, owing to the downgradient migration of soluble organic matter. However, its longevity is significantly shorter compared with ZVI walls and replenishment of the organic substrate may be required once the reactive medium is exhausted. Vegetable oil amendments are commonly used to stimulate biodegradation processes in order to optimize PRB performance.[28]

In biowalls, biodegradation of contaminants may occur under aerobic or anaerobic conditions.

7.3.8.1 Aerobic Conditions

A wide variety of organic contaminants can be efficiently removed *via* aerobic biodegradation. Such contaminants, including petroleum hydrocarbons such as BTEX and methyl *tert*-butyl ether (MTBE), are mostly reduced in Nature.[42]

In aerobic biodegradation, terminal electron acceptors (TEAs) are required. TEAs are chemical compounds that receive or accept an electron during the oxidation of a carbon source. Nitrates, sulfates, O_2 and CO_2 are the most commonly available electron acceptors in the environment. However, molecular oxygen is preferred, as it provides more energy to microbial populations and hence increases the degradation rates. Several methods have been used to release oxygen or create an aerobically active zone in the subsurface. Oxygen diffusers and air spargers blow air into the subsurface, whereas solid oxygen- and nitrate-releasing compounds (ORCs) act as chemical sources of oxygen and nitrate for the microbial populations. Calcium peroxide, hydrogen peroxide, sodium nitrate and sodium percarbonate are some of the most frequently used ORCs.[2,7]

7.3.8.2 Anaerobic Conditions

In the case of anaerobic biodegradation, organic substrates used as reactive media in PRBs serve as the source of electrons, whereas the contaminants serve as the electron acceptors for the metabolic process. Nitrates, sulfates and chlorinated solvents are some of the contaminants more frequently anaerobically biodegraded.

Nitrates can be removed by several species of denitrifying bacteria (*e.g. Paracoccus denitrificans*, *Pseudomonas denitrificans*, *Thiobacillus denitrificans*) in the presence of several inexpensive organic substrates such as alfalfa leaves, peat, sewage sludge, sawdust, wood waste or compost.[43]

Several carbon-based reactive mixtures have been tested for sulfate removal: wood chips, sawdust, composted municipal sewage sludge and leaves. Sulfate-reducing bacteria enable the decomposition of organic matter by using sulfate (SO_4^{2-}) as terminal electron acceptor and reducing it to hydrogen sulfide (H_2S). The anaerobic sulfate reduction process increases the pH and releases other products such as dissolved phosphates, which may be utilized by microbes as nutrients. Under such relatively high pH conditions, heavy metals can precipitate as metal sulfides. The use of compost-based sulfate-reducing bacteria to remove sulfate and precipitate heavy metals, including Cu, Co, Ni, Cd and Zn, has been reported.[44]

Compost, peat and mulch have frequently been used as materials in biobarriers for the degradation of chlorinated solvents. Decomposition of organic media creates a strong bioactive zone that facilitates the anaerobic biodegradation of TCE.[45,46]

7.3.8.3 Bioaugmentation

Bioaugmentation consists in the addition of cultured microorganisms to the saturated zone to enhance the biodegradation of soil and groundwater contaminants. When applied to PRBs, bioaugmentation has been most commonly considered for the bioremediation of chlorinated solvents, either as a sole treatment or as a contingency alternative when degradation stops at intermediate dechlorination products.[2] Bioaugmentation is a feasible option when native dechlorinating species are not present or are poorly distributed.[47]

7.3.9 Combined Media

The application of combined reactive media has aroused increasing interest owing to its advantages over conventional PRB designs:

- treatment of complex contaminant plumes;
- lifetime extension of the barrier;
- increased removal rates.

Combinations of a wide range of reactive media have been described. Mixtures of different metallic particles (nano-Ni^0/Fe^0, Zn^0/ZVI) have been reported to facilitate the removal of redox-sensitive heavy metals and the degradation of TCE.[48] Combinations of vegetable residues, such as compost and mulch, have also been applied to the remediation of chlorinated solvents.[41]

The combination of biowalls with ZVI has also been evaluated for the treatment of complex contaminant plumes, owing to the synergistic effect of reduction and sorption mechanisms. This approach allows the concomitant treatment of different contaminants (heavy metals, As, Se). ZVI treatment and natural biodegradation are compatible treatment processes for many chlorinated solvents. Both are reductive processes that follow first-order reaction kinetics and involve the generation of partially dechlorinated daughter products with reaction rates that are typically slower than those of the parent compound. Under appropriate circumstances, the two processes may be synergistic, as ZVI can enhance downgradient biodegradation rates by creating a more suitable environment for anaerobic bacterial metabolism.

There is currently a wide variety of commercial products based on the combination of ZVI and organic carbon substrates. Table 7.2 summarizes the characteristics and applications of five of the currently commercially available products. ABC+®, EHC® and EOS_{ZVI}® provide a source of organic carbon and nutrients for microorganisms in order to enhance anaerobic reductive dechlorination processes. Others, such as BOS 100® and E-ZVI®, degrade the contaminant abiotically whereas the oil or the food-grade carbon acts as a long-term electron donor source to enhance microbial degradation.

Table 7.2 Characteristics and applications of five of the currently commercially-available products of combined media.

	Biologically enhanced treatment			Chemical treatment	
	ABC+®[49] (Redox-tech, 2018)	EHC®[50] (Peroxychem, 2018)	EOS_{ZVI}®[51] (Trap-and-treat, 2018)	BOS 100®[52] (EOS remediation, 2018)	E-ZVI®[53] (Remquest, 2018)
Constituents					
ZVI	Micro ZVI	Micro ZVI	Carbonyl ZVI	Micro ZVI	Nano-/micro-ZVI
Organic substrate	Lactic acid+fatty acids	Controlled released carbon+nutrients	Water-mixable oil (soybean oil)	Activated carbon (food-grade carbon)	Water-in-oil emulsion+surfactant +food-grade vegetable oil
Applications	Chlorinated solvents and daughter products	Heavy metals Chlorinated solvents Pesticides Hydrocarbons	DNAPLs (dense non-aqueous phase liquids)	Chlorinated solvents	Halogenated hydrocarbons

These products show great versatility, since they can be applied to a wide range of target contaminants and concentrations. One of the main features of these products is their easy application in the field. Preparations can be injected directly into the subsurface by using direct-push or packer injection. Soil mixing, trenching and pneumatic fracturing are also feasible alternatives for their installation.

7.4 Application of Nanomaterials to Reactive Barriers

Emerging technologies for groundwater remediation, such as nanotechnology, can lead towards more cost-effective and environmentally friendly solutions. The direct injection of nanoparticles into the subsurface overcomes some of the drawbacks of conventional PRBs, such as depth restrictions or the use of complex geological media.

One of the advantages of the use of nanomaterials is that they can be injected directly into both shallow and deep aquifers, without conditioning above-ground use. Nanoparticles can move downgradient, allowing treatment over large areas.[54]

As nanoparticles are being applied at an increasing number of sites, more data will become available on performance, cost and environmental aspects. Additional information generated in this way will allow environmental professionals to determine whether the technology might be applicable to their specific sites. Cost estimates show that the injection of nano-ZVI (nZVI) for the treatment of TCE and PCE represents cost savings of 90% over pump-and-treat methods and 80% over conventional PRB options.[55] In addition to the potential cost savings, the amount of time required to clean up a site could be greatly reduced.[56] This shortening of the treatment time would result in a decrease in operating costs.

