# Advancing Natural *In Situ* Remediation for Treatment of Radionuclides in Groundwater through Permeable Reactive Barriers – 11621

Scott D. Warner, CHG, CEG
AMEC Earth and Environment, Inc., Oakland, California 94612

## ABSTRACT

The concept of using natural remediation methods to treat groundwater affected by radioactive constituents is not a new concept. Seldom, however, has the concept been used in full-scale remedies for radioactive-affected groundwater although hundreds if not thousands of pilot tests have been reported. Natural materials, such as zeolites and other minerals, granular iron, and carbon-based plant matter have properties that are well known and have been well studied with respect to their ability to effectively modify the ambient hydrogeochemical environment to promote mobility reduction or elimination of certain radioactive constituents in an aqueous system. Implementing these treatment materials within a hydraulically passive to semi-passive in situ treatment zone, or a permeable reactive barrier (PRB) is consistent with a growing demand to use "green" or sustainable approaches. Natural zeolitic minerals such as clinoptilolite to promote ion exchange reactions that remove strontium-90 from groundwater in exchange for monovalent ions such as sodium and potassium; and granular iron particles that, through abiotic corrosion reactions, promote strongly reducing conditions that reduce redox-sensitive radioactive constituents such as uranium (VI) to low-solubility precipitates composed of uranium (IV), can be applied effectively and economically. Though the responsible geochemical reactions leading to these treatments have been studied for many years if not decades, the general reluctance to install full-scale natural remedies for treatment of radionuclide affected groundwater in situ likely is due to a number of factors including, but not limited to: (1) the general difficulty of implementing a remedial technology in a complex subsurface geologic environment; (2), the uncertainty as to how long such a treatment will be effective considering the long half-lives of many constituents; and (3) the difficulty in achieving regulatory approval for such installations. Examples of recent advances in the application such in situ natural measures, such the comprehensive evaluation, design and application of a natural zeolite to remove Sr-90 from the entire width of a plume of radionuclide-impacted groundwater should give more credibility to this concept. Using the new advances to design innovative approaches that effectively package specific aquifer volumes to promote full treatment of low half-life radionuclides (such as Sr-90 with a half life of approximately 28 years) also could effectively treat an entire plume within a reasonable time-frame. With the growing demand and work in: (1) site decommissioning, (2) treatment of legacy sites, and (3) long-term waste management of nuclear materials including those from mining starts, the needs for economical and sustainable treatment is as great as ever.

This presentation will highlight new advances, lessons learned, and offer new concepts for long-term treatment approaches.

## INTRODUCTION

Remediation technologies for contaminated groundwater has progressed over the past 30 years since the 1980 genesis of the U.S. Superfund Program from using energy-intensive groundwater pumping with above-ground treatment (i.e., pump and treat), to the relatively recent use of hydraulically passive treat-in-place, or *in situ*, methods. While pump-and-treat still is used for many groundwater remediation projects, the generally progression from active to passive technologies has occurred for a number of reasons including the intent to find less expensive, more focused, more resource conservative methods to protect environmental receptors from being negatively impacted by groundwater contaminants.

Since the early 1990s, the advent, development, and progression of PRB technology has allowed passive in situ groundwater remediation to evolve from an "innovative" method to one that is considered accepted and mature for the treatment of industrial contaminants. The PRB technology, which has been the focus of hundreds if not thousands of technical articles and publications, e.g., [1,2,3,4,5,6] is considered a "remediation concept" whereby affected groundwater is allowed to flow through, or is routed through, an emplaced subsurface zone of treatment media that has geochemical or biochemical properties appropriate for either destroying, immobilizing, or altering the molecular form of the contaminant sufficiently to render it harmless (Figure 1).

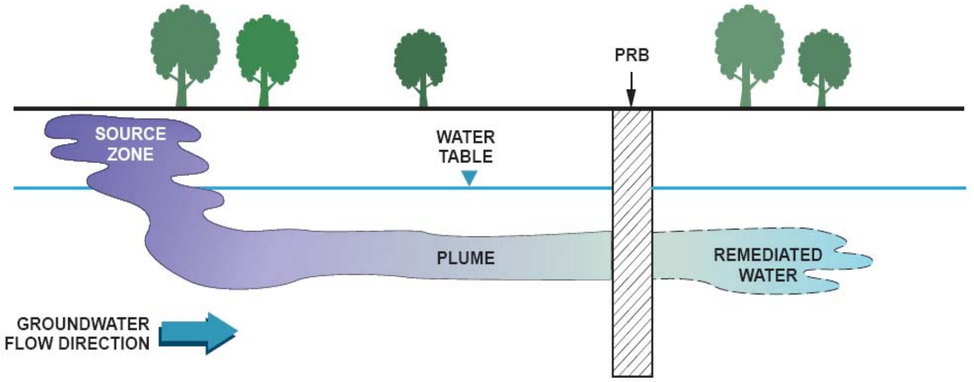

Fig. 1. General concept of a PRB for treating a plume of contaminated groundwater.

