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Environment Canada

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Passive Remediation of Groundwater Using In
Situ Treatment Curtains

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Blowes, D.W., Ptacek, C.J., Cherry, J.A., Gillham, R.W., and Robertson, W.D., 1995. Passive remediation of groundwater using *in situ* treatment curtains. In: Acar, Y.B. and Daniel, D.E. (Eds.), *Geoenvironment 2000, Characterization, Containment, Remediation, and Performance in Environmental Geotechnics*, Geotechnical Special Publication No. 46, Vol. 2, American Society of Civil Engineers, New York, pp. 1588-1607.

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Passive *in situ* groundwater treatment techniques, in which reactive materials are installed in an aquifer in the path of a contaminated groundwater plume, are potential alternatives to conventional groundwater remediation technologies. Using these passive techniques, natural hydraulic gradients transport contaminants to the treatment zone, where chemical reactions remove them from the flowing water. Reactive mixtures for treatment of organic chemicals, including halogenated hydrocarbons and gasoline derivatives, and inorganic contaminants, including dissolved metals, and nutrients such as NO_3^- and PO_4^{3-} are being developed. Field-scale testing of porous reactive zones for treatment of a number of contaminants is in progress.

Management Perspective

Permeable reactive walls are a new technique for treating contaminated groundwater. These walls are installed in the pathway of plumes of contaminated groundwater and lead to the passive removal of the contaminants from the flowing groundwater. Permeable reactive walls have the potential to save energy, save water, and therefore reduce expenses. Because they are designed to be effective for decades or longer, their lifespan is similar to the duration of typical leach periods for sites of contamination. A review of current research on reactive wall technology is provided in this manuscript.

Passive Remediation of Groundwater Using *In Situ* Treatment Curtains

D.W. Blowes¹, C.J. Ptacek^{2,1}, J.A. Cherry¹, R.W. Gillham¹, and
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Abstract

Passive *in situ* groundwater treatment techniques, in which reactive materials are installed in an aquifer in the path of a contaminated groundwater plume, are potential alternatives to conventional groundwater remediation technologies. Using these passive techniques, natural hydraulic gradients transport contaminants to the treatment zone, where chemical reactions remove them from the flowing water. Reactive mixtures for treatment of organic chemicals, including halogenated hydrocarbons and gasoline derivatives, and inorganic contaminants, including dissolved metals, and nutrients such as NO_3^- and PO_4^{3-} are being developed. Field-scale testing of porous reactive zones for treatment of a number of contaminants is in progress.

Introduction

The need to protect groundwater resources, and to remediate contaminated industrial sites has been clearly recognized over the past two decades. Remediation of contaminated groundwater using conventional technologies is costly and, in many cases, it has not been possible to reduce permanently contaminant levels to drinking-water quality standards. It has been possible, however, to control the continued migration of plumes, by groundwater pumping (pump-and-treat) and thereby protect downstream water quality. At many sites, pump-and-treat is expected to continue for

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decades or longer because of the slow release of contaminants from source areas (Mackay and Cherry, 1989; Mackay et al., 1993). Many pump-and-treat systems are expensive because of the cost of construction and operation of treatment facilities and the cost of discharge of the treated water to sewers or other points. Researchers at the University of Waterloo recently have been investigating alternatives to conventional pump-and-treat systems for controlling contamination plumes. Among the most promising alternatives is the passive *in situ* treatment of contaminants using porous reactive and permeable materials that are buried in the aquifer to intercept plumes.

Porous reactive zones are installed in the path of the contaminant plume. Natural groundwater flow transports the contaminants to the zone of reactive materials (Fig. 1). A number of reaction materials or components are currently being studied at the University of Waterloo, and elsewhere, to evaluate their potential for remediation of many types of contaminants, including inorganic contaminants, such as dissolved metals and nutrients, and organic contaminants, derived from industrial solvents and fuel derivatives. The results of current studies show promise that this range of contaminants can be treated in these walls. Components contained in the emplaced reactive zone are selected to maintain reactivity for prolonged periods of time. Because of this longevity, these treatment systems are designed to remain effective as residual contaminants are continually leached from source areas. In this manner, the duration of the treatment system is intended to be compatible with the duration of the release of contaminants from the source zone.

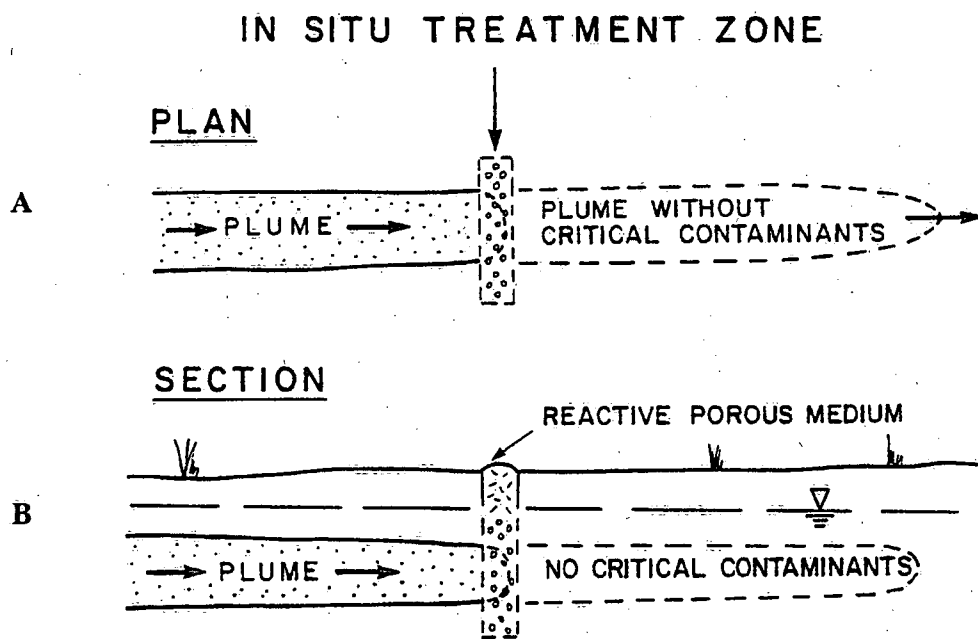


Figure 1. Schematic diagrams showing porous reactive walls for treating contaminated groundwater a) aerial view, b) vertical cross-section.