Despite the apparent potential of nanomaterials as remediating agents, some observed side effects must be assessed. Their increasing application to soil and groundwater remediation will turn nanomaterials into a new source of pollution. nZVI particles have been reported to be adsorbed by cells and also to cause cell death and DNA damage.[55,56]

nZVI is the most commonly used nanomaterial for soil and groundwater remediation. It is a versatile remediation tool able to treat a wide range of dissolved contaminants in water, including heavy metals such as Cr(VI), lead, nickel and mercury, redox-sensitive radionuclides such as U, metalloids, perchlorate and nitrate.[56]

Some modifications have been performed to improve the properties of iron nanoparticles. Some examples of modified nZVI are bimetallic nZVI (using a metal catalyst such as Ni, Cu, Pd, Pt, Ag or Au),[48] amorphous nZVI, emulsified nZVI (coated with food-grade surfactant) and carbon- and sepiolite-supported nZVI.[57–59]

Iron nanoparticles can be surface modified for groundwater treatment. Typical examples of surface-modified nZVI are sulfide-modified nZVI (S-nZVI) and emulsified ZVI (EZVI). The magnetic S-nZVI has shown promising results for its application in the remediation of deep aquifers.[60] EZVI is a water-in-oil emulsion consisting of nano-/micro-scale ZVI, surfactant, food-grade vegetable oil and water. EZVI is a NASA-patented material that was aimed specifically to deliver reactive iron particles, permitting full miscibility with contaminants.[59] Currently, there is an nZVI-based commercial solution that is being applied for the remediation of dense non-aqueous phase liquid (DNAPL)-contaminated sites.

Apart from metallic nanoparticles, nanosorbents, such as carbon nanotubes and nanozeolites, have shown promising performances for groundwater remediation.[61] Carbon nanotubes have been extensively studied for the removal of metalloids such as arsenic compounds, heavy metals such as Cr^{3+}, Pb^{2+} and Zn^{2+} and other organic and inorganic pollutants such as dioxins and various volatile organic compounds.[62]

Zeolites have traditionally been used for the removal of heavy metals, chlorinated solvents and nutrients (phosphate and ammonium) from surface waters. The introduction of new functional groups in the zeolite through several processes of surface modification substantially improves its activity and selectivity for the removal of several contaminants, especially heavy metals.

Nature-inspired nanomaterials are attracting increasing interest for environmental applications, as they are environmentally safe and can be easily degraded. Perminova *et al.*[63] discussed the viability of humic-based PRBs for the remediation of deep subsurface radioactive plumes. Direct injection of ''mineral-adhesive'' humic derivatives was proposed by using a ''fence row'' of wells to create a ''humic curtain'' for the removal of actinides from the contaminated groundwater.

Further developments are needed in the synthesis of new materials with specific and selective properties for environmental applications. Future studies should also address knowledge gaps in the fate and transport of nanoparticles, cost–benefit analyses and public acceptance of nanotechnology for site remediation.[48]

7.5 Construction Technologies for PRBs

Traditionally, the most common type of installation design of PRB is a continuous trench wall filled with reactive medium in the path of a contaminant plume. More recently, PRB design technology has advanced, using single-pass trenching, direct injection, hydraulic and pneumatic fracturing injection technology and large-diameter borehole-filled completions.[1]

The installation method for a PRB system is critical for its successful performance and includes geotechnical and civil design considerations, the method of construction, service and infrastructure, waste management and health and safety requirements. Important factors for suitable construction for a specific site include the following:

- soil quality at the site and soil waste generation;
- designer's and contractor's expertise;

- aquifer and aquitard characteristics;
- construction constraints at the site (space availability for construction of barriers);
- construction budget.

The depth to the groundwater table plays a part in the selection of the construction techniques; for a shallow depth excavation techniques are suitable, whereas for a deeper barrier injection methods are suitable. The soil quality at the contaminated site strongly influences the type of excavation in terms of the side-wall support. In general, the excavation technique generates more spoil than injection-based techniques. However, excavation techniques are relatively easy and straightforward to apply.

Depending on the contaminants present and disposal methods, the soil generated also influences the choice of the construction technique. A thorough understanding of the site stratigraphy and lithology is important when choosing a particular construction method. For instance, the use of sheet piling to construct a reactive gate may not be a good choice where low-permeability layers exist because of the smearing potential. If a low-permeability layer exists at the site, the PRB can be fitted into this layer. If such a layer does not exist at the site, then a hanging wall design can be employed, but the uncertainty regarding plume capture may increase.[64] Hanging barriers will result in significant vertical flow gradients and it is critical that the temporal distribution of vertical flow velocities should be accurately generated.

Usually, the conventional PRB installation techniques require some degree of excavation, which limits the PRB to fairly shallow depths of ~20 m. However, the use of new construction techniques, such as slurry injection and hydrofracturing, is able to overcome this depth limitation.[65]

Continuous trenching excavation involves filling with reactive medium and backfilling simultaneously. Continuous trenches can be dug to install a treatment zone 0.3–0.9 m wide to a depth of 11 m. Although the cost of the continuous trenching equipment is relatively high, the fast trenching rate may make the overall installation cost economical for larger barriers.

Biopolymer trenching is a cost-effective and versatile PRB method. During the excavation of a biopolymer trench, biopolymer slurry such as guar gum is pumped into the trench to provide stability to the trench wall. After the emplacement of the reactive medium in the trench, an enzyme is recirculated to degrade the polymer.[6] This construction technique allows the installation of trenches up to 21 m deep.

Sheet piling generates much less soil than other methods and is a useful construction technique when there are horizontal space limitations.[6] During trench construction, sheet piles are driven around the perimeter of the PRB and the soil. Internal bracing is required as the depth increases. After backfilling is completed, the sheet piling is removed and the groundwater is allowed to flow through the treatment zone. The installation of the sheet pile is relatively quick and easy.

Slurry wall installation is generally used to construct the impermeable funnels in funnel-and-gate PRBs. Soil–bentonite, cement–bentonite and composite slurry walls are the most commonly used preparations.[66] A slurry trench is generally excavated and an appropriate slurry is injected into the trench to maintain its stability. The slurry wall construction process is time consuming and is more expensive than sheet piling.

Unsupported excavation is typically limited to depths of 6 m or less. PRBs can be constructed without any side-wall supports if the trench can remain open for about 4 h without any significant caving in. When deeper placement is required (>6–9 m) and trench side-wall collapse is a risk, trench boxes can be used for stability. Supported excavation for trench side walls can be constructed using trench boxes or hydraulic shores. The depth of the trench should be <6 m. Successful installation depends on an effective site layout, the construction sequence and the selection of heavy equipment, flexibility in the construction method to accommodate unforeseen conditions, an understanding of backfill materials, the potential impact on the community and the environment and the season for the construction work.[19]

The injection method creates a treatment zone within the contaminant boundary by drilling series of boreholes or injection wells and injecting the reactive material (chemical–particulate mixture) into the treatment zone. Potential advantages of this approach include the remediation of deep aquifers and spills below existing buildings. Usually, two or three rows of overlapping, interlocking columns can offer an effective barrier. Nevertheless, it has to be ensured that the contaminant plume is efficiently taken care of and no by-passing or fingering occurs, which may hinder the remediation effect (Figure 7.7).

