Chemistry and Microbiology of Permeable Reactive Barriers for *In Situ* Groundwater Clean up

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ABSTRACT: Permeable reactive barriers (PRBs) are receiving a great deal of attention as an innovative, cost-effective technology for *in situ* clean up of groundwater contamination. A wide variety of materials are being proposed for use in PRBs, including zero-valent metals (e.g., iron metal), humic materials, oxides, surfactant-modified zeolites (SMZs), and oxygen- and nitrate-releasing compounds. PRB materials remove dissolved groundwater contaminants by immobilization within the barrier or transformation to less harmful products. The primary removal processes include: (1) sorption and precipitation, (2) chemical reaction, and (3) biologically mediated reactions. This article presents an overview of the mechanisms and factors controlling these individual processes and discusses the implications for the feasibility and long-term effectiveness of PRB technologies.

I. INTRODUCTION

Analysts estimate that there are between 300,000 and 400,000 sites in the U.S.A contaminated with a wide variety of toxic chemicals, representing total clean up costs in the range of \$500 billion to \$1 trillion (NRC, 1994). Many of these sites experience groundwater contamination by complex mixtures of chlorinated solvents, fuels, metals, and/or radioactive materials. To date, mostly conventional remediation technologies (e.g., pump-and-treat systems) have been applied for the clean up of contaminated groundwater. Even after many years of operation, however, it has proven difficult and costly to meet applicable clean up standards (Mackay and Cherry, 1989). Clearly, more innovative remediation technologies and approaches are needed to mitigate the effects of contaminated subsurface environments.

In the last 5 years, there has been an explosion of activity directed at the development and implementation of permeable reactive barriers (PRBs). This is reflected in Figure 1, which shows a recent sharp increase in the number of publications related to groundwater clean up with iron metal PRBs. Permeable reactive barriers constitute a semipassive, in situ remediation technology that

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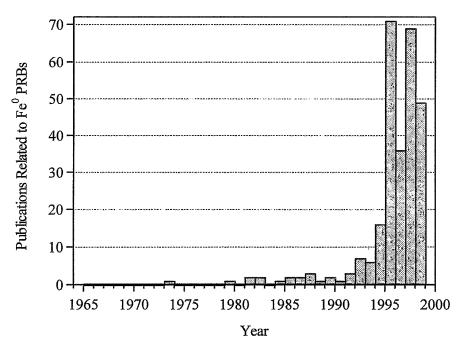


FIGURE 1. Number of publications related to iron metal and PRB development and implementation since 1964. (Adapted from the iron references database maintained by Dr. Paul Tratnyek at the Oregon Graduate Institute: http://cgr.ese.ogi.edu/ironrefs/.)

utilize media which cause chemical or biochemical reactions to transform or immobilize contaminants. The approach involves placing semi-permeable reactive media in the flow path of a plume of contaminants. As the plume moves through the barrier, the contaminants are transformed to nontoxic or immobile products. PRBs are particularly attractive for groundwater remediation because they conserve energy and water and have the potential to be more economical than conventional clean up methods because of low operation and maintenance costs. An additional advantage of PRBs is that reactive media can be used *in situ*, eliminating the need for extensive operating equipment and surface facilities.

Although the reactivity of common barrier materials (e.g., iron metal) with chlorinated compounds was recognized as early 1925 (Rhodes and Carty, 1925), in situ applications were apparently not being considered until recently. The sharp increase in interest in PRBs during the early 1990s (Figure 1) is attributable to a number of seminal studies, but perhaps mostly to those of Robert Gillham and coworkers (Gillham and O'Hannesin, 1992), who first proposed the concept of in situ reactive barriers. More than 20 reactive barriers have been installed in North America from 1994 to 1997, and about an equal number in 1998 (for details about individual sites see U.S. EPA/RTDF, 1999).

Several excellent reviews of PRB technologies have been published recently (Gavaskar et al., 1998; U.S. EPA/RTDF, 1998a). These reviews have focused on PRB design and implementation aspects, including hydrologic considerations,

flow control, and barrier emplacement methods. The chemical and biochemical principles behind barrier media selection have yet to be critically reviewed. Therefore, the emphasis here is to review these fundamental principles in order to provide a framework for the selection and development of materials for use in PRBs and associated technologies.

Following a general review of current PRB applications and the types of media being used as reactive material (Section II), the major processes governing the immobilization and transformation of contaminants in reactive barriers are covered as separate sections. These processes include sorption and precipitation (Section III), chemical reaction (Section IV), and biologically mediated reactions (Section V). A brief introduction of the processes governing each mechanism is presented followed by a discussion of the viability of potential reactive media. Specifically, the media is evaluated based on its ability to (1) transform or immobilize the contaminant at sufficiently rapid rates, (2) maintain adequate permeability and reactivity over long time periods, and (3) release only benign compounds as byproducts of the removal process (Blowes et al., 1995). Finally, this review concludes with a discussion of the effect of microorganisms on PRB permeability and long-term performance (Section VI), and current technical challenges and research needs (Section VII).

II. REACTIVE BARRIER APPLICATIONS

Sacre (1997) reviewed the state of permeable reactive barrier technology and identified 124 projects that are currently using or planning to install PRBs. The main target contaminant groups in these projects are halogenated aliphatics (54%), heavy metals (30%), and radionuclides (12%). The most frequently targeted organic contaminants are trichloroethylene, tetrachloroethylene, and carbon tetrachloride (Figure 2). Typical inorganic contaminants treated by PRBs are hexavalent chromium, lead, molybdenum, arsenic, and cadmium (Figure 3). The majority of these PRB projects are still in the laboratory phase (58%), and commercial applications account for only 16%. Iron metal is the most frequently utilized medium, accounting for approximately 45% of PRB these applications (Figure 4). Nevertheless, there is a wide variety of materials other than iron metal that have been evaluated for use in reactive barrier technologies. Tables 1 and 2 summarize the materials that have been proposed for the treatment of organic and inorganic contaminants, respectively. These materials remove contaminants by two major processes: (1) transformation of the contaminant to a less harmful compound and/ or (2) immobilization of the contaminant within the barrier.

Immobilization of the contaminant within the barrier can occur by sorption to the reactive medium or precipitation from the dissolved phase. Sorption is an abiotic reaction where the contaminant is attracted to the surface via hydrophobic interactions, electrostatic attraction, and/or surface complexation (Westall 1987;

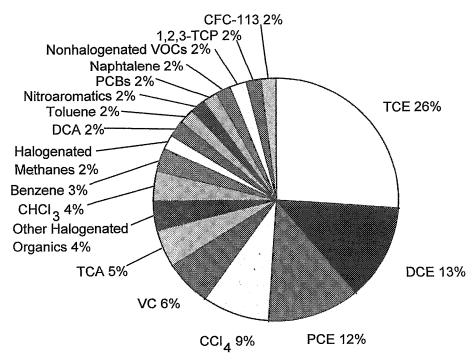


FIGURE 2. Organic contaminants most frequently treated with permeable reactive barrier technology. Percentages are based on a total of 124 projects. (Adapted from Sacre, 1997.)

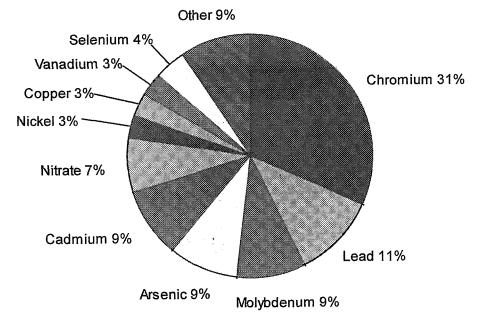


FIGURE 3. Inorganic contaminants most frequently treated with permeable reactive barrier technology. Percentages are based on a total of 124 projects (Adapted from Sacre, 1997.)

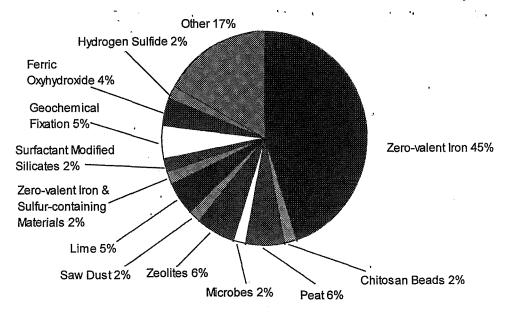


FIGURE 4. Materials used for reactive barrier applications. Percentages are based on a total of 124 projects. (Adapted from Sacre, 1997.)

Schindler, 1990). The most common mechanism for organic compounds (particularly nonpolar organic compounds) is sorption due to hydrophobic expulsion from water. Sorption of chlorinated organics onto activated carbon is an important example of a removal process controlled by hydrophobic expulsion (Perrich, 1981). Metals, on the other hand, tend to sorb via an electrostatic attraction or surface complexation reaction. In addition, metals can be immobilized by manipulating the solubility of the metal by raising the pH or adding excess ions to form an insoluble mineral. Precipitation of metals by reduction to a less soluble form is a combination of a transformation process followed by an immobilization process and is reviewed in the sections on chemical reaction barriers and biological barriers. Both sorption and precipitation processes are generally reversible and therefore may require removal of the reactive materials and accumulated products, depending on the stability of the immobilized compound and the geochemistry of the groundwater.

Transformation of the contaminant to a less harmful compound via irreversible reactions, on the other hand, does not necessarily require removal of the reactive medium (unless reactivity diminishes or clogging occurs). Transformation within a reactive barrier is most commonly an irreversible redox reaction in which the contaminant is reduced or oxidized. The medium may directly supply electrons for reduction (e.g., iron metal and iron minerals) or indirectly stimulate microorganisms to mediate electron transfer by providing an additional electron acceptor (e.g., providing oxygen to stimulate aerobic degradation) or an electron donor (e.g., supplying a carbon source to stimulate heterotrophic denitrification).

TABLE 1
Reactive Media for Treatment of Inorganic Groundwater Contaminants in PRBs

Reactive Medium	Removal Mechanism	Contaminants Removed	References
Ferric ovahudrovide	Mechanism Sorption	uranium, molybdenum,	Morrison and Connector 1002
Ferric oxyhydroxide	borption	chromium	Morrison and Spangler, 1993 Morrison and Spangler, 1996
			Morrison et al., 1995
			Zachara et al., 1987
Peat moss	Sorption	Chromium, copper, zinc, nickel, cadmium, uranium, molybdenum	Crist et al., 1996
			Gosset et al., 1986
			Ho et al., 1995
			McLellan and Rock, 1987
			Morrison and Spangler, 1992
			Sharma and Forster, 1993
Modified Zeolites	Sorption	Lead, chromium, selenium, sulfate, cadmium	Bowman et al., 1995
			Haggerty and Bowman, 1994
			Kesraoui-Ouki et al., 1993
			Lee et al., 1989
			Li and Bowman, 1997, 1998b
Chitosan	Sorption	Mercury, uranium, cadmium,	Mitani et al., 1991
		lead, vanadium, nickel,	
		molybdenum, titanium,	
0	G d	selenium etc.	V. H
Spodic material	Sorption	Arsenic	Lindberg et al., 1997
Sawdust, lignite, coal	Sorption	Molybdenum, uranium	Morrison and Spangler, 1992
Titanium oxide	Sorption	Molybdenum, uranium Uranium	Morrison and Spangler, 1992
Ferric chloride (with	Sorption	Oranium	Morrison and Spangler, 1992
CaCO ₃) Ferric nitrate	Cametinu	Molybdenum	Marriagn and Spanisher 1002
	Sorption	Monyodenam	Morrison and Spangler, 1992
Ferric sulfate Hydroxyapatite	Precipitation	Lead	Ma et al., 1993
Natural apatite	Frecipitation	Dodu	Ma et al., 1994a and b
			Ma et al., 1995
Ferrous sulfate	Precipitation	Molybdenum, uranium	Morrison and Spangler, 1992
Calcium chloride		,	
Barium chloride			
Hydrated lime	Precipitation	Uranium	Morrison and Spangler, 1992
Fly ash			-
Limestone	Precipitation	Acid mine drainage	Hedin et al., 1994
			Turner and McCoy, 1990
Zero-valent iron	Chemical reduction	Chromium, uranium,	A complete set of iron metal
		technetium, nitrate, nitrite,	references can be found at the web site maintained by Dr. Paul
		Molybdenum, silver, sulfate,	Tratnyck of the Oregon Graduate
		mercury	Institute:
			http://cgr.ese.ogi.edu/ironrefs/
Iron minerals	Chemical	nitrate, chromate	Hansen et al., 1996
	reduction		Peterson et al., 1997
Zero-valent iron	Lower redox	Acid mine drainage	Shelp et al., 1995
	potential and metal	-	- · ·
	precipitation		
Organic material	Microbial sulfate	Acid mine drainage	Benner et al., 1997
	reduction and		
	precipitation		
Organic material	Microbial nitrate	Nitrate	Robertson and Cherry, 1995
		1414416	Robertson et al., 1991
	reduction		Augenson et al., 1991