Early versions of the PRB concept were used to neutralize acidic water using limestone filters off of mine tailings piles [7]; the first commercial PRB using granular iron metal was constructed in 1994 to destroy chlorinated aliphatic compounds in groundwater [8] following the development of the technology by researchers at the University of Waterloo [9], and a number of pilot tests of PRBs for treating radioactive constituents in groundwater were attempted in the mid to late 1990s [3]. Reasonably, it makes sense that since the early 1990s, several hundred pilot tests and fewer, though still a substantial number of full-scale remedies involving the PRB concept have been implemented world-wide. Given the great interest in sustainable and “green” remediation concepts, it may be surprising that more systems have not been installed. Particularly, when it comes to the treatment of radioactive constituents, after the early work using PRBs to mitigate plumes of radioactive constituents, there appear to have been few full-scale uses of PRB technology for this. The purpose of this paper is to re-evaluate the PRB as a potential method to sustainably and effectively treat radioactive constituents in groundwater by considering both the challenges and opportunities held by this technology.

## DEFINING NATURAL REMEDIATION

At first glance, groundwater treatment by a PRB may not appear as natural. That is, a PRB is a constructed remediation system. Construction typically involves heavy machinery to remove soil and emplace a reactive media; or in some advancement, involves the use of sophisticated injection equipment to emplace the reactive material at great depths. Thus, even though the PRB happens to be installed in the subsurface so that, aside from the tops of groundwater wells or other such monuments, there are few reminders that a constructed treatment system exists in place, its emplacement involves great activity.

The argument that a PRB is not natural if it must be constructed is reasonable at first glance. With the exception of monitored natural attenuation, which does not involve any human-activity to promote enhanced destruction or immobilization of a contaminant, there are no other groundwater remedies that are 100% natural. Bioremediation methods come close, but even those methods will involve the injection or placement of a material that enhances a subsurface treatment process. Phytoremediation also is very close to 100% natural with the exception that certain trees or plants are planted for the intentional removal, immobilization or destruction of contaminants and often those trees and plants, or foliage from them must be managed as a waste material following remedial application. What we can say, however, is that if designed appropriately the PRB could be sustained for decades with little if any adjustment or maintenance to the system required. From a resource conservation approach, the lack of pumping, energy usage, and even carbon dioxide generation (from energy needs) can be highly beneficial.

What makes the PRB treatment as reasonably close to “natural” as possible, is that affected groundwater is allowed to flow under ambient conditions through the treatment portion of the PRB (groundwater pumps are not applied), and treatment occurs by interaction between the dissolved contaminants in groundwater and the PRB treatment material. These two processes that allow a PRB to function – ambient groundwater flow and treatment by passive interaction between contaminant and treatment material, are tremendous advantages that the PRB may have for treating a contaminant plume over other remedies; providing other criteria are met including:
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1. Contact or residence time within the PRB is sufficient to allow full treatment to occur
2. The longevity of the PRB material is sufficient to be economical
3. No negative byproducts (or more toxic chemicals) are produced by the treatment
4. Chemicals migrate through the PRB; not around, beneath or above it.

5. The PRB is consistent with land use and will not substantially interfere with other site activities.

Consider then examples of treatment materials that are used to promote treatment of contaminants within a PRB as listed in the 2005 guidance on PRBs produced by the Interstate Technology Regulatory Council [6]:

- Compost
- Limestone
- Granular iron
- Zeolites
- Apatite
- Organo-clay

Though the production of these materials may involve milling to an appropriate size fraction, these are not human-invented materials and thus promote natural chemical reactions that work to promote necessary destruction or immobilization of target chemicals. For example; (a) compost promotes bio-active processes that destroy certain organic compounds and promotes retardation of metals and organics; (b) limestone neutralizes pH conditions which helps to mitigate acid-mine drainage; (c) granular iron promote abiotic destruction of chlorinated hydrocarbons, reduces the mobility of certain metals, and promotes the evolution of hydrogen that can promote bioremedial processes; and (d) zeolites and apatite promote ion exchange and reduction of mobility for certain dissolved metals. The PRB can also promote the benefit of other types of remediation; such as the use of phytoremediation in combination with a PRB whereby the PRB (composed of nutrient enriched soil and gravel for example) may enhance both hydraulic conditions and growing conditions whereby plant roots can have greater spread within the subsurface and thus greater uptake of affected groundwater. In no cases, however, are deleterious chemical byproducts being formed, unless the system is inadequately designed and complete treatment does not occur.

