

# Permeable reactive barriers for acid mine drainage treatment: a review

Ayanda N. SHABALALA<sup>a,1</sup>, Stephen O. EKOLU<sup>b</sup> and Souleymane DIOP<sup>a</sup>

<sup>a</sup>Council for Geoscience, Head Office, Engineering Geoscience Unit

<sup>b</sup>Department of Civil Engineering Science, University of Johannesburg, South Africa

**Abstract.** Contaminated water flowing from abandoned mines is one of the most significant contributors to water pollution. Acid mine drainage (AMD) can have severe impacts on aquatic resources, can stunt terrestrial plant growth and harm wetlands, contaminate groundwater, raise water treatment costs, and damage concrete and metal structures. Permeable reactive barriers (PRBs) are one of the passive treatment technologies widely accepted for sustainable in situ remediation of contaminated groundwater and may be used in the management of localised seepage plumes from mine residues that contaminate shallow groundwater. These barriers provide chemical interactions with AMD as the polluted water flows through it. The ability of PRBs to remediate contaminants is dependent on the type of reactive material used. Some of the reactive media remove contaminants through physical contact while others work by altering the biogeochemical processes in the treatment zone, thus providing conditions conducive for contaminant immobilization or (bio) degradation. A variety of materials has been employed to remove contaminants including heavy metals, chlorinated solvents, aromatic hydrocarbons, and pesticides. This paper gives an overview of the PRB technology, which includes the advantages and limitations of the PRB, the types of reactive materials used, laboratory treatability tests used to evaluate suitable reactive materials and to aid in the designing and the implementation of the PRB and the installations schemes used in PRB field application.

**Keywords.** Passive treatment, acid mine drainage, permeable reactive barrier

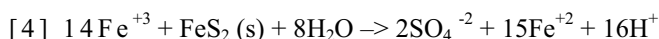
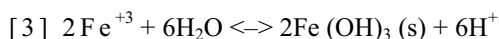
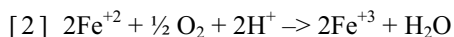
## Introduction

The formation of acid mine drainage (AMD) and the contaminants associated with it have been described as the largest environmental problem facing the mining industry. Commonly referred to as acid rock drainage (ARD) or AMD, acid drainage from mine waste rock, tailings, and mine structures such as pits and underground workings is primarily a function of the mineralogy of the rock material and the availability of water and oxygen [29]. It is a naturally occurring process of weathering and erosion of sulphur and iron (Fe) bearing material, as well as other metallic sulphidic materials. It occurs when groundwater comes into contact with remnant coal and rock that is rich in sulphide. These sulphide minerals oxidise in the presence of water and oxygen, the by-product being a usually but always acidic, typically sulphate (SO<sub>4</sub><sup>2-</sup>) rich drainage [8]. The resulting drainage usually has a low pH and high metal concentration.

---

<sup>1</sup>Corresponding author: Council of Geosciences, Water Geoscience Business Unit, 280 Pretoria Street, Silverton, Pretoria; Email: [ashabalala@geoscience.org.za](mailto:ashabalala@geoscience.org.za)

Contaminated water flowing from abandoned mines is one of the most significant contributors to water pollution. Acid mine drainage (AMD) can have severe impacts on aquatic resources, can stunt terrestrial plant growth and harm wetlands, contaminate groundwater, raise water treatment costs, and damage concrete and metal structures [8]. There are 4 commonly-accepted chemical reactions that represent the chemistry of pyrite weathering to form AMD [9]:



## 1. Brief review of related studies

### 1.1 Treatments technologies

Remediation of acid drainage is difficult and expensive. Treatment falls under two broad categories: active and passive. Active treatment involves physically adding a neutralising agent to the source of the AMD, or directly to the stream that has been impacted. Active treatment can be very successful; however, it necessitates a long-term and continuous commitment to treatment. Weather, equipment failure, and budget reductions can result in lapses in treatment [8].