Background

Sources of Groundwater Contamination

Groundwater contamination has occurred at numerous locations in North America as a result of ineffective or inappropriate material and waste management practices. Many cases of groundwater contamination have resulted even though facility operators generally followed the best available practices. Although a large range of contaminant sources exist, it is possible to distinguish a few distinct contaminant types. These are: dissolved contaminants, including dissolved inorganic contaminants, such as metals, nutrients and toxic nonmetals, for example cyanide, and dissolved organic contaminants, such as dissolved gasoline derivatives; and nonaqueous phase contaminants or immiscible liquids, such as free-product gasoline, PCB oils or industrial solvents. Among the immiscible organic liquids, it is possible to distinguish two basic contaminant types: lighter than water non aqueous phase liquids (LNAPL) and heavier than water (dense) non aqueous phase liquids (DNAPL).

Dissolved inorganic and organic species can be released from a variety of contaminant sources. The extent and duration of contamination depends on the nature and mass of the contaminant source and the hydrogeological setting. Examples of sources of inorganic contaminants include municipal landfills, domestic septic systems and other waste management facilities, such as mine tailings impoundments and industrial waste lagoons. Release of contaminants from these sources depends on the physical nature of the waste disposal site and the chemical characteristics of the waste and the subsurface materials.

For example, until recently, the potential for groundwater contamination was not considered in the design of mine tailings impoundments at many locations in North America. As a result of chemical reactions occurring within the tailings impoundment and the natural hydrogeologic setting, tailings-derived water containing high concentrations of dissolved metals is generated within many impoundments and released to underlying and adjacent aquifers. The principal mechanisms resulting in contaminant release from tailings impoundments are the oxidation of sulfide minerals and the release of dissolved metals (Fig. 2). Contaminants released from these wastes include potentially toxic elements, such as lead, cadmium, chromium, arsenic and selenium. These elements are contained in tailings-derived waters which are typically low in pH and contain high concentrations of dissolved ferrous iron and sulfate. The release of metals to the tailings pore water is controlled by the supply of oxygen to the tailings as a result of the rate of oxygen diffusion and oxygen consumption. Limitations on oxygen transport extend the duration of sulfide oxidation to periods of decades or centuries. As a result of these processes, the release of contaminants from these wastes also is anticipated to continue for prolonged periods of time (Blowes and Jambor, 1990).

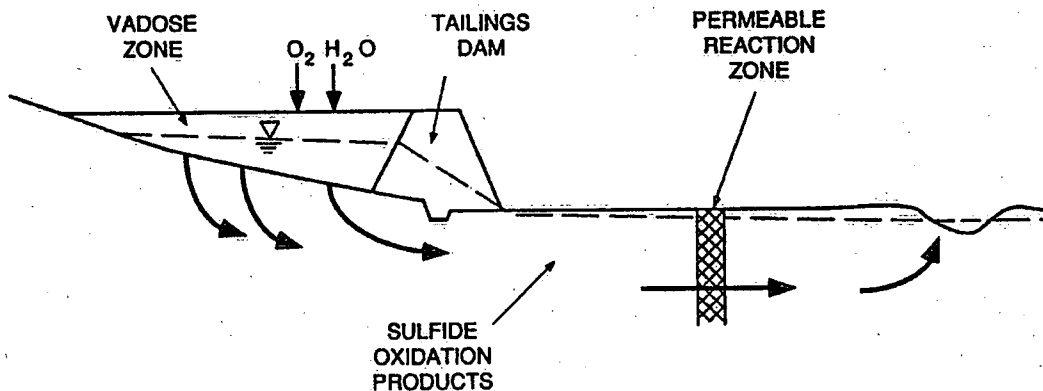


Figure 2. Schematic diagram of an inactive mine tailings impoundment. Sulfide oxidation products generated in the vadose zone are displaced downward into underlying aquifer and ultimately to the surface-water flow system. Interception of the plume within the aquifer using a reactive wall protects groundwater and surface water quality.

Conventional domestic septic systems, in use throughout North America, are significant contributors of nitrate to aquifer systems (Keeney, 1986). These systems are effective in treating domestic waste water, but have no provision for removing nutrients, including nitrate and phosphate from the discharging water (Wilhelm et al., 1994). Monitoring of septic systems in Ontario has indicated some potential for phosphate attenuation (Harman et al., 1994). The attenuating capacity of natural aquifer materials and the potential for the continued release of phosphate after septic system use ceases remains unknown.

When a spill or leak of nonaqueous phase liquids occurs at ground surface, the liquid migrates downward through the unsaturated zone leaving residual product behind (Fig. 3). Fluids that are less dense than water settle on top of the water table, and fluids that are more dense than water continue to migrate downward through the saturated zone until the entire mass is distributed either as residual product (Fig. 3) or until it encounters an impermeable layer. Immiscible liquids contained in the aquifer, either as pooled free product or as residual product retained above the free product, will subsequently dissolve, releasing contaminants to the flowing groundwater (Fig. 3). The duration of contaminant release depends on the mass of the immiscible liquid retained within the aquifer and the rate of dissolution. Dissolution of the immiscible liquid is affected by the solubility of the specific contaminant within the immiscible liquid, and the rate of transport and release of the contaminant from the immiscible liquid to the flowing groundwater. These and other factors result in periods of contamination that are anticipated to persist for years to decades.

Transport of the contaminant through the aquifer will be affected by interaction between the dissolved contaminant and the aquifer materials. Adsorption and precipitation of inorganic species, or sorption of organic contaminants can retard the migration of these contaminants through the aquifer, decreasing their dissolved concentrations, but extending the duration of transport. In the case of organic compounds, and some inorganic species such as cyanide, these attenuating processes can facilitate degradation or biodegradation reactions within the aquifer.

