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Filtration Materials for Groundwater

A Guide to Good Practice

Ivan Kozyatnyk



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5.3 Designs of permeable reactive barriers and examples of full scale treatment

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Andrea Mastorgio*

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Permeable reactive barriers (PRBs) are innovative technologies for the in situ remediation of contaminated groundwater. The technology involves the emplacement, into an excavated zone of the aquifer across the flow path of the contaminated groundwater, of a “reactive” filling material permeable to groundwater to intercept and treat the contaminants as the plume flows through under the influence of the natural hydraulic gradient (Careghini *et al.* 2013).

A wide range of materials are currently available. Some of them remove contaminants through non-destructive mechanisms, such as precipitation, sorption or cation exchange (also promoted by geochemistry modifications in the treatment zone), other through destructive mechanisms, such as abiotic degradation or biological degradation (in biobarriers) (Table 5.3.1). The choice among these is primarily based on the contaminant to remove and the abatement required, but the hydrogeological and biogeochemical conditions of the aquifer may have great influence as well (ITRC, 2011; Obiri-Nyarko *et al.* 2014). Sometimes, concurrently mechanisms acts in removing the pollutants. Multilayer barrier systems can be developed in order to treat groundwater affected by different kinds of pollutants (Obiri-Nyarko *et al.* 2014).

The most used abiotic materials include: (i) zero-valent iron Fe⁰ (ZVI); (ii) activated carbons (ACs); (iii) zeolites; and (iv) apatites.

ZVI has a high reduction potential (−440 mV) and acts primarily as a reductant material. Therefore it can effectively remove pollutants such as heavy metals and radionuclides, nutrients and aliphatic chlorinated solvents. Typically, ZVI grain

size ranges from 0.25 to 2 mm and the surface area from 0.5 to 1.5 m²/g. ZVI has been conventionally used as the reactive media of PRBs and more than 60% of the PRBs installed worldwide are iron-based (ITRC, 2011).

Table 5.3.1 Contaminants, main reactive materials and issues at PRB full-scale applications (ITRC, 2011; Obiri-Nyarko *et al.* 2014).

Contaminants	Reactive Material	Major Issues
Aliphatic chlorinated solvents	ZVI	Iron reactions with groundwater constituents produce OH ⁻ ions and pH increase, which promotes precipitate formation on the reactive material (coating) and a reduced surface contact between Fe(0) and pollutants
	Biobarrier	Anaerobic conditions are required for highly chlorinated compounds Degradation reactions, excessive variation in pH and redox conditions can lead to the solubilization of metals (iron, manganese, arsenic) and potential negative effects (e.g.: total dissolved solids) on the water quality
Monoaromatic solvents Methyl-tert butyl ether	Biobarrier	Aerobic conditions and an external source of oxygen are generally required
Phenols	GAC	Removal is strongly influenced the pH value (low pH values decrease phenol sorption)
Cationic metals	Apatite	Removal is affected by the pH (low pH is necessary to dissolve the apatite to release the phosphate) The contaminant sorption is reversible and they can be released again into groundwater when geochemical conditions favor the mechanism
Arsenic	ZVI	Low pH is favorable to remove arsenic compounds under aerobic condition, while under anaerobic condition, acidic and alkaline pHs seems to be favorable for arsenate and arsenite removal

(Continued)

Table 5.3.1 Contaminants, main reactive materials and issues at PRB full-scale applications (ITRC, 2011; Obiri-Nyarko *et al.* 2014) (*Continued*).