Passive treatment encompasses a variety of techniques that are employed to raise the pH of AMD and consequently reduce metal loadings through a constructed treatment or containment project. While initial costs for passive treatment techniques can be higher than the costs of setting up active treatment, the former do not require continuous chemical inputs and they provide a controlled environment in which naturally occurring chemical and biological processes play a major role in the treatment of AMD [21, 27]. A widely accepted definition of Passive treatment is that it is a deliberate improvement of water quality using only naturally available energy sources (e.g., gravity, microbial metabolic energy, photosynthesis), in systems which require only infrequent maintenance in order to operate effectively over the entire system design life [34]. There are several types of passive treatment systems; they may be used on their own or in combinations, in order to treat difficult effluents. Generally, the selection of an appropriate passive system is based on water chemistry, flow rate, local topography and site characteristics. The primary passive technologies include constructed wetlands, anoxic limestone drains (ALD), successive alkalinity producing systems (SAPS), Limestone ponds and open limestone channels (OLC) [27].

### 1.2 Permeable reactive barriers

Permeable reactive barriers (PRB) usually consist of physical porous media that interact with specific chemicals of concern in the AMD. The PRB is placed in the path of polluted water flow, allowing the water to flow through it easily while the treatment process takes place through chemical or biochemical processes. These methods may

well be used in the management of localised seepage plumes from mine residues that contaminate shallow groundwater.

For PRBs designed to treat acid mine drainage (AMD) with sulphate contamination, the barrier is generally composed of solid organic matter, like municipal compost, leaf compost, and wood chips/sawdust [2]. Construction of PRBs involves the digging of a trench or pit in the flow path of contaminated groundwater, filling the void with reactive materials (a mixture of organic solids and possibly limestone gravel) that are sufficiently permeable to allow unhindered flow of the groundwater [19], as illustrated in Figure 1.

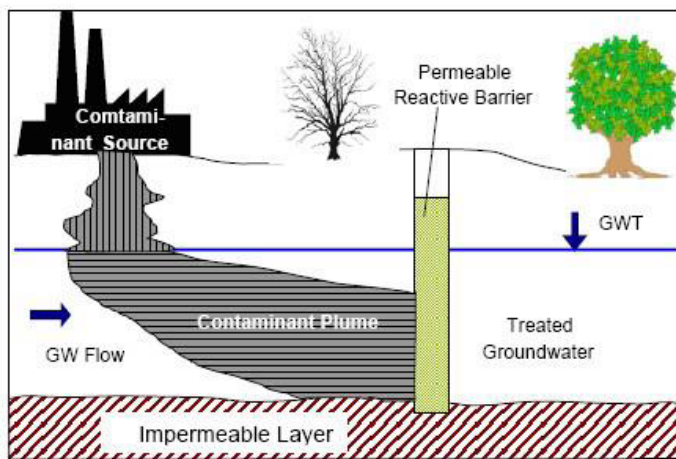
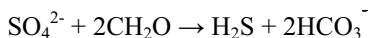
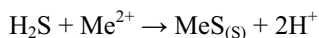


Figure 1. Diagrammatic representation of a PRB [11]

Iron, limestone, and carbon are common types of reactive materials that can be used. The reactive materials promote microbially mediated sulphate reduction, the generation of hydrogen sulphide, and the subsequent precipitation of sparingly soluble iron and other metals, such as Cd, Ni, Co, Cu, Zn, As sulphide minerals [31]. Sulphate-reducing bacteria (SRB) convert  $\text{SO}_4^{2-}$  to sulphide by catalysing the oxidation of organic carbon with the reduction of  $\text{SO}_4^{2-}$ :



The reaction between the  $\text{SO}_4^{2-}$  and the organic substrate consumes  $\text{SO}_4^{2-}$ , results in the production of  $\text{H}_2\text{S}$  and increases bicarbonate alkalinity and the pH. The sulphide produced reacts with dissolved metals ( $\text{Me}^{2+}$ ) and enhances the precipitation of metals as metal sulphides [20]:



The oldest full scale PRB technology was first used to remediate groundwater contaminated with chlorinated solvents. More recent work began in the 1970s and continued through the 1980s, culminating in a pilot-scale PRB installed in 1991 at Borden, Ontario site and a full-scale PRB installed in 1995 at the Intersil Site in Sunnyvale, CA. To date, PRBs have been used to treat a range of contaminants in

groundwater such as organohalogen compounds (e.g. tetrachloroethane (PCE), trichloroethene (TCE), dichloroethene (DCE), metals (e.g. chromium and arsenic), nitrate, and radionuclides such as uranium [4, 16]. The advantages and limitations of the PRB technology are summarized in Table 1 [4, 6, 13, 22, 23, 29, 32].