TABLE 2
Reactive Media for Treatment of Organic Groundwater Contaminants

Reactive Medium	Removal Mechanism	Contaminants removed	References
Zero-valent iron	Chemical reduction	Chlorinated aliphatics,	A complete set of iron metal
		DDT, DDD, DDE,	references can be found at the web
	1	nitroaromatics, some	site maintained by Dr. Paul
	'.	pesticides, azo dyes	Tratnyek of the Oregon Graduate
			Institute:
			http://cgr.ese.ogi.edu/ironrefs/
Bimetallic iron	Chemical reduction	Chlorinated aliphatics,	Grittini et al., 1995
		PCB's	Liang et al., 1997a
			Muftikan et al., 1995
			Orth et al., 1998
Magnesium, tin and	Chemical reduction	Chlorinated aliphatics	Arnold and Roberts, 1998
zinc		1	Fennelly and Roberts, 1998
			Warren et al., 1995
		1	Boronina et al., 1995
			Boronina et al., 1998
		}	Song, et al., 1999
],		Su and Puls, 1999
Iron minerals (oxides,	Chemical	nitroaromatics,	Kriegman-King and Reinhard 199
hydroxides, and	reduction	chlorinated aliphatics	Kriegman-King and Reinhard 199
sulfides)	-	ļ	Kriegman-King and Reinhard 199
			Butler and Hayes 1998
		1	Haderlein and Pecher, 1998
	1		Sivavec, et al., 1997
•		1.	Klausen et al., 1995
Oxygen-releasing	Microbial degradation	BTEX	Bianchi-Mosquera et al., 1994
compounds	Microbian degradation	DILLA	Borden et al., 1997
Nitrate-releasing			Kao and Borden, 1997
compounds	,		Rao and Borden, 1997
Resting-state	Microbial	Chlorinated aliphatics	Duba et al., 1996
microorganisms	cometabolism '		Taylor et al., 1993
Surfactant-modified	Sorption .	Nonpolar organics	Burris and Antworth, 1992
soils			Lee et al., 1989
			Wagner et al., 1994
Surfactant-modified	Sorption	Nonpolar organics	Smith and Galan, 1995
clays			Smith and Jaffé, 1994
	4.	11.	Smith et al., 1990.
Surfactant-modified zeolites	Sorption , ,	Nonpolar organics,	Bowman et al., 1995
Coal, powdered	Sorption	Benzene	Rael et al., 1995
activated carbon, peat,	p]	
activated cathon pear)	1	

The following three sections discuss the types of reactive materials used in sorption (Section III), chemical reaction (Section IV), and biological barriers (Section V). Emphasis is placed on the chemical and biochemical mechanisms governing the applicability and limitations of these media.

III. SORPTION BARRIERS

Sorption reactions remove contaminants from a groundwater plume via partitioning from the dissolved phase to a solid medium. Sorption is a general term that is used to describe several mechanisms by which a contaminant may partition to a surface. Sorption mechanisms are often classified as adsorption, absorption, and precipitation reactions (Brown, 1990). Precipitation reactions involve the formation of a solid of different composition than the solid medium. The precipitate phase is defined by a three-dimensional structure that is not influenced by the solid medium. Adsorption, on the other hand, is defined as accumulation at the solid-water interface without the formation of a three-dimensional structure. Absorption implies that the contaminant has diffused or partitioned within the bulk of the solid medium.

Of the three sorption mechanisms, adsorption has received the most attention as a feasible mechanism for removal of contaminants in PRBs. Adsorption is a combination of three possible mechanisms: (1) hydrophobic expulsion (dislike of water), (2) electrostatic attraction (opposite charges attract), and/or (3) surface coordination reactions (hydrolysis, metal complexation, ligand exchange, or hydrogen bonding) (Westall, 1987; Schindler, 1990). Table 3 outlines various terms used to describe sorption mechanisms and provides examples of contaminants that are strongly influenced by the individual mechanisms. Hydrophobic expulsion is the dominant mechanism for most nonpolar (uncharged) organic compounds (e.g., most chlorinated solvents). Partitioning into organic matter present in soils, however, should be viewed as an absorption process, whereby the organic contaminant dissolves into the soil organic matter (Stumm, 1992). Hence, the degree of partitioning is strongly correlated to both the compound's octanol-water coefficient, K_{ow} , and the fraction of organic matter present in the solid material, f_{oc} (Schwarzenbach and Westall, 1981; Karickhoff, 1984).

Polar compounds (such as metals and inorganic nutrients), on the other hand, tend to sorb via electrostatic attraction and surface complexation reactions. Electrostatic attraction is the weaker of the two forces and involves nonspecific adsorption of a charged compound at an oppositely charged surface. A layer of coordinated water molecules separates the compound from the surface, providing only an indirect attachment to the surface, known as outer sphere adsorption. The replacement of one weak (or outer-sphere) ion with another is also known as ion exchange. Unlike electrostatic interactions, surface coordination reactions, such as metal complexation and ligand exchange, involve direct contact between the surface and the contaminant (Westall, 1986; Dzombak and Morel, 1990; Sposito, 1995). The surface reaction is not influenced by a layer of intervening coordinated water molecules and thus is considered inner sphere or specific adsorption. Surface complexation is the dominant mechanism of sorption for most transition metals (with the exception of some of the alkali and alkaline earth metals, Group I and IIA of the periodic table) (Schindler, 1990).

TABLE 3
Major Adsorption Mechanisms

Mechanism	Other Terminology	Examples
hydrophobic expulsion	partitioning	nonpolar organics (e.g., PCBs, PAHs, etc.)
electrostatic attraction	outersphere nonspecific physisorption, physical ion exchange	some anions (e.g., NO ₃ -) alkali and alkaline earth metals (Ba ²⁺ , Ca ²⁺)
complexation reaction	innersphere specific chemisorption, chemical ligand exchange	Transition metals (e.g. Cu ²⁺ , Pb ²⁺ , CrO ₄ ²⁻)

The success of sorbent materials in reactive barriers will depend primarily on the strength of the sorbed complex and the capacity of the material to sorb a particular contaminant. These materials have the advantage of not introducing any chemicals into the groundwater, but the disadvantage that the efficacy of the material depends on the geochemistry of groundwater (e.g., pH and major anions and cations). Proposed materials for use in reactive barriers include: (1) surfactant-modified zeolites, (2) humic materials, (3) oxides, and (4) precipitation agents. A discussion of the dominant sorption mechanism and the implication for field-scale application of these materials is presented below.

A. Surfactant-Modified Zeolites '

Many natural materials, such as clays and zeolites, have a high capacity for ion exchange, particularly cation exchange. A net negative charge is created on clays and zeolites by substitution of lower-valent cations (e.g., Al³+) for higher-valent cations (e.g., Si⁴+) within the mineral structure (Bohn et al., 1985). The negatively charged surface, in combination with the high surface area of these materials, creates a strong affinity for positively charged contaminants, such as transition metal cations (e.g., Pb²+, Cd²+), but little affinity for anions and nonpolar organic compounds.

Modification of clays and zeolites with sorbed surfactants can substantially change the affinity of these materials for anions and nonpolar organic compounds. Surfactants are amphiphilic substances which contain a hydrophilic portion (com-

monly called the "charged head") and a hydrophobic segment (commonly called the "tail") (Rosen 1989). Exchange of a positively charged surfactant head group with the cations substituted on the surface of the zeolite will orient the hydrophobic portion of the surfactant towards the solution (Ulrich and Stumm 1988). Accumulation of the surfactants at the surface will create a hydrophobic organic coating which has been shown to promote sorption of non-polar organic compounds (e.g., Brownawell et al. 1990; Sheng et al. 1996; Hayworth and Burris 1997; Burris and Antworth, 1992).

The large sorption capacities of surfactant modified zeolites (SMZ) and clays suggest a promising material for treating non-polar organic contaminants. Indeed, organoclays have been proposed for use in landfill liners, slurry walls, and containment barriers (Sheng et al. 1996). The low permeability of clays, however, excludes clays from use in flow-through reactive barriers. Zeolites, on the other hand, tend to have an open framework, with large cavities capable of maintaining a good hydraulic conductivity in permeable barriers. Extensive studies of SMZ's conducted by Bowman and coworkers* suggest that SMZs are capable of removing nonpolar organic compounds (Li and Bowman, 1998a), transition metal cations (Bowman et al., 1995), and inorganic oxyanions (Haggerty and Bowman, 1994; Li and Bowman, 1997; Sullivan et al., 1998). Figure 5 illustrates the proposed removal mechanisms for oxyanions and metal cations.

As discussed earlier, the enhanced sorption of nonpolar organic compounds to surfactant-coated materials has been recognized as a potential remediation technology for several decades (Lee et al., 1989). Although hydrophobic expulsion is considered the dominant mechanism, there is some evidence that the structure of the surfactant monomers at the surface also plays a role in controlling the partitioning of nonpolar organic compounds to the SMZ surface (Li and Bowman, 1998a). The structure of surfactants sorbed on a charged surface have been shown to transition from a single monolayer to a bilayer (admicelle) as the concentration of surfactant in solution is increased (Yeskie and Harwell, 1988; Holsen et al., 1991). Figure 6 provides an illustration of the four *idealized* regions for sorption of a cationic surfactant on a surface with a net negative charge (such as a zeolite). At low surfactant concentrations, sorption of the surfactant is due to electrostatic forces resulting in monomers spread out over the surface (Region I). As the surfactant concentration increases (Region II), the hydrophobic tails begin to associate and form patches of hemimicelles, creating hydrophobic regions that attract further surfactant sorption. The transition to Region III is marked by a decreasing rate of surfactant sorption as the surface charge is neutralized, eliminating the electrostatic attraction. Beyond this point, a second layer of monomers may form, creating an admicelle with the positively charged head groups oriented toward the solution. Finally, when the surfactant concentration exceeds the critical micelle concentration (CMC) (Region IV), the organic interiors of the solution

For up to date information on an SMZ pilot-scale study conducted jointly by New Mexico Institute of Mining and Technology and Oregon Graduate Institute see http://cgr.ese.ogi.edu/smz/p2smz.htm

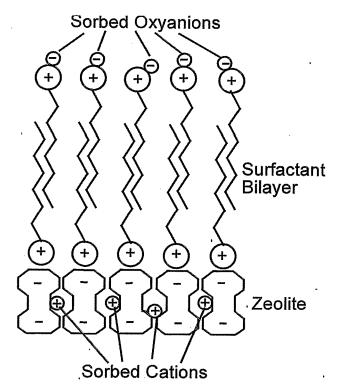


FIGURE 5. Schematic illustrating the proposed mechanisms for oxyanion and metal cation sorption onto surfactant modified zeolites.

