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Treatment of inorganic contaminants using permeable reactive barriers[1]

David W. Blowes [a], Carol J. Ptacek [a], Shawn G. Benner [a],
Che W.T. McRae [a], Timothy A. Bennett [a], Robert W. Puls [b, *]

[a] *Department of Earth Sciences, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1*
[b] *National Risk Management Research Laboratory, US Environmental Protection Agency, R.S. Kerr Laboratory, P.O. Box 1198, Ada, OK 74820, USA*

Abstract

Permeable reactive barriers are an emerging alternative to traditional pump and treat systems for groundwater remediation. This technique has progressed rapidly over the past decade from laboratory bench-scale studies to full-scale implementation. Laboratory studies indicate the potential for treatment of a large number of inorganic contaminants, including As, Cd, Cr, Cu, Hg, Fe, Mn, Mo, Ni, Pb, Se, Tc, U, V, NO_3, PO_4 and SO_4. Small-scale field studies have demonstrated treatment of Cd, Cr, Cu, Fe, Ni, Pb, NO_3, PO_4 and SO_4. Permeable reactive barriers composed of zero-valent iron have been used in full-scale installations for the treatment of Cr, U, and Tc. Solid-phase organic carbon in the form of municipal compost has been used to remove dissolved constituents associated with acid-mine drainage, including SO_4, Fe, Ni, Co and Zn. Dissolved nutrients, including NO_3 and PO_4, have been removed from domestic septic-system effluent and agricultural drainage. © 2000 Elsevier Science B.V. All rights reserved.

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* Corresponding author. Tel.: +1-580-436-8543.

E-mail address: puls.robert@epamail.epa.gov (R.W. Puls).

1. Introduction

Over the past decade, permeable reactive barriers have been developed and used to treat groundwater contaminated by inorganic constituents. Traditional approaches to treating groundwater contaminated by dissolved inorganic constituents have involved removing the contaminant source, pumping, and treating plumes of contaminated groundwater or isolating the source area with low permeability barriers or covers. The use of permeable reactive barriers provides an alternative in situ approach to replace or supplement these existing techniques.

Permeable reactive barriers are placed in the path of a migrating plume of contaminated groundwater. Reactive materials within the barrier are selected to promote geochemical reactions that result in the destruction or stabilization of the groundwater contaminants. Ideally, these materials are sufficiently reactive to treat water for periods of years to decades. Mixtures selected for the attenuation of inorganic species must be designed to maintain their permeability as secondary precipitates accumulate. The barrier design must also ensure that the contaminant will remain immobilized within the aquifer, or can be retrieved with the reactive material following treatment.

The barrier materials should provide treatment at costs that are competitive with other groundwater remediation programs. Costs associated with the implementation of a reactive barrier treatment system include the initial costs associated with the design, installation, and site rehabilitation, and the continuing costs of monitoring the barrier performance. Costs may also be associated with the recovery and disposal of the reactive material following the completion of the treatment program.

Permeable reactive barriers have been developed and demonstrated to be effective for the treatment of dissolved metals (Blowes and Ptacek, 1992; Powell et al., 1995; Cantrell et al., 1995; Blowes et al., 1997b), acid-mine drainage (Waybrant et al., 1995; Benner et al., 1997, 1999), and dissolved nutrients (Robertson and Cherry, 1995; Baker et al., 1997; Schipper and Vojvodic-Vukovic, 1998). A wide range of reaction mechanisms can be employed to remove both negatively charged and positively charged inorganic species from flowing groundwater. These include simple adsorption (Morrison and Spangler, 1993), simple precipitation (McMurty and Elton, 1985), adsorptive precipitation (Baker et al., 1997), reductive precipitation (Blowes and Ptacek, 1992), and biologically mediated transformations (Waybrant et al., 1995; Robertson and Cherry, 1995; Benner et al., 1999). This paper summarizes recent advances in the development of permeable reactive barriers for remediating groundwater contaminated by inorganic species.

2. Treatment of inorganic anions

The principal components of most aquifers are silicate and aluminosilicate minerals, including quartz, feldspars, and clays. Under near neutral pH conditions, which prevail in most shallow aquifers, the surface charge of these minerals is negative. The tendency for negatively charged anions to be attracted to these surfaces is small. The limited tendency for adsorption of anionic contaminants, and the high solubility of minerals

containing oxyanions, results in the persistence of high concentrations of these elements in aquifers (Palmer and Wittbrodt, 1991; White et al., 1991; Dubrovsky et al., 1991; DeSimone et al., 1996).
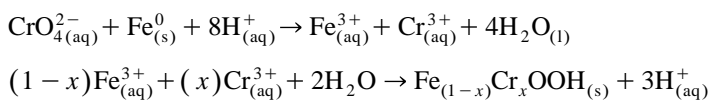
Anions or oxyanions, which occur as groundwater contaminants, include sulfate, arsenic, selenium, chromium, technetium, molybdenum and antimony. In addition, the dissolved nutrient species nitrate and phosphate occur as anions. A variety of reactive materials have been evaluated for treatment of anions using permeable reactive barriers. Laboratory bench-scale studies have been conducted to evaluate the potential for remediation of anionic contaminants, including Cr(VI), NO_3, Se(VI), Se(IV), As(V), As(III), Tc(VII), Mo(VI), PO_4 and SO_4. Pilot-scale field trials have been conducted to assess the potential for treatment of Cr(VI), Tc(VII), Mo(VI), SO_4, NO_3 and PO_4. Full-scale demonstration projects have treated groundwater plumes containing Cr(VI), NO_3, PO_4, Tc(VII) and SO_4.

