Passive *In Situ* Remediation of Contaminated Ground Water Using Permeable Reactive Barrier

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Abstract— Groundwater contamination due to heavy metals, either from natural sources or anthropogenic sources, has become a major concern for the authorities these days. Industrial activities with inadequate and improper water treatment, and then leaching of the same into the water body, make the ground water contaminated and harmful to consume. Passive remediation is one of the recent treatments introduced to counter this problem as it is low in cost but an effective technique. After being widely acknowledged and through research conducted, the most suitable remediation technique found is the permeable reactive barriers (PRBs). PRB is defined as an in *situ* permeable treatment zone filled with reactive materials, designed to intercept and remediate a contaminant plume under natural hydraulic gradients. There have been many findings made from PRB which can be used to remove contaminants such as heavy metal, chlorinated solvents, carbonates and aromatic hydrocarbons. The most crucial criteria in making a successful PRB is the reactive media used to remove contaminants. The current paper presents an overview of the PRB selective medias that have been used and also the unresolved issue on the long-term performance of PRB. This inexpensive but effective technique is crucial as a sustainable technology in order to treat the drainage before it enters water tables to prevent water pollution and can be used as an alternative raw water source.

Key words: In Situ, Heavy Metal, Passive Remediation, Permeable Reactive Barrier, Reactive Media, Water Pollution

I. INTRODUCTION

The deterioration of groundwater and surface water quality is a widespread concern mainly originating from accidental discharges and soil/landfills leaching. Leaching of discharges can cause a lot of effect to the environment and one of the examples is the heavy metal contamination. Heavy metal contamination can give impact through soil, groundwater, and surface water in the form of sludge. Toxic heavy metals are found naturally in the earth, and become concentrated as a result of human caused activities where one of the common sources is from mining.

A permeable reactive barrier (PRB) is a passive treatment which acts as a subsurface emplacement of reactive materials through which a dissolved contaminant plume must move as it flows, typically under natural gradient. Treated water exits the other side of the PRB. This *in situ* method for remediating dissolved-phase contaminants in groundwater combines a passive chemical or biological treatment zone with subsurface fluid flow management. The barrier contains selective media which acts as a remediation agent and will result in less polluted water to flow to the water table.

Mine water pollutions have been arising in centuries (Younger, Banwart, & Hedin, 2002; Blowes, Ptacek, Jambor, & Weisener, 2004). The polluted mine water will leach mostly into groundwater and the water body. One of the treatments for polluted mine water is by remediation. Groundwater remediation removes constituents, or "contaminants," that affect valuable uses of groundwater. Groundwater remediation can remove contaminants biologically in either passive or active methods. Passive groundwater remediation allows contaminants to degrade or disperse *in situ* by using only naturally available energy sources. Normally, passive treatment signifies engineering intervention and implementing a system using much lower long-term operating costs (PIRAMID Consortium, 2003).

The reactive materials in the PRB has evolved from time to time in order to improve and to enhance more contaminants to be remediated. Active groundwater remediation involves either treating contaminated groundwater *in situ* (while it is still in the aquifer) or extracting contaminated groundwater from the aquifer and treating it. Active *in situ* methods generally involve injecting chemicals into the contaminant plume to obtain a chemical or biological removal of the contaminant. The former involves the use of energy (for example, for pumping) and addition of chemicals (for example, lime and caustic soda for *pH* correction), whilst the latter relies on naturally occurring biogeochemical reactions to attenuate mine water pollutants. Extracting and treating contaminated groundwater can involve physical, chemical, and/or biological processes.

Active groundwater remediation systems that extract, treat and discharge the treated groundwater to a water body or inject it back into the aquifer are commonly termed "pump and treat" systems. This pump and treat technology is a conventional method to remediate groundwater contaminations. However, the clean-up goals have become an issue; thus, much research and development have been done to create alternative systems for sustainable remediation techniques (Henderson and Demond, 2007).

Contaminated groundwater can come from a multitude of sources, both naturally occurring and anthropogenic. Examples of naturally occurring contaminants include heavy metals and radioactive constituents and high concentrations of various salts from specific geologic formations or conditions. Groundwater can also be contaminated through anthropogenic sources which are organic, inorganic, and radioactive constituents from many specific sources and other more diffuse and widespread sources. Examples of anthropogenic sources are industrial sites, mining operations, leaking pipelines, landfills, septic systems and agricultural activities. The contaminants that give the most adverse impact on drinking water wells are nitrates, arsenic, pesticides, and industrial and commercial solvents.

