

# Chemical Degradation Methods for Wastes and Pollutants

Environmental and Industrial Applications

edited by

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### Permeable Reactive Barriers of Iron and Other Zero-Valent Metals

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#### I. INTRODUCTION

##### A. Historical Context

The “modern” history of the use of zero-valent metals (ZVMs) in the remediation of contaminated water has been summarized from several perspectives [1–4]. By most accounts, the critical event was the serendipitous discovery that trichloroethene (TCE) is degraded in the presence of the metal casing materials used in some groundwater monitoring wells [5]. This observation led to recognition that granular iron metal might be applicable to the remediation of groundwater that is contaminated with chlorinated solvents. Around the same time, the possibility of engineering permeable treatment zones for in situ treatment of contaminated groundwater had led to a search for suitable reactive media, and granular iron quickly became the most promising reactive medium for application in permeable treatment zones [6]. The confluence of these two developments (granular iron and permeable treatment zones) made the emergence of reactive barriers



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containing granular iron into one of the landmark developments in the history of groundwater remediation technology.

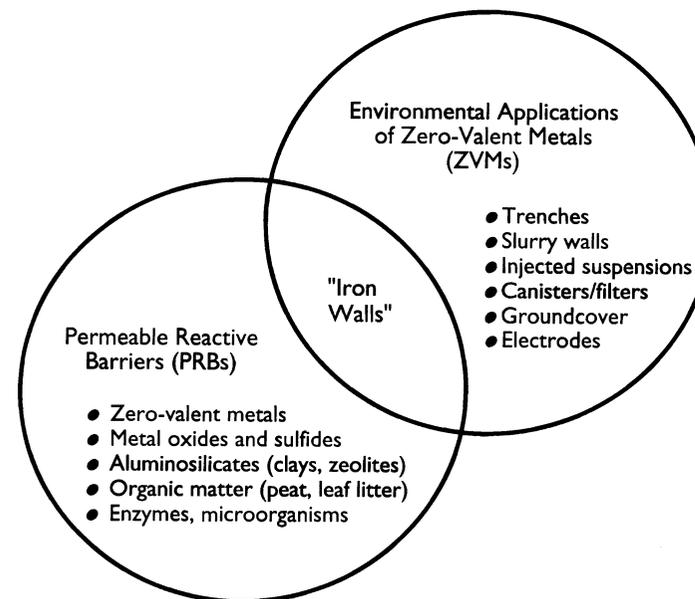
The rapid development of this technology over the last decade has been accompanied by a conspicuous increase in the quantity of published information on the reaction of iron metal with organic and inorganic solutes in aqueous systems. With so much activity in the present, it is easy to overlook how much relevant work was done earlier. For example, the electrolytic deposition of dissolved metals onto ZVMs has long been known to chemists, and the potential for application of this chemistry to water treatment was recognized at least as far back as the 1960s [7]. Similarly, the use of ZVMs to perform selective reductions for organic synthesis was already well documented by the 1920s (e.g., Refs. 8 and 9), and environmental applications had been described by the 1980s [10,11]. In fact, prior to 1990, there had already been several detailed “process-level” studies on the removal of organics (e.g., Refs. 12–15) and inorganics (e.g., Refs. 7, 16, and 17). This early work was very widely dispersed, however, and a unified understanding of the processes responsible for contaminant removal by ZVMs has only recently begun to take shape.

## B. Scope

The scope of this review is centered around permeable reactive barriers (PRBs) of ZVMs. Among the ZVMs used in remediation applications, iron metal (ZVI or Fe<sup>0</sup>) is by far the most important. PRBs of ZVI (sometimes designated FePRBs) are the technology known colloquially as “iron walls.” However, as illustrated in Fig. 1, not all PRBs are made from ZVMs and not all remediation applications of ZVMs are PRBs.

### 1. Permeable Reactive Barriers

Technologies for treatment of subsurface contamination can be divided into “ex situ” methods that involve removal of the contaminated material for treatment at the surface and “in situ” methods where the treatment is applied to the subsurface. In situ treatment technologies include a variety of related methods such as continuous trenches, funnel-and-gates, passive reactive wells, geochemically manipulated zones, and biologically reactive zones. Continuous trenches and funnel-and-gates are the most common types of PRBs [18,19]. At least one formal definition of a PRB has been given [3], but for the present purpose we prefer a slightly narrower and simpler definition: “a permeable subsurface zone constructed of reactive material that is oriented to intercept and destroy or immobilize contaminants.” The major elements of a PRB are shown in Fig. 2.

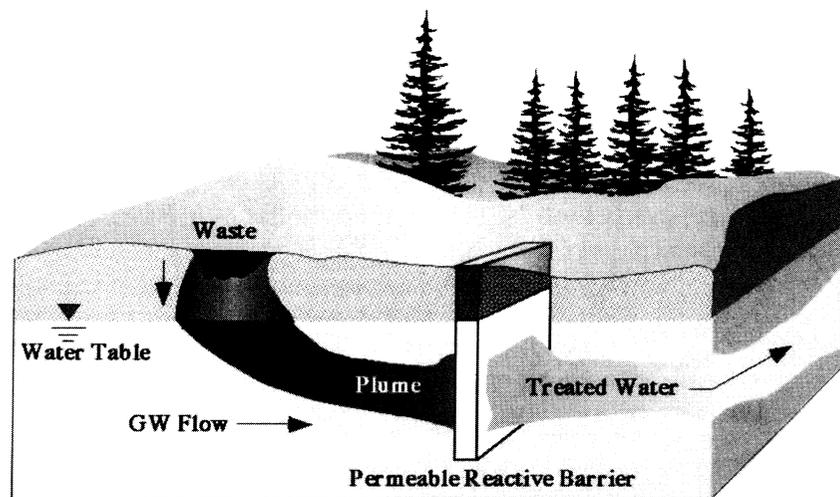


**Figure 1** Venn diagram showing the relationship between various types of PRBs and various remediation applications of ZVMs. The intersection of these two categories represents PRBs with ZVI as the reactive medium (i.e., FePRBs or “iron walls”).

In contrast to the conventional PRB, a permeable reactive treatment zone (PRTZ) is a geochemically manipulated subsurface zone where aquifer material is altered to promote destruction or immobilization of target chemicals (e.g., flushed with sodium dithionite to create a zone of reduced iron [20–23]). Passive reactive wells (PRWs) are a series of wells or caissons containing a treatment material, through which water flows because of a permeability contrast between the wells and aquifer. A biologically reactive barrier (BRB), sometimes called a “biocurtain,” is a subsurface zone where microbiological activity is enhanced or modified to provide treatment of target chemicals.

### 2. Reactive Media

The core function of a PRB (and many related technologies) is to bring the contaminated material in contact with a reactive material that promotes a process that results in decontamination. The range of reactive materials that can be applied in PRBs is quite diverse, as illustrated by Table 1. The



**Figure 2** Typical configuration of a PRB, showing the source zone, plume of contamination, treatment zone, and plume of treated groundwater. (Reprinted with permission, Powell and Associates.)

reactive material can be introduced directly into the subsurface or formed in situ after addition of agents that are not directly involved in reaction with the contaminants. The former is exemplified by ZVMs, whereas the latter is exemplified by the zone of ferrous iron formed by “in situ redox manipulation” [20–23]. In Table 1, we have tried to capture the whole range of reactive media that are currently being used in PRBs, but the remainder of this review will focus on PRBs constructed with ZVMs.

### C. Other Sources of General Information on ZVI and PRBs

The rapid increase in interest and knowledge associated with remediation applications of ZVMs and PRBs has led to a number of reviews on these subjects. To date, these include Refs. 2, 3, 18, and 42–53. In general, these reviews do not attempt to provide comprehensive coverage of the primary literature in this field, as it has already become too vast. Fortunately, most of the primary literature is included in several databases that are available on the World Wide Web. These databases can be found at <http://cgr.ese.ogi.edu/ironrefs> and <http://www.rtdf.org>.

## II. CONTAMINANT-REMOVAL PROCESSES

The processes responsible for contaminant removal by ZVMs and PRBs include both “physical” removal from solution to an immobile phase and “chemical” removal by reaction to form less hazardous products. In the discussion that follows, we will refer to the former as sequestration and the latter as transformation. This distinction has heuristic value, even though sequestration and transformation processes are related for many contaminants.

### A. Removal by Sequestration

For the purposes of this review, we have chosen the term *sequestration* to represent contaminant removal by processes that do not involve contaminant degradation. Although the term is most commonly applied to the fate of organic contaminants [54], it can also be applied to metals and other inorganic contaminants. In older literature on removal of contaminant metals, the term *cementation* was commonly used (e.g., Ref. 55), but this term is not used here.

Sequestration by  $\text{Fe}^0$  occurs mainly by adsorption, reduction, and coprecipitation, although other processes may be involved such as pore diffusion and polymerization. In most cases, *adsorption* is the initial step and

**Table 1** Summary of Reactive Media<sup>a</sup>

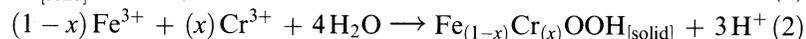
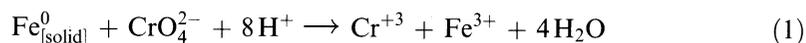
Type	Composition	Applications	Selected references
Zero-valent metals	Fe, Zn, Sn	TCE, Cr(VI), etc.	Numerous <sup>b</sup>
Bimetallic combinations	Fe/Ni, Fe/Pd	PCBs, chlorophenols, chloromethanes,	[24–26]
Metal oxides	Iron oxides	Cr(VI), U(VI)	[20,21,23,27–30]
Metal sulfides	FeS	Chloromethanes, ethanes, and ethenes	[31,32]
Aluminosilicates	Clays, Zeolites	TCE, Cr(VI)	[33–35]
Calcium phosphates	Apatite, bone char	U(VI), Pb	[36,37]
Carbonaceous materials	Peat, sawdust, leaf litter, ground rubber	Phosphate, BTEX, Acid Mine Drainage	[38–41]

<sup>a</sup> Other tables of this type can be found in Refs. 4, 30, and 42.

<sup>b</sup> Complete list at <http://cgr.ese.ogi.edu/ironrefs/>.

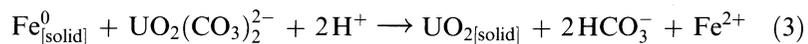
subsequent transformations help ensure that the process is irreversible. In some cases, however, adsorption is the sequestration process of primary importance. This is certainly true with metals that occur as soluble cations, which can be expected to adsorb fairly strongly to iron oxides, but cannot be reduced to insoluble forms by  $\text{Fe}^0$ : e.g.,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Zn}^{2+}$  [56]. It may also be true of toxic heavy metals like Cd, Cu, Hg, Ni, and Pb, which exist predominantly as soluble cations under aerobic conditions, but could be reduced to insoluble species by  $\text{Fe}^0$ . In some cases, the dominant process is unmistakable, such as in the recovery of  $\text{Hg}^0$  using  $\text{Fe}^0$  [57–59]. In other cases, however, the relative importance of adsorption vs. reduction is uncertain because most of the available literature either focuses on adsorption without attention to whether the contaminant metal undergoes a change in valence state (e.g., Ref. 60) or assumes sequestration is due to reduction without distinguishing how much is due to adsorption (or coprecipitation) alone (e.g., Refs. 61 and 62).

Of greater recent interest are metals that exist predominantly as soluble, hazardous oxyanions in oxic groundwaters, but that become relatively insoluble species when reduced, making them candidates for remediation by reductive immobilization. These metals include As(V), Cr(VI), Se(VI), Tc(VII), U(VI), and a few others [51,63,64]. In general, a complex and variable mixture of processes is responsible for sequestration of these contaminants by  $\text{Fe}^0$ . For example, Cr(VI) is at least partially reduced to Cr(III), which is then precipitated as a mixed oxyhydroxide [65–67].



Although further reduction of Cr(III) to  $\text{Cr}^0$  is not thermodynamically favorable with  $\text{Fe}^0$ , reduction of Se(VI) all the way to  $\text{Se}^0$  is expected and has been observed [67]. As(V) can also be reduced by  $\text{Fe}^0$  to  $\text{As}^0$ , but sequestration of As(V) seems to involve mainly As(III) under anaerobic conditions [68,69] and adsorbed As(V) under aerobic conditions [70].

Unlike the other metal oxyanions discussed above, the thermodynamic driving force for reduction of U(VI) by  $\text{Fe}^0$  is only moderately favorable under conditions of environmental relevance. Because the dominant forms of U(VI) in most groundwaters are carbonate complexes, the following overall (reduction and precipitation) reaction might be expected:

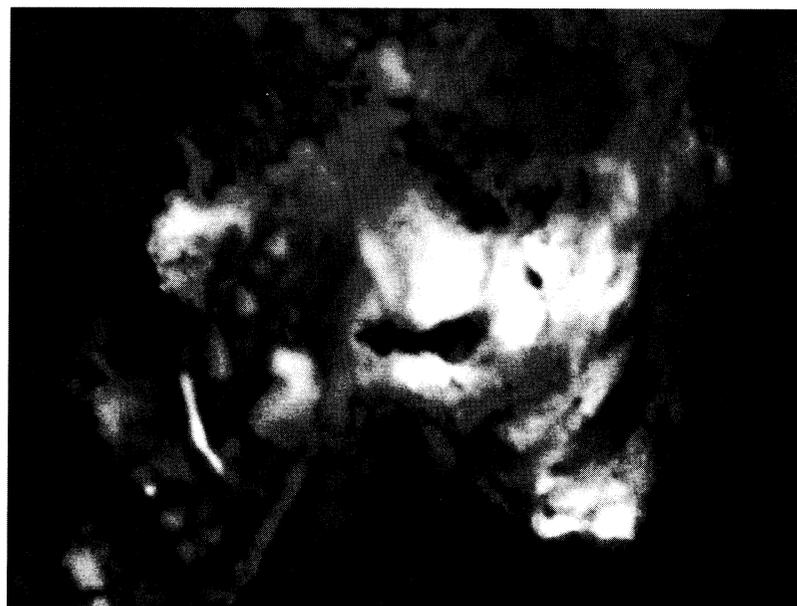


Reactions of this type could be responsible for the sequestration of U(VI) by  $\text{Fe}^0$ , as favored by several investigators [63,71,72]. However, adsorption of U(VI) to iron oxides is known to be strong, and evidence that this process is

the dominant sequestration mechanism has been provided by other investigators [67,73,74]. Recently, detailed studies of samples from the FePRB at the Y-12 site, Oak Ridge, TN (Fig. 3) have shown that the distribution and speciation of uranium in the  $\text{Fe}^0$ -bearing zone is complex, and that sampling and characterization of these materials is challenging [75,76].

## B. Removal by Transformation

To contrast with the term sequestration, we have chosen *transformation* to represent chemical reactions that convert contaminants to distinct products. The transformation of metals from one valence state to another was included in the previous section because the effect of these transformations is mainly to enhance sequestration. In contrast, there are a few nonmetal inorganic contaminants that are transformed by  $\text{Fe}^0$  to soluble but comparatively innocuous products, which are discussed below. Following that,

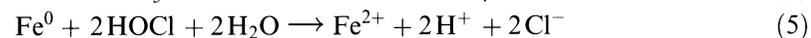
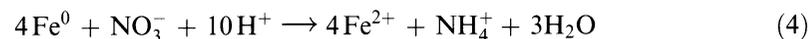


**Figure 3** Scanning electron micrograph of an  $\text{Fe}^0$  grain taken from an FePRB at the Y-12 site at Oak Ridge, TN. The bright spot is mostly U, showing that these deposits are localized on the  $\text{Fe}^0$  surface. These deposits were associated with varying amounts of Fe, S, Si, and Ca. Additional details on the analyses of these samples are in Ref. 76.

we review the reductive transformation of organic contaminants by  $\text{Fe}^0$ , with emphasis on the two most important pathways: dehalogenation of chlorinated aliphatic or aromatic contaminants and reduction of nitroaromatic compounds.

### 1. Inorganic Transformations

The two most notable examples of reductive transformations by  $\text{Fe}^0$  that involve nonmetal inorganic compounds are reduction of nitrate [Eq. (4)] and aqueous chlorine [Eq. (5)].



The reduction of nitrate yields ammonia under most conditions [77–80], but some have suggested that dinitrogen is formed [81]. Possible applications of this process include not only the direct treatment of nitrate-contaminated groundwater, but also the pretreatment of groundwater that is contaminated with both nitrate and radionuclides, in order to allow the development of more strongly reducing biogeochemical conditions (sulfidogenesis or methanogenesis) that are necessary for microbially mediated immobilization of uranium [75].

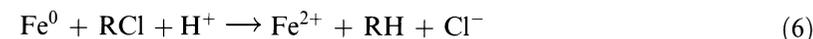
The reduction of aqueous chlorine ( $\text{HOCl}$ ) to chloride by  $\text{Fe}^0$  and other ZVMs [Eq. (5)] has long been known as a major contributor to the decay of residual chlorine disinfectant during distribution in drinking water supply systems that contain metal pipes (e.g., Ref. 82). This reaction can, however, be turned to advantage for the removal of excess residual chlorine, and a variety of proprietary formulations of granular ZVMs are available commercially for this purpose (e.g., KDF Fluid Treatment, Inc. Three Rivers, MI). This application is sometimes called “dechlorination,” but should not be confused with the dechlorination of organic contaminants, which is discussed below.