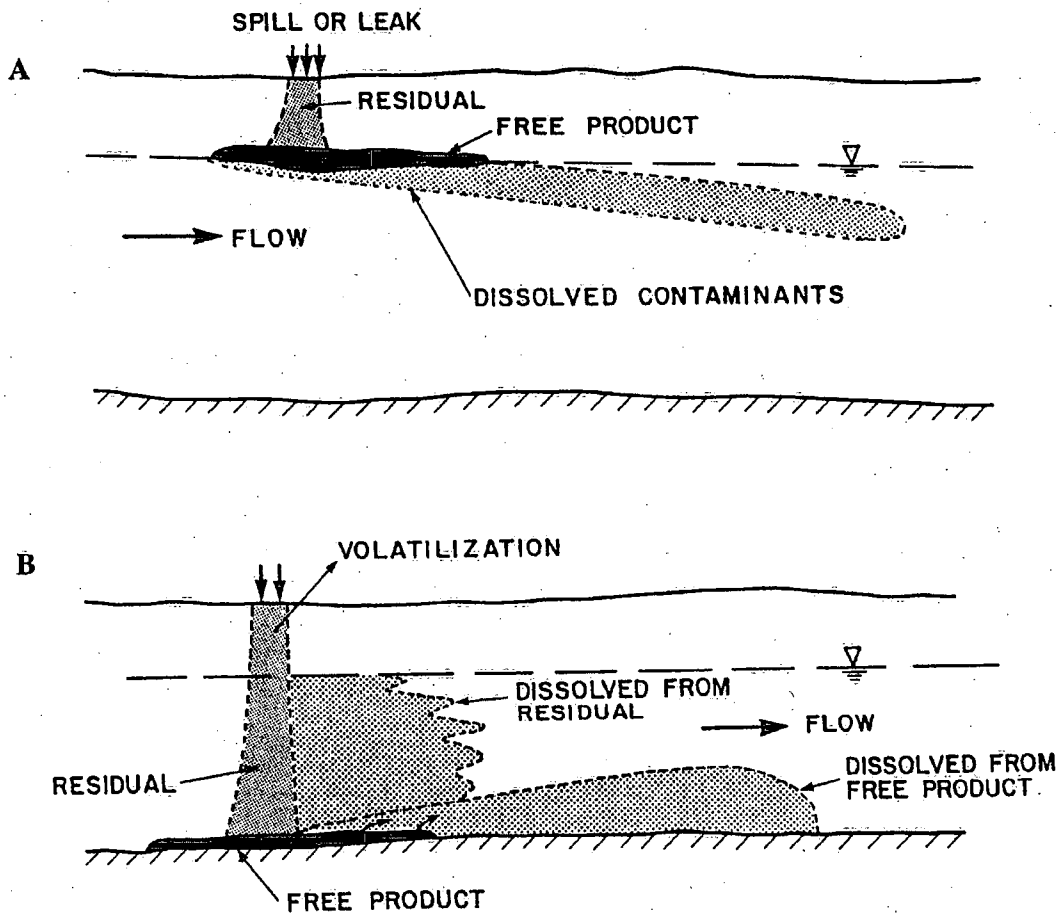


Figure 3. Behaviour of nonaqueous phase liquids in aquifer systems a) lighter than water nonaqueous phase liquid (LNAPL), b) dense nonaqueous phase liquid (DNAPL).

Conventional Approaches to Groundwater Remediation

Pump-and-Treat Systems

The most common approach to remediating contaminated groundwater is extraction of the groundwater by pumping, followed by treatment or removal of the contaminants at ground surface (pump-and-treat). Pump-and-treat systems may

employ a variety of water treatment technologies to remove contaminants. Although pump-and-treat systems have potential to be effective for controlling plume migration, physical and chemical constraints limit their effectiveness as a complete site clean-up strategy (Mackay and Cherry, 1989). Pump-and-treat systems tend to draw groundwater from the most permeable zones in the aquifer. Removal of contaminants retained in lower permeability zones is limited by the transfer of mass from these zones into the higher permeability portions of the aquifer. In addition, the effectiveness of pump-and-treat systems may be inhibited by slow dissolution of mineral phases, or nonaqueous liquids, or by partitioning of contaminants onto the aquifer solids. These physical and chemical limitations may render pump-and-treat systems ineffective for some contaminants, and may extend the duration of these systems for other contaminants.

In some cases, the removal of the contaminants in the aquifer may be accelerated through the use of enhanced pump-and-treat techniques, such as injection of surfactants or injection of co-solvents (Mercer and Cohen, 1990), and complexing agents to enhance the desorption or dissolution (Palmer and Wittbrodt, 1991). Other approaches to groundwater remediation include enhanced biodegradation through the addition of nutrients or electron acceptors through injection wells (Barker, 1992), and the addition of chemical reactants or additives through injection wells to enhance dissolution of inorganic species (Palmer and Wittbrodt, 1991).

In Situ Reactive Zones

In situ reactive zones are installed by excavating a portion of the aquifer material and replacing that material with a porous reactive mixture over the desired depth of treatment. Above the zone of treatment, aquifer material or other backfill is used to fill in the excavation to ground surface. The reactive medium is installed in a zone downgradient from the contaminant source. The distance between the contaminant source and the reactive zone can vary depending on site conditions and the composition of the reactive media used in the wall. Alternatively, reactive zones can be installed as impermeable barriers containing permeable zones or windows (e.g. funnels and gates; Starr and Cherry, 1994).

Preliminary results of laboratory and small-scale field experiments suggest that, at some sites, *in situ* reactive media have the potential to greatly reduce the expense associated with plume control. Because reactive zones are installed downgradient from the source of groundwater contamination, natural hydraulic gradients carry the contaminated groundwater through the treatment zone, avoiding the need for pumping the contaminated groundwater to ground surface, where problems and costs are incurred because of operation of above-ground treatment facilities and release of treated water to sewers or streams or reinjection of the water to the groundwater zone.