Contaminants	Reactive Material	Major Issues
Chromium (VI)	ZVI	<p>The presence of other inorganic species in the aquifer may compete with contaminants for ZVI reactive sites</p> <p>Chromium precipitation (as Cr(III)) progressively blocks reactions sites on iron</p> <p>The formation of mineral precipitates can cause clogging</p> <p>Removal may be influenced by pH, redox potential and dissolved organic carbon in the aquifer</p> <p>The presence of other inorganic species in the aquifer may compete with Cr(VI) for ZVI reactive sites</p>
Uranium	ZVI	<p>Possible clogging due to the formation of mineral precipitates</p> <p>Removal may be influenced by pH, redox potential and dissolved organic carbon in the aquifer</p> <p>The presence of other inorganic species in the aquifer may compete with contaminants for ZVI reactive sites</p>
	Apatite	<p>Removal is affected by the pH (low pH is necessary to dissolve the apatite to release the phosphate)</p> <p>The contaminant sorption is reversible and it can be released again into groundwater when geochemical conditions favor the mechanism</p>
Strontium-90	Zeolites	<p>The use may be influenced by groundwater pH, its constituents (Ca, Mg, Na, SO_4^{2-}, CO_3^{2-}) and dissolved organic carbon</p>

(Continued)

Table 5.3.1 Contaminants, main reactive materials and issues at PRB full-scale applications (ITRC, 2011; Obiri-Nyarko *et al.* 2014) (*Continued*).

Contaminants	Reactive Material	Major Issues
	Apatite	Removal is affected by the pH (low pH is necessary to dissolve the apatite to release the phosphate) The contaminant sorption is reversible and it can be released again into groundwater when geochemical conditions favor the mechanism
Nitrates	Biobarrier	Anaerobic (denitrifying) conditions are required to transform nitrates into N ₂ Nitrous oxide, NH ₄ ⁺ , CH ₄ , CO ₂ can be produced Gases can reduce the hydraulic conductivity in the barrier
Sulphates	Biobarrier	Anaerobic conditions are required to transform sulphates into sulphides
Perchlorate	Biobarrier	Anaerobic conditions are required to transform perchlorate to chlorate and chloride

ACs are carbonaceous materials with high sorption capacity; therefore, pollutant removal occurs mainly through sorption. They have been widely used for phenols, monoaromatic and chlorinated hydrocarbons, although heavy metals have been treated as well. Granular AC (GAC) was one of the materials commonly used in the early stages of the PRB technology (Bone, 2012).

Zeolites are aluminosilicate minerals that have high cation-exchange capacity (200–400 meq/100 g) and large surface area (up to 145 m²/g) (ITRC, 2011). Natural zeolites generally have low organic carbon content, which makes them unsuitable for sorption of organic compounds; however, surface modified zeolites have been developed exhibiting strong affinity with organics. Contaminants that can be removed include heavy metals, radionuclides, NO₃⁻, monoaromatic and chlorinated hydrocarbons (Obiri-Nyarko *et al.* 2014; USEPA, 2015a).

Apatites are phosphate minerals, containing mainly calcium and phosphorus, with net negative charge at neutral and alkaline pH. Apatites may remove inorganic contaminants (perchlorate, cationic metals, radionuclides, nitrate) via sorption to their negative charge surface or via ion-exchange, precipitation as phosphates, carbonates, oxides, and hydroxides, or incorporation into their mineral structure (USEPA, 2015b).

5.3.1 DESIGN

A key aspect of the PRB design is a good understanding of the site and aquifer characteristics, which includes the site geology, aquifer hydrogeology, 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 (Smith *et al.* 2003).

Once the site has been fully characterized, the design of a PRB include selection of the reactive medium, treatability studies at lab scale (batch and column tests) and pilot scale, and engineering design (Obiri-Nyarko *et al.* 2014). Laboratory-based trials are a prerequisite, while field-based pilot trials are recommended, but not obligatory. Nevertheless, is likely that both laboratory and field-scale trials would be conducted prior to full-scale installation, as these are considered the best ways of optimizing the design and minimizing risk of failure of the PRB (Smith *et al.* 2003).

After the reactive material has been selected, the dimension, 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. The “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 (Smith *et al.* 2003).