Other nonmetal inorganic compounds that might be usefully transformed by  $\text{Fe}^0$  include perchlorate, sulfate, and cyanide. Although the energetics for reduction of these compounds are all favorable, the kinetics appear to be unfavorable in the absence of microbial mediation. In the case of perchlorate, it has been reported that biodegradation can be inhibited by  $\text{Fe}^0$  [83]. This means that useful applications of these reactions will have to wait until effective methods of catalyzing these reactions are discovered.

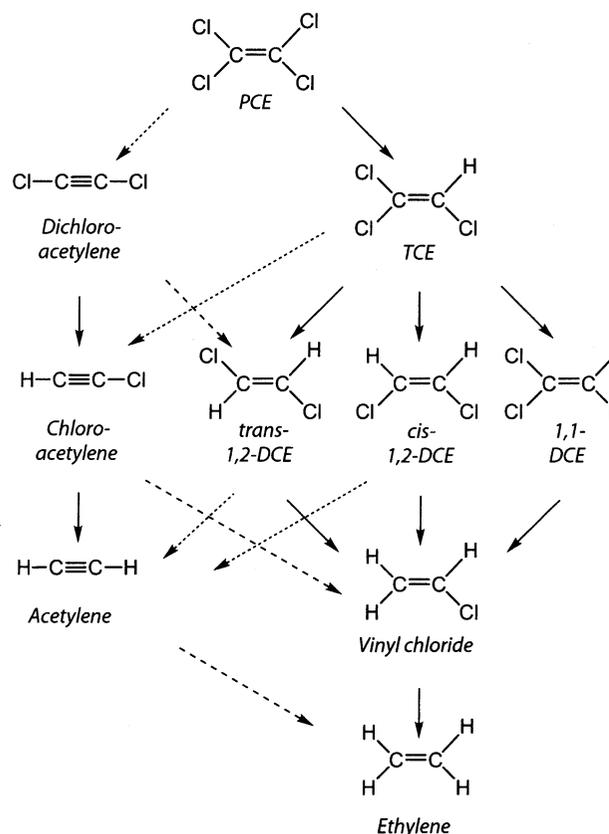
### 2. Dechlorination

Dehalogenation can occur by several reductive pathways. The simplest results in replacement of a C-bonded halogen atom with a hydrogen, and

is known as *hydrogenolysis* or *reductive dehalogenation*. For a general chlorinated aliphatic compound,  $\text{RCl}$ , hydrogenolysis by  $\text{Fe}^0$  corresponds to the overall reaction:



This reaction is the dominant dehalogenation pathway in reduction of halogenated methanes [84] and haloacetic acids [85]. In Fig. 4, this reaction is illustrated for perchloroethene (PCE), where complete dechlorination by this pathway requires multiple hydrogenolysis steps. The relative rates of these steps are a critical concern because they determine whether

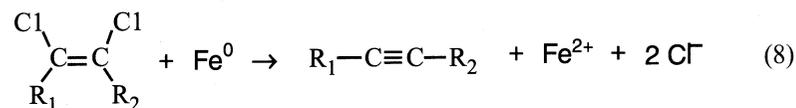
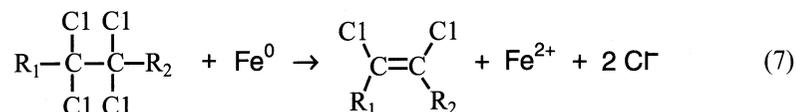


**Figure 4** Scheme showing the branching between hydrogenolysis (solid arrows), reductive elimination (fine dashed arrows), and hydrogenation (course dashed arrows) pathways to produce the major products of chlorinated ethene reduction by ZVMs. (Adapted from Ref. 88.)

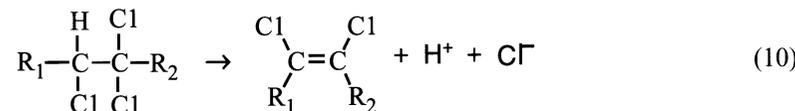
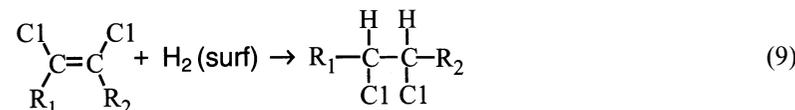
persistent and hazardous intermediates (such as vinyl chloride, VC) will accumulate [86,87].

In principle, aryl halogens can also be subject to hydrogenolysis, although this reaction is likely to be less facile than hydrogenolysis of most alkyl halogens. In fact, the only confirmed example of hydrogenolysis involving aryl halogens by  $\text{Fe}^0$  under environmental conditions is for pentachlorophenol, and the reaction was found similar in rate to literature values for TCE [89]. In contrast, rapid hydrogenolysis of aryl halogens by  $\text{Fe}^0$  has been obtained under extreme conditions, such as in supercritical water [90–92] or at high temperature [93]. These variations are not amenable to use in a PRB, but are discussed along with related enhancements in Sec. V.C.

The other major dehalogenation pathway involves elimination of two halogens, leaving behind a pair of electrons that usually goes to form a carbon-carbon double bond. Where the pathway involves halogens on adjacent carbons, it is known as *vicinal dehalogenation* or *reductive  $\beta$ -elimination*. The fine dashed arrows in Fig. 4 illustrate this process for PCE. Note that this pathway can produce alkynes from vicinal dihaloalkenes [88,94,95], as well as producing alkenes from vicinal dihaloalkanes [96,97].

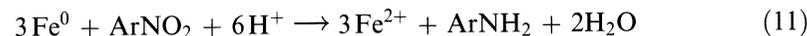


In addition to the two major reductive pathways for dechlorination, there are two additional reactions that have been observed: *hydrogenation*, which involves addition of hydrogens across a C-C double or triple bond [Eq. (9)] and *dehydrohalogenation*, which involves elimination of  $\text{H}^+$  and  $\text{X}^-$  and creation of a new C-C double bond [Eq. (10)]. Hydrogenation has been invoked to explain the distribution of products observed in several studies involving chlorinated alkenes and  $\text{Fe}^0$  [88], and is particularly important where a noble metal like Pd is present to act as a catalyst (see Sec. III.B). Note that we have written  $\text{H}_2(\text{surf})$  in Eq. (9) to represent all of the various forms of surface-activated hydrogen, and do not mean to imply that the reaction necessarily involves adsorbed diatomic molecular hydrogen. Dehydrohalogenation has not received much attention as a reaction that might contribute to degradation of chlorinated ethenes by  $\text{Fe}^0$ , even though it can be base catalyzed [98], which might make it favored under the alkaline conditions that can be created by corrosion of  $\text{Fe}^0$ .

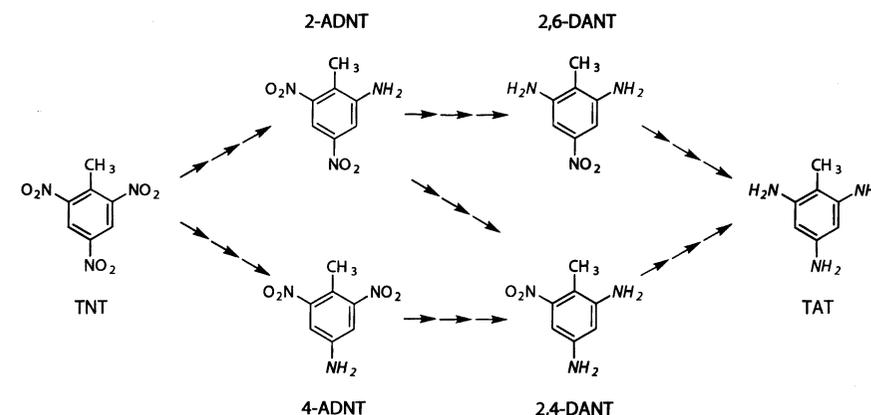


### 3. Nitro and Azo Reduction

In general, reduction of aromatic nitro groups occurs in three steps, via nitroso and hydroxylamine intermediates, to the amine. For nitrobenzene and simple substituted nitrobenzenes reacting with  $\text{Fe}^0$  in batch model systems, the intermediates have been detected in solution, but the dissolved amine alone is usually sufficient for good mass balance [99–103]. Thus, the net reaction is:



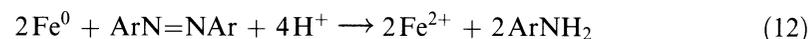
Recently, research on nitro reduction by  $\text{Fe}^0$  has been extended to environmental contaminants with multiple nitro groups, such as TNT and RDX [104–107]. As expected, batch experiments show that TNT and RDX are rapidly reduced by  $\text{Fe}^0$  to a complex mixture of products (Fig. 5). In contrast, column experiments with TNT have shown a very high capacity to



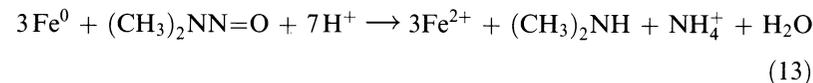
**Figure 5** Scheme showing branching among nitro reduction steps for TNT by zero-valent metal. Triple arrows indicate that each step shown presumably proceeds through three steps with nitroso and hydroxylamine intermediates. (Adapted from similar figures for other reducing systems, including Refs. 109,110.)

convert all products to triaminotoluene [108]. This result suggests that earlier work, all of which appears to have been done in batch experiments, may have led to unrepresentative conclusions regarding the formation of soluble reduction products. Despite this simple FePRBs may be sufficient to reach treatment goals for some explosives under real-field conditions.

In principle, the nitroso, hydroxylamine, and/or amine products of nitro reduction might undergo coupling to form azoxy, azo, and/or hydrazo dimers, but no evidence for these products has been found under the conditions that have been studied to date. One reason that these dimers do not accumulate may be that they are rapidly reduced by Fe<sup>0</sup>. In fact, Fe<sup>0</sup> reduces azo groups to amines [Eq. (12)] very rapidly [111–113], and this reaction may prove to be useful in the remediation of wastewaters contaminated with azo dyes.



Like nitro and azo groups, the nitrosamine moiety is subject to reduction by Fe<sup>0</sup> and is present in some important environmental contaminants. One such contaminant is *N*-nitrosodimethylamine (NDMA), which is reduced by Fe<sup>0</sup> via a complex mechanism that gives the following overall reaction [114,115]:



NDMA is a potent carcinogen that not only occurs in groundwater contaminated with rocket fuels but can be formed from precursors that sometimes occur in groundwater and even drinking water [116]. Another important nitrosamine that is reduced by Fe<sup>0</sup> is the explosive RDX [104–106,117,118]. The products of this reaction are difficult to characterize, but appear to be low molecular weight, polar, N-containing compounds, which are likely to be analogous to the products formed from NDMA [Eq. (13)].

#### 4. Other Organic Transformations

In principle, there are other organic functional groups that might be reduced by Fe<sup>0</sup> under environmental conditions, including aldehyde, ketone, quinone, diamine, nitrile, oxime, imine, sulfoxide, and disulfide moieties [119–121]. Recently, the reduction of quinonoid redox indicators by Fe<sup>0</sup> has been explored in an educational context [122], but we are not aware of any application of FePRBs for remediation of groundwater contaminants that contain these moieties. It is likely, however, that examples will emerge in the future. In addition, it is to be expected that other types of transformations will become accessible as “enhanced” and hybrid technologies involving ZVMs become available. A few of these are discussed in Sec. V.C.

To conclude this section, it is worth noting some of the chemistry that is not expected in association with FePRBs. In general, any compound that is easily oxidized will be a poor candidate for reduction. Such compounds include saturated or aromatic hydrocarbons (including the constituents of gasoline, coal tar, creosote, etc.), ethers and alcohols (including MTBE, glycols, etc.), and phenols (e.g., cresols, various residues from digestion lignin into paper pulp). At the same time, care should be taken not to presume that a contaminant is transformed by reduction just because it is found to be removed by contact with Fe<sup>0</sup>. This is illustrated by recent reports that Fe<sup>0</sup> degrades the pesticides carbaryl [123] and benomyl [124], both of which were attributed to reduction. However, these pesticides do not contain any readily reducible functional groups. It is more likely that Fe<sup>0</sup> degrades carbaryl by catalyzing alkaline hydrolysis of the phosphate ester moiety, and benomyl by catalyzing alkaline hydrolysis of the amide moiety.

### III. REACTIVE MEDIA AND THEIR PROPERTIES

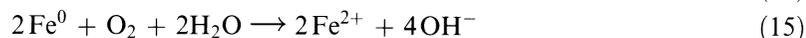
There are two types of metals that are of interest as reactive media in PRBs: (1) corrodable, base metals, which have equilibrium potentials for dissolution that are below the potential for reduction of water or any strongly oxidizing solutes, and (2) noble, catalytic metals, which are not subject to oxidative dissolution under environmental conditions but which participate in reduction of solutes as catalysts. The corrodable, base metals (Fe, Zn, Sn, etc.) are discussed in Sec. III.A, and the role of noble, catalytic metals (Pd, Ni, etc.) in PRBs is discussed in Sec. III.B.

#### A. Iron and Other Corrodable Metals

Although the majority of interest in remediation applications of corrodable metals revolves around Fe<sup>0</sup>, other possibilities have been investigated, including magnesium, tin, and zinc. The bulk of this work has used Zn<sup>0</sup> as a model system for comparison with Fe<sup>0</sup> (e.g., Refs. 95, 96, 125, and 126), but a few studies have surveyed a range of metals as possible alternatives to Fe<sup>0</sup> in environmental applications other than PRBs (e.g., Refs. 127 and 128).

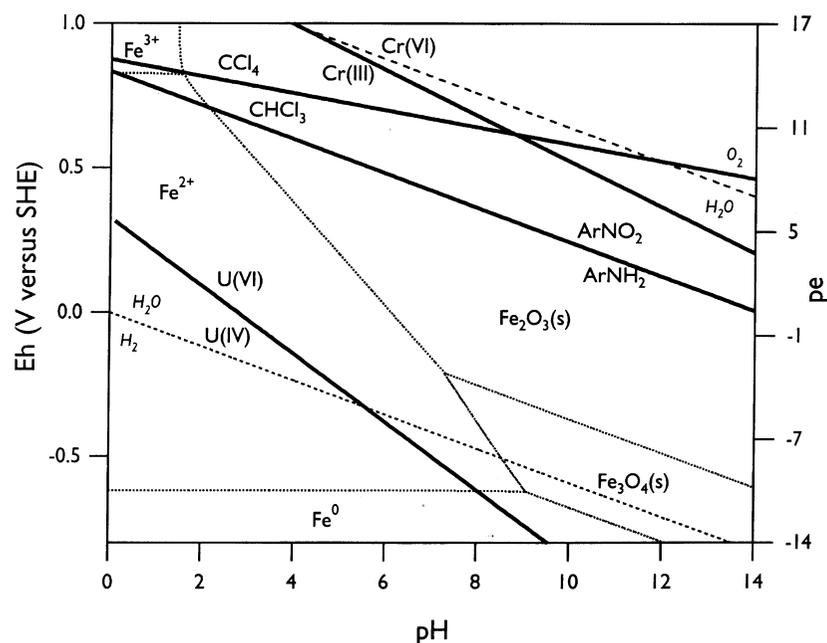
##### 1. Corrosion Chemistry

The corrosion reaction involving water [Eq. (14)] is slow but presumably ubiquitous, whereas corrosion of Fe<sup>0</sup> by reaction with dissolved oxygen [Eq. (15)] is rapid as long as O<sub>2</sub> is available.



The presence of a reducible contaminant in an  $\text{Fe}^0\text{-H}_2\text{O}$  system provides another reaction [in addition to Eqs. (14)–(15)] that can contribute to the overall corrosion rate. This is exemplified in Eq. (6) for the hydrogenolysis of a generic chlorinated hydrocarbon, Eq. (11) for nitro reduction, and Eq. (12) for azo compounds.

For simplicity, we have written and balanced these equations for acidic conditions, but the speciation of iron and some contaminants, as well as the thermodynamic potentials for the associated redox half-reactions, will vary with pH. The most efficient way to represent the effects of pH is in an Eh-pH diagram, such as Fig. 6. This particular diagram shows that reduction of three contaminants ( $\text{CCl}_4$ ,  $\text{ArNO}_2$ , and  $\text{Cr(VI)}$ ) by  $\text{Fe}^0$  is thermodynamically favorable over a wide range of pH, even though the speciation of the  $\text{Fe(II)}$



**Figure 6** Eh-pH diagram for the  $\text{Fe}^0\text{-H}_2\text{O}$  system where total dissolved  $\text{Fe} = 1 \times 10^{-6}$  M,  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  are assumed to be the solubility limiting phases, and  $[\text{ox}] = [\text{red}]$  for all redox active species. Other Eh-pH diagrams for  $\text{Fe}^0\text{-H}_2\text{O}$ -contaminant systems can be found in Refs. 42, 84, and 129–131.

that is formed changes considerably. In contrast, reduction of  $\text{U(VI)}$  by  $\text{Fe}^0$  switches from favorable to unfavorable where the pH increases above 8.

## 2. Common Types of Granular Iron

The  $\text{Fe}^0$  that has been used for contaminant degradation includes construction-grade material, used primarily in field applications, and reagent-grade material, used primarily in laboratory studies. Construction-grade granular iron is prepared from scrap “gray” or ductile cast iron by grinding and sieving, and annealed under an oxidizing atmosphere. The resulting material usually has a thick outer layer of iron oxide, which sometimes includes considerable amounts of inorganic carbon. Reagent-grade granular iron is usually prepared by electrolytic precipitation, is then ground, sieved, and sometimes annealed under a reducing atmosphere leaving a bright metallic surface.