For the *in situ* reactive system to be effective, three basic requirements must be met. First, the contaminant must be sufficiently reactive that suitable transformations take place during the time the contaminated groundwater flows through the treatment zone. Without sufficient reaction rates, only partial transformation and removal of the contaminant will occur, leading to incomplete treatment or, in some cases, formation of byproducts that are less desirable than the original contaminant. The second requirement is the need for the reactive media in the treatment zone to be sufficiently abundant and have persistent reactivity so that it performs well for an economically viable period of time. As discussed, contaminant plumes can exist for decades or longer, thereby requiring the treatment system be active for a similar length of time. Under some geochemical settings the reactive materials selected for use in the reactive *in situ* plume treatment may require replacement after several years or decades. Under other settings, design of a system for operation over the entire period of contaminant release may be feasible. Design of a reactive wall for a given application requires an optimal balance when selecting a reactive mixture so that it is sufficiently reactive to remove a contaminant at site velocities yet sufficiently stable to remain in place for an economically viable period of time. The physical and geochemical conditions at a site will dictate the design criteria for a specific system. The third requirement is that the reactive media itself not release additional contaminants that would be unacceptable in groundwater on the downgradient side of the treatment zone. The groundwater that has passed through the reaction zone will generally be significantly different in chemical composition than the ambient groundwater, however the goal is for the water to meet regulatory requirements, which are usually drinking water standards.

Selection of Treatment Media

At the University of Waterloo, and elsewhere, research is under way in an effort to evaluate reactive media for use with *in situ* treatment systems and to assess various engineering systems for configuration and emplacement of the systems. These include reactive mixtures for the treatment of either organic or inorganic contaminants, and the co-treatment of both inorganic and organic contaminants. The research focus is currently directed at solid particles that are conveniently formed or mixed to provide porous, permeable media. Other relevant research involves systems for slow-rate, long-term release of dissolved chemicals in reaction zones. In this paper, we describe only the solid-phase media.

Treatment Systems for Organic Contaminants - Chlorinated Solvents As a consequence of their extensive use by industry as cleaning agents, solvents and degreasers, chlorinated organic compounds are among the most common groundwater contaminants. In addition to their wide-spread occurrence, drinking water limits are generally low (commonly on the order of 5 µg/L) and they are highly persistent in most natural groundwater environments. Over the past two decades, much effort has been directed at developing methods for degrading chlorinated organic compounds in aqueous solution. Though research has encompassed both abiotic and biological

processes, because of the generally low rates of abiotic processes, much of the effort has been focused on biological technologies. Useful reviews of this topic are provided in Vogel et al. (1987) and Freedman and Gossett (1989).

Over the past five years, there has been rapidly growing interest in the use of zero valent metals for enhancing the degradation of chlorinated organic compounds (Senzaki and Kumagai, 1988; Senzaki, 1991; Gillham and O'Hannesin, 1992, 1994; Lipczynska-Kochany et al., 1994; Matheson and Tratnyek, 1994, for example). Though metals have been used in the processing and transformation of organic chemicals for over a century, the potential for environmental applications (transformations in dilute aqueous solution) appears to have been first recognized by Sweeny and Fischer (1972), who were issued a patent for waste water treatment in 1972. However, their application was not commercialized, nor published in the scientific literature and therefore went unrecognized. The present resurgence in the technology can be attributed in part to rediscovery of the technology in a new form most relevant to *in situ* groundwater treatment by Gillham and O'Hannesin (1992), as well as the pressing need for effective groundwater remediation technologies.

Early studies at the University of Waterloo involved batch tests, and were focused on a survey of degradation of chlorinated methanes, ethanes and ethenes in the presence of granular iron (Gillham and O'Hannesin, 1994). Of 14 compounds tested, all, with the exception of dichloromethane, showed significant rates of degradation, with half-lives (normalized to 1 m² of iron surface area per mL of solution) about 5 to 15 orders of magnitude lower than those reported in the literature for natural abiotic degradation. For the compounds tested, hexachloroethane gave the shortest half life (0.013 hr) and c1,2-dichloroethene the longest (19.7 hr). The reaction was proposed to be abiotic reductive dechlorination and represented by pseudo-first order kinetics with respect to the organic substrate. In a subsequent study using flow-through column procedures (Orth, 1992), the degradation of trichloroethylene (TCE) was shown to be pseudo-first order, and over the range of 1.3 to 61 mg/L of TCE in the source water, the rate of degradation was independent of the initial concentration. For an initial TCE concentration of 4.7 mg/L, Figure 4 shows the decline in TCE concentration versus distance along the column, as well as the production of non-chlorinated hydrocarbons generated as degradation products. The primary product was ethene (43%), followed by ethane (19%), with methane and a range of C₃ and C₄ hydrocarbons accounting for about 10% of the degraded TCE. In addition to the nonchlorinated hydrocarbons, about 3% of the initial TCE appeared as chlorinated degradation products, including the three dichloroethene (DCE) isomers and vinyl chloride. Of these, c1,2-DCE appeared in the highest concentrations. As shown in Gillham and O'Hannesin (1994), the DCE isomers and vinyl chloride degrade in the presence of granular iron, though at lower rates than TCE. In addition to demonstrating rapid rates of degradation of TCE (normalized half life of 0.68 hr) no persistent toxic degradation products were identified, the process was consistent with a pseudo-first order kinetics model and the evidence indicated that the process was not stepwise dechlorination.

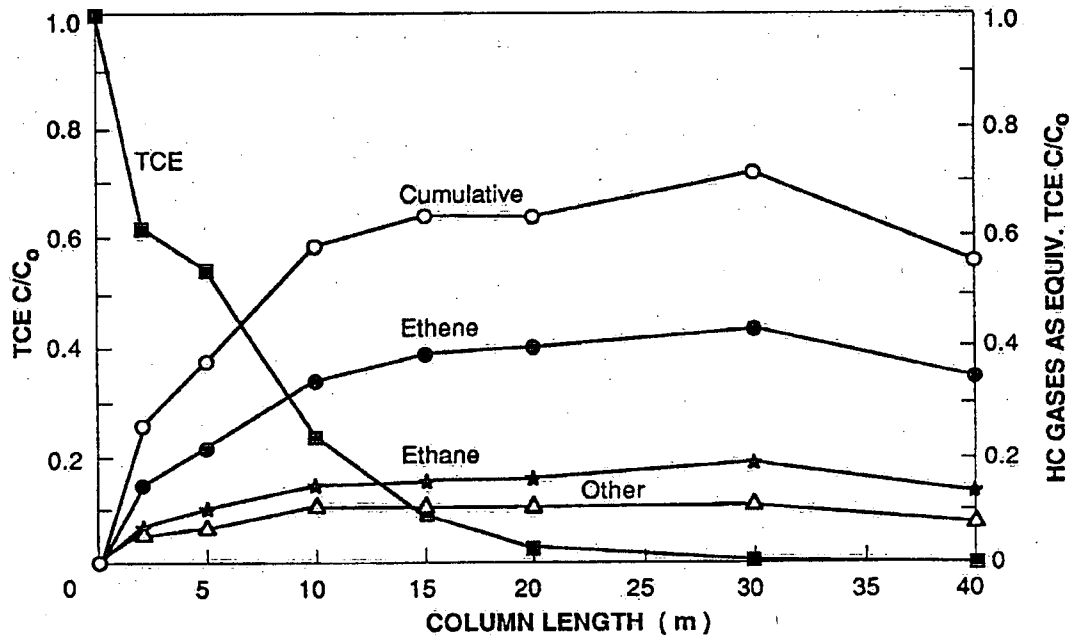


Figure 4. Decline in TCE concentrations and accumulation of hydrocarbon products versus distance along the column (adapted from Orth, 1992).

