Zero-Valent Iron Permeable Reactive Barriers: A Review of Performance

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ZERO-VALENT IRON PERMEABLE REACTIVE BARRIERS:
A REVIEW OF PERFORMANCE

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<tr>
<td>DoD</td>
<td>U.S. Department of Defense</td>
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<tr>
<td>DOE</td>
<td>U.S. Department of Energy</td>
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<tr>
<td>EPA</td>
<td>U.S. Environmental Protection Agency</td>
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<td>FRTR</td>
<td>Federal Remediation Technologies Roundtable</td>
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<tr>
<td>HDPE</td>
<td>high-density polyethylene</td>
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<tr>
<td>KCP</td>
<td>Kansas City Plant</td>
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<tr>
<td>MCL</td>
<td>maximum contaminant level</td>
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<tr>
<td>NFESC</td>
<td>Naval Facilities Engineering Service Center</td>
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<tr>
<td>ORNL</td>
<td>Oak Ridge National Laboratory</td>
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<tr>
<td>PRB</td>
<td>permeable reactive barrier</td>
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<tr>
<td>RTDF</td>
<td>Remediation Technologies Development Forum</td>
</tr>
<tr>
<td>SCFA</td>
<td>Subsurface Contaminants Focus Area</td>
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<td>TIO</td>
<td>Technology Innovation Office</td>
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EXECUTIVE SUMMARY

This report briefly reviews issues regarding the implementation of the zero-valent iron permeable reactive barrier (PRB) technology at sites managed by the U.S. Department of Energy (DOE). Initially, the PRB technology, using zero-valent iron for the reactive media, was received with great enthusiasm, and DOE invested millions of dollars testing and implementing PRBs. Recently, a negative perception of the technology has been building. This perception is based on the failure of some deployments to satisfy goals for treatment and operating expenses. The purpose of this report, therefore, is to suggest reasons for the problems that have been encountered and to recommend whether DOE should invest in additional research and deployments.

The principal conclusion of this review is that the most significant problems have been the result of insufficient characterization, which resulted in poor engineering implementation. Although there are legitimate concerns regarding the longevity of the reactive media, the ability of zero-valent iron to reduce certain chlorinated hydrocarbons and to immobilize certain metals and radionuclides is well documented. The primary problem encountered at some DOE full-scale deployments has been an inadequate assessment of site hydrology, which resulted in misapplication of the technology. The result is PRBs with higher than expected flow velocities and/or incomplete plume capture.

A review of the literature reveals that cautions regarding subsurface heterogeneity were published several years prior to the full-scale implementations. Nevertheless, design and construction have typically been undertaken as if the subsurface was homogenous. More recently published literature has demonstrated that hydraulic heterogeneity can cause so much uncertainty in performance that use of a passive PRB is precluded. Thus, the primary conclusion of this review is that more attention must be given to site-specific issues. Indeed, the use of a passive PRB requires an unusually comprehensive hydrologic characterization so that the design can be based on a thorough understanding of subsurface heterogeneity rather than on average values for hydraulic parameters.

Scientists and engineers are capable of conducting the level of investigation required. However, design costs will increase, and the pre-design field work may demonstrate that a passive PRB is not suitable for a particular site. In such cases, an option to consider is hydraulic augmentation, such as pumping (in which the system is no longer passive) or gravity flow from drains. In these circumstances, operation of the treatment media is under known hydraulic conditions. These systems typically contain the treatment media in a vault or in drums. Most of the media problems in such systems have been related to the exclusion of air and can be addressed by better engineering design or by frequent maintenance.

Finally, a number of outstanding issues require resolution for further application of this technology. Of particular interest to DOE is resolving the removal mechanisms for uranium and technetium. Few data are available for the latter, and for the former, the technical literature is contradictory. Determining the mechanisms has long-term cost implications; engineers must consider whether it is appropriate to remove or simply abandon a barrier that is no longer functioning. Other issues that are unresolved include determining how hydraulic performance is affected by the emplacement method and quantifying the effects of varying groundwater types on barrier longevity.
1. INTRODUCTION

The U.S. Department of Energy (DOE) has invested millions of dollars in permeable reactive barriers (PRBs) through research, pilot studies, and full-scale installations. As experience with full-scale deployments has increased, a perception has grown that the technology is not performing as well as expected. The purpose of this document is to review the present status of the technology with a view toward understanding the source of the negative perception and to provide recommendations regarding DOE’s future investments in the technology. This report was prepared with limited time and budget. The effort, therefore, relied significantly on infrastructure that exists because of the DOE Subsurface Contaminants Focus Area (SCFA) project, “Permeable Reactive Barriers Performance Monitoring and Verification.” That project (Appendix A) is an interagency effort with the U.S. Department of Defense (DoD) and the U.S. Environmental Protection Agency (EPA) that provided a sufficient network within the federal government and private industry to ensure a comprehensive view of the status of the technology.

2. SCOPE

The scope of the project was a review and synthesis of data from existing PRBs. No fieldwork was performed. Although there are various barrier media, this review was limited primarily to the use of granular zero-valent iron—the most widely used PRB media.