A great deal of empirical testing has been done to determine which types of iron are most reactive with a particular contaminant, but little of this work has been reported in the peer-reviewed literature. A few studies have summarized readily available properties of a significant range of iron types [126,132], but these efforts fall far short of forming the basis for a systematic understanding of the relative reactivity of granular metals. The role of some physical properties of granular  $\text{Fe}^0$  are well established, as discussed in Sec. IV.A.1 and V.B.1, so these properties are summarized in Table 2 for selected construction- and reagent-grade irons.

**Table 2** Summary of Iron Properties

Supplier	$\alpha_s$ ( $\text{m}^2 \text{g}^{-1}$ ) <sup>a</sup>	$\rho_s$ ( $\text{g cm}^{-3}$ ) <sup>b</sup>	$\rho_b$ ( $\text{g cm}^{-3}$ ) <sup>c</sup>
Connelly iron aggregate (ETI CC-1004)	1.8 (2)	7.55	1.9
Peerless cast iron aggregate (ETI 8/50)	$0.9 \pm 0.7$ (11)	7.39	2.2
Master builder	$1.3 \pm 0.7$ (14)	7.38	2.7
Fisher electrolytic	$0.2 \pm 0.2$ (9)	9.49	2.6
Fluka filings	$0.03 \pm 0.06$ (5)	8.58	3.8

<sup>a</sup> Average of reported specific surface areas in  $\text{m}^2$  per gram of  $\text{Fe}^0$  as summarized in Ref. 80. Statistics are based on independently reported values from the literature: uncertainties are one standard deviation and the number of averaged values are given in parenthesis.

<sup>b</sup> Specific density in grams per liter of  $\text{Fe}^0$  volume [133]. For comparison, typical literature values are  $7.87 \text{ g cm}^{-3}$  for pure elemental iron, 7.2–7.3 for cast and malleable iron, and 4.9–5.3 for hematite [134].

<sup>c</sup> Bulk density in grams per liter of total volume. Construction-grade  $\text{Fe}^0$  can be prepared with bulk densities from 1.4 to  $3.5 \text{ g cm}^{-3}$  (90 to 220  $\text{lb ft}^{-3}$ ), but currently available products are about  $2.4 \text{ g cm}^{-3}$  (150  $\text{lb ft}^{-3}$ ) (David Carter, Peerless Metal Powders and Abrasives, personal communication).

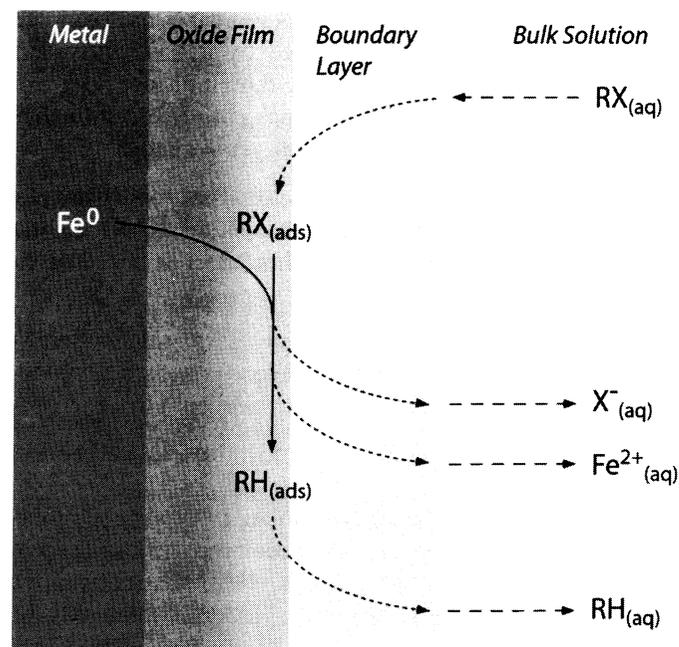
## B. Bimetallic Combinations

In addition to transformation by corrodable metals (such as  $\text{Fe}^0$  and  $\text{Zn}^0$ ), bimetallic combinations of a catalytic metal with a corrodable metal (such as Pd/Fe or Ni/Fe) have also been shown to transform a variety of contaminants. In most cases, rates of transformation by bimetallic combinations have been significantly faster than those observed for iron metal alone [26,96,135–139]. Not only have faster transformation rates been observed with bimetallic combinations, but, in some cases, transformation of highly recalcitrant compounds, such as polychlorinated biphenyls (PCBs), chlorinated phenols, and DDT has been achieved [24,140,141]. The mechanism responsible for the enhanced reactivity with bimetallic combinations is still unclear; however, it has been suggested that electrochemical effects, catalytic hydrogenation, or intercalation of  $\text{H}_2$  may be responsible. A likely limitation to the full-scale application of bimetallic combinations to groundwater remediation is deactivation of the catalytic surface either by poisoning (e.g., by sulfide) or by formation of thick oxide films [136,142,143].

## IV. MICROSCALE PROCESSES

Almost everything that is known about the fundamental processes that are responsible for contaminant removal by ZVMs has been derived from laboratory experiments done with bench-scale model systems. Of this work, the majority has been done in batch reactors consisting of dilute slurries of  $\text{Fe}^0$  particles suspended in small bottles. Batch experiments are simple to perform and the results can be easy to analyze, but this method can be limiting, and questions remain about how well it models conditions that are relevant to the field. Recently, a few other small-scale laboratory model systems have been described that offer greater control over key experimental variables, e.g., (rotating) iron disk electrodes [101,144], recirculating batch reactors [100], and small columns operated in “miscible-displacement” mode [145]. Future developments along these lines may greatly improve our understanding of the fundamental chemistry that controls the performance of this technology.

Through the many studies that have now been done in well-controlled model systems, a general conceptual model has emerged of the processes controlling contaminant reduction on  $\text{Fe}^0$ . Some of the key elements of this model are summarized in Fig. 7, using a generic chlorinated hydrocarbon, RX, as the model contaminant. First, RX must be conveyed to the stagnant boundary layer at the oxide-water interface, then it must diffuse across the boundary layer and form a complex with a reactive site either on or in the oxide film (or directly on the  $\text{Fe}^0$  through a defect in the oxide film [146]). Only then can reduction occur (with electrons that ultimately come from the



**Figure 7** Schematic of the primary steps involved in dehalogenation of RX at  $\text{Fe}^0$ -oxide- $\text{H}_2\text{O}$  interface. Coarse dashed arrows represent mass transport between the bulk solution and the particle surface, fine dashed arrows denote diffusion across the stagnant boundary layer and surface complexation, and solid arrows show electron transfer and bond rearrangement on the surface. (Adapted from Ref. 147.)

underlying  $\text{Fe}^0$ ), followed by desorption and diffusion of products away from the surface.

### A. Reaction at the Surface

#### 1. Basic Kinetic Model

Most of the primary kinetic data that have been obtained from bench-scale model systems suggest that reaction with  $\text{Fe}^0$  is first order in the concentration of solution phase contaminant,  $C$ . Thus, we can write the following rate law in differential and integrated forms:

$$-dC/dt = k_{\text{obs}}C \quad (16)$$

$$\ln(C_t/C_0) = -k_{\text{obs}}t \quad (17)$$

where  $k_{\text{obs}}$  is the pseudo-first-order rate constant. Experimental values of  $k_{\text{obs}}$  are routinely obtained from the slope of the regression line for  $\ln(C_t)$

or  $\ln(C_t/C_0)$  vs. time. However,  $k_{\text{obs}}$  will only be constant for a limited range of experimental conditions, as it can be influenced by a host of system properties. Two of the best characterized factors that influence  $k_{\text{obs}}$  are addressed below. Others, such as pH [84,148–150], are not discussed further here because general models for their effects are not yet available.

**Effect of Iron Concentration.** Among the factors that influence  $k_{\text{obs}}$ , the effect of the amount of iron surface area that is accessible to the contaminant has received the most attention. This effect is most often described by a linear relationship:

$$k_{\text{obs}} = k_{\text{SA}}\rho_a \quad (18)$$

where  $k_{\text{SA}}$  is the specific reaction rate constant ( $\text{L hr}^{-1} \text{m}^{-2}$ ) and  $\rho_a$  is the concentration of iron surface area ( $\text{m}^2 \text{L}^{-1}$  of solution). Deviations from this linear relationship have been reported [151–153], but their general significance is not yet well established.

Data for  $k_{\text{SA}}$  that were available as of November 1995 were summarized in Refs. 86 and 132, but many more data have been reported since then. Selected values of  $k_{\text{SA}}$  are given in Table 3. In addition, quantitative structure-activity relationships (QSARs) have been reported that may be suitable for estimating values of  $k_{\text{SA}}$  that have not been measured [87,88, 154–156].

The other term in Eq. (18),  $\rho_a$ , can be calculated from:

$$\rho_a = a_s\rho_m \quad (19)$$

where  $a_s$  is the specific surface area ( $\text{m}^2 \text{g}^{-1}$ ) of a type of  $\text{Fe}^0$ , usually measured by BET gas adsorption, and  $\rho_m$  is the mass concentration of  $\text{Fe}^0$

(grams of Fe per liter of solution volume). For batch studies,  $\rho_m$  can be calculated from

$$\rho_m = \frac{M_{\text{Fe}}}{V_{\text{H}_2\text{O}}} = \frac{M_{\text{Fe}}}{V_{\text{Tot}} - M_{\text{Fe}}/\rho_s} \quad (20)$$

where  $M_{\text{Fe}}$  is the mass of  $\text{Fe}^0$  (g),  $V_{\text{H}_2\text{O}}$  is the volume of solution (L),  $V_{\text{Tot}}$  is the total system volume (L), and  $\rho_s$  is the density of the iron ( $\text{g L}^{-1}$  occupied by the  $\text{Fe}^0$ ).

**Effect of Temperature.** Several studies have shown that the kinetics of contaminant reduction in batch experiments exhibit temperature dependencies that conform to the Arrhenius equation [86,87,132,159,160]. Thus, we can write the following expression relating the rate constants at  $T_1$  and  $T_2$  (in °K):

$$\frac{k_{T_2}}{k_{T_1}} = e^{\left(\frac{-E_a}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} \quad (21)$$

where  $E_a$  is the activation energy ( $\text{kJ mol}^{-1}$ ) and  $R$  is the gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ). Adapting the approach taken in several previous publications [49,161], we have used Eq. (21) to calculate correction factors ( $k_{T_2}/k_{T_1}$ ) as a function of groundwater temperature ( $T_2$ ), assuming a reference temperature ( $T_1$ ) of 23°C and appropriate values for  $E_a$ . Five values of  $E_a$  were selected to generate Fig. 8: 55  $\text{kJ mol}^{-1}$  is nearly the value reported for  $\text{CCl}_4$  reacting with Fluka  $\text{Fe}^0$  [144], 45  $\text{kJ mol}^{-1}$  is approximately the value reported for vinyl chloride reacting with Fisher  $\text{Fe}^0$  [159], 35  $\text{kJ mol}^{-1}$  approximates the average  $E_a$  for TCE reacting with both reagent- and construction-grade  $\text{Fe}^0$  [160], 25  $\text{kJ mol}^{-1}$  represent regimes that are transitional between reaction and mass transfer control [101], and 15  $\text{kJ mol}^{-1}$  represents kinetics that are entirely limited by mass transfer [162]. In general terms, Fig. 8 shows that reactions with  $\text{Fe}^0$  will occur about half as rapidly in the field as they do at temperatures that are typical of the laboratory. Note that there is less effect of temperature on rates that are influenced by mass transport.

## 2. Multiprocess Kinetic Models

**Competition for Reactive Sites.** Recently, it has become widely recognized that  $k_{\text{obs}}$  can vary with the concentration of the contaminant. In most cases, this effect has been attributed to saturation of reactive sites on the  $\text{Fe}^0$  surface. One kinetic model that has been used to describe these data is of the form:

$$-\frac{dC}{dt} = \frac{AC}{B + C} \quad (22)$$

**Table 3** Selected Rate Constants for Reduction by  $\text{Fe}^0$

Contaminant	$k_{\text{SA}}^a$ ( $\text{L hr}^{-1} \text{m}^{-2}$ )
Carbon tetrachloride ( $\text{CCl}_4$ )	$1.2(\pm 1.5) \times 10^{-1}$ (11) <sup>b</sup> ; $1.5 \times 10^{-1}$ [157]
1,1,1-Trichloroethane (TCA)	$1.1 \times 10^{-2}$ [158]; $4.6 \times 10^{-1}$ [96]
Trichloroethene (TCE)	$3.9(\pm 3.6) \times 10^{-4}$ (12) <sup>b</sup> ; $3.3(\pm 5.2) \times 10^{-4}$ (4) <sup>c</sup> ; $1.1 \times 10^{-3}$ (2) <sup>d</sup>
Vinyl chloride (VC)	$5.0(+1.5) \times 10^{-5}$ (3) <sup>b</sup> ; $8.2 \times 10^{-6}$ (5) <sup>e</sup>
2,4,6-Trinitrotoluene (TNT)	$5.0(\pm 0.7) \times 10^{-2}$ (5) <sup>f</sup>

<sup>a</sup> For data that are derived from multiple independent experiments, the values in parentheses are the standard deviation of the estimate, followed by the number of experiments.

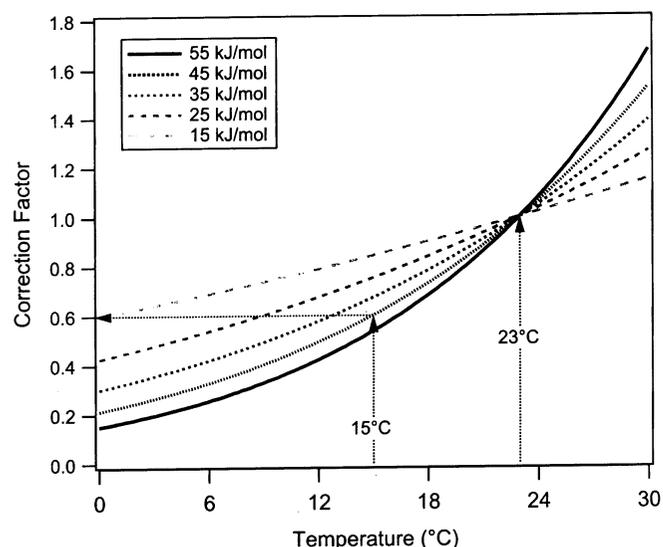
<sup>b</sup> Represents average of all published data as of November 1998 [86].

<sup>c</sup> Average of values from four types of  $\text{Fe}^0$  [69].

<sup>d</sup> From Ref. 152.

<sup>e</sup> From regression of  $k_{\text{obs}}$  vs.  $\rho_m$  [159].

<sup>f</sup> Batch experiments done with Peerless iron [107].



**Figure 8** Correction factors for the effect of temperature on the rate of reduction by  $\text{Fe}^0$ . Arrows indicate the reference temperature around which most laboratory data are obtained ( $23^\circ\text{C}$ ), and a more representative temperature for groundwater ( $15^\circ\text{C}$ ). Assuming  $E_a \approx 45 \text{ kJ mol}^{-1}$  for TCE [160], the corresponding correction factor shown is 0.6 (i.e., rates will be slower in the field by 60%).

where  $A$  and  $B$  are constants [163]. Several studies have equated  $A$  and  $B$  with  $V_m$  and  $K_{1/2}$ , by analogy to the Michaelis-Menten model for enzyme kinetics [86,111,147]. Other studies have associated  $A$  with  $k_0$ , the zero-order rate constant observed when surface sites are fully saturated [152], and equated  $A/B$  with  $k_{\text{obs}}$  when  $B \gg C$  [107,152].

Site saturation kinetics can also be described with a kinetic model of the form:

$$-\frac{dC}{dt} = \frac{DC}{1 + EC} \quad (23)$$

where  $D$  and  $E$  are constants. Some studies have defined  $D$  and  $E$  in accord with the Langmuir-Hinshelwood-Hougen-Watson (LHHW) model for surface catalyzed reactions [88,125,164–166], whereas others have defined  $D$  and  $E$  in terms derived from a surface complexation model [146]. Although the Michaelis-Menten and LHHW models were derived for different systems and conditions, the mathematical forms of these models [represented by Eqs. (22) and (23)] are essentially equivalent. Consequently, it can be shown that  $A = D/E$  and  $E = 1/B$ .

In addition to competition by the contaminant for a limited supply of reactive surface sites (*intraspecies competition*), there is evidence for competition among different species for surface sites (*interspecies competition*). Interspecies competition effects can arise between combinations of contaminants (e.g., Ref. 167) or between contaminants and other adsorbates [102,146,147,159,168–170]. The kinetics that arise from interspecies competition have been modeled by adding appropriate terms to Eq. (22) or Eq. (23). However, in most cases the parameterization of these models has been rather preliminary and their sensitivity to uncertainties in these parameters has not yet been thoroughly investigated.

*Competition Among Reactive and Nonreactive Sites.* In addition to competition among different adsorbates for reactive sites, there is also competition among different surface sites for adsorbates. In principle, it is easy to imagine that granular  $\text{Fe}^0$  under environmental conditions might present surface sites with energies that vary widely for adsorption and reaction. To date, however, most of the available data have been explained using a simple binary model that assumes surface sites are either reactive or nonreactive (i.e., just adsorptive) and that the distribution of reactant between these sites and the solution phase is in quasi-equilibrium. Assuming that contaminant transformation rates are dependent on its aqueous phase concentration and that most adsorption is to nonreactive sites, then a kinetic model for transformation that accounts for sorption can be written

$$-dC_T/dt = k_a C_a^N \quad (24)$$

where  $C_T$  and  $C_a$  are the total system and aqueous phase concentrations,  $k_a$  is the rate constant for transformation, and  $N$  is the reaction order [171]. This model has been applied for PCE and TCE [171,172] and cis- and trans-1,2-dichloroethene [173]. The results are easily interpreted for PCE and TCE, because both gave  $N \approx 1$ . However, the dichloroethenes both gave  $N > 1$ , which suggests that Eq. (24) was not entirely adequate to describe the system behavior.