2.1. Reduction and precipitation using zero-valent iron

Treatment of chromate, Cr(VI), has been more extensively tested, and demonstrated than other anionic inorganic contaminants. Chromium commonly occurs in two oxidation states, Cr(III) and Cr(VI). Trivalent Cr(III) is a micronutrient, which forms sparingly soluble hydroxide precipitates under conditions prevalent in most surficial aquifers. Hexavalent Cr(VI) is a known carcinogen, which forms relatively soluble precipitates, and does not adsorb readily, and relatively high concentrations of dissolved Cr(VI) are often found in aquifers impacted by Cr contamination.

A range of solid-phases containing reduced iron have been observed to promote the reduction and precipitation of Cr(VI), including elemental iron, iron sulfides, and iron-bearing oxyhydroxides and aluminosilicate minerals. Iron bearing reductants have been evaluated as potential candidate materials to promote Cr(VI) reduction (Bostick et al., 1990; Blowes and Ptacek, 1992; Powell et al., 1995; Blowes et al., 1997a,b). Comparison of reaction rates observed using elemental iron (Fe^0), pyrite (FeS_2), and siderite ($FeCO_3$), indicate that more rapid Cr(VI) reduction is attained using Fe^0 (Blowes and Ptacek, 1992; Blowes et al., 1997b).

Reduction of Cr(VI) to Cr(III) by reaction with Fe^0, and subsequent precipitation of Cr(III) oxyhydroxides occurs through the reaction sequence:

$$CrO_{4(aq)}^{2-} + Fe_{(s)}^0 + 8H_{(aq)}^+ \rightarrow Fe_{(aq)}^{3+} + Cr_{(aq)}^{3+} + 4H_2O_{(1)}$$

$$(1-x)Fe_{(aq)}^{3+} + (x)Cr_{(aq)}^{3+} + 2H_2O \rightarrow Fe_{(1-x)}Cr_xOOH_{(s)} + 3H_{(aq)}^+$$

The extent and rate of Cr(VI) removal by Fe^0 has been evaluated in laboratory batch tests (Blowes and Ptacek, 1992; Powell et al., 1995), column tests (Blowes and Ptacek, 1992; Blowes et al., 1997b), pilot-scale field trials (Puls et al., 1995) and a full-scale field demonstration (Blowes et al., 1997b; Puls et al., 1998). The results of these studies indicate that the rate of Cr(VI) reduction by Fe^0 and removal through precipitation is sufficiently rapid for use in groundwater remediation systems.

In the laboratory studies, the removal of Cr(VI) from solution is accompanied by a sharp decrease in Eh, from initially oxidized conditions (Eh > 100 mV) to very reduced

conditions $(Eh < -300$ mV$)$. Mineralogical study indicates the dominant reaction product derived from these laboratory studies is a mixed Fe–Cr oxyhydroxide phase with the mineral structure of goethite $(\alpha FeOOH)$. The distribution of Cr throughout the goethite structure is variable, suggesting incorporation through solid-solution substitution (Blowes et al., 1997b). X-ray photoelectron spectroscopy (XPS) indicates that the Cr within the precipitate is exclusively in the Cr(III) oxidation state, and that Fe present in the precipitate is in the Fe(III) oxidation state (Pratt et al., 1997). Auger electron spectroscopy indicates that at the precipitate surface, Fe(III) and Cr(III) are found in the hematite (Fe_2O_3) structure, distinct from the goethite structure of the bulk phase. The presence of the distinct structure suggests Cr(III) exsolution and formation of a chromite-like (Cr_2O_3) phase at the precipitate surface (Pratt et al., 1997).

In 1996, a continuous trenching machine was used to construct a permeable reactive barrier at a US Coast Guard Facility in Elizabeth City, North Carolina (Bennett et al., 1997). The barrier is 46-m long, 0.6-m thick, and 8-m deep. The installation of the barrier was completed in less than a day. The reactive barrier has been monitored quarterly since installation. The results of this monitoring program indicate consistent removal of Cr(VI) from influent concentrations of up to 8 mg l^{-1} to < 0.01 mg l^{-1} (Fig. 1). The removal of Cr(VI) is accompanied by a sharp decrease in Eh, to values < -600 mV, and a sharp increase in pH from initially near neutral conditions $(5.8 < pH < 6.5)$ to more basic conditions $(9.5 < pH < 11)$ (Blowes et al., 1997a; Puls et al., 1998). The reductive precipitation of Cr(VI) at the Elizabeth City site occurs concurrently with the reductive dehalogenation of trichloroethylene, dichlorethylene, and vinyl chloride. Simultaneous treatment of organic and inorganic contaminants provides an additional level of efficiency to the reactive barrier treatment system.