A draft report was prepared by the author and provided to the various reviewers for comment. Appendix B provides comments from R. Puls, EPA; J. Vogan, EnviroMetal Inc.; and Gerald Eykholt, University of Wisconsin. Arun Gavaskar, Battelle, responded that he agreed with the draft report and had no specific comments. Liyuan Liang, Oak Ridge National Laboratory (ORNL), and Charles Reeter, Naval Facilities Engineering Service Center (NFESC), provided comments in marked-up text. Those comments have been incorporated. Reeter also recommended inclusion of the information in Appendix A. Finally, the SCFA requested the Lead Lab to review the report and provide comments to the author. These comments are presented in Appendix C, which also describes the actions taken.

3. WORKING HYPOTHESIS

The author’s working hypothesis was that most problems were a result of engineering application and were not inherent to the technology. Indeed, research published in the peer-reviewed geochemical and hydrological literature has been sufficient to predict or warn of the problems that have been observed (see Sect. 7). In other words, the science has been sound, but not the execution. Specific aspects of this working hypothesis are listed below:

1. The original excitement regarding the technology as portrayed in trade magazines and by word-of-mouth exceeded the potential for performance and widespread application.

2. Because of the unrealistic expectations, many in the engineering and regulatory community perceived that this technology would work in most circumstances. Thus, insufficient attention was given to the problems of manipulating the subsurface. Moreover, the unrealistic expectations resulted in regulatory negotiations with unrealistic cleanup goals.
3. With respect to subsurface manipulation, the effects of hydrologic heterogeneity (e.g., range of hydraulic conductivity over the zone of the barrier) have not always been sufficiently investigated prior to construction.

4. The effects, if any, of the construction process have not been defined. Examples include the ability to ensure that walls are continuous and determining whether there is construction-induced smearing or compaction that causes mounding or bypass.

5. The performance of the reactive media itself is not a primary cause of the negative perceptions. Nevertheless, there are sites where reactive media problems have been experienced. In these instances, insufficient attention was given to effects of the groundwater geochemistry prior to construction.

4. THREE CASE HISTORIES FROM DOE SITES

This section reviews three DOE case histories that support the working hypothesis described. Only full-scale deployments were considered. Most pilot-scale deployments have been deemed successes because hydraulic problems are not apparent when only a small portion of the plume is treated.

4.1 KANSAS CITY

The Kansas City Plant (KCP) has a 130-ft continuous zero-valent iron barrier that was installed in late summer of 1998 to replace a pump-and-treat system. A July 1999 report states the following regarding this PRB: “Sidegradient wells were installed ... to confirm that the contamination is not going around the wall. Results of a January 16, 1999, sampling event indicate that all compliance wells are below MCLs [maximum contaminant levels]” (EPA 1999). Yet, one year later, the KCP has resumed use of their pump-and-treat system. The regulators required the resumption of pump-and-treat because a portion of the plume was not intercepted by the PRB. Thus, unless one is following the circumstances closely, the site can be considered an unequivocal success or an abject failure.

Reports prepared 7–8 years prior to construction of the KCP barrier and prior to operation of the pump-and-treat system show either that the historical plume width is incorrect or the barrier is not wide enough. In fact, the pump-and-treat system had narrowed the plume in the area where the PRB was installed. Apparently, the PRB installation contractor did not review historical reports and did not wait long enough after the pump-and-treat system was turned off to investigate the plume width. Hence, as time passed after the wall was installed and the pump-and-treat system was turned off, the plume returned to its former width and is not entirely captured by the barrier.

Unfortunately, misjudgment of the plume width is not the only problem with the KCP barrier. Most of the subsurface at the KCP is relatively homogenous with 2–4 ft of basal gravel underlying a silty clay. The exception to this homogeneity is found in the contaminated location referred to as the Northeast Area—the location where the iron wall was installed. Formerly, the Blue River flowed through this area in a large meander loop that was removed when the river was channelized. Hence, the area where the wall was installed is hydraulically heterogeneous with overbank deposits and buried organic debris, such as logs. A pumping test was performed in order to determine a design hydraulic conductivity. The value determined and used in the PRB
design was 34 ft/day. A more recent test, utilizing a pumping test in a sandy zone, found a hydraulic conductivity of 250 ft/day. Single well tests in the various wells and boreholes indicated that in some locations the hydraulic conductivity was <1 ft/day. The further problem for the KCP, therefore, is whether it is feasible to design a continuous barrier with such large contrasts in hydraulic conductivity. As noted in the literature review section, the uncertainty inherent in such an installation probably precludes construction.

4.2 ROCKY FLATS

The Rocky Flats Mound Site (Colorado) system was installed in 1998. This system differs from a conventional barrier in that groundwater is collected in a trench lined on the downhill side with an impermeable liner. At the bottom of the trench, the water enters a perforated pipe and flows under the force of gravity into tanks containing zero-valent iron. Thus, the system is passive, and hydraulic heterogeneities are circumvented because the drain intercepts all of the water flowing down the hill. There have been criticisms of the treatment portion of the system because it apparently does not exclude air from the iron. Thus, “problems” have been described for this site because a hard crust formed on the iron medium. The crust had to be broken up every few days, sometimes with a jackhammer. Operating experience, however, led to a modification in which coarser iron mixed with gravel is used at the top. Now the top of the medium is periodically raked to prevent crust formation. The operators consider the project a success. The system is passive with low maintenance and complete treatment is achieved.