There are a few passive systems that can practise passive remediation but the most innovative technologies that have been used for *in situ* treatment is by using PRBs

(Tratnyek, 2000; U.S. EPA, 2000). Since the invention of the PRB technology in the early 1990s, its ability in removing contaminants has been vigorously investigated. The results are always extraordinary, thereby making the PRB technology as a suitable alternative for the pump and treat technology (Korte, 2001; Carey, Fretwell, Mosley, & Smith, 2002; Wilkin and Puls, 2003; Puls, 2006; Skinner and Schutte, 2006; Henderson and Demond, 2007; Chen, Li, Lei, & Shim, 2011).

PRB offers a passive alternative to pump-and-treat systems, where in other words, PRB is a zone of reactive materials emplaced within a void space where the flow path of contaminated ground water takes place, such that polluted ground water is improved in quality as it flows through the PRB. The majority of full scale PRBs constructed to date have been designed to totally remove or reductively degrade contaminants. There are many published documents and reviews on PRBs but there are also reports on pollution swapping in some PRBs (Schipper, Robertson, Gold, Jaynes, & Cameron, 2010) of the decontamination of the groundwater which usually occurs within the barrier, depending on the type of the reactive media used (Carey et al., 2002; Wilkin and Puls, 2003; Puls, 2006; Henderson and Demond, 2007; Chen et al., 2011).

Pollution swapping is where when one element contaminant has successfully degraded leads to an increasing rate of other contaminants. Hence this paper will present an overview of PRBs, the reactive media used so far as well as the advantages and also the limitations of PRBs. This review is important in order to keep up to date with the latest environmental technology in the field of passive treatment and also to keep track of the advantages and limitations of PRBs. By gathering the knowledge of PRB, especially in terms of its limitations, it can then be reconsidered and improved from time to time. Although there are many published documents and reviews on PRBs itself, this paper focuses mainly on the overall view of the PRB technology, from the reactive media used so far, the design and construction as well as the long term performance of PRBs.

II. ENVIRONMENTAL TECHNOLOGY OF PRBS

The PRB technology was first used to remediate groundwater contaminated with chlorinated solvents. After proving to be effective in treatment, this technology was extended to include other contaminants. In the early stages, the most reactive material used is the zero valent iron (ZVI) filled barriers, which could treat limited number of contaminants. There are many published papers studied and reviews on PRB technology; however, most of the studies used zero valent iron as the reactive materials (Scherer, Richter, Valentine, & Alvarez, 2000; Korte 2001; Henderson and Kemond, 2007; Noubactep, 2010). Zero valent iron has high reduction potential hence producing high removal rate of contaminants.

After the success of using ZVI as reactive materials, the productions of new reactive materials have been conducted seriously in order to remove more contaminants at one time. Thus, the term "biobarrier id" was introduced which allowed the use of organic materials to remove contaminants (Yang, Fan, & Erickson, 1995). With the production of biobarriers, there is higher possibility production of using inexpensive organic substrates to be used as the filling of biobarriers to enhance growth and activities of autochthonous or inoculated microbes in order to facilitate the degradation of contaminants (Yerushalmi, Manuel, & Guiot, 1999 Wilson, Mackay, & Scow, 2001; Vesela, Nemecek, Siglova, & Kubal, 2006). For example, in the removal of nitrogen, the use of denitrifying bioreactors have been most commonly used and proven with a high removal of nitrate based contaminants (Robertson and Cherry, 1995).

Although nitrogen contributes as a major nutrient to plants in addition to potassium and phosphorus, excessive nitrogen can lead to a process called "eutrophication" and is able to leach into groundwater and surface water in the form of nitrate hence affecting the quality of the water. A bioreactor called "the denitrifying bioreactor" has been invented and introduced to remove nitrate by using solid carbon substrates to achieve contaminant removal of nitrate. Not just also that, it also helps to remove pathogens, pharmaceutical compounds and pesticides in agricultural drainage (Schipper et al., 2010).

