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NGWA Workshop on Permeable Reactive Barriers in Ground Water Workshop Organizer: Robert W. Puls, Ph.D., National Risk Management Research Laboratory, USEPA

Introduction:

Information is required for ground water professionals to better understand the application of in situ permeable reactive barriers for the remediation of contaminated ground water. This workshop will describe this innovative technology, provide examples of where it has been successfully applied, discuss site characterization needs for successful implementation, reactive materials selection, the conduct of pre-installation feasibility tests, methods of emplacement (already demonstrated and others currently being researched), and acceptable approaches for compliance and performance monitoring of emplaced systems.

Workshop Sessions:

I. Permeable Reactive Barrier Design Considerations
David W. Blowes, Ph.D., University of Waterloo, Waterloo, Ontario, Canada

II. Site Characterization
Robert M. Powell, Powell & Associates Science Services
For ManTech Environmental Research Services Corp.

III. Emplacement Methods For Optimized Design & Cost Effectiveness
Dale S. Schultz, Ph.D., Dupont Central Research & Development

IV. Compliance and Performance Monitoring
Robert W. Puls, Ph.D., USEPA National Risk Management Research Laboratory
Ada, OK.

V. Installed Treatment Wall Demonstrations and Applications
John Vogan, Envirometal Technologies Inc., Guelph, Ontario, Canada

I. Permeable Reactive Barrier Design Considerations

David W. Blowes, Ph.D., University of Waterloo, Waterloo, Ontario, Canada

Introduction:

Permeable reaction walls are an emerging technology for the treatment of contaminated groundwater. Successful treatment of contaminated groundwater using this technique requires that the contaminant be rendered innocuous or immobile during transport through the in-situ treatment zone. The extent of treatment, and the success of the permeable barrier system depends on the nature of the contaminant, the selection of the reactive material, the physical design of the treatment system, and site conditions.

Selection Of The Reactive Material

The selection of the reactive material for use in the permeable reactive barrier is dependent on the type, concentration and mobility of the contaminant to be treated. Much of the reactive barrier research conducted to date has focused on the use of zero metals, principally iron to treat halogenated hydrocarbons and dissolved electroactive metals. Elemental iron (Fe°) has been demonstrated to accelerate the dechlorination of numerous halogenated hydrocarbons, including the common groundwater contaminants trichloroethylene (TCE), dichloroethylene (DCE) and vinyl chloride (VC). Fe° has also been demonstrated to reduce electroactive metals, including hexavalent chromium (Cr(VI), selenium (Se(VI), and uranium (U(VI), resulting in the formation of sparingly soluble precipitates that effectively remove these metals from the flowing groundwater.

Although Fe° has been studied extensively, other reactive materialsf, including bimetal combinations, organic carbon, ferric oxyhydroxides, and surfactant enhanced zeolites and clays have been used or proposed for use in reactive barriers. Bimetal combinations, such as iron-palladium mixtures, iron-copper mixtures, and iron-nickel mixtures have been proposed for use in reactive walls, and have been tested in the laboratory, and in small-scale field trials. The advantages of these bimetal combinations include more rapid reaction kinetics, and the potential for treatment using smaller volumes of reactive materials. These advantages become most significant when dealing with plumes containing high concentrations of contaminants, very deep plumes, or installation systems which provide limited treatment media volumes. Organic carbon has been used as a reactive material for the treatment of dissolved metals, acid mine drainage, and nitrate. In all of these cases, the organic carbon serves as a substrate for facultative bacteria, which catalyze reduction reactions, resulting in the removal of the contaminant from solution. Organic carbon is inexpensive, and readily available at most locations. In addition to reactive barriers that result in a change in the chemical nature of the contaminant, barriers that result in the adsorption or retardation of contaminants have also been studied. Potential adsorbents include iron oxyhydroxide phases, added as solid precipitates or as a slurry of colloidal material, and surfactant enhanced zeolites and clays, which can be engineered to remove metals, anions, or organic compounds.