4.3 Y-12 PLANT

Construction for the Y-12 Plant (Oak Ridge, Tennessee) barriers, consisting of Pathways 1 and 2, was completed in November and December 1997. The Pathway 1 system was designed to capture groundwater in a gravel-filled, high-density-polyethylene (HDPE)-lined trench and to treat it within a vault that contains zero-valent iron. Unfortunately, flow through the barrier is much less than expected. The system was designed on the basis of inaccurate characterization data; the hydraulic heads in certain parts of the Pathway 1 site are higher than modelers expected. Researchers are also attempting to determine whether work at the site has unexpectedly introduced a recharge zone or has impacted vertical gradients. The problems, therefore, are related to vertical upward gradients and/or recharge from above. The naturally low permeability of the site has been the primary reason for low flow. There was also high iron discharge at this site because of the corrosive nature of the groundwater (low pH, high nitrate, and bicarbonate). The treatment media, however, effectively removes uranium and nitrate from the water that passes through it.

At Pathway 2, a permeable trench exists, oriented subparallel to the direction of groundwater flow. The trench is about 2 ft wide and about 225 ft long. It consists of a 26-ft long zone of zero-valent iron flanked by zones of gravel backfill. The trench, which has been installed into a saprolite and silt area that extends into the shale bedrock, ranges from about 22 to 30 ft deep. The trench and iron at Pathway 2 were initially installed to obtain hydraulic information (i.e., conduct a pump test on the trench), to determine if this type of trench design (i.e., parallel to groundwater flow) would work hydraulically in a passive mode, and to assess the in situ treatment effectiveness of zero-valent iron. Hydraulic head, tracer study tests, and geochemical data show that the groundwater gradient and flow are consistent in direction from upgradient to downgradient even during storm events. Groundwater sampling and coring data indicate that the iron is effectively removing uranium and nitrate. The data also show that the uranium is removed rapidly when the contaminant plume encounters the iron. Some mineral precipitation is occurring that warrants continued monitoring, although impacts on hydraulic gradients have not been observed.
Furthermore, while sampling and analyses indicate that the Pathway 2 barrier is still removing uranium in the middle of the iron, the concentration of uranium in groundwater is increasing in the two multi-port piezometers installed in the upgradient portion of the reactive media. These data suggest that some of the removal/reductive capacity is decreasing in this upgradient zone. This observation calls for continued monitoring because it has significant implication on the long-term effectiveness and probable life-span of the iron.

Because the demonstration system at Pathway 2 was deemed to be working, the trench was extended in 1999 to increase the capture zone, and a siphon was installed at the end of the trench extension. Siphon pipe was run approximately 800 ft down the valley to a new treatment box. There have been problems getting the siphon to work effectively. It stops flowing, apparently because the siphon is broken because of degassing from the aquifer, typically 4 days after the siphon is primed. Thus, the Y-12 installations have required repeated intervention to keep the water flowing through the media. In summary, both operational and design problems have been encountered at Pathways 1 and 2 on the Oak Ridge Reservation. Continuing work will determine whether the problems can be overcome or whether these locations are too complex for a passive technology.

4.4 OTHER EXPERIENCE

The issues described in Sects. 4.1, 4.2, and 4.3 are not limited to PRBs within the DOE system. Other barriers exhibit some of the same problems. For example, the EPA has been investigating PRBs at Elizabeth City, North Carolina, and at the Denver Federal Center. There is some underflow at Elizabeth City and severe mounding and bypass flow at the Denver Federal Center. The underflow at Elizabeth City, however, is not related to the chromium removal for which the project was designed. Indeed, both the site owners and the regulators are completely satisfied that the PRB is performing as designed (see comments of R. Puls in Appendix B). The DoD PRB at Alameda, California, is also not performing as expected. Scientists evaluating the latter site have suggested that the site is probably too hydraulically and chemically complex for a passive PRB (A. R. Gavaskar. Battelle, Columbus, Ohio, personal communication with N. Korte, February 2000).

5. GEOCHEMICAL UNCERTAINTIES

There are a few geochemical uncertainties related to the long-term performance of a PRB. These are briefly reviewed in this subsection.

5.1 REMOVAL MECHANISMS FOR URANIUM AND TECHNETIUM

A controversial issue for DOE is the uncertainty in removal mechanisms for uranium and technetium. Initially, it was believed that both elements would be removed by reductive precipitation. The reduced forms of these elements are insoluble and would provide the longest and safest long-term immobilization. However, at the Durango, Colorado, site, all of the immobilized uranium was oxidized (MSE 1999). Similarly, a published study suggested that a significant portion of the uranium removed by iron would remain in the oxidized form (Fiedor et al. 1998, Farrell et al. 1999). In contrast, another report indicated that uranium removed by an iron barrier was reduced (Gu et al. 1998). At present, whether these seemingly contradictory results are related to sample handling or differences in groundwater and barrier geochemistry is unknown. The removal mechanism for technetium is unknown, but the questions with uranium
have led to concern that technetium might not be reduced. Kentucky regulators who are providing oversight for the PRB field treatability program planned at the Paducah site, for example, have questioned the technetium removal mechanism. It should be noted that the mobile forms of uranium and technetium in groundwater are chiefly oxyanions. Other oxyanion elements include arsenic, which is removed by iron by absorption without a change in oxidation state (Lackovic et al. 2000), and chromium, which is removed by reductive precipitation (Blowes et al. 1997).