Reductive precipitation of other anion-forming elements, using elemental iron as a reductant, has been investigated at the laboratory scale, field pilot scale, and large-scale demonstrations. Laboratory experiments conducted to evaluate the treatability of Tc(VII) indicate rapid reduction using elemental iron (Bostick et al., 1990; Del Cul et al., 1993; Cantrell et al., 1995). Large-scale treatment of Tc(VII) was evaluated at the US Department of Energy, Oak Ridge National Laboratory Y-12 site. Preliminary results indicate that Tc(VII), U(VI), and NO_3 are removed by the zero-valent iron contained in the treatment system. Incomplete treatment of some contaminants by the barrier has been attributed to insufficient residence times. Bone char phosphate, amorphous iron oxide, and Fe^0 were assessed for their ability to remove U in pilot field scale reactive barriers at Fry Canyon, Utah (Naftz et al., 1999). The average influent concentration over approximately 2 years was 2.5 mg l^{-1}. Total percentage of mass removed by each mixture over the 2 years was 99.5% for the bone char phosphate, 42.6% for the amorphous iron oxide, and 99.9% for the Fe^0.

Arsenic commonly occurs as a dissolved species in two oxidation states, As(V) and As(III). Both of these oxidation states form protolytic acids, which dissociate to oxyanions as the pH increases. Arsenic reduction and precipitation using zero-valent iron has been proposed as a potential method for treatment of groundwater contaminated by dissolved arsenic (McRae et al., 1997). In batch tests conducted using elemental iron, McRae et al. (1997) observed rapid removal of As(V) from concentrations of 1000 to < 3 μg l^{-1} over a 2-h period (Fig. 2). Similar experiments using As(III) and mixtures
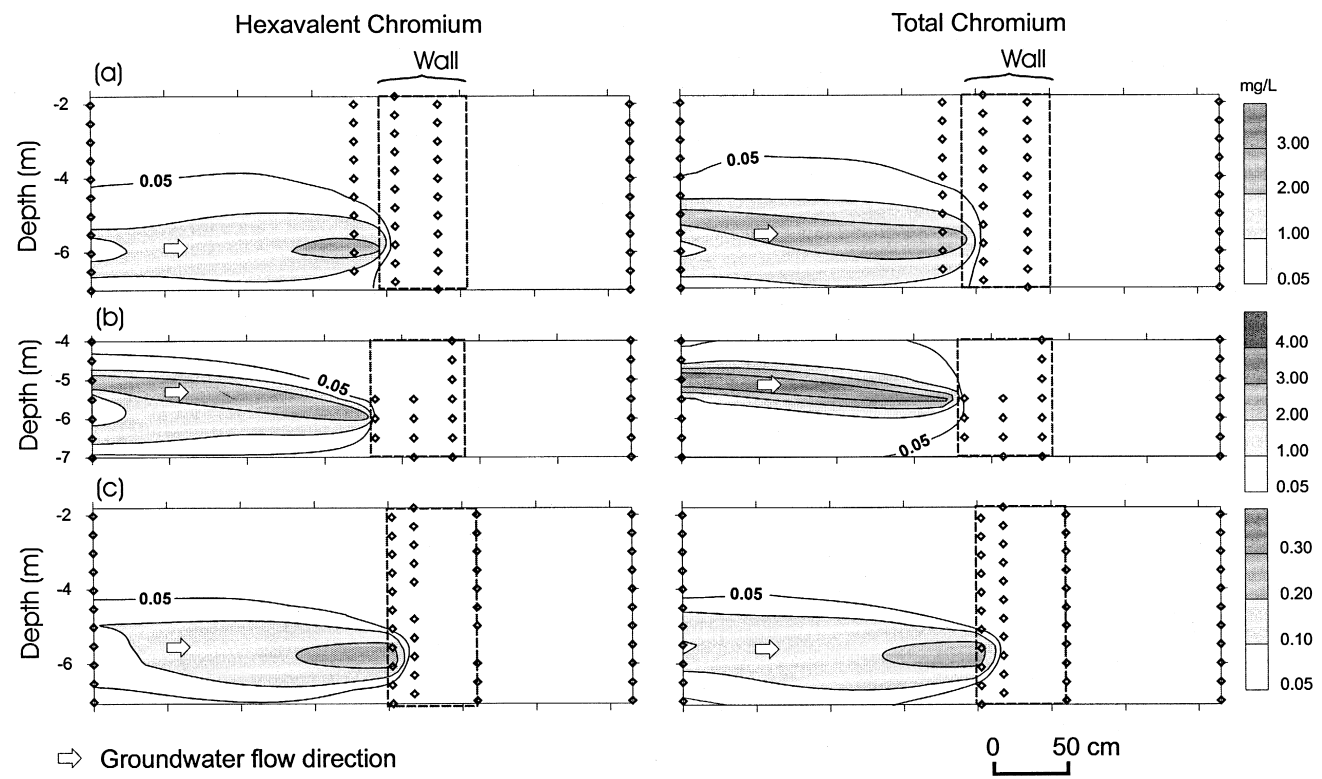
Fig. 1. Cross-section diagrams showing the position of the reactive barrier at the Elizabeth City site and the concentrations of hexavalent and total chromium in mg 1^{-1}. Results are shown from three separate transects through the reactive barrier February 1997, Day 240 after installation (from Bennett et al., 1997).
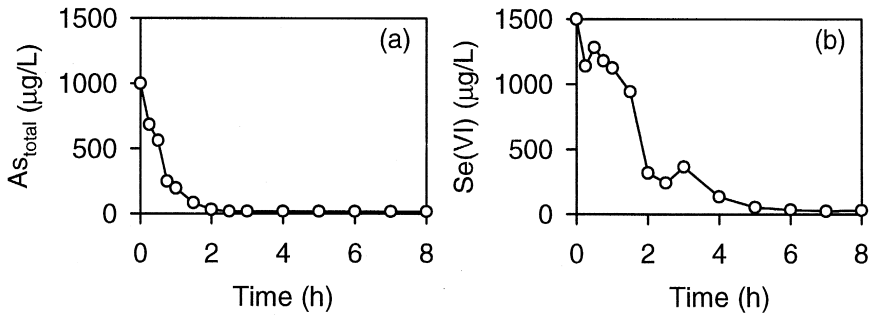
Fig. 2. Results of batch experiments showing (a) removal of 1000 mg l^{-1} As(Total), as 500 mg l^{-1} As(III) and 500 mg l^{-1} As(V), using zero-valent iron as the reactive media and (b) removal of 1500 mg l^{-1} Se(Total) as Se(VI) using zero-valent iron.