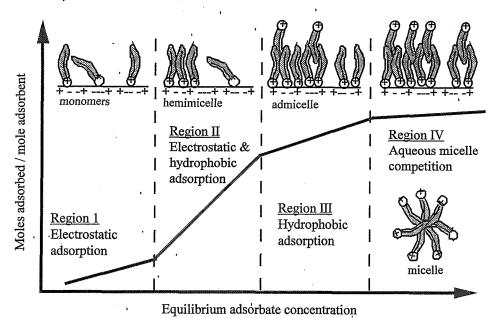


FIGURE 6. Relationship between growth of surfactant aggregates and surfactant adsorption isotherm. Schematic drawn for sorption of a cationic surfactant on a polar surface. (Adapted from Chandar et al., 1987; Yeskie and Harwell, 1988.)

micelles will start to compete with the surface causing the extent of surfactant sorption to level off.

Removal of nonpolar organic contaminants by SMZs has been shown to occur in all Regions (from low concentrations up to concentrations exceeding the CMC) (Li and Bowman, 1998a). Experiments with common groundwater contaminants, such as BTEX compounds (benzene, toluene, ethylbenzene, p-xylene) and chlorinated solvents (perchloroethene, 1,1,1-trichlorethane, and pentachloroethane) have demonstrated the effectiveness of SMZs. Removal efficiency, however, as measured by the organic carbon normalized partition coefficient (K_{oc}), was found to decrease as a surfactant bilayer (admicelle) began to form (Figure 6, Region III). The decrease in efficiency is most likely due to the formation of a positively charged surface, which no longer provides a hydrophobic coating to promote sorption of the nonpolar organic compound (Bowman et al., 1995). Therefore, the most effective removal of nonpolar organic contaminants will be achieved at concentrations below where admicelles form (i.e., submonolayer or monolayer coverage, Figure 6, Regions I and II).

The sorption of inorganic anions, on the other hand, is favored by the formation of a positively charged surfactant bilayer (Sullivan et al., 1998). Based on the negative charge of the unmodified zeolite, and the hydrophobic surface of the SMZ, little or no anion sorption was expected on SMZs (Haggerty and Bowman, 1994). batch experiments with the cationic surfactant, Yet. hexadecyltrimethylammonium (HDTMA) and the zeolite, clinoptilolite, revealed significant sorption of chromate (CrO₄²⁻), selenate (SeO₄²⁻), and sulfate (SO₄²⁻). Spectroscopic evidence and competition experiments suggest that the anions are sorbing via an ion exchange mechanism with the counterions sorbed to the surface of the positively charged surfactant bilayer (see Figure 5) (Sullivan et al., 1998; Li et al., 1998b). The ability to exchange inorganic anion contaminants, such as chromate, was found to vary depending on the counterion. Specifically, a trend of increased chromate sorption was found with the counterions: Cl⁻ < Br < HSO₄⁻. The ability to sorb transition metal cations is only slightly lowered by the surfactant treatment of natural zeolites. One explanation is that HDTMA and other large surfactant cations only occupy the external surface of the zeolite. As illustrated in Figure 5, the internal exchange sites are then still available for sorption of small cations, such as Pb²⁺ (Bowman et al., 1995).

The ability to remove nonpolar organic compounds, metals, and anions make SMZs a promising, low-cost alternative for treating mixed contaminant plumes with PRBs. There are, however, several factors to consider in the application of SMZs as a sorbent media in reactive barriers. First, the surfactant concentration influences the sorption of both anions and nonpolar organic compounds. Unfortunately, sorption of nonpolar organic compounds is favored at low concentrations (in the submonolayer or monolayer Regions I and II of Figure 6), whereas sorption of anions is favored at high concentrations (where a positively charged bilayer forms, Region III of Figure 6). Second, counterions, and therefore the composition

of the groundwater will have a significant effect on anion sorption. Large-scale studies are currently being conducted to evaluate the capacity of the SMZs for each type of contaminant and potential removal or regeneration strategies for saturated material. The influence of both surfactant concentration and groundwater composition on the ability of SMZs to sorb anions will require careful characterization of the groundwater geochemistry to ensure optimum conditions.

B. Humic Materials

Humic materials, particularly peat and activated carbon, have been used as effective sorbents in wastewater treatment for many years (Perrich, 1981; Couillard, 1994). Humic materials are complex organic molecules with molecular weights ranging from 500 to 20,000 (Leventhal, 1980). Humic materials contain a wide variety of functional groups, including phenolic and carboxylic groups, which provide exchange sites for the sorption of cations, such as heavy metals (e.g., Pb²⁺ and Cd²⁺) and anions (e.g., CrO₄²⁻, MoO₄²⁻). In addition, the high carbon content of these materials may make humic materials a suitable sorbent for nonpolar organic compounds.

The sorption efficiency of several humic materials, including sawdust, lignite, peat moss, Cercona Bone-Char, and subbituminous coal has been studied for the removal of uranium (U), and molybdenum (Mo) (Morrison and Spangler, 1992; Gu et al., 1998). Coal removed roughly 50% of the initial Mo and U. Sawdust removed about 90% of the U, but only small amounts of Mo. Lignite showed a U removal efficiency of 98%, but was relatively ineffective for removing Mo. Of the five organic materials evaluated, peat moss was only material that effectively removed both U and Mo.

Peat moss is a widely available and inexpensive natural substance that has a large specific surface area (>200 m²/g) and a high porosity (McLellan and Rock, 1988). The uptake of metals by peat materials is considered an ion exchange reaction where the metal displaces either a proton (at low pH) or existing metal (at high pH) from the anionic functional groups (Crist et al. 1996). The exchange reaction is highly dependent on pH. Anions, such as CrO₄²⁻ and MoO₄²⁻ are removed more effectively at low pH (<3) because of the positively charged surface created by protonation of the surface functional groups (Morrison and Spangler, 1992; Sharma and Forster, 1993). When the pH increases, little removal of anions. such as arsenite and arsenate, is observed (Lindberg et al., 1997). Cations, on the other hand, such as UO22+, Ni2+, Cu2+, Zn2+, and Cd2+, are more effectively removed at high pH values (Morrison and Spangler, 1992; Gosset et al., 1986; Ho et al., 1995; Crist et al., 1996). Based on the above studies, it appears that peat moss is an effective ion-exchange material for the removal of heavy metals and some anions. The removal efficiency for cations can become close to 100% at low pH, but both the strong pH dependency and the initial metal ion concentration have to be considered.

Although humic materials appear to be effective at removing heavy metals, the removal of non-polar organic compounds does not look promising. The high fraction of organic carbon in humic materials, such as coal and sawdust, does not appear to be effective for retaining benzene (Rael et al., 1995). Activated carbon, on the other hand, has been shown to remove benzene when sufficiently long enough residence times were used. The long residence times, however, are not feasible for current PRB technologies.

C. Oxides

The sorption and exchange of anions and cations to naturally occurring oxides and clays has been recognized for well over a century (Thomas, 1977). Sorption onto these natural materials has been used for the treatment of industrial wastewaters (Aoki and Munemori, 1982) and may provide a promising alternative for containment of metals (Morrison et al., 1995; Morrison and Spangler, 1993). Natural oxides that have been investigated for use in a reactive barrier include: amorphous ferric oxide (Fe(OH)₃), goethite (α -FeOOH), hematite (α -Fe₂O₃), magnetite (Fe₃O₄), and hydrous titanium oxide (Ti(OH)₄). In addition, the sorption of metals onto a variety of oxides and clays has been studied extensively to determine the fate and transport of metals in subsurface environments (Zachara et al., 1987; Ainsworth et al., 1989; Ford et al., 1997; Raven et al., 1998; Robertson and Leckie, 1998).

The sorption of an ion at a charged oxide surface can be a combination of both electrostatic attraction and surface complexation. In general, metal ions tend to sorb via a complexation reaction (Buffle and Altmann, 1987). Both mechanisms are strongly influenced by solution pH, and it is experimentally difficult to distinguish between the two without direct spectroscopic measurements (Wersin et al., 1984; Charlet and Manceau, 1992). Example reactions describing the surface complexation of U(VI), Mo(II), and Cr(VI) are represented by Eqs. 3.1 through 3.3 (Morrison and Spangler, 1992; Zachara et al., 1987).

$$SOH + UO_2^{2+} + 3 H_2O \div SOH - UO_2(OH)_3 + 2 H^+$$
 (3.1)

$$2 \text{ SOH} + \text{MoO}_4^{2-} + 2 \text{ H}^+ \div (\text{SOH}_2)_2 - \text{MoO}_4$$
 (3.2)

$$SOH + CrO_4^{2-} + H^+ \div (SOH_2^+ - CrO_4^{2-})^{-}$$
(3.3)

where S =oxide surface site

Anions, such as molybdenate and chromate, tend to sorb more at lower pH values because of increased surface protonation, which creates a more positively charged surface. Cations, on the other hand, tend to sorb more at higher pH because

of the deprotonation of the surface, which creates a negatively charged surface. The sorption of uranium (UO₂²⁺), for example, increases significantly at pH values greater than four. The removal of both anions and cations will require careful control of the pH within the barrier. Batch studies conducted by Morrison and Spangler found that a pH value of six was effective for the removal of both molybdenate and uranium (Morrison and Spangler, 1992). An additional drawback to the use of oxides as a sorbent material in PRBs is the competition of other anions (such as sulfate and carbonate) for surface sites (Zachara, 1987; Morrison and Spangler, 1993 and 1995).

Spodic soil materials (B horizon soils) are comprised of various aluminum and iron oxides that have the potential for surface complexation and ion exchange processes. Lindberg and co-workers have shown that spodic material can effectively remove arsenic from groundwater (Lindberg et al., 1997). In natural waters, arsenic exists in two oxidation states, As(III) and As(V). As(III), or arsenite, exists primarily as an uncharged species (H₃AsO₃), whereas the dominant forms of As(V) are anions (H₂AsO₄ and HAsO₄²-). The performance and lifetime of spodic soil material, however, may vary significantly with different soil samples. As found with other sorbent materials (e.g., humic materials), the effect of competing or complexing ions, such as sulfate and carbonate, has to be considered.

The sensitivity to geochemical changes, such as pH and presence of competing ions, will require careful management of field applications that use oxides as a sorbent material. It may be necessary to incorporate additional materials to maintain optimal pH conditions. The optimal pH range depends on both groundwater composition and contaminant speciation.

D. Precipitation Agents

Immobilization of contaminants via precipitation is a significantly different mechanism than adsorption to a solid medium. Precipitation of a mineral or oxide occurs when the solubility limit is exceeded in solution. The precipitate phase has a three-dimensional structure that is not influenced by the surface of the solid medium (Brown, 1990). Therefore, PRBs that are based on a precipitation mechanism typically involve solution amendments that manipulate the solubility limit. The most common methods of manipulating solubility limits are to raise the pH by the addition of a base, such as hydrated lime (Ca(OH)₂), or to add excess ions to form an insoluble mineral.

The addition of lime (CaO), hydrated lime, or limestone (CaCO₃) is a common method for raising the pH of a number of engineered (e.g., sludge treatment) and natural systems. Limestone has been used as a passive treatment technology for acid mine drainage (AMD) for several years (Hedin et al., 1994; Davis et al., 1999). The high concentrations of dissolved Fe and Mn result in waters with very high mineral acidity. The use of a treatment wall containing limestone, known as anoxic

limestone drains (ALDs), has the potential for increasing the pH and alkalinity of the mine water before it enters a wetland system for precipitation. Potential problems of ALDs are the low solubility of limestone and the coating of the limestone with ferric hydroxides if strict anoxic conditions are not maintained. The ALD concept has been extended to consider removal of metals and nutrients in PRBs (Morrison and Spangler, 1992; Baker et al., 1998). The addition of small amounts of hydrated lime was found to effectively remove uranium from aqueous solution, presumably due to the precipitation of a calcium uranate (Morrison and Spangler, 1992). A mixture of crushed limestone and sand was found to reduce the concentration of phosphate, again most likely due to the formation of a calcium phosphate precipitate (Baker et al., 1998).