5.2 CALCIUM MASS BALANCE/COLLOID FORMATION

The question of calcium in the barrier is also of interest. At the Moffett field site in Mountain View, California, (Gavaskar et al. 1998) and at the site in Durango, Colorado, (DOE 1999) there was a poor mass balance for calcium. In other words, more calcium was removed by the barrier than could be accounted for in precipitates within the iron. It has been speculated that colloidal particles are ejected from the barrier. There has been no detailed study to prove or disprove this conjecture. Loss of colloids would be important to DOE because of the potential for facilitated transport of metals and radionuclides. It should be noted, however, that detailed, sequential filtration at the Elizabeth City site showed no evidence of colloid transport (see comments of R. Puls, Appendix B), and that an adequate calcium mass balance was obtained at one site (see comments from J. Vogan and R. Focht, Appendix B).

5.3 EFFECTS OF GROUNDWATER CHEMISTRY ON BARRIER LONGEVITY

Little work has been published on the effects of groundwater geochemistry on barrier longevity. One field study demonstrated that “after two years, there was no evidence of precipitation or cementation and after four years there was no cementation” (O’Hannesin and Gillham 1998). However, cementation has been observed in small portions of the barrier at Y-12 (Watson et al. 1999) and in laboratory (MacKenzie et al. 1995) and pilot studies (Liang et al. 1997, Korte et al. 1997). Similarly, biological activity at the same barrier studied by O’Hannesin and Gillham (1998) remained low after two years (Matheson 1994) while some laboratory (Gu et al. 1999) and pilot studies (Liang et al. 1997) did observe significant increases in biological activity with time. These varying results can be related to differences in groundwater geochemistry, as recently reviewed by Liang et al. (2000). In general, when the groundwater is more highly buffered, that is, when alkalinity and sulfate are high, the pH change within the iron is moderated, and both precipitation and microbial activity are enhanced. The existing DOE SCFA project “Permeable Reactive Barriers Performance Monitoring and Verification” is attempting to quantify the relationships between groundwater geochemistry and precipitation and microbial activity within the barrier (Appendix A).

6. CONSTRUCTION UNCERTAINTIES

Uncertainties associated with PRB construction are also hampering use and acceptance. Three uncertainties are briefly reviewed in this section: construction-induced compaction, difficulties in testing barrier integrity, and difficulties with the accuracy of installation of monitoring wells.

6.1 CONSTRUCTION-INDUCED COMPACTION

No case studies clearly document problems from construction-induced compaction. However, the mounding and bypass observed at some PRB deployments have led to considerable
speculation that compaction might have occurred during installation. Such compaction could take the form of skin effects caused by trenching or driving sheet piling. Skin effects would be analogous to the recognized problem encountered with monitoring well installations and slug testing of monitoring wells. The potential for skin effects is believed to increase with the amount of clay in the soil. However, compaction and consequent loss of permeability caused by vibration when installing sheet piling has also been implicated as a potential cause of permeability loss at PRB sites with coarse-grained soils. Finally, at sites where jet grouting or pneumatic or hydraulic fracturing is used to inject iron, material is added to the surface and none is removed. Hence, some amount of compaction must occur. Nevertheless, whether any of these scenarios explain hydraulic problems at some PRBs is unknown. Thus, determining the extent, if any, of permeability loss induced by construction would remove a frequently cited uncertainty related to PRB construction.

6.2 DIFFICULTIES TESTING BARRIER INTEGRITY

There are no accepted methods for determining the integrity of PRBs installed by grouting or fracturing. At DOE's Paducah installation, electrical resistance tomography will be attempted, but the method is unproven so far and, in any case, will be difficult to validate. Without an accepted method for separating problems caused by construction from problems caused by inadequate characterization, validating performance of deep PRBs may be prohibitively expensive, requiring many deep monitoring wells and testing with an array of tracers at multiple depths.

6.3 DIFFICULTIES WITH THE ACCURACY OF INSTALLATION OF MONITORING WELLS

The accuracy with which a PRB can be installed perpendicular to the surface and subsurface is uncertain—particularly for deep PRBs. Similarly, the same potential problem exists for monitoring wells used to monitor a PRB. For barriers that are deep (e.g., approximately 100 ft), installing monitoring wells close enough to the barrier can be very difficult. If the borehole and/or the barrier itself vary by a few percent in inclination, the error at depth could be 5 to 10 ft. Deep barriers to date have been installed by grouting or fracturing and in these methods, the iron layer is thin—so thin that it is conceivable that a well installed to monitor an iron layer that has a few percent error from vertical could be upgradient of the barrier at the surface and downgradient at depth. These problems can be overcome or identified, but the expense and difficulty are such that some site owners are deterred from installing a PRB.

7. LITERATURE REVIEW

The technical literature indicates that the apparent gap between theory and practice should not have existed. In fact, a field project had indicated that hydraulic problems would be a concern several years prior to the installations described in Sect. 4. Smyth (1995) described “installation of a funnel and gate system downgradient of a 16-year plume.” These investigators reported that the hydraulic conductivity of the gate was not high enough and postulated that a “skin” effect from installation or problems with packing the reactive material caused the system to perform poorly. They concluded that “a substantial amount of optimization work is needed.” Indeed, imperfections when designing and constructing barriers should be expected, as noted by Tachavises and Benson (1997), “All cut-off walls contain defects, such as poor seams, punctures, zones of higher hydraulic conductivity (e.g., windows) or inadequate keys.”
Other examples indicating that the scientific community understood the uncertainties in PRB performance are found in the proceedings of a conference co-sponsored by DOE in 1995 (Rumer and Mitchell 1995). The following quotations are contained in those proceedings:

- “Since it is desired that all of the contaminated groundwater flow through the PRB, careful attention needs to be given to development of a groundwater flow model for the site. The groundwater flow model enables evaluation of ... the need for hydraulic control augmentation.” (p. 310) Specifically, the text states a few pages later the possibility of using downgradient pumping to increase the hydraulic gradient. The authors acknowledge that the pumped water would have to be discharged but suggest that reinjection upgradient might be a solution.