**Table 1.** The advantages and limitations of the PRB technology [4, 6, 13, 22, 23, 29, 32]

Advantages	Limitations
(a) Results in reduced costs due to the semi-permanent installation, low energy input, focused cleanup on only the area of contamination, conservation of clean water, and continued productive use of the site almost immediately after installation	(a) It can be expected that the long-term performance would be inhibited by clogging and armouring by aluminium and manganese precipitates. Armouring with aluminium hydroxide or manganese oxides would decrease the reactive surface area and may cause clogging of the pore spaces, restricting the flow of groundwater through the PRB
(b) They have the potential to mitigate the spread of contaminants that have proven difficult and expensive to manage with other cleanup methods	(b) Design flaws such as improper hydraulic and/or geological characterization of a site prior to PRB installation can result in limited capture of the plume, diversion and partial or total by-pass of the groundwater around the PRB and, overall, loss of hydraulic control
(c) Allows for treatment of multiple contamination plumes since more than one barrier can be used	(c) Limited field data concerning longevity of barriers
(d) Requires occasional monitoring to ensure that barriers are functioning properly	(d) Reactive media may have to be removed or be replaced during operation
(e) They typically rely on passive processes, and are considered an environmentally sustainable treatment technique	(e) Long time-frames (decades) may be required to manage risks associated with a long-lived or persistent contaminant source
(f) Minimise volume of soils and groundwater that need to be physically handled	(f) Deeper plumes can present problems for construction and monitoring
(g) They have potential operational lives of decades	

## 2. Materials and methods

### 2.1 Reactive media for heavy metal removal

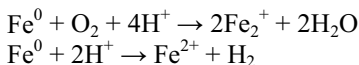
The ability of PRBs to remediate contaminants is dependent on the type of reactive material used. Some of the reactive media remove contaminants through physical contact while others work by altering the biogeochemical processes in the treatment zone, thus providing conditions conducive for contaminant immobilization or (bio) degradation. The choice of the reactive material is generally influenced by: (i) the type of contaminants to be treated (i.e., organic and/or inorganic), their concentrations, and the mechanisms needed for their removal (e.g. biodegradation, sorption or precipitation); (ii) the Hydrogeological and biogeochemical conditions of the aquifer; (iii) the environmental/ health impacts; (iv) mechanical stability (capacity of the material to preserve its hydraulic conductivity and reactivity over time), and (v) the availability

and cost of the material [22]. A suitable material must have the following characteristics [5, 12, 14, 24, 31]:

- Increase the pH of the groundwater to a level that causes metals such as Fe and Al to precipitate out of solution
- Provide reactive sites for the precipitation to take place
- Have a permeability and effective porosity that allows groundwater to pass freely through the barrier
- Longevity: with time, reactive materials may be consumed by reactions taking place and the reactive sites may become armoured by the precipitates that form
- Environmental compatibility: must not release toxins into the environment
- Must be abundant and low cost

### 2.1.1 Zero-valent iron

Zero-valent iron is currently the most common reactive material used in a PRB. It has been broadly used as a reactive material in PRBs for groundwater remediation and demonstrates very good removal efficiency for several inorganic (e.g. Cr, Cu, Ni, As, Zn) and organic contaminants. It consumes oxygen, establishing thus anaerobic conditions which favour growth of sulphate reducing bacteria. [3, 10, 33].



The first granular iron-filled wall was constructed inside a sheeted excavation by the University of Waterloo in 1991. This installation was monitored for a period of 5 years, and performed successfully and consistently. Granular iron has been effective in degrading a wide range of halogenated organic contaminants, such as trichloroethene, in groundwater and has now been implemented at over 20 sites [6].

Other types of media have been implemented in PRB. However, studies [16] have shown that particular media are more effective in removal of certain contaminants and not effective in others. For example, it has been shown that the effective media for removal of heavy metals are ZVI, apatite, bioreactors, and slag whereas only bioreactors are known to be capable of sulphate removal.