Hydraulic/pneumatic fracturing consists in intentional fracturing of a subsurface using pumped water and/or air under high pressure. As the confining pressures are exerted in the borehole, fractures will open and propagate out laterally from an initiation point. A fracture fill slurry composed of the reactive medium can then be injected into the fracture to form a reactive treatment zone. Fractures have a preferred direction of propagation; they are therefore asymmetric with respect to the borehole and they climb in the preferred direction of propagation. Fractures can be controlled to occur either horizontally or vertically. This technique allows the emplacement of a barrier to depths > 2.5 m. Fracturing causes minimal disturbance, does not generate contaminated soils and is inexpensive. Fractured zones may also be applied to direct groundwater flow towards the gates in a funnel-and-gate system. Some drawbacks of emplacement by hydraulic fracturing include difficulty in controlling the fracture direction and the limited soil conditions in which it can be used effectively.[65]

High-pressure jetting is an established practice for injecting grouting agents to improve the structural characteristics of soil for construction purposes. Recently, injection of grout has been used to construct funnel walls. This technique only requires the use of small equipment, which results in a lower mobilization cost.

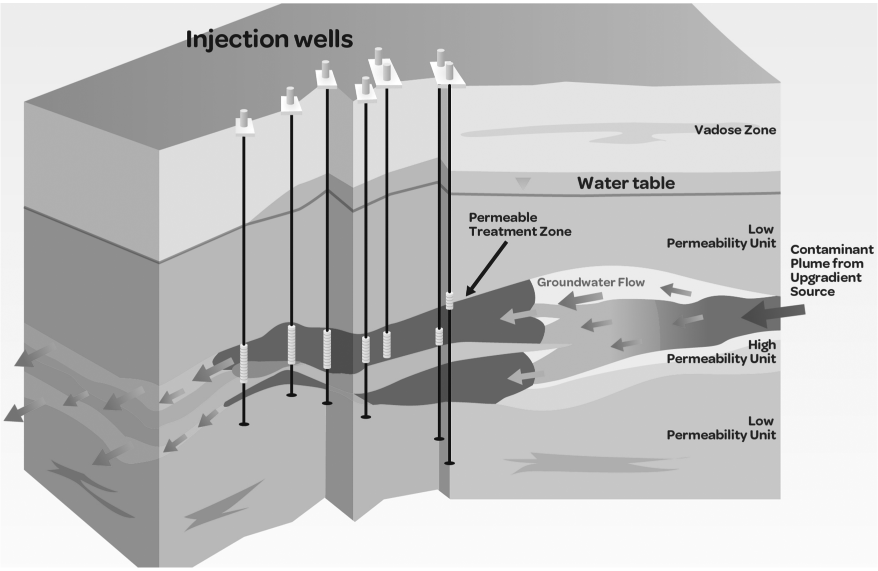

Figure 7.7 Diagram of an injection system.

Deep-soil mixing can be used at depths up to 40 m, creates minimal spoils and has a higher production rate with lower costs than jet grouting. Soil mixing generally achieves greater PRB uniformity compared with the injection and fracturing techniques. The mixing results in higher hydraulic conductivities and, consequently, a slight increase in the capture zone of the wall. Mixing can also be applied upstream of the barrier in order to maintain parallel flow lines entering the PRB.

Another alternative to conventional construction techniques is passive groundwater capture and treatment by *in situ* reactor cells. This option involves the emplacement of reactor cell(s) in the subsurface consisting of reactive medium and capturing the contaminated plume in the reactor for treatment.[5] This system does not involve any pumping equipment and the plume is directed into the reactor by siphoning or by natural gradient.

7.6 Performance Monitoring

Performance monitoring plays a decisive role in determining whether the PRB is meeting regulatory compliance and performance criteria. Monitoring programmes should be developed according to the regulatory specifications. Regulatory guidelines usually include recommendations about the location and configuration of the monitoring boreholes in addition to the sampling frequency and physicochemical parameters to be controlled. Nevertheless, the design of the monitoring programme should be tailored to specific site conditions.

Effective performance monitoring is based on an adequate site characterization, to provide a baseline for later comparison. A hydrogeological conceptual model of the site will determine the location of the monitoring wells. Understanding the mechanisms that control contaminant transformation, destruction or immobilization within the reaction zone is critical to the interpretation of performance monitoring data.

The development of long-term monitoring protocols should be aimed at providing an early warning of incipient barrier failure, which would minimize maintenance operations. Performance monitoring plans should be able to detect processes that may jeopardize PRB performance, such as

- loss of reactivity;
- decrease in permeability;
- decrease in contaminant residence time in the reaction zone;
- short-circuiting or leakage in the funnel walls.

In performance monitoring plans, the contaminants of concern and general water quality are periodically controlled. However, it may also be of interest to monitor other parameters, such as contaminant degradation products, precipitates, hydrological parameters and geochemical indicators. For instance, the concentration of contaminant degradation products can be used as an indicator of incipient breaches in the barrier.

The design of the surveillance programmes must take into account aspects such as flow velocity or type of contaminant in order to determine the frequency of sampling. The frequency of performance sampling will be dictated by site-specific hydrogeochemical conditions, system design and performance sampling objectives, which should be specified prior to installation of the system. These objectives should be agreed among the interested stakeholders, environmental regulators and the operators of the contaminated facility.

Complementary to traditional groundwater sampling, passive and semi-passive samplers are an interesting option for site monitoring. These types of samplers allow more detailed performance monitoring of the barrier to be applied, as these devices can be used to determine the temporal and spatial variability of the contaminants of interest. The use of passive diffusion bags (PDBs) is a cost-effective alternative to standard sampling techniques. These passive samplers are especially interesting when long-term monitoring is required. PDBs can also provide inexpensive and precise vertical contaminant concentration profiles that can be used to optimize remedial systems.

Currently, on-line monitoring systems are being introduced for the monitoring of contaminated sites. *In situ* sensors and telemetry systems allow real-time monitoring of the site chemical and hydrological parameters and can provide an early warning of barrier failure.

In order to prevent the hydraulic failure of the barrier, hydrological changes should also be closely monitored to detect changes in permeability or leakages through funnel walls. Head measurements, electromagnetic and nuclear techniques, tracer tests and *in situ* flowmeters can be used to monitor changes in the system permeability and alteration of flow paths over time.

The monitoring programme for a PRB should be dynamic and subjected to periodic revisions. As the PRB ages, the monitoring plan will likely require adjustments to assess variability in both hydraulic and chemical conditions.

7.7 Longevity of PRBs

Suthersan *et al.*[17] defined longevity, in the case of PRBs, as ''the ability of the PRB to sustain the critical performance criteria (*i.e.* hydraulic capture, residence time and reactivity) for the requisite operation lifetime''. The longevity of the PRB system and the need, frequency and extent of media maintenance will depend on site-specific conditions and the PRB characteristics.

The cost-effectiveness of a PRB system will be determined by the longevity of the reactive media and the long-term hydraulic capture of a system. The useful lifetime of a PRB is estimated to range from 10 to 30 years. However, there are several threats to the longevity of the barrier. Mineral precipitation seems to be the critical factor limiting the longevity of PRBs, as mineral fouling may lead to a decline in reactivity and hydraulic capture, but several studies have also noted a reduction in the effectiveness of PRBs with time due to microbial activity and corrosion processes. Documented degradation processes include the following:[6,67–72]

- clogging of the barrier due to mineral precipitation (mainly carbonate and sulfate);
- loss of reactivity and a decrease in hydraulic residence time;
- gas production (H_2, CH_4) and subsequent decrease in permeability;
- competition for or loss of reactive sites due to corrosion;
- mineral fouling or precipitation.

Knowledge gained over 20 years from established systems and long-term performance studies showed that 80–90% of all ZVI PRBs work successfully and most PRBs show an adequate performance after more than a decade of operation.[19] Documented premature PRB failures have been mainly attributed to poor site characterization and inadequate hydraulic designs.[73]

Long-term performance data show that conventional funnel-and-gate systems are more vulnerable to performance failures than other PRB configurations. Continuous barriers are more robust systems than conventional funnel-and-gate structures, owing to their lower sensitivity to design and construction defects.[19]

Maintenance frequency and strategy may differ as a function of the site-specific conditions and PRB design characteristics. Maintenance operations, necessary to ensure the PRB longevity, can range from a simple clearing of clogged sections or the venting of gas accumulations to the replacement of the reactive media.