- “The site groundwater gradient, flow direction, hydraulic conductivity, and water balance are developed using standard methods. Uncertainties in these parameters can be particularly significant in the design of a PRB.” (p. 311)

- “…seasonal recharge effects and heterogeneity and anisotropy of the aquifer … may cause local variations in flow rate and contaminant flux, often by an order of magnitude or more from one point to another.” (p. 311)

The issues raised in the latter two points are not being addressed routinely when a PRB is designed. Instead, pumping tests are used to obtain average values of hydraulic conductivity, and seasonal data are not obtained prior to installation. As noted by Eykholt et al. (1999), “Natural aquifers are rarely homogenous, yet this assumption is often made to simplify design and because data needed to characterize homogeneity are unavailable.” In other words, the pre-construction investigations are not sufficiently detailed at some sites. Instead, once deployment problems have been recognized, large, expensive investigations have ensued to explain the observed problems.

Another major conference on PRBs was held in February 1997. A paper on hydraulic issues with PRBs noted, “…the presence of layers of high hydraulic conductivity may exert major control over contaminant migration, and it may be a technical challenge to design a permeable barrier....” (Smyth et al. 1997). At the same conference, a paper about another hydraulic investigation of a PRB described a failed tracer test and concluded that heterogeneities in the flow field caused the loss of tracer (Focht et al. 1997).

Further caution was expressed in a 1998 book: “Modeling studies and barrier design at most existing permeable barrier sites so far have been primarily based on the assumption that the aquifer sediments in the vicinity of the permeable barrier are homogenous.” The authors further state, “The general implications of heterogeneity are that a more detailed site characterization is required and more complex models are needed. The symmetrical capture zones seen in homogenous sediments become asymmetrical and difficult to predict without detailed characterization and modeling” (Gavaskar et al. 1998). These statements are supported by the performance problems observed at some barriers and by cautions expressed in a 1998 report from EPA (1998).

In summary, the circumstances with PRB construction illustrate an oft-encountered problem when implementing an innovative technology. More investigation is needed than for conventional methods and the detailed investigation may conclude that the innovative technology is not suitable for the particular site. On the other hand, if no problems are found, then the extent of investigation needed might appear to be overkill upon completion. Usually there is significant
resistance to spending money a priori on an expensive investigation that either might not be needed or might preclude the use of the chosen technology.

8. RECOMMENDATIONS

Remedies to the present circumstances and growing dissatisfaction with in situ PRBs are the following:

1. The most important recommendation is that hydrologic characterizations must be sufficient to support designs of specified reliability. In addition, the barrier must be designed on the basis of variability in hydraulic conductivity rather than average values. There must also be recognition that at some sites hydraulic conductivity contrasts can be so great or complex that a passive barrier system cannot be used.

2. Expectations and regulator negotiations must be realistic. A PRB is often a cost-effective approach for eliminating most of a contaminant plume’s potential impacts. In other words, combining an iron barrier with monitored natural attenuation may be a realistic and inexpensive remedy in contrast with insisting that the barrier yield less than MCLs (maximum contaminant levels) at all downgradient locations. An effective means of ensuring realistic expectations may be to engage outside experts as reviewers at critical stages of the project. Similarly, risk-based designs (Eykholt 1999) should be used to ensure that stakeholders have realistic expectations.

3. Sufficient attention must be paid to the groundwater geochemistry. Sites with high levels of dissolved oxygen and/or high levels of carbonates and sulfate are much more susceptible to clogging and buildup of microbial biomass than are systems that are poorly buffered and have low levels of dissolved solids. (An iron barrier might have a role at highly buffered sites, but expectations regarding performance and longevity have to be consistent with the groundwater geochemistry.)

4. Issues regarding the oxidation state or exact mechanism of uranium and technetium removal need to be resolved.

5. In conjunction with points 3 and 4, development and testing of media with respect to longevity and ultimate disposition of PRBs (e.g., will retrieval be required?) are needed.

6. Whether construction-induced smearing or compaction affect barrier performance needs to be determined.

7. A consistent approach (field tools, analyte lists, modeling, etc.) for monitoring performance is required. In some respects, this issue is related to point 2. The success or failure of barriers with similar operating characteristics may be differently perceived because of differences in expectations rather than differences in their technical performance.
9. LITERATURE CITED


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OVERVIEW OF THE TRI-AGENCY (EPA, DoD, DOE) PROGRAM FOR MONITORING AND VERIFYING BARRIER PERFORMANCE
APPENDIX A: OVERVIEW OF THE TRI-AGENCY (EPA, DoD, DOE) PROGRAM FOR MONITORING AND VERIFYING BARRIER PERFORMANCE

Approximately two years ago, representatives of the U.S. Department of Defense (DoD), U.S. Environmental Protection Agency (EPA), and U.S. Department of Energy (DOE) met at a Remediation Technologies Development Forum (RTDF) workshop to discuss issues of long-term performance and various uncertainties associated with the use of the permeable reactive barrier (PRB) technology. It was clear that not only would these uncertainties cause installation costs of PRBs at contaminated sites to be quite variable and unpredictable, but also that PRB longevity concerns were also inhibiting use of the technology. During subsequent meetings, it also became evident that there were a great variety of lessons to be learned from existing PRB sites, and that each agency had different and yet complementary expertise. Furthermore, it became clear that the least expensive and fastest approach to solving these apparent problems was for each agency to maintain close cooperation and communication with the others, while maintaining a focus on their own PRB sites and their particular strengths. To that end, the EPA Technology Innovation Office (TIO) has recently provided its support in this cooperative effort under their leadership of the Federal Remediation Technologies Roundtable (FRTR). The EPA has assigned a contractor to coordinate communication and maintain a database of information regarding the progress.