The second method of enhancing precipitation is through the addition of an excess ion. For example, high concentrations of phosphate in the presence of Pb²⁺ will cause the precipitation of insoluble lead phosphates. Phosphate minerals, such as apatites (Ca₁₀(PO₄)₆(OH)₂), can be used for *in situ* treatment technologies, such as PRBs, for precipitation of low solubility metal phosphates (Ma et al., 1993; Ma et al., 1994a; Ma et al., 1994b; Ma et al., 1995; Chen et al., 1997). The major mechanism for Pb²⁺ removal appears to be the formation of hydroxypyromorphite [Pb₁₀(PO₄)₆(OH)₂]. Other removal mechanisms, however, such as ion exchange and surface adsorption may be important in the phosphate-based removal of Cd and Zn (Chen et al., 1997). Aqueous aluminum, cadmium, copper, ferrous iron, nickel and tin can hinder the removal of lead by precipitation of phosphate minerals. The presence of anions, such as nitrate, chloride and sulfate, do not significantly affect lead removal; however, high carbonate concentrations result in lower lead removal efficiency due to lower hydroxyapatite solubility at increased pH values.

The significant lead removal by hydroxyapatite, the rapid reaction rate, and the stable products indicate the high potential for lead removal by hydroxyapatites from groundwater. While the efficiency of hydroxyapatite for lead removal is greater than the efficiency of naturally occurring phosphate rock, the advantage of the latter might be the lower cost factor. The effect of the precipitation of the pyromorphite material on the hydraulic conductivity of the surrounding soil may be an important issue with respect to the application of apatite and phosphate rock in reactive subsurface barriers.

Immobilization by precipitation has the advantage that precipitation reactions tend to be less dependent on groundwater conditions than adsorption reactions. For example, precipitation agents, such as limestone and apatite minerals, often provide some control of pH. Sorption reactions, on the other hand, can be highly dependent on pH. A disadvantage of precipitation reactions, however, is that groundwater additions are often required that may degrade the groundwater composition (e.g., adding limestone will significantly increase the hardness of the groundwater). The most significant challenge for both immobilization techniques

(i.e., adsorption and precipitation) is assessing the stability of the contaminant and the risk of future remobilization by desorption or dissolution.

IV. CHEMICAL REACTION BARRIERS

Chemical reaction barriers, unlike sorption or precipitation barriers, transform contaminants into different chemicals. The goal is to produce chemicals that are less toxic or less mobile than the original compound. Transformation within a chemical reaction barrier most often involves a redox reaction in which the contaminant is reduced (gains electrons) and the reactive medium is oxidized (loses electrons). The transfer of electrons from the reactive medium to the contaminant needs to be both thermodynamically favorable (i.e., $\Delta G_{rxn} < 0$) and kinetically facile for the medium to be effective. Viable media that have been proposed include zero-valent metals and reduced minerals.

A. Zero-Valent Metals

1. Iron Metal

Zero-valent metals such as iron, tin, and zinc are moderately strong reducing agents that are capable of reducing many common environmental contaminants. Of these metals, granular iron metal has received a great deal of attention because of the pioneering work of Gillham and O'Hannesin, (Gillham and O'Hannesin, 1992; Gillham and O'Hannesin 1994). Early studies of reduction by iron metal focused primarily on chlorinated aliphatics (RCl), and, only recently, has the reduction of other compounds such as metals (Cantrell et al. 1995; Powell et al., 1995; Liang et al., 1996; Blowes et al., 1997; Pratt et al., 1997; Fiedor et al., 1998), nitrate (Huang et al., 1998; Till et al., 1998; Zawaideh and Zhang, 1998), munition wastes (Agrawal and Tratnyek, 1996; Devlin et al., 1998; Singh et al., 1998a), and pesticides (Sayles et al., 1997; Eykholt and Davenport, 1998; Singh et al., 1998b) received significant attention.*

It was quickly recognized in the early studies with chlorinated aliphatics that reduction by iron metal was a well-known process to both organic chemists and corrosion scientists (Gillham and O'Hannesin, 1994; Johnson and Tratnyek 1994; Lipczynska-Kochany et al., 1994; Matheson and Tratnyek, 1994; Schreier and Reinhard, 1994). The transformation process is a redox reaction where the iron metal is oxidized and the chlorinated aliphatic is reduced. Iron metal is powerful reductant with a reduction potential of -0.44 V (Eq. 3.4). The relative

A complete set of iron metal references can be found at the web site maintained by Dr. Paul Tratnyek of the Oregon Graduate Institute: http://cgr.ese.ogi.edu/ironrefs/

$$Fe^0 \to Fe^{2+} + 2e^-$$
 (3.4)

stability of iron in the presence of three common environmental contaminants is represented as a function of redox potential (E_h) and pH in Figure 7. The relative position of each line in Figure 7 provides information about the stability of the individual compounds. For example, both iron metal (Fe^0) and dissolved ferrous iron (Fe^{2+}) are oxidized in the presence of oxygen (because the $O_2 \rightarrow H_2O$ line is higher). The relative positions of the perchloroethene (C_2Cl_4), nitrobenzene ($ArNO_2$), and chromate (CrO_4^{2-}) lines indicate that Fe^0 is thermodynamically capable of reducing these common environmental contaminants.

Originally, three general pathways were hypothesized for the reduction of chlorinated aliphatics (specifically, carbon tetrachloride) by iron metal (Matheson

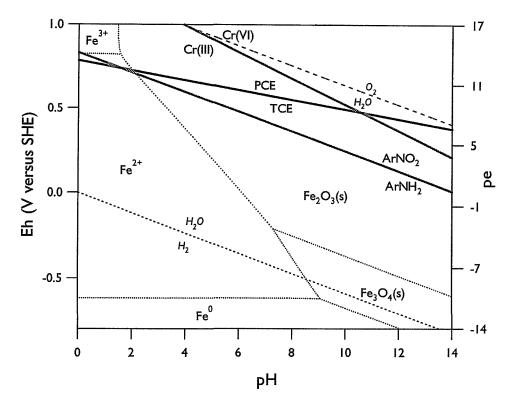


FIGURE 7. Eh-pH diagram (or Pourbaix diagram) showing equilibria with water, iron, and common environmental contaminants including perchloroethene (PCE), nitrobenzene (ArNO₂), and chromate (Cr(VI)). Hematite (α -Fe₂O₃) and magnetite (Fe₃O₄) are assumed to be the controlling phases for iron speciation. The stability lines for the reduction nitrobenzene (ArNO₂) to aniline (ArNH₂), Cr(VI) to Cr(III), and PCE to TCE are superimposed to show the instability of Fe⁰ in the presence of these contaminants.

and Tratnyek, 1994). The first pathway (Figure 8A) involves direct transfer of electrons from the iron metal to the chlorinated aliphatic. The second pathway (Figure 8B) involves reduction of the chlorinated aliphatic by dissolved or surface Fe²⁺ ions formed from the oxidation of iron metal by water (also known as anaerobic corrosion, Eq. 3.5).

$$Fe^{0} + 2 H_{2}O \rightarrow H_{2(g)} + 2 OH^{-} + Fe^{2+}$$
 (3.5)

The third pathway (Figure 8C) involves reduction of the chlorinated aliphatic by dissolved or surface hydrogen generated as a product of anaerobic corrosion. Both dissolved Fe²⁺ and hydrogen were eliminated as potential reductants based on the results of control experiments with FeCl₂ and H₂ saturated water. However, neither surface-bound Fe²⁺ (Fe²⁺_(sur)) or surface-bound H₂ (possibly as H• or H⁻) could be excluded as potential contributors to the reduction of carbon tetrachloride.

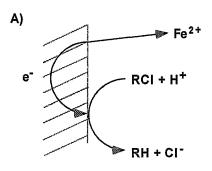
In addition to multiple reducants, there are also multiple pathways for the reduction of chlorinated aliphatics. The predominant pathway for chlorinated methanes appears to be reductive dechlorination (also called hydrogenolysis, Eq 3.6). For chlorinated ethenes, in addition to hydrogenolysis, significant amounts of reductive elimination have also been reported (Roberts et al., 1996; Campbell et al., 1997; Fennelly and Roberts, 1998).

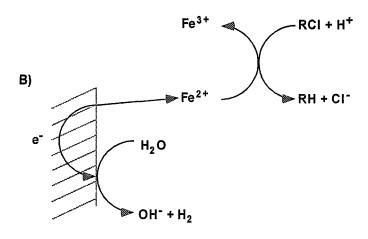
$$RC1 + H^+ + 2 e^- \rightarrow RH + X^-$$
 (3.6)

Both pathways involve a net transfer of two electrons. Hydrogenolysis involves replacement of a chlorine atom with a hydrogen atom (e.g., reduction of PCE to TCE), whereas reductive elimination involves removal of either two chlorines, or a hydrogen and a chlorine, and formation of a C-C double bond or triple bond (e.g., reduction of PCE to dichloracetylene). The resulting product distributions will be significantly different and additional studies are needed to quantify the relative contributions of each pathway before the impact on Fe⁰ PRBs can be assessed.

Despite the uncertainty regarding the dominant reductive dechlorination pathway and the identity of the actual reductant (i.e., Fe^0 , $Fe^{2+}_{(sur)}$, or H_2), it is clear that the transformation process is a surface reaction that requires close contact of the reactive medium and the contaminant (Weber, 1996). Surface redox reactions are comprised of a series of physical and chemical processes including: (1) mass transport of the dissolved contaminant from a well mixed bulk solution to the surface (2) sorption of the contaminant to the surface (e.g., precursor complex formation or surface complex formation), (3) transfer of electrons (ET) from the surface to the contaminant, and (4) desorption of the contaminant from the surface (Stumm, 1992). Any one of these four steps can limit the rate of contaminant reduction by Fe^0 .

The first step, mass transport to the surface, has been shown to have little influence on the reduction rate of chlorinated aliphatics at a bare Fe⁰ electrode





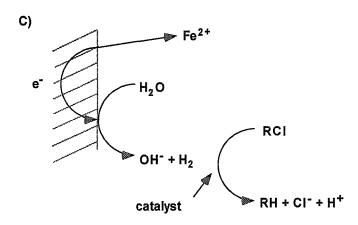


FIGURE 8. Scheme showing proposed pathways for reductive dehalogenation in Fe^0 - H_2O systems: (A) direct electron transfer from iron metal at the metal surface; (B) redcution by Fe^{2+} , which results from corrosion of the metal; (C) catalyzed hydrogenolysis by the H_2 that is formed by reduction of H_2O during anaerobic corrosion (Matheson and Tratnyek, 1994). Stoichiometries are not shown. (Reprinted with permission from the American Chemical Society.)

(Scherer et al., 1997). Reduction rates of chlorinated aliphatics, however, are significantly slower than some other classes of environmental contaminants, such as nitro aromatics (Agrawal and Tratnyek, 1996; Devlin et al., 1998; Scherer et al., 1999) and azo dyes (Weber, 1996; Nam and Tratnyek, 1999). The faster reduction rates of azo dyes and nitro aromatics suggest that mass transport effects may be more significant for these contaminants. Indeed, both batch and column experiments have revealed significant mass transport limitations for nitro aromatics (Agrawal and Tratnyek, 1996; Devlin et al., 1998; Scherer et al., 1999) and azo dyes (Weber, 1996; Nam and Tratnyek, 1999). It is important to note that additional mass transport limitations may arise in Fe⁰ PRBs due to pore diffusion (i.e., intraparticle diffusion) through the highly porous oxide layer that forms on the surface of the metal (Burris et al., 1998). The implications of mass transport limitations on the design and implementation of Fe⁰ PRBs has yet to be addressed.