Based on the strength of the laboratory results, a permeable reactive curtain was installed across the path of a small contaminant plume created as a controlled field experiment in a sand aquifer at the Canadian Forces Base Borden field site (O'Hannesin, 1993). The contaminant plume contained about 250 mg/L TCE and 43 mg/L of tetrachloroethylene (PCE) and emanated from a source of residual solvent installed below the water table as part of a previous experiment (Rivett et al., 1992). The reactive curtain consisted of a mixture of 22 wt% granular iron and 78 wt% sand. Figure 5 shows the concentration of both TCE and PCE to decrease rapidly as the plume enters the reactive wall, with the rate of decline decreasing with travel distance across the wall. Approximately 90% of the TCE and 86% of the PCE was removed within the reactive wall. The concentration in the effluent was well above drinking water limits; however, greater removal and possibly complete remediation could have been achieved if a higher percentage of iron had been used in the reactive mixture. As in the laboratory tests, the three DCE isomers were identified as breakdown products, though no vinyl chloride was detected. About 10% of the initial TCE and PCE appeared as the DCE isomers; however, as in the laboratory tests, these also degraded within the residence time in the wall. There was no apparent change in performance of the reactive wall over a 16 month period of monitoring and core samples collected 24 months after installation indicated no substantial change in the physical characteristics of the reactive material.

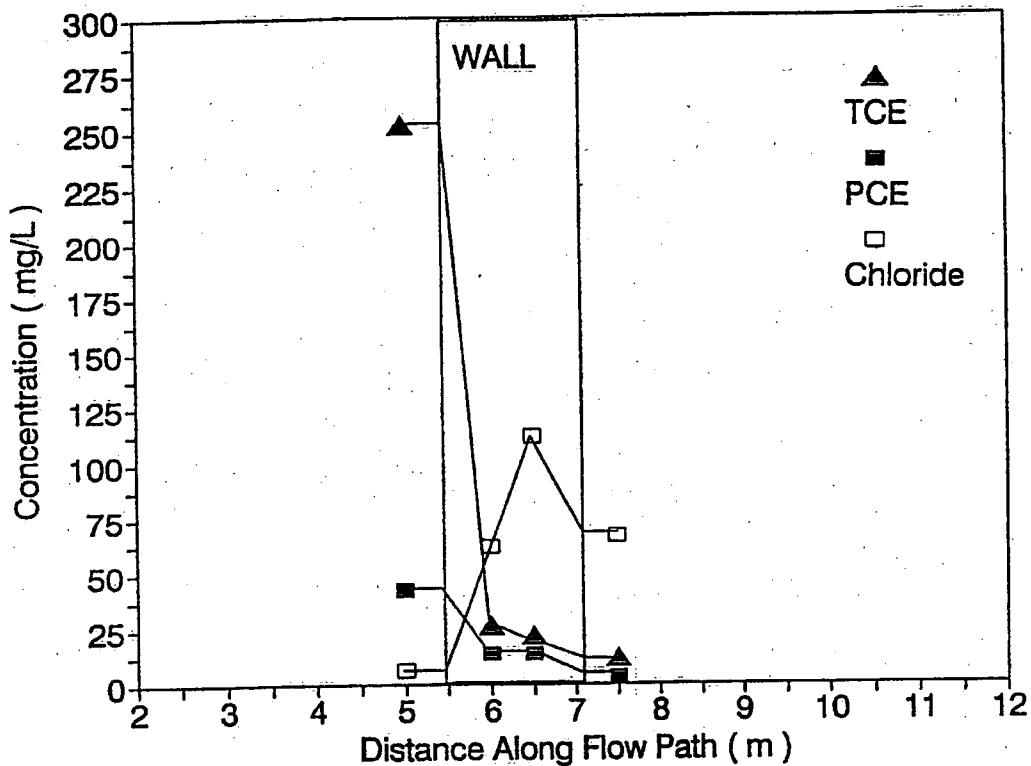


Figure 5. Graph showing the decrease in TCE and PCE concentrations across the *in situ* reactive wall at the Borden field site (Gillham et al., 1994).

Experimental results suggest great potential for the use of zero-valent iron for *in situ* remediation of groundwater contaminated by chlorinated organics. Though the process of degradation is widely accepted as reductive dechlorination, details of the mechanism remain uncertain. From studies of the degradation of carbon tetrachloride, Matheson and Tratnyek (1994) proposed direct electron transfer on the iron surface. Continuing studies will undoubtedly reveal the details of the mechanism(s) with the potential for improved efficiency in application. Pilot scale trials of iron technology are expected to take place in 1995 at several sites of industrial contamination in the United States.