The performance of PRBs over time can be predicted by simulation of longevity scenarios with the aid of numerical models.[9] Numerical models are commonly used to support experimental data and to deepen the understanding of the processes involved in the material degradation and the formation of secondary minerals.[7,74]

The migration of contaminants in the subsurface environment is influenced by various physical processes such as flow and non-reactive transport mechanisms, in addition to geochemical processes. Understanding these processes is the key to developing reactive transport models that are able to simulate accurately the contaminant transport in the subsurface.

Reactive transport modelling is an essential tool for the assessment of PRB design and performance scenarios. MODFLOW[75] in combination with MODPATH[76] is commonly used for contaminant fate modelling.[77]

MODFLOW is a finite difference-based three-dimensional groundwater flow model. It is the most widely used model for simulating groundwater flow. In order to evaluate the capture zone of the PRBs, the model results should be compatible with the use of particle tracking algorithms. MODPATH[76] is a widely used particle tracking code designed to work with MODFLOW. Geochemical modelling tools such as MINTEQA2[78] and PHREEQC[79] have frequently been used to predict the mineral phases that may be formed and changes in geochemical parameters such as pH and E_h. Process-based reactive transport modelling can become a versatile tool for building reliable PRB performance simulations.[80] Assessment and evaluation of the performance of a PRB also require the integration of complex biogeochemical processes occurring in the heterogeneous subsurface.[81]

The use of numerical models eases the choice of the reactive materials and can help in understanding the geochemical processes that may hinder the PRB performance.[82] Table 7.3 provides an overview of mathematical models applied to the evaluation of PRBs performance:

7.8 Closure

Little information about the closure and decommissioning of PRBs is currently available owing to the longevity of the existing facilities. Since the first PRBs were installed, several ideas have been postulated for closing or decommissioning a PRB. The proposed alternatives included clean closure (*i.e.* excavating a spent PRB), cementing up grouting in a spent PRB or the isolation of the system. Strategies for the closure of contaminated facilities may vary as a function of the site conditions and the nature of the pollutant (*i.e.* heavy metals, radionuclides, organics, *etc.*).[15]

Once the remediation goals have been achieved and approval from the regulators has been obtained, two different approaches concerning the future of the barrier have been considered: decommissioning and removal from the site or left in site.

Table 7.3 Summary of numerical models used for the assessment of PRB performance. Adapted from ref. 82 with permission from Taylor and Francis, Copyright 2014.

Model	Important features	Examples of model applications
PHREEQC	1D reactive transport model Performs speciation, solubility and reaction path calculations for aqueous, mineral, gas, surface ion-exchange solution equilibrium Inverse modelling tool Dual porosity	ZVI-PRB for the remediation of U[83] Influence of precipitates on PRB hydraulic performance (modelling 1D column filtration experiments)[84] Mineralogy of a mature PRB for acidic mine water[85]
MINTEQA2	Equilibrium speciation model Performs speciation, solubility and reaction path calculations for aqueous, mineral and gas phases	Column experiments: Granular Fe for removing Cr(VI)[86] Apatite for treating acid mine drainage[87]
MODFLOW (coupled with non-reactive transport models MT3DMS and RT3D)	MODFLOW – groundwater flow model RT3D and MT3D models can simulate the groundwater pollutant transport	PRB for treating acidic groundwater[88] Prediction of PRB performance for removal of BTEX[89]
PHT3D: MT3DMS – PREEQC	Reactive transport model	Nitrate removal by ZVI[90] Degradation of TCE by ZVI in column experiments[91]
PHAST	3D simulator for the groundwater flow, pollutant transport involving multicomponent geochemical reactions Geochemical reactions governed by PHREEQC	ZVI-PRB for the remediation of U[83]
MIN3P	Formulation for kinetically controlled reactions Multicomponent reactive transport model	ZVI-PRB for remediation of As[92]

Most PRBs are expected to remain in place once the reactive medium is exhausted or the remediation process has been completed. If the environmental restoration of the contaminated site does not include the removal of the PRB, post-closure monitoring can be required by the regulatory authorities in order to guarantee that a possible remobilization of the absorbed pollutants may not pose a risk to human health or the environment. In these cases, post-closure monitoring plans should be developed to detect changes in the hydrological and geochemical conditions of the site that may favour the mobilization of the pollutants.

PRBs designed for the treatment of chlorinated solvents and organics do not usually accumulate contaminants, hence removal of the reactive media is not necessary for the site restoration. In the case of PRBs used for the retention of short-lived radionuclides (*e.g.* ^{90}Sr, ^{137}Cs), the strategy proposed for the closure of the site is to keep the PRB until radiation levels reach exemption limits by radioactive decay.

One of the most widely accepted options for metals and long-lived radionuclides is the removal of the barrier, as potential problems may arise from the ageing of the reactive media. These problems may include desorption of pollutants or alteration of groundwater flow paths caused by the decrease in permeability of the PRB due to clogging effects. If the PRB is removed from the contaminated facility, the reactive medium should be extracted and transported to a suitable disposal facility, which will be conditioned by the type of contaminant and its concentration in the reactive medium. Dewatering may also be necessary prior to backfilling the PRB area with "clean" geological materials. Once backfilled, the area should be conditioned for revegetation in order to favour the site's integration in the surrounding area.[2]

Conditions for the closure, decommissioning and final facility closure should be agreed between the most relevant stakeholders and regulator(s) and addressed in the design and working plans developed prior to the construction of the PRB.

7.9 Costs

Several publications have reported estimated installation costs as a function of the construction technique and the characteristics of the PRB (depth and width).[55] However, in addition to construction costs, the estimation of the overall cost of a PRB system should also include the following:[93]

- Site characterization costs.
- Design costs:
  - treatability desk and laboratory studies costs;
  - modelling costs.
- Construction costs:
  - purchase and installation of reactive media;
  - licensing fees;

  - reporting;
  - monitoring costs.
- Operating and maintenance costs:
  - periodic monitoring;
  - media replacement/rejuvenation;
  - institutional controls/regulatory oversights;
  - other maintenance costs.
- Closure and restoration costs.

Estimating the costs of a PRB installation requires an economic analysis of several aspects, some of which are generally poorly documented. There is an overall lack of accurate information on the cost–performance of existing PRBs. Capital and operating costs of PRB systems are highly variable depending on the site-specific circumstances, the nature of the contaminant and the characteristics of the PRB (depth, length, width, type of reactive medium, *etc.*).