The remaining three steps are a series of chemical reaction steps that are difficult to distinguish among. There is some evidence that step (2), sorption, influences the reduction rate by limited availability of reactive surface sites (Arnold and Roberts, 1997; Johnson et al., 1998; Scherer et al., 1998b) or sorption to nonreactive surface sites (Burris et al., 1995; Allen-King et al., 1997; Campbell et al., 1997; Burris et al., 1998). A study of four different types of iron metal suggest that sorption without immediate dechlorination is occurring at exposed graphite inclusions and is strongly dependent on the hydrophobicity of the contaminant (Burris et al., 1998). Identification of nonreactive sites as graphite inclusions may explain why similar behavior has not been observed in studies conducted with higher purity iron metal (Johnson et al., 1998).

Although it is difficult to distinguish between sorption (step 2) and electron transfer (step 3), a strong correlation between reduction rates of chlorinated aliphatics, and a variety of measures of electron affinity suggests that ET plays a significant role in the reduction process (Scherer et al. 1998a). Several lines of indirect evidence, including (1) negligible hydrogen production during dechlorination at a bare Fe⁰ electrode, and (2) a strong correlation between dissolved ferrous iron and carbon tetrachloride concentrations, suggest that most of the observed reduction is due to reaction with Fe⁰ or Fe²⁺(sur), and little, if any, involves H₂ (or H• or H⁻) at near neutral pH values (Johnson and Tratnyek, 1995; Scherer et al., 1997). Three mechanisms of electron transfer between the Fe⁰-oxide interface and the chlorinated aliphatic have been hypothesized (Scherer et al. 1998b). The first pathway involves ET from the bare metal exposed to solution at defects (e.g., pits) in the oxide layer (Figure 9A). The pitting mechanism is a localized form of corrosion that can lead to catalytic dissolution pathways. The second pathway involves ET from the conduction band of the oxide (i.e., the oxide is treated as a semiconductor) or localized states within the oxide (Figure 9B). The final pathway involves reduction by a sorbed or lattice Fe(II) surface site (Figure 9C). The significance of the individual ET pathways in reduction by Fe⁰ has yet to be resolved; however, there is some evidence that ET from granular Fe⁰ is not occurring by ET from the oxide conduction band (Balko and Tratnyek, 1998).

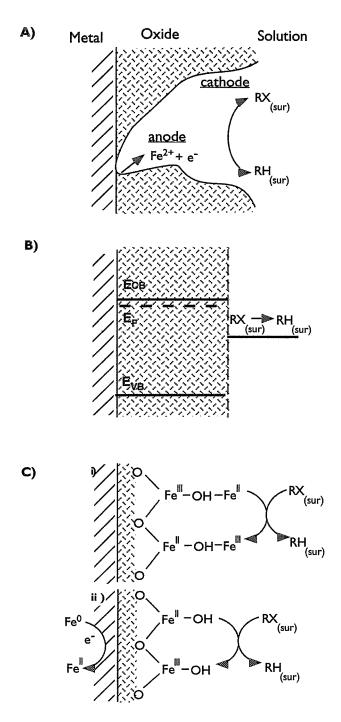


FIGURE 9. Conceptual models of electron transfer (ET) mechanisms at Fe^0 -oxide-water interface: (A) ET from bare iron metal exposed by pitting of the oxide layer; (B) ET from conduction bands in the oxide layer; (C) ET from adsorbed or lattice Fe(II) surface sites.

As with most surface reactions, the rate of reduction by Fe⁰ is dependent on the metal surface area concentration (ρ_a). In most cases, a linear relationship has been observed between reduction rates and iron metal surface area concentration (Gillham and O'Hannesin, 1994; Sivavec and Horney, 1995; Johnson et al., 1996), although there are some reports of leveling off behavior at high surface area-loadings (Gotpagar et al., 1997). If reduction rates are directly proportional to surface area, a surface area normalized rate constant (k_{SA}) can be calculated by dividing the observed rate constant (k_{obs}) by the iron metal surface area (i.e., $k_{SA} = k_{obs} / \rho_a$). Average surface area normalized rate constants have been used in a one-dimensional, steady-state advection dispersion model to predict the barrier width require to achieve a 1000-fold reduction in contaminant concentration (Tratnyek et al., 1997).

Athough much of the work with iron metal has focused on chlorinated aliphatics, substantial work has also been done with munition wastes, pesticides, nitrate, and metals.² As discussed earlier, removal of metals by Fe⁰ is a combination of a transformation process and immobilization process, where the metal is reduced to a less soluble form. The reductive precipitation of Cr(VI) and U(VI) are two examples that have received a significant amount of attention (Powell et al., 1995; Pratt et al., 1997; Gu et al., 1998; Fiedor et al., 1998). Just as with the precipitation barriers discussed in Section III, the significant challenge with the removal of metals by reductive precipitation is the potential risk of remobilization due to dissolution. Remediation of munition wastes formed during the manufacturing of explosives, such as TNT and RDX, involves the reduction of the nitro (NO₂) group, which has been studied with model nitro aromatic compounds (Agrawal and Tratnyek, 1996; Devlin et al., 1998; Singh et al., 1998a). Pesticides are more complex chemicals (e.g., alachlor, metolachlor, DDT, and atrazine), but have also been shown to be amenable to reduction by Fe⁰ (Sweeney, 1981a; Sweeny, 1981b; Sayles et al., 1997; Eykholt and Davenport, 1998; Singh et al., 1998b).

2. Other Metals and Bimetallic Couples

Iron metal is not the only metal capable of reducing environmental contaminants. Both single metals and bimetallic couples have been evaluated as potential reductants. Single metals, such as zinc and tin (Arnold and Roberts, 1998; Fennelly and Roberts, 1998; Warren et al., 1995; Boronina et al., 1995; Boronina et al., 1998; Kim and Carraway, 1999; Song, et al., 1999; Su and Puls, 1999), have been shown to reduce several chlorinated aliphatics, as well as the insecticide methyl parathion (Butler et al., 1981). Oxidation of these metals, however, often results in the release of harmful metal ions, such as Zn²⁺, that limits the use of these metals in *in situ* barriers. To overcome this problem, a combination of zinc metal and hydroxyapatite has been proposed (Song et al., 1999) to remove the dissolved Zn²⁺ by precipitation of low solubility metal phosphates (see Section III.D).

Bimetallic couples have received significant attention due to the markedly faster reduction rates reduction rates compared with iron metal alone (Fennelly and Roberts, 1998; Liang et al., 1997a; Muftikian et al., 1995 and 1996; Appleton, 1996; Wan et al., 1999). Bimetallic couples, such as Pd/Fe, have also been shown to rapidly dechlorinate some of the more recalcitrant compounds such as polychlorinated biphenyls (PCBs) and chlorinated phenols (Grittini et al., 1995; Neurath et al., 1997). Several hypotheses have been suggested to explain the observed rate increase in the presence of bimetallic couples: (1) corrosion effects introduced by the presence of a metal with a more positive reduction potential (i.e., weaker reductant), (2) catalytic hydrogenation, and (3) formation of a more powerful reductant by intercalation of hydrogen gas within the palladium lattice (Sivavec et al., 1997; Cheng et al., 1997).

A significant problem with bimetallic couples is the observed loss of reactivity over time (Sivavec et al., 1997; Muftikian et al., 1996). Surface analysis of Ni/Fe and Pd/Fe systems suggest that deactivation is caused by the formation of a thick oxide layer. Although initial laboratory- and pilot-scale studies of bimetallic systems look promising because of the fast reduction rates, there is still a great deal of uncertainty regarding the reaction mechanism, product formation, and long-term efficiency.

B. Minerals

There is substantial evidence suggesting that minerals are viable reductants for a host of environmental contaminants. Both iron and sulfide minerals have been shown to reduce chlorinated aliphatics (Kriegman-King and Reinhard, 1991; Kriegman-King and Reinhard, 1992; Kriegman-King and Reinhard, 1994; Butler and Hayes, 1998; Haderlein and Pecher, 1998; Sivavec et al., 1997), substituted nitrobenzenes (Klausen et al., 1995), and inorganic groundwater contaminants (Hansen et al., 1996; Peterson et al., 1997). Reduction by iron oxides appears to involve a surface Fe(II) species, although it is unclear how the surface Fe(II) species is formed. Surface Fe(II) species can originate from (1) reductive dissolution of Fe(III) phases and adsorption of the dissolved Fe(II), or (2) "structural" (Stucki, 1988) Fe(II) ions within the oxide lattice or within a freshly precipitated oxide coating (e.g., mixed-valent iron minerals such as magnetite and green rust). Both adsorbed Fe(II) sites and lattice Fe(II) sites (Figure 9C) have been shown to catalyze redox reactions in the presence of iron minerals. Reduction by iron sulfide minerals on the other hand has been attributed to both surface bound Fe(II) species (Sivavec et al., 1997) and surface-bound sulfur species (Kriegman-King and Reinhard, 1994).

The extent of reactivity for both iron oxides and iron sulfide minerals, however, varies dramatically depending on which mineral is present (Klausen et al., 1995; Pecher et al., 1997; Sivavec et al., 1997). Before iron minerals can be

considered a viable material for use in PRBs, additional work needs to be done to determine the capacity of these minerals to reduce contaminants and the effect of groundwater composition on the reactivity of iron minerals.

V. BIOLOGICAL BARRIERS

Many environmental pollutants such as petroleum hydrocarbons are highly reduced. Hence, the oxidation of these reduced pollutants to inocuous compounds (e.g., carbon dioxide and water) is thermodynamically feasible. On the other hand, some pollutants such as chlorinated solvents and nitrate are highly oxidized and are prone to undergo reduction. Microorganisms commonly mediate such redox reactions, often exploiting contaminant degradation as a metabolic niche to obtain energy and materials for cell synthesis.

Oxidative biodegradation requires the presence of electron acceptors that microbes use to "respire" the electrons removed from the target contaminants. This transfer of electrons releases energy to drive microbial life functions. Under aerobic conditions, molecular oxygen is utilized for this purpose. Under anaerobic conditions, nitrate, ferric iron, sulfate, and carbon dioxide can serve as electron acceptors. Often, a sequential utilization of electron acceptor is observed in contaminated sites, in preferential order of oxidation potential. Oxygen is preferentially utilized over anaerobic electron acceptors because this yields more energy to the microbial community and results in faster contaminant oxidation rates. Nevertheless, the available oxygen is often exceeded by the biochemical oxygen demand exerted by the contaminants, and anaerobic conditions often develop in highly contaminated areas. Thus, oxygen is often supplied to contaminated sites to stimulate in situ bioremediation (Lee et al., 1988). Reactive barriers containing oxygen-releasing compounds have been used successfully to stimulate aerobic biodegradation of monoaromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylenes (BTEX). Examples of such barriers are given in Section V.A.

Oxygen, however, can have a detrimental effect associated with the incidental oxidation of reduced minerals such as ferrous iron. Subsequent precipitation of metal oxides may lead to a severe reduction in aquifer permeability (Morgan and Watkinson, 1992). Such (site-specific) problems have motivated the addition of nitrate as a cost-effective approach to supplement the electron acceptor pool (Anid et al., 1993; Alvarez and Vogel, 1995; Hutchins et al., 1991; Werner, 1985). Reactive barriers containing nitrate-releasing compounds have been used to enhance microbial oxidation of toluene and xylenes under denitrifying conditions. Examples of such barriers are also given in Section V.A.

Reductive biodegradation, on the other hand, requires a source of electrons, which are transferred by the microorganisms to the target pollutants. Suitable electron donors tend to be abundant in anaerobic environments. Thus, anaerobic

microbial communities readily transform reducible pollutants such as trichloroethylene, hexavalent chromium, sulfate, and nitrate. Nevertheless, such pollutants tend to persist in aerobic systems with a low reduction capacity. Therefore, barriers containing reducing equivalents (e.g., organic material) have been used to intercept and stimulate the anaerobic biodegradation of such redox-sensitive contaminants. Such barriers are discussed in Section V.B.