Treatment Systems for Organic Contaminants - Gasoline Derivatives

Groundwater contamination by gasoline derivatives occurs at thousands of sites throughout North America (Bianchi-Mosquera et al., 1994). Gasoline derivatives, including benzene, toluene, ethylbenzene and xylene (BTEX) degrade aerobically, in the presence of oxygen. Anaerobic biodegradation of some BTEX compounds has

been observed, but bacterial growth on benzene as a substrate has not been demonstrated (Barker, 1992). It is probable, therefore, that complete degradation of BTEX compounds relies on the presence of oxygen as an electron acceptor. Bianchi-Mosquera et al. (1994) examined the potential use of a proprietary solid peroxide formulation oxygen releasing compound for *in situ* treatment of BTEX compounds. In a controlled field experiment at the Canadian Forces Base Borden site the oxygen releasing compound was installed in the path of an injected groundwater plume containing benzene and toluene. The plume also contained Br^- , as a conservative tracer, and NO_3^- , as a nutrient. The experiment included trials using two different forms of the oxygen releasing compound. In one trial the oxygen releasing compound was installed in the aquifer as a 60 % (vol/vol) slurry of the oxygen releasing compound and water. In the second trial the compound was mixed with cement to form briquets. Two control studies were conducted, one using briquets with no oxygen releasing compound, and one with natural aquifer material. In the control cases degradation of toluene was observed, but there was no decline in benzene concentrations. Toluene degradation was assumed to have occurred through anaerobic biodegradation with NO_3^- as the electron acceptor. In both trials where the oxygen releasing compound was present loss of both benzene and toluene was observed. In addition, dissolved oxygen concentrations were observed to be similar to concentrations predicted through laboratory studies. Monitoring of the experiment indicated that oxygen release continued for a period of at least 10 weeks. Bianchi-Mosquera et al. (1994) concluded that the oxygen releasing compound could be used to introduce dissolved O_2 to flowing groundwater, and that this addition can lead to enhanced biodegradation of BTEX compounds. In a follow-up study, Thomas (1994) buried the same oxygen releasing compound in the Borden aquifer and observed effective oxygen release for a period of one year. Prospects are good for new versions of the compound to provide even longer release periods.

Treatment Systems for Inorganic Contaminants

The design of treatment systems for inorganic contaminants has focused on the treatment of metals, including those derived from mine wastes and from industrial sources; and the treatment of nutrients, including nitrate and phosphate, derived primarily from septic system effluent.

Removal of Metals Systems evaluated for the treatment of metals can be divided into two categories, those that cause the contaminant to be converted to a lower oxidation state, which causes removal from water by chemical precipitation or co-precipitation and those that lead to the transformation of a second dissolved species present in the groundwater, which is not hazardous. This, in effect, results in the removal of the contaminants of concern.

An example of a reactive mixture designed to cause the direct removal of the target contaminant is the removal of hexavalent chromium (Cr(VI)) by reaction with zero-valent iron (Fe^0) (Blowes and Ptacek, 1992, 1994; Gillham et al., 1994). The principle behind this system is the reduction of Cr(VI) , by reaction with solid-phase

Fe⁰, to Cr(III). Cr(III) subsequently precipitates to form a mixed Cr(III)-Fe(III) oxyhydroxide. These combined reactions lead to extremely low aqueous concentrations of Cr(VI). At pH > 5, concentrations of Cr(III) are also very low. The resulting concentrations of total Cr are less than recommended drinking-water limits established for Cr. Iron filings, the same particulate medium that performs well for treatment of chlorinated solvents, is an effective form of Fe⁰ for the chromium removal.

Results of laboratory trials using iron filings suggest that this reactive mixture is suitable for removing Cr from flowing groundwater at residence times that are less than those observed in many aquifers. In these experiments, fine-grained iron filings were mixed with a small percentage of calcite, added to maintain the moderate pH conditions needed for the formation of the insoluble oxyhydroxide solid, and coarse-grained quartz sand, added to maintain a high permeability. This mixture has been successfully used to treat more than 150 pore volumes of a 20 mg/L Cr(VI) solution at a flow rate of 800 cm/year. In developing a treatment system for the removal of Cr(VI), Blowes and Ptacek found that coarse-grained iron chips and a number of Fe(II)-bearing solids also lowered aqueous concentrations of Cr(VI) from solution, but the reaction rates were insufficient for the treatment of Cr(VI) at typical groundwater velocities. The use of a mixture containing fine-grained Fe⁰ for the rapid treatment of Cr(VI) and other electroactive metals, therefore, is recommended. Under the experimental conditions assessed by Blowes and Ptacek, minimal clogging of the porous media resulted from the formation of the Cr(III)-Fe(III) precipitate. A field evaluation of this system is currently under way.

An example of the indirect removal of metals is a system described by Blowes and Ptacek (1994) and Blowes et al. (1994a,b) which involves the indirect removal of metals from a plume of mine-tailings derived groundwater. In this system, SO₄²⁻ also present in the mine-drainage water, is reduced to hydrogen sulfide by sulfate-reducing bacteria which require supplemental organic carbon. The hydrogen sulfide produced through this reaction combines with many of the metals present in the mine-drainage water resulting in metals immobilization due to the formation of insoluble metal-sulfide solids. In addition to the formation of hydrogen sulfide, the bacterially-mediated sulfate-reduction reaction is accompanied by an increase in alkalinity and pH, favouring the formation of carbonate and hydroxide containing solids.

In a series of laboratory batch and column tests, a number of organic carbon sources were evaluated to assess their ability to promote sulfate reduction and metal sulfide precipitation (Blowes et al., 1994b). For the majority of organic carbon sources evaluated, after an initial incubation period of 30 - 40 days, concentrations of SO₄²⁻, Fe and other metals were observed to decline rapidly to very low concentrations, suggesting the formation of insoluble metal sulfide solids. A small-scale field trial was initiated in October, 1993 in a portion of an aquifer receiving mine tailings effluent containing high concentrations of Fe(II), SO₄ and lower

concentrations of other metals (Blowes et al., 1994b). Preliminary results obtained from this field trial indicate that sulfate concentrations were reduced from $> 3,000$ mg/L to < 20 mg/L and dissolved Fe concentrations were reduced from > 600 mg/L to < 5 mg/L (Fig. 6).

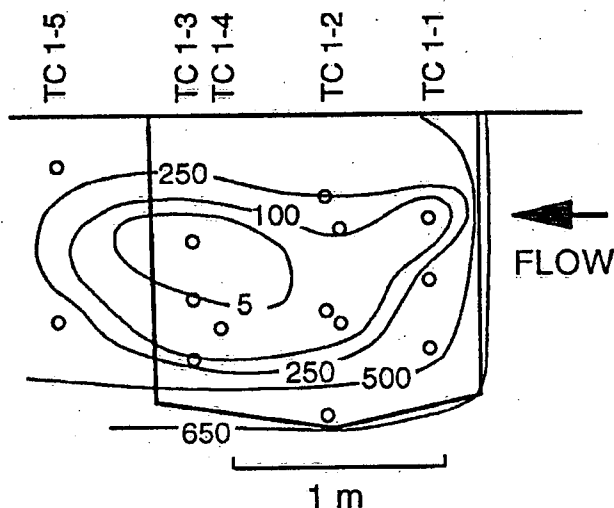


Figure 6. Cross section through the Nickel Rim test cell. Water entering the cell contains > 600 mg/L Fe. Within the cell this concentration decreases to < 5 mg/L.