The largest capital costs are associated with the installation of the PRB. They are site specific, but depend strongly on the geometry (length and depth) of the wall. Depth is a crucial factor since the installation costs increase with increasing depth of the aquifer.[94] Trenching accounts for 70% and the reactive material 10–15% of the total costs. For some materials, such as mulch, the only costs are related to handling and transport to the site. For ZVI, the costs depend on the grain size; fine-grain material is usually more expensive than coarse-grain material.[2]

The main operational and maintenance costs include the long-term performance, monitoring and the replacement of the reactive medium. The replacement costs are difficult to quantify, since little is known about the long-term performance of most reactive materials used in PRBs. However, once the reactive material is depleted, exhausted or clogged with precipitates, rejuvenation or replacement is needed, resulting in an increase in maintenance costs.[44]

Compared with the conventional pump-and-treat technology, PRB systems typically involve higher installation costs; however, the operational and maintenance costs are lower and offer cost savings over the project life, depending on the useful life of the reactive medium. Hence the longevity of the reactive medium and adequate long-term hydraulic capture will dictate whether the PRB system will be cost-effective. PRB systems appear to be cost-effective compared with groundwater pump-and-treat systems if the useful life of the reactive medium approaches 10 years. For instance, in the case of the PRB installed in the USGC Elizabeth City (NC, USA) facility, estimated costs were \$585 000 (\$500 000 in capital and \$85 000 in operational and maintenance costs), which correspond to \$225 per 1000 gallons of groundwater treated. According to the estimations, by using a PRB the USGC would have saved nearly \$4 000 000 in construction and long-term maintenance costs in comparison with a typical pump-and-treat system.[95]

The Guide to Documenting and Managing Cost and Performance Information for Remedial Projects[95] provides guidelines for calculating and reporting the cost data of remediation projects. Another useful tool for estimating the cost of a PRB installation is the Remedial Action Cost Engineering and Requirements System (RACER), developed by the US Department of Defense, which offers a database of costs for activities such as trenching or drilling.[93]

7.10 Lessons Learned

Since 1991, when the first pilot testing of a PRB was installed at Borden, Ontario, Canada, the PRB concept has evolved from being an emerging technology to a well-established remediation method. Lessons learned from the last 25 years of PRB operation will help in advancing towards more cost-efficient deployments. The use of local and abundant green materials will facilitate the universalization of this remediation technique. The development of cheaper construction methods and the use of green compost-native sorptive materials (*e.g.* sawdust, wood chips) will promote the application of this technology in economically disadvantaged areas to protect sensitive water resources.[96]

Knowledge gained over the last two decades has led to significant improvements in design and construction issues. These advances have been based at an increasing level of detail on site characterization. Based on past experiences, poor performances are usually related to the hydraulic failure of the PRB rather than poor chemical treatment performance.

Whereas the treatability of a reactive medium can be tested under laboratory conditions, hydraulic efficacy must rely on numerical calculations that are often based on limited, incomplete or inadequate site characterization and field hydraulic information. Additionally, the aquifer system may undergo structural changes during PRB construction. Hence the capacity to predict and ensure appropriate hydraulic performance becomes substantially limited.

In order to minimize the risk of PRB failure, field-based pilot trials are recommended prior to full-scale installation.[8] In any case, field designs should incorporate potential uncertainty in the design so that the treatment remains sustainable and functional throughout the life of the project.[2]

Operating experience with PRBs shows two main areas of improvement: characterization techniques and construction methods. The development of characterization techniques will provide improved site characterization. Construction methods should also advance towards more cost-effective technologies that can be implemented under more complex conditions (*e.g.* complex hydrogeology, multicomponent plumes, deep aquifers).

Currently, there is a lack of information about the cost–performance of existing deployments, especially those involving novel reactive media. An extensive database would facilitate estimations of the long-term cost-effectiveness of PRB technology and would ease decision-making processes about the suitability of a PRB for a particular site.

7.11 Future Directions

Lessons learned during the last two decades have allowed continuous improvement in all aspects of PRB technology, especially in design and construction. The development of more cost-effective concepts will continue as ongoing research will provide novel reactive materials and site characterization and construction techniques will continue to improve.

The construction methods for deep emplacements must advance substantially, primarily in terms of the ability to install thicker barriers or barriers with fast-reacting media. Verification methods for these deeper barriers will be one of the more important advancements, as comprehensive assurance of emplacement is currently a cost and technical limitation.[2]

Other technical advancements may also involve the development of longer emplacements using advances in horizontal drilling capabilities and emplacement under existing surface structures and buildings. One of the challenges that PRB technology faces is upscaling. Knowledge gained during recent years has already proved the successful performance of commercial PRBs. In future years, this technology will extend its potential use to the remediation of contaminated megasites.

Advances in combined geophysical and hydrophysical methods will provide more efficient and effective site characterization. The development of reliable and easy-to-build three-dimensional transient models will greatly improve PRB designs. The development of novel reactive materials with greater contaminant specificity and higher reaction rates will allow the deployment of deeper and thinner designs.

Hydraulic performance assessment of standard PRB designs confirmed a significant potential for improvement. Some of the PRB design enhancements proposed for controlling residence time and capture variations are as follows:[97]

- customized downgradient gate faces;
- velocity equalization walls (VEWs), consisting of the elongation of the funnel in the downflow direction;
- deeper emplacement of the funnel than the gate;
- careful manipulation of the hydraulic conductivity ratio between the gate and the aquifer.

Advances in PRB hydraulic designs together with the development of new reactive materials will allow the treatment of mixed plumes and emerging compounds. Biological reactions in PRB systems that use facultative bacteria or cometabolic processes may be particularly promising in this context. The development of sustainable and cost-effective PRBs for common environmental contaminants, such as nitrates and pesticides, will become more necessary owing to the increasing impact on water resources.[2] The use of cheap local green materials will favour the generalization of PRB technology in economically disadvantaged areas. Access to cost data of existing installations will ease the decision about the suitability of a PRB for a particular site.

One of the greatest challenges for PRB technology is to increase the useful lifetime of the reactive media. Greater longevity will rely on the results of current and future research on the biogeochemical processes that may hinder PRB performance as the PRB ages.

Owing to the increasing use of PRBs for the removal of heavy metals and radionuclides, it is expected that regulators will possibly require the design of closure and decommissioning plans prior to the construction of the PRB.

7.12 Alternatives to Conventional PRBs

Conventional construction techniques used for the installation of PRBs imposed several technical limitations related to the depth and width of the barrier. *In situ* chemical reactive barriers (CRBs) represent a cost-effective alternative to conventional trench-and-fill technology as neither excavation nor replenishment of the reactive medium is required.

An injection system can control large and deep plumes even if the extension is irregular. Nevertheless, it is necessary to ensure that the contaminant plume is being efficiently treated and no bypassing or fingering occurs, which may hinder the remediation effect. In this case, recovery of the reactive material is practically impossible. Therefore, degradation is the preferred approach, since otherwise reinjection of reactive material may be necessary.[98] The installation of horizontal CRBs could be an interesting option for the containment or isolation of point pollution sources. Durmusoglu and Corapcioglu[99] proposed the installation of a horizontal CRB by injecting gelling colloidal silica solutions through horizontal and vertical wells to isolate the downward migration of non-aqueous phase liquids in the subsurface.

Polymer inclusion membranes (PIMs) have been proposed as an attractive alternative for the *in situ* selective removal of heavy metals from aqueous solution by an ion-exchange process.[100] PIMs are thin and stable films that exhibit excellent stability and versatility. Their mechanical properties are similar to those of filtration membranes. However, PIMS present great flexibility in membrane composition, which enables them to achieve the desired selectivity and separation efficiency.

7.13 Conclusion

PRBs represent a green and sustainable remediation technique and have evolved in recent years from an emerging to a developed technology. Owing to their passive nature, PRBs are a cost-effective alternative to *ex situ* technologies, as they involve no operational and maintenance costs.

PRB design needs to be tailored to provide a site-specific solution to meet the site remediation objectives. A successful PRB performance will depend on several factors, such as detailed high-resolution site characterization, selection of the reactive material and the PRB hydraulic design.

Prior to construction, the PRB performance over time needs to be addressed. Despite the fact that numerical simulations of longevity scenarios can help to support laboratory data, they usually fail to predict long-term performance accurately. Further work needs to be done to deepen insight into aspects related to PRB ageing, such as the decline in reactivity and permeability of the reactive medium. Currently, contingency plans have already been incorporated in the event of the barrier failure.