A more complete and mechanistically explicit model has been described that allows for competitive adsorption to reactive and nonreactive sites on  $\text{Fe}^0$ , as well as partitioning to the headspace in closed experimental systems and branching among parallel and sequential transformation pathways [174,175]. This model represents the distinction between reactive and nonreactive sites by a parameter called the “fractional active site concentration.” Simulations and sensitivity analysis performed with this model have been explored extensively, but application of the model to experimental data has been limited to date.

In cases where sorptive equilibrium is reached rapidly and transformation is much slower, the aqueous phase concentration of contaminant may show a rapid initial decrease due to adsorption followed by a slower decline due to transformation. Under these conditions, the kinetic model represented by Eq. (16) is sufficient to describe the kinetics of transformation after the initial data have been excluded. This approach has been taken for TCE [168], vinyl chloride [176], and probably in many other studies where the exclusion of initial rate data was not clearly documented.

**Competition Among Parallel Reaction Pathways.** The third form of competition that complicates the kinetic description of contaminant degradation by  $\text{Fe}^0$  involves branching among parallel pathways (and/or mechanisms) of transformation by the contaminant. Simple manifestations of this effect—such as the transformation of TCE to form chloroacetylene, *trans*-1,2-dichloroethene, *cis*-1,2-dichloroethene, or 1,1-dichloroethene from TCE—can be described with “branching ratios” [132]. However, a more general approach is to divide rate constants for reactant disappearance into separate rate constants for each product formation pathway. Because first-order rate constants are additive (for reactions occurring in parallel), we can write the following for disappearance of TCE by the four pathways noted above:

$$k_{\text{SA}} = k_{\text{chloroacetylene}} + k_{\text{trans-1,2-DCE}} + k_{\text{cis-1,2-DCE}} + k_{\text{1,1-DCE}} \quad (25)$$

This approach has been taken for the reaction of chlorinated ethenes with  $\text{Zn}^0$  [125,165] and  $\text{Fe}^0$  [88,166], resulting in separate rate constants for all the reactions shown in Fig. 3. Care must be taken in using these parameters in predictive modeling, however, as it is not yet known how sensitive the relative values of these rate constants are to pH, thickness and composition of the oxide film, etc. The same caution applies where the approach represented by Eq. (25) is used to describe parallel mechanisms of transformation. For example, it has recently been reported that several experimental factors influence the relative contributions of dissociative electron transfer, hydrogen atom transfer, and reductive elimination to the dechlorination of carbon tetrachloride and TCE by  $\text{Fe}^0$  [177].

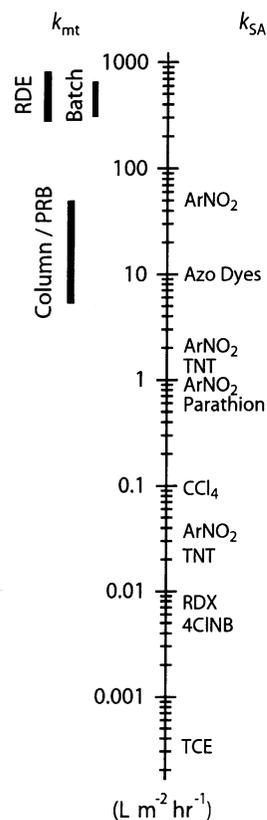
## B. Mass Transport to the Surface

The overall reaction occurring at an  $\text{Fe}^0$  surface involves a series of steps including: (1) mass transport to the reactive site, (2) chemical reaction at the surface (e.g., sorption, electron transfer, etc.), (3) desorption, and (4) mass transport to the bulk solution (recall Fig. 7). Any one of these steps can limit the rate of contaminant removal by  $\text{Fe}^0$ , so the observed

rate ( $k_{\text{SA}}$ ) can be represented as a series of resistances due to transport and reaction:

$$\frac{1}{k_{\text{SA}}} = \frac{1}{k_{\text{rxn}}} + \frac{1}{k_{\text{mt}}} \quad (26)$$

where  $k_{\text{SA}}$  is the overall surface area-normalized rate coefficient,  $k_{\text{mt}}$  is the mass transport coefficient, and  $k_{\text{rxn}}$  is the first-order heterogeneous reaction-rate coefficient. Mass transport resistances can be due to either



**Figure 9** Comparison of previously reported values of  $k_{\text{SA}}$  for reduction by  $\text{Fe}^0$  with external mass transport coefficients estimated for batch, column, and rotating disk electrode reactors. References for the overall rate coefficients are given in Fig. 1 of Ref. 101. Mass transport coefficients were estimated for the batch and column reactors based on empirical correlations discussed in Refs. 125 and 101. Mass transport coefficients for the RDE were calculated using the Levich equation [178].

external transport to the surface or internal transport through the oxide layer (i.e., pore diffusion). Various forms of Eq. (26) have been used to evaluate the role of external mass transport in contaminant reduction by  $\text{Fe}^0$  and  $\text{Zn}^0$  [101,111,144,165].

Because rates of reduction by  $\text{Fe}^0$  vary considerably over the range of treatable contaminants, it is possible that there is a continuum of kinetic regimes from purely reaction controlled, to intermediate, to purely mass transport controlled. Fig. 9 illustrates the overlap of estimated mass transport coefficients ( $k_{\text{mt}}$ ) and measured rate coefficients ( $k_{\text{SA}}$ ). The values of  $k_{\text{SA}}$  are, in most cases, similar to or slower than the  $k_{\text{mt}}$  values estimated for batch and column reactors. The slower  $k_{\text{SA}}$  values suggest that  $k_{\text{rxn}} < k_{\text{mt}}$ , and therefore removal of most contaminants by  $\text{Fe}^0$  should be reaction limited or only slightly influenced by mass transport effects (i.e., an intermediate kinetic regime).

Direct evidence of mass transport limitations for the more highly reactive contaminants has been observed in RDE experiments and batch and column reactors with  $\text{Fe}^0$ . The measured  $k_{\text{rxn}}$  of  $\text{ArNO}_2$  reduction at a bare  $\text{Fe}^0$  electrode was about 10 times faster than the mass transport coefficient estimated in a PRB [101]. In addition, evidence for mass transport effects have been observed in both batch and column  $\text{Fe}^0$  experiments where rates of nitro aromatic [99,100] and azo dye [111] removal were dependent on mixing speed or flow rate. The observed dependence of reduction rate on mixing intensity and the similarity between rates of surface reaction and mass transport suggest that mass transport may limit removal rates of these highly reactive contaminants in FePRBs. An interesting implication of these results is that for highly reactive compounds (such as  $\text{ArNO}_2$  and TNT), hydraulic designs that increase mass transport rates (e.g., funnel-and-gate systems) may be useful for improving contaminant removal rates by FePRBs.

## V. MACROSCALE PROCESSES

The microscale processes reviewed in the previous section may be sufficient to describe the behavior of well-mixed model systems, but packed bed systems (including columns, canisters, and PRBs) are also characterized by processes that are manifest on length scales of meters and time scales of hours. Progress toward understanding the macroscale processes associated with FePRBs has been comparatively slow, in part because it has to be built on a thorough understanding of the microscale processes occurring at the metal-water interface, and the latter is still emerging. On the other hand, the ultimate objective of FePRBs is remediation on the aquifer scale, so

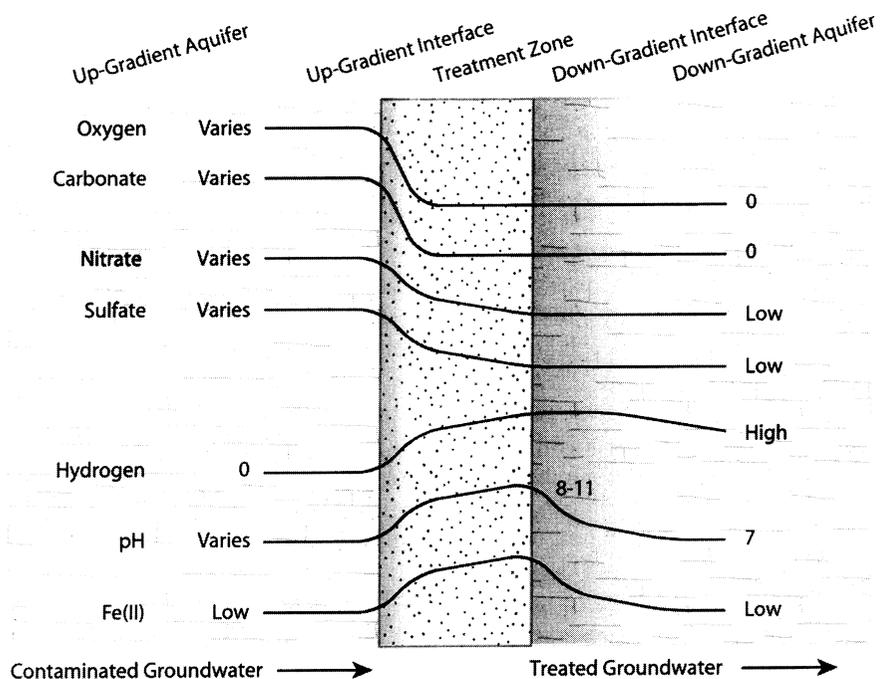
advancing our understanding of biogeochemical processes at the macro scale is where many of the most significant advances can be expected as the FePRB technology matures in the future.

### A. Geochemical Gradients and Zones

Unlike well-mixed batch systems, columns and field conditions result in the development of steep chemical gradients within the iron-bearing zone, at the interfaces between the iron-bearing zone and the surrounding material, and downgradient where the plume of treated water interacts with the native aquifer material. Although some early work recognized that these gradients could be significant (e.g., Refs. 179–181), further characterization of these geochemical gradients has been needed at the field scale before their effects on contaminant fate could be accurately assessed. Recently, considerable progress on this topic has been made through integrated monitoring and modeling studies associated with several field sites, including Moffett Field in Mountain View, CA [182–184], the U.S. Coast Guard Support Center in Elizabeth City, NC [185–188], and the Y-12 uranium processing plant in Oak Ridge, TN [75,131,189,190].

The major geochemical gradients that have been observed associated with FePRBs are summarized in Fig. 10. They involve (1) dissolved oxygen, which is completely removed within a few millimeters of where groundwater enters the iron-bearing zone, (2) dissolved  $\text{H}_2$ , which rises over the width of the iron-bearing zone to near saturation, (3) pH and dissolved Fe(II), both of which usually rise rapidly inside the wall and then decline gradually in the downgradient region, (4) dissolved  $\text{CO}_2$ , which precipitates near the upgradient interface as iron carbonates, (5)  $\text{NO}_3^-$ , which is abiotically reduced to ammonia, and (6)  $\text{SO}_4^{2-}$ , which is reduced by anaerobic bacteria to sulfide, much of which then precipitates as iron sulfides. Note that lateral diffusion is very slow into the plume of treated groundwater, so reoxygenation by this mechanism is expected to be minimal and the anaerobic plume may eventually extend a considerable distance downgradient from an FePRB.

As a consequence of the gradients in groundwater geochemistry described above, zones of authigenic precipitates develop along the flow path of FePRBs and columns designed to simulate these conditions. A considerable amount of research has been done on the iron oxides and carbonates that accumulate near the upgradient interface because these solids can cement grains and decrease porosity and thereby prevent contaminated groundwater from flowing through the treatment zone [131,189,193–196]. The effect of these precipitates on overall rates of contaminant reduction is not entirely clear, however, because most field



**Figure 10** Schematic of a cross section of an FePRB showing the major gradients in groundwater geochemistry, zones of precipitation, and expected regions of microbiological influence. (Adapted from figures in Refs. 75, 184, 191, and 192.)

data suggest that contaminant reduction occurs mainly near the upgradient interface, where precipitation of oxide and carbonates might contribute to passivation of  $\text{Fe}^0$  surfaces and, therefore, slower overall rates of corrosion.

The zone of precipitation that develops on the native aquifer material beyond the downgradient interface has received comparatively little attention to date. It is known, however, that most of the dissolved iron that is released by the treatment zone precipitates on the downgradient aquifer material, resulting in the accumulation of Fe(II)-containing oxyhydroxides (and favoring a decrease in pH). These changes minimize undesirable changes in groundwater geochemistry that might be caused by an FePRB. In addition, the accumulation of highly-reactive forms of Fe(II) creates a zone that may result in further contaminant degradation by abiotic and biologically mediated pathways (e.g., Refs. 197–201).

## B. Design and Scaling of Conventional PRBs

In the last few years, a number of documents have appeared that are largely devoted to providing guidance for the design of FePRBs [161,202–204]. These guidelines reflect a mixture of scientific, engineering, and regulatory considerations that is certain to evolve as the relevant science and technology matures. The following addresses some of the major issues involved in preliminary calculations for scaling from the batch to the field.

### 1. Steady-State Design Calculations

From an engineering perspective, a central consideration in the design of an FePRB is how to ensure enough contact between contaminated groundwater and the treatment zone to reach the required treatment goal. This can be expressed as

$$W = V_{\text{lin}} t_c \quad (27)$$

where  $W$  is the necessary barrier width,  $V_{\text{lin}}$  is the linear velocity of groundwater, and  $t_c$  is the required contact time. One way to get  $t_c$  is by solving Eq. (13) to give

$$t_c = \frac{-\ln(C_{\text{eff}}/C_{\text{inf}})}{k_{\text{SA}} \rho_A} \quad (28)$$

where  $C_{\text{inf}}$  and  $C_{\text{eff}}$  are the concentrations of contaminant in the influent and effluent, respectively. For preliminary design calculations,  $C_{\text{inf}}$  is usually taken to be the maximum concentration in site groundwater and  $C_{\text{eff}}$  is the treatment goal required by local regulations. As described above,  $\rho_a$  can be calculated from  $a_s$  and  $\rho_m$  using Eq. (19). However, for packed systems,  $\rho_m$  may be more conveniently estimated from:

$$\rho_m = \frac{\rho_s \rho_b}{(\rho_s - \rho_b)} \quad (29)$$

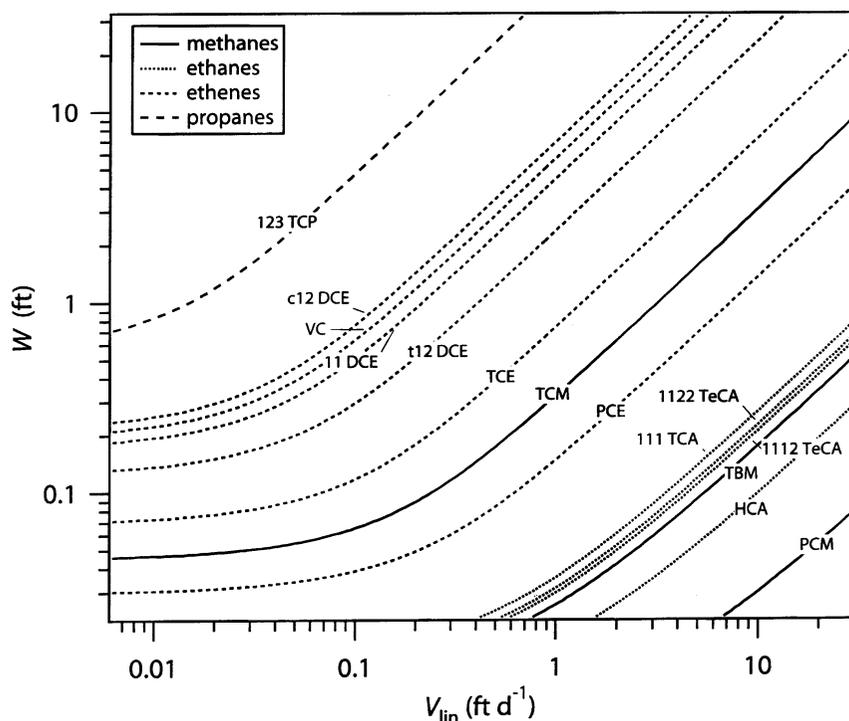
where  $\rho_b$  is the bulk density of the iron (g of Fe per L of total volume). Some values of  $\rho_s$  and  $\rho_b$  are given in Table 2.

### 2. Reactive Transport Modeling

The reactive transport of contaminants in FePRBs has been modeled using several approaches [179,184,186,205–208]. The simplest approach treats the FePRB as an ideal plug-flow reactor (PFR), which is a steady-state flow reactor in which mixing (i.e., dispersion) and sorption are negligible. Removal rates (and therefore required wall widths,  $W$ ) can be estimated based on first-order contaminant degradation and residence times calculated from the average linear groundwater velocity [Eq. (27)]. The usefulness of

PFR models are limited, however, because of the slow velocities encountered in groundwater aquifers and the tendency for many contaminants (particularly hydrophobic organic compounds) to sorb. More appropriate but more complex models based on various forms of the advection-dispersion equation (ADE) have been used by several researchers to incorporate more processes, such as dispersion, sorption, mass transfer, sequential degradation, and coupled chemical reactions.