In the past year at DoD’s request, the DOE has supported this collaborative effort in providing assistance through performing hydraulic assessments at the Lowry Air Force Base and Dover Air Force Base PRB sites. The DoD has also requested additional assistance of DOE ORNL scientists to help evaluate the Watervliet Army Depot and Cape Canaveral Air Station PRB sites this summer (2000). The field data collected by the DOE and DoD are identifying the proper role and selection of borehole flowmeters for evaluating the hydraulic performance of PRBs. Each agency has been using different approaches in their evaluation of specific aquifer hydraulic properties, and each approach has led to different PRB designs with unique limitations and strengths. Comparisons of these data should result in clear and concise solutions to the PRB performance and longevity concerns in future usage of this innovative remediation technology.

In addition to collaborating on fieldwork, the principal investigators of each agency have participated in bimonthly conference calls and two “face-to-face” meetings. During these meetings, a great deal of additional information has been shared regarding the overall performance of the PRB technology. For example, the collective tri-agency experience of assessing the longevity of PRBs through coring of the reactive iron cell is presently being compiled and will soon be posted on the FRTR Web site.

Over the next two years this collaborative effort will produce a series of joint publications and guidance manuals that will enable site operators to make better choices regarding PRB design and monitoring methods. Considering the long-term investment of implementing various remedial alternatives to clean up contaminated property, the recommendations from this tri-agency group can save millions of dollars in PRB installation and monitoring costs. Without our ability to share data between DOE, DoD, and EPA, we would not have access to adequate information and or expertise. Quite simply, there would not be sufficient funds for us to acquire the data necessary to satisfy the program objectives of evaluating PRB performance and longevity concerns without the collaboration of the tri-agencies (DOE, DoD, and EPA).
APPENDIX B

COMMENTS FROM GERALD EYKHOLT, UNIVERSITY OF WISCONSIN; R.W. PULS, USEPA; AND JOHN VOGAN AND ROBERT FOCHT, ENVIROMETAL, INC.
APPENDIX B: COMMENTS FROM GERALD EYKHOLT, UNIVERSITY OF WISCONSIN; R.W. PULS, USEPA; AND JOHN VOGAN AND ROBERT FOCHT, ENVIROMETAL, INC.

COMMENTS FROM GERALD EYKHOLT, UNIVERSITY OF WISCONSIN

From Executive Summary, second paragraph:

The most important finding of this review is that the most significant problems have been the result of poor engineering implementation. Although there are legitimate concerns regarding the longevity of the media, the principal problem at full-scale deployments has been an inadequate assessment of site hydrology. This has resulted in PRBs where bypass and/or incomplete plume capture has occurred.

I suggest that you also note the higher than anticipated velocities in the barrier, which lead to higher effluent concentrations.

Response: The recommended changes were made.

From Executive Summary, second paragraph:

I suggest that one additional recommendation be that new jobs involve more external review, possibly through involvement of outside technical experts at critical stages of the projects.

Response: This recommendation, also made by John Fruchter, was included.

From 3.0 Working Hypothesis, Aspect 2:

Because of point 1, unrealistic expectations propagated through the engineering and regulatory community. It was believed that this technology would work in all circumstances. In particular, insufficient attention was paid to the problems of manipulating the subsurface. Moreover, the unrealistic expectations resulted in regulatory negotiations with unrealistic cleanup goals.

I think the engineering and regulatory community was cautious at first—yet excited by the lab and early field trials that showed good performance. The appeal was strong, especially as PRBs served as a remedy to the inefficiencies of pump and treat systems. Given a situation of inadequate characterization and lack of scrutiny regarding the reliability of designs, some designs should be expected to fail.

Response: Agreed, no action necessary.
From 4.0 Review of Existing Barriers:

This section reviews three DOE case histories, which support the working hypothesis described above. Only full-scale deployments were considered. Most pilot-scale deployments have been deemed successes because hydraulic problems are not apparent when the entire plume is not being treated.

Instead of the last statement (underlined), I suggest that it read, “…when only a small portion of the plume is treated.”

Response: Change made as suggested.

From Section 4.3 Construction for the Y-12 Barriers:

Midway through the second paragraph you note that: “At this site, the hydraulics worked as predicted and modeled.”

I think more detail is needed here. I don’t have the details, but I’m skeptical about this statement. The modeling I saw was based on homogeneous assumptions.

Response: The sentence is misleading and was deleted.

Under Literature Review:

Reference to Tachavises and Benson (1997) is good, but there is an important distinction between poorly performing cutoff walls for hydraulic containment and the performance of a cutoff wall with a defect when a PRB is present. The distinction deals with the head loss over the defect, which is expected to be much lower when a PRB allows most of the flow through it.