Owing to the ageing of existing barriers, the design of closure and decommissioning plans is becoming an increasingly important issue.

Knowledge gained over the last two decades has allowed the identification of several potential improvement areas. The development of novel materials and improvements in construction and monitoring methods will result in a reduction in costs and mitigation of the environmental impact.

Additional Resources

The following literature and Internet resources may be of interest for deepening knowledge on the application of PRBs to groundwater remediation.

Guides

The Interstate Technology and Regulatory Council (ITRC) has produced during the last 20 years several guides addressing the fundamentals and the future directions of this technology:

Regulatory Guidance for Permeable Reactive Barriers Designed to Remediate Chlorinated Solvents (1999). http://www.itrcweb.org/Documents/PBW-1.pdf.

Regulatory Guidance for Permeable Reactive Barriers Designed to Remediate Inorganic and Radionuclide Contamination (1999). https://www.itrcweb.org/Guidance/GetDocument?documentID=67.

Design Guidance for Application of Permeable Reactive Barriers for Groundwater Remediation (2000). https://www.itrcweb.org/Guidance/GetDocument?documentID=59.

Permeable Reactive Barriers: Lessons Learned/New Directions (2005). https://www.itrcweb.org/GuidanceDocuments/PRB-4.pdf.

Permeable Reactive Barrier: Technology Update (2011). https://www.itrcweb.org/GuidanceDocuments/PRB-5-1.pdf.

Books

In the last 20 years, a number of books have been published on *in situ* remediation technologies and more specifically on PRBs. The books listed below may provide further insight into the design and implementation of PRBs.

Handbook of Groundwater Remediation Using Permeable Reactive Barriers: Applications to Radionuclides, Trace Metals and Nutrients, ed. D. L. Naftz,

S. J. Morrison, J. A. Davis and C. C. Fuller, Academic Press, San Diego, 2002, 550 pp., ISBN: 0125135637.

Permeable Reactive Barrier: Sustainable Groundwater Remediation, ed. R. Naidu and V. Birke, CRC Press, Boca Raton, 2015, 320 pp., ISBN: 9781482224474.

Long-term Performance of Permeable Reactive Barriers, ed. K. E. Roehl, T. Meggyes, F. G. Simon and D. I. Stewart, Elsevier Science, Amsterdam, 2005, 224 pp., ISBN: 9780444515360.

Remediation Engineering, ed. S. S. Suthersan, J. Horst, M. Schnobrich, N. Welty and J. McDonaugh, CRC Press, Boca Raton, 2017, 511 pp., ISBN: 9781498773270.

Barrier Systems for Environmental Contaminant Containment and Treatment, ed. C. C. Chien, H. I. Inyang and L. G. Everett, CRC Taylor & Francis, Boca Raton, FL, 2005, 380 pp., ISBN: 1008493404.

Advanced Groundwater Remediation: Active and Passive Technologies, ed. F.-G. Simon, T. Meggyes and C. McDonald, Thomas Telford Publishing, London, 2002, 360 pp., ISBN: 9780727731210.

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Additional resources on PRB applications can be found at the following websites (last accessed October 2018):

Interstate Technology and Regulatory Council (ITRC):
https://www.itrcweb.org/team/Public?teamID=20
USEPA:
https://archive.epa.gov/ada/web/html/prb.html
http://www.clu-in.org/download/rtdf/prb/reactbar.pdf
http://clu-in.org/download/techdrct/tdfieldapp_prb.pdf
http://large.stanford.edu/courses/2015/ph241/khalaf2/docs/bronstein.pdf
http://www.cluin.org/techfocus/default.focus/sec/Permeable_Reactive_Barriers%2C_Permeable_Treatment_Zones%2C_and_Application_of_Zero-Valent_Iron/cat/Application/
Federal Remediation Technologies Roundtable (FRTR):
http://www.frtr.gov/matrix2/section4/4-41.html
Naval Facilities Engineering Command (NAVFAC):
https://www.navfac.navy.mil/navfac_worldwide/specialty_centers/exwc/products_and_services/ev/erb/tech/rem/biobarrier.html
Remediation Technologies Development Forum (RTDF):
https://rtdf.clu-in.org/PUBLIC/permbarr/prbsumms/default.cfm
German Permeable Reactive Barrier Network – RUBIN:
http://www.rubin-online.de/english/introduction/index.html

References

1. Batelle Memorial Institute, Permeable Reactive Barrier Cost and Performance Report. Final technical report, *Naval Facilities Engineering Command*, Port Hueneme, CA, 2012, p. 85.

2. ITRC (Interstate Technical and Regulatory Council), *Permeable Reactive Barrier: Technology Update*, Interstate Technology & Regulatory Council. PRB: Technology Update Team, Washington, D.C., 2011, p. 234.
3. AFCEE, 2011, *Sustainable Remediation Tool (SRT™)*, Version 2.2, User Guide.
4. D.O.N (U.S. Department of Navy), *SiteWise™ User Guide Version 3.1.*, NAVFAC Engineering and Expeditionary Warfare Center, Port Hueneme, CA, 2015, p. 96.
5. D. N. Bekele, R. Naidu, V. Birke and S. Chadalavada in *Permeable Reactive Barrier: Sustainable Groundwater Remediation*, ed. R. Naidu and V. Birke, CRC Press, Boca Raton, 2014, p. 41.
6. A. R. Gavaskar, *J. Hazard. Mater.*, 1999, **68**, 41.
7. F. Obiri-Nyarko, J. Grajales and G. Malina, *Chemosphere*, 2014, **111**, 243.
8. J. Smith, G. Boshoff and B. Bone, *Land Contam. Reclam.*, 2003, **11**(4), 411.
9. S. Saponaro, E. Sezena and A. Mastorgio, in *Filtration Materials for Groundwater: A Guide to Good Practice*, ed. I. Kozyatnyk, IWA Publishing, London, 2016, p. 114.
10. J. Muegge, An Assesment of Zero Valent Iron Permeable Reactive Barrier Projects in California, *Office of Pollution Prevention and Technology Development*, California Department of Toxic Substances Control, Sacramento, CA, 2008, p. 154.
11. S. D. Abadzic and J. N. Ryan, *Environ. Sci. Technol.*, 2001, **35**(22), 4502.
12. Y. Furukawa, J. W. Kim, J. Watkins and R. T. Wilkins, *Environ. Sci. Technol.*, 2002, **36**(24), 5469.
13. A. R. Kacimov, H. Klammler, N. Il'yinskii and K. Hatfield, *J. Eng. Math.*, 2011, **71**(4), 319.
14. P. J. Vikesland, J. Klausen, H. Zimmerman, A. L. Roberts and W. P. Ball, *J. Contam. Hydrol.*, 2003, **64**(1–2), 3.
15. ITRC (Interstate Technical and Regulatory Council), *Regulatory Guidance for Permeable Reactive Barriers Designed to Remediate Inorganic and Radionuclide Contamination*, Interstate Technology and Regulatory Cooperation Work Group - Permeable Reactive Barriers Work Team, Washington, D.C., 1999, p. 53.
16. ITRC (Interstate Technical and Regulatory Council), *Permeable Reactive Barriers: Lessons Learned/New Directions*, Interstate Technology & Regulatory Council. Permeable Reactive Barriers Team, Washington, D.C., 2005, p. 202.
17. S. S. Suthersan, J. Horst, M. Schnobrich, N. Welty and J. McDonaugh, in *Remediation Engineering*, CRC Press, Boca Raton, 2017, p. 511.
18. W. E. Jones, M. E. Denham, M. A. Phifer, F. C. Sappington and F. A. Washburn, in *Handbook of Groundwater Remediation using Permeable Reactive Barriers. Applications to Radionuclides, Trace Metals and Nutrients*, ed. D. L. Naftz, C. F. Fuller, S. J. Morrison and J. A. Davis, Academic Press, Cambridge, 105.