Installation Technique:

Two basic designs have been proposed for the installation of reactive barriers, continuous walls, which intercept the entire plume width with reactive material, and Funnel and Gate™ systems, which use impermeable barriers to direct contaminated water into a smaller treatment zone containing reactive materials. The selection of the installation technique is highly dependent on the site characteristic, and, to a lesser degree on the cost and availability of the reactive material. Continuous wall systems tend to spread the reactive material over a greater cross sectional area, and tend to result in little disruption of natural groundwater flow patterns. Continuous barriers, therefore, may be preferable at sites where walls are installed within an aquifer, with no underlying impermeable layers. At these sites minimizing the disturbance to the groundwater flow system may provide greater protection against directing groundwater flow beneath the reactive barrier, and the reactive materials. Funnel and Gate ™ configuration. Sites where plumes are contained in aquifers underlain by low permeability fine grained materials, or bed rock are particularly well suited to the use of Funnel and Gate™ systems, because the potential for underflow beneath the wall is minimized. Funnel and Gate™ systems are well suited to remedial techniques that require the use of expensive reactive materials. In these cases, the costs associated with the installation of the impermeable portion of the barrier is offset by decreased costs for reactive materials. At sites where inexpensive reactive materials will be used (e.g. organic carbon), the costs associated with the installation of the impermeable Funnel may not be warranted.

Site Specific Conditions:

The successful installation of a reactive barrier will rely on an understanding and incorporation of site specific conditions into the design of the reactive barrier. Site conditions that may affect barrier performance include the rate, direction and variability of groundwater flow, the concentration, and the variability of concentration of the contaminant, and the geochemical nature of the groundwater. The rate and variability of groundwater flow is a critical design parameter that must be determined by field investigations. The effect of the observed variability can be assessed through computer modeling techniques. Variations in the contaminant concentrations also should be assessed through site investigations, and the robustness of the treatment media assessed through treatability studies and computer simulations which incorporate this information. The composition of the site groundwater may provide the potential for enhanced groundwater treatment through the provision of reactive solutes, or in the case of biologically active walls, essential nutrients. High concentrations of dissolved constituents within site ground waters may enhance the potential for clogging of the reactive material or blinding to reactive surfaces.

II. Site Characterization

Robert M. Powell, Powell & Associates Science Services
ManTech Environmental Research Services Corp.

A complete site characterization is of critical importance for the installation of a reactive barrier. The plume location and extent ground water flow direction, and contaminant concentrations must be accurately known to achieve the required performance. In addition, information on stratigraphic variations in permeability, fracturing, and aqueous geochemistry is needed. The plume must not pass over, under, or around the barrier and the reactive zone must reduce the contaminant to concentration goals without rapidly plugging with precipitates or becoming passivated. The barrier design, location, emplacement methodology, and estimated life expectancy are based on the site characterization information; therefore, faulty information could jeopardize the entire remedial scenario.

As with any ground water remediation technique, adequate site characterization must be done to understand the ground water flow patterns and the distribution of the contaminant plume. This is especially important for the installation of a permeable reactive subsurface barrier since the entire plume must be directed through the reactive zone of the barrier. To attain a "passive" remediation system, the barrier must be placed in a location that allows the plume to move through the reactive zone using the natural ground water gradient. It must also be designed to eliminate the possibility that portions of the plume could flow around the barrier in any direction. This requires a complete understanding of the four-dimensional extent of the plume, the width, depth, length and how these dimensions can be expected to change over the lifetime of the reactive wall. Information that must be obtained includes the piezometric surfaces and gradient, the hydraulic conductivity, permeability, porosity, and the other hydrologic parameters typical of a careful and complete subsurface characterization.

It is also important to understand seasonal changes in flow direction and flux, since the reactive wall must be designed to accommodate these changes. Beyond general hydrologic factors, the stratigraphy and lithology of the site will often dictate the type of barrier design chosen. It is desirable to "key" the barrier into a low-permeability clay layer to prevent contaminant underflow, for example. If such a layer is not available at a reasonable depth, then a "hanging" design might be necessary. This type of system must be engineered tp prevent contaminant underflow. Understanding the vertical variation in stratigraphy is also important for choosing the zone(s) that the barrier will intersect. Clearly if the contaminant is moving through a highly permeable layer, the barrier should be placed vertically to encompass this layer. Therefore, a careful evaluation of the stratigraphic variability at the location of the reactive wall, and the continuity of this stratigraphy with respect to the upgradient plume, is necessary for having confidence in the installation.