## PRB TREATMENT FOR RADIOACTIVE CONSTITUENTS

Groundwater under natural conditions may contain radioactive constituents in trace quantities due to the interaction between groundwater and its host aquifer material (e.g., the dissolution of granite under aqueous conditions can lead to an increase in the concentration of radioactive potassium – $^{40}$K – as a fraction of the ionic content of groundwater). Since the 1940s, the advent of using radioactive materials for defense and energy purposes, as well as other direct commercial needs and activities including medical equipment, safety products, mining operations, and product coloring has lead to the release of radioactive contaminants to soil and eventual impact to underlying aquifers. These impacts are found around the globe; both in areas where direct releases occurred, and where radioactive constituents have spread due to particulate transport by atmospheric processes.

While non-anthropogenic-derived trace occurrence of radioactive constituents in the subsurface generally is tolerated from an environmental perspective, the presence of above background amounts of these constituents typically are regarded as hazardous to environmental receptors and become the focus of remediation programs. The remediation technologies typically available for ridding subsurface ground of excess radioactive content may be greatly expensive, difficult to implement, and may not be always effective at removing or isolating all radioactive content for a number of reasons, including the complexity of the subsurface environment. Remediation of radioactive constituents in the subsurface does not lead to the destruction of these constituents; rather, the strategy employed typically is to isolate the contaminants in place or remove and dispose the contaminated material at offsite locations designed to accept and manage radioactive waste materials. All radioactive constituents eventually will lose radioactivity due to natural decay; however, the time frame for most of these contaminants to decay to the point of being non-hazardous (due to radioactivity) are substantially longer than reasonable (e.g., thousands to millions of years). Some radioisotopes with relatively short decay times (such as $^{90}$Sr at approximately 28 years and tritium at about 12.3 years) may be managed under reasonable human-scale periods; however, this is not typical for many radioactive constituents of concern.

With few exceptions, the radioactive constituents dissolved in groundwater needing treatment are metals (the primary exception being tritium) such as uranium and include the alkaline earth metals strontium and radium. As metals, geochemical processes can be conceived that will immobilize the constituent and remove it from flowing groundwater. Most metals can either be immobilized through reduction (e.g., uranium) or through sorption and ion-exchange (e.g., strontium). Generally, PRBs are well suited for promoting these reactions – granular iron metal is a strong reductant and promotes the reduction and precipitation of uranyl phosphates or carbonates; Sr-90 is exchanged for monovalent cations (such as K or N) in the structure of clinoptilolite.

Challenges exist, however. Radioactivity is not reduced if a mineral precipitate is formed or if an ion exchange reaction occurs. Though immobilized from the flow system, radioactivity will slowly be focused in the treatment zone; which is reasonable and can be managed, but must be considered. Also, assuring that the subject contaminant plume flows through the PRB is perhaps most important so as not to divert affected groundwater to non-contaminated areas or to sensitive receptors currently not at risk. With many metals, competition for reactive sites (such as in ion exchange processes) and reversal of the geochemical conditions that may cause dissolution of a previously precipitated state must also be considered. This leads to the issue of long-term management and care to assure that a treatment zone remains protected for perhaps decades and longer. Tritium poses a special problem due to it replacing the stable hydrogen isotope in water; essentially, tritiated water is not easily remediated by chemical processes unless a material is used to effectively reduce the permeability of the aquifer flow system and thus retard the tritium until it decays sufficiently to below regulatory limits.

## PRB ADVANCES FOR REMEDIATING RADIOACTIVE GROUNDWATER

A major potential benefit for using PRB technology in mitigating a plume of groundwater affected by radioactive constituents stems from not having to remove the contaminant from the subsurface. This reduces the potential that secondary exposure and above ground management of the contaminant is necessary. Because the PRB concept is intended to be designed to site specific needs, there is great flexibility in conceiving a PRB system that can effectively remove or substantially limit the migration of radionuclides in the subsurface.

As demonstrated more than 15 years ago, the use of natural materials, such as natural phosphate minerals, granular iron, and bone char can effectively retard and remove uranium isotopes from groundwater [3]. This type of system is highly sustainable and may be operational for decades with little maintenance required.