of As(III) and As(V) indicated equally rapid removal rates. Mineralogical examination using XPS of the reaction products obtained from these experiments indicated that As(V) was reduced and coprecipitated with Fe in goethite at the zero-valent iron particle surface (McRae, 1999). McRae (1999) conducted column experiments using a reactive mixture containing 10 wt.% Fe^0. In these experiments, McRae (1999) observed continuous removal of As from a solution containing 500 $\mu g\ l^{-1}$ As(III) and 500 $\mu g\ l^{-1}$ As(V). The effluent concentration of total As remained below 3 $\mu g\ l^{-1}$ for more than 320 pore volumes.
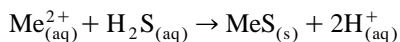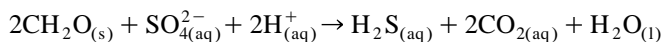
Dissolved Se occurs in groundwater in two oxidation states, Se(VI) and Se(IV) and, like As, both oxidation states hydrolyze to form oxyanions under most pH conditions found in groundwater. Reduction of Se(VI) by elemental iron, and precipitation of elemental selenium (Se^0) is favored thermodynamically. McRae et al. (1997) observed removal of 1500 $\mu g\ l^{-1}$ of Se(VI) from solution in laboratory batch experiments using elemental iron (Fig. 2). Column experiments conducted by McRae (1999) demonstrated the removal of Se(VI) from 1.0 to < 0.1 mg l^{-1} for more than 250 pore volumes. The secondary reaction product was not isolated or identified in these column experiments. Amrhein et al. (1998) demonstrated removal of Se(VI) by Fe^0 with dissolved O_2 present. Although zero-valent iron promotes highly reducing environments, the presence of O_2 prevents Eh values from decreasing substantially. Amrhein et al. (1998) did not detect Se(VI) in any of the reaction products. Reduced Se(IV) was associated with ferric oxyhydroxide phases.

2.2. Biologically mediated reduction and removal

Biological processes are involved in the cycling of numerous elements, including nitrogen and sulfur. Treatment strategies employing these biologically mediated reactions have been proposed for direct treatment of nitrate (Robertson and Cherry, 1995) and sulfate (Blowes et al., 1995; Waybrant et al., 1995, 1998; Blowes et al., 1998; Benner et al., 1999), and for indirect removal of other anions through precipitation as

sulfide phases. A system for removing nitrate from groundwater affected by discharge from on-site wastewater disposal systems through denitrification has been developed by Robertson and Cherry (1995). This system intercepts a plume of nitrate-bearing ground-water with a reactive barrier containing solid-phase organic carbon. In the presence of organic carbon, under anaerobic conditions maintained below a water cover in the subsurface, reduction of NO_3 to N_2 gas is thermodynamically favored. Robertson and Cherry (1995) evaluated permeable reactive barriers for treating NO_3 at several domestic and institutional septic systems. The results of these studies indicate that denitrification occurs rapidly, leading to effective treatment. Nitrate is reduced from concentrations typically observed in the effluent of on-site wastewater disposal systems (5–90 mg l^{-1} NO_3–N) to below the World Health Organization drinking water standard (10 mg l^{-1} NO_3–N). Long-term monitoring of effluent from several nitrate removal systems indicated continued treatment over a period of several years (Robertson et al., 2000). A similar approach for removing agricultural nitrate was evaluated by Schipper and Vojvodic-Vukovic (1998) who installed a permeable reactive barrier that contained 30% v/v sawdust. Concentrations of nitrate entering this barrier ranged from 5 to 16 mg l^{-1} NO_3–N. The effluent nitrate concentration was < 2 mg l^{-1}.