In the two cases described for the removal of metals, the precipitates formed are expected to be relatively stable under moderate pH and reducing conditions. If these geochemical conditions remain present, and the site is suitable, there may be no need to excavate the metals accumulated in the reactive curtain. At sites where the reaction products are not expected to remain stable in the long term, removal of the reactive materials at some later date may be necessary.

Other potential reactive materials for removing metals from contaminated groundwater include those that promote the precipitation of insoluble metal hydroxides and carbonates through a simple increase in pH, and those in which ion exchange or adsorption reactions are promoted through the addition of additives. For example, McMurry and Elton (1985), propose the use of reactive barriers containing pH-neutralizing materials to remediate acidic groundwater containing high concentrations of Cr(III).

Removal of Nutrients Nitrate and phosphate are commonly released to shallow aquifers as a result of the release of domestic waste waters and some industrial processes. Several technologies for providing enhanced attenuation of nitrogen from

septic systems have been available for about a decade, including the "Ruuk" system (Laak et al., 1981), the peat bed system (Brooks et al., 1984), recirculating sand filters (e.g. Sikora and Keeney, 1976), among others. Recently, however, detailed plume mapping studies (i.e. Robertson et al., 1991; Harman et al., 1994) have demonstrated that NO_3^- , from even small septic systems, can persist in the groundwater zone for distances of hundreds of meters, undiluted, and above the drinking water limit (10 mg/L as N). This finding has promoted a renewed interest in nitrogen removal technology.

Research currently underway is investigating the use of NO_3^- -reactive porous media barriers to achieve enhanced attenuation of septic system NO_3^- . The goal is to reduce NO_3^- concentrations to levels below the 40 mg/L NO_3^- (10 mg/L NO_3^- -N) drinking water limit. The barriers use solid organic carbon (i.e. sawdust, cellulose, straw, etc.) as electron donors for heterotrophic denitrification. The barriers can be constructed as layers positioned below a conventional septic system infiltration bed at the time of installation, or as a vertical wall intercepting a downgradient horizontally flowing plume. The advantages of this technology are that it is of relatively low cost and simple to construct, requiring no additional tanks or plumbing, and treatment is passive so that potentially no maintenance is required for a long period of time.

To date, the research has included laboratory studies to assess the usefulness of various solid carbon sources for denitrification (Vogan, 1993) and pilot scale field trials using both the layer and wall configuration (Robertson and Cherry, 1995) and in combination with funnel-and-gate technology (Carmichael, 1994). The field trials, which have been in operation for periods of up to two and a half years, have achieved 70-100% attenuation of input NO_3^- levels of up to 125 mg/L. Reactive barriers of similar composition have also been tested for use in treating NO_3^- from farm field runoff (Blowes et al., 1994c) and NO_3^- in landfill leachate plumes (Byerley, 1994). Presently, the research is focused on establishing the reactivity and longevity of the various carbon source materials used in the barriers.

Phosphate is a nutrient of significant environmental concern, particularly in soft, fresh-water lakes which are sensitive to eutrophication due to phosphate loading. Researchers at the University of Waterloo have recently developed a reactive particulate mixture, suitable for use in a reactive curtain or funnel-and-gate system, that has demonstrated the potential to remove more than 90% of phosphate from an input solution of 10 mg/L (as P) (Baker, 1993; Ptacek et al., 1994). Field testing of this reactive mixture in a funnel-and-gate system has resulted in a decrease in phosphate concentrations from > 1 mg/L P to < 0.02 mg/L P (detection limit of the analytical method) (Ptacek et al., 1994). The particulate materials used in the laboratory and field experiments are inexpensive and available in large quantities, suggesting that treatment of domestic septic system leachate and preservation of soft water lakes is viable.

Engineering Aspects of the Subsurface System

In the above discussion, the focus was primarily on the selection of reactive media for use in *in situ* reactive walls. This discussion considered approaches taken to optimize a system based on the geochemistry of the site and the treatment system. A second aspect of the treatment system that can be optimized to attain adequate treatment of a contaminant is the physical configuration of the system. The following discussion will focus on potential methods that can be used to most efficiently take advantage of the properties of a reactive mixture at a given field site.

Installation Method

There are a number of ways in which a reactive wall can be installed at a field site. The wall can be installed by first inserting steel sheet piling into the formation, followed by excavation of the native aquifer materials, insertion of the reactive medium, and the withdrawal of the sheet piles to allow groundwater to flow through the reactive medium. The replacement materials can consist of a single reactive medium, or a mixture of materials. If appropriate, local aquifer material can be blended together with the reactive materials to reduce installation costs. The primary physical constraint is that the permeability of the mixture be similar to, or greater than, that of the native aquifer materials. This requirement prevents groundwater from bypassing the reactive materials.

Alternative installation methods include walls excavated using biodegradable, low-permeability slurries to hold the aquifer materials in place while excavation takes place. These slurries later biodegrade allowing the permeability to be regained and normal flow of the groundwater to return. Reactive media may also be installed through the use of *in situ* mixing techniques that blend the reactive material with the aquifer material in the zone through which the contaminated groundwater flows. This latter method may be less likely to ensure a continuous zone is created in the aquifer, and may lead to incomplete treatment of the contaminant. Any installation technique that allows replacement of aquifer materials with the reactive materials to form a relatively continuous treatment zone without destroying permeability is likely to be suitable.

Installation Design

Reactive zones can be installed as a broad, continuous curtain that extend the entire width of a contaminant plume for treatment or it can be installed as one or more discrete zones joined to segments of impervious walls. This configuration is known as a funnel-and-gate system. The impervious wall segments direct the plume through the gaps where the permeable medium is placed (Starr and Cherry, 1994). In both cases, the wall can either be installed through the entire aquifer depth or it can be installed slightly deeper than the maximum depth of the contaminant zone (a hanging wall). The geochemical and physical conditions at a site will determine the suitability of a given design.