### 2.1.2 Pervious concrete

Pervious concretes are commonly used in parking lots, sidewalks and pathways, low traffic areas to reduce the peak flows along stream and drainage channels and reduces the risk of floods. They minimize stormwater-related flooding by allowing the infiltration of surface runoff through the pavement. Furthermore, these pavements are effective in reducing the pollutant loads in stormwater runoff. Runoff waters that pass through porous pavements contain lower pollutant loads than those from a reference catchment. This is said to be due to the accumulation of metallic micro-pollutants from runoff waters on the surface of the pervious pavement [28].

Absorption, straining and decomposition of microbiological organisms in soils have been suggested as the main removal mechanisms by pervious concrete pavements. Properly designed pervious concrete can be effective in treating polluted or acidic water, not only by raising its pH value but also by efficiently removing most of the

undesirable contaminants including sulfate, iron, zinc, sodium, magnesium, manganese and most other metals. Furthermore, the use of pervious concretes in pavements can lead to a reduction in oil and grease, and petroleum products (polycyclic aromatic hydrocarbons (PAHs)) from the water effluent drained through pervious concrete. For these reasons, pervious or permeable concrete is becoming more extensively promoted in light of its environmental sustainability impacts [7].

## *2.2 Batch and column tests*

In order to evaluate the suitability of the reactive materials, laboratory tests concerning the rate and mechanism (including the formation of by-products) of pollutant removal are performed. These laboratory treatability tests coupled with site characterization information are the basis for the design and the implementation of the PRB. These tests assess the effectiveness and rate of pollutants removal of potential barrier materials, evaluate the reaction products that are formed in the remediation process and their eventually toxicity and estimate the working life time of the reactor. The treatability tests can be performed under no flow conditions (batch tests) or under gravitational or imposed flow conditions (column tests). Batch studies evaluate the rate in the remediation of pollutants and the longevity of different materials under controlled conditions. It is the test more appropriated for the selection of the reactive materials for the barrier. Different samples consisting of a mixture of the reactive material to test and an aqueous solution containing dissolved contaminants are prepared. The mixtures react for a given period of time and the concentrations of the contaminants at the beginning and at the end of the contact time are measured [1].

In Column studies: the conditions of this test, like flow velocity, should be similar to those in the field site. Based on these studies, one can obtain the residence time of the contaminant in the reactive zone that can be used, with the flow rate, to determine the thickness of the media [26]. The test consists of the percolation of the solution of the contaminant through a cylindrical column filled with the reagent material. Concentration variation and physical–chemical parameters are typically monitored in the effluent and in different points along the height of the column. Hence, the profile of concentration of the contaminant and of its by-products along the column is obtained. Furthermore, distinct degradation rates can be determined for every value of flow rate. Samples of solutions from all recipients are collected and submitted to chemical analyses to determine concentration changes and to obtain physico–chemical parameters such as the pH, redox potential and electric conductivity [15]. A schematic diagram of a fixed-wall column is shown in Figure 2. Although batch tests are quick to perform, column experiments provide dynamic flow conditions which closely approximate those expected in a PRB system in field deployments and can be useful for the estimation of long term performance [1, 22].

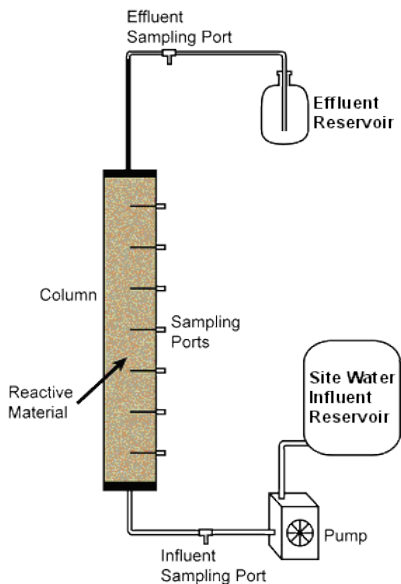


Figure 2. Schematic diagram of fixed-wall column [16]