Response: Agreed, no changes necessary.

When you discuss our paper (Eykholt et al. 1999), you can remove one of the two citations.

Response: Change made as suggested.

Under Recommendations:

Under item 2, you say that, “…characterizations must be sufficient.”

Characterization should be sufficient to help deliver designs that achieve a stated level of reliability. Effectiveness of the designs should be evaluated with regard to the reductions of uncertainty in performance (minimizing probability of failure).
With this, some mention should be made of risk-based designs.

Response: These statements are incorporated into both recommendations 1 and 2.

Another recommendation deals with an earlier comment that designs and methods for new PRBs be reviewed more broadly, and that a portion of the development budget be allotted for outside reviewers at critical stages of the project. This would help document the designs, as well as to address concerns and decisions leading to the designs.

Response: This comment is addressed in the first recommendation.

COMMENTS ON DOE WHITE PAPER
ROBERT W. PULS, PH.D., CHIEF, SUBSURFACE REMEDIATION BRANCH, NATIONAL RISK MANAGEMENT RESEARCH LABORATORY, USEPA

I generally concur with the conclusions and recommendations presented in the paper and appreciate the opportunity to offer comments.

The formation of precipitates in zero-valent iron media under saturated conditions is expected. One of the objectives of the current tri-agency project is to evaluate under what geochemical conditions this buildup of precipitates may be so rapid as to significantly affect performance and costs. As yet, we have not seen such a condition.

Where there has been less than optimal performance of PRBs installed to date, causes can be universally traced to two conditions:

1) Inadequate characterization of the hydrologic flow system to maximize plume capture, and

2) A rush to implement the technology (and join the party), resulting in inadequate characterization and design.

These conditions are certainly true for most of the sites you address in the paper. We emphasize this point in the RTDF training we are currently doing for the state and federal regulators and environmental consultants. It is thoroughly covered in the site characterization portion of the course and in case studies as well. At the Elizabeth City site, both the site owners and the regulators are completely satisfied that the wall is performing as designed and containing the contaminants emanating from the plating shop on the USCG site (I just came from a meeting of both groups in Raleigh, North Carolina, this day, June 1, 2000). The only problem at the Elizabeth City site is the occurrence of other sources of chlorinated compounds at the site (not the plating shop) whose sources have yet to be delineated by the USCG and its contractor. However, the USCG and the state are in the process of not only agreeing to work, which will remove the plating shop source area, but also of dealing with the other VOC source areas. Zero-valent iron is a prime candidate for future measures based on the success of the iron wall for the chrome plating shop plume. I take exception to inferences that the Elizabeth City wall is performing less than desired.
We have investigated the potential for colloid transport at the Elizabeth City USCG site and have observed no evidence for this as a significant transport mechanism. Lack of mass balance for calcium based on core analysis is shaky at best, particularly when the core collection methods do not ensure collection of the first few inches of the upgradient wall interface. This is where the bulk of the precipitation is occurring, and I am not satisfied that this has been done adequately in these systems. Detailed sequential filtrations at the Elizabeth City site show no evidence of this transport mechanism. I spent a fairly large portion of my scientific career investigating colloid transport, and in my experience, it is somewhat unusual for it to be a significant transport pathway, with the exception of high level radioactive elements, and it is often brought about by transient changes in subsurface geochemical perturbations.

Once again, thank you for the opportunity to comment (albeit short notice), and if I can be of further assistance, let me know.

Response: The statements regarding Elizabeth City and regarding colloid transport were explicitly incorporated into the text to ensure that there are no misconceptions.
Comments from John Vogan and Robert Focht, EnviroMetal, Inc.

To: Nic Korte, Oak Ridge National Laboratory

From: John Vogan, EnviroMetal Technologies, Inc. (ETI)

Date: 31 May 2000

Re: Comment on Draft “White Paper” entitled “A Review of Permeable Reactive Barrier Performance” - 316010

Nic:

In response to your request, we (Rob Focht and I) have reviewed the draft “white paper” you have prepared concerning permeable reactive barrier performance. As you are aware, we have been involved at ETI in the design, construction, and monitoring of several PRBs using granular zero-valent iron for remediation of chlorinated volatile organic compound (VOC) plumes. Your discussion of removal mechanisms for uranium and technetium is beyond the scope of our expertise and experience, however, I hope you find the following comments on the remainder of the paper of use.

We concur with the general conclusions of the paper. Our experience to date indicates that the iron PRB technology appears quite robust in a geochemical sense, in terms of promoting the requisite VOC degradation under field conditions. However, there are at least six PRB systems that we know of where underestimation of hydraulic (aquifer) and/or plume variability during design has led to perceived “failure” and/or retrofits of the system. Indeed, the need to characterize the plume in detail during PRB design is one of the major “messages” we are trying to deliver in the EPA PRB short course.

As a result of numerous discussions with designers, owners, and regulators over the past few months, we feel that there is a growing recognition that reasonable “site-specific” objectives for PRB performance need to be identified, partly as a result of the uncertainties in design. These objectives may involve (1) the use of a PRB to reduce a large percentage of VOC mass flux; (2) making use of natural attenuation processes downgradient of the PRB; or (3) design of sequenced treatment processes, as opposed to meeting MCLs at the PRB itself. In many cases, this will also improve the cost-effectiveness of the technology.
Comments regarding specific sections of the text follow:

Section 3.0

One of the “unrealistic expectations” we have encountered is the presumption that the existing plume downgradient of a PRB will dissipate in a short time frame. Most PRBs are installed within a plume. The detection of VOCs downgradient of the PRB (for an extended period) has caused considerable consternation among regulators and designers.