Recent advances in the development of ion-exchange PRBs for Sr-90 [10, 11, 12] pushes the technology by providing new insights on the potential exchange capacity of natural minerals and on construction techniques (one-pass trenching) amenable to shallow PRB delivery. For deeper systems, advents in using large-diameter borings to place treatment media at depth, and injection methods for enhancing a native aquifer with natural materials (such as phosphatic, iron, and other amendments) has been demonstrated.

For radioactive plumes developing a remedial scheme that creates managed treatment "packages" may be a consideration to effectively mitigate entire plumes and put less reliance on other more energy inefficient methods such as groundwater pumping. For example, it is reasonable for plumes Sr-90, or Tritium, whose half live values are each less than 30 years, to be managed as illustrated in Figure 2 where the plume is divided into sections based on treating half-life volumes of water. That is, the amount of affected groundwater expected to pass through a PRB represents one half-life of water, or the volume for which the isotope will decay by one half-life by the time it migrates through the PRB. Using this approach, the activity of the entire plume will be reduced in half within the half-life period of time.

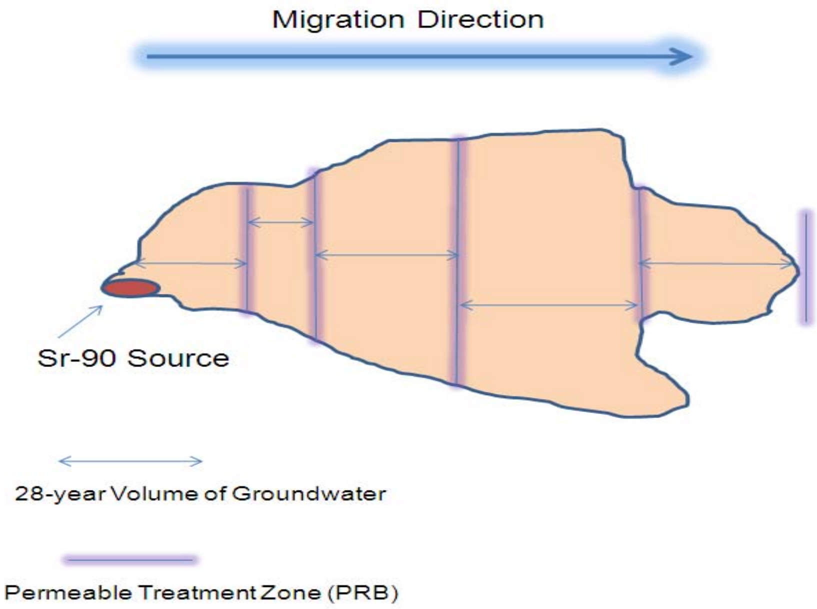

Fig.2. Conceptual layout of PRBs for management of "half-life" packages of groundwater.

## CONCLUSION

The ability to use PRBs, or any other remedy to treat or destroy mobile radioactive constituents is dependent on many issues, including cost and constructability, but notably, effective and complete site characterization. Advances in PRB development, notably in the use of natural materials, and in assessing the effective longevity of PRB materials will continue to develop, and will continue to provide practitioners with a bevy of new options intended to be highly effective, and also highly cost efficient

Because this is a passive technology that is not easily adjusted once installed, an accurate conceptual model must be developed and most important data gaps must be filled before a PRB can be designed. A PRB will fail to meet project objective, and thus be considered a failure, if it designed based on data that are incomplete and/or inaccurate. The PRB may not be the correct remedy to select for many contaminant remediation schemes, however, the several decade experience that our profession has with the PRB technology opens up many more potential opportunities for reducing cost, impact, and secondary treatment issues that characterize the difficulty in mitigating radioactive plumes. Technologies for implementing PRBs will continue to improve and develop (such as injection and deep well PRB installation); the benefits of not having to pump groundwater nor supply ongoing energy for treatment will be the primary drivers for the development of new technologies. We will find that more natural materials effectively create geochemical conditions that remove a contaminant from the flow field, or alter its chemical makeup to less harmful forms.

This paper was not intended to provide substantial detail on PRB development because of the great amount of technical and peer reviewed resources currently available to most interested parties. However, the goal of this paper, to open up the discussion of greater consideration for PRB use in mitigating plumes of radioactive constituents is achieved. Additional technical papers are expected to be written in 2011 as sites report specific additional advances; also, new training sessions on the use of PRBs are expected during the year.

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