The hydraulic conductivity of the filling material is usually selected at a value one order of magnitude higher than the aquifer hydraulic conductivity. In order to obtain this condition, the reactive material is usually mixed with sand to achieve the suitable permeability (Muegge, 2008). However, PRB interior changes its hydraulic properties during operation, as chemical reactions and/or bacterial growth may cause clogging/fouling (Abadzic & Ryan, 2001; Furukawa *et al.* 2002; Kacimov *et al.* 2011; Lampron *et al.* 2001; Vikesland *et al.* 2003).

The performance of the PRB over time needs to be addressed. The oldest PRB is close to two decades, but this is still not enough to provide sufficient information to help in adequately understanding and predicting their long-term performance. This can be predicted by simulation of longevity scenarios with the aid of numerical models. However, most of them do not take into consideration the changes in reactivity of the material over time. More recent models are able to incorporate the declining reactivity and permeability of the material in order to adequately represent long- term performance (Kouznetsova *et al.* 2007; Jeen *et al.* 2011).

There may be potential for generation of polluting substances within the barrier as a consequence of secondary reactions not considered as part of the PRB design for its target pollutants (Cheng *et al.* 1997).

5.3.2 FULL-SCALE TREATMENTS

A few sites where a full-scale PRB has been installed are reported in Table 5.3.2.

Table 5.3.2 Performance of a few full-scale PRBs.

Site	Reactive Medium	Pollutants	Max Inflowing Concentration	Remedial Goal	Installation Date	Pollutant Removal	Reference
Sunnyvale (California, USA)	ZVI	Perchloroethene (PCE)	1.8 mg/l	600 µg/l	2003	90.6%	ITRC (2011)
Avigliana (Italy)	ZVI	Trichloroethene (TCE)	80 µg/l	30 µg/l (as the sum of chlorinated compounds)	2005	99.7	(Sethi <i>et al.</i> 2007)
Belfast (Ireland)	ZVI	TCE	390 mg/l	500 µg/l	1995	97.5%	ITRC (2011)
Vandenberg (California, USA)	ZVI	TCE	270 µg/l	5 µg/l	2009	60%	ITRC (2011)
Elizabeth City (North Carolina, USA)	ZVI	TCE	42 mg/l	5 µg/l	1996	98.7%	ITRC (2011)
Grain silo (Midwest, USA)	ZVI	Carbon tetrachloride	4.7 mg/l	50 µg/l		99.9%	
Altus (Oklahoma, USA)	Biobarrier	TCE	1000 µg/l	5 µg/l	2005	99%	ITRC (2011)
Port Hueneme (California, USA)	Biobarrier	MTBE	8 mg/l	5 µg/l	2002	>99%	ITRC (2011)
Chalk River (Ontario, USA)	Zeolite	Strontium-90	400 µg/l	5 µg/l	2000	98.7%	ITRC (2011)
Pork facility (Oklahoma, USA)	Biobarrier	Nitrates	85 Bq/l	5 Bq/l	1998	99.5%	ITRC (2011)
East Helena (Montana, USA)	ZVI	Arsenic	>25 mg/l	10 mg/l	2002		ITRC (2011)
				10 µg/l	2005	>92%	ITRC (2011)

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Groundwater is a source for drinking and industrial water supply and pollution created by active industrial sites which often cause social, health, and environmental problems. This groundwater eventually drains into adjacent water sources.

Filtration Materials for Groundwater: A Guide to Good Practice presents the up-to-date technology of purification of polluted ground water, its treatment for industrial and human needs and the remediation of polluted sites.

The book examines:

- Types of pollutants in ground water including the main inorganic and organic pollutants and their behaviour
- Filtration materials for water treatment and principles of their choice. How to choose suitable filtration materials according to targeted compounds and estimate its efficiency
- Technologies for ground water treatment.
- Cost and risks estimation of treatment facilities. Lifetime, risks and cost estimation of technology
- Examples of modern ongoing facilities for ground water treatment and polluted sites remediation.

This book is of interest to scientists and engineers who deal with the problem of purification of groundwater for different purposes and the remediation of polluted sites.



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