Using results from the column tests, the residence time required to attain prescribed treatment follows a first-order decay equation [16, 21]

$$C_t = C_o e^{-kt}$$

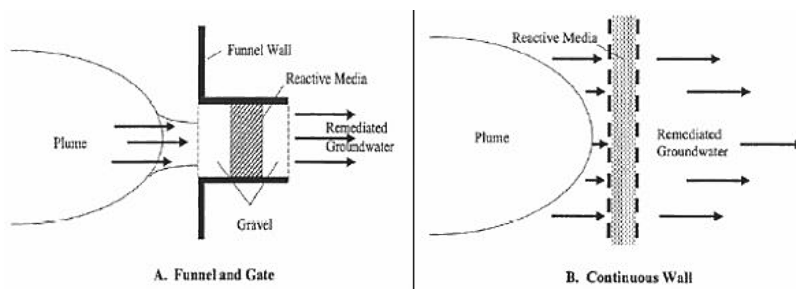
Where,  $C_o$  =the concentration of the contaminant entering the PRB,  $C_t$  = target concentration down-gradient of the PRB and  $k$  is the rate of reaction. If the decay rate (which depends on chemistry of the polluted water and media type), is known, only two sets of data are needed to estimate the residence time by re-arranging the decay equation into:

$$t = - \ln (C_t/C_o)/k$$

### 2.3 Installations schemes used in PRB field application

Two installation schemes are more frequently used in field applications of a PRB; Continuous and Funnel-and-Gate systems. The continuous PRB configuration consists of a single reactive zone installed across the contaminant plume, while the funnel-and-gate system consist of a permeable gate (reactive zone) placed between two impermeable walls that direct the contaminated plume towards the reactive zone. The choice between the two configurations is influenced by both the hydrogeological characteristics of the site and the reactive material cost. When a high cost reactive material is used, funnel-and gate configuration is preferred since the reactive zone requires less material. However, construction cost of continuous type barrier is much cheaper than funneland- gate system. Multi-sequenced reactive barriers are also being installed, especially on sites with multiple groundwater contaminants such as gas works sites. Multi-sequenced PRBs use multiple reactive materials in more than one reactive

zone to treat the contaminated groundwater [25, 30]. Diagrams of PRBs are shown in Figure 3.



**Figure 3.** Typical configurations of a permeable reactive barrier [18]

#### 2.4 Barrier design

Steps in the design of a permeable reactive barrier are shown in Figure 4. The main issues that need to be considered in the design of a permeable reactive barrier will be [4, 10, 17]:

- The selection of the treatment process and specification of reactive material including chemical composition, surface area, grain size, and density of placement
- The influence of the PRB on the groundwater flow and geochemical regime;
- The PRB's ability to retain its hydraulic properties (i.e. permeability) and treatment capacity in the long-term
- The location of the PRB in relation to contaminated groundwater and site constraints;
- The type and configuration of barrier
- The residence time to ensure that the contaminants of concern are treated to a level that protects identified receptors
- The treatment process does not result in any detrimental impacts to the environment, and in particular to groundwater quality or flow
- The seasonal and long-term variation in groundwater flow and contaminant flux can be accommodated by the PRB design;
- The treatment process can be monitored;
- The possible requirement to replace or rehabilitate the reactive media, as well as to decommission the PRB
- Whether a combination of remedial options may be required to meet the remedial objectives, i.e. the PRB forms part of an integrated treatment approach;
- Potential environmental impacts associated with implementing a PRB.





#### 4. Conclusions

PRBs have been successfully used for the treatment of a variety of contaminants, including the treatment of AMD and the remediation of streams polluted by heavy metals. PRBs are practical, have low maintenance costs, require low energy input and are a more sustainable alternative to traditional pump and treat methods. Although Zero-valent iron is currently the most common reactive material used in a PRB, the spectrum of contaminants that can be treated has been broadened, owing to other types of media that have been implemented in PRB such as zeolites, limestone, organic substrates and activated carbon.

The selection of the reactive material is crucial; it must be chemically effective to eliminate the target contaminant(s) and must maintain an adequate permeability to ensure flow through the PRB. In order to evaluate the suitability of the reactive materials, treatability laboratory tests (batch and column) should be performed. These tests assess the effectiveness and rate of pollutants removal of potential barrier materials, evaluate the reaction products that are formed in the remediation process and their eventually toxicity and estimate the working life time of the reactor. Continuous and Funnel-and-Gate systems are two installation schemes frequently used in field applications of a PRB. Even though considerable laboratory-based research has been done on PRB technology, more research is still required to determine the long term-performance of PRBs, which have somewhat affected their acceptability and full-scale implementation.