Historically, plume dimensions have been determined using the installation of monitoring wells. However, these are expensive, time-consuming to install and sample, and require special multi-level installations to provide adequate delineation of the plume in the vertical dimension. The use of push technologies, such as Geoprobe«, Hydropunch«, and cone penetrometers are rapidly becoming the tools of choice for evaluating shallow plume locations. These can be driven rapidly and relatively inexpensively, allowing more points to be sampled than could be accomplished with monitoring wells for the same amount of time and money. Additionally, they can be used to collect samples over very narrow vertical intervals, allowing better delineation of the contaminant concentrations in the plume than could normally be acquired with exploratory monitoring wells. Following this characterization, monitoring wells can be installed where appropriate, with much less guesswork.

Information on contaminant concentrations is necessary for any remedial operation, whether pump and treat or in situ technologies are used, since the remediation technique must be effective up to the maximum concentrations that will be encountered. This is especially important for reactive barriers because once emplaced, it is difficult to change the thickness of the reactive zone. Since permeable reactive barriers are generally placed downgradient of the plume center-of-mass, it is important that the barrier be designed to accommodate the higher upgradient concentrations, should they arrive at the barrier unattenuated. This requires sufficient contaminant characterization to accurately determine this high concentration zone. It is also clearly desirable to know whether this zone is moving downgradient over time or whether a steady-state has been achieved that could suggest natural attenuation is occurring. If this is so, the barrier could be designed for attenuating only the lower downgradient concentration(s) for the protection of nearby receptors or to eliminate migration beyond site boundaries.

Site/plume geochemical information is needed for reactive barrier implementation and to further our understanding of the expected lifetime of these systems. It has been shown, for example, that water passing through a reactive barrier of zero-valent iron undergoes radical geochemical changes, including a change in pH up to 9 or 10, elimination of oxygen with Eh reduction to minus several hundred millivolts, and a reduction in carbonate alkalinity. Often, sulfate is reduced to sulfide and dissolved iron appears. Other changes might be observed, dependant upon the contaminants being reacted. Some of the geochemical changes can result in precipitation on the reactant surfaces, potentially reducing the permeability of the reactive zone over time.

One area of site characterization for reactive barriers that needs further study is microbial activity. The interactions of native microbial populations, contaminants, and reactive barrier materials are likely to be quite complex, and have the potential for either beneficial or detrimental effects on the remediation. Beneficial effects could include enhanced contaminant degradation; for example the further reduction in Eh due to the presence of sulfate-reducing bacteria might increase the rates of contaminant reduction. Adverse effects could include the potential loss of permeability of the reactive zone due to biofouling. Additional laboratory and field studies are needed to understand these interactions and learn how to enhance the positive effects and reduce the negative effects of native microorganisms.

III. Emplacement Methods for Optimized Design and Cost Effectiveness

Dale S. Schultz, DuPont Central Research & Development

Permeable reactive barriers can be an attractive alternative to conventional means of groundwater treatment. The challenge is to optimize the design of these systems and the means of emplacing them in the ground so as to implement them as cost-effectively as possible.

In this paper, it will be shown how laboratory reaction kinetics data and basic knowledge of the plume characteristics and the remediation goals may be used to estimate the required amount of reactive material per unit cross-section of the plume. The value of this parameter has important implications regarding the choice of permeable barrier design and emplacement method. The specific application of granular iron to treat groundwater contaminated with chlorinated solvents is considered here, but the methodology may be applicable to other types of media and contaminants.

Thus far, most field applications of permeable reactive barriers have employed the funnel-and-gate design. That is, the reactive material is placed into excavated regions (gates) and groundwater is directed to them by means of impermeable walls (funnels). Experience has shown that the most expensive element is construction of the gates. Therefore, there is increasing interest in implementing continuous permeable zones across the entire width of plumes. If such zones can be emplaced at costs similar to those of impermeable walls, then considerable cost savings would be expected. Emplacement methods being considered include the use of trenching machines, driven mandrels, high pressure jetting, and deep soil mixing. Each of these methods offer different capabilities and costs. Recent developmental efforts aimed at applying these methods to implement permeable reactive barriers are discussed.

IV. Compliance and Performance Monitoring

Robert W. Puls, Ph.D., USEPA National Risk Management Research Laboratory Ada, OK.