During the early stage of the technology, only a single barrier has been used in most of the PRB applications and a single barrier means a single reactive material used (ITRC, 2011). These barriers were mainly used for contamination plumes containing one contaminant or contaminants of similar nature; for example, heavy metals. However, these barriers are very ineffective for most sites with a mixture of different physical and chemical properties (Kober, Schafer, Ebert, & Dahmke, 2002).

Apart from the inability to attenuate multi-contaminant plumes, most researchers had to deal with the issue of pollution swapping, which is defined as the inadvertent generation or release of new potential hazardous contaminants (Stevens and Quinton, 2009; Healy, Ibrahim, Lanigan, Serrenho, & Fenton, 2012). A number of studies report that the usage of denitrifying bioreactors and single barriers can produce a phenomenon called "pollution swapping". Hence, the technology has introduced a multi-barriers concept to make PRBs a more sustainable technology and to broaden the field of application.

A multi-barrier system is a two or more barriers that are filled with different or same reactive materials. The reactive materials can also be mixed. This system helps in the removal of contaminants constantly as well as to eliminate pollution swapping from occurring and, consequently, this concept is relatively efficient and has been receiving attentions from many interested parties (Kober et al., 2002; Birke et al., 2007). One of the examples which prove that multi-barriers can eliminate pollution swapping is the Permeable Reactive Interceptors (PRI) in denitrifying bioreactors. Fenton et al. (2014) suggests that the PRI is suitable as a solution for remediating agricultural activities as it gives the best result in minimizing pollution swapping so far.

Advantages	Limitations
a) A very cheap technology for passive remediation; for example inexpensive but effective reactive materials can be used, low energy cost, little or no disposal cost for treated wastes and; relatively low maintenance and monitoring costs with the exception of initial cost of installation	(a) Only contaminants flowing in the direction of the barrier can be treated
b) More than one barrier can be used, hence more contamination plume will take place	(b) It requires all aspects of site assessment explorations, site characterizations and accurate delineations of the contaminants prior to installation of barriers
c) Can treat a wide range of contaminants	(c) Only restricted to plumes 20m beneath the ground surface
d) The aboveground contaminated site can still be used while the treatment is still ongoing down under	(d) No proper length of time in longevity of the barriers
e) No cross-media contamination since contaminants remain underground	(e) Problems may be present in terms of performance and maintenance in underground structure
f) Only requires occasionally monitoring	(f) Reactive media may need to be replaced during operation

Table 1: Advantages and limitations of PRBs (Obiri-Nyarko, F., Grajela-Mesa, S.J. & Malina, G. 2014)

III. REACTIVE MEDIA USED IN PRBS

One of the important factors in designing a successful PRB is the selection of reactive media. Based on previous studies, there are a variety of media which can be used and most media can treat different contaminants. The main objective of PRB is to deliver the contaminant to the reactive zone under natural gradient to be treated. Previous studies have come out with a wide range of reactive materials made available. The first and most common reactive media used is ZVI.

Other reactive materials are activated carbons, zeolites, saw dust, and oxygen releasing compound. Amos and Younger (2003) have performed various experiments and combinations from manure and slurry screenings (mostly cattle), limestone chips, organic compost, and pea gravel. Besides that, the use of sawdust as the reactive material has been conducted as it can remediate a highly toxic thallium T1 (I) contaminated groundwater (Musmarra, Di Natale, Bortone, Erto. & Ciarmiello, 2015). The first step in building PRB is to collect all site characterization information. Once it is obtained, then only the reactive materials for the barriers are selected.

The choice for the suitable reactive media depends on a few factors namely (i) reactivity, a medium that has higher half-lives; (ii) stability, it is highly important to ensure that the medium will maintain reactivity over a length of time; (iii) availability and cost, a cheaper and easy to get medium is highly preferred than the expensive but limited version; (iv) hydraulic performance, this is concerned with the particle size of the reactive medium in order to achieve high quality hydraulic performance; (v) environmental compatibility, it is relatively crucial to ensure that the by-products are not harmful to the environment; (vi) construction method; the finer the particle size of the medium, the more innovative construction method can be produced (Gavaskar et al., 2000). There are two categories in the mechanism of removing the contaminant, which is firstly through the destructive abiotic or biotic process where toxic contaminants are transformed into a nontoxic contaminant; for example, the biodegradation or dechlorination process and secondly the non-destructive processes such as adsorption, cation exchange, surface complexation and precipitation. These processes are needed to enhance the removal efficiencies of the materials and designs, where the removal rate do not rely heavily on the reactive materials used (U.S. EPA, 1998; Gu et al., 2002). In this review, a few materials commonly used as reactive media are discussed.