Biologically mediated reduction of sulfate to sulfide, accompanied with the formation of metal sulfides can be expressed by the reaction sequence:

$$2CH_2O_{(s)} + SO_{4(aq)}^{2-} + 2H_{(aq)}^+ \rightarrow H_2S_{(aq)} + 2CO_{2(aq)} + H_2O_{(l)}$$

$$Me_{(aq)}^{2+} + H_2S_{(aq)} \rightarrow MeS_{(s)} + 2H_{(aq)}^+$$

where CH_2O represents organic carbon and Me^{2+} represents a divalent metal cation. Biologically mediated sulfate reduction has been used to treat metal cations derived from mining activities in permeable reactive barriers (Blowes et al., 1995, 1998; Waybrant et al., 1995, 1998; Benner et al., 1997, 1999; McGregor et al., 1999). Although these systems are designed to promote the removal of dissolved metals, these barriers also effectively remove sulfate. In laboratory studies, Waybrant et al. (1995) observed sulfate removal at rates of 0.14 to 4.23 mg l^{-1} day^{-1} g^{-1}.

2.3. Adsorption and precipitation of inorganic anions

Inorganic anions that are not electroactive are not suitable for removal by reductive or oxidative processes. Phosphate (PO_4^{3-}) derived from anthropogenic sources is a limiting nutrient in many aquatic ecosystems (Schindler, 1977). In many regions, phosphate from on-site wastewater disposal systems, such as septic systems or sewage lagoons, result in excess release of phosphorous. Baker et al. (1997, 1998) used a mixture of iron oxide, calcium oxide, and limestone to promote adsorption and coprecipitation of phosphorous. The solid phase sink for phosphorous was identified as hydroxyapatite ($Ca_5(PO_4)_3OH$). Phosphate was removed rapidly in batch experiments. In column experiments extending over 4 years and 1500 pore volumes, influent PO_4 concentrations of 4 mg l^{-1} PO_4–P, were removed to < 0.3 mg l^{-1} PO_4–P, with more than 90% removal of the phosphate

over this prolonged period (Fig. 3). A field-scale demonstration at an institutional septic system resulted in removal of phosphate from impact concentrations of 1 to 2 mg l^{-1} PO_4–P to less than 0.1 mg l^{-1} PO_4–P (Baker, 1996). Test systems, installed at on-site wastewater treatment systems, indicate potential for PO_4 removal from wastewater under continuous flow conditions. The effluent concentrations achieved by this technique are sufficiently low to prevent eutrophication of surface water flow systems in which PO_4 is the limiting nutrient (Baker et al., 1997).

The reactive material used by Baker et al. (1998) was also evaluated for its potential to remove As and Se (McRae, 1999). Laboratory batch tests indicate the potential for this mixture to remove As(III) and As(V) from concentrations of up to 1000 to < 3 μg l^{-1}. Column experiments indicate potential for removal of As from a mixed solution containing 500 μg l^{-1} As(III) and 500 μg l^{-1} As(V) to < 3 μg l^{-1} total As. Treatment continued for a period of > 250 pore volumes. After 250 pore volumes, the As concentration gradually increased with only As(V) detected in the effluent water. Similar evaluation for Se indicated little potential for Se treatment using this material.
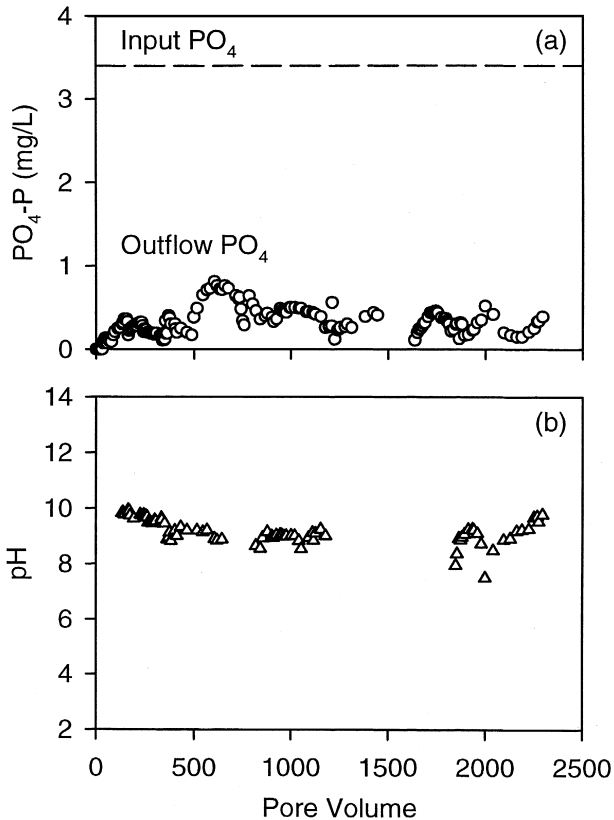

Fig. 3. Results from a laboratory column experiment showing the removal of PO_4–P using Fe/Ca oxide as the reactive media.