#### References

- [1] Ambrosini, G. 2004. Reactive Materials for Subsurface Remediation through Permeable Reactive Barriers. Diss. ETHNo.15784 (2004).
- [2] Blowes, D. W., Ptacek, C. J., Benner, S. G., McRae, C.W.T., Bennett, T. A. and Puls, R. W. 2000. Treatment of inorganic contaminants using permeable reactive barriers. *Journal of Contaminant Hydrology*, 45, 123-137.
- [3] Bazdanis, G., Komnitsas, K., Sahinkaya, E. and Zaharaki, D. 2011. Removal of heavy metals from leachates using permeable reactive barriers filled with reactive organic/inorganic mixtures. Third International Conference on Environmental Management, Engineering, Planning and Economics, Skiathos island, Greece (June 19-24, 2011).
- [4] Carey, M.A., Fretwell, B.A., Mosley, N.G. and Smith, J.W.N. 2002. Guidance on the use of permeable reactive barriers for remediating contaminated groundwater. *National Groundwater & Contaminated Land Centre report NC/01/51*.
- [5] Cocos, L.A., Zagury, G.J., Clément, B., Samson, R. 2002. Multiple factor design for reactive mixture selection for use in reactive walls in mine drainage treatment. *Water Research* 32, 167-177.
- [6] Day, S.R., O'Hannesin, S.F. and Marsden, L. 1999. Geotechnical techniques for the construction of reactive barriers. *Journal of Hazardous Materials* B67, 285-297.
- [7] Ekolu, S.O., Azene, F.Z. and Diop, S. 2013. A concrete reactive barrier for acid mine drainage treatment. *Institution of Civil Engineers publishing*. Paper 1300035.
- [8] Fripp, J., Sienkiewicz, P.F., Charkavorki, H. 2000. Acid mine drainage treatment. EMRRP Technical Notes Collection (ERDC TN-EMRRPSR-14), U.S. Army Engineer Research and Development Center, Vicksburg, MS.
- [9] Ford, K.L. (2003). Passive treatment systems for acid mine drainage. Technical Note 409. BLM/ST/ST 02/001+3596. Bureau of Land Management Web based report available online at <http://www.blm.gov/nstc/library/techno2.htm>
- [10] Gavaskar, A.R. 1999. Design and construction techniques for permeable reactive barriers. *Journal of Hazardous Materials* 68, 41-71.
- [11] Geranio, L. 2007. Review of Zero Valent Iron and Apatite as reactive materials for Permeable Reactive Barrier. Term Paper SS 07/08, major in Biogeochemistry and Pollutant Dynamics Department of Environmental Sciences, ETH Zurich.