Compliance monitoring typically involves the monitoring of the contaminants of interest at a particular hazardous waste site discovered to exceed regulatory limits during a remedial investigation. General water quality monitoring is also often included such as determinations for major cations and anions and other water quality indicator parameters such as pH, alkalinity, specific conductance etc. For permeable reactive barriers, similar monitoring requirements are necessary; however, the placement and design of monitoring wells or monitoring points and the methods used to sample ground water may be different.

Well placement and design are important to ensure assessment of system performance. In addition to upgradient and downgradient wells, wells should be located to ensure that contaminated water is not flowing around or under the barrier wall. Selection of screen length should be compatible with sampling program objectives and site conditions.

Performance monitoring of permeable reactive barriers includes the monitoring of physical, chemical and mineralogic parameters over time. It begins with adequate site characterization to provide a baseline for later comparison and its objective is to evaluate permeable barrier wall performance as designed over time. A performance monitoring program should address and be able to detect loss of reactivity, decrease in permeability, decrease in contaminant residence time in the reaction zone, short circuiting or leakage in the funnel walls and verification of emplacement. In addition to monitoring the contaminants of concern and general water quality, the following are also recommended: degradation products, precipitates, hydrologic parameters and geochemical indicator parameters. Understanding of the mechanisms controlling contaminant transformation, destruction or immobilization within the reaction zone is critical to interpretation of monitoring data.

Geochemical indicator parameters which provide some measure of system performance include: pH, Eh, alkalinity, dissolved oxygen, and ferrous iron. These parameters provide indications that iron corrosion is proceeding and provide some indication of the extent of precipitate formation within the barrier which may eventually decrease wall performance over time. When included with general water quality monitoring and used in conjunction with geochemical modeling, these geochemical parameters can support modeling projections concerning potential precipitate formation. Coring of the reactive mixture and surface mineralogic analyses of the iron surfaces should be done periodically to assess precipitation build-up which might eventually lead to system plugging and failure over time. Hydrologic changes over time should also be closely monitored. Head measurements, tracer tests and in-situ flow meters can be used to monitor for changes in system permeability and alteration of flow paths over time.

This workshop session will expand the above discussion and also provide recommendations on sampling methods, onsite analysis, and sampling materials useful for both compliance and performance monitoring of this emerging innovative remedial technology.

V. Installed Treatment Wall Demonstrations and Applications

John Vogan, Envirometal Technologies Inc., Guelph, Ontario, Canada

In-situ permeable reactive barriers can provide a cost-effective alternative to pump and treat techniques for control of dissolved phase contaminant plumes. Six full-scale and five pilot-scale *in-situ* systems using permeable iron treatment sections have been installed at several sites in the past two years for remediation of chlorinated solvents (VOCs). At most sites, a funnel and gate configuration has been employed where impermeable barrier sections (funnels) consisting of sheet piling or slurry wall are used to direct the groundwater plume towards permeable iron treatment sections (gates). Continuous reactive walls and an *in-situ* reaction vessel have also been constructed at other facilities. The systems have been installed to depths of about 40 feet to date, and are treating VOCs in the range of 10's of ppb to 100's of mg/L.

This section of the workshop will present several case histories of these installations to illustrate how site specific hydrologeologic and geotechnical characteristics were addressed in system design and installation. Construction of these systems has also involved addressing concerns common to many types of subsurface construction, including dewatering needs, unexpected lithological changes, soil disposal options and health and safety issues. Problems encountered and overcome in this regard will also be described.

Little data has been published regarding the costs of *in-situ* permeable treatment walls. As part of this section, capital costs for the full-scale systems installed to date till be presented, and compared to the estimates developed for alternative treatment remedies. Costs of constructing the same size of system using different construction techniques will also be compared.

A brief summary of operating results to date will conclude this section. The longest operating *in-situ* permeable treatment wall, installed at the University of Waterloo test site at CFB Borden, Ontario has been operating for five years. Commercial installations have been in place for up to two years. Geochemical data from these installations will be presented in the context of the performance predicted for these systems in the design phase.

Notice

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16. ABSTRACT

Permeable reaction walls are an emerging technology for the treatment of contaminated groundwater. Successful treatment of contaminated groundwater using this technique requires that the contaminate be rendered innocuous or immobile during transport through the in-situ treatment zone. The extent of treatment, and the success of the permeable barrier system depends on the nature of the contaminant, the selection of the reactive material, the physical design of the treatment system, and site conditions.

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