A. Oxygen- and Nitrate-Releasing Compounds to Stimulate BTEX Degradation

Petroleum hydrocarbons, such as BTEX, are common groundwater contaminants. In the United States more than 380,000 confirmed gasoline releases from underground storage tanks have contaminated local aquifers with BTEX compounds (U.S. EPA, 1998b). Fortunately, BTEX degrade relatively fast under aerobic conditions. Thus, one approach to enhance BTEX biodegradation *in situ* is to provide sufficient oxygen. To this end, oxygen-releasing compounds (ORCs) represent a passive alternative to introduce oxygen. This passive approach conserves energy, and through long-term low operating and maintenance costs, has the potential to be less costly than conventional oxygen injection approaches.

Potential oxygen releasing substances include magnesium peroxide (MgO₂), calcium peroxide (CaO₂), sodium percarbonate (Na₂CO₃≈1.5H₂O₂) and urea hydrogen peroxide (urea-H₂O₂) (Borden et al., 1997). Oxygen is released when water reacts with these materials, as shown for calcium peroxide in Eq. 5.1.

$$2CaO_2 + 2H_2O \rightarrow 2Ca(OH)_2 + O_2$$
 (5.1)

These oxygen-releasing compounds are commonly powdered substances that can also be incorporated into a cement matrix to obtain an ORC concrete. This concrete can be prepared as briquettes to avoid significant reductions in aquifer permeability. The total available oxygen is about 5.2% by weight in mixture with concrete at 20% ORC (Bianchi-Mosquera et al., 1994).

Laboratory experiments have shown that urea peroxide and sodium percarbonate are most likely not acceptable for use in long-term projects due to a rapid depletion of oxygen-release capabilities. The relatively high solubility of these compounds would require encapsulation for sustaining oxygen release capabilities. In contrast, a cement mix of 14% MgO₂ or 14% CaO₂ cement can release oxygen for hundreds of days (Bianchi-Mosquera et al., 1994). One major advantage of commercial CaCO₂ (prepared at a mass purity of 60 to 80%) over commercial MgO₂ (prepared at a mass purity of 15 to 25%) is that the former generally delivers three to four times more oxygen (White et al., 1998). In addition, CaCO₂ is less expensive and easily produced in the field by heating lime with hydrogen peroxide (Vol'nov, 1966). The rate of oxygen release can be controlled by the size of the concrete

briquettes containing the ORCs, with smaller briquettes generally resulting in higher release rates (Borden et al, 1997). Field experiments found that ORCs are able to maintain elevated dissolved oxygen concentrations, typically between 6 and 19 mg/L (Bianchi-Mosquera et al., 1994).

There are some potential disadvantages regarding the use of ORC compounds. Clogging of the aquifer is a potential problem with all strategies associated with oxygen delivery, including ORCs, when high levels of dissolved Fe²⁺ are present in the groundwater. In such cases, increased oxygen availability leads to iron oxide precipitation and reduced aquifer porosity (Borden et al., 1997). Another potential problem with these barriers is a pH increase in the groundwater caused by concrete dissolution. The increased pH could inhibit bacteria and decrease biodegradation rates (Kao and Borden, 1997).

Nitrate-releasing materials (e.g., NaNO₃, K₃PO₄, fly ash, sand, and water blended at a ratio of 1:1:4:7:15:5 by weight) can also be incorporated into subsurface permeable barriers to increase the electron acceptor pool and enhance the degradation of toluene, ethylbenzene, and xylenes under denitrifying conditions (Kao and Borden, 1997). Benzene, however, is recalcitrant under denitrifying conditions (Alvarez and Vogel, 1995). Thus, introducing nitrate in anoxic zones is unlikely to significantly attenuate benzene migration.

One concern about nitrate-based bioremediation is that unreacted nitrate represents a water quality problem due to its potential to cause methemoglobinemia. Kao and Borden (1997) proposed to address this problem by installing a peat barrier downgradient from the point of nitrate release. Peat can serve as electron donor to stimulate bacterial denitrification of any excess residual nitrate in the ground water, as discussed in the next section. In such cases, sorption of nondegraded organic compounds by the peat might further attenuate the migration of the (moderately hydrophobic) BTEX compounds (Kao and Borden, 1997).

In summary, oxygen- and nitrate-releasing compounds in subsurface barriers can enhance oxidative biodegradation processes. Yet, the individual characteristics of the aquifer and groundwater constituents (e.g., ferrous iron concentration, initial BTEX concentration, and the presence of other substrates or toxicants) determine the applicability and success of these systems (Borden et al., 1997).

B. Organic Material to Stimulate Reductive Biotransformations

Adding organic matter to subsurface barriers is a novel approach to create *in situ* reactive zones where anaerobic biotransformations are stimulated. This allows a wide variety of redox-sensitive contaminants to be treated, including chlorinated solvents, hexavalent chromium, nitrate, sulfate, nitroaromatic explosives, and radionuclides (Fruchter et al., 1996). Two applications of organic barriers that have been proven successful in field applications include (1) sulfate reduction and iron precipitation in the treatment of acid mine drainage (Benner et al., 1997), and (ii) stimulation of het-

erotrophic denitrification to remove nitrate (Robertson and Cherry, 1995; Schipper and Vojvodiĉ-Vukoviĉ, 1998). Each of these approaches are discussed below.

Acidity (H⁺) production in mine drainage often results from the oxidation of sulfide minerals and the subsequent oxidation of dissolved metals such as ferrous iron. This is illustrated in Eqs. 5.2 and 5.3 for pyrite (FeS₂):

$$FeS_2(s) + 3.5 O_2 + 2 H_2O \leftrightarrow 2 SO_4^{2-} + Fe^{2+} + 2 H^+$$
 (5.2)

$$Fe^{2+} + 0.25 O_2 + 2.5 H_2O \leftrightarrow Fe(OH)_3(s) + 2 H^+$$
 (5.3)

The generated sulfate (SO₄²⁻) can be respired to hydrogen sulfide by sulfate-reducing bacteria in the organic barrier (Eq. 5.4). In this equation, CH₂O represents the organic carbon that serves as electron donor and carbon source for sulfate reducers. The resulting sulfide can subsequently form metal precipitates, as shown in Eq. 5.5.

$$2 SO_4^{2-} + 4 CH_2O + 4 H^+ \leftrightarrow 2 H_2S + 4 CO_2 + 4 H_2O$$
 (5.4)

$$Fe^{2+} + H_2S \leftrightarrow FeS(s) + 2 H^+$$
 (5.5)

Note that acidity production by both pyrite oxidation (Eq. 5.2) and iron precipitation (Eq. 5.5) is balanced by acidity consumption during sulfate reduction (Eq. 5.4). Thus, microbial sulfate reduction attenuates the decrease in pH.

The maintenance of anoxic conditions is essential for sulfate reduction to proceed. This condition is easily met because the organic substrates exert a relatively high biochemical oxygen demand that rapidly depletes dissolved oxygen. A well-balanced ratio of carbon, nitrogen, and phosphorous is also important for microbial activity in the mixture. Waybrant et al. (1998) tested a variety of mixtures of organic materials in bench-scale experiments. Sewage sludge, leaf mulch, wood chips, sheep manure, and sawdust were effective for use in organic barriers to treat acid mine drainage, producing reactive mixtures with a permeability within 10^{-4} to 10^{-2} cm/s. Within 65 days, sulfate concentrations decreased from 1200 to 4800 mg/L to less than 10 mg/L, iron decreased from between 105 and 1400 mg/L to between 0.1 and 50 mg/L, and cadmium and nickel decreased from 135 and 148 mg/L, respectively, to less than 0.05 mg/L. In a field application, an organic barrier made of municipal compost, leaf compost, and wood chips stimulated sulfate reduction and removed more than 90% of the soluble Fe²⁺, mostly as iron sulfide (Benner et al., 1997). A 10-fold increase in alkalinity was also observed.

The lifetime of barriers containing organic matter can easily be in the range of tens of years, keeping maintenance requirements low (Benner et al., 1997). However, the effect of metal sulfide precipitation on barrier conductivity and long-term hydraulic performance has not yet been systematically investigated.

Organic barriers can also be used to stimulate heterotrophic denitrification to remove nitrate (NO₃) from contaminated groundwater. Nitrate is a priority pollutant due to its

potential to cause infant methemoglobinemia, and there is circumstantial evidence linking nitrate to gastric cancer and birth defects (Mirvish, 1985). Nitrate contamination is a major ground water quality problem in the United States (Nolan et al., 1997), which is reflected in a recent survey that found 23% of all primary drinking water standard violations to be due to high nitrate concentrations (Kapoor and Viraraghavan, 1997).

In aerobic groundwater zones, nitrate is mobile and not significantly utilized by microorganisms (Robertson et al., 1991). Yet, nitrate can be respired by facultative denitrifiers when anoxic conditions prevail. The denitrification reaction is represented by Equation 5.6, where CH₂O represents an organic carbon source (Robertson and Cherry, 1995).

$$5 \text{ CH}_2\text{O} + 4 \text{ NO}_3^- \leftrightarrow 5 \text{ CO}_2 + 2 \text{ N}_2 + 3 \text{ H}_2\text{O} + 4 \text{ OH}^-$$
 (5.6)

Potential barrier materials providing organic carbon include peat, sawdust, leaf compost, and seeds (Kao and Borden, 1997; Schipper and Vojvodiĉ-Vukoviĉ, 1998; Waybrant et al., 1998). The denitrification barrier could be installed in a horizontal or vertical arrangement, depending on the application. A silt matrix containing organic material can effectively provide the required anaerobic conditions and maintain water saturation within the barrier. The treatment efficiency for nitrate attenuation can be high (72 to 97%) and decreases with increasing loading rate (Robertson and Cherry, 1995). *In situ* denitrification rates as high as 906 ng of N g⁻¹ have been reported for a 30% (v/v) sawdust barrier (Schipper and Vojvodiĉ-Vukoviĉ, 1998).

One concern with organic barriers is that the resulting reducing conditions can stimulate reductive dissolution of ferric oxyhydroxide from soil minerals. Solubilization of ferrous (Fe²⁺) iron represents a potential problem because Fe²⁺ subsequently can be oxidized downgradient to ferric (Fe³⁺) iron under aerobic conditions. As mentioned before, ferric iron readily forms hydroxides and precipitates at circum-neutral pH, which eventually results in clogging of aquifer material or well screens (Robertson and Cherry, 1995).

Organic barrier permeability and performance can also be reduced by filtration and accumulation of suspended solids in the pore spaces and by microbial production of nitrogen gas bubbles during denitrification (Eq. 5.6). Studies with denitrifying systems have demonstrated that the accumulation of N_2 gas bubbles in porous media can significantly reduce the hydraulic conductivity (Soares et al., 1988, 1989, and 1991). Thus, N_2 bubbles could increase the pressure and divert groundwater flow around the barrier, bypassing the treatment system.

VI. BIOGEOCHEMICAL INTERACTIONS

A. Effects of Microorganisms on Barrier Permeability

The longevity and enduring efficiency of reactive barriers are major uncertainties currently being addressed by several researchers (Gu et al., 1999). Microbial

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geochemical processes could play an influential role in the long-term performance of a barrier, affecting contaminant removal both within and downgradient of the barrier matrix. For example, microorganisms could hinder or enhance the hydraulic performance of a reactive barrier. Depending on aquifer chemistry, microorganisms could reduce porosity (and induce clogging) by forming a biofilm, or by contributing to mineral precipitation, or by producing gas bubbles that restrict water flow. Conversely, microorganisms could enhance the permeability of a barrier by contributing to mineral dissolution or by consuming gas bubbles produced by abiotic processes. Controlled experiments that address the significance and extent of such phenomena on the hydrodynamic characteristics of reactive barriers are lacking. Therefore, biogeochemical interactions affecting barrier permeability are discussed primarily from a theoretical point of view.