A. Zero valent iron (ZVI)

Zero valent iron is the first and the most commonly used reactive media in both laboratory studies and field applications for PRBs. Although ZVI can treat a limited number of contaminants, it has a high reduction potential and, as a result, acts as a reductant in the flow systems. Among the contaminants that can be removed by ZVI are mostly chlorinated hydrocarbons (for example, TCE, PCE, VC and DCE), heavy metals and metalloids (Gallinati et al., 1995; Orth and Gillham, 1996; O'Hannesin and Gilham, 1998; Vogan, Focht, Clark, & Graham, 1999; ITRC, 2005; Da-Silva, Johnson, & Alvarez, 2007; Handerson and Demond, 2007). Its rates of contaminant removal are proven to be effective but depend mostly on the specific grain size and surface areas. The mechanism for ZVI usually uses destructive and non-destructive processes, namely through adsorption, degradation and transfer of ions in anaerobic conditions. Extensively, the removal of these contaminants is influenced by pH, redox conditions and dissolved organic carbon (DOC). ZVI are mostly installed in the forms of chips, iron foams and pallets.

B. Activated carbons (AC)

Activated carbons, or granular activated carbons, are carbon contained materials which possess highly chemical heterogeneous surfaces with adsorption capacity. Many studies have shown that AC can remove contaminants such as phenols, BTEX, PTE, TCE and heavy metals (Scherer et al., 2000; Nakagawa et al., 2003). Apart from ZVI, AC is also one of the most common reactive materials used in PRBs (Bone, 2012). The mechanism for removal using AC usually

involves sorption process where the substances are attached to one another and is influenced by the pH value. However, adequate characterization of aquifer and effective managements are needed before using AC as the barrier material.

C. Transformed red mud (TRM)

Another reactive media that has been used is the transformed red mud (TRM). However, the use of TRM as removal agents is still under investigation. TRM is alkaline in nature (pH 8-10.5) and is formed when brine is mixed with red mud generated during the production of aluminium in bauxite industries. TRM is an alternative of limestone in treating acid mine drainage (AMD) (Munro et al., 2004), which is a phenomenon whereby mine water turns acidic due to the accelerated oxidations of iron pyrite and other sulphidic minerals. In addition, TRM mainly contains hydrated aluminium and oxides from iron. Lapointe, Fytas, & McConchie (2006) report that TRM is able to remove 99% of Fe, Cu, Zn, Ni and Pb. Also, Cappai et al. (2012) have proven that TRM is also capable of treating Cr. Relatively, TRM has to be mixed with sand or gravel to increase permeability due to its fine texture.

D. Lime and other alkaline materials

Alkaline materials are often used to treat acidic waters that are harmful to the environment. The most common alkaline materials used to treat acidic conditions, namely AMD is limestone (Dixon, J.B., Weed, S.B., & Dinauer, R.C., 1989; Triay et al., 1989; Conca et al., 2002). AMD is an environmental problem of major concern in areas where iron pyrite (FeS_2) is oxidised with sulphide materials and turns mine waters to be acidic (Burns et al., 2012). Sulphate-rich waters with low pH are produced from natural oxidation of metallic sulphide ores and from industrial activities (Sanchez-Andrea, Sanz, Bijmans, & Stams, 2014). AMD is acidic and contains precipitation of metals because most metals have the tendency to become more soluble when the pH is low. The application of these alkaline materials is done in order to adjust the pH of the groundwater from acidic to neutral. These materials have mostly been used to treat heavy met and to reduce the solubility, and to turn it into precipitation instead. For example, a study by Baker et al. (1998) show that a mixture of crushed lime stone and sand can result in the precipitation of phosphate and thus reduce the solubility and acidity of groundwater. However, the disadvantage of using alkaline materials is that the precipitation formed could easily clog the barrier and affect the hydraulic performance of PRBs. Other than that, it can increase directly the hardness of groundwater and carbon dioxide contents, which lead to other environmental problems connected to greenhouse gas. Pang et al. (2009) also indicate that, since these alkaline materials are affected by pH adjustment, it is important to identify the ideal pH conditions in order to maintain the barriers during their use.