Continuous Curtain Installation of a continuous reactive curtain is desirable at sites where installation is relatively inexpensive, such as in a shallow formation, where a contaminant plume is relatively narrow in width, and where the treatment media is inexpensive. Continuous walls have the advantage of minimizing the groundwater flow velocity through the treatment zone, maximizing contact with individual grains of reactant. With the funnel-and-gate system, the presence of low permeability sections leads to increased velocities within the treatment zones (i.e. in the gates).

Funnel-and-Gate System There are a number of methods that can be used to install funnel-and-gate systems. The impermeable zones can be constructed of impermeable materials, such as sheet piling, or low permeability materials, such as bentonite slurry. The primary advantage of the funnel-and-gate system is improved control of the reaction zone, because of its smaller dimensions, the potential for improved control on the groundwater flow system, and the potential for reduced installation expenses.

In one example of a funnel-and-gate system developed at the University of Waterloo, sheet piling is installed to form impermeable sections of the wall (funnels), and openings containing reactive mixtures are constructed within the wall (gates) (Fig. 7). The openings are unique in that they are constructed by inserting sheet piling perpendicular to the funnels. The reaction gates can be filled with a single reactive media or, if needed, different media can be installed in series (Fig. 7). The funnel-to-gate length ratio can be adjusted to optimize residence times within the gate sections.

The funnel-and-gate design allows control of the treatment zone. The effectiveness of the treatment process can be efficiently monitored with less instrumentation than would be needed for a continuous curtain. For systems requiring removal and or replacement of the reactant after a given time period, the funnel-and-gate system provides an efficient method for locating the treatment zone. With the addition of cassettes (Starr and Cherry, 1994), the reactive media can be removed and replaced when it is exhausted. If a reactive mixture is determined to be less effective than desired, or if an improved treatment mixture is developed, the cassettes allow easy replacement.

A disadvantage of the funnel-and-gate technology is the increased velocities that will occur within the treatment zone. Reactions that proceed relatively quickly can tolerate high velocities and high funnel-to-gate length ratios, whereas those that proceed slowly may require low funnel-to-gate length ratios. An alternative method to increase the residence time for the contaminant within the gate section is to increase the length of the gate in a direction parallel to flow. This increase will result in an increased contact time with the reactive mixture as a whole, but not with an individual particle. The final design of a system requires characterization of the physical hydrogeology and chemistry of the site, and an understanding of the rates

and nature of reactions taking place in the treatment zone.

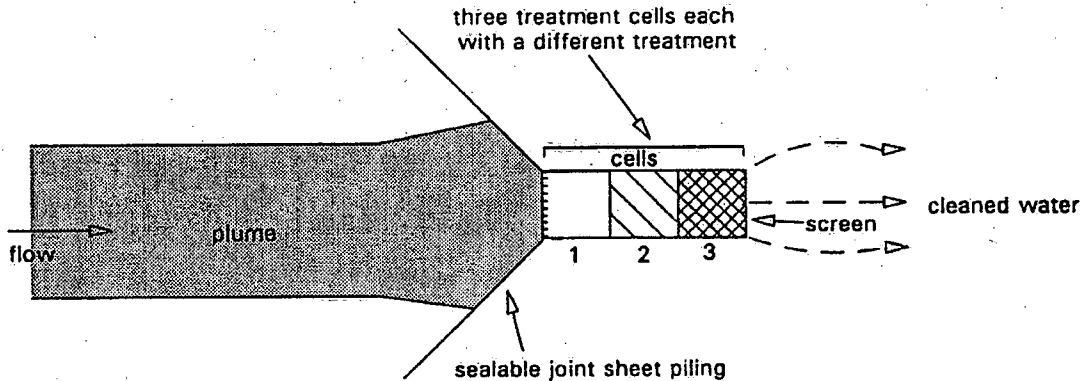


Figure 7. Aerial view schematic of a Funnel-and-Gate system. This is a multiple gate system for treating complex contaminants.

Conclusions

The conventional approach to remediation of contaminated groundwater is to pump the water to ground surface where it is treated. When used for permanent aquifer restoration, this approach is limited by difficulties in extracting contaminants retained within low permeability zones of the aquifer and those strongly adsorbed to particle surfaces, precipitated or coprecipitated as moderately soluble minerals, or present as separate immiscible liquid phases. To alleviate this problem, injection-withdrawal techniques are being developed to enhance the removal of contaminants by the addition of agents that will result in the release of the contaminants prior to or coincident with the application of pump-and-treat techniques. While many advances are being made using techniques that rely on removal of groundwater and treatment at ground surface, they remain inappropriate at many sites due to excessive cost or wastage of water resources. At these sites, *in situ* treatment techniques may be more suitable.

One type of *in situ* treatment system is porous reactive zones. A permeable reactive mixture is placed in the path of the flowing groundwater where removal of the contaminant occurs passively. The system can consist of a continuous curtain, covering the entire width of the plume, or a discontinuous wall (funnel-and-gate system), which has impermeable sections joined to gaps where reactive media are inserted. Reactive mixtures have been developed for removing a variety of contaminants from groundwater, including organic and inorganic contaminants. The funnel-and-gate method was introduced to assist in the installation of the reactive mixtures, and to ensure optimal reaction conditions during passage of the contaminant through the treatment zone and to more efficiently monitor the reaction progress.

Results from several years of laboratory tests and several field installations suggest *in situ* porous reactive walls have the potential to efficiently remediate a variety of contaminant types, present both as single contaminants or as combinations. Although the initial investment required is high, due to installation costs, *in situ* reactive curtains have the potential to be economical. Because of their passive nature, pumping is not required, therefore energy savings can be large and groundwater resources are not wasted. The system is passive in the sense that the contaminated groundwater is naturally carried to the treatment zone. These, and other, advantages potentially make *in situ* reactive curtains a viable remediation alternative. *In situ* reaction curtains and funnel-and-gate systems have advanced rapidly from the laboratory research stage to field prototype trials. We expect that the next stage in technology development, from the prototype stage to the full scale site use will occur in the next few years.

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