One of the simplest forms of the ADE that has been applied to an FePRB includes both dispersion and sorption [205]. A one-dimensional steady-state ADE was used to estimate  $W$  for 1000-fold reduction in contaminant concentrations at a groundwater velocity of  $1 \text{ ft day}^{-1}$ . Applying the model to chlorinated aliphatic compounds (using rate coefficients summarized in Ref. 86) gave the results shown in Fig. 11. These estimates,



**Figure 11** Calculated width of an FePRB ( $W$ ) required to reduce contaminant concentrations 1000-fold, as a function of linear velocity of groundwater ( $V_{lin}$ ). (Based on representative values of  $k_{SA}$  from Ref. 86. A simplified version of this plot was published previously [132]. This version used with permission of J. Eykholt.)

however, are based solely on the degradation rate of the parent compound and do not consider more complex degradation schemes involving multiple sequential and parallel reactions (e.g., Fig. 3). One approach that can be used to accommodate the complexity of multiple reactions is to design the wall for the least reactive product [132] and apply a safety factor [209].

Another approach has been to model sequential reactions by using multiple advection-dispersion equations [207]. The use of multiple ADEs provides a more realistic model where each reactant can degrade, sorb, and disperse. Simulations using this type of model reveal that breakthrough of degradation products could occur despite complete removal of the parent compound, TCE [207]. Additional simulations were used to explore the effect of slow sorption (i.e., nonequilibrium sorption), and the results suggest that it is reasonable to assume that an FePRB will reach steady-state conditions under typical field conditions.

Nonequilibrium sorption due to mass-transfer limitations (including slow external or internal diffusion) and sorption to two different sorbents have been incorporated into a single ADE to evaluate the conditions under which mass-transfer processes may be important [206]. Simulations with this model, using mass-transfer parameters estimated from empirical correlations, reveal nonequilibrium conditions (i.e., mass-transfer limitations) when groundwater velocities increase (such as those that might occur in a funnel-and-gate system).

The most sophisticated models applied to FePRBs to date combine multiple ADEs (i.e., multicomponent transport) with coupled chemical reactions [184,186,208]. These multicomponent reactive transport models were used to simulate the geochemical evolution in FePRBs for the treatment of TCE [184] and for remediating mixtures of Cr(VI) and chlorinated solvents [186,208]. The models are capable of reproducing the spatial distribution of field-observable parameters such as the concentrations of the chlorinated solvents, pH, Eh, alkalinity,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$  [184,186,208], although some discrepancies were observed for  $\text{Mn}^{2+}$  [186] and  $\text{Ca}^{2+}$  [184]. These discrepancies were attributed to processes that were not incorporated into the models, such as coprecipitation, sorption, ion exchange [186], and surface complexation [184]. The selection of secondary minerals was found to be the critical factor for accurately simulating the inorganic geochemistry throughout the wall [184]. Concentration profiles of the chlorinated solvents, however, were adequately described by reaction with  $\text{Fe}^0$  only, and it was not necessary to model the reaction of the solvents with secondary minerals as separate processes [186,208].

Multicomponent reactive transport models can also be used to estimate the potential for barrier clogging due to secondary mineral formation [186,208]. In addition, processes such as the microbially mediated degrada-

tion of sulfate and degassing of hydrogen gas within the barrier, as well as geochemical interactions of treated groundwater with the aquifer matrix downgradient of the barrier were considered [208].

All of the above modeling has assumed uniform flow fields, even though heterogeneity in the hydraulic conductivity of the barrier and surrounding aquifer can lead to preferential flow patterns. Some of the implications of preferential flow have been investigated by varying input parameters in the models described above [209–211].

## C. Variants and Integrated Technologies

### 1. Coupling with Natural Attenuation (Microbiological Effects)

Early studies of  $\text{Fe}^0$  systems found little microbial contribution to contaminant degradation [191], and this caused most investigators to focus on abiotic processes during the early development of FePRBs. There are, however, many ways by which microbial activity could influence the performance and longevity of FePRBs, and evidence for some of these effects is being reported with increasing frequency. Most of what was known about this topic as of 1999 was reviewed by Scherer et al. [42], but there have already been significant advances since that time (e.g., Refs. 117, 190, and 212–214).

The main types of effects that microorganisms might have on FePRBs involve (1) biocorrosion, (2) cometabolism, (3) dissolution/precipitation, and (4) biofouling. It is expected that these effects will be localized in and around an FePRB in accord with the strong gradients in chemical conditions that are created by the barrier. For example, the high pH within a treatment zone containing  $\text{Fe}^0$  will inhibit most types of microbial activity, whereas the effluent from the treatment zone might stimulate microbial activity downgradient due to elevated levels of dissolved hydrogen and iron. Some of the key spatial relationships are represented in Fig. 10 for a conventional FePRB; however, microbial effects can also be engineered into sequences of treatment zones, as described in the section below.

Early work on biocorrosion led to the notion that  $\text{H}_2$ -utilizing bacteria accelerate anaerobic corrosion by “cathodic depolarization”, i.e., utilizing the  $\text{H}_2$  produced by anaerobic corrosion of  $\text{Fe}^0$  [Eq. (14)] and thereby favoring further corrosion by this reaction. Several studies have shown that microbial utilization of the  $\text{H}_2$  from anaerobic corrosion of  $\text{Fe}^0$  can lead to accelerated cometabolism of contaminants. For example, combining  $\text{Fe}^0$  with active ( $\text{H}_2$ -consuming) methanogenic consortia significantly enhances both the rate and extent of transformation of chlorinated methanes, ethanes, and ethenes [215–218]. Experiments conducted with pure cultures of methanogens showed that  $\text{H}_2$  can enhance microbial reduction of chlorinated

solvents even when  $\text{H}_2$  does not serve as growth substrate [219]. Some of the effects of *Methanosarcina thermophila* on degradation of carbon tetrachloride and chloroform may be due to a proteinaceous extracellular factor that is excreted when the bacteria are exposed to  $\text{Fe}^0$  [220]. It has also been shown that autotrophic denitrification is synergistic with the abiotic reduction of nitrate by  $\text{Fe}^0$  [221].

Surprisingly little attention has been given to the possibility that the precipitation and dissolution of iron oxides downgradient from an FePRB will be strongly influenced by microbial activity. Although the basic geomicrobiology of Fe(II)-oxidizing and Fe(III)-reducing bacteria is well known [222], the environment downgradient from an FePRB provides an exceptional opportunity for synergistic effects between microbial iron metabolism and contaminant transformation reactions. Of particular interest are dissimilatory iron-reducing bacteria (DIRB), which can use a variety of Fe(III)-containing minerals as electron acceptors, resulting in reductive dissolution of iron and cometabolism of a variety of contaminants [223]. Evidence for both of these effects in the presence of  $\text{Fe}^0$  has been reported recently in studies with *Shewanella alga* BrY and  $\text{CCl}_4$  [212].

Until recently, evidence for *biofouling* of in situ FePRBs has been notably absent. Recently, a study of the in situ FePRB at the Y-12 Plant Site, Oak Ridge, TN [131,190] concluded that microbial biomass was 1–3 orders of magnitude higher in the  $\text{Fe}^0$ -bearing zone than in the surrounding aquifer based on phospholipid fatty acid analysis (PLFA) and DNA probe results. This result suggests that some conditions may favor microbial growth within FePRBs; although the collective experience with in situ FePRBs to date suggests that macroscopic biofilms or other gross manifestations of biofouling are not observed.

### 2. Other Variations and Modifications

For the most part, the scope of this chapter has been restricted to core issues related to the “classical” FePRB, consisting of a single in situ treatment zone containing granular, construction-grade, zero-valent iron. In parallel with developments on classical FePRBs, however, a wide range of variations have been described. The growing diversity of variations on the classic FePRB makes them difficult to classify, but the better known variations can be grouped into general categories, as shown in Table 4. Many of these variations are designed to overcome limitations of the classical FePRB by extending the range of contaminants that are treatable by  $\text{Fe}^0$  and/or extending the range of situations where  $\text{Fe}^0$  can be applied. Other variations are simply efforts to make the classical FePRB more efficient or cost-effective.

**Table 4** Variations and Enhancements of the Basic FePRB

Variation	Application/benefit	References
Acid mine drainage	Lower pH, adsorbs metals	[224]
Cyclodextrins	Solubilizes organics, prevents settling	[225,226]
Electroenhanced	Faster reduction	[227–232]
Fenton (Fe <sup>0</sup> /H <sub>2</sub> O <sub>2</sub> )	Oxidative degradation	[233–239]
Vapor phase	PCBs	[93,240,241]
High temperature	PCBs	[93]
Nanoparticles	Enhanced reactivity, avoids settling	[153,242–249]
Photoenhancement	Faster reduction, alters products	[250]
Slurry walls	Barrier to diffusing contaminants	[251]
S(II) or pyrite amended	Chlorinated ethenes, chlorinated phenols	[94,252–254]
Sub/supercritical solvents	PCBs	[90–92,255]
Surfactants	Solubilizes contaminants	[34,168,170,256]
Sequential reactive treatment zones (SRTZs)	Recalcitrant intermediates, decreased risk	[257,258]
Ultrasound	Fast degradation, alters products, restores activity of passivated metals	[157,259–261]
Vadose zone soils	Pesticides	[262]

## VI. LIST OF SYMBOLS

$\rho_a$	surface area concentration (m <sup>2</sup> of Fe surface area L <sup>-1</sup> of solution volume)
$\rho_b$	bulk density (g of Fe L <sup>-1</sup> of total volume)
$\rho_m$	mass concentration (g of Fe L <sup>-1</sup> of solution volume)
$\rho_s$	specific density (g of Fe L <sup>-1</sup> of Fe volume)
$\Gamma$	surface concentration of reactive sites (mol m <sup>-2</sup> )
$A, B, D, E$	constants defined in Eqs. (22) and (23)
$a_s$	specific surface area (m <sup>2</sup> Fe surface area g <sup>-1</sup> of Fe)
$C_a$	concentration of contaminant in the aqueous phase
$C_0$	concentration at $t=0$
$C_{\text{eff}}$	concentration in effluent
$C_{\text{inf}}$	concentration in influent
$C_t$	concentration at $t=t$
$C_T$	total concentration of contaminant (dissolved and adsorbed)
$E_a$	activation energy (kJ mol <sup>-1</sup> )
$k_0$	zero-order rate constant
$k_1$	first-order rate constant
$k_2$	second-order reaction rate constant (L mol <sup>-1</sup> hr <sup>-1</sup> )

$k_a$	rate constant for transformation
$k_{\text{mt}}$	mass transport coefficient
$k_{\text{obs}}$	observed pseudo-first-order disappearance rate constant (hr <sup>-1</sup> )
$k_{\text{overall}}$	overall surface area-normalized rate of reaction
$k_{\text{RXN}}$	first-order heterogeneous reaction rate constant
$k_{\text{SA}}$	observed reaction rate ( $k_{\text{obs}}$ ) normalized to surface area (L m <sup>-2</sup> hr <sup>-1</sup> )
$k_{T_1}$	rate constant at temperature $T_1$
$k_{T_2}$	rate constant at temperature $T_2$
$K_{1/2}$	concentration of $P$ at $V_m/2$ (mol L <sup>-1</sup> )
$M_{\text{Fe}}$	mass of Fe <sup>0</sup> (g)
$N$	reaction order
$N_{1/2}$	number of half-lives needed to reach a treatment goal
$[P]$	molar concentration of contaminant $P$ (mol L <sup>-1</sup> )
$R$	gas constant (8.314 J K <sup>-1</sup> mol <sup>-1</sup> ).
$t_c$	contact time necessary to achieve a treatment goal
$V_m$	maximum reaction rate (mol L <sup>-1</sup> s <sup>-1</sup> )
$V$	velocity of groundwater
$V_{\text{H}_2\text{O}}$	volume of solution (L)
$V_{\text{Tot}}$	total system volume (L)
$W$	width of barrier

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## REFERENCES

- Gillham RW. Resurgence in research concerning organic transformations enhanced by zero-valent metals and potential application in remediation of contaminated groundwater. 209th National Meeting, Anaheim, CA, American Chemical Society 1995; 35(1):691–694.
- Tratnyek PG. Putting corrosion to use: remediation of contaminated groundwater with zero-valent metals. Chem Ind (London) 1996; 499–503.
- Powell RM, Powell PD. Iron metal for subsurface remediation. In: Myers RA, ed. Encyclopedia of Environmental Analysis and Remediation. New York: Wiley, 1998; 8:4729–4761.

4. Warner SD, Sorel D. Ten years of permeable reactive barriers: lessons learned and future expectations. 221st National Meeting of the Chemical Society, San Diego, CA, American Chemical Society 2001; 41(1):1104–1112.
5. Reynolds GW, Hoff JT, Gillham RW. Sampling bias caused by materials used to monitor halocarbons in groundwater. *Environ Sci Technol* 1990; 24:135–142.
6. Gillham RW, Burris DR. Recent developments in permeable in situ treatment walls for remediation of contaminated groundwater. Proceedings of the Sub-surface Restoration Conference, Dallas, TX. Houston, TX: Rice University, 1992:66–68.
7. Young GK, Bungay HR, Brown LM, Parsons WA. Chemical reduction of nitrate in water. *J Water Pollut Control Fed* 1964; 36:395–398.
8. Rhodes FH, Carty JT. The corrosion of certain metals by carbon tetrachloride. *Ind Eng Chem* 1925; 17:909–911.
9. Lyons RE, Smith LT. Die reduktion von nitroverbindungen mit eisen und löslichen chloriden. *Chem Ber* 1927; 60:173–182.
10. Sweeny KH. Reductive degradation treatment of industrial and municipal wastewaters. Water Reuse Symposium. Denver, CO: American Water Works Association Research Foundation 1979; 2:1487–1497.
11. Butler LC, Staiff DC, Sovocool GW, Davis JE. Field disposal of methyl parathion using acidified powdered zinc. *J Environ Sci Health* 1981; B16:49–58.
12. Senzaki T, Yasuo K. Removal of chlorinated organic compounds from wastewater by reduction process. I. Treatment of 1,1,2,2-tetrachloroethane with iron powder. *Kogyo Yosui* 1988:2–7.
13. Senzaki T, Yasuo K. Removal of chlorinated organic compounds from wastewater by reduction process. II. Treatment of trichloroethylene with iron powder. *Kogyo Yosui* 1989:19–25.
14. Senzaki T. Removal of chlorinated organic compounds from wastewater by reduction process. III. Treatment of trichloroethylene with iron powder. *Kogyo Yosui* 1991; 391:29–35.
15. Khudenko BM. Feasibility evaluation of a novel method for destruction of organics. *Water Sci Technol* 1991; 23:1873–1881.
16. Gould JP. The kinetics of hexavalent chromium reduction by metallic iron. *Water Res* 1982; 16:871–877.
17. Khudenko BM. Mechanism and kinetics of cementation processes. *Water Sci Technol* 1985; 17:719–732.
18. Day SR, O'Hannesin SF, Marsden L. Geotechnical techniques for the construction of reactive barriers. *J Hazard Mater* 1999; 67:285–297.
19. Starr RC, Cherry JA. In situ remediation of contaminated ground water: the funnel-and-gate system. *Ground Water* 1994; 32:465–476.
20. Amonette JE, Szecsody JE, Schaef HT, Templeton JC, Gorby YA, Fruchter JS. Abiotic reduction of aquifer materials by dithionite: a promising in-situ remediation technology. Proceedings of the 33rd Hanford Symposium on Health & the Environment In-Situ Remediation: Scientific Basis for Current

- and Future Technologies, Pasco, WA. Richland, WA: Battelle Pacific Northwest Laboratories, 1994; 2:851–881.
21. Fruchter JS, Cole CR, Williams MD, Vermeul VR, Amonette JE, Szecsody JE, Istok JD, Humphrey MD. Creation of a subsurface permeable treatment zone for aqueous chromate contamination using in situ redox manipulation. *Ground Water Monit Remediat* 2000; 20:66–77.
22. Istok JD, Amonette JE, Cole CR, Fruchter JS, Humphrey MD, Szecsody JE, Teel SS, Vermeul VR, Williams MD, Yabusaki SB. In situ redox manipulation by dithionite injection: intermediate-scale laboratory experiments. *Ground Water* 1999; 37:884–889.
23. Szecsody JE, Williams MD, Fruchter JS, Vermeul VR, Evans JC, Sklarew DS. Influence of sediment reduction on TCE degradation. In: Wickramanayake GB, Gavaskar AR, Chen ASC, eds. *Chemical Oxidation and Reactive Barriers: Proceedings of the Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Monterey, CA, 20–25 May 2000. Columbus, OH: Battelle Press, 2000; C2–6:369–376.
24. Grittini C, Malcomson M, Fernando Q, Korte N. Rapid dechlorination of polychlorinated biphenyls on the surface of a Pd/Fe bimetallic system. *Environ Sci Technol* 1995; 29:2898–2900.
25. Graham LJ, Jovanovic G. Dechlorination of p-chlorophenol on a Pd/Fe catalyst in a magnetically stabilized fluidized bed; Implications for sludge and liquid remediation. *Chem Eng Sci* 1999; 54:3085–3093.
26. Wan C, Chen YH, Wei R. Dechlorination of chloromethanes on iron and palladium–iron bimetallic surface in aqueous systems. *Environ Toxicol Chem* 1999; 18:1091–1096.
27. James BR. The challenge of remediating chromium-containing soil. *Environ Sci Technol* 1996; 30:248A–251A.
28. Benjamin MM, Sletten RS, Bailey RP, Bennett T. Sorption and filtration of metals using iron–oxide-coated sand. *Water Res* 1996; 30:2609–2620.
29. Martinez CE, McBride MB. Coprecipitates of Cd, Cu, Pb and Zn in iron oxides: solid phase transformation and metal solubility after aging and thermal treatment. *Clays Clay Miner* 1998; 46:537.
30. Morrison SJ, Spangler RR. Chemical barriers for controlling groundwater contamination. *Environ Prog* 1993; 12:175–181.
31. Kriegman-King MR, Reinhard M. Transformation of carbon tetrachloride by pyrite in aqueous solution. *Environ Sci Technol* 1994; 28:692–700.
32. Butler EC, Hayes KF. Kinetics of the transformation of trichloroethylene and tetrachloroethylene by iron sulfide. *Environ Sci Technol* 1999; 33:2021–2027.
33. Kriegman-King MR, Reinhard M. Transformation of carbon tetrachloride in the presence of sulfide, biotite, and vermiculite. *Environ Sci Technol* 1992; 26:2198–2206.
34. Li Z, Jones HK, Bowman RS, Helferich R. Enhanced reduction of chromate and PCE by pelletized surfactant-modified zeolite/zerovalent iron. *Environ Sci Technol* 1999; 33:4326–4330.