E. Combination of reactive materials

There are a lot of reactive materials which can be used but the technology of PRBs has evolved; from using single or individual materials to combinations of materials. Single or individual materials have been frequently applied at the early stages of the PRB technology. The combinations of materials have been applied as developed modifications to eliminate any pollution swapping, providing multiple mechanisms for contaminants removals and also enhancing the rates of removals (Obiri-Nyarko, Grajales-Mesa, & Malina, 2014). The combinations of reactive materials can be done not just to increase removal rates but also to allow multi contaminant plumes. This combination of materials has been carried out by Ma and Wu (2008) where they used two abiotic materials, namely zero-valent zinc and ZVI, to remove TCE. Based on the result, the rate of TCE removal occurred to be three times faster with the mixture than using ZVI alone. Moraci and Calabro (2010), in addition, conducted a study on a mixture of iron and pumice which were found to be effective in the removal of copper and nickel as well as in the maintaining of the long term hydraulic conductivity of PRBs. Combinations of reactive materials produce effects on the performance of PRBs depending on a few factors including the ratio of materials in the mixture. Among the factors that need to be considered when combining reactive materials are the contaminants that need to be treated, any removal mechanisms needed, availability and cost materials, as well as the effects on the longevity and long term performances of the materials and the PRBs.

IV. PRB DESIGNS AND CONSTRUCTIONS

The design of PRB comprises a few important steps that include a preliminary assessment, characterization of the site where the barrier need to be constructed, followed by the selection of reactive media which is one of the most step need to be considered, treatability studies (batch and column tests), engineering design, choice of the construction method, and formulation of the monitoring plan (Gavaskar et al., 2000).

In constructing the PRB, it is essential to understand completely the key aspect of the design which is in the characteristics of the site and aquifer, the site geology, hydrochemistry and hydrogeology aquifer (Puls, 2006) and also any microbial activity and the contaminated plume delineation (Powell et al., 1998; Erto et al., 2011). As for the selection of reactive media, the important key aspect is the hydraulic performances including screens and reactive media. Permeability within the barrier should be higher to avoid problems due to permeability changes with time as a result of the precipitation of iron oxides/ hydroxides, carbonates and or other metal precipitations (U.S. EPA, 1998). After the selection of reactive material has been conducted, the dimension, location and orientation of the barrier have to be defined.

After the process of preliminary assessment and selection of reactive media, then comes the site characterization of the PRB. A site must be characterized in detail to ensure an efficient design and installation of a PRB. Other than that, to consider this technology as feasible, the physical settings and the site's regulatory constraints must be accounted. This is fairly important because, although it is designed as passive treatment, it must intercept and capture the containment plume in order to produce an effective system.

The physical settings that need to be considered include topography, structures at the surface, underground

utilities and structures, surface water features and ecological features. The PRB technology comes with several construction methods. Among the methods are deep soil mixing, vibrated beam, continuous deep trenching machines, vertical hydraulic fracturing (Puls, 2006), sheet pile walls, backhoe excavation, jetting and caissons method. All these methods depend mainly on the PRB dimensions, depth to the aquifer, and sediments or rocks (Gavaskar et al., 2000). This is indeed necessary as the methods used are different at different dimensions. For example, several PRBs are installed using the backhoe method at 30m reachable for effective excavation rate but, when it needs to dig deeper than 70m, another method needs to be installed, which is the clamshell excavators, although the method could need more skill (Sethi, Day, & Di Molfetta, 2011).

V. CONCLUSION

The technology of PRBs for sustainable groundwater treatment has been invented for a long time and many academic papers and reviews have been published in order to improve PRBs. Clearly, it has been shown that, although the technology is considered new, much research has been conducted so far, improving the technology and producing solutions to arising problems, modifications in reactive materials, improving PRB performances and slowly transitioning it from an innovative to a developed technology. The discoveries of new reactive materials have contributed to solving environmental problems related to groundwater contaminations. Hence, based on previous research and studies that have been discussed and reviewed here, *in situ* passive remediation is not just cost effective but also effective and can be reliable in the process of in removing contaminants. In a nutshell, the main aspects for a proper and effective design of the technology are adequate knowledge in site characterizations, understanding of groundwater flow conditions, site assessments and contaminant transport modellings. The PRB technology is a promising technology and can bring sustainability towards a greener environment.

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