3. Treatment of inorganic cations

3.1. Reduction by zero-valent iron

Reduction by zero-valent iron and precipitation of sparingly soluble solids has been proposed for treating groundwater contaminated with inorganic cations. Treatment of cation-forming electroactive metals, including mercury, uranium, and copper by reduction with elemental iron and coprecipitation within secondary precipitates has been investigated on the laboratory scale. Laboratory batch experiments indicate rapid removal of UO_2^{2+} [U(VI)] from solutions in contact with elemental iron (Bostick et al., 1990; Amrhein et al., 1998; Gu et al., 1998). Strongly reducing conditions must be attained for uranium reduction and precipitation to proceed. In addition, if oxidizing conditions recur, the reduced uranium may become reoxidized and remobilized (Gu et al., 1998). Other metal cations potentially treatable by reduction with zero-valent iron include Cu and Hg.

3.2. Biologically mediated reduction and precipitation

Biologically mediated reduction reactions can promote the attenuation of inorganic cations through direct reduction of the cation or through indirect precipitation resulting from the oxidation or reduction of an inorganic anion.

Indirect precipitation of inorganic cations results from the reduction of an anion-forming species, usually sulfate. Laboratory studies indicate that many metals, including Ag, Cd, Co, Cu, Fe, Ni, Pb and Zn, are treatable using this approach (Waybrant et al., 1995, 1998). Column experiments, conducted using a range of organic substrates demonstrated the potential to remove a range of dissolved metals at groundwater velocities similar to those observed in groundwater contaminated aquifers (Waybrant et al., 1995).

In 1995, a full-scale continuous reactive barrier was installed in an aquifer down gradient from an inactive mine tailings impoundment at the Nickel Rim mine site, Sudbury, Ontario (Benner et al., 1997, 1999). The barrier was installed into a confined bedrock valley by a cut-and-fill technique. The barrier is 15-m long, 3.7-m deep, and 4.3-m wide. It is composed of a reactive mixture containing municipal compost, leaf compost, and wood chips to promote bacterial sulfate reduction and metal sulfide precipitation. These organic materials were mixed with pea gravel to attain a permeability greater than that of the aquifer. One-meter wide buffer zones containing coarse sand were installed on the up and down gradient sides of the reactive material.

One year after installation, concentrations of SO_4 decrease from 2400–3800 mg l^{-1} to 110–1900 mg l^{-1} as groundwater passes through the permeable barrier. The concentrations of Fe decrease from 740–1000 to < 1–91 mg l^{-1}, and alkalinity values increase from 60–220 mg l^{-1} (as $CaCO_3$) to 850–2700 mg l^{-1} (as $CaCO_3$) (Fig. 4). A comparison of the equivalents of potential acidity to the equivalents of alkalinity indicate that the water entering the barrier will generate acidity when exposed to atmospheric oxygen. The water leaving the barrier has an excess of alkalinity and will consume acidity when discharged from the aquifer. As a result of the barrier, the plume
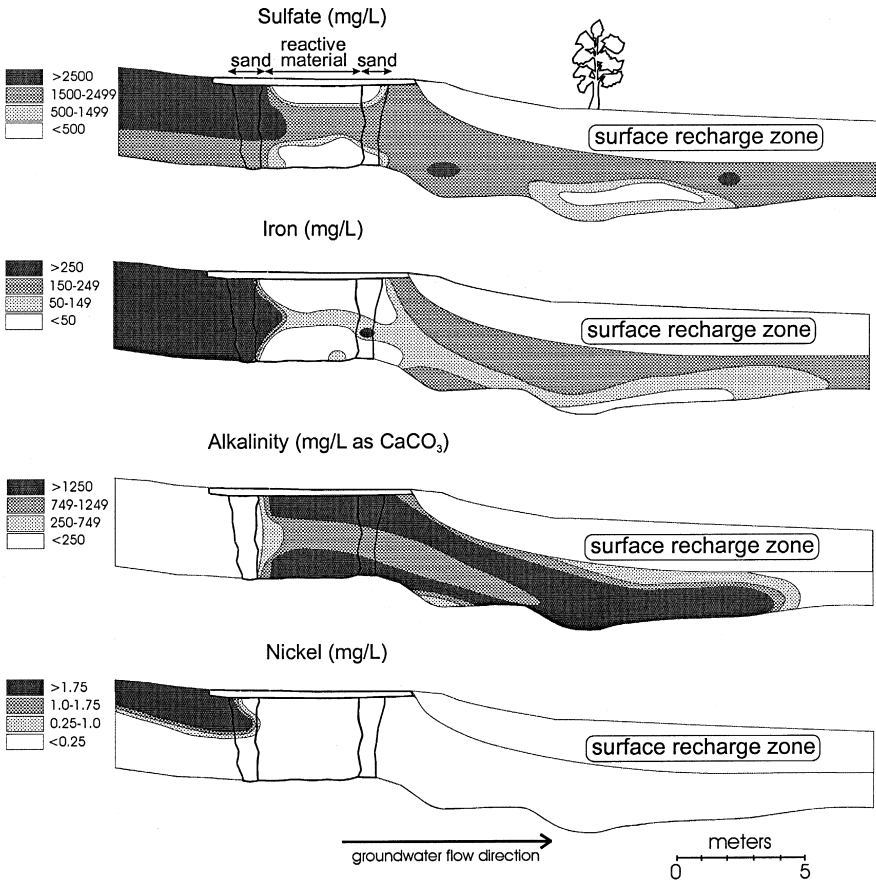
Sulfate (mg/L)

reactive
sand material sand

>2500
1500-2499
500-1499
<500

surface recharge zone

Iron (mg/L)