The formation of cell aggregates and biofilms that reduce the available pore space is a potential clogging mechanism of concern (Taylor and Jaffe, 1990; Vandevivere and Baveye, 1992). A combination of excessive microbial growth and mineral precipitation could result in a significant reduction porosity and permeability over a longer period of time. The inherent diversion of groundwater flow around the barrier could then reduce the treatment efficiency. The formation of a precipitate could also contribute to an early decrease in reaction rates and treatment efficiency (Allen-King et al., 1997). The development of a biofilm on the medium surface can also affect the reactivity of the barrier. Biofilms could block reactive sites and hinder abiotic reactions, or enhance biological degradation processes. The overall effect is probably system specific and has not yet been evaluated scientifically.

An important mechanism responsible for reduced permeability in Fe^0 barriers is the abiotic production of (water-derived) hydrogen gas bubbles during anaerobic Fe^0 corrosion (Eq. 3.5). Field pilot tests have shown that venting of H_2 bubbles may be required to maintain water flow (Korte et al., 1997; Liang et al., 1997b). Nevertheless, microorganisms that can utilize H_2 as an energy source are ubiquitous in anaerobic environments (Atlas and Bartha, 1993). Consequently, microbial consumption of cathodic H_2 could be a favorable mechanism to attenuate the decrease in permeability and enhance the long-term hydraulic performance of Fe^0 barriers.

B. Microbial Ecology of Fe⁰ Barriers

The microbial ecology of Fe⁰ barriers has received very little attention in the literature. Nevertheless, theoretical considerations suggest that Fe⁰ is likely to stimulate a wide variety of geochemical transitions and associated microbial population shifts as a result of ferrous iron dissolution, dissolved oxygen consumption, and cathodic hydrogen production during Fe⁰ corrosion. Hypothetical zones of biogeochemical and microbiological influence surrounding an Fe⁰ barrier are

illustrated in Figure 12 (Matheson, 1994). If the incoming groundwater is aerobic, iron-oxidizing bacteria might exploit the increased availability of ferrous iron that dissolves during Fe⁰ corrosion near the upgradient face of the barrier. These aerobic bacteria produce ferric oxides that could precipitate and reduce the reactivity and permeability of the barrier. Whether iron-reducing bacteria can reverse this passivation process by reducing the ferric oxide and hydroxide coating within the barrier to the more soluble ferrous form has not been investigated.

The depletion of dissolved oxygen and the production of cathodic hydrogen by Fe⁰ corrosion would provide a reducing environment favorable to a wide variety of hydrogen-consuming anaerobic microorganisms. These include methanogens, sulfate reducers, and iron-reducers within and downgradient of the barrier. The relative abundance of such microorganisms would depend on the concentration of hydrogen and on the availability of sulfate and mineral containing ferric iron. Iron-reducing bacteria have a greater affinity for hydrogen than sulfate reducers and methanogens (Lovley and Goodwin, 1988). In addition, iron reducers have a thermodynamic advantage over sulfate reducers and methanogens (Zehnder and Stumm, 1988). Therefore, if ferric iron is not limiting, iron reducers might keep hydrogen concentrations low enough to hinder the proliferation of sulfate reducers and CO₂-reducing methanogens. Similarly, sulfate reducers are likely to outcompete hydrogenotrophic methanogens when sulfate is not limiting.

The zone of influence of hydrogen-utilizing anaerobic microorganisms would extend downgradient, up to a point where hydrogen is consumed and/or oxygen diffusion makes redox conditions unfavorable for their survival. Iron oxidizers might prevail also further downgradient at the aerobic edge of the dissolved ferrous iron plume. Therefore, Fe⁰ barriers may provide an interesting environment to study the ecology of different types of hydrogenotrophic microorganisms and the biogeochemical cycling of iron.

C. Combined Microbial- Fe^o Systems -

Early studies of Fe⁰ systems found little microbial contribution to contaminant degradation (Matheson, 1994), and research has focused primarily on abiotic processes. Therefore, the role of microorganisms on the surface reactivity of Fe⁰ has not been addressed systematically. Nevertheless, the potential for microorganisms to enhance reductive treatment with Fe⁰ has been demonstrated conclusively in recent laboratory experiments.

Microbial utilization of cathodic hydrogen has been shown to be a critical link between biogeochemical interactions and enhanced contaminant removal (Weathers et al., 1997; Till et al., 1998). Specifically, hydrogen can serve as electron donor for the biotransformation of reducible contaminants. For example, combining Fe⁰ with an active (hydrogen-consuming) methanogenic consortium significantly enhanced both the rate and extent of transformation of chlorinated methanes

(Weathers et al., 1997). Further experiments were conducted with pure cultures of methanogens, including hydrogenotrophic species that could grow on hydrogen (i.e., *Methanosarcina barkeri*) as well as aceticlastic species that could not (i.e., *Methanosarcina thermophila* and *Methanosaeta concillii*) (Novak et al., 1998a). These experiments demonstrated that cathodic hydrogen could enhance microbial reduction of chlorinated solvents, even when hydrogen does not serve as growth substrate. In addition, Fe⁰ stimulated *M. thermophila* to excrete an extracellular factor with protein-like characteristics that degraded both carbon tetrachloride and chloroform (Novak et al., 1998b). This suggests that some microbial-Fe⁰ interactions can significantly enhance the efficacy of Fe⁰ barriers.

Theoretical considerations suggest that some biogeochemical interactions may be particularly beneficial to treat mixtures of reducible contaminants, such as chlorinated solvents and hexavalent chromium. For example, aerobic corrosion of Fe⁰ rapidly induces anoxic conditions favorable for anaerobic biotransformations and increases the pH to a range that favors heavy metal precipitation:

$$2Fe^{0} + O_{2} + 4H^{+} \rightarrow 2Fe^{2+} + 2H_{2}O$$
 (6.1)

Thus, Fe⁰ can enhance microbial participation in the clean up process by removing potentially co-occurring inhibitory pollutants such as Cr(VI) (Powell et al., 1995). In addition, cathodic hydrogen production represents an increase in the bioavailability of an excellent substrate to support microbial reduction of the target compounds and the further degradation of some dead-end chlorinated products that may accumulate during abiotic reduction by Fe⁰ (Helland et al., 1995; Matheson and Tratnyek, 1994; Roberts et al., 1996). In theory, hydrogenotrophs could also remove the passivating cathodic H₂ layer from the Fe⁰ surface (i.e., cathodic depolarization), which could enhance the reactivity of Fe⁰. As mentioned previously, microbial consumption of H₂ gas bubbles could also enhance the permeability of the barrier. This would offset any decrease in permeability resulting from microbial growth.

Pure cultures of methanogenic, homoacetogenic, sulfate reducing, and denitrifying bacteria have demonstrated the ability to use cathodic hydrogen (Eq. 2.5) as an energy source for growth in short-term, batch experiments (Daniels et al., 1987; Rajagopal and LeGall, 1989; Till et al., 1998). Many such organisms have also been shown to reduce redox-sensitive pollutants that react with Fe⁰, such as chlorinated solvents, Cr(VI), TNT, and U(VI) (e.g., Bouwer et al., 1981; Lovley et al., 1991; Wang et al., 1989). Thus, it seems plausible that an indigenous hydrogenotrophic microbial consortium could develop around Fe⁰ barriers to exploit cathodic depolarization and pollution degradation as metabolic niches. This notion is supported by field sampling of a pilot test after 6 months of operation, which revealed the presence of methanogens, sulfate reducers, metal reducers, and trichloroethylene-degrading bacteria (Liang et al. 1997b; Korte et al., 1997).

Whether bioaugmentation of Fe⁰ barriers with specialized hydrogenotrophs can enhance treatment performance is yet to be determined. However, the potential for this approach to enhance contaminant removal kinetics and end product distribution has been demonstrated in bench-scale systems. As an example of such combined microbial- Fe⁰ treatment systems, let us consider iron-supported denitrification (Till et al., 1998). This example provides a forum to discuss some biogeochemical interactions that may also be applicable to the removal of other redox-sensitive priority pollutants in Fe⁰ systems.

Although numerous physicochemical processes have been proposed for removal of nitrate from water, many of these have proven marginally cost-effective and/or have detrimental side-effects on water quality. The use of autotrophic, hydrogen-utilizing denitrifiers is an attractive technique, due primarily to the cleanliness of the process (Haring and Conrad, 1991; Liessens et al., 1992; Smith, et al., 1994). Because CO₂ is the carbon source for autotrophic growth, there is no need to remove residual organic substrates. H₂ gas is inherently clean and only slightly soluble in water (0.78 mg/L at 1 atm, 25°C). Autotrophic growth also leads to lower cell yield and less biomass production. The overall reaction proceeds as follows (Kurt et al., 1987):

$$2 \text{ NO}_3^- + 5 \text{ H}_2 \rightarrow \text{ N}_2 + 4 \text{ H}_2\text{O} + 2 \text{ OH}^-$$
 (6.2)

Hydrogen is one of the most thermodynamically favorable electron donors for denitrification, and its high diffusivity through biofilms is conducive to enhanced nitrate removal. However, its relatively high cost, low solubility, and hazardous (explosive) properties during handling and storage limit the use of hydrogen in engineered denitrification systems. Nevertheless, these limitations could be overcome by exploiting Fe⁰ corrosion to continuously generate cathodic hydrogen to sustain denitrification (Eq. 3.5).

Fe⁰ can also reduce nitrate by a surface-mediated reaction, leading to ammonium as the primary end product (Huang et al., 1998; Till et al., 1998). This reaction is proposed to proceed as follows:

$$4 \text{ Fe}^0 + \text{NO}_3^- + 7 \text{ H}_2\text{O} \rightarrow 4 \text{ Fe}^{2+} + \text{NH}_4^+ + 10 \text{ OH}^-; \quad \Delta G^{\circ'} = -620 \text{ kJ} \quad (6.3)$$

Ammonium, however, has an adverse aesthetic impact on drinking water and can interfere with subsequent disinfection processes (Jafvert and Valentine, 1992). Thus, reductive treatment of nitrate with Fe^0 can be enhanced by the presence of autotrophic denitrifiers, which offer an alternative pathway-reducing nitrate to more innocuous products such as N_2O and N_2 (Figure 10). The overall reaction, which is given by combining Eqs. 2.5 and 6.2, is thermodynamically more feasible than abiotic nitrate reduction with Fe^0 :

$$5 \,\text{Fe}^0 + 2 \,\text{NO}_3 + 6 \,\text{H}_2\text{O} \rightarrow 5 \,\text{Fe}^{2+} + \text{N}_2 + 12 \,\text{OH} \quad \Delta G^{\circ \prime} = -1147 \,\text{kJ} \quad (6.4)$$

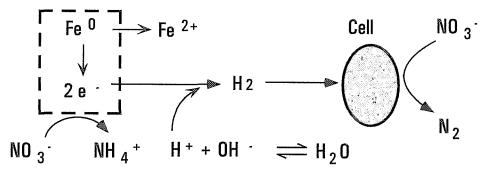


FIGURE 10. Concept of Fe(0)-supported denitrification. (Adapted from Till et al., 1998.)

This reaction could increase the pH beyond the tolerance range of common denitrifiers. Thus, the system may have to be buffered against large pH increases. This could be accomplished by adding carbon dioxide (Kappor and Viraraghavan, 1997) or by combining Fe⁰ with (acidic) aluminosilicate minerals that enhance proton generation at the Fe⁰ surface (Dejournett and Alvarez, 1999; Powell and Puls, 1997).