35. Bowman RS, Li Z, Roy SJ, Burt T, Johnson TJ, Johnson RL. Pilot test of a surfactant-modified zeolite permeable barrier for groundwater remediation. In: Smith JA, Burns SE, eds. *Physicochemical Remediation of Contaminated Subsurface Environments*. New York: Kluwer, 2000:161–185.
36. Chen XB, Wright JV, Conca JL, Peurrung LM. Effects of pH on heavy metal sorption on mineral apatite. *Environ Sci Technol* 1997; 31:624–631.
37. Hodson ME, Valsami-Jones E, Cotter-Howells JD. Bone meal additions as a remediation treatment for metal contaminated soil. *Environ Sci Technol* 2000; 34:3501–3507.
38. James BR, Rabenhorst MC, Frigon GA. Phosphorus sorption by peat and sand amended with iron oxides or steel wool. *Water Environ Res* 1992; 64:699–705.
39. Kershaw DS, Crouthamel Kulik B, Pamukcu S. Ground rubber: sorption media for ground water containing benzene and o-xylene. *J Geotech Geoenviron Eng* 1997; 123:324–334.
40. Guerin TF, Horner S, McGovern T, Davey B. An application of permeable reactive barrier technology to petroleum hydrocarbon contaminated groundwater. *Water Res* 2002; 36:15–24.
41. Benner SG, Blowes DW, Gould WD, Herbert RB Jr, Ptacek CJ. Geochemistry of a permeable reactive barrier for metals and acid mine drainage. *Environ Sci Technol* 1999; 33:2793–2799.
42. Scherer MM, Richter S, Valentine RL, Alvarez PJJ. Chemistry and microbiology of reactive barriers for in situ groundwater cleanup. *Crit Rev Environ Sci Technol* 2000; 30:363–411.
43. Gillham RW, Blowes DW, Ptacek CJ, O'Hannesin S. Use of zero-valent metals for in situ remediation of contaminated ground water. *Proceedings of the 33rd Hanford Symposium on Health & the Environment In-Situ Remediation: Scientific Basis for Current and Future Technologies*, Pasco, WA. Richland, WA: Battelle Pacific Northwest Laboratories 1994; 2:913–930.
44. Shoemaker SH, Greiner JF, Gillham RW. Permeable reactive barriers. In: Bodocsi A, Ryan ME, Rumer RR, eds. *Barrier Containment Technologies for Environmental Remediation Applications (Final Report of the International Containment Technology Workshop, Baltimore, MD, 29–31 August 1995)*. New York: Wiley, 1995:301–353.
45. Gillham RW. In situ treatment of groundwater: metal-enhanced degradation of chlorinated organic contaminants. *Recent Advances in Ground-Water Pollution Control and Remediation*, NATO Advanced Study Institute, Kemer, Antalya, Turkey. New York: Kluwer Academic, 1996:249–274.
46. Palmer PL. Reactive walls. In: Nyer EK, Kidd DF, Palmer PL, Crossman TL, Fam S, Johns FJ II, Boettcher G, Suthersan SS, eds. *In Situ Treatment Technology*. Boca Raton, FL: CRC, 1996:271–288.
47. Gillham RW, Burris DR. Recent developments in permeable in situ treatment walls for remediation of contaminated groundwater. In: Ward CH, Cherry JA, Scalf MR, eds. *Subsurface Restoration*. Chelsea, MI: Ann Arbor, 1997:343–356.

48. Grathwohl P, Dahmke A. Direkte sanierung verschmutzter grundwässer. *Spektrum Wiss* 1998; (April):89–94.
49. Powell RM, Puls RW, Blowes DW, Vogan JL, Gillham RW, Powell PD, Schultz D, Landis R, Sivavic T. *Permeable Reactive Barrier Technologies for Contaminant Remediation*, U.S. Environmental Protection Agency, EPA/600/R-98/125, Ada, OK, 1998.
50. Yin Y, Allen HE. *In Situ Chemical Treatment, Ground-Water Remediation Technologies Analysis Center (GWRTAC)*, TE-99-01, Pittsburgh, PA, 1999.
51. Blowes DW, Ptacek CJ, Benner SG, McRae CWT, Bennett TA, Puls RW. Treatment of inorganic contaminants using permeable reactive barriers. *J Contam Hydrol* 2000; 45:123–137.
52. U.S. Environmental Protection Agency. *Field Applications of In Situ Remediation Technologies: Permeable Reactive Barriers*, USEPA, Office of Solid Waste and Emergency Response, EPA-542-R-99-002, Washington, D.C., 1999.
53. Bigg T, Judd SJ. Zero-valent iron for water treatment. *Environ Technol* 2000; 21:661–670.
54. Luthy RG, Aiken GR, Brusseau ML, Cunningham SD, Gschwend PM, Pignatello JJ, Reinhard M, Traina SJ, Weber WJ Jr, Westall JC. Sequestration of hydrophobic organic contaminants by geosorbents. *Environ Sci Technol* 1997; 31:3341–3347.
55. Khudenko BM, Gould JP. Specifics of cementation processes for metals removal. *Water Sci Technol* 1991; 24:235–246.
56. Pourbaix M. *Atlas of Electrochemical Equilibria in Aqueous Solutions*. Oxford: Pergamon, 1966:644.
57. Grau JM, Bisang JM. Removal and recovery of mercury from chloride solutions by contact deposition on iron felt. *Chem Biotechnol* 1995; 62:153–158.
58. Biester H, Schuhmacher P, Müller G. Effectiveness of mossy tin filters to remove mercury from aqueous solution by Hg(II) reduction and Hg(0) amalgamation. *Water Res* 2000; 34:2031–2036.
59. Bostick WD, Beck DE, Bowser KT, Bunch DH, Fellows RL, Sellers GF. Treatability study for removal of leachable mercury in crushed fluorescent lamps, Oak Ridge National Laboratory, K/TSO-6, Oak Ridge, TN, 1996.
60. Smith EH. Uptake of heavy metals in batch systems by a recycled iron-bearing material. *Water Res* 1996; 30:2424–2434.
61. Makhloufi L, Saidani B, Hammache H. Removal of lead ions from acidic aqueous solutions by cementation on iron. *Water Res* 2000; 34:2517–2524.
62. Ku Y, Chen C-H. Kinetic study of copper deposition on iron by cementation reaction. *Sep Sci Technol* 1992; 27:1259–1275.
63. Cantrell KJ, Kaplan DI, Wietsma TW. Zero-valent iron for the in situ remediation of selected metals in groundwater. *J Hazard Mater* 1995; 42:201–212.
64. Morrison SJ, Metzler DR, Dwyer BP. Removal of As, Mn, Mo, Se, U, V and Zn from groundwater by zero-valent iron in a passive treatment cell: reaction progress modeling. *J Contam Hydrol* 2002; 56(1–2):99–116.

65. Pratt AR, Blowes DW, Ptacek CJ. Products of chromate reduction on proposed subsurface remediation material. *Environ Sci Technol* 1997; 31:2492.
66. Blowes DW, Ptacek CJ, Lambor IL. In-situ remediation of Cr(VI)-contaminated groundwater using permeable reactive walls: laboratory studies. *Environ Sci Technol* 1997; 31:3348–3357.
67. Qiu SR, Lai HF, Roberson MJ, Hunt ML, Amrhein C, Giancarlo LC, Flynn GW, Yarmoff JA. Removal of contaminants from aqueous solution by reaction with iron surfaces. *Langmuir* 2000; 16:2230–2236.
68. Lackovic JA, Nikolaidis NP, Dobbs GM. Inorganic arsenic removal by zero-valent iron. *Environ Eng Sci* 2000; 17:29–39.
69. Su C, Puls RW. Arsenate and arsenite removal by zerovalent iron: kinetics, redox transformation, and implications for in situ groundwater remediation. *Environ Sci Technol* 2001; 35:1487–1492.
70. Farrell J, Wang J, O'Day P, Conklin M. Iron mediated reductive precipitation of arsenic from contaminated groundwater. 220th National Meeting, Washington, DC, American Chemical Society 2000; 40(2):794–796.
71. Gu B, Liang L, Dickey MJ, Yin X, Dai S. Reductive precipitation of uranium(VI) by zero-valent iron. *Environ Sci Technol* 1998; 32:3366–3373.
72. Morrison SJ, Metzler DR, Carpenter CE. Uranium precipitation in a permeable reactive barrier by progressive irreversible dissolution of zerovalent iron. *Environ Sci Technol* 2001; 35:385–390.
73. Fiedor JN, Bostick WD, Jarabek RJ, Farrell J. Understanding the mechanism of uranium removal from groundwater by zero-valent iron using X-ray photoelectron spectroscopy. *Environ Sci Technol* 1998; 32:1466–1473.
74. Charlet L, Liger E, Gerasimo P. Decontamination of TCE- and U-rich waters by granular iron: role of sorbed Fe(II). *J Environ Eng* 1998; 124:25–30.
75. Gu B, Watson DB, Phillips DH, Liang L. Biogeochemical, mineralogical, and hydrological characteristics of an iron reactive barrier used for treatment of uranium and nitrate. In: Naftz DL, Morrison SJ, Davis JA, Fuller CC, eds. *Groundwater Remediation Using Permeable Reactive Barriers*. San Diego: Academic Press, 2002:305–342.
76. Matheson LJ, Goldberg WC, Bostick WD, Harris L. Analysis of uranium-contaminated zero-valent iron media sampled from permeable reactive barriers installed at U.S. Department of Energy sites in Oak Ridge, Tennessee and Durango, Colorado. In: Naftz DL, Morrison SJ, Davis JA, Fuller CC, eds. *Groundwater Remediation Using Permeable Reactive Barriers*. San Diego: Academic Press, 2002. In press.
77. Cheng IF, Muftikian R, Fernando Q, Korte N. Reduction of nitrate to ammonia by zero-valent iron. *Chemosphere* 1997; 35:2689–2695.
78. Kielemoes J, DeBoever P. Influence of denitrification on the corrosion of iron and stainless steel powder. *Environ Sci Technol* 2000; 34:663.
79. Rahman A, Agrawal A. Reduction of nitrate and nitrite by iron metal: implications for ground water remediation. 213th National Meeting, San Francisco, CA American Chemical Society 1996; 37(1):157–159.

80. Alowitz MJ, Scherer MM. Kinetics of nitrate, nitrite, and Cr(VI) reduction by iron metal. *Environ Sci Technol* 2002; 36:299–306.
81. Chew CF, Zhang TC. Abiotic degradation of nitrates using zero-valent iron and electrokinetic processes. *Environ Eng Sci* 1999; 16:389–401.
82. Özdemir M, Tüfekci M. Removal of chlorine residues in aqueous media by metallic iron. *Water Res* 1997; 31:343–345.
83. Shrouf JD, Parkin GF. Inhibition of anaerobic perchlorate biotransformation by Fe(0). In: Wickramanayake GB, Gavaskar AR, Gibbs JT, Means JL, eds. *Case Studies in the Remediation of Chlorinated and Recalcitrant Compounds: Proceedings of the Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Monterey, CA, 20–25 May 2000. Columbus, OH: Battelle Press, 2000; C2–7:107–113.
84. Matheson LJ, Tratnyek PG. Reductive dehalogenation of chlorinated methanes by iron metal. *Environ Sci Technol* 1994; 28:2045–2053.
85. Hozalski RM, Zhang L, Arnold WA. Reduction of haloacetic acids by Fe<sup>0</sup>: implications for treatment and fate. *Environ Sci Technol* 2001; 35:2258–2263.
86. Johnson TL, Scherer MM, Tratnyek PG. Kinetics of halogenated organic compound degradation by iron metal. *Environ Sci Technol* 1996; 30:2634–2640.
87. Scherer MM, Balko BA, Gallagher DA, Tratnyek PG. Correlation analysis of rate constants for dechlorination by zero-valent iron. *Environ Sci Technol* 1998; 32:3026–3033.
88. Arnold WA, Roberts AL. Pathways and kinetics of chlorinated ethylene and chlorinated acetylene reaction with Fe(0) particles. *Environ Sci Technol* 2000; 34:1794–1805.
89. Kim Y-H, Carraway ER. Dechlorination of pentachlorophenol by zero valent iron and modified zero valent irons. *Environ Sci Technol* 2000; 34:2014–2017.
90. Yak HK, Wenclawiak BW, Cheng IF, Doyle JG, Wai CM. Reductive dechlorination of polychlorinated biphenyls by zerovalent iron in subcritical water. *Environ Sci Technol* 1999; 33:1307–1310.
91. Wu QX, Majid A, Marshall WD. Reductive dechlorination of polychlorinated biphenyl compounds in supercritical carbon dioxide. *Green Chem* 2000; 2:127–132.
92. Hinz DC, Wai CM, Wenclawiak BW. Remediation of a nonachloro biphenyl congener with zero-valent iron in subcritical water. *J Environ Eng* 2000; 2:45–48.
93. Chuang F-W, Larson RA, Scully Wessman M. Zero-valent iron-promoted dechlorination of polychlorinated biphenyls. *Environ Sci Technol* 1995; 29:2460–2463.
94. Campbell TJ, Burris DR, Roberts AL, Wells JR. Trichloroethylene and tetrachloroethylene reduction in a metallic iron–water–vapor batch system. *Environ Toxicol Chem* 1997; 16:625–630.
95. Roberts AL, Totten LA, Arnold WA, Burris DR, Campbell TJ. Reductive elimination of chlorinated ethylenes by zero-valent metals. *Environ Sci Technol* 1996; 30:2654–2659.

96. Fennelly JP, Roberts AL. Reaction of 1,1,1-trichloroethane with zero-valent metals and bimetallic reductants. *Environ Sci Technol* 1998; 32:1980–1988.
97. Totten LA, Jans U, Roberts AL. Alkyl borimides as mechanistic probes of reductive dehalogenation: reactions of vicinal dibromide stereoisomers with zerovalent metals. *Environ Sci Technol* 2001; 35:2804–2811.
98. Roberts AL, Jeffers PM, Wolfe NL, Gschwend PM. Structure–reactivity relationships in dehydrohalogenation reactions of polychlorinated and polybrominated alkanes. *Crit Rev Environ Sci Technol* 1993; 23:1–39.
99. Agrawal A, Tratnyek PG. Reduction of nitro aromatic compounds by zero-valent iron metal. *Environ Sci Technol* 1996; 30:153–160.
100. Devlin JF, Klausen J, Schwarzenbach RP. Kinetics of nitroaromatic reduction on granular iron in recirculating batch experiments. *Environ Sci Technol* 1998; 32:1941–1947.
101. Scherer MM, Johnson K, Westall JC, Tratnyek PG. Mass transport effects on the kinetics of nitrobenzene reduction by iron metal. *Environ Sci Technol* 2001; 35:2804–2811.
102. Klausen J, Ranke J, Schwarzenbach RP. Influence of solution composition and column aging on the reduction of nitroaromatic compounds by zero-valent iron. *Chemosphere* 2001; 44:511–517.
103. Mantha R, Taylor KE, Biswas N, Bewtra JK. A continuous system for Fe<sup>0</sup> reduction of nitrobenzene in synthetic wastewater. *Environ Sci Technol* 2001; 35:3231–3236.
104. Singh J, Comfort SD, Shea PJ. Iron-mediated remediation of RDX-contaminated water and soil under controlled Eh/pH. *Environ Sci Technol* 1999; 33:1488–1494.
105. Singh J, Comfort SD, Shea PJ. Remediating RDX-contaminated water and soil using zero-valent iron. *J Environ Qual* 1998; 27:1240–1245.
106. Hundal LS, Singh J, Bier EL, Shea PJ, Comfort SD, Power WL. Removal of TNT and RDX from water and soil using iron metal. *Environ Pollut* 1997; 97:55–64.
107. Tratnyek PG, Miehr R, Bandstra JZ. Kinetics of reduction of TNT by iron metal. *Groundwater Quality 2001: Third International Conference on Groundwater Quality, Sheffield, UK. IAHS Press, 2002; 275:427–433.*
108. Miehr R, Bandstra JZ, Po R, Tratnyek PG. Remediation of 2, 4,6-trinitrotoluene (TNT) by iron metal: kinetic controls on product distributions in batch and column experiments. 225th National Meeting, New Orleans, LA, American Chemical Society 2003; 43(1).
109. Elovitz MS, Weber EJ. Sediment-mediated reduction of 2,4,6-trinitrotoluene and fate of the resulting aromatic (poly)amines. *Environ Sci Technol* 1999; 33:2617.
110. Hofstetter TB, Heijman CG, Schwarzenbach RP. Complete reduction of TNT and other (poly)nitroaromatic compounds under iron-reducing subsurface conditions. *Environ Sci Technol* 1999; 33:1479–1487.
111. Nam S, Tratnyek PG. Reduction of azo dyes with zero-valent iron. *Water Res* 2000; 34:1837–1845.