>250
150-249
50-149
<50

surface recharge zone

Alkalinity (mg/L as CaCO₃)

>1250
749-1249
250-749
<250

surface recharge zone

Nickel (mg/L)

>1.75
1.0-1.75
0.25-1.0
<0.25

surface recharge zone

groundwater flow direction

meters
0   5

Fig. 4. Cross-sectional diagrams showing the concentrations of SO_4 and Fe (mg l^{-1}) and potential acidity (mEq l^{-1}) at the Nickel Rim reactive barrier in Sudbury, Ontario, June 1996 (from Benner et al., 1997).

water will begin to neutralize the pH of the receiving surface-water system. Concentrations of dissolved Ni of up to 30 mg l^{-1} up gradient of the barrier are decreased to < 0.2 mg l^{-1} within and down gradient of the barrier. Enumeration of sulfate-reducing bacteria indicates an abundance of these species within the barrier, and elevated numbers in the down gradient aquifer (Benner et al., 1999).

In March 1997, a pilot-scale, compost-based reactive barrier was installed at an industrial site in Vancouver, Canada (McGregor et al., 1999). The barrier was installed in the path of a plume of groundwater containing Cd, Cu, Ni, Pb and Zn. The barrier was installed by trenching using biodegradable slurry. Dissolved Cu concentrations decrease from 300 mg l^{-1} to < 5 μg l^{-1} within the barrier. The concentrations of Cd, Ni, Pb and Zn showed similar decreases, with effluent concentrations generally below instrument detection limits.

4. Long-term performance

Reactive barriers have a finite treatment capacity. The barrier life may be limited by the chemical characteristics of the barrier, including the total mass of reactive material within the barrier, and rate of reaction within the barrier. Barrier life may also be limited by physical changes to the barrier, including decreases in porosity and permeability.

The chemical characteristics of the barrier, and the duration of reactivity depend on the reaction rate and on the reaction mechanisms. Reaction mechanisms and rates vary dramatically between reactive barrier types. The initial rate of Cr(VI) removal in the zero-valent iron barrier at Elizabeth City, NC is on the order of 1.0 mol l^{-1} day^{-1} (Mayer, 1999). The initial rate of sulfate reduction in the organic carbon barrier at Nickel Rim, Ontario is on the order of 1.3×10^{-4} mol l^{-1} day^{-1} (Benner, 2000). The rate of the reaction or process leading to treatment and the concentration of the contaminant dictates the required residence time within the barrier.

At many sites, the total reactive material within a barrier installation is theoretically sufficient to remove the target contaminant from groundwater for tens, or hundreds of years. For example, at the Elizabeth City site, the maximum Cr(VI) concentration is 10 mg l^{-1} and the groundwater velocity is approximately 10 cm per day, resulting in an annual flux of Cr(VI) for a 1 m^2 cross-sectional area of the aquifer of 35 mol a^{-1} m^{-2} (Blowes et al., 1997a,b). The barrier thickness is 60 cm, and, assuming a porosity of 0.5, a 1 m^2 vertical cross-sectional area of the barrier contains 2.7×10^4 mol Fe^0. Assuming that the ratio of removal is 1:1 Cr(VI) to Fe^0, the Elizabeth City barrier can theoretically remove Cr(VI) from the groundwater for 750 years. However, the reactive material within the barrier will be consumed by dissolved species other than the target constituent. For example, most of the SO$_4$ entering the Elizabeth City barrier (15–120 mg l^{-1}) is reduced. The reduction of sulfate by the zero-valent iron can be expressed by the reaction:

$$4Fe^0 + SO_4^{2-} + 9H^+ \Rightarrow 4Fe^{2+} + HS^- + 4H_2O$$
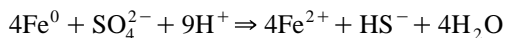
This reaction consumes approximately 50 times more Fe^0 than that consumed by reduction and precipitation of Cr(VI) (Mayer, 1999). Numerical reactive transport modeling conducted by Mayer (1999) suggests that the iron is consumed by reactions with a series of oxidants including Cr(VI), dissolved oxygen, sulfate, dissolved inorganic carbon and water. All of these reactions will gradually deplete the mass of zero-valent iron. The results of laboratory column studies conducted using site groundwater suggest that the barrier life will be approximately 20 years, much less than the 750 years estimate based on the total Fe^0 present and assumption of a single oxidant (Bennett et al., 1997). This comparison highlights the importance of performing treatability studies with groundwater from the proposed site of the reactive material installation.