19. V. Birke and H. Burmeier, in *Permeable Reactive Barrier: Sustainable Groundwater Remediation*, ed. R. Naidu and V. Birke, CRC Press, Boca Raton, 2014, p. 275.
20. S. Y. Chen, W. H. Chen and C. J. Shih, *Water Sci. Technol.*, 2008, **58**(10), 1947.
21. F. Alshaebi, W. Z. Yaacob and A. R. Samsuldin, *Eur. J. Sci. Res*, 2009, **33**(2), 214–219.
22. S. J. Morrison, D. L. Naft, J. A. Davis and C. C. Fuller in *Handbook of Groundwater Remediation using Permeable Reactive Barriers*, ed. D. L. Naft, S. J. Morrison, J. A. Davis and C. C. Fuller, Elsevier Science, San Diego, 2002, p. 1.
23. M. M. Rahman, M. Adil, A. M. Yusof, Y. B. Kamaruzzaman and R. H. Ansary, *Materials*, 2014, **7**(5), 3634.
24. M. Wolowiec, B. Muir, T. Bajda, K. Ziabada, B. Kijak and F. Wojciech, *Desalin. Water Treat.*, 2017, **94**, 120.
25. L. J. Westholm, E. Repo and M. Sillanpää, *Environ. Sci. Pollut. R.*, 2014, **21**(15), 9109.
26. C. S. Dunets and Y. Zheng, *Environ. Technol.*, 2014, **35**(22), 2852.
27. M. Rigali, P. V. Brady and R. Moore, *Am. Mineral.*, 2016, **101**(12), 2611.
28. C.-K. Lee, H.-S. Kim and J.-H. Kwon, *Environ. Eng. Res.*, 2005, **10**(5), 205.
29. C. Ardau, P. Lattanzi, R. Perettin and A. Zucca, *Environ. Technol.*, 2014, **35**(24), 3060.
30. V. K. Gupta and S. Sharma, *Environ. Sci. Technol.*, 2002, **36**(16), 3612.
31. G. De Gioannis, A. Muntoni, R. Ruggeri and J. J. P. Zijlstra, *J. Environ. Sci. Health, Part A.*, 2008, **43**(8), 969.
32. W. Huang, S. Wang, Z. Zhu, L. Li, Y. Xiangdong, V. Rudolph and F. Haghseresht, *J. Hazard. Mater.*, 2008, **158**(1), 35.
33. A. Bhatnagar, J. P. Vilar, M. S. Botelho and A. R. Boaventura, *Environ. Technol.*, 2011, **32**(3), 231.
34. H. Lu, J. Wang, M. Stoller, T. Wang, Y. Bao and H. Hao, *Mater. Sci. Forum*, 2016, **2016**, 10.
35. J. Giménez, M. Martínez, J. de Pablo, M. Rovira and L. Duro, *J. Hazard. Mater.*, 2007, **141**(3), 575.
36. C. D. Hsi and D. Langmuir, *Geochim. Cosmochim. Acta*, 1985, **49**(9), 1931.
37. L. Weng, W. H. Van Riemsdijk and T. Hiemstra, *J. Environ. Qual.*, 2012, **41**(3), 628.
38. M. Okazaki, K. Takamidoh and I. Yamane, *Soil Sci. Plant Nutr.*, 1986, **32**(4), 523.
39. K. Fukushi and D. A. Sverjensky, *Geochim. Cosmochim. Acta*, 2007, **71**(1), 1.
40. C. A. J. Appelo, M. J. J. Van Der Weiden, C. Tournassat and L. Charlet, *Environ. Sci. Technol.*, 2002, **36**(14), 3096.
41. K. A. Morris, *Remed. J.*, 2009, **20**(1), 59.
42. A.-K. Ghattas, F. Fischer, A. Wick and T. A. Ternes, *Water Res.*, 2017, **116**(1), 268.

43. Y. Gilbert, Y. L. Bihan, G. Bihan, G. Aubry, M. Veillette, C. Duchaine and P. Lessard, *Bioresource Technol*, 2008, **99**(10), 4495.
44. R. D. Ludwig, R. G. McGregor, D. W. Blowes, S. G. Benner and K. Mountjoy, *Groundwater*, 2002, **40**(1), 59.
45. C.-T. Kao and C. C. Wang, *Water Res.*, 2000, **34**(13), 3413.
46. Z. Özturk, B. Tansel, Y. Katsenovich, M. Sukop and S. Laha, *Chemosphere*, 2012, **89**(6), 665.
47. C. Scheutz, N. D. Durant and M. M. Broholm, *Biodegradation*, 2014, **25**(3), 459.
48. S. R. Kanel in *Nanoscale Multifunctional Materials: Science and Applications*, ed. S. M. Mukhopadhyay, John Wiley & Sons, Inc., New York, 2011, p. 271.
49. Redox-tech, *ABC+*, 2018 [accessed September 2018], Available from: https://www.redox-tech.com/abc-2/.
50. PeroxyChem, *EHC*, 2018 [accessed May 2018], Available from: http://www.peroxychem.com/markets/environment/soil-and-groundwater/products/ehc-iscr-reagent.
51. Trap-and-treat, *EOSZVI*, 2018 [accessed May 2018], Available from: http://www.trapandtreat.com/products/bos-100/.
52. BOS100, *EOS remediation*, 2018 [accessed May 2018], Available from: https://www.eosremediation.com/eos-zvi-product-information/.
53. Remquest, *>E-ZVI*, 2018 [accessed May 2018], Available from: http://remquestonline.com/ezvi.
54. C. Macé, S. Desrocher, F. Gheorghiu, A. Kane, M. Pupeza, M. Cernik, P. Kvapil, R. Venkatakrishnan and W. Zhang, *Remed. J.*, 2006, **16**(2), 23.
55. EPA, *Cost Analysis for Selected Groundwater Cleanup Projects: Pump and Treat Systems and Permeable Reactive Barriers*, U.S. Environmental Protection Agency, Washington D.C., 2001, p. 24.
56. B. Karn, T. Kuiken and M. Otto, *Environ. Health Perspect.*, 2009, **117**(12), 1823.
57. G. Quan, J. Zhang, J. Guo and Y. Lan, *Water, Air, Soil Pollut.*, 2014, **225**(6), 1979.
58. N. C. Mueller, J. Braun, J. Bruns, M. Acernak, P. Rissing, D. Rickerby and B. Nowack, *Environ. Sci. Pollut. R.*, 2012, **19**(2), 550.
59. J. Quinn, C. Geiger, C. Clausen, K. Brooks, C. Coon, S. O'Hara, T. Krug, D. Major, W.-S. Yoon, A. Gavaskar and T. Holdsworth, *Environ. Sci. Technol.*, 2005, **39**(5), 1309.
60. Y. Su, A. Adeleye, A. Keller, Y. Huang, C. Dai, X. Zhou and Y. Zhang, *Water Res.*, 2016, **74**, 47–57.
61. D. Pramudita, I. Iskandar and A. Indarto, in *Bio-Geotechnologies for Mine Site Rehabilitation*, ed. M. Narasimha Vara Prasad, P. J. Campos Favas and S. K. Maiti, Elsevier, Amsterdam, 2017, p. 201.
62. L. Camilli and N. Bahramifar, *Membr. Technol.*, 2014, **2014**(3), 8.
63. I. V. Perminova, S. N. Kalmykov, N. S. Schcherbina, S. A. Ponomarenko, V. A. Kholodov, A. P. Novikov, R. G. Haire and K. Haitfield, in *Nanomaterials for Environmental Protection*, ed. B. I. Kharisov,