- [12] Gibert, O., de Pablo, J., Cortina, J.L., Ayora, C. 2004. Chemical characteristics of natural organic substrates for biological mitigation of acid mine drainage. *Water Research* 38 (2004) 4186–4196.
- [13] Gibert, O., Rötting, T., Cortina, J.L., de Pablo, J., Ayora, C. and Carrera, J. 2011. In-situ remediation of acid mine drainage using a permeable reactive barrier in Aznalcóllar (Sw Spain). *Journal of Hazardous Materials* 191, 287–295.
- [14] Golab, A.N., Peterson, M.A. 2006. Selection of potential reactive materials for a permeable reactive barrier for remediating acidic groundwater in acid sulphate soil terrains. *Journal of Engineering geology and hydrogeology*, 39, 2006, 209–223.
- [15] Gusmão, A.D., Tácio Mauro Pereira de Campos, Manoel de Melo Maia Nobre and Eurípedes do Amaral Vargas Jr. 2004. Laboratory tests for reactive barrier design. *Journal of Hazardous Materials* 110, 105–112.
- [16] Henderson, A.D. and Demond, A.H. 2007. Long-Term Performance of Zero-Valent Iron Permeable Reactive Barriers: A Critical Review. *Environmental Engineering Science*, 24, 401–423.
- [17] ITRC Technology update team. 2011. Permeable Reactive Barrier: Technology Update. Technical/Regulatory Guidance. Retrieved from <http://www.itrcweb.org/GuidanceDocuments/PRB-51.pdf>
- [18] ITRC Mining Waste Team. (2005). Permeable Reactive Barrier Systems. ITRC. Retrieved from [http://www.itrcweb.org/miningwaste-guidance/to\\_permeable.htm](http://www.itrcweb.org/miningwaste-guidance/to_permeable.htm)
- [19] Johnson, D.B. and Hallberg, K.B. 2005. Acid mine drainage remediation options: a review. *Science of the Total Environment* 338, 3 – 14.
- [20] Ludwig, R.D., McGregor, R.G., Blowes, D.W., Benner, S.G., Mountjoy, K. 2002. A permeable reactive barrier for treatment of heavy metals. *Ground water*, vol. 40, No.1:59–66.
- [21] MEND. 1996. Review of passive systems for treatment of acid mine drainage Phase II. Prepared by Kilborn Inc. for Mine Environmental Neutral Drainage (MEND) programme.
- [22] Obiri-Nyarko, F., Grajales-Mesa, S.J. and Malina, G. 2014. An overview of permeable reactive barriers for in situ sustainable groundwater remediation. *Chemosphere* 111, 243–259.
- [23] Park, J., Lee, S., Lee, J. and Lee, C. 2002. Lab scale experiments for permeable reactive barriers against contaminated groundwater with ammonium and heavy metals using clinoptilolite (01-29B). *Journal of Hazardous Materials* B95, 65–79.
- [24] Pagnanelli, F., Viggi, C.C., Mainelli, S., Toro, L. 2009. Assessment of solid reactive mixtures for the development of biological permeable reactive barriers. *Journal of hazardous materials* 170, 998–1005.
- [25] Phillips, D.H. 2009. Permeable reactive barriers: A sustainable technology for cleaning contaminated groundwater in developing countries. *Desalination* 248, 352–359.
- [26] Powell, R.M., Puls, R.W., Blowes, D.W., Vogan, J.L., Gillham, R.W., Powell, P.D., Schultz, D., Sivavec, T. and Landis, R. 1998. Permeable reactive barrier technologies for contaminant remediation- *Environmental Protection Agency*, Office of research and development, Washington DC 20460, Office of Solid Waste and Emergency Response, Washington DC 20460, EPA/600/R-98/125.
- [27] Skousen, J. 1990. Overview of passive systems for treating acid mine drainage. West Virginia University. Retrieved 10/08/2010 from <http://www.wvu.edu/~agexten/landrec/passtr/passtr.htm>
- [28] Solpuker, U., Sheets, J., Kim, Y. and Schwartz, F.W. 2014. Leaching potential of pervious concrete and immobilization of Cu, Pb and Zn using pervious concrete. *Journal of Contaminant Hydrology* 161, 35–48.
- [29] USEPA (United States Environmental Protection Agency). 1998. Permeable reactive barrier technologies for contaminant remediation. USEPA, Washington, DC. 1 pp.
- [30] Thiruvenkatachari, R., Vigneswaran, S. and Naidu, R. 2008. Permeable reactive barrier for groundwater remediation. *Journal of Industrial and Engineering Chemistry* 14, 145–156.
- [31] Waybrant, K.R., Blowes, D.W., Ptacek, C.J. 1998. Selection of reactive mixtures for use in permeable reactive walls for treatment of mine drainage. *Environmental science and technology* 32, 1972–1979.
- [32] Wanner, C., Zink, S., Eggenberger, U. and Mäder, U. 2013. Unraveling the partial failure of a permeable reactive barrier using a multi-tracer experiment and Cr isotope measurements. *Applied Geochemistry* 37, 125–133.
- [33] Wilkin, R.T. and McNeil, M.S. 2003. Laboratory evaluation of zero-valent iron to treat water impacted by acid mine drainage. *Chemosphere* 53, 715–725.
- [34] Younger, P.L., Banwart, S.A. and Hedin, R.S. 2002. *Mine water*. Kluwer Academic Publishers London, 442 pp