112. Cao J, Wei L, Huang Q, Wang L, Han S. Reducing degradation of azo dyes by zero-valent iron in aqueous solution. *Chemosphere* 1999; 38:565–571.
113. Weber EJ. Iron-mediated reductive transformations: investigation of reaction mechanism. *Environ Sci Technol* 1996; 30:716–719.
114. Gui L, Gillham RW, Odziemkowski MS. Reduction of N-nitrosodimethylamine with granular iron and nickel-enhanced iron. 1. Pathways and kinetics. *Environ Sci Technol* 2000; 34:3489–3494.
115. Odziemkowski MS, Gui L, Gillham RW. Reduction of N-nitrosodimethylamine with granular iron and nickel-enhanced iron. 2. Mechanistic studies. *Environ Sci Technol* 2000; 34:3495–3500.
116. Tomkins BA, Griest WH. Determinations of N-nitrosodimethylamine at part-per-trillion concentrations in contaminated groundwaters and drinking waters featuring carbon-based membrane extraction disks. *Anal Chem* 1996; 68:2533–2540.
117. Wildman MJ, Alvarez PJJ. RDX degradation using an integrated Fe(0)-microbial treatment approach. *Water Sci Technol* 2001; 43:25–33.
118. Oh B-T, Just CL, Alvarez PJJ. Hexahydro-1,3,5-trinitro-1,3,5-triazine mineralization by zerovalent iron and mixed anaerobic cultures. *Environ Sci Technol* 2001; 35:4341–4346.
119. Rinehart KL Jr. *Oxidation and Reduction of Organic Compounds*. Englewood Cliffs, NJ: Prentice-Hall, Inc., 1973; 148.
120. Macalady DL, Tratnyek PG, Grundl TJ. Abiotic reduction reactions of anthropogenic organic chemicals in anaerobic systems. *J Contam Hydrol* 1986; 1:1–28.
121. Tratnyek PG, Macalady DL. Oxidation–reduction reactions in the aquatic environment. In: Mackay D, Boethling RS, eds. *Handbook of Property Estimation Methods for Chemicals: Environmental and Health Sciences*. Boca Raton, FL: Lewis, 2000:383–415.
122. Tratnyek PG, Reilkoff TE, Lemon A, Scherer MM, Balko BA, Feik LM, Henegar B. Visualizing redox chemistry: probing environmental oxidation–reduction reactions with indicator dyes. *Chem Educ* 2001; 6:172–179.
123. Ghauch A, Gallet C, Charef A, Rima J, Martin-Bouyer M. Reductive degradation of carbaryl in water by zero-valent iron. *Chemosphere* 2001; 42:419–424.
124. Ghauch A. Degradation of benomyl, picloram, and dicamba in a conical apparatus by zero-valent iron powder. *Chemosphere* 2001; 43:1109–1117.
125. Arnold WA, Ball WP, Roberts AL. Polychlorinated ethane reaction with zero-valent zinc: pathways and rate control. *J Contam Hydrol* 1999; 40:183–200.
126. Su C, Puls RW. Kinetics of trichloroethene reduction by zerovalent iron and tin: pretreatment effect, apparent activation energy, and intermediate products. *Environ Sci Technol* 1999; 33:163–168.
127. Boronina T, Klabunde KJ, Sergeev G. Destruction of organohalides in water using metal particles: carbon tetrachloride/water reactions with magnesium, tin, and zinc. *Environ Sci Technol* 1995; 29:1511–1517.
128. Schlimm C, Heitz E. Development of a wastewater treatment process:

- reductive dehalogenation of chlorinated hydrocarbons by metals. *Environ Prog* 1996; 15:38–47.
129. Hardy LI, Gillham RW. Formation of hydrocarbons from the reduction of aqueous CO<sub>2</sub> by zero-valent iron. *Environ Sci Technol* 1996; 30:57–65.
  130. Agrawal A, Tratnyek PG, Stoffyn-Egli P, Liang L. Processes affecting nitro reduction by iron metal: mineralogical consequences of precipitation in aqueous carbonate environments. 209th National Meeting, Anaheim, CA, American Chemical Society 1995; 35(1):720–723.
  131. Liang L, Korte N, Gu B, Puls R, Reeter C. Geochemical and microbial reactions affecting the long-term performance of in situ “iron barriers”. *Adv Environ Res* 2000; 4:273–286.
  132. Tratnyek PG, Johnson TL, Scherer MM, Eykholt GR. Remediating groundwater with zero-valent metals: kinetic considerations in barrier design. *Ground Water Monit Remediat* 1997; 17:108–114.
  133. Miehr R, Tratnyek PG, Bandstra JZ, Scherer MM, Alowitz M, Bylaska EJ. The diversity of contaminant reduction reactions by zero-valent iron: role of the reductate. In preparation.
  134. Weast RC, ed. *Handbook of Chemistry and Physics* 56th ed. Cleveland, OH: CRC Press, 1975.
  135. Liang L, Korte N, Goodlaxson JD, Clausen J, Fernando Q, Muftikian R. Byproduct formation during the reduction of TCE by zero-valence iron and palladized iron. *Ground Water Monit Remediat*. Winter 1997:122–127.
  136. Muftikian R, Nebesny K, Fernando Q, Korte N. X-ray photoelectron spectra of the palladium–iron bimetallic surface used for the rapid dechlorination of chlorinated organic environmental contaminants. *Environ Sci Technol* 1996; 30:3593–3596.
  137. Muftikian R, Fernando Q, Korte N. A method for the rapid dechlorination of low molecular weight chlorinated hydrocarbons in water. *Water Res* 1995; 29:2434–2439.
  138. Appleton EL. A nickel–iron wall against contaminated groundwater. *Environ Sci Technol* 1996; 30:536A–539A.
  139. Mackenzie K, Koehler R, Weiss H, Kopinke F-D. Dechlorination of chlorohydrocarbons in ground-water using novel membrane-supported Pd catalysts. In: Wickramanayake GB, Gavaskar AR, Chen ASC, eds. *Chemical Oxidation and Reactive Barriers: Proceedings of the Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Monterey, CA, 20–25 May 2000. Columbus, OH: Battelle Press 2000; C2–6:331–338.
  140. Neurath SK, Ferguson WJ, Dean SB, Foose D, Agrawal A. Rapid and complete dehalogenation of chlorinated phenols by Fe–Pd bimetallic reductants in bench-scale reactors: implications for soil and ground water remediation. 213th National Meeting, San Francisco, CA, American Chemical Society 1997; 37(1):159–161.
  141. Engelmann MD, Doyle JG, Cheng IF. The complete dechlorination of DDT by magnesium/palladium bimetallic particles. *Chemosphere* 2001; 43:195–198.

142. Sivavec TM, Mackenzie PD, Horney DP. Effect of site groundwater on reactivity of bimetallic media: deactivation of nickel-plated granular iron. 213th National Meeting, San Francisco, CA, American Chemical Society 1997; 37(1):83–85.
143. Gui L, Gillham RW. Preparation and regeneration of nickel–iron for reduction of organic contaminants. 221st National Meeting, San Diego, CA, American Chemical Society 2001; 41(1):1132–1137.
144. Scherer MM, Westall JC, Ziomek-Moroz M, Tratnyek PG. Kinetics of carbon tetrachloride reduction at an oxide-free iron electrode. *Environ Sci Technol* 1997; 31:2385–2391.
145. Casey FXM, Ong SK, Horton R. Degradation and transformation of trichloroethylene in miscible displacement experiments through zerovalent metals. *Environ Sci Technol* 2000; 34:5023–5029.
146. Scherer MM, Balko BA, Tratnyek PG. The role of oxides in reduction reactions at the metal–water interface. In: Sparks DL, Grundl TJ, eds. *Mineral–Water Interfacial Reactions: Kinetics and Mechanisms*. Washington, DC: American Chemical Society, 1998; ACS Symp. Ser. 715:301–322.
147. Johnson TL, Fish W, Gorby YA, Tratnyek PG. Degradation of carbon tetrachloride by iron metal: complexation effects on the oxide surface. *J Contam Hydrol* 1998; 29:377–396.
148. Chen J-L, Al-Abed SR, Ryan JA, Li Z. Effects of pH on dechlorination of trichloroethylene by zero-valent iron. *J Hazard Mater* 2001; 83:243–254.
149. Hu H-Y, Goto N, Fujie K. Effect of pH on the reduction of nitrite in water by metallic iron. *Water Res* 2001; 35:2789–2793.
150. Zawaideh LI, Zhang TC. The effects of pH and addition of an organic buffer (HEPES) on nitrate transformation in Fe<sup>0</sup>–water systems. *Water Sci Technol* 1998; 38:107–115.
151. Gotpagar J, Grulke E, Tsang T, Bhattacharyya D. Reductive dehalogenation of trichloroethylene using zero-valent iron. *Environ Prog* 1997; 16:137–143.
152. Wüst WF, Köber R, Schlicker O, Dahmke A. Combined zero- and first-order kinetic model of the degradation of TCE and cis-DCE with commercial iron. *Environ Sci Technol* 1999; 33:4304–4309.
153. Choe S, Chang YY, Hwang KY, Khim J. Kinetics of reductive denitrification by nanoscale zero-valent iron. *Chemosphere* 2000; 41:1307–1311.
154. Tratnyek PG, Scherer MM. Kinetic controls on the performance of remediation technologies based on zero-valent iron. Proceedings of the 1998 National Environmental Engineering Conference: Water Resources in the Urban Environment, Chicago, IL. American Society of Civil Engineers 1998:110–115.
155. Burrow PD, Aflatooni K, Gallup GA. Dechlorination rate constants on iron and the correlation with electron attachment energies. *Environ Sci Technol* 2000; 34:3368–3371.
156. Perlinger JA, Venkatapathy R, Harrison JF. Linear free energy relationships for polyhalogenated alkane transformation by electron-transfer mediators in model aqueous systems. *J Phys Chem* 2000; 104:2752.

157. Hung H-M, Hoffmann MR. Kinetics and mechanism of the enhanced reductive degradation of  $\text{CCl}_4$  by elemental iron in the presence of ultrasound. *Environ Sci Technol* 1998; 32:3011–3016.
158. Gillham RW, O'Hannesin SF. Enhanced degradation of halogenated aliphatics by zero-valent iron. *Ground Water* 1994; 32:958–967.
159. Deng B, Burris DR, Campbell TJ. Reduction of vinyl chloride in metallic iron–water systems. *Environ Sci Technol* 1999; 33:2651–2656.
160. Su C, Puls RW. Temperature effect on reductive dechlorination of trichloroethene by zero-valent metals. In: Wickramanayake GB, Hinchee RE, eds. *Physical, Chemical, and Thermal Technologies: Proceedings of the First International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Monterey, CA, 18–21 May 1998. Columbus, OH: Battelle Press, 1998; 1(5):317–322.
161. Gavaskar A, Gupta N, Sass B, Janosy R, Hicks J. Design Guidance for Application of Permeable Barriers for Remediate Dissolved Chlorinated Solvents. Columbus, OH: Battelle Press, Final, 2000.
162. Lasaga AC. Rate laws of chemical reactions. In: Lasaga AC, Kirkpatrick RJ, eds. *Kinetics of geochemical processes*. Washington, DC: Mineralogical Society of America, 1981; 8:1–68.
163. Scherer MM, Tratnyek PG. Dechlorination of carbon tetrachloride by iron metal: effect of reactant concentrations. 209th National Meeting, Anaheim, CA, American Chemical Society 1995; 35(1):805–806.
164. Arnold WA, Roberts AL. Development of a quantitative model for chlorinated ethylene reduction by zero-valent metals. 213th National Meeting, San Francisco, CA, American Chemical Society 1997; 37(1):76–77.
165. Arnold WA, Roberts AL. Pathways of chlorinated ethylene and chlorinated acetylene reaction with  $\text{Zn}(0)$ . *Environ Sci Technol* 1998; 32:3017–3025.
166. Arnold WA, Roberts AL. Inter- and intraspecies competitive effects in reactions of chlorinated ethylenes with zero-valent iron in column reactors. *Environ Eng Sci* 2000; 17:291–302.
167. Devlin JF, Morkin M, Repta C. Incorporating surface saturation effects into iron wall design calculations. In: Wickramanayake GB, Gavaskar AR, Chen ASC, eds. *Chemical Oxidation and Reactive Barriers: Proceedings of the Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Monterey, CA, 20–25 May 2000. Columbus, OH: Battelle Press, 2000; C2-6:393–400.
168. Tratnyek PG, Scherer MM, Deng B, Hu S. Effects of natural organic matter, anthropogenic surfactants, and model quinones on the reduction of contaminants by zero-valent iron. *Water Res* 2001; 35:4435–4443.
169. Deng B, Hu S, Burris DR. Effect of iron corrosion inhibitors on trichloroethylene reduction. In: Wickramanayake GB, Hinchee RE, eds. *Physical, Chemical, and Thermal Technologies: Proceedings of the First International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Monterey, CA, 18–21 May 1998. Columbus, OH: Battelle Press, 1998; 1(5):341–346.

170. Loraine GA. Effects of alcohols, anionic and nonionic surfactants on the reduction of PCE and TCE by zero-valent iron. *Water Res* 2001; 35:1453–1460.
171. Burris DR, Campbell TJ, Manoranjan VS. Sorption of trichloroethylene and tetrachloroethylene in a batch reactive metallic iron–water system. *Environ Sci Technol* 1995; 29:2850–2855.
172. Burris DR, Allen-King RM, Manoranjan VS, Campbell TJ, Loraine GA, Deng B. Chlorinated ethene reduction by cast iron: sorption and mass transfer. *J Environ Eng* 1998; 124:1012–1019.
173. Allen-King RM, Halket RM, Burris DR. Reductive transformation and sorption of cis- and trans-1,2-dichloroethene in a metallic iron–water system. *Environ Toxicol Chem* 1997; 16:424–429.
174. Gotpagar JK, Grulke EA, Bhattacharayya D. Reductive dehalogenation of trichloroethylene: kinetic models and experimental verification. *J Hazard Mater* 1998; 62:243–264.
175. Gotpagar J, Lyuksyutov S, Cohn R, Grulke E, Bhattacharyya D. Reductive dehalogenation of trichloroethylene with zero-valent iron: surface profiling microscopy and rate enhancement studies. *Langmuir* 1999; 15:8412–8420.
176. Deng B, Campbell TJ, Burris DR. Kinetics of vinyl chloride reduction by metallic iron in zero-headspace systems. 213th National Meeting, San Francisco, CA, American Chemical Society 1997; 37(1):81–83.
177. Li T, Farrell J. Rate-limiting mechanisms for carbon tetrachloride and trichloroethylene reactions at iron surfaces. 221st National Meeting, San Diego, CA, American Chemical Society 2001; 41(1):1154–1159.
178. Levich VG. *Physicochemical Hydrodynamics*. Englewood Cliffs, NJ: Prentice-Hall, 1962.
179. Fryar AE, Schwartz FW. Modeling the removal of metals from groundwater by a reactive barrier: experimental results. *Water Resour Res* 1994; 30:3455–3469.
180. Johnson TL, Tratnyek PG. A column study of carbon tetrachloride dehalogenation by iron metal. *Proceedings of the 33rd Hanford Symposium on Health & the Environment In-Situ Remediation: Scientific Basis for Current and Future Technologies*, Pasco, WA. Richland, WA: Battelle Pacific Northwest Laboratories 1994; 2:931–947.
181. Tratnyek PG, Johnson TL, Schattauer A. Interfacial phenomena affecting contaminant remediation with zero-valent iron metal. *Emerging Technologies in Hazardous Waste Management VII*. Atlanta, GA: American Chemical Society, 1995:589–592.
182. Gupta N, Sass BM, Gavaskar AR, Sminchak JR, Fox TC, Snyder FA, O'Dwyer D, Reeter C. Hydraulic evaluation of a permeable barrier using tracer tests, velocity measurements, and modeling. In: Wickramanayake GB, Hinchee RE, eds. *Designing and Applying Treatment Technologies: Proceedings of the First International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Monterey, CA, 18–21 May 1998. Columbus, OH: Battelle Press, 1998; 1(6):157–162.
183. Sass BM, Gavaskar AR, Gupta N, Yoon W-S, Hicks JE, O'Dwyer D, Reeter C. Evaluating the Moffett Field permeable barrier using groundwater

- monitoring and geochemical modeling. In: Wickramanayake GB, Hinchee RE, eds. *Designing and Applying Treatment Technologies: Proceedings of the First International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Monterey, CA, 18–21 May 1998. Columbus, OH: Battelle Press, 1998; 1(6):169–175.
184. Yabusaki S, Cantrell K, Sass B, Steefel C. Multicomponent reactive transport in an in situ zero-valent iron cell. *Environ Sci Technol* 2001; 35:1493–1503.
  185. Puls RW, Paul CJ, Powell RM. The application of in situ permeable reactive (zero-valent iron) barrier technology for the remediation of chromate-contaminated groundwater: a field test. *Appl Geochem* 1999; 14:989–1000.
  186. Blowes DW, Mayer KU. An in situ permeable reactive barrier for the treatment of hexavalent chromium and trichloroethylene in ground water: Volume 3, Multicomponent Reactive Transport Modeling, U.S. Environmental Protection Agency, EPA/600/R-99/095c, Ada, OK, 1999.
  187. Blowes DW, Puls RW, Gillham RW, Ptacek CJ, Bennett TA, Bain JG, Hanton-Fong CJ, Paul CJ. An in situ permeable reactive barrier for the treatment of hexavalent chromium and trichloroethylene in ground water: Volume 2, Performance Monitoring, U.S. Environmental Protection Agency, EPA/600/R-99/095b, Ada, OK, 1999.
  188. Blowes DW, Gillham RW, Ptacek CJ, Puls RW, Bennett TA, O'Hannesin SF, Hanton-Fong CJ, Bain JG. An in situ permeable reactive barrier for the treatment of hexavalent chromium and trichloroethylene in ground water: Volume 1, Design and Installation, U.S. Environmental Protection Agency, EPA/600/R-99/095a, Ada, OK, 1999.
  189. Phillips DH, Gu B, Watson DB, Roh Y, Liang L, Lee SY. Performance evaluation of a zerovalent iron reactive barrier: mineralogical consequences. *Environ Sci Technol* 2000; 34:4169–4176.
  190. Gu B, Watson DB, Wu L, Phillips DH, White DC, Zhou J. Microbial characteristics in a zero-valent iron reactive barrier. *Environ Monit Assess* 2002; 77(3):293–309.
  191. Matheson LJ. Abiotic and Biotic Reductive Dehalogenation of Halogenated Methanes. Ph.D thesis, Oregon Graduate Institute, 1994.
  192. Johnson TJ. Surface Mediated Reduction of Chlorinated Solvents by Zero-Valent Iron. Ph.D thesis, Oregon Graduate Institute, 1997.
  193. Vogan JL, Butler BJ, Odziemkowski MS, Friday G, Gillham RW. Inorganic and biological evaluation of cores from permeable iron reactive barriers. In: Wickramanayake GB, Hinchee RE, eds. *Designing and Applying Treatment Technologies: Proceedings of the First International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Monterey, CA, 18–21 May 1998. Columbus, OH: Battelle Press, 1998; 1(6):163–168.
  194. Mackenzie PD, Horney DP, Sivavec TM. Mineral precipitation and porosity losses in granular iron columns. *J Hazard Mater* 1999; 68:1–17.
  195. Roh Y, Lee SY, Elless MP. Characterization of corrosion products in the permeable reactive barriers. *Environ Geol* 2000; 40:184–194.