The fact that Fe⁰ could serve as electron donor to sustain autotrophic denitrification via cathodic hydrogen production was first demonstrated by (Till et al., 1998), using a dual-flask apparatus (Figure 11). Cathodic H₂ from a flask containing Fe⁰ was allowed to diffuse to another (anoxic) flask containing a pure culture of Paracoccus denitrificans, where denitrification and microbial growth occurred. Further experiments studied the ability of P. denitrificans to enhance nitrate removal in Fe⁰ systems. Batch reactors were prepared with either steel wool or Fe⁰ powder, and replicate reactors were inoculated with P. denitrificans. Steel wool, with a smaller surface area, was less reactive and its corrosion did not significantly increase the pH of the solution. This allowed for a greater participation of denitrifiers in the nitrate removal process, which increased nitrate removal rates and transformed a greater portion of the added nitrate to innocuous gases rather than to ammonium (Till et al., 1998). Combining denitrifiers with the more reactive Fe⁰ powder, however, did not increase removal rates or decrease the proportion of nitrate reduced to ammonium. This was attributed to a combination of relatively fast abiotic removal rates, and a corrosion-induced increase in pH above the tolerance range of the bacteria (pH > 10). This suggests that there is kinetic competition between the biological and the abiotic nitrate reduction pathways. Therefore, sustaining autotrophic denitrification with a lower surface area concentration of Fe⁰ might be more beneficial to enhance the biological pathway and thus the end product distribution.

The potential for a combined Fe⁰-microbial approach to sustain nitrate removal in a continuous flow system was also demonstrated (Till et al., 1998). Flow-through columns packed with steel wool were seeded with autotrophic denitrifiers, and denitrification was sustained during the 4-month duration of the experiment. The relative importance of microbial and abiotic nitrate removal pathways was

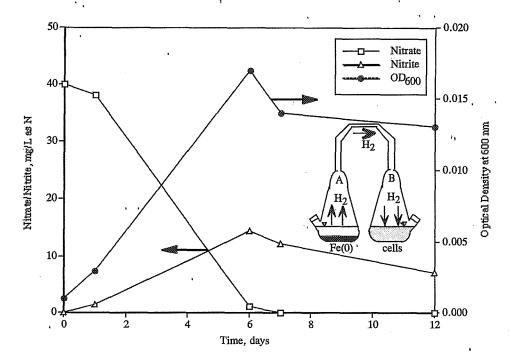


FIGURE 11. Autotrophic growth of *P. denitrificans* in a dual-flask apparatus. (Adapted from Till et al., 1998.)

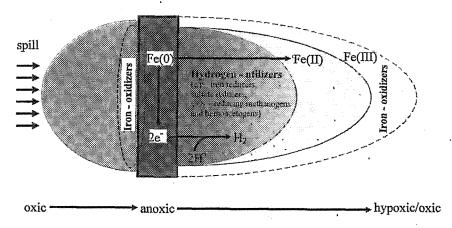


FIGURE 12. A plan view of the hypothetical domains of microbial activity surrounding an Fe^o barrier. (Adapted from Matheson, 1994.)

influenced by the hydraulic retention time. Increasing the hydraulic retention time from 0.67 to 2.33 days increased both the nitrate removal efficiency and the relative importance of biological denitrification, leading to a lower fraction of nitrate reduced to ammonium. Thus, longer retention times are beneficial to enhance the end product distribution. While longer retention times may be a concern due to increased reactor volume requirements, the typically slow flow velocity of groundwater (e.g., 1 cm/d) (Schnoor, 1996) ensures long retention times because contaminated groundwater flows through typical Fe⁰ barriers (50 to 150 cm thick).

Using scanning electron microscopy, Dejournett and Alvarez (1999) investigated bacterial colonization of solid surfaces in a denitrifying flow-through column packed with sand and Fe⁰ filings (15% by weight). Bacteria were observed on the surface of Fe⁰ filings, but not in sand grains. Apparently, denitrifiers selectively colonized Fe⁰ surfaces to facilitate microbial uptake of relatively insoluble cathodic H₂. This suggest that indigenous microorganisms are likely to colonize Fe⁰ barriers to exploit cathodic depolarization as a metabolic niche.

A similar approach, based on cathodic hydrogen utilization, could be used to stimulate sulfate reduction and attenuate acid mine drainage. The resulting sulfide production could provide an ancillary benefit associated with heavy metal precipitation. However, such benefits would need to be evaluated against a reduction in barrier porosity (and thus reduced permeability) as a result of metal-sulfides precipitation.

VII. TECHNICAL CHALLENGES AND RESEARCH NEEDS

Permeable reactive barriers are currently treating a host of groundwater contaminants. Indeed, numerous sites have been successfully remediated with PRB technologies (primarily iron metal PRBs). However, despite the success of PRBs in recent field applications, there are still significant limitations that arise from the physical and biogeochemical characteristics of individual sites. The most important limitation is the lack of information on the long-term effectiveness of the fullscale process. Even though some field tests are promising (e.g., O'Hannesin and Gillham, 1998) and suggest lifetimes for several media in the range of decades, care has to be taken in predicting field degradation rates from short-term laboratory data. Field degradation rates may be influenced by long-term processes such as aging of the reactive material (Allen-King et al., 1997) or decreased permeability due to precipitation (Mackenzie et al., 1997), microbial growth (Taylor and Jaffe, 1990; Vandevivere and Baveye, 1992), or gas accumulation (Soares et al., 1988, 1989, and 1991) that are not operative in short-term laboratory experiments. For example, a potential technical challenge with iron barriers is the oxidation of ferrous iron and the precipitation of oxides that may clog the pore space or serve as a physical barrier to surface reactive sites (Figure 9A). Alternative strategies for removing oxides that are being investigated include ultrasound technologies and pH control. In addition, as discussed earlier, microorganisms may be able to mediate mineral dissolution reactions. Microbial processes might also help alleviate pore volume reduction due to the formation and entrapment of hydrogen gas (H₂) from anaerobic iron corrosion (Eq. 3.5) (Mackenzie et al., 1997). As the technology is implemented at more sites, the data from these field experiments form a stronger basis for barrier design.

The goal in the design of a barrier system is the complete capture of the migrating contaminant plume with a minimum amount of reactive material. There are currently two basic design configurations, continuous trench and funnel gate systems. Selection of the appropriate configuration depends on plume size, accessibility, and groundwater flow characteristics. Both configurations have been utilized for relatively wide barriers of up to 1000 ft (Gayaskar et al., 1998), but are limited to relatively shallow depths on the order of a few tens of feet. Deep barriers generally require the use of steel sheet piling to control flow in conjunction with or as a replacement for bentonite-slurry walls. Biodegradable polymers have often been used instead of conventional bentonite-slurries to avoid subsequent plugging of aquifer material by residual slurry material (Gavaskar et al., 1998; Vidic and Pohland, 1996). Based on current emplacement technologies, it is doubtful that barriers can be cost-effective for treating contamination in deep aquifers (e.g., below a depth of 100 ft), or at locations that are geologically difficult to access. The injection of reactive material (e.g., iron colloids) via hydraulic fracturing, deep soil mixing, or jet grouting may be an alternative that overcomes the depth limitations associated with commercial excavation technologies (Cantrell and Kaplan, 1997; Gavaskar et al., 1998; Kaplan et al., 1996).

In addition to the physical limitations imposed by the site geology and conventional excavation techniques, there are several unresolved issues regarding the removal process within the PRB. Ideally, the contaminants are either permanently immobilized or transformed to non-hazardous substances. Several classes of compounds, however, are transformed to more toxic substances that are more resistant to degradation than the parent compound. For example, the reduction of chlorinated ethenes by iron metal has been shown to produce vinyl chloride, a compound which has greater health concerns associated with it then the more highly chlorinated ethenes (e.g., trichloroethene and perchloroethene) (Liang et al., 1997a; Orth and Gillham, 1996). Additional research is needed to better understand the mechanisms controlling reaction pathways and subsequent product distributions.

For Fe⁰ barriers, one unresolved mechanistic issue is the role of ferrous iron, surface precipitates, and impurities in the reduction process. In theory, these compounds could serve not only as reductants, but also as catalysts. As discussed earlier, surface-bound and complexed ferrous iron may be the active species most directly responsible for the reduction of a contaminant (see Figure 9C). Furthermore, the strength of ferrous iron as a reductant could be significantly affected by the ligands present in the system, including organic matter and metal oxides that

form inner-sphere complexes with Fe⁺² (Stumm, 1992). There is also some uncertainty regarding the rate-limiting step in the removal process. In a broad sense, transformation rates within a PRB can be controlled by either transport to the surface or reaction at the surface (Stumm, 1992; Scherer, 1997). The effects of mass transport on PRB degradation rates have yet to be resolved or even addressed for many of the reactive materials being proposed.

The significant challenge remaining for immobilization techniques, such as sorption and precipitation, is to develop methods to control the groundwater conditions that favor immobilization and reduce the potential for remobilization of the contaminants. Current immobilization techniques, such as adsorption to surfactant-modified zeolites, humic materials, and oxides are strongly dependent groundwater conditions, including pH, surfactant concentrations, and presence of competing ions. Effective field-scale implementation of these technologies will require a method for either ensuring optimal conditions or removal of barrier material after the plume is treated.

The interactions of abiotic and biotic degradation processes represent a particularly difficult research challenge because of the complexity of potential synergistic or antagonistic effects. For example, short-term laboratory experiments suggest that combining microorganisms with Fe⁰ offers advantages such as faster kinetics and better end product distribution (Novak et al., 1998a and 1998b; Till et al., 1998; Weathers et al., 1997). However, the effect that microorganisms have on the permeability and long-term reactivity of the barrier is a major uncertainty. There is also a need to address numerous questions related to the feasibility of bioaugmenting Fe⁰ barriers for example, Do we need to add exogenous microorganisms, or will an indigenous hydrogenotrophic consortium eventually develop around Fe⁰ barriers to fill a metabolic niche associated with cathodic depolarization? How long does it take for such a natural hydrogenotrophic consortium to develop? Which microbial-Fe⁰ interactions are beneficial and which are detrimental to contaminant removal efficiency? Which indigenous microorganisms fill which niches in Fe⁰ barriers? How well do added specialized strains adapt and survive?) Other questions should be addressed to obtain basic criteria for process design and operation, for example, How thick should bioaugmented barriers be? What should be the Fe⁰ surface area concentration to optimize desirable biogeochemical interactions? How long does Fe⁰ or the added bacteria remain active? How do pH, temperature, and redox conditions affect contaminant removal kinetics and end product distribution? Can we use thinner barriers as a pretreatment step to enhance the degradability of recalcitrant contaminants by (downgradient) indigenous microorganisms?) Finally, there are basic mechanistic questions that should be answered to contribute to the rational development of reactive barriers as a waste management technology, for example, How do bacteria affect the reactivity of the Fe⁰ surface? How does Fe⁰ corrosion affect microbial physiology and population dynamics?)

Most work to date has focused on barriers that contain metals that bring about a chemical reduction of a contaminant. This limits the usefulness of barriers to

only a few classes of redox-sensitive compounds. A need exists for alternative barrier materials. A provocative idea is the creation of an oxidative barrier that relies on advanced oxidation processes such as hydroxyl radical generation. Recently, Mill and Su reported on the use of Fe⁰ barriers with hydrogen peroxide as a means of producing these reactive species (Mill and Su, 1997). Another approach could be the electrochemical production of oxidants. An oxidative barrier could potentially be used to treat a much different and broader category of contaminants, although process feasibility would probably depend on the ability to control alternative oxidant sinks. Quite logically, combining several types of barriers could be done to exploit specific chemical reactions that ultimately lead to the most effective and complete transformation of contaminant mixtures.

In summary, many opportunities exist to improve treatment barrier technology. Clearly, a better understanding of process mechanisms, kinetics of the rate-limiting steps, biogeochemical interactions, and effects of groundwater chemistry should lead to unifying principles that facilitate process design. As our understanding of the fundamental processes controlling the removal mechanisms improves, so will the use of barrier technology.

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