The rate of reaction leading to treatment can also decline with time. The rate of iron removal by sulfide precipitation in the Nickel Rim barrier declined 45% from an initial rate of 2100 to 1000 mg l^{-1} a^{-1}, 3 years after installation (Benner, 2000). In contrast, the rate of Cr removal in the Elizabeth City barrier remains sufficiently rapid to remove all Cr to less than 0.01 mg l^{-1} prior to the first sampling point 10–20 cm into the barrier, 3 years after installation.

Potential processes leading to a decreased reaction rate include consumption of reactive material, depletion of the reactive component of a reactive mixture, and declining reactive surface area resulting from precipitating secondary minerals on reactive surfaces, clogging and preferential flow. The Nickel Rim barrier contains sufficient organic carbon to theoretically remove all SO_4 and Fe for > 100 years (Benner et al., 1997). The declining rate of treatment at this site has been attributed to the depletion of the more reactive portion of the organic carbon within the barrier. The rate of treatment at this site is caused, in part, by preferential channeling of groundwater flow through portions of the barrier. Improved treatment can likely be achieved by increasing the thickness of the barrier or by more uniformly distributing flow through the barrier (Benner, 2000).

The formation of secondary precipitates within the reactive barrier can potentially impact barrier performance by accumulating on the reactive material and decreasing effective reactive surface area. The impact of coatings on performance was documented in the column studies of Blowes et al (1997a,b); the accumulation of (oxy)hydroxide coatings was observed to migrate through the column. After 100 pore volumes, when the coatings were observed over the entire length of the column, concentrations of Cr in the effluent increased dramatically. Mass balance calculations indicate that only a small fraction of Fe^0 was consumed after 100 pore volumes and breakthrough was attributed to decreased reactivity of the Fe^0 as a result of the (oxy)hydroxide coatings.

Barrier longevity may also be limited by changes in the physical characteristics of the barrier, such as clogging or the development of preferential flow channels. In some barriers, the accumulating secondary mineral may be unrelated to the treatment of the target contaminant. The accumulation of secondary precipitates may be sufficient to decrease porosity, potentially decreasing flow through the barrier. In zero-valent iron barriers, precipitation of sulfides, Ca, Mg, and Fe(II) carbonates and Fe and Al (oxy)hydroxides may occur due to the large decrease in Eh and increase in pH that results from the iron corrosion reaction. Accumulations are expected to be greatest when the incoming groundwater contains elevated dissolved concentrations.

In many reactive barriers, inorganic contaminants are transferred to the solid phase. The method by which the contaminant is sequestered will determine its long-term stability and will dictate if the reactive material and contaminants must be eventually removed from the aquifer. The preferred mechanism of removal is often precipitation of the target contaminant in an insoluble mineral phase, in which case, the long-term stability and solubility of that mineral must be assessed.

In sulfate reduction barriers, dissolved metals are removed by the precipitation of a sulfide mineral phase. The stability of these metals is controlled by sulfide mineral solubility. The solubility of most sulfide phases is low and equilibrium dissolution under anaerobic conditions will result in very low dissolved concentrations of metals. Oxidation of the sulfides could result in the rapid release of the metals at high concentrations. At the Nickel Rim site, the flux of oxygen downwards into the barrier is limited by a 20 cm saturated clay cap. Furthermore, because water flows horizontally through the barrier, an oxidizing agent must travel the entire 100-m flow length from the recharge zone in the tailings impoundment. This flow path includes 10 m of unoxidized sulfide-rich tailings that consume dissolved oxygen contained in the groundwater prior

to arrival at the barrier. In the unlikely case of groundwater arriving at the barrier fully saturated with oxygen, the resulting dissolved Fe(II) concentration from pyrite oxidation would be $10–20$ mg l^{-1}, much lower than the original plume concentration. Therefore, the contaminants within this barrier are quite stable and it is likely that this barrier can remain within the aquifer indefinitely.

The mechanism of Cr(VI) removal in zero-valent iron barriers is reduction to Cr(III) and precipitation as a mixed Fe(III) − Cr(III) (oxy)hydroxide mineral phase (Pratt et al., 1997; Blowes et al., 1997a,b). The long-term stability of this phase was assessed in column studies (Blowes et al., 1997a,b) in which dissolved Cr(VI) was pumped through the columns containing Fe^0 for approximately 100 pore volumes. After that time, Cr-free input water was pumped through the column. After two pore volumes, Cr concentrations declined to less than the level of detection $(0.01$ mg $l^{-1})$ and remained at that level until the experiment was terminated for an additional 350 pore volumes. This experiment suggests that Cr(III) solids formed in a zero-valent iron barrier will remain stable after the input of dissolved Cr(VI) ceases. In situations where leaching of the target contaminant occurs at unacceptable concentrations, excavation of the barrier would be required. It is desirable, therefore, to design barriers in which long-term stability of the precipitating phase will limit the concentrations of the contaminant exiting the barrier into the foreseeable future.

The relatively short history of the reactive barrier technology results in a lack of long-term performance data. Routine sampling is presently underway at several permeable reactive barrier installations. This monitoring will provide an excellent basis for the assessment of the long-term performance of permeable reactive barriers.

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