O. V. Kharissova and H. V. Dias, John Wiley & Sons, Inc., New York, 2014, p. 483.

64. H. I. Inyang and S. J. Piet, in *Barrier Systems for Environmental Contaminant Containment and Treatment*, ed. C. C. Chien, H. I. Inyang and L. G. Everett, CRC Taylor & Francis, Boca Raton, 2005, p. 62.
65. R. Thiruvenkatachari, S. Vigneswaran and R. Naidu, *J. Ind. Eng. Chem.*, 2008, **14**(2), 145.
66. F.-G. Simon, S. Ludwig, T. Meggyes, D. I. Stewart and K. E. Roehl, in *Long-term Performance of Permeable Reactive Barriers*, ed. K. E. Roehl, T. Meggyes, F.-G. Simon and D. I. Stewart, Elsevier, Amsterdam, 2005, p. 311.
67. N. E. Korte, *Zero-Valent Iron Permeable Reactive Barriers: A Review of Performance Environmental*, U.S. Department of Energy, Washington, D.C., 2001, p. 36.
68. L. A. Roberts, W. P. Ball, P. Searson, H. Fairbrother, P. J. Vikesland, P. J. Klausen, R. Kamath and H. J. Zimmermann, *Influence of Groundwater Constituents on Longevity of Iron-Based Permeable Barriers. Final Report for the SERDP Project CU-1125*, Air Force Research Laboratory, Tyndall, 2002, p. 273.
69. L. Liang, A. Sullivan, O. West, G. Moline and W. Kamolpornwijit, *Environ. Eng. Sci.*, 2003, **20**(6), 635.
70. R. T. Wilkin and R. W. Puls, *Capstone Report on the Application, Monitoring and Performance of Permeable Reactive Barriers for Groundwater Remediation: Volume 1. Performance Evaluations at Two Sites*, U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Cincinnati, 2003, p. 135.
71. R. C. Borden, Effective distribution of emulsified edible oil for enhanced anaerobic bioremediation, *J. Contam. Hydrol.*, 2007, **94**(1–2), 1.
72. V. Zolla, et al., *J. Environ. Qual.*, 2009, **38**(3), 897.
73. A. D. Henderson and A. H. Demond, *Environ. Eng. Sci.*, 2007, **24**(4), 401.
74. S.-W. Jeen, R. W. Gillham and A. Przepiora, Predictions of long-term performance of granular iron permeable reactive barriers: Field-scale evaluation, *J. Contam. Hydrol.*, 2011, **123**(1), 50.
75. A. W. Harbaugh, *MODFLOW-2005. the U.S. Geological Survey modular Groundwater Model – the Groundwater Flow Process*, U.S. Geological Survey, Reston, 2005, p. 253.
76. D. W. Pollock, *User guide for MODPATH Version 7 – A particle-tracking model for MODFLOW*, U.S. Geological Survey, Reston, 2016, p. 41.
77. J. P. Richardson and J. W. Nicklow, *Soil Sediment Contam.*, 2002, **11**(2), 241.
78. J. D. Allison, D. S. Brown and K. J. Novo-Gradac, *MINTEQA2/PRODEFA2. A Geochemical Assessment Model for Environmental Systems*, U.S. Environmental Protection Agency, Athens, 1991, p. 107.
79. D. L. Parkhurst, K. L. Kipp, P. Engesgaard and S. Charlton, PHAST – A program for simulating groundwater flow, solute transport and

multicomponent geochemical reactions, *U.S. Geological Survey Techniques and Methods*, vol. 6-A8, 2004, p. 154.

80. R. T. Amos, K. U. Mayer, D. W. Blowes and C. J. Ptacek, *Environ. Sci. Technol.*, 2004, **38**(11), 3131.
81. K. Mayer, S. Benner and D. W. Blowes, *J. Contam. Hydrol.*, 2006, **85**(3–4), 195–211.
82. S. Chadalavada, M. Wegner and R. Naidu, in Permeable Reactive Barriers: Sustainable Groundwater Remediation, ed. R. Naidu and V. Birke, CRC Press, Boca Raton. 2015, p. 63.
83. S. Kwong, J. Small and B. Tahir, Modelling the remediation of contaminated groundwater using zero-valent iron barriers, in *WM'07 Conference*, Tucson, AZ, 2007.
84. B. Courcelles, A. Modaressi, D. Gouvenot and A. Esnault-Filet, Influence of Precipitates on Hydraulic Performance of Permeable Reactive Barrier Filters, *Int. J. Geomech.*, 2011, **11**(2), 142.
85. M. A. Caraballo, E. Santofimia and A. P. Jarvis, *Am. Mineral.*, 2010, **95**(11–12), 1642.
86. S. W. Jeen, D. W. Blowes and R. W. Gillham, *J. Contam. Hydrol.*, 2008, **95**(1–2), 76.
87. J. C. Choi, T. R. West and Y. Seol, *Environ. Eng. Geosci.*, 1997, **III**(2), 217.
88. B. Indraratna, P. U. Pathirage, R. K. Rowe and L. Banasiak, Coupled hydro-geochemical modelling of a permeable reactive barrier for treating acidic groundwater, *Comput. Geotech.*, 2014, **55**, 429.
89. Y. Chung, J. W. Kim and S.-H. Kong, *Int. J. Environ. Sci. Dev.*, 2011, **2**(2), 138.
90. Q. Wu, C. Zheng, J. Zhang and F. Zhang, *J. Earth Sci.*, 2017, **28**(3), 447.
91. H. Prommer, et al., *J. Contam. Hydrol.*, 2008, **97**(1–2), 13.
92. S.-W. Jeen, *Water*, 2017, **9**(11), 890.
93. V. Mikita, T. Madarász, K. S. Tothné and B. Kovács, in *Filtration Materials for Groundwater: A Guide to Good Practice*, ed. and I. Kozyatnyk, Iwa Publishing, London, 2016, p. 71.
94. A. Gavaskar, B. Sass, N. Gupta, E. Drescher and W.-S. Yoon, *Cost and Performance Report - Evaluating the Longevity and Hydraulic Performance of Permeable Reactive Barriers at Department of Defense Sites*, Batelle Memorial Institute, Columbus. 2002, p. 70.
95. *Guide to Documenting and Managing Cost and Performance Information for Remediation Projects - Revised Version*, Prepared by the Member Agencies of the Federal Remediation Technologies Roundtable EPA 542-B-98-007, 1998.
96. W. D. Scott, in *Permeable Reactive Barrier: Sustainable Groundwater Remediation*, ed. R. Naidu and V. Birke, CRC Press, Boca Raton, 2015, p. 25.
97. B. D. M. Painter, *Groundwater*, 2004, **42**(4), 609.

98. F.-G. Simon, T. Meggyes and T. Tünnermeier, in *Advanced Groundwater Remediation*, ed. F.-G. Simon, T. Meggyes and C. McDonald, Thomas Telford Publishing, London, 2002, p. 3.
99. E. Durmusoglu and M. Corapcioglu, *J. Environ. Eng.*, 2000, **126**(9), 833.
100. I. Zawierucha, C. Kozlowski and G. Malina, in *Groundwater Quality Sustainability*, *International Association of Hydrogeologists. Selected Papers*, ed. P. Maloszewski, S. Witczak and G. Malina, CRC Press/ Balkema, Leiden, 2013, p. 370.