196. Gu B, Phelps TJ, Liang L, Dickey MJ, Roh Y, Kinsall BL, Palumbo AV, Jacobs GK. Biogeochemical dynamics in zero-valent iron columns: implications for permeable reactive barriers. *Environ Sci Technol* 1999; 33:2170–2177.
197. Klausen J, Tröber SP, Haderlein SB, Schwarzenbach RP. Reduction of substituted nitrobenzenes by Fe(II) in aqueous mineral suspensions. *Environ Sci Technol* 1995; 29:2396–2404.
198. White AF, Peterson ML. Reduction of aqueous transition metal species on the surfaces of Fe(II)-containing oxides. *Geochim Cosmochim Acta* 1996; 60:3799–3814.
199. Williams AGB, Scherer MM. Kinetics of chromate reduction by carbonate green rust. 220th National Meeting, Washington, DC, American Chemical Society 2000; 42(2):666–668.
200. Schultz CA, Grundl TJ. pH dependence on reduction rate of 4-Cl-nitrobenzene by Fe(II)/montorillonate systems. *Environ Sci Technol* 2000; 34:3641–3648.
201. Amonette JE, Workman DJ, Kennedy DW, Fruchter JS, Gorby YA. Dechlorination of carbon tetrachloride by Fe(II) associated with goethite. *Environ Sci Technol* 2000; 34:4606–4613.
202. Suthersan SS. *Remediation Engineering: Design Concepts*. Boca Raton, FL: Lewis, 1997:362.
203. Gavaskar AR, Gupta N, Sass B, Janosy R, O'Sullivan D. *Permeable Barriers for Groundwater Remediation: Design, Construction, & Monitoring*; Columbus, OH: Battelle, 1998:188.
204. Interstate Technology and Regulatory Cooperation Work Group (ITRC). *Regulatory Guidance for Permeable Reactive Barriers Designed to Remediate Inorganic and Radionuclide Contamination*, Interstate Technology and Regulatory Cooperation Work Group (ITRC), Regulatory Guidance, 1998. See <http://www.itreweb.org>.
205. Eykholt GR, Sivavec TM. Contaminant transport issues for reactive-permeable barriers. In: Acar YB, Daniel DE, eds. *Geoenvironment 2000*, Vol 2, Characterization, Containment, Remediation, and Performance in Environmental Geotechnics. New York: American Society of Civil Engineers, 1995:1608–1621.
206. Hatfield K, Burris DR, Wolfe NL. Analytical model for heterogeneous reactions in mixed porous media. *J Environ Eng* 1996; 122:676–684.
207. Khandelwal A, Rabideau AJ. Transport of sequentially decaying reaction products influenced by linear nonequilibrium sorption. *Water Resour Res* 1999; 35:1939–1945.
208. Mayer KU, Blowes DW, Frind EO. Reactive transport modeling of an in situ reactive barrier for the treatment of hexavalent chromium and trichloroethylene in groundwater. *Water Resour Res* 2001; 37:3091–3104.
209. Eykholt GR. Uncertainty-based scaling of iron reactive barriers. In: Evans J, Reddi L, eds. *In Situ Remediation of the Geoenvironment*. New York: American Society of Civil Engineers, 1997:41–55.

210. Benner SG, Blowes DW, Molson JWH. Modeling preferential flow in reactive barriers: implications for performance and design. *Ground Water* 2001; 39:371–379.
211. Eykholt GR, Elder CR, Benson CH. Effects of aquifer heterogeneity and reaction mechanism uncertainty on a reactive barrier. *J Hazard Mater* 1999; 68:73–96.
212. Gerlach R, Cunningham AB, Caccavo FJ. Dissimilatory iron-reducing bacteria can influence the reduction of carbon tetrachloride by iron metal. *Environ Sci Technol* 2000; 34:2461–2464.
213. Schäfer A, Bouwer EJ. Toluene induced cometabolism of cis-1,2-dichloroethylene and vinyl chloride under conditions expected downgradient of a permeable Fe(0) barrier. *Water Res* 2000; 34:3391–3399.
214. Sfeir HA, Reinhart RD, Chopra M, Clausen C, Geiger C. Biotic attenuation and zero-valent iron permeable barrier technology. In: Wickramanayake GB, Gavaskar AR, Chen ASC, eds. *Chemical Oxidation and Reactive Barriers: Proceedings of the Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Monterey, CA, 20–25 May 2000. Columbus, OH: Battelle Press, 2000; C2–6:323–329.
215. Weathers LJ, Parkin GF, Alvarez PJ. Utilization of cathodic hydrogen as electron donor for chloroform cometabolism by a mixed, methanogenic culture. *Environ Sci Technol* 1997; 31:880–885.
216. Gregory KB, Mason MG, Picken HD, Weathers LJ, Parkin GF. Bioaugmentation of Fe(0) for the remediation of chlorinated aliphatic compounds. *Environ Eng Sci* 2000; 17:169–181.
217. Chiu PC, Lee M, Cha DK, Radosevich M, Rhine ED. Characterizing a culture that dechlorinates TCE with Fe(0). In: Wickramanayake GB, Gavaskar AR, Chen ASC, eds. *Chemical Oxidation and Reactive Barriers: Proceedings of the Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, 20–25 May 2000, Monterey, CA. Columbus, OH: Battelle Press, 2000; C2–6:425–432.
218. Lampron KJ, Chiu PC, Cha DK. Reductive dehalogenation of chlorinated ethenes with elemental iron: the role of microorganisms. *Water Res* 2001; 35:3077–3084.
219. Novak PJ, Daniels L, Parkin GF. Enhanced dechlorination of carbon tetrachloride and chloroform in the presence of elemental iron and *Methanosarcina barkeri*, *Methanosarcina thermophila*, or *Methanosaeta concillii*. *Environ Sci Technol* 1998; 32:1438–1443.
220. Novak PJ, Daniels L, Parkin GF. Rapid dechlorination of carbon tetrachloride and chloroform by extracellular agents in cultures of *Methanosarcina thermophila*. *Environ Sci Technol* 1998; 32:3132–3136.
221. Till BA, Weathers LJ, Alvarez PJJ. Fe(0)-Supported Autotrophic Denitrification. *Environ Sci Technol* 1998; 32:634–639.
222. Ehrlich HL. *Geomicrobiology*. 2nd ed. New York: Marcel Dekker, 1990:646.
223. Lovley DR. Dissimilatory Fe(III) and Mn(IV) reduction. *Microbiol Rev* 1991; 55:259–287.

224. Shokes TE, Möller G. Removal of dissolved heavy metals from acid rock drainage using iron metal. *Environ Sci Technol* 1999; 33:282–287.
225. Bizzigotti GO, Reynolds DA, Kueper BH. Enhanced solubilization and destruction of tetrachloroethylene by hydroxypropyl- $\beta$ -cyclodextrin and iron. *Environ Sci Technol* 1997; 31:472–478.
226. Navon D, Loehr RC, Liljestrand HM, Daniel DE Jr. Impact of biodegradable trenching slurry on iron treatment wall performance. *Water Sci Technol* 1998; 38:49–53.
227. Lin CH, Tseng SK. Electrochemically reductive dechlorination of pentachlorophenol using a high overpotential zinc cathode. *Chemosphere* 1999; 39:2375–2389.
228. Roh Y, Lee SY, Elless MP, Moon HS. Electro-enhanced remediation of trichloroethene-contaminated groundwater using zero-valent iron. *J Environ Sci Health, Part A* 2000; 35:1061–1076.
229. Roh Y, Lee SY, Elless MP, Cho KS. Electro-enhanced remediation of radionuclide-contaminated groundwater using zero-valent iron (A35, pg. 1043, 2000). *J Environ Sci Health, Part A* 2000; 35:1995.
230. Roh Y, Lee SY, Elless MP, Cho KS. Electro-enhanced remediation of radionuclide-contaminated groundwater using zero-valent iron. *J Environ Sci Health, Part A* 2000; 35:1043–1059.
231. Scherer MM, Westall JC, Tratnyek PG. An electrochemical interpretation of carbon tetrachloride reduction at an oxide-free iron electrode. 214th National Meeting, Las Vegas, NV, American Chemical Society 1997; 37(2): 247–248.
232. Ho SV, Athmer C, Sheridan PW, Hughes BM, Orth R, McKenzie D, Brodsky PH, Shapiro A, Thornton R, Salvo J, Schultz D, Landis R, Griffith R, Shoemaker S. The Lasagna technology for in situ soil remediation. 1. Small field test. *Environ Sci Technol* 1999; 33:1086–1091.
233. Deng N, Luo F, Wu F, Xiao M, Wu X. Discoloration of aqueous reactive dye solutions in the UV/Fe<sup>0</sup> system. *Water Res* 2000; 34:2408–2411.
234. Lücking F, Köser H, Jank M, Ritter A. Iron powder, graphite and activated carbon as catalysts for the oxidation of 4-chlorophenol with hydrogen peroxide in aqueous solution. *Water Res* 1998; 32:2607–2614.
235. Doong R-A, Chang W-H. Photodegradation of parathion in aqueous titanium dioxide and zero valent solutions in the presence of hydrogen peroxide. *J Photochem Photobiol A Chem* 1998; 116:221–228.
236. Doong R-A, Chang W-H. Photoassisted iron compound catalytic degradation of organophosphorus pesticides with hydrogen peroxide. *Chemosphere* 1998; 37:2563–2572.
237. Pulgarin C, Schwitzguebel JP, Péringer P, Pajonk GM, Bandara J, Kiwi J. Abiotic degradation of atrazine on zero-valent iron activated by visible light. 209th National Meeting, Anaheim, CA, American Chemical Society 1995; 35(1):767–770.
238. Balarama Krishna MV, Chandrasekaran K, Karunasagar D, Arunachalam J. A combined treatment approach using Fenton's reagent and zero valent iron

- for the removal of arsenic from drinking water. *J Hazard Mater* 2001; B84:229–240.
239. Arienzo M, Chiarenzelli J, Scudato R, Pagano J, Falanga L, Connor B. Iron-mediated reactions of polychlorinated biphenyls in electrochemical peroxidation process (ECP). *Chemosphere* 2001; 44:1339–1346.
  240. Uludag-Demirer S, Bowers AR. Adsorption/reduction reactions of trichloroethylene by elemental iron in the gas phase: the role of water. *Environ Sci Technol* 2000; 34:4407–4412.
  241. Uludag-Demirer S, Bowers AR. Gas phase reduction of chlorinated VOCs by zero valent iron. *J Environ Sci Health Part A* 2001; 36:1535–1547.
  242. Wang C-B, Zhang W-X. Synthesizing nanoscale iron particles for rapid and complete dechlorination of TCE and PCBs. *Environ Sci Technol* 1997; 31:2154–2156.
  243. Zhang W-X, Wang C-B. Rapid and complete dechlorination of TCE and PCBs by nanoscale Fe and Pd/Fe particles. 213th National Meeting, San Francisco, CA, American Chemical Society 1997; 37(1):78–79.
  244. Lien H-L, Zhang W-X. Complete reduction of chlorinated ethylenes by nanoscale bimetallic particles. 215th National Meeting, Dallas, TX, American Chemical Society 1998; 38(1):29–30.
  245. Lien H-L, Zhang W-X. Transformation of chlorinated methanes by nanoscale iron particles. *J Environ Eng* 1999; 125:1042–1047.
  246. Schrick B, Ponder SM, Mallouk TE. Remediation of chlorinated hydrocarbons using supported zero valent nickel-iron nanoparticles. 220th National Meeting, Washington, DC, American Chemical Society 2000; 42(2):639–640.
  247. Lien H-L, Zhang W-X. Nanoscale iron particles for complete reduction of chlorinated ethenes. *Colloids Surf A Physicochem Eng Asp* 2001; 191:97–105.
  248. Ponder SM, Darab JG, Mallouk TE. Remediation of Cr(VI) and Pb(II) aqueous solutions using supported, nanoscale zero-valent Iron. *Environ Sci Technol* 2000; 34:2564–2569.
  249. Elliott DW, Zhang W-X. Field assessment of nanoscale bimetallic particles for groundwater treatment. *Environ Sci Technol* 2002.
  250. Balko BA, Tratnyek PG. Photoeffects on the reduction of carbon tetrachloride by zero-valent iron. *J Phys Chem B* 1998; 102:1459–1465.
  251. Rabideau AJ, Shen P, Khandelwal A. Feasibility of amending slurry walls with zero-valent iron. *J Geotech Geoenviron Eng* 1999; 125:330–333.
  252. Butler EC, Hayes KF. Factors influencing rates and products in the transformation of trichloroethylene by iron sulfide and iron metal. *Environ Sci Technol* 2001; 35:3884–3891.
  253. Hassan SM. Reduction of halogenated hydrocarbons in aqueous media: I. involvement of sulfur in iron catalysis. *Chemosphere* 2000; 40:1357–1363.
  254. Lipczynska-Kochany E, Harms S, Milburn R, Sprah G, Nadarajah N. Degradation of carbon tetrachloride in the presence of iron and sulphur containing compounds. *Chemosphere* 1994; 29:1477–1489.
  255. Yak HK, Lang Q, Wai CM. Relative resistance of positional isomers of

- polychlorinated biphenyls toward reductive dechlorination by zerovalent iron in subcritical water. *Environ Sci Technol* 2000; 34:2792–2798.
256. Alessi DS, Li Z. Synergistic effect of cationic surfactants on perchloroethylene degradation by zero-valent iron. *Environ Sci Technol* 2001; 35:3713–3717.
  257. Sequenced Reactive Barriers for Groundwater Remediation. In: Fiorenza S, Oubre CL, Ward CH, eds. Boca Raton, FL: Lewis, 2000.
  258. Morkin M, Devlin JF, Barker JF, Butler BJ. In situ sequential treatment of a mixed contaminant plume. *J Contam Hydrol* 2000; 45:2302–2833.
  259. Hung H-M, Ling FH, Hoffmann MR. Kinetics and mechanism of the enhanced reductive degradation of nitrobenzene by elemental iron in the presence of ultrasound. *Environ Sci Technol* 2000; 34:1758–1763.
  260. Clausen CA, Geiger CL, Reinhart DR, Ruiz N, Farrell K, Toy P, Lau Chan N, Cannata M, Burnwinkle S, Quinn J. Ultrasonic regeneration of permeable treatment walls: laboratory/field studies. In: Wickramanayake GB, Gavaskar AR, Chen ASC, eds. Chemical Oxidation and Reactive Barriers: Proceedings of the Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, 20–25 May 2000. Columbus, OH: Battelle Press, 2000; C2–6:385–392.
  261. Ruiz NE, Reinhart DR, Clausen CA, Geiger CL, Lau N. Enhanced zero-valent iron degradation of chlorinated solvents using ultrasonic energy. In: Wickramanayake GB, Hinchey RE, eds. Designing and Applying Treatment Technologies: Proceedings of the First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, 18–21 May 1998. Columbus, OH: Battelle Press, 1998; 1(6):71–76.
  262. Comfort SD, Shea PJ, Machacek TA, Gaber H, Oh B-T. Field-scale remediation of a metolchlor-contaminated spill site using zerovalent iron. *J Environ Qual* 2001; 30:1636–1643.