Section 4.1 Kansas City

As you are aware, there is some difference of opinion as to the reason for incomplete plume capture by the PRB at the Kansas City Plant (i.e., the degree of influence of geologic control versus historical plume width). In any event, we concur that the high hydraulic conductivity zone identified at one end of the PRB (where plume bypass is occurring) represents a significant challenge to any retrofit.

Section 4.2 – Rocky Flats

The need to periodically scarify (rake) the top of the media was identified in the design. It is our understanding that this was not done frequently in the first several months following system startup and may have exacerbated the “crusting” problem.

Section 4.4 – Denver Federal Center

The mounding at the Federal Center was expected by ETI given the funnel to gate ratio employed at the site. We performed two dimensional modeling assuming homogeneous aquifer properties during design that predicted mounding similar to that subsequently observed and a smaller capture zone than may have been expected by the design team. The same conclusions can be reached by reviewing the USGS modeling that was used for the design. This modeling shows about 8 ft of head difference across the funnel and an upgradient capture zone of about 400-500 ft. In perfect hindsight, the potential for underflow and bypass due to this mounding should have been evaluated in more detail.
Alameda

Part of the iron treatment gate in the Alameda demonstration of a sequenced PRB treatment system was “exposed” to aquifer concentrations of cis-1,2-dichloroethene and vinyl chloride of 200 mg/l or more, an order of magnitude higher than concentrations used in the design. Subsequent experiments by Dr. Rick Devlin and his colleagues at the University of Waterloo have shown that the lower than expected field degradation rates (i.e., the cause of the lack of performance) are due to concentration impacts on zero-valent iron reaction rates. ETI has also recognized this in several subsequent studies. We attempt to take this into account during design, assuming the site consultants know what concentrations to expect. There has also been a novel “mixing zone” concept suggested for the front of the PRB at Alameda which could conceivably lower and homogenize influent VOC concentrations across the gate.

Section 5.2

We were able to obtain reasonable mass balance between precipitated calcium carbonate and calcium removed from groundwater at a pilot-scale PRB in New York after two years of performance (Vogan et al, 2000). However, we agree that colloid transport does merit study.

Section 5.3

In comparing the performance of PRBs, it is not only important to recognize the influence of groundwater geochemistry on longevity, but also the composition of the material in the PRB. For instance, the Borden PRB (O’Hannesin and Gillham 1998) is composed of a 22% by wt iron mixture and sand in a relatively low to moderate alkalinity (about 160 mg/L as HCO₃⁻) and dissolved oxygen (2 to 5 mg/L DO) groundwater. The fact that this was an iron/sand mixture may have a significant impact on why there was no evidence of cementation.

It is interesting that the research microbial activity in PRBs appears to have changed from a focus on possible adverse effects (fouling) to a focus on possible positive effects (i.e., enhanced microbial dechlorination activity in and downgradient of the barrier due to hydrogen gas production in the iron). This is an area of considerable current research.
Summary

As noted previously, we are in general agreement with your recommendations. One recommendation to add might involve the realistic costing of both PRBs and their alternatives (e.g., pump and treat). We have seen several cases where costs of both have been underestimated. In the case of PRBs, this underestimation involves assuming little or no maintenance over a decade-long (30-year) time frame. The operating and maintenance requirements for pump and treat systems also appear frequently lower than operating experience would suggest.

Thank you for the opportunity to provide these comments. Please call us to discuss them.

Response: The comment regarding calcium mass balance was added to the text. The remainder of the discussion supported the comments in the report.
APPENDIX C

COMMENTS RECEIVED FROM THE LEAD LAB

The SCFA requested the Lead Lab to review the report and provide comments. The first four pages of this appendix provide the comments received. The following page discusses the changes that were made to the report.
APPENDIX C: COMMENTS RECEIVED FROM THE LEAD LAB

Responses to Lead Lab Comments:

John Fruchter’s suggestion to engage outside experts at critical stages is contained in Section 8.0.

The wording change recommended by Everett Springer was incorporated.

Terry Sullivan provided the following comments.

1. The suggestion was made to change the title to be specific to zero-valent iron. This change was made as requested.

2. The comment was made that blaming “engineering implementation” was misleading. The section was revised to clarify. However, the problem is related to engineering because projects such as these are typically subcontracted to an engineering firm, and it is the professional engineers in charge of construction who perform or select the data used for construction.

3. Clarification was recommended regarding what was meant by hydraulic augmentation. The clarification was provided to make it clear that systems with pumping are not PRBs.

4. The statement that “the science has been sound” was challenged. However, as noted in comment 2, the problem is engineering application, not the research supporting barrier use. No change was made.

5. Wording changes were suggested in point 5 of the working hypothesis. These changes were made.

6. Diagrams for the case histories were suggested. This was not done because of the small scope of funding.

7. Problems with the Y-12 system were not clearly described. The text has been changed to clarify that wells that had been referred to as upgradient are in the barrier, and that degassing is believed to be the cause of the siphon stopping.

8. The recommendations were reorganized to put the most important ones first.

9. The comments about risk-based designs are addressed through the work of Gerald Eykholt, which is referenced. Additional emphasis was added to the original statements.
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